

The Conference, the Chloroplast, the Charisma

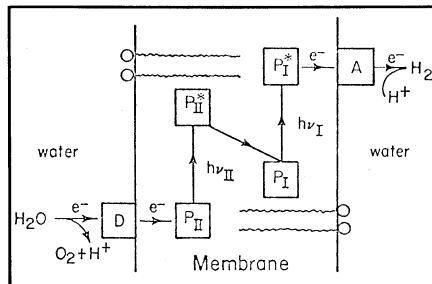
It seemed appropriate at the solar energy conference last week in Boulder, Colo., that the first spotlight should shine on Melvin Calvin. For forty-five years, this University of California at Berkeley chemist has pioneered several different areas of research that relate to the subjects included at the conference. And Calvin broke exciting ground in opening the meeting—the Third International Conference on Photochemical Conversion and Storage of Solar Energy sponsored by the Solar Energy Research Institute (SERI)—when he presented the culmination of “a lifetime” in the field of green plants and energy conversion: a report on the development of a synthetic chloroplast.

A synthetic chloroplast mimics the ability of plant chloroplasts to convert solar energy to stored chemical energy. In natural chloroplasts, sunlight is captured at the photosynthetic membrane where it drives the reaction, $H_2O + CO_2 \rightarrow$ stored chemical energy + O_2 . The photosynthetic job is done in two steps: Photosystem I (PS I) generates electrons; Photosystem II (PS II) generates oxygen. While the electrons generated in green plants furnish the power to convert the CO_2 to sugar (stored chemical energy), those generated in synthetic chloroplasts can combine with hydrogen ions (H^+) to produce molecular hydrogen (H_2), an alternative fuel source.

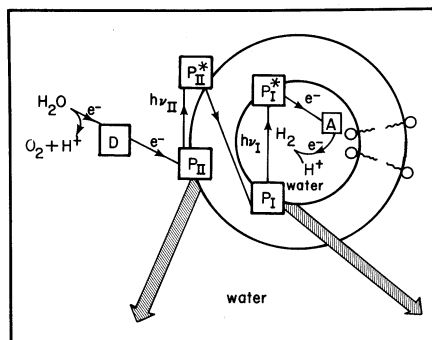
But the novelty of Calvin's synthetic model lies not in the production of molecular hydrogen—other systems have achieved this—but rather in its analog to the oxygen-generating step of photosynthesis. In Calvin's system this process begins when light “excites” a complex manganese (Mn)-containing molecule, causing it to pass an electron to an acceptor (A) molecule. After a second light reaction, the resulting molecule, Mn^{IV} , splits water, scooping up the oxygen atom.

The oxygen atom kidnapped by the manganese molecule is a highly reactive atom that can be picked up by any other molecule with an unshared electron pair. “That's the message; that's the thing that is different,” Calvin says. “Rather than making [molecular] oxygen [O_2] we've caught the oxygen atom.” Because the captured atom is highly reactive, it can be used to oxidize other molecules, forming useful products that now are expensive to synthesize. Propylene oxide, for example—4 billion tons are produced annually in the United States for foams, fibers and film—could be synthesized in Calvin's chloroplast by allowing a propylene molecule to pick up a kidnapped oxygen atom.

The hydrogen-generating and oxygen-capturing systems of Calvin's design occur across artificial membranes called vesi-



Simplified version of Photosystems I and II in the membrane of the chloroplast.



Model version of a photosynthetic vesicle.

cles, the spherical membranes composed of two layers of fat (phospholipids) that lie tail-to-tail (diagrammatically represented by a zig-zag line attached to the round “head” of the phospholipid). In the oxygen-capturing system, the manganese complex inside the vesicle passes its excited electron to an acceptor molecule on the outside surface of the vesicle. In a separate vesicle, an electron-donor molecule on the vesicle surface must pass an electron to an appropriate molecule inside the vesicle to drive the hydrogen-evolving reaction.

And therein lies the major wrinkle in Calvin's artificial chloroplast: The oxygen-capturing and hydrogen-generating systems are not coupled. In natural chloroplasts, the two photosystems are connected so that the electron-acceptor in PS II becomes the electron donor in PS I. This gives green plants a perfect catalytic method for splitting water. In Calvin's system, acceptor and donor molecules must be continually fed into the system because they are not recycled. But Calvin is optimistic about combining the different components of the artificial system into one comprehensive system; after all, he says, “The coupling was achieved long ago in nature.”

Calvin's work on the synthetic chloroplast is one of several paths being paved in the field of photochemical conversion. While Calvin is attempting to mimic the overall reactions of photosynthesis, other researchers—James Bolton and colleagues at the University of Ontario in London (SN: 8/2/80, p. 68), for example—are concentrating on individual steps of photosynthesis, building models for each component of the process. Still other researchers—such as Michael Grätzel of the Institut de Chimie Physique in Lausanne, Switzerland—are concerned with photochemically generating hydrogen fuel using systems that do not model the photosynthetic process.

But all paths cross the same finish line, filling this field with competitive spirit. “There is a lot of credit, a lot of money and several Nobel Prizes at stake,” Grätzel explains. When water is finally photochemically and efficiently split, “the world's energy problems will be solved.” And, says Grätzel, “We're close to home now.” □

