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PHOTOSYNTHESIS AS A RESOURCE FOR ENERGY AND MATERIALS

Melvin Calvin

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PHOTOSYNTHESIS AS A RESOURCE FOR ENERGY AND MATERIALS

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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 again become economic in the light of increasing costs of recovery of hydrocarbon from fossil sources and improved fermentation technology. It may also be possible to produce hydrocarbon directly by direct fermentation of relatively labile carbohydrates in seaweed. Even the direct photosynthetic production of hydrocarbon from known sources (Hevea, etc.), or newly bred ones, seems possible in view of the large number of species. Finally, more distantly, synthetic systems constructed on the basis of our growing knowledge of the photosynthetic processes may produce fuel, fertilizer and power.

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First of all, I want to thank you not only for the honor you have done me in inviting me to present the first Arturri I. Virtanen Memorial Lecture, but also for the opportunity that this gives me to pay my respects to the memory of one of the great scientists of the world in what I hope will be an active and creative way, as nearly reminiscent of Virtanen's own style as I can be. Because his interests were so wide and varied, I have felt both the impulse and the freedom to discuss not only some of the things in which he himslf had a personal interest and to the knowledge of which he contributed so much, but to other activities in which I know I know a man of his broad scope would have been interested. It is in this context that I have undertaken to discuss "Photosynthesis as a Resource for Energy and Materials", not only in and of itself but as a model for synthetic systems which may one day be important.

INTRODUCTION

In order to give you some background for the current concern with the dimensions of the energy problem, I have introduced in Figure 1 a diagram of the flow of energy in the United States in 1970 only because I do not have such information for Finland.[1] However, I will indicate the major differences (insofar as I know them) as we go along. The information on this figure has three major components: on the left are the primary energy sources, in the center are the ways in which that energy is used and collected, and on the right are the ways in which the energy

losses accumulate.* As you can see, by far the largest source of energy, at least in the United States (and I suspect everywhere else as well) is the collected remains of ancient photosynthesis in the form of what we call fossil fuels; these include natural gas, coal and petroleum. Three additional sources of energy supply are being used to a very small extent in electric generation. For example, something less than 15% of the electric energy installed capacity in the United States is hydro power. In Finland, however, this figure rises to 40% of the installed electric capacity. As you will see later, hydro power is in effect a use of solar energy and in that sense Finland is already making better use of solar energy resources than is the United States.

The right-hand portion of Figure 1 indicates that roughly one-half of the total energy used in the United States is actually lost as low temperature heat. Only the remaining half is eventually converted into some useful form. This is partly due to the inefficiencies of the thermal engines which convert the potential energy of the fossil fuel into some useful form.

Let me also call your attention to the fact that approximately 15% of the total use of hydrocarbon (fossil fuels) is for non-energy (that is, chemical and other material) purposes.[2]

A number of factors have recently combined to focus our attention on this very high rate of consumption of all of our non-renewable fossil fuel resources, particularly of the petroleum and natural gas components.[3] The relative ease of recovery of both oil and natural gas and the convenient ways in which these fuels may be used, compared to coal, have in the past

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* The units used here are at 10^{15} Btu. Keep in mind that one Btu is 252 cal and that 1 kilowatt is 3412 Btu/hr.

several decades produced this very high rate of consumption of these particular materials. This has contributed to the resultant increase in their costs.

To give you some concept of what has happened to the cost of these fossil fuels, I have reproduced in Figure 2 a plot of the price of the three major fossil fuels over the last fifteen years, and the evidence of the last four years clearly shows why our interests are now turning to other ways of providing for our needs for energy and materials. That, taken together with the recognitiion that it is necessary for us to maintain the quality of the environment in which we live at the same time as we supply the energy and material needs of the population, has induced a search for other sources in addition to nuclear. The principal source of energy which has captured our attention (as scientists, and especially as chemists, biochemists and physicists who have an interest in life processes--particularly photosynthesis) is the sun itself.[3] Of course, the sun is also "nuclear". However, it is such a distance from us that the only component of the nuclear reaction which reaches the surface of the earth in any great amount is in thy form of electromagnetic radiation.

The amount and distribution of the solar energy which reaches the surface of the earth is shown in Figure 3, a map of the earth upon which are given the incident energy contour lines in terms of kcal/cm^2/year. (The conversion factor to watts/m^2 is 1.33.) As is clearly indicated, the most intense solar radiation, averaged over the entire earth, is not at the equator but at about 30° north and south of the equator, largely because of the atmospheric conditions. In the northern hemisphere, there

are only two regions in which the average annual insolation is over 200 watts/m^2. These are in the North African and Middle Eastern deserts and the Southwest desert of the United States. Because of the lack of water in these regions, they are not very fruitful in terms of total agricultural productivity. However, if synthetic processes could be developed, basedupon upon knowledge we may have (or gain) of the natural process of solar conversion which takes place in green plants, it may be possible to make use of this high solar influx even in regions of little water. It is exactly this situation which is a major component of our interest in trying to reproduce some of the processes which take place in green plants without the necessity for agriculturally competent environments.

Finland, and most of Northern Europe, do not appear in the high color regions of the world map in Figure 3 which is average insolation over the entire earth. Nevertheless, for some periods of the year, even in Finland, there are some long days, shown in Figure 4, which is a comparison of data from weather stations with the following geographical distributions: One near the equator (Trivandrum), one at 33° north of the equator (Phoenix, Arizona) and Helsinki at 60° north. Of course, the most northerly location naturally has the largest fluctuation of sunlight and the lowest overall average insolation. However, for at least part of the year suitable devices for solar energy collection might be made to work, provided storage facilities were also available.

The "natural" storage for solar energy takes place in the form of reduced carbon which ultimately becomes the fossil fuel, and we will speak more of that later.

Let us now look at the quality of the solar radiation which comes to the earth's surface. The distribution of solar radiation as a function

of wavelength plotted both in terms of photons and in terms of energy content is shown in Figure 5. The a) curve is the incident solar radiation at the top of the atmosphere and the b) curve is what actually impinges on the surface of the earth. The major absorption above 9000 A is due to carbon dioxice and water vapor, which reduces the energy content which comes to us at such long wavelengths very materially. Similarly, below 3300 A there is very little solar radiation impinging on the earth's surface due to upper atmosphere absorption, particularly of ozone. In fact, our biggest supply of solar energy lies between 4000 A and 7000 A. This, of course, is precisely the region of wavelengths for which living organisms have been most efficiently evolved.

Let me remind you of a fact I mentioned earlier, along with our first projection, namely, that about one-half of the energy consumption by man, at least in the United States, was lost as low temperature heat because most of it is used in some kind of a thermal engine whose mechanical efficiency for conversion to useful work is limited by the Carnot law. Thus, because of limitations of our materials the highest temperatures at which we can work are limited, and because of the fact that the coolest temperatures which we have to run the low temperature side of a heat engine are limited by the cooling agents (mostly water or air), the most efficient engines which we have evolved for large scale generation of electricity may run only as high as 35-38%. On the other hand, most of our transport engines run at nothing like that efficiency, rather less than 25% efficient.

METHODS OF CAPTURING SOLAR ENERGY

It is for this reason that I have divided the methods of capturing solar radiation into general categories, shown in Figure 6.[4] The upper group represents the conventional ways of using solar radiation by first degrading it to lower temperature than would correspond to its origin (about 5000°C), i.e., somewhere in the region of below 500°C, and then using this heat in various ways. The lower group of processes does not degrade the solar radiation but uses the incoming quanta in quantum conversion processes in which the excitation of electrons by the absorption of visible and ultraviolet quanta is the primary process. Following this excitation, some system of trapping and converting that electromagnetic excitation into a long-lived form occurs in all three of the quantum collection processes indicated in Figure 6. In a sense, a quantum collecting device using the solar energy at its emitted temperatures (around 5000°C) can be theoretically, at least, highly efficient. The trapping process, however, requires a certain loss in efficiency to prevent the back reaction by either thermal degradation or emission. As yet, we do not know what that limiting loss must be. There have been cases described in which the conversion efficiency may be as high as 70%. However, there are other problems,as yet unsolved, in connection with this type of use of solar energy.

Heat Collection

Returning now to the heat collection devices, listed in Figure 6: Two of these have long been in use. The oldest, of course, is the windmill in which the heat of the sun has been used to generate temperature differences in the atmosphere which result in the flow of air from one area to another. This flow can be passed through a suitable device, known as a

windmill, which converts it into mechanical energy. Another system for collecting solar heat is water evaporation from the surface of lakes and oceans into the atmosphere. The water vapor is then condensed at higher altitudes into clouds which move from one part of the earth's surface to another, over mountainous areas, where the water droplets condense and fall from the clouds. The water is then collected at high points on the earth's surface in reservoirs (usually in dams) of some kind, from which the further fall of the liquid water may be used to run turbines and generate mechanical or electrical power.

The use of focussing devices to generate high pressure vapors which can then be used to run turbines is a feasible engineering system and is being extensively explored. This may be one of the earliest of the new ways developed for capturing additional solar energy.

Another natural heat collector, of course, is the surface of the sea, and it may very well be possible to build heat engines based upon the small temperature difference between the surface of the sea and the cooler region some distance below it to make use of the enormous amounts of heat which can flow between these two temperatures.

Finally, building conditioning is being used in a small way in many parts of the world, even today. This method would be more difficult to use in the northern latitudes in which the heat of the summer must be stored for use in the winter.

Quantum Collection

I would now like to spend some time in discussion of the quantum collection processes for solar energy, not only because these have the

possibility of generating both energy and material but also because of their intrinsic capability of high energy efficiency.

The natural process by which solar energy is converted into food, fuel and material is the process of photosynthesis, which takes place in all green plants.[5] It is a process in which Professor Virtanen himself was greatly interested. His contribution to the knowledge of the long-term storage of food and fodder was of extreme importance to countries in the northern latitudes where the long summer day must be used to put by the needs for the short winter days. It was Virtanen's contribution to this capability, stemming from his basic scientific knowledge as well as his great practical interests, which has remained such an important component of agriculture.

Another quantum collection process for solar energy conversion is one which I have called photochemistry. By this I mean the direct sensitized absorption of light used to produce a useful fuel. The third process, photoelectric, is probably better known to most of you in terms of solid state devices in which the direct excitation of electrons from valence to conduction band leads to separation of charge and creation of an electrical potential. There is also a hybrid of these last two quantum collection processes which might be called photoelectrochemical in which the surface properties of the absorber are such as to lead directly to the production either of oxygen or hydrogen in a suitable physical arrangement, including the external flow of electrons.[6]

BIOLOGICAL (AGRICULTURAL) PHOTOSYNTHETIC CONVERSION OF SOLAR ENERGY

Since Virtanen's time we have learned a good deal about the way carbohydrate and protein is made by the green plant. A diagrammatic representation of this process is shown in Figure 7 where the photoelectrochemical cell in the center produces a separation of charge in which the negative charge may eventually become molecular hydrogen and the positive charge becomes molecular oxygen. In normal photosynthesis the nascent hydrogen is used to reduce carbon dioxide, through a complex cycle of compounds (here indicated by the circle). Some of the intermediate separated charge is used to generate the auxiliary compound, adenosine triphosphate (ATP), which is necessary to assist in that reduction process and various other processes of synthesis in the plant. We have learned a great deal about the way in which the chemical reduction process occurs in the green plant, from carbon dioxide to fats, proteins, nucleic acids and hydrocarbons. On the other hand, our knowledge of the primary quantum conversion process (represented by the gray box in the center of Figure 7) is still rudimentary. I will speak more of what we know of this process later.

Carbohydrate Utilization

AT present, let us explore how the natural process of photosynthesis might be used in ways to increase the supply of fuel and material. Most of you are undoubtedly aware of the fact that the major product of carbon dioxide reduction by green plants is carbohydrate, in one form or another. Some simple carbohydrates, such as sucrose, can be stored in large amounts in certain plants. For example, sugar from cane or beets

is created by this natural photosynthetic process and has become a direct source of human food. In some plants the principal carbohydrate storage material may be a more complex polysaccharide, such as starch, which is still directly digestible. In such plants as rice, and other grains, as well as potatos, this carbohydrate is thus a source of human food. The largest use of cellulose (wood, cotton, etc.) is as a structural material because of its crystal limitations and physical character. This carbohydrate may be processed by certain animals who harbor within them mechanisms capable of hydrolyzing the cellulose so that the animal may make use of it.

Most carbohydrates, when finally hydrolyzed to their simple sugars, can be converted, usually by fermentation processes, into a variety of useful products, not only food but fuel and materials as well.[7] The chemical reactions by which this occurs are shown in Figure 8, and the numbers clearly indicate that the process can be highly conservative of the energy values contained in the carbohydrate.

There was a time, in the recent past, when our principal source of industrial alcohol, and all things made from it, was such primarily produced photosynthetic carbohydrate. The history of this situation is given in Figure 9, showing the sources of industrial alcohol in the United States over the past thirty years. During World War II practically all of the industrial alcohol in the United States was made from grain. In recent times, however, with the availability of low cost petroleum, other sources of alcohol have given way to ethylene which, in turn, is derived from fossil fuel. The reason for this has been the very low price at which ethylene could be obtained from fossil sources and the ease with which it could be hydrated to form alcohol. The process of hydration can, of course, be reversed, and if the price of the raw material, namely, ethylene, rises

sufficiently high, it may become economic once more to go back to other ways, deriving the ethylene from ethanol rather than deriving the ethanol from ethylene. Such ethanol would have to come from renewable carbohydrate resources.

There was a time, about a year ago, when I believed one might even use the very efficient carbohydrate producer, sugar cane, as a source of that carbohydrate which could be used for ethylene. However, the shortage of sugar for human food which has come about during the last year makes it unlikely that this very easy source of ethanol will be available soon for material purposes.

Rather, we will have to find ways of making use of the enormous amount of waste carbohydrate which is now returned to the air, lakes and oceans as a result of human and animal activity. A great deal of technological effort is now going forward in many parts of the world to find ways to convert waste products of human and animal activity into useful materials, either directly by bacterial hydrolysis of the carbohydrate before fermentation or direct conversion by fermentation to methane (not to ethanol). Some of this is already being done today, but it must be expanded manyfold if it is to have any great impact.

Another possible source of carbohydrate which is not today exploited to the extent it might be is the seaweed (algae) which grows off most of the coasts of the continents.[8] Its use today is very specialized, primarily in the production of certain kinds of materials used in drugs, coatings and food additives. But the enormous productivity of seaweed is attracting attention as a resource for large scale production of fermentable carbohydrate which could be used in the ethanol or methane route to produce useful materials. The giant kelp beds which occur off the coast of California are particularly attractive for this purpose, but related varieties grow even

in the northern latitudes such as the North Sea and the Baltic Sea. Whether they can be harvested on a sufficient scale to be useful for anything more than cattle food supplements, or fertilizer, remains to be seen.

Hydrocarbon Production

I would like to remind you of the possibility that some plants not only produce carbohydrate but can reduce the carbon even further to make hydrocarbon itself directly. The best example, of course, is the latex-bearing plant, Hevea, which is today grown on plantations in Southeast Asia and some in Africa, and, of course, grows wild in Brazil. There are some 3000 species of latex-bearing plants which have not been explored as a source of hydrocarbon since their latex does not produce rubber. The hydrocarbon content and the nature of the hydrocarbon in these latex-bearing plants has yet to be thoroughly explored and exploited. If one accepts these plants as a source of hydrocarbon rather than as a source of elastomer (rubber), the fact that the yield of plantation Hevea was raised in the last thirty years from 400 lbs/acre/year to 2400 lbs/acre/year is an indication of the potential for breeding which is inherent in the wild species.[9]

Figure 10 shows the annual productivity of these three renewable plant resources for comparison purposes. Perhaps the most important of this group is the potential 40 tons/acre which the kelp seems to be capable of producing, almost ten times the dry weight productivity of the best carbohydrate producer we know today in agriculture.

If this type of agricultural effort - i.e., development of plant breeding for hydrocarbon production -- could be developed (and there is no obvious reason why it could not be done) it may constitute a resource,

not competitive with human food production, in addition to those which we have already explored.

The mechanism by which the green plant produces these various materials (including carbohydrate and hydrocarbon) are shown in detail in Figure 11. Here the two sites for harvesting the carbon reduction cycle are clearly shown: The carbohydrate in the upper left hand corener of the cycle and the hydrocarbon group in the lower right. In this diagram the primary quantum conversion act has been reduced to a small "black box" in the center of the cycle, in which the light enters and from which reduced pyridine nucleotide and adenosine triphosphate are evolved to drive the carbon reduction cycle, expelling oxygen to the atmosphere. Knowing as much as we do about the way in which the green plant manipulates carbon it should be possible to add to the usual plant breeding efforts additional chemical efforts to control the direction in which the synthetic sequences occur, thus altering the storage products of the plant. Work toward this end has been going forward in our laboratory for many years, and we have already found a number of ways in which the flow of carbon is regulated in this cycle.[10]

MODEL SYSTEMS OF PHOTOSYNTHETIC SOLAR ENERGY CONVERSION

In addition to our efforts to learn more of the intricacies of the carbon reduction cycle in photosynthesis and to possibly develop some additional methods of regulating the cycle for development of certain types of products (hydrocarbon, carbohydrate), we are very much concerned with the nature of the quantum conversion process itself, not only in green plant systems but in model systems as well.[11-14]

In the green plant we know that the quantum conversion process takes place in the chlorophyll-bearing organelles of the plant (chloroplasts)

which themselves have a microstructure, as shown in Figure 12. The quantum conversion process occurs in the lamellar layers, which are shown as dark layers stained with osmium. (We will discuss the detailed structures of these lamellae in more detail later.)

The details of the quantum conversion process which takes place in these plant organelles is shown in Figure 13. Here the emphasis of Figure 11 is reversed; the major carbon reduction is placed in a circle to the right and the "black box" of Figure 11 is expanded to be the entire focus of interest. It is evident that two successive quanta are required to move electrons from the water to the highly reduced acceptor, (trap I) even more reduced than molecular hydrogen itself. The beginning of the electron flow from the water is induced by the absorption of light by pigment P680 to an excited state. This excited electron then flows back down the potential gradient through plastoquinone and cytochrome f. In the course of this movement, some high energy phosphate is generated from ADP and ortho-phosphate, returning eventually to the hole left by a second excitation in pigment P700. Excitation of this pigment brings the electron to a very high reduction level which can give rise to molecular hydrogen or reduced carbon dioxide.

The structure of this pigment system and electron transport system is not yet known in detail, but the fact that there are two quite different enzymatic processes at either end of the system has already been discovered.

On the oxygen end of the process (on the left side of the figure) there is some polynuclear manganese complex involved in the generation of the molecular oxygen. The details of the structure of that polynuclear manganese compound have yet to be determined. It is rather labile in

terms of its complexing properties since almost every effort to isolate it as a complex has so far resulted in the isolation of uncomplexed manganese ion. A few cases have been reported in which some rather labile protein complex of manganese has been claimed as the oxygen generating catalyst, but its structure has yet to be determined.

Photochemical Hydrogen Production

At the other end of the photosynthetic system, i.e., production of hydrogen, a good deal more is known. Here in some plants if oxygen is excluded or minimized and carbon dioxide withheld, the potential reducing agent may appear as molecular hydrogen itself. When it does, there is present in the plant an enzyme (hydrogenase) which gives rise to the molecular hydrogen.[15] The electron passes through an iron-sulfide protein known as ferredoxin on the way either to molecular hydrogen or carbon dioxide. The basic structure of this group of complexes is now known. The chemistry involved in photosystem II (known as II only because it was the second one discovered) shown in Figure 13 involves the absorption of light and the excitation of an electron, leaving behind a highly oxidized "hole", presumably in pigment P680. This may either directly, or indirectly, remove electrons from a manganese compound (whose structure is not yet known) which, in turn, will oxidize water to produce molecular oxygen and reduced manganese for further reaction. A diagrammatic description of this process is shown in Figure 14. It involves a binuclear manganese complex moving from two ^{+2}Mn ions up to two ^{+4}Mn ions, and returning, with the evolution of oxygen.

Following excitation by photosystem II the excited electron passes through the connecting cascade to the hole left behind in photosystem I (pigment P700) to return the pigment to its initial condition. The

electron excited by photosystem I is transferred eventually to ferredoxin and hydrogenase on its way to molecular hydrogen. The structure of the group of iron-sulfide proteins which contain both ferredoxin, hydrogenase and even nitrogenase, is rapidly being determined.

The crystalline structure of bacterial ferredoxin (as opposed to plant ferredoxin) has been recently elucidated.[16] The active center of this material appears to be a 4-iron/4-sulfide distorted cube, as shown in Figure 15. A model compound representing this distorted cube has been synthesized using benzylmercaptide to replace the cysteine groups of the ferredoxin protein, and its crystal structure has also been determined, shown in the right-hand side of Figure 15.[17] As yet, the structure of green plant ferredoxin has not been so completely determined. However, it is known to be a 2-iron/2-sulfide protein whose core structure is shown in Figure 15 and for which models have indeed been synthetized. In fact, the hydrogenase itself seems to be such a 2-iron/ 2 sulfide protein of a similar type.

While a model substance of the 2-iron/2-sulfide protein has indeed been made, using two ortho-xylylene dimercaptide molecules, the two halves of the molecule are not tied together. Upon reduction of that model substance, the molecule is unstable, and it is for this reason that we are presently making an attempt to produce a model substance for the hydrogenase in which all <u>four</u> mercaptide groups are part of a single molecule. This is most readily achieved in terms of a dodecapeptide, modeled on bacterial ferredoxin in which each of the four cysteine groups is separated from its neighbors by two intermediate peptides.[18]

We believe that if and when such a (hopefully cyclic) 2-iron/2-sulfide/4-mercaptide compound is constructed it will be capable of adding

two electrons without falling apart and may give rise to the evolution of hydrogen when two electrons are added to it in the presence of protons. If our knowledge of the manganese compound could be developed to the same extent, it is conceivable that such a compound could be placed in a system so that the two successuve quanta involved in the transfer of an electron from water to hydrogen go through two separate stages, one through manganese and the other stage through the iron. The proposed juxtaposition of these two catalysts will be discussed again later.

It is worthwhile at this point to remind you of Professor Virtanen's interest in the enzyme required for the fixation of molecular nitrogen from the atmosphere which is found in certain plants. This enzyme is called nitrogenase. Nothing was known of its structure at the time Virtanen worked on it, and he made surmises as to how the nitrogen was chemically changed on its way to ammonia. Today a good deal more is known about the structure of nitrogenase.[19] It appears to be a combination of an iron-sulfur protein, such as ferredoxin, and a molybdenum-iron protein of a similar sort. The molybdenum-iron compound absorbs the nitrogen and the reduced iron-sulfur protein in combination with magnesium and ATP reduces the nitrogen so bound, as shown in Figure 16.

Chloroplast Structure

Let us return to our earlier discussion of the chloroplasts in which all of the hydrogen and oxygen generating complexes are located, and examine in more detail an electron micrograph of such a chloroplast (Figure 18). This photograph is the result of the method of "freeze-etching" in which the sample is frozen, the ice sublimed away and the resulting structure shadowed with heavy metal or carbon. One can see a lamellar

structure in great detail, and if the photograph is magnified still further, one can see the details within these lamellae; this latter is shown in Figure 19. Here, the lamellae are shown to be coated with particles (protein) of different size. It is not unreasonable to suppose (and it is a current hypothesis) that the low oxidation catalysts which generate hydrogen and the high oxidation catalysts which generate oxygen are on opposite sides of these lamellae, and they may be contained in the particles visible in Figure 19. A diagrammatic representation of these lamellae is shown in Figure 20.[20] Here the two different kinds of particles are clearly visible. Whether they do indeed represent the oxidizing and reducing sides of the photosynthetic system remains to be established. They may, however, represent two aspects of the same particle in which the two catalysts are separately mounted.

Photoelectric Membrane

The question of whether the electrons are physically able to move from one side to the other of the molecule or membrane while, at the same time, the two sides are in some way prevented from reacting with each other remains This prevention of back reaction may be achieved by mounting the electron donors and the electron acceptor molecules on opposite sides of a membrane and requiring that only the excited electron can actually pass the membrane (perhaps by a tunnelling mechanism) while the ground state electron on the acceptor molecule cannot, thus providing a barrier to the back reaction.

An alternative structure would be to surround each individual molecule with such a nonconducting hydrocarbon-rich barrier through which the excited electron must pass and through which the ground state acceptor electron cannot return. Whether either or both of these ideas plays a

role remains to be established. However, that there are mobile charges generated in such a lamellar system seems to be established.

We have recently measured a Hall effect dielectric loss in chloroplasts and Figure 21 shows the results of such an experiment. Part C shows the photoinduced dielectric loss without any external magnetic field, due only to charge separation. Part B shows the behavior of the dielectric loss when the magnetic field adds the motion of the electron to the zero field effect. Part A shows the situation in which the magnetic field is reversed and the electromagnetic effect is subtracted from the dielectric loss. It is clear that the electron mobility is high and is short-lived whereas the hole mobility, which moves in the opposite direction, is low and has a longer life.[21] In both cases, the evidence is good for mobile charges of both signs, and this is depicted more clearly in Figure 22.

Using this notion of charges mobile through a membrane, one can construct a synthetic system in which hydrogen might be evolved on one side of the membrane and oxygen on the other. Such a concept, shown in Figure 22, is still hypothetical.[22] However, the idea is that the separated electron is taken off the membrane by means of an iron-sulfide catalyst which will generate hydrogen with protons from the medium. The hole, on the other hand, is filled by the manganese complex (as yet unknown) which, in turns, removes an electron from hydroxyl to generate molecular oxygen and a proton. Similarly, a proton carrier, such as alkylnitrophenol, is built into the membrane to transmit the protons through the membrane. The basic principle of this system (shown in Figure 23) is the tunneling of the electron from the excited state, represented by S^*, through some 20 A to the conducting system represented, in this case, by the carotenoid.[23] At the other end of the carotenoid will be an acceptor molecule, such as quinone, and the electron will then pass out through

quinone, to the iron-sulfide catalyst. The manganese and iron might very well be mounted on the membrane itself and not be free to move in the medium.

Finally, one can conceivably suggest that each of these catalysts might be individually surrounded by the electron and proton permeability barriers so that the back reaction is prevented. It is also possible to remove the excess electrons on one side of the barrier and neutralize the hole on the other side of the barrier by means of a redox system which, in turn, through a pair of electrodes could deliver useful current and voltage in an external circuit.[24] (Figure 24).

CONCLUSION

As we learn the detailed structures of each of these crucial components in the photoelectron transport system (quantum conversion process) and how they are constructed, it should be possible to reconstruct the photochemical system for generating molecular hydrogen from water in a relatively stable synthetic system without the need of an agricultural environment. The hydrogen so generated could be used directly as fuel, or be a component in the construction of hydrocarbon fuels from hydrogen-poor sources such as coal and shale. It might even be possible to reconstruct the carbon dioxide reduction system of the green plant as well, and thus have the capability of generating reduced carbon in a similar synthetic system.

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 future, be another source of capturing the energy of the sun and producing electricity directly from it.

PHOTOSYNTHESIS AS A RESOURCE FOR ENERGY AND MATERIALS

FIGURE CAPTIONS

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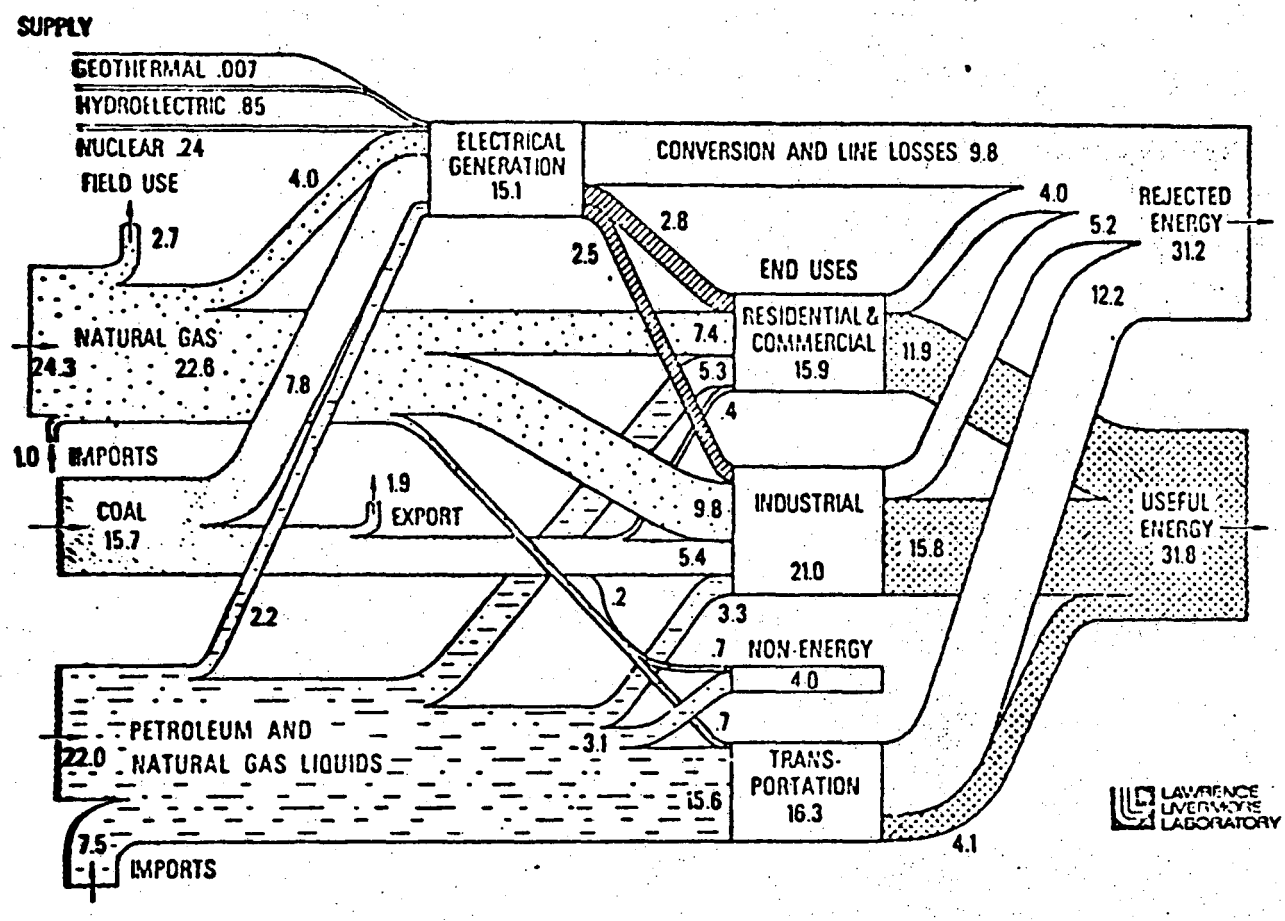
Figure 16 (XBL 741 5015)	Proposed structure of green plant ferredoxin and hydrogenase

Figure 17 (XBL 7411 7887)	Schematic representation of events during turnover of nitrogenase
Figure 18 (BC 1211)	Electron micrograph of chloroplast (Bassham)
Figure 19 (XBB 7411 7523)	Details of chloroplast lamellae
Figure 20 (XBB 7411 7524)	Diagrammatic representation of deep etch surfaces
Figure 21 (XBL 723 4569A)	Hall effect experiment; photoinduced microwave losses showing positive and negative carriers in the chloroplasts
Figure 22 (XBL 724 4627)	Scheme for photosynthetic electron transport system
Figure 23 (XBL 7411 7888)	Photochemical cell modeled on photosynthetic membrane
Figure 24 (XBL 731 4636)	Proposed synthetic membrane system for photoelectron transport and direct conversion to electric power

U. S. ENERGY FLOW PATTERNS, 1970



(NOTE: ALL VALUES ARE x 10^{15} Btu. TOTAL PRODUCTION =71.6 x 10^{15} Btu.)

XBL741-5007

Fig. 1.

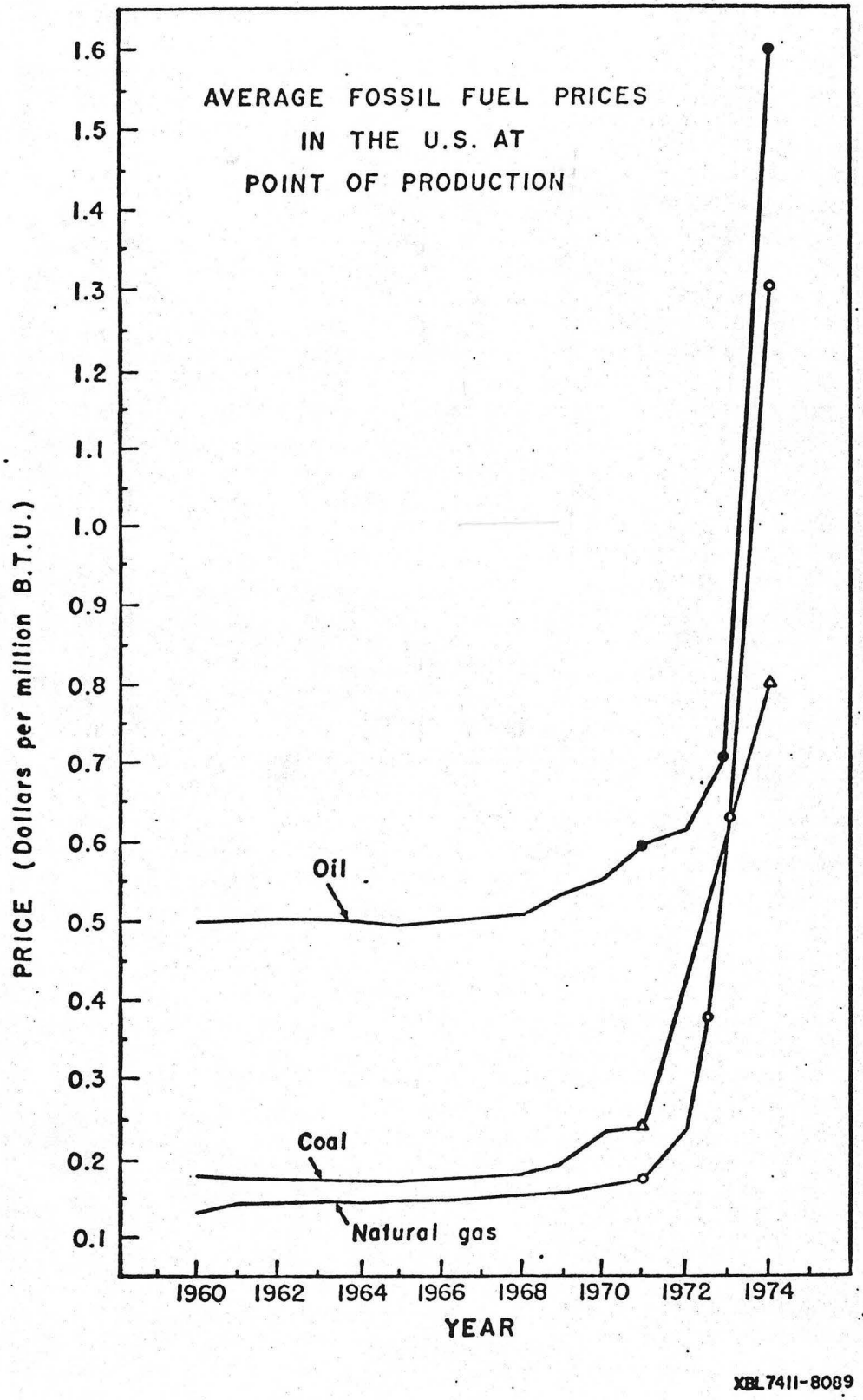
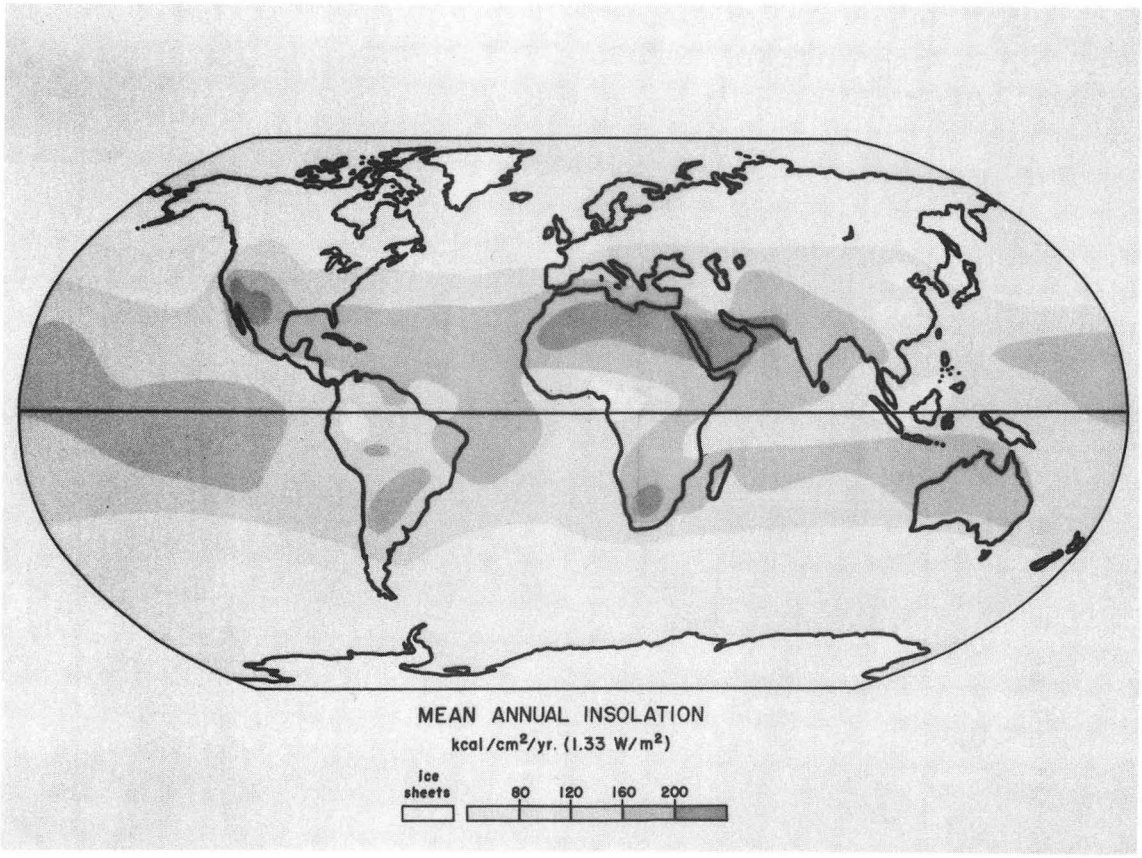

AVERAGE FOSSIL FUEL PRICES
IN THE U.S. AT
POINT OF PRODUCTION
PRICE (Dollars per million B.T.U.)
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
Oil
Coal
Natural gas
1960
1962
1964
1966
1968
1970
1972
1974
YEAR
XBL7411-8089

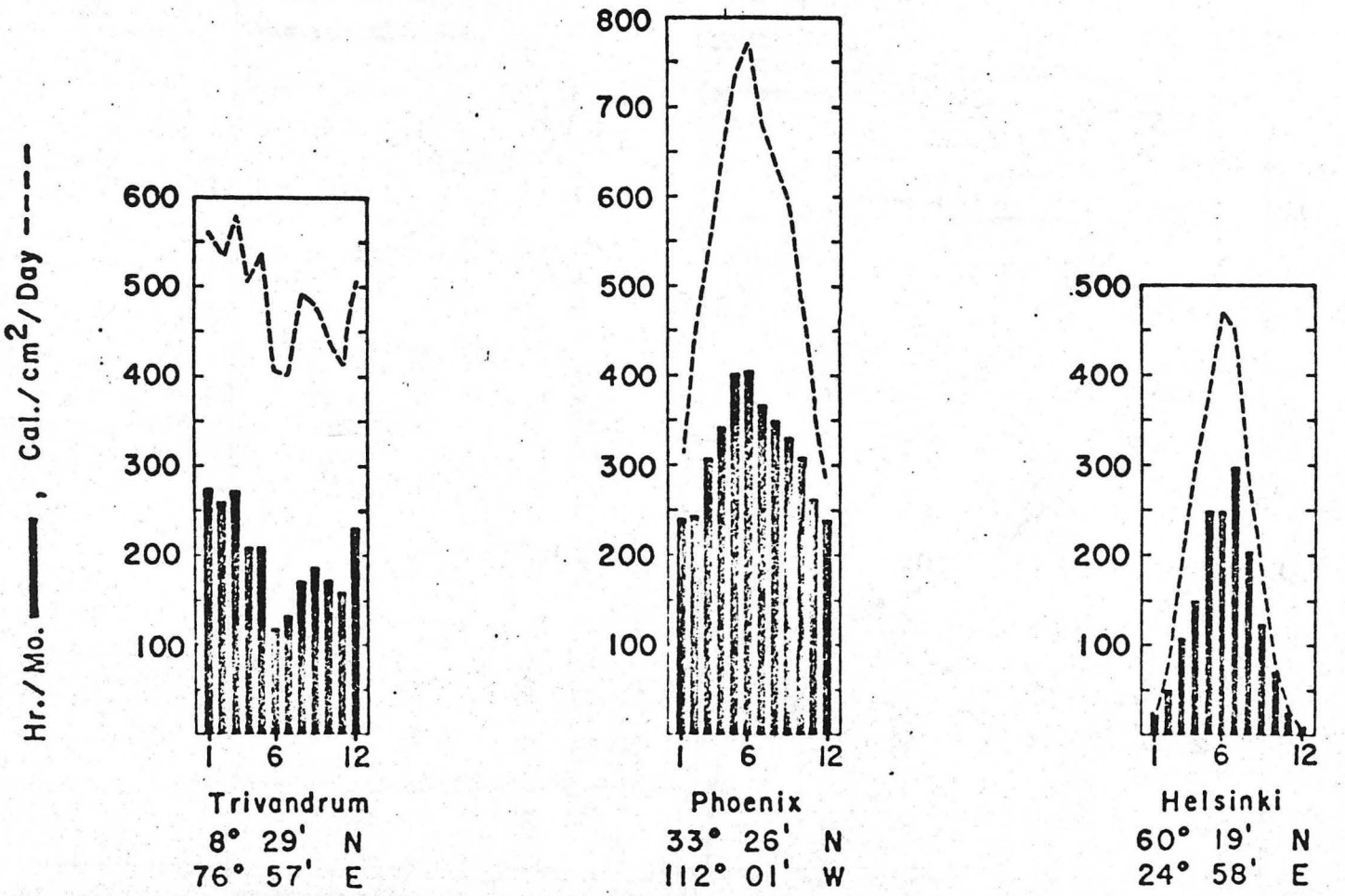
Fig. 2.



CBB 7410-6758

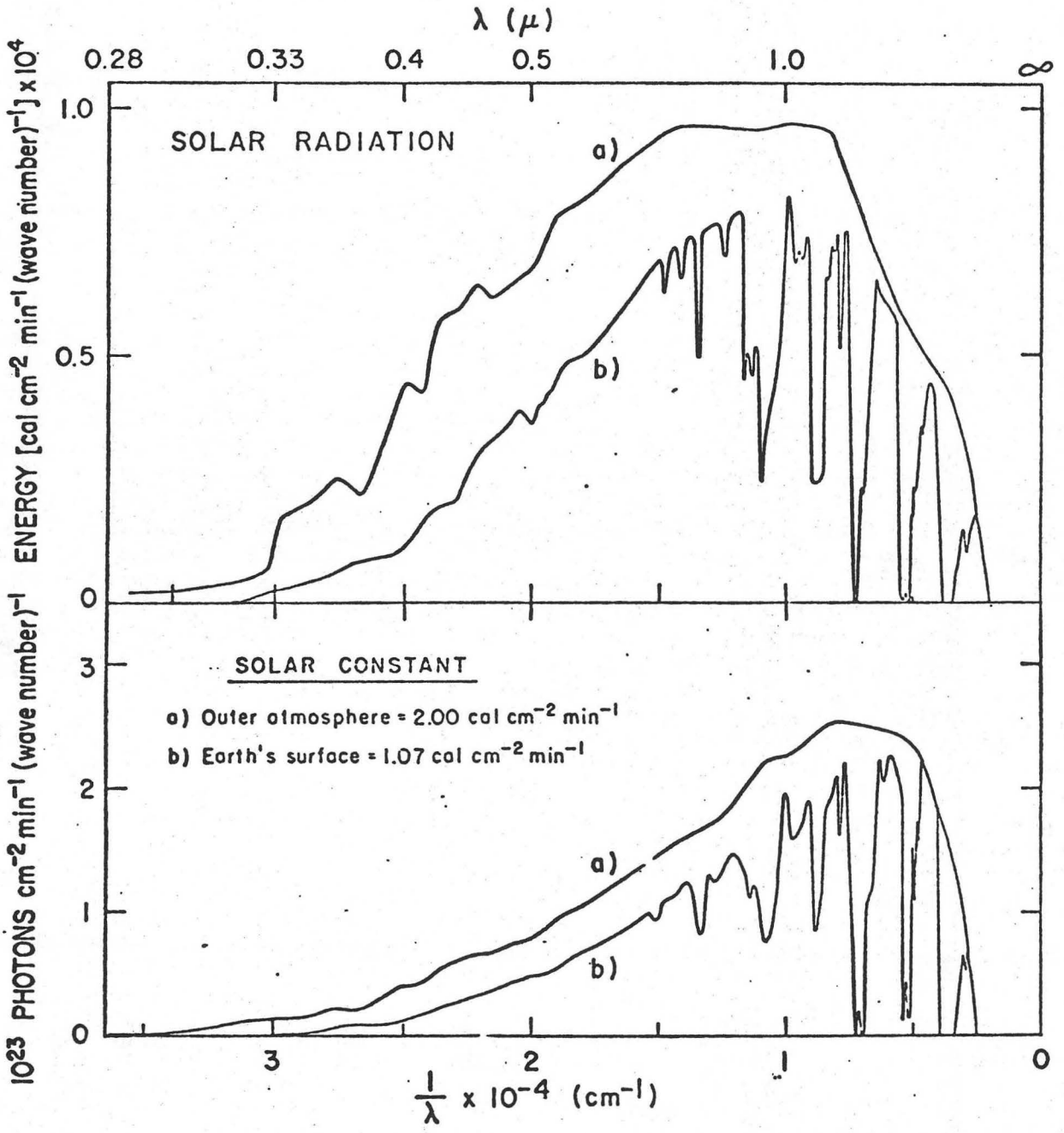
Figure 3.

0 0 0 4 3 0 1 0 0 5



XBL7410-8050

Fig. 4.



XBL722-4521

Fig. 5.

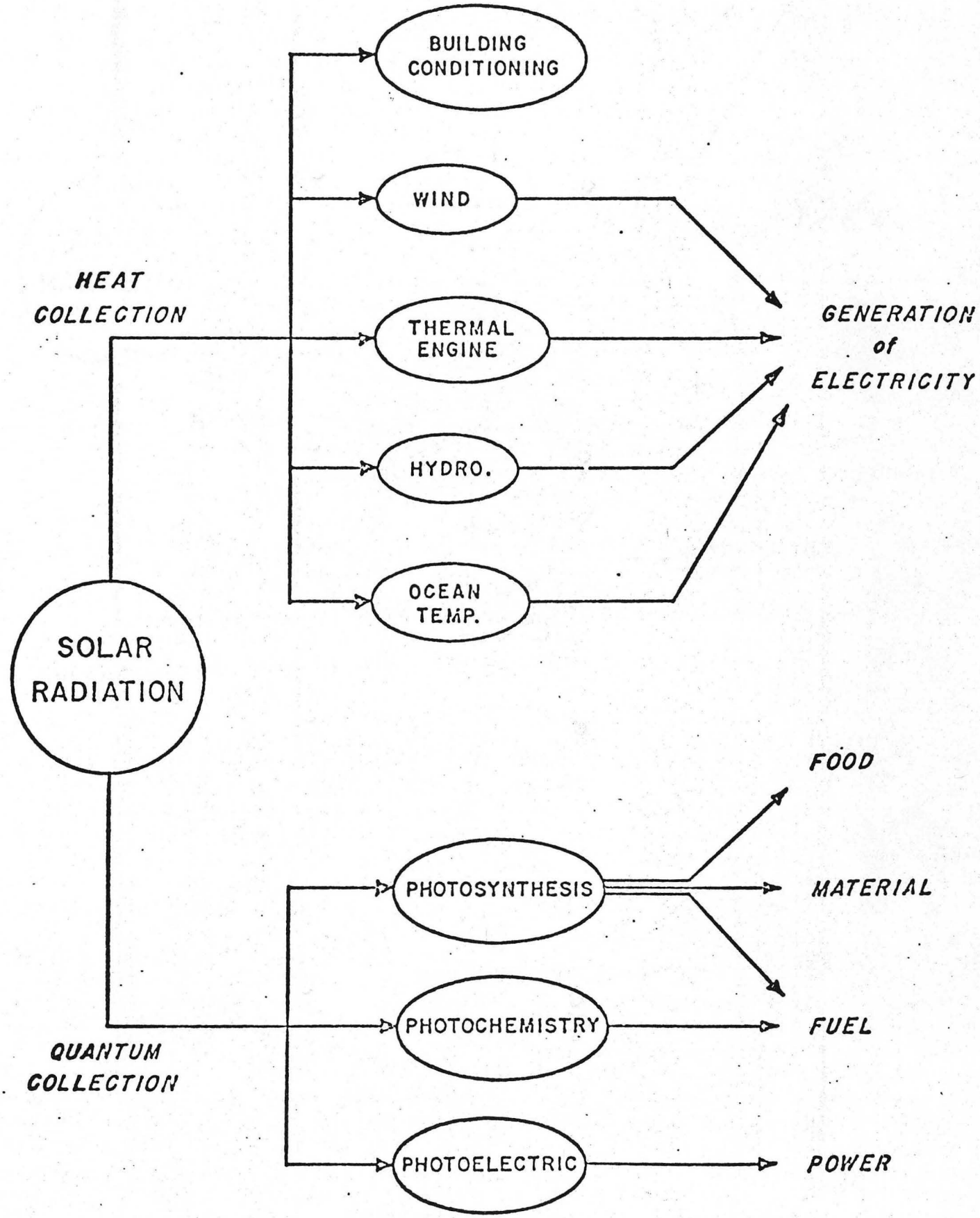
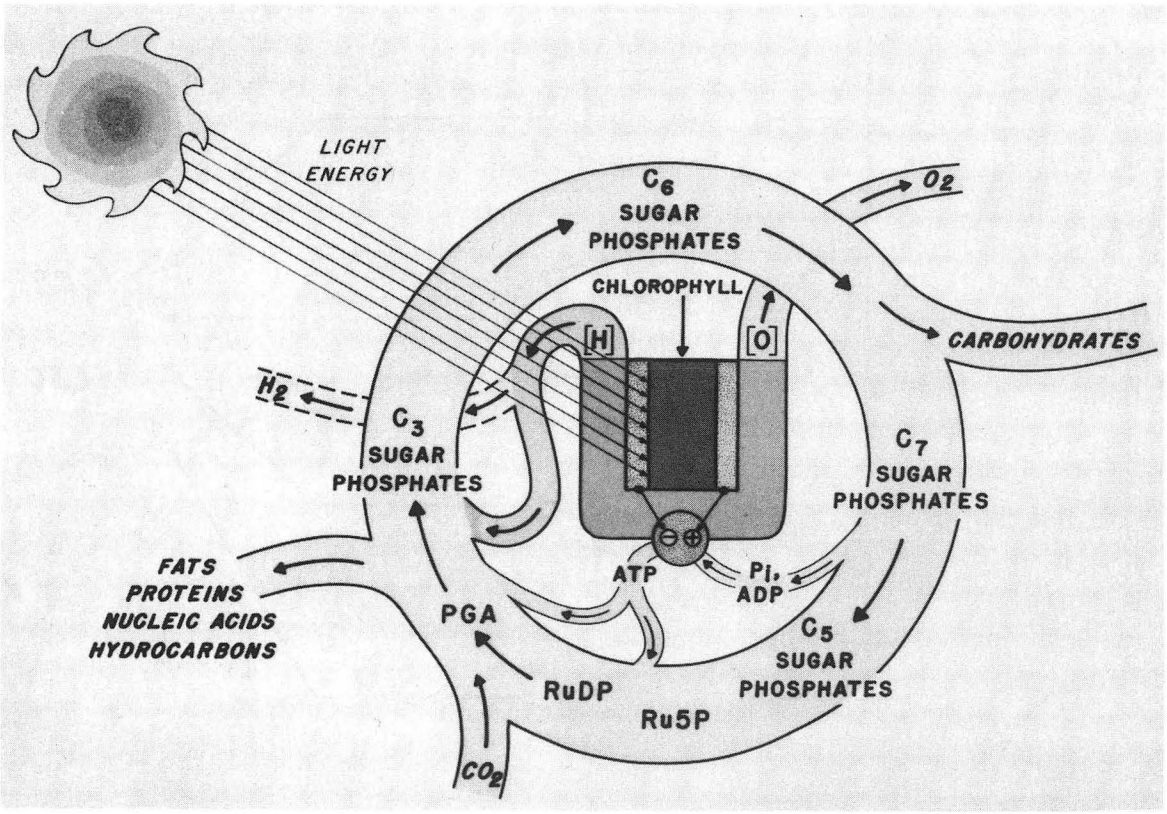


Fig. 6.

XBL743-5077



CBB 7410-6756

Figure 7.

0 0 0 0 4 3 0 1 0 0 7

$$C_6H_{12}O_6 \longrightarrow 2\,C_2H_5OH + 2\,CO_2$$

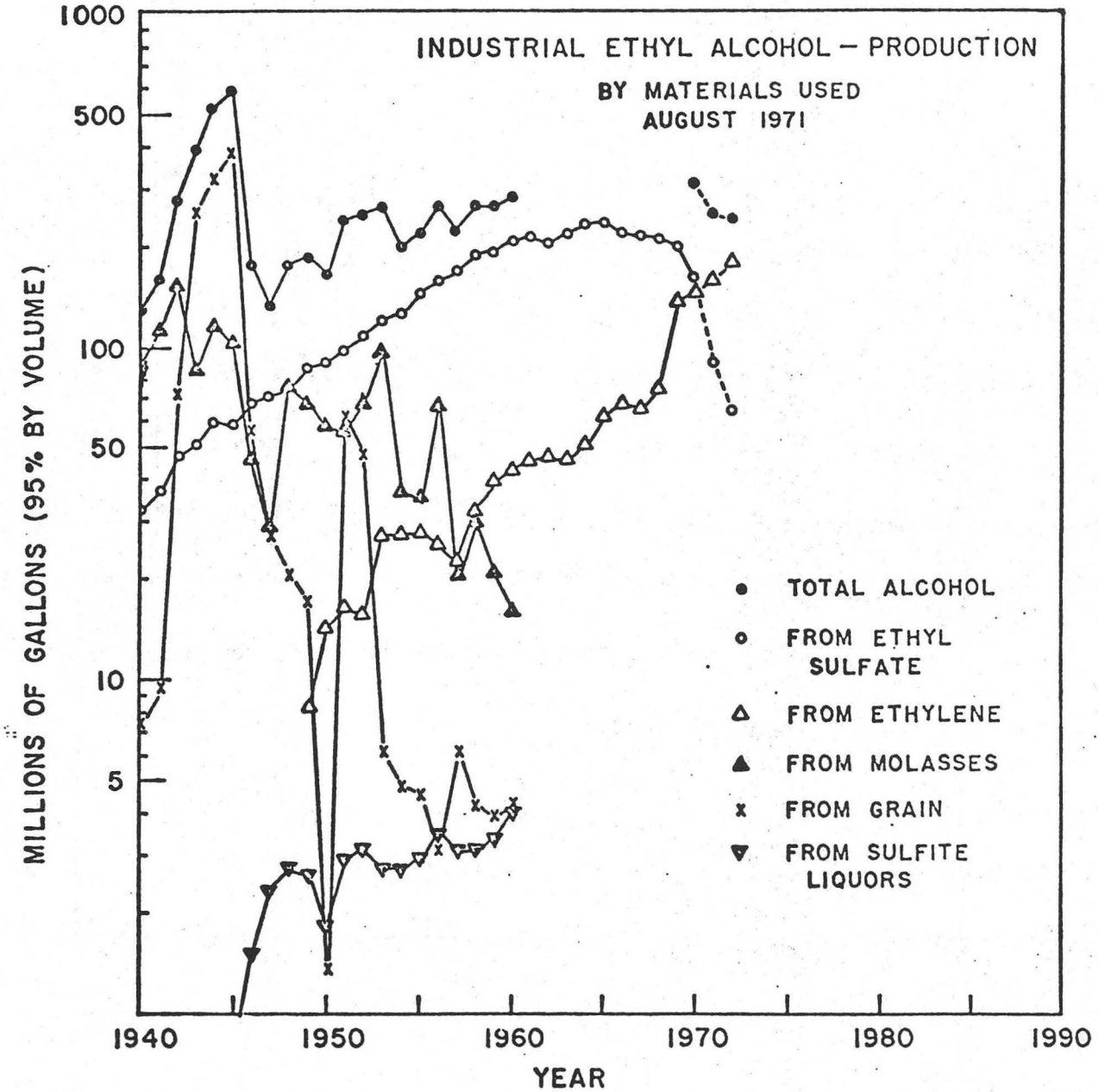
180 gm	92 gm
(673 Kcal)	(655 Kcal)

12.88 lbs $\longrightarrow$ 1 gal. (84,356 B.T.U.)

Cost / gal. = raw material + ~20¢ process cost

XBL7411-8086

Fig. 8.



XBL741-5011

Fig. 9.

ANNUAL PRODUCTIVITY

HEVEA

Present: 1 T/acre rubber
(0.2 % of incident sun)

Potential: 2-4 T/acre

CANE

4 T/acre sugar (0.23 % of incident sun)
2 T ethanol
1.2 T ethylene

4 T/acre bagasse

KELP (dry weight carbohydrate)

Present: 4 T/acre

Potential: 40 T/acre (~2 % of incident sun)

XBL7411-8087

Fig. 10.

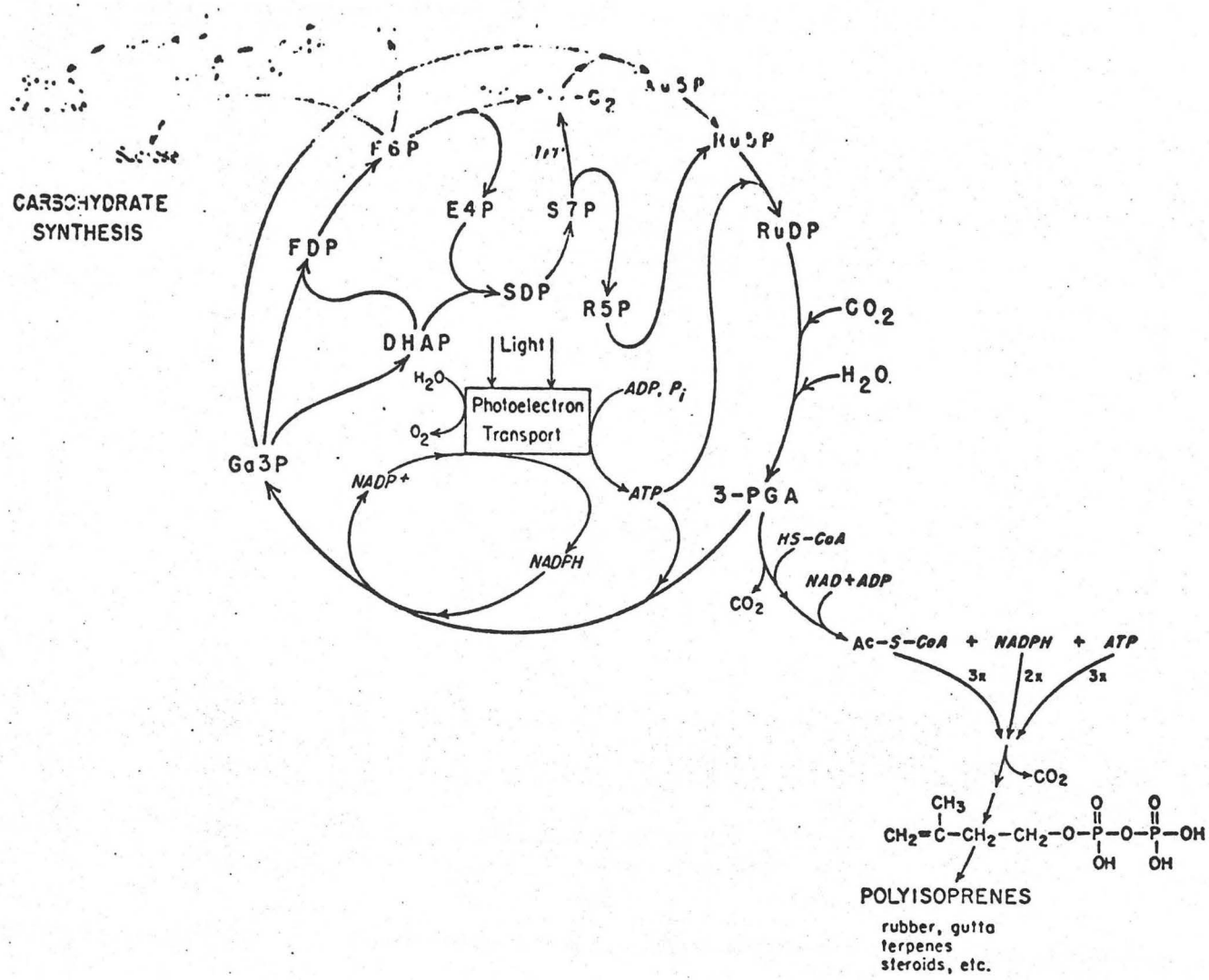
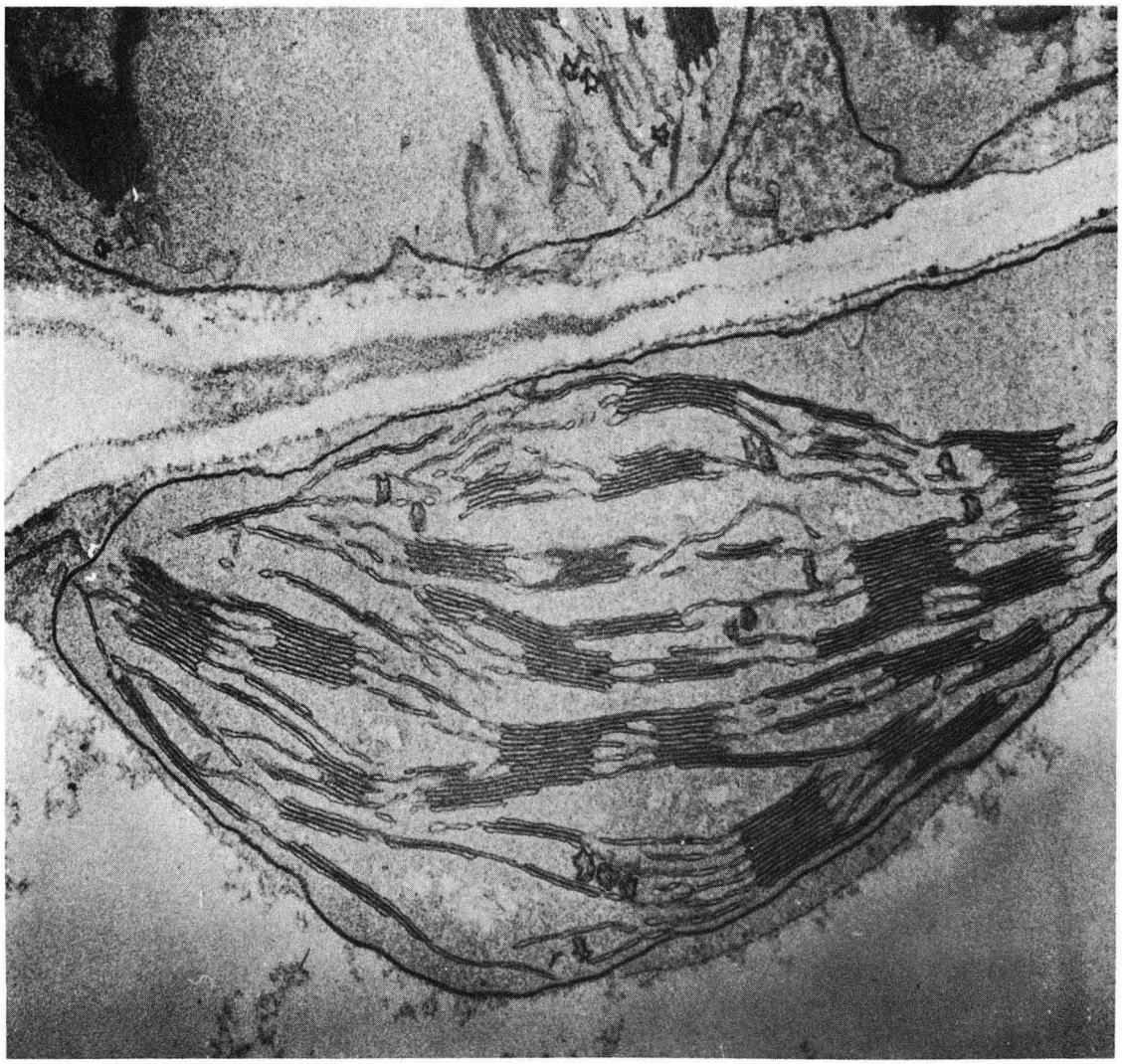


Fig. 11.

XBL685-4219 L



XBB 7411-7521

Figure 12.

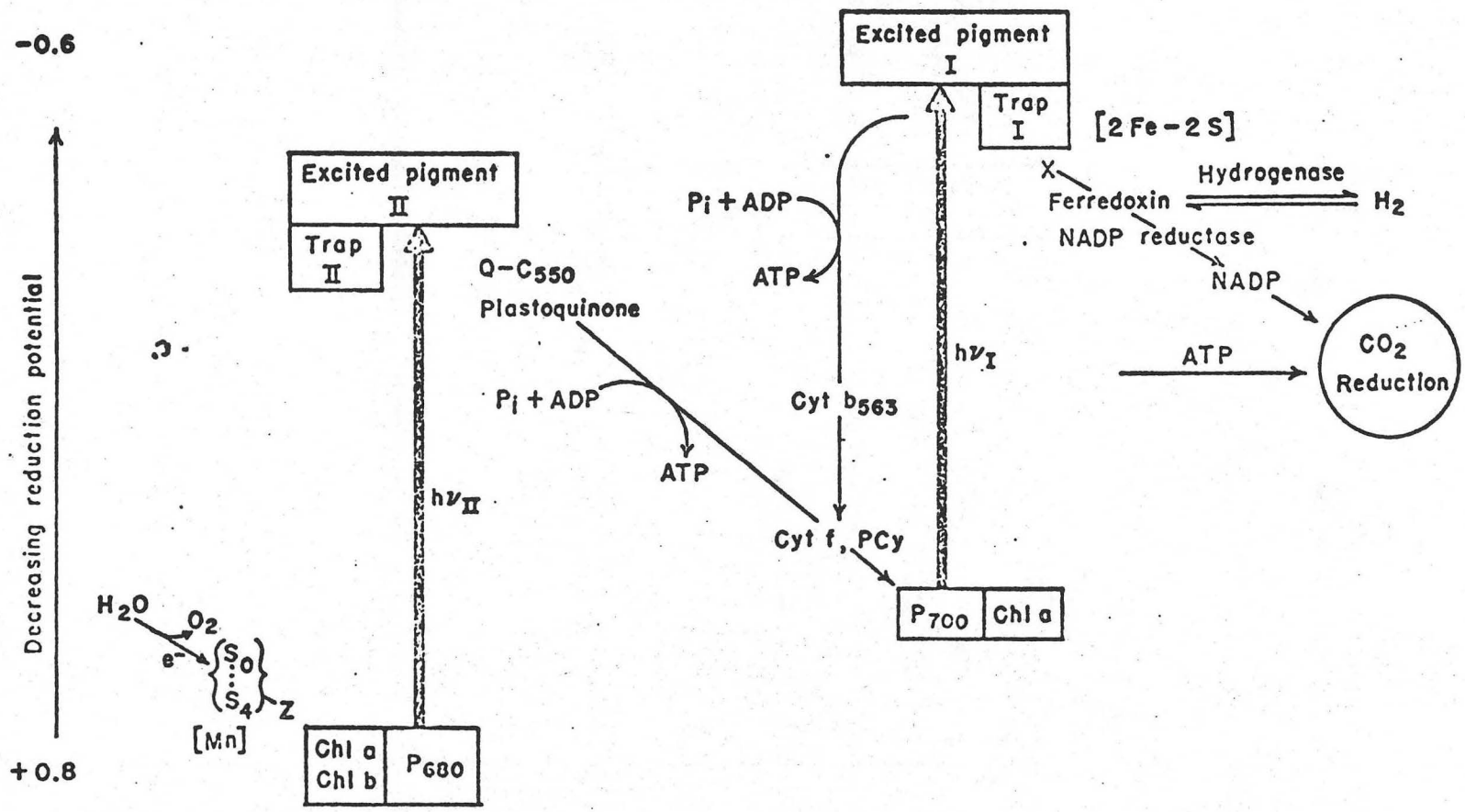
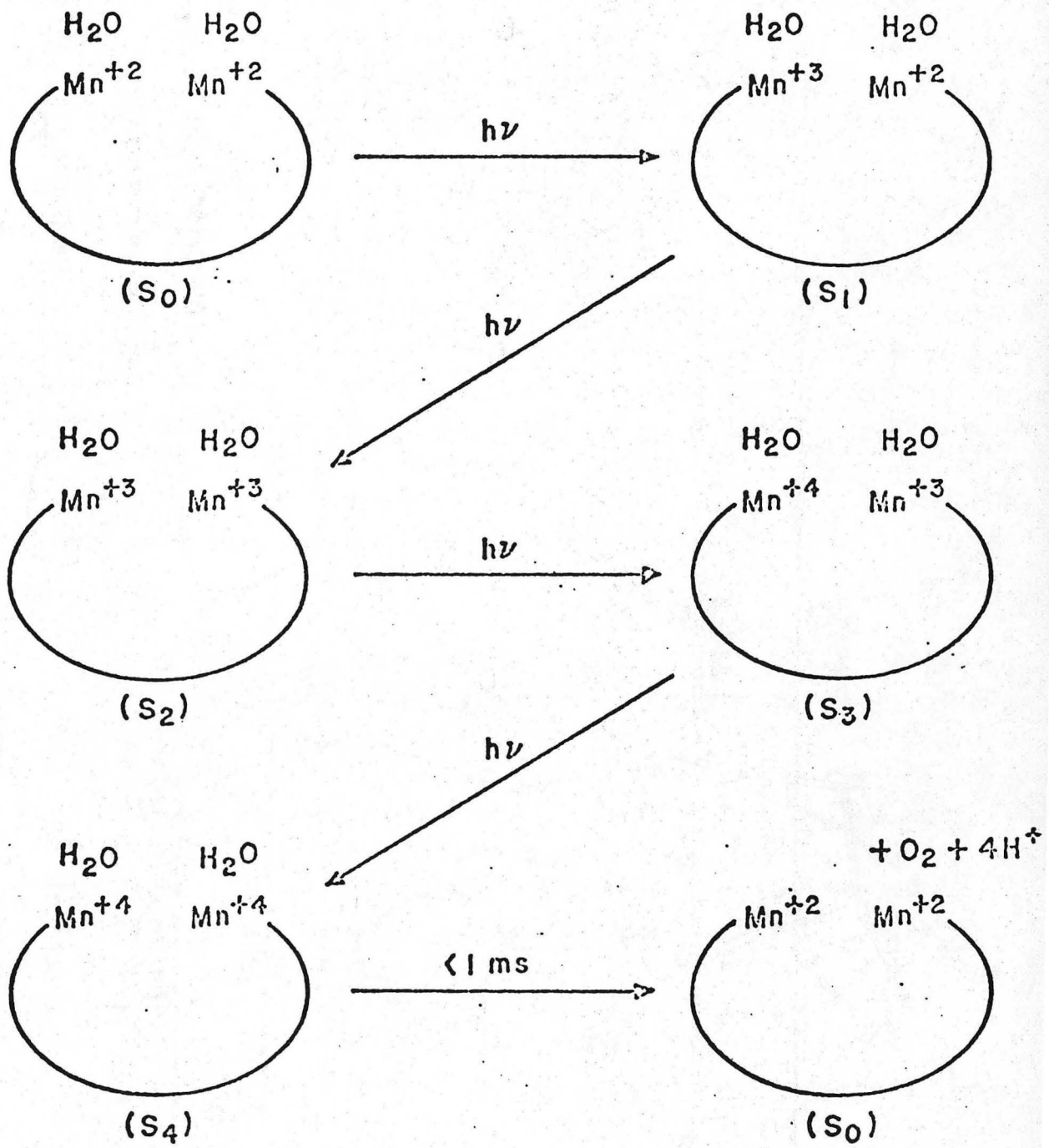


Fig. 13.

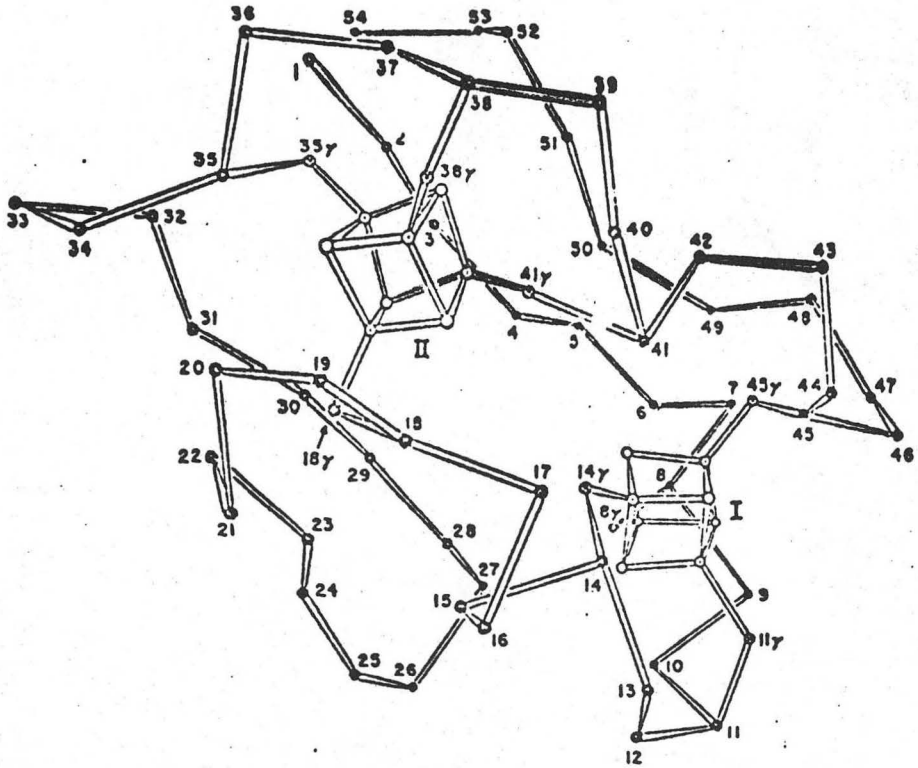
XBL7410-5395 B

POSSIBLE MECHANISM OF PHOTOSYNTHETIC OXYGEN EVOLUTION



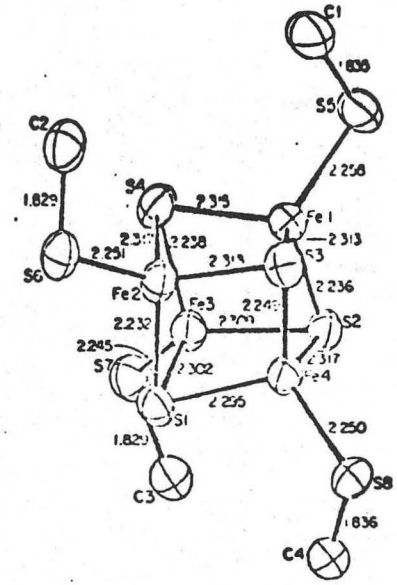
XBL 7412-7772

Fig. 14.



Bacterial Fd

(from Adman et al., 1973)



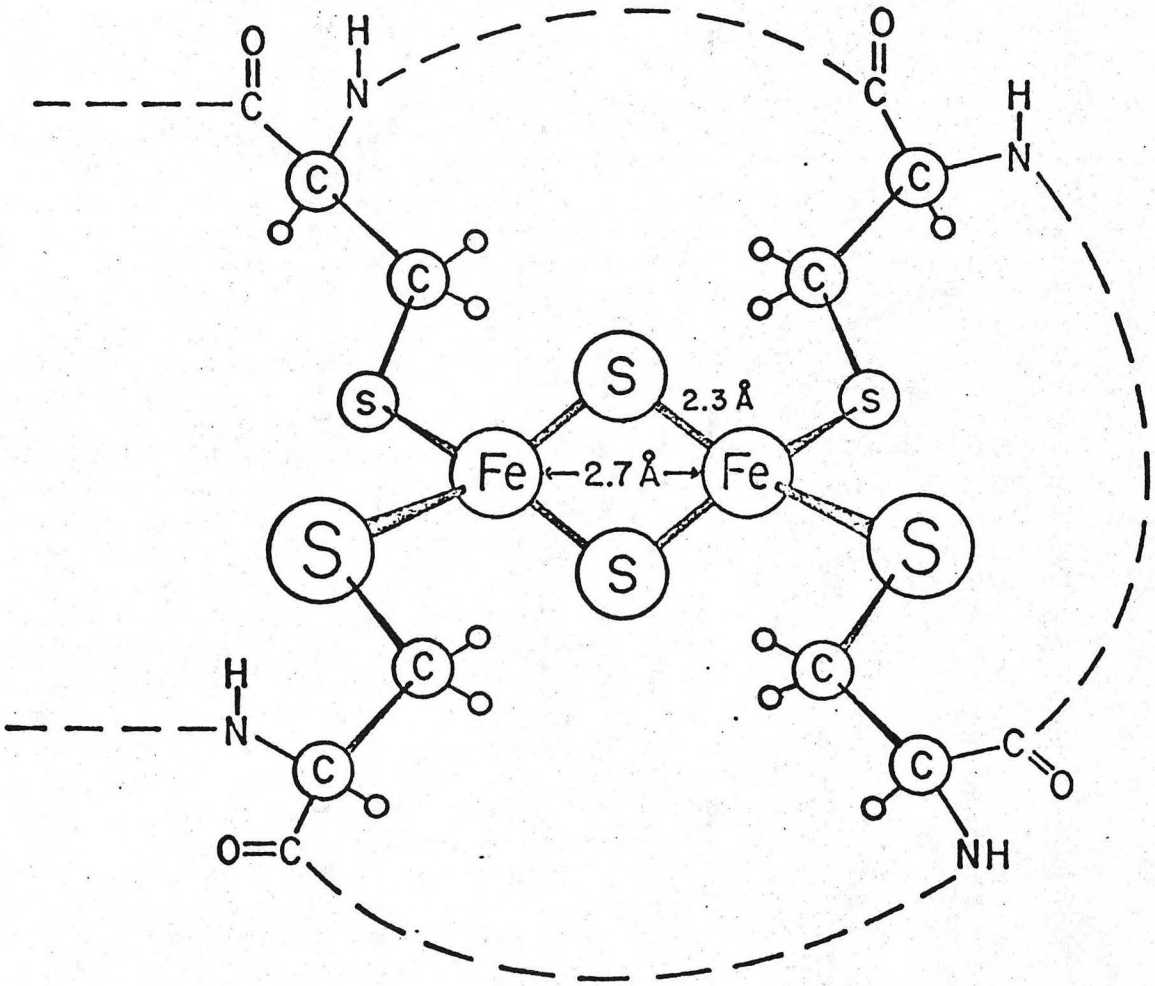
Distorted cube of

$[Fe_4S_4(SCH_2\phi)_4]^{-2}$

(from Herskovitz et al., 1972)

XBL741-5004

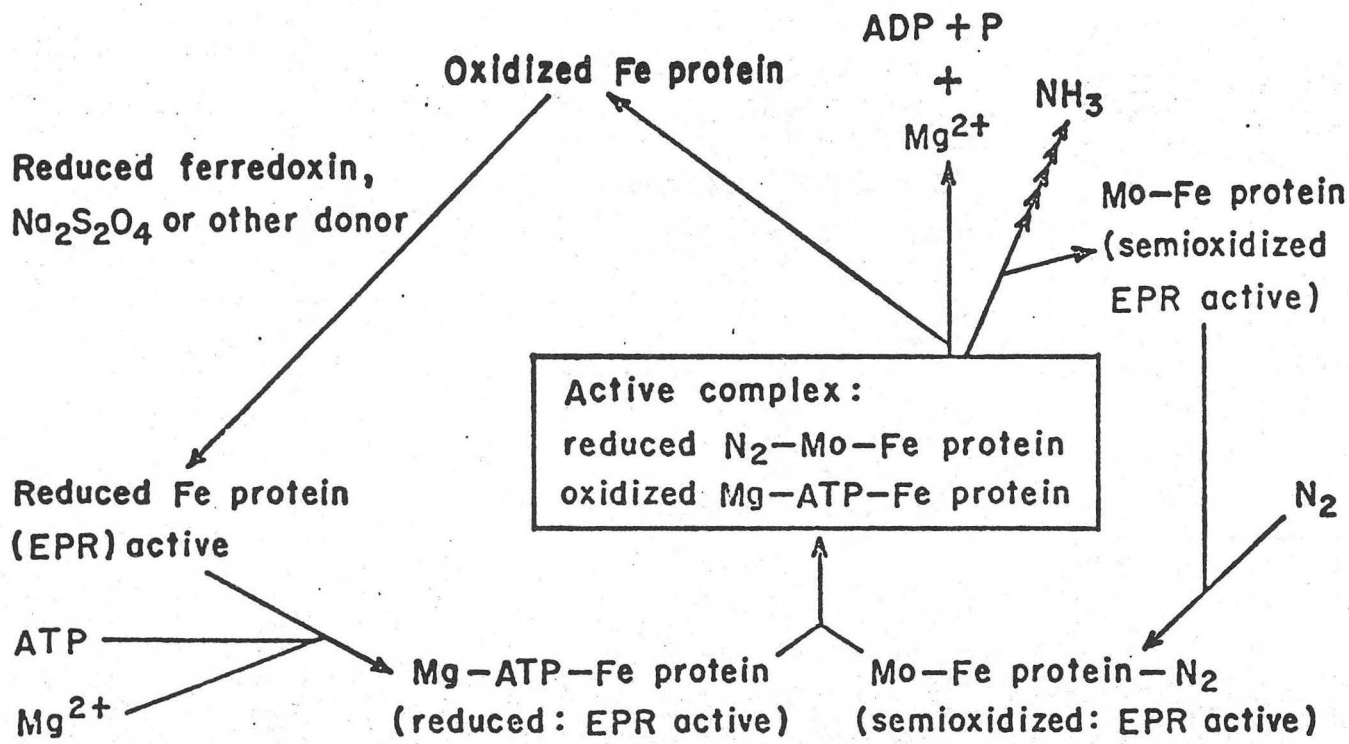
Fig. 15.



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

XBL741-5015

Fig. 16.

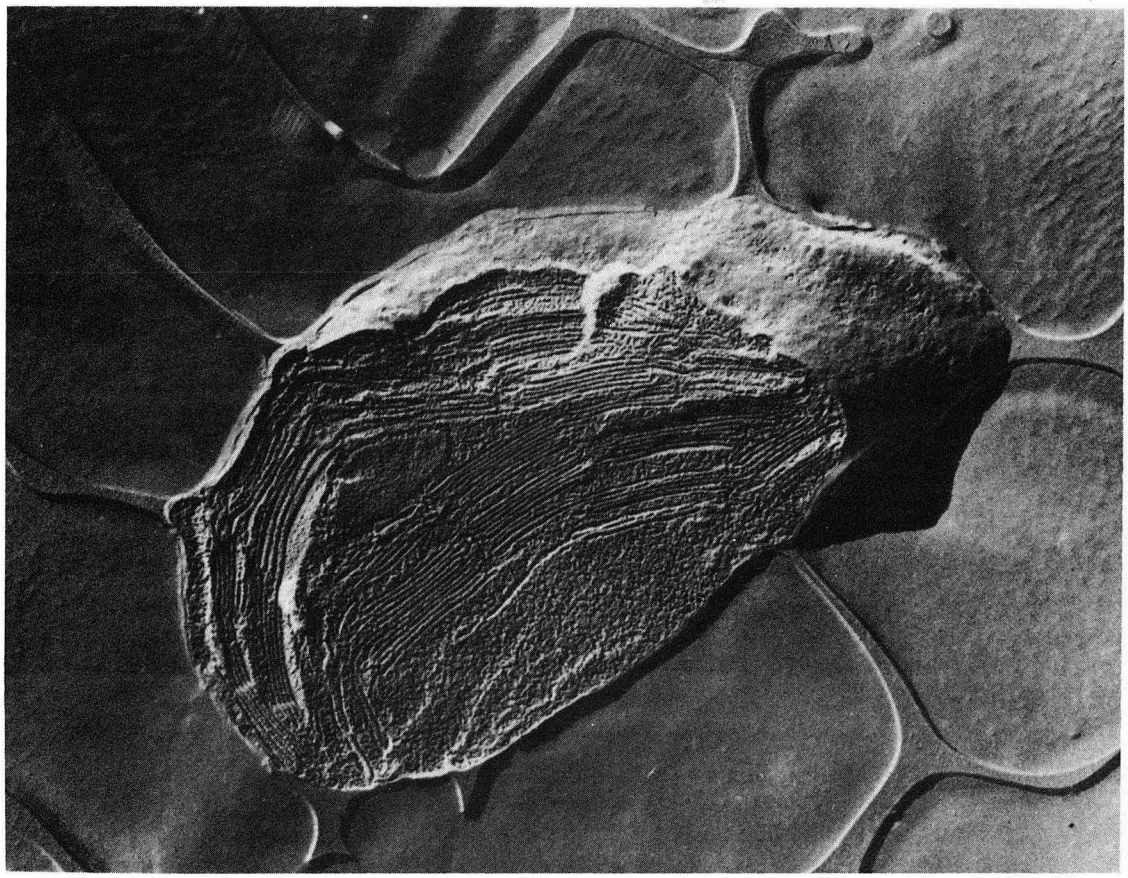


From Eady & Postgate, Nature (1974)

XBL7411-7887

Fig. 17.

0 0 0 0 4 3 0 1 0 1 2



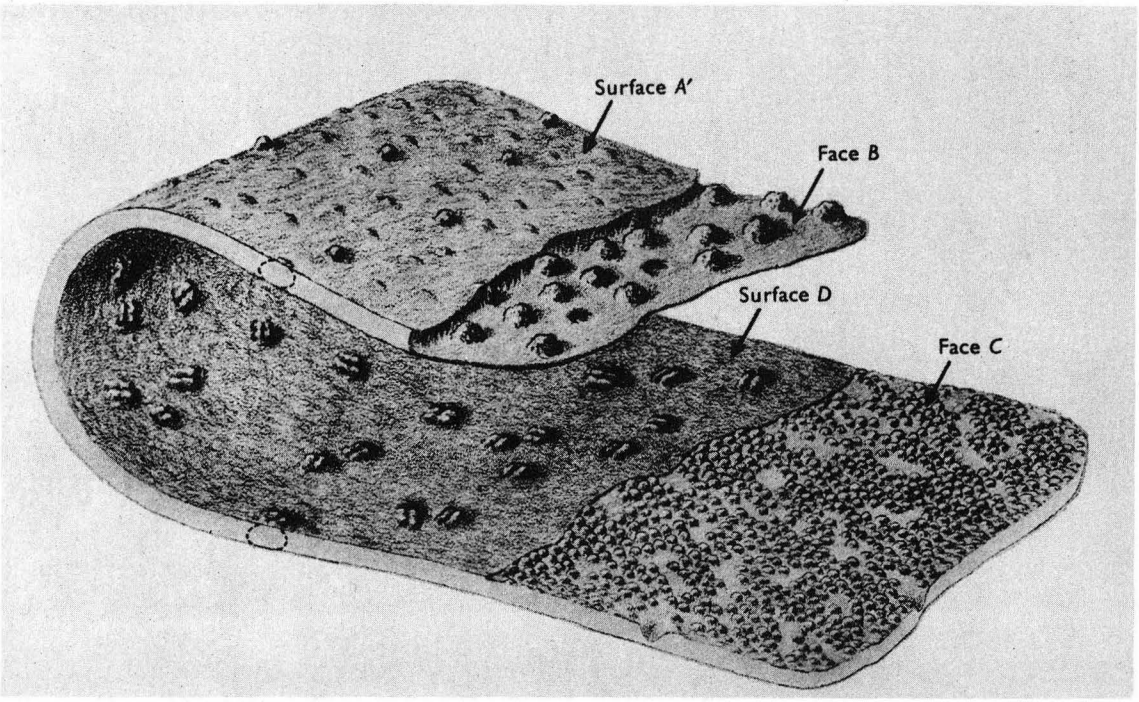
BC-1211

Figure 18.

XBB 7411-7523

Figure 19.

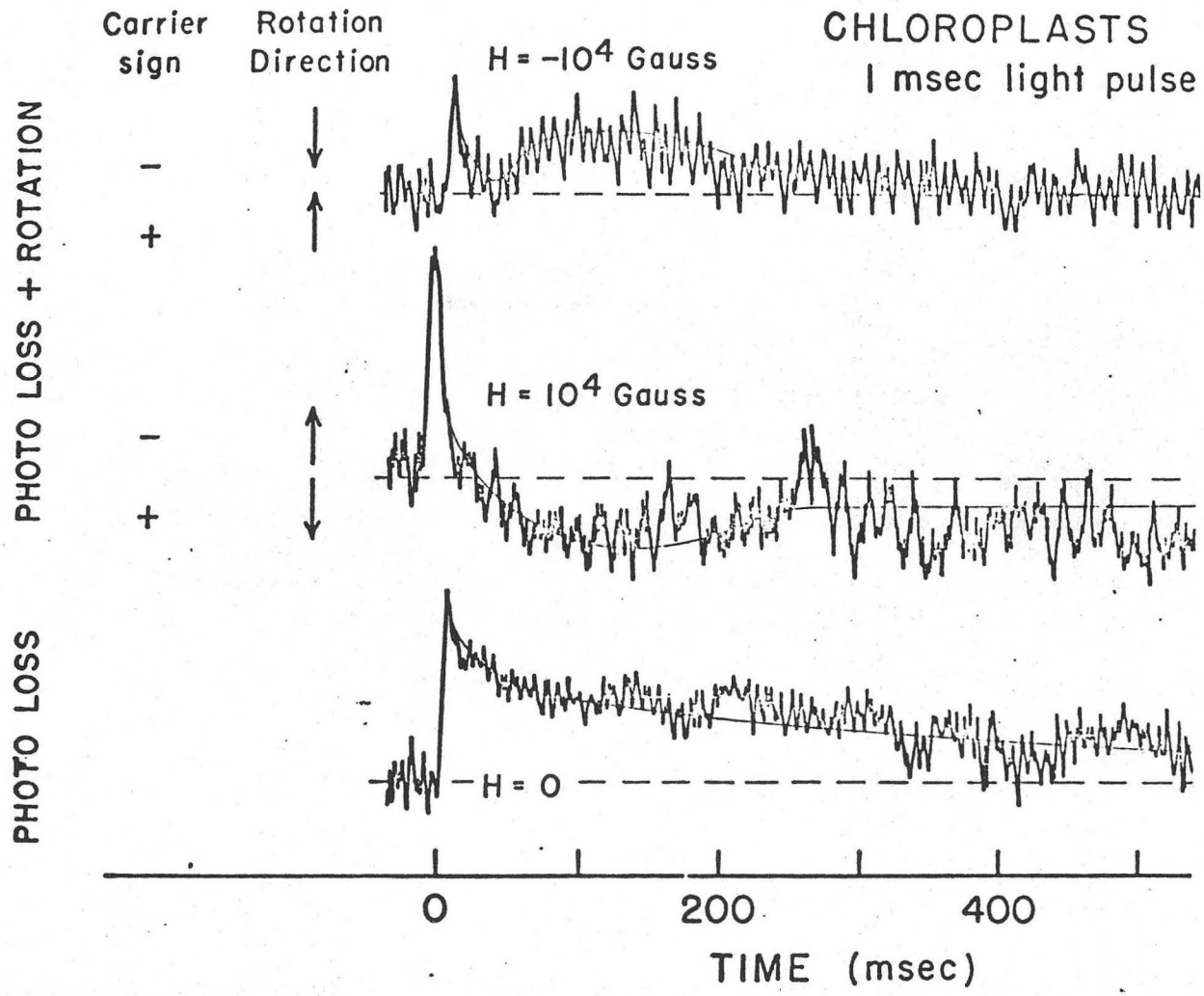
0 0 0 0 4 3 0 1 0 1 3



Diagrammatic representation of the deep etch surfaces (*A′*, *D*) and fracture faces (*B*, *C*) commonly seen in thylakoids.

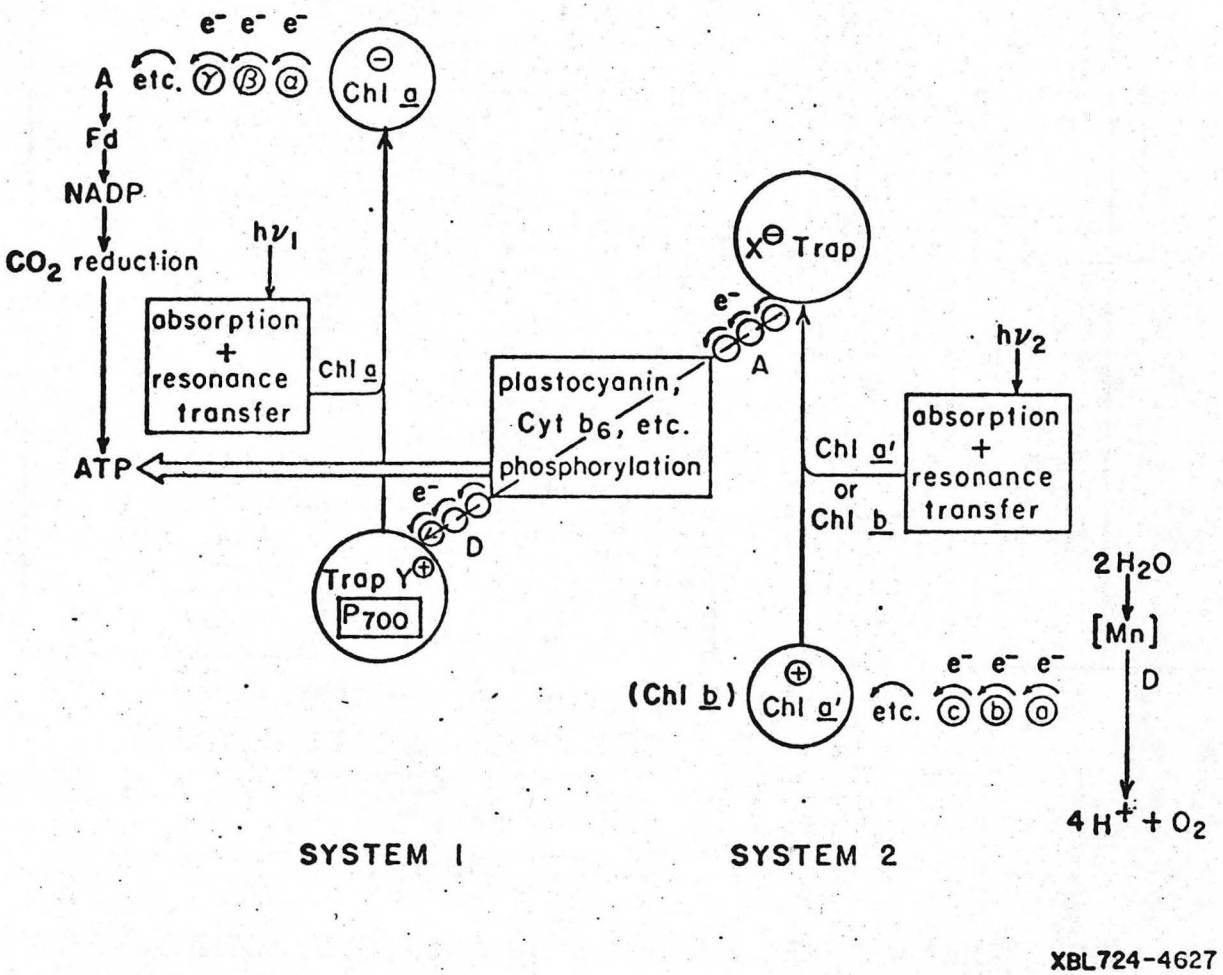
XBB 7411-7524

Figure 20.



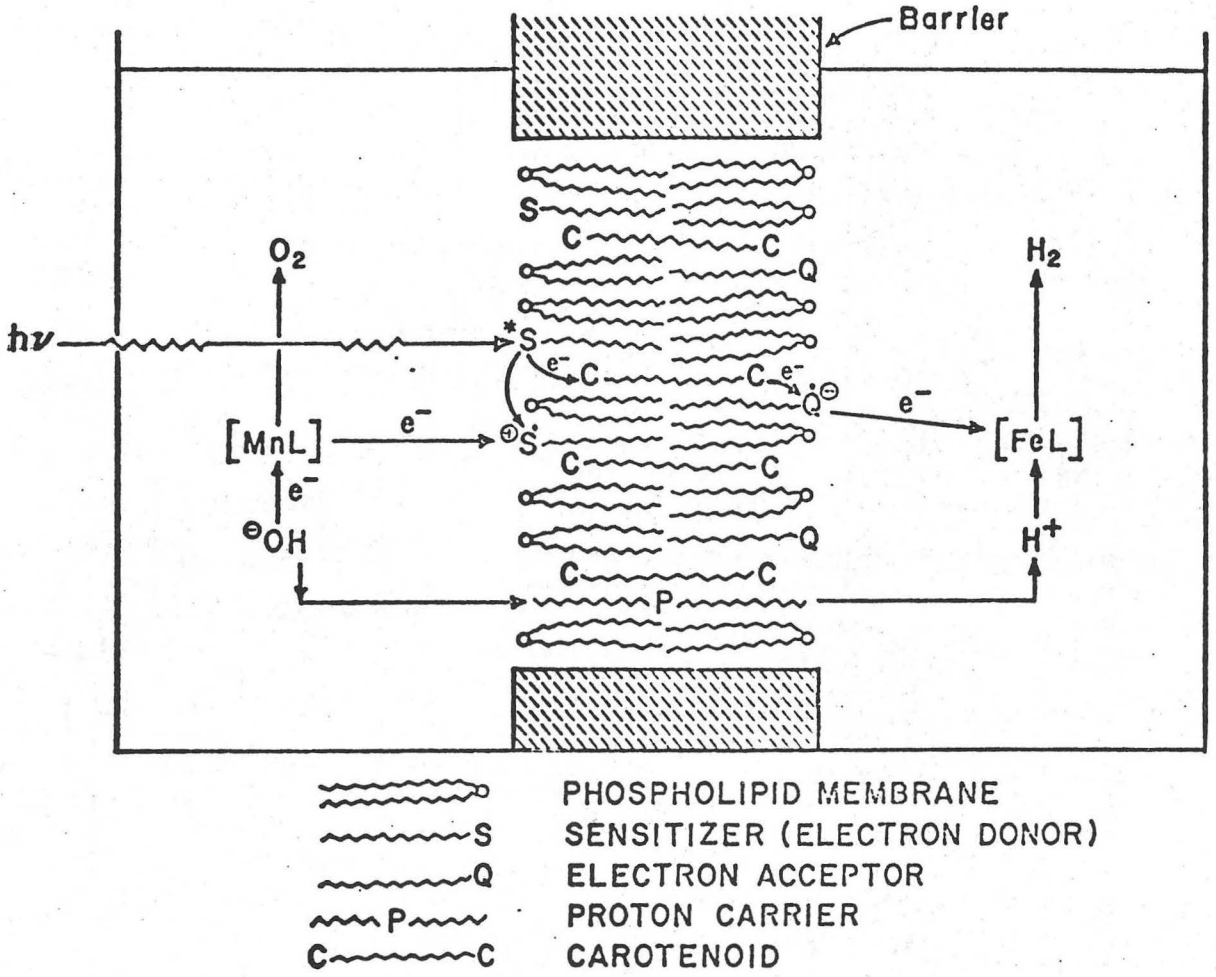
XBL723-4569A

Fig. 21.



XBL724-4627

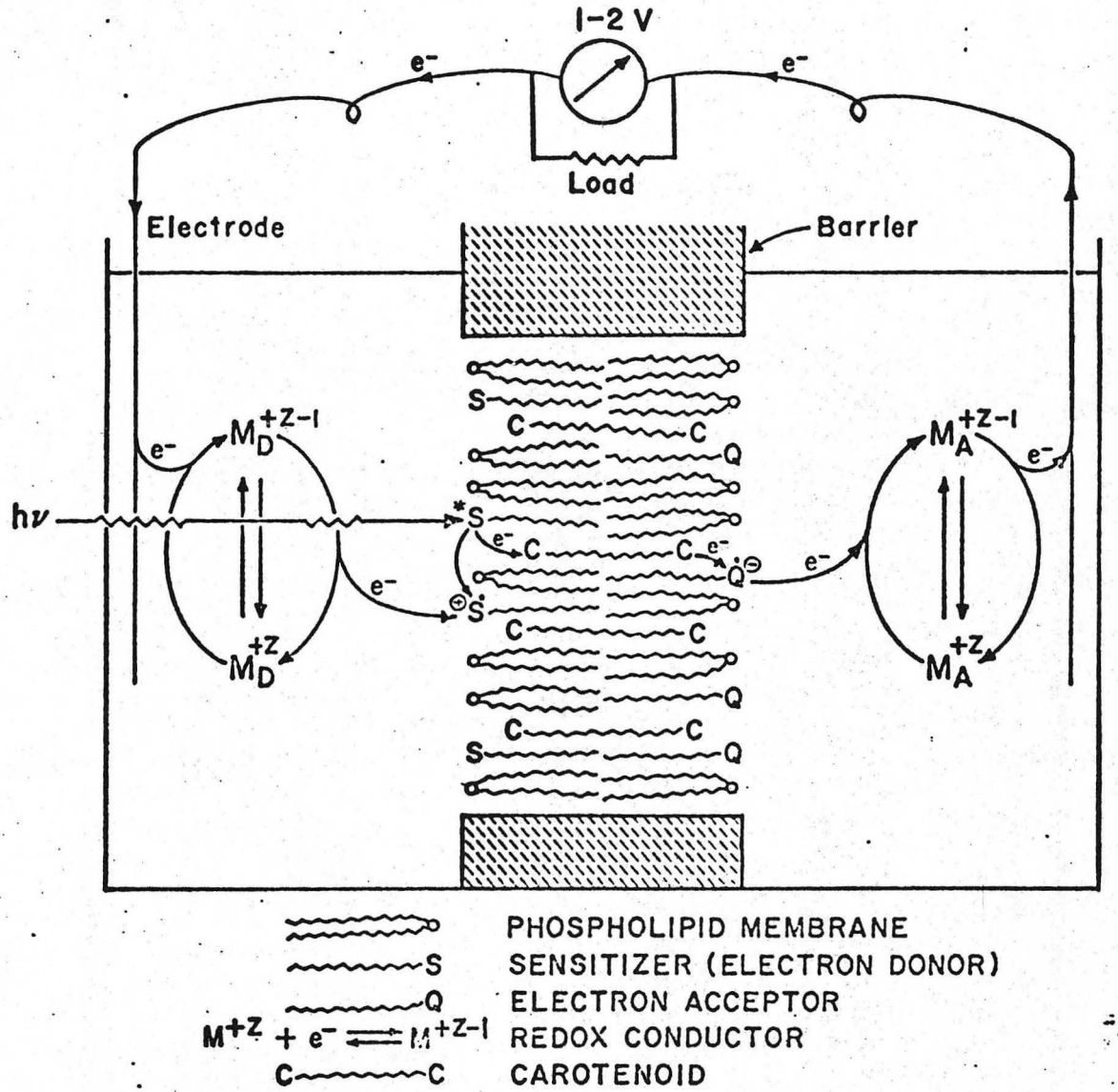
Fig. 22.



PHOTOCHEMICAL CELL MODELED ON PHOTOSYNTHETIC MEMBRANE

XBL7411-7888

Fig. 23.



PHOTOELECTROCHEMICAL CELL MODELED ON PHOTOSYNTHETIC MEMBRANE

XBL731-4636

Fig. 24.

0 0 0 - 4 3 0 1 0 1 6

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