

PHOTOCATALYTIC GENERATION OF HYDROGEN FROM WATER

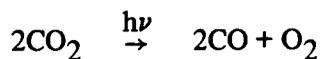
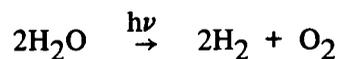
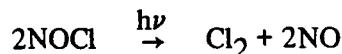
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INTRODUCTION

The dissociation of simple molecules provides a potentially efficient method of storing energy in a transportable form. Among the numerous chemical systems that have been proposed for energy conversion are the following:



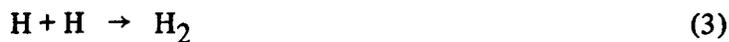
Hydrogen offers the advantages of being a clean burning fuel, easily stored in gas, liquid, or hydride form, and efficiently transferable. It may be used as a fuel for a variety of energy conversion processes including fuel cells and rocket engines as well as conventional heat engines. In conjunction with a water dissociation process, it holds forth the promise of providing a closed cycle, photon powered, energy system where photon energy may be efficiently stored for future use and converted to thermal or electrical energy on demand. In this paper we will discuss a new concept which is designed to overcome the problems encountered when using photodissociation for the generation of hydrogen.

Two fundamental problems limiting the efficiency of photodissociation of water are the separation of the photolysis products and the high energy photons necessary for the reaction. Although there has not been a great deal of work with metal-water systems, it has been shown that the dissociation energy of a large number of molecules is catalytically reduced when these molecules are in intimate contact with a surface of certain metals (ref. 1). The spontaneous dissociation of water has been demonstrated for Cu (ref. 2), Fe (ref. 3), and Ni (ref. 4) at room temperature in the dark. We suggest the possibility of engineering a surface which will take advantage of this catalytic shift in dissociation energies to reduce the photon energy required to produce hydrogen. This same catalytic surface can be used to separate the reaction products if it is made so that one of the dissociations products is soluble in the metal and others are not. This condition is met by many metal systems such as platinum group metals which have been used commercially (ref. 5) to separate hydrogen from other gases and liquids.

Chemistry

The generation of hydrogen by unassisted photolysis of water is an inefficient process. This inefficiency arises from the high photon energies required for direct photodissociation, the energy lost in secondary reactions, and rapid recombination of the products into water. The maximum quantum efficiency measured by Chen and Taylor (ref. 6) was 30 percent; however, that required photons in the 1650 Å range, intense illumination, and flowing water vapor. In a static system, the quantum yield was about 1 percent. Since the energy stored in each hydrogen molecule is equivalent to about 4000 Å, Chen and Taylor's overall efficiencies ranged from 0.4 percent to 12 percent. It is well to remember that there is no solar flux in the 1650 Å region, so such a system is not suitable for solar conversion.

The photodissociation of water to produce hydrogen and oxygen proceeds in the ultraviolet around 1650 Å mostly by the reactions



The energy required for the first step is equivalent to 180 kcal/mole if a single photon is absorbed or approximately 117 kcal/mole thermally. The difference is due to the Frank-Condon principle which requires that a photon be absorbed to a high energy state, followed by exothermic dissociation. The overall reaction

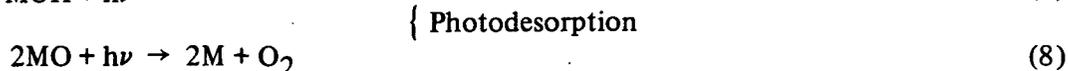
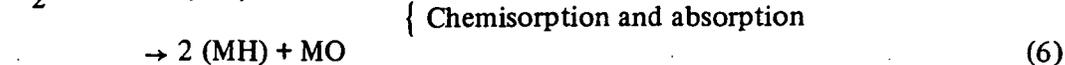


on the other hand, requires 68 kcal/mole because the recombination of the H and OH radicals is exothermic. If reaction (4) could be done in a single step with a photon, the photon wavelength would have to be 4000 Å or less. Water is not absorbing at this frequency, thus some intermediate reactions are necessary for efficient generation of hydrogen from water using visible light.

Numerous photocatalytic paths have been suggested including salt compounds, semiconductors, and dyes (ref. 4) to improve the efficiency of photolysis of water. Molecules adsorbed in surface complexes on metals are capable of multistep processes not possible in gas or liquid phase. The presence of the surface alters the molecular bonds, and the proximity of the molecules to each other and to the surface provides the possibility of intermediate reactions and lower activation energies for direct reactions.

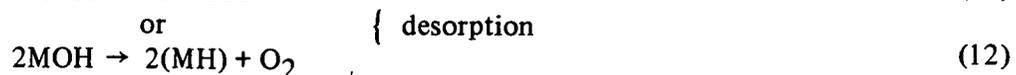
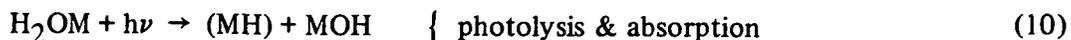
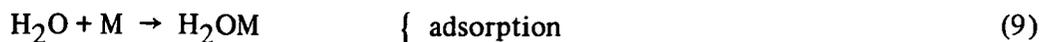
Depending on the chemisorptive activity, the dissociation process on a metal surface may be photoassisted in one of or a combination of the following ways. [(MH) denotes a metal hydride.]

1. Strongly Chemisorptive Case



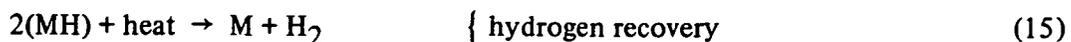
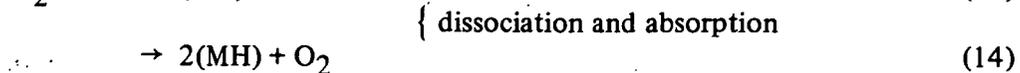
Contact with the water molecules causes the breakdown of the H_2O into absorbed hydrogen and strongly adsorbed OH or oxygen complexes. This behavior proceeds at room temperature and in the absence of illumination. The photoassisted step is therefore directed toward breaking the OH or oxygen complex bond with the surface, thus opening additional sites for continuation of the dissociative process.

2. Mildly Chemisorptive Case



The H_2O molecule is adsorbed onto the surface nondissociatively. Surfaces become saturated with adsorbed H_2O , and subsequent illumination breaks the H_2O molecule allowing the hydrogen to be absorbed into the metal or metal alloy and releasing the remaining dissociation products into the solution.

3. Strongly Hydrogen Absorptive Case



H_2O on the surface is dissociated; the hydrogen atom is strongly absorbed into the metal or metal alloy, and the oxygen and OH radicals either evolve into the solution or are weakly held onto the metal surface.

Final separation of the hydrogen from the hydride form may involve a physical separation of the metal hydride from the reaction region or diffusion through a film of metal and evolution from

the other side. Energy is added to remove the hydrogen from the metal or metal alloy. Since this is a bulk rather than surface effect, energy must be added as heat, rather than light, although the light may be converted to heat on the particle surface.

A more detailed look at the adsorption process in transition metals indicates that water molecules are adsorbed with the oxygen atom close to the surface (ref. 8). Probably one of the hydrogen atoms is also close to the surface and the other is free to move about. Adsorption energies are about 11 kcal/mole for copper and will probably be similar for other transition metals (ref. 9). A metal that forms a hydride will attract the hydrogen atoms into inner lattice bonds, and if the hydride is to be useful, the metal hydride bond must be of approximately the same strength as the H₂ bond. Thus the reaction



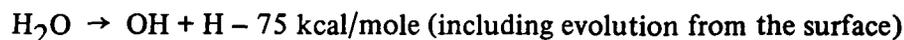
is in equilibrium or slightly exothermic.

A possible compound is LaNi₅, recently found to be a candidate for storage of hydrogen in hydride form (ref. 10). If we assume the surface behaves like Ni, then we may write

$$(\text{MH}) \cong 53 \text{ kcal/mole}$$

$$\text{M-O} \cong 58 \text{ kcal/mole}$$

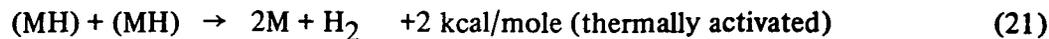
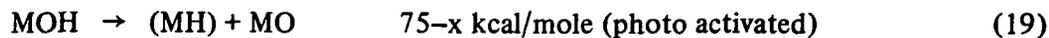
$$\text{H}_2\text{O-M} \cong 7 \text{ kcal/mole (to liquid state)}$$



These estimates arise from

1. The slightly exothermic nature of hydrogen absorbing in the metal.
2. The binding energy of NiO.
3. The adsorption energy of water vapor to copper, which is similar to that on nickel.

The reactions will be a combination of all three processes discussed previously.



The metal hydride to hydrogen evolution step is performed after the physical separation of the particles from the fluid or on the back side of a thin film. If $x = 50$ kcal/mole, reaction (18) requires radiation at 5600 \AA and the 25 kcal/mole, remaining for reaction (19) correspond to about 0.9μ . Assuming light of these colors can be delivered to the appropriate bonds, the catalytic decomposition of H_2O into free hydrogen and oxygen may be achieved. The strength of the M-OH bond will determine the relative endothermicity of the reactions 18 and 19. An increase in the bond strength, however, will most likely mean an increase in the metal oxide bond strength and a subsequent energy requirement for cleaning the oxygen off the surface (reaction 20).

OPTICAL PROCESSES

As mentioned previously, the separation of water into hydrogen plus oxygen would require photons of 4000 \AA or less if it could be accomplished in a single step. The absorption spectrum of water vapor (fig. 1), however, shows that there is virtually no absorption at wavelengths longer than about 1800 \AA (ref. 11). Thus any energy efficient process will require that water be broken down into hydrogen plus oxygen via one or more intermediate states. These intermediate reactions, then, may be selected so they are affected by visible radiation.

If one assumes that the reactions 18 and 19 can indeed be photoactivated, then the possibility of high conversion efficiency is conceivable. Two particular cases are important: the first is the conversion of laser energy to hydrogen, and the second is the conversion of solar energy. Since the bandwidth of a laser is very narrow, optimization of a surface for laser conversion is quite different from the optimization for solar conversion.

Theoretically, laser light may be converted with 100 percent efficiency into hydrogen gas; obviously such an efficiency will never be achieved. The value of x in equations 18 and 19 will probably be determined by the absorption spectra of the adsorbed surface compound. This will be somewhat determined by surface engineering and selection of metals, but may well be somewhere in the near infrared where water vapor absorption bands are known to lie. Such a level would require either two different lasers, or one laser driving a multiple photon process, to achieve enough energy to favor the water to hydrogen reaction.

As can be seen from figure 2, the amount of solar radiation with wavelengths shorter than 4000 \AA is small: hence the need for a two-step process for efficient solar conversion. One hydrogen molecule would then be formed for each pair of photons whose energy sums to the equivalent of 4000 \AA . In that manner a large portion of spectrum of the solar radiation may be used. Even the far infrared might contribute by heating the catalyst, thus aiding with desorption of surface compounds, the diffusion of hydrogen or, if concentrated at another location, with desorption of absorbed hydrogen from metal particles.

A calculation of the efficiency for such a device cannot be made until the surface properties of the catalyst are known. The optical absorption bands associated with the surface compounds, and the way in which these will react when optically excited, must be studied. It is clear, however, that a particle slurry or very porous surface can be made to appear black. Thus most of the visible and infrared light is absorbed. Any light absorbed that does not produce a hydrogen atom will heat the catalyst or surrounding medium. Thus the catalytic activity may also change with exposure to light.

Since the molecules will be complexed with the metal surface, absorption bands are broadened and shifted. Energy may be transferred by direct photon absorption into a surface complex, or by absorption by the bulk of the particle. Most metal particles tend to be reflective: thus photons not absorbed by a surface compound are likely to be reflected and may be absorbed by some other surface molecule. A rough metal film surface (ref. 12) or a large number of suspended particles will allow multiple reflections until absorption occurs. Photons absorbed by the particles or the solution, or by both, will heat the surfaces and aid with oxygen/OH desorption.

An optimum situation will exist if one photon with somewhat greater energy than 0.8μ first interacts with the water-catalyst to create an absorbed hydrogen atom and a surface compound. A second photon, with lower energy, then reduces the surface compound, freeing the remaining oxygen and leaving the hydrogen in the catalyst. Subsequent heat (perhaps also derived from electromagnetic radiation) then releases the hydrogen.

Referring again to equations 17 through 21, we can estimate the efficiency as a function of x . The energy regained by combustion of H_2 is 68 kcal/mole assuming the water is condensed from vapor phase. Assuming optimistically that any photon with energy higher than x for reaction 18 and $75-x$ for reaction 19 will be absorbed and cause the reactions to proceed, the energy efficiency may first be calculated.

$$\eta = \left(\frac{68 \text{ kcal/mole}}{\text{sum of average energy of both photons}} \right) \cdot$$

(percent of solar radiation with energy $\geq x$) \cdot (percent of solar radiation with energy $\geq 75-x$).

One extreme of course is reached if $x = 75$; that is, only light with wavelength shorter than $\sim 0.4\mu$ is useful. Then $\eta \cong \left(\frac{68}{80}\right) \cdot (0.05) (100) \cong 4$ percent. If $x = 0$ the same efficiency is found. Optimum conversion occurs if $x = 95/2$, or $\eta \cong \frac{68}{100} \cdot 0.6 \times 0.6 \cong 24$ percent. Figure 3 is a plot of η vs x assuming the thermal photons do not contribute.

If the photons are reflected around until they are absorbed and the heat of condensation is recovered

$$\eta = \left(\frac{68 \text{ kcal/mole}}{\text{sum of average energy of both photons}} \right) \cdot (\text{percent of solar radiation with energy } \geq x)$$

\cdot (percent of solar energy with rad. $\geq 75-x$ + percent of solar energy between x and $75-x$)

The percentage of energy between $75-x$ and x varies from ~ 95 percent if $x = 0$ to 0 if $x = 75/2$. This treatment introduces a quadratic factor into the efficiency as shown in figure 4. Thus $x \cong 50$ will provide a peak of approximately 30 percent conversion efficiency.

SEPARATION PROCESSES

Thin Films

Thin films of palladium and palladium alloys are used for industrial purification of hydrogen. The diffusion of hydrogen through palladium has been known for over a century (ref. 13) although the particulars of the diffusion mechanism have not yet been determined. At low temperatures palladium absorbs hydrogen up to about 60 percent H/Pd atom ratio as is shown in figure 5, then the material alters structure from what is termed the α phase to the β phase. As figure 5 indicates, the β phase may also be achieved at higher temperatures and lower concentrations, and above 295°C no α phase exists at all.

Diffusion is observed in both phases. Diffusion rates approximately 10cc/cm²/sec for films about 1 μ thick are easily achieved. Very thin films remain in the α phase even at high temperatures and can be efficiently used as separators.

Two major problems must be overcome if films are to be used. Even if photo induced dissociation of H₂O can be achieved on the surface, the small absorption cross section of the surface region will not allow many photons to be absorbed. Most photons will pass through and reflect off into space. The second difficulty is to promote hydrogen evolution from the back surface and not the front. Otherwise a vacuum must be maintained on the back and the hydrogen subsequently repressurized resulting in a decreased energy efficiency.

Some headway has already been made toward the solution of both these problems. The surface roughness can be controlled by thin film fabrication techniques and extremely rough surfaces have been made (ref. 14). Such a surface may be treated to form a palladium black layer thereby increasing the optical cross section and enhancing hydrogen uptake (ref. 15). Work on inhibiting the evolution of hydrogen from palladium points toward the creation of an alloy or coating on the front surface, thus forcing evolution from the rear surface only. Copper alloys of palladium have been shown to inhibit hydrogen evolution (ref. 16). Figure 6 shows schematically an arrangement for separation of hydrogen using a thin film diffusion barrier.

Particle Suspension

A suspension of finely ground particles in water or air is an alternative configuration for separation. Particles have the advantage of large surface to volume ratios, thus a suspension would expose more surface area to the incident radiation and water molecules than would a thin film. Figure 7 shows in diagrammatic form a conceivable arrangement for activating and separating the particles.

The optical scattering cross section of small particles is very dependent on size and wavelength. Generally speaking, particles on the order of the wavelength of the light are strong scatterers. Sizes on the order of 1 μ or so in diameter can easily be seen (e.g. cigarette smoke). Even in the atmosphere, particles of this size have a coat of water surrounding them.

A concentration of particles of some easily hydrated metal such as Pd, LaNi₅, would ideally act as light scatterers unless one of the adsorbed water molecules or surface compounds was to

absorb the radiation. Thus, photons arriving would be scattered numerous times before being absorbed. This multiple scattering alleviates the problem of mono-molecular layers of water molecules not being capable of absorbing the light.

An absorbed photon would either heat the particle or release a hydrogen atom into the particle. Typical solar fluxes unconcentrated range about 10^{19} photons/cm²/sec. Thus each 1- μ diameter particle would see on the order of 10^{11} photons/sec, assuming low absorption. The water solution is, of course, virtually transparent to photons with energies greater than about 2.5 μ , thus most of the photons in the frequency range of interest would be seen by the particles.

The surface area of a 1- μ particle is about 10^{-7} cm². Generally speaking, surface densities range around 10^{15} molecules/cm², so a typical particle would attract 10^8 water molecules around it. The volume of the 1- μ particle is about 4×10^{-12} cm³ and the atom density $\sim 10^{13}$ /cc; thus there are on the order of 4×10^{11} atoms of metal. Since saturation occurs at about 50-60 percent hydrogen-to-metal ratio, each particle is capable of holding 2×10^{11} hydrogen atoms or the equivalent of 10^{11} hydrogen molecules. At STP this hydrogen would occupy 3×10^{-9} cc or about 1000 times the volume of the particle.

If the absorption cross section of adsorbed water in the region of interest is low, $\sigma \cong 10^{-20}$ cm², then the water around each particle will absorb 10^{-4} of the 10^{11} photons/sec seen by the particle. If 50 percent of the solar flux is in the region of interest, 2×10^{-7} sec of exposure per particle will be necessary for the creation of one hydrogen atom. Saturation of each particle, therefore will take on the order of 40000 sec, or a couple of weeks. This approximation is mitigated by several factors.

1. Unabsorbed photons are scattered, thus the number of photons/cm²/sec seen by each particle is increased by the number of times a particle is scattered before being absorbed. Reference to Figure 1 indicates that each photon may be scattered four to five times before there is a 90 percent chance of absorption.

2. Absorption of a photon by the metal rather than the adsorbed water might also couple to the water since the photon still must be absorbed on the surface. This effect will be important for achievement of high efficiencies unless the absorption cross section of the adsorbed water molecule can be made greater than 10^{-18} cm² or so.

The addition of other metals (Cu, Ag, Au) has been shown to increase the heat of solution for hydrogen. The explanation proposed for this is that the interstitial sites are enlarged by increasing the percent of alloying metal thereby making the hydrogen interstitials more stable (ref. 17). Assuming this model is correct, we can expect to adjust the heat of solution for hydrogen and control the heat required to release hydrogen from the metal hydride.

Summary

A system involving separation of hydrogen from water will most likely proceed on a mildly chemisorptive surface, using a transition metal or transition metal alloy whose activation energy for hydrogen absorption is several kilocalories per mole thus providing stable storage of hydrogen in the hydride form at room temperature. Such a metal may be palladium, an alloy of palladium and silver

or copper, or LaNi_5 . The adsorption of water molecules on the surface will produce light absorbing bands in the infrared, visible, and ultraviolet portions of the spectrum. Although the optical cross sections of some of the bands may be small, the depth of the suspension and particle concentration or the surface roughness can be made large to totally absorb the incident light energy. The absorbed energy will promote dissociation of adsorbed species by the direct excitation of electrons out of their bonding orbitals. Additional energy absorbed by the particles will produce localized heating and will further facilitate dissociation and desorption.

Separation by diffusion will involve a thin film of palladium or palladium alloy through which the hydrogen will diffuse and evolve on the back side. The diffusion of hydrogen through palladium is a well known phenomenon currently used for hydrogen purification. The flow rate through such a film is determined by the partial pressure on either side, the thickness of the film, and the temperature. Flow rates on the order of 10 cc/sec/cm^2 are easily achievable. Thus the flow limiting step will be the hydrogen uptake at the active surface. A simple calculation shows that the diffusion limit for a $51\text{-}\mu$ film at 500°C would be the energy equivalent of approximately 100 kW/m^2 .

Separation by particles from the suspension may proceed by numerous techniques. Settling tanks or filtration probably are the least expensive, but for magnetic alloys, magnetic separation may be attractive. In either case, the adsorbed hydrogen may be reclaimed by heating or lowering the pressure below equilibrium. Particles may then be recirculated in the system.

The process described here is in many ways similar to the observed behavior of palladium. Palladium, or the other platinum group catalysts, are used to enhance the probability of specific reactions occurring by breaking selective bonds, thereby allowing certain molecules to rearrange their structure. This process frequently involves the removal of hydrogen from a particular functional group and placement in another. Because of the solubility of hydrogen, palladium is preferred for hydrogen-transfer type reactions (ref. 18). Typically, hydrogenation-dehydrogenation reactions use nickel or palladium alloys suspended on carbon, alumina, or any of a variety of substrates. An alternatively used method, however, is a slurry of particles which are mixed with the solution and subsequently filtered out. (See, for example, ref. 19.) This separation process is operational on an industrial scale and could probably be adapted to the separation problem discussed here.

It appears to be possible to produce a system for the generation of hydrogen by the photolysis of water. The information available in the current scientific literature supports the essential principles underlying the concept including the reduction of the dissociation energy and the separation of the reaction products using a metal alloy system. The efficiency of such a scheme will depend on the optical cross sections and the relative reaction rates for the various processes involved. There remains, at this point, a serious question about the ultimate efficiency of such a scheme. Although we can make both optimistic and pessimistic assessments of the outlook, the answer will be known only after an experimental program has been carried out.

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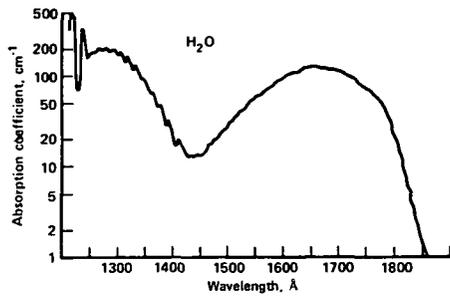


Figure 1.— Absorption spectrum of water vapor.

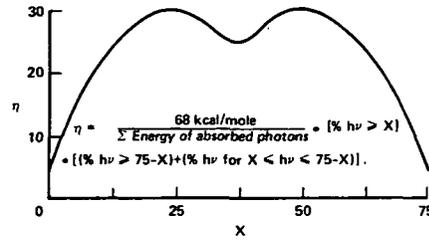


Figure 4.— Potential efficiency, including solar irradiance effects.

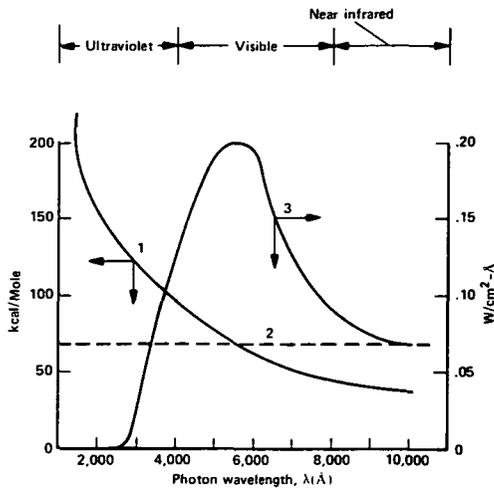


Figure 2.— Photon energy (1), water dissociation (2), and solar irradiance (3) versus photon wavelength.

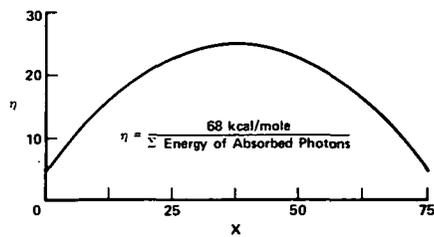


Figure 3.— Potential process efficiency.

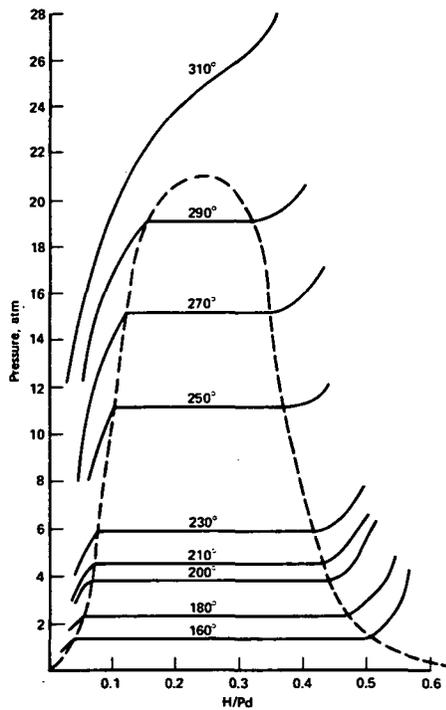


Figure 5.— Plots of $p C$ relationships.

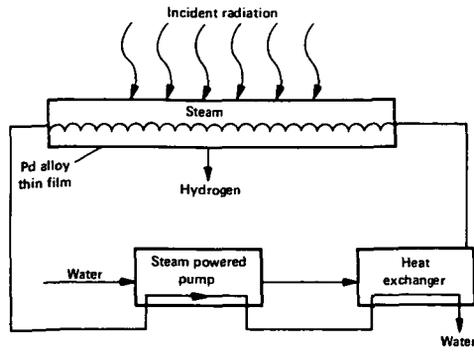


Figure 6.— Hydrogen generator using thin film separator.

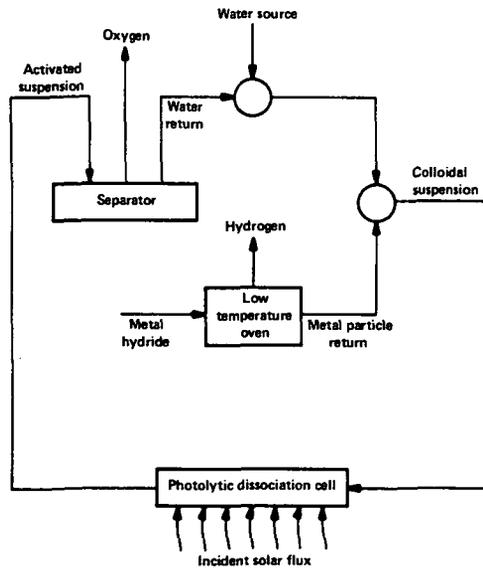


Figure 7.— Catalytic separation of hydrogen from water.

DISCUSSION

Dick Miles, Princeton University — I have a comment. I just want to say that there are two problems — which was not entirely clear. The first one is the use of the laser. It appears that if we can reduce the activation energy such that one can use 4000 Å or so and create hydrogen in either a hydride form or evolving to the surface, then we have a very high laser conversion efficiency. Solar conversion is a very different question — requiring two photons since the solar spectrum doesn't have very many 4000 Å photons. Thus it will be necessary to use a two step process which of course will require an intermediate state which would be either the breaking of an OH band off the surface or getting one hydrogen into a metal hydride and the other into the OH. That's why there are two considerations here. However, from the point of view of laser conversion, it doesn't have to be a double step process.

Dick Pantell, Stanford — Is there a deterioration of the palladium catalyst, do you have to replace it periodically?

Answer: No. First of all let me say we are speaking about a system that has not yet been built. But the deterioration of hydrogenation catalysts in the petroleum industry is only associated with the available carbon. We shouldn't have that problem. So the question is will we remove the catalysis products, will we oxidize them. We suspect the answer is no, unless we have contamination of the feed stream.

Mark Wrighton, M. I. T. — You are essentially separating hydrogen and oxygen on a catalyst and the stability comes in because of the complex which is formed.

Answer: It's very stable.

Mark Wrighton, M. I. T. — But if you ever wish to make large amounts of hydrogen and oxygen in that system, you will decompose back to water since platinum is an extremely good catalyst for that.

Answer: That's just the point. You see, we are removing the reaction products as the reaction takes place. In the thin film situation we are keeping the concentration of the reaction products down by, on the front surface, continually replenishing with fresh water and, on the back surface, by removing the hydrogen. In the case of the colloidal particle we are talking about the same situation. When the particle comes reasonably near the saturation point where you have to worry about back reactions, its gone since another particle takes its place.

Mark Wrighton: Another question. If you have this material in there, all that's going to happen is that its going to heat up. I don't see the advantage over using a piece of black paper and letting the laser heat it.

Answer: That's not true at all. In fact if it were, *you* would have problems also.

Mark Wrighton: Yes, but in my system there are discrete photochemical reactions which correspond to electronic transitions — optical transitions. In this case, I don't know of any examples of photochemical reactions on surfaces.

Answer: Well, photochemical reactions that Greg has done in solution are exactly the same thing.

Dick Miles: Let me comment. This is something we are going to be studying. Obviously what we do will depend upon the absorption band of the surface complex. We hope to be able to couple to the vibrational absorption bands and increase the probability of this reaction going over the thermal probability. That is what the apparatus we just showed is set up to demonstrate.

Bill Bottoms: The question is basically, if we are just absorbing the energy directly into the palladium its just going to heat up and you are right, its just going to get hot. If, however, we are absorbing the energy into the surface complex, then we have the same kinds of transitions available that anyone else does that is irradiating a complex of metal and water.

Karlheinz Thom, NASA Headquarters – In both talks we've heard that the speakers have avoided considering the use of uv photons because they are too expensive. But photochemists feel that they will make progress in their fields and they should allow, therefore, that the laser people will make progress in their field also. Being an optimist, I predict that we will have cheap uv photons in the not too distant future and we shouldn't neglect this possibility.

Bill Bottoms: These uv photons are expensive, not because its expensive to buy a laser, but because the energy you can get back is less than the energy you have invested with the uv photon. So its expensive in terms of chemistry. When you burn water you don't get as much energy back as you put in with one uv photon, so you want to bring down the photon energy to as low a value as possible.

Max Garbuny: Because of the great interest in isotope separation it is quite likely that work of this type will be investigated thoroughly in the near future.

Bill Bottoms: Thank you for the interesting comment. However, I must point out that the literature has data on the diffusion through palladium of both hydrogen and deuterium and, unfortunately, they are disturbingly similar! The rates are not as far apart as one would like.