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Melvin Calvin

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SOLAR RADIATION AND LIFE*

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INTRODUCTION

What I will discuss today stems from a combination of interests, two of very long standing and one of more recent vintage. The two of very longstanding interest are the problem of energy transduction by living plants -- the way in which a plant converts solar energy into chemical energy (and we have been concerned with this problem for over 25 years) -- and the other is the question of chemical evolution and the origin of life. It is a combination of those two interests which has provided the original impetus for putting together the kind of discussion which I am about to undertake. In addition to that, a more recent interest has been developing, related, really, to the first problem of energy transduction (solar energy conversion). This has to do with the subjects of energy, population, resources, and other questions of this sort. It is a combination, then, of those three kinds of interests (two old ones and one relatively new one) that has given rise to my desire to weave together the various ideas and themes in a coherent way today.

* Opening address, VI International Photobiology Congress, Bochum, Germany, August 21, 1972.

** The work described in this paper was sponsored, in part, by the U.S. Atomic Energy Commission.

We want to know, first, something about the sun -- its actual sources of energy, how the earth is related to it, the quality of solar energy and why we think of "solar" energy -- or, for that matter, all sorts of energy which comes from a variety of stars -- in connection with the way in which life evolved on the surface of the earth. Following that will be a discussion of the ways in which solar energy is converted by the green plant, and model systems which we have constructed on the basis of those ideas. The last part of the discussion will be concerned with comments about the available sources of energy for practical use in human life today compared to the input of solar energy on a daily basis.

Figure 1 shows a generalized diagram of the solar system itself, to give an idea of how it is constructed and where the earth is in respect to the sun. The dimensions shown are, relatively speaking, correct, regarding both the size of the bodies and the distances between them. The earth is relatively close to the sun (90 million miles) compared to most of the other planets, and this has, of course, been a factor in its overall development. In Figure 2 the earth is shown from a satellite about 30,000 miles away. You can see at a glance that a very large fraction of the light which strikes the earth from the sun is immediately reflected from it, as visible light. We will discuss the percentages in various wavelength regions later.

What is the actual reaction which gives rise to the sun's energy? The principal source of solar energy is a sequence of fusion reactions shown in Figure 3, with the final amount of solar energy emitted as 3×10^{32} Joules/day, which corresponds to a conversion of mass of 10^{16} kg/day. This is, of course, a tremendous amount of energy which the sun radiates every day, but the total solar mass is actually 10^{30} kg. Because of the mass of

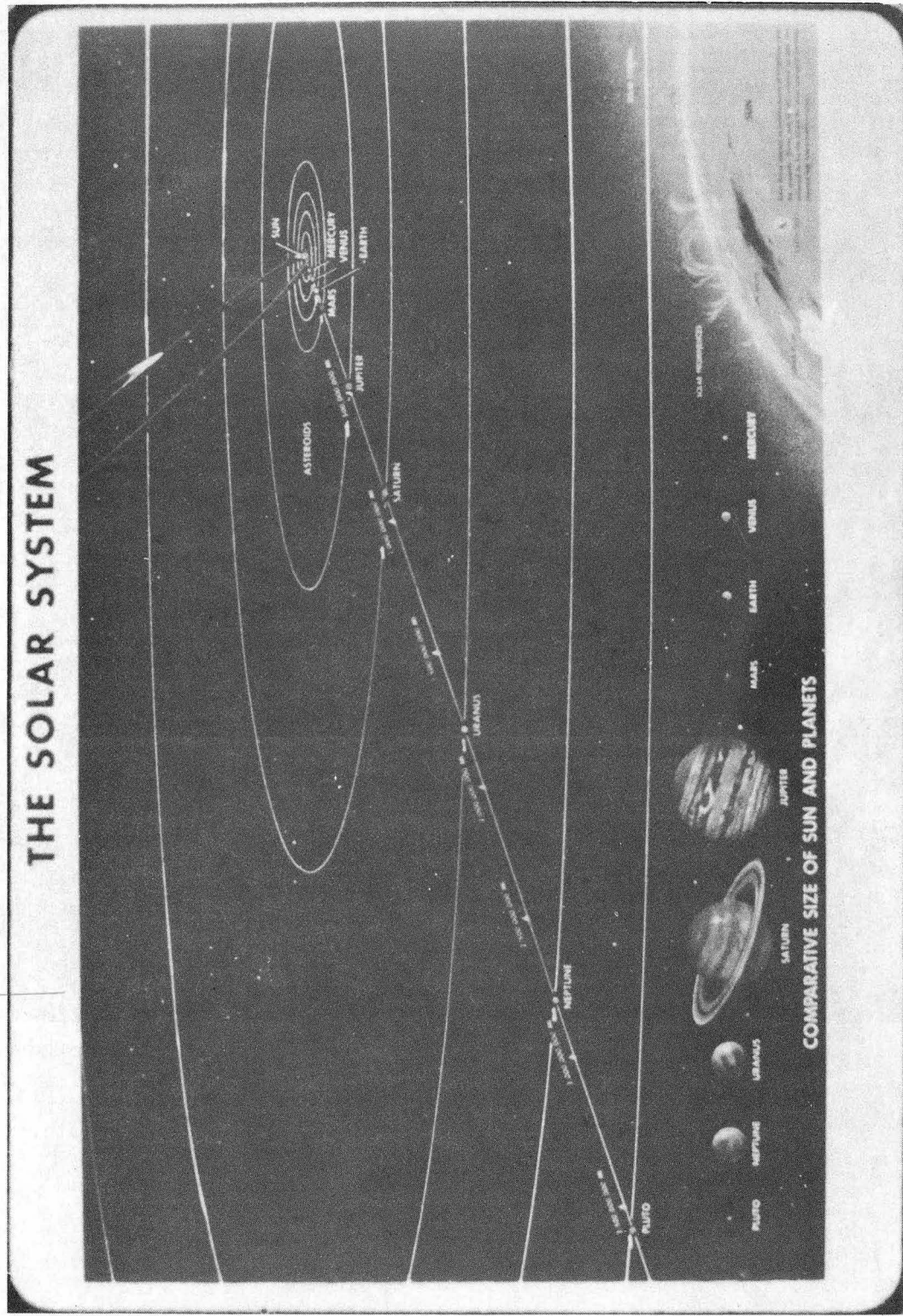


Fig. 1

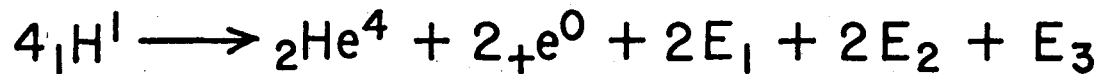
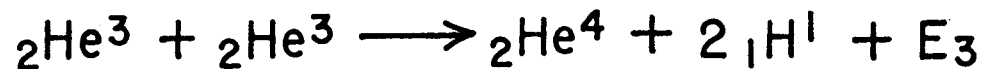
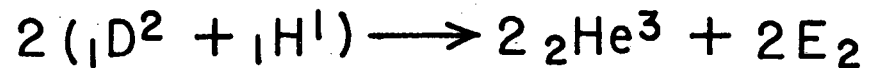
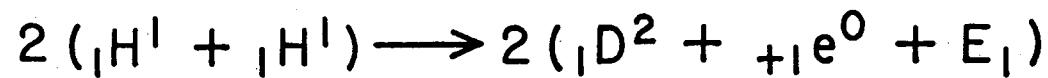
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Fig. 2. The earth as viewed from a satellite.

PRIME SOURCE OF SUN'S ENERGY



$$2E_1 + 2E_2 + E_3 = 26.7 \text{ MeV per He}^4 \text{ formed}$$

$$\text{Solar Emission Day}^{-1} = 3 \times 10^{32} \text{ J} \equiv 10^{16} \text{ Kg} \text{ (} S_{\text{mass}} = 10^{30} \text{)}$$

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Calvin Figure 3

Nuclear sources of solar
energy

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of the sun itself, even with the tremendous amount of solar energy radiated on a daily basis, it is unlikely that the sun will be exhausted as an energy source during the lifetime of the earth.

INTERSTELLAR MOLECULES

The sun has played a rather central role in the origin and character of living things on the surface of the earth. Many of the experiments, which have led to the notion that biological molecules (biogenic molecules) can be derived from the primitive atmosphere which the earth had, have been performed over the past 20-25 years. I had originally intended to review some of these experiments in which the various energy inputs on the primitive earth's atmosphere converted the primeval molecules into more complex ones of biological interest, eventually leading to the biopolymers which, in turn, gave rise to the highly organized state of matter which we know as a living cell. But since these have been reviewed a number of times recently and certain information which might be relevant to this step in life's origin has come to light, it seemed worthwhile to devote what time we had available for this part of the discussion to the newer concepts which might be added to the older ones.

In recent years it has become apparent that there were several other ways in which the biogenic molecules arose. A number of molecules have been discovered in interstellar space itself as individual, free living, molecules. The number of the molecules is of the order of one per cubic meter in interstellar space. If these molecules begin to aggregate in interstellar space, you can see that many of the reactions which have been postulated as requiring the input of energy from a star into the earth's atmosphere (or cosmic rays, meteoritic impact, radioactivity,

lightning, etc. are not necessarily the only way in which these biologically important molecules arose.

Table 1 shows the list of the various molecules which have been discovered in interstellar space up until the end of last year. You can see that long ago CH and CN were found in interstellar space and then there was an interregnum of some 20 years before hydroxyl (OH) was discovered in 1963. Subsequently there was an "information explosion" after 1968 when many more biologically important molecules were discovered. These molecules are described by virtue of their absorption in the microwave region. The whole impetus for this kind of research came when the larger radiotelescopes were developed.

The earliest known interstellar molecules (cyanogen, hydroxyl, ammonia and water) have been known for quite some time and constituted some of the basic primitive molecules which were used earlier to describe the process of chemical evolution on the surface of the earth. However, previously we thought it was necessary to have a solar energy input in order to create these primitive chemicals. It turns out, however, that HCN itself has been discovered in interstellar space. One of the more interesting of the interstellar molecules which was described recently is cyanoacetylene, which has also been created by chemical evolutionary experiments in the laboratory of the type I mentioned earlier. Cyanoacetylene, really, was what was needed to generate most of the compounds of biological interest if it is condensed in the presence of ammonia, water, etc., and a solid catalyst; there is a great deal of energy stored in the cyanoacetylene in the four pi-bonds which are present. In other words, there is a lot of chemistry which can be done with cyanoacetylene.

Calvin

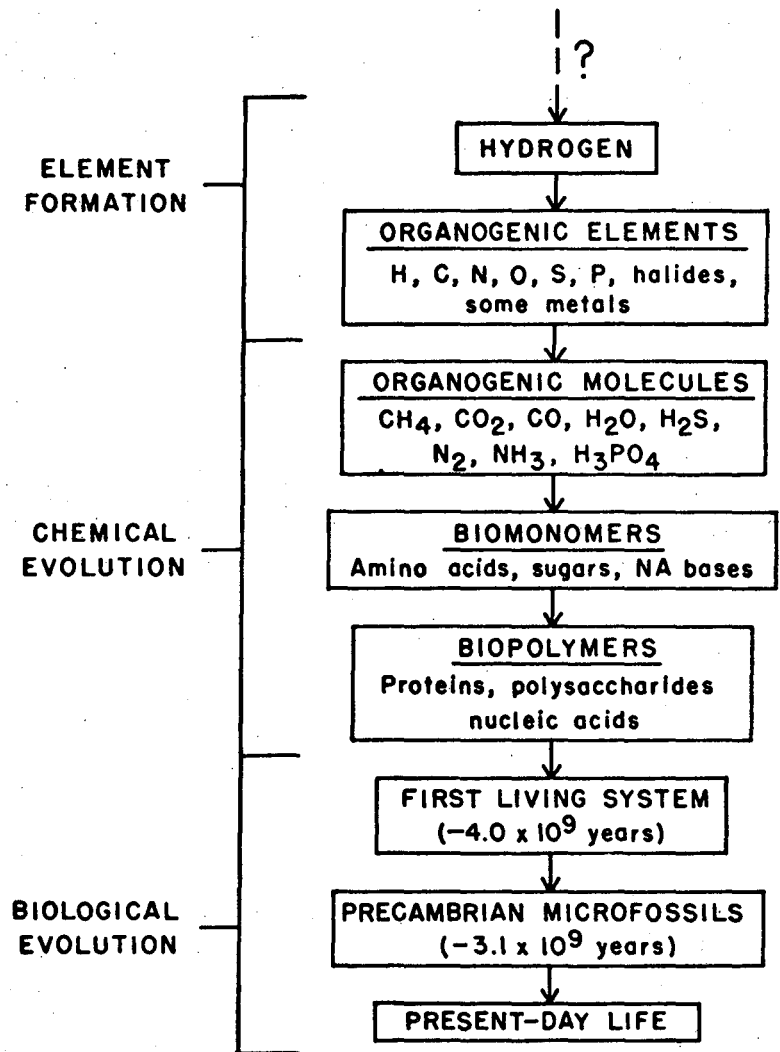
Table 1

Molecules Found in the Interstellar Medium

Year	Molecule	Symbol	Wavelength
1937		CH	4300 Å
1940	Cyanogen	CN	3875 Å
1941		CH ⁺	3745-4233 Å
1963	Hydroxyl	OH	18, 6.3, 5.0 and 2.2 cm
1968	Ammonia	NH ₃	1.3 cm
1968	Water	H ₂ O	1.4 cm
1969	Formaldehyde	H ₂ CO	6.2, 2.1 and 1 cm; 2.1 and 2.0 mm
1970	Carbon monoxide	CO	2.6 mm
1970	Cyanogen	CN	2.6 mm
1970	Hydrogen	H ₂	1100 Å
1970	Hydrogen cyanide	HCN	3.4 mm
1970	X-ogen	?	3.4 mm
1970	Cyano-acetylene	HC ₃ N	3.3 cm
1970	Methyl alcohol	CH ₃ OH	36 and 1 cm; 3 mm
1970	Formic acid	CHOOH	18 cm
1971	Carbon mono- sulphide	CS	2.0 mm
1971	Formamide	NH ₂ CHO	6.5 cm
1971	Silicon oxide	SiO	2.3 mm
1971	Carbonyl sulphide	OCS	2.7 mm
1971	Acetonitrile	CH ₃ CN	2.7 mm
1971	Isocyanic acid	HNCO	3.4 mm; 1.4 cm
1971	Hydrogen iso- cyanide	HNC	3.3 mm
1971	Methyl-acetylene	CH ₃ C ₂ H	3.5 mm
1971	Acetaldehyde	CH ₃ CHO	28 cm
1971	Thioformaldehyde	H ₂ CS	9.5 cm

Chemical Evolution. When the presence of cyanoacetylene was discovered in the interstellar medium, I felt the work which we had done in the laboratory for the previous 20 years, trying to generate these compounds by electrical discharge, or direct ultraviolet irradiation of methane-ammonia-water (corresponding, if you like, to the solar energy input) while they were useful and interesting experiments in and of themselves, were not necessarily the only way in which the complex biologically important molecules such as amino acids and heterocyclic bases were generated. All of the various molecules which have so far been discovered in interstellar space -- even the more recent ones such as isocyanic acid, hydrogen isocyanide, methylacetylene, acetaldehyde and thioformaldehyde -- are important intermediates for the creation of biogenic molecules.

I will not, therefore, discuss the whole history of the experimental work which was done in the laboratory from 1950-1970 trying to create, by various energy inputs, the important biogenic molecules for chemical evolution. I think there is no doubt now that there are ways, in the laboratory and in interstellar space, of synthesizing all of the simple molecules which are needed for the evolution of a living system. At this stage, I wish merely to describe in general terms the scheme of the process leading from element formation to biological evolution, which is shown in Figure 4. We have first the organogenic elements (H,C,N,O,S,P, etc.), which, in turn, under the influence of various types of energy, can create the organogenic biomonomeric molecules (methane, carbon dioxide, water, hydrogen sulfide, etc.). Unfortunately, when this



Calvin

Figure 4

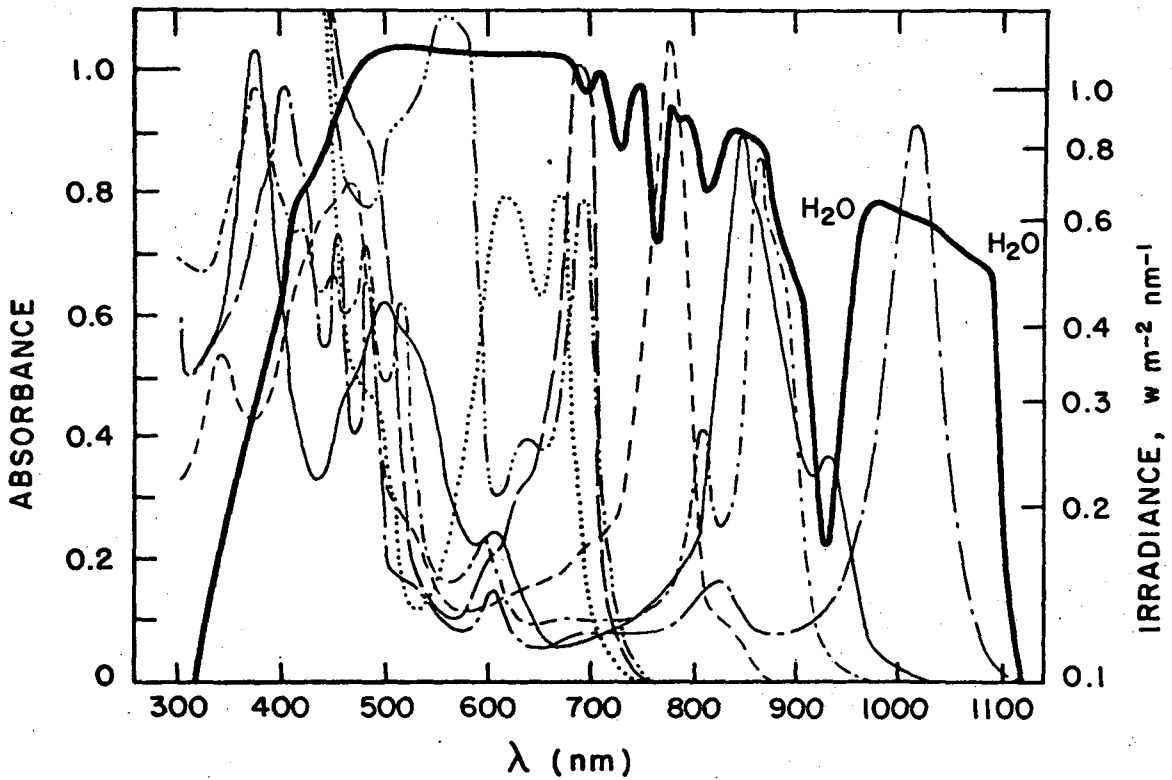
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General scheme for chemical and biological evolution

drawing was made, I did not have the information about the more recent discoveries of such molecules as cyanoacetylene, thioformaldehyde, etc., in interstellar space. Therefore, the figure should be modified to include this information. From the organogenic molecules, the biomonomers (amino acids, sugars, nucleic acid bases) are formed. Most of these materials were created from methane-ammonia-water-carbon monoxide, etc. under the influence of various kinds of energy, in simulated primitive earth atmospheres. In general, electrical discharge was used as the energy source, but ultraviolet light was also used. Both of these originally had their source in solar energy. At the moment, we are now trying to find how the biomonomers can be condensed into the biopolymers (proteins, polysaccharides, nucleic acids) in a spontaneous way. This has also been achieved to a large extent in the laboratory.

Evolution of Photosynthetic Organisms. Practically all of the energy which was available for continuing existence was solar energy. A question is: Does there exist today a collection of living organisms which makes use of the whole spectrum of solar energy? Figure 5 shows a collection of what are probably primitive photosynthetic organisms, showing how they use the entire available solar energy spectrum. The dark line shows the intensity which is proportional to the intensity of the solar spectrum at the earth's surface. The absorption spectrum of various organisms which have evolved on the earth's surface are shown, and there is a rather large variety of mostly unicellular organisms which absorb at various wavelengths. These organisms take up most of the useful wavelengths of the sun which strike the earth's surface. Any

- ····· *Porphyridium* (red alga)
- *Rps. spheroides* (red bac.)
- *Chlorella* (green alga)
- *Synechococcus* (blue-green alga)
- *Rps. viridis* (red bac.)
- *Chromatium vinosum* (red bac.)
- **AVAILABLE SOLAR ENERGY**
- ····· *Chloropseudomonas ethylica* (green bac.)



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Calvin Figure 5

Evolution of photosynthetic organisms showing use of entire visible solar energy spectrum

thing much longer is not at a high enough energy to get directly into electronic excitation; it involves vibrational and rotational excitation. Anything much shorter than 3000 A is not available. Therefore, the evolution of living organisms as represented in Figure 5 did indeed encompass all the wavelength regions which were available on the surface of the earth from the sun.

PHOTOSYNTHETIC CONVERSION OF SOLAR ENERGY

I would now like to discuss the way in which we now use the sun's energy which presently comes to the surface of the earth. We use this energy in the form of agricultural materials, but actually most of our energy sources came, ultimately from the sun, now in the form of fossil fuels which are presently being used up very rapidly. Let us compare the rate at which we are using up what has been stored over the millenia from the sun with the rate at which the sun is now irradiating the earth; this is shown in Table 2. As we mentioned earlier, the sun's daily energy output is 3×10^{32} Joules, and the earth receives impinging on it 1.5×10^{22} Joules. Of this, only a very small fraction is captured by the green plants of the earth in the process of photosynthesis (40×10^{17} Joules/day). One part in 10,000 of the solar energy which strikes the earth is used in the process of photosynthesis, and is transformed into plant organic material. The number is somewhat uncertain because of the relationships of the process of photosynthesis during the illumination period and the respiration which takes place in the dark. I did not try to correct for the amount which is lost in the dark respiration segment of the photosynthetic process. The daily consumption of energy, both in the United State and worldwide, is also pointed out in Table 2. The world's daily

Calvin Table 2

TERRESTRIAL ENERGY BALANCE (1970)

Sun's Daily Output (10^{16} Kg)	3×10^{32} J
Earth's Daily Receipt	1.5×10^{22} J
Earth's Daily Photosynthesis	40×10^{17} J
U.S. Daily Consumption	2×10^{17} J
World Daily Consumption	$\sim 8 \times 10^{17}$ J

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total energy consumption is about one-fifth of the total photosynthesis which takes place on the surface of the earth (on land and sea). Agricultural (useful) photosynthesis is actually a very small percentage of the average daily photosynthetic energy on the surface of the earth, probably only one part in one thousand. The idea I wanted to promulgate here is that the world as a whole is using up energy at a rate beginning to approach the total rate of its photosynthetic capture on the earth's surface, even though much of that is not in a daily useful form, but is partially used in restoring the fossil fuel level. Obviously, the fossil fuel level is being restored at a much slower rate than it is being consumed. The figures which are given in Table 2 are as of 1970, and I am sure that you have repeatedly heard that the rates are increasing logarithmically, especially in the United States but worldwide as well. The question of how soon those rates will pass the 40×10^{17}

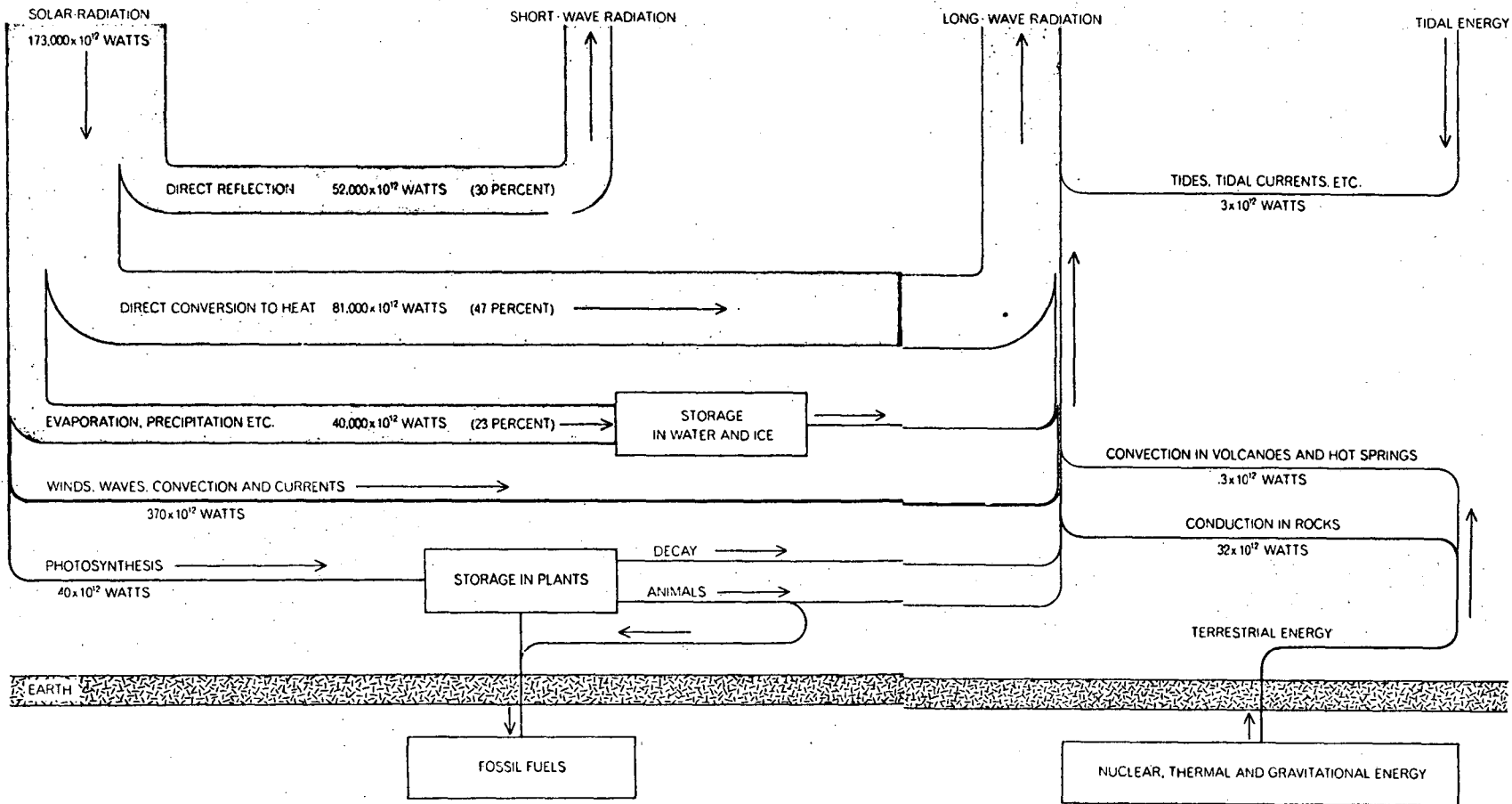
Joules/day, which is the amount of energy used daily in the process of photosynthesis, can be answered by noting it will probably be less than one decade. At the moment it appears that the it is being used up at the annual rate of 5% -7%/year.

Let us return to the more fundamental question of how the photosynthetic conversion of solar energy is achieved. I feel that ultimately we will have to use some such method for the capture of energy for future use. One of the reasons that we are interested in this problem is that we will have to devise systems for making use directly of some of that solar energy, because we are approaching the exhaustion of the solar energy which has been stored over the millenia in the form of fossil fuel. Therefore, we are returning to a more serious study of how the

plant actually makes the direct photoconversion into chemical potential. If we could learn enough of that process, we might be able, perhaps, to extract some ideas about how to produce synthetically a converting system which would not be as slow and would not be as indirect and involve so many other "demands". I am now thinking of the life of the plant itself which loses so much of the solar energy, which is devoted to keeping it alive and keeping it ordered. Perhaps we can offer some suggestions as to how this might be done, and the basis of that knowledge as far as it has gone.

In order to devise systems which might be more useful and efficient for solar energy conversion, we have to know something of the wavelength distribution of the energy which is available. Figure 6 shows the solar energy balance of the earth. Directly reflected as possibly useful short-wave radiation is about 30% of the total and the reflected long-wave radiation (the energy which is converted from the visible and near infrared into heat and reradiated) is 47%; the two together constitute 77% of the total energy of the sun impinging on the earth. Roughly 23% is used for evaporation, with precipitation, some is stored in water and ice and can be used as water power. Some of the solar energy is converted into winds, waves, convection currents, which is a small fraction, and photosynthesis is even smaller fraction of the stored solar energy. Actually only a very small fraction of photosynthesis is stored in terms of fossil fuels. There is, of course, a certain amount of energy in the interior of the earth, gravitational-nuclear-thermal, but this is a very small fraction of the total which is reirradiated.

What we are talking about is trying to capture some of this large amount of the solar energy before it is degraded into heat and reirradiated



Calvin Figure 6

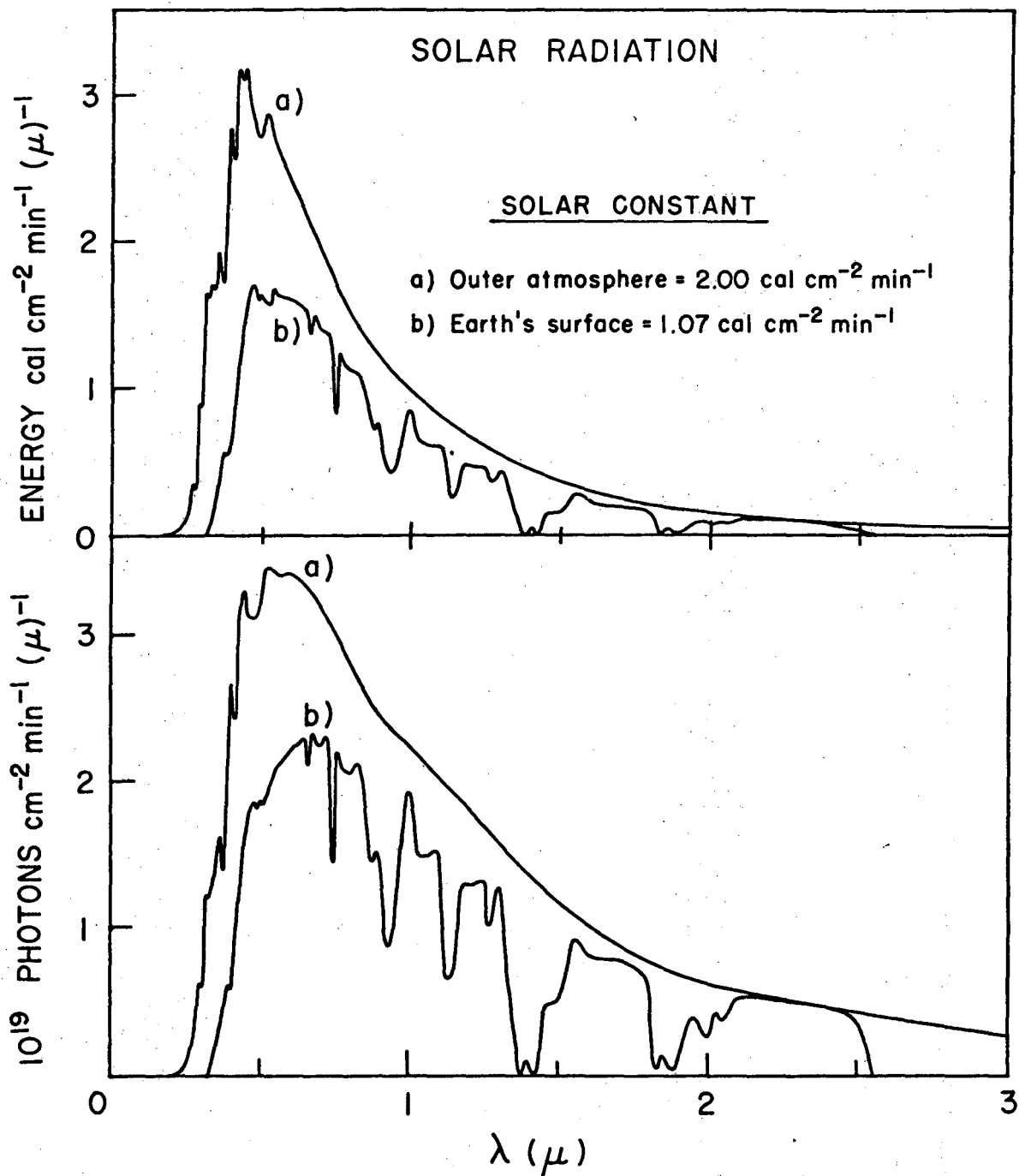
Solar energy balance on the earth (1970)

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(either as short or longwave radiation). We would like to "catch" the solar energy before it gets into that degraded, or "low class", condition. Figure 7 shows the wavelength distribution of solar energy, and Figure 8 shows the fraction of total solar radiation as a function of wavelength. The energy at 10,000 A or shorter, which is a major fraction of the energy coming in from the sun, can be used for direct electronic excitation. If the wavelength is longer than 10,000 A, it is difficult to find electronic systems which can handle it for direct conversion into useful electronic energy. You can see from these figures that about half of the energy is able to get through to the earth's surface, the other half being degraded as it comes through the atmosphere and reirradiated back to space as heat. This shows what type of energy is available and what the wavelength distribution is.

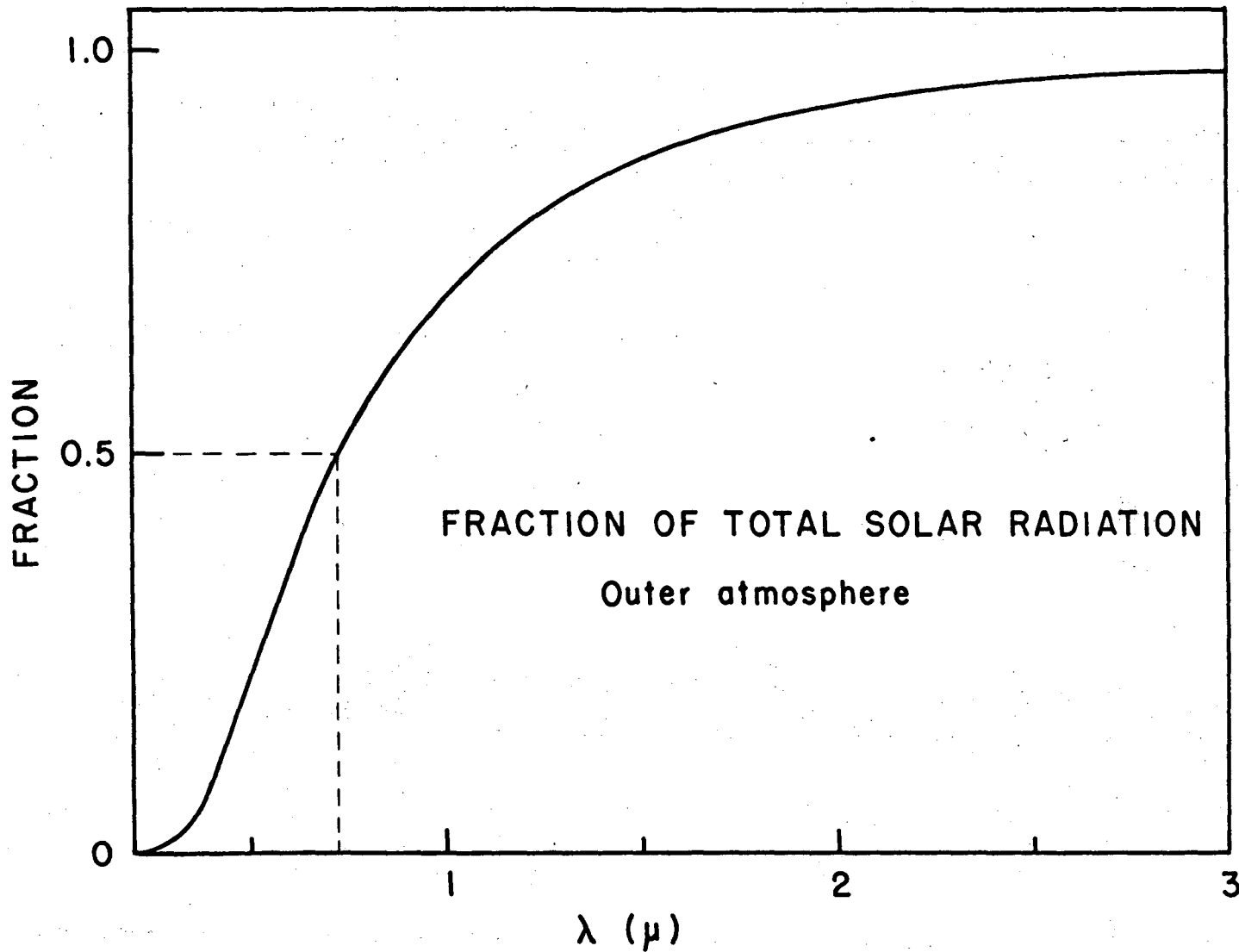
Path of Carbon in Photosynthesis and Quantum Conversion in Photosynthesis. I would now like to discuss our investigations which began 25 years ago on how the green plant actually achieves the conversion of light into chemical potential. At the end of World War II we began our investigation by trying to learn how the chemical energy was created from the carbon in its lowest energy source, that is carbon dioxide; i.e., how carbon was reduced. We succeeded in this search, and Figure 9 is a summary of the photosynthetic carbon reduction process. This shows how the carbon dioxide enters, by reaction with a 5-carbon sugar, goes through a complex cycle of carbon compounds, which is driven by the light. The carbon dioxide and water are transformed to sugar and oxygen, and the whole cycle is driven by the light in some kind of direct electron transport reaction system. It is the "black box" in the diagram which is the key to the photosynthetic process --



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Calvin Figure 7

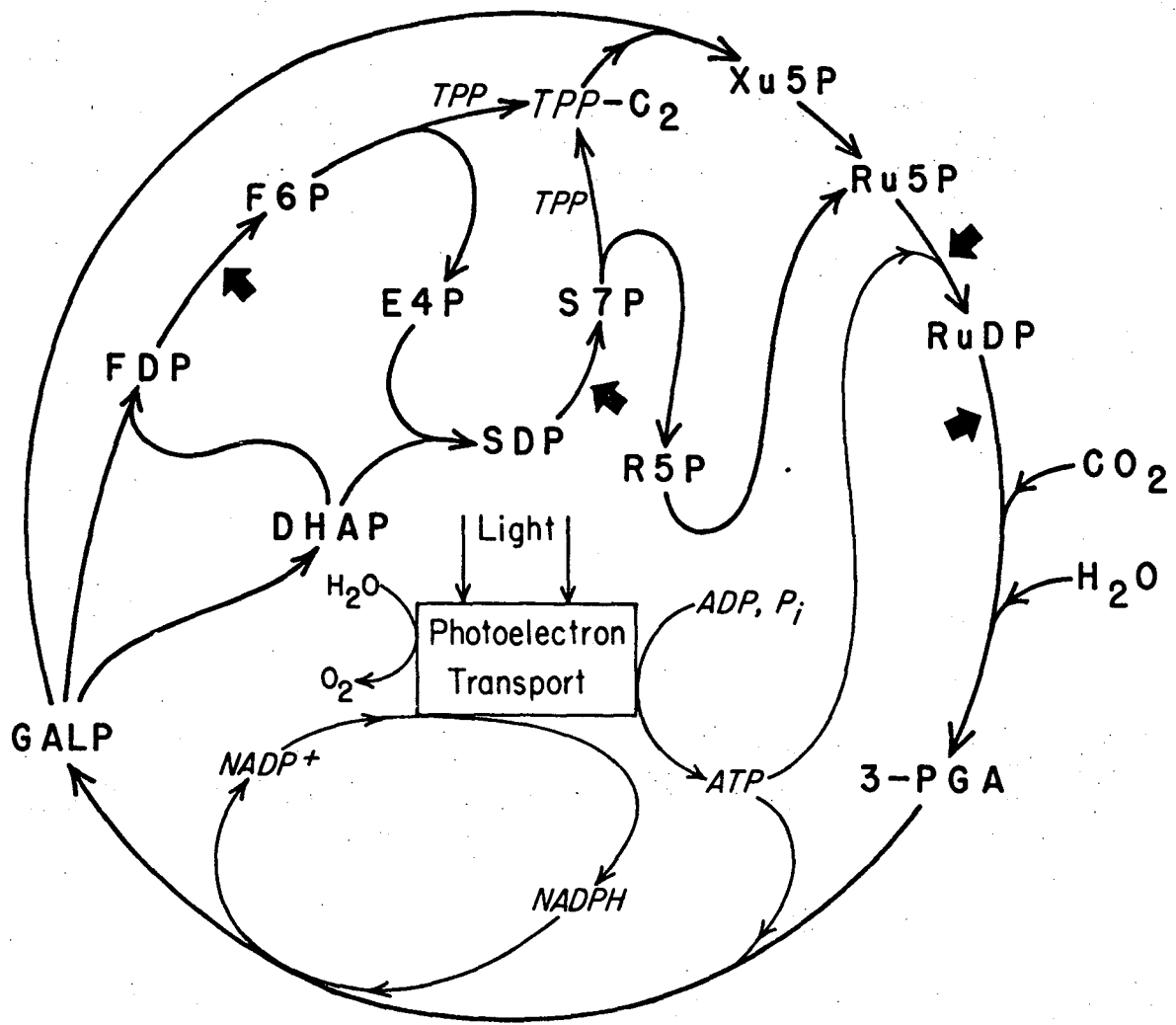
Wavelength distribution of
solar energy



Calvin Figure 8

Fraction of total solar radiation as function of wavelength

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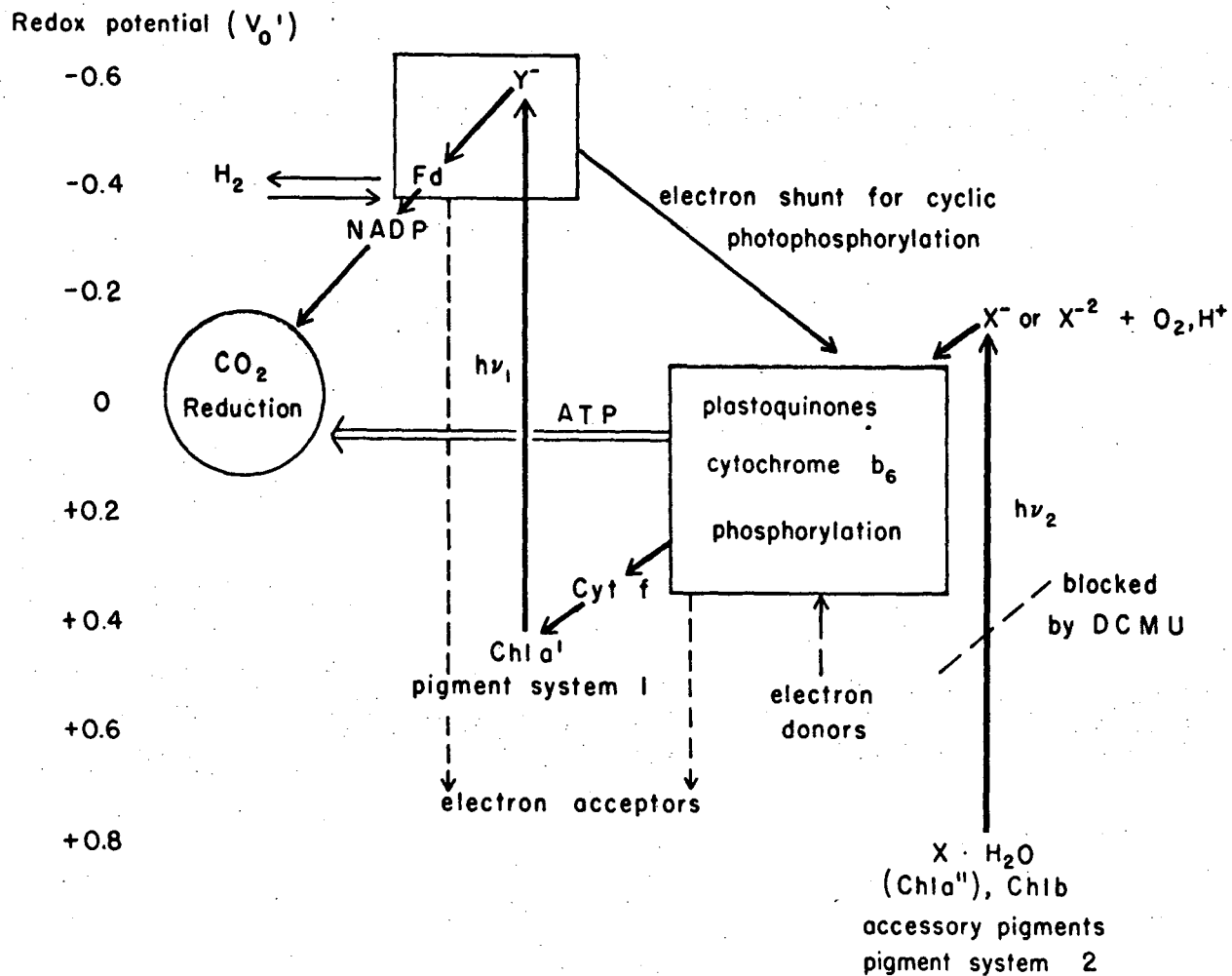
Calvin Figure 9
 Photosynthetic carbon
 reduction cycle

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how does the light produce these reagents, here labeled ATP and NADPH, to drive this cycle and store the energy. We have tried to determine what takes place between the entry of the photon and the generation and use of ATP and NADPH, those two molecules which are required for the storage of chemical energy.

There has been a great deal of research done all over the world, particularly in the last 10-15 years, to elucidate the primary quantum conversion process of photosynthesis. A scheme has been evolved which gives us some ideas about how the light actually works in this complex process. That scheme, as it stands roughly today, in a generalized form, is shown in Figure 10. At one end of the scheme we have the water, and at the other end we have the carbon dioxide. In between there are two photo reactions, one involving chlorophyll which eventually oxidizes the water to give oxygen; the other photo reaction involves the excitation of chlorophyll a, requiring a separate photo reaction. An attempt was made to trace the path not only of the energy but also the corresponding path of the electrons in terms of a redox potential chart beginning with water on the right. On the left, a second electron excitation occurs, raising it to a still higher redox potential. The two processes can then be coupled by having the electron excited by the first process (system 2) pass down into the vacancy created by the second process (system 1) to generate ATP which is used in the photosynthetic carbon cycle. The second electronic excitation path (system 1) generates NADPH which, together with the ATP, is responsible for running the photosynthetic cycle which was shown in Figure 9. This (Figure 10) is, really, the same chart as shown in Figure 9, but the cycle has been reduced to a circle (carbon dioxide reduction) and the black box has been expanded to show the two photo reactions.



Calvin Figure 10

Photosynthetic electron transfer scheme

Each of these two systems has been worked out in detail to some extent, but there are still many unknown areas to be explored, particularly in the two photo reactions. We know that an electron raised to a redox potential of -0.1 volt by system 2 will react with the vacancy which is created at $+0.4$ volt after excitation by system 1. The electron drops down drop energy scale through plastoquinone, cytochrome b, etc. and generates ATP in so doing. (I will not discuss the biochemical part of that electron transport process, which is an enzymatic biochemical process which takes place in a similar fashion in mitochondria.)

We are really concerned in trying to learn how the quantum, which is absorbed by chlorophyll in each of the two pigment systems and which produces an electronic excitation, is converted into some useful chemical form. The first thiwe know fairly certainly is that the quanta are absorbed by antenna chlorophyll molecules which then move by resonance transfer to special sites. The next concept of which we are confident is that there must be a separation of charge. The oxidation product created by removing the electron, must in some way be separated from the electron. In physical terms we can discuss this separation as a separation of a hole, or positive charge, from the excited electron, which is the negative charge. Between those two steps -- the excitation of the electron in the chlorophyll molecule into its excited state represented by the absorption peak at about 7000 A and the resultant separation of charge -- is where I want to focus your attention. If we could get this in a separate system such as would occur in a silicon photoconverter, we would have some direct method (if the plant uses such a method) of converting a quantum into not merely chemical potential, which we have defined in Figure 10, but prior to that into real electrical potential.

We might then be able to take this charge out as an external electronic current. This is really the status of the notion, as of this moment.

There is at least one intermediate step. We know something about the arrangement of the energy-capturing apparatus of the plant. It consists mostly of chlorophyll contained in separate entities within the plant cell, called chloroplasts, and the accessory pigments are also associated with the chloroplasts, actually with substructures in the chloroplast. Some years ago I gave the name "quantasome" to a substructure of the chloroplast lamellae. This is the simplest energy-converting entity inside the chloroplasts. The quantasomes are composed not only of chlorophyll a and chlorophyll b but also of carotenoids, proteins and a variety of other materials.

The idea of electron transfer gave rise to several rather important experiments, one of which was the demonstration that all of the chlorophyll is not involved in the direct conversion of the excited state into charge separation; only certain centers are involved, the so-called "traps". However, all of the chlorophyll is involved in the initial light absorption. Otherwise, the plant would be very inefficient because the number of "traps" is very small compared to the total number of chlorophyll molecules. Somehow after the absorption of the light by the chlorophyll molecule and the creation of an excited state in the chlorophyll, that excitation energy must migrate around amongst the chlorophyll molecules until it finds the "trap" where electron transfer can occur. This is called resonance transfer, and the demonstration of resonance transfer not only between chlorophyll molecules but from the carotenoids to the chlorophyll molecules is one of some considerable standing now. The next step, then, after excitation is resonance transfer from chloro-

phyll to chlorophyll, until a particular site is reached. In Figure 10 that particular site is designated as X^- or Y^- .

The separation of charge is not really very clearly defined, and, in fact, some 10-15 years ago I recognized that this separation did indeed have to exist in order to give rise to an efficient energy storage apparatus. At that time, I suggested there might be some kind of semiconductor mechanism which would involve that separation of charge. All of the experiments which we have done in the ensuing period, following that suggestion in 1958, failed to demonstrate any such phenomenon. Although many experiments were performed, we never did demonstrate with any confidence that one did generate charge carriers which moved as electrons move in a semiconductor, and which could give rise to separation of charge. The common type of experiment was to perform a model experiment, placing some chlorophyll, or chlorophyll-protein complex, between a pair of electrodes, one of them being transparent, and then shine light on the material to see if it would be possible ^{to} demonstrate mobile charges by photoconductivity or other means. Many hundreds of experiments of this type were done, but none of them were really convincing. In other words, we couldn't really say definitely that this was the way the plant was doing it. It was always necessary in these experiments to put a potential on the materials to separate the charges, and we did not know that the charges were separable without the externally applied potential. It is very difficult to place electrodes on individual quantasomes within the chloroplast; it is not really possible to measure the conductivity across the chloroplast membrane, or the photoinduced voltaic effect, if there is one.

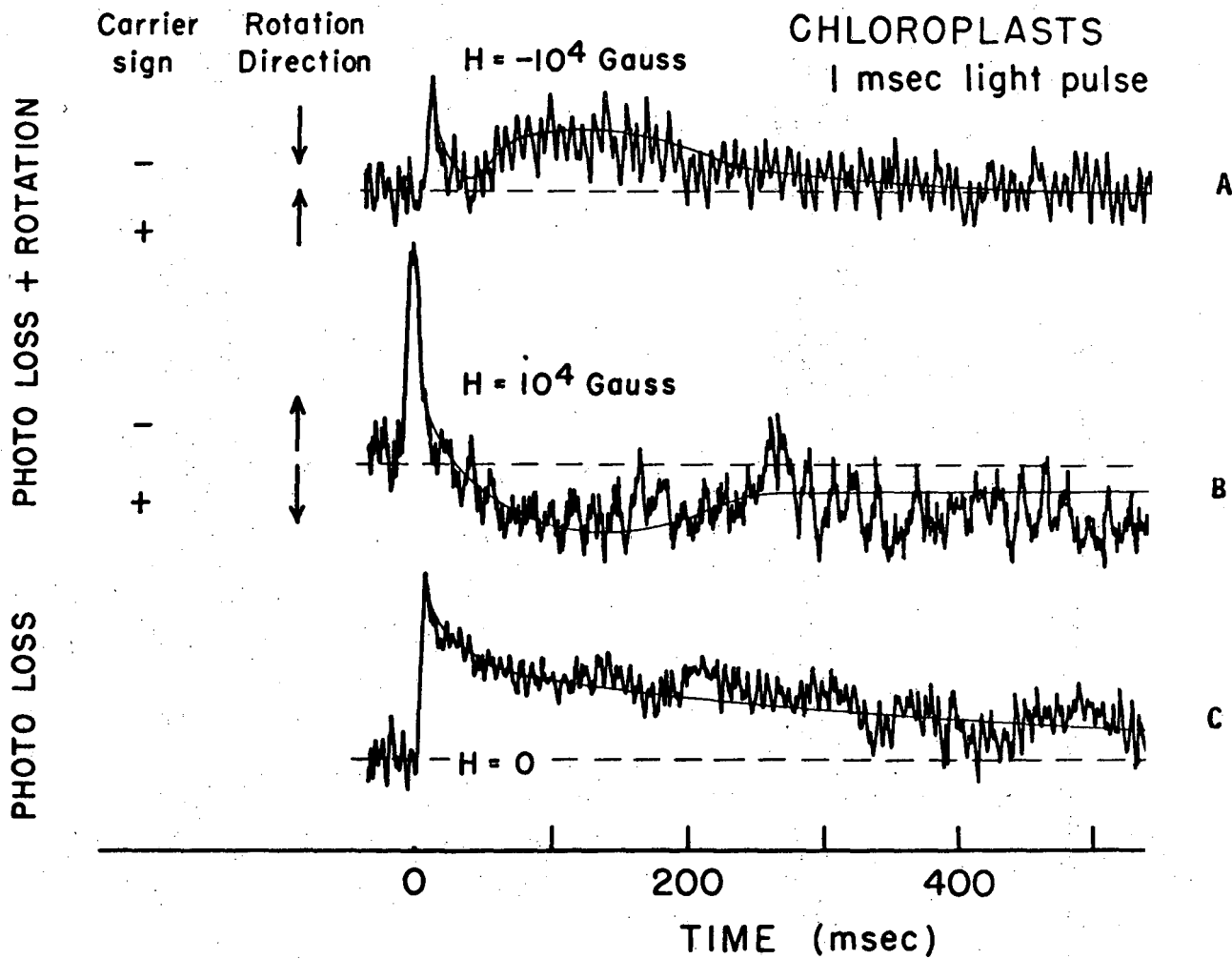
Therefore, we had to seek an indirect way of measuring this effect. For a while, I thought we could locate the electrons by using the ordinary

ESR techniques, and, indeed, we did find that when the light was turned on the chloroplast (or on the whole plant, for that matter) unpaired electrons were generated which could be recognized by their electron spin signals, in the same way that free radicals can be recognized by the unpaired electron spin signals. We found that we could not unequivocally identify the nature of the electrons which gave rise to the unpaired spin signals; we could not find out what environment they were in, because they were too diffuse in their nature. We could say there were two different kinds of spins, as there were two different lifetimes, but they actually behaved more like organic radicals than electrons in a semiconductor system. It was not possible to say that this type of signal was any evidence for the original notion.

Dielectric Loss Experiments. The next experiment which I wish to describe is one which we have just completed a few weeks ago, in which we measured the generation of movable charge in the chloroplasts without electrodes, by putting the chloroplasts in a 2 cm cavity microwave apparatus and measuring the photo-induced dielectric loss. You can see that if the light is turned on to sua system to create mobile electrons, then the fact that they are mobile will induce a loss of energy from the oscillating field which is proportional to the number of such mobile electrons which are created. This is one way of measuring the induced "looseness" of electrons. The next question was: Could we see the charge separation? In order to see separation of charge it is necessary to have negative charge moving in one direction and positive charge moving in the other direction. In order to define whether it is negative or positive charge, it is necessary to do a Hall/experiment, that is, to put the semiconductor in a magnetic field.

If there is moving charge, then as the charge tries to cross the magnetic field, if it is negative it will move in one direction and if it is positive it will move in the other. In this way, by measuring the effect of the magnetic field on the photoinduced dielectric loss, following a pulse of light, it should be possible not only to determine whether or not electrons are generated by the pulse of light, or, actually, a charge generated by the pulse of light, but also what the sign of the charge is and how long it takes to move from its first generation until its loss as a mobile charge into the fixed ions such as the X^- and chlorophyll⁺.

We performed that experiment, after a couple of years of model work. Figure 11 shows the result of that experiment. It (Figure 11c) shows that when the light is turned on there is indeed a very large increase in the dielectric loss; the photoinduced loss increases and then decays. What happens if we put this in a magnetic field of 10,000 gauss? You will notice that the photoinduced loss increases, at first, goes down below the base line, decreases and then returns (Figure 11b). Inverting the magnetic fields shows that the dielectric losses due to the initial light flash are depressed and the later losses are increased (i.e., the slower decay loss, Figure 11a). The first thing that is shown is a rapidly produced electron, at relatively high mobility, which decays in about 5 milliseconds. Then, the other sign of charge takes over, and the positive migration takes about 100 milliseconds. When the field is reversed, the negative charge loss is depressed and the positive charge loss is increased. The symmetry of these two curves, with respect to the bottom one, is the essential experimental result. It shows that there are two kinds of mobile charge carriers present, one positive and one negative, with different lifetimes.

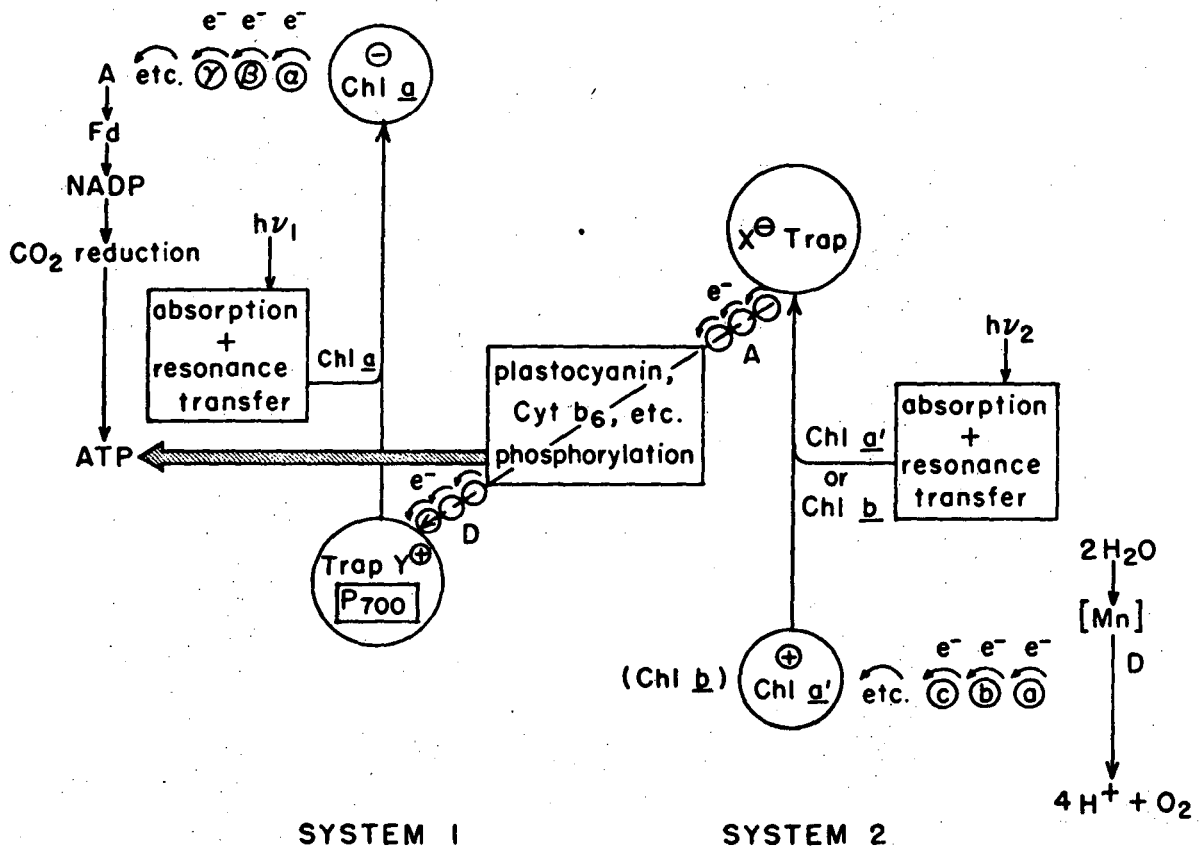


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Calvin Figure 11

Photoinduced microwave losses showing both positive and negative carriers in the chloroplasts

We would therefore state that there are two kinds of carriers, with two different lifetimes, possibly as a result of two different light acts, which are involved in the quantum conversion process of photosynthesis. One is that which operates in photo system 1. This can be represented by having the chlorophyll in the excited state, and then an electron is transferred to the lower vacant orbital in the excited chlorophyll from some source which gives rise to a negative ion. The electron can then hop from chlorophyll to chlorophyll until the final acceptor is reached, in the form of something just preceding ferredoxin. It then goes on down to NADP. The fact that the electron migration takes such a long time is evidence that it is not really a true semiconduction process, but a hopping mechanism. At this point, we do not know how many "hops" there are from the first trap to the final trap, where it becomes a definite chemical species. The other side of the process is an excited chlorophyll which transfers its electron to the trap, instead of getting an electron from the trap. Here the positive chlorophyll is filled by electron migration, process, ultimately from the water, involving manganese in some way. The mechanism is a positive charge migration, also an electron "hopping" mechanism. The vertical arrows in Figure 10 represent absorption and resonance transfer to the ionization point, followed by charge migration in two different directions. This is shown more explicitly in Figure 12.



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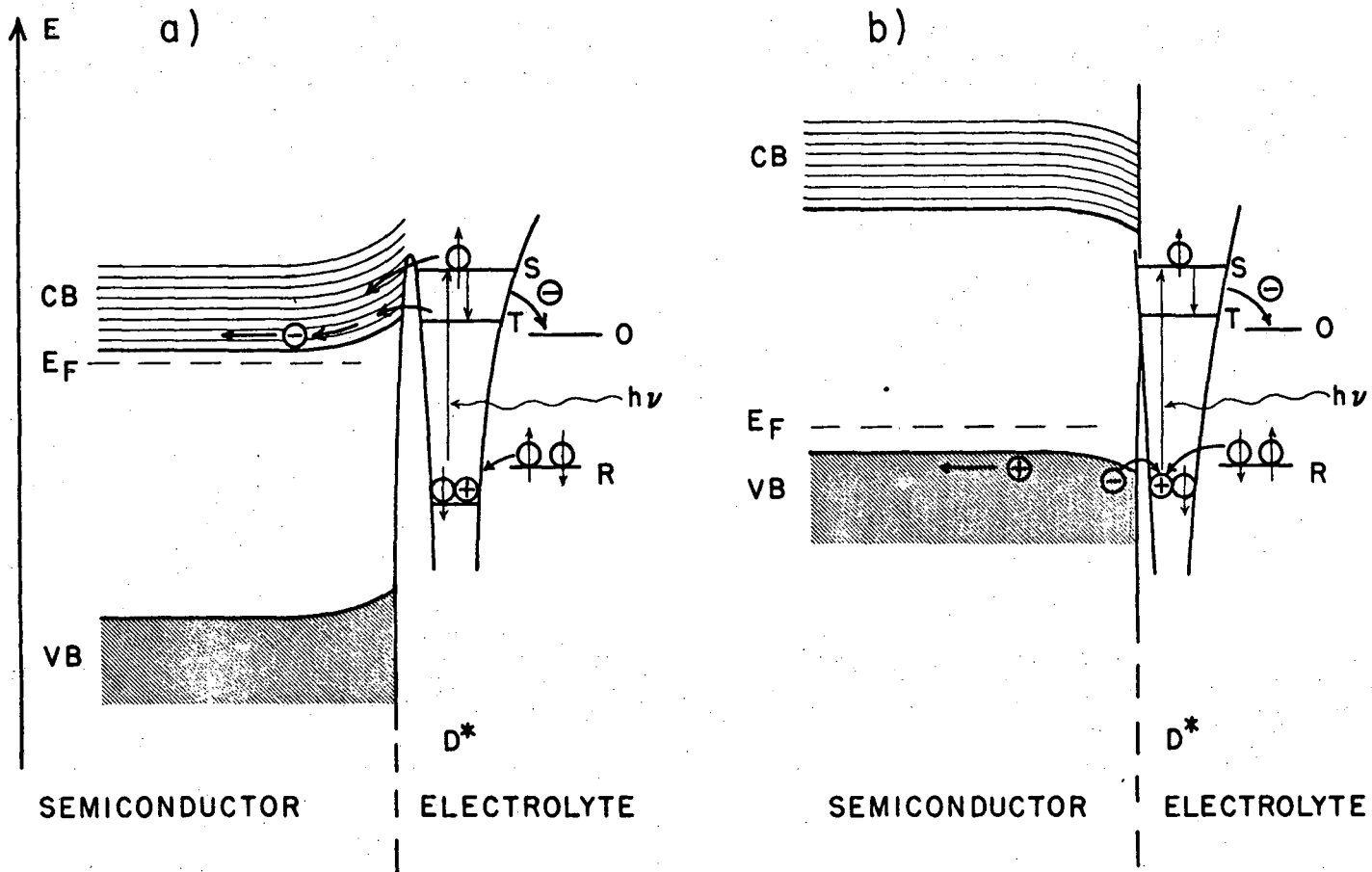
Calvin Figure 12

Photosynthetic electron transfer scheme showing proposed regions for electron and hole migration

Photoelectrochemical Energy Conversion. The result of a model experiment using zinc oxide and chlorophyll is shown in Figure 13. Figure 13a shows the chlorophyll (represented by D) in which the excited electron is given to some acceptor, leaving behind a positive ion. Figure 13b is the case in which the excited chlorophyll receives an electron from the valence band of the zinc oxide, or cadmium sulfide, which corresponds to photo system 1. We have seen evidence for both photo systems using zinc oxide and cadmium sulfide. We have done the reverse experiment also, by taking one semiconductor and different dyestuffs, with different energy levels, to show both types. This experiment shows the result of successful modeling of what has turned out to be possibly the reality in the chloroplast itself.

We have been successful with model experiments (zinc oxide and chlorophyll) with respect to generating a photovoltaic cell (zinc oxide is the semiconductor and chlorophyll is the light-capturing agent). We can remove current from these model systems as long as the light is turned on. However, this is only the beginning of this type of experimentation, as the chlorophyll is eventually destroyed, after roughly 10,000 electrons/chlorophyll molecule have been transformed. This merely shows that we must learn to use other sensitizers which are more stable and which are not irreversibly destroyed but which will keep their energy systems intact.

We have thus developed a "photoelectrochemical" system which is capable of making a photovoltaic cell. This is exactly analogous to the solid-state silicon system developed by the physicists, except we are doing it by a "photoelectrochemical" method instead of photophysical method. Although the experiments were done with single crystals of



0 0 0 0 5 6 0 2 0 8 7

Calvin Figure 13

XBL 706-5243

Model experiment for photochemical energy conversion using zinc oxide (or cadmium sulfide) for photo system 1

zinc oxide, it is not necessary to have single crystals of semiconductors for this purpose. It will probably be possible to use microcrystalline material.

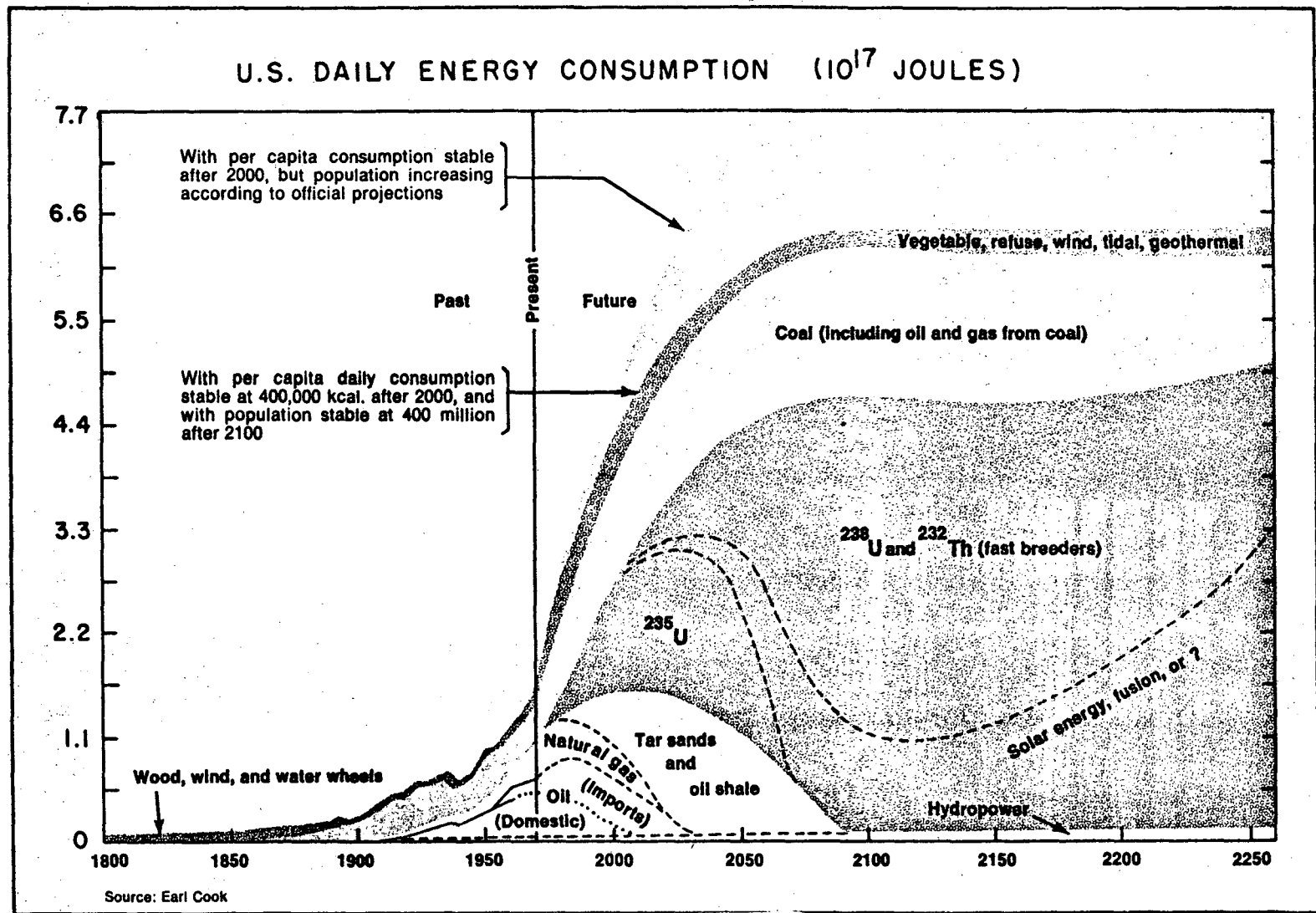
Therefore, it seems likely that we will be able to create not only square inches, or square meters, of photovoltaic cells, but square miles of them. The idea of making square miles of silicon converters, of course, is at least dismaying to the physicists, even though single crystals are not needed. However, I recently read that a combination of four serious companies in the Boston area has proposed that silicon converters be made of roughly $15,000 \text{ m}^2$ each and send them up in a space ship, where they will receive $2 \text{ cal/cm}^2/\text{sec}$ instead of the $1 \text{ cal/cm}^2/\text{sec}$ as they would on the earth surface, convert the energy into microwaves, beam it down to the earth, to be transformed into useful electrical energy.

CONCLUSION

It seems possible, by using the "photoelectrochemical" method, even with the $1 \text{ cal/cm}^2/\text{sec}$, which is available on the earth's surface, to generate electrical energy in quantities sufficient to be useful and economic. It turns out that even on the surface of the earth we need only an area 100 mi. sq. (10^4 square miles of Arizona desert, for example) covered with this type of material which could produce the total energy needs of the earth today. This is no small job, even so, although 100 mi. sq. is not much, in Arizona, in terms of desert. The real problem is an engineering one, because you can see that only about 2 volts are generated, in a very thin system, and the problem of collection is very difficult.

Why do I even discuss this at all? I am sure that many of you have been exposed to some of the more recent discussions of the energy problem. The problem is profound and worldwide. Some months ago, a chart was published in Chemical & Engineering News (Figure 14) which gave some estimates of the world energy needs in relation to sources. At the present time, 96% of the U.S. energy is coming from fossil fuels (oil, natural gas, coal). You can see that the U.S. domestic oil supply is already not adequate for the needs of the population, and natural gas may last another ten years, and then will start to be inadequate. Figure 14 shows that twenty years from now nuclear power will be very important as an energy source, and even that source will decline within another hundred years. Solar energy and fusion may be the methods of the future to ensure the energy supply for the world. I feel that it will be necessary to develop solar energy sources almost immediately, and I am not at all certain that we can use nuclear power (fission or fusion) to the extent that this chart requires, again for a variety of reasons.

The only really clean energy and the only really unlimited energy within man's lifetime which is available is solar energy. Therefore, I feel that one objective that scientists could keep in mind is the development of systems for usefully capturing that solar energy. There are four quite different ways in which that solar energy can be captured. It can be captured by an engineering method (a thermal engine), or the silicon converter developed by the physicists, the photoelectrochemical method being developed by chemists, and the development and evolution of more efficient and more useful biological energy capturing systems and converters.



Calvin Figure 14

Possible energy sources for the next one hundred years

XBL 722-4547

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