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**REVIEW OF SOLAR FUEL-PRODUCING QUANT.  
CONVERSION PROCESSES**

By  
D. B. Peterson  
J. R. Biddle  
T. Fujita

May 1, 1984

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Jet Propulsion Laboratory  
Pasadena, California

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AUTH: A/PETERSON, D. B.; B/BIDDLE, J. R.; C/FUJITA, T. PAA: A/(San Diego Univ.); B/(California State Polytechnic Univ., Pomona)

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ABS: The status and potential of fuel-producing solar photochemical processes are discussed. Research focused on splitting water to produce dihydrogen and is at a relatively early stage of development. Current emphasis is primarily directed toward understanding the basic chemistry underlying such quantum conversion processes. Theoretical analyses by various investigators predict a limiting thermodynamic efficiency of 31% for devices with a single photosystem operating with unfocused sunlight at 300 K. When non-idealities are included, it appears unlikely that actual devices will have efficiencies greater than 12 to 15%. Observed

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# Review of Solar Fuel-Producing Quantum Conversion Processes

D.B. Peterson (Consultant, University of San Diego)  
J.R. Biddle (Consultant, California State Polytechnic University, Pomona)  
T. Fujita

May 1, 1984

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## ABSTRACT

The single most important factor in determining the cost of fuel produced by a commercial-scale solar photochemical plant is the overall efficiency which is limited primarily by the relatively low efficiency of the solar photochemical process. The results of that study are summarized in Section III of this report. A more detailed account is given in "Solar Photochemical Process Engineering for Production of Fuels and Chemicals."

Because of the pivotal role of photochemical efficiency in determining the economic viability of fuel production, the current status and potential of fuel-producing solar photochemical processes are discussed in this report.

Research has focused almost exclusively on splitting water to produce dihydrogen and is at a relatively early stage of development. Current emphasis is primarily directed toward understanding the basic chemistry underlying such solar quantum conversion processes.

Theoretical analyses by various investigators predict a limiting thermodynamic efficiency of 31% for devices with a single photosystem operating with unfocused sunlight at 300 K. When non-idealities are included, it appears unlikely that actual devices will have efficiencies greater than 12 to 15%. Observed efficiencies are well below theoretical limits. Cyclic homogeneous photochemical processes for splitting water have efficiencies considerably less than 1%. Efficiency can be significantly increased by addition of a sacrificial reagent; however, such systems are no longer cyclic and it is doubtful that they would be economical on a commercial scale. The observed efficiencies for photoelectrochemical processes are also low but such systems appear more promising than homogeneous photochemical systems.

Operating and systems options, including operation at elevated temperature and hybrid and coupled quantum-thermal conversion processes, are also considered.

## FOREWORD

This report covers a part of a study of solar photochemical quantum conversion processes for producing fuels and chemicals that addressed engineering feasibility issues and reviewed the status of solar quantum conversion processes. Results of the study are summarized in the following two complementary reports (which include the present report):

- (1) Solar Photochemical Process Engineering for Production of Fuels and Chemicals.
- (2) Review of Solar Fuel-Producing Quantum Conversion Processes.

The first report investigates engineering feasibility by analyzing processes with characteristics determined by a review of solar quantum conversion processes. The second report documents the review of quantum processes and delves into specific aspects of the chemistry associated with these processes. The engineering and economic feasibility issues from the first report provide a framework within which specific processes are reviewed in the second report. The first report is intended for those primarily concerned with engineering issues and their implications with regard to research directions for solar photochemical processes. The second report is directed toward those whose primary interest is the chemistry of quantum conversion processes.

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The authors acknowledge the supportive management direction and encouragement for the study provided by Marvin R. Christensen, the Program Manager for Fuels and Chemicals at the Jet Propulsion Laboratory (JPL), and Gerald Katz, the Program Coordinator for Solar Fuels and Chemicals at the U.S. Department of Energy/San Francisco Operations Office (DOE/SAN). The technical inputs of Chris England of the Engineering Research Group, who collaborated with the authors during all phases of the study, is especially appreciated. The study also benefited from technical reviews provided by Gerry Nix and Dave Johnson of the Solar Energy Research Institute (SERI).

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## DEFINITION OF SYMBOLS

|             |                                                                                                                                                                                             |
|-------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| AM          | Air Mass. AM is followed by a number that indicates the relative air mass through which solar radiation has passed (e.g., AM 0 is the solar insolation just outside the Earth's atmosphere) |
| CR          | Concentration ratio                                                                                                                                                                         |
| E           | Energy                                                                                                                                                                                      |
| $E_g$       | Band-gap energy. Only photons with $E \geq E_g$ can initiate the quantum conversion process                                                                                                 |
| h           | Plank's constant                                                                                                                                                                            |
| M           | Molar concentration. Moles of solute per liter of solution                                                                                                                                  |
| mol         | Mole. One gram-molecular mass                                                                                                                                                               |
| $T_0$       | Ambient temperature                                                                                                                                                                         |
| $T_Q$       | Photochemical reaction temperature                                                                                                                                                          |
| E           | Fraction of incident solar energy that can initiate the quantum conversion process                                                                                                          |
| $\eta_o$    | Overall system efficiency. Ratio of energy content of product gas to incident solar flux                                                                                                    |
| $\eta_Q$    | Estimated overall efficiency of the solar quantum converter (includes absorption and product collection efficiencies)                                                                       |
| $\eta_{QT}$ | Limiting thermodynamic efficiency of a solar quantum conversion process                                                                                                                     |
| $\lambda$   | Wavelength                                                                                                                                                                                  |
| $\lambda_g$ | Band-gap wavelength. Only radiation with $\lambda \leq \lambda_g$ can initiate the quantum conversion process                                                                               |
| $\nu$       | Frequency                                                                                                                                                                                   |
| $\phi$      | Quantum yield. The number of molecules of product per photon absorbed                                                                                                                       |



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## EXECUTIVE SUMMARY

### INTRODUCTION

Photochemical processes seem to be a promising method for conversion of solar energy to fuels and chemicals because of the possibility of direct conversion of the photon energy to chemical energy. These processes involve the production of electronically excited species as a result of the absorption of photons of appropriate energy from the incident solar flux. The energy of these excited species is directed into chemical energy stored in a high energy product, the fuel. Because the overall efficiency is expected to be relatively low, there is concern that photochemical processes may suffer from high costs associated with the distribution of reactors over large areas and, concurrently, costs associated with transporting the reagents and product gases to and from the reactors.

Higher efficiency systems hold promise of reducing energy costs by yielding smaller field sizes for the same plant output. Concentrated solar radiation focused on the reactor will increase the efficiency as long as temperature increases are limited by reactor cooling. These concentrating systems provide better performance but are more technically sophisticated and costly. By scoping the engineering cost and performance of commercial-size baseline non-concentrating and concentrating photochemical plants for fuel production, guidelines can be established for selection of the most promising and appropriate photon-driven technologies.

A brief, general description of currently available processes for direct conversion of solar energy into storable chemical energy is given in the Solar Photochemistry section. This information provides the photochemical basis for defining the baseline systems used in the engineering feasibility study that follows in the Engineering Assessment of Solar Photochemical Dihydrogen Production section. Current research pertinent to fuel producing quantum conversion processes, which is the focus of this report, is reviewed in the State of the Art section. Systems and operating options, such as coupled and hybrid systems and photochemistry at elevated temperatures, are discussed in the Systems and Operating Options section. Finally, the conclusions from this study are summarized together with recommendations for further work.

### SOLAR PHOTOCHEMISTRY

Photochemical processes convert solar energy directly into chemical energy. Devices based on such processes are classified as quantum converters because they are initiated by the electronic excitation of an absorber by photons of appropriate energy, a quantized event. The required photon energy is called the threshold or band-gap energy ( $E_g$ ), and it is usually large enough that less than half of the solar spectrum can initiate photochemistry.

Photochemical processes differ from thermal processes in a number of important aspects. In photochemistry, absorber molecules, often present at low concentration, are selectively excited. In thermal processes, excitation is

essentially non-specific. Thermal systems also differ in that the molecules involved in reaction almost invariably remain in their ground electronic states. Because of these differences, the reaction products may differ markedly when the same system is excited photochemically rather than thermally.

The following are some general requirements for solar photochemical systems that produce fuels or chemicals:

- (1) The process should constitute a closed cycle with respect to all species except the feedstock and its decomposition products (e.g.,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ , and  $\text{O}_2$  in the photochemical splitting of water).
- (2) They should operate over a wide band of the solar spectrum.
- (3) The quantum yield should be high.<sup>1</sup>
- (4) The product(s) should be easily separated, stored, and transported.
- (5) The materials of construction and the reagents involved must be inexpensive and relatively abundant.

Considering such factors as process chemistry and the cost and availability of feedstock, it seems unlikely that fuels will be produced on a large scale from feedstocks other than water, carbon dioxide, and dinitrogen ( $\text{N}_2$ ).

Most of the research related to development of solar photochemical processes for the production of fuels has focused on splitting water to produce dihydrogen.

#### Homogeneous Photochemical Water Splitting

Direct solar photolysis of water to produce dihydrogen is not practical because of the large band-gap energy involved. However, indirect photolysis is possible in the presence of an appropriate sensitizer. The sensitizer absorbs energy over a wide band in the solar spectrum and uses the energy to drive a cyclic process, the net result of which is decomposition of water into dihydrogen and dioxygen.

A typical process is represented schematically in Figure 1. The sensitizer, S, absorbs photons to produce the electronically excited state,  $\text{S}^*$ , which transfers an electron to the quencher, Q, resulting in formation of  $\text{Q}^-$  and  $\text{S}^+$ . The latter species undergo catalyzed redox reactions with water to produce  $\text{H}_2$  and  $\text{O}_2$ .

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<sup>1</sup>The quantum yield is the number of molecules of product divided by the number of photons absorbed.



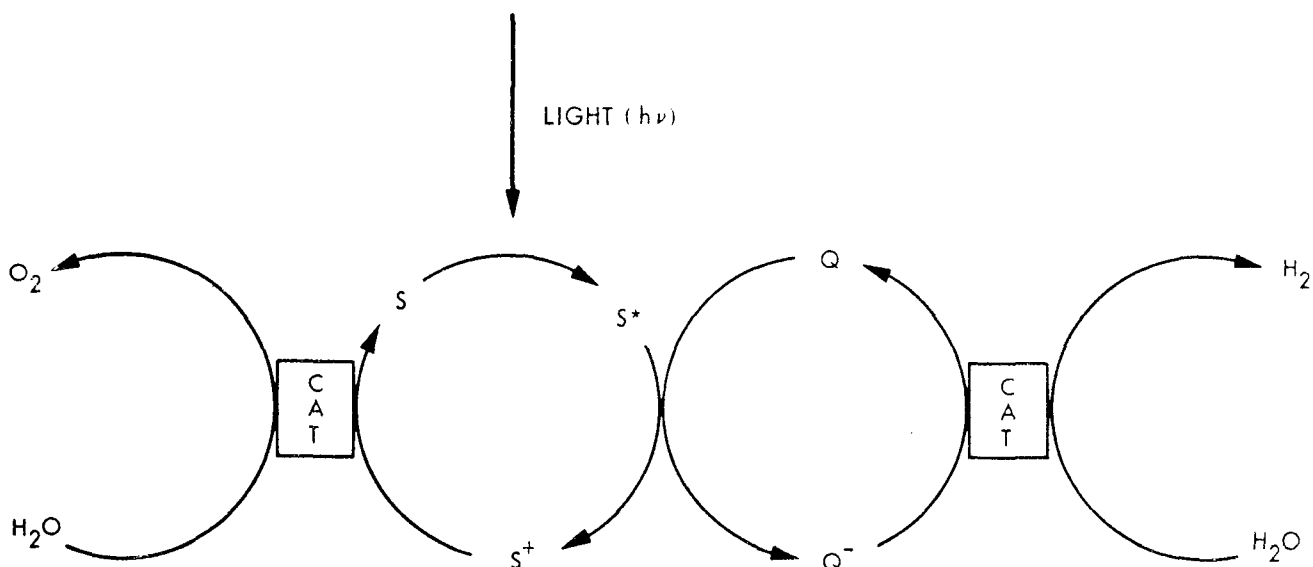


Figure 1. Schematic Diagram for Cyclic Photochemical Water Splitting

### Photoelectrochemical Processes

The distinguishing feature of photoelectrochemical processes is that the fuel-producing chemical reactions<sup>2</sup> occur at electrodes, one or both of which is an illuminated semiconductor. Illumination of the semiconductor results in excitation of electrons from the valence to the conduction band.

The resulting electron-hole pairs migrate to the electrodes where the chemical reactions occur. Various cell configurations are possible. A schematic diagram of a photoelectrochemical cell with a single semiconductor electrode is shown in Figure 2. In such cells, the counter electrode is an inert conductor such as platinum or carbon. Photons absorbed at the photoelectrode provide the only energy input.

Other configurations include those in which both electrodes are illuminated semiconductors and cells in which the photoelectrochemical cell is reduced to colloidal dimensions. In the latter case, platinized colloidal particles of the semiconductor are dispersed in the electrolyte to produce what are, in effect, wireless photoelectrochemical cells.

Voltage-assisted photoelectrolysis is another option. In this configuration, an external power source is used to bias the electrodes, and the energy input includes both radiant energy and electrical energy.

<sup>2</sup>Photoelectrochemical devices may also be designed to convert solar photons directly to electricity. Such devices, usually referred to as photogalvanic cells, are not considered in this report.

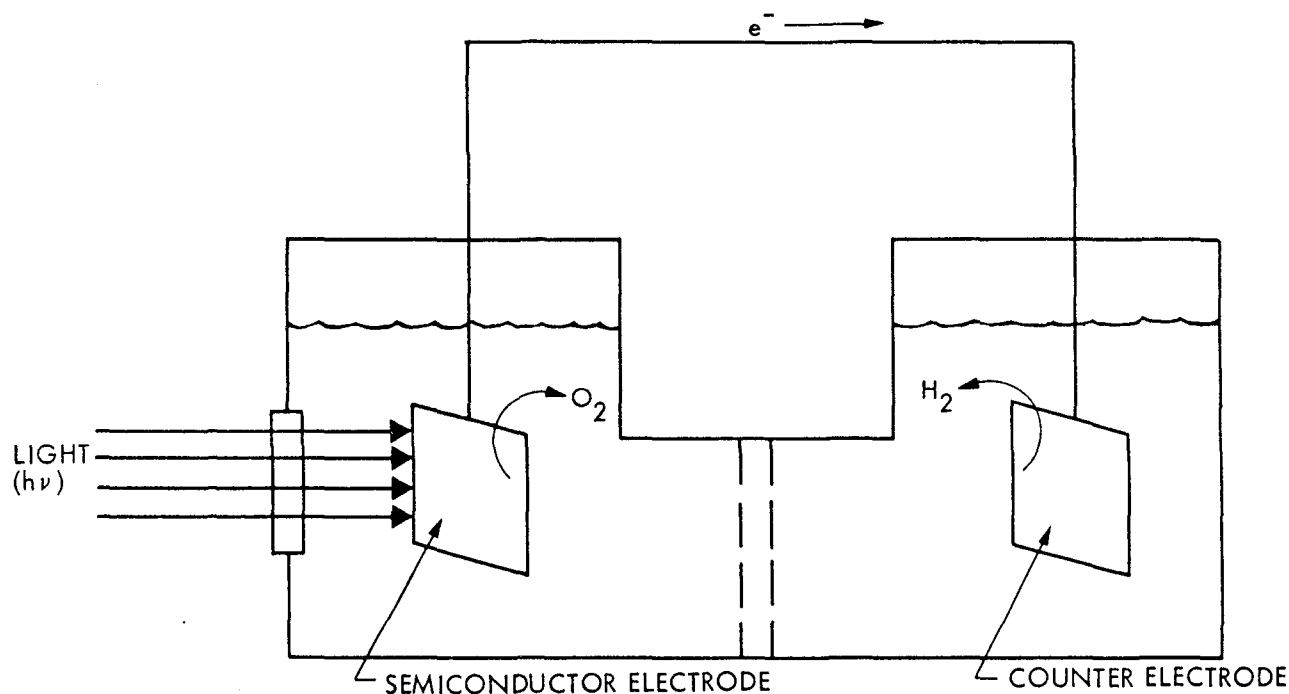


Figure 2. Photoelectrolysis Cell With a Single Semiconductor Electrode

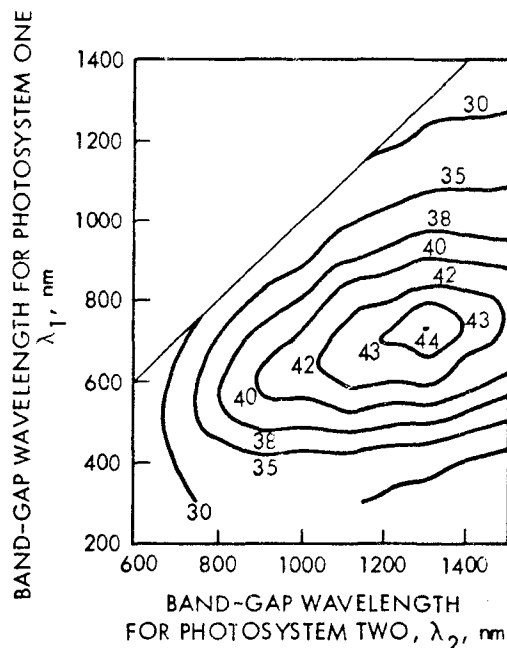
## Efficiency

Limiting Thermodynamic Efficiency. Both thermodynamic and kinetic factors limit the efficiency with which solar energy can be converted directly to work and/or storable chemical energy. The limiting thermodynamic efficiency,  $\eta_{QT}$ , has been examined by several investigators.

There is general agreement that for quantum converters with a single photosystem and unfocused sunlight,  $\eta_{QT}$  has a maximum of about 31% for AM 0 and 300 K. The relatively low value is inherent in the quantum nature of the conversion process and the consequences of the second law and, as such, is independent of the mechanistic details of the process.

Haught and Bilchak, et al, have shown that the limiting thermodynamic efficiency increases approximately two percentage points for each tenfold increase in solar intensity and decreases by about that same amount for each 50 K increase in temperature. Thus, if solar concentration is to be employed for the purpose of increasing efficiency, it will probably be necessary to cool the reactor.

The efficiency,  $\eta_{QT}$ , can be increased by using two or more separate photosystems involving different absorbers with different band-gap or threshold energies. Figure 3 shows contours of  $\eta_{QT}$  (as a percentage) as a function of  $\lambda_1$  and  $\lambda_2$  for a system with two photosystems subjected to AM 1.2 solar energy. One absorber absorbs all light with  $\lambda \leq \lambda_1$ ; the other absorbs all light with  $\lambda_1 \leq \lambda \leq \lambda_2$ . A maximum  $\eta_{QT}$  of 44% is predicted for  $\lambda_1 = 830$  nm and  $\lambda_2 = 1320$  nm.



NOTE:

AM 1.2 (AIR MASS 1.2) CORRESPONDS TO THE INSOLATION AT THE EARTH'S SURFACE WHERE THE SUN PASSES THROUGH 20% MORE AIR MASS THAN AT ITS ZENITH ON A CLEAR DAY

Figure 3. Efficiency Contours for a Quantum Converter Using Two Photosystems and Unfocused AM 1.2 Solar Energy

Efficiencies of Real Systems. Real systems, producing chemically stored energy, will have efficiencies that are significantly lower than  $\eta_{QT}$ , the limiting thermodynamic efficiency. For example, the values of  $\eta_{QT}$  are calculated assuming that the absorber is ideal, i.e., all photons with  $\lambda \leq \lambda_g$  are absorbed. In real photochemical systems, the absorption characteristics of the photosensitizer are such that not more than 70 to 80% of these photons are likely to be absorbed. Also, not all of the photochemical product will be collected from the system. Collection efficiency is unlikely to be greater than 90%, especially when a gas is generated in a liquid system. There are also kinetic limitations that reduce the efficiency of processes that store energy chemically. If the product is to be kinetically stable, there must be an energy barrier to prevent its back reaction. It is estimated that this kinetic effect will reduce the limiting efficiency for a quantum converter using a single photosystem from about 31% to about 21%. When all of these factors are considered, it seems unlikely that the overall efficiency of a real quantum converter of this type will exceed 12 to 15%.

## ENGINEERING ASSESSMENT OF SOLAR PHOTOCHEMICAL DIHYDROGEN PRODUCTION

The object of this phase of the study is to identify engineering requirements associated with solar photochemical systems and scope the costs of a commercial scale plant for producing fuels. The nominal plant size chosen produces 25,000 scmd (850,000 scfd) of dihydrogen gas at 50 atm. Production of dihydrogen from water was selected because it has received the most attention.

### Non-Concentrating System

The initial system investigated is based on a non-concentrating, flat-plate design. Characteristics of this design are given in Table 1. The collector/reactor for this system is shown in detail in Figure 4. It is, essentially, two 1.22 x 3.66 m (4 x 12 ft) glass sheets, 2.54 cm (1 in.) apart, surrounded by an extruded, aluminum frame. Water is pumped to the unit (inclined at 35 deg) where solar energy is collected and the photochemical reaction occurs. The product gases (dihydrogen and dioxygen) are assumed to be separated. Twelve of these individual units are field assembled into a gang and gangs are laid out in a field such as that shown in Figure 5. Dihydrogen gas is piped to a central site where it is compressed to 50 atm (typical gas pipeline transmission pressure). All field piping is uninsulated carbon steel and almost 90% is 0.95 cm (3/8 in.) size.

The capital cost breakdown for this non-concentrating baseline flat-plate system is shown in Table 2. The balance of plant (BOP) includes site preparation, construction, plant facilities, and plant equipment. All costs are based on 1983 dollars. These capital costs are translated into energy costs by an economics model widely used in solar energy studies. The results, as a function of overall plant system efficiency, are shown in Figure 6. Fixed charge rates of 0.20 (typical of utility industry economics) and 0.30 (typical of chemical industry economics) are used and operating and maintenance are assumed to be 2% of the plant capital cost. The overall system efficiency includes photochemical, separation, and compression efficiencies. For the baseline system efficiency of 10.3%, the energy cost ranges from \$34 to \$56/10<sup>6</sup> kJ (\$36 to \$59/10<sup>6</sup> Btu).

Table 1. Characteristics of the Baseline Non-Concentrating System

| Characteristics           | Selected Conditions         |
|---------------------------|-----------------------------|
| Feedstock                 | Water                       |
| Product                   | Dihydrogen gas              |
| Operating Pressure        | 1 atm                       |
| Operating Temperature     | 54°C (130°F)                |
| Nominal Plant Size        | 25,000 scmd                 |
| Overall System Efficiency | 10.3%                       |
| Nominal Collector Area    | 120,000 m <sup>2</sup>      |
| Annual Solar Flux         | 2430 kWh/m <sup>2</sup> /yr |

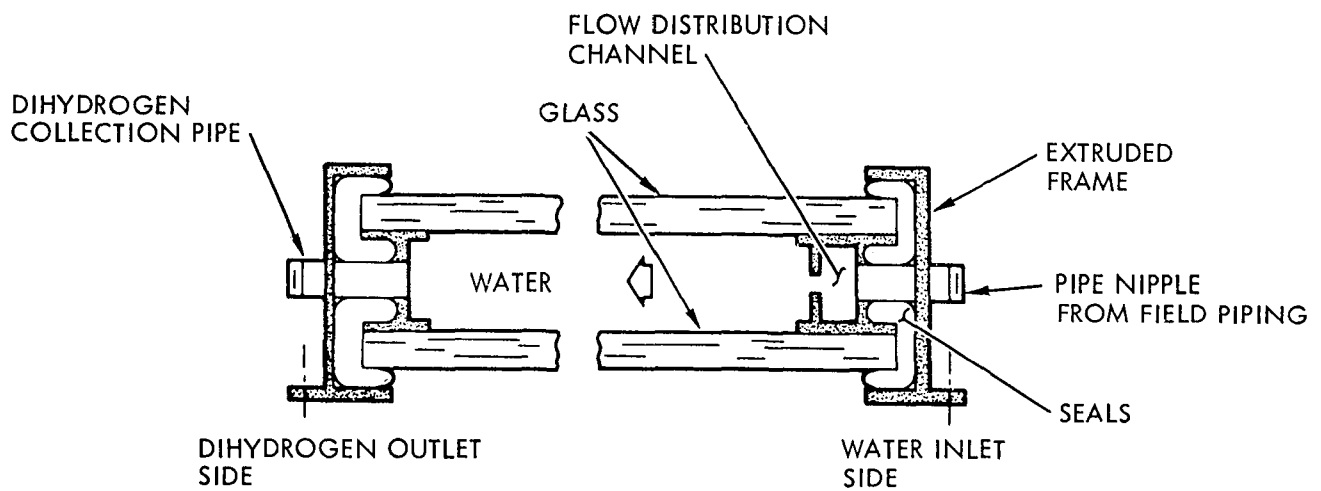


Figure 4. Baseline Flat-Plate Collector/Reactor Configuration

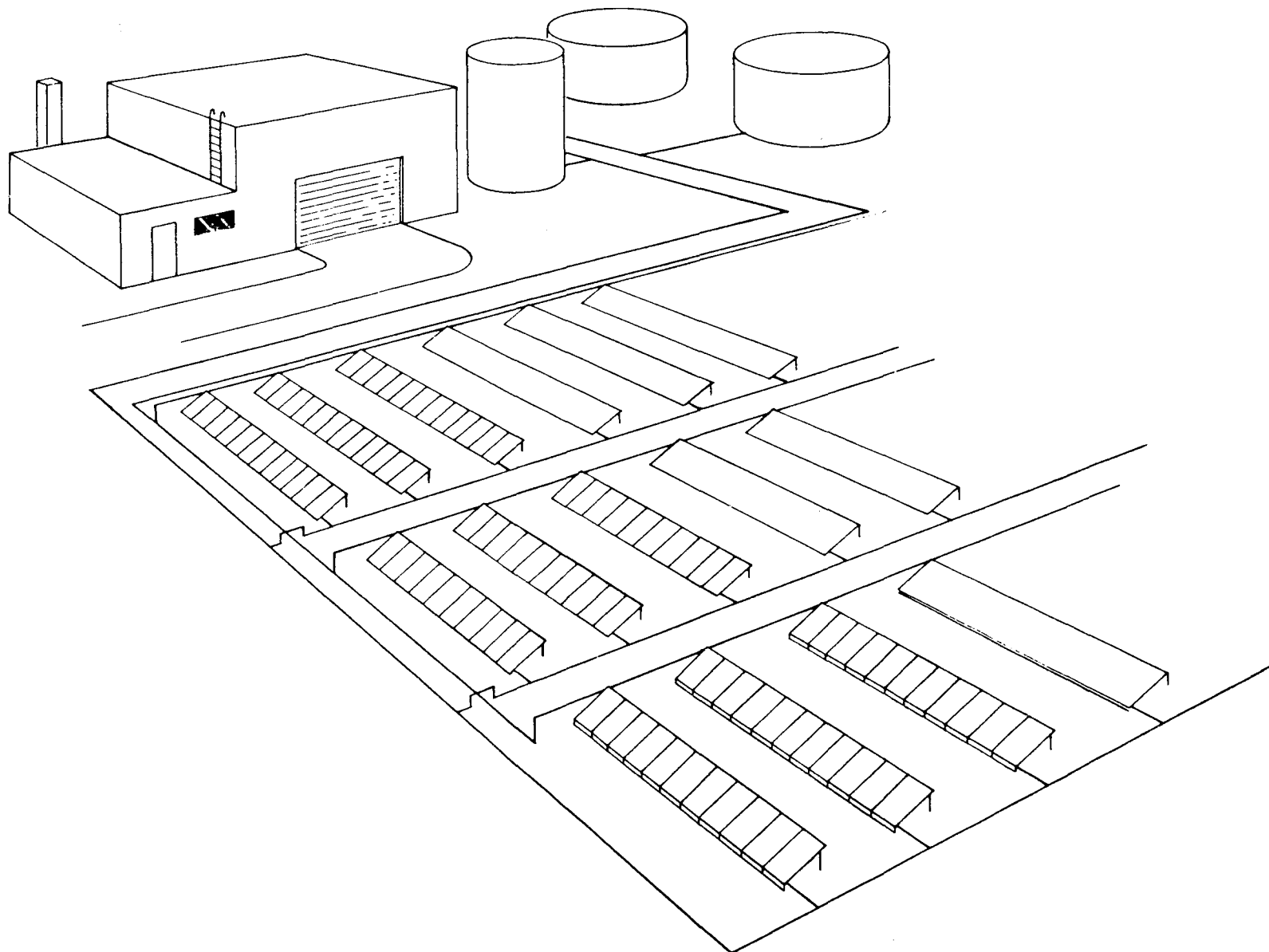


Figure 5. Artist's Conception of Flat-Plate Photochemical Plant

Table 2. Capital Cost Breakdown for Baseline Flat-Plate System

| Subsystem                  | Cost, \$ x 10 <sup>3</sup> |
|----------------------------|----------------------------|
| Collector/Reactor          | 7,096                      |
| Piping and Reactor Support | 1,305                      |
| Field Piping               | 1,483                      |
| Gas Compression            | 1,160                      |
| Balance of Plant           | <u>8,410</u>               |
| Total                      | 19,454                     |

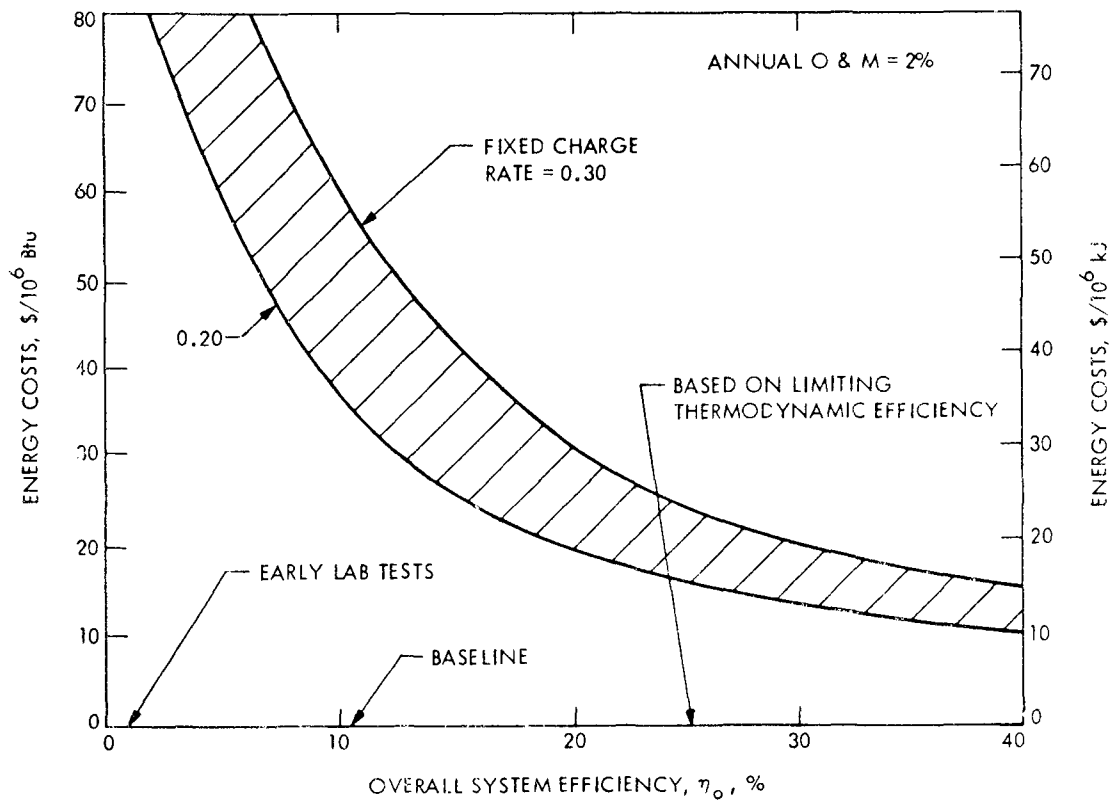


Figure 6. Cost of Dihydrogen from the Baseline Flat-Plate System

## Concentrating Systems

Because energy costs are dominated by the efficiency, it was decided to investigate the use of concentrated solar radiation. This might increase the system efficiency and reduce energy costs by reducing the field size and associated piping and BOP costs.

Characteristics of the baseline concentrating system chosen are given in Table 3. A parabolic trough collector (Figure 7) was selected for the baseline because it has a moderate concentration range and is commercially available. The major modification required is the redesign of the receiver tube to serve as a reactor for the photochemical process. However, it was determined that, if left uncooled, the reaction temperature could approach 250°C. To provide for reactor cooling, a concentric glass tube arrangement was proposed. In the baseline system, the photochemical solution is in the core and the cooling water circulates through the annular region.

The receiver/reactor consists of concentric glass tubes with diameters of 5.1 cm (2 in.) and 2.5 cm (1 in.) in a parabolic trough with a 2.1-m (7-ft) aperture, giving a concentration ratio of 42.8. The trough length was 6.1 m (20 ft). Four of these troughs are assumed to be coupled in series

Table 3. Characteristics of the Baseline Concentrating System

| Characteristics           | Selected Conditions         |
|---------------------------|-----------------------------|
| Feedstock                 | Water                       |
| Product                   | Dihydrogen gas              |
| Operating Pressure        | 1 atm                       |
| Operating Temperature     | 29°C (85°F)                 |
| Nominal Plant Size        | 25,000 scmd                 |
| Overall System Efficiency | 11.6%                       |
| Nominal Collector Area    | 125,000 m <sup>2</sup>      |
| Annual Solar Flux         | 2150 kWh/m <sup>2</sup> /yr |
| Concentration Ratio       | 43                          |



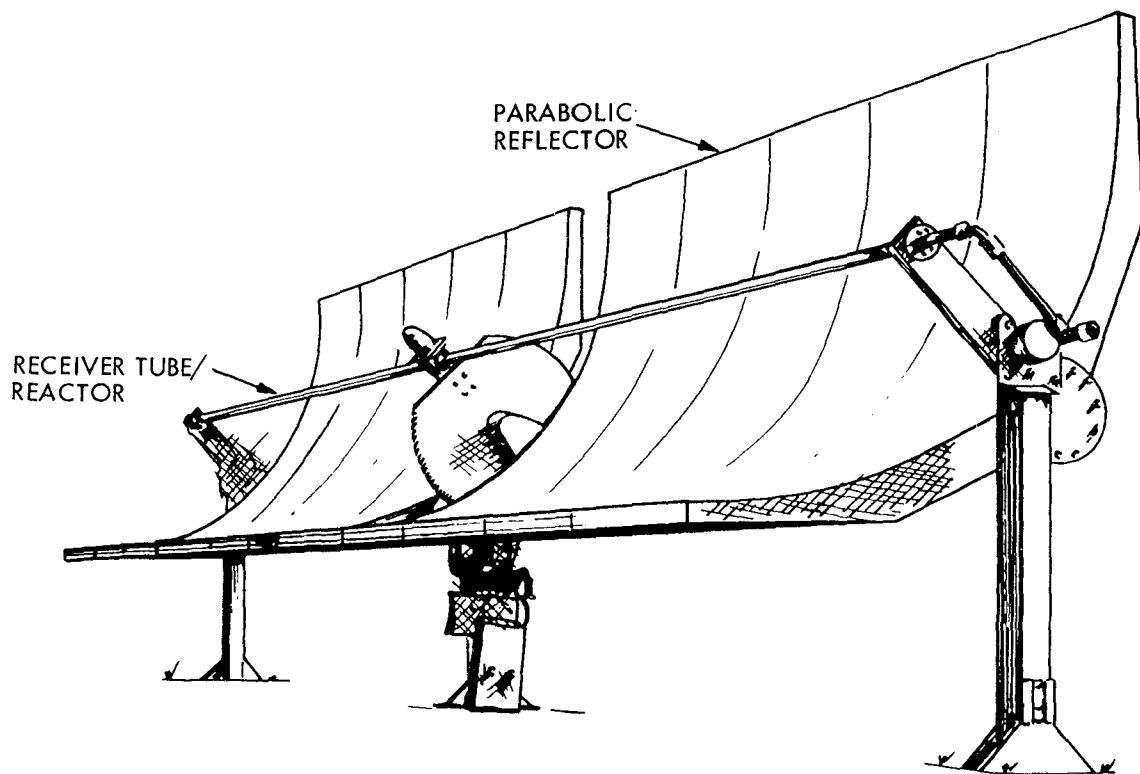


Figure 7. Parabolic Trough Collector/Reactor

to form an 80-ft-long string. Strings were laid out in an east-west field orientation shown in Figure 8. About 64% of the field piping for gas and liquid transport is 0.95 cm (3/8 in.).

The capital cost breakdown for the baseline concentrating system is given in Table 4. Energy costs are presented in Figure 9 as a function of the overall system efficiency. Comparison with the flat-plate system reveals that, for the baseline concentrating system shown, energy costs are two to three times greater than those for the non-concentrating system, depending on the fixed charge rate used. For the baseline system (overall efficiency of 11.6%), the energy cost would be from \$94 to \$141/10<sup>6</sup> kJ (\$99 to \$149/10<sup>6</sup> Btu). This dramatic difference in energy costs can be attributed to the higher cost for the collection system (the tracking parabolic trough collectors). Any small advantage gained in the photochemical efficiency due to increased concentration is lost because of the much higher costs for collection and lower annual energy collection efficiency that results because the concentrating system does not use the diffuse component of solar radiation.

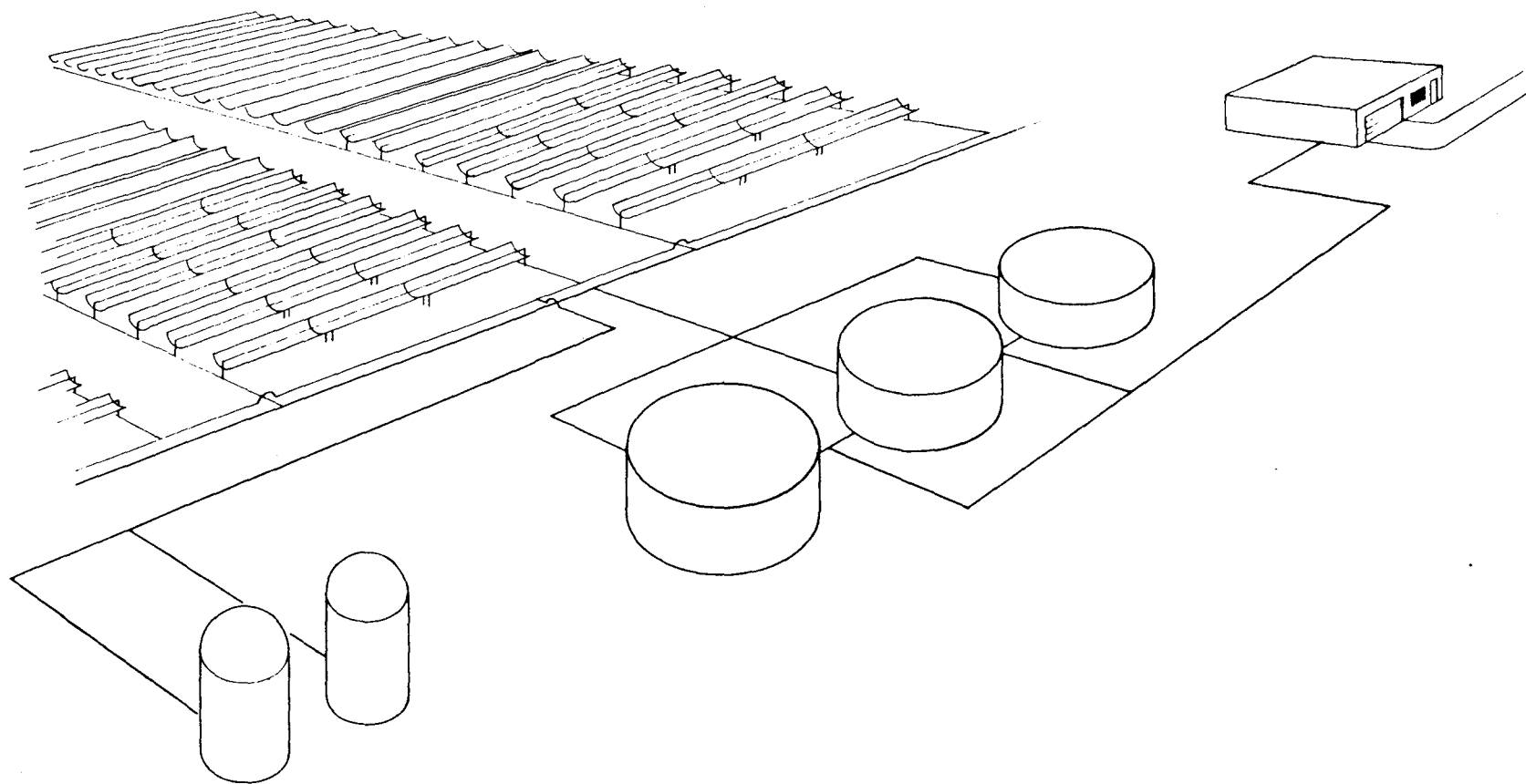


Figure 8. Artist's Conception of Parabolic Trough Photochemical Plant

Table 4. Capital Cost Breakdown for Concentrating System

| Item              | Cost, \$ x 10 <sup>3</sup> |
|-------------------|----------------------------|
| Collector/Reactor | 30,658                     |
| Coolant Equipment | 2,170                      |
| Field Piping      | 553                        |
| Gas Compression   | 1,160                      |
| Balance of Plant  | <u>13,646</u>              |
| Total             | 48,187                     |

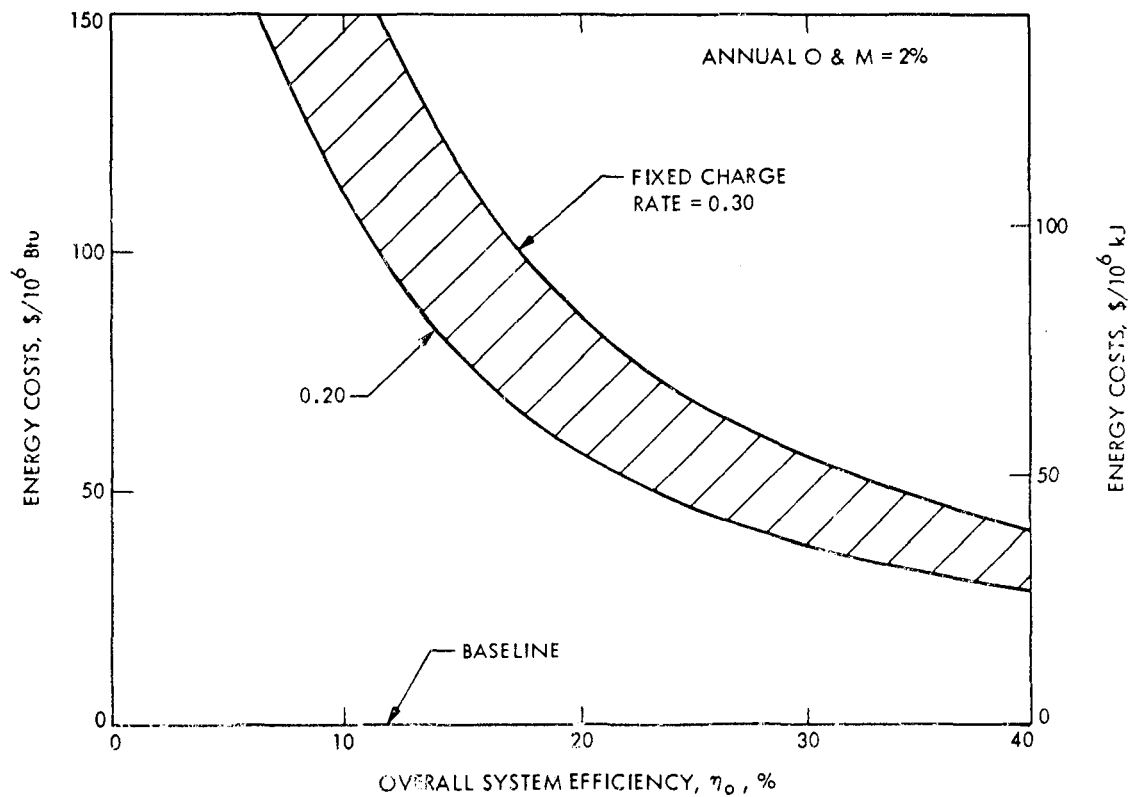


Figure 9. Cost of Dihydrogen from the Baseline Concentrating System

## STATE OF THE ART

The current status of fuel-producing photochemical and photoelectrochemical processes is reviewed to provide background and perspective for the study of engineering feasibility. As of this date, such research has concentrated almost exclusively on splitting water to produce dihydrogen.

### Cyclic Photoredox Processes

These processes are cyclic in the sense that all species are regenerated except water and its decomposition products,  $H_2$  and  $O_2$ . Because only a very small fraction ( $\ll 1\%$ ) of solar radiation is at wavelengths short enough to initiate direct photodecomposition of water, a sensitizer is required. The sensitizer is electronically excited by the absorption of solar photons of appropriate energy ( $E \geq E_g$ ), and uses its excitation energy to drive a sequence of reactions that result in the decomposition of water to  $H_2$  and  $O_2$  (Figure 1).

Complexes of transition metals with appropriate organic ligands that absorb strongly in the visible are among the more widely used sensitizers and the viologens, particularly methyl viologen, are the most widely used quenchers.

Cyclic processes of this general type have efficiencies of less than one percent. The major reason for the low efficiencies observed in such systems seems to be the very rapid non-productive back reaction between the charge pairs.

### Sacrificial Reagents

Significantly higher yields of  $H_2$  can be obtained by introducing a sacrificial reagent, however, such systems are no longer cyclic. The sacrificial reagent may inhibit charge recombination by scavenging one of the ions via an irreversible redox reaction in which the sacrificial reagent is consumed. The unscavenged ion is then able to produce  $H_2$  or  $O_2$ .

Mild reducing agents are effective sacrificial reagents if dihydrogen is the desired product, and the highest efficiency observed is about 13%.

Systems requiring a sacrificial reagent might be practical for commercial sale production of  $H_2$  if an inexpensive reagent were available. At the present stage of development, studies with sacrificial reagents are used primarily to obtain kinetic data and to evaluate various components of photoredox/systems.

### Organized Assemblies

In natural photosynthesis, non-productive charge recombination is inhibited by separating charge pairs in highly specialized thylakoid membranes. Photochemists are attempting to mimic this natural process by using organized assemblies of molecules such as micelles and vesicles. The work is in a relatively early stage of development and it is not possible to say whether such assemblies will be useful in commercial-scale processes.

## Photoelectrochemical Water Splitting

These processes involve production of the fuel via chemical reactions at the surface of electrodes, one or both of which is a semiconductor. Various cell configurations are possible.

Voltage-Assisted Photoelectrolysis. In 1972, Honda and Fujishima reported that water could be decomposed to  $H_2$  and  $O_2$  at voltages well below the theoretical decomposition potential in a cell with a n-TiO<sub>2</sub> photoanode and a platinum cathode.

Since then, a number of semiconductors have been used in voltage-assisted photoelectrolysis but, in general, conversion efficiencies with solar radiation have been relatively low, 3% or less. A conversion efficiency of 12% has been reported for photoelectrolysis of aqueous 1M HCl - 2M KCl to produce  $H_2$  and  $Cl_2$ . The cell employed a platinized p-In photocathode and a platinum anode. This is the highest efficiency that has been reported for any fuel-producing solar quantum converter.

Unbiased Cells with a Single Photoelectrode. In these devices, one electrode is an illuminated semiconductor and the counter electrode is an inert conductor, such as platinum or carbon (see Figure 2). Light absorbed at the photoelectrode is the only energy input. Sustained photoelectrolysis of water without application of an external voltage was first achieved using a UV-illuminated, n-SrTiO<sub>3</sub> photoanode, and a platinum cathode. However, the band-gap energy in this case is so large (3.2eV) that the efficiency would be unacceptably low with solar radiation.

Major problems are the poor match of semiconductor band-gap with the solar spectrum and photocorrosion of semiconductor electrodes. The spectral response can be improved by sensitization of the semiconductor electrode with dyes or molecular substrates attached to the surface. A number of semiconductor-sensitizer combinations have been investigated, but efficiencies remain low.

Unbiased Cells with Two Photoelectrodes. In this case, two photons are absorbed (one at each photoelectrode) to generate one net electron-hole pair for the fuel-producing reaction. Such devices may be able to use lower band-gap semiconductors that better utilize the solar spectrum. A variety of such cells have been investigated but, thus far, efficiencies have been low, less than a few percent.

Colloidal Semiconductor Systems. Cells have been designed in which colloidal n-TiO<sub>2</sub> particles loaded with ultrafine deposits of RuO<sub>2</sub> and platinum act as wireless cells with an n-TiO<sub>2</sub> photoanode short-circuited to a platinum cathode. However, the efficiency is extremely low with solar radiation because of the large band-gap energy of TiO<sub>2</sub>. Grätzel and his coworkers are attempting to extend the spectral response into the visible by surface-doping the colloidal TiO<sub>2</sub> particles with transition metals. Sustained water cleavage with visible light has been observed with aqueous suspensions of TiO<sub>2</sub> particles doped with  $Cr^{3+}$ . The observed quantum efficiency for production of  $H_2$  is approximately 1%.

Particle systems are attractive because their relative simplicity could result in lower construction and maintenance costs. However, unlike cells with well separated electrodes, particle systems produce a mixture of gases which must be separated.

## SYSTEMS AND OPERATING OPTIONS

### Photochemistry at Elevated Temperatures

Because of the significant difference in the specificity of the excitation process, and the fact that electronically excited molecules may react quite differently than ground-state molecules, the reaction products may differ when the same system is excited photochemically rather than thermally. Since increased temperature will reduce this specificity, there is usually no incentive to operate photochemical systems at elevated temperatures. There are also other factors that mitigate against using high temperatures. For example, absorbers well matched to the solar spectrum are usually rather complex molecules that may be expected to undergo increased degradation when the temperature is increased. In most fuel-producing photochemical systems, the absorber must survive repeated cycling if the process is to be cost effective.

Another factor that must be considered is the decrease in the limiting thermodynamic efficiency of all quantum converters with increasing temperatures. The limiting efficiency decreases approximately two percentage points per 50 K increase in temperature. Nonetheless, experimental results have been reported that show significant increases in yield with temperature for chemical systems operating well below the thermodynamic limit. In such cases, favorable kinetic effects are responsible for the observed increases in yield. Because real systems will almost certainly operate below the limiting efficiency, there may be advantages to operating water-splitting systems at temperatures above ambient.

### Thermochemical-Photochemical Hybrids

Pure solar thermochemical processes for water splitting receive the necessary driving energy as heat. Such processes are expected to have greater efficiencies because they use the solar spectrum more efficiently and are not subject to some of the losses inherent in quantum conversion (e.g., internal conversion).

Thermochemical water splitting can be carried out indirectly by a series of chemical reactions that constitute a closed cycle with respect to all species except water and its decomposition products, dihydrogen and dioxygen. Preliminary analyses indicate that some of the cycles have efficiencies as high as 40 to 45%.

In some cycles, at least one step is driven primarily by the input of electrical work. These so-called thermochemical-electrochemical hybrids are designed to eliminate a difficult processing step(s) or to close a cycle that includes a step that is thermally unworkable.

By analogy, it might be expected that a hybrid cycle could incorporate a photochemical step. However, hybrids of this type do not appear to be viable because of the low efficiency of solar photochemical processes.

### Coupled Systems

Haught has examined the efficiency of a system consisting of a quantum converter coupled to a thermal converter at a common temperature. Figure 1 shows the efficiency of such a system as a function of temperature. The efficiency of the quantum converter decreases with increasing temperature while that of the thermal converter increases. It is clear from Figure 2 that there is little incentive to couple the two converters in this fashion unless the quantum converter is significantly cheaper than the thermal device. In that case, a coupled system might be useful up to about 600 K.

As an alternative, the quantum converter could be operated at near ambient temperatures and the thermal converter at high temperatures. The shorter wavelengths of the solar spectrum would be used to drive a photochemical process in the quantum converter and the long wavelengths would be collected by the thermal converter. In this case, the quantum converter would produce chemically stored energy and the thermal converter would probably produce electricity. For example, the heliostats of a central receiver solar-thermal power plant might be made with a mirror coating that is highly reflective in the infrared, but highly transparent in the visible and near-ultraviolet. The quantum converter would be located beneath the mirrored surface.

### CONCLUSIONS AND RECOMMENDATIONS

The study effort was focused on: (1) the assessment of selected baseline systems for hydrogen production, and (2) the identification of the potential for improvement via options that differ from the baseline systems. Major conclusions pertaining to these two efforts are summarized below:

#### Baseline Systems for Hydrogen Production

- (1) Major improvements in photochemical conversion efficiencies in excess of the baseline values are required for economic viability.
- (2) Potential for plant cost reduction is limited and depends on finding low-cost substitutes for glass and reflective surfaces of collectors.

#### Potential and Options for Improvement

- (1) Multiple photon systems can potentially provide the required efficiencies in excess of target baseline values (~40% greater).

- (2) Novel solar collection concepts, such as a shallow solar pond with a thin photochemical reaction layer, can avoid the high cost of materials associated with the baseline systems and warrant further study.
- (3) Coupled systems, wherein the portion of the solar spectrum applicable to photochemical conversion is allowed to enter the reactor while the remainder is used to generate thermal energy, can potentially utilize hardware in a synergistic manner and warrant further study.

The pursuit of the above identified options having potential for improvement form the basis for the recommendations resulting from this effort. Key recommendations are to:

- (1) Pursue photochemical research leading toward identification of practical concepts utilizing efficient multiple photon conversion processes.
- (2) Investigate novel solar collection concepts such as a shallow solar pond that has potential for avoiding the high cost of materials associated with the baseline systems.
- (3) Investigate systems that can potentially utilize hardware in a synergistic manner, e.g., heliostats with surfaces that transmit a selected portion of the solar spectrum to drive a photochemical process in a reactor located beneath the surface while reflecting the remainder of the flux to the tower of a central receiver solar thermal power plant.



## SECTION I

### INTRODUCTION

#### A. BACKGROUND

Solar photochemical processes appear to be an attractive method for conversion of solar energy to fuels and chemicals because of the possibility of direct conversion of photon energy to chemical energy. Water splitting processes to produce dihydrogen (gaseous  $H_2$ ), such as those using essentially homogeneous photochemical reactions in solution and photoelectrolysis, have received the most attention. There is concern, however, that because of low efficiencies, these processes may suffer from high costs associated with the distribution of collector/reactors over large areas.

One method of reducing such costs is to use concentrated solar radiation. Although this may reduce the combined reactor and piping system costs, it will change the thermal and flux characteristics of the reactor. Because the limiting thermodynamic efficiency of photochemical processes increases with intensity, but decreases with temperature, reactor cooling may be required.

To guide research in the areas of fuel-producing solar photochemistry and photoelectrochemistry, it would be helpful to develop estimates of the engineering performance and costs even before the chemical details have been characterized. If, for example, the costs of distribution and recovery of materials strongly dominate the process, the chemical process details could be irrelevant to potential practicality.

#### B. OBJECTIVES AND SCOPE

The study is divided into two separate, but complementary, areas: (1) the engineering performance and costs of a commercial-scale dihydrogen-producing solar quantum conversion plant, and (2) the identification of potentially useful fuel-producing photochemical processes. Although these were generally separate and parallel tasks, there were interactions throughout the study. These interactions provided the necessary scientific background for the engineering analyses, and potential engineering constraints gave practical perspective to the review of photochemical processes.

The engineering assessment of a dihydrogen-producing solar quantum conversion plant was the focus of a companion report, "Solar Photochemical Process Engineering for Production of Fuels and Chemicals." In this report, the primary emphasis is on the current status of research on fuel-producing solar quantum conversion processes.

A general description of photochemical and photoelectrochemical processes for direct conversion of solar energy into storable chemical energy is given in Section II, together with a brief discussion of both limiting thermodynamic efficiencies and probable efficiencies for real systems. Section III provides a summary of the results of the engineering assessment which is described in greater detail in the companion report, mentioned above.

Sections IV and V are reviews of the current research pertinent to fuel-producing solar quantum conversion processes, both photochemical and photoelectrochemical. That review is the major focus of this report. Its purpose is to identify and assess candidate processes for potential production of fuels on a commercial scale. Section VI is a discussion of operating and systems options.

Finally, the conclusions from this study are summarized in Section VI, together with recommendations for further work.

## SECTION II

### SOLAR PHOTOCHEMISTRY

#### A. INTRODUCTION

Photochemical processes are among the options available for the production of fuels and chemicals from solar energy. They convert solar energy directly into chemical energy and can be classified as quantum converters in contrast to thermal converters which are essentially solar heat engines.<sup>1</sup> They are quantum converters because they are initiated by the electronic excitation of an absorber by photons of appropriate energy. The excitation process is a quantized event that requires photons with energies equal to, or in excess of, the threshold or band-gap energy ( $E_g$ ). In general, the band-gap energy is the minimum energy required to excite the absorber from its ground electronic state to the lowest allowed excited electronic state. It is usually large enough in magnitude that less than half of the solar spectrum is capable of initiating photochemistry.

Photochemical processes differ from thermal processes in a number of important aspects. In photochemistry, absorber molecules are selectively excited resulting either in their dissociation or their conversion to an electronically excited state. If the electronically excited state is sufficiently long-lived, it may react with suitable substrates or transfer energy to appropriate acceptor molecules with resultant chemical changes. In thermal processes, excitation is essentially non-specific, i.e., the average energies of all molecules present in the system are increased. Chemical reaction occurs if a sufficiently large fraction of reactant molecules acquire the necessary energy of activation. Thermal systems also differ in that the molecules involved in reaction almost invariably remain in their ground electronic states. Heating the system results in shifts in the translational, rotational, and vibrational energy distributions, but the energy available is usually not sufficient for electronic excitation. Because of the significant difference in the specificity of excitation, and the fact that electronically excited molecules may react differently than ground-state molecules, the reaction products may differ markedly when the same system is excited photochemically, rather than thermally.

The following are some general requirements for solar photochemical systems that produce fuels or chemicals:

- (1) The process should constitute a closed cycle with respect to all species except the feedstock and its decomposition products (e.g.,  $H_2O$ ,  $H_2$ , and  $O_2$  in the photochemical splitting of water).
- (2) They should operate over a wide band of the solar spectrum.

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<sup>1</sup>This includes thermochemical cycles which produce storable chemical energy.

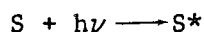
- (3) The quantum yield should be high.<sup>2</sup>
- (4) The product(s) should be easily separated, stored, and transported.
- (5) The materials of construction and the reagents involved must be inexpensive and relatively abundant.

Considering such factors as process chemistry and the cost and availability of feedstock, it seems unlikely that fuels will be produced on a large scale from feedstocks other than water, carbon dioxide, and dinitrogen (N<sub>2</sub>).

Most of the research related to development of solar photochemical processes for the production of fuels has focused on splitting water to produce dihydrogen. A brief description of both homogeneous photochemical and photoelectrochemical processes for water splitting is given in Section II-B and II-C. A discussion of the limiting thermodynamic efficiency of quantum conversion processes, including some remarks on the probable conversion efficiencies of real systems, follows in Section II-D.

## B. HOMOGENEOUS PHOTOCHEMICAL WATER SPLITTING

Direct solar photolysis of water to produce dihydrogen is not practical because of the large band-gap energy involved.<sup>3</sup> However, indirect photolysis is possible in the presence of an appropriate sensitizer. The sensitizer absorbs energy over a wide band in the solar spectrum<sup>4</sup> and uses that energy to drive a cyclic process, the net result of which is decomposition of water into dihydrogen and dioxygen. Absorption of photons by the sensitizer, typically present at low concentrations (10<sup>-4</sup> to 10<sup>-5</sup>M), results in its electronic excitation. The excited sensitizer (S\*) then transfers an electron with an appropriate quencher or relay, also present at relatively low concentrations. Depending upon the nature of the quencher, electron transfer may be either from or to S\*, i.e., via Equation (2-1) or (2-2).




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<sup>2</sup>The quantum yield is the number of molecules of product divided by the number of photons absorbed.

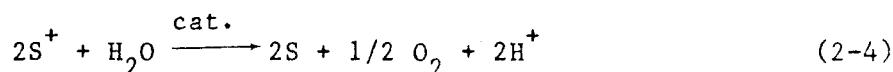
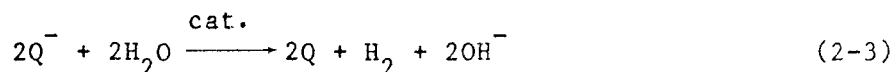
<sup>3</sup>Direct photolysis of water requires wavelengths less than 190 nm. Much less than 1% of the solar spectrum falls in that range.

<sup>4</sup>Ideally, the sensitizer should absorb strongly between 400 and 900 nm. Below 400 nm, the solar intensity is very low. Above 900 nm, the excitation energy is likely to be too low to drive the process.

or



Ideally, the products of this quenching then produce dihydrogen and dioxygen by redox reactions with water, such as Equation (2-3) and Equation (2-4), to complete the cycle. Because of the nature of its role in this process, the quencher is often referred to as an electron relay.



The process is illustrated schematically in Figure 2-1. Ideally, the photo-sensitizer and any other species required are completely recycled so that the only net chemistry is the decomposition of  $H_2O$  to  $H_2$  and  $O_2$  in stoichiometric amounts. Real systems are not likely to be completely closed. Side reactions will result in some loss of reagents; a major problem will be to hold such losses to an acceptable level.

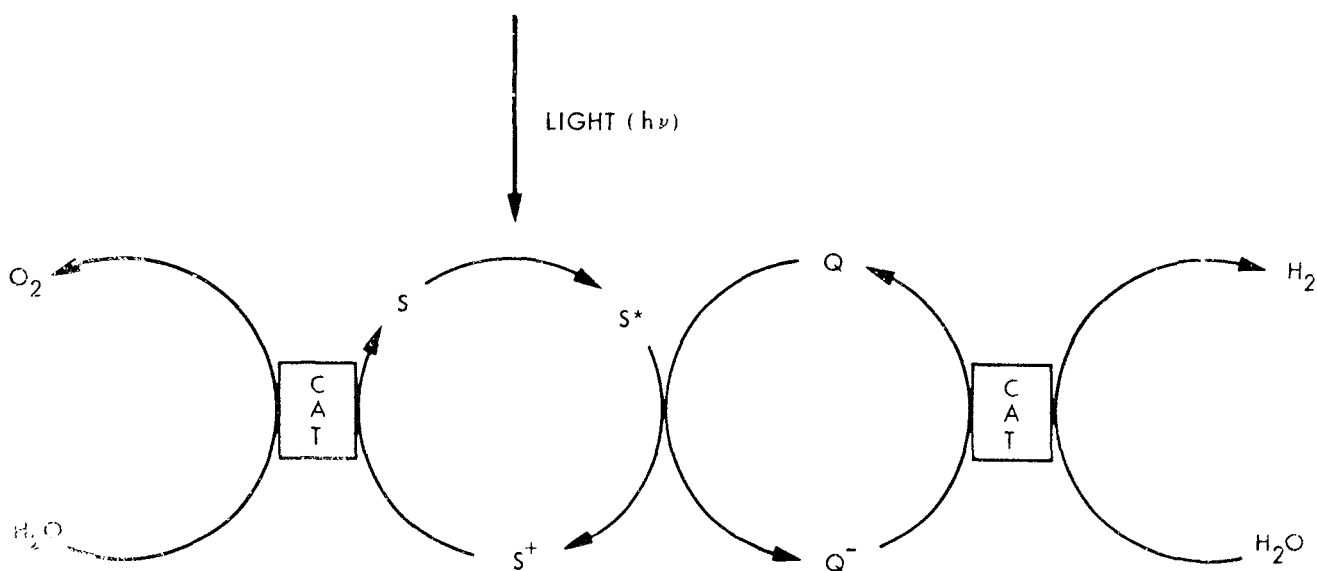


Figure 2-1. Schematic Diagram for Cyclic Photochemical Water Splitting

The process described above involves a single photosystem. Processes with two or more photosystems are also of interest because of their higher limiting thermodynamic efficiencies (see Section II-D).

The state of the art of homogeneous water splitting is reviewed in Section IV.

### C. PHOTOELECTROCHEMICAL PROCESSES

The distinguishing feature of photoelectrochemical processes is that the fuel-producing chemical reactions<sup>5</sup> occur at electrodes, one or both of which is an illuminated semiconductor. Illumination of the semiconductor results in excitation of electrons from the valence to the conduction band. The resulting electron-hole pairs separate in the electric field that is produced spontaneously at the semiconductor-electrolyte interface, and migrate to the electrode surfaces where the chemical reactions occur. Various cell configurations are possible. A schematic diagram of a photoelectrochemical cell with a single semiconductor electrode is shown in Figure 2-2. In such cells, the counter electrode is an inert conductor such as platinum or carbon. Photons absorbed at the photoelectrode provide the only energy input.

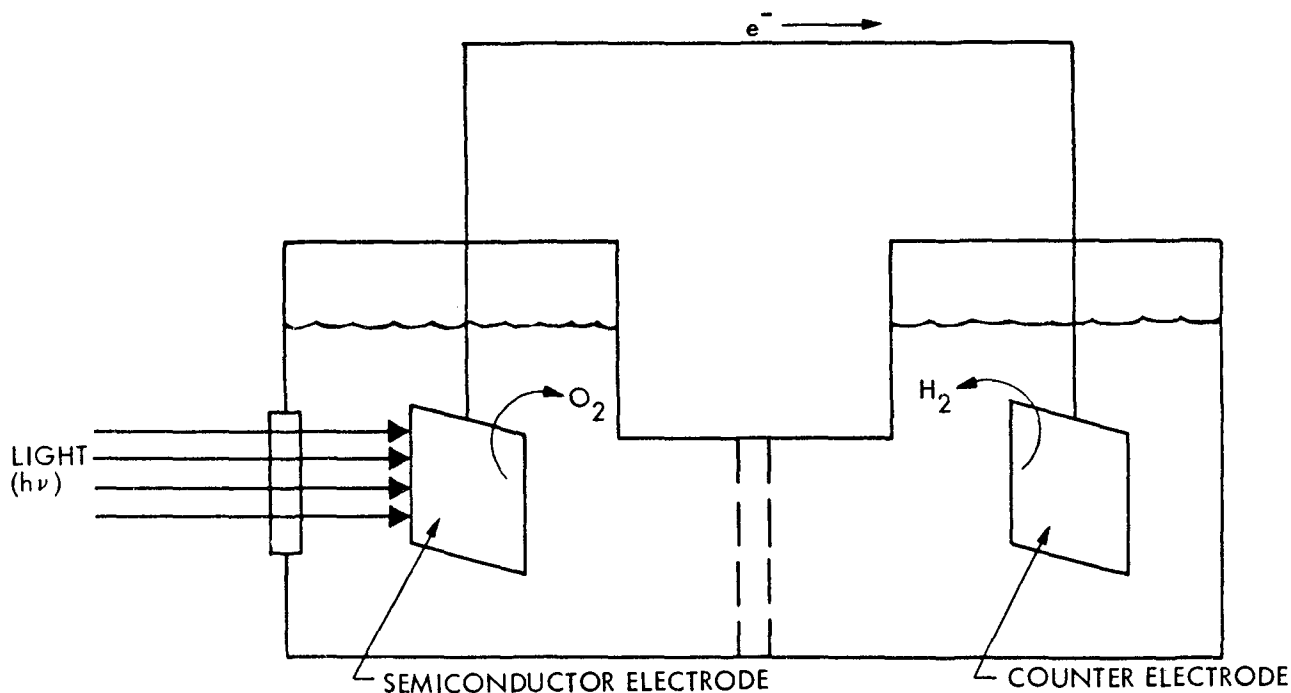


Figure 2-2. Photoelectrolysis Cell with a Single Semiconductor Electrode

<sup>5</sup>Photoelectrochemical devices may also be designed to convert solar photons directly to electricity. Such devices, usually referred to as photogalvanic cells, are not considered in this report.

The current state of the art of the photoelectrochemical processes is reviewed in Section V.

#### D. EFFICIENCY

##### 1. Limiting Thermodynamic Efficiency

Both thermodynamic and kinetic factors limit the efficiency with which solar energy can be converted directly to work and/or storable chemical energy. The limiting thermodynamic efficiency of such devices, usually classified as quantum converters,<sup>6</sup> has been examined by several investigators (References 1 through 10).

A schematic diagram of a solar quantum converter is shown in Figure 2-3. It is a threshold device because the energy conversion process is initiated by electronic excitation of an absorber, a quantized event. The minimum energy ( $E_g$ ) required for such excitation is called the threshold or band-gap energy, and only photons with energies equal to or greater than  $E_g$  can initiate the energy conversion process.

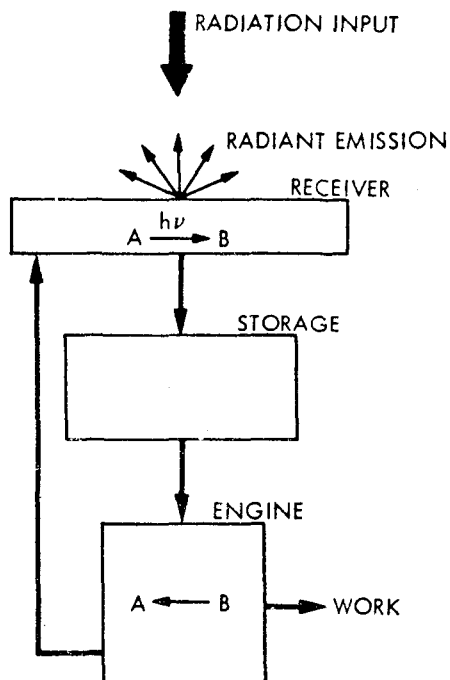


Figure 2-3. A Generalized Quantum Converter

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<sup>6</sup>Quantum converters are devices that convert radiant energy to work or chemical potential energy in a process initiated by the electronic excitation of the absorber, a quantized event.

The thermodynamic analysis usually involves a number of assumptions, among which are the following:

- (1) The converter is a perfect absorber; all photons with energy equal or greater than  $E_g$  are completely absorbed<sup>7</sup> and induce electronic excitation of the absorber with unit quantum yield.<sup>8</sup>
- (2) All photons with  $E \geq E_g$  are converted to the same amount of chemical energy; high energy photons generate no more chemical energy than low energy photons.<sup>9</sup>

Several approaches have been used to calculate the limiting thermodynamic efficiency,  $\eta_{QT}$ . One of the most general is due to Haught (Reference 9). His analysis is based on Planck's and Kirkoff's laws, the thermodynamic requirement that the entropy of an interacting system is a maximum at equilibrium, and the principle of detailed balance. These arguments will not be reproduced here, but Bolton, et al (Reference 10), have given an excellent review of the subject, including a number of different approaches to the derivation of  $\eta_{QT}$ . There is general agreement that the limiting thermodynamic efficiency for quantum converters with a single photosystem and unfocused sunlight is about 31% for AM 0<sup>10</sup> and 300 K.

Figure 2-4 shows the variation in  $\eta_{QT}$  with  $\lambda_g$ , the band-gap wavelength. The relatively low values for the limiting thermodynamic efficiency are inherent in the quantum nature of the conversion process and the consequences of the second law and, as such, are independent of the mechanistic details of the process. As Bolton, et al (Reference 10), have pointed out, "This limitation is thermodynamic and fundamental: it cannot be overcome by the choice of a different photosystem, use of catalysts, or any other strategem."

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<sup>7</sup>Complete absorption is assumed because this analysis is intended to yield the maximum thermodynamic efficiency.

<sup>8</sup>The quantum yield ( $\phi$ ) is the number of molecules of product (in this case, molecules of an electronically excited absorber) divided by the number of photons absorbed.

<sup>9</sup>This is equivalent to assuming rapid internal conversion of higher electronic states to the lowest excited state, which is assumed to be thermally equilibrated at the temperature of the photoconverter. There is considerable evidence to support such an assumption.

<sup>10</sup>AM signifies air mass. AM 0 corresponds to the insolation just outside Earth's atmosphere (i.e., air mass zero). AM 1 corresponds to the solar radiation at the Earth's surface with the sun at its zenith on a clear day.



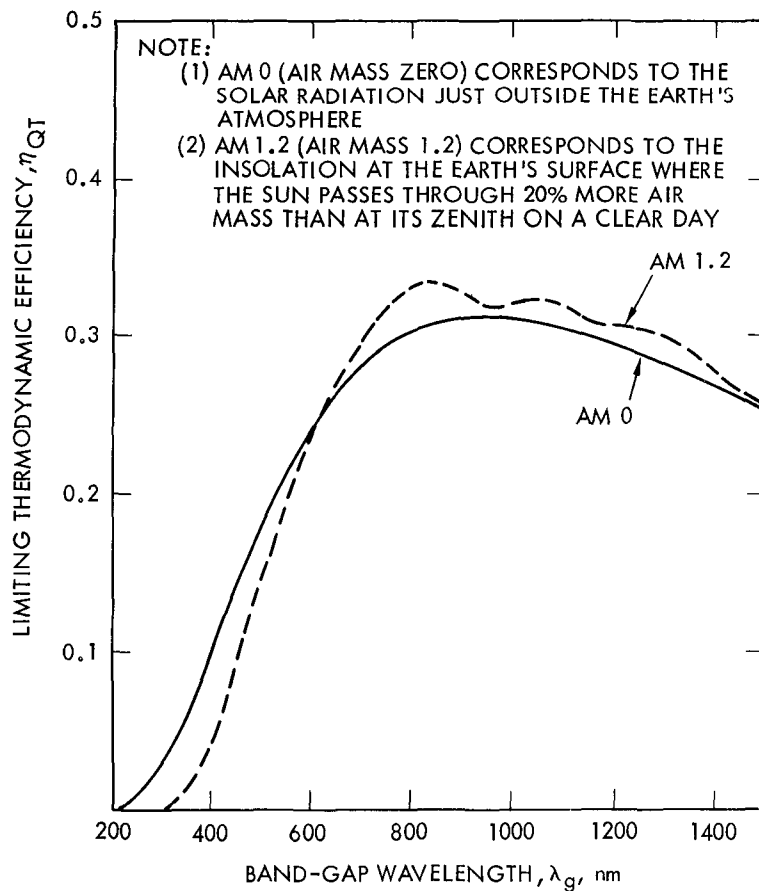


Figure 2-4. Limiting Thermodynamic Efficiency for an Ideal Quantum Converter as a Function of Band-Gap Wavelength

Figure 2-4 applies to quantum converters using a single photosystem operated at 300 K with unfocused sunlight. Haught (Reference 9) and Bilchak, et al (Reference 11), have examined the influence of both temperature and solar concentration on the limiting efficiency. The variations in  $\eta_{QT}$  with solar concentration for a single photosystem operated at AM 1.2, and various temperatures from 300 to 500 K, are listed in Table 2-1. The efficiency ( $\eta_{QT}$ ) increases by about two percentage points for each tenfold increase in intensity, and decreases by that same amount for each 50 K increase in temperature. These data reveal that the gain in efficiency, resulting from a tenfold increase in intensity, will be offset by a 50 K increase in temperature. Thus, if solar concentration is to be employed for the purpose of increasing efficiency, it will probably be necessary to cool the reactor. Solar concentration may have other advantages that would make it cost effective even without a significant increase in efficiency, e.g., reduction in the cost of the reactor.

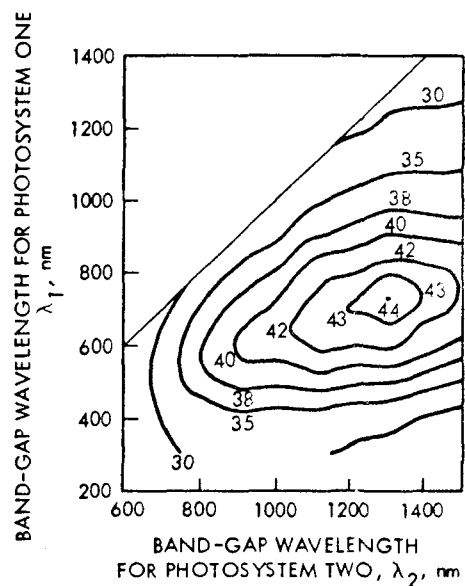
Table 2-1. Limiting Thermodynamic Efficiencies for AM 1.2 Solar Radiation at Various Intensities and Absorber Temperatures (Reference 11)  
( $\lambda_g = 840$  nm)

| Intensity,<br>suns | Absorber Temperature, K |      |      |      |      |
|--------------------|-------------------------|------|------|------|------|
|                    | 300                     | 350  | 400  | 450  | 500  |
| 1                  | 32.3                    | 30.2 | 28.1 | 26.1 | 24.0 |
| 10                 | 34.1                    | 32.3 | 30.5 | 28.7 | 26.9 |
| $10^2$             | 35.9                    | 34.4 | 32.8 | 31.3 | 29.8 |
| $10^3$             | 37.7                    | 36.5 | 35.2 | 34.0 | 32.7 |
| $10^4$             | 39.5                    | 38.5 | 37.6 | 36.7 | 33.7 |

The efficiency ( $\eta_{QT}$ ) can also be increased by using two or more separate photosystems involving different absorbers with different band-gap or threshold energies. Figure 2-5 shows contours of  $\eta_{QT}$  (as a percentage) as a function of  $\lambda_1$  and  $\lambda_2$  for a system with two absorbers subjected to AM 1.2 solar energy (Reference 6). One absorber absorbs all light with  $\lambda \leq \lambda_1$ ; the other absorbs all light with  $\lambda_1 < \lambda \leq \lambda_2$ . A maximum of  $\eta_{QT}$  of 44% is predicted for  $\lambda_1 = 830$  nm and  $\lambda_2 = 1320$  nm. Figure 2-6 is a schematic diagram for such a device that has been suggested by Bolton (Reference 7). Two photons are absorbed for each electron transferred in the overall reaction. D and A are the two absorbers (photosensitizers) which drive the water splitting reaction and N and M are charge-storage catalysts which permit oxidation of water to dioxygen and reduction of protons to dihydrogen in concerted redox reactions. The two photosystems are separated by a semipermeable membrane which permits transport of electrons and protons between photosystems. A real device of this type has not yet been developed.

## 2. Efficiencies of Real Systems

The efficiencies discussed in the previous paragraphs are limiting or ideal thermodynamic efficiencies. Real systems, producing chemically stored energy, will have significantly lower efficiencies. For example, the limiting values, discussed earlier, assume the absorber is ideal, i.e., all photons with  $\lambda \leq \lambda_g$  are absorbed. In real photochemical systems, the absorption characteristics of the photosensitizer are such that not more than 70 to 80% of these photons is likely to be absorbed. Also, not all of the photochemical products will be collected from the system. Collection efficiency is unlikely to be greater than 90%, especially when a gas is



NOTE:

AM 1.2 (AIR MASS 1.2) CORRESPONDS TO THE INSOLATION AT THE EARTH'S SURFACE WHERE THE SUN PASSES THROUGH 20% MORE AIR MASS THAN AT ITS ZENITH ON A CLEAR DAY

Figure 2-5. Efficiency Contours for a Quantum Converter Using Two Photosystems and Unfocused AM 1.2 Solar Energy

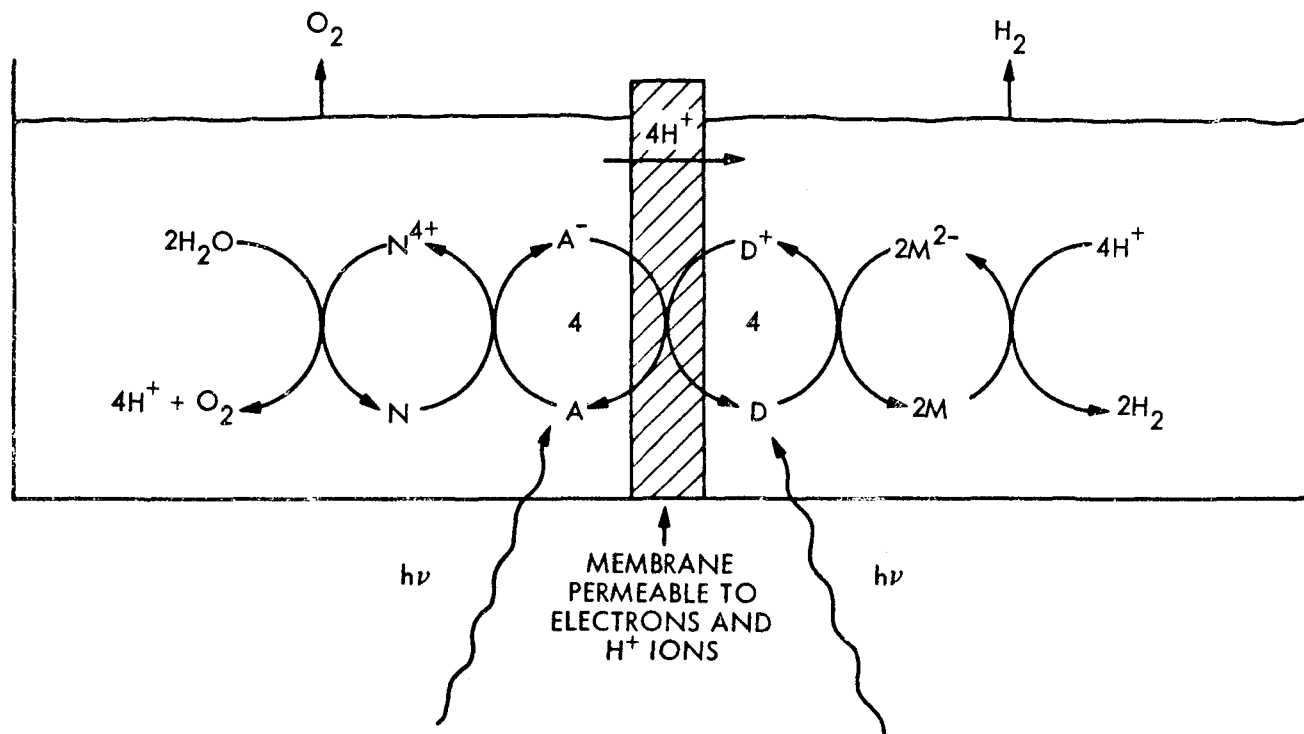


Figure 2-6. A Photochemical Scheme for Splitting Water Using Two Photosystems

generated in a liquid system. There are also kinetic limitations that reduce the efficiency of processes that store energy chemically. If the product is to be kinetically stable, there must be an energy barrier to prevent its back reaction (Figure 2-7). This energy barrier is provided at the expense of the excitation energy ( $E_g$ ). Bolton has estimated that this effect will reduce the limiting efficiency for a quantum converter using a single photosystem from about 31 to 21% (Reference 6). On the basis of these considerations, it seems unlikely that the overall efficiency of a real quantum converter of this type will exceed 12 to 15%.

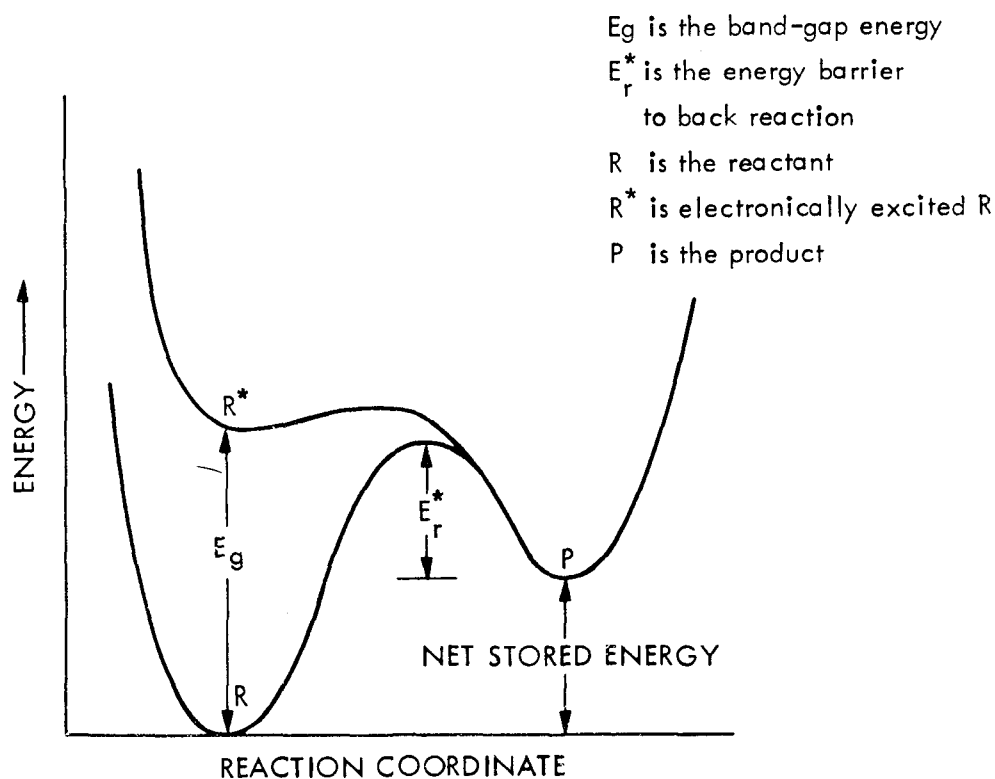


Figure 2-7. The Kinetic Barrier,  $E_r^*$

## SECTION III

### ENGINEERING ASSESSMENT OF SOLAR PHOTOCHEMICAL DIHYDROGEN PRODUCTION

#### A. APPROACH AND METHODOLOGY

The purpose of this phase of the study is to identify engineering requirements associated with solar photochemical systems and to scope the costs of a prototype system for producing fuels on a commercial scale. The results are presented in greater detail in a companion report. Here the major findings of that analysis are summarized to provide perspective for the discussion of the state-of-the-art review of fuel-producing solar quantum conversion processes that is the major topic of this report.

For purposes of the engineering assessment, the photochemical process is specified only to the extent that it is assumed to produce dihydrogen from water. The nominal plant size chosen was 25,000 scmd (850,000 scfd) with the product gas, dihydrogen, at a pressure of 50 atm. The analysis is intended to provide a reasonably clear indication of the engineering design limitations on the development of solar-photochemical systems for large-scale production of fuels. Major factors influencing performance and costs include reaction efficiency, solar concentration ratio, and the operating temperature and pressure. Parametric studies of these factors were made to permit an estimate of the range of operating conditions that can be used and the quality of solar concentrators needed, if any.

Two baseline collector/reactor designs were chosen for this study. One involves a flat-plate, non-concentrating collector/reactor and the other is a cylindrical parabolic trough with a solar concentration ratio of 43. Both baseline systems were analyzed to include realistic performance projections and a broad scoping of costs including: collector/reactor, fluid piping, peripheral equipment, temperature control of the reactor (if necessary), and balance of plant (BOP). A design constraint used throughout this engineering feasibility study was that the system components should be based on currently available technology and equipment whenever possible.

#### B. NON-CONCENTRATING SYSTEM

The major design parameters for the baseline non-concentrating system are summarized in Table 3-1.

This baseline system is composed of a field of flat-plate collectors. The photochemically reactive solution is pumped to the collector/reactors where sunlight initiates the reaction, generating dihydrogen and dioxygen gas at essentially atmospheric pressure. The dihydrogen gas, at approximately 54°C (130°F), is separated and transported by another piping network to a gas cleanup and compression unit where the pressure is raised from 1 atm to a normal gas pipeline pressure of 50 atm. For the baseline plant size of

Table 3-1. Characteristics of the Baseline Non-Concentrating System

| Characteristics           | Selected Conditions         |
|---------------------------|-----------------------------|
| Feedstock                 | Water                       |
| Product                   | Dihydrogen Gas              |
| Operating Pressure        | 1 atm                       |
| Operating Temperature     | 54°C (130°F)                |
| Nominal Plant Size        | 25,000 scmd                 |
| Overall System Efficiency | 10.3%                       |
| Nominal Collector Area    | 120,000 m <sup>2</sup>      |
| Annual Solar Flux         | 2430 kWh/m <sup>2</sup> /yr |

25,000 scmd, the collector field area required is 120,000 m<sup>2</sup>, assuming an overall plant efficiency of approximately 10%.

The final conceptual design of the collector/reactor units is essentially two glass sheets, 2.54 cm (1 in.) apart, surrounded by an extruded aluminum frame (Figure 3-1). Collector/reactor units, 1.2 x 3.66 m (4 x 12 ft), are combined together in gangs of 12 to give modules that are 14.63 x 3.66 m (48 x 12 ft). Figure 3-2 shows the field layout and piping connections for 1/8 section of the field. The total field is shown in Figure 3-3.

The central location for the collection of the dihydrogen gas from the field includes a compressor station to compress the gas to 50 atm, which is the typical pressure for pipeline transmission. The total field area for the 25,000 scmd plant is about  $3.08 \times 10^6$  m<sup>2</sup> (83 acres). This includes the collector/reactor area, maintenance corridor area, and field perimeter area.

Total capital cost for such a plant is \$19,454,000. The cost breakdown given in Table 3-2 reveals that the collector/reactor and BOP are the major cost components.

Balance of plant includes a variety of costs such as architects and engineers (A&E) fees, construction management fees, contingencies, buildings, roads, parking lots, fencing, vehicles, collector washing equipment, and spares.

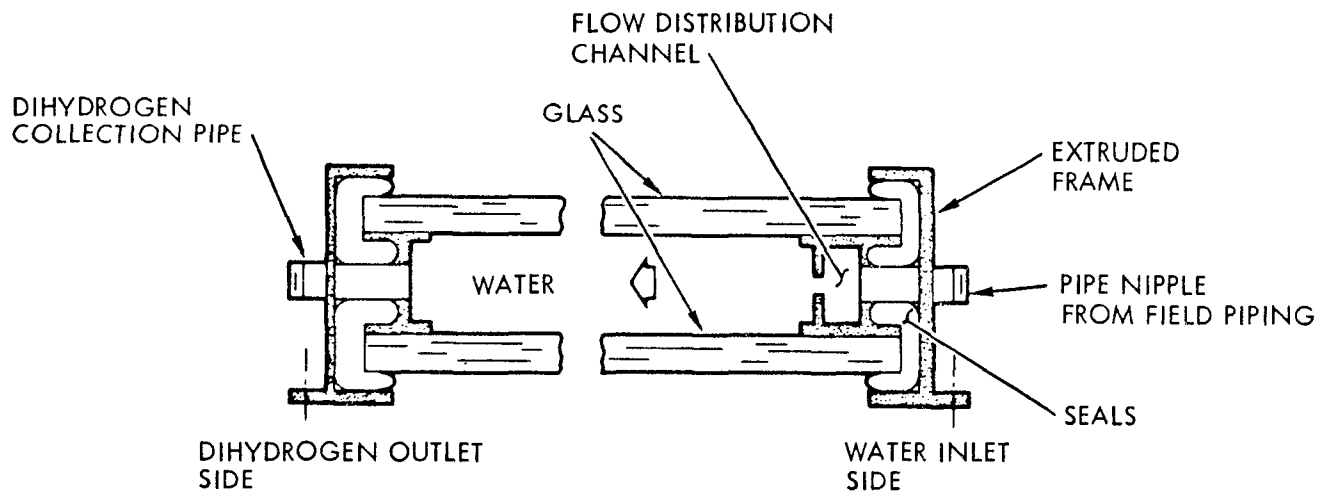


Figure 3-1. Baseline Flat-Plate Collector/Reactor Configuration

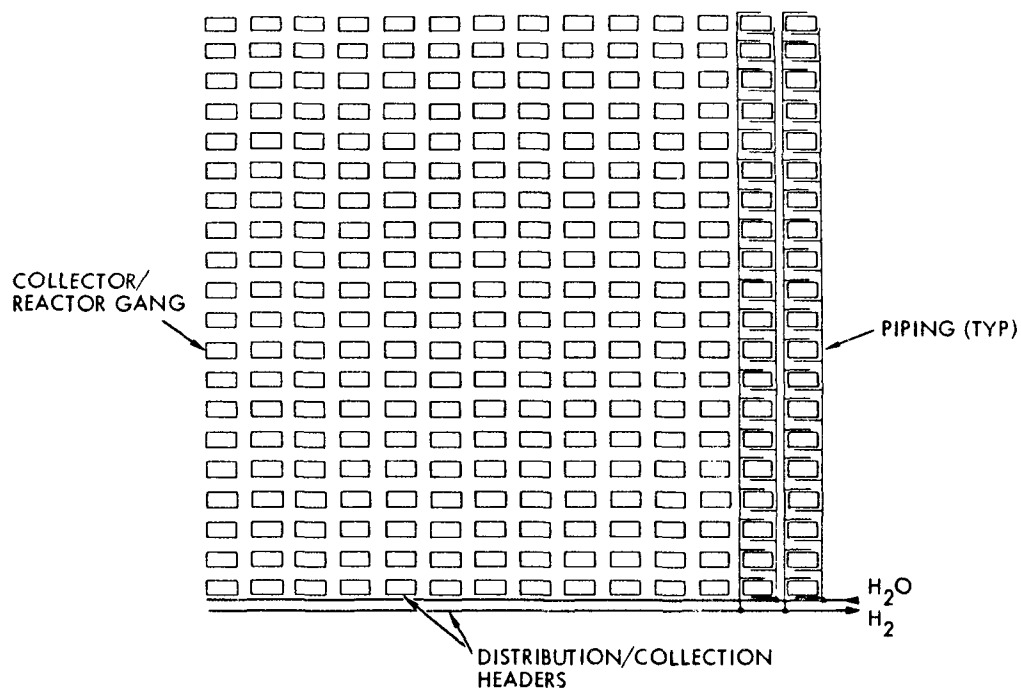


Figure 3-2. Flat-Plate Field Layout Showing Piping Connections

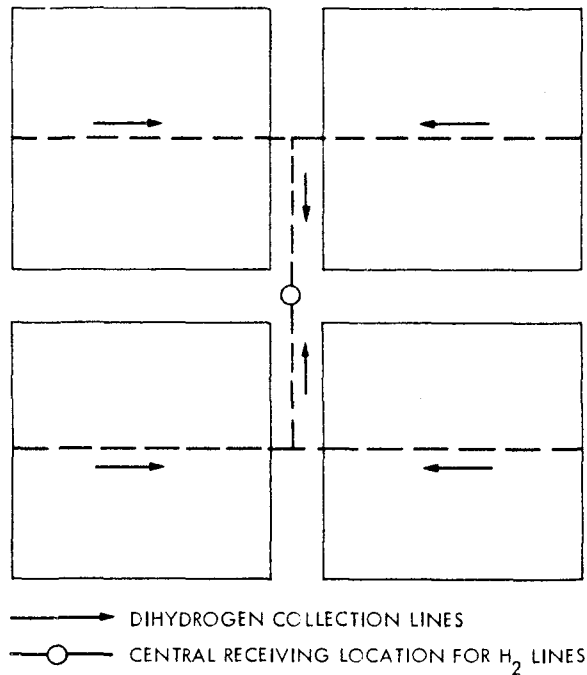


Figure 3-3. Plant Layout for Baseline Flat-Plate System

Table 3-2. Capital Cost Breakdown for Baseline Flat-Plate System

| Subsystem                    | Cost, \$ x 10 <sup>3</sup> |
|------------------------------|----------------------------|
| Collector/Reactor            | 7,096                      |
| Piping and Collector Support | 1,305                      |
| Field Piping                 | 1,483                      |
| Gas Compression              | 1,160                      |
| Balance of Plant             | 8,410                      |
| Total                        | 19,454                     |



Capital costs were translated into energy costs using an economics model widely used in solar energy studies (Reference 12). Fixed charge rates of 0.20 and 0.30 were used, and operating and maintenance was assumed to be 2% of the plant capital cost. The fixed charge rate of 0.20 is typical of utility industry economics, and 0.30 typical of chemical industry economics. A photochemical fuel-producing plant is likely to involve a fixed charge rate in this range. A plot of energy costs as a function of the overall system efficiency is shown in Figure 3-4. For the baseline case of 10.3% overall efficiency, the energy cost ranges from \$34 to \$56/10<sup>6</sup> kJ (\$36 to \$59/10<sup>6</sup> Btu).

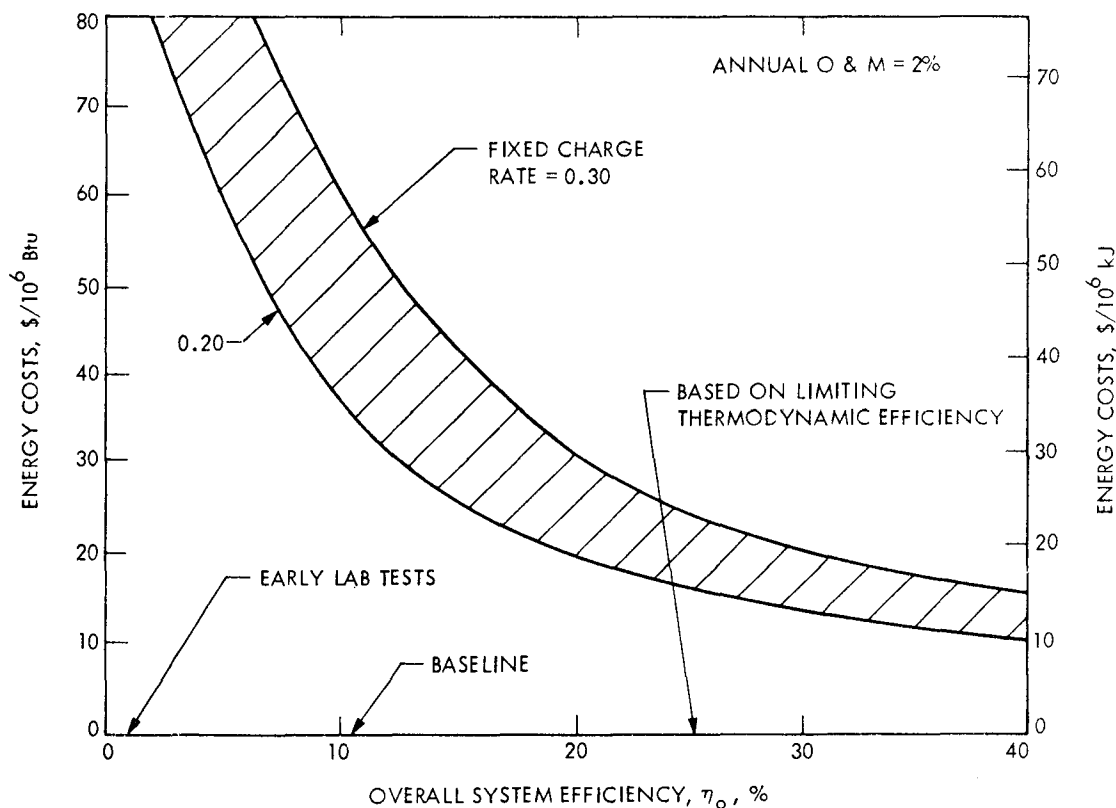


Figure 3-4. Cost of Dihydrogen from the Baseline Flat-Plate System

### C. CONCENTRATING SYSTEM

Because of the relatively low efficiency of 10% assumed for the baseline flat-plate system, energy costs are quite high. The low efficiency results in the distribution of collector/reactors over a large area with associated increases in liquid and gas transport piping and BOP items. One method of reducing these costs might be the use of concentrated solar radiation. Increasing the concentration ratio increases the limiting thermodynamic efficiency of the quantum conversion process, however, increased operating temperatures will tend to decrease efficiency. In the baseline design, collector/reactor cooling is employed to keep reactor temperature at 100°C or less.

After considering several concentrating collector types, a parabolic trough collector was selected for the baseline case because of its moderate concentration range and its commercial availability. The major design parameters for the baseline concentrating system are contrasted with those of the baseline flat-plate system in Table 3-3. In both cases, 25,000 scmd of dihydrogen is produced at a pressure of 50 atm. The parabolic trough collectors has a baseline concentration ratio (CR) of 43 and overall system efficiency is 11.6%, a 12.6% increase over the non-concentrating system.

The parabolic trough collector used for a baseline in this study is similar to the one shown in Figure 3-5. The glass receiver tube, located at the focal line of the concentrator, contains the photochemical reagents. Dihydrogen gas is separated and collected by a field piping network. The baseline collector chosen is 6.1 m (20 ft) long with an aperture of 2.1 m (7 ft) and a rim angle of 90 deg. The concentration of solar energy on the receiver tube will cause the photochemical solution temperature to rise. It is estimated that, if left uncooled, the photochemical reactor could reach temperatures in excess of 250°C (482°F).

Various methods of cooling the photochemical layer were considered. The use of exterior filters (or reflective coatings) on the glass receiver tube could reduce the infrared (IR) load on the receiver and possibly eliminate or substantially reduce the need for active cooling. A commercially available IR

Table 3-3. Comparison of the Baseline Non-Concentrating and Concentrating Systems

| Characteristics           | Non-Concentrating           | Concentrating               |
|---------------------------|-----------------------------|-----------------------------|
| Feedstock                 | Water                       | Water                       |
| Product Gas               | Dihydrogen                  | Dihydrogen                  |
| Operating Pressure        | 1 atm                       | 1 atm                       |
| Operating Temperature     | 54°C (130°F)                | 29°C (84°F)                 |
| Nominal Plant Size        | 25,000 scmd                 | 25,000 scmd                 |
| Photochemical Efficiency  | 12.9%                       | 14.6%                       |
| Overall System Efficiency | 10.3%                       | 11.6%                       |
| Nominal Collector Area    | 120,000 m <sup>2</sup>      | 125,000 m <sup>2</sup>      |
| Annual Solar Flux         | 2430 kWh/m <sup>2</sup> /yr | 2150 kWh/m <sup>2</sup> /yr |
| Concentration Ratio       | 1                           | 43                          |

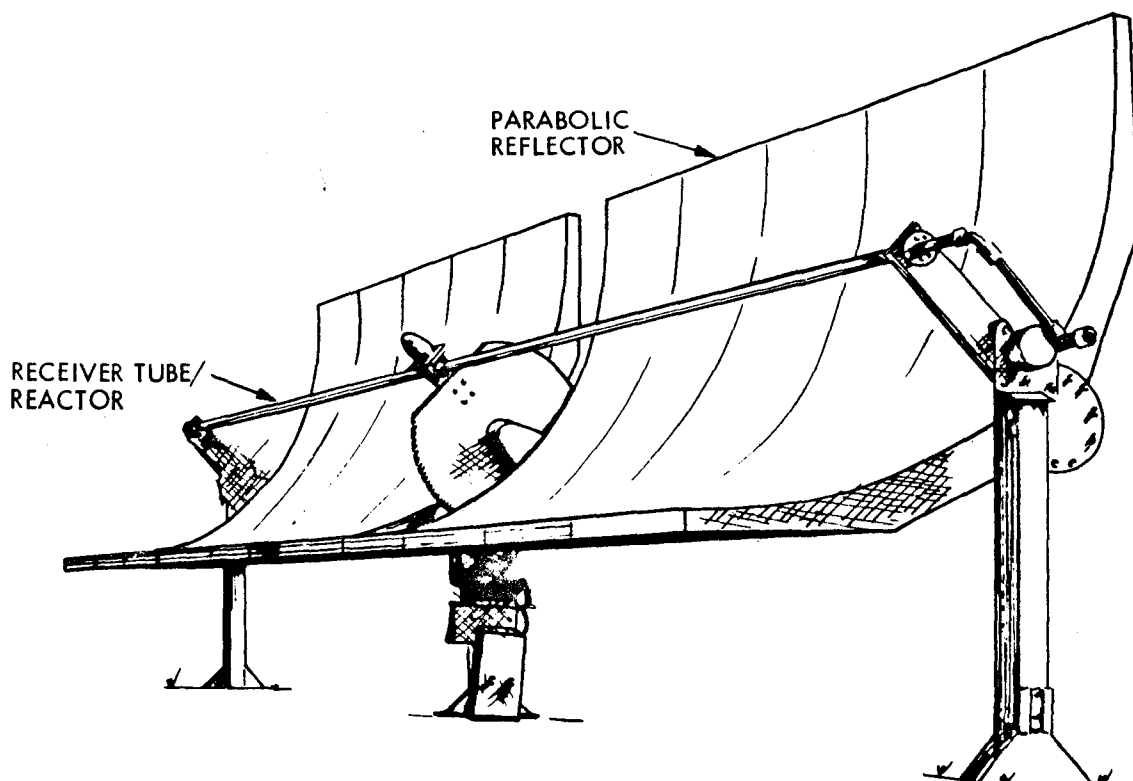


Figure 3-5. Parabolic Trough Collector/Reactor

reflective coating was found which exhibits relatively high transmission (78%) in the visible and high reflectivity in the IR region (90% reflectance for wavelengths greater than  $2\mu\text{m}$ ). However, it is expected to cost two-to-three times as much as uncoated glass and, although the thermal load is decreased by about 50%, the dihydrogen production is also decreased by 38% because of transmission losses. Thus, the use of available IR reflective coating is not economically attractive at this time.

Another type of system studied for temperature reduction of the photochemical layer was an active cooling method using water as the coolant. A cylindrical receiver geometry with two concentric tubes is employed. Two different arrangements are possible. The first possibility is to place the photochemical solution in the inner tube surrounded by the coolant fluid in the annular region, i.e., front-side cooling. The second possibility for active cooling is to place the water coolant in the inner tube, or core region, while the photochemical layer is located in the annular region, i.e., core cooling.

Thermal loads are essentially identical for core and front-side cooling because the total water coolant and photochemical solution thicknesses remain the same. However, thermal loads in the two zones are different. From the analyses of thermal loads to be removed, there would seem to be no major differences between front-side cooling and core cooling. The deciding factors may be product gas separation design considerations and/or second order photochemical effects factors not considered in this study.

The baseline collector/receiver geometry chosen incorporates a 5.1-cm (2-in.) glass tube concentric with a 2.5-cm (1-in.) tube with front-side cooling and a 2.1-m (7-ft) aperture, giving a concentration ratio of 42.8. This geometry is quite similar to the commercially available parabolic trough collectors illustrated in Figure 3-5. Modifications include the design of the receiver tube, which now must serve as the photochemical reactor with cooling, and the addition of a heat rejection loop on the back side of the trough.

Total system capital costs are \$48,187,000, as shown in Table 3-4. The dominant cost item for the concentrating system is the collector/reactor costs which account for 64% of the overall cost. Balance of plant amounts to 28%, while coolant equipment, field piping, and compressors amount to minor percentages. Energy costs (using the same economics model used for the baseline non-concentrating system discussed previously) are given in Figure 3-6 as a function of overall system efficiency.

Comparison with the flat-plate system (see Figure 3-4) shows that, for the baseline concentrating system chosen, energy costs are two-to-three times those for the non-concentrating system, depending on the fixed charge rate used. For the baseline system overall efficiency of 11.6%, the energy cost would be from \$94 to \$141/10<sup>6</sup> kJ (\$99 to \$149/10<sup>6</sup> Btu). This dramatic difference in energy costs can almost completely be attributed to the higher cost for the collection system (the tracking parabolic trough collectors).

Table 3-4. Capital Cost Breakdown for the Concentrating System

| Subsystem         | Cost, \$ x 10 <sup>3</sup> |
|-------------------|----------------------------|
| Collector/Reactor | 30,658                     |
| Coolant Equipment | 2,170                      |
| Field Piping      | 553                        |
| Gas Compressors   | 1,160                      |
| Balance of Plant  | 13,646                     |
| Total             | 48,187                     |

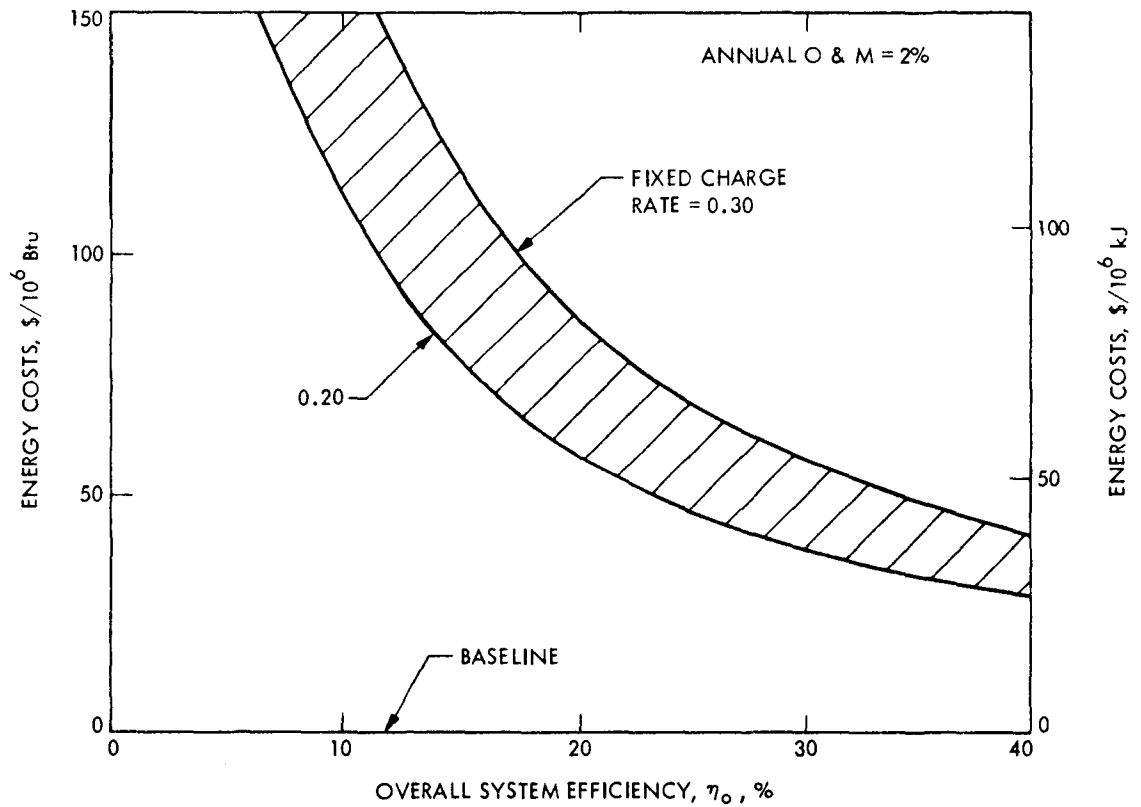


Figure 3-6. Cost of Dihydrogen from the Baseline Concentrating System

Any small advantage gained in the photochemical efficiency due to increased concentration is lost because of much higher costs for collection and lower annual energy collection efficiency. The latter of these is a result of the inability of the concentrating system to use the diffuse component of solar radiation. The basic problem is that the baseline collector chosen is a sophisticated device designed to produce high temperatures. However, in photochemical applications, the refined optics and sophistication to produce such high temperatures are counterproductive. It may prove better to employ a less optically sophisticated design using less costly materials. However, lowering the costs of the collector/receiver to a level competitive with non-concentrating systems may prove to be very difficult.



## SECTION IV

### SOLAR FUEL-PRODUCING PHOTOCHEMICAL PROCESSES: STATE OF THE ART

#### A. INTRODUCTION

Research related to production of fuels using solar photochemical processes has focused almost exclusively on splitting water to produce dihydrogen. Essentially, all of this research has been at a very fundamental level and no process has yet been identified that is suitable for sustained production of dihydrogen on a commercial scale. The major constraint is low conversion efficiency, typically, a few percent or lower. Research is currently aimed primarily at understanding the process mechanism in sufficient detail to suggest modifications that might lead to increased conversion efficiency.

Section IV-B is devoted to homogeneous water splitting processes that involve a single photosystem, i.e., there is only one photon absorbing species and, hence, a single band-gap energy for the system. Multiple photosystem processes, which involve more than one absorbing species each with its own band-gap energy, are discussed in Section IV-C. These processes have higher limiting thermodynamic efficiencies than those that involve a single photosystem.

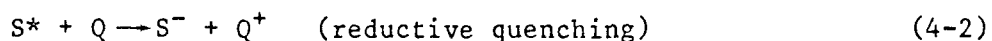
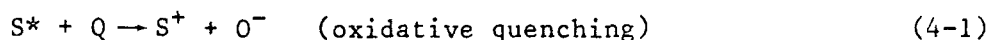
#### B. HOMOGENEOUS WATER SPLITTING PROCESSES USING A SINGLE PHOTOSYSTEM

As noted earlier, direct photodecomposition of water to produce dihydrogen is not practical with solar radiation because of the large band-gap energy involved.<sup>11</sup> However, indirect photolysis is possible with an appropriate sensitizer. The sensitizer absorbs energy over a wide band in the solar spectrum<sup>12</sup> and uses that energy to drive a cyclic photoredox process, the net result of which is decomposition of water into dihydrogen and dioxygen. Absorption of photons by the sensitizer, typically present at low concentrations ( $10^{-4}$  to  $10^{-5}$  M), results in its electronic excitation. Excited sensitizer,  $S^*$ , then transfers an electron with an appropriate quencher or relay, also present at relatively low concentrations. Depending upon the nature of the quencher, electron transfer may be either from or to  $S^*$ , i.e., quenching may be either oxidative or reductive.

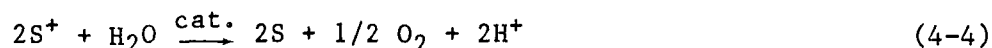
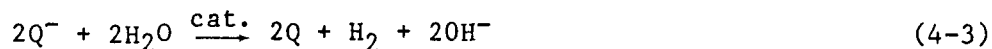
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<sup>11</sup>Direct photolysis of water requires wavelengths less than 200 nm and, hence, much less than one percent of the solar spectrum is available.

<sup>12</sup>Ideally, a sensitizer should absorb strongly between 400 and 900 nm. Below 400 nm, the solar intensity is very low and above 900 nm, the excitation energy is likely to be too small to drive the process.



The products of the quenching reaction then produce dihydrogen and/or dioxygen by redox reactions with water such as (4-3) and (4-4). Because of the nature of its role in this process, the quencher is often referred to as an electron relay. If a single photosystem is involved, there is only one absorber (sensitizer) species with a single band-gap energy. (Systems with multiple photosystems are discussed in IV-C.)



Reaction (4-3) requires two electrons per molecule of  $H_2$  produced and reaction (4-4) requires concerted action of four holes per molecules of  $O_2$ . Since the redox reagents ( $S^+$  and  $Q^-$ , in this case) usually only exchange one electron per molecule, some method of charge accumulation is required. Colloidal platinum appears to be the best charge-storage catalyst<sup>13</sup> for production of  $H_2$ , and ruthenium oxide,  $RuO_2$ , is preferred for production of  $O_2$ . In addition to storing charge, these substances facilitate the formation of the gaseous products.

Complexes of transition metals with appropriate organic ligands, such as the polypyridines, have been widely used to sensitize photochemical water splitting. These complexes absorb strongly in the visible to produce electronically excited states which possess favorable lifetimes and redox properties.<sup>14</sup> The most frequently employed sensitizer of this type is tris (2,2'-bipyridine) ruthenium (II) cation, hereafter written as  $Ru(bpy)_3^{2+}$ .

Metalloporphyrins, such as Zn meso-tetra (N-methyl-4-pyridal) porphine (see Figure 4-1) (References 16 through 23) and porphyrin derivatives, such as proflavin (References 24 and 25), have also been used to photosensitize water splitting. Gray (References 26 and 27) has employed dinuclear, metal-to-metal-bonded bridge compounds such as the dimeric rhodium (I) complex with four 1,3-diisocyanopropane ligands as bridges. The prophyrins are attractive sensitizers because they absorb over a very wide band in the solar spectrum. Some can absorb up to 50% of the incident solar energy.

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<sup>13</sup>Recent work by Matheson, Lee, and Meisel (Reference 13) indicates that Pt may act as a storage site for hydrogen atoms rather than electrons.

<sup>14</sup>Balzani and Scandola (Reference 14) and Sutin and Creutz (Reference 15) have discussed the properties of ideal sensitizers.



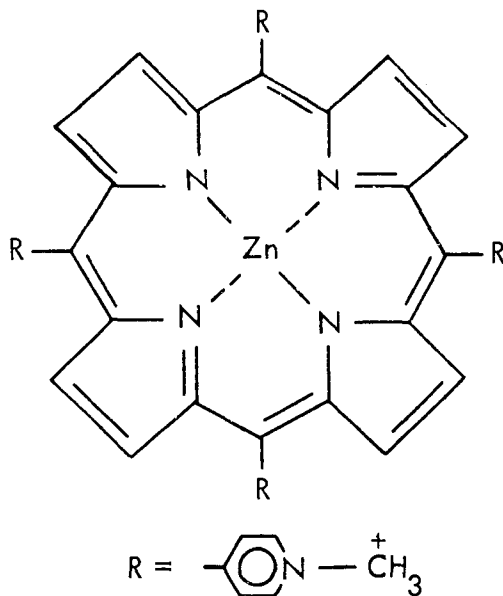
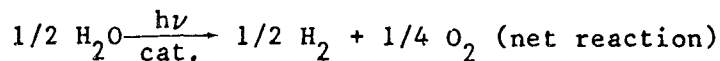
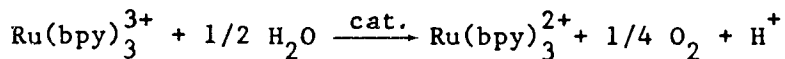
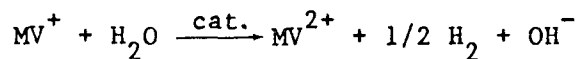
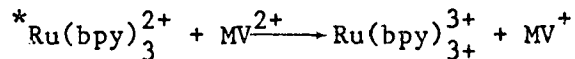
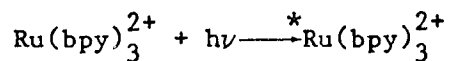


Figure 4-1. Structure of Zn (II) Meso-Tetra (N-Methyl-4-Pyridyl)

The viologens, particularly methyl viologen (N,N-dimethyl-4,4'-bipyridium cation, hereafter written as  $MV^{2+}$ ), are the most widely used quenchers. Other species, such as  $Rh(bpy)_3^{3+}$  (References 28 through 30),  $Eu^{3+}$ ,  $V^{3+}$  (References 31 and 32), and  $Fe^{2+}$  (References 21 through 33) have also been employed, but they are less efficient than the viologens.

### 1. Cyclic Processes

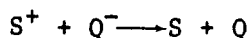
If the water-splitting process is to be cyclic, both sensitizer and quencher must be regenerated. The following is an example of such a cycle:



Photodecomposition of water to produce both dihydrogen and dioxygen in a cyclic process has met with only limited success. Kalyanasundaram and Grätzel obtained both  $\text{H}_2$  and  $\text{O}_2$  from aqueous solutions using the system described above, i.e., with  $\text{Ru}(\text{bpy})_3^{2+}$  as sensitizer, methylviologen as quencher, and  $\text{RuO}_2$  and protected colloidal Pt as catalysts (Reference 34). They observed a quantum yield for production of  $\text{H}_2$  of only  $1.5 \times 10^{-3}$  and production of  $\text{H}_2$  stopped after a few hours of irradiation. Buildup of  $\text{O}_2$  in the system leads to reoxidation of the reduced form of methylviologen, thereby lowering the yield of  $\text{H}_2$ . At sufficiently high concentration of  $\text{O}_2$ , production of dihydrogen ceases.

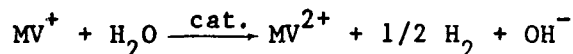
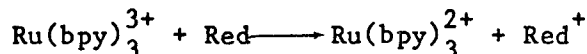
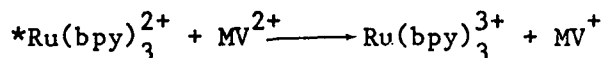
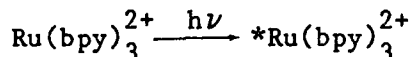
## 2. Sacrificial Reagents

One of the major reasons for the low conversion efficiencies of cyclic photoredox processes, such as those discussed in Section IV-B-1, is the rapidity of the non-productive back reaction between charge pairs, i.e.:



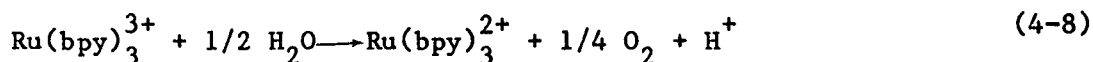
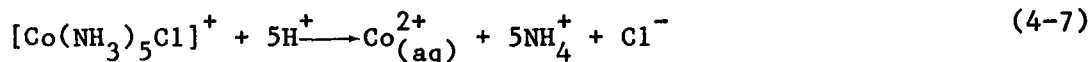
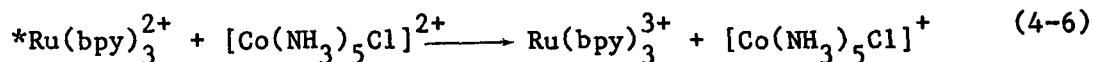
One strategy for inhibiting this charge-recombination reaction involves the introduction of a sacrificial reagent. The sacrificial reagent undergoes an irreversible reaction with either  $\text{S}^+$  or  $\text{Q}^-$ , leaving the unscavenged species,  $\text{Q}^-$  or  $\text{S}^+$ , free to produce either  $\text{H}_2$  or  $\text{O}_2$  via (4-3) or (4-4).

Mild reducing agents, such as ethylenediaminetetraacetic acid (EDTA) and triethanolamine (TEOA), are effective sacrificial reagents if dihydrogen is the desired product. As an example, consider a system in which  $\text{Ru}(\text{bpy})_3^{2+}$  is the sensitizer and methylviologen ( $\text{MV}^{2+}$ ) is the quencher or electron relay. In the presence of the sacrificial reagent, Red, the photoredox process proceeds as follows:



Grätzel, et al (Reference 35), report a quantum efficiency of about 13% for the above process with EDTA as sacrificial reagent. In the absence of a sacrificial reagent, the quantum yield of  $H_2$  is only about 0.1%. A still higher quantum efficiency, 30%, has been reported for a system in which a zinc porphyrin is sensitizer,  $MV^{2+}$  is quencher, and EDTA is the sacrificial reagent (Reference 19).

Formation of  $O_2$  in the presence of sacrificial reagents has also been studied. Shafirovich, et al, have reported generation of  $O_2$  from aqueous solutions using  $Ru(bpy)_3^{2+}$  as sensitizer, and  $[Co(NH_3)_5Cl]^{2+}$  as a sacrificial reagent (Reference 36). In this case, the sacrificial reagent quenches excited sensitizer via a rapid irreversible reaction (4-6) to form  $Ru(bpy)_3^{3+}$  which oxidizes water by reaction (4-8). The proposed mechanism includes the following steps:



$[Co(NH_3)_5Cl]^+$ , formed in the quenching step, is rapidly and irreversibly converted to stable  $Co_{(aq)}^{2+}$ , thus permitting  $Ru(bpy)_3^{3+}$  to escape back reaction and, subsequently, produce  $O_2$ .

Borgarello, et al, have also reported formation of  $O_2$  using zinc meso-tetra (N-methyl-4-pyridyl) porphine ( $ZnTMPyP^{4+}$ ) as sensitizer with electron acceptors, such as iron (III), in the presence of a  $RuO_2$ - $TiO_2$  catalyst (Reference 33). Harriman, et al, however, were unable to generate  $O_2$  from systems of this type (Reference 21). The major difference in these two studies was the preparation of the  $RuO_2$ - $TiO_2$  catalyst. Since this system probably involves injection of electrons into the conduction band of the semiconductor, it is more appropriately discussed in Section IV-C.

When a sacrificial reagent is employed, the system is no longer cyclic and either, but not both, dihydrogen or dioxygen may be produced. The use of a sacrificial reagent would be unacceptable in a practical system for producing  $H_2$  on a large scale unless a very inexpensive and abundant species were

available.<sup>15</sup> Nonetheless, studies of these systems are an important source of kinetic data and a valuable method of testing and optimizing the various components of photoredox processes. For example, systems such as the one outlined above have been used to evaluate charge-storage catalysts for dihydrogen formation.

### 3. Organized Assemblies

Non-productive charge recombination can also be inhibited via a biomimetic approach that involves organized assemblies of molecules such as micelles and vesicles. In natural photosynthesis, charge recombination is inhibited by the separation of charged pairs in the potential field developed in highly specialized thylakoid membranes.

Micelles are approximately spherical aggregates of 50 to 100 molecules that are readily formed by addition of a surfactant to an appropriate solvent. Surfactant molecules have an ionic or polar head and a non-polar hydrocarbon tail which is typically 8 to 20 carbon atoms in length. In water, such molecules form aggregates or micelles, about 300 to 600 nm in diameter, in which the polar or ionic head groups are on the surface in contact with water (see Figure 4-2). Micelles form over a relatively narrow range of surfactant concentration called the critical micelle concentration.

If a hydrophobic substrate is present in an aqueous solution containing micelles, it will undergo rapid solubilization into the interior of the micelle.<sup>16</sup> Hydrophilic substrates, however, will remain in the bulk solution. If one of the members of a charge pair is sufficiently more hydrophobic than the other, the pair will be physically separated from one another and the surface potential on the micelle will inhibit charge recombination.

Several sensitizer-quencher combinations, including various geometric arrangements of sensitizer and quencher, have been studied in micellar systems (References 40 through 55). The application of this method is best illustrated by reference to a specific example. Consider an aqueous solution containing  $\text{Ru}(\text{bpy})_3^{2+}$  as sensitizer and N-tetradecyl-N-methylviologen,  $\text{C}_{14}\text{MV}^{2+}$ , as quencher in the presence of the surfactant, cetyl (trimethyl) ammonium chloride (CTAC). Electron transfer from an excited sensitizer converts relatively hydrophilic  $\text{C}_{14}\text{MV}^{2+}$  to  $\text{C}_{14}\text{MV}^+$  which is hydrophobic. Thus, the quenching reaction between  $\text{C}_{14}\text{MV}^{2+}$  and  $\text{*Ru}(\text{bpy})_3^{2+}$  occurs exclusively in the aqueous phase, while the  $\text{C}_{14}\text{MV}^+$  that is formed is rapidly solubilized by the cationic micelles formed by the surfactant, CTAC. The oxidized sensitizer,  $\text{Ru}(\text{bpy})_3^{3+}$ , is repelled by the positive surface charge on the cationic micelles

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<sup>15</sup>Lehn has suggested the possibility of obtaining such reagents from organic wastes or biomass (Reference 37) and Sakata and Kawai (Reference 38) report that urine and cockroaches can be used as sacrificial electron donors in related semiconductor systems.

<sup>16</sup>Recent studies suggest that different solutes can be solubilized in different sites within the micelle. This includes sites which are moderately polar, possibly interfacial sites (Reference 39).

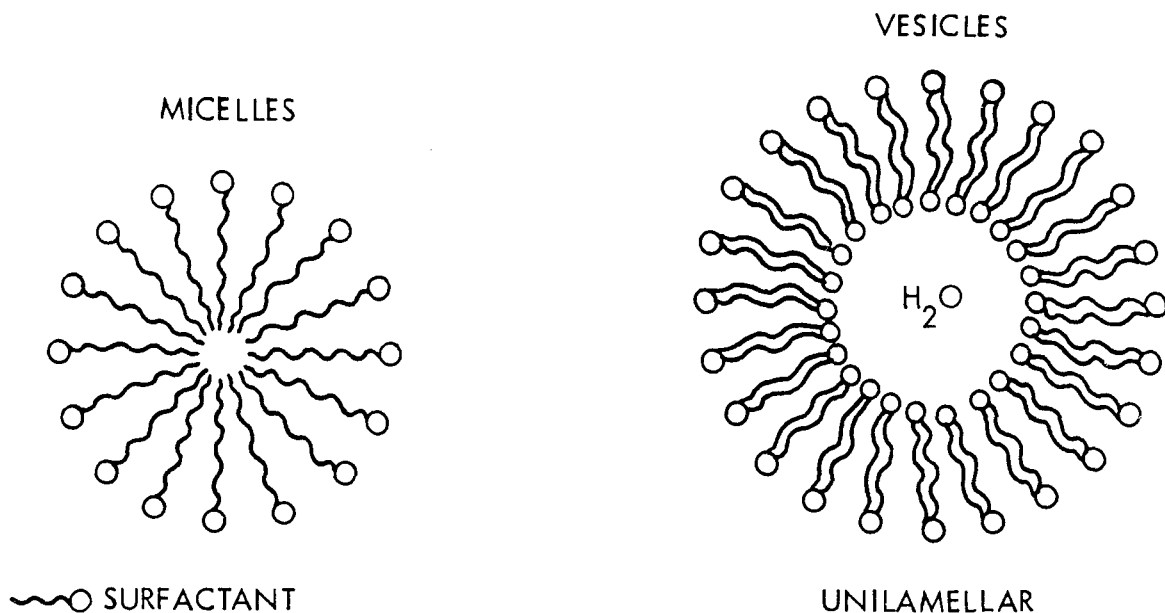


Figure 4-2. Structural Features of Organized Assemblies

and, hence, the back reaction between it and  $C_{14}MV^+$  is strongly inhibited. When the sensitizer is either  $Ru(bpy)_3^{2+}$  or the porphyrin derivative,  $ZnTMPyP^{4+}$ , the rate of the back reaction is decreased by a factor of 500 in the presence of cationic micelles (Reference 54).

Vesicles are closed bilayer structures formed from two layers of surfactant molecules with their non-polar tails facing one another, as illustrated in Figure 4-2. These aggregates, which are spherical or ellipsoidal, may be single-(unilamellar) or multi-(multilamellar) compartmented. The former, typically, have diameters of 2,000 to  $10^5$  nm, while multilamellar vesicles may have diameters of  $10^4$  to  $10^5$  nm. Vesicles can be formed from long-chain surfactants such as dialkyldimethylammonium halides and dialkyl phosphates, sulfonates, and carboxylates by sonic dispersal. Surfactant vesicles have long-term stabilities and entrain molecules in their compartments. The mechanism for inhibiting charge recombination is similar to that described above for the case of micellar assemblies. Recent work is described in References 56 through 62.

As in the case with sacrificial reagents, studies with organized assemblies have been used thus far primarily to obtain basic kinetic data. It is too early to determine whether such assemblies will lead to practical processes for producing fuels on a commercial scale.

#### C. PHOTOCHEMICAL PROCESSES WITH MULTIPLE PHOTOSYSTEMS

All of the photochemical processes considered in Section IV-B involve a single photosystem. Since one photon is required per electron transferred, two photons must be absorbed for each molecule of  $H_2$  produced. Bolton and others (References 6 and 10) have pointed out that solar processes using two

or more photosystems have higher limiting thermodynamic efficiencies than those with a single photosystem.<sup>17</sup> The majority of photons in the solar spectrum are at relatively low energies and, hence, processes that use multiple photons of lower energy to transfer a single electron are inherently more efficient than those that use a single photon of significantly higher energy.

A two-photosystem process is illustrated schematically in Figure 2-2. It consists of an oxidation half-cell separated from a reduction half-cell by a semipermeable membrane which permits transport of electrons and protons. Such an arrangement is attractive because  $H_2$  and  $O_2$  are produced in separate compartments.<sup>18</sup> Two photons are used per electron transferred, i.e., four photons per molecule of  $H_2$  produced.

The two absorbers (photosystems) should be arranged in series so that the incident radiation strikes the absorber with the larger band gap first. This first photosystem absorbs all photons with  $\lambda \leq \lambda_1$  and the second absorbs those with  $\lambda_1 < \lambda \leq \lambda_2$ .<sup>19</sup>

In Section II, it was noted that the optimum system of this type has a limiting thermodynamic efficiency of 44%. The corresponding efficiency for a process using a single photosystem is 31%.

Despite the predicted advantage in efficiency, no one has yet proposed a specific fuel-producing photochemical process that incorporates more than one photosystem. This is perhaps not surprising in light of the greater complexity of processes involving multiple photosystems.

#### D. CONCLUSION

No solar photochemical process has yet been identified that is suitable for sustained production of a fuel from a cheap and abundant feedstock. Major emphasis has been on splitting water to produce  $H_2$ , but conversion efficiencies are very low, typically less than one percent for cyclic processes that produce both  $H_2$  and  $O_2$ . The major reason for the low efficiency is non-productive charge recombination. Such recombination can be inhibited by the use of sacrificial reagents or by stabilization of charge

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<sup>17</sup>See Section II-D for details.

<sup>18</sup>This not only eliminates the need to separate the gases, but also may avoid undesired short-circuit processes if the catalysts are not highly specific.

<sup>19</sup> $\lambda_1$  and  $\lambda_2$  are the band-gap wavelengths for the two photosystems.

pairs within organized assemblies such as micelles and vesicles. Quantum efficiencies for production of dihydrogen as high as 30%<sup>20</sup> have been observed in the presence of sacrificial reagents. However, sacrificial reagents are unlikely to be practical for commercial-scale production of fuels unless a very inexpensive reagent can be found. The use of organized assemblies is a relatively new and rapidly developing technique which may prove useful for large-scale systems.

All of the solar fuel-producing photochemical processes developed thus far employ a single photosystem. Yet, thermodynamic analysis reveals that processes employing multiple photosystems have significantly higher limiting efficiencies. The greater complexity of multiphoton processes is undoubtedly the major reason for this lack of development. Nonetheless, the opportunities for significantly higher efficiencies justifies placing greater emphasis on the development of multiphoton systems.

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<sup>20</sup>Conversion efficiencies for solar photochemical systems would be less than half this value because less than half of the solar spectrum is capable of initiating photochemistry, and the sensitizer is not a perfect absorber.





## SECTION V

### SOLAR FUEL-PRODUCING PHOTOELECTROCHEMICAL PROCESSES: STATE OF THE ART

#### A. INTRODUCTION

The basic principles underlying photoelectrochemistry have been presented in a number of review articles (References 63 through 67). Characteristically, photoelectrochemical devices involve the formation of a junction between a semiconductor and an appropriate electrolyte, usually a liquid.

A space charge develops spontaneously in the semiconductor if there is a difference in the chemical potential of electrons in the two phases that form the junction. The chemical potential in the semiconductor is given by the so-called Fermi level, and in the electrolyte by the Nernst potential of the relevant redox couple associated with the electrolyte. Electrons flow spontaneously in the direction of lower chemical potential and, as a consequence, an electric field is established at the surface of the semiconductor extending to depths that typically range from 5 to 500 nm, depending upon the degree of doping. This region is usually referred to as the space charge or depletion layer. The term "depletion layer" is derived from the fact that the region is depleted in majority carriers, electrons in n-type and holes in p-type semiconductors.

The energetics associated with semiconductors-electrolyte junctions are conveniently represented in terms of energy-level diagrams, as shown in Figure 5-1 which illustrates the bending of the conduction and valence bands of the semiconductor at the interface. If the photogenerated electron-hole pairs are to drive redox reactions, the electrical potential of these couples must lie between the conduction,  $E_{CB}$ , and the valence band,  $E_{VB}$ , energies.<sup>21</sup>

Photons with energies equal to or greater than  $E_g$ , the band-gap energy, absorbed within the depletion layer, produce electron-hole pairs which will separate in the electric field formed spontaneously at the junction. Majority carriers move toward the interior of the semiconductor and minority carriers move to the surface. Thus, if an n-type semiconductor is illuminated with photons with  $E \geq E_g$ , photogenerated holes migrate to the electrode

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<sup>21</sup>More recently, it has been shown that with certain semiconductor-electrolyte combinations, the band edges can become unpinned, i.e., can shift with respect to electrolyte redox energy levels. The result is that redox reactions can be driven which have potentials that lie outside the band gap (References 63, 68, and 69).

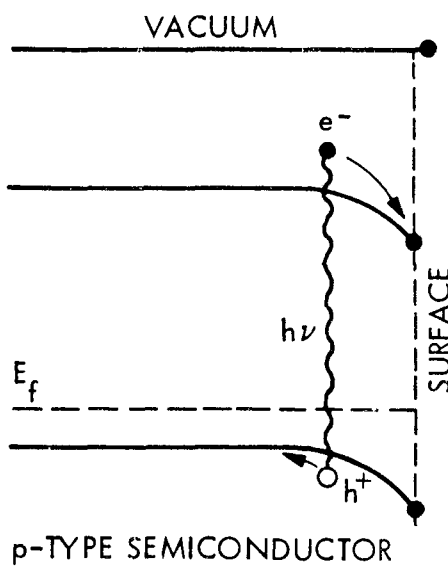
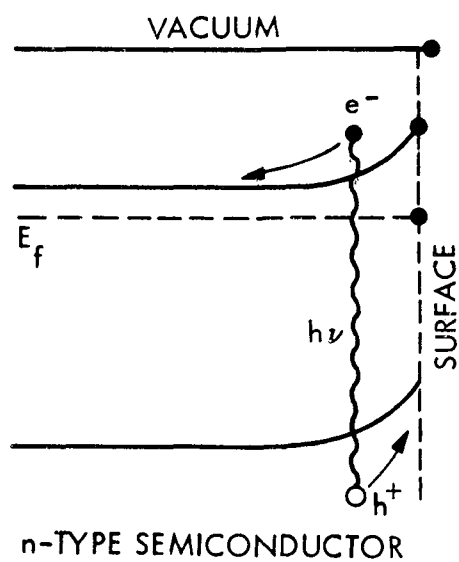
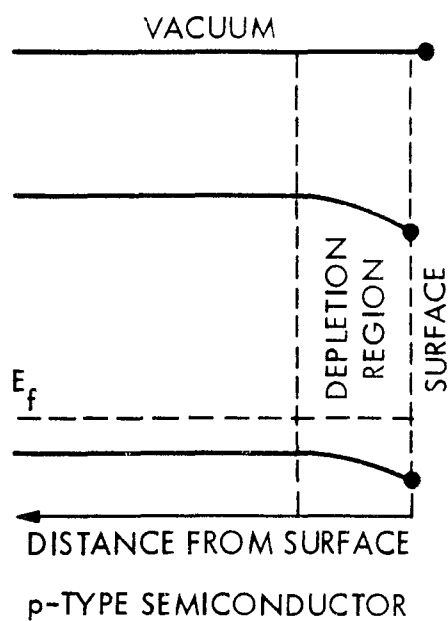
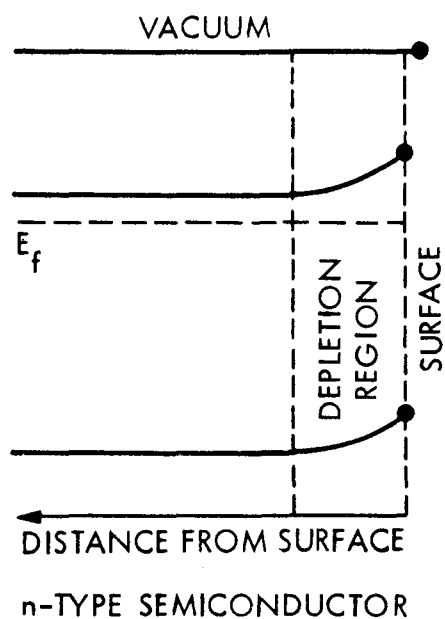


Figure 5-1. Schematic Representation of Semiconductor-Electrolyte Interfaces (a) and Electron-Hole Generation (b)

surface where they can oxidize an appropriate electron donor, D, present in the electrolyte,

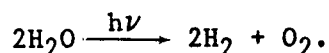


At the same time, electrons travel through the external circuit to an inert counter electrode where they can reduce an appropriate acceptor, A,



For a given semiconductor, the nature of these redox reactions will depend upon the choice of electrolyte. If the anode reaction is simply reversed at the cathode (i.e., if  $A^- = D$  and  $D^+ = A$ ), no chemical change occurs in the electrolyte and the device is referred to as a photogalvanic or wet photovoltaic cells. Such cells convert the incident radiation energy directly into electrical energy. Devices of this type are not considered in this report.<sup>22</sup>

If, however, different redox reactions occur at the two electrodes, there will be a net chemical change in the electrolyte. These devices are classified as a photosynthetic or photoelectrolysis cells. For example, if water is reduced to  $H_2$  at the cathode and oxidized to  $O_2$  at the anode, the net result is photoelectrolysis of water,



Such cells provide a method for the direct conversion of the energy of solar photons to storable chemical energy.

## B. CELL CONFIGURATIONS

Photoelectrolysis cells can be conveniently classified on the basis of cell configuration.

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<sup>22</sup>See, for example, W. J. Albery, "Development of Photogalvanic Cells for Solar Energy Conversion," *Acc. Chem Res.*, Vol. 15, pp. 142-148, 1982.

## 1. Voltage-Assisted Photoelectrolysis

In 1972, Fujishima and Honda reported that water could be electrolyzed at voltages well below the thermodynamic decomposition potential in cells incorporating an illuminated n-TiO<sub>2</sub> anode (Reference 70). Their work stimulated great interest in photoelectrolysis and photoelectrochemistry, generally. Voltage-assisted photoelectrolysis is used either when the band gap is too small or when band edges are not properly located with respect to the electrical potentials of the desired redox reactions. A variety of semiconductors have been used in this configuration (References 71 and 72), but most have exhibited conversion efficiencies of less than 6%. A schematic diagram of this type of cell is shown in Figure 5-2.

Unfortunately, efficiency calculations are not always made on the same basis. Perhaps the most useful form for reporting efficiency would be the following: Efficiency = (100) (chemical energy of H<sub>2</sub> produced minus electrical energy supplied)/incident solar energy.

In some cases, the efficiencies reported are calculated upon the basis of the amount of electrical energy saved in using photoassisted electrolysis vis à vis that required when the photoelectrode is replaced by a platinum electrode. Thus, Heller and Vadninsky (Reference 73) report an efficiency of

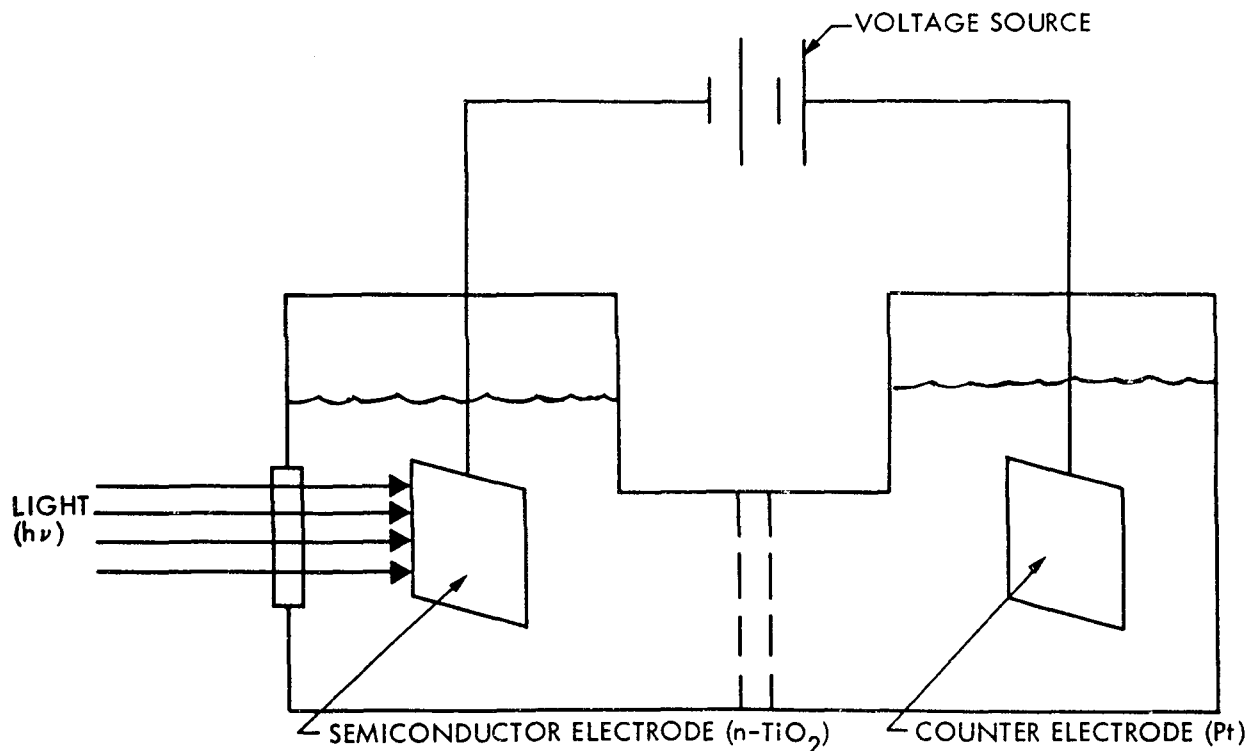


Figure 5-2. Voltage-Assisted Photoelectrolysis

12% (based on electrical energy saved) using a platinized<sup>23</sup> p-InP photocathode and a platinum anode. The electrolyte was aqueous 1M HCl-2M KCl and the products were H<sub>2</sub> and Cl<sub>2</sub>. P-InP is the most efficient H<sub>2</sub>-generating photocathode that has been reported to date. The band gap for p-InP is nearly ideally matched to the solar spectrum and, as a p-type semiconductor, it is quite stable against corrosion. An important factor in achieving this efficiency is the formation of a surface monolayer of chemisorbed oxygen. Apparently, the surface layer of oxide greatly reduces recombination losses.

## 2. Unbiased Cells with a Single Photoelectrode

In this configuration, one electrode is an illuminated semiconductor and the counter electrode is an inert conductor such as platinum or carbon (see Figure 2-2). Light absorbed at the photoelectrode is the only energy input. Sustained production of both H<sub>2</sub> and O<sub>2</sub> from water without application of an external voltage was first achieved using a UV-illuminated n-SrTiO<sub>3</sub> photoanode and a platinum cathode (References 74 through 76). The band gap, however, is so large (3.2 eV) that the efficiency is unacceptable with solar radiation.

Theoretically, water splitting should require 1.23 eV per electron transferred (i.e., 2.46 eV per molecule of H<sub>2</sub>). However, because of the overvoltages associated with evolution of H<sub>2</sub> and O<sub>2</sub> and the unavoidable losses associated with entropy production, about 2.2 eV is probably required in practice (References 65, 67, and 69). Also, the band edges of the semiconductor must be properly situated with respect to the electrical potentials for oxidation and reduction of water. For example, TiO<sub>2</sub> has a sufficiently large band gap (2.9 eV) to split water. However, a bias voltage must be applied because the conduction band edge is 0.2 V more positive than the H<sub>2</sub> evolution potential (Reference 77).

One method of increasing the spectral response of large band-gap semiconductors is to bond a photosensitizing substrate to the surface of the photoelectrode. The sensitizer absorbs strongly in the visible to produce an electronically excited state, S\*, which undergoes rapid electron transfer with the semiconductors. The direction of charge transfer depends upon the relative positions of the energy levels of S\* and the semiconductor. If S\* transfers an electron into the conduction band of the semiconductor, the electron will move into the bulk of the semiconductor under the influence of the electric field generated at the junction; S<sup>+</sup> will remain at the surface of the electrode. Subsequently, the electrons can reduce protons to H<sub>2</sub> at a metal cathode, and S<sup>+</sup> can oxidize water to produce O<sub>2</sub>. A number of semiconductor-sensitizer combinations have been investigated, but the efficiencies are low (References 63 and 78 through 83). Thin layers of sensitizer are required in order to have efficient charge transfer between S\*

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<sup>23</sup>Platinization is necessary because the semiconductor is a relatively poor surface for generating H<sub>2</sub>. Incorporation of fine islands of noble metals greatly enhances H<sub>2</sub> evolution.

and the semiconductor, but thin layers result in incomplete absorption and low efficiency. Recombination processes and trapping by surface states of the semiconductor also contribute to low efficiencies. Elegant, new techniques are being used to explore decay mechanisms for excited sensitizer on semiconductor surfaces (Reference 84).

A somewhat related approach is to surface-dope large band-gap semiconductors with transition metal ions (References 85 through 88). Although response is extended into the visible, efficiencies are still only about one percent.

The other major problem area is photoelectrochemical corrosion of the semiconductor electrode. Photogenerated holes and electrons may undergo redox reactions with the semiconductor itself leading to its irreversible dissolution or surface corrosion. This problem appears to be more severe with n- than p-type semiconductors and, in general, stability against corrosion decreases with decreasing band gap. Both kinetic and thermodynamic factors determine which redox reactions will predominate in a given system. Bard and Wrighton (Reference 89) and Gerischer (Reference 90) have examined these factors in some detail and a variety of techniques for inhibiting corrosion have been investigated. Among these are the application of a protective coating (References 91 through 93) and chemical derivatization of the semiconductor surface (References 94 and 95). Although these methods have led to some improvement in the stability of semiconductor electrodes, photoelectrochemical corrosion continues to be a major problem in designing practical systems.

### 3. Cells with Two Photoelectrodes

In this case, two photons are absorbed, one at each photoelectrode, to generate one net electron-hole pair for the fuel-producing reaction. Such devices, which are often referred to as photochemical diodes, may permit the use of lower band-gap semiconductors which are able to better use the solar spectrum.

A variety of such water-splitting photoelectrochemical cells have been investigated, but conversion efficiencies are quite low, typically, less than one percent (References 96 through 100). Heller and co-workers have reported moderate efficiencies for photoelectrolysis of aqueous solutions of HBr to  $H_2$  and  $Br_2$  and of HI to  $H_2$  and  $I_2$  (Reference 101). The cells employed a p-InP photocathode with catalytic (noble metal) islands on the surface and either an n-MoSe<sub>2</sub> or an n-WSe<sub>2</sub> photoanode. Conversion efficiencies were calculated by two different methods: one based upon electrical energy saved in the electrolysis, and the other upon stored free energy. For HBr, the first method leads to an efficiency of 11.2% for monochromatic light at 632.8 nm. This calculation is based on the electrical energy saved by using the photoelectrolysis cell relative to what would have been required for electrolysis in a cell with platinum electrodes. An efficiency of 7.8% is obtained when the calculation is based upon the amount of electrical energy that could be produced from the photoelectrolysis products ( $H_2$  and  $Br_2$ ),

using an ideal fuel cell. Somewhat lower values, 6.9 and 5.2%, respectively, are reported for photoelectrolysis of aqueous HI.<sup>24</sup>

#### 4. Colloidal Semiconductor Systems

Grätzel and his colleagues have developed systems in which colloidal  $\text{TiO}_2$  particles, loaded with ultrafine deposits of  $\text{RuO}_2$  and platinum, split water into  $\text{H}_2$  and  $\text{O}_2$  (References 85 and 102 through 107). Such particles (see Figure 5-3) are, in effect, wireless photoelectrochemical cells with a photoanode and a platinum cathode. In the early studies,  $\text{Ru}(\text{bpy})^{2+}$  was used as a sensitizer with  $\text{MV}^{2+}$  as relay. Reduced viologen,  $\text{MV}^+$ , produced by reaction of excited sensitizer and  $\text{MV}^{2+}$ , injects electrons into the conduction band of  $\text{TiO}_2$ . After transport to platinum sites, these electrons reduce protons to generate  $\text{H}_2$ . At the same time,  $\text{RuO}_2$  catalyzes formation of  $\text{O}_2$  from the photogenerated holes, a process which is accompanied by reduction of  $\text{Ru}(\text{bpy})^{3+}$  back to  $\text{Ru}(\text{bpy})^{2+}$ . It has since been shown that the electron relay is unnecessary (Reference 104), i.e., electronically excited sensitizer can inject electrons directly into the conduction band of  $\text{TiO}_2$ . In this case, only that fraction of sensitizer that is absorbed on the surface of the particles is photoactive.

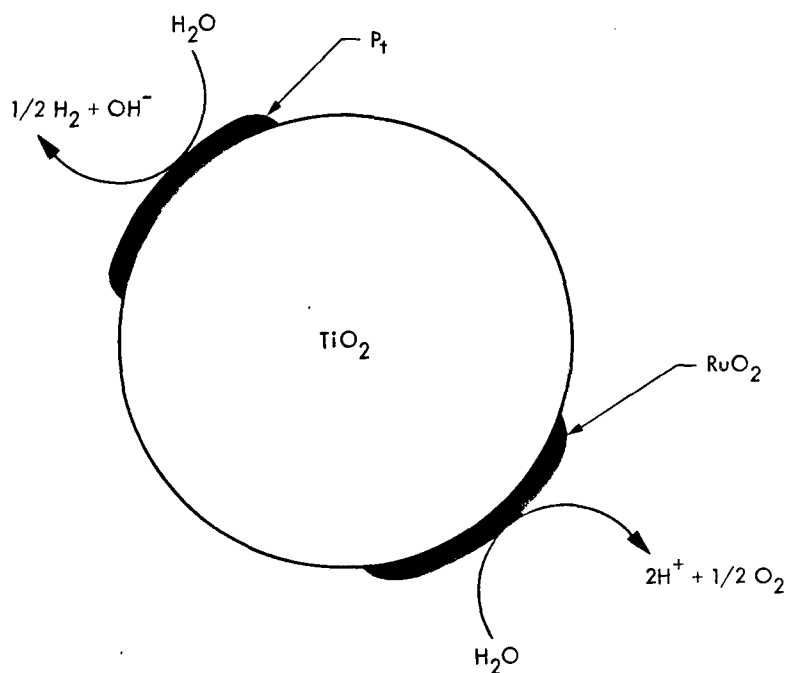


Figure 5-3. Colloidal Systems ( $n\text{-TiO}_2$  Loaded with  $\text{Pt}$  and  $\text{RuO}_2$ )

<sup>24</sup>This cell is unusual in that both electrical and chemical energy is produced in the photoelectrochemical process.

Also, water can be split with relatively high quantum efficiency by direct band-gap excitation of the semiconductor, i.e., in the absence of sensitizer (Reference 104). However, the efficiency is extremely low with solar radiation because of the large band-gap energy of  $\text{TiO}_2$ . Grätzel and his co-workers are attempting to extend the spectral response into the visible by surface-doping the colloidal  $\text{TiO}_2$  particles with transition metals. Sustained water cleavage with visible light has been observed with aqueous suspensions of  $\text{TiO}_2$  particles doped with  $\text{Cr}^{3+}$  (Reference 85). As in the previous cases, the colloidal particles also carried ultrafine deposits of Pt and  $\text{RuO}_2$  as redox catalysts. The observed quantum efficiency is estimated to be 1%, using visible light.

Particle systems are attractive because their relative simplicity could result in lower construction and maintenance costs. However, unlike cells with well-separated electrodes, particle systems produce a mixture of gases which must be separated. Also, the buildup of  $\text{O}_2$  reduces the efficiency of water splitting because of competition between  $\text{O}_2$  and protons for electrons. However, Grätzel (References 85 and 105) reports that colloidal  $\text{TiO}_2$  absorbs  $\text{O}_2$  produced during photolysis. Although some of this absorption is spontaneous, the majority is photoinduced. Details of the mechanism are not entirely clear, but the concentration of  $\text{O}_2$  in solution is kept very low. Grätzel has suggested that if capacity for  $\text{O}_2$  uptake can be increased, it may be possible to produce essentially pure  $\text{H}_2$  during solar photolysis and release  $\text{O}_2$  during dark periods.

### C. CONCLUSION

At present, solar photoelectrochemical devices produce fuels with greater efficiencies than cyclic homogeneous photochemical processes, but efficiencies are still relatively low and no system has been identified that would be capable of sustained production of hydrogen from water on a commercial scale. Research has been and continues to be directed at understanding fundamental principles.

The most efficient photocathode yet reported is p-InP. Photo-assisted electrolysis of aqueous  $\text{KCl}/\text{HCl}$ , in a cell with a p-InP photocathode and a platinum anode, results in production of  $\text{H}_2$  and  $\text{Cl}_2$  with a reported efficiency of 12%, using sunlight. This efficiency is based on the electrical energy saved by using the photoelectrolysis cell rather than an electrolysis cell with two platinum electrodes. Unassisted photoelectrolysis of aqueous  $\text{HBr}$ , in a cell with a p-InP photocathode and either a  $\text{MoSe}_2$  or a  $\text{WSe}_2$  photoanode, results in production of  $\text{H}_2$  and  $\text{Br}_2$  with a reported efficiency of 11.2%, using monochromatic (632.8 nm) light. This efficiency is calculated on the same basis as the previous figure, but is for monochromatic radiation rather than sunlight.

The use of semiconductor particles with surface deposits of redox catalysts is an attractive approach because of its relative simplicity. However, conversion efficiencies are low because of the poor spectral response. Attempts to extend this response have not been very successful as of this time.



The two major problems common to photoelectrochemical water splitting are photocorrosion and the poor match between the semiconductor band gap and the solar spectrum.



## SECTION VI

### SYSTEMS AND OPERATING OPTIONS

#### A. INTRODUCTION

The basic solar photochemical and photoelectrochemical processes for producing fuels and chemicals are described in Section II and their current research and development status is reviewed in Sections IV and V. In this section, systems and operating options are considered. The possibility of operating at elevated temperatures is one such option. The others are hybrid and coupled systems.

As the term is used here, a hybrid system is a solar thermochemical-photochemical hybrid that produces a fuel in a cyclic process in which an appropriate feedstock (e.g., water) and solar energy are the only net inputs. Other substances may be required, but they are regenerated in the cycle. Such hybrids are essentially thermochemical cycles in which at least one step is photochemical. The various steps in such cycles are generally carried out at different temperatures.

Coupled systems combine a photochemical process (quantum converter) with a thermal converter operating at a common temperature. The processes associated with the two converters are specified only to the extent that one (the quantum converter) is a threshold device,<sup>25</sup> while the other (the thermal converter) is not. The final systems concept considered is one in which the photochemical process is operated at or near ambient temperature, and the thermal converter is operated at high temperatures.

#### B. PHOTOCHEMISTRY AT ELEVATED TEMPERATURES

If solar photons are used to drive photochemical processes, operating temperatures will be significantly above ambient unless some type of cooling strategy is employed. This will be especially important if concentrated sunlight is used. Thus, it would be of interest to determine whether there are photochemical processes for producing fuels or chemicals that would benefit from operation at elevated temperatures. Elevated temperatures, in this case, means about 350 to 370 K for non-concentrating systems and perhaps 500 to 600 K (or higher) in concentrating systems.<sup>26</sup>

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<sup>25</sup>Threshold devices require photons with energies equal to or in excess of a threshold or band-gap energy,  $E_g$ .

<sup>26</sup>In both concentrating and non-concentrating systems, the temperature of the photosystem will depend upon a number of variables.

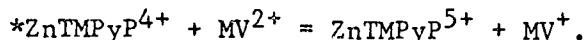
Photochemical excitation is highly specific. Absorber molecules, often at low concentration, are selectively excited, resulting either in their dissociation or their conversion to an electronically excited state. If the latter is sufficiently long lived, it may react with suitable substrates to produce chemical changes. When a system is heated, excitation is essentially non-specific; there is an increase in the average energies of all molecules present in the system, and no electronic excitation occurs.

Because of the significant difference in the specificity of excitation, and the fact that electronically excited molecules may react quite differently than ground-state molecules, the reaction products may differ when the same system is excited photochemically rather than thermally. Because thermal processes will reduce this specificity, there is usually no incentive to operate photochemical systems at elevated temperatures. There are also other factors that mitigate against using high temperatures. For example, absorbers well matched to the solar spectrum are usually rather complex molecules that may be expected to undergo increased degradation when the temperature is increased.<sup>27</sup> In most fuel-producing photochemical systems, the absorber functions as a photosensitizer which must survive repeated cycling if the process is to be cost effective.

Another factor that must be considered is the decrease with increasing temperature in the limiting thermodynamic efficiency of all quantum converters. The limiting efficiency decreases approximately two percentage points per 50 K increase in temperature (see Section II-D).

If a photochemical system is operating at efficiencies below the limiting thermodynamic value, increasing temperature may lead to an increase in efficiency because of favorable kinetic consequences. Thus, Grätzel, et al, report a 50-fold increase in the yield of H<sub>2</sub> from photochemical cleavage of water when the temperature is increased from 298 to 348 K (Reference 104). This particular system is relatively complex and the increased yields of H<sub>2</sub> are rationalized in terms of favorable effects of increased temperature upon a number of kinetic factors. Richoux, in a much simpler system, has shown that increasing temperature increases the efficiency of photo-induced charge separation in aqueous solution of zinc tetramethylpyridylporphyrin (ZnTMPyP<sup>4+</sup>) and methyviologen (MV<sup>2+</sup>) (Reference 108).

This is interesting because non-productive charge recombination reactions contribute significantly to the low efficiencies of homogeneous, photochemical water-splitting processes. Absorption of photons by the porphyrin produces an electronically excited state which undergoes an electron transfer reaction with MV<sup>2+</sup>,




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<sup>27</sup>The polypyridine complexes of the transition metals, and the metalloporphyrins that have been used as photosensitizers for splitting water, appear to be stable up to at least 353 K (References 104 and 108).

Richoux reports that the relative quantum yield of the separated ions,  $\text{ZnTPyP}^{5+}$  and  $\text{MV}^+$ , more than doubles when the temperature is increased from 293 to 353 K. This increase is attributed to an increase with temperature in the specific rate of separation of geminate charge pairs. The rate of recombination, which competes with separation, is assumed to be essentially independent of temperature.

Because increased efficiency in the separation of photo-induced charge pairs should favor increased efficiency of water splitting, these results (like those of Grätzel) may appear to contradict the argument that the limiting thermodynamic efficiency of all quantum converters decreases with an increase in temperature. However, in both cases, the photochemical system is operating far below the limiting thermodynamic efficiency. For example, in the zinc porphyrin/ $\text{MV}^{2+}$  system, the efficiency at 298 K is less than 1%.

Because real systems will almost certainly operate below the limiting efficiency, there may be kinetic advantages to operating water-splitting systems at temperatures of the order of 350 K. Sensitizers are likely to be sufficiently stable in this temperature range and cooling requirements can be reduced with some saving in system costs.

A search of the scientific literature was conducted to determine the extent of photochemical work at elevated temperatures to identify photochemical processes that might benefit from operation at elevated temperature. A computer-based search of Chemical Abstracts for the period 1967-1982 was conducted using the Dialog Information Retrieval Service. The computer was instructed to retrieve abstracts which contained a combination of either the words "high temperature" or "elevated temperature" with "photochemistry" or "photolysis." None of the abstracts retrieved contained information that would suggest a possible photochemical process for producing fuels or important chemical products at elevated temperatures. However, it should be emphasized that this was only a cursory search of the literature.

In concluding this discussion of photochemistry at elevated temperatures, it should be noted that Haught (Reference 9) has shown that it will be generally more efficient to use solar thermal converters at temperatures in excess of about 500 K. At such temperatures, thermal systems have higher limiting efficiencies than quantum converters, and this superiority increases with further increases in temperature.

### C. THERMOCHEMICAL-PHOTOCHEMICAL HYBRIDS

Pure solar thermochemical processes for water splitting receive the necessary driving energy as heat. Such processes are expected to have greater efficiencies because they use the solar spectrum more efficiently and are not subject to some of the losses inherent in quantum conversion (e.g., internal conversion).

In principle, the simplest example of a pure thermochemical process would be direct thermolysis of water into dihydrogen and dioxygen. However, temperatures of 2500 K, or higher, are required to achieve significant

decomposition and, hence, materials and separation problems are severe. As a result, direct thermochemical splitting of water has received relatively little attention. Funk and Reinstrom (Reference 109) were the first to suggest that thermochemical decomposition of water could be carried out indirectly at significantly lower temperatures by a series of chemical reactions that constitute a closed cycle with respect to all species except water and its decomposition products, dihydrogen and dioxygen. Hundreds of cycles have been proposed, but fewer than a dozen have been studied in sufficient detail to confirm that they are workable on a laboratory scale. Preliminary analyses indicate that some of the cycles have efficiencies as high as 40 to 45% (Reference 110).

In some cases, at least one step in the cycle is driven primarily by the input of electrical work. These so-called thermochemical-electrochemical hybrids are designed to eliminate a difficult processing step(s) or to close a cycle that includes a step that is thermally unworkable. Examples are the Westinghouse (References 110 and 111) and EURATOM-Mark 11 sulfuric acid cycles (References 110 and 112).

By analogy, it might be suggested that hybrid cycles could be devised which incorporate a photochemical step. However, no such hybrid has been reported in the literature, probably because of the low efficiency of solar photochemical processes. As shown in Section II-D, such processes have a limiting efficiency of about 30% and for real systems, the efficiency is not likely to exceed 15%. Thus, inclusion of a photochemical step would considerably reduce overall cycle efficiency.

Also, it would be difficult to use proposed strategies for optimizing the plant capacity factor of solar thermochemical cycles if such hybrids were developed. Capacity factor will be an important consideration because thermochemical plants will be highly capital intensive. When a solar heat source is used, the high temperature step(s) of the cycle will have a low capacity factor, assuming high temperature-heat storage is not available. This can be mitigated to some degree by sizing these units so that the lower temperature steps in a cycle can be operated continuously. In general, the units operated continuously can be built at about one-fifth the maximum capacity of the high-temperature part of the plant. If, however, one of the low temperature steps is photochemical, the effectiveness of this sizing strategy would be significantly compromised.

On the basis of these arguments, thermochemical-photochemical cycles do not seem to be an attractive option.

#### D. COUPLED SYSTEMS

Haught has examined the efficiency of a system consisting of a quantum converter coupled to a thermal converter (Reference 9). A schematic diagram of such a device is shown in Figure 6-1. Note that both converters operate at a common temperature. Figure 6-2 shows the efficiency of such a system as a function of temperature. The efficiency of the quantum converter decreases with increasing temperature while that of the thermal converter increases. It is clear from Figure 6-2 that there is little incentive to couple the two

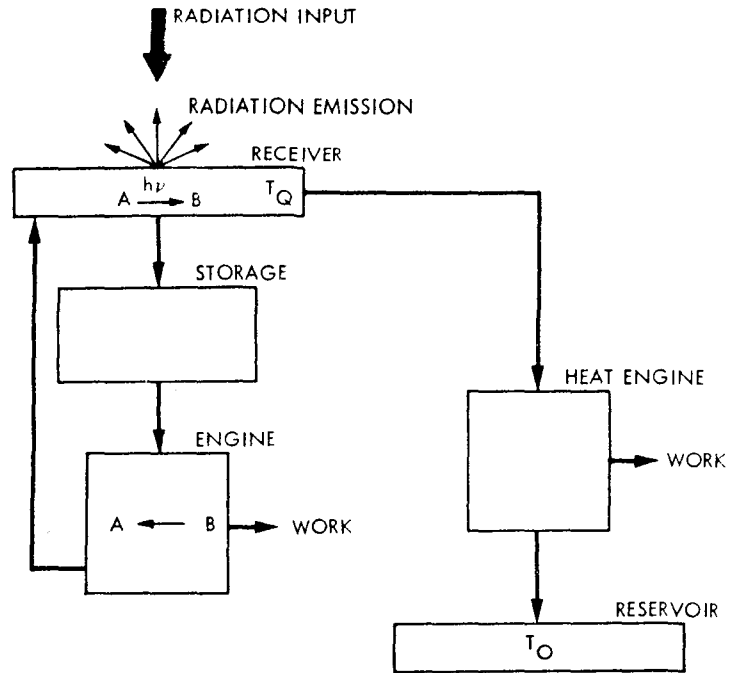


Figure 6-1. Coupled Quantum/Thermal Converter

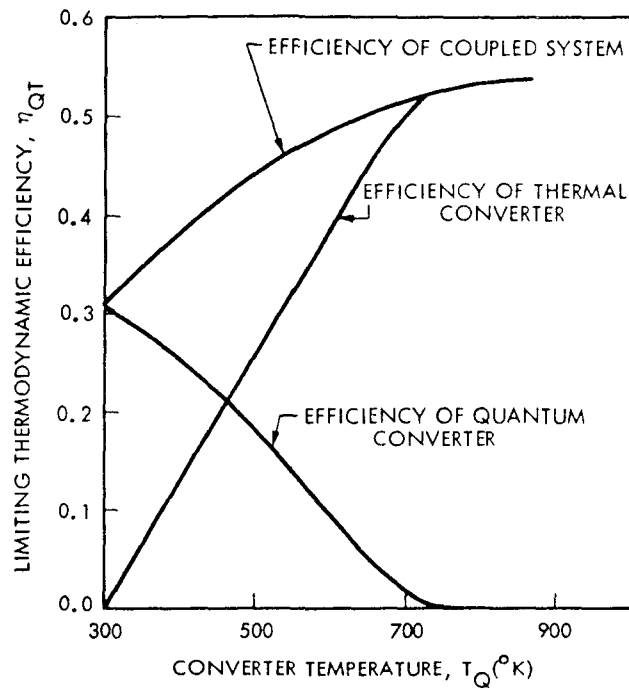


Figure 6-2. Conversion Efficiency Versus Temperature for a Single Collector Coupled Quantum/Thermal System

converters in this fashion unless the quantum converter is significantly cheaper than the thermal device. In that case, a coupled system might be useful up to about 600 K.

As an alternative, the quantum converter could be operated at near ambient temperatures and the thermal converter at high temperatures. The shorter wavelengths of the solar spectrum would be used to drive a photochemical process in the quantum converter and the long wavelengths would be collected by the thermal converter. In this case, the quantum converter would produce chemically stored energy and the thermal converter would probably produce electricity. For example, the heliostats of a central receiver solar-thermal power plant might be made with a mirror coating that is highly reflective in the infrared, but highly transparent in the visible and near-ultraviolet. The quantum converter would be located beneath the mirrored surface.

This type of coupling could be an attractive strategy for siting quantum conversion devices that produce chemically stored energy. The tracking heliostats would increase the average intensity for the quantum converter and the reflection of infrared radiation to the central receiver would permit the quantum converter to operate more efficiently because of the lower operating temperature. The increased cost of the more complex heliostats would have to be justified by the value of the fuel produced by the quantum converter.

As an example, an infrared reflective coating, produced by Liberty Mirror, has the optical properties shown in Figure 6-3. This glass was

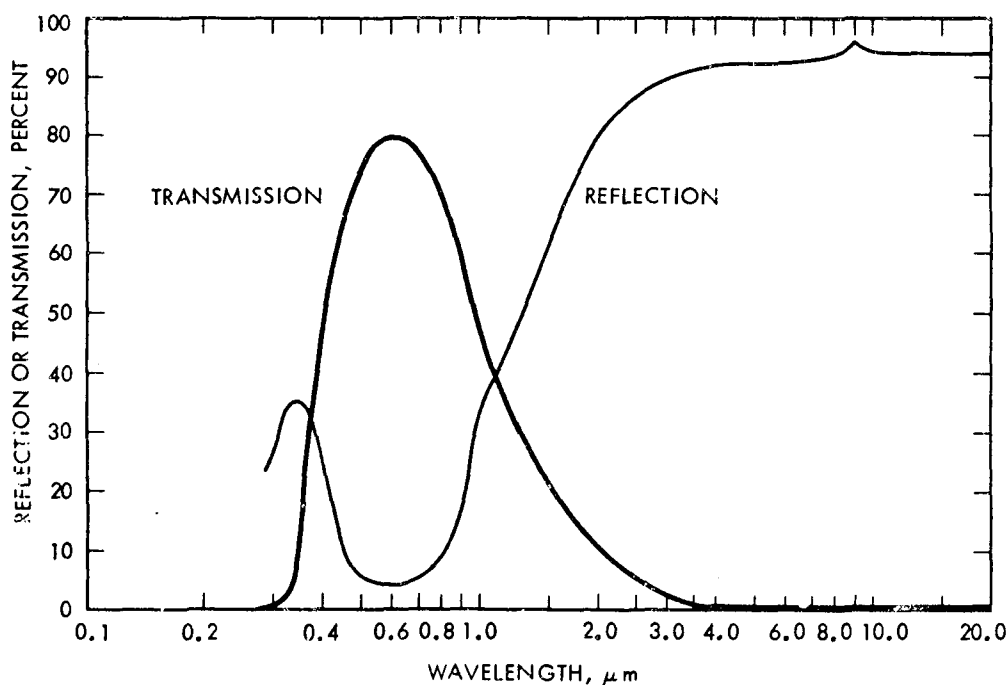


Figure 6-3. IR-81-E Conductive Infrared Reflection Coating



considered as a possible construction material for a photochemical reactor that could be used with concentrated sunlight (Section III-C). In that case, the idea was to reduce the heating of the reactor by reflecting most of the infrared radiation. Incomplete transmission in the visible and ultraviolet, however, leads to a reduction in overall efficiency of 38% if the absorber is assumed to be ideal.

Nonetheless, mirrored surface may be developed that will have acceptable optical properties. If so, this might prove to be a desirable option for siting quantum conversion devices. Johnson has recently carried out a thermodynamic analysis of systems of this general type, which he refers to as thermally decoupled systems (Reference 113). He finds a significant advantage for the thermally decoupled systems, vis-à-vis, those in which the thermal and quantum converter operate at a common temperature.



## SECTION VII

### CONCLUSIONS

- (1) The overall system efficiency is the single most important factor in determining the cost of fuel produced by a photochemical process. The overall system efficiency is dominated by the relatively low efficiency of the photochemical process.
- (2) Fuel-producing solar quantum converters employing a single photosystem are unlikely to have efficiencies greater than about 15%. If multiple photosystems are used, higher efficiencies should be possible. For example, the limiting thermodynamic efficiency for a device with two photosystems could be as much as 40% greater than one with a single photosystem.
- (3) Almost all research on fuel-producing solar quantum conversion processes has focused on splitting water to produce dihydrogen.
- (4) Essentially, all of the research has been at a fundamental level and no process has yet been identified that is suitable for sustained production of dihydrogen on a commercial scale.
- (5) The cyclic homogeneous photochemical processes that have been studied thus far have very low efficiencies. It may be possible to increase efficiency by a biomimetic approach using organized assemblies such as micelles and vesicles, but this approach is at a very early stage of development.
- (6) The highest efficiencies observed thus far in bench-scale work have been achieved for photo-assisted electrolysis and for p/n photochemical diodes in which a p-InP cathode is combined with a photoanode such as n-MoSe<sub>2</sub>.
- (7) Particulate systems, in which semiconductor particles of colloidal dimensions surface-coated with redox catalysts function as wireless photoelectrolysis cells, are promising because of their relative simplicity. Currently, efficiencies with solar radiation are too low, about 1%, for practical application.
- (8) A number of factors have been identified that mitigate against operating solar photochemical systems at elevated temperatures. The most general, and probably the most important factor, is the decrease in limiting thermodynamic efficiency,  $\eta_{QT}$ , with increased temperature. For systems operating below  $\eta_{QT}$ , favorable kinetic consequences resulting from increased temperature may, in some cases, outweigh thermodynamic considerations.
- (9) It is unlikely that solar thermochemical-photochemical hybrid cycles will be viable options for production of fuels or chemicals. The low efficiency of a photochemical step would result in a considerable reduction in overall cycle efficiency.

- (10) The siting of solar fuel-producing quantum converters beneath the mirrored surface of heliostats of a central-receiver power station may prove attractive if a suitable mirror surface can be developed. Photons corresponding to  $\lambda > \lambda_g$  would be reflected to the central receiver; those with  $\lambda \leq \lambda_g$  would be transmitted to the quantum converter.

## SECTION VIII

### RECOMMENDATIONS

- (1) Research should focus on fuel-producing solar quantum conversion processes that promise high efficiencies. Greater emphasis should be given to processes that employ multiple photosystems.
- (2) Research on photoelectrochemical processes, particularly p/n photochemical diodes and colloidal semiconductor systems, should be encouraged because they are among the options that appear most likely to achieve acceptably high efficiencies.
- (3) An engineering feasibility study should be made of siting fuel-producing quantum converters within IR-reflecting heliostats at central receiver power plants.



## SECTION IX

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