

Maintenance:

- Rinse porous cup well after each use, particularly before putting into

storage. Handle with care; it will break if dropped.

- Zinc electrodes will last longer if coated with film of mercury.

Theory and History:

The Voltaic Cell, named after its inventor, Count Alessandro Volta, is based upon principles discovered by Luigi Galvani in 1790, a biologist experimenting with a pair of frogs' legs freshly dissected and suspended from a copper wire. Galvani noticed the legs jerk as if alive when touched by an iron knife. Wondering if lightning would have this effect, he hung the legs outside during a thunderstorm

on a brass hook connected to an iron bar. The legs kicked after the storm passed, which Galvani attributed to electricity in the muscles of the frog.

Volta arrived at a different conclusion: that the metals reacted chemically with body fluids to generate electric current which caused the twitching. He tested this by demonstrating that a potential difference is generated by two different conductors in contact with liquid containing ions to conduct electricity. One type of cell based on this principle is the **Voltaic Cell**.

A basic Voltaic Cell transforms *chemical* energy into *kinetic* energy. A rod of zinc and copper are placed in dilute sulfuric acid, for example. The rods are the *electrodes* (conductors) and acid is the *electrolyte* (liquid which conducts electricity.) The metal rods are arranged so they do not touch. If wires are connected to the rods and a voltmeter, the needle on the voltmeter is deflected. This shows that a potential difference exists between two dissimilar conductors. The wires and voltmeter form a conducting path termed a circuit.

How Voltaic Cells Work:

All metal tends to dissolve in liquid in varying degrees. In the example in this diagram, the copper and zinc electrodes tend to dissolve when placed in sulfuric acid. As each zinc atom dissolves, it loses two electrons and forms a charged particle, or **ion**, represented by the symbol Zn^{++} . The "lost" electrons collect on the zinc rod, which is charged negatively. As additional Zn^{++} ions form, many are attracted to the zinc electrode, which is growing increasingly negative. The Zn^{++} ions form a concentrated positive charge in the liquid near the zinc electrode. The charge stops growing when a

Zn^{++} ion returns to the electrode for each zinc atom that dissolves. A *dynamic equilibrium* condition now prevails, since atoms and ions are continuing to form although the total charge stops increasing.

The copper electrode shows a similar reaction. Since copper atoms have less tendency to dissolve, they reach equilibrium more quickly. The charge on the copper rod is less strong and less negative than on zinc. The copper electrode is positive in comparison with the zinc. In a Voltaic Cell, the metal that dissolves more readily is always negative. The cell's chemical action establishes a *potential difference* between the two electrodes.

When the electrodes of this zinc-copper cell are lined externally by means of connecting wire, electrons begin to drift through the conductor (wire) from the negative (zinc) electrode to the positive (copper) electrode. The charge of each decreases and the Cell renews its chemical action. Electrons flow from zinc to copper by way of the wire, and back from copper to zinc by way of the solution.

In **Diagram 1**, where dilute sulfuric acid is used as the electrolyte, the sulfuric acid contains the ions H_3O^+ , HSO_4^- , and SO_4^{--} . H_3O^+ ions are repelled toward the copper electrode as Zn^{++} ions form. At the copper electrode each H_3O^+ ion acquires one free electron. This helps the copper electrode hold a positive charge relative to the zinc electrode.

Similarly, SO_4^{--} and HSO_4^- ions drift through the solutions to the zinc electrode. Here they tend to combine with Zn^{++} ions and keep these ions from plating out onto the zinc electrode. The cell continues to turn chemical energy into kinetic energy of moving ions and electrons until either the acid or the zinc is used up.

No electrons flow through the electrolyte solution, although there is a constant flow of charged particles or ions.

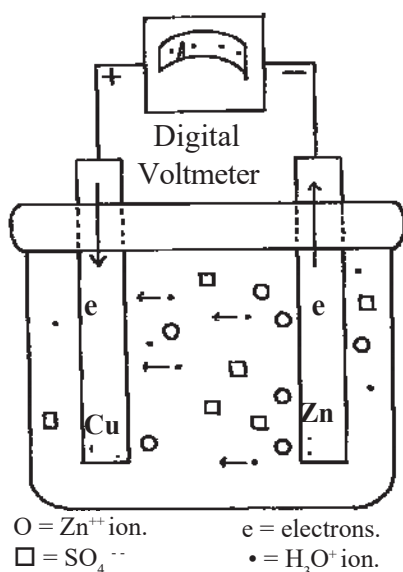


Diagram 1 - Voltaic Cell

The kinetic energy of these moving particles adds to the total energy produced by the chemical reaction. The energy available in the external circuit is always less than the total energy created by the cell. This total energy constitutes the **electromotive force** (emf) of the electrical energy source, defined as the potential difference between the terminals when the current is zero. It is measured in volts or joules per coulomb of charge.

The Voltaic Cell may be compared to a furnace in which zinc is the fuel burned to furnish energy. The energy produced is partly in the form of heat, partly an electric current. The electrolyte may be compared to a fire. The copper electrode may be compared to a tool which is inserted into the cell to remove the electricity but which takes no part chemically in the entire process. Therefore, these three elements are required to make a Voltaic Cell: a metal which may be consumed; a chemical to consume or oxidize it; and an inactive element which serves merely to collect the electricity.

The voltage (EMF) output of a Voltaic Cell varies depending upon which two dissimilar metals are used as electrodes. EMF is determined by the position of the chosen metals in the electrochemical series. A table of oxidation-reduction potentials lets you predict the amount of EMF generated by any combination of electrodes in a Voltaic Cell. The

Table

(page 4) lists different **cells** with their individual characteristics.

Polarization and local action are defects of chemical cells. Polarization refers to the adherence of gas bubbles on the positive (copper) electrode, which results in decrease in electric current. To prevent this, a chemical that can oxidize the hydrogen gas to water is often introduced to the cell, termed a depolarizer.

Local action, a second defect, occurs when zinc forms on one of the electrodes. Minute impurities present in commercial zinc interact with the electrolyte and with adjacent zinc atoms to form many microscopic local cells. These extra cells use up the zinc that could otherwise be contributing to chemical energy by giving off heat. The zinc is consumed by the acid no matter whether the electric current is used or not.

This wasteful effect can be neutralized, although not totally prevented, by amalgamating the zinc with mercury, a process that involves coating the zinc electrode with a mercury shield. Since most of the impurities in the zinc are insoluble in mercury, they will not interact with the electrolyte.

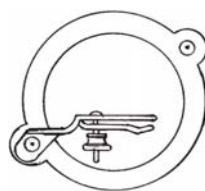
A number of different chemicals avoid polarization when added to the electrolyte. There are also a number of different electrolytes and elements that make a more satisfactory cell than Volta's original invention.

To Assemble:

Attach assembled brackets to long screws protruding from plastic ring and fasten with knurl nuts. Electrode brackets should attach to plastic ring loosely enough to swing inside ring, so you can position your electrodes as desired.

Attach copper and zinc electrodes to electrode brackets. Unscrew knurl nuts slightly to allow brackets to open. Slide one end of electrode through opened bracket as shown; screw knurl nuts tight.

One short and long electrode bracket fastened to plastic ring with knurl nut



and electrolytes such as lemon juice.

Additional Materials:

- voltmeter
 - vinegar (5% acetic acid)
 - (optional) dilute lemon juice
 - 2 lengths hookup wire
 - various electrodes
- (if 10-175 Basic Cell purchased)

Construct a Voltaic Cell:

- **Attach electrodes to brackets.**

Open electrode brackets with knurl nuts, slide zinc and copper electrodes, top down, between electrode brackets so electrode points into jar.

- **Fill jar with vinegar.**

Fill container with vinegar (5% acetic acid) or other electrolyte 2/3 full, so electrodes protrude into the electrolyte. If you need more liquid than can be held by an 8 oz jar, use a pint or quart jar.

(10-180 Cell is designed so rim fits standard Mason jar.)

- **Hook up cell to digital voltmeter.**

Hook your voltaic cell to a voltmeter by clipping one end of hookup wire to the thumb nut on either the electrode holder or the plastic rim. Repeat for second hookup wire. Clip free ends of both wires to the terminals on your voltmeter.

- **Measure the amount of electrical volt age generated.**

You should generate about 1.5 volts. The zinc electrode should have negative readings.

Experiment with different electrodes

Construct A Coulometer:

Additional Materials:

- 2 copper electrodes
- ammeter
- analytical balance
- stop watch or clock
- copper sulfate solution
- 6v storage battery plus rheostat or adjustable power source

The coulometer can be used to measure the amount of copper in solution by passing a known current through it for a known period of time.

A coulometer measures an unknown quantity of electricity as it passes through. It does so by measuring the mass of copper deposited on one of its electrodes. Use it to determine **Faraday's Constant** - the quantity of electricity needed to deposit a gram equivalent of any ion.

Start with clean electrodes and practice on a test run. Time is of the essence in this procedure.

- **Connect electric circuit as shown in Diagram 2.**

Test to make sure your electric circuit is properly connected. Connect in series: **power source** (either an adjustable power supply {recommended} or a 6-volt battery (plus rheostat), your **coulometer**, and an **ammeter**. Make sure the positive terminal is connected to **anode** (loss plate) and negative terminal is connected to **cathode** (gain plate).

Select one copper plate to be the gain plate (negative.) Clean by rinsing in clean water, then dipping in alcohol. Wave in air to dry, then set on sheet of clean paper until needed.

- **Weigh both anode and cathode on analytical balance.**

Position the electrode to be weighed on a clean sheet of paper on the left pan. Subtract the weight of the paper from the final result. Try to handle the clean electrodes by the edges to keep them as clean.

- **Fill the Coulometer with a solution of copper sulfate.**

The volume of solution should be

high enough to cover most of the electrode but not so high that it is in danger of splashing onto the clamps: about 2/3 full in an 8 oz. container.

- **Just before starting the experiment, place the electrodes in the coulometer.**

Open electrode brackets with knurl nuts, slide both copper electrodes, top down, between electrode brackets with electrode pointing down into jar.

Since copper is slightly soluble in copper sulfate electrolyte, it is important not to immerse them until a few minutes before starting the current to prevent damage and inaccurate results.

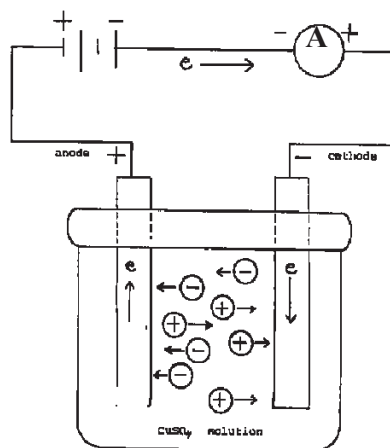
- **Turn on current.**

Pass a known current through the chemical cell for a known period of time. The amount of current used is crucial. Too great a current density (current density is the *current per unit*

area) results in the flaking off of the deposit which collects on the gain plate. For copper the optimum current density is approximately 20 milliamperes per square centimeter. Adjust the rheostat, or adjustable power source, until an appropriate current is reached. It is necessary to have the rheostat or power source connected in such a way that you will be able to increase or decrease the current at a later point.

- **Let current flow for a minimum of 20 minutes.**

Use a stopwatch to take accurate note of start and stop times. (If you are conducting a test run at this point, it is not necessary to let the current run for the entire length of time.) Remove gain plate from cell, taking care not to knock off any loose grains of metal adhering to it. Rinse the cathode in clean water, then in alcohol, and dry. Weigh it again on the analytical balance.



e = electrons + Copper ions
A = Ammeter - Sulfate ions

Diagram 2 - Coulometer

observations, using a different amount of current for a different length of time. This will help test the dependence of the mass deposited upon the quantity of electricity. **The purpose of this experiment is to determine Faraday's Constant, or *k*.**

This is the quantity of electricity necessary to deposit a gram equivalent of the substance, to the current, and to the time. This relationship is expressed as:

- **Compare current weight to its initial weight.**

Compute the gain in weight. This gain is due to the copper that has been deposited on it.

It is a good idea to take a second set of

$$m = kc It$$

where **m** is the mass deposited, **c** is the electrochemical equivalent (atomic weight/valence), **I** the current flow through a solution, **t** time, and **k** Faraday's Constant. A sample problem follows.

m

where **m** is gain in weight on the copper cathode, **c** is electrochemical equivalent, **I** is current flow and **t** is length of time. The electrochemical equivalent is defined as the *mass of material deposited electrolytically per unit quantity of electricity*, or the mass deposited by a unit current flowing steadily for a unit time, usually expressed in grams per coulomb. The mass in grams which is equal numerically to the chemical equivalent of an ion is called a gram equivalent.

In the case of copper, the gram equivalent is **31.8** grams. That is, if a quantity of electricity equal of **Faraday's Constant (k)** is passed through an electrolyte, it will liberate 31.8 grams of copper. This number derives from the atomic weight divided by the number of charges. For copper, it is 63.6/2 or 31.8.

Compute Faraday's Constant:

Sample Problem:

Since $m = kc It$ then

$$k = c I t$$

Take the case where an electric current of 1 ampere liberates 1.186 grams of

copper over 1 hour.

m therefore equals 1.186 grams. A current of 1 ampere/hour becomes 3,600 coulombs/hour, since an ampere is defined as *one coulomb per second* and there are 3,600 seconds in an hour.

c is 31.8 grams of copper by definition (63.2/2).

Inserting these figures yields:

$$k = \frac{31.8g (3600 \text{ coul/hr}) (1 \text{ hr})}{1.186 g}$$

$$1.186 g$$

Cancelling out the measurements of **g** and **hr** results in:

$$k = 31.8 \text{ (3600 coul)} = 1144800 \text{ coul} \\ \frac{1.186}{1.186}$$

$$k = 96,526.14 \text{ coulombs}$$

The actual Faraday's Constant is defined to be:

$$\frac{1}{96,500} \text{ coulombs}$$

It will take 96,500 coulombs of electricity to deposit a mass **m** which is equal to the chemical equivalent of an ion.

Construct A Storage Cell:

Additional Materials:

- 2 lead electrodes(you provide)
- dilute sulfuric acid
- 3v power source

- **Fill jar 2/3 full with dilute sulfuric acid.**

Pour 10 to 20 ml of concentrated sulfuric acid slowly into 200 ml of tap water. Stir slowly. Do not use until solution cools to 40° C or lower.

- **Define one electrode as positive.**

Connect to positive terminal of a battery having an emf of at least 3 volts. Clip one end of hookup wire to thumb nut on either the electrode holder or plastic rim. Connect negative terminal of battery to other lead electrode with second clip lead.

- **Let current flow 5 -10 minutes.**

Gas should begin to rise from both electrodes. After the current has flowed, disconnect the cell. Both lead electrodes were charged as the current passed through them. The anode will have a reddish coating of **lead dioxide** (PbO₂). The negative electrode remains pure lead.

- **Use the electricity you have stored.**

Your cell should have enough energy to ring a bell, light a bulb or run a small motor for a short time. Your cell would have greater capacity if you used grids filled with a paste of lead oxides instead of flat electrodes of solid lead.

Cell Type	Positive	Porous Cup	Negative	Outside
	Electrode (<i>in cup</i>)	Electrolyte	Electrode (<i>outside</i>)	Electrolyte
Bunsen	Carbon	10% HNO ₃	Zinc	10% H ₂ SO ₄
Bunsen	Carbon	H ₂ CrO ₄	Zinc	10% H ₂ SO ₄
Chromic Acid (single fluid)	Carbon	No cup	Zinc	H ₂ SO ₄ & H ₂ Cr O ₄ dilute, mixed
Daniel *	Copper* (cathode)	5%H ₂ SO ₄	Zinc (anode)	CuSO ₄ **
Storage	Lead	No cup	Lead	10% H ₂ SO ₄
Poggendorf	Carbon	No cup	Zinc	H ₂ SO ₄ & K ₂ CrO ₄
Niadut	Carbon	CaCl ₂	Zinc	NaCl
Fuller ***	Carbon ***	ZnCl ₂	Zinc	K ₂ Cr ₂ O ₇ *** & HCl

* Place copper and sulfuric acid inside cup. **Dilute 5g copper sulfate with 100 ml water.
*** Place carbon K₂Cr₂O₇ and HCl **outside** cup. Place Zn and ZnCl₂ **inside** cup.

The porous cup is needed if each electrode requires a separate electrolyte. The cup contains the second electrolyte and will ensure that the two electrolytes do not mix. At the same time it allows ions to pass in and out through its walls.

Caution:

- **Sulfuric acid is corrosive.**
- **Charging liberates hydrogen gas.**
- **Keep away from flame and gas.**

How Storage Cell Works:

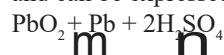
A storage cell is created by running an electric current through two lead electrodes and dilute sulfuric acid. As it generates current, lead dioxide on the positive electrode changes to lead sulfate. Lead sulfate also coats the negative electrode. This removes sulfate ions from dilute sulfuric acid with the result that the acid solution grows weaker.

When a storage cell is exhausted, it can be **recharged** by connecting a source of direct current to its terminals in the opposite direction - that is, by forcing electrons to enter at the negative terminal. This removes sulfate coatings from both positive and negative electrodes.

How To Use:

A storage or **secondary** cell differs from a **primary** cell in that it will not produce an electric current until it has been charged by passing an electric current through it. The energy of the charging current changes into chemical energy, which in turn produces electricity when the cell is again discharged. The **total amount** of energy is the same before and after discharge, since the secondary cell merely serves as a convenient way to **store** energy.

When the storage cell is fully recharged, the positive electrode is again coated with lead dioxide and the negative electrode is pure lead. The chemical equation for this reaction is reversible and can be expressed as:



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