LA-UR-78-652

CONF-771246--1

TITLE: Thermochemical Production of Hydrogen from Water*

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MASTER

SUBMITTED TO: To be included in the Proceedings of the DOE sponsored workshop on "Supply and Demand of Hydrogen as a Chemical Feed Stock," December 12-14, 1977 at the University of Houston, Houston, Texas.

*Work completed under the auspices of the Department of Energy

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INTRODUCTION

Currently there is widespread interest in the development of a "hydrogen economy" as an eventual solution to many of the problems associated with the increasing energy crisis. Many papers have been published that discuss the advantages and problems associated with the widespread use of hydrogen as a medium for energy storage, energy transmission and indeed for large-scale use as a non-polluting fuel. However, in addition to the potential for a hydrogen economy, it is important to emphasize that hydrogen is a very valuable chemical that is used in large volume for the production of ammonia and in chemical processing. Requirements for such applications are increasing rapidly and it is clear that an expanded production of hydrogen will be required in the future even if the "hydrogen economy" is only partially realized. It is equally clear that fossil energy sources will become inadequate and that eventually large scale hydrogen production must utilize nuclear fission, fusion and/or solar energy for the decomposition of water by electrolysis, or by thermochemical cycles, and perhaps, by hybrid combinations of these methods.

The potential higher efficiency and lower cost for thermochemical methods, versus the overall electrolysis path has been rather widely recognized. As a consequence, several laboratories throughout the world are conducting programs to develop thermochemical processes for water decomposition. A large number of thermochemical cycles have been conceived. Unfortunately, many have been published without experimental verification

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of the reactions in the cycle. As a result of this, most evaluations and/or comparisons of thermochemical processes for process efficiency or cost have been based on assumed data or on reaction conditions that have not actually been achieved. Nevertheless, several cycles have now been published where all of the reactions have been demonstrated experimentally. As a consequence, the development of methods for engineering and cost analyses for this new technology can be based on the actual chemistry involved in demonstrated cycles. It is probable that such engineering assessment will reveal serious problems in most cycles, but in many cases changes in process flow sheets will be possible that minimize the problem identified. It is anticipated that this iterative process will not only lead to improvements in existing cycles, but also to the development of criteria to guide the search for and evaluation of new and possibly better cycles.

THERMOCHEMICAL WATER DECOMPOSITION

In its most general sense, thermal water decomposition implies the splitting of water into its elements, hydrogen and oxygen, by the use of heat. Water has an extremely high enthalpy and free energy of formation (-286 and -237 kJ/mol) that decrease slowly as the temperature increases. For this reason, direct or one-step processes to split water are impractical. Temperatures in excess of 3000 K are required to obtain a reasonable yield of hydrogen and one is faced additionally with separating this hydrogen from oxygen and the unreacted water before the products recombine. The reaction is also favored by low pressure which is detrimental if the final product is hydrogen at pipeline pressure. (1)

To improve on direct water-splitting, researchers have tried methods that decompose water in a number of steps. These processes, by which water is decomposed by a set of chemical reactions at various temperatures with complete recycling of the intermediate reactants, are known as thermochemical cycles.

Thermochemical cycles appear promising due to the following reasons:

- Overall heat-to-hydrogen efficiencies of the order of 50-60 percent may be obtained as compared to 25-30 percent by conventional electrolysis.
- The only raw material is water.
- Little or no net work may be required in a cycle if exothermic (reject) heat is used to generate work.
- No major technological breakthroughs are required to develop cycles from the conceptual stage to the laboratory and later to a plant. Modern chemical engineering practice has developed a high degree of sophistication in separation technology as exemplified by the petrochemical industry.

Thermochemical Efficiency

Processes for the production of hydrogen utilize liquid water as the raw material. The definition of efficiency, η, adopted by the International Energy Agency, (2) is the ratio of the theoretical energy required, ΔH^o, (286 kJ) to the total heat input required, Q_t, for the decomposition process. Thus,

$$\eta = \frac{\Delta H^o}{Q_t} = \frac{286}{Q_t} \qquad 1)$$

The upper limit on thermochemical cycle thermal efficiency, η, was defined by Funk and Reinstrom (3) as:

$$\eta \leq \frac{\Delta H^o}{\Delta G^o} \cdot \frac{T_h - T_c}{T_h} \qquad 2)$$

where, T_h and T_c represent the upper and lower operating temperatures in the cycle.

This efficiency has an upper limit of 1.2 times the Carnot efficiency of an engine operating between the same higher and lower temperatures in the cycle. For the temperatures 1000 K and 400 K, a cycle effiency of 72% is theoretically possible.

The Step-Wise Decomposition of Water

The basic thermochemistry involved in the step-wise decomposition of water was published in 1966 by Funk and Reinstrom. (3) They pointed out that a large ΔS value would be required for the $T\Delta S$ term to equal the ΔH term in the high temperature reaction of a two-step cycle and concluded that simple two-step cycles would not be possible for temperatures available from practical heat sources. In more recent years, several authors have considered the thermochemistry of water decomposition cycles and essentially confirmed the conclusions of Funk and Reinstrom. Bowman has repeated the analysis (4) in order to point out that specific values for the sum of the ΔS^o terms and the sum of the ΔH^o terms are required for the endothermic reactions if maximum heat efficiencies are to be realized. These specific and related values depend on the maximum temperature at which heat is available and the ΔG^o of H_2O at the low temperature. Thus, for a general two-step decomposition cycle

1. $R + AB \rightarrow RA + B$ at T_1
2. $RA \rightarrow R + A$ at T_2

"ideal" ΔS^o and ΔH^o values are given by

$$\text{ideal } \Delta S^o = \frac{-\Delta G^o(AB)}{(T_2 - T_1)} \qquad 3)$$

$$\text{ideal } \Delta H^o = \Delta S^o \times T_2 \qquad 4)$$

For decomposition of water with $T_1 = 400$ K and $T_2 = 1100$ K, i.e.,

3. $R + H_2O \rightarrow RO + H_2$ at 400 K

4. $RO \rightarrow R + 1/2\ O_2$ at 1100 K

For reaction 4, $\Delta S^o \sim 320$ J/K, and $\Delta H^o \sim 350$ kJ.

The striking feature of the above analysis is the large ΔS^o values required for the decomposition reactions. Typically, reactions such as 4, exhibit ΔS^o changes of about 100 J/K. Thus, it is quite clear that simple two-step cycles for H_2O decomposition will not be found unless higher temperatures are used.

Examination of the ideal ΔS^o values emphasizes the value of reactions with large entropy changes in water splitting cycles in order to minimize the number of reactions required. This, of course suggests gaseous reactants or reaction products to provide the large entropy changes.

Practical considerations that have to be met before a conceptual cycle becomes a matter of reality include the selection of the following problems:

Process:
- Availability of Accurate Thermodynamic and Equilibrium Data
- Kinetic Data

- Effect of Losses of Intermediates
- Effect of Competing Reactions and Side Products

Engineering:
- Development of Separation Methods to allow for Reactant Recycle and Product Separation
- Minimization of Heat Exchange Area
- Materials to withstand High Temperature and Hostile Environments

These reasons are the primary ones that explain why cycles have not yet been developed at the pilot plant stage. Mention has already been made of the large amount of scientific activity in this field; most of it is devoted to laboratory testing of the key reactions in the cycles.

Thermochemical Hydrogen Cycles under Research and Process Development

Thermochemical cycles are being studied in this country and in other laboratories abroad. Some of the more promising cycles under investigation are described below:

The Sulfuric Acid Hybrid Cycle

Hybrid cycles are those in which some of the reactions proceed thermally and others are effected by electrolysis at a lower voltage than that for water electrolysis. This is one of the hybrid cycles studied early in the LASL Program. (5) The "two-step" cycle may be written as:

5. $SO_2 + 2H_2O \xrightarrow{elect.} H_2SO_4 + H_2$ 300 K

   $E^o = -0.17V$ for 1 M H_2SO_4 and 1 atm. SO_2

6. $H_2SO_4 \longrightarrow H_2O + SO_2 + 1/2\ O_2$ 1144 K

The cycle is shown schematically in Figure 1. Hydrogen is generated electrolytically in an electrolysis cell which anodically oxidizes sulfurous

acid to sulfuric acid while simultaneously generating hydrogen at the cathode. Sulfuric acid formed in the electrolyzer is then vaporized, using thermal energy from a high temperature heat source. The vaporized sulfuric acid (sulfur trioxide-steam mixture) flows to an indirectly heated reduction reactor where sulfur dioxide and oxygen are formed. Wet sulfur dioxide and oxygen flow to the separation system, where oxygen is produced as a process coproduct and the sulfur dioxide is recycled to the electrolyzer. Workers at the Westinghouse Electric Corporation are concentrating on developing the cycle. They have made excellent progress in experimental programs to improve the electrolysis reaction and have achieved higher current densities at higher sulfuric acid concentrations than those reported earlier by LASL. They have also conducted extensive studies on the catalytic thermal decomposition of sulfuric acid. In addition, engineering evaluations of the process, its performance as a function of operating parameters, and its economics have been performed.

In a recent Progress Report (6) Farbman reported that for 50 wt% sulfuric acid produced at 50°C and current densities of 2000 A/m^2, total cell voltages of 600 mV for the electrolysis step were attained. Eventually, the Westinghouse workers hope to achieve their "target" conditions of 75 wt% sulfuric acid at a current density of 2000 A/m^2 and a cell voltage of 480 mV.

Under these conditions, a process evaluation, in which a very high temperature nuclear reactor (VHTR) was used as the heat source, indicated an overall thermal efficiency of 54% for the sulfuric acid hybrid cycle.

The Westinghouse workers have also estimated the cost of hydrogen produced by the hybrid cycle; assuming their "target" conditions and assuming what may be described as an advanced method of power production, they derived a very optimistic cost of $5.27/GJ (see cost section below). This may be the reason why the cycle has achieved popularity. At any rate, the Julich Nuclear Research Center in West Germany has initiated a large developmental effort on the cycle. (7) Workers at the Euratom Joint Research Center in Ispra, Italy are also maintaining an active interest in the cycle. (8)

The Sulfuric Acid-Hydrogen Iodide Cycle

At the First World Hydrogen Energy Conference (March 1976), the General Atomic Co. presented their Sulfuric Acid-Hydrogen Iodide cycle. (9) The cycle may be written simply as:

7.	$2H_2O + SO_2 + x\ I_2 \rightarrow H_2SO_4 + 2\ HI_x$ Aqueous	300 K
8.	$2HI_x \rightarrow x\ I_2 + H_2$	573 K
9.	$H_2SO_4 \rightarrow H_2O + SO_2 + 1/2\ O_2$	1144 K

where the HI_x represents the mixture of several polyiodides formed in the initial solution. Seperation of the H_2SO_4 and HI_x takes place under gravity, as the two acids are almost immiscible. The upper phase contains most of the H_2SO_4, and the lower phase contains most of the HI_x.

After physical separation, the sulfuric acid must be dried (concentrated) before it is decomposed at high temperature. Rather extensive drying, distillation and recycle operations are the principal disadvantages of the process. The availability of iodine and a system for adequate iodine recovery may also prove disadvantageous. However,

overbalancing these disadvantages, perhaps, is the potential for a continuous process involving essentially only liquids and gases.

A process flowsheet illustrating the major operations and material transfers is presented in simplified form in Fig. 2. Process engineering, involving the coupling of this cycle to a high temperature gas-cooled reactor (HTGR), indicates an efficiency in the 40-50% range.

Prior to the G.A. disclosure, workers at the Euratom Joint Research Center (Ispra) had discovered essentially the same method for separation of the H_2SO_4 and HI. Vigorous development of the cycle is continuing at both Laboratories. The work involves corrosion studies and the evaluation of process equipment and containers as well as attempts to improve yields via changes in process conditions.

Thermochemical Cycles from Los Alamos Scientific Laboratory

The Los Alamos program may be described as a combined theoretical and experimental effort to develop criteria required for an ideal process and to search for thermochemical cycles that approximate the criteria in practice, (10) conceptual cycles are subjected to experimentation in order to verify the concept (usually, of course, it is found that at least one of the reactions will not occur). If the reactions can be demonstrated, additional data are obtained in order to permit initial evaluation and also comparison with other cycles.

Process development and engineering analysis activities have been directed primarily to experimental studies of reactions relevant to cycles employing sulfuric acid as an intermediate substance. These cycles include the sulfuric acid-hydrogen bromide cycle, the hybrid sulfuric

acid cycle (Westinghouse) and the sulfuric acid-iodine cycle (General Atomic). The rationale for this work is to avoid the large heat penalties incurred on drying sulfuric acid solutions. The approach taken in the case of sulfuric acid-hydrogen bromide cycle has been to devise means of decomposing anhydrous hydrogen bromide which is produced with essentially pure sulfuric acid in one of the cycle steps making water evaporation unnecessary. In the work supporting the development of the hybrid cycle and the icdine cycle, the approach is slightly different. The use of an insoluble, non-hydrated, metal sulfate precipitated from sulfuric acid solutions as a means of recovering sulfur trioxide (and hence sulfur dioxide) without having to dry the acid is being continued. Efforts have been devoted to the engineering design and analysis of these modifications which produce smaller heat penalties as compared to the existing forms of the cycles. Results are an expected increase in cycle efficiency.

A preliminary view of cycles having maximum reaction temperatures in the 1500-1700 K range is being undertaken. These temperatures may be attained in magnetic fusion energy schemes. Magnetic fusion energy may thus incorporate thermochemical cycles in the production of synthetic fuels.

Use of Metal Sulfates in the H_2SO_4 Cycles

In the H_2SO_4 hybrid cycle (reactions 5-6) large amounts of heat are needed to dehydrate the sulfuric acid. A significant saving in energy might be achieved by forming a suitable metal sulfate from the H_2SO_4. The alternative hybrid cycle may be represented by:

10. $SO_2 + 2H_2O = H_2SO_4$ (aq.) $+ H_2$, electrochemical

11. $H_2SO_4 + MO = MSO_4 + H_2O$

12. $MSO_4 = MO + SO_3$

13. $SO_3 = SO_2 + 1/2O_2$

The same is true for the H_2SO_4 - HI cycle (reactions 7-9) in which sulfuric acid is dehydrated prior to thermal decomposition.

The metal sulfate used in reactions 11-12 should have low solubility and form an anhydrous sulfate. A survey and assessment of the literature were made for antimony and bismuth sulfates, both of which satisfy these criteria.

14. $Bi_2O_3 \cdot 3SO_3 = Bi_2O_3 \cdot 2SO_3 + SO_3$

15. $Bi_2O_3 \cdot 2SO_3 = Bi_2O_3 \cdot SO_3 + SO_3$

$Bi_2O_3 \cdot 3SO_3$ decomposes with increasing temperature to SO_3 and a series of oxide sulfates terminating in Bi_2O_3 itself. The equilibrium SO_3 pressure for reaction 14 is 1 atm at 860 K, and $Bi_2O_3 \cdot 2SO_3$ in reaction 15 is reported to decompose at 1050 K. Final decomposition to form Bi_2O_3 occurs at higher temperatures. The options for generating SO_3 over a temperature range that includes intermediate temperatures, in addition to high temperatures for SO_3 decomposition, should be useful in achieving efficient extraction of heat from the circulating helium coolant of a high-temperature gas-cooled nuclear reactor.

A preliminary evaluation of the energy efficiency of the bismuth sulfate alternate to the hybrid sulfuric acid cycle has been completed. Reduction in the heat requirements for the acid concentration step as well as for the acid decomposition step show a potential gain of 12% in efficiency on adopting the metal sulfate method of solution concentration.

The Sulfuric Acid-Hydrogen Bromide Cycle

A hybrid cycle involving hydrogen bromide was identified at LASL. It is now under study at the Euratom-Joint Research Center, Ispra, Italy (11) and at the Institute of Gas Technology in the U.S.A. (12)

Labelled Mark-13 at the Ispra Laboratory, the cycle may be represented by:

16. $2H_2O + SO_2 + Br_2 = H_2SO_4\ (\ell) + 2HBr\ (g)$ 440 K

17. $H_2SO_4 = H_2O + SO_2 + 1/2\ O_2$ 1144 K

18. $2HBr\,(g) = H_2 + Br_2$ electrochemical 300 K

For the electrolytic reaction, $\Delta G^o = +\ 112$ kJ or $E^o = -\ 0.58V$. The cycle should prove attractive as it involves reactions in which data have already been obtained. The electrolytic decomposition of HBr is the key step. Electrode reactions on graphite are currently being investigated in this regard.

Heat Sources for Thermochemical Processes

Most discussions of thermochemical hydrogen production tacitly assume that heat will be supplied by dedicated high-temperature, process-heat reactors. For a process to be efficient then, its heat requirements must match the heat delivery characteristics of the reactor. Engineering analyses under this assumption very quickly reveal that isothermal endothermic reactions near the temperature maximum are very undesirable steps. Further, solution drying steps are very disadvantageous if the necessary heat must be derived from the primary high-temperature source. Therefore, at this time it is important to emphasize the fact that after 3-5 years of development in several countries, essentially all of the cycles that have been demonstrated experimentally

contain solution drying or solution concentration steps. Therefore, it seems reasonable to suggest that thermochemical hydrogen plants be located where they can be combined with systems that yield low-temperature heat as a by-product.

Solar energy heat sources are sometimes mentioned for use with thermochemical cycles. Usually it is assumed, at least tacitly, that they will be too expensive. This may be true, but solar towers, mirrors and trough concentrators are getting cheaper. Therefore, it is relevant to note that for a solar heated process, low temperature heat can probably be delivered at significantly lower cost per unit of heat than heat at the maximum temperature. Thus, solution chemistry may be more useful. In addition, an isothermal step near the maximum temperature may be a very useful way of absorbing high temperature heat from a solar tower. Certainly, it seems prudent to seriously consider the possible adaptation of solar heat sources to thermochemical processes.

In the long term, magnetic fusion reactors or laser fusion reactors may become available for synthetic fuel production. Such reactors, in particular laser fusion reactors, may be advantageous for coupling with thermochemical processes since rather large quantities of "recycle power" must be used and, hence, significant quantities of low temperature waste heat can be made available.

Estimates of Costs of Thermochemical Hydrogen

In discussions of thermochemical processes, the question of costs usually is asked quite early. In one sense, the questions are premature since this new technology is only in the initial definition stage. Nevertheless, cost is an important question and early attempts at cost

estimates are valuable not only as a means to develop the methodology for eventual realistic cost estimates, but also to guide experimental development programs. Up to the present time, most cost estimates have been made for conceptual cycles that have not been validated experimentally. The cost estimates given below were made for cycles that have been proved by experimentation even though conditions assumed for the different reactions are for the most part projected conditions that have not actually been adequately demonstrated in an experimental program. Thus, it is difficult to determine whether a particular cost estimate is optimistic or pessimistic since knowledge that conditions are uncertain can lead to conservatism in equipment estimates.

Table I contains a few estimates of the cost of hydrogen produced by electrolysis. No attempt has been made to select estimates where uniform assumptions have been made. In each case, the author used assumptions that they deemed appropriate. Table II contains estimates of the cost of hydrogen produced by thermochemical cycles whose reactions are known to occur in the laboratory. Cycle A is the hybrid sulfuric acid process, and cycle B is the thermochemical sulfuric acid-hydrogen iodide cycle being developed by the General Atomic Co. and by Euratom-Ispra.

Table I

Cost Estimates for Electrolytic Hydrogen

Author	Reference	Current Technology	Advanced Technology	Dollar Type
Escher Donakowski	17	$9.36/GJ	$4.81/GJ	Mid-1975
Steeman	13	5.55	-	1975
Broggi	16	9.76	7.48	1975
Farbman	14	6.65	-	Mid-1974
Nuttall	18	-	5.08	1976

Table II

Cost Estimates for Thermochemical Hydrogen

Author	Reference	Cycle	Cost	Dollar Type	Note
Steeman	13	A	$7.18/GJ	1975	1
Farbman	6	A	5.27	1976	1
Knoche & Funk	15	A	7.15	1976	1,2
Broggi	16	B	5.95	1975	3

Note 1. All of the cost estimates of the hybrid sulfuric acid cycle were based on the Westinghouse "target" conditions rather than the much less favorable conditions that have been achieved in the laboratory up to the present time.

Note 2. The methodology for the cycle evaluation developed by Professor Knoche and Professor Funk will be very useful for evaluating cycles, particularly initial and comparative evaluations. The authors themselves stress the value of the method for indicating directions for improving flow-sheets and processes. Thus, they stress that the sulfuric acid decomposition step in cycles a and b can be improved and costs lowered.

Note 3. The cost estimates made by Broggi assume the production of 60 wt% sulfuric acid in the process. It seems questionable as to whether this concentration can be achieved. Broggi also estimates a cost of $5.40/GJ for a cycle in which an insoluble sulfate is formed (and decomposed) rather than sulfuric acid. The potential insoluble sulfate was not identified.

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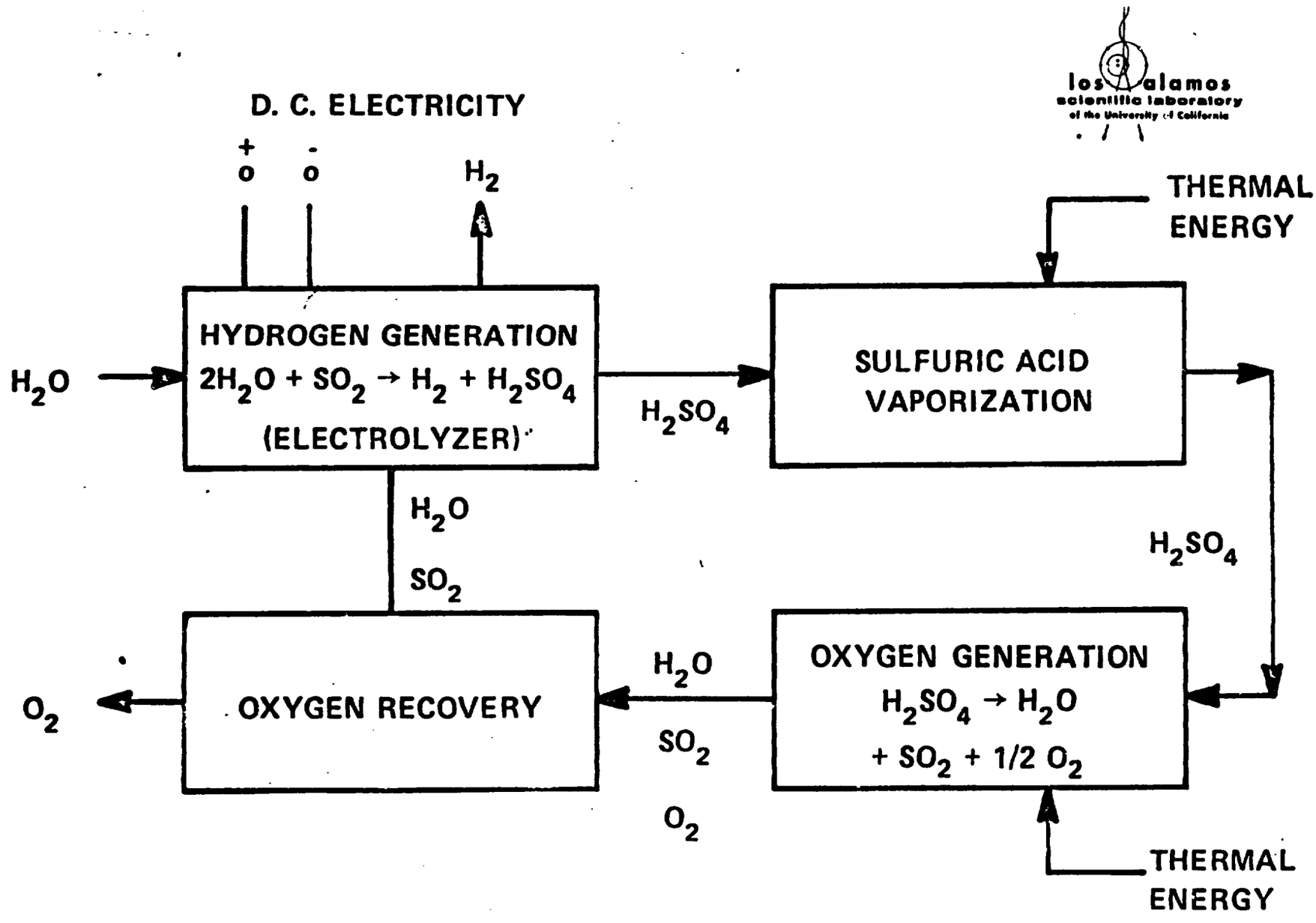

Figure 1 SULFURIC ACID HYBRID CYCLE SCHEMATIC DIAGRAM

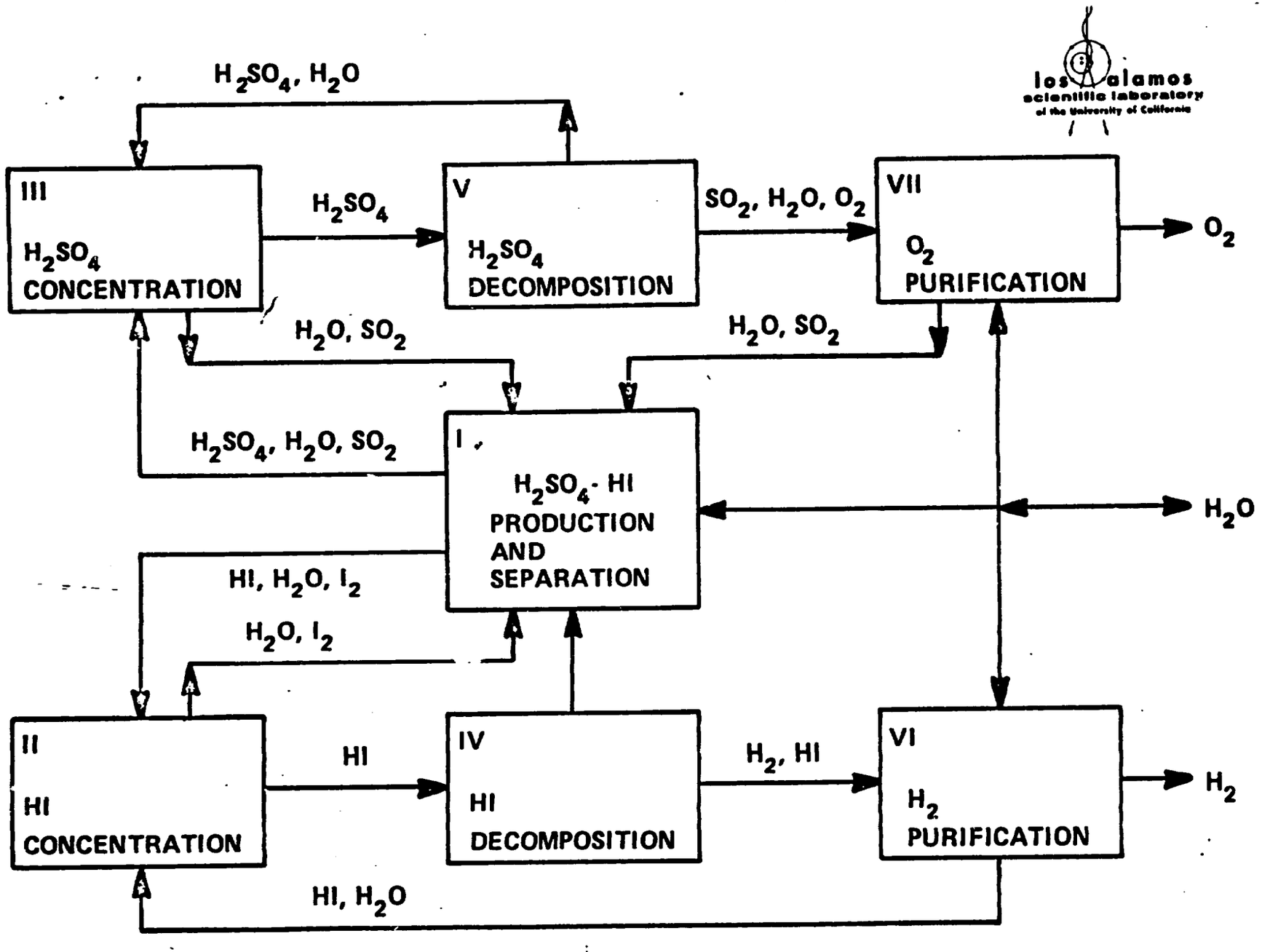

Figure 2 SULFURIC ACID-HYDROGEN IODIDE CYCLE SCHEMATIC DIAGRAM