

Using redox chemistry to create a homemade battery

Chemistry 401

May 8, 2013

Introduction

A. What is electrochemistry?

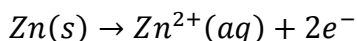
Electrochemistry is the branch of science linking electricity and chemistry. Molecules contain groups of atoms held together by chemical bonds. Molecular bonds consist of electrical forces between electrons and protons. While a molecule may be stable on its own, it can also donate or accept electrons when it interacts other molecules, which will lead to charge separation and energy transfer.

B. What is a redox reaction?

Reduction-oxidation or redox reactions are electrochemical reactions that are characterized by a transfer of electrons between species, resulting in changes in oxidation states of the oxidation and reduction reactants. Redox reactions take place in a solution called an *electrolyte*, which acts as a conductive medium for electron transport.

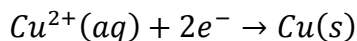
The redox process can be written into two *half reactions*. An example for a zinc and copper redox system is shown below, which is what we will use in our experiments.

i. Oxidation reaction



Here, zinc is the reducing agent and is being oxidized; it is giving up electrons to reduce the copper. This reaction occurs at the *anode*, which is then surrounded by positive charge. An easy way to remember this is that *oxidation* occurs at the *anode* – both begin with vowels, while *reduction* occurs at the *cathode* (both consonants). The oxidation number of the reactant *Zn* is 0, while the oxidation number of the product Zn^{2+} is 2.

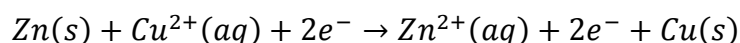
ii. Reduction reaction



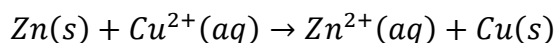
Here, copper is the oxidizing agent and is being reduced; it is gaining the electrons given up by the zinc. This reaction occurs at the cathode.

Electrons from the anode are transferred to the cathode, forming a region of negative charge. The ions in the electrolyte neutralize and correct the charge imbalance between half cells and continually allow for electrons to flow as the reaction progresses.

The oxidation and reduction half reactions can be combined to write the full redox reaction:



The reaction can be simplified further by cancelling the $2e^{-}$ from both sides:

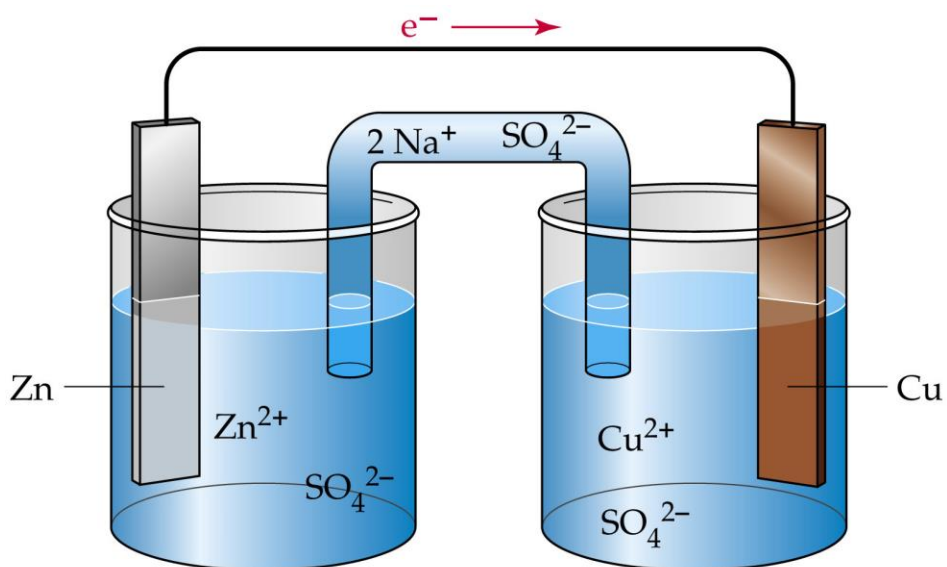


A mnemonic to help remember redox equations is “LEO GER” – Leo the lion goes “grrr.” *Losing electrons is oxidation, gaining electrons is reduction!*

C. Electrochemical cell

Redox reactions take place in an electrochemical cell. Electrochemical cells may be galvanic (also known as voltaic) or electrolytic. In galvanic cells, reactions are spontaneous, while they are non-spontaneous in electrolytic cells. *How do you know if a reaction is spontaneous?*

A cell diagram can be used to trace the path of the electrons in the electrochemical cell. For example, here is a cell diagram of the Daniell cell, invented by John Frederic Daniell in 1836.



http://wps.prenhall.com/wps/media/objects/602/616516/Chapter_18.html

The reduction and oxidation reactions take place in separate half-cells. At the zinc anode, oxidation occurs as the zinc forms its ion and electrons. At the copper cathode, copper is reduced as electrons combine with copper ions in solution to deposit additional copper. The half-cells are connected by a membrane or a salt bridge. *What do you think the role of the salt bridge is?*

The cell gains energy from the electron transport process, which can then be input into another process to do work. The net voltage generated by the two half-cell reactions is called electromotive force. Redox reactions can thus be used as batteries, as we will do in our experiment today.

Questions

Solving and balancing redox equations

1) Using the provided standard potential table below, rank and explain the following elements in their ease of oxidation: Gold, Aluminum, Lithium, Copper, Zinc, and Iron.

2) Determine the half-cell and total redox potential equations for the following reactions. Which are being oxidized and reduced?

a. Lithium/Silver

b. Potassium/Nickel

c. Gold/Magnesium

d. Copper/Barium

STANDARD REDUCTION POTENTIALS IN AQUEOUS SOLUTION AT 25°C

Half-reaction	$E^0(\text{V})$
$\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-$	2.87
$\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$	1.82
$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}(\text{s})$	1.50
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-$	1.36
$\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.23
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^-$	1.07
$2\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}$	0.92
$\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}(\text{l})$	0.85
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}(\text{s})$	0.80
$\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow 2\text{Hg}(\text{l})$	0.79
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	0.77
$\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-$	0.53
$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}(\text{s})$	0.52
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	0.34
$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	0.15
$\text{Sn}^{4+} + 2\text{e}^- \rightarrow \text{Sn}^{2+}$	0.15
$\text{S}(\text{s}) + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{S}(\text{g})$	0.14
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0.00
$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.13
$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}(\text{s})$	-0.14
$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.25
$\text{Co}^{2+} + 2\text{e}^- \rightarrow \text{Co}(\text{s})$	-0.28
$\text{Tl}^+ + \text{e}^- \rightarrow \text{Tl}(\text{s})$	-0.34
$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}(\text{s})$	-0.40
$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$	-0.41
$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.44
$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}(\text{s})$	-0.74
$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}(\text{s})$	-1.18
$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}(\text{s})$	-1.66
$\text{Be}^{2+} + 2\text{e}^- \rightarrow \text{Be}(\text{s})$	-1.70
$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.37
$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71
$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}(\text{s})$	-2.87
$\text{Sr}^{2+} + 2\text{e}^- \rightarrow \text{Sr}(\text{s})$	-2.89
$\text{Ba}^{2+} + 2\text{e}^- \rightarrow \text{Ba}(\text{s})$	-2.90
$\text{Rb}^+ + \text{e}^- \rightarrow \text{Rb}(\text{s})$	-2.92
$\text{K}^+ + \text{e}^- \rightarrow \text{K}(\text{s})$	-2.92
$\text{Cs}^+ + \text{e}^- \rightarrow \text{Cs}(\text{s})$	-2.92
$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.05

<http://www.docstoc.com/docs/80140979/STANDARD-REDUCTION-POTENTIALS-IN-AQUEOUS--SOLUTION-AT-25oC-Half>

D. Redox calculations

i. Standard electrode potential

In electrochemistry, the standard electrode potential, or E° , is the measure of electric potential of an electrode at STP (standard temperature and pressure) and solute concentrations of 1 mol/L. Greater positive values of E° indicate that reactants are more easily reduced, and they are more likely to act as oxidizing agents.

As previously mentioned, redox reactions occur spontaneously in galvanic cells. This implies that the Gibbs free energy ΔG° is negative, and by virtue of the following equation, E° must be positive:

$$\Delta G_{cell}^\circ = -nFE_{cell}^\circ$$

Where:

n is moles of electrons per mole of products

F is the Faraday constant, which is 96485 C/mol

We can thus use E_{cell}° to determine if a cell is galvanic or electrolytic:

If $E_{cell}^\circ > 0$, then $\Delta G_{cell}^\circ < 0$. Thus, the cell is galvanic because the process is spontaneous.

If $E_{cell}^\circ < 0$, then $\Delta G_{cell}^\circ > 0$. Thus, the cell is electrolytic because the process is not spontaneous.

In battery cell applications, both the cathode and the anode standard electrode potentials contribute to the total potential of the cell:

$$E_{cell}^\circ = E_{cathode}^\circ - E_{anode}^\circ$$

Where E_{anode}° is the standard potential at the anode and $E_{cathode}^\circ$ is the standard potential at the cathode as given in the table of standard electrode potential.

ii. Nernst Equation

When the standard electrode potential is used, it is assumed that the reactant concentrations are fixed at 1M and STP. However, this is generally not the case in active batteries. The Nernst equation relates the conditions at a specific time to the observed

potential at that time. Factors such as concentration and temperature will change the potential as the reaction proceeds.

We can derive the Nernst equation by first using Gibbs theory, which is used to predict whether a chemical reaction is spontaneous based on the free energy.

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

Where:

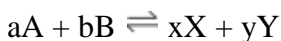
ΔG is change in Gibbs free energy

T is absolute temperature

R is the gas constant, 8.314 J/mol*K

Q is reaction quotient

The reaction quotient, Q , can be calculated using the concentration of the reactants and the products, assuming equilibrium. We can write the expression for Q for the following reaction:



The reaction quotient, Q , is thus defined as:

$$Q = \frac{X^x * Y^y}{A^a * B^b}$$

The Gibbs free energy can be expressed as its electrochemical equivalent. Then the relation between the reaction quotient, Q , and the Gibbs free energy for an electrochemical cell is expressed as follows:

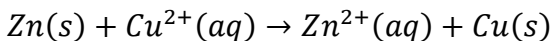
$$\Delta G^{\circ} = -nFE_{cell}^{\circ}$$

$$-nFE_{cell} = -nFE_{cell}^{\circ} + RT \ln(Q)$$

After simplifying the equation, we obtain the Nernst equation:

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

Example:



If we have 5 M of ZnSO_4 and 0.3 M of CuSO_4 and respective Zn/Cu electrodes, what is the cell voltage? Assume STP.

$$Q = 5/0.3 = 16.7$$

$$n = 2 \text{ (2 electrons transferred)}$$

$$E = (1.10) - (0.0257/2) * \ln(16.7) = 1.10 - 0.0362 = 1.0638 \text{ V}$$

Questions

- 3) 3 M of LiCl and 1 M AgNO_3 are used for a voltaic cell, what is the cell voltage? The standard reduction potential table can be found previously.

- 4) Using the gold and magnesium battery from problem 2c), a total cell voltage of 10.09 V was observed. What was the reaction quotient Q?

- 5) Using the same battery and reaction quotient from problem 4, now an increased temperature of 500K is used. What is the new cell voltage?

- 6) According to the Nernst Equation, why does a battery's voltage output decrease over a period of time as the reaction proceeds?

Experiment: Creating your homemade battery

Objective:

Create a voltaic cell using copper/zinc electrodes and electrolyte solutions of Gatorade, lemons, potatoes, and soda.

Experimental Procedure:

- 1) Each group should have 1 potato, 1 lemon, 1 LED, and a beaker of Gatorade or soda (can be refilled). A voltmeter, alligator clips, and zinc/copper electrode should be provided as well.
- 2) Place the copper and zinc electrodes in a beaker of deionized water and attach them to the voltmeter. The reading should be near zero. *If not, what does this indicate about the water?*
- 3) Next, place the copper and zinc electrodes in a potato and attach them to the voltmeter. Try to place them relatively near each other and sufficiently deep.
- 4) Record the voltage seen.
- 5) Repeat steps 3-4 for the lemon, Gatorade and/or soda. For the liquid electrolytes, use enough to sufficiently cover the electrode contacts.
- 6) Test the battery with the provided LED and see if it can power it.

Post-Lab Questions:

- 1) What are some common similarities between each of the electrolytes tested?

- 2) How is our experimental cell different from the typical Daniell voltaic cell?

3) Draw a diagram of the experimental battery similar to the one provided of the Daniell cell found on page 3. Identify the cathode, anode, and electron flow.

4) Why do some electrolytes produce a higher voltage than others? What makes a “good” electrolyte?

5) Determine the reaction quotient, Q for each of the electrolytes tested. Assume STP conditions.

6) How can we increase the EMF produced by our system?

Bonus questions:

Even though we have a high voltage, why will our system not initially light the LED?
(Hint: what two inputs contribute to power production?)

What are some ways we can increase the output voltage of the battery system while still using the same materials? Feel free to test out your hypotheses with the LED.