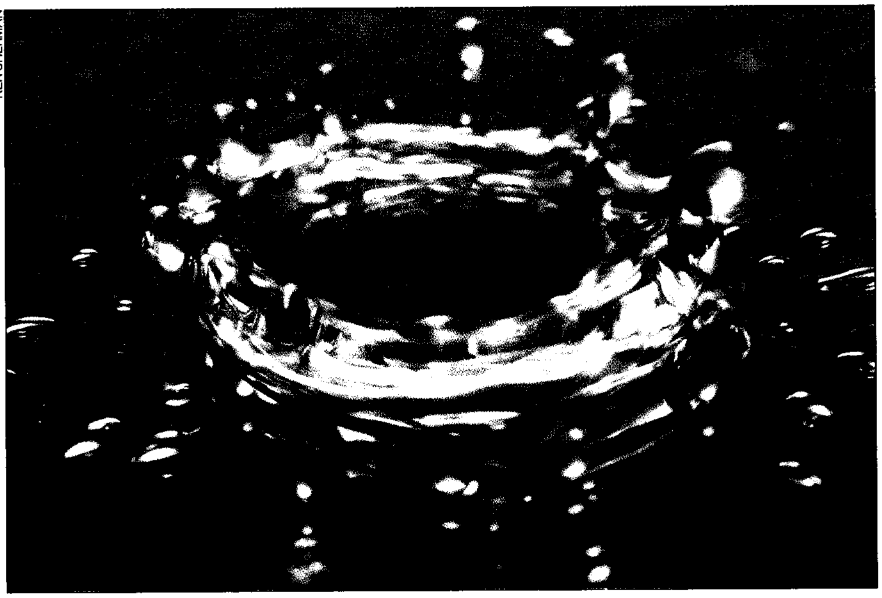
SPLITTING WATER

KEN SHERMAN



The fuel of the future may be hydrogen gas, separated from water by artificial photosynthesis

by PAMELA WEINTRAUB

I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light...
—Jules Verne, 1874
The Mysterious Island

Like so many other of Jules Verne's writings, this prophecy may become reality. If the hydrogen on earth were readily accessible, it could become a major and virtually unlimited source of energy. Passed through fuel cells, it could generate electricity. Cooled and liquefied, it could serve as fuel for modified internal-combustion engines; in liquid form it contains two and a half times the energy of an equivalent weight of gasoline. And hydrogen has a great environmental advantage as a fuel: the product of its combustion is water.

But most terrestrial hydrogen is locked up, bound with oxygen in the form of water. Electric current, passed through water in a process called electrolysis, can break that powerful bond, releasing hydrogen as well as oxygen. But there is one important drawback: the amount of electricity needed to produce practical amounts of hydrogen is prohibitively expensive. Nature has a better way. For hundreds of millions of years, green plants have been splitting water into hydrogen and oxygen with chloroplasts, tiny cellular factories energized only by the rays of the sun.

Now man is copying nature. Nobel laureate Melvin Calvin, a chemist at the University of California at Berkeley, has produced synthetic chloroplasts. Natural chloroplasts, found in the cells of green plants, are disc-shaped structures that manufacture the basic carbohydrates needed to sustain nearly every creature on earth. They produce this food by photosynthesis, a chemical process involving sunlight, water, and carbon dioxide. In essence, sunlight striking a chloroplast splits hydrogen from water, allowing the hydrogen to combine with carbon dioxide from the air to form the carbohydrates needed for the plant's growth. The oxygen released from the split water molecules drifts away to become part of the atmosphere.

Calvin's artificial chloroplasts—minute spheres of oil floating in water in his Berkeley laboratory—are different from the real thing in one essential way: they are not designed to help hydrogen combine with carbon dioxide to form new plant material. Instead, as the diagram on the opposite page shows, they release hydrogen in the form of a gas.

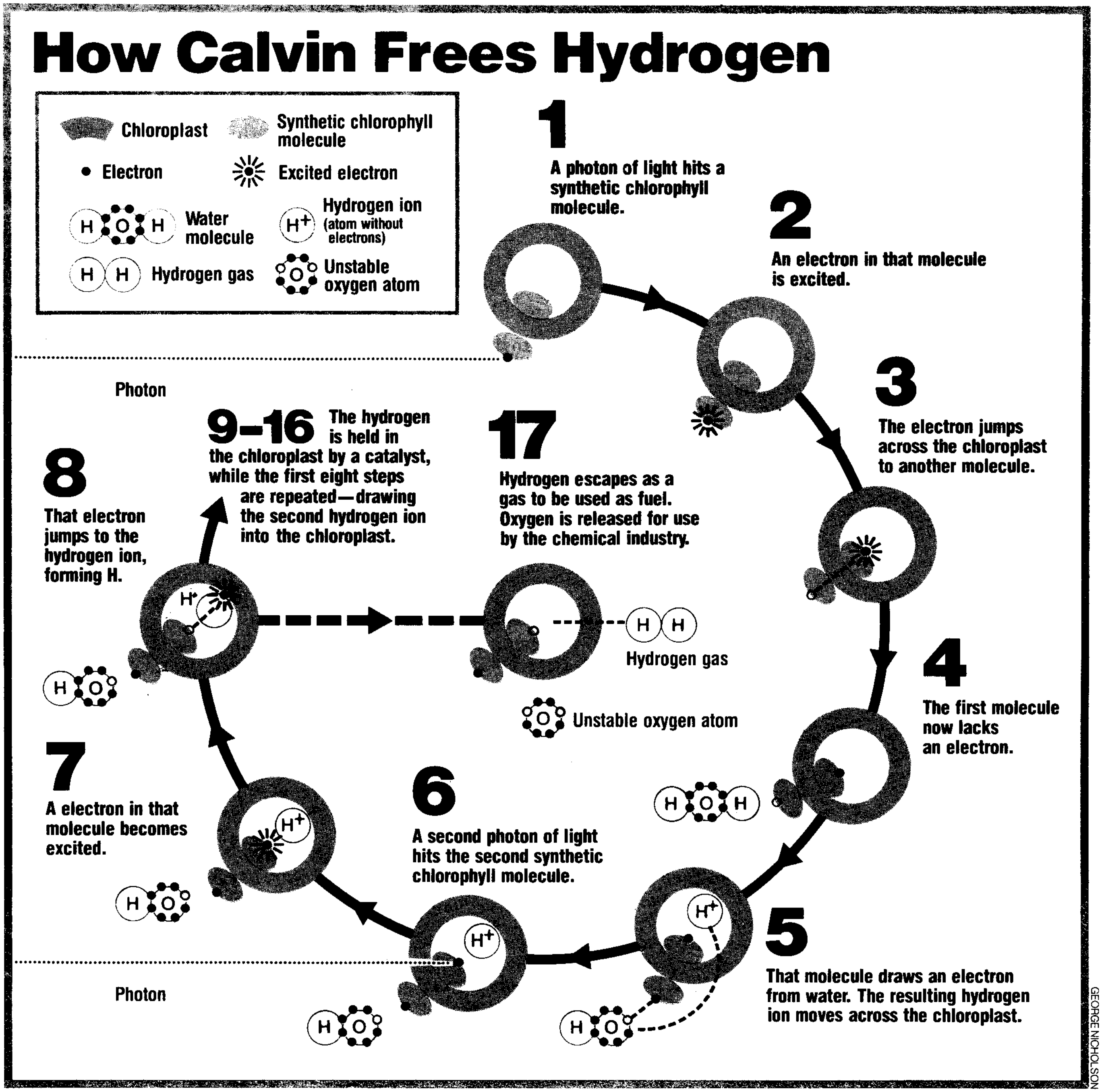
When Calvin completed mapping the photosynthesis of carbohydrates, the feat for which he won his Nobel in 1961, some scientists believed that the day was not far off when ample quantities of hydrogen could be produced economically. Achieving that goal, however, turned out to be extraordinarily difficult. It required learning about the hundreds of chemical reactions that take place during the first phase of photosynthesis. Calvin and others have spent the past 20 years trying to decipher those reactions.

What they finally unraveled was a wondrously complex process. The membranes surrounding a natural chloroplast are lined, inside and out, with molecules of chlorophyll, the green pigment that gives a plant its color. Whenever a photon, a unit of light, strikes a chloroplast, energy is transferred to an electron in a chlorophyll molecule. The energized electron leaps from the molecule, leaving it with a "hole" that would ordinarily pull the electron back. But the electron passes through the chloroplast membrane, which traps it and allows it to be captured by a second molecule of chlorophyll located inside the membrane.

At this point water, brought up through the roots and present in the plant tissue, enters the reaction. Because the chlorophyll molecule has lost an electron and has a hole, it is unstable. Seeking a replacement, it pulls an electron from a molecule of water. Now the water molecule becomes unstable. But because it can find no replacement for its electron, it breaks up, losing one of its two hydrogen atoms in the process. That hydrogen, now stripped of its electron and in the form of a positively charged ion, passes through the membrane to the interior of the chloroplast. A second photon then supplies the remaining energy needed to combine the captured electron with the hydrogen ion and carbon dioxide that the chloroplast absorbs from air. The steps are repeated to split the second hydrogen atom from water, and oxygen escapes to the atmosphere. The result of all this: carbohydrates.

From the time the first photon of light strikes the plant until the second photon strikes, only a few billionths of a second pass.

In the cycle diagrammed below, a synthetic chloroplast splits a single molecule of water, shown at stage 4, into the hydrogen and oxygen gases shown as atoms at stage 17



JOHN MCDERMOTT

Melvin Calvin with light-testing equipment used in developing the synthetic chloroplast

After that, the reactions leading to the formation of carbohydrates require five or six minutes. Calvin decades ago identified these later reactions, but they are irrelevant to the process of splitting water. In order to separate hydrogen from water in usable form—as a gas—Calvin had to alter the initial interplay between particles and catalysts, complex chemicals that help the reaction to occur.

Scientists are still trying to determine the precise chemical structures of the catalysts and the detailed sequence of events in the first part of the reaction. But by the early 1970s Calvin and others had learned enough to produce small quantities of hydrogen gas by altering photosynthetic reactions within real chloroplasts: they isolated chloroplasts from spinach and added natural catalysts that prevented electrons and hydrogen ions from combining with carbon dioxide. Instead of forming carbohydrates, hydrogen escaped to the atmosphere as a gas. As a result, many scientists came to believe that hydrogen-producing chloroplasts harvested from vast green fields of spinach would one day provide energy for all of civilization.

But Calvin eventually had to face the fact that for billions of years evolution had honed green plants to synthesize carbohydrates, not produce hydrogen fuel. Thus plant chloroplasts proved at best to be only 4 per cent efficient in generating hydrogen gas. Calvin speculated that man-made chloroplasts would be about 30 per cent efficient, giving them a better than sevenfold advantage over the natural variety. He also reasoned that synthetic chloroplasts would last longer; real chloroplasts degenerate rapidly.

The artificial chloroplast developed by Calvin over the past few years is far simpler than the natural one, but it functions in much the same way. To build it, Calvin substituted synthetic molecules for the plant molecules and tried to mimic the complex electron pathways. To imitate chlorophyll's light-absorbing and water-splitting ability, he synthesized dyes from chemical compounds called porphyrins. He used metals like platinum and ruthenium and organic chemicals like viologen to create artificial catalysts that released hydrogen instead of transforming it into carbohydrates. He even created artificial membranes by mixing water with fatty substances called phospholipids to form spheres about a millionth of an inch in diameter, roughly the same size as the smallest natural chloroplast. It all seems to work; the artificial chloroplasts now floating in test tubes at Calvin's lab release tiny bubbles of hydrogen and oxygen.

Calvin is currently working on a device that will both generate and gather these products; it is essentially a water-filled glass cylinder containing hundreds of hollow tubes, each about six inches long and thinner than a human hair. Made of the same kind of membranes used in kidney dialysis machines, these fibers function like long, thin chloroplasts. Whenever the sun shines, photons strike the dyes and catalysts embedded in the membrane walls, generating a stream of hydrogen gas at one end of the cylinder and oxygen at the other. "We haven't perfected the system yet, and no doubt there will be lots of unforeseen mechanical problems," Calvin says. "But I don't see any fundamental scientific difficulties."

Although Calvin's major goal is the efficient generation of hydrogen, the first commercial use of the artificial chloroplast may well be to produce oxygen. For instead of releasing oxygen gas to the air in its normal, molecular form (O_2), the artificial chloroplast generates highly unstable atomic oxygen (O). Because this type of oxygen is used in making fibers, foams, and many other materials, Calvin believes that there would be an immediate market for his synthesizer; it could make atomic oxygen at a fourth of the current cost. He predicts that "people who make useful products with oxygen will invest money to build synthetic chloroplast factories." Then, he believes, the availability of the other product of these factories—hydrogen gas—will encourage the building of engines, furnaces, and other devices that can use hydrogen gas as fuel. Once these devices are developed, he says, "the hydrogen will become more important than the oxygen, and factories turning out only hydrogen will be the result." ■