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TITLE: THERMOCHEMICAL PRODUCTION OF HYDROGEN FROM WATER

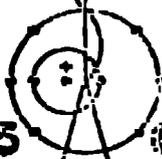
AUTHOR(S): MELVIN G. BOWMAN

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LOS ALAMOS, NEW MEXICO 87544

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MASTER

REA

THERMOCHEMICAL PRODUCTION OF HYDROGEN FROM WATER

Melvin G. Bowman

**LOS ALAMOS SCIENTIFIC LABORATORY
P. O. BOX 1663
LOS ALAMOS, NM 87545, U.S.A.**

ABSTRACT

The advantages of hydrogen as a medium for energy storage, energy transmission and possible large-scale use as a non-polluting fuel have led to the concept of a "hydrogen economy." However, even if this does not fully materialize, accelerating requirements for hydrogen demonstrate that efficient, low-cost methods for production based on non-fossil heat sources will become extremely valuable.

Theoretical advantages for thermochemical production methods have led to the publication of many conceptual cycles prior to experimental testing and to efficiency and cost estimates based on assumed data for non-verified processes. Finally, however, laboratories in several countries have published details of cycles that have been demonstrated by experimental studies.

In this paper the chemistry of experimentally valid cycles is discussed in some detail. Thermochemical criteria for efficient cycles are also presented. It seems probable that the development of low-cost processes must be the result of experiments not yet performed. However, valid cycles have been demonstrated in a variety of chemical systems and one may hope that an efficient low-cost process will be developed.

Some cost estimates have finally been made on valid cycles, although mostly on assumed conditions. At the present time, such studies are most useful for guiding process improvement, and also to develop methodology for process evaluation.

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Melvin G. Bowman

LOS ALAMOS SCIENTIFIC LABORATORY
P.O. BOX 1663
LOS ALAMOS, NM 87545, U.S.A.

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 and/or solar energy for the decomposition of water by electrolysis, by thermochemical cycles, possibly by photoelectrochemical techniques and/or, 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 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.

The purpose of this paper is to discuss the current status of thermochemical hydrogen processes that are (in the author's opinion) based on experimentally verified conceptual cycles.

A. Thermochemical Efficiency

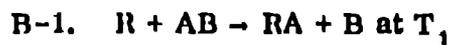
Processes for the production of hydrogen will utilize liquid water as the raw material. Since the standard heat (enthalpy) of formation of water at 298 K is -285.9 kJ/mol, the decomposition of liquid water to form one mole of hydrogen gas will require a minimum energy input of 285.9 kJ. Therefore, in this paper we have accepted the definition of efficiency adopted by the International Energy Agency [1], i. e., the ratio of the theoretical energy required (285.9 kJ) to the total heat input required for the decomposition process. Thus,

$$E (H_2) = \frac{285.9}{\sum \Delta H_d^0} \quad 1)$$

The $\sum \Delta H_d^0$ term must include the heat required to produce any work utilized to promote the decomposition.

B. 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 [2]. 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. We have also repeated the analysis [3] in order to point out that specific values for the sum of the ΔS^0 terms and the sum of the ΔH^0 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_f^0 of H_2O at the low temperature. Thus, for a general two-step decomposition cycle

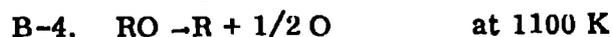


"ideal" ΔS^0 and ΔH^0 values are given by

$$\text{ideal } \Delta S^0 = \frac{-\Delta G_f^0 (AB)}{(T_2 - T_1)} \quad 2)$$

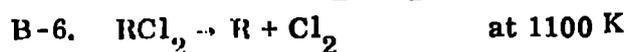
$$\text{ideal } \Delta H^0 = \Delta S^0 \times T_2 \quad 3)$$

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

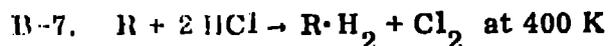


$$\Delta S^\circ (B-4) \sim 320 \text{ J/K}, \Delta H^\circ (B-4) \sim 350 \text{ kJ.}$$

It is of interest to consider two-step decomposition cycles for HCl and HBr since such subcycles are contained in some water splitting cycles. For the reactions (where R can be a reactant or a reaction),



or for the reaction

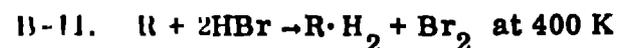


$$\Delta S^\circ (B-6 \text{ or } B-8) \sim 275 \text{ J/K}, \Delta H^\circ \sim 305 \text{ kJ.}$$

Similarly, for the reactions



or for the reactions



$$\Delta S^\circ (B-10 \text{ or } B-12) \sim 160 \text{ J/K}, \Delta H^\circ \sim 175 \text{ kJ.}$$

The striking feature of the above analyses are the large ΔS° values required for the decomposition reactions. Typically, reactions such as B-4 exhibit ΔS° changes of about 100 J/K. Thus, it is quite clear that simple two-step cycles for H_2O decomposition will not be found (as indicated by Funk and Reinstrom). It is also of value to note that typical ΔS° values for reactions such as B-6 and B-10 are ~ 140 - 170 J/K. Therefore, simple two-step reactions for HCl decomposition (ideal $\Delta S^\circ \sim 275$ J/K) should not be expected, but one should be able to find two-step cycles for HBr decomposition (ideal $\Delta S^\circ \sim 160$ J/K).

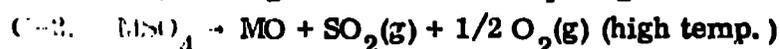
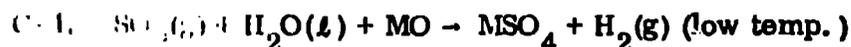
Examination of the ideal ΔS° values emphasizes the value of reactions with large entropy changes in water splitting cycles in order to minimize the number of

reactions required. This, of course suggests gaseous reactants or reaction products to provide the large entropy changes.

C. Thermochemical Cycles From Los Alamos Scientific Laboratory

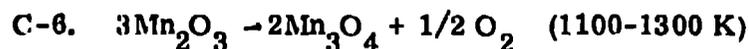
The Los Alamos program may be described as a combined theoretical and experimental effort to develop criteria required for an ideal process and to search for thermochemical cycles that approximate the criteria. In practice, conceptual cycles are subjected to experimentation in order to verify the concept (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. At this point, the cycle is "set aside" so that new concepts can be tested. Of course, it is hoped that a cycle will be demonstrated that is so promising that efforts can be directed almost exclusively to its development. Despite the fact that two cycles identified in the LASL program are now under additional development at other laboratories, we have not found a cycle that seemed to merit the commitment of a major fraction of the program effort to its development and to rigorous engineering and cost analyses.

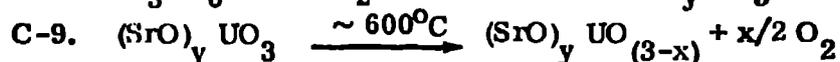
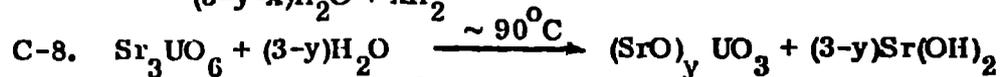
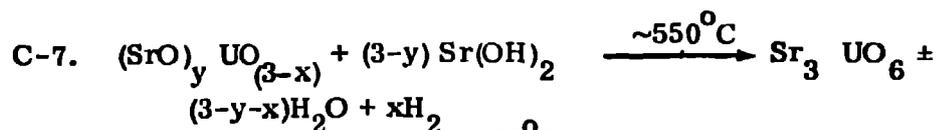
In our search for new thermochemical cycles, we have looked for reactions with large entropy changes as outlined in section B above. In our early program, we conceived a possible two-step reaction cycle based on the decomposition of metal sulfates [3] to give two gaseous decomposition products. Thus:



Typical ΔS° (298) values for C-2 type reactions are ~ 280 J/K and the cycle is conceptually valid. However, despite an extensive effort, we have been unable to find conditions where the low temperature reactions will occur.

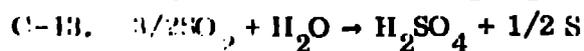
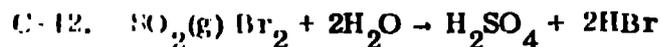
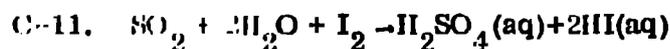
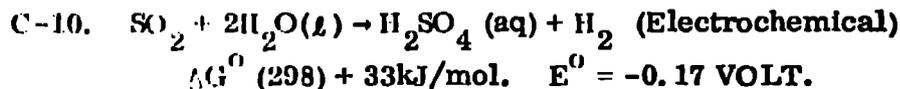
Also in the early program, cycles were conceived in which a desired oxidation state in an oxide is stabilized by compound formation with another oxide. We named such cycles complex oxide cycles and experimentally demonstrated a lithium-carbonate-manganate cycle, a sodium manganate cycle and a strontium uranate cycle. The last two cycles can be illustrated as follows:





In such cycles, it is apparent that at least one of the high temperature steps involves the formation of more than one gaseous product. The cycles were set aside since leaching steps were included and the resultant carbonate or hydroxide solutions require drying operations and since the hydrogen and oxygen are produced at less than atmospheric pressures.

Consideration of sulfate chemistry led to cycles based on four reactions to form sulfuric acid, as follows:

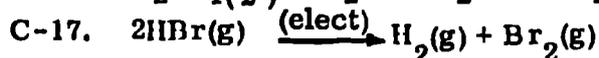
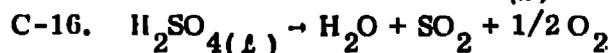
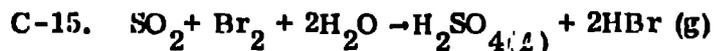


The thermochemical decomposition of sulfuric acid may be represented as follows:



We have studied the decomposition and have found rapid and near equilibrium decomposition with suitable catalysts at high temperature (900-1200 K).

Two hybrid electrochemical-thermochemical cycles have been identified and studied as part of the effort on sulfuric acid. One of these consists of reactions C-10 and C-14 written above. Experimental results were presented to the October 1974 meeting of the Electrochemical Society [4]. A second hybrid cycle was identified in reference [3]. It may be illustrated as follows:



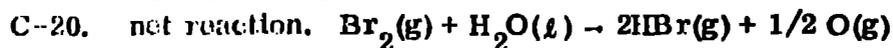
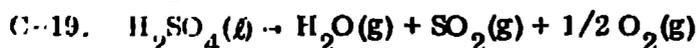
$$\Delta G(400 \text{ K}) = + 112 \text{ kJ}$$

$$E^\circ = -0.59 \text{ VOLT}$$

From our results, we concluded that these hybrid cycles might be feasible. However, it seemed too early in the search for thermochemical cycles to abandon the potential additional advantages of "pure" cycles in favor of hybrid cycles. The cycles are now undergoing additional development at other laboratories and one may expect an eventual realistic evaluation of their potentials.

1.0 The Sulfuric Acid-Hydrogen Bromide Cycle

If one forms sulfuric acid by means of reaction C-12 and then decomposes it at high temperature by means of reaction C-14, the two reactions comprise a sub-cycle for the formation of hydrogen bromide and oxygen from bromine and water. That is (using $\text{Br}_2(\text{g})$ as a reactant),

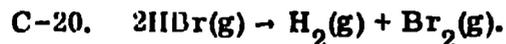


Reaction C-18 is exothermic. Reaction C-19 is endothermic with $\Delta H_{298}^{\circ} = +275.3 \text{ kJ}$ for the formation of $\text{H}_2\text{O}(\text{g})$ rather than $\text{H}_2\text{O}(\text{l})$. The theoretical heat requirement for the net reaction (ΔH_{298}°) is 182.5 kJ. Therefore, assuming $\Delta G^{\circ} = 0$ for C-19 and perfect heat exchange between reactants and products, the maximum efficiency for the sub-cycle is $182.5/275 = 0.66$.^{*} The value of 275 kJ for reaction C-19 assumes the formation of liquid H_2SO_4 (no excess water) in reaction C-18. Our laboratory experiments have

* Professor Pank [5] has used the term "stage efficiency" to describe efficiencies of sub-processes. We have decided to adopt the name.

produced very concentrated H_2SO_4 with the maximum concentration not determined. It should be possible to achieve 99% H_2SO_4 by the reaction [6].

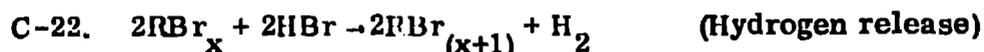
In order to complete the cycle for water decomposition, a process for the net decomposition of HBr is required, i. e.



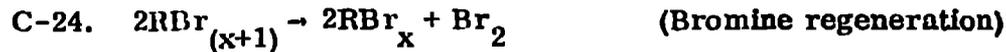
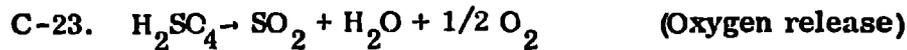
The theoretical heat requirement for this second stage is 103.4 kJ. Therefore, since the major heat requirement is in the first stage and since its potential efficiency is quite high, the stage efficiency for a process to decompose HBr could be rather low and the efficiency of an overall water splitting process still be relatively high.

One conceptual cycle may be described by the following reactions.

Low Temperature Heat Rejecting Reactions



High Temperature Heat Absorbing Reactions

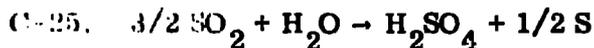


In principle, this cycle could be more efficient than the other sulfuric acid cycles under study. Reaction C-21 yields nearly 100% H_2SO_4 rather than ~ 50% H_2SO_4 that is formed in the other cycles. Thus, the rather large heat requirements for "drying" sulfuric acid can be avoided. In addition, typical ΔS° for metal bromide decompositions are very near the value required for an "ideal" two-step decomposition of HBr. From literature data, the VBr_2 - VBr_3 couple and the CrBr_2 - CrBr_3 couple have ΔH° values near the value required for the efficient decomposition of HBr. However, in both cases the low temperature reaction of HBr with the dibromide (to evolve H_2) is far too slow.

Recently, satisfactory reaction rates were demonstrated for reactions involving chromium bromide hydrates [7]. However, the heat requirement for dehydration appears to be too high for an efficient cycle. Several interesting (perhaps promising) methods for HBr decomposition are still under study. However (except perhaps for electrolytic decomposition), we have not achieved a really satisfactory HBr sub-cycle. The program is continuing.

2.0 Sulfuric Acid-Sulfur Cycles

If one forms sulfuric acid by means of reaction C-13 and then decomposes it as indicated in reaction C-14, the two reactions in effect form a sub-cycle for the decomposition of one-half mole of SO_2 . Thus:



Reaction C-25 actually represents equilibrium in the SO_2 - H_2O system [8] and although the reaction rate is extremely slow, it is possible to use catalysts and achieve adequate rates. This reaction can then form the base for a large number of thermochemical cycles. In the LASL program, many reactions have been studied that effect the second stage of the cycle (i. e. , the net reaction of S with H_2O to produce SO_2 and H_2). These reactions have been described in previous publications [9, 10] and will not be reproduced here. Two of the cycles have been subjected to a preliminary engineering analysis by the General Atomic Co. [1]. This study indicated a high capital cost. In view of this and the fact that some of the reaction steps are "difficult", the cycles have been "tableted" for the present.

3.0 The Cerium Chloride Cycle

This cycle may be written as follows:



Experimental studies of reactions in the cycle may be summarized as follows:

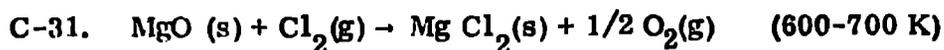
(a.) Reaction C-27 exhibits a very rapid reaction rate at 1250 K, but the reaction equilibrium leaves about 11 moles of unreacted H_2O for each mole of H_2 produced. Despite this, it seems necessary to add additional H_2O to the reaction products in order to separate the H_2 from HCl . The resultant HCl in solution must be separated from the H_2O in a separate step. This is one of the serious problems in the cycle.

(b.) Reaction C-28 has been found to decrease with time in the temperature range where equilibrium yields are most favorable. However, it is apparent that equilibrium yields should increase with increasing reaction pressures and initial results from the difficult high pressure studies indicate not only the expected increase in equilibrium, but also an apparent very large increase in reaction rates even at lower temperatures. It is still not certain, however, if an adequate reaction rate can be achieved with the rather refractory CeO_2 produced in reaction C-27.

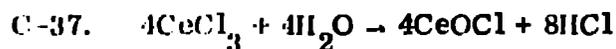
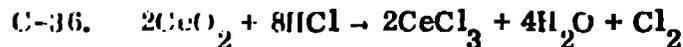
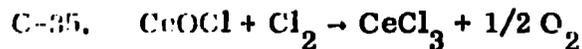
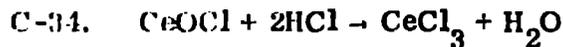
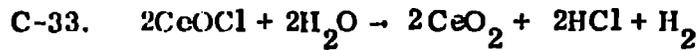
(c.) Reaction C-29 exhibits rapid reaction rates and excellent yields at the indicated temperatures.

(d.) Reaction C-30 is the reverse Deacon Reaction. The reaction occurs at high temperature where the reactants are the products of reaction C-28. Again, however, the addition of H_2O to the effluent from reaction C-30 seems necessary in order to separate the O_2 and unreacted Cl_2 from the HCl . The extra H_2O in the cycle is disadvantageous.

In principle, a two-step reaction sequence can be substituted for the reverse Deacon Reaction. Ulrichson [12] has conducted preliminary studies on the following reaction pair.



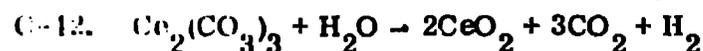
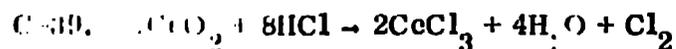
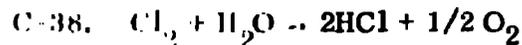
His results indicate that the reactions will be feasible. Recently, Martin [13] has suggested the use of CeOCl to replace MgO in the above reactions. It seems probable that similar reaction sequences can be used to separate H₂ from HCl in the effluent from reaction C-27 above. Using CeOCl for both purposes, one can write a revised cerium chloride cycle as follows:



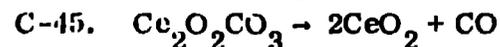
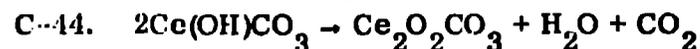
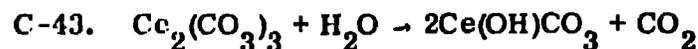
The variations of the cerium chloride cycle will be tested experimentally and finally compared through flow sheets and cost estimates based on experimental results.

4.0 Cerium Chloride-Carbonate Cycles

In a continuing study of cerium chemistry, all reactions have been verified for a cycle described by the following reactions.



If the moist or hydrated Ce₂(CO₃)₃ from reaction C-42 is heated in the absence of additional water, the decomposition (with increasing temperature) may be described by the following reactions.



It is interesting to note that the cycle is capable of "splitting" either H₂O or CO₂. However, one must also note that the sum of the ΔS⁰ values for the endothermic hydrolysis reactions and the sum of the ΔS⁰ values for the endothermic carbonate decomposition reactions are each sufficiently high for a water splitting cycle with maximum temperatures near 1100 K. Therefore, for the overall cycle, the ΔS and ΔH values are not optimum for a highly efficient process. In addition, the removal of CeCl₃ from solution represents an additional endothermic step. However, these

disadvantages are partially compensated by the lower maximum temperature required (perhaps 800-850 K). Therefore, if a source of less-costly, low temperature heat is assumed for the solution drying step, the cycle might be competitive on a cost basis. Actually, in our continuing experimental program attempts are being made to combine reactions or to find substitute paths that require less heat.

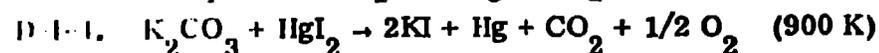
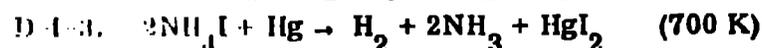
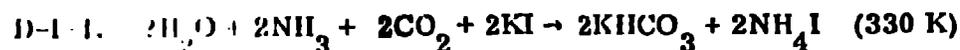
D. Unique Cycles From U.S.A. Programs

Thermochemical hydrogen programs at Argonne National Laboratory, at Lawrence Livermore Laboratory and at Oak Ridge National Laboratory have each produced thermochemical cycles that are each different in type from cycles under development at other laboratories. In each case, the cycles have been demonstrated experimentally and merit serious attention.

D-I. Argonne National Laboratory

The program at ANL "is directed toward the invention, the experimental investigation and the bench scale assessment of thermochemical water splitting cycles."

At the present time, the program seems to be directed primarily to the development and demonstration of the ANL-4 cycle. This cycle may be described as follows [14]:



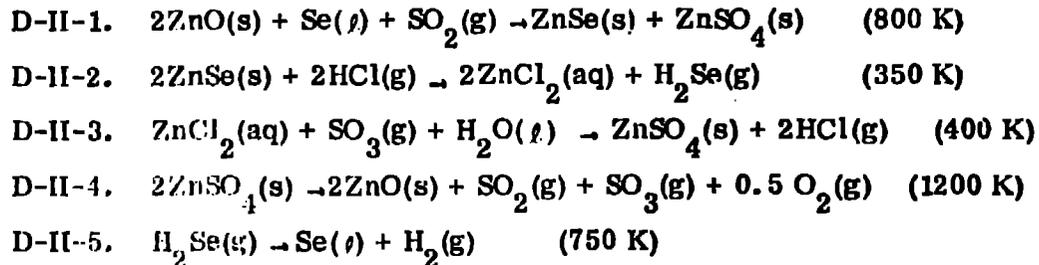
The workers at Argonne report that all reactions can be carried out under conditions where reasonably rapid rates are obtained and the yields of the high-temperature reactions are essentially 100%. The highest temperature required is 900 K. The chemistry of the reactions follows the equations and there are no harmful side reactions. Thus, ANL-4 belongs to the relatively small and select group of cycles that can actually be conducted in the laboratory.

The program at Argonne is continuing. Alternative reactions that do not utilize mercury are being studied and methods are being sought for minimizing heat requirements for drying solutions.

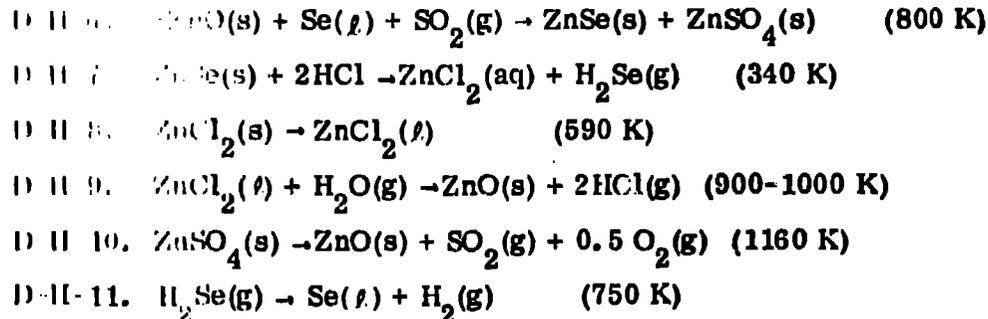
D-II. Lawrence Livermore Laboratory

The program at LLL for developing processes for thermochemical hydrogen production has involved chemical systems significantly different than those studied by other investigators. A cycle based on the formation of ZnSe and ZnSO_4 has been

described by the Livermore Group for which all reactions have been demonstrated experimentally [15]. The cycle may be described by the following major reaction steps.



Engineering and preliminary cost analyses by the Livermore group revealed the disadvantage that most of the heat requirement is for the decomposition of two moles of ZnSO_4 (reaction D-II-4). Since this occurs over a narrow temperature interval near the maximum temperature available, it is a serious difficulty where heat must be extracted from a heat exchanger, e.g., where a nuclear reactor is the heat source. As a result of this, the Livermore workers have made modifications of the cycle to minimize the disadvantages [15]. The modified cycle may be described by the following major reaction steps.

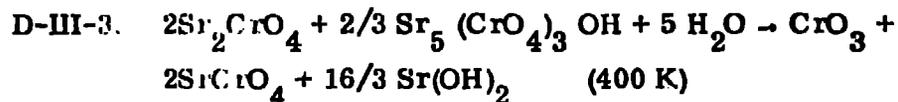


In the new version of the cycle, only one mole of ZnSO_4 is decomposed at the high temperature (reaction D-II-10). The ZnSe is separated from the ZnSO_4 before it is reacted with HCl (reaction D-II-7). The hydrolysis of one mole of ZnCl_2 (reaction D-II-9) not only occurs at a lower temperature than reaction D-II-10, but also requires less heat than the decomposition of one mole of ZnSO_4 for which it substitutes. Therefore, the new cycle will exhibit higher efficiency.

The progress revealed by the two Livermore cycles is considered to be an example of how innovative changes in chemistry can improve cycles after specific problems have been revealed by engineering analysis.

D-III. Oak Ridge National Laboratory

Workers at ORNL have worked principally on a type of cycle involving the formation and "hydrolytic" disproportionation or decomposition of mixed oxide compounds. The strontium chromate cycle is an example of the cycle type [17]. It may be written as:



All of the reactions have been demonstrated experimentally. Efficiency estimates cannot be made until the thermochemistry of $\text{Sr}_5(\text{CrO}_4)_3 \text{OH}$ has been determined. This determination is now under way.

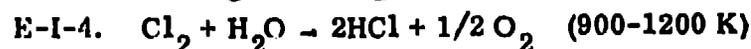
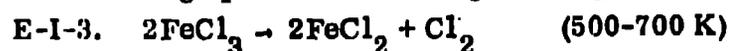
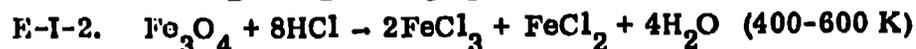
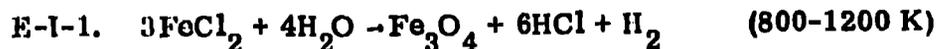
New and interesting cycles of the same general type are being evaluated at ORNL [18].

E. Cycles Common to Several Programs

There are four thermochemical or hybrid processes under serious development and evaluation by more than one laboratory worldwide. These are: The Iron Chloride Cycle, The Sulfuric Acid-Hydrogen Iodide Cycle (the General Atomic Co. "Prima Cycle"), The Sulfuric Acid Hybrid Cycle, The Sulfuric Acid-Hydrogen Bromide Hybrid Cycle.

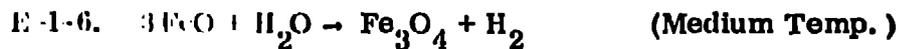
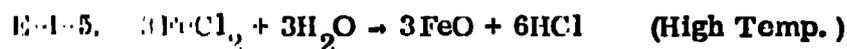
E-I. Iron Chloride Cycles

Several different versions of the iron chloride cycle have been published by Laboratories in Europe, Japan and the U.S.A. Apparently, the cycle was originated by Pangborn and Associates at the Institute of Gas Technology and of the many versions published, the IGT B-1 cycle seems to be the only one fully verified by extensive experimental studies. The cycle may be written as [19].



The disadvantages of the cycle include: 1) The problem of separating H_2 from HCl and unreacted H_2O from reaction E-I-1. 2) The fact that gaseous Fe_2Cl_6 sublimes along with the formation of Cl_2 in reaction E-I-3 and, since Fe_2Cl_6 does not decompose, the decomposition of $FeCl_3$ is a difficult step in the cycle. 3) The problem of separating $Cl_2 + O_2$ from the $HCl + H_2O$ in reaction E I-4.

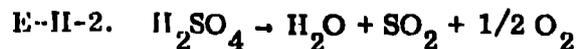
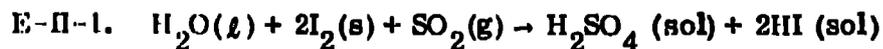
Workers at the Euratom Joint Research Center, Ispra, Italy, have apparently discontinued development of the cycle [20, 21]. Primarily, because of the difficulties with reactions E-I-1 and E-I-3, but also because of their greater interest in their Mark-16 cycle (see below). Development of the cycle is continuing at IGT where workers have invented a clever diffusion-based method for separating Cl_2 from Fe_2Cl_6 and promoting reaction E-I-3 [19]. Knoche and co-workers at the RWTH, Aachen, West Germany, are also continuing to develop the cycle. In their latest modification of the cycle, Knoche and co-workers [22] have achieved some success in combining reactions E-I-2 and E-I-3 (above) by moving the Fe_3O_4 up an increasing temperature gradient while the $HCl-H_2O$ gas mixture flows in a counter direction. They are also attempting to avoid the difficult H_2 separation step associated with reaction E-I-1 by conducting the reaction in two steps, i. e.,



The formation of Fe_3O_4 in reaction E-I-4 is prevented by the presence of some H_2 . This, together with some HCl , is recycled into the reaction without a complete separation step being necessary. In principle, the "clean" hydrogen from reaction E-I-5 can be evolved at fairly high pressure.

E-II. The General Atomic Co. Prime Cycle

At the First World Hydrogen Energy Conference (March 1976), the General Atomic Co. presented their Sulfuric Acid- Hydrogen Iodide cycle that had been kept "proprietary" until that time [23]. The cycle may be written simply as:



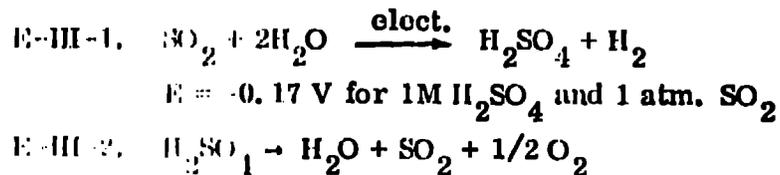
Several laboratories had considered the cycle, but credible methods for separating HI from the sulfuric acid solution were not suggested. The critical discovery by G. A. was that with excess I_2 and excess SO_2 , two liquid phases are formed. The $H_2O - H_2SO_4$ phase contains nearly all the H_2SO_4 and the $I_2-SO_2-HI_x$

(higher density) phase nearly all the HI. 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.

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 from the reaction E-II-1. 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 process conditions.

E-III. The Sulfuric Acid Hybrid Cycle

As indicated above, this is one of the hybrid cycles studied early in the LASL Program. The "two-step" cycle may be written as:



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. Their results demonstrate this reaction can be a part of a technological process. Many important features of the Westinghouse Program were included in four papers presented at the First World Hydrogen Energy Conference [24, 25, 26, 27].

In a recent Progress Report [28] Farbman reported that for 50 wt% sulfuric acid produced at 25°C and current densities of 2000 A/m², total cell voltages of 800-900 mV for the electrolysis step appear attainable. Eventually, the Westinghouse workers hope to achieve their "target" conditions of 75 wt% sulfuric acid at a current density of 2000 A/m² and a cell voltage of 450 mV.

The Westinghouse workers have estimated the cost of hydrogen produced by the hybrid cycle; assuming their "target" conditions and assuming what may be

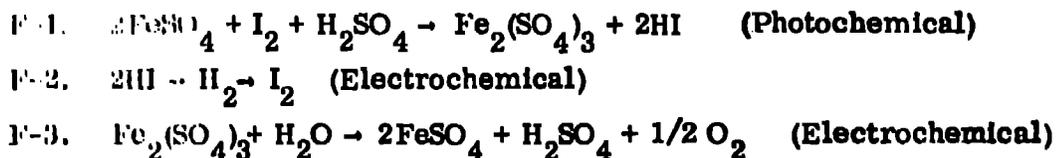
described as an advanced method of power production [29]. They derived a very optimistic cost of \$4.65/GJ (see cost section below). This may be the reason why the cycle has achieved popularity. At any rate, the Julich Nuclear Research Center in West Germany has initiated a large developmental effort on the cycle [30]. Workers at the Euratom Joint Research Center in Ispra are maintaining an active interest in the cycle [21] and it is reported (so far unsubstantiated) that a large program on the cycle is now under way in France.

E-IV. The Sulfuric Acid-Hydrogen Bromide Hybrid Cycle

The possible advantages of this hybrid cycle, versus the sulfuric acid hybrid have been mentioned above (Section C-1). The electrolytic decomposition of HBr is the key step. Development on the cycle is continuing at Euratom-Ispra [21,31] and the Institute of Gas Technology is conducting a small program to evaluate the electrolysis step [32].

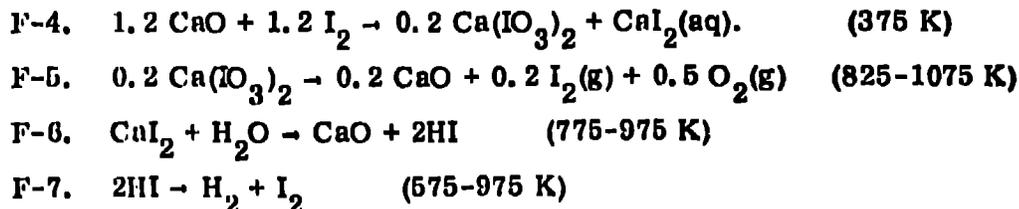
F. Thermochemical Hydrogen Cycles From Japan

There appears to be a serious effort in Japan to develop thermochemical processes for hydrogen production. Many conceptual cycles have been published and these include most of the reactions and cycles published by other laboratories throughout the world. These cycles will not be reviewed here. However, attention should be drawn to two of the cycles since they are not only different from cycles under serious consideration in other countries, but are also based on experimental studies. One of these cycles is a hybrid photochemical-electrochemical cycle designated Yokohama Mark 5 by Ohta and co-workers [33]. It may be written as:



The authors have identified several serious problems that must be solved before the cycle can approach practicality. Nevertheless, it is possible that the problems could be solved or that the unique approach could be applied to different systems.

A second Japanese cycle is the calcium-iodine cycle described by Fujii and co-workers [34]. It may be written as:



These equations oversimplify the cycle, for example the HI formed in reaction F-6 is partially decomposed during the reaction. However, the difficulties with the cycle are recognized by the authors, they have been evaluated in what appears to be a sound experimental program, and the cycle apparently is considered to be a sound candidate for further development.

G. 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

* This potential advantage of solar heat was first pointed out to the author by Jon Pangborn and John Gahlmer of IGT during discussions of their cadmium hydroxide hybrid cycle [35].

(and continuously) consider the possible adaptation of solar heat sources to thermochemical processes.

In the long run, 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 "by-cycle power" must be used and, hence, significant quantities of low temperature waste heat can be available. For example, in a current conceptual design of a laser fusion reactor [36] with a power production efficiency of 50%, approximately 35% of that power must be recirculated, primarily to fire the lasers. Thus,

systems including such reactors will always be a source of heat that could be used in low temperature applications.

H. 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 a 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 he 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. Cycle b is a thermochemical sulfuric acid/methanol process that is described in reference 42 and 43 and cycle c 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

<u>Author</u>	<u>Reference</u>	<u>Current Technology</u>	<u>Advanced Technology</u>	<u>Dollar Type</u>
Escher Donakowski	37	\$9.36/GJ	\$4.81/GJ	Mid-1975
Steeman	38	5.55	-	1975
Broggi	39	9.76	7.48	1975
Farbman	29	6.65	-	Mid-1974
Nuttall	40	-	5.08	1976

TABLE II

COST ESTIMATES FOR THERMOCHEMICAL HYDROGEN

<u>Author</u>	<u>Reference</u>	<u>Cycle</u>	<u>Cost</u>	<u>Dollar Type</u>	<u>Note</u>
Steeman	38	a	\$7.18 /C.J	1975	1
Farbraun	29	a	4.65	Mid-1974	1
Knoche & Funk	41	a	7.15	Mid-1976	1,2
Funk & Knoche	43	b	11.65	Mid-1976	2,3
Broggi	39	c	5.95	1975	4

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 (see Section E-III).

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 both cycle a and cycle b can be improved and costs lowered.

Note 3. The cost of \$11.65/GJ for the methanol-sulfuric acid cycle given in reference 43 are higher than the value of ~ 10.00 given in an early paper [42]. The primary difference is in the assumed capital recovery factor.

Note 4. The cost estimates made by Broggi assume the production of 60 wt% sulfuric acid in the process. It seems questionable 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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