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Chemical Conversion of Solar Energy

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It has long been recognized that the fossil fuels of the earth are rapidly being exhausted. The mineral fuels present in the earth, including sources of nuclear energy, are also limited. The rate at which the fossil energy sources are being replaced by photosynthesis is not sufficiently rapid to balance the energy needs of our civilization. It is therefore obvious that the energy of the sun must be used in a more efficient manner than it is in photosynthesis (*1, 2*). Man's utilization of solar energy involves consideration of the following processes.

1) *Collection of sunshine, either with or without concentration.* Any common material—particularly one having high heat capacity—will collect solar energy in the form of heat. Rocks, sand, and large bodies of water serve this purpose in nature. In a more selective fashion, the green leaf collects sunshine for a specific use. A common device for the collection of sunshine as heat is the flat-plate collector, which is used in solar air and water heaters. To concentrate solar energy—as, for instance, in solar furnaces—mirrors and lenses are usually employed.

2) *Conversion of solar radiation into other forms of energy.* Roughly half the sunlight incident on the earth's surface is in the infrared portion of the spectrum and is directly absorbed as molecular heat. The visible part of the spectrum and is directly absorbed as molec-can be converted into more serviceable forms of energy in a variety of ways. For instance, in the green plant, conversion is a chemical reaction in which chlorophyll participates. In solar batteries, conversion consists of the ionization of an atom, with consequent migration of charged particles to produce an electric current. Other useful methods of conversion of solar energy include photochemical, photoelectric, and photogalvanic processes.

3) *Storage of potential energy in a readily available and convenient form.* Storage of energy depends generally on the arrangement of matter—it requires energy, for instance, to set flywheels in motion, to stretch springs, and to create reservoirs of water above sea level. Chemical potential energy is a particularly desirable kind of energy that appears in many different forms.

4) *Generation of power.* A variety of engines are known that transfer potential energy into kinetic energy.

5) *Application of power to do useful mechanical work.* Having outlined the scope of the solar energy field, I shall now focus attention on the conversion of radiant energy into chemical potential energy and will detail some of the methods by which this may be accomplished. Thus, the collection of solar energy and utilization of power fall outside the range of this paper.

Energy Storage in Nature

Biological storage of energy from the sun is primarily a chemical process. In the photosynthetic process, carbon dioxide is reduced, forming a sugar, and water is split, producing oxygen. Radiant energy produces this change, and when the resultant sugar is burned, its energy is recovered either as chemical energy in the body or as heat from wood and coal. Thus, the production of sugar, as well as its subsequent transformation to starch by the plant, is an example of the conversion of radiant energy into chemical energy and of the storage of energy in the form of a stable endothermic compound.

Although the conversion of monochromatic solar energy by the green plant under optimum conditions in the laboratory is 25 to 66 percent (*3*), the conversion of incident sunlight in the field under natural conditions is about 0.3 percent for corn and eucalyptus, 0.13 percent for wheat, and less than 0.1 percent for aspen (*4, 5*). Furthermore, the reduction of carbon dioxide can be accomplished only by the green plant cell, although preliminary reports (*6*) of the fixation of carbon dioxide by chloroplasts have appeared. A popular picture of this situation has been presented by comparing the leaf action with that of a coffee mill (*7*). In this picture, carbon dioxide and water are poured into the top of the coffee mill, and the handle is turned (which amounts to putting the energy of sunlight into the mill); sugar and oxygen then come out of the bottom of the mill. The moment, however, that one opens the mill to find out what happens inside, the evolution of products stops. The process of opening the coffee mill is equivalent to cutting open a green plant cell; because of this limitation, energy utilization by the green plant could formerly be studied only on a macroscopic scale.

It was a great advance, therefore, when Hill (*8*) found in 1937 that chloroplasts, the small chlorophyll-bearing bodies inside the green plant cell, are able to evolve oxygen from water when they are illuminated in the presence of certain ferric compounds. This photolysis of water is today known as the Hill reaction. It is carried on by isolated chloroplasts or chloroplast fragments in the presence of water and some electron acceptor, which then is reduced in place of carbon dioxide. There appears to be little doubt that the Hill reaction is closely analogous to the oxidizing half of the photosynthetic reaction (*9*).

The Hill reaction has been extensively studied on a laboratory scale. Its velocity can be measured by following the formation of three different products—

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oxygen, hydrogen ion, or the reduced form of the electron acceptor (*10*). Consequently, the Hill reaction provides a useful tool in the study of photosynthesis.

Electron-Transfer Spectra

So far I have spoken mainly of the storage part of the solar energy problem. Let us look more closely now at the conversion part of the problem—the manner in which solar energy is converted into chemical energy. A perfectly general description of this conversion is that an electron transfers from one compound to another against the gradient of chemical potential. The Franck-Condon principle (*11–14*) tells us that the transfer of the electron itself is rapid compared with the nuclear motions that precede it. Thus, part of the energy required for electron transfer is used for atomic rearrangements that make the electron transfer possible (*15, 16*). The conclusion of many investigators—whose work has been reviewed by Rabinowitch (*17*), Platzman and Franck (*18*), and Orgel (*19*)—is that the energy required for such an electron transfer against the gradient of chemical potential is faithfully reflected in some region of the absorption spectrum of the species concerned—the electron-transfer spectra. Although this definition is couched in terms of electron transfer, it does not exclude conversion reactions in which the primary light absorption step appears to involve the breaking of chemical bonds. Reactions of this type have been discussed, among others, by Calvert (*20*). The remainder of this section is concerned exclusively with photochemical electron transfers that occur in inorganic species.

The absorption bands due to electron transfer frequently occur in the ultraviolet region of the spectrum. One requirement for the identification of a particular absorption peak or limit as an electron-transfer spectrum is a very high extinction coefficient—of the order of 10^4. Another requirement is that the absorption peaks for a periodic series vary as does some electronic characteristic (ionization energy or electron affinity, for instance) of that series. In the case of the halides, for instance, light absorption in the ultraviolet catalyzes the reaction:

$$X^- + H_2O \rightarrow \tfrac{1}{2}H_2 + \tfrac{1}{2}X_2 + OH^- \quad (1)$$

The difference in energy of absorption peaks of two halide ions is very similar to the difference in the sum of their electron affinities and hydration energies (*17*). Such a correlation strongly supports the identification of these absorption peaks as electron-transfer spectra. The electron transfer is known to take place in both directions—that is, from the central ion of the absorbing species (oxidative case) and to the central ion of the absorbing species (reductive case). The direction of the electron transfer appears to be a function of the electronic parameters (*21*).

Oxidative case. Some of the absorption peaks that have been identified as belonging to electron-transfer reactions of the type

$$X^n + H_2O \rightarrow \tfrac{1}{2}H_2 + X^{n+1} + OH^- \quad (2)$$

are listed in Table 1. In some of these reactions, the production of hydrogen atoms (which appear as intermediates) was proved by the formation of polymers from the corresponding monomer solution (*21*)—a process that is known to be initiated by hydrogen atoms. Table 2 lists some other absorption peaks that have been identified as belonging to electron-transfer spectra, but they have not been studied as thoroughly as those listed in Table 1.

For the halogen reactions listed in Table 1, it has been found that the quantum yield varies linearly with the hydrogen-ion concentration. This indicates that a reaction scheme of the following kind applies (*18*):

$$X^n \cdot H_2O \overset{h\nu}{\rightleftarrows} X^{n+1} \cdot H_2O^- \quad (3)$$

$$X^{n+1} \cdot H_2O^- + H^+ \rightarrow X^{n+1} \cdot H_2O + H \quad (4a)$$

$$\text{or} \quad X^{n+1} \cdot H_2O^- \rightarrow X^{n+1} + H + OH^- \quad (4b)$$

$$2H \rightarrow H_2 \quad (5)$$

Here only one water molecule out of the hydration sheath surrounding the absorbing ion is indicated specifically. It is thought that the absorption of light by $X^n \cdot H_2O$ involves ionization of the central ion X^n and removal of the electron to one of the ligands or to a nearby acceptor molecule. The state of charge separation will obviously not persist (a lifetime of 10^{-12} seconds is estimated for this intermediate, *18*), and the unstable product of Eq. 3 may then fluoresce, dismute (Eq. 4*b*), or react with a hydrogen ion (Eq. 4*a*). Discussion of the kinetics of reactions such as Eqs. 4*a* and 4*b* is presented at the end of this section.

It appears to be useful to treat electron-transfer spectra by means of thermodynamic cycles of the Born-Haber kind (*17, 22, 23*). Such a cycle was used by Platzman and Franck (*18*) in the analysis of the electron-transfer spectra of the halide ions. The term level diagram describing this cycle is shown in Fig. 1. One of the terms in these cycles is the energy *hν* of the light absorbed in the electron-transfer spectrum; the only other unknown term is generally the energy difference between the reduced form of the absorbing complex and a bound electron, on the one hand, and the reduced form of the absorbing complex and a gaseous electron, on the other hand. This energy difference can be calculated by judicious choice of a model. The use of a model in which the electron is smeared out over the first few hydration layers of the absorbing species for about 10^{-12} seconds led Platzman and Franck (*18*) to a calculation of the level in the potential well to which the electron is excited. The values of the excitation energy that they calculated in this manner matched the positions of the observed absorption peaks of the halide ions.

The use of a model in which the transferred electron remains with one of the ligands in the absorbing species led to a thermodynamic cycle in which the unknown term is the difference between the free energies of formation of the two species (*24*). This energy difference is approximated on an electrostatic basis and agrees qualitatively with observed values.

Reductive case. Although the transfer of an electron to the central ion of an absorbing species has been studied much less thoroughly than the oxidative case, some absorption peaks of this type have been identified as electron-transfer spectra. Some examples found in the litera-

Table 1. Electron-transfer spectra: oxidative case—the reaction $M^n \cdot H_2O + H^+ \rightarrow M^{n+1} \cdot H_2O + H$. E^0 is the half-cell potential.

Ion	λ (A)	hc/λ (kcal/mole)	$E_M{}^0$ kcal/mole	Reference
F^-	1500	191	94	(*17, 18*)
Cl^-	1900	150	56	(*17, 18*)
Br^-	1995	143	44	(*17, 18*)
I^-	2320	123	29	(*17, 18*)
Co^{+2}	2200	130	42	(*21*)
Ni^{+2}	2200	130		(*21*)
Mn^{+2}	2250	127	35	(*21*)
Fe^{+2}	2850	100	18	(*21*)
V^{+2}	3500	81	− 5	(*21*)
Cr^{+2}	3800	75	− 9	(*21*)
Eu^{+2}	$\geqq$ 3660	$\leqq$ 78	− 10	(47)

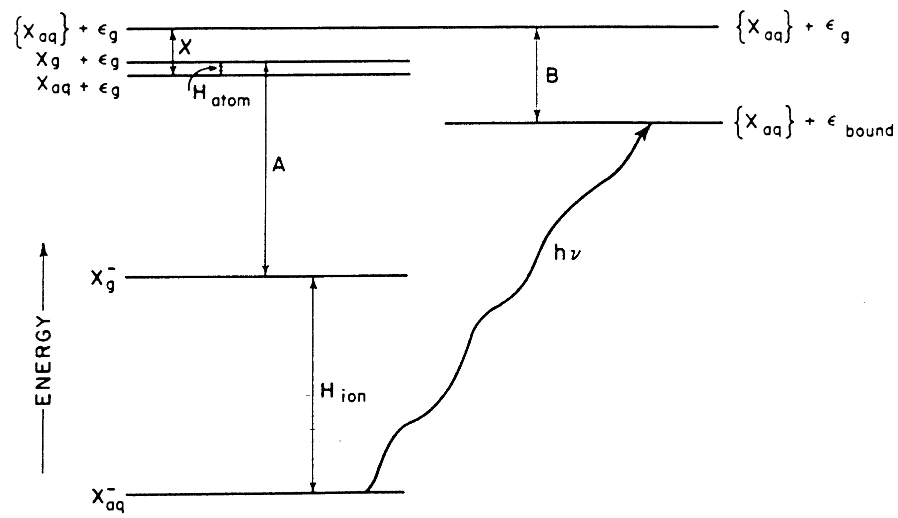

Fig. 1. Energy-level scheme for the electron-transfer spectrum of an ion in aqueous solution. [After Platzman and Franck, *18*]

ture are listed in Table 3. The initial step in these reactions always appears to be charge separation and, when water is the electron donor, the end-product is always oxygen. The reaction scheme is thus analogous to the oxidative case:

$$X^n \cdot H_2O \overset{h\nu}{\rightleftarrows} X^{n-1} \cdot H_2O^+ \qquad (6)$$

$$X^{n-1} \cdot H_2O^+ + OH^- \rightarrow X^{n-1} \cdot H_2O + OH \qquad (7a)$$

or

$$X^{n-1} \cdot H_2O^+ \rightarrow X^{n-1} + H^+ + OH \qquad (7b)$$

$$2OH \rightarrow \rightarrow H_2O + \tfrac{1}{2}O_2 \qquad (8)$$

The reduced product may in turn be used in some reaction in which its energy is permanently stored. Thus, it was found in a study of the photo-reactions of uranium ions that U^{+3}, produced by the photoreduction of U^{+4} at low temperatures, reacted in turn with the solvent to produce hydrogen (*25*). A proposal for inorganic photosynthesis along these lines has been made by Uri (*26*), using the reaction

$$Pb^{II}Cl^+ \xrightarrow{h\nu} Pb^+ + Cl \qquad (9)$$

where the course of the electron transfer was verified by initiation of vinyl polymerization by chlorine atoms. In the presence of an organic substrate that takes up chlorine atoms, the unstable metal ion Pb^+ would be able to reduce organic acids, carbon dioxide, or even water to produce hydrogen. In preliminary experiments, it was found that such a system, when it was illuminated with light of wavelengths in the region 2800 to 3200 angstroms, was able to reduce the dye Janus Green in neutral solution. The oxidation potential of the dye in neutral solution is of the order of + 250 millivolts. Similar reactions involve use of $FeCl_4^-$ as photocatalyst (*27*).

The discussion of this section has so far centered on the light absorption of complex species, which may be handled by the methods of statistical thermodynamics. Very little can be said about the kinetics of the reactions given by Eqs. 4 and 7. Alternative *b* is in each of these cases a dismutation of a transitory complex. Alternative *a*, on the other hand, is in each case an electron-transfer reaction. Various models for such electron-transfer reactions have recently been reviewed (*16, 28*).

A special case: electron-transfer reactions of chlorophyll. An interesting application of the foregoing ideas to the question of energy conversion by chlorophyll has been made by Levitt (*29, 30*). He suggests that it is the magnesium atom that is really active in photosynthesis and that any theory of the conversion of light energy into chemical energy by chlorophyll inevitably has to take the valence changes of the magnesium atom of chlorophyll into account. Levitt arrived at this suggestion by the following reasoning.

1) The organic part of chlorophyll, pheophytin, is photochemically inactive in an electron-transfer sense.

2) The absorption spectra of chlorophyll and pheophytin are quite similar, so that the presence of magnesium in chlorophyll causes no gross change in the spectrum of the molecule.

3) Comparison of the principal absorption bands of chlorophylls *a*, *b*, and *c* with the emission lines of Mg and Mg^{+1} shows a one-to-one correspondence. In particular, this comparison shows that the blue absorption band of chlorophyll coincides with Mg lines, whereas the red absorption band of chlorophyll coincides with Mg and Mg^{+1} lines.

The univalent magnesium ion is not a common chemical species in aqueous solution; its transitory existence has only recently been discovered (*31*) in the course of the anodic oxidation of magnesium. This reaction has been used as an example of the tremendous stabilizing effect of solvation (*28*). Figure 2 is a schematic diagram that shows the stabilization of the unfamiliar univalent state of magnesium by solvation. A magnesium atom from the electrode at point *A* may be ionized to form gaseous magnesium ions, as shown by the upper two curves, but may also coordinate with the solvent at the Helmholtz double layer *B* to form the stable species in solution *C*, as shown by the lowest curve. A similar coordination with the solvent will stabilize the univalent ion *D*, and the height of the barrier *E* will determine the lifetime of the univalent ion in solution.

A similar stabilization of the magnesium ions may be predicted if one considers chlorophyll as a magnesium solvated by pheophytin. Levitt postulates that the 3*s* electrons of such a structure are successively excited by light and finally pass to the electron acceptor. If this model applies, the reaction scheme of the electron-transfer reactions of chlorophyll is that of the oxidative case, which I have already discussed; the oxidized chlorophyll then reacts with water to form oxygen and to regenerate chlorophyll.

Criteria for Practical Chemical Conversion Systems

Having examined briefly the theoretical aspects of the conversion of solar energy to chemical energy, one can see that there is much to be gained by reexamining the problem of energy storage in endothermic compounds. The following requirements come to mind when one thinks about new energy-storage reactions.

1) The system must be simple. Although any energy stored represents a triumph in the effort to reduce waste of otherwise unused sunlight, the first cost of the necessary equipment must be low enough to make its use feasible, at least in energy-poor areas of the world.

2) Operation and fuel costs must be

Table 2. Electron-transfer spectra: oxidative case.

Ion	λ (A)	hc/λ (kcal/mole)	Reference
OH^-	1870	153	(*17*)
SH^-	2270	126	(*17*)
CNS^-	2240	128	(*17*)
NO_3^-	1980	145	(*17*)
UCl_3	4000	72	(*25*)

low. In effect, this means that some extremely common substance, such as air, carbon dioxide, water, or sand, must be used as the primary reactant. The green plant utilizes carbon dioxide by means of many successive oxidation-reduction equilibria, each of which returns to its original state after the reduction of carbon dioxide has been accomplished. Carbon dioxide is thus catalytically reduced by the operation of many successive cyclic systems in the green plant.

3) The fuel produced by the converting reaction must be easily separable from the reaction mixture. This means it should separate out as a solid or as a gas.

4) The fuel produced by the converting reaction must be capable of being economically used to generate electric power.

5) The proposed system should be efficient in the use of available solar energy.

The fifth point has been put last for three reasons. (i) The energy necessary to induce endergonic chemical reactions is large compared with the energies available in the greater part of the solar spectrum. Photosynthesis appears to be the chemical reaction that can take place at longest wavelength (see Table 3) (*20*). (ii) Since any energy taken from the sun is a gain, efficiency in the amount of sunlight converted in the part of the solar spectrum utilized is important only as it affects the cost of the process. (iii) The characteristics of absorption can be changed by complexing of the absorber with organic or inorganic ligands (*19*).

Utilization of Hydrogen

It appears from these considerations that one of the best energy-storing reactions would be the photoreduction of water resulting in the formation of hydrogen. The use of water as primary reactant fulfills criterion 2. The production of hydrogen, which comes off as a gas, fulfills criterion 3. The use of hydrogen as a fuel (criterion 4) is discussed in the following paragraphs, and three different methods for its photocatalytic production (criterion 1) are discussed in succeeding sections.

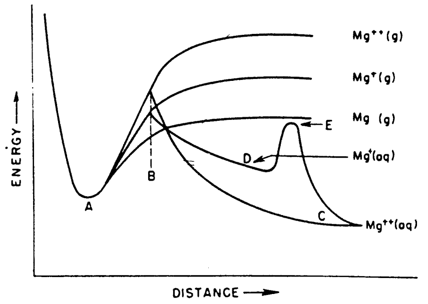

Fig. 2. Section through potential-energy surface for electrolysis of magnesium showing stabilization of ions by hydration. [After Zwolinski, Marcus, and Eyring, *28*]

Table 3. Electron-transfer spectra: reductive case.

Ion	λ (A)	*hc*/λ (kcal/mole)	Reference
Hg^{+2}	1800	159	(*17*)
$HgCl_4^{-2}$	2285	125	(*17*)
$HgBr_4^{-2}$	2500	115	(*17*)
HgI_4^{-2}	3230	89	(*17*)
Cu^{+2}	2000	143	(*17*)
$CuCl_4^{-2}$	2500	114	(*17*)
$CuBr_4^{-2}$	2810	102	(*17*)
Pb^{+2}	2085	137	(*17*)
$PbCl^+$	2260	127	(*17*)
$PbBr^+$	2358	121	(*17*)
PbI^+	2645	108	(*17*)
$PbCl_4^{-2}$	2720	105	(*17*)
$PbBr_4^{-2}$	3040	94	(*17*)
PbI_4^{-2}	3633	79	(*17*)
$SnCl_4^{-2}$	2185	131	(*17*)
$SnBr_4^{-2}$	2450	117	(*17*)
SnI_4^{-2}	2900	99	(*17*)
$CdCl_4^{-2}$	1875	153	(*17*)
$CdBr_4^{-2}$	2155	133	(*17*)
CdI_4^{-2}	2570	111	(*17*)
Fe^{+3}	~2300	124	(*17*)
$FeCl^{+2}$	~3200	89	(*17*)
$FeBr^{+2}$	~3800	75	(*17*)
$FeCNS^{+2}$	~4600	62	(*48, 17*)
ZnI_4^{-2}	2385	120	(*17*)
UCl_4	3000	95	(*25*)
Ce^{+4}	~3200	89	(*17*)
$Co(C_2O_4)_3^{-3}$	2450	117	(*49*)

Endothermic compounds that store solar energy have been utilized by burning. Fossil fuels such as oil and coal have been burned to produce steam, which in turn can generate electric power. Alternatively, sugars and starches made by the green plant are utilized in oxidation cycles (food for plants and animals) that are closely related to the reduction cycle of photosynthesis. It is probable that hydrogen can be used as a fuel in much the same manner that our present organic or atomic fuels are used. The characteristics of hydrogen flames have been studied by Bartholomé and Sachsse (*32*). Enough information is available today to generate power from a hydrogen-fired steam plant with an efficiency of about 30 percent (*33*)—approximately the same efficiency as a coal-burning generator. A direct way of generating power is to mount two hydrogen-burning ram jets firing in opposite directions on a rotating bar connected to a generator. Such use of hydrogen as a fuel is presently possible with an efficiency of 5 to 10 percent. Were the gas turbine to be modified to utilize hot flames, it could probably develop power from hydrogen with 20-percent efficiency. Another attractive possibility for future development is the use of hydrogen-air mixtures in an internal-combustion engine (*34–36*). Here the heat developed is no deterrent, because the burning in each cylinder is intermittent. The efficiency of such an engine may vary from 20 to 47 percent (*35*).

An interesting conversion of hydrogen to electric power has been reported of F. B. Bacon (*37*). In this process, oxygen is forced through a porous nickel electrode. At the other side of the electrode, the gas meets a continuously circulating 27-percent potassium hydroxide solution, thus producing excess hydroxyl ions in the electrolyte and leaving positive charges on the electrode. Hydrogen ions are produced at the edge of a similarly constructed hydrogen electrode, leaving electrons behind. The two electrodes are then connected to form a battery. The cell efficiencies vary from 54 to 67 percent at voltages between 0.8 and 1.0 volt and current densities of 100 to 400 milliamperes per square centimeter at 240°C and pressure of 800 pounds per square inch. Such a unit has already been operated continuously for more than 800 hours.

Production of Hydrogen

Several photochemical means of producing hydrogen appear to exist. The initiation of each of these by visible radiation is discussed in the preceding sections. These reactions will now be considered from the point of view of practicality for hydrogen production. For reference purposes, all of these reactions are gathered together in Fig. 3 in a schematic form that shows the relationship of these reactions to the oxidation-reduction potential of the initial photocatalyst, which is designated by the letter *X*.

Oxidative case. The photooxidation of both anions and cations in aqueous solution, with consequent production of hydrogen, has been well studied. These reactions seldom proceed against the gradient of chemical potential. Upon completion of the reaction, therefore, the absorbing species is in its more stable oxidation state, and considerable energy would have to be expended to reduce it again. For this reason, photooxidation of a light-absorbing species does not appear to be a good way to store energy.

This state of affairs is represented in Fig. 3 by the length of the arrow that connects the initial state of the photochemical catalyst *X* with its final state, X^+. It appears that most of these reactions take place with light absorption in the far ultraviolet, as is indicated in Table 1. Again, it is probably fair to assume that this is due to the necessity of the intermediate production of hydrogen atoms, which is endergonic by 2.1 electron volts.

Reductive case. The photoreduction of the complex ions of many elements, with consequent production of oxygen, has been reported frequently, although the products of such reactions have not been extensively studied. These reactions proceed more frequently against the gradient of chemical potential and thus are able to store radiant energy in the form of chemical energy (*38*). This fact has been indicated in Fig. 3 by the somewhat shorter arrow leading from the initial photocatalyst X to its reduced form, X^-. The conversion of radiant energy to chemical energy represented by this reaction may not persist, however, unless the chemical energy is stored in the form of a stable endergonic compound and thus is removed from the reaction mixture. It appears that this can be accomplished when the oxidation-reduction potential of the absorbing species is more positive than the quantity

$$E = (RT/nF)\ \ln\,[H^+]$$

where F = Faraday and $E > 0.414$ at *p*H 7. In this case the reduced species will react with water to produce hydrogen and thus to regenerate itself. It is necessary to emphasize that this latter reaction is a thermal reaction and is not concerned with light absorption. This possibility has been indicated in Fig. 3 by the arrow pointing upward from the reduced form of the photocatalyst X. The reaction scheme in this case will be

Photoreduction

$$2X + H_2O \xrightarrow{h\nu} 2X^- + \tfrac{1}{2}O_2 + 2H^+ \quad (10)$$

Thermal oxidation

$$2X^- + 2H^+ \rightarrow 2X + H_2 \quad (11)$$

Net reaction

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2 \quad (12)$$

The proposal of Uri for inorganic photosynthesis (*26*), which has been referred to previously, is a reaction that falls into the reductive case. In this particular context, however, the difficulty with this proposal appears to be that the initial form of the photocatalyst, which in this case is the complex ion $PbCl^+$, is not regenerated, but rather the chloride ion has been lost to some substrate. The discovery by Freed and Sancier (*25*) of the photoreduction of uranium tetrachloride also belongs to this particular reaction class. In this reaction, uranium tetrachloride was reduced to the trichloride by the action of light, and the trichloride reacted thermally with the solvent to produce hydrogen and to regenerate the oxidized form. However, this reaction was carried out in a nonaqueous solvent at very low temperatures; there is some doubt that these particular species of uranium could be maintained in aqueous solutions. Furthermore, the previous comment about losing 1 molecule of chlorine from the original form of the photocatalyst also applies here. Work on similar systems in aqueous solution is presently being carried on in this laboratory.

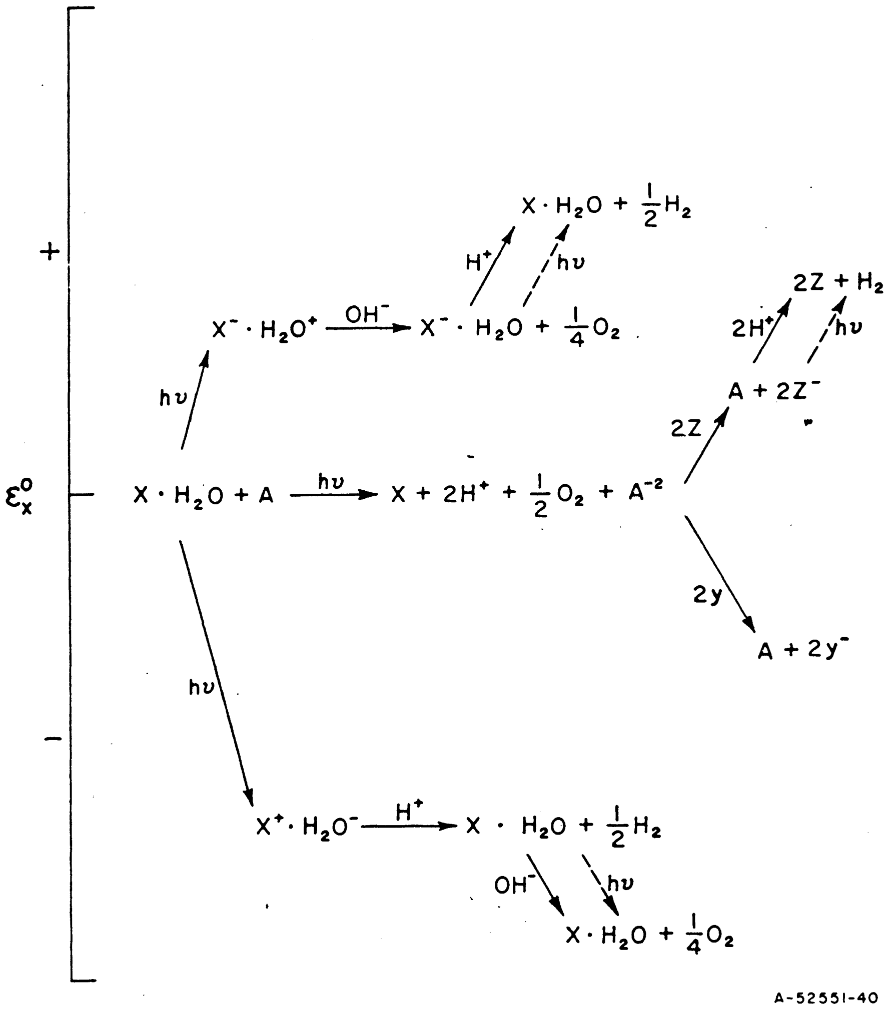

Fig. 3. Relationship of the various routes of hydrogen production to the reduction potential $E_x{}^0$ of a photocatalyst.

The requirements for the magnitude of the oxidation-reduction potential of the photocatalyst become less stringent if the reducing form of the photocatalyst is also photoactive. In this case another photoreaction may restore the original form of the photocatalyst and produce hydrogen at the same time. This is the principle that was used by Heidt (*39, 40*) in designing a system for the cyclic production of hydrogen. This system involved the photoreduction of ceric ion, which resulted in the formation of oxygen, and the subsequent photooxidation of cerous ion, which resulted in the formation of hydrogen. Heidt pictures his scheme with the following efficiencies:

Photoreduction

$$2Ce^{+4} + H_2O \xrightarrow{h\nu} 2Ce^{+3} + \tfrac{1}{2}O_2 + 2H^+ \quad \text{(36 percent)} \quad (13)$$

Photooxidation

$$2Ce^{+3} + 2H_2O \xrightarrow{h\nu} 2Ce^{+4} + H_2 + 2OH^- \quad \text{(0.1 percent)} \quad (14)$$

Net reaction

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2 \quad (15)$$

In the laboratory study of this reaction, the 2537 line of a high-intensity mercury arc was used to photocatalyze the reaction. In ordinary sunlight, however, the efficiency of the reaction is quite low. Under the conditions employed by Heidt, several days' illumination of his absorption system by sunlight resulted in the formation of about 10^{-8} mole of hydrogen. The following difficulties come to mind in a discussion of cyclic reactions in which both halves are photocatalyzed.

1) The rates of both reactions should be the same and should be such that no appreciable photostationary concentrations of intermediates appear. Otherwise such intermediates may absorb light that is needed to make the reaction proceed. In the afore-mentioned scheme, the initial production of hydrogen is encouraged by use of very low initial concentrations of ceric ion.

2) When two ions of the same element but of different charge are present

in aqueous solution, they will often exchange electrons. In the present case, such an electron exchange would be

$$Ce^{*+3} + Ce^{+4} \rightarrow Ce^{*+4} + Ce^{+3} \quad (16)$$

The theory of such electron-exchange reactions has been treated by several authors (*15, 16, 28*). Such exchange reactions interfere with the cyclic production of hydrogen in at least two different ways. (i) Although the actual electron transfer is fast, the atomic adjustments required by the Franck-Condon principle take time, and the ions are unavailable for hydrogen production during that time (*39*). (ii) Some electron-exchange reactions may proceed by a photocatalytic, as well as a thermal, path. The cerium exchange reaction is one of these. Gryder and Dodson (*41*) attributed the rapid ceric ion exchange in perchloric acid to an excited cerous species that lies about 2000 cm^{-1}, or 572 calories/mole, above the ground state. For the thermal reaction, one can expect from the Boltzmann probability that 10^{-3} percent of the cerous ions exist in the excited state at room temperature; this percentage will rise considerably when radiation is present. When ultraviolet light is available, even higher states may be populated, so that the electron-exchange reaction may be considerably favored over the hydrogen-producing reaction.

3) As is shown in the reaction scheme, the two photocatalytic reactions will always be *p*H-dependent in opposite ways. Thus, if the cycle cannot be run at about *p*H 7, one reaction will always be faster than the other, with a resulting disturbance of the photostationary state.

It has also been reported (*20*) that Heidt has produced hydrogen by using ferrous and ferric ions according to this scheme. In that instance, some hydrogen appears to have been evolved at 5900 angstroms, although from Tables 1 and 2 one would expect this reaction to proceed in the ultraviolet only.

(*Note added in proof*: In a private communication, L. J. Heidt (MIT) states that he has never reported that he could produce hydrogen by using ferrous ions with light of any wavelength except 2537 A.)

Hill reaction. A photooxidation that occurs in nature is the Hill reaction, which is briefly discussed in the first section of this paper. Here one may think in terms of chlorophyll donating 2 electrons, in two separate acts of light absorption, to some intermediate, which in turn passes these electrons on to an electron acceptor. This is indicated by the middle branch of Fig. 3.

The electron acceptors most frequently used in laboratory studies of the Hill reaction are ferric compounds, primarily ferricyanide. The reduction of ferricyanide to ferrocyanide is exergonic and, hence, stores none of the light energy used in the photolysis of water. This is indicated in Fig. 3 by the reaction of A^{-2} with the electron acceptor Y. It has never been determined how hard chloroplasts can "push"—that is, whether an electron acceptor can be found that will use part of the light energy for reduction and, thus, store such light energy. This can be determined in an equilibrium system by the use of electron acceptors with varying half-cell potentials. Several quinones and dyes have been used for this purpose at concentrations at which they are supposed to be nonpoisonous to the chloroplast.

Wessels (*42*) found that illuminated chloroplasts could not reduce oxidants E_0' ($E_0' = E_0$ at *p*H 6.5) greater than -40 millivolts. The value of E_0' for ferricyanide is -440 millivolts at the potassium-ion concentrations used. If the oxygen liberated by the Hill reaction is taken off immediately, however, so that back oxidation of the electron acceptor does not occur, Wessels found that dyes of E_0' as high as 100 millivolts can be reduced.

MacDowall (*43*) studied the normal potential (that is, the extent of reduction) of a series of dyes. The highest potential reached was 250 millivolts for toluylene blue, and MacDowall thinks that even this potential was not the reducing limit of the chloroplast. Vishniac and Ochoa (*44*) observed that triphosphopyridine nucleotide (TPN) can function as a Hill-reaction oxidant when its reduced form is removed by coupling to an appropriate enzyme system. Since the oxidation potential of the TPN system is about 300 millivolts, one concludes that the illuminated chloroplast has a potential of at least this magnitude. Lumry, Spikes, and Eyring (*45*), in reviewing these data, came to the conclusion that the Hill reaction is completely nonspecific (in concentrations where no oxidant-poisoning effects occur) with respect to the E_0 of the oxidant, as long as the latter is below some as yet undetermined limit. At the time of this writing, preliminary reports of the fixation of carbon dioxide by chloroplasts have appeared (*6*).

It thus appears possible that some electron acceptor, designated by Z in Fig. 3, may be found which can accept electrons in the course of the Hill reaction and thus store some of the energy evolved in this reaction. If the chloroplasts can push hard enough to reduce Z when $E_Z{}^0 > 0.414$ at *p*H 7, then this electron acceptor Z can in turn react with hydrogen ion to form hydrogen. This problem is currently being studied in this laboratory. The reaction can be pictured in the following manner.

Hill reaction

$$2H_2O + 4Z \xrightarrow{h\nu} 4H^+ + O_2 + 4Z^- \quad (17)$$

Thermal oxidation

$$4Z^- + 4H^+ \rightarrow 4Z + 2H_2 \quad (18)$$

Net reaction

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2 \quad (19)$$

In an unpublished paper, Spikes (*46*) has pointed out another interesting possibility. This concerns an electron acceptor Z whose reduced form would be photoactive. Thus, another photoreaction would occur that would convert the reduced form of the electron acceptor (Z^-) back to its original form, with consequent production of hydrogen. This is the kind of reaction that would occur if, for instance, ceric ion were an electron acceptor in the Hill reaction. The reaction scheme would be, in this case:

Hill reaction

$$2H_2O + 4Z \xrightarrow{h\nu} 4H^+ + O_2 + 4Z^- \quad (20)$$

Photooxidation

$$4Z^- + 4H_2O \xrightarrow{h\nu} 4Z + 2H_2 + 4OH^- \quad (21)$$

Net reaction

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2 \quad (22)$$

Conclusion

In this paper (*50*) I attempt to show the directions that developments in chemical storage systems of solar energy are likely to take. This is done by examining the requirements that nature and economy impose on the storage system. In the course of such an examination, it becomes clear that the simplest chemical storage system of energy is the gas hydrogen. Some of the ways in which hydrogen can be used to supply energy are mentioned briefly, together with the efficiency to be expected from each use. After a short review of the present knowledge of energy conversion (in terms of electron-transfer spectra), the various paths available for the production of hydrogen from water are discussed. It is shown that each of these paths depends on the cyclic oxidation and reduction of a photocatalyst.

Thus, a review of the fundamental concepts of light absorption and of the chemical effects that occur upon light absorption provides a comprehensive picture of the possibilities and mechanisms for conversion of solar energy into chemical energy. It can easily be appreciated that the photochemical approach to the conversion of solar energy avoids some of the thermodynamic problems that are inherent in the black-body degradation of solar energy. It is to be hoped that this collation of available facts will encourage a quick and successful attack on this urgent problem of the storage of solar energy.

References and Notes

1. Anon., *Chem. Eng. News* 31, 2056 (1953).
2. F. Daniels, *ibid.* 31, 3868 (1953).
3. E. Rabinowitch, *Photosynthesis and Related Processes* (Interscience, New York, 1945).
4. F. Daniels, in *Centennial* (AAAS, Washington, D.C., 1950).
5. H. A. Spoehr, *Photosynthesis* (Chemical Catalog Co., New York, 1926).
6. D. I. Arnon, M. B. Allen, F. R. Whatley, *Nature* 174, 394 (1954); D. I. Arnon, *Science* 122, 9 (1955).
7. C. S. French and H. Milner, *Symposia Soc. Exptl. Biol.* 5, 232 (1951).
8. R. Hill, *Nature* 139, 881 (1937).
9. A. S. Holt and C. S. French, in *Photosynthesis in Plants,* J. Franck and W. E. Loomis, Eds. (Iowa State College Press, Ames, 1949), Chap. 14.
10. J. D. Spikes, *Arch. Biochem. and Biophys.* 35, 101 (1952).
11. E. U. Condon, *Phys. Rev.* 28, 1182 (1926).
12. ———, *ibid.* 32, 858 (1928).
13. J. Franck, *Trans. Faraday Soc.* 21, 536 (1926).
14. ———, *Z. physik. Chem.* A120, 144 (1926).
15. R. J. Marcus, B. J. Zwolinski, H. Eyring, *J. Phys. Chem.* 58, 432 (1954).
16. J. Weiss, *Proc. Roy. Soc. London* A222, 128 (1954).
17. E. Rabinowitch, *Revs. Mod. Phys.* 14, 112 (1942).
18. R. Platzman and J. Franck, in *L. Farkas Memorial Volume,* A. Farkas and E. P. Wigner, Eds. (Research Council of Israel, Jerusalem, 1952), Chap. 5.
19. L. E. Orgel, *Quart. Revs. London* 8, 422 (1954).
20. J. G. Calvert, *Ohio J. Sci.* 53, 293 (1953).
21. F. S. Dainton and D. G. L. James, *J. chim. phys.* 48, No. 9/10, C17 (1951).
22. J. Franck and F. Haber, *Sitzber. kgl. preuss. Akad. Wiss.* 1931, 250 (1931).
23. J. Franck and G. Scheibe, *Z. physik. Chem.* A139, 22 (1929).
24. H. L. Schlaefer, *Z. physik. Chem.* NF3, 222, 263 (1955).
25. S. Freed and K. M. Sancier, *J. Chem. Phys.* 22, 928 (1954).
26. N. Uri, *ibid.* 20, 348 (1952).
27. ———, *Chem. Revs.* 50, 375 (1952).
28. B. J. Zwolinski, R. J. Marcus, H. Eyring, *ibid.* 55, 157 (1955).
29. L. S. Levitt, *Science* 118, 696 (1953).
30. ———, *ibid.* 120, 33 (1954).
31. R. L. Petty, A. W. Davidson, J. Kleinberg, *J. Am. Chem. Soc.* 76, 363 (1954).
32. E. Bartholomé, *Naturwissenschaften* 36, 171, 206 (1949); H. Sachsse and E. Bartholomé, *Z. Elektrochem.* 53, 183 (1949).
33. Figures on the expected efficiency of hydrogen utilization were supplied by Robert H. Eustis of Stanford Research Institute.
34. R. O. King, *Can. J. Research* F26, 228 (1948).
35. R. O. King and M. Rand, *Nature* 174, 975 (1954).
36. R. O. King, W. A. Wallace, B. Mahapatra, *Can. J. Research* F26, 264 (1948).
37. Anon., *Ind. Eng. Chem.* 46, No. 10, 11A, 13A (1954).
38. F. S. Dainton, *The Kinetics and Mechanism of Inorganic Reactions in Solution,* K. W. Sykes, Ed. (Chemical Society, London, 1954), pp. 18–40.
39. L. J. Heidt, *Proc. Am. Acad. Arts Sci.* 79, 228 (1951).
40. L. J. Heidt and A. F. McMillan, *Science* 117, 75 (1953).
41. J. W. Gryder and R. W. Dodson, *J. Am. Chem. Soc.* 73, 2890 (1951).
42. J. S. C. Wessels and E. Havinga, *Rec. trav. chim.* 72, 1076 (1953).
43. F. D. H. MacDowall, *Science* 116, 398 (1952).
44. W. Vishniac and S. Ochoa, *J. Biol. Chem.* 195, 75 (1952).
45. R. Lumry, J. D. Spikes, H. Eyring, *Ann. Rev. Plant Physiol.* 5, 271 (1954).
46. J. D. Spikes, "The energy conversion reactions in photosynthesis," *The Physical and Economic Foundation of Natural Resources: Photosynthesis—Basic Features of the Process* (Interior and Insular Affairs Committee, U.S. House of Representatives), in press.
47. D. L. Douglas and D. M. Yost, *J. Chem. Phys.* 17, 1345 (1949).
48. R. H. Betts and F. S. Dainton, *J. Am. Chem. Soc.* 75, 5721 (1953).
49. T. B. Copestake and N. Uri, *Proc. Roy. Soc. London* A228, 252 (1955).
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Study Center for Behavioral Scientists

Ralph W. Tyler

The Center for Advanced Study in the Behavioral Sciences, located on a knoll a mile west of the Stanford University campus, is a place where each year 50 selected students of human behavior come on postdoctoral fellowships to study individually and with others in seeking to broaden and deepen their competence. The center was established by the Ford Foundation on the unanimous recommendation of a committee of 12 scientists and academic administrators as one major means for the further development of the behavioral sciences.

Obviously, the center is not the only important way of facilitating this development. More time and funds for research, greater attention to fundamental problems, better Ph.D. training, greater incentives for able minds to devote themselves to the study of human behavior, more opportunities for competent research workers to free themselves periodically from activities that distract them from intensive research efforts, and more encouragement in universities for interdepartmental communication on common problems would all help to speed up the development of the behavioral sciences. The center offers one kind of opportunity not previously available. For 1 year, it provides the scholar both with free time to devote entirely to his own study and with access to colleagues of the same and related disciplines who are interested in some of the same problems.

This concept of the center was outlined by a planning committee of scientists and submitted to the Ford Foundation, which in the summer of 1952 approved the proposal and appropriated $3.5 million to establish the center and to pay for 5 years of operation. The foundation also appointed a board of directors who were to incorporate the center as a nonprofit institution and to take full responsibility for it. The directors are Frank Stanton, psychologist, president of Columbia Broadcasting System, who is chairman of the board; Paul H. Buck, historian of Harvard University; F. F. Hill (*1*), economist, provost of Cornell University; Clark Kerr, economist, chancellor of the University of California at Berkeley; Robert K. Merton, sociologist of Columbia University; Robert R. Sears, psychologist, Stanford University; Alan T. Waterman, physicist, director of the National Science Foundation; and Theodore O. Yntema, economist, vice president-finance of the Ford Motor Company. The directors invited me to become executive director of the center, and I began this work on 1 October 1953. The year 1953–54 was spent in finding a site, erecting buildings, and selecting the fellows for the first year of operation, which began in September 1954. Hence comments about the way in which the center is serving the purposes intended are based on the first year of operation.

The original plan for the center con-

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