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SOLAR ENERGY BY PHOTOSYNTHESIS: ARE WE ABLE TO RAISE ENOUGH CANE TO GET IT?

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SOLAR ENERGY BY PHOTOSYNTHESIS:

ARE WE ABLE TO RAISE ENOUGH CANE TO GET IT?*

Melvin Calvin**

ABSTRACT: Photosynthesis, both natural and as a model process, is examined as a possible annually renewable resource for both material and energy. The conversion of carbohydrate from cane, beets and other sources through fermentation alcohol to hydrocarbon may soon again become economic in thelight of increasing costs of recovery of hydrocarbon from fossil sources and improved fermentation technology. Even the direct photosynthetic production of hydrocarbon from known sources (*Hevea*, etc.) or newly bred ones seems possible. Finally, more distantly, synthetic systems constructed on the basis of growing knowledge of the photosynthetic processes, may produce both fuel and power.

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* Transcription of address presented at Stanford University Energy Seminar Series, Stanford, California, Jan. 28, 1974.

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INTRODUCTION

Current solar energy utilization is quite different from discussions of fossilized solar resources. As yet, we do not have any strong indication as to the nature of its environmental disadvantages. I plan to discuss the way in which photosynthetic solar energy conversion can be used to help us in our present and future energy problems.

An examination of the energy flow patterns in the United States [1,2] shows that electrical generation is supplied from all sources of energy, including hydro, geothermal and nuclear, while non-energy uses (chemicals, plastics, etc.) depend mainly on liquid petroleum sources, with some contribution from coal and gas. Also, when resources are used for energy value only, roughly half is lost in non-useful ways. Finally, note that 6% of the total fossil resource input is for a non-energy end use, i.e., as a mat erial or as a chemical source. I wish to emphasize this "material" use as a target for renewable resources in a later discussion.

One set of factors causing us to be concerned with this energy flow pattern is the cost of hydrocarbons (natural gas and petroleum) which are the major source of energy as well as hydrocarbon material source for chemicals.[2] The price of hydrocarbon has risen considerably, and I am sure that most of you have had your personal experience with this factor. Average fossil fuel prices in the United States at the point of production have remained fairly constant for nearly a decade and then began a rather precipitious rise in 1970. The commercial price of LPG, for example, rose (at a retail level) from 20¢/gallon (0.13×10^6 Btu*) six months ago to 40¢/gallon last week (January 1974). This propane-butane mixture comes mostly from liquid hydrocarbon and is somewhat more expen-

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* A million Btu of natural gas is about 1000 cu ft: a barrel of oil contains about 5.8 million Btu.

sive than natural gas, which is mostly methane. Because the prices of such materials are rising so steeply, many of the suggestions which appear here will become realistic in economic terms whereas they may not have been realistic even as late as a year ago.

You should, of course, recognize that all three of the materials mentioned above (oil, coal, natural gas) are the result of photosynthetic conversion of solar energy, which has accumulated over geological time. We are using these materials at a rate very much faster than they are being accumulated each year. The question now arises as to whether we can make direct use of the solar energy every year as we run out of the stored energy which the hydrocarbon represents.[1b] In order to make some estimate of this possibility, we must evaluate the magnitude of the solar energy resource. The highest annualized impingement is in the region of the Sahara Desert ($\sim$280 w/m^2*) and there is another high intensity region in the southern United States and Northern Mexico (about 260 w/m^2). Let's relate that to the solar energy constant, i.e., the total energy of the sun coming in at normal incidence outside the earth's atmosphere, which is about 2 cal/cm^2/min or 1 kw/m^2. Only about half of that reaches the earth's surface, and this amount varies considerably, depending upon the weather conditions. Figure 1 is a map of the United States showing the annual average insolation annualized over day and night, winter and summer, to take care of the variability which exists. You can see the region in the 260 w/m^2 contour line, consisting of most of New Mexico and Arizona with parts of Nevada and Southern California. The other high points are in Southern Florida and in Southern Louisiana, and I will refer to these last two regions later in the discussion, in connection with agricultural solar energy conversion.

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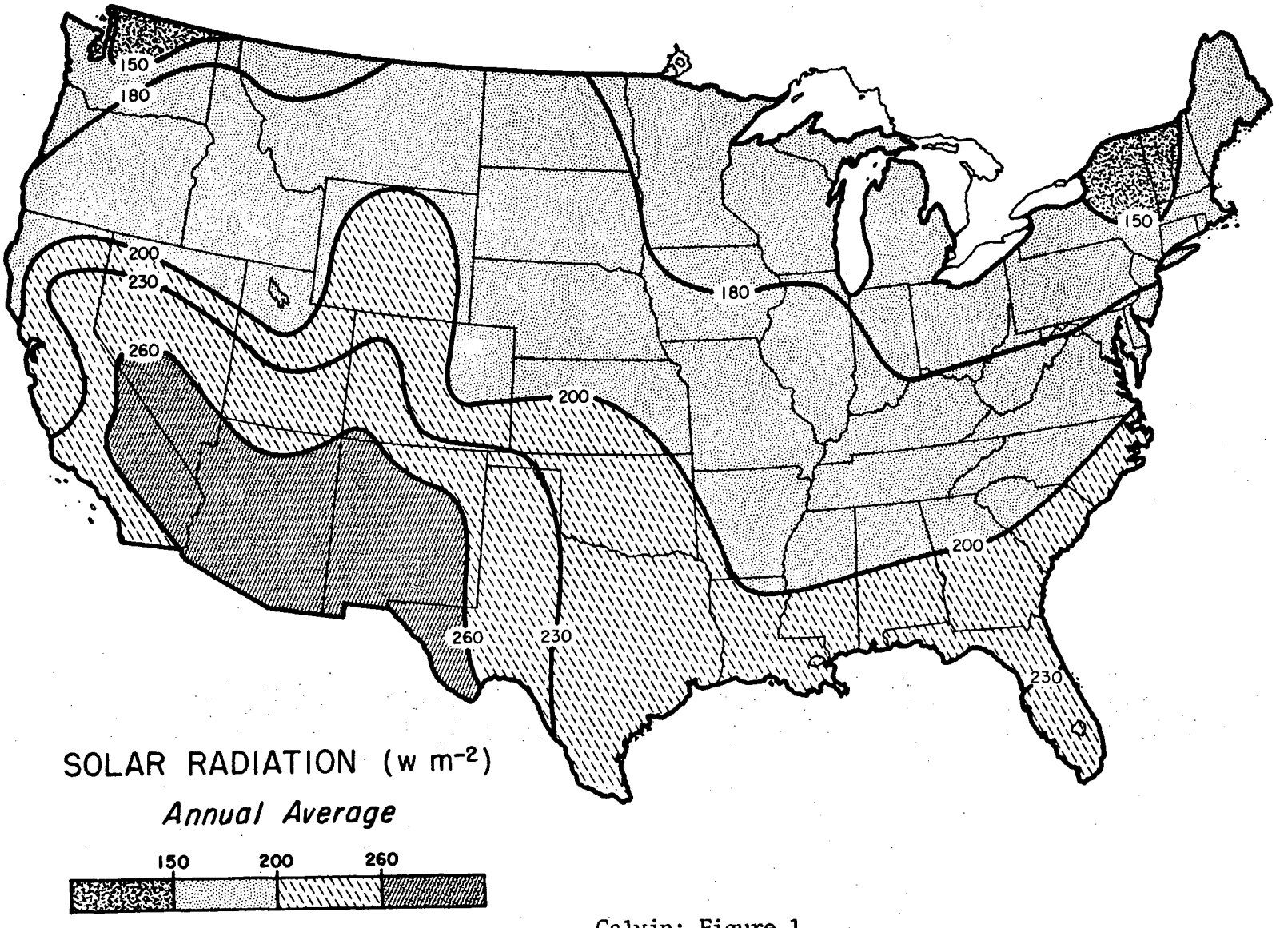
* 1 kcal/cm^2/yr is 1.33 watts/m^2.



Calvin: Figure 1

Annual insolation,
United States

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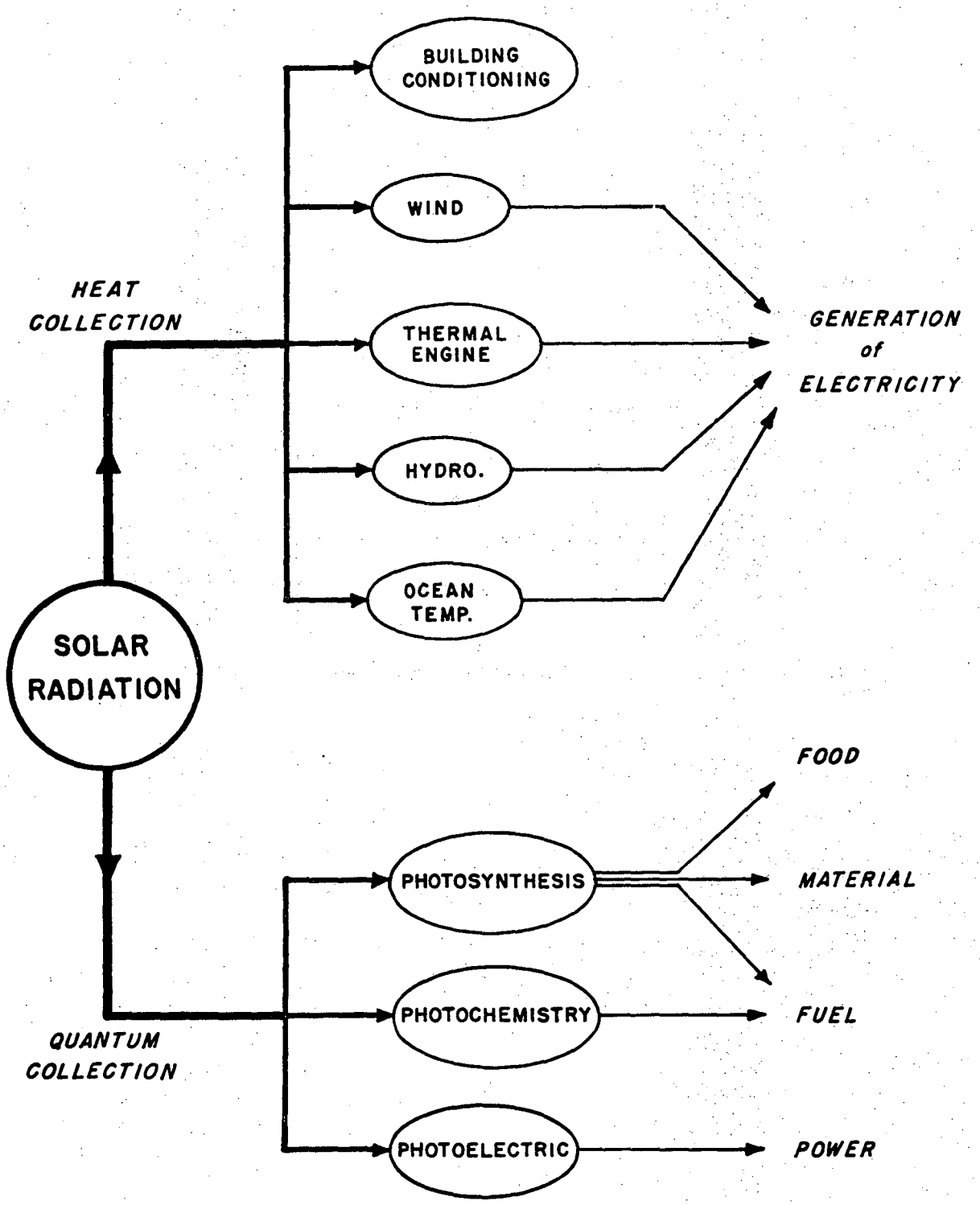
We have, then, roughly one-quarter kw/m^2 of solar energy to deal with on an annualized basis. What can we do with this amount of energy? Figure-2 is a chart of almost all of the possibilities open to us for solar energy utilization. I have divided these possibilities into two major categories, based upon a fundamental difference in the way in which the two categories collect and convert the solar energy. The upper group is labeled "heat collection" and contains all those devices and systems in which the solar energy must pass through a thermal stage for use. The lower group is labeled "quantum collection" and in these the electromagnetic energy of the sun is used, in the first instance, to excite electrons in molecules, or atoms, and the energy in these excited states is stored directly as chemical or electrical energy.

The major difference between the two collecting systems is not only the size of the energy packet which is converted but its quality (entropy) as well. In the heat collecting systems, the very largest packages are of the order of 2 kcal, most of them being much smaller, whereas in the quantum collecting process the packages are of the order of 40-50 kcal. In addition, the thermal system is subject to relatively severe limitation through the Carnot efficiency (<35%), while quantum conversions, because they take place at such a high equivalent temperature (~5500°K), can have very high efficiencies of conversion, at least theoretically.

Another way of dividing these eight collection systems was used by the National Science Foundation[3] in a study in which the division was on the basis of natural collection vs. technological collection. Natural collectors were those which already exist in nature, including wind, rain (hydro), ocean temperatures and photosynthesis. The technological



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Calvin: Figure 2

Systems for conversion of solar energy to electricity

collection methods would include building conditioning, thermal collectors and the engines operating on them as well as the photochemical and photoelectrical quantum devices.

It is not my purpose in this discussion to try and examine the devices based on heat collection, nor even to discuss in any detail the photoelectric systems based on known solid state devices (such as silicon cells or cadmium-copper sulfide cells). As the title indicates, we will be limited to an examination of the photosynthetic process itself as such and to technologically constructed systems modeled on what we know of the natural photosynthetic apparatus. I will suggest two such model systems for the direct photoconversion of the quantum into useful energy, one of them to produce storable energy (probably in the form of hydrogen), and the other to use a synthetic system based on the concepts of the structure of biological membranes and taking the converted quantum off as electrical potential.

While the hydrogen proposal and experiments are not biological photosynthesis, they are based upon what we know about the photosynthetic process. It is a "synthetic" system, in which we expect to sensitize the photodecomposition of water to hydrogen and oxygen. The hydrogen can be a fuel which can be used in various ways. The collection of solar energy by a natural quantum collection process includes the generation of hydrogen or the reduction of carbon dioxide. The nromal way for the quantum to be used in photosynthesis is in the reduction of carbon dioxide.

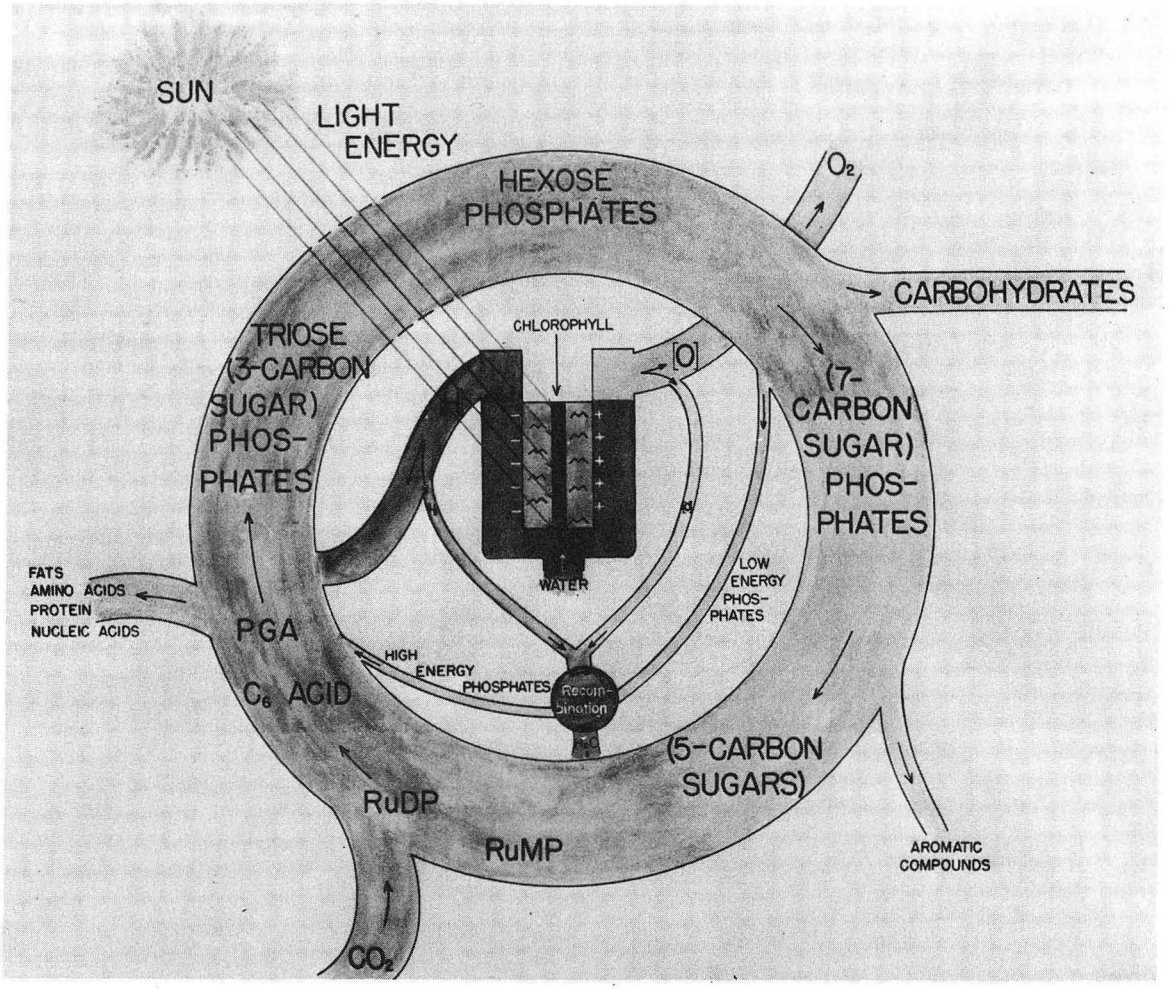
Roughly 6% of the energy use in the United States is for non-energy purposes, in chemicals or materials. For this purpose, power generation or hydrogen production can be only adjuncts: only reduced carbon can contribute directly in making materials and chemicals. I therefore distinguish

between the materials and fuel (Figure 2). The photochemical system, as now conceived, can produce only hydrogen whereas photosynthesis itself can produce either hydrogen or reduced carbon.

BIOLOGICAL (AGRICULTURAL) PHOTOSYNTHETIC CONVERSION OF SOLAR ENERGY

What is the biological model which is the conceptual source of these two processes?[5] That model is both the green plant and bacterial photosynthesis as we have learned to understand it in the last 20 years, a generalized scheme of which is shown in Figure 3. This is a diagrammatic scheme of what is occurring. The green part of the plant, represented in the center, is absorbing the sunlight and separating the positive and negative charge. The positive and negative charge can be used by the enzymatic apparatus of the green plant. The hydrogen atoms representing the negative charge can be used to reduce carbon dioxide and generate sugar; and the positive side represented by oxygen atoms can be used to oxidize water and generate molecular oxygen. The center of the diagram is the quantum converting apparatus. The carbon reduction cycle (the large circle on the outside) uses the primary reducing power produced in the chlorophyll-containing part of the plant to reduce the carbon dioxide.[6] Following the entry of carbon dioxide into the photosynthetic carbon cycle all the various plant components are synthesized (fats, hydrocarbons, proteins, carbohydrates, amino acids, nucleic acids). One can use the information about the two parts of the photosynthetic process -- the photochemical generation of [H] and [O] and carbon reduction -- in two separate ways.

How can the photosynthetic carbon reduction cycle be used as an energy source and as a material source?[7] It does not seem possible to



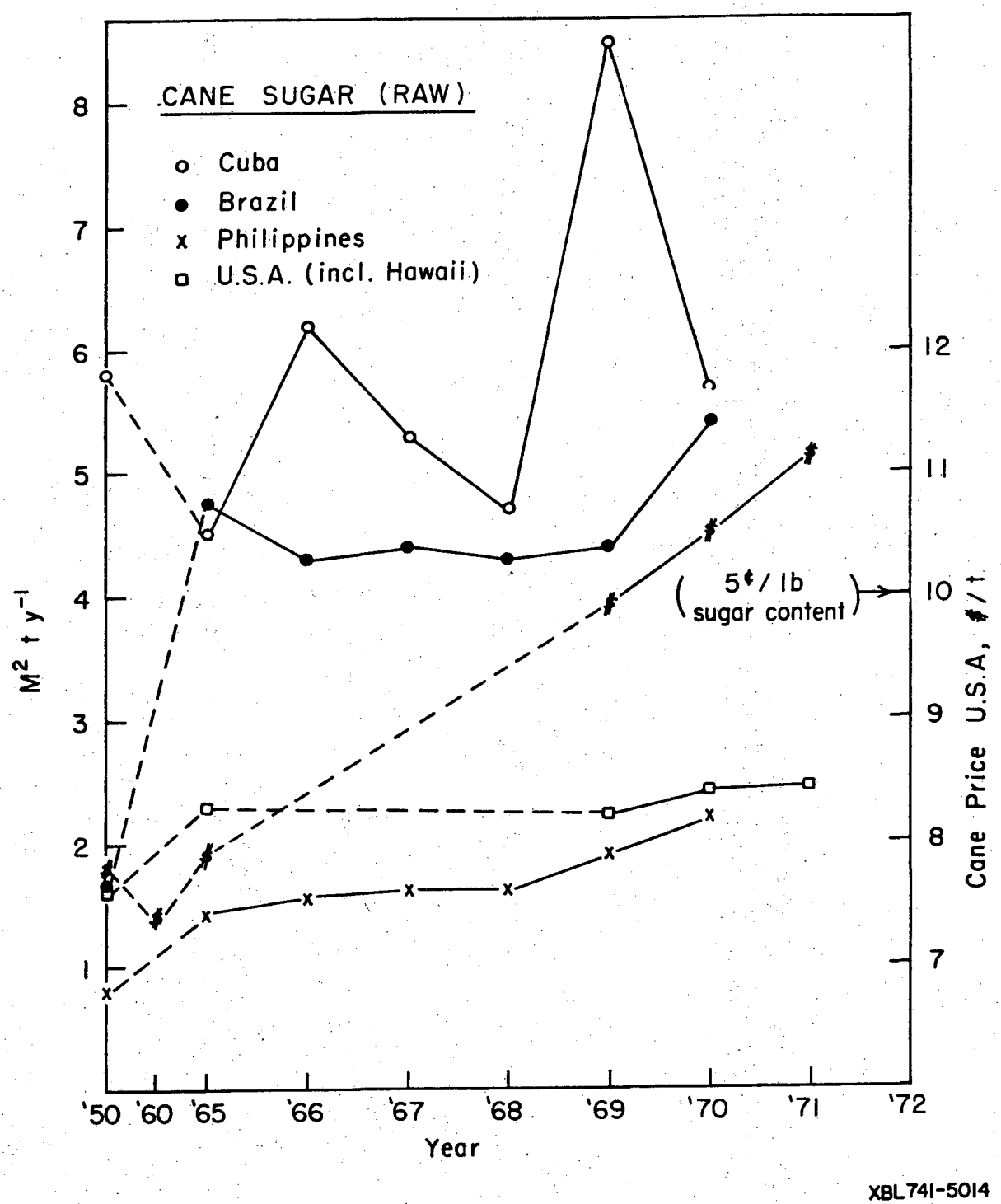
Bio-Chem. 355A

Calvin: Figure 3
Photosynthetic conversion of sunlight to energy and reduced carbon

use directly the photoelectric system for a material source. It generates electric power, or hydrogen, neither of which are substances from which the materials which we need can be constructed. These materials are primarily the chemicals and other non-energy uses mentioned in Figure 1 which constitute about 6% of our total energy requirement (the equivalent of about 2 M^2 barrels of crude oil per day).

One way of beginning to examine the photosynthetic cycle as an energy and material source is to ask: What about the natural photosynthetic productivity in terms of reduced carbon which is spread over the earth's surface? The greatest production of reduced carbon is mainly along the equator; not the areas of the earth where the highest insolation occurs, but, rather, where the best conditions for year-round growth exist. The equatorial areas grow a very large amount of natural vegetation because of the presence of water. The overall annual production is of the order of one kilogram of carbon per square meter per year, mostly in the form of sugar. I say "mostly in the form of sugar" because the principal product (generally about 50%) of plant photosynthesis is carbohydrate.

When that fact is realized, we should then ask ourselves which plants are capable of raising that productivity from 1 kilo $C/m^2/yr$ to something more useful. The natural efficiency is very low, a few hundredths of a percent. There is little doubt about which type of plants to use. The principal plant known today which has the highest yield of annualized photosynthesis is sugar cane.[8] In Figure 4 is shown the quantity of cane sugar produced worldwide in millions of tons per year. Cuba and Brazil are the two highest producing countries, with the United States (including Hawaii) producing about 3 million tons annually. I want to give some idea of the costs involved, relating them now to the costs of petroleum. The cane price in the United



Calvin: Figure 4

Cane sugar production and
U.S. fresh sugar cane price

States (mostly Louisiana and southern Florida) is about $10/ton and cane makes 10% of its wet weight in sucrose. What can we do with that sugar, which is the most common useful product of photosynthesis presently known? The overall efficiency is about 0.6% and this will be compared with several other types of plants later.

I want to suggest the use of sugar as an industrial raw material and also suggest its end uses. You could burn sugar -- it is carbohydrate as is cellulose and has the same caloric content. However, there are more efficient methods than burning, and one is to convert the sugar and cane cellulose into alcohol. The scheme for this process is shown in Table 1, and you will notice that the thermal efficiency is very good, with practically no loss in going from sugar to alcohol. It takes 12.9 pounds

Table 1. Fermentation of alcohol: efficiency and price

$C_6H_{12}O_6$	$\longrightarrow$	$2\ C_2H_5OH$	+	$2\ CO_2$
	180 gm			92 gm
H_{comb}	673 Kcals			655 Kcals

12.88 lbs	$\longrightarrow$	1 gal (84,356 Btu)
at 5¢/lb	$\longrightarrow$	64¢ $\simeq$ 20¢ process cost
Petroleum source		12/73 55¢ (controlled)
actual price:		offshore >$1.00

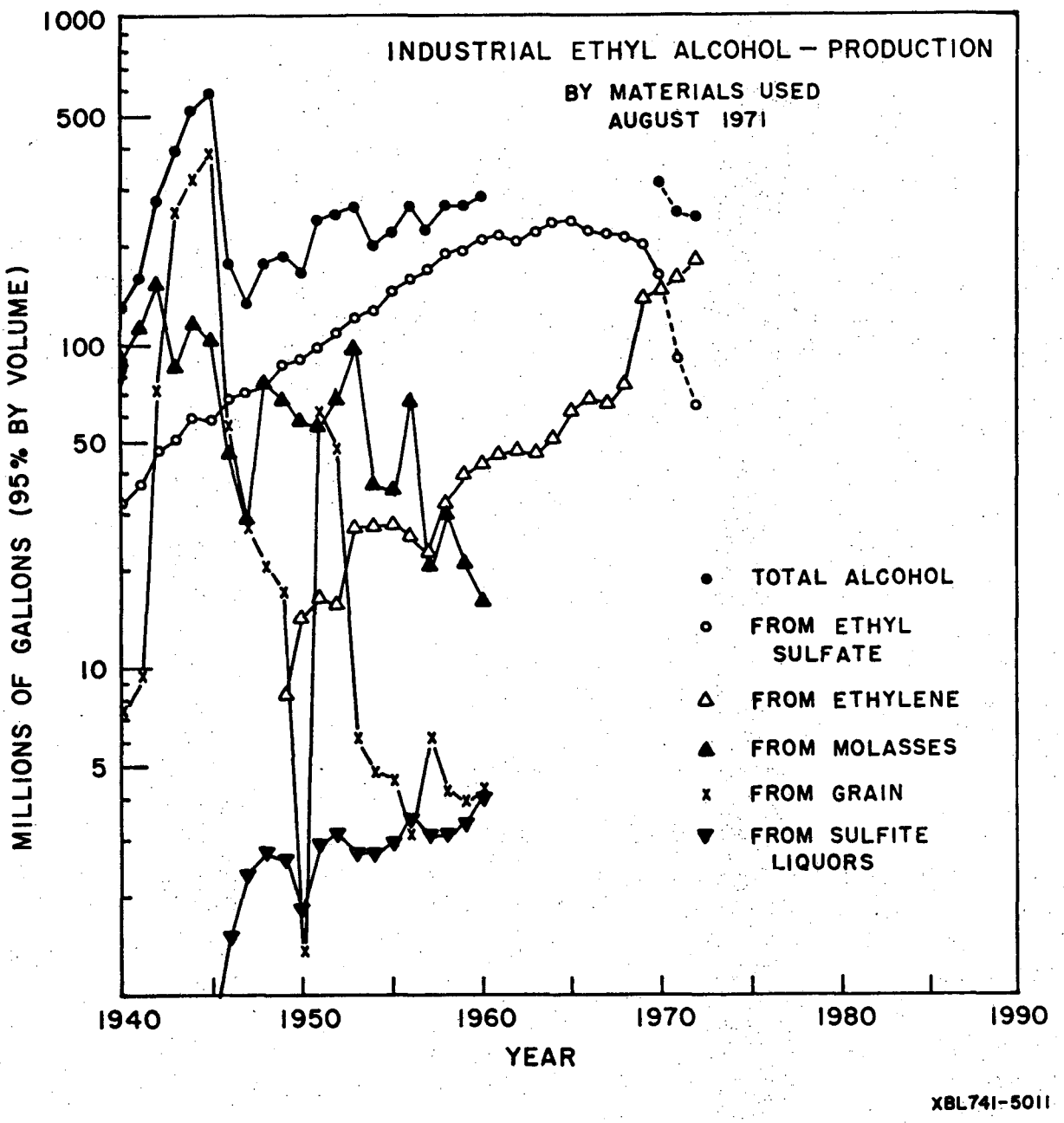
of sugar to make one gallon of alcohol, i.e., 64¢ worth of sugar at 1971-1972 sugarcane price to make one gallon of alcohol. It costs about 20¢ to convert the sugar, making a toal of 84¢ per gallon for alcohol by fermen-

tation. Today(January 1974) the controlled price of the petroleum source alcohol is 66¢/gallon, if you can find any. However, the actual offshore price for petroleum source alcohol is over $1.00/gallon. The reason I have given these numbers is that at a price of 85¢/gallon for fermentation alcohol, even on a thermal basis, if nothing else, we are already nearly economic in the use of alcohol at least as an additive to fuel gasoline. These sources are coming closer economically.

Just to illustrate how the economics of this kind of chemistry have effected the sources of alcohol in the last fifty years, I want to show you a graph of the industrial ethyl alcohol production since 1940 (Figure 5). The top line is total alcohol in millions of gallons per year. It is interesting to note that from 1940-45 (during World War II) the alcohol was made mostly by fermentation from molasses, sulfite liquors and grain (natural sources of carbohydrate). When petroleum became available as a cheap source of alcohol around 1950 it took over, entirely, the alcohol market. Ethylene is obtained by cracking liquid hydrocarbon down and hydrating the ethylene to make ethanol. The fermentation sources of ethanol disappeared entirely after 1960 because ethylene was only 2¢/lb and the conversion cost was very small. Therefore, ethylene entirely replaced fermentation as a resource for industrial alcohol.

The price of ethylene is roughly of the order of 10¢/lb and rising, whereas a year or two ago it was around 2¢/lb. Thus, the economic facts of high price and scarce supply have brought back the possibility that fermentation alcohol could become a significant source of hydrocarbon.

I have summarized these comments on photosynthetic crop sources of hydrocarbon in Table 2. Sugar cane makes four tons of sugar per acre per year, from which is obtained 2 tons of ethanol and 1.2 tons



Calvin: Figure 5

Industrial alcohol production

Table 2. Annual Productivity: Hevea, Cane, Beet

Hevea

1 t/acre rubber

45×10^6 Btu (0.2% of incident sun)

Cane

4 t/acre sugar

2 t ethanol

1.2 t ethylene

68×10^6 Btu (0.23% of incident sun)

4 t/acre bagasse

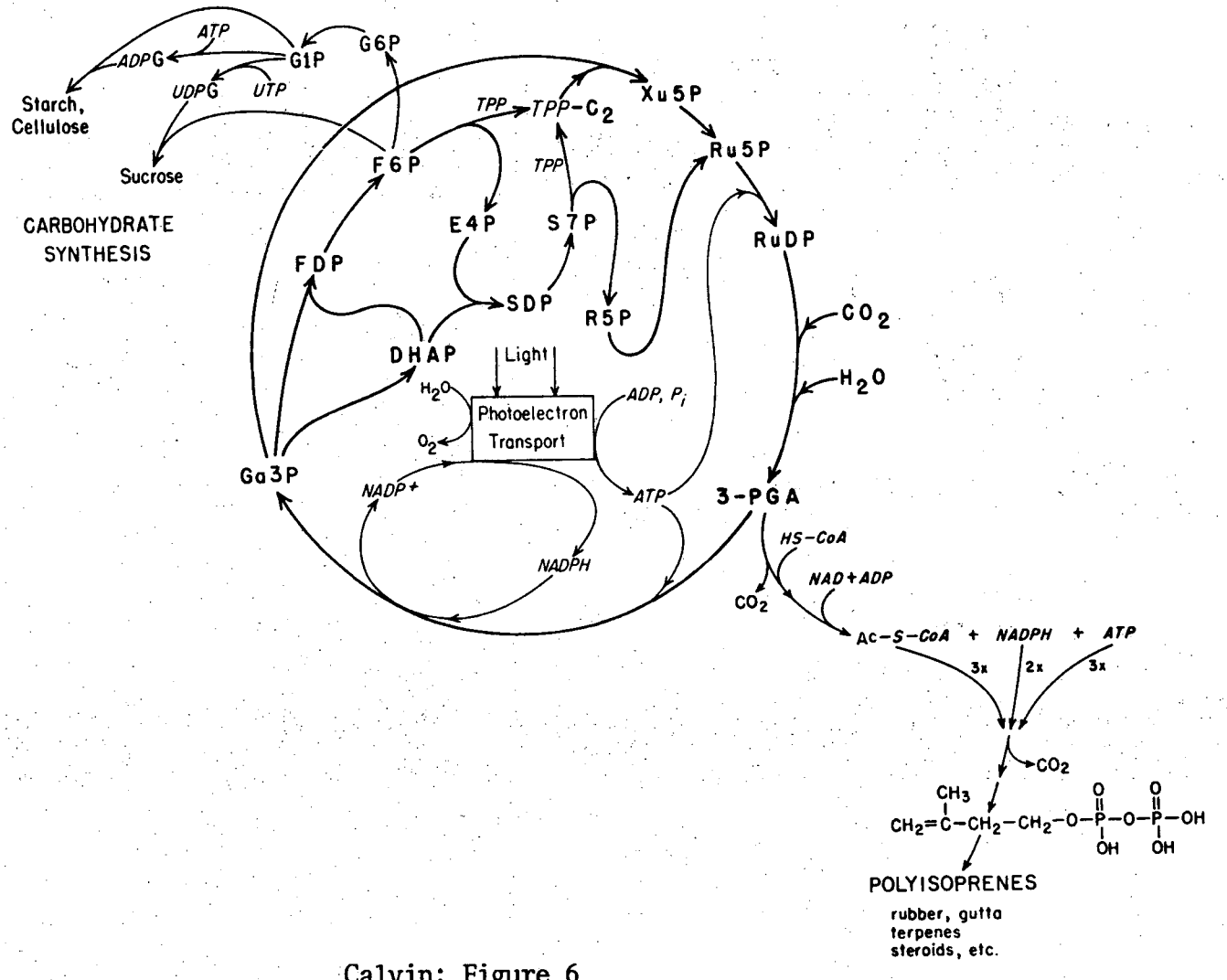
Beet

2.3 t/acre sugar

0.7 t/acre pulp

of ethylene, with an overall efficiency of 0.23% of incident sunlight, if only the sucrose is counted. There is, however, an equal amount of cellulose present in the cane, in the form of bagasse (the cellulose residue of the sugar cane) with a yield of 4 tons of bagasse per acre per year. The total therefore appears to be 8 tons of carbohydrate per acre of cane, raising the efficiency of solar energy conversion (agricultural solar energy conversion) for cane to about 0.5%. Sugar beets give 2.3 tons of sugar per acre, with 0.7 ton of pulp per acre, per year, but beets, unlike sugar cane, do not grow on a year-round basis.

It occurred to me that we are going to a great deal of trouble to convert a carbohydrate (sugar) into a hydrocarbon (ethanol-ethylene-polyethylene). Would it not be possible to find a plant source which would make hydrocarbon directly? (see Figure 6). There is at least one already



Calvin: Figure 6

Photosynthetic carbon cycle, including carbohydrate and polyisoprene production

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available, very well known, the Hevea rubber plant which was first found wild in Brazil and now is grown almost exclusively in plantations in Malaysia and Indonesia. Today the yield of rubber (which is already a hydrocarbon with no oxygen in it) is about one ton per acre per year, which is about half the yield of cane and only about 20% less in terms of ethylene potential. The rubber growers are very optimistic that they can, and will, be able to raisethe yield of rubber from one to three tons per acre per year.[9] If they are able to harvest three tons of rubber per acre per year (i.e., three tons of hydrocarbon), this type of plant may also become a serious possibility for a direct photosynthetic source of hydrocarbon for use in chemicals and materials.

The rubber story is very similar to the industrial alcohol (ethanol) story, and, in a sense, is even a little more spectacular. After World War II, synthetic rubber (i.e., butadiene and styrene) made from petroleum practically eliminated rubber plantations as a source of this material. The rubber growers then began to improve the yield, which at the end of World War II was only about 400 pounds of rubber per acre per year.[10] The figure today is about 2300 pounds of rubber per acre per year. About one-third of the rubber used today comes from natural sources, and two-thirds from synthetic sources.

If the price of petroleum continues to rise and the yield of natural rubber can be raised another two-fold, we will again have reached another crossing point where a natural photosynthetic system for converting carbon dioxide and sunlight into hydrocarbon can be used. There are also many other types of hydrocarbon resources such as gutta, terpenes, etc., which have not yet been explored for this particular purpose. It is quite possible that breeding programs, such as have been devised to

improve the Hevea rubber plant yield from 400 pounds to 2400 pounds per acre per year, could be used to develop other sources of natural hydrocarbon. This could perhaps be done in a shorter period of time than was required for Hevea (a seven-year crop) if some of the annual plants were explored and without the special requirement of elasticity.

Probably the first natural photosynthetic process which will be developed economically as a hydrocarbon source will be the conversion of carbohydrate. In fact, as you all know, gasoline rationing began in Hawaii today, January 28, 1974. If the Hawaiian sugar planters would convert about one-third of their molasses directly into fuel alcohol, they would not have to purchase the 15 million gallons of petroleum which they now do to run their agricultural machinery. This is a particularly localized situation which could give rise to immediate action and may bring this type of natural photosynthetic process into operation very soon as a source of hydrocarbon.

Another special situation seems to be developing in Nebraska which has about 7 M^2 bushels of spoiled grain per year. This should yield more than 20 M^2 gallons of alcohol, which, as a 10% additive to gasoline, would give 200 M^2 gallons of "gasohol". This is the name used by the Nebraska legislature to designate a composition which would qualify for a 3¢ state tax credit. It has even been suggested that there are 0.5 M^2 acres of unused land available in Nebraska for such a purpose, an acreage that could produce another 500 M^2 gallons of "gasohol".*

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* See Chemical Week, January 30, 1974, page 33. Is alcohol next candidate for fuel pumps? Also, National Inquirer: Alcohol from grain could help ease gasoline shortage, tests show. Chemical Marketing Reporter, February 11, 1974: Energy Help from Plant Alcohol. Letters to the Editor, Science, 183, 698 (1974): Gasoline Substitutes

As a final comment on the natural photosynthetic sources of hydrocarbon, let me remind you of our use of about 2 M^2 barrels per day of oil equivalent as a source of chemicals and materials. If we were to try and supply this entire need from sugar cane we would require about 60 M^2 acres of cane if we used only the sucrose and only about 30 M^2 acres if the cellulose could be used as well, a capability soon to arrive.[11] In 1971 there were 0.7 M^2 acres under cane cultivation and about 1.4 M^2 acres in sugar beets in the United States.

MODEL SYSTEMS OF PHOTOSYNTHETIC SOLAR ENERGY CONVERSION

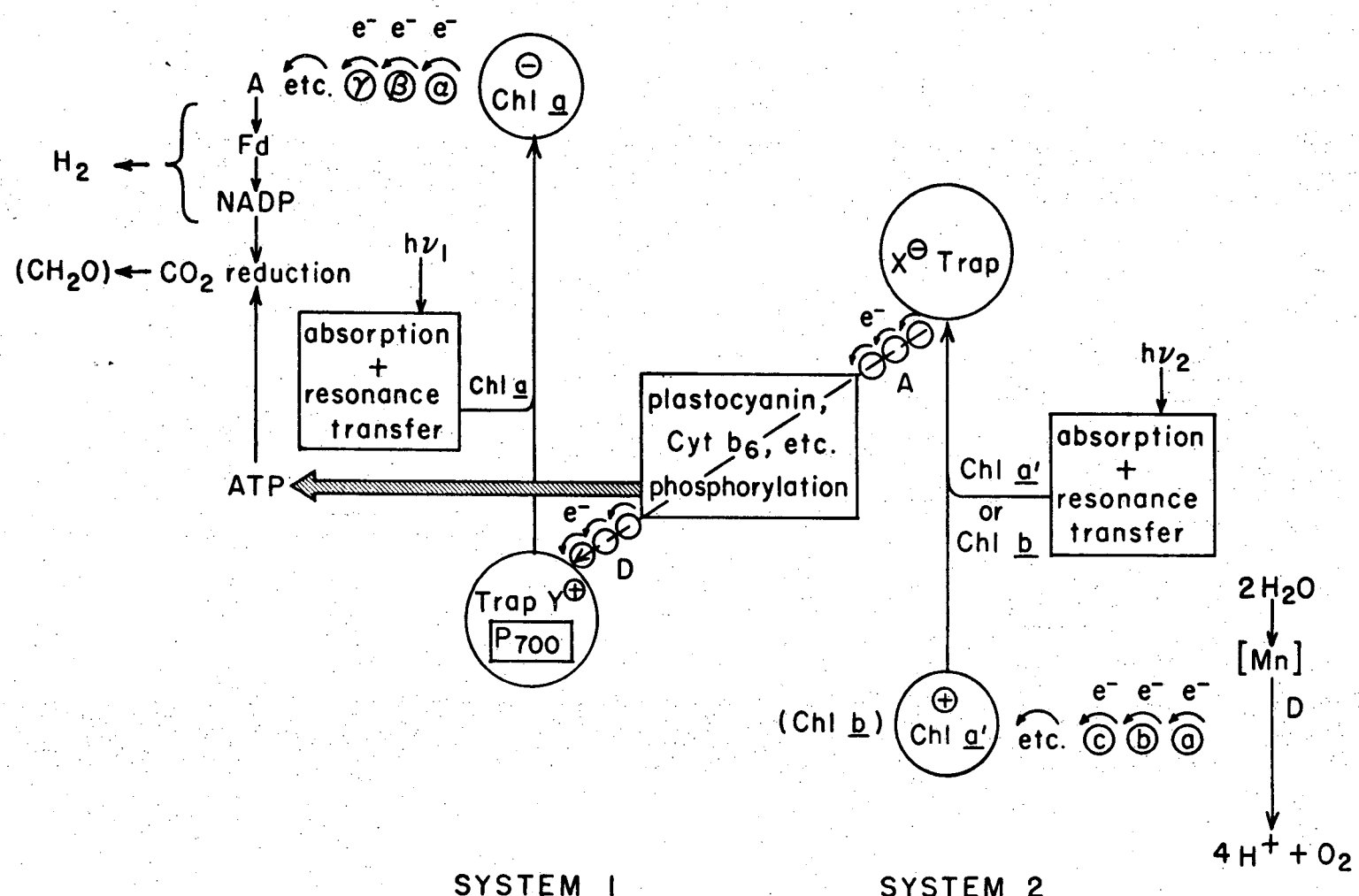
We have learned in great detail about how the plant makes carbohydrate; we also know how the plant makes hydrocarbon (polyisoprene--rubber). We are learning more about the way in which the plant captures the quantum of energy.[12-15] The knowledge of the plant's quantum conversion system is not nearly as complete as the knowledge of the photosynthetic carbon reduction cycle and subsequent processes. The primary quantum conversion process is still uncertain, but we are learning more about it constantly. Using what knowledge we have of the quantum conversion process, we can ask if the concepts generated in photosynthesis research -- how the plant actually captures the quantum and converts it into useful potential, or electron flow -- can guide us in simulating some parts of that process by purely synthetic methods. We then might be able to use that quantum conversion (solar energy conversion) process to help solve some of the energy problems with which we are faced.

However, before I leave the general subject of agricultural productivity of photosynthesis, I wish to review Figure 6 which is

the same photosynthetic carbon cycle shown in Figure 3 but much more elaborately displayed. You can see in some detail the entry of carbon dioxide into the photosynthetic carbon cycle and the exit of carbon into sucrose, starch and cellulose, as well as hydrocarbon, which we have just discussed. The energy which drives the carbon cycle is represented by the photoelectric cell shown in the center of Figure 3. Here, in Figure 3, light enters the black box, which takes oxygen from the water and expels it into the atmosphere, and uses the remaining hydrogen to generate the reduced pyridine compound (NADPH) which, together with the adenosine triphosphate (ATP), drives the carbon reduction cycle. I won't go into the biochemical details of how this process works. All of the driving chemicals -- the ATP and NADPH -- come from the light source.

How much do we know about this "black box"? We know a good bit about what is occurring inside the "photoelectric cell" of the green plant, shown in Figure 7. There are two successive quantum absorptions, the first one (photosystem II) producing a strong oxidant and an intermediate reductant energy state, i.e., taking the electron up so that it may pass through electron transfer agents back to another previously oxidized chlorophyll molecule at a lower oxidation potential.[14] After it has reduced the second chlorophyll to its normal state, it is again raised by another light act (photosystem I) to a still higher reduction potential and then it comes down through a series of carriers, of which NADPH is one, and eventually goes into the carbon dioxide reduction process. While Figure 6 emphasized the carbon reduction cycle, Figure 7 emphasizes the quantum conversion (electron transfer) scheme of photosynthesis.

An analysis of this photosynthetic electron transfer scheme can give us some clues as to how we might be able to construct a system which



Calvin: Figure 7

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Scheme for photosynthetic electron transport system

might be a device for converting solar energy into some useful form. One method might simply be to try and isolate a particle which would contain the entire system asymetrically arranged with an acceptor, perhaps ferredoxin (FD), on one side and an oxygen generator on the other, and use that particle (if it exists) in an asymmetric membrane. Light would then transfer electrons from the oxygen-generating side (donor) of the system to the acceptor (or hydrogen-generating) side. Suitable electrode-active redox couples could be placed in the solutions on either side of the membrane to couple this electron transfer process to electrodes, and so generate a current for use. While the successful construction of such a system would be very illuminating, it is not likely to be easily constructed or very stable if, as now appears, it must depend on complex structures isolated from plants and placed in an unnatural environment.

Photochemical Hydrogen Production

In some green plants and bacteria it is possible to modify the end result of this type of photochemistry. Instead of the active hydrogen reducing carbon dioxide to make sugar, it is possible to limit the amount of carbon dioxide available to the plant and, by keeping the oxygen level very low, induce the plant to use the light energy to generate molecular hydrogen.[16] The oxygen must be swept out, or used up, because the enzyme system which generates the molecular hydrogen is sensitive to oxygen. This is one of the problems. However, it appears possible to alter the conditions in such a way that the photosynthetic apparatus will generate hydrogen instead of reducing carbon. Thus we know that it is possible to have catalytic systems in

the plant which can use sunshine (solar energy) to generate hydrogen from the water.[17] This fact has been known for over twenty years,[16] but recently a system was described in which a blue-green algae, Anabena, which contains in it the entire photosynthetic apparatus and, additionally, a heterocyst cell which has no oxygen-producing apparatus but has in it the hydrogen-generating apparatus.[18] The reduced compounds are made in the green part of the plant (the oxygen-producing cells) and then diffuse into the non-green part (heterocyst) with resultant evolution of hydrogen.

The fact that the plant has in it an apparatus capable of capturing the quanta and liberating molecular hydrogen was sufficient to make me feel that if I knew more about the details of the quantum conversion[19] and about the enzymatic systems involved I might be able to devise a simpler set of chemicals which would perform the same function, i.e., generate hydrogen and oxygen from water. It would not be necessary, then, to reduce carbon, or have the whole skeleton of construction of a green plant which is required to make another green plant. I wanted to derive a system which would not be as complex as the one the green plant has in order to reproduce itself. To do that, however, it was necessary to have a concept of how the hydrogen is evolved and how the oxygen is evolved, and put the two processes together conceptually and, ultimately, synthetically.

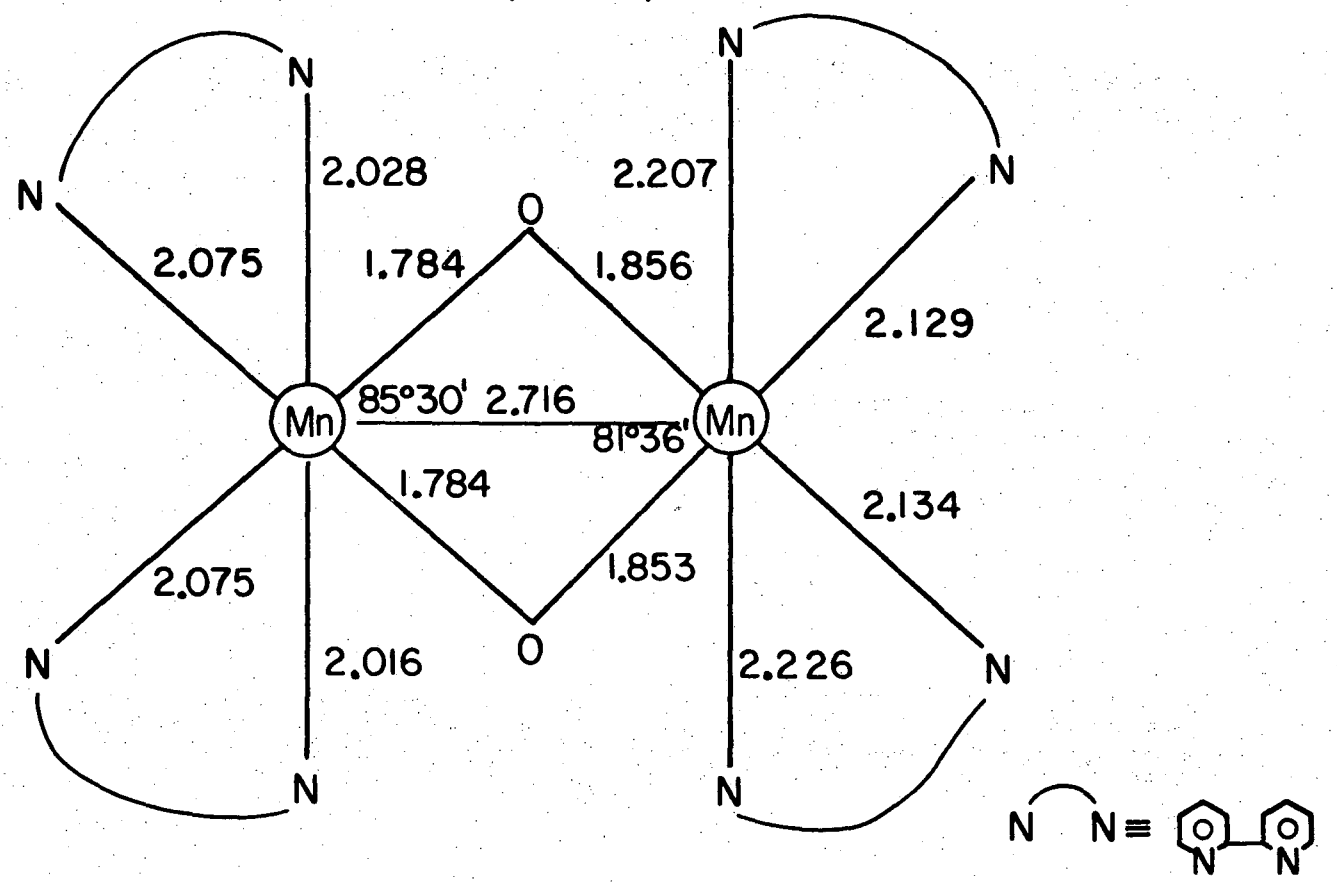
The right side of Figure 7 shows that the oxygen comes from the water, and the water molecule has only one oxygen atom in it, while the oxygen molecule has two. A total of four electrons are involved in converting two molecules of water into a molecule of oxygen and four hydrogen atoms. In order to generate oxygen molecules from the water

molecules it is necessary to bring two oxygens together and remove four electrons. It is known that manganese is involved in this part of the system,[20] but a single manganese ion by itself seems unable to remove four electrons. However, it appeared to me that if two manganese atoms, each of which would have oxidation number changes from +2, to +3, to +4, were put together in the same complex, there would be a source of the required electrons without the necessity of generating free oxygen atoms or hydroxyl radicals. This process could be performed entirely in the double manganese complex. Thus arose the notion of a binuclear manganese complex containing two water molecules and which could be used in the quantum conversion process. The light, sensitized or direct, could induce a ligand-to-metal charge transfer, thus generating reduced metal ions and virtual hydrogen peroxide on the way to molecular oxygen. The reduced metal ions could then be the source of electrons for another quantum act, giving rise to molecular hydrogen. This was the theoretical basis on which the next experiment was performed. The idea was that we needed two manganese atoms in one complex. Could we find a system which could generate oxygen or hydrogen in separate quantum acts?

The structure of the dimanganese complex which we used is shown in Figure 8.[21] It turns out that if this molecule is irradiated in a suitable aqueous solution, oxygen is indeed given off. Figure 9 shows oxygen evolution by this binuclear manganese compound upon turning on the light. We thus have a system which will generate oxygen when the light is turned on.[23]

The overall scheme representing the light act on the binuclear manganese catalyst which generates oxygen and reduced catalyst is shown

Structure of di-μ-oxo-tetrakis (2,2' bipyridine) dimanganese (III, IV) perchlorate



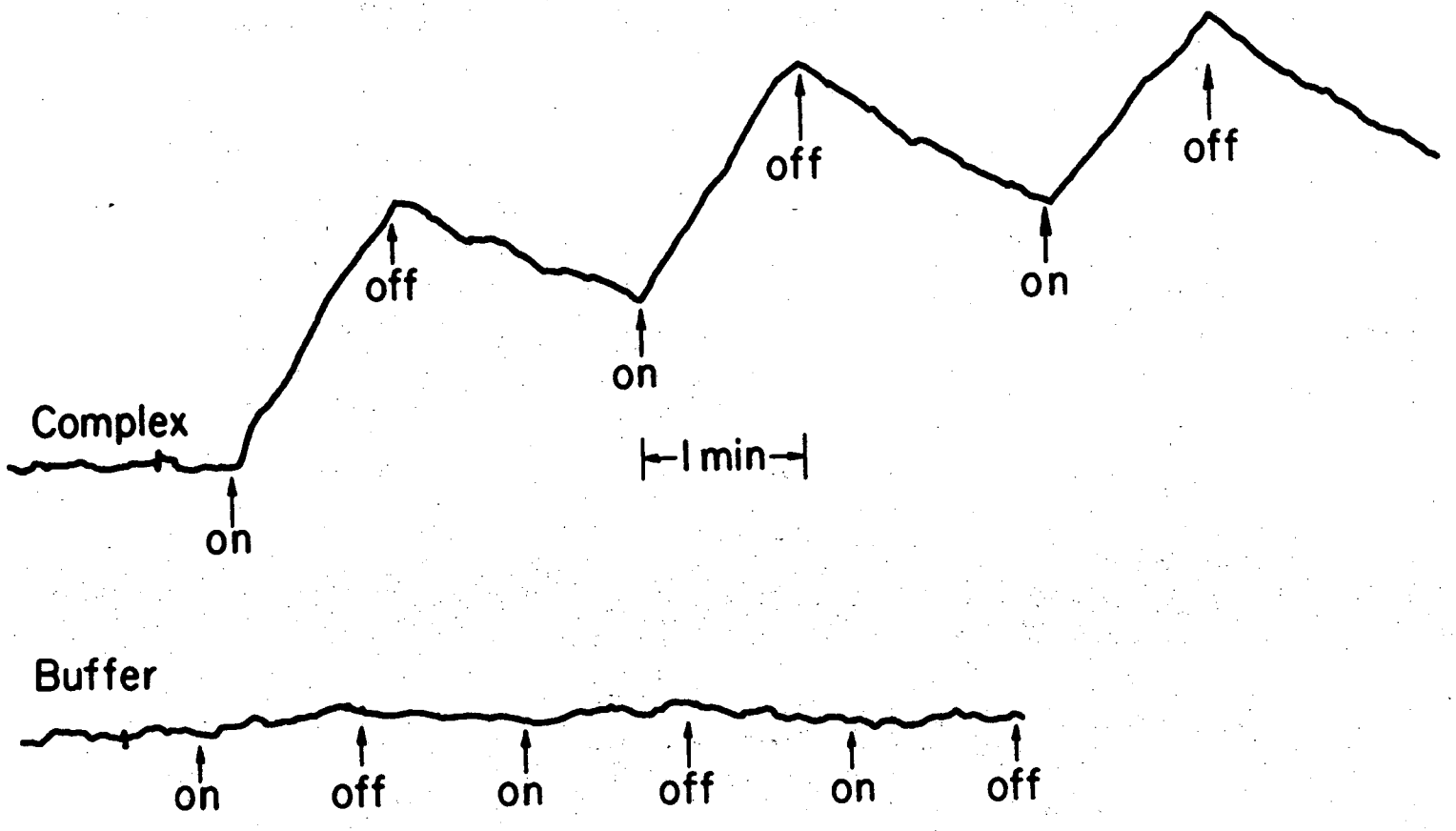
P.M. Plaksin, R.C. Stoufer, M. Mathew, G.J. Palenik, JACS 94 2121 (1972)

Calvin: Figure 8

XBL 7310-4202

Structure of the binuclear manganese photocatalyst

Photoinduced oxygen evolution by $(bipy)_2$ Mn^{III} O O Mn^{IV}
$(bipy)_2(ClO_4)_3$ 1.65×10^{-2} M in pH 4.5 0.05 M
bipy | bipy H^+ClO_4 – buffer (10 % CH_3COCH_3)



Calvin: Figure 9

XBL7310-4201

Oxygen production by photolysis of binuclear manganese compound

as reaction (1) in Chart 1. The reduced catalyst can move to the place where the hydrogen-liberating enzyme exists (presumably near ferredoxin) and another quantum act could then move the electron into an acceptor (the ferredoxin) and reoxidize the catalyst (reaction 2). The reduced ferredoxin plus protons with either one of the hydrogen-liberating enzymes, hydrogenase or nitrogenase, would then liberate hydrogen and recover the oxidized ferredoxin[24] (reaction 3).

Chart 1. Proposed reactions for photochemical hydrogen production

$$1/2\ H_2O \xrightarrow[{[cat.]_{ox.}}]{h\nu_{II}} 1/4\ O_2\uparrow + \underset{[cat.]_{red.}}{[H]} \qquad (1)$$

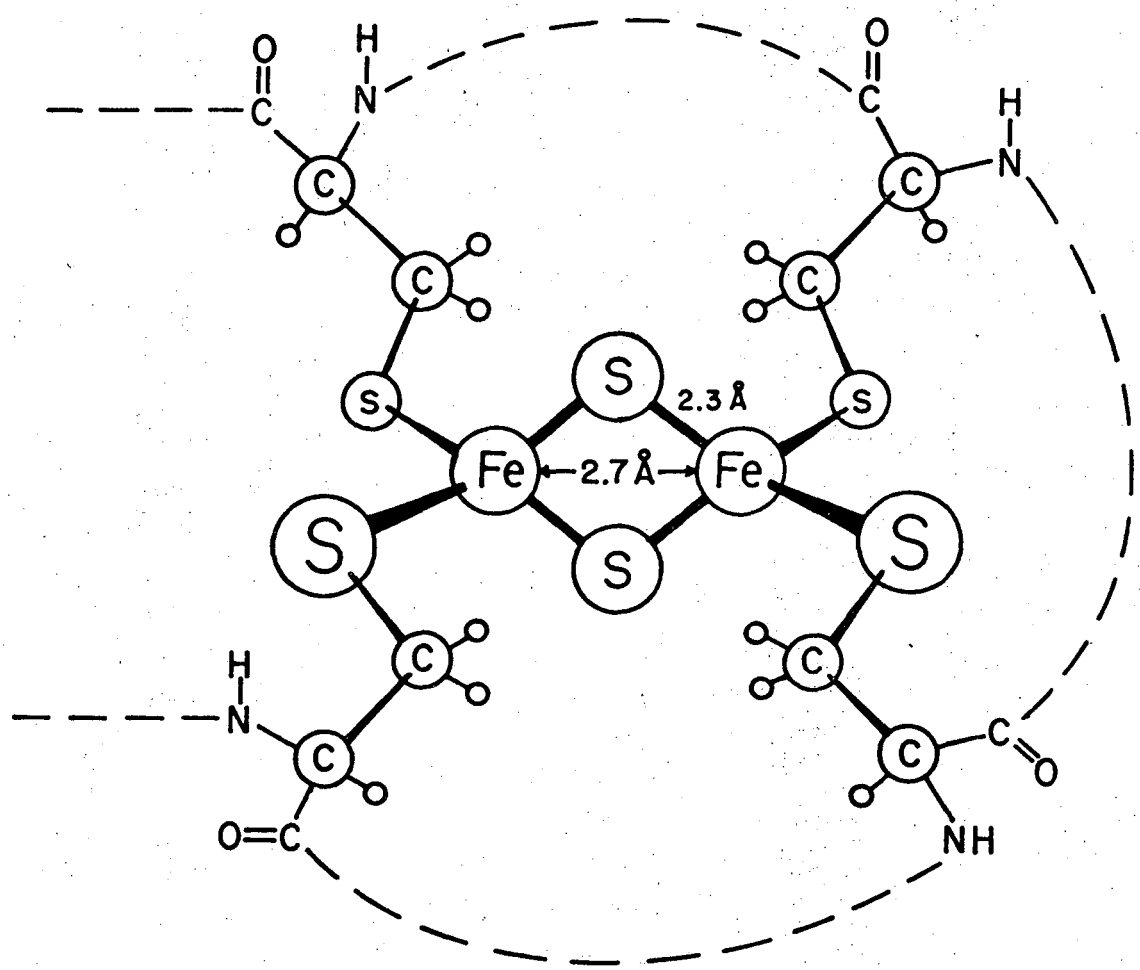
$$\underset{[cat.]_{red.}}{[H]} + Fd^{+3} \xrightarrow{h\nu_{I}} Fd^{+2} + [cat.]_{ox.} \qquad (2)$$

$$2\ Fd^{+2} + 2H^{+} \xrightarrow[2)\ \text{Hydrogenase}]{1)\ \text{Nitrogenase / or}} H_2\uparrow + 2\ Fd^{+3} \qquad (3)$$

What I have shown you so far is some experimental evidence for the first reaction only. We have produced a reduced catalyst, whose structure is still unknown, and we are, of course, actively pursuing its elucidation. We are also in the process of deciding how to achieve the second step. For this purpose we have had to examine the structure of the green plant ferredoxin and of the hydrogen-liberating enzymes. It appears that these two substances

have certain elements of structure in common, if they are not identi-cal. Both their functional groups are iron atoms completely coordinated by sulfur atoms of various kinds. The bacterial ferredoxin contains the unit of 4 Fe atoms and 4 S atoms, arranged at the alternate corners of a distorted cube, the entire cube supported or contained in a polypeptide framework by the four mercaptide sulfur atoms of cysteine molecules in the peptide chain.[25,26] A somewhat simpler structure, consisting of two iron, two sulfur and four cysteine mercaptides, is suggested for both plant ferredoxin and hydrogenase in Figure 10.[27a,b,c] The binuclear iron center contains each iron, tetrahedrally surrounded by four sulfur atoms, two of which are $S^{=}$ bridges between the two Fe atoms. The remaining four are mercaptides, from a presumed surround of peptide. This latter structure (Figure 10) has simple analogues which can be synthesized. By tying all the mercaptides together into a macrocyclic structure it should be possible to add two electrons to such a system of iron and sulfur atoms without causing the separation of the iron and sulfur atoms. The reduced complex, with the two sulfur atoms so close together, could provide the centers for the addition of protons and the ejection of molecular hydrogen, and thus return to the oxidized form.

If we can succeed in this construction we will then have available the components of a totally synthetic system which sensitizes the photochemical decomposition of water into hydrogen and oxygen in two different places. There are various methods of engineering this process, and I am not much concerned about that problem. Once the two separate reactions are achieved as two separate reactions, the construction of the system will go forward. At present, we have demonstrated the first half of this synthetic system and we are on the road to the second part.



Suggested $Fe_2S_2(CyS^-)_4$ center of green plant Fd and for hydrogenase

XBL741-5015

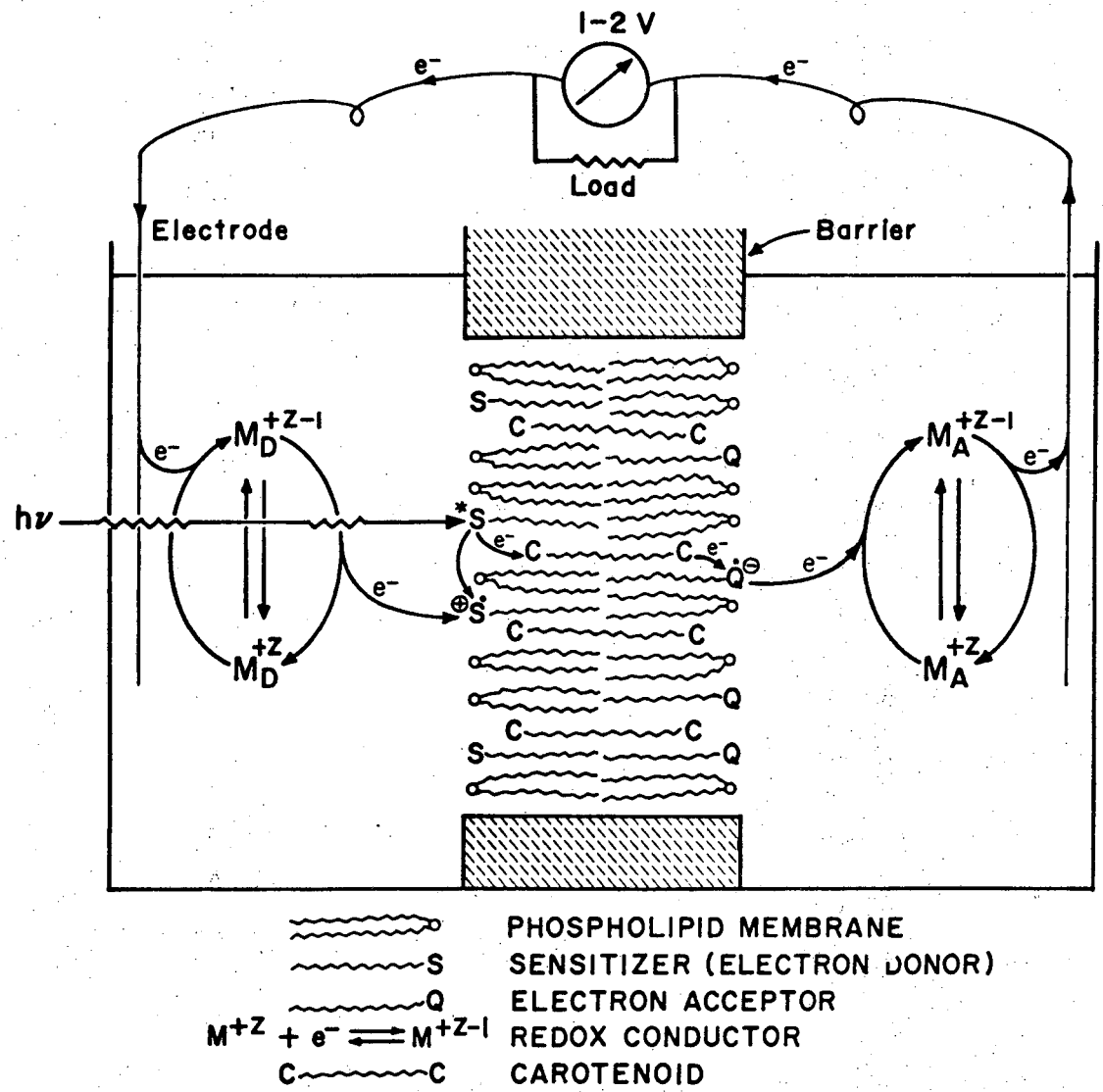
Calvin: Figure 10

Proposed structure of plant ferredoxin and hydrogenase

Photoelectric Membrane

Another type of notion has evolved from an examination of the nature of the primary quantum conversion act in the green plant. As was shown earlier, the primary quantum conversion apparatus in some ways simulates a solid state device in which impinging light separates charge--positive and negative, electrons and holes. We have used this concept for the last fifteen years, trying to learn if and how such a system might work in the green plant.[17] In the last couple of years we have found that it is possible to demonstrate that the intact chloroplasts of the green plant, when light of the proper wavelength is shone on them, do indeed behave as though there were "conduction electrons" developed by incident light.[28] We were able to demonstrate a Hall effect in illuminated chloroplasts. By placing the chloroplasts in a magnetic field and shining the light on them, two different carriers are evolved, one positive and one negative, having different lifetimes and moving in opposite directions in the magnetic field.

This result encouraged us to design sensitized systems for separating charge, using various dyestuffs whose photoactivity resembles that of chlorophyll.[29,30] Figure 7 shows some of the details of such two-quantum details of such two quantum processes. Instead of allowing the evolution of oxygen, and hydrogen or carbohydrate, it may be possible using this quantum conversion system to take the holes and electrons off as current, across a suitable device. The device I am about to propose is an example.[21] I have seen the designs of other such devices.[29] It is a photoelectrochemical cell[29] modeled on the photosynthetic membrane itself, using the idea of photoelectron transfer and generating voltage and a current (Figure 11).[30] There is a sensitizer (S) on one side of the synthetic



PHOTOELECTROCHEMICAL CELL MODELED ON PHOTOSYNTHETIC MEMBRANE

XBL731-4636

Calvin: Figure 11

Photoelectrochemical cell modeled on photosynthetic membrane

membrane which, upon the absorption of a quantum, transfers its excited electron (by tunnelling 10-20 A) to a carotenoid (C) which resembles a wire inside the membrane. The electron delocalized in the carotenoid travels through the membrane and is captured by an electron acceptor (Q) on the other side, which then goes through the cycle of a dyestuff (M_A) to deliver the electrons to the electrode. Similarly, the hole remaining (S^+) is fed an electron from another pair of dyestuffs (M_D) at a different potential. The dyestuffs are electroactive on the electrodes, thus generating a voltage and a current which can be taken off, and dependent on incident light which transfers the electron from one side of the membrane to the other. Such systems are under construction. Components have been made, for example, in which the bilipid membrane has a donor system on one side and an acceptor on the other, without the conductor, only two lipid layers thick (about 60 A). The idea of a conductor is to produce various conducting channels through a thicker membrane which will allow only the excited electron to pass through but be thick enough to be stable.[33]

This kind of a totally synthetic system which emulates and simulates in some ways the chloroplast membrane activity of the green plant may very well, in the more distant future, be another means of capturing the energy of the sun and producing electricity directly from it.

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