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PHOTOCHEMICAL PRODUCTION OF HYDROGEN FROM WATER

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ABSTRACT

The energy flux in sunlight is 40 000 kW per head of the world population. Theoretically much of this energy can be used to photolyze water, in presence of a sensitizer, to H_2 (and O_2) for a hydrogen economy. The main difficulty in a homogeneous medium is the back-reaction of the primary products. According to the "membrane principle", the reducing and the oxidizing primary products are released on opposite sides of asymmetric membranes, and so prevented from back-reacting. In essence, this is the mechanism of the photosynthetic machinery in plants and bacteria. This therefore serves as an example in the artificial construction of suitable asymmetric, "vectorial", membranes. Relatively small areas of photolytic collectors, e.g. in tropical deserts, could cover the energy needs of large populations through hydrogen.

INTRODUCTION

The bulk of the technical hydrogen now comes from limited, fossil, raw materials, namely, coal and oil. However, alternative processes are available or under development that are based on an unlimited raw material, water. On utilization in combustion this hydrogen returns to the form of water so that the cycle is closed. Water requires for the splitting into $H_2 + 0.5 O_2$ 56.7 kcal (237 kJ) in the liquid and 68.3 kcal (285 kJ) in the gas form per mole. This dissociation energy can come either from a limited, i.e., exhaustible, or from an inexhaustible, regenerative, source.

An old alternative process is electrolysis. This process is technically simple, but is bound to remain expensive. The conversion of heat, e.g. from nuclear reactors, into electric energy is burdened with the huge loss due to the Carnot factor, in practice hardly less than 60%. Moreover, the yield in technical electrolysis is far removed from the theoretical value.

A more recent group of processes is called "thermochemical". The energy source is always heat from nuclear reactors. More or less complicated cycles of reactions involving inorganic reactants in the end lead to the production of hydrogen. Many different cycles



have been proposed. Formally, the totality of the participating reactants can be considered as a catalytic system for water splitting. Again a Carnot factor cannot be avoided.

The process for the production of hydrogen from water to be discussed here is photochemical. The dissociation energy of 1 mole H_2O (237 kJ) equals the energy of 1 mole (einstein) of green light. Thus thermodynamically there is no obstacle to the "photolysis" of 1 mole H_2O by 1 quantum of green, blue or violet light, and with 2 quanta of yellow or red light the process could also be carried out. The photolysis of water may be possible at room, or similar, temperature and is altogether expected to be a clean, nonhazardous and convenient process. Because of the high temperature to be ascribed thermodynamically to sunlight, even to diffuse sunlight, the Carnot loss is not large. The existing or envisaged processes for the photolysis of water are biotic or abiotic.

The possible scope of water photolysis can be judged from the flux of light energy that comes, uninterruptedly, to the Earth: $1,7 \cdot 10^{14}$ kW, corresponding to 40 000 kW per head of the world population. Any light, whether direct or diffuse, is useful photochemically. While the light flux varies during the day and the year and also according to the weather, this is not a decisive drawback in a process where the product (primarily, hydrogen) is stored quite easily.

In a "solar hydrogen", in contrast to a "nuclear hydrogen", economy, no additional energy is introduced into the biosphere, and this is therefore not heated up. It is true that large-scale photochemical hydrogen factories might influence the local albedo, but this is a second-order effect, and measures can be taken against it.

HYDROGEN FROM PLANT PHOTOSYNTHESIS

In photosynthesis, the plants extract about 10^{11} tons of carbon per year from the air, twenty times more than is returned now to the air in the combustion of fossil fuels. Several authors have recently discussed the global effects of photosynthesis (1,2).

About 40 years ago it has been established by the genius from the Netherlands, the microbiologist C.B. van Niel (3), that the essence

of plant photosynthesis consists precisely in the splitting of water. The energy of visible light is captured by plant pigments and transferred to an enzyme system for the photolysis of H_2O . Now normally the hydrogen from the water does not appear as the gas, which would be from the standpoint of the plant be useless. The hydrogen - more precisely: its electron - rather serves, in some reactive form, for the reductive assimilation of the CO_2 . Van Niel's theory has superseded older hypotheses, according to which the action of light consists in the direct photochemical splitting of CO_2 .

It has later become known through the work of D.I. Arnon (4) that the primary reductant, which subsequently enters the dark reactions of photosynthesis, consists of the reduced form of ferredoxin, a well-defined iron-containing protein. The standard electrochemical redox potential of ferredoxin is about -0.4 volts and consequently coincides with the potential of the couple H_2/H_2O . Thus from a thermodynamical point of view the achievement of the plant in reducing ferredoxin is as great as if it had produced free hydrogen. The cycle of dark reactions has been elucidated by M. Calvin (5).

(In the analysis of the mechanisms of plant photosynthesis, comparison with the photosynthetic bacteria is of extraordinary value (1). These bacteria are the ancestors of the plants. Their most direct descendants among the plants are the blue-green algae, recently often called "blue bacteria". The photosynthetic machinery of the bacteria is simpler and less efficient than that of the plants, including the blue-green algae. This fact is expressed in the fundamental result established by H. Molisch that bacteria never release O_2 . They cannot break the bond between hydrogen and oxygen, and so they require "easier" source of hydrogen, e.g. H_2S . Indeed many photosynthetic bacteria are intolerant of oxygen and are strict anaerobes. Nevertheless, the broad features of bacterial photosynthesis are similar to those of plant photosynthesis.)

It has been found by H. Gaffron (6,7) that in certain artificial conditions plants do produce H_2 as a product of their photosynthesis. Larger amounts can be made by photosynthetic bacteria. The release of hydrogen is explained by the presence in such organisms of a hydrogenase. This enzyme transfers an electron, as soon as this has been lifted to a high negative potential by the energy of light, to

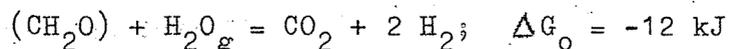


an ion of hydrogen. In the plants, the hydrogenase normally is latent, and therefore must be induced. The hydrogenase also is rather inefficient, and it is easily poisoned by oxygen, itself a product of photosynthesis. Therefore plants are unlikely ever to serve directly as a major source of hydrogen through photosynthesis (7).

To improve yields, components of plants have been combined with more strongly acting hydrogenases of bacterial origin (9). However, such hydrogenases are also oxygen-sensitive, and the hydrogen yields are still modest. Moreover, such systems must be carefully prepared from living organisms. They are expensive and deteriorate quickly.

ENERGY FARMING

Another approach to hydrogen production through biotic processes is "energy farming" (10,11). The biomass of productive plants, e.g., alfalfa, poplar trees or sugar cane, can be subjected to hydrogen fermentation. However, yields of hydrogen would not be high; methane fermentation gives more fuel. Practically complete conversion of biomass to hydrogen (plus CO₂) could be obtained by steam reforming, similar to the well-known process for the production of hydrogen on the basis of coal:



(CH₂O) indicates unit quantity of carbohydrate, the main component of biomass - not formaldehyde!

However, even assuming that this process were economical, the fundamental obstacle would remain that any possible farming area could better be used to make food, feedstuff or technical raw materials rather than hydrogen. This would apply also if blue-green or green algae, as many hope, could be grown economically in tanks or basins (12,13) so that no, or practically no, area would be diverted from ordinary agriculture. In this case, too, biomass would best be used otherwise. In the consideration of energy farming it must furthermore not be forgotten that high yields require heavy investment of fossil energy through fertilizers, pesticides and transport (14).

What remains of energy farming is the possibility to produce hydrogen (or methane) from waste like straw, corn cobs, sawdust, agricultural or town effluents (15). Important though such processes certainly are, no independent increase in output is possible. The amount of waste remains linked to agricultural or silvicultural production and to population size.

WATER PHOTOLYSIS WITH MEMBRANES

Single- and double-phase systems

One approach to direct water-splitting is to let light act on water or a single-phase aqueous solution (an abiotic system) in presence of a sensitizer, also known as a photocatalyst. The sensitizer would play the role of chlorophyll A in the plants. The energy of the light would be transferred to the water and used for its photolysis. Such single-phase systems have so far not been successful (16). Whenever hydrogen was observed, its concentration was stationary and small. Moreover, in most cases only UV light (typically, 254 nm) proved active. Such light does not occur naturally at ground level.

The basic difficulty in the experiments with the homogeneous aqueous solutions consists in the appearance, at close distances, of both reducing and oxidizing primary products. These "complementary" products may or may not be free radicals. The products rapidly meet by diffusion, back react with each other to water, and disappear ("geminate reaction"). This has also so far been the experience with solutions of complexes of transition metals, e.g. Fe or Ru (18). Such complexes are hoped to provide separate sites for subsequent reaction steps in photolysis.

In double-phase systems it is in principle possible to separate spatially the complementary primary products, and so to prevent, partly or wholly, their recombination and mutual annihilation. Systems with one liquid and one solid bulk phase have been studied (19). Often the solid is a semiconductor. In some cases an external potential was applied, and the energy of light was used only to supplement the electric energy invested (photoassisted electrolysis).

Here we shall rather concentrate on heteroabiotic systems consisting of two liquid phases ("compartments")(20). The phases obviously must



be separated by a more or less permanent membrane, consisting of solids and or liquids, which may contain the sensitizer and catalysts. The energy transducing machinery is distinguished by an asymmetric structure and is arranged in such a way that some of the primary products of photolysis appear in one liquid compartment, the other (complementary) products in the other liquid compartment. In this way, a "vectorial" rather than a "scalar" reaction takes place; the membrane can simply be called a "vectorial membrane".

The membrane principle

Vectorial membranes have never as yet been constructed by man in a planned way. But Nature has "learned" their construction and utilization soon after life arose, 3-4 gigayears (10^9 years) ago, although at first the membranes were not photosynthetic (1). No living cell exists now that does not make use of this "membrane principle", as it might be called. While the importance of membranes in bioenergetics has long been known, the contribution of P. Mitchell (21) should be singled out, who in his "chemiosmotic" theory gave a central role to asymmetric biomembranes.

Let it first be recalled that already the enzyme molecules, indispensable components of even the most ancient and primitive bacteria, carry out vectorial reactions. Each enzyme molecule has at least one reactive site, which accepts reactant(s) coming from some (not all) directions, and releases product(s) into some (not all) directions. However, with dissolved enzymes the vectoriality is obscured by the disorientation of the enzyme molecules within the solution. This applies, e.g. to the enzymes of lactic acid or alcoholic fermentation. One could speak of "microvectoriality". Vectoriality emerges more clearly as soon as enzyme molecules are positioned in an ordered way within permanent structures, i.e. in membranes ("macrovectoriality").

Presumably the first macrovectorial system in the evolution of organisms was that for "active transport". This is defined as the energy-driven transport across membranes, notably the membranes surrounding the cells. Such systems are more or less specific for particular substrates, and can transport them even against large

gradients of the electrochemical potential. This is defined as

$$\Delta \bar{\mu} = RT \ln(a_2/a_1) + nEF$$

where a_1 and a_2 are the activities inside and outside, n the charge of an ion (if it is an ion), E the electric potential difference, and F the faraday. For example, bacteria generally transport K ions actively inward, and H ions outward. Active transport is by definition endergonic, i.e. it requires free energy.

The most ancient bacteria are not photosynthetic, but derive their energy from fermentation processes. However, with the energy of sunlight the bacteria tapped later in evolution a tremendous, additional, source of energy. Experience shows that the photosystems of the bacteria (and also of higher organisms) are without exception contained exclusively within membranes. The asymmetry of the membranes that served and serves active transport has also been exploited to ensure the vectoriality of the primary processes in photosynthesis: the separation of the complementary products.

(The similarity of the working principles of photosynthesis in all organisms, bacteria and plants, and also the similarity of the chemical constituents of the photosystems leave hardly any doubt that all photosynthesizers are monophyletic, i.e. that in evolution photosynthesis arose only once. All later, and more efficient, photosynthetic organisms descended from earlier, and more primitive, photosynthetic organisms. Yet fairly recently one important exception has become known: *Halobacterium halobium* (22), a photosynthetic bacterium living in brines, has a qualitatively different kind of photosystem and apparently arose independently and fairly late (23). But this organism likewise carries its photosystem within the cell membrane.)

In the simplest plants, the "prokaryotic" blue-green algae, the photosynthetic, water-splitting, membranes are usually contained as a network within the protoplasm. In the higher ("eukaryotic") plants such networks are restricted to specialized, intracellular, "organelles", the chloroplasts. Otherwise the photosynthetic machineries in lower and higher plants are nearly identical. Now, how do these photosynthetic membranes ("thylakoid" membranes) work ?

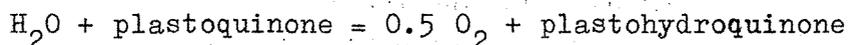


Two photosystems in succession

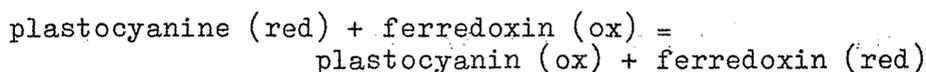
Before answering this question, an important feature of plant photosynthesis (24,25) must be mentioned. As pointed out, the synthesis of (CH_2O) from CO_2 and H_2O (by plants) requires far more energy than from CO_2 and H_2S (by bacteria). The figures are 112 and 12 kcal (480 and 50 kJ) per mole, respectively. To overcome the enormous endergonicity of water splitting, the plants are found to apply 2 light quanta for each reduction equivalent (electron) that is transferred from water to ferredoxin, and therefore, in physiological conditions, to CO_2 . According to the "Z scheme" put forward first by Hill and Bendall (26) each electron is lifted first (in "photosystem 2") by the energy of 1 quantum to a primary acceptor. Some non-photosynthetic ("dark", i.e., exergonic) steps follow, after which the electron is present within a different kind of molecule, and this molecule then serves as electron donor for "photosystem 1". As sensitizers, both systems contain chlorophyll A, but in different forms. Ferredoxin is reduced only through the action of photosystem 1.

An ordered sequence of 2 different, collaborating, photoreactions in different places is again an achievement of Nature that man has not yet equalled. Now what are the primary products, the two couples of complementary compounds, in the two subsequent photoreactions? Though the investigation of the photosynthetic machinery of the plants is still in flux, we already have broad knowledge of the primary (and also of the subsequent) reaction steps.

The first photostep in the plants leads to the reaction



and the second photostep to the reaction



In either case, the first-named product is formed at the inside of the thylakoid membrane. The reactions are here written down in a purely formal way, and transient, very short-lived, intermediates are not taken into account. Each of the two photosteps requires an energy per electron of about 77 kJ, corresponding to light of

about 1500 nm. For the release of each molecule of O_2 and for the concomitant reduction of each atom of carbon to the level of carbohydrate the lifting of 4 electrons is needed, each by 2 steps.

Photolysis with visible light

It has been said that the photolysis of water cannot be carried out with visible light because the primary step, the breaking of a O-H bond, needs too much energy: 460 kJ per mole, corresponding to 1 einstein of UV light (260 nm). This is wrong. In fact, Nature has demonstrated to us that light around 700 nm (more precisely: about 700 in photosystem 1, and 680 in photosystem 2) is sufficient, i.e. long-wave visible light. One reason is that Nature has avoided unduly strong endergonic steps, notably the uncompensated breaking of O-H bonds. Expressed in terms of energy per mole, the limiting energies for the two photosteps mentioned before are only near 170 kJ.

Indeed the energy balance in the natural system is even more favourable than has appeared so far. Ferredoxin (red) and O_2 are not the only products of electron flow from the first donor, H_2O , to the last acceptor, ferredoxin (ox). The electron flow is enzymatically coupled to the simultaneous endergonic synthesis of adenosine triphosphate (ATP) from its precursors adenosine diphosphate (ADP) and orthophosphate (27). The ATP is needed, along with ferredoxin (red), for the assimilation of the CO_2 . It also serves other essential purposes of the living cell.

(Photosynthetic bacteria can utilize light of even longer wave length, namely, infrared light. The mechanistic analysis, from the point of view of photochemistry, is most interesting, but cannot be undertaken here).

The energy yield in the overall process of plant photosynthesis can be estimated by comparing the light energy absorbed with the energy available in the back-conversion of the product into the starting materials, H_2O and CO_2 . In sufficient approximation, this is measured as the heat of combustion of the biomass. In optimum conditions with microscopic algae, the energy yield has the astonishingly high value of 33%. By optimum conditions is meant not only that the plants are



healthy and active, but also that light without excess energy is applied, i.e. red light. With larger quanta (short-wave light) the quantum yield remains the same, but part of the energy of each quantum is wasted.

Artificial photolytic membranes

The basic task in the artificial photolysis of water is, then, the construction of photoactive vectorial membranes that release the complementary products to opposite sides. These products may be H_2 and O_2 directly or at least products of the photoredox reaction that in subsequent dark steps give these gases. For instance one could think of reduced ferredoxin as an intermediate stage on the way to H_2 if a hydrogenase-active catalyst were present. Possibly such artificial vectorial membranes can be constructed ab initio on the basis of our knowledge of physical chemistry. Alternatively, we may learn from the plants and be "inspired" by them (28,29,30). For the purpose it is necessary not only to understand photosynthesis in depth, but its essential features must also be distinguished from these that have been dragged along from an evolutionary past. After all, the plants were not designed and optimized at a green table, but they could evolve only from their ancestors. This evolution needed advance in small steps, as is true for evolution in general.

"Structured systems" (20) have been built that contain micelles or microscopic vesicles. The insides are separate compartments. In a few cases, notably by Henglein and his colleagues (31,32,33), it has been observed that quantum yields in micellar systems may be far higher than in homogeneous solution. Obviously the spontaneously formed membranes are asymmetric and geminate recombination is, because of the compartmentation, inhibited. Work has also been started with "black" lipid bilayer membranes ("BLM")(34) and with monolayer assemblies (35). A further possibility are macroscopic synthetic systems. e.g. on the basis of polymer membranes. They may perhaps at the beginning be difficult to approach, but from a technical point of view such systems may in the end have the highest feasibility.

ESTIMATE OF TECHNICAL POSSIBILITIES

The ultimate goal is a massive contribution of water photolysis to a hydrogen economy. According to theory, the rate of hydrogen production would, within wide limits, be just proportional to light flux. The hydrogen would be collected at the rate made possible by sunshine at the given time and place, stored as a gas or in the form of organic fuels, e.g. methanol or hydrocarbons, and transported to the consumption centres.

Current estimates for mean light energy fluxes through all time are 110 watts/m² in England or Southern Sweden, 185 in the USA, and 250 in the Sahara, with 300 in a few ultra-hot places. These differences are not excessive, and as soon as photolysis works at all, it will have to be considered not only for hot, but also for temperate climates. Of course, few large contiguous areas are free in Europe or the USA, but even so such areas may be found, e.g. in Arizona. Moreover, decentralisation of the hydrogen factories would be an advantage from more than one point of view.

Nevertheless, the utilization of tropical deserts would be especially attractive. To paraphrase Kurt Mendelssohn, the Sahara is, by common consent, immensely large and immensely useless. Ocean water would feed the hydrogen factories; there is no obvious reason why salt water should not directly be used as a photolyte. Nor would the quantity be prohibitive. Be it mentioned that of the water consumed in the irrigation of plants 999 parts are lost by transpiration and only 1 part is used for photolysis.

While the light collecting areas will be provided best by developing countries, the know-how and the equipment will for a long time have to be supplied by the developed countries. Clearly socio-political problems will arise that ought to be studied in time, but problems there will be whatever the energy sources of the future! At some future time, photolytic hydrogen factories might also be built at sea.

For a rough estimate, we assume an energy flux, infrared included, of 250 watts/m², and an energy yield in the form of hydrogen of 10% of the theory. With these assumptions made, hydrogen energy is



obtained at a rate of 25 000 kW per km² (18 t H₂/day). With a consumption of 1 kW of thermal energy per head, as is typical of large parts of the world now, about 40 km² would be needed per million people. Even with 10 kW per head, about the present world record value, only 400 km² per million would be required. This is to be compared with the area of the Sahara of some 10 million km².

Here it has not been assumed that the radiation is concentrated (focussed) or that the photoactive, collecting, area is enclined towards the sun. Though in either way savings in photoactive area can be made, no total economy of area would be expected, and presumably investment per unit photoactive area would go up considerably.

It may be premature to guess the economics. However, we can approach the question from the back end. We allow a price of hydrogen, per unit calorific (joulific?) value, equal to that of crude oil, and capital service (interest and depreciation) of 10% per annum. No operating costs are taken into account, as they are entirely unknown, but probably relatively modest. On this basis, one would arrive at a break-even line with an investment of 20 million dollars/km², or 20 dollars/m², accessory equipment (piping, etc.) included.

In spite of the fact that the basis of these estimates may still appear optimistic, it will not be easy to come down to the break-even line given. But as the price of fossil fuel will undoubtedly go up steeply in the future, the break-even line must rise correspondingly. Moreover, for the comparison with hydrogen from thermochemical (nuclear) cycles, many, not only economic, factors will have to be taken into account.

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