Voltaic Cells

INTRODUCTION

An oxidation-reduction reaction can be broken into two half reactions. For example, the net ionic reaction

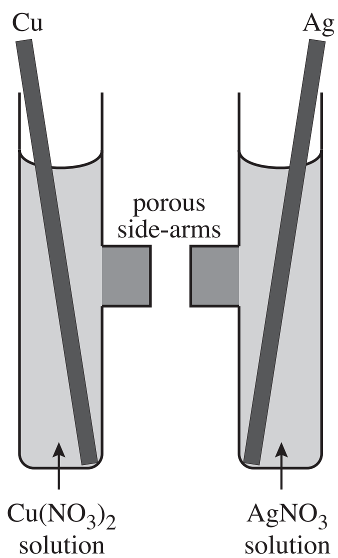
$$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2\ Ag(s)$$

can be shown as the two half reactions

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2\ e^{-} \quad \text{and}$$

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

Half-cells are half reactions engineered into physical entities. A half-cell consists of the oxidized and reduced forms of a substance in contact with one another. Electrons and ions must be able to freely flow into or out of a half-cell. To construct half-cells out of the two half reactions shown above, for example, we could construct two setups as follows:



In the half-cell on the right, the bar of silver extending into the cell provides both the reduced form of the substance *and* the medium for getting electrons into or out of the cell. The $AgNO_3$ solution provides the Ag^{+} ion, which is the oxidized form of the substance. The NO_3^{-} ions are spectator ions in this half-cell. The porous sidearm shown on the side of the container allows ions to flow into or out of the solution but keeps the solution from spilling out. Sintered glass, ionic gelatin solutions, and wet cellulose are three materials in common usage. A common shorthand method of showing this half-cell is:

$$Ag^{+}(aq) \mid Ag(s)$$

The line indicates that the silver ions are in physical contact with the solid silver bar. The order of writing the chemical symbols shows the reaction taking place, that is

$$Ag^{+} + e^{-} \rightarrow Ag$$

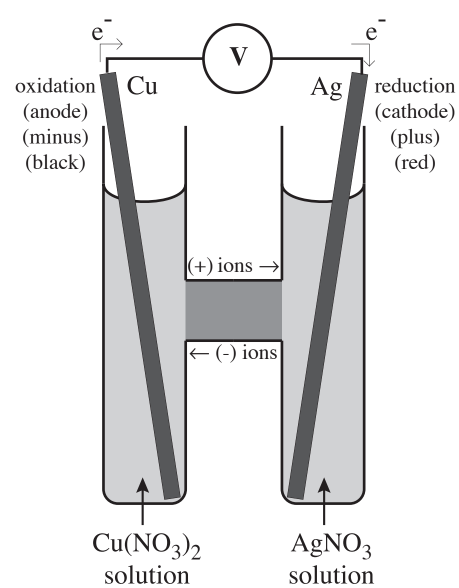
Half-cells are not shown doubled or tripled as half reactions are in balanced equations. The lowest whole-number-ratio reduction or oxidation reaction is shown. The copper half-cell is shown as

$$Cu(s) \mid Cu^{2+}(aq)$$

since the copper is oxidized in this reaction. The statements about electron and ion flow made for the silver half-cell also apply to the copper half-cell.

For ***standard cells***, all aqueous solutions are 1 molar. Concentrations other than 1M are indicated in the half-cell diagram. For example, we will be using a copper half-cell in this experiment which is $Cu(s) \mid Cu^{2+}(0.1M)$.

Voltaic cells are constructed by connecting two half-cells so that electrons flow through an external circuit. Sliding the copper and silver half-cells together so the porous side-arms join, and then connecting the two pieces of metal with a wire would produce a voltaic cell. A voltmeter is shown connected between the copper and silver electrodes. Any electrical device could be in place of the voltmeter, although the power output of this cell is limited.



Electrons flow through the wire from the copper half-cell to the silver half-cell. Notice on the diagram the names and the color code commonly used for the oxidation and reduction portions of the cell. Ions flow through the mated porous side-arms, positive ions from the copper side flow to the silver side, negative ions in the opposite direction. The porous sidearm connection is called a salt bridge. The diagram for this cell would be:

$$Cu(s) \mid Cu^{2+}(aq) \parallel Ag^{+}(aq) \mid Ag(s)$$

The double vertical line symbolizes the salt bridge.

VOLTAGE

The voltage produced by electrochemical cells depends upon the nature and the concentrations of the substances in the half-cells. Half reactions are commonly listed with a ***standard reduction voltage***. The six half reactions which are used in this experiment are:

$Br_2(l)$	+	$2e^-$	$\rightarrow$ $2Br^-(aq)$		1.07V
$Fe^{3+}(aq)$	+	e^-	$\rightarrow$ $Fe^{2+}(aq)$		0.77V
$I_2(s)$	+	$2e^-$	$\rightarrow$ $2I^-(aq)$		0.54V
$Cu^{2+}(aq)$	+	$2e^-$	$\rightarrow$ $Cu(s)$		0.34V
$Fe^{2+}(aq)$	+	$2e^-$	$\rightarrow$ $Fe(s)$		-0.44V
$Zn^{2+}(aq)$	+	$2e^-$	$\rightarrow$ $Zn(s)$		-0.76V

The voltages given for each half reaction are relative voltages. They only have meaning compared to each other. The values are for 1 molar solutions and 25°C temperatures.

To get a full reaction, two half reactions are required. One of them must be reversed, since reduction only takes place in conjunction with oxidation. The reaction that is reversed has its voltage change sign. For example, the Br_2 reaction shown in oxidation form would be:

$$2Br^-(aq) \rightarrow Br_2(l) + 2e^- \qquad -1.07V$$

The full reaction is then the sum of the half reactions, one in reduction form, one in oxidation form, and the voltage is the sum of the two half reaction voltages.

The voltage gives the energy per coulomb of electrons. Even if a half reaction is multiplied by a factor to get the proper number of electrons, the voltage remains the same.

If the concentration of ions is other than 1 molar, the ***Nernst Equation*** can be used to calculate the voltage, for half reactions or for full reactions:

$$E = E^{\circ} - \frac{0.0592\,V}{n}\log Q$$

- E° refers to the standard voltage for the reaction.
- 0.0592 V is a constant derived from the standard temperature and the value of the Faraday.
- n is the number of electrons in the balanced equation.
- Q for the silver/copper reaction taking place in the

copper/silver cell shown on the left would be $\frac{[Cu^{2+}]}{[Ag^{+}]^2}$.

See the balanced equation at the beginning of the experiment to verify this.

In Part 1 of this experiment, you will construct voltaic cells and measure their voltages to see how the calculated voltages correspond with the list of standard reduction voltages given on this page.

In Part 2, you will observe how concentration changes voltage.

In Part 3, you will construct a cell in a way that allows you to use the voltage of the cell to calculate a K_{sp}.

EXPERIMENT

Supplies:

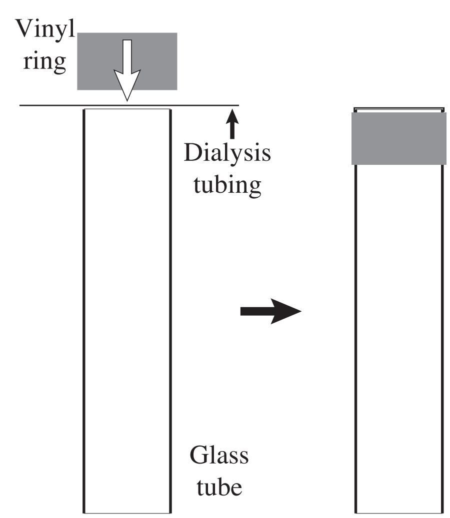
- 6 dialysis membranes
- 1 voltmeter with leads (if you have your own digital multimeter, please bring it and use it).
- Chemical solutions, substances and quantities given on page 81, may be measured directly from the containers into the half-cells or beakers, using the marked transfer pipets attached to each bottle.

From the storeroom, a kit containing:

- 6 vinyl rings, and 6 glass tubes.
- 1 inert metal electrode (platinum).
- 2 copper strips, 1 zinc strip, and 1 iron nail.
- 1 piece of sandpaper.
- 1 file
- 1 battery

Part 1: Cell Potentials.

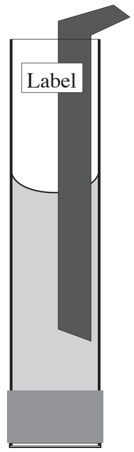
a) Construct 6 half-cell containers as shown:



The dialysis membranes are soaking in deionized water. The dialysis tubing is porous to water molecules and small ions. The vinyl ring should be pushed past the edge of the glass. Add deionized water to each tube to check for leaks. If the vinyl ring is too loose, ask the instructor for a replacement.

b) Now make the half-cells.

Identify each half-cell with masking tape. Make sure you clearly identify the two half-cells containing iron. One is the Fe^{2+} | Fe reaction, and the other is the Fe^{3+} | Fe^{2+} reaction. Set the assembled cells in a 250 ml beaker. Lightly sand each piece of metal used in the first three cells. Electron flow is provided by an inert electrode (platinum) in the last three cells. Only one inert electrode will be used. It will be placed in each of those three cells as needed. ***The mixes for the last three cells should be made in a small beaker, then poured into the cells.***

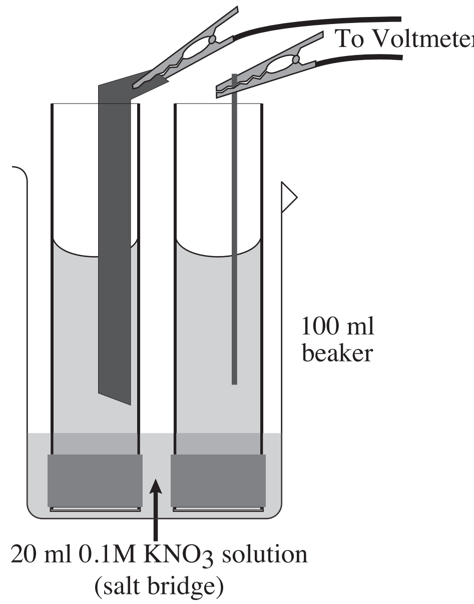


- Cu^{2+} | Cu: 6 ml 0.1M $Cu(NO_3)_2$, 1 of the strips of copper metal.
- Fe^{2+} | Fe: 6 ml 0.1M $FeSO_4$, 1 iron nail (head down).
- Zn^{2+} | Zn: 6 ml 0.1M $Zn(NO_3)_2$, the strip of zinc metal (use in Parts 1 &2).
- Br_2 | Br^- | Pt: 3 ml of saturated Br_2 solution and 3 ml of 0.1M KBr.
- Fe^{3+} | Fe^{2+} | Pt: 3 ml 0.1M $FeCl_3$ and 3 ml 0.1M $FeSO_4$.
- I_2 | I^- | Pt: 3 ml 0.05M I_2 (solution in methanol) and 3 ml 0.1M KI.

c) For each cell, you must experimentally find out which half-cell is being oxidized, which is being reduced.

An easy way to do this is to check the voltmeter with a 1.25 or 1.5 volt battery. See page 108 for information on the mV meter. Turn the voltmeter on, set it to the millivolt function, and press one clamp to the (-) terminal and the other to the (+) terminal of the battery. If you see a negative voltage displayed, switch clamps. When you have a positive voltage displayed, use masking tape to mark the clamp attached to the (-) terminal of the battery as the ***oxidation*** (anode) connection. Any time the voltmeter is showing a positive voltage, electrons are coming out of the half-cell that is attached to the connection you have marked, and therefore, oxidation is taking place in that half-cell. The other half-cell is undergoing a reduction reaction. An alternate method for determining which terminal on the voltmeter shows oxidation and which shows reduction is to read the manual for the instrument.

F or each cell you put together in this part of the experiment, attach the clamps to the half-cells in a way that gives a positive voltage. ***Make sure the clamps are firmly connected.*** Occasionally, the clamps become corroded to the point where they should be filed clean. If you are seeing erratic shifts in the voltage, check the clamps. The half-cell attached to the clamp you marked is the one where oxidation is taking place. In the diagram below, the right hand half-cell shows a platinum electrode, the left hand half-cell a strip of metal, either copper, zinc, or iron. Use the platinum electrode in the bromine, iodine, and iron(II)/iron(III) half-cells. Use the same KNO_3 for each cell you make. Place the proper half-cells in the beaker to make the desired cell.



d) Measure the voltage of cells made up of the copper half-cell with each of the other 5 half-cells. If the voltage shows a minus value, shift clamps. Record the voltage in the data table. Write the voltage as volts, not millivolts (which the meter displays). Record which is the oxidation half-cell and which the reduction half-cell.

e) Make up a sixth cell using two half-cells, neither of which is copper. Choose two half-cells that you think will give the largest voltage possible. Base your choice on the voltages of the first five cells. (Hint: The copper half-cell will be the anode in one of the previous five cells, and the cathode in another of the previous five cells. Choose the two non-copper half-cells from these two.)

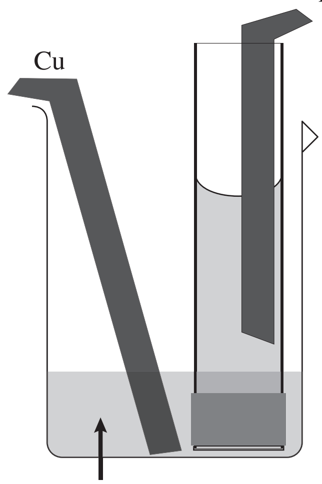
f) Use the standard voltages for the half-cells given on page 80 to calculate the standard voltages for each cell you measured. Remember to reverse the half-cell that you determined was the oxidation half-cell, and to change the sign on the voltage shown for that cell. Then add the voltages from the reduction half-cell and the oxidation half-cell together.

Concentration and internal resistance factors will cause the measured voltages and the calculated voltages to vary by 0.1 or 0.2 V.

Part 2: Voltage and Concentration

Give careful attention to the diagrams on this page.

Construct a cell as follows:



Connect the zinc cell to the oxidation clamp, the copper cell to the reduction clamp. Record the voltage. The voltage should be essentially the same as the zinc/copper cell in Part 1.

Add 3 ml of 6M NH_3 solution to the beaker and stir. Record the voltage.

Now add 5 ml of 2M Na_2S solution. Stir. Again record the voltage.

A negative voltage means that the electrons are actually traveling in the opposite direction.

When NH_3 is added, the following reaction takes place:

$$Cu^{2+}(aq) + 4\ NH_3(aq) \rightarrow Cu(NH_3)_4^{2+}(aq)$$

This lowers the $[Cu^{2+}]$ in the copper half-cell.

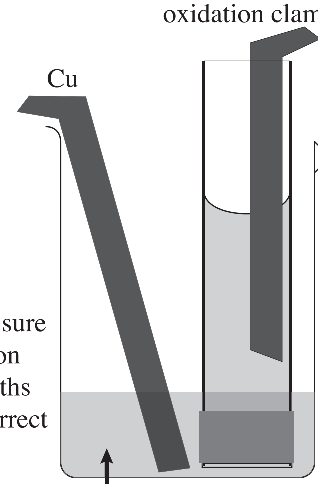
When Na_2S is added, the reaction is

$$Cu^{2+}(aq) + S^{2-}(aq) \rightarrow CuS(s)$$

This lowers the $[Cu^{2+}]$ in the copper half-cell to an extremely low level. The reaction actually reverses direction. The Zn^{2+} ions are now present in such large numbers compared to the Cu^{2+} ions that their cumulative attraction for electrons is greater than that of the few copper ions available.

Part 3: K_{sp} from Cell Voltage

Set up a cell as follows:



First place the 25 ml of 1.0M Na_2CO_3 solution in the beaker, then add 5 drops of $Cu(NO_3)_2$, and stir well to mix the blue precipitate in the solution. Now place the other components in the beaker. Attach the Cu from the glass tube to the oxidation clamp and the Cu in the beaker to the other clamp. Record the voltage. It should be negative.

This is an interesting setup. The oxidation reaction is:

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2\ e^-$$

and the reduction reaction is:

$$CuCO_3(s) + 2\ e^- \rightarrow Cu(s) + CO_3^{2-}(aq)$$

Adding these two reactions together gives:

$$CuCO_3(s) \rightarrow Cu^{2+}(aq) + CO_3^{2-}(aq)$$

Since all concentrations are 1 M, this is a standard cell. The Nernst equation,

$$E = E^o - \frac{0.0592\ V}{n} \log Q$$

for a cell at equilibrium, becomes:

$$0 = E^o - \frac{0.0592\ V}{n} \log K$$

then

$$E^o = \frac{0.0592\ V}{n} \log K$$

and for this reaction, with n = 2,

$$\log K_{sp} = \frac{2\ E^o}{0.0592\ V} \qquad (1)$$

Solve the equation for K_{sp} using the measured E°.

Waste disposal: When you finish the experiment, pour the straight **copper, iron and zinc solutions and the sodium carbonate** solution from Part 3 into the beaker marked **"Metal Waste"**. Pour the **iodine and bromine** solutions into the beaker marked **"Halogen Waste"**. Pour the **sulfide** containing liquid from Part 2 into the beaker marked **"Sulfide Waste"**. Pour the KNO_3 solution into the beaker marked "KNO_3 Waste". Take the half cells apart. Dispose of the dialysis tubing in the garbage. Clean and dry the metal strips, vinyl rings, glass tubes, and platinum wire. Neatly reassemble the kit and return it to the storeroom.

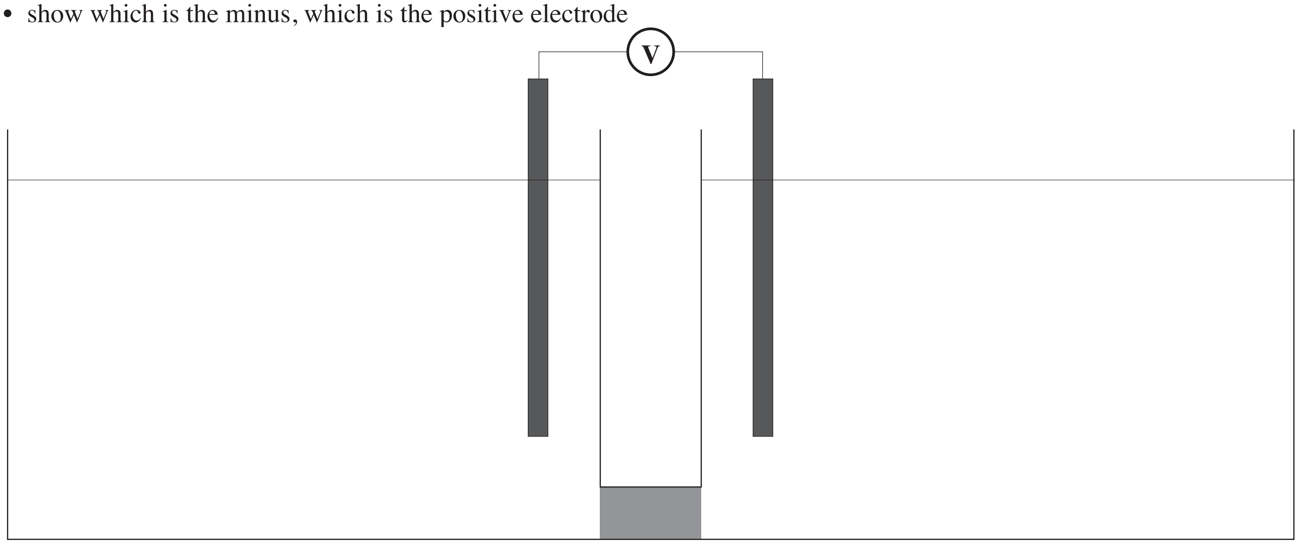
Data Table, Part 1

all shown in reduction form	show in oxidation form			from table on page 2	
Half-cell Combinations (Concentrations are not standard)	Oxidation Half-cell	Reduction Half-cell	Experimental Voltage	Standard Voltage, E°	ΔE (E_{exp} - E°)
Cu^{2+} | Cu and Fe^{2+} | Fe					
Cu^{2+} | Cu and Zn^{2+} | Zn					
Cu^{2+} | Cu and Br_2 | Br^-					
Cu^{2+} | Cu and Fe^{3+} | Fe^{2+}					
Cu^{2+} | Cu and I_2 | I^-					

The non-copper cell:

Show in detail what is going on in the voltaic cell using the Cu^{2+} | Cu and Br_2 | Br^- cells. Remember, one of the half-cells is reversed. Indicate the following on the diagram below:

- direction of electron flow in the wire
- direction of ion flow in each direction through the porous plug
- list the content in each half-cell (including spectator ions)
- list the substances making up the electrodes
- show where oxidation and reduction is taking place
- show which half-cell is the anode, which the cathode
- show which is the minus, which is the positive electrode



Write out the balanced equation for the cell:

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Name______________________________________ Grade__________ Date __________

Part 2

Initial voltage ___________ Voltage after NH_3 ___________ Voltage after S^{2-} ___________

Write out the balanced equation for the Cu/Zn cell:

Use Le Chátelier's Principle to explain why the voltage dropped as you added the reagents.

What would you do to the concentrations of Cu^{2+} and Zn^{2+} to make this cell give maximum voltage?

Part 3

Voltage __________ Use equation (1) on the bottom of page 4 to calculate the following:

log K_{sp} ___________ K_{sp} ___________

The book value for the K_{sp} of $CuCO_3$ is 2.5×10^{-10} M^2. Use the same equation to calculate what voltage the cell should give to get this value.

Voltage __________

What is the % difference between your result and this value?__________

$$\frac{V_{exp} - V_{calc}}{V_{calc}} \times 100 = \% \text{ Difference}$$

It takes very careful control of variables to do precise and reproducible measurements with voltaic cells. In this last measurement, not only the electrical connections, but time…the time it takes to reach equilibrium, is of importance.