CONF-780449--2

LA-UR-78-1052

TITLE: Solar-Thermochemical Production of Hydrogen from Water.*

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SUBMITTED TO: To be presented and included in the Proceedings of the Solar Tower Test Facility (STTF) Users Association Annual Meeting, 11-12 April 1978 Golden, Colorado.

*Work completed under the auspices of the Department of Energy.

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Form No. 836
St. No. 2629
1/78

UNITED STATES
ENERGY RESEARCH AND
DEVELOPMENT ADMINISTRATION
CONTRACT W-7405-ENG. 36

Abstract

There is a widespread interest in the development of a "hydrogen economy" as an eventual solution to many of the problems associated with the growing energy crisis. Hydrogen is also valuable as a chemical intermediate. As fossil sources become inadequate, large scale hydrogen production must utilize energy sources such as solar energy for the decomposition of water by thermochemical cycles, electrolysis or perhaps, by a hybrid combination of these methods.

The potential higher efficiency and lower cost for thermochemical methods, versus the overall electrolysis path has been rather widely recognized. This paper details the criteria for the selection of an appropriate thermochemical cycle for matching with a high temperature solar heat source. Advantages of a thermochemical cycle based on a solid sulfate decomposition that makes use of isothermal high temperature energy is detailed and a plan for the implementation of such a cycle on a central tower solar receiver is given.

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Introduction

The use of solar energy has not yet become widespread due largely to the costs of its collection, conversion and storage. As conventional fuel costs continue to escalate, solar energy has become more cost-effective for a number of applications such as business and residential heating and cooling.

To efficiently use solar energy as a major source of energy, it is highly desirable to convert it and store it in a concentrated form that can easily be transported. This has been the traditional case with fossil fuels, which represent solar energy that has accumulated over a much longer time period, i.e., millenia. Today, faster and more efficient methods of solar energy conversion to a form of chemical (stored) energy are clearly indicated.

A candidate system that appears to offer high potential for solar energy conversion and storage is that of the decomposition of water into its elements, hydrogen and oxygen. Hydrogen is a substance that can be stored in a number of ways, transported with relative ease, and used either in direct combustion to supply thermal energy or converted to electricity via fuel cells. In addition, with water as the only feedstock and the product on combustion, the use of hydrogen would be environmentally acceptable and would help alleviate the world's growing pollution problems (such as the CO_2 problem caused in large measure by our increasing dependence on coal). Additionally, the hydrogen produced would supply the growing demands for hydrogen as a chemical feedstock that has tripled in the last decade.

The use of hydrogen as an energy medium, transferring energy from abundant, clean, massive, renewable energy sources such as the sun to uses in industry, transportation, househoulds and as a basic chemical intermediate has been termed the "hydrogen economy." (1)

It is not the purpose of this paper to engage in the debate regarding the relative merits of hydrogen vs. electricity as media for energy transfer and use, but rather to detail the means by which solar energy can be transfromed into hydrogen.

Hydrogen Production

Most of the hydrogen we use today is derived from fossil fuels. Hydrogen is produced from natural gas by steam reforming and from naphtha by partial oxidation processes. Future production methods for hydrogen will use water as the feedstock. Six possible water-splitting schemes are detailed in Table I below.

TABLE I

Water-Splitting Schemes for Hydrogen Production

1. Electrolysis
2. Direct Thermal Decomposition
3. Thermochemical Decomposition
4. Hybrid, Mixed Electrolytic and Thermochemical Decomposition
5. Hybrid Photochemical-Thermochemical Decomposition
6. Photolysis

With the exception of photolysis, these methods require a high temperature heat source to achieve reasonable conversion efficiencies to hydrogen. Photolysis hinges on the discovery of a chemical system with high quantum yields and broad-band absorption characteristics, which as yet remains undiscovered.

Among the thermal methods, the direct thermal decomposition of water appears to be impractical because of the low partial pressure of hydrogen and oxygen produced even for temperatures of 3000 K and also because of practical engineering difficulties and low efficiencies for methods conceived for separating the hydrogen, oxygen and water.(2) Direct decomposition of carbon dioxide (rather than water) followed by the shift conversion reaction to produce hydrogen offers the advantage of much larger reaction yields, but formidable separation problems remain.

Electrolytic conversion of water to hydrogen and oxygen is well-known technology. It however requires a power cycle to convert thermal energy to electricity and is thus inherently limited by thermodynamic constraints. Electricity obtained directly from sunlight via photovoltaic cells suffers from a low conversion efficiency (10-20%) and at today's prices, high capital cost ($10-20 per peak watt). The latter situation could change drastically if a pricing breakthrough is achieved in photovoltaics. (DOE's goal is $0.50 per peak watt by 1985). The efficiencies and relative costs of generating hydrogen by these techniques and thermochemical processing have been surveyed.(3)

A thermochemical step added to a photochemical or a photo-assisted electrolytic step could lead to a "hybrid" type of process for water decomposition which offers greater flexibility in the use of solar energy than either photolytic process on its own. Hybrid cycles of this nature are being studied for future potential as hydrogen producers at LASL.

In the thermochemical process for water-splitting, water is chemically reacted with intermediate chemical species to yield hydrogen or other compounds. These compounds are thermally decomposed at relatively low temperatures (∿ 1000 K) in turn and yield other intermediates or oxygen. All chemical intermediates are recycled internally within the process or "cycle" so that water and thermal energy are the only inputs and hydrogen and oxygen plus a small amount of reject heat are the only outputs.

The prime purpose for pursuing thermochemical cycles as a means of producing hydrogen is the promise of a higher conversion efficiency of heat to hydrogen as contrasted to other methods for this transformation such as water electrolysis. This expected higher efficiency (defined as the ratio of higher heating value of hydrogen, 286 kJ/mol, to all thermal inputs to the cycle) in turn, would yield a lower cost for the hydrogen product. Although no thermochemical cycles are as yet commercialized, there appears to be good reason based on results to date, that thermochemical cycles can be devised within the range of current or near-term technology to yield hydrogen at rates comparable with electrolytic hydrogen at present-day electricity costs. The above is based on laboratory studies that have demonstrated all of the individual steps comprising a single cycle. Promising cycles are being investigated (in the USA) at the Los Alamos Scientific Laboratory, Lawrence Livermore Laboratory, Argonne National Laboratory, the Institute of Gas Technology, the General Atomic Company and the Westinghouse Electric Corporation. Extensive research in this novel area of energy research is also being conducted in Western Europe, primarily by Euratom at Ispra, Italy and also in Japan.

Major technical problems with proposed cycles are those of heat transfer, heat recuperation (internal heat recycle), and chemical species separation. Engineering approaches are being taken to solve these problems so that thermochemical cycle performance may be demonstrated in the near future.

Criteria for Thermochemical Cycle Selection

On a fundamental level, the energy requirements for the thermal decomposition of water can be disscussed in terms of chemical thermodynamics. This approach was first taken by Funk and Reinstrom, who laid the foundation for the concept of thermochemical water splitting.(4) 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 temperature around 1000 K available from heat sources such as the high temperature (nuclear) reactor (HTR, or VHTR). We have also repeated the analysis (5) 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_f of water (237 kJ/mol) at the low temperature. Thus for a two-step decomposition cycle,

1. $R + AB = RA + B$ at T_1 (K)
2. $RA = R + A$ at T_2 (K)

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

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

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

For the decomposition of water with T_1 at 400 K and T_2 at 1100 K,

3. $R + H_2O = RO + H_2$ 400 K
4. $RO = R + 1/2\ O_2$ 1100 K

ΔS^o (reaction 4) = 320 J/K and ΔH^o = 350 kJ/mol of H_2.

The striking feature of the above analysis are the large ΔS^o values required for the decomposition reactions. Typically, reactions such as 4 exhibit ΔS^o changes of about 100 J/K. However by raising the temperature, these thermochemical constraints are no longer so stringent. At temperatures approaching 2500 K, the required ΔS^o value drops to 140 J/K approaching the ΔS^o values that can be obtained in metal sulfate and metal oxide decomposition reactions. It should therefore be possible to devise a thermochemical cycle consisting of from two to three steps that provide the necessary ΔS^o changes required for maximum efficiency at elevated temperatures.

Suggested Cycles for Hydrogen Production from Solar Energy

A few cycles have already been suggested for matching to a solar energy source. These include the General Atomic (GA) cycle (6); a zinc oxide cycle, (Bilgen, 7); an iron oxide cycle, (Nakamura, 2); and a hybrid (involving electrolysis) bismuth sulfate cycle being developed at the Los Alamos Scientific Laboratory (LASL, 8). Brief descriptions of these cycles follow with details on the General Atomic and LASL concepts.

The GA cycle has been described by Schuster (6), and is characterized by three reactions:

5.	$2H_2O + SO_2 + x\ I_2 = H_2SO_4 + 2\ HI_x$	Aqueous	300 K
6.	$2HI_x = x\ I_2 + H_2$		500 - 600 K
7.	$H_2SO_4 = H_2O + SO_2 + 1/2\ O_2$		1150 K

GA discovered in the laboratory that if excess iodine is added to the first reaction, a separation of the liquid phases into a HI_x-rich layer and a sulfuric acid layer occurs. These acids are readily separated and can be thermally decomposed to yield the desired hydrogen and oxygen as well as iodine and SO_2 for recycle.

The basic problem in coupling a solar energy source to a thermochemical cycle is one of effectively using the time-variant solar thermal input to "drive" the individual cycle reactions. In the GA scheme, the process works due to the availability of intermediate compound storage. In the GA conceptual scheme, the low temperature solution reaction is conducted 24 h/day, producing H_2SO_4 and HI_x. During daylight hours, the sulfuric acid is decomposed at high temperature (1150 K). An intermediate heat transfer loop, possibly using an eutectic salt, stores thermal energy and supplies heat over the 24 h/day period to perform HI_x decomposition. For the sulfuric acid decomposition reaction, a central receiver solar tower might perform adequately; a fixed mirror solar concentrator (FMSC), invented by John Russell at GA is contemplated for heating the intermediate temperatute eutectic.

The work reported by Bilgen was done in conjunction with Ducarroir, Foex, Sibieude and Trombe at the French (CRNS) solar facility at Odeillo.(7) The cycle chosen is seen below:

8. $2ZnO\ (l) = 2Zn\ (g) + O_2\ (g)$ 2340 K
9. $2Zn\ (g) + 2H_2O\ (g) = 2ZnO\ (s) + 2H_2(g)$ 1500 K

The zinc oxide was diluted in a refractory oxide and a dynamic inert atmosphere was used. A theoretical efficiency of 51% was calculated for this cycle.

Nakamura (2) suggests a conceptual cycle that has the following steps:

10. $3FeO + H_2O = Fe_3O_4 + H_2$ 450 K
11. $Fe_3O_4 = 3FeO + 1/2\ O_2$ 2500 K

Reaction 11 has been studied experimentally by Ducarroir at Odeillo.(8) Fe_3O_4 was heated to 2100 K in the solar furnace at that facility and decomposed partially to give a mixed FeO and Fe_3O_4 material.

Fifty percent efficiency can be obtained if half the heat of the decomposing iron oxide is recoverable. With zero heat recovery, the efficiency would drop to 36 percent which is the upper limit of a thermal-electrolytic alternate process for hydrogen production. Needless to say, a number of engineering problems, particularly heat transfer as well as the kinetics of solid-gas reactions at high temperature need to be solved for this process to function.

The LASL hybrid-bismuth sulfate cycle employs the first step of the corresponding hybrid cycle being developed by Westinghouse,(9) this step is the electrolytic oxidation of SO_2 to give sulfuric acid and hydrogen as seen below:

12. $2H_2O + SO_2 \xrightarrow{\text{electrolysis}} H_2SO_4\ (aq.) + H_2$ 300 K

Rather than completing the cycle by the decomposition of sulfuric acid as seen in reaction 7, a reaction in which a solid sulfate is precipitated follows,

13. H_2SO_4 (aq.) + 1/3 Metal Oxide(s)
= 1/3 Metal Oxide Sulfate(s)

The metal oxide Bi_2O_3 is being considered, and the metal oxide sulfate is $Bi_2O_3 \cdot 3SO_3$. The next reaction is a high temperature, endothermic decomposition of this metal oxide sulfate and further decomposition of the evolved SO_3.

14. $1/3\ Bi_2O_3 \cdot 3SO_3 \overset{\Delta}{=} 1/3\ Bi_2O_3 + SO_2 + 1/2\ O_2$

The high temperature process heat obtained from the solar furnace will be used to drive this decomposition reaction, part of it being diverted to electricity generation for the electrolysis step, 12. To complete the cycle, O_2 is separated from the SO_2 and O_2 gas mixture and the SO_2 is recycled to the process.

A principal reason for the introduction of a metal oxide species into the thermochemical cycle is to eliminate the large amounts of heat required for the dehydration of sulfuric acid; this requirement is characteristic of the already-mentioned sulfuric acid hybrid and sulfuric acid-iodine cycles. The separation by precipitation of the solid metal oxide sulfate from a relatively low concentration sulfuric acid solution rather than evaporation of

Figure 2 depicts a preliminary process flow diagram proposed for $H_2SO_4/Bi_2O_3 \cdot 3SO_3$ thermochemical cycle. The sulfate decomposition rate should be governed by heat transfer to the decomposing particles. If $Bi_2O_3 \cdot 3SO_3$ particles were adequately dispersed, heat transfer might not be a limiting factor, and, assuming the decomposition takes place in less than one minute, a decomposer might operate as a series of countercurrent moving-bed reactors. The bismuth sulfate particles (100-200µm in size) would be circulated through the decomposer system, the $Bi_2O_3 \cdot 3SO_2$ particles would decompose and emerge as Bi_2O_3.

The SO_3, SO_2, and O_2 product gases may have to pass through a catalyst bed to ensure that the SO_3 is decomposed. Equilibrium conversions of the SO_3 to SO_2 and O_2 should be achieved at 1500 K within ∿ 98% at moderate pressures. The solar furnace could also supply this energy. Conceptually, the $SO_3/SO_2/O_2$ gas stream may be used as a primary heat-transfer (direct-contact) medium used to drive the decomposition reactions. The bismuth oxide is physically separated from the product gases and is returned to a (chemical) reactor in which occurs contact with H_2SO_4 solution from the electrolyzer to form bismuth sulfate. The gaseous products are separated, the SO_2 is recycled, and O_2 is discarded after purification. As seen in Fig. 2 a conceptual 1513 MWt (equivalent) hydrogen plant requires 1318 MWt of high-temperature process heat, 1190 MWt of electrical energy, 640 MWt of moderate to low temperature heat; this cycle operates with an overall efficiency of ∿ 0.48.

This introduction of the metal oxide into the solar thermochemical cycle creates an interesting engineering problem. For an efficient cycle, the significant sensible, latent and transformation heats must be recovered from the

Bi_2O_3 decomposition reaction product; and electricity must be generated, perhaps by using the lower temperature process heat.

Other engineering problems requiring attention that stem from the solar energy aspects of the process are control problems relating to the transient nature of the energy source during daylight hours, as for example, when a cloud shields the sun, and the problems caused by the storage and transfer of intermediate reactants and products during the diurnal solar cycle. Variation in seasonal solar insolation would appear to also present a difficuly unless the solar-thermochemical process was located at Southwestern USA site where seasonal changes are not highly significant.

These engineering and related problems do not appear to be insurmountable. The transport of large masses of solids appears similar to processes used in other heavy-chemical industries and should present no serious difficulty. Indeed, some of the solid processing problems would appear similar to those proposed by other authors at this symposium, i.e., the processing of molybdenite ore (Skaggs) and the pyrolysis of biomass (Antal).

Immediate development of thermochemical means for hydrogen production by water-splitting should be a matter of top priority in solar energy research.

Conclusions

Hydrogen, a versatile element, has a tremendous potential as an energy storage medium. Its production from solar energy using water as the only raw material would open the way to a truly recyclable energy system based on renewable resources.

There are several water-splitting schemes that may be adaptable to use with solar energy, in particular, a concentrated, high temperature heat source such as the solar tower. Among the thermochemical cycles proposed for water-splitting, the "hybrid" bismuth sulfate cycle being developed at LASL appears to offer potential as a high efficiency solar heat to hydrogen conversion process. This cycle is presently being researched in the laboratory and a concurrent design study (funded by the DOE's Office of Fusion Energy) is being done at LASL to match the cycle's thermal requirements to that of a fusion source for the ultimate production of hydrogen.

Coupling this cycle to a solar energy source would also be an alternate source of clean, non-polluting energy in the form of hydrogen.

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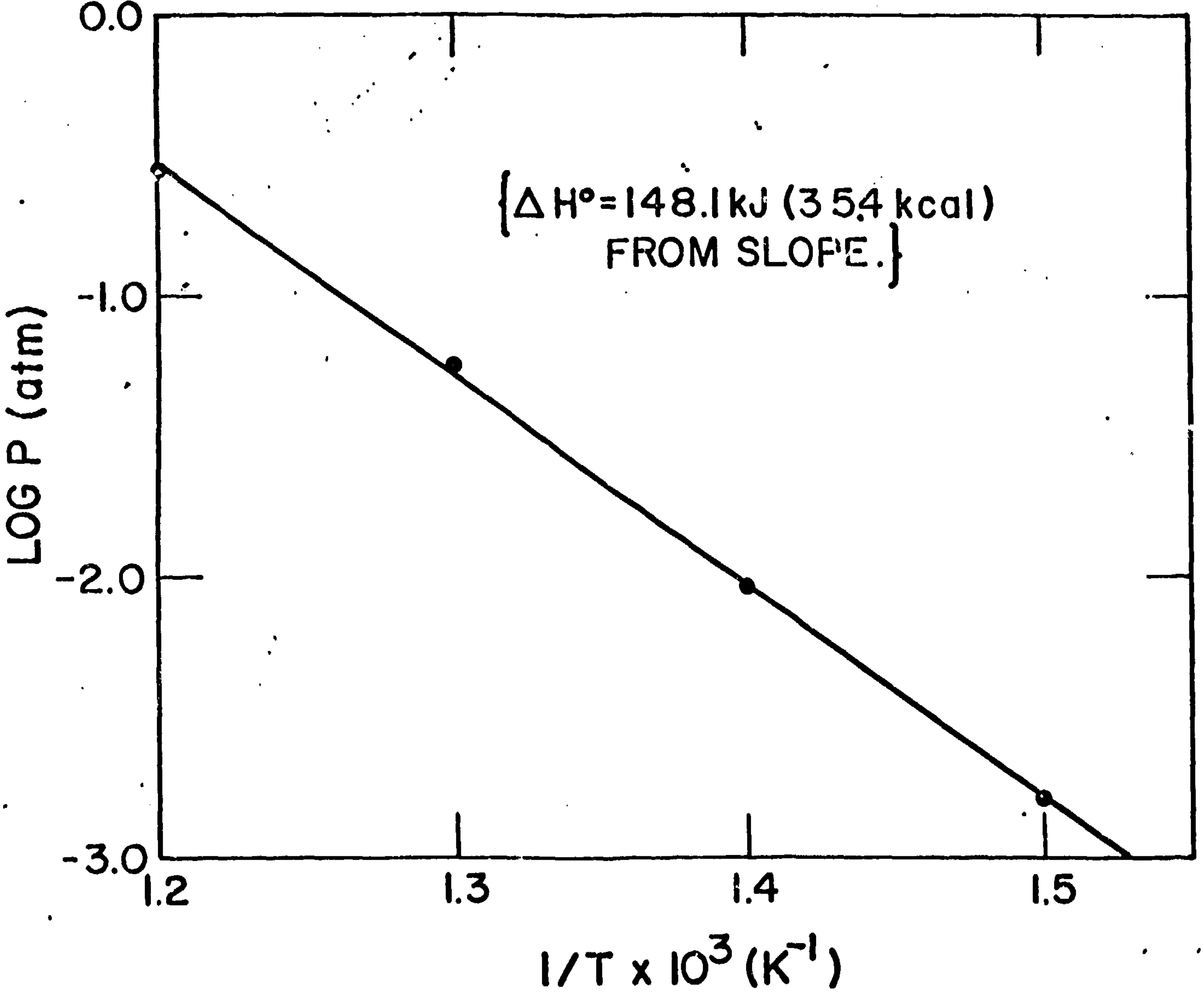

Fig. 1. Results of Bismuth Sulfate Decomposition.

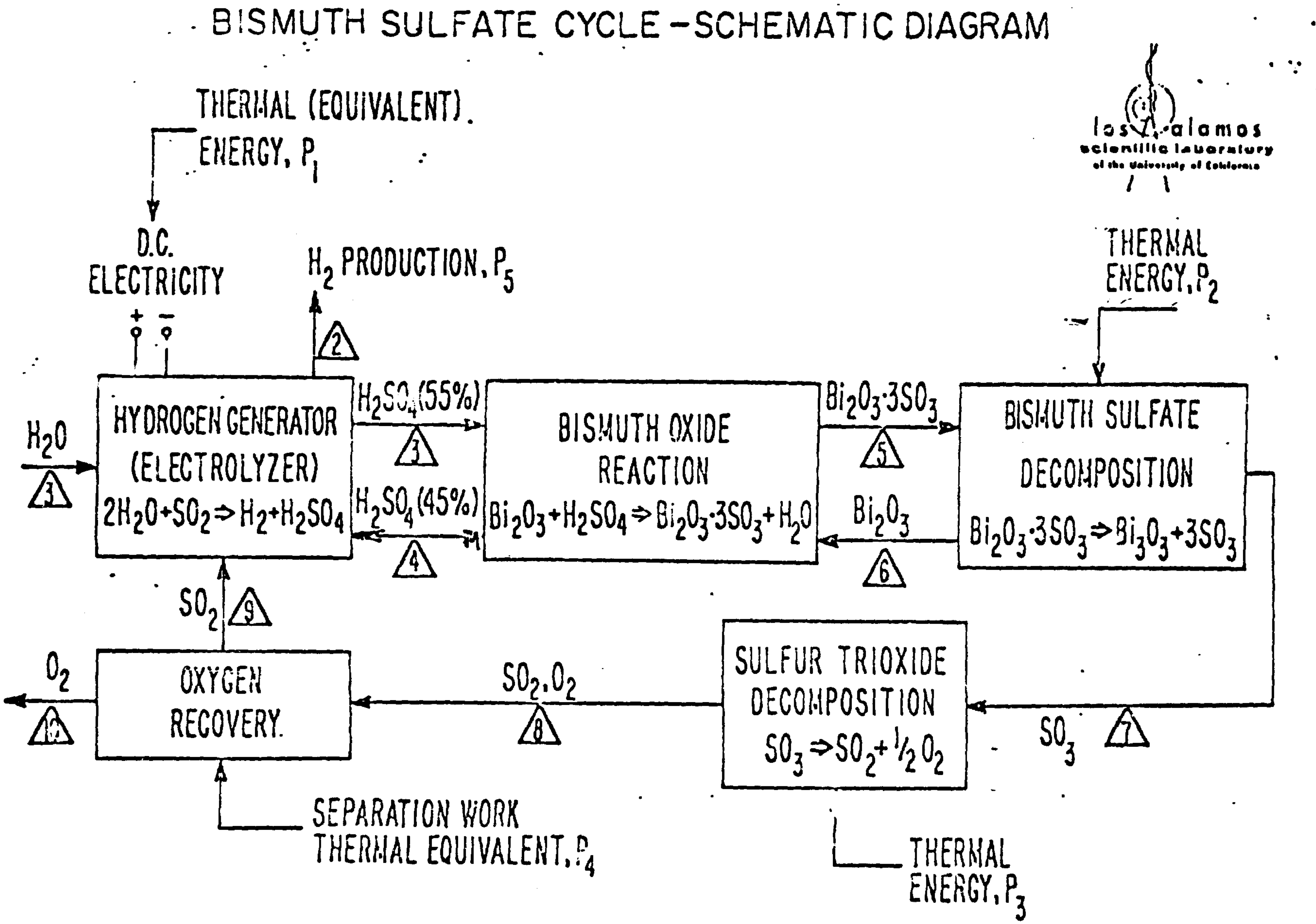

Fig. 2. Schematic diagram of the process flow envisaged for a bismuth-sulfate thermochemical cycle.