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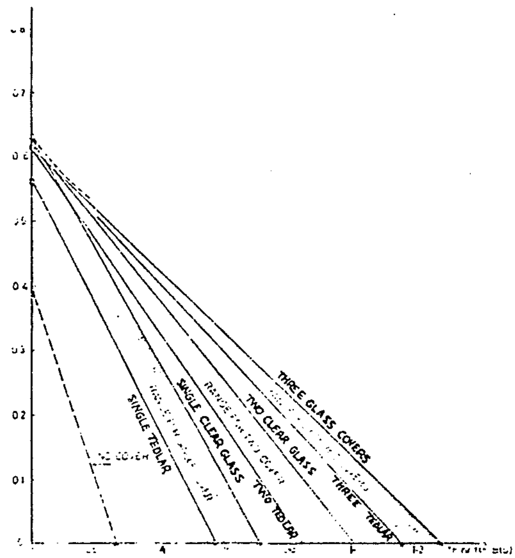

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The Utilization of Solar Energy by Way of Hydrogen Production.

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Summary. It is suggested to produce hydrogen gas by photolytic splitting of water, and to feed it into a hydrogen economy. One approach to obtain good yields in photolysis consists in the application of asymmetric membranes that release the different, reactive, primary products of the photochemical reaction on opposite sides of the membranes so that a back reaction is prevented. Through this solar-chemical option a very large part of the energy needs of mankind could be covered in the long run.

Solar energy flows to the Earth at the tremendous rate of 170 (European) billion kilowatts ($1{,}7 \cdot 10^{14}$ kw). This energy ~~amounts~~ corresponds to 40 000 kw per head of the world population and can be compared to a typical consumption of about 4 kw of primary energy in Europe. Thus a very small fraction of solar energy would be sufficient to cover all reasonable requirements of mankind.

For the utilization of the radiation three main options exist: solar-thermal, solar-electric and solar-chemical. The importance of the third option is generally not sufficiently appreciated, and in some of the official documents on solar energy it is not even mentioned. Yet this option may well, in the long run, turn out to be the most important of all. It uses diffuse as well as direct sunlight.

The object of the photochemical approach is the production of hydrogen gas through the photolysis of water. As in electrolysis, the energy is to be used for the splitting of water into its compounds H_2 and O_2. As soon as one has a sufficient amount of cheap hydrogen, one has, so-to-speak, everything. Hydrogen can be burned for residential and industrial heat, it can be used to make electricity through combustion engines or, better, through galvanic fuel cells, Hydrogen is a raw material for chemical industry, e.g. for the reduction of CO_2 to liquid fuels, hydrogen can place coal or coke as a metallurgical reductant, and hydrogen can even be fed to bacteria that serve as a source of protein.

Hydrogen has many pleasant qualities. It is easily stored and cheaply transported to pipelines. It is, given certain precautions, a non-polluting fuel, and there is no radioactivity. Solar hydrogen does not heat up the biosphere, as no additional source of energy is introduced. No CO_2 is added to the air. A hydrogen economy has already been studied by many authors in connection with nuclear energy, i.e. for hydrogen produced with heat from fission in "thermochemical cycles".

How can photolysis be done? According to simple physico-chemical data 57 kilocalories (240 kilojoules) per mole are needed for the overall decomposition of H_2O to $H_2 + 0{,}5\ O_2$. That amount of energy is contained in 1 mole (1 einstein) of quanta of green light. Thus from a thermodynamic point of view green light has enough energy for water splitting, and blue or violet light would be even better. In the case of yellow or red light, the energy of 2 quanta would have to be combined for each molecule of water.

It might therefore be expected that one could shine light on water or an aqueous solution and draw off a mixture of hydrogen and oxygen. Of course, the water, being transparent to visible light, would have to contain a suitable light-absorbing pigment. E. Rabinovitch, F.Daniels and others have tried this experiment, but unfortunately it never worked properly. Very quickly a stationary state was set up, in which the concentration of the hydrogen was exceedingly low. The reason is rather obvious. The primary products of photolysis are not really the stable molecules, but rather reactive entities, notably free radicals, including H and OH. In the homogeneous system used, these radicals are born at small distances from each other all over the volume. Therefore they meet rapidly, recombine and annihilate each other. In this back reaction, water is reformed, and the energy dissipated as heat.

Is, then, a technical photolysis of water an impossibility? Against this it must be emphasized that no law of nature is in the way of the process. In fact, Nature has demonstrated to us on a gigantic scale for a period of 3 gigayears (3 thousand million years) that the photolysis of water is a real possibility. In our time, about 100 milliard tons of carbon per year are extracted from the atmosphere through photosynthesis. Visible light of every wavelength is used by the plants. In optimum conditions in the laboratory energy yields of up to 30% are obtained, i.e. that percentage of the light energy absorbed is found as chemical energy of biomass, and is released on its combustion.

From a historical point of view it is interesting that the role of light as an energy source in photosynthesis was first postulated by nobody else but Julius Robert Mayer, the discoverer of the First Law of Thermodynamics, the law of conservation of energy. True, the need for light in photosynthesis had been found first by Ingen-Housz from the Netherlands in his experiments in 1779. But that pioneer did not explain the role of light. In fact, that role could not be defined before conservation of energy was established. It was Mayer who in 1845 wrote: "The plants take up a force, light, and produce a force: chemical difference." At that time the term "force" was used for what is now called "energy".

However, not every kind of energy is good enough. The Second Law of Thermodynamics shows that only energy poor in entropy can do work. It was Ludwig Boltzmann, who explained the Second Law in atomistic terms, and it was he who wrote in 1886: "The general struggle of the organisms for existence is not a struggle for the chemical elements, nor for energy, which is richly present in every body in the form of heat, unfortunately unchangeable. It is rather a struggle for entropy (more exactly: negentropy, E.B.) which becomes available through the transition of the energy from the hot Sun to the cold

Earth. To exploit that transition as far as possible, the plants spread out the immeasurable areas of their leaves and force solar energy in a way as yet unexplored to carry out chemical syntheses of which one has no inkling in our laboratories so far."

But do the plants really produce hydrogen? The layman may think that in photosynthesis CO_2 is split, and this was also the view of science until fairly recently. So thought Richard Willstätter, the great authority on photosynthesis, and so thought the great biochemist Otto Warburg to the end of his days. However, now the alternative theory of Cornelius Van Niel is generally accepted that the primary process in plant photosynthesis is the splitting of H_2O. Only secondarily the hydrogen produced is utilized for the reduction of CO_2 to biomass. Concomitantly, oxygen is released from the water, and this is practically the only source of the oxygen in the atmosphere.

But where is, then, the hydrogen? ~~Indeed,~~ Normally, plants do not set free hydrogen, although in particular, unphysiological, conditions Hans Gaffron has indeed demonstrated hydrogen production by plants. From the point of view of the plant a release of hydrogen gas would not make sense. The hydrogen would be lost. Instead, the plants use the electron of the hydrogen to make a strong reductant, which in a subsequent stage enables the reduction of CO_2 to biomass. The hydrogen ion (proton) of the hydrogen, which remains after the transfer of the electron, is given off as such.

The reductant in question is the reduced form of "ferredoxin". This is a well defined protein which also contains iron and sulphur in inorganic linkage, and was discovered less than two decades ago. This substance is now well characterized and can be crystallized, and even purchased. Ferredoxin in its reduced form, containing twovalent iron, is a rather strong reductant with a redox potential in standard conditions of -0,42 Volts. This standard potential happens to be the same as that of hydrogen gas in neutral solution. Thus the tendency of reduced ferredoxin to transfer an electron is just as great as that tendency of hydrogen. In other words, the thermodynamic achievement of the plants in making reduced ferredoxin is as great as if the plant had made hydrogen gas.

(In brackets it should be explained that Nature did not create plants with their tremendous photochemical capabilities in one step. Rome was not built in one day. Rather, the plants were preceded by photosynthetic ancestors, the purple and green bacteria, of which some species happily (for science) still exist. These more primitive creatures cannot yet split H_2O, but they must take their hydrogen from other source compounds where the hydrogen is more loosely bound, notably from H_2S or from certain organic substances. The far greater achievement of the plant has necessitated the construction of more complicated machinery, in which 2 light quanta in succession are used to promote each electron from water to ferredoxin. Incidentally, such ordered summation of several quanta to force a difficult photochemical process is another magnificent invention of Nature, and has never been carried out with an abiotic system by man in the laboratory or elsewhere.)

Considering that plants are so efficient, why do we not just use them for the production of technical fuels? Indeed, some eminent authors like Melvin Calvin argue for "energy farming", where fast-growing plants like poplars, alfalfa or sugar cane are fermented or otherwise transformed to give convenient liquid or gaseous fuels. The objection against energy farming consists in the scarcity of land. Wherever it is suited for agriculture, it will be used for the production of food or technical raw materials like fibres rather than that of fuel. Some other excellent authors have suggested the growing of unicellular algae in suspension for fuel, as in this case much land would be needed per unit biomass production rate. However, even algae, if they could be produced economically, would be employed as food rather than as a source of fuel. It appears that fuel should be made from biomass on the basis of farming or forestry wastes. Enormous amounts of such wastes exist and are indeed wasted now: corn cobs, straw, sawdust, etc. The economic utilization of such material has enormous importance. But this is a different matter from energy farming.

We have seen that the plants succeed in water photolysis. How do they do it? They likewise meet the difficulty of recombination of the primary products of photolysis in back reactions. To overcome this difficulty, already the photosynthetic bacteria made a momentous invention, and later they handed it over to their offspring, the plant cells. The bacteria developed the "membrane principle", i.e. photosynthetic membranes that produce complementary products on opposite sides. The reductant made from the substrate, say H_2O, comes out on one side, and the oxidant comes out on the other side of the membrane. In this way, the complementary (opposed) primary products do not meet, and no backreaction takes place.

Such membranes must clearly be asymmetric, so that the products "know" on which side they ought to come out. It may be said that such membranes are capable not only of "scalar", but also of "vectorial" reactions. Such asymmetric membranes may themselves be called vectorial membranes. No such membranes were ever constructed by man, but they are found, without exception, in every photosynthetic cell in the world. Consequently, the artificial construction of such membranes is one of the great challenges to science and technology in our time. It is not suggested here to use for this construction biogenic components, which will always be difficult and expensive to obtain, and will decompose easily. The idea is rather to learn from Nature how such asymmetric membranes might be constructed, and thereafter to build them up entirely from man-made, cheap and stable materials.

The solar-chemical option may well become important even to countries with temperate climates. But clearly the best conditions exist in the enormous, unused, hot deserts. A crude calculation shows that with an energy yield of 10% an area of the order of 100 km^2 would be sufficient to supply 1 million people with primary energy at the rate of 1 kW, typical of energy consumption in many parts of the world now. But the area of the Sahara alone is of the order of 10 million km^2. It is no objection against this idea that water is needed for photolysis and must be carried to the hydrogen factories. The amount is not prohibitive. This is illustrated by the fact that plants in irrigated fields dissipate about 99,9% of the water in transpiration, and utilize only the minute rest for photolysis.

The task of developing vectorial membranes will not be easy, and considerable work and time will be needed. However, in the case of nuclear energy 30 years passed between the fundamental discovery of nuclear fission and the completion of worth-while, large-scale, power stations. ~~and~~ Untold milliards of dollars were invested in the problem. In contrast, practically nothing was spent on solar energy until very recently, and of the tiny amounts that were spent only a tiny fraction went into photochemistry. For instance, in the USA as late as in 1973 only 4 million dollars were devoted by the Government on solar energy, while year after year amounts of the order of 500 million dollars went into nuclear research and development. The ratio has improved recently, but still far too little is being done for solar energy all over the world.

What is needed first, is first-class minds, i.e. excellent scientists to apply unorthodox thoughts to the problems of solar energy, including the photochemical option. First-class minds will come in only if they are provided with fine working conditions and a congenial environment. Yet such work will not be excessively expensive. In contrast, e.g., to the international nuclear and high energy research institutions like CERN, no precision machinery extending over kilometers, no advanced electronic equipment of giant dimensions, and no mammoth computers will be needed. However, international integration of solar research would be highly desirable to prevent dissipation of financial and human ressources. Moreover , first-class brainpower will be obtained most easily for an international crash programme.