

In 1800, William Nicholson and Anthony Carlisle announced that they had achieved the chemical decomposition of ordinary water with an electric current supplied by the "galvanic apparatus" of Alessandro Volta. The work was published in Nicholson's *Journal of Natural Philosophy, Chemistry, and the Arts*, where it caught the attention of a poetic young experimenter by the name of Humphry Davy. Immediately, Davy began to wonder what other kinds of electrochemical changes might be possible with that marvelous new invention: the battery.

Davy's electrochemical investigations were interrupted in 1801 when he was appointed to a lectureship at the Royal Institution. Davy was a highly successful public speaker. His science lectures became as popular and as fashionable as the latest piece of literature. The stylish London audiences were thrilled to have the latest advances in physics and electrochemistry reproduced before their eyes.

In addition, the income helped sup-

Experiments In Electrochemistry

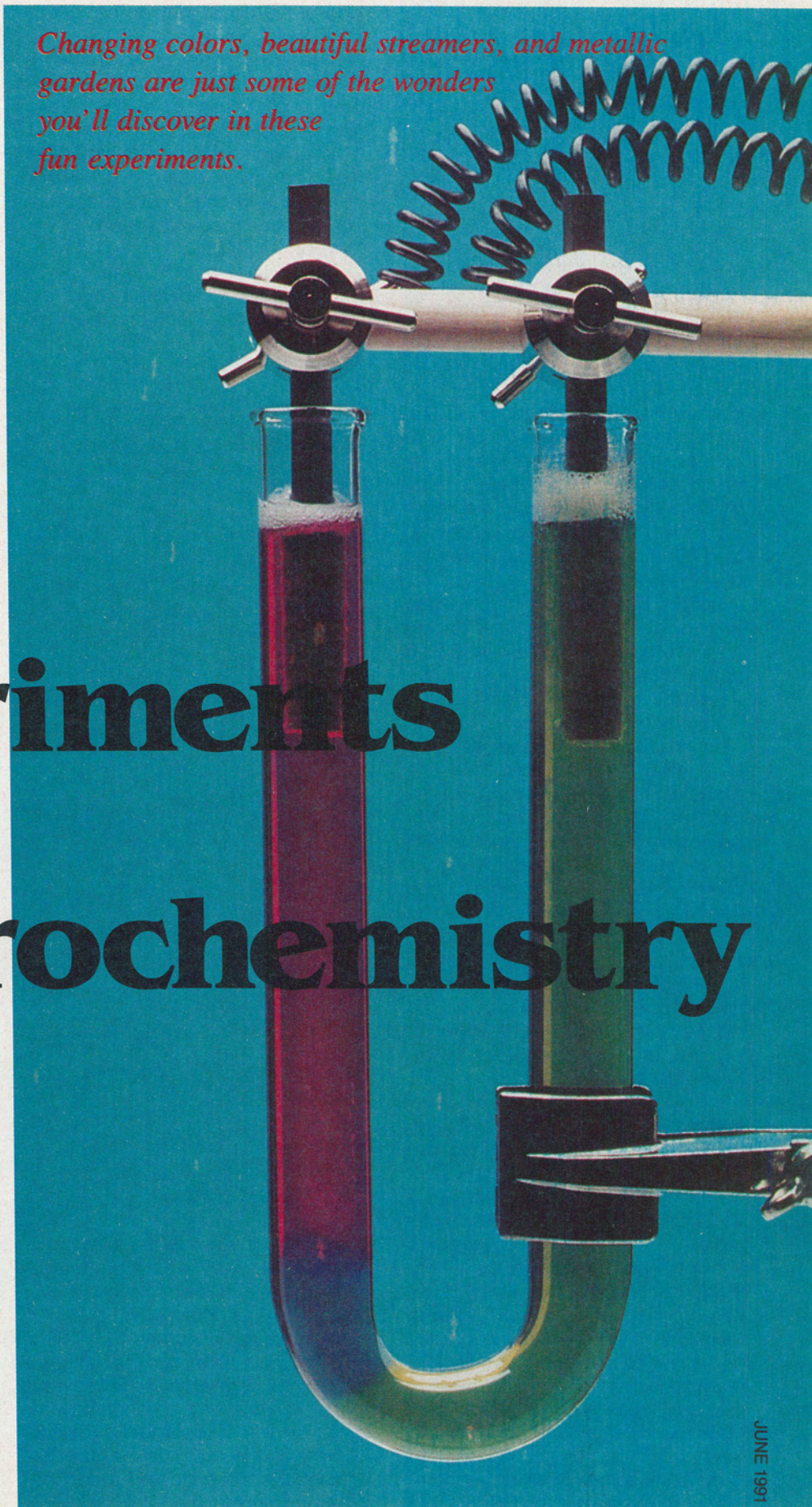
BY
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port the Royal Institution and provided the money necessary for the pursuit of natural philosophy in a well-equipped workshop. And that's just what happened. Humphry Davy's large London laboratory became one of the finest in all of western Europe.

The Discovery of Potassium. Davy returned to his electrochemical studies in 1806. His thinking on the subject was already very far advanced. He was confident that with the new electrochemical techniques, it might someday be possible to identify and even manipulate the "true elements" of the physical world.

In 1807, Davy began a famous series of experiments involving the decomposition of potash (potassium carbonate). He placed a small amount of

Changing colors, beautiful streamers, and metallic gardens are just some of the wonders you'll discover in these fun experiments.



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potash into a platinum spoon and attached the spoon to the positive pole of a battery. A flame was placed beneath the spoon to melt the chemical. When a wire connected to the negative pole of the battery was touched to the hot potash, a ball of fire appeared over the point of contact.

Humphry Davy knew that something special was being collected at the negative wire. He also knew that a slightly different technique would be necessary in order to isolate the collected material.

So, he moistened the potash with a bit of water to make it conductive and repeated the experiment without the heat. This time, tiny metallic globs appeared at the end of the negative wire. Some of the pieces, once again, caught fire; but some remained and became covered with a white film.

Here, at last, in free form, was the material he had been looking for. He called it potassium, one of the "true elements" from which potash is made. The results of the experiments were reported to the Royal Society on November 19, 1806.

Leaves and Seeds. Davy's discovery of potassium, as well as sodium and a number of other alkali metals, has become a classic example of electrochemical decomposition. But there's more: A close reading of Davy's lecture "On Some Chemical Agencies of Electricity," delivered originally in 1806, reveals work with various organic materials like laurel leaves, mint plants, and strips of beef. He even experimented with seeds. In a somewhat cryptic footnote, he says: "Seeds, I find, when placed in pure water in the positive part of the circuit, germinate much more rapidly than under common circumstances; but in the negative

part of the circuit they do not germinate at all."

Clearly, Humphry Davy was fascinated by the physical transformations which so often occur in electrochemical circuits of all kinds. Indeed, he even imagined certain similarities between the effects of electrochemical change and the mystic visions of the alchemical philosophers. Maybe you will too.

Early Warning. There's no getting around it: the chemicals and reactions

PARTS AND MATERIALS LIST FOR EXPERIMENTS IN ELECTROCHEMISTRY

Copper sulfate
Hydrochloric acid, 20% solution (muriatic acid)
Potassium iodide
Red cabbage, shredded
Sodium bisulfate
Sodium chloride (table salt)
Tin chloride
Burette clamp
Carbon rods (2)
6-12-volt DC power supply
Glass vessels for mixing and storage
Hook-up wire
Ringstand
Two-way rod clamps (3)
U-tube, 6 inch (Hagenow catalog no. 42, or similar)
Wooden dowel-rod

Note: Chemicals, glassware, and laboratory equipment are available from the following suppliers:

Hagenow Laboratories, 1302 Washington Street, Manitowoc, WI 544220. The Hagenow catalog is \$1.50

Chem-Lab Supplies, 1060-C Ortega Way, Placentia, CA 92670. Tel. 714-630-7902. The Chem-Lab catalog is \$5.00

Analytical Scientific, Post Box 675, Helotes, TX 78023. Tel. 512-684-7373. The Analytical catalog is \$3.00.

discussed in this article are potentially dangerous. Every effort has been made to minimize the risks involved. But, the possibility of an accident still exists.

Please keep all of the following in mind while running your experiments:

- Do not allow any of these solutions or materials to come into contact with your hands, arms, fingers, face, or clothing. Take no chances whatsoever with poisonous or corrosive substances.
- Perform all experiments in a well-ven-

tilated room. The room should be free of any open fire or flame. Keep your face away from the apparatus and do not inhale any gas or chemical dust.

- Do not experiment with large quantities of any chemical solid or solution. For one thing, it's just not necessary. All of the effects discussed are perfectly visible in a small vessel containing only a small amount of conductive material.
- If at all possible, use regular laboratory glassware. Chemicals do not belong in pots, pans, plastic cups, and paper plates. They do belong in glass beakers, flasks, tubes, and graduates.
- Be very careful not to spill anything. Accidental spills can be very frightening and very hazardous. Work slowly and pay close attention to what you're doing. When transferring solutions from one vessel to another, use a good glass funnel whenever necessary.
- Do not, under any circumstances, work on a valuable surface. Run your experiments, for example, on a heavy slab of plywood that will never be used for anything else.
- Never store chemicals of any kind in unmarked containers. Keep a supply of gummed labels handy and put one on every beaker, bottle, or jar containing any type of experimental substance whatsoever.

Setting up your Lab. Electrochemical experimentation involves the use of some specialized hardware and glassware. You'll need some electrodes, a U-tube, and a dependable way of holding the whole system in a stable vertical position. A good many electrochemical effects require electrodes made of a material that will not react with the conductive solution (electrolyte). One such material is carbon. Carbon rods (you'll need at least two) may be obtained by cutting open a

FURTHER READING

On Some Chemical Agencies of Electricity, Humphry Davy., W. Blumer, 1807

Great Scientific Experiments, Rom Harre, Oxford University Press, 1983

"The Chemical Philosophy of Humphry Davy," Robert Siegfried, *Chymia*, Volume 5, pp. 193-201, 1959

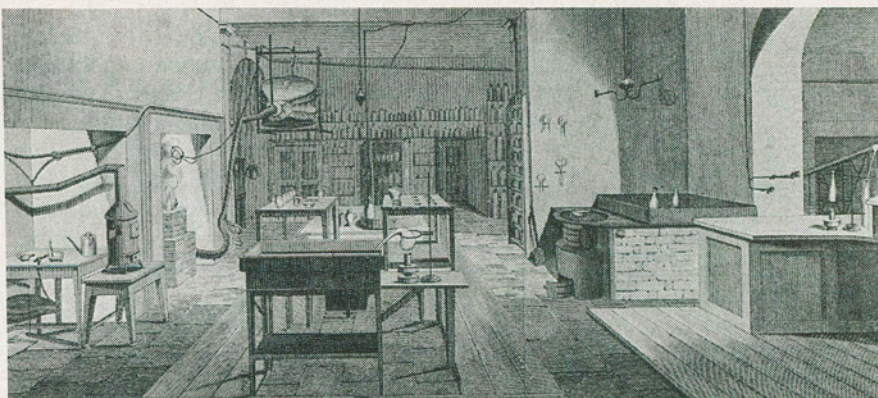
Chemistry Magic, Kenneth Swezey, McGraw-Hill, 1956

"Humphry Davy," L.P. Williams, *Scientific American*, Volume 202, pp. 106-116, June 1960

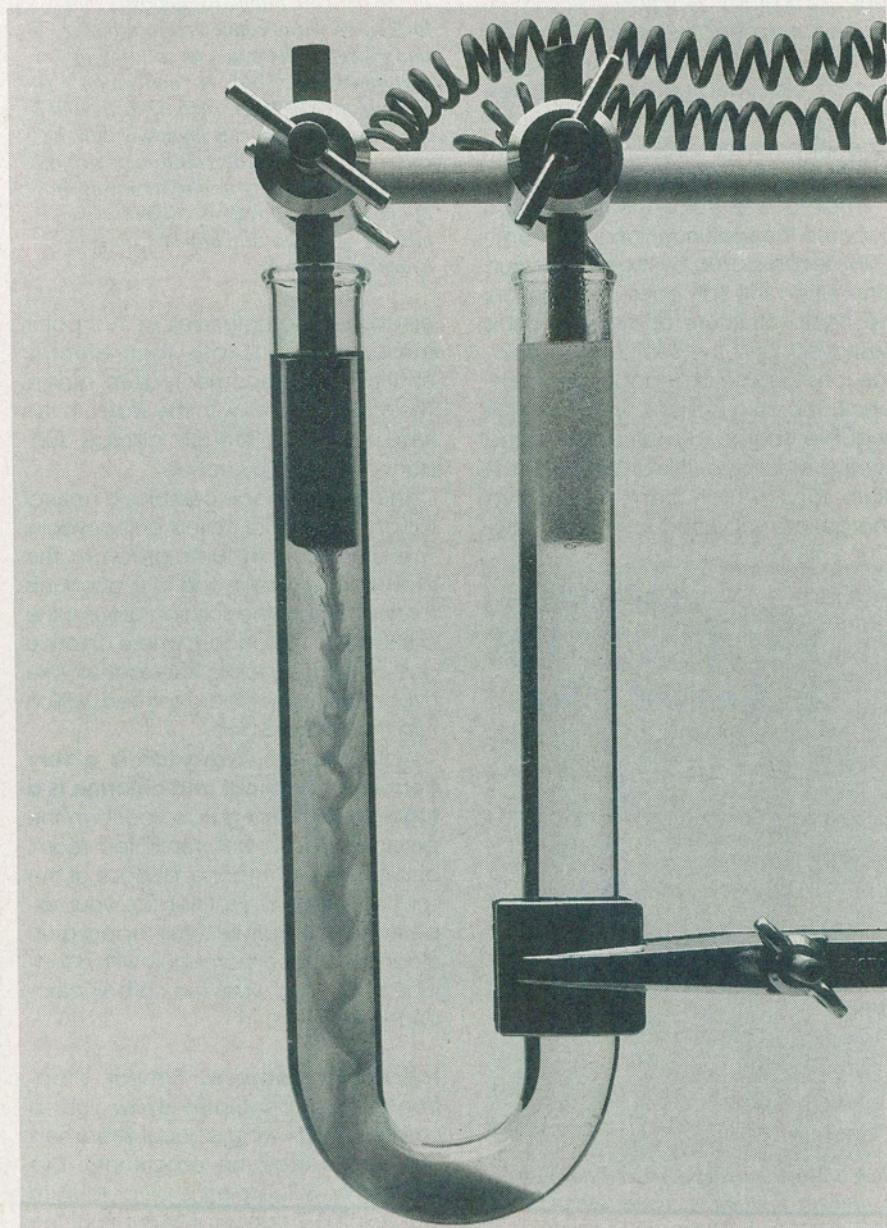
couple of ordinary 1.5-volt dry cells. Do not use nickel-cadmium or lithium batteries; they do not contain carbon.

Good quality carbon rods are also available at many large building supply stores in the form of carbon-arc welding rods. Such rods are often covered with a thin layer of copper. The copper coating can usually be removed by slitting the material with a sharp knife and then, very gently, peeling it off. The carbon electrodes in the photographs are about a $\frac{1}{4}$ inch in diameter and were cut to a length of about 3 inches each.

Next, you'll need a peculiar piece of laboratory glassware sometimes called a U-tube. A clear glass U-tube will ac-



Humphry Davy's large laboratory at the Royal Institution in London was one of the finest in all of western Europe. It was here that Davy performed his famous electrochemical experiments in the early years of the 19th century. This engraving appeared originally in William Thomas Brande's Manual of Chemistry (1819).



The electrochemical decomposition of potassium iodide in water releases iodine at the positive electrode. The iodine dissolves in the potassium-iodide solution and sinks down to the bottom of the tube.

commodate the carbon rods nicely and provide an unobstructed view of the electrochemical reactions. U-tubes come in a number of sizes. The examples in the photographs are about 6 inches long and hold about $1\frac{1}{2}$ fluid ounces (or about 50 ml).

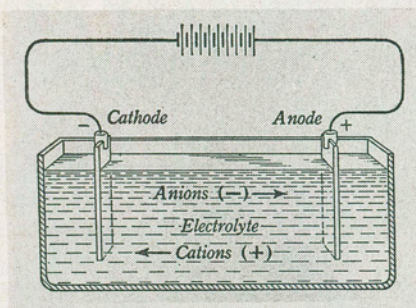
U-tubes are available from many laboratory supply houses. If you can not locate one locally, they can be bought through the mail from Hagenow Laboratories, a science supply company in Wisconsin. The catalog number is 42 and the 6-inch length must be specified. See the Parts and Materials List for more information.

When you get your U-tubes, order several, if possible. U-tubes are difficult to clean and notoriously easy to break.

Finally, we must deal with the problem of holding the entire electrochemical system in a stable vertical position. That can be done by attaching the U-tube to a ring stand with a burette clamp and suspending the carbon electrodes over the U-tube from a non-conductive wooden dowel rod. The carbons are fastened to the wooden rod with a couple of two-way laboratory rod clamps. The power cables are then connected directly to the rod clamps. The wooden rod is attached to the ring stand with another two-way clamp.

That arrangement facilitates wiring and makes it easy to remove the electrodes for cleaning. If you do not wish to reproduce the electrode support structure that appears in the photographs, a similar mechanism can be made with a couple of large alligator clips. You can even use modified clothespins.

Complete the set-up by attaching the carbon rods to a variable 6–12-volt DC power supply with two long pieces of hook-up wire. And remember, polar-



All simple electrolytic systems operate in the same way. A direct current of electricity is applied to a conductive solution. The conductive solution is usually called an electrolyte. All conductive solutions contain ions. The ions that carry a negative charge (anions) are attracted to the positive electrode (anode); the ions that carry a positive charge (cations) are attracted to the negative electrode (cathode).



Ordinary table salt (sodium chloride) dissolved in a cup of dilute red cabbage juice makes a conductive solution that will actually change color when subjected to the influence of a direct current of electricity. The solution around the negative electrode will turn green. The solution around the positive electrode will become a pinkish-red.

ity is important, so check to make sure you know which electrode is which before you start experimenting.

Chameleon Colors. One of the simplest, as well as one of the prettiest, electrochemical experiments you can perform involves the use of little more than tap water, table salt, and a bag of red cabbage. It's an experiment you'll want to perform again and again for your family and friends. Here's what to do:

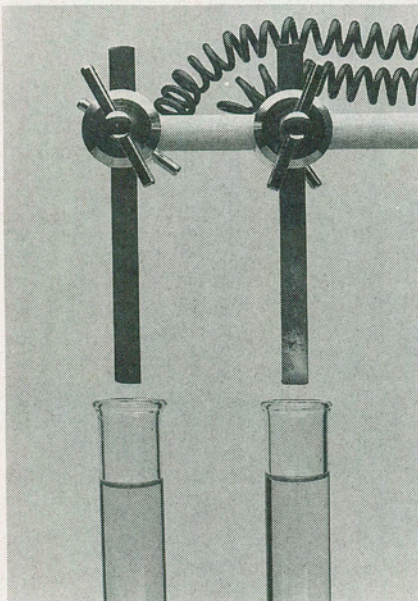
Obtain some fresh red cabbage at the local supermarket. If possible, get the pre-shredded kind; it's a lot easier to work with. Place one large handful of cabbage in a heat-resistant container and add 7 or 8 ounces of plain water. Now, boil the mixture until the liquid becomes a deep purplish-red. Allow the vessel with its contents to cool. Pour the red cabbage extract (the liquid) into a labeled bottle and save it. You've made enough extract for several demonstrations.

When you're ready for the experiment, mix about 1 ounce of cabbage extract with about 1 ounce of clear water. Then add about ½ teaspoon of sodium chloride (ordinary table salt) and agitate the mixture to dissolve as much of the solid as possible. The liquid should now be a semi-transparent grayish-blue or bluish-purple.

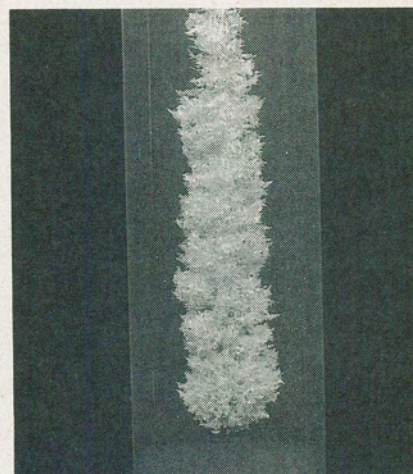
Now, set up one of your U-tubes and fill it with the red-cabbage/sodium-chloride solution. Then, insert the two carbon electrodes. For a good visual effect, illuminate the tube from the rear with small desk lamp.

Finally, plug in your power supply and turn up the voltage until the electrodes begin to bubble. Keep your eyes on the tube. Almost immediately, the mixture around the negative electrode turns green, while the solution around the positive electrode becomes an iridescent pink. In a few minutes, the entire tube will become occupied by the two electrochemical colors.

What you see inside the tube occurs because the sodium chloride is chemically decomposed by the electric current. When the salt goes into solution, the crystal structure of the material is destroyed, and the sodium and chloride ions assume an independent existence. The chloride ions, which carry a negative charge, are attracted to the positive electrode (the anode). The sodium ions, which carry a positive charge, are attracted to the negative



When a direct current is passed through an aqueous solution of copper sulfate, pure copper will appear on the negative electrode (the one on the right). Sodium bisulfate has been added to the solution to improve its conductivity.



Early in the 19th century, Freiherr Theodor Von Grothus became interested in the delicate plant-like deposits that formed on wires connected to a battery and placed in an aqueous solution of certain metallic salts. He noticed a resemblance between such deposits and the crystalline growths known within the European alchemical tradition as arbores (trees). Here, a tiny tree of tin forms on the negative electrode in a conductive mixture of water, tin chloride, and hydrochloric acid.

electrode (the cathode). At that point, the sodium ions lose their electric charge and become sodium atoms. The sodium unites with the water in the tube to form a strongly alkaline substance, sodium hydroxide.

The red cabbage contains a natural indicator material called anthocyanin. The anthocyanin turns green in the presence of alkalis, and that accounts for the color of the solution around the cathode. At the anode, where chlorine gas develops, acidic substances (like hypochlorous acid) are formed, which turn the indicator red.

Note: **Sodium hydroxide is a very corrosive chemical and chlorine is a highly poisonous gas**, so perform the experiment in a well-ventilated room, and, when you're done, dispose of the solution properly. To finish up your experiment, dismantle your apparatus, clean the U-tube thoroughly with a test-tube brush, and wash the carbon electrodes.

Iodine Streamers. Similar electrochemical principles allow you to create long, flowing, sinuous streamers of iodine. Here's the experiment: Dissolve 2 or 3 teaspoons of potassium iodide in 1-1/2 ounce of water. Pour the solution into your U-tube and insert the electrodes.

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When a current is applied to the solution, the iodide ions, which carry a negative charge, are attracted to the positive electrode. There, atoms of iodine are formed as the ions lose their electric charge. Immediately, the iodine sinks and dissolves in the potassium iodide solution, leaving the streamers as they fall. If the power is left on for a few minutes, the material will begin to accumulate at the bottom of the tube.

Note: **Iodine is very poisonous stuff. Please be extremely careful with it. Do not spill the solution, and throw it away as soon as you're through.**

Homemade Copper. Here's how to make your own copper metal in a matter of minutes. The copper can't really be used for anything; the quantity created is much too small. But still, it's genuine electrolytic copper.

Place 1 teaspoon of copper sulfate in 1½ ounces of water. Agitate the liquid until the solid has dissolved. Now, to improve the conductivity of the solution, add a ½ teaspoon of sodium bisulfate.

Pour the solution into a clean U-tube, insert your electrodes, and turn on the current. The copper ions, which carry a positive charge, are attracted to the cathode. And there, at the lower end of the negative electrode, you'll soon see a thin layer of reddish-brown copper.

Note: Copper sulfate is sometimes used to make insecticides and sodium bisulfate is sometimes used to clean drains. Both of these chemicals are **highly poisonous** and should be treated with a great deal of respect. Be very careful with the solution, and, when you're finished, dispose of it quickly.

Metallic Vegetation. Humphry Davy wasn't the only one running electrochemical experiments in the early years of the 19th century. Another observer of galvanic effects was a young German nobleman by the name of Freiherr Theodor Von Grotthaus. Von Grotthaus was living in Rome at the time.

Von Grotthaus became interested in the delicate plant-like deposits that formed on wires connected to a battery and placed in an aqueous solution of certain metallic salts. He noticed a resemblance between such deposits and the crystalline growths known within the European alchemical tradition as

arbors. Arbor, or *arbo*, is a Latin word meaning tree. Arbors appeared when one metallic material in a solution was displaced by another.

Von Grotthaus found that the old alchemical arbors could be produced with electricity. Writing in 1807, he called all such growths *vegetation metallique* (metallic vegetation). But, do the formations really resemble vegetation? Let's find out:

Place about ⅛ teaspoon of tin chloride in 1½ ounces of water. That's not a lot of chemical; but, for our purposes, a little goes a long way. Now, very carefully, add ½ ounce of hydrochloric acid, 20% solution. Wait a few minutes for the undissolved solid to settle to the bottom of your mixing vessel. Note: Hydrochloric acid at 20% concentration is available at many hardware stores where it is also known as muriatic acid.

Please remember that hydrochloric acid is a corrosive and poisonous material. It's nasty stuff, and you must be extremely careful when working with it. Moreover, **the electrolysis creates a small amount of poisonous chlorine gas, so perform the experiment in a well-ventilated room. Hydrogen, a combustible gas, is also released, and that means keeping all open flames far away from your equipment.**

The arbor requires a special surface on which to grow. Obtain a 3- or 4-inch piece of stranded hook-up wire and remove all of the insulation. Twist the bare copper strands into a firm cable and straighten the piece with your fingers. Next, replace the negative carbon rod with your new stranded-wire electrode.

When the electrode is ready, pour the tin-chloride/acid mixture slowly and carefully into your U-tube. Note: If the solution is cloudy or milky to the point of being opaque, you've used too much tin chloride. Lower the electrodes into the tube and make sure the twisted wire is connected to the negative side of your power supply.

Next, turn on the current and watch the wire. Within seconds, the electrode becomes covered with a mass of bubbles. Then, tiny fern-like laminations of pure tin begin to appear on the surface. The arbor grows before your eyes and soon extends a dense collection of gleaming crystal branches down towards the bottom of the tube.

Von Grotthaus was right. It really does look like something pulled from some weird electrochemical garden. ■