

1. Electrochemistry I: Chemical Cells

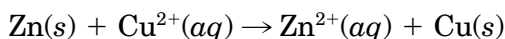
Objective

Oxidation/reduction reactions find their most important use in the construction of voltaic cells (chemical batteries). In this experiment, several such cells will be constructed and their properties studied.

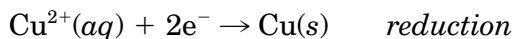
Introduction

Electrochemistry is the detailed study of *electron-transfer* (or oxidation/reduction) reactions. Electrochemistry is a very wide field of endeavor, covering such subjects as batteries, corrosion and reactivities of metals, and electroplating. This experiment will briefly examine some of these topics.

Consider the following reaction equation:



In this process, metallic elemental zinc has been added to a solution of dissolved copper(II) ion. Reaction occurs, and the metallic zinc dissolves, producing a solution of zinc ion. Concurrently, metallic elemental copper forms from the copper(II) ion that had been present in solution. To see what really is happening in this reaction equation, it is helpful to split the given equation into two *half-reactions*:



The zinc half-reaction is called an *oxidation* half-reaction. **Oxidation** is a process in which a species *loses electrons* to some other species. In the zinc half-reaction, metallic zinc loses electrons in becoming zinc(II) ions. The copper half-reaction is called a *reduction* half-reaction. **Reduction** is a process in which a species *gains electrons* from some other species. In the copper half-reaction, copper(II) ions gain electrons (i.e., the electrons that had been lost by the zinc atoms) and become metallic copper.

In the zinc/copper reaction, metallic zinc has *replaced* copper(II) ion from a solution. This has happened because metallic zinc is *more reactive* than metallic copper, and zinc is more likely to be found *combined* in a compound rather than as the free elemental metal. The common metallic elements have been investigated for their relative reactivities and have been arranged into what is called the **electromotive series**. A portion of this series follows:

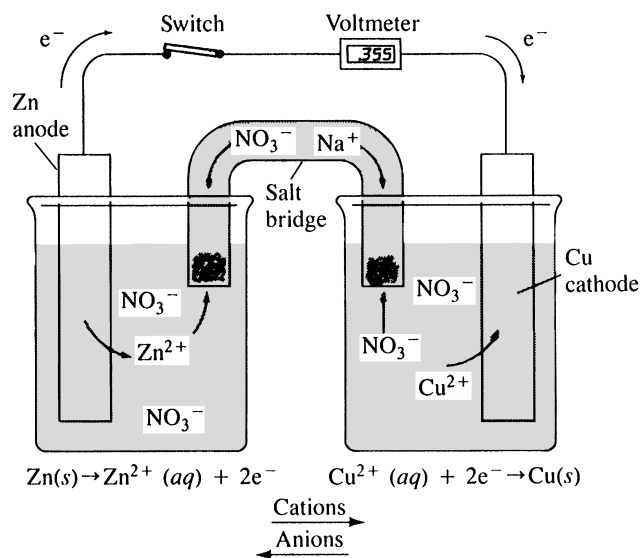
K, Na, Ba, Ca, Mg, Al, Mn, Zn, Cr, Cd, Fe, Co, Ni, Sn, Pb, H, Sb, Bi, As, Cu, Hg, Ag, Pt, Au

The more reactive elements are at the *left* of this series, and the elements become progressively less reactive moving toward the right of the series. For example, you will notice that zinc comes considerably *before* copper in the series, showing that zinc is more reactive than copper.

Notice that H appears in the series. Metals to the left of H are capable of replacing hydrogen ion (H^+) from acids, with evolution of gaseous elemental hydrogen (H_2). In fact, the first four elements of the series are so reactive that they will even replace hydrogen from pure cold water. Elements in the series that come to the *right* of H will *not* replace hydrogen from acids and will consequently generally *not* dissolve in acids. You will note that the elements at the far right side of the series include the so-called noble metals: silver, platinum, and gold. These metals are used in jewelry because they have such low reactivities and can maintain a shiny, attractive appearance. In addition to hydrogen, an element at the left of the electromotive series can replace any element to its right.

While the fact that a reactive metal can replace a less reactive metal from its compounds might be interesting in itself, there is much more implied by the electromotive series. In the zinc/copper reaction discussed at the beginning of this introduction, we considered putting a piece of metallic zinc into *direct contact* with a solution of copper(II) ion so that electrons could flow directly from zinc atoms to copper ions. A far more useful version of this same experiment would be to set up the reaction so that the zinc metal and copper(II) ion solution are *physically separate* from one another (in separate beakers, for example) but are connected *electrically* by a conducting wire. (See Figure 1-1.) Since the reaction that occurs is a transfer of electrons, this can now occur through the wire, thereby producing an electrical current. We could place a motor or light bulb along the wire joining the zinc/copper beakers and make use of the electrical current produced by the reaction. We have constructed a **battery** (or voltaic cell) consisting of a zinc half-cell and a copper half-cell. A second connection will have to be made between the two beakers to complete the electrical circuit, however.

FIGURE 1-1
A zinc/copper voltaic cell. Electrons flow spontaneously through the wire from the zinc half-cell to the copper half-cell when the switch is closed.



In common practice, a glass tube containing a nonreactive salt solution is used to do this (a **salt bridge**), or alternatively a porous porcelain cup is used to contain one half-reaction, with the porcelain cup then being placed in a beaker containing the second half-reaction. Reactions of voltaic cells are exergonic. They take place with the *release* of energy. This energy can be put to use if the cell is set up correctly.

It was indicated earlier that gold is the least reactive metal in the electromotive series. This would mean that metallic gold could not be produced by some more active metal replacing gold ions from solution. Yet gold is quite commonly electroplated from solutions of Au(III) ions onto more common, cheaper metals. The reduction of Au(III) ions to metallic gold is an endergonic process, requiring the *input* of energy from an external source to overcome the reluctance of Au(III) ions to undergo reduction. If an electrical current of sufficient voltage from an outside source is passed through a solution of Au(III) ions, it will provide the required energy, and metallic gold will be produced. When an electrical current is used to force a reaction to occur that would ordinarily not be capable of spontaneously occurring, **electrolysis** is said to be taking place. You will perform several electrolysis reactions in experiment “Electrochemistry II: Electrolysis”.

In this experiment, you will examine the relative reactivity of some metals and determine a small portion of the electromotive series. You will also set up several batteries and measure the voltage delivered by the cells.

SAFETY PRECAUTIONS

- **Wear safety glasses at all times while in the laboratory.**
- **Salts of metal ions may be toxic. Wash hands after use.**
- **Dispose of all solutions as directed by the instructor.**
- **Wash hands after using sulfuric acid. Although the acid used in this experiment is dilute, it will become more concentrated as water evaporates from it.**

Apparatus/Reagents Required

Equipment for voltaic cells (beakers, porous porcelain cup, voltmeter), 1 *M* sulfuric acid, 1 *M* magnesium sulfate, 1 *M* copper(II) sulfate, 1 *M* sodium sulfate, 1 *M* zinc sulfate, 0.1 *M* copper sulfate, 0.1 *M* zinc sulfate, small strips of metallic zinc and copper, magnesium turnings, 24-well plate, 4-inch strips of magnesium, copper, and zinc metals

Procedure

Record all data and observations directly in your notebook in ink.

A. The Electromotive Series

In separate wells of the 24-well test plate, add 10 drops of solutions of one of the following: 1 *M* sulfuric acid, 1 *M* magnesium sulfate, 1 *M* copper(II) sulfate, 1 *M* sodium sulfate, and 1 *M* zinc sulfate. Place a small strip of metallic zinc in each well so that the metal is partially covered by the solution in the test plate.

Allow the solutions to stand for about 15 minutes. Examine the zinc strips for evidence of reaction, both during the 15-minute waiting period and after removing from the test tubes. Determine which ionic species zinc is capable of *replacing* from solution and write equations for the reactions that take place.

Repeat the process using new 10-drop samples of the same solutions, but substituting first copper and then magnesium in place of the zinc metal.

On the basis of your results, arrange the following elements in order of their activity: H, Mg, Cu, Zn, Na.

B. Voltaic Cells

Using strips of copper, zinc, and magnesium metals as electrodes, and solutions of the sulfates of these metals, you will set up three voltaic cells, and will measure the cell potentials (voltages). The following procedure is described in terms of a copper/zinc voltaic cells. You will also set up copper/magnesium and zinc/magnesium voltaic cells.

Obtain a porous porcelain cup from your instructor and place it in a 400-mL beaker of distilled water for 5 minutes to wet the cup.

Add 15–20 mL of 1 M CuSO_4 to a 100-mL beaker. Obtain a 4-inch strip of copper metal and clean it with sandpaper. Place the copper metal strip into the beaker containing the copper sulfate solution to serve as an electrode.

Add 10–15 mL of 1 M ZnSO_4 to the porous porcelain cup you have soaked in water. The porcelain cup is very fragile and expensive: be careful with it. Obtain a 4-inch strip of zinc metal and clean it with sandpaper. Place the zinc metal strip into the porous cup containing the zinc sulfate solution to serve as an electrode.

Connect one lead of the voltmeter to the copper strip, and the other lead of the voltmeter to the zinc strip.

Place the porous cup containing the $\text{Zn}|\text{Zn}^{2+}$ half cell into the beaker containing the $\text{Cu}|\text{Cu}^{2+}$ half cell. Allow the cell to stand until the voltage reading on the voltmeter has stabilized, then record the highest voltage obtained.

Using the table of standard reduction potentials in your textbook, calculate the *standard potential* for the copper/zinc voltaic cell. Calculate the *% difference* between your experimentally determined voltage and the standard voltage.

Using the same method as discussed for the copper/zinc cell, construct copper/magnesium and zinc/magnesium cells and measure their potentials. Calculate the standard cell potential for both of these cells, and the *% difference* between your experimental voltage and the standard voltage.

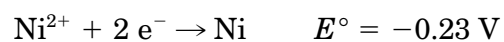
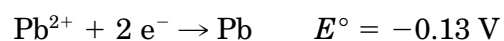
C. Effect of Concentration on Cell Potential

Prepare a copper/zinc voltaic cell as in Part B, using 1 M ZnSO_4 solution as before, but replace the 1 M CuSO_4 solution with 0.1 M CuSO_4 solution. Measure the voltage of the cell. How does the decrease in concentration affect the voltage of the cell?

Prepare a copper/zinc voltaic cell as in Part B, using 1 M CuSO_4 solution as before, but replace the 1 M ZnSO_4 solution with 0.1 M ZnSO_4 solution. Measure the voltage of the cell. Does the decrease in concentration of Zn^{2+} ion affect the voltage measured? Why?

3. How is the voltage (potential) developed by a voltaic cell dependent on the concentrations of the ionic species involved in the cell reaction?

4. Given the following two standard half-cells and their associated standard reduction potentials, what cell reaction occurs when the half-cells are connected to form a battery? What is the standard potential of the battery?



Electrochemistry I: Chemical Cells

Date: Student name:
Course: Team members:
Section:
Instructor:

Results/Observations

A. Electromotive Series

Observations for reactions of metallic zinc

with 0.1 M sulfuric acid

with 1 M MgSO₄

with 1 M CuSO₄

with 1 M Na₂SO₄

Observations for reactions of metallic copper

with 1 M sulfuric acid

with 1 M MgSO₄

with 1 M ZnSO₄

with 1 M Na₂SO₄

Observations for reactions of metallic magnesium

with 1 M sulfuric acid

with 1 M CuSO₄

with 1 M ZnSO₄

with 1 M Na₂SO₄

Write balanced equations for any reactions that occurred.

Order of activity

B. Voltaic Cells

Copper/zinc cell

Observation of zinc electrode

Observation of copper electrode

Voltage measured for the cell % difference from E°

Balanced chemical equation for the cell reaction:

Copper/magnesium cell

Observation of magnesium electrode

Observation of copper electrode

Voltage measured for the cell % difference from E°

Balanced chemical equation for the cell reaction:

Zinc/magnesium cell

Observation of magnesium electrode

Observation of zinc electrode

Voltage measured for the cell % difference from E°

Balanced chemical equation for the cell reaction:

C. Effect of Concentration on Cell Potential

Voltage measured with 0.1 M Cu(II)

Why is the voltage measured lower when [Cu(II)] is decreased?

Voltage measured with 0.1 M Zn(II)

How was the measured voltage affected by the decrease in Zn(II) concentration? Why?

3. Use a table of standard reduction potentials to calculate E° and E for each of the following voltaic cells at 25°C .

