2

microLAB
ENGAGING THE NEXT GENERATION IN SCIENCE

ELECTROCHEMISTRY

Experiments for College/University Introductory and General Chemistry Laboratory courses.

About this Experiment Series:

Electrochemistry is somewhat of a step-child in the general chemistry curriculum. Often left for quick treatment at the end of the semester, "hands-on" electrochemistry labs are thought to be difficult and expensive.

This need not be true. Here are some new tools and ideas that will make electrochemistry understandable, affordable, and easy and fun to teach – and learn! They are designed to help students visualize and understand rather than just memorize chemical concepts.

MicroLab's team are all practicing or recently-retired college/university faculty. Recognizing that the best experiments are those the instructor "tuned" for their course goals and the background of their students, our fellow faculty are invited to freely use these ideas, text, or art as they develop lab materials for their students.

*Except for the first experiment, Conductivity / Electroplating, all experiments in this Electrochemistry suite use transparent MicroLab software to organize and to quickly graph experimental data. This creates a quick visual and conceptual link between the experiment and the student. Software may be downloaded from the MicroLab web site **www.microlabinfo.com.***

Voltage measurements may be read directly into this software by MicroLab instruments, or hand-entered if observations are made with a digital voltmeter.

Typical student results are included within this experiment text so that faculty may evaluate the experiment. If desired, these results may be removed during edit for student use.

CITRUS BATTERIES

AN INTRODUCTION TO SPONTANEOUS ELECTROCHEMICAL REACTIONS AND THE ELECTROCHEMICAL SERIES

Overview:

This Citrus Battery experiment is fast, safe, fool-proof, and inexpensive. It quickly produces a lot of data which, when organized with MicroLab's Electrochemistry Series software, identifies several basic electrochemical concepts.

The experiment begins with a flashlight battery, and then shifts to three citrus fruits – a lemon, lime, and orange, using them as salt bridges for simple galvanic cells. Three electrodes are used: A steel nail, a zinc-coated galvanized nail, and a copper wire. Each electrode is used successively as a "reference electrode" generating, for each citrus fruit, a three-element list ordered according to each element's ability to gain electrons from the other elements in the list.

There are six measurements made with each fruit, for a total of 18 for the experiment. To speed up the experiment, individual lab groups could run only one citrus fruit, and then compare results. The measurements, however, are fast.

The lesson from the experiment is that a list of elements ordered by ability to gain electrons is the same regardless of the choice of reference electrode. The choice of citrus fruit has no effect on this natural order – the citrus fruit is acting only as a salt bridge. This natural order of electron-attracting ability is expanded into the Electrochemical Series in the next experiment.

Concepts:

- A galvanic cell or battery is formed when two different metal/ion pairs are connected through a solution that allows movement of both positive and negative ions. This solution is called a "salt bridge".
- There is a natural order among elements in their ability to attract electrons. This order is called "The Electrochemical Series".
- The reactions taking place at the metal surfaces in a galvanic cell are by convention written as reduction reactions.
- The vertical position of an element or reaction in the Electrochemical Series is not affected by the identity of the reference electrode or salt bridge.
- A reference electrode is arbitrarily assigned a value of O volts.
- The voltage observed for a given element/reaction, as compared to the zero-value reference electrode, is known as the reduction potential for that element/reaction. Reduction potentials presented in textbooks always refer to a "standard hydrogen" electrode as an international reference. To compare reduction potentials, everyone has to agree on a common reference electrode.
- The voltage produced by a battery is equal to the difference in reduction potentials of the two elements.

Materials:

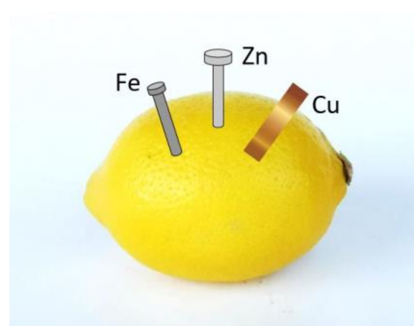
- An AA flashlight battery.
- Small citrus fruits – lemons, limes, and oranges.
- For each group – a steel nail, a galvanized (Zn) nail, and about 2" of copper wire. Number 14 copper wire may be purchased at hardware stores and its insulation removed.
- A voltage measuring device – A MicroLab 238 USB voltmeter, a MicroLab 252 Electronic Half-cell Module, a MicroLab FS-522 or FS-528 lab measurement system, or a digital voltmeter.
- A computer with MicroLab *Electrochem Series* software loaded.

Resource Materials:

- Check the MicroLab web site www.microlabinfo.com under "Help" for short video clips.

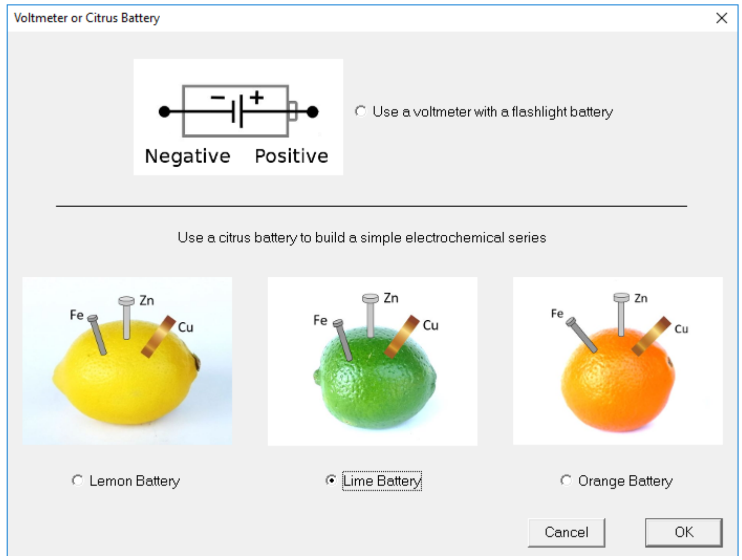
Citrus Batteries Part I: Batteries and Voltage Measurement

Batteries are "electron pumps" that can extract useful work from two complementary electron-transfer reactions. One of these reactions pushes out electrons (the "oxidation" reaction), and the other pulls them in (the "reduction" reaction). The two reactions are separated by a material that called a "salt bridge" will allow mobile positive and negative ions to move from one reaction to the other to maintain electrical charge balance, but keep the reactions separated. Thus electrons are forced to travel though external wires from one "half-cell" to the other. The moving electrons can operate a "load" such as a light bulb where the energy of the moving electrons can be harvested.



These batteries were initially called "Galvanic Cells" or "Voltaic Cells", after the two Italian scientists who independently discovered them: Luigi Galvani and Alessandro Volta. Volta's name ultimately provided the unit for electrical force, the *Volt.*

This experiment will use simple batteries made of citrus fruits (lemon, lime, and an orange) and three metal electrodes – a steel nail, a galvanized nail covered with zinc, and a copper wire. The metals will be used two-at-a-time, and the citrus fruit will act as a salt bridge to move positive and negative ions between the two reactions.



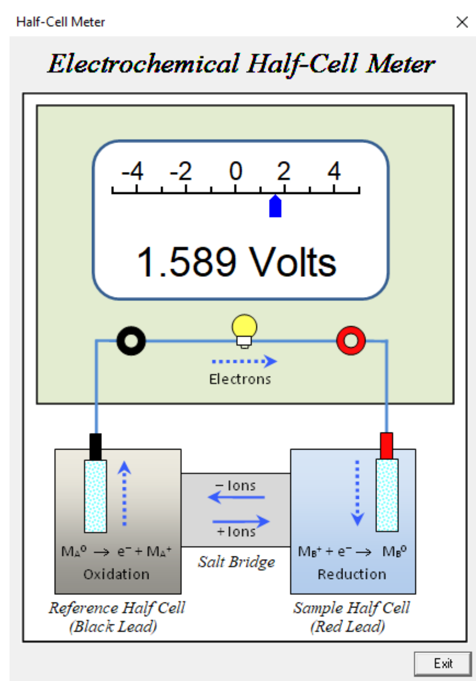
We will use measurements from these citrus batteries to illustrate several important concepts of electron-transfer chemistry.

First, however, we need a way to measure voltage. Here are four options. The first three will read voltage information directly into the MicroLab electrochemistry software. You can hand-enter data from a digital voltmeter into MicroLab electrochemistry software as a fourth option.

1. A MicroLab Model 238 USB voltmeter. This will read ± 5 volts with a resolution of 0.00015 volts, or 0.15 millivolts.
2. A MicroLab Model 232 Electronic Half-cell module. This has the same voltage measurement specifications at the 238 USB voltmeter.
3. A MicroLab 522/524/528 lab interface. This will read ± 2.5 volts, with a resolution of 0.00076 volts, or 0.076 millivolts
4. A digital voltmeter. Most DVM's, when operated on the ± 2.0 volt range, have a resolution of 0.001 volts, or 1 millivolt.

Part I: Learning to Measure Voltage: Measure the voltage of an AA flashlight battery.

Open the Citrus Battery Electrochemistry MicroLab software. Select "Flashlight battery". The MicroLab Electrochemistry Voltmeter will appear. If you are using options 1, 2, or 3, above, for voltage measurement, connect your black/red wire voltage lead to the black and red voltage input terminals on your MicroLab device.



Connect your red voltage lead to the positive terminal of an AA flashlight battery, and the black lead to the negative terminal. You should see a reading like the figure to the right. A new AA alkaline battery has a voltage of about 1.6 volts. However, there are several kinds of information presented in this voltmeter display:

1. The electrical force exerted on electrons that travel from the negative pole to the positive pole of the battery is 1.589 volts in this example. It is presented both digitally and on an analog meter scale. The analog meter scale accents the direction of electron flow in the circuit.
2. The blue arrow shows that electrons are coming out the terminal of the battery connected to the black lead, and running back in the terminal connected to the red lead.

3. The graphics below the meter show two "half-cell" reactions. On the left is an oxidation reaction. In this case the metal of the battery case is giving up electrons. Each atom gives up two electrons and goes from a M (O) oxidation number to a M 2+ oxidation number. On the other side, Ions of a different metal are attracting and gaining electrons. These ions are being reduced, becoming metal (0) charge or oxidation number.
4. To keep electrical charge balanced in both "half-cells", negative ions move through the "salt bridge" from right to left to balance charge of the newly created positive metal ions, and positive ions move from left to right to balance the charge of the newly unbalanced negative ions formed as metal ions touching the electrode pick up electrons to become metal (0).

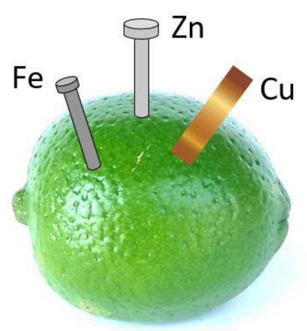
Now turn your battery over. The direction of electron movement should reverse, the voltmeter will read negative instead of positive, and the oxidation and reduction reactions will change positions in the graphic.

You can use this voltmeter to show direction of electron motion, to identify oxidation and reduction reactions, and to measure the voltage exerted on electrons as one reaction pushes them out and the other pulls them in.

The electrical force or voltage exerted on the electrons as they move from one half-cell to the other is measured as a "voltage difference" between the two reactions.

To maintain a consistent vocabulary, the reaction connected to the black voltmeter lead is called a "*reference electrode*" and is arbitrarily assigned a voltage of zero.

The sample reaction or electrode connected to the red lead reads + 1.598 volts in this example. On a scale of electron attracting ability, it is 1.598 volts more positive than the reaction connected to the black voltmeter lead.



Part II: Creating a battery with two spontaneous electron-transfer reactions.

In this experiment we will try to order three elements – Fe, Zn, and Cu, in terms of their ability to gain electrons.

We will also use the three citrus fruits as the substrate or salt bridge for the experiment. The citrus fruit plays two roles. First, the juice in it serves as a medium in which positive and negative ions may freely move. In its second role, the citric acid in the fruit will slightly dissolve some of the metals inserted, providing positive metal ions at the surface of the solid metal.

The presence of both the metal and the positive metal ion adjacent to each other on the metal surface gives the reactions the possibility of running in either direction:

$$Fe^{2+} + 2e \rightleftarrows Fe^{0}$$

$$Zn^{2+} + 2e \rightleftarrows Zn^{0}$$

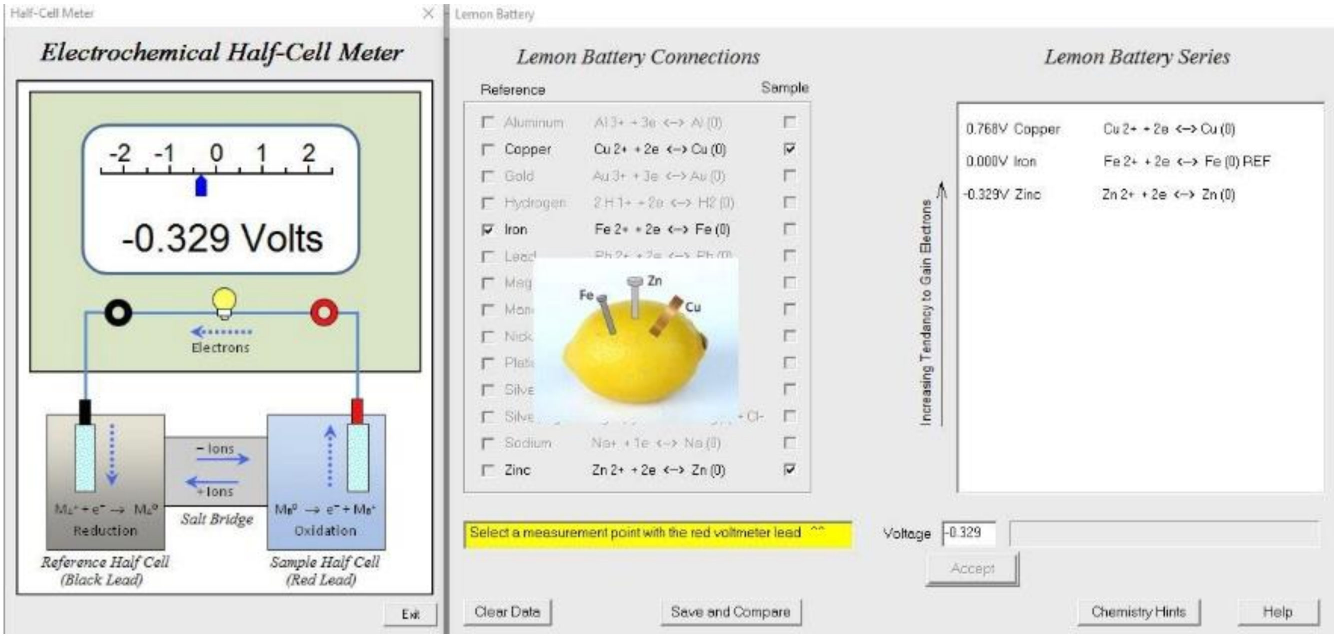
$$Cu^{2+} + 2e \rightleftarrows Cu^{0}$$

There are two experimental questions:

1. Does the identity of the reference electrode change the ordering of these elements in terms of their ability to attract electrons?
2. Does the identity of the citrus fruit – the salt bridge – change the ordering of these elements in terms of their ability to attract electrons?

Procedures:

1. Reload the MicroLab “Citrus Battery” software again. As the software comes up, a box will appear asking you want to measure a flashlight battery or run a citrus battery experiment. For now, choose one of the citrus batteries.



The screen will show a voltmeter, a list of elements, and a blank table in which software will arrange reactions in order of their ability to gain electrons.

While there are a dozen elements in the table, only copper, iron, and zinc are used for this experiment.

For each of the citrus fruits, we can make three batteries, each using one of the three elements as a reference electrode.

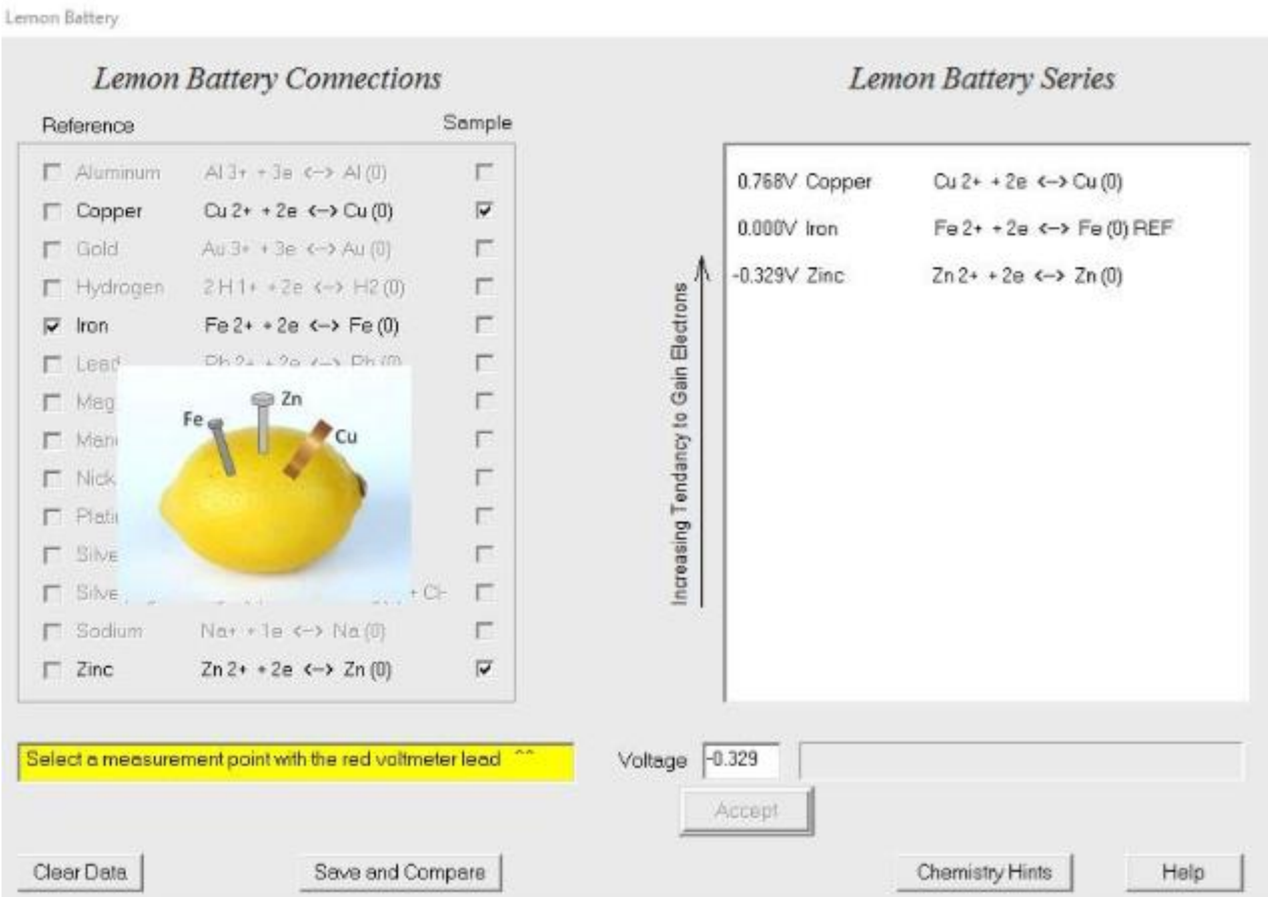
Each battery will have a reference electrode and one other element.   You can select your reference electrode (the black voltmeter lead connects to this) by clicking the element in the left column. This example started with iron as a reference.

Connect your red voltage lead to the copper electrode. Click “Copper” in the right-hand sample column.   Observe the voltage and click “Accept” when the voltage reading stabilizes. The software will place the copper reaction in the appropriate order with respect to the (iron) reference electrode.

Now connect your red voltage lead to the Zinc electrode.   Click its name in the right-hand “sample” column and click “Accept” when the voltage reading stabilizes. The software will add the reading in the proper order, again with respect to the iron reference electrode. The screen capture below shows the result for two batteries made with an iron reference and copper and zinc electrodes.

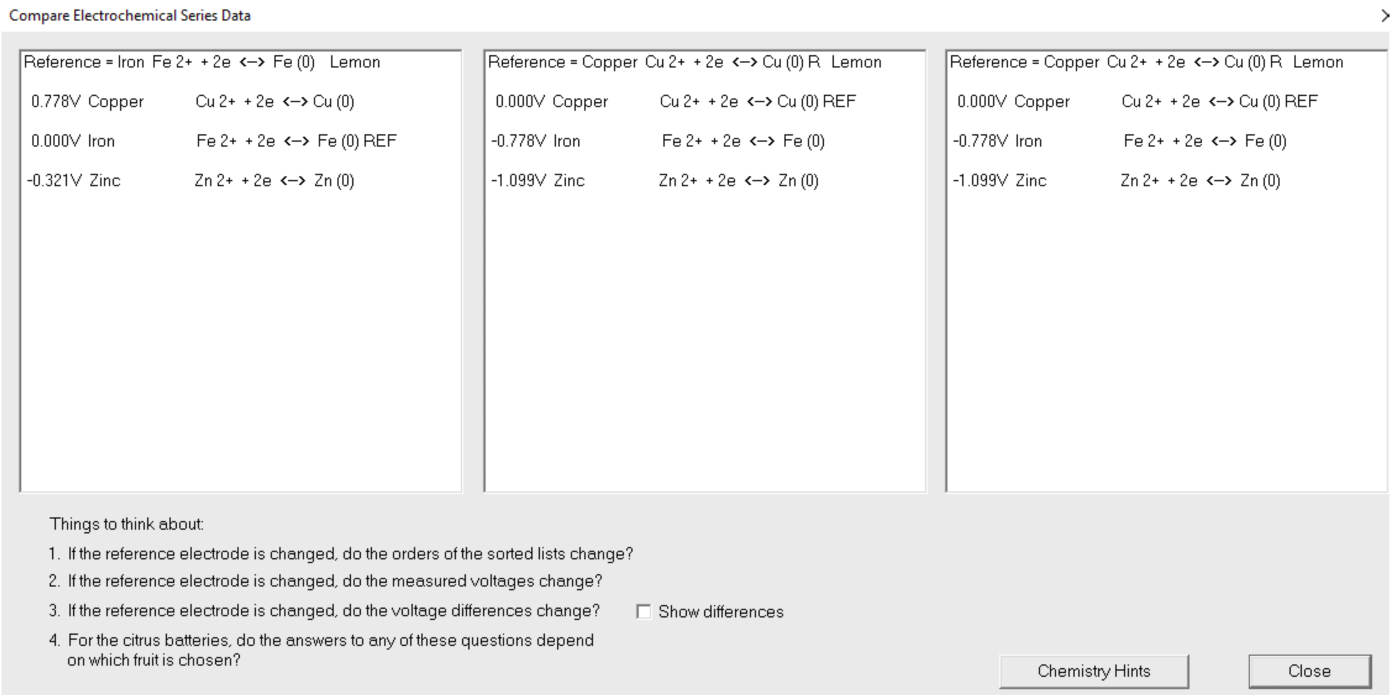
This ordered list presented in the sample data below says that, of these three elements, copper has the greatest attraction for electrons, iron is next, and zinc has the least.

The associated voltage readings refer to an arbitrarily assigned "zero" for the iron reference electrode. Reference electrodes are always assigned a value of zero.



When you have collected data from batteries formed by the copper and zinc electrodes using an iron reference electrode, click "Save and Compare". Pick "Sample 1". You can store this data for comparison with your next two experiments – one battery made with a copper reference, and the other with a zinc reference.

Now run the experiment again with Copper as a reference electrode, and a third time with Zinc as a reference electrode, each time saving data as the experiment is completed.



When you have gathered data with all three citrus fruits, call up the three results and compare them. Note the questions at the bottom of the comparison screen.

Click the "show differences" box. The software will calculate the differences between each of the half-cell reduction potentials in the list.

Note that, although the voltage readings (reduction potentials) are different for each reaction when the reference (zero) electrode is changed, both the order of elements and the difference in reduction potential between the reactions is the same.

This list of elements arranged by ability to gain electrons is a natural order and is the same regardless of what element is chosen as an arbitrary "zero" reference.

You will find that it is also the same regardless of the identity of the substrate/salt bridge. The salt bridge just moves positive and negative ions to maintain overall charge balance at each electrode of the battery.

Try this experiment again using a lime and then an orange as the substrate / salt bridge.

CONCLUSIONS

This experiment has asked you to make a number of relatively simple tests and observations. Can you use your experiments and observations to create a clear explanation (a model) of how you think the following things work? Can you support these proposals with observations *other than the ones you used to initially create the model*?

The content objectives listed at the beginning of the experiment are presented below, with several related questions. For each of these questions, describe briefly how you think it works (a model) *and the experimental evidence you have collected that supports your belief:*

- A galvanic cell or battery is formed when two different metal/ion pairs are connected through a solution that allows movement of both positive and negative ions. This solution is called a "salt bridge".
    - What property of the two metal/ion pairs must differ to make the battery create a voltage?
    - How can you predict which direction electrons will move between the two external electrodes?
    - Why must a salt bridge be placed between the two reactions?

- There is a natural order among elements in their ability to attract electrons. This order is called "The Electrochemical Series". Given the identity of two elements and their ions, can you use the electrochemical series to predict whether one element/ion pair can take electrons from another? And if so, which way the electrons will move?

- The reactions taking place at the metal surfaces in a galvanic cell are by convention written as reduction reactions.
- The vertical position of an element or reaction in the Electrochemical Series is not affected by the identity of the reference electrode or salt bridge.
- A reference electrode is arbitrarily assigned a value of O volts.

- The voltage observed for a given element/reaction, as compared to the arbitrarily-assigned zero-value reference electrode, is known as the ***reduction potential*** for that element/reaction. Reduction potentials presented in textbooks always refer to a "standard hydrogen" electrode as an international reference. To compare reduction potentials, everyone must agree on a common reference electrode. In this experiment, we successively and arbitrarily chose iron, copper, and zinc as reference electrodes, to prove that the identity of the reference electrode does not change the order of the electrochemical series. For most experiments, the identify of the reference electrode does not matter, because one is usually watching change in the reduction potential or position in the electrochemical series for one element/reaction. What matters is that the reference electrode sit still electrochemically, and that everyone involved agrees to that element serving as a zero reference.

  Standard hydrogen electrodes – the international standard for electrochemistry - are very hard to assemble, but Silver/Silver Chloride (Ag/AgCl) reference electrodes are stable, inexpensive to manufacture, and are commonly used in pH and REDOX electrodes. In the next experiment, we will consider using an Ag/AgCl reference electrode as we expand our understanding of the electrochemical series.

- The voltage produced by a battery is equal to the difference in reduction potentials of the two elements. Given the reduction potential table developed with an iron reference electrode (the first experiment), can you predict the voltage that would be produced by a zinc / copper battery?