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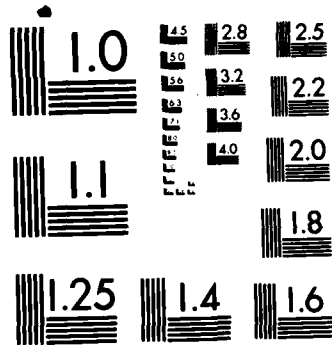
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OFFICE OF NAVAL RESEARCH

Contract N00014-82-K-0523

TECHNICAL REPORT NO. 7

High-Temperature Solar Energy Research  
at the University of Minnesota

by

Edward A. Fletcher, Professor  
Department of Mechanical Engineering  
University of Minnesota  
Minneapolis, MN 55455

Accepted for Publication

in

Proceedings, 1986 American Association of Mechanical Engineers  
Solar Energy Conference  
Anaheim, California

D. Turner, Chairman  
Department of Mechanical Engineering  
Texas A&M University  
College Station, TX 77843

November 15, 1985

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER TR-7	2. GOVT ACCESSION NO. AD-A162	3. RECIPIENT'S CATALOG NUMBER 047
4. TITLE (and Subtitle) High-Temperature Solary Energy Research at the University of Minnesota		5. TYPE OF REPORT & PERIOD COVERED Technical Report, Int. 07/01/84 - 10/31/85
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Edward A. Fletcher		8. CONTRACT OR GRANT NUMBER(s) N00014-82-K-0523
9. PERFORMING ORGANIZATION NAME AND ADDRESS Edward A. Fletcher, Dept. of Mechanical Engng. University of Minnesota, 111 Church St. S.E. Minneapolis, MN 55455		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-625-830 NR-359-830X
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research, 612A: BAR Dept. of the Navy, 800 North Quincy St. Arlington, VA 22217		12. REPORT DATE November 15, 1985
		13. NUMBER OF PAGES 11
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Director, Office of Naval Research Detachment, Chicago, 536 South Clark St. Chicago, IL 60605		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Proceedings, 1986 American Association of Mechanical Engineers Solar Energy Conference, Anaheim, CA; D. Turner, Chairman, Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843 (CONT A p B)		
18. SUPPLEMENTARY NOTES Proceedings, 1986 American Association of Mechanical Engineers Solar Energy Conference, Anaheim, CA, D. Turner, Chairman, Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Solar, electrolysis, metallurgy, zinc, zinc oxide, solar thermal, solar thermoelectrochemical.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Solar energy, coming from a 5800K source, has thermodynamic value that is now becoming widely recognized for use in thermoelectrochemical processes. For about ten years a small group at the University of Minnesota has been conducting analytical and experimental studies which have the objective of using the sun's thermodynamic potential, both for chemical processing and		

20. Abstract, continued...

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**HIGH-TEMPERATURE SOLAR ENERGY RESEARCH  
AT THE UNIVERSITY OF MINNESOTA**

**Edward A. Fletcher, Professor  
Department of Mechanical Engineering  
University of Minnesota  
Minneapolis, MN 55455, U.S.A.**

**to be presented at**

**1986 ASME Solar Energy Division Conference  
Grand Hotel, Anaheim, California  
April 14-17, 1986**

## ABSTRACT

Solar energy, coming from a 5800K source, has thermodynamic value that is now becoming widely recognized. For about 10 years a small group at the University of Minnesota has been conducting analytical and experimental studies which have the objective of using the sun's thermodynamic potential, both for chemical processing and for solar energy storage. This paper summarizes our published work, describes ongoing as yet unpublished work, and suggests future work. The emphasis is on both shorter and long range applications to industrial processes.

## INTRODUCTION

Solar energy offers earthlings unique opportunities because the sun is a 5800K heat reservoir. In pursuing earthly objectives, we take available substances at ambient temperature, do something to them, such as change them into something more useful, or generate electric or mechanical power to do work, transforming them into something less useful, and return them to ambient temperature. From a thermodynamic standpoint, the best processes are those that least degrade our ability to do work, because work is the highest form of energy transfer.

High temperature process heat is almost the thermodynamic equivalent of work! The sun can thus be made to do some things that conventional and nuclear fuels can't, and to do others more efficiently. The highest temperatures of burning fossil fuels in air is about 2300K. If we want to use the energy, we have

to use it at much lower temperatures. If we need high temperature heat, we must convert some of the energy to electric power, degrade it by resistance, induction, or an arc, introducing contaminants, complication, and substantial loss of its work equivalent.

On earth's surface the theoretical limit for solar energy conversion to work for all devices, including perfect so-called quantum devices, is about 0.95. An ideal heat engine would have 90% of that efficiency if the highest temperature in its cycle were only about 2000K. It should therefore be possible, if we work at it, to use almost the full thermodynamic potential of this unique heat reservoir at high, but manageable, temperatures.

Moreover, if we expand our work arena to include the moon and space, sunlight, as solarthermal energy, becomes our most valuable, unique, and reliable source. Its intensity there is substantially greater, the sink temperature could probably be made lower, and the vacuum of space would be a significant asset to many solarthermal processes, including power production.

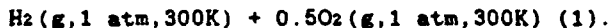
For about ten years a small group at The University of Minnesota has been studying the use of sunlight as the energy source for chemical processes<sup>1-22</sup>. We have conducted both theoretical and experimental studies. We have built a solar furnace<sup>15, 18</sup> which achieves concentration ratios as high as 7000 solar intensities and conducted, among other experiments, preliminary experimental studies of the thermolysis and quenching of water and hydrogen sulfide, the formation of nitric oxide, and high temperature electrolysis, this paper summarizes some of our past work, describes ongoing but as yet uncompleted work, and makes suggestions for future studies.

## SOME THERMODYNAMIC CONSIDERATIONS

### Thermochemical Processes

We propose to split water into hydrogen and oxygen in the black box shown in Figure 1. Most of us might first suggest that it should be an electrolysis cell. But electric power is not a prime energy source. It must be manufactured from more primitive sources. Thus, the power plant must be included in the black box as one of the components of our water splitting device. It may, however use materials (fuels or other reactants) or heat (or mechanical work, if that's available) from outside sources.

At first we don't have to know what is in the black box or how it works. We may even overlook some good ideas if we are too specific. We know that energy must be supplied to the box in the process. For each mole of water it uses 285.8kJ,  $\Delta H$ , of the reaction,



That is a necessary but not sufficient condition. Obviously, heat won't just flow into water from a 400K reservoir and decompose it. We could, however, run a Carnot engine in the box between a 400K source and the surroundings to generate electric power to electrolyze the 300K water. We would use 237.2kJ of electrical work,  $\Delta G$  of reaction 1. The power plant uses 948.8kJ from the 400K reservoir and the electrolysis cell takes up 48.6kJ as heat from its surroundings. If we had used a 600K reservoir, we would have needed only 474.4kJ from it.

In general, any isothermal chemical transformation that requires work input can be identified with a Carnot cycle.<sup>12, 23, 24</sup> The higher the temperature of the source, the less energy we need to effect the reaction. A substantial part of our effort has been aimed at inventing mechanisms by which it might be done.<sup>5, 7, 8, 9, 11, 12, 17, 20, 21</sup>

### Thermoelectrochemical Processes

Solar energy should also be considered as a source of high-temperature process heat in electrolytic processes.<sup>4</sup> If work, such as electrical work, is needed to effect a chemical change, the amount is  $\Delta G$  of the reaction. The total amount of energy needed is  $\Delta H$  of the reaction. The difference can be process heat. As electrolysis proceeds, the cell maintains its temperature constant by heat exchange with the surroundings.

The enthalpies and gibbs free energies of formation of stable metallic oxides are large negative numbers. The recovery of the metal from an oxide ore at ambient or low temperatures thus requires either the use of a great deal of electric power or the use of a reducing reactant such as carbon.

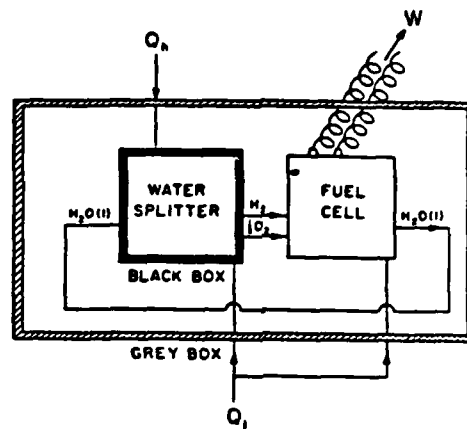


Figure 1. Intellectual construct for the thermodynamic analysis of an endothermic chemical reaction. The reactor (the black box) is a device which receives ambient temperature and pressure liquid water and produces ambient temperature and pressure products. It exchanges heat with high- or ambient-temperature reservoirs. The fuel cell is a construct we use to understand the limitations of the reactor. The electrical work of the fuel cell measures hydrogen and oxygen production. When water from the cell returns to the reactor, the system is closed. The grey boundary then encloses a heat engine. If it is reversible, it is a Carnot engine (Reference 1).

The variation of  $\Delta H$  of a reaction with temperature depends on the difference between the heat capacities of its products and reactants, which is small. But the variation of the gibbs free energy depends on  $\Delta S$  of the transformation, which is a larger positive number if the reactants are condensed phases and the products include gases. The enthalpies of formation of many metallic oxides are therefore quite independent of temperature; their gibbs free energies decrease with temperature. Thus, the electrolytic reduction of many ores at elevated temperatures should require that less-and-less of the energy need be furnished as electric power as the electrolysis temperature is raised.

### Concentration Ratios and the Efficiency of Energy Use

As solar furnaces operate at higher and higher temperatures, their reradiation losses increase as the fourth power of the temperature and directly as the area from which they reradiate. To minimize such losses, we use high solar concentration ratios.

The overall system efficiency of any solar thermochemical or electrothermal process is most appropriately defined as the work-equivalent of returning the product to its original (reactant) state, divided by the



solar energy intercepted by the collecting system. It is the product of a solar collection efficiency and the thermal efficiency of the heat engine which correlates with it. The maximum (reversible) efficiency depends on the solar concentration ratio and on the highest temperature used in the thermochemical process. These maximum efficiencies<sup>1</sup> are shown in Figure 2. It is evident that there is a thermodynamic advantage to be achieved in working with furnaces that have high concentration ratios. We have built and are using such a furnace, shown in Figure 3, for our work<sup>5,18</sup> and have studied a number of representative systems to acquire experience and create benchmarks for future studies. Some of the results of these studies, which are continuing, are described in this paper.

#### SOME REPRESENTATIVE PROCESSES

##### Hydrogen and Sulfur from Hydrogen Sulfide

We think of hydrogen sulfide only as a disagreeable industrial waste product. Instead, it should be sought as a mineral and as a heretofore untapped source of hydrogen<sup>2, 18, 19, 20, 21</sup>

In 1979, in the United States, 1.76 million tons of sulfur was recovered from natural gas, and 2.31 million tons from petroleum. In Canada, 6.1 million tons was recovered. Most of it was first retrieved as hydrogen sulfide. Its hydrogen, had it been recovered, might have fixed 2.5 million metric tons of atmospheric nitrogen as ammonia. Its heating value,  $9.1 \times 10^{11}$  J would have been equivalent to that of 17 million barrels of gasoline. Or, it might have been used to hydrogenate one million tons of coal to produce 59 million barrels of high-grade liquid hydrocarbon, about 3% of that we imported in 1980.

One estimate of the organically bound sulfur in recoverable fossil fuels in the United States alone places it at at least 40 billion metric tons<sup>25</sup> The associated hydrogen would come to about 2.7 billion tons. Regardless of exactly how much is actually there to be recovered, there will be much hydrogen sulfide in our future.

The idea of recovering both hydrogen and sulfur from hydrogen sulfide was considered by Raymont<sup>26</sup> and by others<sup>27-30</sup>

Accordingly, we conducted a series of studies of the feasibility of using solar energy to recover hydrogen and sulfur from hydrogen sulfide. In a series of preliminary experiments in a solar furnace, we obtained substantial amounts of hydrogen and sulfur by simply quenching the effluent. In the temperature range 1600-1800K at 0.05-0.15atm we achieved quench fractions as high as 85% of the theoretical maximum.

Thus encouraged, we did concurrent more detailed experimental measurements of the

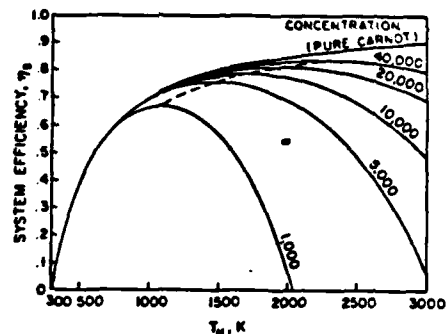


Figure 2. Variation of the system efficiencies of reversible systems with reactor temperature. The uppermost curve is for a Carnot engine. The other curves are for devices which are otherwise reversible, but which, using the sun as a source, must necessarily reradiate energy at a rate which is proportional to the fourth power of their temperature. The parameter is concentration ratio. The dashed curve shows the maxima of the other curves (Reference 2).



Figure 3. The 4.2 meter concentrating solar furnace of the University of Minnesota. The heliostat rotates on two axes to redirect sunlight to the concentrating array of 312 hexagonal-in-plan-form spherical mirrors whose centers are located on the surface of a sphere. The concentrating mirrors are all brought as nearly as possible to a focus at the aperture of a cavity receiver, which serves as the reactor.

conversion of hydrogen sulfide in a solar furnace<sup>21</sup> and a theoretical study to assemble information which could be used to evaluate the economic viability of such a solar process<sup>20</sup> and to compare it with some non-solar alternatives. Some pertinent experimental results are shown in Figures 4-9.

Figure 4 shows the variation of the hydrogen production rate with hydrogen sulfide feed rate at 380 torr and 1700K. Although the production rate continued to rise with hydrogen sulfide feed rate, suggesting

that we were not yet reaching any limitation imposed by the power available from the furnace, the yield, Figure 5, showed a small variation with feed rate, going through a maximum of about 0.45 at a feed rate of about 1.9 moles/sec. This suggests that at the highest feed rates the yields were becoming rate limited with respect to the forward (dissociation) reactions, whereas at the lowest flow rates the reverse reactions were fast enough to decrease the product yield. Kinetic calculations suggest that if the only reactions of concern were gas-phase reactions, the recombination reactions should have been orders of magnitude slower. Our experimental observations are thus in agreement with the experimental observations of Bandermann and Harder<sup>31</sup> who observed that alumina surfaces increase the rates of these reactions dramatically. Our observations that we could bracket the flow regimes over which the yield can go through a maximum suggests that hydrogen sulfide will be a good benchmark reference reactant for evaluating the performance of reactors in general. The quench fractions corresponding to the yields of Figure 5 are shown in Figure 6.

The variation of hydrogen production rate with temperature, at a feed rate near that for maximum yield at a pressure of 300 torr is shown in Figure 7. The corresponding yields are shown in Figure 8 and the quench fractions, the fractions of the theoretical maxima for very slow reactions, in Figure 9. These results bear out the expectations of our preliminary study and enhance the significance of our economic evaluation.<sup>20</sup>

We compared the payback times for the capital cost of a solar facility with those for two alternatives, one which uses electric power exclusively and one which uses electric power only when the sun is not shining. A sample result is shown in Figure 10.

When electric power is cheap, 5¢ per kWh, electric power may be the more attractive alternative. As electric power becomes more expensive, there is a crossover, and at 15¢ per kWh solar is the clearly to-be-preferred alternative. The extent to which high quench fractions can be achieved in various configurations will be an important factor in determining the economic viability of such a process, and other related processes as well. We are therefore continuing and refining our studies of this interesting system.<sup>22</sup>

#### Hydrogen and Oxygen from Water

Solar thermochemical water splitting in a one-step process is of abiding interest.<sup>33-39</sup> Bilgen<sup>40</sup> did analytical and experimental studies and considered the possibility of quenching hot equilibrium products. A group at Los Alamos<sup>41</sup> concluded that it could not be done. Lede, Lapique, and Villiermaux<sup>42</sup> concluded that equilibrium was quickly established when H<sub>2</sub>O was heated. They also quenched the streams which emerged from the

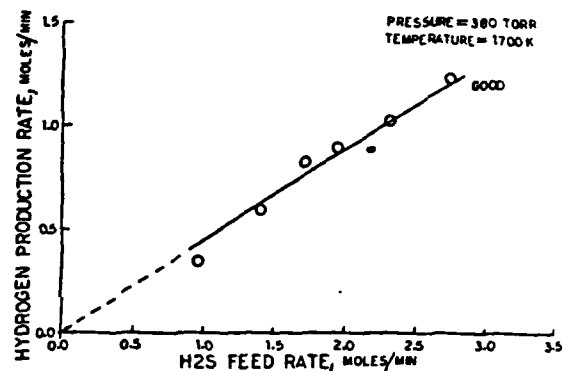


Figure 4. Variation of the hydrogen production rate with hydrogen sulfide feed rate at 300 torr and 1700K.

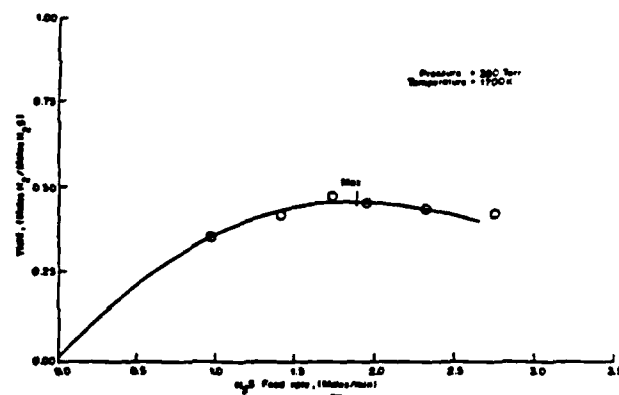


Figure 5. Variation of product yield with hydrogen sulfide feed rate at 300 torr and 1700K.

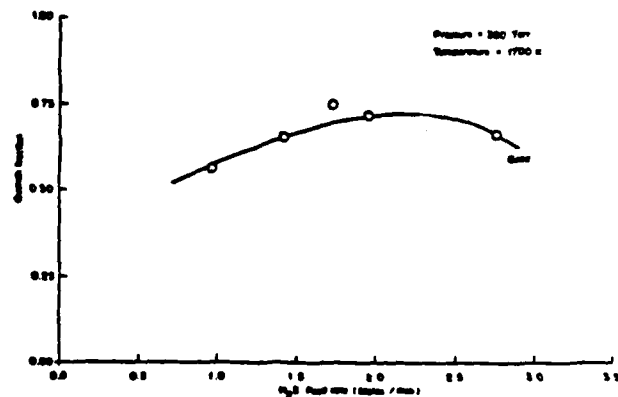


Figure 6. Variation of quench fraction with hydrogen sulfide feed rate at 300 torr and 1700K.

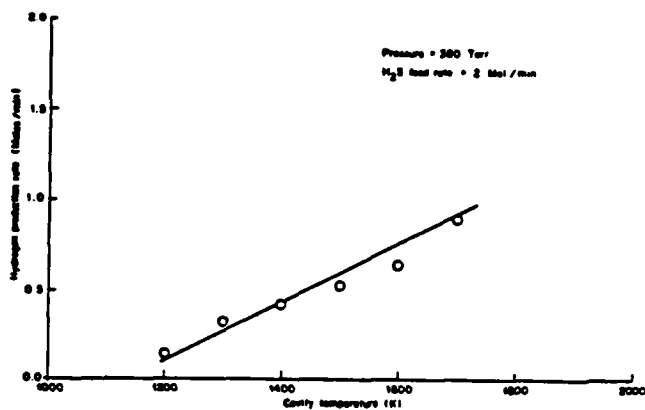


Figure 7. Variation of hydrogen production rate from hydrogen sulfide with cavity temperature at 380 torr, at a constant feed rate of 2 moles/min.

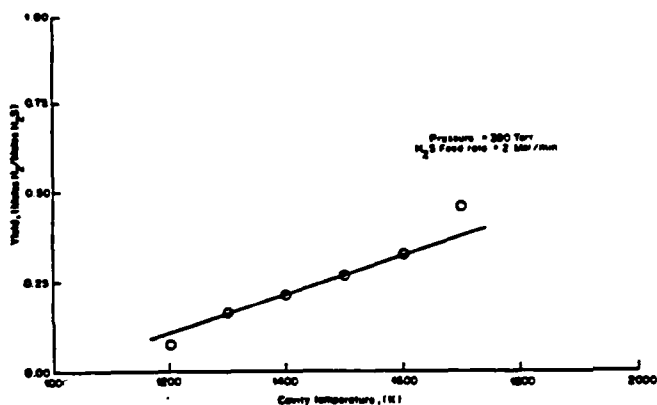


Figure 8. Variation of hydrogen yield from hydrogen sulfide with cavity temperature at 380 torr at a constant feed rate of 2 moles/min.

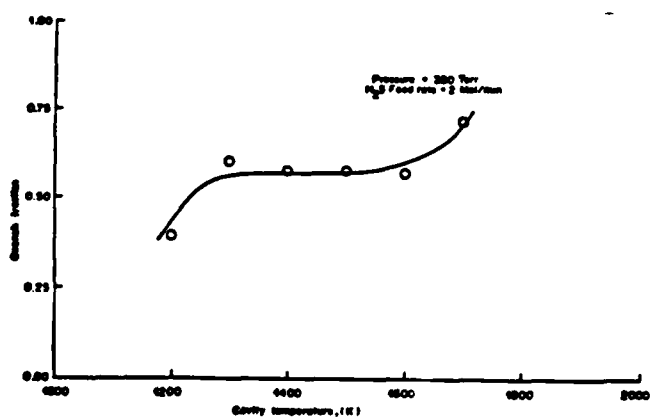


Figure 9. Variation of the quench fraction with cavity temperature for hydrogen sulfide at 380 torr at a constant feed rate of 2 moles/min.

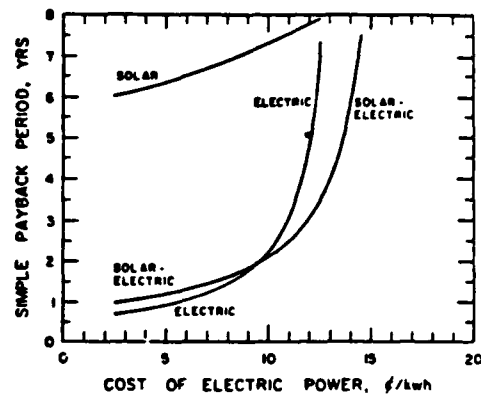


Figure 10. Variation of the payback period of alternative schemes with the cost of electrical energy. The all-solar facility is assumed to be operable 20% of the time, the others 100%. The reactor temperature is 1600K, the pressure is 1 atm, and the design point quench fraction is assumed to be 0.7. The plant produces 100 gram moles per second each of hydrogen and sulfur.

focus of an arc image furnace. Our analytical studies<sup>1, 7-9, 11</sup> emphasized high-temperature separation rather than quenching. We believe that quenched mixtures should be avoided, at least until they can be safely handled. Quenched mixtures from which most of the H<sub>2</sub>O has been removed are explosive over a wide range of compositions<sup>3, 4</sup>. Nevertheless, in view of the interest of the solar community in quenching water and some kinetic calculations<sup>45</sup> that suggested that we could, indeed, quench the reaction in our facility, we tried it at 0.02atm and 2125K. It worked. The product was, indeed, explosive<sup>17</sup>. The conversion was about 0.0045, about 10% of the maximum that could have been expected at that temperature and pressure. The result suggests that quenching may well be a viable way of splitting water, but that what may be needed to make that process industrially attractive is a safe technique for handling the low-temperature, explosive mixtures until they can be separated. Accordingly, we have emphasized research on high temperature separation schemes.

Our first generation devices embodied effusional reactor-separators which achieve a partial separation of the products. They require recirculation of a great deal of water. Thus, from a thermodynamic standpoint, their heat exchangers are wasteful. Moreover, we have not yet fabricated a successful effusion membrane. We then sought ways to minimize the amount of working fluid which must be circulated.

In the meantime, others evaluated one-membrane systems which effect the separation by removing one of the components, oxygen,

from the high-temperature equilibrium system by diffusion of the oxygen under the influence of a pressure gradient or an emf<sup>46-50</sup>. We expected that such systems might also entail substantial recirculation.

Accordingly, our second generation was an extension of an earlier idea<sup>51-52</sup>. It was a two-membrane reactor-separator, the ROC<sup>1</sup>, which achieves a complete separation in a single pass of the water and thus requires no recirculation.

#### One Membrane Devices

Fally's<sup>50</sup> patent describes the prototype one-membrane device. Others<sup>46-49, 51</sup> differ from his in that they use an emf, rather than pressure alone, to facilitate or effect transport of oxygen through the membrane. They are thus sometimes referred to as electrolysis cells. But, from a thermodynamic standpoint, at a given temperature a pressure difference and an emf difference across a boundary have the same effect. Although Fally claims that his device will effect virtually 100% separation, the accumulation of hydrogen on the high-pressure side of the membrane and concomitant reduction of the oxygen pressure, should make separation increasingly difficult and require the recirculation of a substantial fraction of the feedwater. The use of electrolysis to boost the oxygen transport against an adverse pressure gradient will probably permit a substantial reduction of the amount of water which need be recirculated.

#### Two Membrane Devices--the ROC

Ford<sup>51</sup> and Nakamura<sup>52</sup> suggested two-membrane reactor-separators. In their systems, high-temperature water is introduced into a chamber whose walls are equipped with a hydrogen passing membrane as well as an oxygen passing membrane. Ihara<sup>53</sup> extended their work. Ford considered the use of palladium and its alloys as hydrogen passing membranes. He thus had to operate at low temperatures with high chamber pressures and inordinately high pressure drops across the membranes. Nakamura, who was concerned with the need to minimize pumping losses concluded that the reactor-separator would have to operate at temperatures above 3000K, a requirement that would make solar collection efficiencies very low and virtually eliminate the possibility that other energy sources might be used or that suitable membrane materials might be found.

In addressing this problem<sup>1</sup> we concluded that optimum temperatures for such systems would be much lower than those envisioned by Nakamura. Ihara<sup>53-55</sup> has since agreed. Our studies suggested that particular geometries and membrane conductances might ameliorate materials problems by controlling oxygen activity. Thus, we might use more reactive refractory metals for hydrogen passing membranes, and operate at higher temperatures than Ford's. We called our device

the ROC, an acronym for reduced oxygen concentration. It seemed appropriate. It was the name of the "fabulous bird of Arabia so huge that it bore off elephants to feed its young"<sup>56</sup> that was duped by Sindbad the Sailor<sup>57</sup> into serving him.

It is pertinent to ask: "Would it be advantageous to combine the features of ROC's with those of electrolysis to achieve water splitting?"

Superficially, it would appear that the work of electrolysis at the high reactor temperatures would be equivalent to the low temperature pump work required to create the pressure drop across the oxygen-passing membrane in the ordinary ROC, and that they are therefore thermodynamically equivalent. We therefore examined what would be the effect on the thermal efficiency of the ROC if it were to be enhanced by the use of high-temperature electrolysis, or if electrolysis were to be used in place of the pump, thus replacing it completely. The results are shown in Table 1. The EROC is a device which uses an electrical boost only on the oxygen membrane. The DERO uses an electrical boost on both.

Table 1 shows that the semi-idealized ROC is superior to its semi-idealized electrical modifications. The slight differences in the first efficiencies arise from the substitution of thermodynamically more

Table 1. Performance of the ROC Configurations<sup>10</sup>

	ROC	EROC	DEROC
heat flux to reactor, kW	285.64	243.71	172.13
pump work, kW	15.41	9.70 <sup>a</sup>	
electrical work, kW		42.13 <sup>b</sup>	113.71
thermal efficiency <sup>c</sup>	0.776	0.761	0.717
thermal efficiency <sup>d</sup>	0.731	0.635	0.520

a. hydrogen pump only; b. oxygen pump only; c. defined as the net work equivalent of one mole of hydrogen minus the pump and electrical work required to achieve it, divided by the heat to the reactor-separator; d. defined as the work equivalent of one mole of hydrogen divided by the heat input required by the reactor-separator plus that required to produce the electric power required for electrolysis and the pumps with an efficiency of 0.4.

valuable electrical work for heat in the reactor-separator. The greater differences shown in the second efficiency reflect the likelihood that electric power will be furnished by a heat engine, whose efficiency has been taken, arbitrarily, to be 0.4.

The EROC may require an order of magnitude more heat exchange than its competitors, but it does offer a potential advantage. Electrolytic pumping of oxygen would permit it to operate at a much lower temperature. Palladium and platinum thus become attractive candidate materials for hydrogen passing membranes. Such a device, operating at 1400K and 30 atm might be expected to produce a "residue" containing mole fractions of 0.9, 0.1, and  $10^{-11}$  water, hydrogen, and oxygen, respectively, from which the hydrogen might be separated by palladium membrane. It would require substantially less recirculation. Heat exchanger losses would thus be substantially reduced.

It is evident that a great deal of research, analytical as well as experimental, should be done on these interesting systems. In our laboratory we have fabricated and tested<sup>5</sup> zirconia electrodes with which we have been able to pump oxygen across adverse pressure gradients and effect separations. A negative development has been the observation that at higher-and-higher temperatures the passage of oxygen in the direction of the pressure gradient competes with the electrolytic transport, but the good news is that that will make it easier to fabricate a ROC.

#### Hydrogen Bromide and Hydrogen Bromide-Water Mixtures

The kinetics of the hydrogen bromide reaction is probably one of the most studied and well understood problems of chemical kinetics. We have done theoretical studies of hydrogen bromide as a candidate material for solarthermal solar energy storage<sup>4, 13</sup>, with encouraging results. We have also done unpublished thermodynamic calculations involving hydrogen bromide-water mixtures as the working fluid and concluded that at temperatures high enough to make hydrogen bromide an attractive candidate, water acts essentially as an inert diluent. The non-equilibrium mixtures that one hopes to achieve in a quenching process would be rendered extremely easy to separate into its elementary components by the addition of a small amount of water. They might be used, for example, in a fuel cell. From an applications standpoint, both neat hydrogen bromide and hydrogen bromide-water are attractive.

Moreover, because its kinetics are so well known, hydrogen bromide is also an attractive bench-mark system to be used in obtaining a data base which will be useful in organizing our knowledge of quench processes and relating fundamental reaction kinetics to the performance of chemical systems in real hardware.

#### Nitric Oxide from Air

Fixing atmospheric nitrogen as nitric oxide at high temperatures is the well-known dream of Farrington Daniels. That small, low-temperature non-equilibrium concentrations of nitric oxide are obtained when one cools nitrogen-oxygen mixtures from high temperatures is well known to those who deal with nitric oxide emissions from combustion processes. This is confirmed by our experiments as well. Our thermodynamic calculations suggest that we cannot expect high yields of useful products from this system; nevertheless, it is an interesting system because of its kinetics and because the effects of fixing atmospheric nitrogen cheaply would be so far reaching.

Although we have not yet published on the formation of nitric oxide from air in a solar furnace, we have done thermodynamic calculations and some preliminary quench experiments in which we have not attempted to optimize yields, we have measured non-equilibrium concentrations of nitric oxide in the quenched products from our solar furnace that are about 16% of the high temperature equilibrium concentrations and, of course, many orders of magnitude higher than the ambient temperature concentrations.

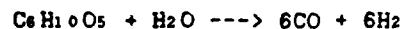
#### Carbon Dioxide

At high temperatures, carbon dioxide disproportionates to carbon monoxide and oxygen. The extent of disproportionation depends on the pressure, lower pressures increasing it. Combustion experience suggests that in the absence of hydrogen, the recombination reaction should be quite slow. Carbon dioxide disproportionation is therefore an interesting reaction since, depending on the pressure, the disproportionation can become quite extensive.

The numbers in Table 2 suggest that, if the recombination reaction in a solar furnace is indeed low, as one would expect from the results of combustion studies, that it should be easy to recover substantially non-equilibrium quantities of carbon monoxide from the solar thermolysis of carbon dioxide, storing a substantial amount of solar energy in the process.

#### Synthesis Gas from Cellulose and Water

The isothermal reaction



is endothermic to the extent 582kJ. That means that the conversion of one formula weight of cellulose by its reaction with water, to give synthesis gas, increases the heating value by 582kJ. This is thus a means of storing solar energy in one of its most useful forms, as the potential energy of a chemical reaction.

Table 2. Equilibrium Extent of Disproportionation of Carbon Dioxide

T, K	P, atm			
	1	0.1	0.01	0.001
1000	$1.08 \times 10^{-7}$	$2.2 \times 10^{-7}$	$4.67 \times 10^{-7}$	$1.33 \times 10^{-5}$
1800	0.0025	0.0049	0.0106	0.0231
2000	0.0084	0.0171	0.0372	0.0820
2200	0.0202	0.0477	0.1057	0.2221
2400	0.0345	0.0757	0.2180	0.4077

Fluidized beds, with which we have done previous studies on nitric oxide formation in combustion processes<sup>5,8a</sup> seem to be appropriate for such reactions, although there is, at present, not much experience with them. We are now beginning to do some experimental work which is aimed at the development of fluidized bed reactors for solar furnaces.

Table 3 shows the mole fraction of the product which would be synthesis gas issuing forth from an inert, or if it turns out to be necessary, catalytic, bed to which cellulose is being fed and which is being fluidized by water, if it can be made to achieve equilibrium.

Table 3. Mole Fraction of Synthesis Gas in the Product of Cellulose-Water

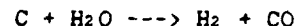
Temp., K	Mole Fr.
1000	0.922
1200	0.944
1400	0.962
1600	0.975
1800	0.986
2000	0.992
2200	0.996
2400	0.999

Relatively low bed temperatures could give excellent results, especially if non-equilibration during the quench were enhanced by departure of the gas from the heterogeneous region of the bed.

Alternatively, the products could be made, catalytically, carbon dioxide and methane, at some sacrifice in the solar energy storage.

#### Synthesis Gas from Coal (coke)

A related reaction is the conversion of carbon in a fluidized bed, using water as the fluidizing phase. This reaction also stores a lot of solar energy. The changes of enthalpy and gibbs function at various temperatures for the reaction



are given in Table 4.

Table 4. Variation of Enthalpies and Gibbs Functions of the Carbon-Water Reaction, kJ, with Temperature

T, K	$\Delta H$	$\Delta G$	remark
298	+131.29	+91.266	eq lies far to the left
1000	+135.875	-7.611	spontaneous to right
1500	+135.156	-79.262	spontaneous to right
2000	+132.959	-150.423	spontaneous to right
2500	+130.143	-220.949	spontaneous to right

It is evident from the table that this reaction stores a lot of solar energy in the product and that sunlight is uniquely suited to effect it. It, like the previous reaction, is highly endothermic, but it will proceed spontaneously at temperatures that are easily achieved in our solar furnace. It thus stores solar energy as the potential energy of the product, requiring no input of additional electrical or mechanical work.

#### Zinc from Zinc Oxide

This is an example of a chemical reaction which does not become spontaneous at atmospheric pressure (to yield the separated elements) at any temperature. It requires some work input. The amount of work, which is easily furnished by electrolysis, decreases with temperature<sup>4</sup> Zinc oxide, at one atmosphere, sublimates to give a mixture of monatomic zinc and (principally) molecular oxygen at about 2250K<sup>5,8,82</sup> Thus, the work required to separate zinc oxide into its elements decreases continuously, corresponding to the work of simply unmixing the two gases if it is done on the vapor phase.

We have measured the electrolytic decomposition potential of zinc oxide in our solar furnace over a temperature range 600-1400K<sup>3,84</sup> in a variety of high-temperature

electrolytes made from mixtures which contained sodium hydroxide, zinc fluoride, sodium fluoride, aluminum fluoride, and calcium fluoride, and have indeed observed a diminution of the decomposition potentials with increasing temperature, Figure 11.

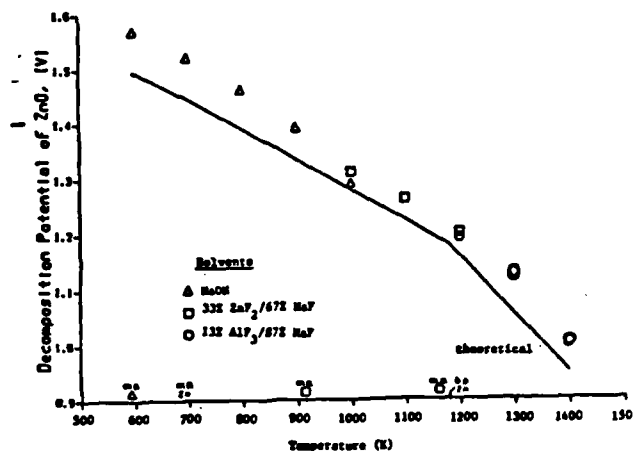


Figure 11. Variation of the decomposition potential of zinc oxide in a variety of solvent with temperature in a solar furnace. The solid curve is the theoretical decomposition potential. The differences between the experimental and theoretical values are the overpotentials.

We have also done a few preliminary experiments in which we have demonstrated that we can, by imposing the appropriate emf, recover zinc from zinc oxide by electrically pumping oxygen from zinc oxide vapor in the vapor phase against a pressure gradient, which exhausts it to the atmosphere<sup>6</sup>

In the temperature range 1200-1800K the vapor pressure of zinc oxide is substantially below 0.01atm. Nevertheless, we have recovered elemental zinc from zinc oxide vapor in this range, exhausting it to the air across a zirconia membrane by imposition of an external emf across it, i.e., we have produced one of the components of an EROC, and have achieved a little progress in fabricating what should be electron-conducting zirconia membranes, which should permit us to fabricate a ROC.

#### ACKNOWLEDGEMENTS

The research described in the paper is the work of many graduate students and several post-doctoral research associates. I would like to express a special note of appreciation to R.B. Diver, J.E. Noring, and Todd Kappauf. Additional thanks are due to the many people with whom I coauthored the references cited in this paper. The work could not have been done without a generous series of free grants from the Northern

States Power Company, and the financial support of The Office of Naval Research and the Department of Energy.

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