RUSSIAN CHEMICAL REVIEWS
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August 1980

Translated from *Uspekhi Khimii*, **49**, 1457-1497 (1980)

U.D.C. 535.217; 541.128; 541.141; 620.91; 620.92

Possible Approaches to the Development of Photo-catalytic Solar Energy Converters

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Possible approaches to the development of photo-catalytic solar energy converters, and their perspectives, are discussed with special reference to the conversion of solar energy into chemical energy by the photo-catalytic decomposition of water into hydrogen and oxygen. 408 references.

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I. INTRODUCTION

According to recent estimates[1-4] the annual consumption of energy by mankind is currently 5×10^{16} kcal, rising rapidly and doubling every 15–20 years. On the other hand the known reserves of mineral fuels, which at present form the basis of our energy balance, are limited to an estimated energy equivalent of 10^{19} kcal. Thus the search for new sources of energy is a problem of fundamental importance. The most promising approaches appear to be the use of thermonuclear energy (based on deuterium) and the use of solar energy[1-18]. The large-scale exploitation of both these sources of energy presents serious difficulties, but it is important to note that whereas controlled thermonuclear fusion is still at the research stage solar energy is continuously reaching the Earth in amounts far exceeding the rapidly growing needs of mankind.

Thus the amount of solar energy which is incident on our planet is estimated[1,16,17] to be 1.2×10^{21} kcal per annum, but some of this energy is reflected by the atmosphere and by the Earth's surface and is irreversibly lost, while the remainder is absorbed by the atmosphere (2×10^{20} kcal), by the oceans and seas (4.2×10^{20} kcal), and by the land masses (1.8×10^{20} kcal). Part of this absorbed energy (6×10^{17} kcal per annum) is converted into chemical energy by the photosynthetic process in plants and micro-organisms. However, only a very small part of this energy is used by mankind: 8×10^{15} kcal per annum as fuel and other materials and 4×10^{15} kcal per annum as food. The amount of solar energy converted into electrical energy by hydroelectric and wind-operated power stations is also quite small: 4×10^{15} kcal per annum.

The most important attribute of solar energy is its ecological purity, i.e. the possibility of carrying out energy cycles without emitting harmful products into the surroundings and without additional heating of the Earth.

The wide-scale exploitation of solar energy must await practical solutions to the following three problems: 1) the relative diffuseness of solar energy (even outside the Earth's

atmosphere the flux of solar energy is only 1.395 kW m^{-2} = 12260 kW-h m^{-2} $year^{-1}$ = 3.33×10^{-5} kcal cm^{-2} s^{-1}),[19-24] 2) the annual, seasonal, and daily variations of the energy flow reaching the Earth's surface, and 3) the need to convert the energy of the light quanta into a more convenient form.

Let us consider the importance of the first two of the above factors. In the vicinity of the Earth a power of 1 GW (typical of a modern electric power station) is carried by the Sun's rays falling on a square 850 m in side: the area of such a square is comparable to that occupied by a thermal power station having that output. Of course, on the Earth's surface the insolation is much lower, since the Sun shines for only part of the day, and its rays are partly reflected by the atmosphere. But even in the middle latitudes of the USSR—in the region of Moscow or of Novosibirsk, say—the total amount of radiation falling on the surface of the Earth is staggeringly large: more than 1000 kW-h m^{-2} $year^{-1}$.[19,20] This is only 2.5 times lower than the radiation in the sunniest region of the Earth (near the Red Sea[20,22]). In Soviet Central Asia the total solar radiation is as high as 1600 kW-h m^{-2} $year^{-1}$. A simple calculation shows that an amount of energy equal to the annual output of a 1 GW electric power station is contained in the Sun's rays falling on a square 3 km in side in the middle latitudes of the USSR or 2.3 km in side in Central Asia. It is equally easy to show that the amount of energy produced by the combustion of 600 million tonnes of petroleum (the annual production of the USSR) is contained in the Sun's rays falling on a square 67.4 km in side in Central Asia: we note that just the Kara-Kum desert can accommodate over 60 of these squares.

An amount of energy of 1300 billion kW-h, equal to the annual output of electrical energy planned for 1980 in the USSR, could be collected in Central Asia from a square 64.7×64.7 km^2 in area assuming a conversion efficiency of 20%. Even in the region of Novosibirsk the annual output of electrical energy of the Novosibirsk hydro-electric station (1.7×10^9 kW-h)[25] could be matched with a square 2.9 km in side (again, assuming 20% conversion efficiency), which is very much less than the area of the Ob' sea which feeds the hydroelectric station (1070 km^2). For comparison we may note that in the USA the area of the existing network of hard-surfaced roads (having a total length of 6 million km in 1972[26]) is greater than the area of a square 150 km in side. Thus, in spite of the relatively low density of the solar energy flux and of its dependence on local conditions, even a complete change-over of our energy consumption to solar energy is not (in principle) an engineering impossibility. More detailed estimates have confirmed the economic justification for the development of energetics based on solar radiation[27-59]. However, the effective exploitation of solar energy awaits the development of economically acceptable methods of concentration, conversion, and storage of the Sun's energy.

II. METHODS OF SOLAR ENERGY CONVERSION

Existing methods of conversion of the Sun's energy can be arbitrarily classified into four types: 1) thermal, 2) photophysical, 3) photochemical (including photo-electrolysis), and 4) photobiological (based on natural photosynthesis).

The thermal conversion of solar energy is the simplest: it consists in heating heat-transfer media with ordinary or with concentrated Sun's rays. Many variants of the thermal method are currently in use, or are being developed: they are used for cooling or heating buildings, in solar kitchens and high-temperature furnaces, for powering mechanical engines and electrical generators, for feeding thermo-electric converters, in the desalination of water, etc. (see previous reviews[4,12,27-39]). In principle the efficiency of the conversion of the Sun's radiant energy into heat is quite high, and with a very simple concentrator it can reach 50–70% at noon[23,27,28,38,39,60]. Therefore even in the near future we can expect relatively large-scale use of thermal methods of solar energy conversion, matched to local needs. However, in the subsequent conversion of thermal into electrical or mechanical energy the efficiency (daily average) falls to 3–5% because of the low efficiency of heat engines and of the low effectiveness of the concentrators except at noon[23,27]. For these reasons thermal conversion of solar energy is still not being used for large-scale energy production.

Recent advances in the direct conversion of solar energy into electrical or chemical (fuel) energy have made these methods potentially more attractive for large-scale energy production.

The direct photophysical conversion of solar into electrical energy is most effectively realised in semiconductor $p-n$ junction converters[4,22,28,51-55,61,62]. In these devices the absorption of a light quantum of energy $h\nu$ (greater than the energy gap) transfers an electron from the valence to the conduction band. The resulting hole–electron pair is separated by the electric field of the $p-n$ function (see Fig. 1), causing electrical polarisation of the semiconductor wafer and thus producing an e.m.f. and a current i. Semiconductor converters based on crystalline silicon, with efficiencies up to 14%, have been developed and are being used successfully[51-55,61,62]. Even more effective semiconductor converters based on hetero-junctions (e.g. gallium arsenide) are also being developed: their efficiency can be as high as 20% or more[52-55]. This method of converting solar into electrical energy is attracting most of the research effort at the moment, and it appears to offer the best prospect of success†. A plan to set up a semiconductor electrical power station in space capable of re-transmitting the energy to the Earth in the form of UHF radiation is also being discussed[24].

The widespread use of semiconductor converters awaits practical solutions to two main problems: the high cost of the semiconductor converters themselves (currently[53-55] 10–15 thousand dollars per kW of power production capability), and the difficulty of combining semiconductor photo-electric converters with high-power electrical circuits. The former problem will be rapidly overcome by current advances in semiconductor production technology (it is estimated[53-55] that economically acceptable converters costing 200–250 dollars per kW, i.e. matching the cost of modern thermal converters, will be available in the mid-1980's). However, the second limiting factor, which applies to all Earth stations, is more serious. It stems from the annual, seasonal, and daily

† Work is proceeding also on photo-electrochemical converters of solar into electrical energy ("wet photocells"). According to their operating mechanism, these can be classified into two types: the photosensitive semiconductor electrode type[11,59,63-93] and the photosensitive electrolyte type[94-110]. Recent converters of the photosensitive electrode type have shown very promising efficiencies (up to 7.5% for CdSe with a polysulphide electrolyte[88]). However, much more work is needed before the true potential of the method can be assessed. The All-Union Research and Technical Information Institute (VINITI) issues a special bulletin entitled "Ekspress-informatsiya. Pryamoe Preobrazovanie Teplovoi i Khimicheskoi Energii v Elektrichestvo" (Express Information. The Direct Conversion of Thermal and Chemical Energy into Electricity), which summarises current foreign publications on the conversion of solar energy into electrical energy by photo-electric cells (including "wet cells").

variations of the energy output of the semiconductor converters. The consumption of electrical energy cannot be tailored to suit these variations. Energy accumulators (or buffers) have been based on the chemical energy of fuels or on the potential energy of water in reservoirs. The large-scale use of solar energy will also require some form of *accumulation* of this energy, preferably in the most effective form currently known (i.e. as a *chemical fuel*).

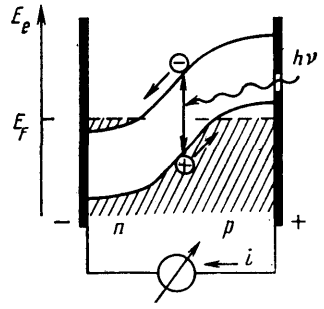


Figure 1. Basic operation of the semiconductor element. The potential energy of the current carriers (E_e) is plotted vertically. The thin full lines are the edges of the energy gap; the cross-hatched region denotes the energy levels filled with electrons; E_F is the Fermi level. The arrows show the direction of motion of the charges (electrons and holes) separated by the light in the region of the step in electrical potential.

Many experts consider hydrogen to be the most promising fuel[1,13–15,56–59,111–116]. Hydrogen is not only an exceptionally good fuel, whose combustion does not contaminate the environment, but it is also a valuable chemical product. The current world production of hydrogen is more than 30 million tonnes per annum, with an annual growth rate of 10%.[14,57] Given solar energy converters having an efficiency of 20% this amount of hydrogen could be produced in Central Asia from a square with 55.4 km sides.

One possible way of converting solar energy into chemical energy in the form of hydrogen is the electrolysis of water, using the electrical energy produced by semiconductor p–n junction converters. Assuming an efficiency of 14% for the conversion of solar into electrical energy (which has already been achieved in modern silicon photocells), and an efficiency of 70% for the conversion of electrical into chemical energy (i.e. the efficiency of present-day industrial apparatus for the electrolysis of water), the overall efficiency for the conversion of solar energy into the chemical energy of hydrogen is 10%. This is an encouraging figure, especially since there are very real prospects of further improvements in the efficiency of semiconductor converters of radiant into electrical energy. Converters based on this two-stage scheme could in principle be operating now, but so far they have not been economically viable because of the existence of cheaper (natural) organic and nuclear fuels.

In addition to this two-stage method we can envisage the direct photochemical conversion of solar energy into fuel energy without intermediate production of electrical energy. Most of the photochemical conversion methods rely on the use of *photo-catalytic* processes. One of these methods is the photo-electrolysis of water on a semiconductor surface (e.g. an oxide), acting as a heterogeneous catalyst for the decomposition of water[117–119]. This method is attracting a great deal of attention at the moment[11,59,117–188] (see also Refs. 63–93).

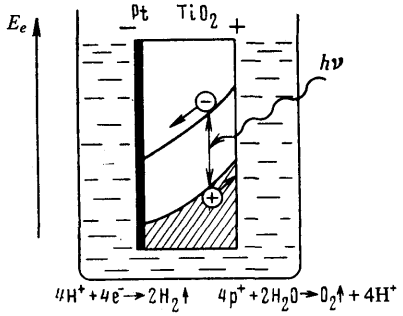


Figure 2. Operation of a semiconductor photo-catalyst for the decomposition of water; symbols as in Fig. 1.

In the most thoroughly investigated system, which uses titanium dioxide as the photo-catalytic semiconductor, the photo-electrolysis process can be described as follows[87,178]. The light generates a conduction electron and a hole in the semiconductor, and the two carriers are separated by the electric field at the semiconductor–electrolyte interface. The holes diffuse to the surface of the semiconductor catalyst, where they oxidise the water with evolution of molecular oxygen (see Fig. 2), and the conduction electrons reach the metal electrode (e.g. platinum) where they reduce the water with evolution of molecular hydrogen. Unfortunately the efficiency of the conversion of solar into chemical energy on TiO_2 is quite low (less than 1%) because this oxide has a wide band-gap (~ 3 eV) and hence the photo-catalytic process in this case requires u.v. quanta, which are present in small numbers in the Sun's spectrum.

Worthwhile progress in this area can be made only by changing to semiconductors which can decompose water under the influence of visible radiation, such as iron oxide[116,182,183] and tungsten oxide[182,183], though other semiconductors also could be used. However, in the absence of reliable quantitative measurements we cannot yet assess the efficiency of solar energy conversion with hydrogen accumulation on these photo-catalysts. Furthermore, most of these materials suffer strong photo-corrosion in aqueous solutions. There is evidence that the photo-corrosion of semiconductor photo-catalysts may be suppressed by chemical modification of the semiconductor surface (by introducing surface impurities, or by adsorption of special reagents). Surface modification can be used also to control the surface field which separates the photo-generated charge pairs.

Thus any progress in the exploitation of these converters will be determined to a large extent by advances in the surface chemistry of semiconductors.

Another method of direct conversion of solar energy into chemical energy relies on molecular photo-catalytic systems. These systems are found, for example, in natural photobiological converters such as plants and bacteria capable of photosynthesis[7,13,56,189–192]. In plants the energy of the Sun's radiation is converted mainly into chemical energy of

carbohydrates, synthesised by the reduction of carbon dioxide and the oxidation of water. The initial step of the photosynthesis is reminiscent of the formation of a conduction electron and a hole in semiconductors. The light quantum absorbed by a chlorophyll molecule (Chl) transfers one electron from the ground state to an excited level (Fig. 3), from which it can fall into the lower-lying levels of other molecules (the acceptors, A). On the other hand the hole which is formed at the same time in the ground level of the Chl molecule can accept an electron from the higher-lying levels of other molecules (the donors, D). As a result, the initial step of the photosynthesis process

$$A + D \xrightarrow[Chl]{h\nu} A^- + D^+ , \qquad (1)$$

produces a pair of particles (the reducing agent A^- and the oxidising agent D^+) analogous to the hole–electron pair of semiconductors.

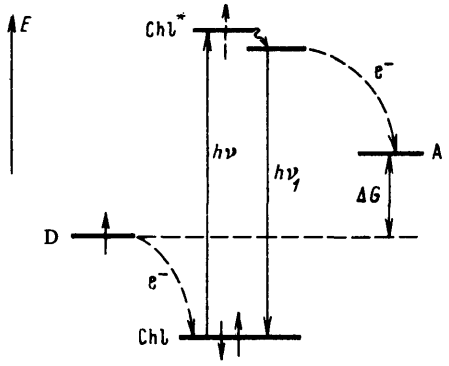


Figure 3. Charge separation by an electronically excited dye molecule (chlorophyll, Chl). Electron energy is plotted vertically, $h\nu$ is the absorbed light quantum, the wavy arrow denotes the conversion into a longer lived excited state, $h\nu_1$ is the luminescence quantum, and ΔG is the chemical energy stored as a result of the process.

During photosynthesis in plants the reducing agent A^- is used (through a complicated chain of catalytic reactions) to reduce CO_2 to sugars:

$$4A^- + 3H_2O + CO_2 \rightarrow 4A + {}^1/_6(C_6H_{12}O_6) + 4OH^- , \qquad (2)$$

and the oxidising agent D^+ completes the cycle of reactions by oxidising water to molecular oxygen:

$$4D^+ + 4OH^- \rightarrow 4D + 2H_2O + O_2\uparrow . \qquad (3)$$

Thus the overall photosynthesis process in plants can be described by the catalytic reaction scheme

$$H_2O + CO_2 \xrightarrow[Chl,\,A,\,D]{h\nu} 1/6\,(C_6H_{12}O_6) + O_2\uparrow \qquad (4)$$

in which an amount of free energy $\Delta G \cong 120$ kcal mole^{-1} O_2 is stored. In order to carry out one such cycle a plant needs no fewer than eight quanta of red light, each with an energy of ~40 kcal Einstein^{-1}.[7]

Theoretical calculations (see below) suggest that the maximum possible efficiency of the conversion of solar energy by the eight-quantum reaction (4) is 15% of the incident Sun's light. This value can be treated as the theoretical limit of the efficiency of photo-biological energy converters. In some water plants (e.g. *chlorellae*) the experimentally measured efficiency of solar energy conversion is as high as 6%.[12,193–195] Among cultivated (agricultural) plants the highest efficiencies are found in maize (3.2%), sorghum (3.2%), and sugar cane (2.4%).[194] Thus the best cultures of water plants offer an acceptably efficient conversion of solar into chemical energy. Economically sound processes for the microbiological fermentation of the products of plant photosynthesis to give convenient forms of fuel for large-scale energy production have already been suggested: hydrogen (see Fig. 4), methane, or ethanol[13,50,196–200]. Large Government programmes aimed at replacing hydrocarbon motor fuels by ethanol (obtained from sugar cane) are already in progress in Brazil and in the Philippines.[13]

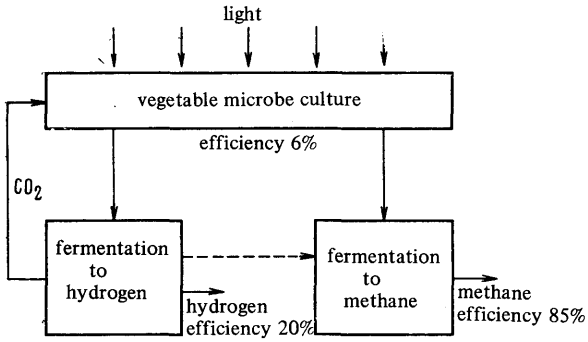


Figure 4. Microbiological conversion of solar energy and efficiencies achieved in the different steps.

Obviously, a major advance in the conversion of solar into chemical energy would be the development of synthetic molecular photo-catalytic systems with a narrow "chemical specialisation", which could be more efficient than plants[1]. If these systems could be handled in simple industrial plant, and manufactured from cheap starting materials, they could even be cheaper than existing semiconductor p–n junction devices. The problem of designing molecular photo-catalytic systems for the conversion of solar into chemical energy was fully formulated only recently[1], and is still in its initial stages of development. The various approaches to its solution are the main theme of the present review.

As will be shown below, molecular and semiconductor photo-catalytic converters have very similar mechanisms. Hence many of the data quoted in this paper can be applied also to calculations involving semiconductor photo-catalytic systems.

III. POSSIBLE PROCESSES FOR THE CONVERSION OF SOLAR INTO CHEMICAL ENERGY

The basic thermodynamic requirement which applies to chemical reactions for accumulating solar energy in the form of chemical energy is that the reaction should be endothermic in the dark. The condition is $\Delta H > 0$ (if the stored energy is to be used for the production of heat) or $\Delta G > 0$ (if the energy is being stored for the production of a more "noble" form of energy, e.g. the electrical energy of fuel cells). In order to allow their storage, transport, and use in practical situations the photo-reaction products must be stable, i.e. the reverse (exothermic) reactions must be slow.

Chemical energy can be stored either directly as the internal energy of molecules (for example, by converting a substance under the influence of light into an energy-enriched form such as a valency isomer), or as reaction products which can be used as fuels (combustibles and oxidisers), and which interact with evolution of energy in a useful form[13,56-59,122,179,201-208].

The exploitation of photochemical converters for large-scale energy production implies the storage and transport of hundreds of millions of tonnes of photo-catalytic reaction products in the form of useful fuels. Therefore the starting materials used in these reactions should be readily available, cheap, convenient to use, and easily transportable. The accumulation of energy in an intramolecular form obviously implies the use of fairly complex compounds[122,179,201,208-216], and this method will probably be limited to satisfying local needs even if very efficient forms of the method are developed. The same is true of converters relying on phase transitions[217,218] or on corrosive or dangerous materials such as SO_2, Cl_2, etc.[208]

Within the Earth's atmosphere the most convenient way to exploit chemical energy is to allow a fuel to react with the atmospheric oxygen. Hence the most attractive working processes for the conversion of solar energy are those leading to the reduction of readily available materials (as in natural photosynthesis).

Table 1. Possible reactions for the storage of solar energy as fuel.

No.	Reaction	n	ΔG^0_{298}, kcal mole^{-1}	ΔH^0_{298}, kcal mole^{-1}	ΔG^0_{298} (for 1 electron), eV	λ_{thr}, nm
1	$H_2O \rightarrow H_2 + {}^1/_2 O_2$	2	56.71	68.25	1.23	1008
2	$2H_2O + CO_2 \rightarrow CH_4 + 2O_2$	4	195.54	212.8	2.12	588
3	$2H_2O + CO_2 \rightarrow CH_3OH + {}^3/_2 O_2$	6	167.92	173.64	1.21	1025
4	$3H_2O + 2CO_2 \rightarrow C_2H_5OH + 3O_2$	12	318.34	336.82	1.15	1077
5	${}^3/_2 H_2O + {}^1/_2 N_2 \rightarrow NH_3 + {}^3/_4 O_2$	3	81.09	91.44	1.17	1059
6	$2H_2O + N_2 \rightarrow N_2H_4 + O_2$	4	181.33	148.74	1.97	629

Note. The thermodynamic data quoted are for liquid H_2O, CH_3OH, C_2H_5OH, and N_2H_4; n is the number of electrons transferred; λ_{thr} is the threshold wave length for the n-quantum mechanism (see Section IV).

In the light of the requirements outlined above the most convenient starting materials are water and atmospheric gases, and we must turn towards these materials (at least, initially) in our search for large-tonnage photo-catalytic energy production methods. Some processes potentially suitable for the storage of energy in a chemical form are listed in Table 1. In every case the product is a valuable chemical raw material. All these processes take place in living organisms (photosynthesis followed by fermentation of the photosynthesis products to H_2, CH_4, or alcohols, or fixation of atmospheric nitrogen). As was pointed out above, reaction No.1 of Table 1 has been achieved under artificial conditions on semiconductor photo-catalysts. Reactions No.2[219] and Nos.5 and 6[220] have also been observed on TiO_2 and $SrTiO_3$ photo-catalysts under the influence of u.v. light, though their quantum efficiency is still very low. The distinguishing feature which all these processes have in common is the oxidation of water with evolution of molecular oxygen. As we shall show below, this reaction step is the most difficult to implement.

The absorption of solar energy by the compounds listed in Table 1 is negligibly small, and photochemical conversion is necessary: this is provided by an additional intermediate agent (the photo-catalyst) which strongly absorbs the Sun's light and which is fully regenerated at the end of the working cycle. Many photo-catalytic reactions, both homogeneous and heterogeneous, have been described (see, for example, Refs.221 and 222 respectively). However, the effort currently devoted to the search for really effective catalytic processes for the conversion of solar energy is still inadequate.

The most promising chemical process for the conversion of solar energy at present is the photo-catalytic decomposition of water into hydrogen and oxygen. Water, of course, is a universally available, cheap, and very convenient starting material. The product of the reaction—hydrogen—is not only an excellent fuel but also an important raw material for the chemical industry, used on an enormous scale. Furthermore, existing information on chemical reaction mechanisms suggests that the photo-dissociation of water may be the most easily implemented of all the processes so far proposed for the accumulation of solar energy. Therefore we shall examine in detail the problems posed by the conversion of solar into chemical energy by this process.

IV. MAXIMUM THEORETICAL EFFICIENCY OF THE CONVERSION OF SOLAR INTO CHEMICAL ENERGY

The efficiency of the conversion of solar energy (η) is defined as the ratio of the amount of energy stored to the total amount of solar energy (E_0) falling on the converter. The latter quantity is equal to the product of the area of the system (S) and of the total flux of solar energy (i.e. of the flux of light quanta of all energies).

For thermal methods of solar energy conversion the efficiency is limited essentially by the use of the Carnot cycle for heating the working fluid in the first stage of the process, and by the conversion of heat into mechanical, electrical, or chemical energy in the later stages[23,60]. Other losses (such as incomplete absorption of radiation) are avoidable in principle to a large extent, and are being overcome as new technological improvements are introduced.

The photo-catalytic conversion of light energy also suffers losses of different types: incomplete absorption of the light by the system (or ineffective absorption by photochemically inactive parts of the system), partial recombination of the useful intermediates during the photochemical reaction, partial loss of energy (as heat) in overcoming activational barriers or in forming energy-consuming intermediates, etc. All these losses can be avoided to a large extent by improved photo-reactor design and by choosing a more effective cycle of chemical reactions.

However, the maximum theoretical efficiency of the photochemical conversion of solar into chemical energy is limited by a factor which is unavoidable in principle and is unrelated to the Carnot cycle: the same factor which sets a limit to the maximum theoretical efficiency of semiconductor p–n junction energy converters. This is the quantum character of the photochemical and photophysical changes[7,59,223].

The elementary endo-energetic photochemical processes all require the absorption of a quantum of light energy greater than some threshold value determined by the free energy ΔG of the process: $h\nu_{thr} = \Delta G$. The only exceptions are the multi-photon processes which take place in high-intensity light fluxes such as laser beams. The real threshold value $h\nu'_{thr}$ can be higher than $h\nu_{thr}$, since the activational barrier may have to be overcome in a system which does not absorb at the frequency ν_{thr}.

All the light quanta having an energy $< h\nu'_{thr}$ fail to induce the photochemical reaction and are wasted; on the other hand when quanta having an energy $> h\nu'_{thr}$ are absorbed only a fraction of their energy ($h\nu_{thr}$) is converted into chemical energy.

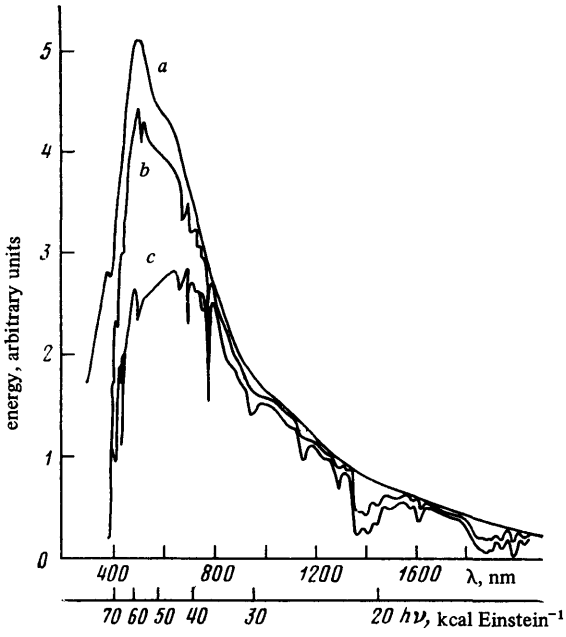


Figure 5. Spectral composition of solar radiation outside the atmosphere (*a*) and on the Earth's surface on a clear summer day at noon (*b*) and in the evening (c)[21].

Knowing the energy distribution function $\rho(\nu)$ of the quanta of solar energy (see Fig.5) we can easily calculate the maximum possible efficiency of a photochemical conversion for different assumed mechanisms. Thus in the simplest case of a one-quantum chemical reaction the stored useful energy E is equal to the product of the number N of acts of reaction (which under optimum conditions is given by the number of incident quanta with an energy $> h\nu'_{thr}$) and of ΔG or ΔH (depending on the final use of the stored energy) for a single act. For example, if the product is to be used in the production of electrical energy we can write $E = \Delta G \cdot N$, where $N = S\int_{\nu'_{thr}}^{\infty} \rho(\nu) d\nu$; furthermore $E_0 = S\int_0^{\infty} h\nu\rho(\nu) d\nu$, so that

$$\eta = \Delta G \int_{\nu'_{thr}}^{\infty} \rho(\nu)\, d\nu \Big/ \int_0^{\infty} h\nu\rho(\nu)\, d\nu.$$

The maximum efficiency theoretically achievable in the complete absence of losses#, i.e. for $h\nu'_{thr} = h\nu_{thr} = \Delta G$,[223] is

$$\eta = \Delta G \int_{\nu_{thr}}^{\infty} \rho(\nu) d\nu \Big/ \int_0^{\infty} h\nu\rho(\nu)\, d\nu = \nu_{thr} \int_{\nu_{thr}}^{\infty} \rho(\nu)\, d\nu \Big/ \int_0^{\infty} \nu\rho(\nu)\, d\nu. \quad (5)$$

According to the second law of thermodynamics we should decrease η by a factor of $\sim (T_0 - T)/T_0$, where $T_0 \cong 5800$ K is the Sun's temperature and T is the temperature of the absorber of quanta. However, this correction is unimportant in practice because $T_0 \gg T$.

Plots of the efficiency calculated by this formula against the threshold quantum energy for the $\rho(\nu)$ distributions which describe the solar spectrum outside the Earth's atmosphere and on the Earth's surface respectively are shown in Fig.6. These plots go through a maximum, where the efficiency reaches ~40% for photochemical processes with threshold energies corresponding to quanta in the red and near-i.r. regions. The existence of an optimum value of ν_{thr} indicates the interplay of two opposing tendencies as ν_{thr} increases: a decrease in the total number of quanta absorbed and an increase in the degree of utilisation of the energy of each of the quanta absorbed.

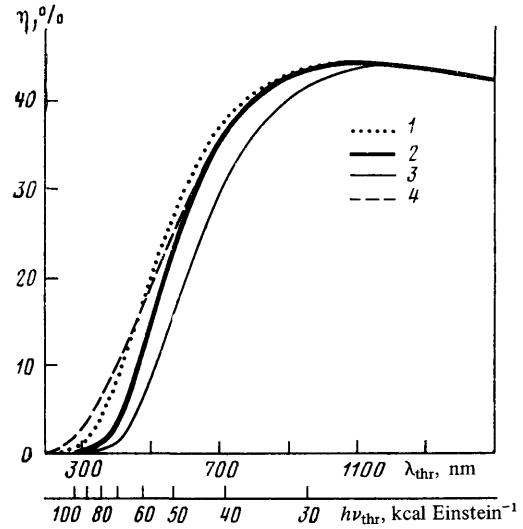


Figure 6. Maximum theoretical efficiency (η) of the one-quantum photochemical reaction against wave length of the threshold light quantum ($\lambda_{thr} = c/\nu_{thr}$) for solar radiation outside the Earth's atmosphere (*1*), on a clear summer day at noon (*2*) and in the evening (*3*), and for a perfect black body at 5800 K (*4*). Data on the solar spectrum taken from Refs.21 and 20.

In another possible situation (which exists, for example, during photosynthesis in plants) n quanta are needed for the chemical change, each quantum producing one particular active compound (the cation radicals of chlorophyll in the case of photosynthesis), and therefore we have

$$\eta = \Delta G \int_{\nu'_{thr}}^{\infty} \rho(\nu)\, d\nu / n \int_0^{\infty} h\nu\rho(\nu)\, d\nu, \quad (6)$$

where $h\nu'_{thr}$ is the threshold energy quantum for an individual photochemical reaction (for example, for the production of Chl^+), and ΔG is the energy stored as a result of the overall process [for example, as a result of reaction (4)].[7,224] In the optimum case $h\nu'_{thr} = h\nu_{thr} = \Delta G/n$, and formula (5) again applies. The following parameters apply to photosynthesis in plants (see Section II): $\Delta G \cong 120$ kcal mole^{-1} O_2, $n = 8$, $h\nu'_{thr} \cong 40$ kcal Einstein^{-1} (the red edge of the chlorophyll absorption band active in photosynthesis). Inserting into formula (6) these values together with the function $\rho(\nu)$

calculated from Fig.5*b* or 5*c* we arrive at $\eta \cong 15\%$ as the maximum efficiency of the photosynthesis process in plants. For the four-quantum ($n = 4$) dissociation of water discussed below ($\Delta G = 113.4$ kcal mole^{-1} O_2) the threshold quantum $h\nu_{thr} = \Delta G/4 = 28.4$ kcal Einstein^{-1} ($\lambda_{thr} = 1008$ nm) lies exactly at the maximum of the curve in Fig.6. This means that a maximum solar energy conversion efficiency of $\eta \cong 40\%$ could be achieved in the decomposition of water by a four-quantum mechanism.

The maximum conversion efficiency could be increased by using several endo-energetic reactions, with different ΔG, in the converter. In this case the photo-catalytic apparatus could be designed in such a way that quanta of low and of high energy are used in reactions with low and with high ΔG respectively. An analogous method of raising the efficiency has been proposed[225] for semiconductor photo-cells. However, there is a danger that chemical systems of this type will be so complex that their usefulness will suffer (as compared to that of the single endo-energetic process). Therefore an efficiency of $\eta \cong 30-40\%$ is perhaps the most realistic estimate which can be made at present.

Table 2. Standard electrode potentials of reactions involving water and its fragments in aqueous solutions.

No.	Reaction	E^0, V	ΔG^0_{298}, kcal mole^{-1}	Refs.
1	$e^-(aq) = e^-$	−2.7	62	227
2	$H^- = {}^1/_2H_2 + e^-$	−2.251	51.93	228
3	$H = H^+ + e^-$	−2.106	48.61	226
4	$H^- = H^+ + 2e^-$	−1.125	51.93	229
5	$2OH^- + H_2 = 2H_2O + 2e^-$	−0.828	19.1	226
6	$O_2^- = O_2 + e^-$	−0.32	7.4	226
7	$H\dot{O}_2 = O_2 + H^+ + e^-$	−0.13	3.0	228
8	$H_2 = 2H^+ + 2e^-$	0.000	0	226
9	$\dot{O}(g) + H_2O = O_2 + 2H^+ + 2e^-$	0.037	1.7	229
10	$HO_2^- = O_2 + H^+ + 2e^+$	0.338	15.6	229
11	$2OH^- = H_2O + {}^1/_2O_2 + 2e^-$	0.401	18.5	226
12	$H_2O_2 = O_2 + 2H^+ + 2e^-$	0.682	31.5	228
13	$\dot{O}H + H_2O = H_2O_2 + H^+ + e^-$	0.72	17	228
14	$2H_2O = O_2 + 4H^+ + 4e^-$	1.228	113.4	226
15	$O_2 + 2OH^- = O_3 + H_2O + 2e^-$	1.24	57.2	226
16	$H_2O_2 = H\dot{O}_2 + H^+ + e^-$	1.5	35	228
17	$3H_2O = O_3 + 6H^+ + 6e^-$	1.511	209.3	229
18	$OH^- + H_2O = HO_2^- + 2H^+ + 2e^-$	1.706	78.76	229
19	$2H_2O = H_2O_2 + 2H^+ + 2e^-$	1.776	81.72	229
20	$OH^- = \dot{O}H + e^-$	2.02	46.6	226
21	$O_2 + H_2O = O_3 + 2H^+ + 2e^-$	2.076	95.56	226
22	$H_2 = H + H^+ + e^-$	2.106	48.61	229
23	$H_2O = \dot{O}'(g)' + 2H^+ + 2e^-$	2.421	111.72	226
24	$H_2O = \dot{O}H + H^+ + e^-$	2.8	65	228

It is often suggested that the use of thermal processes in photochemical converters is irrational because of the low efficiency of the conversion of thermal into chemical energy. However, this shortcoming is compensated by the possibility of full conversion into heat of all the quanta contained in the Sun's light. As a result the overall losses may be lower than those encountered in quantum converters, in which we know that more than half of the energy can be lost. Evidently, photo-catalytic systems which exploit the advantages of the thermal and of the quantum conversion methods at the same time could be designed, thus overcoming their disadvantages to some extent. For example, a system could be designed in which the chemical equilibrium at various stages of the photo-catalytic process is shifted towards useful products by heating the system (or part of it) with photochemically inactive i.r. light. Several possible conversion systems with heating will be considered in the following Section.

V. THE PHOTO-CATALYTIC DECOMPOSITION OF WATER

1. Thermodynamics of the Water Decomposition Processes

The decomposition processes in the gaseous and the liquid phase are accompanied by the following changes in free energy and in enthalpy[226]:

$$H_2O(g) \rightarrow H_2(g) + {}^1/_2O_2(g);\ \Delta G^\circ_{298} = 54.6 \text{ kcal mole}^{-1},\ \Delta H^\circ_{298} = 57.8 \text{ kcal mole}^{-1};$$
$$H_2O(l) \rightarrow H_2(g) + {}^1/_2O_2(g);\ \Delta G^\circ_{298} = 56.7 \text{ kcal mole}^{-1},\ \Delta H^\circ_{298} = 68.3 \text{ kcal mole}^{-1}.$$

For the reaction involving the liquid phase ΔG decreases by ~ 3 kcal mole^{-1} when the temperature is increased from 25 to 100 °C.

The standard electrode potentials E^0 and the corresponding values of ΔG°_{298} for a number of one-electron and multi-electron reduction and oxidation processes involving water and its reaction products in aqueous solutions are listed in Table 2. We can see from the Table that from the electrochemical standpoint the decomposition of water into H_2 and O_2 is a four-electron process§ with a potential difference $\Delta E^0 = 1.23$ V and $\Delta G^0 = 113.4$ kcal mole^{-1} (obtained by combining reactions No.8 and No.14 of Table 2).

Most of the reactions in Table 2 involve the ions H^+ and OH^-. The electrode potentials of these reactions depend on the pH of the medium. The standard potentials listed in Table 2 correspond to pH = 0 for reactions involving H^+ and pH = 14 for reactions involving OH^-. At other pH values the E^0 values should be replaced by the formal oxidation–reduction potentials (ORP) E_m.[228]

Plots of E_m against pH for reactions No.14 and No.8 (evolution of oxygen and of hydrogen respectively) are shown in Fig.7.[229] Since the H^+ ions do not appear in the overall equation

$$H_2O \rightarrow H_2 + {}^1/_2O_2,$$

the difference between the E_m values for reactions No.14 and No.8 is independent of pH (1.23 V). Any oxidising agent with an E_m value lying above the "oxygen" line is thermodynamically able to evolve O_2 from water, and similarly any reducing agent with E_m below the "hydrogen" line can evolve H_2 from water[228–230].

As usual, removal of the reaction products assists the reaction: a rise in the "hydrogen" line and a fall in the "oxygen" line are clearly shown in Fig.7 in response to a decrease in the hydrogen and the oxygen pressure over the solution respectively.

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§ The terms "one-electron" and "multi-electron" process are often used in a different context: they are applied to the number of electrons transferred through the electrical circuit in order to carry out the stated reaction by electrolysis. In papers on electron transfer reactions the same terms denote the number of electrons transferred in each elementary act. In this review we shall use the terms "one-electron" and "multi-electron processes (or reactions)" in the electrochemical sense, and the terms "one-electron" and "multi-electron mechanisms" with reference to the mechanism of the elementary act.

2. Requirements for Photo-catalysts for the Decomposition of Water by Visible Light

By comparing the above thermodynamic data with the photochemical properties of water and with the spectral characteristics of solar radiation we can formulate the most important requirements for photo-catalytic systems for the decomposition of water.

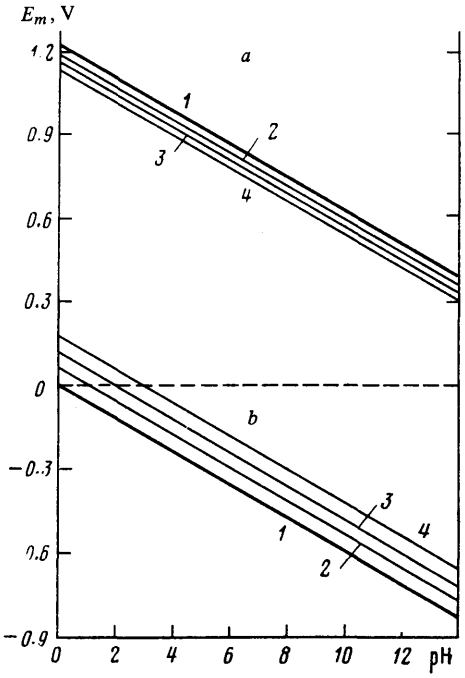


Figure 7. Formal ORP for the evolution of oxygen (*a*) and hydrogen (*b*) from water against the pH of the solution for different partial pressures of oxygen and hydrogen[229]: *1*) 1, *2*) 10^{-2}, *3*) 10^{-4}, *4*) 10^{-6} atm.

As Fig.5 shows, the solar spectrum at the Earth's surface contains practically no quanta corresponding to wave lengths < 300 nm, i.e. with an energy > 95 kcal Einstein^{-1}. At the same time the least endothermic of the possible monomolecular photo-dissociation processes

$$H_2O \rightarrow H_2 + O\ ,$$

requires an energy of 116 kcal mole^{-1} for a gas-phase reaction[222,231-233]. The lowest electronically excited state of water ($^3B_1$) is stated[234,235] to have an excitation energy $\geq$ 116 kcal mole^{-1}. This means that neither the direct nor the sensitised (by excited states) photolysis of water can be used for the conversion of solar into chemical energy. For the same reason it would be useless to try known heterogeneous photo-catalysts for the decomposition of water by hard u.v. radiation with λ < 250 nm (such as BeO and Al_2O_3[222,231,232]).

Thus the key element of any effective molecular system for the decomposition of water by solar radiation is the photo-catalyst: a dye K which can absorb the Sun's light without itself being decomposed by it and initiate a cycle of reactions in which water is reduced and oxidised. In natural photosynthesis the photo-catalyst is based on chlorophyll.

From the thermodynamic point of view any electronically excited K molecule (like chlorophyll, see Fig.3) can induce the photo-catalytic redox reaction

$$D + A \xrightarrow[K]{h\nu} D^+ + A^- \ . \qquad (7)$$

However, in practice these reactions take place only if the dye is excited into the "charge transfer bands"[202,236]. Hence the search for photo-catalysts should be confined to compounds which possess charge transfer bands in the visible region. This property is found in many organic dyes, though transition-metal compounds also seem promising in this respect. The latter compounds offer not only suitable absorption bands but also the ability to change their state of oxidation by several units, which should favour many-electron changes. Lastly, transition-metal compounds are able (in principle) to coordinate the Ḣ and ȮH free radicals formed by the one-electron reduction and oxidation of water. As will be shown below, this should lower the energy losses accompanying the photo-decomposition of water.

Since two molecules of H_2O have to be decomposed in order to produce one molecule of O_2 the total energy expenditure of a catalytic cycle cannot be less than 113.4 kcal mole^{-1}: in other words, the photo-catalytic decomposition of water cannot be a single-quantum process. A two-quantum process would need light of wave length < 504 nm (in the green region of the spectrum). As Fig.6 shows, the maximum efficiency at this wave length is less than the optimum by a factor of 2 or 3. The threshold wave length for a three-quantum process is 756 nm. Light of this wave length is found to offer the optimum conversion efficiency, but the decomposition of water involving fewer than four photons implies the simultaneous transfer of more than one electron under the influence of a single quantum. Until recently no such process had been reported, and therefore a serious discussion of three-quantum and two-quantum mechanisms for the decomposition of water would be inappropriate at present. However, there is no fundamental reason why one quantum should not induce the transfer of several electrons, and therefore we should continue to search for systems capable of reactions of this type[204].

The most rational process for the decomposition of water at present appears to be a four-quantum, sequential mechanism induced by red light, in which each light quantum is used to transfer one electron. As we have already pointed out, the threshold wave length for the decomposition of water in this case is $\lambda_{thr} = 1008$ nm, which corresponds to the optimum efficiency value. The fact that a non-optimum eight-quantum scheme is used in natural plant photosynthesis has been explained by the need to compensate for energy losses in long chains of redox reactions, or by evolutionary effects[192,237]. There is no reason to assume that an eight-quantum scheme is essential also in artificial photo-catalytic systems for the decomposition of water[1].

The energy ΔG stored by the photo-catalyst K for the absorption of one light quantum is equal to the difference in energy between the excited and the ground state of the photo-catalyst. However, the energy available for subsequent reactions is usually less than the energy of the light quantum because of the fast, spontaneous transition (conversion) of the K molecule from the primary excited state to some lower and longer-lived state, which then takes part in the chemical changes. The long life-times of these metastable excited states are due to the difference between their spin multiplicity and that of the ground state. These chemically active excited states are often luminescent, and therefore the energy stored by the photo-catalyst ($\Delta G = h\nu_1$) can

be determined by measuring the wave length ν_1 of the emitted light.

Knowing the formal redox potentials E_m for the ground state of the photo-catalyst, and the energies of its excited states, we can calculate the E_m values for the latter states. Obviously, in order to decompose water we must select a photo-catalyst whose excited states have E_m values consistent with the evolution of H_2 or O_2 from water. For example, in the case of isolated molecules of chlorophyll-*a* (Chl) we know[238] the formation potentials of the Chl^+ cation radical ($E^+ = +0.72$ V) and of the anion radical Chl^- ($E^- = -0.88$ V), and also the energies of the singlet (S) and of the triplet (T) excited state ($E_S = 1.86$ eV, $E_T = 1.26$ eV). The formal oxidation potential of the excited chlorophyll singlet state, i.e. the potential of the reaction

$$^{S}Chl + e^- \rightarrow Chl^{\div} ,$$

with respect to the normal hydrogen electrode, is $E_S^- = E^- + E_S = +0.98$ V, and the reduction potential of the same state, i.e. the potential of the reaction

$$^{S}Chl \rightarrow Chl^{+} + e^- ,$$

is $E_S^+ = E^+ - E_S = -1.14$ V. Similarly we find for the triplet state $E_T^- = +0.38$ V and $E_T^+ = -0.54$ V. These values agree exactly with direct electrochemical measurements of the potentials of the excited states of chlorophyll[238].

It follows from the relative values of E^+ and E^- that both the singlet and the triplet state of chlorophyll are potentially capable of reducing water with evolution of hydrogen, whereas only the singlet state (or the cation radical) can oxidise water with evolution of oxygen, at pH $\gtrsim$4 or 8 respectively (see Fig. 7).¶ The E_m value for the anion radical Chl^- obtained in the first reaction is sufficient in principle for the reduction of water, i.e. it is able to initiate the decomposition cycle.

We should note that many thermodynamically strong one-electron oxidising agents such as Ce^{4+}(aq), with $E^0(Ce^{4+}/Ce^{3+}) = 1.61$ V, cannot in practice cause oxidation of water because the reaction rate is very low. Their potential is probably not high enough to give a high enough rate to the first energetically unfavourable step. (This step is the one-electron oxidation of water to the $\dot{O}H$ free radical, which we shall discuss below in detail.) However, in the presence of catalysts (such as metallic platinum, or manganese or cobalt oxide) which allow the reaction to take place without formation of $\dot{O}H$ radicals in the free state the oxidation of water by Ce^{4+}(aq) is fairly fast[242].

3. Possible Mechanisms for the Decomposition of Water

The data listed in Table 2 allow us to compare the efficiencies of various theoretically possible mechanisms for the photo-catalytic decomposition of water. Thus we note that the reduction or oxidation of water by successive one-electron transfer reactions to give $\dot{H}$ or $\dot{O}H$ radicals in the free state require large (and unproductive) consumptions of energy, since in the subsequent reactions of these particles a significant fraction of their chemical energy is uselessly converted into heat. For example, the one-electron reaction

$$H_2O \rightarrow \dot{H} + \dot{O}H$$

(the difference between reactions No. 24 and No. 3) requires a heat input of 4.9 eV = 113 kcal mole^{-1}. At the same time the overall reaction

$$2H_2O \rightarrow 2H_2 + O_2$$

can store only 1.23 eV = 28.4 kcal mole^{-1} of energy for each transferred electron. In other words, ~75% of the chemical energy of the $\dot{H}$ and $\dot{O}H$ radicals is unavoidably converted into heat.

The effectiveness of the process may be increased in two ways: 1) by carrying out the reaction so that the $\dot{H}$ and $\dot{O}H$ particles are formed in a coordinated or adsorbed state as opposed to a free state, which lowers their energy of formation by an amount equal to the free energy of coordination (complex formation or adsorption), and 2) by avoiding the formation of $\dot{H}$ and $\dot{O}H$ particles through the use of multi-electron elementary acts. The possibility of two-electron transfer processes has been demonstrated[243,244], and even more complex, four-electron processes are believed[245,246] to be possible.

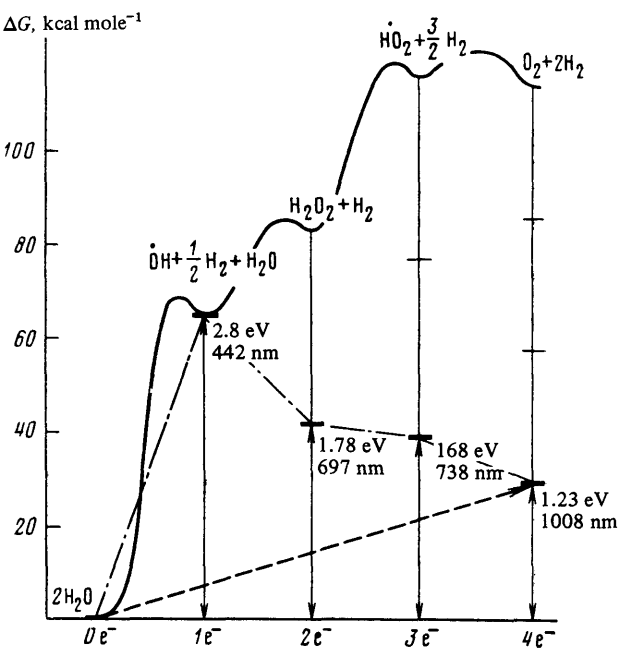


Figure 8. Energy profile of the decomposition of water to molecular hydrogen and the products of its one-, two-, three-, and four-electron oxidation. The numbers denote the energies and wave lengths of the threshold quanta for the transfer of one electron by the four-quantum mechanism of decomposition of water. The dot-and-dash line and the broken line show the changes in stored free energy (expressed for one transferred electron) attending the decomposition of water through the intermediate formation of $\dot{O}H$, H_2O_2, and $H\dot{O}_2$, and by its decomposition directly into H_2 and O_2 respectively.

As an illustration of the use of the data in Table 2 for estimating the effectiveness of various theoretically possible mechanisms of water decomposition we have shown in Fig. 8 an energy profile for conditions in which water is reduced

¶ According to the most recent views, the oxidation of water in natural photosynthesis occurs not on isolated molecules of chlorophyll-*a* but on associated groups of the dihydrated molecule $(Chl\text{-}a \cdot 2H_2O)_n$, with $n \geq 2$ and $E^+ = +0.92$ V[239-241].

directly to H_2 by a two-electron mechanism, and oxidised by sequential one-electron processes with formation of free $\dot{O}H$, H_2O_2, and $H\dot{O}_2$. It is evident from Fig. 8 that hydrogen peroxide (when formed through $\dot{O}H$(ads) or by a two-electron mechanism) is a far more effective intermediate than the $\dot{O}H$ free radical. Over 70% of the stored chemical energy is retained when this intermediate decomposes with evolution of O_2. Active catalysts for the decomposition of hydrogen peroxide are well known[244]. The same approach can be used to estimate the effectiveness of other possible mechanisms.

We conclude from Table 2 and Fig. 8 that the most favourable energy profile is obtained if the water is decomposed directly into H_2 and O_2, without going through the intermediate formation of free $\dot{H}$, $\dot{O}H$, H_2O_2, $H\dot{O}_2$, etc. The possibility of reducing water to H_2 (and of oxidising it to O_2) on the surface of heterogeneous catalysts while avoiding the formation of free $\dot{H}$ and $\dot{O}H$ particles follows directly from data on the electrolysis of water on metal electrodes. Thus at low current densities the overvoltage for the evolution of H_2 on a platinum cathode is of the order of 0.01 V, and the O_2 overvoltage of a cobalt anode is 0.2 V. These potentials are insufficient for the formation of $\dot{H}$ and $\dot{O}H$ in significant quantities.

It has recently been suggested[247,248] that the first step in the electrolytic reduction of water is the formation of adsorbed (as opposed to free) $\dot{H}$ particles:

$$H_3O^+ + e^- \rightleftarrows \dot{H}(ads) + H_2O ,$$

and that molecular hydrogen is formed directly from these particles by the reactions

$$2\dot{H}(ads) \rightleftarrows H_2\uparrow \quad \text{or} \quad \dot{H}(ads) + H_3O^+ + e^- \rightleftarrows H_2\uparrow + H_2O .$$

The stronger the adsorption of atomic hydrogen on the electrode, the faster is the hydrogen evolution and the lower the overvoltage.

The first (and slowest) step in the oxidation of water on precious metal electrodes is thought to be[247]

$$OH^-(ads) \rightarrow \dot{O}H(ads) + e^- \quad \text{or} \quad H_2O(ads) \rightarrow \dot{O}H(ads) + H^+ + e^- ,$$

This is followed by the fast step

$$2\dot{O}H(ads) \rightarrow \dot{O}(ads) + H_2O$$

or

$$\dot{O}H(ads) \rightarrow \dot{O}(ads) + H^+ + e^-$$

and finally

$$2\dot{O}(ads) \rightarrow O_2\uparrow .$$

On common metal electrodes the oxide film which covers the electrode can take part in the oxygen evolution process: for example,

$$MO + H_2O \rightarrow MO_2 + 2H^+ + 2e^-$$
$$2MO_2 \rightarrow 2MO + O_2\uparrow .$$

Thus the water electrolysis processes are essentially heterogeneous catalytic reactions taking place on the electrodes through the formation of adsorbed active particles. Effective heterogeneous catalytic systems for the conversion of electrical into chemical energy by the electrolysis of water are known, and therefore it should be possible in principle to develop similar systems for the conversion of solar energy.

4. Possible Organisation Schemes for the Photo-catalytic Process

Four different organisation schemes for the photo-catalytic decomposition of water can be suggested.

Scheme 1. The primary electron donor (or acceptor) for the excited state of the photo-catalyst is the water molecule itself, or its fragments OH^- and H^+, and the primary oxidation (or reduction) product goes into the solution, where it undergoes further reactions whilst the reduced (or oxidised) state of the photo-catalyst is potentially able to complete the water decomposition cycle in the dark, i.e. this species is a strong enough reducing (or oxidising) agent.

Scheme 2. Analogous to scheme 1 except that the oxidation (or reduction) product does not go into solution but remains coordinated (adsorbed) either on the photo-catalyst or on another compound until it takes part in further reactions.

Scheme 3. The primary photochemical reaction does not cause oxidation (or reduction) of water or its fragments, but it forms a strong oxidising agent and a strong reducing agent at the same time, which can decompose water in the dark.

All the three cases listed above imply a sequential four-quantum mechanism for the decomposition of water, and in every case the effectiveness of the process as a whole is determined by the effectiveness of the electrochemical charge separation process (to form a strong oxidising agent and a strong reducing agent), and of the evolution of hydrogen and of oxygen.

Scheme 4. In the initial step water is dissociated on the surface of a heterogeneous catalyst [for example, with formation of $\dot{H}$(ads), $\dot{O}H$(ads), or $\dot{O}$(ads)], or in the coordination sphere of a homogeneous catalyst. The light is used to cause recombination of the adsorbed (coordinated) intermediates with formation of H_2 and O_2 molecules and the photodesorption of these molecules.

Combinations of these schemes may be used in real water decomposition processes.

a) Photo-catalytic Decomposition of Water by Scheme 1

The main advantage of this scheme is its simplicity. Since one-electron oxidation or reduction of water is assumed even in the initial act of the photochemical reaction the use of a catalyst for the H_2 or O_2 evolution step becomes unnecessary, and the catalyst can consist (in principle) of a single component: the dye. The fast (and uncatalysed) recombination of the $\dot{O}H$ and $\dot{H}$ free radicals leads to evolution of O_2 or H_2, and the reduced or the oxidised form of the dye can be used to produce H_2 or O_2 if this is allowed by the redox potential. The need for stability of the dye in the presence of very reactive free radicals suggests that the most effective photo-catalysts will be found among inorganic compounds.

Data on the complexes and on the organic compounds which can evolve hydrogen (as H_2 or H) or oxygen as O_2 or $\dot{O}H$) from water under the influence of light are summarised in Tables 3 and 4. Unfortunately most of these materials are photochemically active only in the ultraviolet region of the spectrum. Photo-oxidation and photo-reduction processes in water have been reported also in the presence of inorganic anions (halide ions, S^{2-}, SO_4^{2-}, etc.)[202,249,278], but these too require energetic u.v. radiation. It is convenient to examine separately the formation of the oxidised (K^+) and of the reduced (K^-) form of the catalyst in the primary photochemical act (the oxidation and the reduction case).

Photo-oxidation in aqueous solutions with evolution of gaseous hydrogen is well known in aquo complexes of the transition metals in their lower states of oxidation (see Table 3).

The quantum yield of hydrogen in these reactions can be quite high: for example, a yield of 80% has been observed[255] for $Cu^+(aq)$. This suggests that both steps of the process have a high efficiency: the charge separation in the primary photochemical reaction and the evolution of H_2 in the subsequent dark reactions†. The effectiveness of charge separation is determined by the quantum yield of the formation of K^+ and $\dot{H}$ in the primary photochemical act:

$$K + H^+ \xrightarrow{h\nu} K^+ + \dot{H} ,$$

and by the relative rates of the different reactions which consume $\dot{H}$ particles:

$$\dot{H} + \dot{H} \rightarrow H_2\uparrow \quad (8)$$

$$K^+ + \dot{H} \rightarrow K + H^+ \quad (9)$$

$$4K^+ + 2H_2O \rightarrow 4K + O_2\uparrow + 4H^+ . \quad (10)$$

Table 3. Compounds which evolve hydrogen from aqueous solutions in the light.

Initial compound (K)	E_m (K/K+), V	Highest quantum yield of H_2, %* (λ of radiation, nm)	Red edge of charge transfer band**, nm	References
Co^{2+} (aq)	+1.82	>0***	220	202,249,250
Ce^{3+} (aq)	+1.61	0.14 (254)	350	202,236,249—254
Mn^{2+} (aq)	+1.51	>0***	225	99,202,249,250
Fe^{2+} (aq)	+0.77	15 (254)	285	202,236,249,250,287
$Fe(CN)_6^{4-}$	+0.36	<66 (254)	300	249
Cu^+ (aq)	+0.15	80 (275)	>313	249,250,253—255
Ti^{3+} (aq)	+0.1	<1(290)	>290	253,254
V^{2+} (aq)	−0.26	15 (313)	350	202,249,250,253,254
Ti^{2+} (aq)	−0.37	>0	330	249,250
Cr^{2+} (aq)	−0.41	30 (254)	380	236,249,250,253,254
Eu^{2+} (aq)	−0.43	14 (365)	366	202,249,250,253,254, 256,257
U^{3+} (aq)	−0.61	>0	400	202,249,250
Ni^{2+} (aq)	—	0***	220	202,249,250
$Mo_2(SO_4)_2^{4-}$	—	17 (254)	—	258,259

* Depends on the nature of the counter-ion and on the pH of the medium.
** Depends on the nature of the counter-ion.
*** Only the photo-oxidation of K was reported.

The probability of formation of radicals from electronically excited states of molecules cannot yet be predicted theoretically. Therefore photo-catalysts offering a high quantum yield can be chosen only empirically at present.

As regards the relative rates of the subsequent reactions of the free radicals, that for scheme 1 should favour the formation of useful final products. For example, in the case of oxidation (which we are considering) the rate constant of reaction (8) ($\sim 10^{10}$ litre mole^{-1} s^{-1})[279] is usually not less than, and often significantly greater than, the rate constant of reaction (9),[227] and the H radicals formed under the influence of light will be evolved from the solution as gaseous hydrogen in high yield and without the need for a catalyst as long as accumulation of the oxidised form of the dye (K^+) is avoided.

† We should note that direct experimental proof of the formation of $\dot{H}$ (or $\dot{O}H$) free radicals is not available for all the systems listed in Tables 3 and 4. Hence (in some cases at least) the reaction may follow scheme 2 rather than scheme 1.

In the photo-catalytic decomposition of water under static conditions accumulation of K^+ is unavoidable, because of the slowness of reaction (10), even if an active catalyst is used to accelerate the multi-electron process. Therefore the practical realisation of scheme 1 implies the use of flow conditions, arranged so that the evolution of O_2 (or H_2) in the light and the complementary evolution of H_2 (or O_2) in the dark take place in different parts of the apparatus [for example, by pumping the solution enriched in the K^+ (or K^-) form through a reactor containing a catalyst for the evolution of O_2 (or H_2)].

Table 4. Compounds which evolve oxygen (or $\dot{O}H$) from aqueous solutions in the light.

Initial compound (K)	E_m (K−/K), V	Highest quantum yield of O_2 (or $\dot{O}H$), %* (λ of radiation, nm)	Red edge of charge transfer band**, nm	Refs.
Ce^{4+} (aq)	+1.61	36 (254)	400	202, 236, 252
Mn^{3+} (aq)	+1.51	>0 (400)	470	261
Fe (bipy)$_3^{3+}$	+1.1	0.8 (365)	700	236, 260
Fe (phen)$_3^{3+}$	+1.1	1 (365)	700	236, 260
Ag^+ (aq)	+0.799	3.2 (254)	260	262
Fe^{3+} (aq)	+0.77	19 (313)	365	202, 236, 248, 250, 263—265
$Mo(CN)_8^{3-}$	+0.73	>10 (365)	—	236, 260
$W(CN)_8^{3-}$	+0.457	>10 (366)	—	236
UO_2^{2+}	+0.05	>0	—	268, 269
Pb^{2+} (aq)	—	>0	320	262
V^{3+} (aq)	−0.255	>0***	—	270—273
Eu^{3+} (aq)	−0.43	>0 (190)	—	257, 274
Methyl Viologen (MV^{2+})	−0.44	1 (254)	—	275, 276
U^{4+} (aq)	−0.61	>0	300	202, 236
Quinones	+0.4÷+0.8	>10 (313)	—	266, 267
1,10-phenanthroline (phen)	—	0.01 (300)	—	277

* Depends on the nature of the counter-ion and on the pH of the medium.
** Depends on the nature of the counter-ion.
*** Only the photo-reduction of K was reported.

Of the systems listed in Table 3 the following aquo-complexes have a redox potential E_m high enough to complete the water decomposition cycle: Ce^{4+}(aq), Co^{3+}(aq), and Mn^{3+}(aq), the oxidised forms of Ce^{3+}(aq), Co^{2+}(aq), and Mn^{2+}(aq). For the Ce^3(aq)−Ce^{4+}(aq) system the photo-catalytic decomposition of water was observed and fully investigated[251,252] in the 1950's. It was shown that water is decomposed under the influence of u.v. light and in low yield, but we should note that the low quantum yield may have been due to the failure to use flow conditions in those experiments.

Methods of completing the cycle have been suggested even for systems in which the oxidised form K^+ is thermodynamically unable to evolve oxygen from water under normal conditions (for example, for the Cu^+(aq)−Cu^{2+}(aq) system[254]). Thus the E_m value of the K/K^+ couple can be increased by changing the temperature in the dark part of the apparatus. For aquo-complexes, say, the large (up to 20–40 e.u.) difference in entropy between the oxidised and the original form causes a shift in the equilibrium towards the evolution of oxygen upon heating.

In principle the oxidation photo-catalyst could also be a compound which yields a hydrated electron under illumination, since in acid solutions this species is immediately converted into the $\dot{H}$ radical[236,249,260,280]:

$$H_3O^+ + e^-(aq) \rightarrow \dot{H} + H_2O .$$

However, because of the large reduction potential ($E^0 = -2.7$ V), the energy losses in processes involving $e^-(aq)$ can be expected to be even greater than those of processes involving radicals. There is a report[281] of the production of hydrated electrons by green light (as opposed to u.v. light) in micellar heterophase systems. Of course, under these conditions the ORP of K^+ is not high enough to evolve O_2 from water, but it may be high enough in a photo-excited state of K^+. Thus the scheme could be realised in practice only for the decomposition of water by an eight-quantum mechanism.

Photo-reduction (the evolution of oxygen or ȮH radicals by light) has been observed in aqueous solutions of some transition-metal complexes in a higher state of oxidation as well as in some organic compounds (see Table 4). In this case the evolution of oxygen is the fast step as a result of the high chemical activity of the ȮH radicals[279]:

$$2\dot{O}H \rightarrow H_2O_2,\ 2H_2O_2 \rightarrow 2H_2O + O_2\uparrow .$$

As regards completing the cycle of the water decomposition process the most promising systems are UO_2^{2+}–UO_2^+, $U^{4+}(aq)$–$U^{3+}(aq)$, and MV^{2+}–MV^{+}, according to the E_m values in Table 4, but the photo-catalytic decomposition of water has not so far been observed in these systems (though ȮH radicals have been detected in the UO_2^{2+} and MV^{2+} systems).

It is generally thought that the generation of free radicals in an aqueous solution must necessarily imply the use of u.v. radiation, with a disastrous effect on the efficiency of the solar energy conversion. In fact, the ȮH radical can be formed in an acid solution (pH = 0) at room temperature and for a zero value of E_m of the K/K^- couple by a quantum of $\lambda = 442$ nm (blue light), with an efficiency of $\eta \cong 5\%$, and furthermore the same radical can be formed in an alkaline solution (pH = 14) by a quantum of $\lambda = 612$ nm (orange light) with a very adequate conversion efficiency ($\eta \cong 20\%$, see Fig. 6). Of course, in order to complete the cycle of water decomposition reactions in this solution at room temperature we have to use light with $\lambda \leq 442$ nm, since a reducing agent with $E_m < -0.828$ V is needed for the evolution of hydrogen in alkaline solutions.

The formation of Ḣ in acid solution (pH = 0) is also possible in light of reasonably long wave length ($\lambda = 558$ nm), but it is again impossible to complete the cycle at constant temperature without using u.v. light, because an oxidising agent with $E_m > +1.23$ V has to be generated in addition to the Ḣ radicals, and light with $\lambda = 371$ nm is required for this.

Nevertheless the decomposition of water by this mechanism under the influence of light of reasonably long wave length is possible in principle if the H_2 and O_2 evolution steps are separated. This can be attempted in two ways: by arranging for the H_2 and O_2 evolutions to occur at different pH, or at the same pH but different temperatures. The latter approach is the more attractive because it does not require unrecoverable additions of acids and alkalis. The rise in temperature of the solution needed to shift the equilibrium in the required direction could be obtained by exploiting the photochemically inactive long-wave quanta of the solar spectrum, thus raising the efficiency of the overall conversion. We also note that the lower energy losses expected from the relative simplicity of scheme 1 should compensate (at least partially) for the loss in efficiency associated with the irreversible conversion into heat of some of the energy of the Ḣ and ȮH radicals.

Thus the main problem to be overcome before scheme 1 can be used in practice is to find photochemically active dyes with charge transfer bands at sufficiently long wave lengths. All the compounds examined so far, listed in Tables 3 and 4, have this band in the u.v. region of the spectrum. It may be necessary to sensitise the evolution of H_2 and O_2 by adding to the solution an auxiliary dye which absorbs strongly in the visible region and can transfer this absorbed radiant energy to the chemically active excited levels of the photo-catalyst.

b) Photo-catalytic Decomposition of Water by Scheme 2

As we have already pointed out, the effectiveness of the utilisation of the solar spectrum could be substantially increased by arranging for the Ḣ and ȮH radicals produced in the primary photochemical act to be in the coordinated or adsorbed state (as opposed to the free state). The absence of free radicals would also make it easier to use organic photo-catalysts (as compared with scheme 1).

Complexes of the active intermediates of the decomposition of water with transition-metal compounds in excited states have recently been detected experimentally. These include hydroxylated chromium(III) complexes in an electronically excited state[282] and protonated complexes of the aquo uranyl ion (UO_2H^{2+}),[283,284] bipyridyl ruthenium(II) complexes[285,286], and binuclear molybdenum complexes[259].

Kinetic data on the photochemical evolution of hydrogen from acid aqueous solutions of the aquo complexes $Eu^{2+}(aq)$[253–255] are consistent with the hypothesis that the active role in this process is played by complexes of the metal with free radicals:

$$\begin{gathered} Eu^{2+}(aq) + H_2O \xrightarrow{h\nu} [EuOH \cdot H]^{2+} \\ [EuOH \cdot OH]^{2+} + H^+ + Eu^{2+}(aq) \rightarrow EuOH^{2+} + Eu^{3+}(aq) + H_2\uparrow . \end{gathered} \qquad (11)$$

A similar scheme applies to the photochemical evolution of hydrogen from acid solutions of the $Fe^{2+}(aq)$ aquo complex[287]. Detailed studies of acidity changes in organic dyes during electronic excitation are also in progress[277,288–290].

Existing experimental data are insufficient for a meaningful discussion of the application of scheme 2 to homogeneous reactions. We shall only point out that hydrogen evolution from a protonated excited state

$$K^* + H^+ \rightarrow KH^+$$

requires the collision of these protonated forms either in pairs

$$2KH^+ \rightarrow 2K^+ + H_2\uparrow$$

or with a strong reducing agent [e.g. as in reaction (11)], or alternatively it requires further protonation in a secondary excitation:

$$KH^+ + H^+ \xrightarrow{h\nu} KH_2^{3+} \rightarrow K^{3+} + H_2\uparrow .$$

In the first case the effectiveness of the process may be raised by adding a dehydrogenation catalyst, and in the second by choosing a compound in which the protonated excited forms are long-lived.

The most promising media for the realisation of scheme 2 may be heterogeneous systems, especially supported catalysts and zeolites containing adsorbed, attached, or interstitial dye molecules (organic or inorganic). The affinity of Ḣ and ȮH radicals for adsorption on these heterogeneous surfaces should favour the charge separation in the primary photochemical act and the subsequent recombination of the adsorbed radicals with evolution of H_2 and O_2 (as in catalytic electrodes during electrolysis).

The formation of ȮH radicals in the adsorbed state during irradiation with visible or near-u.v. light has been observed in suspensions of ZnO, TiO_2, and V_2O_5 in water[118,291], and in Aerosil containing adsorbed Methyl Viologen bi-cations[276]. Hydrogen evolution by illumination of freshly precipitated iron(II) hydroxide has also been reported[292], but the mechanism of this process was not studied in detail.

Some recent papers describe the decomposition of water under the influence of solar radiation in the presence of silver-substituted type Y and A zeolites[208,293,294]. The following reaction is assumed to take place with a high quantum yield:

$$2Ag^+ + 2ZO^- + H_2O \xrightarrow{h\nu} 2Ag^0 + 2ZOH + {}^1/_2O_2\uparrow .$$

The water decomposition cycle is completed in the dark by heating the system to 600 °C. Clusters are thought to be formed in the zeolite under these conditions, and these clusters are assumed to have an enhanced reducing power:

$$2Ag_n^0 + 2n\ ZOH \xrightarrow{T} 2n\ Ag^+ + 2nZO^- + n\ H_2\uparrow .$$

The main advantage of this type of scheme is the ease with which the final products (H_2 and O_2) can be separated. Furthermore these catalysts can be operated over a much wider range of temperature than homogeneous catalysts.

By replacing the silver by a metal with a greater reducing power in its lower state of oxidation it may be possible to avoid the need for a high temperature during the dark step. Auxiliary dyes may also be added to the zeolite to improve the sensitivity to long-wavelength light.

Another possibility is the photo-catalytic decomposition of water on metal-containing zeolites without the participation of electronically excited states. As in aqueous solutions, the entropy of interstitial transition-metal ions in zeolites is very sensitive to the degree of oxidation of the ions. Therefore a change in temperature will strongly affect the redox properties of the ions, and this should allow the decomposition of water by cyclic changes in the temperature of the catalyst (for example, using concentrated solar radiation). There is evidence[295] that such a cyclic process would be thermodynamically possible in zeolites containing Cr^{3+}, In^{3+}, or Cu^{2+} ions.

Table 5. Systems which evolve hydrogen by scheme 3.

No.	Dye (K)	Acceptor (A)	Donor (D)	Catalyst	Refs.
1	Proflavin; Acridine Orange	MV^{2+}	ethylenediamine-tetra-acetic acid (EDTA)	hydrogenase	296
2	Methylene Blue, acridine	cytochrome → acridine → MV^{2+}*	Fe^{2+}(aq), allyl-thiourea, isopropanol, ethanol, toluene, ascorbic acid, EDTA	not stated	297
3	Acridine Yellow, tripaflavin	salicylato complexes of V(III) and Eu(III)	cysteine, triethanol-amine, EDTA, H_2S	PtO_2, colloidal Pt	298
4	Acridine Yellow	MV^{2+}	EDTA	Pt	298
5	Benzophenone	V^{3+}(aq), Cr^{3+}(aq), Eu^{3+}(aq)	ethanol, isopropanol	PtO_2	299
6	Immobilised chloroplast	MV^{2+}	glycerol, H_2O	hydrogenase, metallic Pt	224
7	Immobilised chloroplast	immobilised ferredoxin	H_2O	hydrogenase	300
8	$Ru(bipy)_3^{2+}$	MV^{2+}	EDTA	hydrogenase	296
9	$Ru(bipy)_3^{2+}$	$Rh(bipy)_2Cl_2^+$	triethanolamine	collodial Pt	301

* A chain of acceptor was used.
** The scheme proposed for completing the cycle involves O_2 evolution by heating the system with Fe^{3+} to 50–350 °C.

In principle scheme 2 can offer the maximum efficiency for the conversion of solar energy. Therefore further work on these problems is of the utmost importance.

c) Photo-catalytic Decomposition of Water by Scheme 3

In spite of the simplicity of schemes 1 and 2, most of the research now in progress is devoted to scheme 3, in which the primary photochemical act does not decompose the water but produces strong one-electron oxidising (D^+) and reducing agents (A^-) simultaneously, able to evolve oxygen and hydrogen from water in the absence of light. The interest in this scheme is not fortuitous: it stems from its similarity to natural photosynthesis.

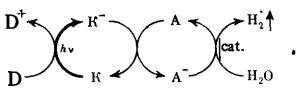
The main difficulty in the practical implementation of scheme 3 is that the complex multi-electron processes leading to the evolution of oxygen and hydrogen from water by the D^+ and A^- species have to compete with the recombination of D^+ and A^-. Therefore the reduction to practice of scheme 3 is possible only if an adequate method of charge separation is available.

Many photo-catalytic systems able to evolve hydrogen from water with a good quantum yield are known (see Table 5). However, in every case the electron donor is not water but a special reducing agent which is consumed irreversibly. Photo-catalytic systems for the evolution of oxygen from water have also been described: chlorophyll and coproporphyrin of iron(III) adsorbed at an octane–water interface[302] or on a vesicle membrane[303]. But in this case the electron acceptor is not water but $Fe(CN)_6^{3-}$, which is again consumed irreversibly. Thus it has not yet been possible to complete the water decomposition cycle without using structures of biological origin#.

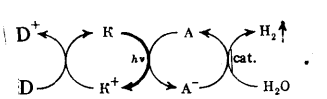
All the systems listed in Table 5 attempt to model the photosynthetic system of bacteria and the "photo-system I" of plant photosynthesis, which synthesises reduced forms of carbon from CO_2 by using good electron donors[189–192].

We note that in system No. 3 of Table 5 (as in the photosynthesis of sulphur bacteria) the electron donor is hydrogen sulphide (an analogue of water, but with more marked reducing properties), which can be oxidised fully by the transfer of only two (as opposed to four) electrons.

The choice of an appropriate photo-catalyst is of the utmost importance for the decomposition of water by scheme 3. Thus, in systems Nos. 1–5 of Table 5 (using benzophenone and organic dyes of the xanthene, acridine, and fluorescein type as the photo-catalyst, i.e. compounds with a fairly high oxidation potential in their initial state) the reaction takes place by the "reduction mechanism"§



However, even the excited form of the photo-catalyst could not bring about the oxidation of water. In systems Nos. 6–9 of Table 5 [for which the photo-catalysts are chloroplasts immobilised in micelles, or the *tris*-bipyridyl complex of ruthenium(II)] the reaction took place by the "oxidation mechanism":



A complete water decomposition cycle has been reported[304] for monolayers of the surface-active bipyridyl complex of ruthenium(II), but many attempts at repeating the experiment have proved unsuccessful[305–310].

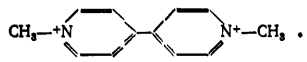
§ The double arrow denotes the instant when radiant energy is stored.

The range of compounds potentially suitable as photo-catalysts for the decomposition of water by scheme 3 is still very narrow. It includes chlorophyll and its nearest analogues, and also bipyridyl (and similar) complexes of ruthenium(II)[311-341], osmium(II)[311,312,320,342,343], and probably also iron(II)[344-347] and chromium(III)[330,348]. Thus the field is wide open for further research.

There are qualitative reports of the production of the very strong oxidising agents Co^{3+}(aq), Mn^{3+}(aq), Ce^{4+}(aq), and Ag^{2+}(aq) by the excited state of uranyl[349-351], and of the reduction of Zn^{2+}(aq) to Zn^0 by the excited state of Mn^{2+}(aq), which becomes oxidised to MnO_2.[352] If a charge separation process with an acceptable quantum yield were available these systems could be of interest as components of the photo-catalytic system.

Special mention is due of the *tris*-bipyridyl complexes of ruthenium, which are not decomposed under the action of light, are not hydrolysed, and offer a unique set of redox properties in their ground and their triplet excited state: as a result, they can take part in both the "oxidation" and the "reduction" mechanism of decomposition of water in solutions of practically any acidity. For the *tris*-bipyridyl complex of ruthenium(II) the following energy levels have been reported[333]: $E^- = -1.3$, $E^+ = +1.3$, $E_T^+ = +0.8$, and $E_T^- = -0.8$ V. The evolution of oxygen from water in the dark by the oxidised states of these[353] and of the corresponding iron complexes[354-358] is well characterised.

Fairly rigid limits are imposed on the intermediate donor D and acceptor A. For example, the E_m value of the acceptor must lie below the "hydrogen" line of Fig.7, but it must also be higher than the E_m value of the K^-/K couple (for the "reduction mechanism") or of the K/K^+ couple (for the "oxidation mechanism"). In the systems listed in Table 5 the intermediate acceptors which satisfy this condition are V(III) and Eu(III) complexes [for example, V^{3+}(aq) and Eu^{3+}(aq)], and also the bipyridyl complex of rhodium(III) and the organic bi-cation[359] Methyl Viologen (MV^{2+})



Reduced forms of all these acceptors in the presence of a catalyst can evolve hydrogen from water at the appropriate pH. Intermediate donors D for the oxidation of water are still unknown.

Let us consider possible ways of increasing the efficiency of charge separation in the primary photochemical reaction. The effective charge separation in natural chloroplasts (systems Nos.6 and 7 of Table 5) is evidently the result of their rigid structure. The molecules of chlorophyll and of the primary electron acceptor (still not definitely identified) are separated by a significant distance (>13 Å) in the chloroplast membranes[360]. Fast charge separation in this system (the process $Chl^* + A \rightarrow Chl^+ + A^-$) can only occur by a tunnel mechanism[360,361]. The reverse process (the tunnelling transfer of an electron from A^- to Chl^+) is much slower[360]. This may be due to the rapid conversion into heat of part of the energy stored in the Chl^+ and A^- particles (since changes in the energy of the system can disturb the conditions favourable to tunnelling transitions[361-363]), or alternatively it may be due to rapid conformational changes in the membrane produced by the forward reaction, which can increase the distance between the reactants[360,362,363].

By analogy with natural photosynthesis we can expect that a spatial separation of the photo-catalyst from the primary acceptor by ~10–20 Å (on a solid carrier surface, in a lipid membrane, or in a micellar solution) will improve the efficiency of charge separation in artificial systems also. Stabilisation of the charge separation by the "tunnel" principle can be attempted also in a homogeneous solution, for example by using rigid molecules within which charge transfer can occur (from one fragment to another) under the influence of light[364-381]. After charge separation of this type the molecule can behave bifunctionally, i.e. both as an oxidising agent and as a reducing agent.

It has been found experimentally that charge separation is assisted by fast chemical changes (for example, protonation or deprotonation) of the D^+, A^-, K^+, or K^- species. Thus fast protonation of the reduced form of the dye in reactions Nos.1–5 of Table 5 is the most probable explanation of the substantial decrease in the recombination rates of D^+ and K^-; furthermore, protonation leading to the formation of hydride complexes of rhodium may occur also in system No.9 of Table 5.

Effective chemical stabilisation of the separated charges by deprotonation of the phenothiazine cation radical has been observed[382] as a result of the interaction with the *tris*-bipyridyl complex of ruthenium(II) in an excited state.

Since chemical stabilisation requires a stabilisation rate greater than the recombination rate the only likely candidates are the fast stabilisation processes involving unimolecular decomposition, conformational transitions, or interactions with substances present in very high concentration (e.g. the solvent).

Stabilisation mechanisms other than the tunnel mechanism and the chemical mechanism discussed above may be considered. One of these consists in precipitating as a solid phase (or extracting from the aqueous solution) the product of the primary photochemical act (e.g. A^-). Thus the elemental sulphur produced by the oxidation of hydrogen sulphide in system No.3 of Table 5 is precipitated into a solid phase. Precipitation as a hydroxide may also be effective: for example, by varying the state of oxidation of metal aquo ion used in the cycle. Stabilisation of the separated charges by extraction was demonstrated in the 1960's for a system consisting of thionine (an organic dye) and the iron(II) aquo ion[383]: the same stabilisation mechanism was later applied to the thionine–thallium(I) aquo ion system[384].

However, phase transformations and extraction are relatively slow processes. Hence we may assume that an initial stabilisation is provided by chemical effects in every case (reconstruction of the solvation shells, dimerisation, etc.), followed at a later stage by the phase transformation.

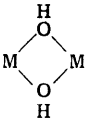
Yet another stabilisation method depends on using an electric field for charge separation, as in the semiconductor energy converters. In liquids, very high electric field gradients are easily obtained at the surface of colloidal particles (for example, the micelles of ionogenic surface-active particles, knots of polymer chains containing ions, etc.)[385,386]; high electric field gradients can exist also in zeolite holes[387]. Thus if singly charged cations are used as the initial forms of the photo-catalyst and of the electron acceptor, and if these cations are adsorbed on the surface of anionic micelles in the form of a Stern layer[385], the doubly charged cation of the photo-catalyst formed by the transfer of an electron under the influence of light will be adsorbed even more strongly in the Stern layer whereas the uncharged form of the acceptor will pass into the bulk of the solution. In this way charge stabilisation may be obtained as a result of the increase in the rate of reaction of the excited photo-catalyst with the acceptor produced by the increased local concentrations resulting from adsorption on the micelle (micellar catalysis)[388,389], combined with the decrease in the rate of recombination of the reaction products. This stabilisation mechanism was studied for a reaction in aqueous solutions containing an anionic surface-active compound or an ion-containing polymer[334,335]:

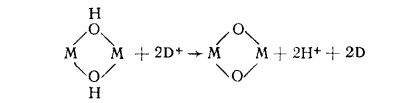
$$Ru(bipy)_3^{2+} + Cu^{2+}(aq) \xrightarrow{h\nu} Ru(bipy)_3^{3+} + Cu^{+}(aq) \cdot$$

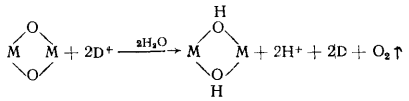
No fundamental difficulties can be foreseen in the evolution of hydrogen from a solution containing a strong one-electron reducing agent. Effective catalysts for this process are known: for example, finely divided or colloidal platinum, or the enzymes nitrogenase and hydrogenase (see Table 5). Of course, the main problem is to choose the most effective and stable catalyst for the specific experimental conditions.

More serious difficulties are found in the oxygen evolution step. In the absence of a catalyst this step proceeds very slowly if at all, even if very strong oxidising agents such as $Ce^{4+}(aq)$ or PbO_2 are present. On metallic catalysts (such as platinum) the reaction takes place only if the oxidation potential is raised well above the thermodynamic minimum value[242]: this is true even in the presence of an oxidising agent as strong as $Ru(bipy)_3^{3+}$. Heterogeneous catalysts of the PtO_2, IrO_2, and RuO_2 type are also not very effective towards the oxidation of water by Ce^{4+} and $Ru(bipy)_3^{3+}$ ions: in this case quantitative evolution of oxygen in acid solutions is observed only after several hours[390,391].

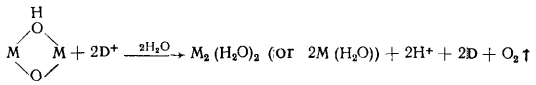
There are reports that the O_2 evolution catalyst in plant photosynthesis systems includes polynuclear manganese and copper complexes[1,13,392], but neither their composition nor their structure has yet been determined. Homogeneous O_2 evolution catalysts were unknown until quite recently. Thus the development of catalysts for the evolution of oxygen from water under mild conditions is the most difficult of the problems which must be solved before photo-catalytic converters relying on scheme 3 can be used in practice.

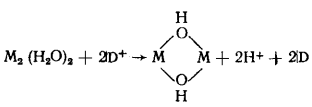
The writers have recently developed effective homogeneous catalysts for the evolution of oxygen from water by one-electron oxidising agents (D^+) of the $Ru(bipy)_3^{3+}$ type[393]. The mechanism of the action of these catalysts is still being investigated, but there is evidence of a catalytically active intermediate with the binuclear μ-dihydroxo  structure (where M is a metal atom), so that the evolution of oxygen and the regeneration of the intermediate occur by successive one-electron oxidations. For example, the catalytic action of partially hydrolysed bipyridyl complexes of iron(III)[296] could be described by one of the following schemes:





or





so that the overall equation is

$$4D^+ + 2H_2O \xrightarrow{cat} 4H^+ + 4D + O_2\uparrow$$

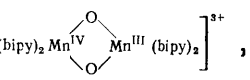
[where M = Fe(III), and $D^+ = Ru(bipy)_3^{3+}$, $Fe(bipy)_3^{3+}$, or $Fe(phen)_3^{3+}$].

We have also observed[393] catalytic effects in some compounds of Co(II) (see also Ref. 394), Cu(II), Ni(II), Mn(II), Ir(III), and Ru(III). Especially interesting catalytic effects were found[393] in the water-soluble cobalt(II) phthalocyanines: we should note that the cobalt(II) and iron(III) phthalocyanines are now considered to be the most effective catalysts for the cathodic (electrolytic) reduction of oxygen in aqueous solutions (i.e. for the reverse of the oxygen evolution reaction)[395].

The evolution of oxygen from water should be favoured by alkaline conditions (see Fig. 7), and therefore the search for photo-catalytic systems operating in alkaline solutions is of interest. Data on the photochemical oxidation of water by iron[292,263,265] or cerium[252] hydroxides are relevant in this context. We note that the ability of hydroxo complexes to form polynuclear structures may be an important factor in the development of multi-electron processes for the decomposition of water.

The mechanism of oxygen evolution from water by oxidising agents (such as MnO_4^- [358,396,397]) stronger than $Ru(bipy)_3^{3+}$ is currently being studied, and so is the mechanism of the electro-catalytic oxidation of water[394,398].

The work on the intermediate steps of the decomposition of water has generated a great deal of interest in the photochemical reduction of binuclear complexes of the type of[56,204,399,400]



as well as in the light-induced generation of hydrogen from solutions of hydride complexes such as[204,401-403]

$$\text{iso-Co(phen)}(PR_3)_2H_2^+ \xrightarrow{h\nu} \text{Co(phen)}(PR_3)_2^+ + H_2\uparrow$$

$$2HIr(PF_3)_4 \xrightarrow{h\nu} (PF_3)_4Ir{-}Ir(PF_3)_4 + H_2\uparrow$$

$$[Rh_2(AA)_4HJCl^{2+} + H^+(aq) + Cl^- \xrightarrow{h\nu} [Rh_2(AA)_4Cl_2]^{2+} + H_2\uparrow$$

$$[Mo(\eta^5\text{-}C_5H_5)_2H_2] \xrightarrow{h\nu} [Mo(\eta^5\text{-}C_5H_5)_2] + H_2\uparrow$$

(where phen = 1,10-o-phenanthroline, and AA = 1,3-diisocyanopropane), and also in the reaction[258,259]

$$Mo_2(SO_4)_2^{4-} + H^+(aq) \xrightarrow{h\nu} Mo_2(SO_4)_2^{3-} + {}^1/_2H_2\uparrow.$$

The binuclear complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ has also been found[404] to evolve hydrogen from potential donors under the influence of light.

The semiconductor photo-catalysts discussed in Section II (e.g. TiO_2) can also be classified with the converters operating by scheme 3.

The main distinguishing feature of semiconductor converters (as opposed to molecular converters) is the primary charge separation by electronic transitions between the collective levels (bands) of the solid under the influence of light, as opposed to transition between levels in individual molecules. With this exception, however, the mode of action of semiconductor converters is not very different from that of molecular converters. Thus the electron and the hole formed by the charge separation in semiconductors contribute to the decomposition of water in exactly the same way as the A^- and D^+ particles formed in molecular systems.

The spatial separation of the electron and hole is assisted by the internal electric field in the surface layer of the semiconductor (i.e. in the region where the light is absorbed). As was stated above, separation of the A^- and D^+ particles by an electric field is one method of stabilisation in molecular converters. The electrons and holes which have failed to recombine diffuse to the electrode surface where (as in molecular systems) they can take part in catalytic reactions leading to the reduction of water with hydrogen evolution

(in the case of the electron) or to the oxidation of water with oxygen evolution (in the case of the hole).

The main shortcomings of the present semiconductor photo-catalysts (see Section II) are their low photosensitivity in the visible region, and also inadequate charge separation in the surface field and low catalytic activity towards the later steps (oxygen and hydrogen evolution). In order to suppress the recombination of electrons and holes, and to impose on them an oxidation–reduction potential sufficient to decompose water at an acceptable rate, additional potentials must be applied from an external voltage source to the semiconductors in existing systems.

These shortcomings may be overcome by the use of semiconductors with a narrower (1–1.5 eV) energy gap and by doping their surface layer (see Section II). The addition of electron donor or acceptor species to the surface layer may generate stronger electric fields and thus allow effective charge separation without resorting to an external source of potential. Sensitisation by adsorbed or "grafted" dye molecules could produce sensitivity to visible light even in wide-gap semiconductors. Lastly, it may be possible to raise the catalytic activity of the semiconductor surface towards hydrogen and oxygen evolution by doping it with suitable impurities.

Thus there is no fundamental difference between the mechanisms of semiconductor and of molecular photo-catalytic converters, and current approaches to the development of molecular photo-catalysts may be expected to apply equally to the development of semiconductor photo-catalysts.

d) Photo-catalytic Decomposition of Water by Scheme 4

Very few data are available on the photo-catalytic decomposition of water by scheme 4. Nevertheless this scheme seems extremely promising. It was recently shown[219] that the following reaction can take place on illuminated single crystals of the semiconductors TiO_2 and $SrTiO_3$:

$$2H_2O\ (gas) + CO_2 \xrightarrow{h\nu} CH_4 + 2O_2 .$$

The first step of this reaction is believed to be the dark dissociative adsorption of water, followed by light-induced desorption of the products. There are also reports[405,406] of the photo-decomposition of gaseous water by visible light on the surface of another semiconductor (monocrystalline germanium).

The dissociative chemisorption of water on metal surfaces (e.g. Raney nickel[407], and possibly iron[408]) is well known. It is assisted by the high heats of adsorption of hydrogen and oxygen atoms on some metals. These results suggest at least the possibility of practical exploitation of scheme 4 on metallic catalysts in the future.

At the present stage of development in science and technology a substantial penetration of solar energy into the energy balance of mankind seems to be a soluble problem, deserving very serious study. At the moment the semiconductor (p–n junction) and thermal methods of solar energy conversion are nearest to large-scale practical application. Existing information on the mechanisms of catalytic and photochemical reactions confirm the reality (in principle) of photo-catalytic energy conversion (using both molecular and semiconductor systems), initially at least as applied to the photo-catalytic decomposition of water. Semiconductor photo-catalysts able to decompose water into hydrogen and oxygen are already known. Though their efficiency is still low, the way is clear to the achievement of higher efficiencies by varying the chemical composition of the surface layer and by using narrow-gap semiconductors. Another realistic (though difficult) goal is the development of molecular photo-catalytic systems for the conversion of solar energy: simpler analogues of the photosynthetic systems found in living organisms.

From the practical view-point—the development of energy converters offering the maximum possible efficiency—the most promising systems are those which do not depend on the formation of free radicals and atoms in the intermediate steps. Nevertheless we should not dismiss the systems in which radicals are formed in the free state. They are simpler, and therefore they may (at least initially) offer more favourable efficiencies than the more complex systems. Hence, elements developed on simple systems may in future find applications in more advanced types of converter.

Combined energy converters, in which visible light is used to induce photochemical changes and infrared light to heat the reactants in order to displace chemical equilibria in the desired direction, are a particularly imaginative development. The maximum theoretical efficiency of these converters must be greater than that of systems relying purely on quantum effects, since the Sun's light is more fully utilised in them.

The decomposition of water on molecular as well as on semiconductor photo-catalysts occurs in three steps: light-induced charge separation (to give a strong oxidising agent and a strong reducing agent), evolution of oxygen from the water by the strong oxidising agent, and evolution of hydrogen from the water by the strong reducing agent.

The main stumbling block on the way to the realisation of the first step is the fast recombination of the strong oxidising agent and the strong reducing agent, which uselessly converts the stored energy into heat. However, it may be assumed that means will be found to suppress this recombination by one of the methods of stabilising charge separation discussed above (based on tunnelling, chemical, phase separation, or electrostatic effects). Of the remaining two steps the evolution of oxygen is the more difficult to carry out in practice. Whereas effective catalysts for the evolution of hydrogen from water by strong reducing agents are already known, equally effective catalysts for oxygen evolution have not yet been reported. The search for these catalysts has become a problem of the greatest importance.

Work on the photo-catalytic conversion of solar energy began only recently, and is still in the research stage. This review has attempted to examine the essential aspects of the problem against the background of the general state of solar energy conversion, and to point out possible solutions. There is every reason to believe that the photo-catalytic method will lead to the development of systems for the conversion of solar energy into chemical fuel (hydrogen) energy with an acceptable efficiency. However, the problem is not an easy one, and its solution needs further extensive studies in the fields of catalysis, photochemistry, and photophysics.

Only the future can show which of the many theoretically possible methods of solar energy conversion will prove to be the most economical.

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