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## **Thermochemical Processes for Hydrogen Production**

**January 1—July 31, 1977**

Compiled by

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# THERMOCHEMICAL PROCESSES FOR HYDROGEN PRODUCTION

JANUARY 1 — JULY 31, 1977

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## ABSTRACT

The Thermochemical Hydrogen Program at the Los Alamos Scientific Laboratory is continuing its investigation of practical schemes to decompose water thermochemically for production of hydrogen.

Current efforts were directed to experimental studies of reactions relevant to the sulfuric acid-hydrogen bromide thermochemical cycle. The use of insoluble bismuth sulfate as a means of concentrating aqueous sulfuric solutions is also under investigation.

Preliminary calculations show a significant cycle efficiency increase if solid sulfate and subsequent sulfur trioxide decomposition steps replace the sulfuric acid concentration and decomposition steps proposed in other cycles.

## INTRODUCTION

In the development of practical thermochemical cycles for hydrogen production from water, the approach adopted by the Los Alamos Scientific Laboratory (LASL) has been to verify proposed cycle reaction schemes by experiment. The verification involves the careful determination of equilibria, reaction yields and rates, as well as the thermochemistry of individual reactions in the cycle under a wide variety of operating conditions. After

demonstration of the cycle's scientific feasibility, a preliminary engineering analysis is attempted to evaluate cycle efficiency and cost. Further experimentation is carried out to optimize the cycle as indicated by the above analysis. Typically, enhanced reaction yield leads to lower internal recycle rates and thus to a lesser energy expenditure involved in the separation of reaction products. Reaction velocity increase reduces reactor residence times and thus contributes to a lower capital cost for the overall cycle.

Should a cycle appear promising after the initial evaluation described, a final phase of process development would involve a bench-scale, closed-loop test that provides data for more realistic engineering evaluation and cost analyses.

In the semiannual period under consideration, the process development and engineering analysis activities have been directed primarily to experimental studies of reactions relevant to sulfuric acid-hydrogen bromide cycles and to the use of insoluble metal sulfates as a means of concentrating sulfuric acid. The latter scheme may prove advantageous in two cycles that are now under development elsewhere. These two cycles are the hybrid sulfuric acid cycle under study at the Westinghouse Research Laboratories and the sulfuric acid-iodine cycle being pursued by the General Atomic Company.

Some work was done on reactions that formed part of the LASL base-line cycle. Work in this area has been "tabled" at present. Kinetic studies on cerium chloride cycles have been terminated under this program. A lesser effort to provide a basic understanding of gas-solid reactions and their control mechanism—in this case, diffusion through a solid product layer—is being continued with cerium compounds under DBES support.

## THE SULFURIC ACID-HYDROGEN BROMIDE CYCLE

The conceptual cycle may be described by the following reactions.

### Low-Temperature Heat-Rejecting Reactions

1.  $2\text{H}_2\text{O} + \text{SO}_2 + \text{Br}_2 = \text{H}_2\text{SO}_4 + 2\text{HBr}$  (water absorption)
2.  $2\text{RBr}_x + 2\text{HBr} = 2\text{RBr}_{x+1} + \text{H}_2$  (hydrogen release)

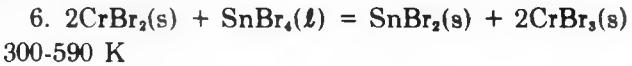
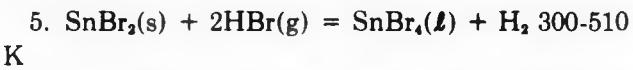
### High-Temperature Heat-Absorbing Reactions

3.  $\text{H}_2\text{SO}_4 = \text{SO}_2 + \text{H}_2\text{O} + 1/2\text{O}_2$  (oxygen release)
4.  $2\text{RBr}_{x+1} = 2\text{RBr}_x + \text{Br}_2$  (bromine regeneration)

In principle, this cycle could be more efficient than the other sulfuric acid cycles under study. Reaction 1 yields nearly 100%  $\text{H}_2\text{SO}_4$  rather than ~50%  $\text{H}_2\text{SO}_4$  that is formed in the other cycles.

Thus, the rather large heat requirements for "drying" sulfuric acid can be avoided. In addition, typical  $\Delta S^\circ$  for metal bromide decompositions are very near the value required for an "ideal" two-step decomposition of HBr. From literature data, the  $\text{VBr}_2\text{-VBr}_3$  couple and the  $\text{CrBr}_2\text{-CrBr}_3$  couple have  $\Delta G^\circ$  values near the value required for the efficient decomposition of HBr. However, in both cases the reaction of HBr with the lower bromide (to evolve  $\text{H}_2$ ) is far too slow.

Earlier, satisfactory reaction rates were demonstrated for reactions involving chromium bromide hydrates.<sup>1</sup> Consequently, in an attempt to promote the chromium bromide reactions in the absence of water, we investigated reactions 5 and 6 of the following sequence.



The thermochemical properties of the  $\text{SnBr}_2\text{-SnBr}_4$  couple would permit it to act as an oxidation-reduction catalyst to achieve the summation reaction. We have previously used oxidation-reduction catalysts, notably the Ru(II)-Ru(III) couple, to obtain very fast reduction of HBr by moist  $\text{CrBr}_3\text{-}6\text{H}_2\text{O}$  and  $\text{VBr}_3\text{-}6\text{H}_2\text{O}$ ; however, these systems are unfavorable because of the heat penalty in decomposing the trivalent bromide hydrates. The  $\text{SnBr}_2\text{-SnBr}_4$  pair appeared to offer several additional advantages: the low melting point of  $\text{SnBr}_4$  (303 K) insures that  $\text{SnBr}_2$  will not be covered by a coating of product in reaction 5. The  $\text{SnBr}_4$ , even when present in small amounts, might act as a reaction medium. The low melting points of the tin bromides ( $\text{SnBr}_2$ , 498 K) would permit phase separation in case of an incomplete reaction 6.

Recently, we have found rather rapid evolution of  $\text{H}_2$  from the reaction of HBr with molten  $\text{SnBr}_2$  (at a temperature of 513 K) in the presence of  $\text{CrBr}_2\text{-CrBr}_3$  and palladium black. Apparently, the increased reaction rate was associated with the presence of the chromium bromides since the reaction of HBr with pure molten  $\text{SnBr}_2$  (513 K, palladium black present) was found to be only 0.3% per h.

Results of reactions of HBr with mixtures containing known amounts of  $\text{SnBr}_2$ ,  $\text{CrBr}_2$ , and  $\text{CrBr}_3$  at a temperature of 516 K (in the presence of palladium black) are presented in Table I. Hydrogen formation was rapid only when palladium was present, whether initially or added. The  $\text{H}_2$  pressure in a given run approached its final experimental value according to the integrated first-order rate law,

$$\frac{P}{P_\infty} = 1 - \exp(-kt)$$

with

$$k = 0.693/t_{1/2}$$

It is important to note that the reaction rates are about 50 times greater than those obtained previously (except for those with the unusable diethylketone medium). This is apparently due to a catalytic effect of one or both of the chromium bromides on reaction 5. It is seen that the  $\text{H}_2$  formed essentially corresponds to the initial  $\text{SnBr}_2$  and reaction 5 rather than the initial  $\text{CrBr}_2$  and the sum of reactions 5 and 6. The measured  $\text{SnBr}_4$  formed also corresponds to reaction 5. Nevertheless, we suspect that a small amount of the  $\text{H}_2$  in experiments 2 and 4 (corresponding to the difference between the  $\text{SnBr}_4$  and total  $\text{H}_2$  formed) did arise from the sum of reactions 5 and 6, that is, from catalytic action of  $\text{SnBr}_2$ - $\text{SnBr}_4$ ; in these cases the final weight of the solids after  $\text{SnBr}_4$  removal is in good agreement with that predicted when the contribution of the tin-catalyzed reaction is included.

The specific rate constant for this reaction ( $0.693/t_{1/2}$ ) is proportional to a ratio,  $R = [\text{Pd}/(\text{SnBr}_2)]_0$ . With a constant amount of palladium, this means that the rate of  $\text{H}_2$  formation is proportional to the amount of  $\text{SnBr}_2$ . This behavior can be used to minimize the cost of reaction materials. Experiments 5 and 6 refer to slow reactions with no chromium bromides present; half-times were derived from initial rates. At the same R ratio the presence of the chromium bromides from reaction 6 increases the rate constant by a factor of 130. The best prospect for increasing reaction rates further lies in more efficient utilization of the present catalyst, as by mounting on ceramic pellets (palladium black is known to clump, reducing effective catalyst area), and in trying new catalysts, such as the perovskites being investigated for automobile exhaust systems.

The reason for the completeness of reaction 5 under the conditions of the above static experiments is that the  $\text{SnBr}_4$  condensed in the cold zone of the reactor. Thus in reaction 5 for these experiments we should consider  $\text{SnBr}_4(l)$  as replaced by  $\text{SnBr}_4(g)$  that is kept at a low partial pressure in the reaction zone by the condensation. In an actual flow reactor at moderate pressures, the  $\text{SnBr}_4(g)$ ,  $\text{H}_2$ , and HBr should be present in equilibrium proportions. It would be favorable to increase the total operating pressure beyond that at which  $\text{SnBr}_4$  condenses so as to increase the degree of conversion of reaction 5. At 513 K the equilibrium constant  $K_p$  is estimated to be about 0.6. The condensation of  $\text{SnBr}_4$  would provide phase separation from  $\text{H}_2$  and HBr. The

TABLE I

FORMATION OF  $\text{H}_2$  FROM REACTION OF HBr WITH MIXTURES OF  
 $\text{SnBr}_2$ ,  $\text{CrBr}_2$ , and  $\text{CrBr}_3$ , IN THE PRESENCE OF Pd AT 516 K  
(Amounts of Materials in Millimoles)

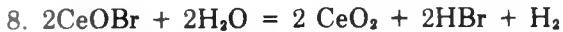
Expt.	$(\text{SnBr}_2)_0$	$(\text{CrBr}_2)_0$	$(\text{CrBr}_3)_0$	$(\text{Pd/SnBr}_2)_0$	$(\text{SnBr}_4)_f$	$(\text{H}_2)_f$	$t_{1/2}$ (min)
1	0.114	0.046	0.229	0.36	0.090	0.107	13
2	0.312	0.136	0.622	0.28	0.276	0.293	17
3	0.312	0.098	0.623	0.17	0.312	0.305	33
4	0.342	0.171	0.864	0.17	0.305	0.360	34
5	0.597	---	---	0.065			$1.2 \times 10^4$
6	0.645	---	---	0.17			$4.4 \times 10^3$

separation of the latter two might be accomplished by a palladium membrane or by utilizing the high solubility of HBr relative to H<sub>2</sub> in mesitylene.

The role of chromium bromides in greatly increasing the reaction rate is not understood other than through the possibility of forming electron transfer complexes with the tin bromides. An experiment with SnBr<sub>2</sub> and CrBr<sub>2</sub>, and another with SnBr<sub>2</sub> and CrBr<sub>3</sub>, gave rates which were intermediate between those with and without the chromium bromide products of reaction 6 (about the geometric mean when compared at the same R ratio).

Results obtained for reaction 6 are summarized in Table II. Apparently a palladium catalyst does not affect the rate significantly, nor does stirring seem important (experiments 3 and 5). Failure to obtain more complete reaction could be due to formation of a stable compound with CrBr<sub>2</sub>, which would prevent its complete reaction. For example, formation of a compound CrBr<sub>2</sub>(SnBr<sub>2</sub>)<sub>2</sub> or Cr(SnBr<sub>2</sub>)<sub>2</sub> would allow only 80% of the CrBr<sub>2</sub> in reaction 6 to be reduced.

A second halide hydrolysis sequence is also being evaluated as a possible subcycle for HBr decomposition. The cycle is composed of reactions 8 and 9 in the following 3 reactions.



The important observation was made that the product of reaction 9 conducted at temperatures of 875 and 775 K contained only CeOBr. At 675 K, both CeOBr and CeBr<sub>3</sub> were produced and at 575 K, only CeBr<sub>3</sub>. The formation of the phase CeOBr at

some temperature above 675 K in quasiequilibrium with H<sub>2</sub>O suggests that the step involving CeBr<sub>3</sub> may be eliminated and that the very endothermic reaction 10 can be avoided.

A series of experiments on reaction 8 has been conducted. In these experiments measured quantities of H<sub>2</sub>O were passed over CeOBr at the reaction temperature and the rate of hydrogen evolution was determined. Equilibrium pressure data have been obtained over a temperature span of ~180° with tests for equilibrium of three of the four temperatures of experimentation.

The experimental data have been reduced and are given in Table III. A plot of log K<sub>p</sub> vs 1/T is presented in Fig. 1.

It appears that these data were, in the most part, obtained under quasiequilibrium conditions; conditions in which the systems were saturated with water vapor. A doubling of the rate of water injected resulted in a decrease of the equilibrium constant, K<sub>p</sub>. This effect is most pronounced at the lower temperatures where true equilibrium is difficult to attain even under static (closed-system) conditions. Because of the limited temperature span, small changes in K<sub>p</sub> drastically change the slope of a line passing through these points as plotted in Fig. 1 (a measure of the ΔH of reaction). An increase in the rate of water injected is shown to produce an increase in the apparent ΔH, removing it further from an estimated value. The above suggest continued study of the system using much lower rates of water delivery.

From our estimates of the thermochemistry of CeOBr, we expect reactions 8 and 9 to exhibit

TABLE II  
RESULTS OF EXPERIMENTS ON REACTION 6

<u>Expt.</u>	<u>Temp. (K)</u>	<u>Time (h)</u>	<u>Catalyst</u>	<u>%CrBr<sub>3</sub> Reacted</u>
1	563	15	Pd	83
2	560	4	Pd	82
3	586	2	None	86
4	600	1	None	80
5	586	1	None; Stirred	73

TABLE III  
EXPERIMENTAL DATA FOR THE CeOBr HYDROLYSIS REACTION

$K_p$	$\Delta G$ (cal.)	Temp. (K)	$\log K_p$	$10^4/T$ (K)
$9.25 \pm 2.10 \times 10^{-4}$	$17\ 352 \pm 507$	1250	-3.03	8.00
$2.34 \pm 0.52 \times 10^{-4}$	$19\ 889 \pm 484$	1197	-3.63	8.35
$2.26 \pm 0.77 \times 10^{-4}$	$19\ 865 \pm 689$	1191	-3.65	8.40
$4.45 \pm 1.15 \times 10^{-5}$	$22\ 622 \pm 502$	1136	-4.35	8.80
$1.90 \pm 0.47 \times 10^{-5}$	$24\ 539 \pm 498$	1136	-4.72	8.80
$5.88 \pm 3.15 \times 10^{-6}$	$25\ 608 \pm 911$	1070	-5.23	9.35
$3.40 \pm 1.54 \times 10^{-6}$	$26\ 826 \pm 796$	1072	-5.47	9.33

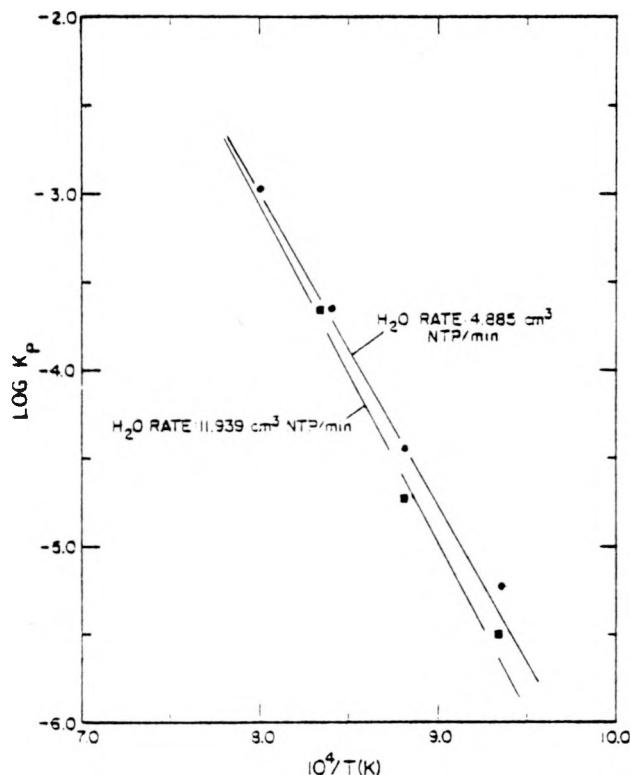


Fig. 1.  
Plot for cerium oxybromide hydrolysis.

positive  $\Delta G^\circ$  values at practical reaction temperatures. Thus, they constitute a "hybrid" cycle for HBr decomposition in which mechanical work is used in the place of electrical work in the more

familiar electrochemical-thermochemical hybrid cycle. The total positive  $\Delta G^\circ$  requirement will be reduced by an important  $\Delta T \cdot \Delta S^\circ$  term, however, and will be significantly lower than the room temperature  $\Delta G^\circ$  for HBr decomposition.

#### USE OF METAL SULFATES IN THE $H_2SO_4$ HYBRID CYCLE AND IN THE $H_2SO_4-I_2$ CYCLE

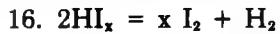
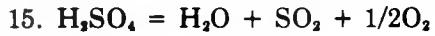
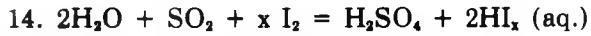
In the  $H_2SO_4$  hybrid cycle (reactions 11-13) large amounts of heat are needed to dehydrate the sulfuric acid for the acid concentrations currently

11.  $SO_2 + 2H_2O = H_2SO_4$  (aq.) +  $H_2$ , electrochemical
12.  $H_2SO_4$  (aq.) =  $SO_3 + H_2O$
13.  $SO_3 = SO_2 + 1/2O_2$

produced in reaction 11. 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

11.  $SO_2 + 2H_2O = H_2SO_4$  (aq.) +  $H_2$ , electrochemical
- 11a.  $H_2SO_4 + MO = MSO_4 + H_2O$
- 12a.  $MSO_4 = MO + SO_3$
13.  $SO_3 = SO_2 + 1/2O_2$

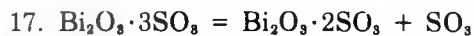
The same is true for the  $\text{H}_2\text{SO}_4$  -  $\text{I}_2$  cycle (reactions 14-16)



in which sulfuric acid produced in reaction 14 and phase-separated from  $\text{HI}_x$  is dehydrated prior to thermal decomposition. The sulfate should have low solubility, form an anhydrous sulfate, and be relatively unstable with respect to 12a. An oxide sulfate may replace metal oxide. A survey and assessment of the literature were made for antimony and bismuth, both of which satisfy the first two criteria.

$\text{Sb}_2(\text{SO}_4)_3$  decomposes to  $\text{SO}_2$  and  $\text{Sb}_2\text{O}_4$ . Unfortunately  $\text{Sb}_2\text{O}_4$  decomposes to  $\text{Sb}_2\text{O}_3$  and  $1/2\text{O}_2$  with unfavorable high-temperature thermodynamics. The formation of sulfate in 11a is also extremely slow even at the boiling points of  $\text{H}_2\text{SO}_4$  solutions.

Published thermogravimetric work<sup>2</sup> indicates that  $\text{Bi}_2\text{O}_3 \cdot 3\text{SO}_3$  decomposes with increasing temperature to  $\text{SO}_3$  and a series of oxide sulfates terminating in  $\text{Bi}_2\text{O}_3$  itself. The first two oxide sulfates to be formed are  $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$  and  $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3$ . We estimate that the equilibrium  $\text{SO}_3$  pressure for reaction 17 is 1 atm at 860 K. With much greater uncertainty, we estimate that the pressure for reaction 18 is 1 atm at 1050 K.



Final decomposition to form  $\text{Bi}_2\text{O}_3$  occurs at higher temperatures. The options for generating  $\text{SO}_3$  over a temperature range that includes intermediate temperatures (in addition to the high temperatures for  $\text{SO}_3$  decomposition in reaction 13) should be useful in achieving efficient extraction of heat from the circulating helium gas of a high-temperature gas-cooled nuclear reactor. Apparatus is being prepared for measuring  $\text{SO}_3$  pressures in the  $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3$  system.

The oxide sulfates from intermediate to high temperatures are returned to low temperature for reaction 11a with  $\text{H}_2\text{SO}_4$  solution. Literature data indicate that anhydrous  $\text{Bi}_2\text{O}_3 \cdot 3\text{SO}_3$  is the stable solid phase at 298 K above 52.6 wt%  $\text{H}_2\text{SO}_4$ . This is the equilibrium concentration for reaction 19.

Anhydrous  $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$  is the stable phase down to 2.7 wt%  $\text{H}_2\text{SO}_4$ . Some flexibility may thus be



possible in utilizing dilute acid and decreased electrochemical work.

Preliminary laboratory work performed at 371 K (98°C) with  $\text{Bi}_2\text{O}_3$  and 58.5 wt%  $\text{H}_2\text{SO}_4$  indicates that the species  $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$  was formed. Reaction times appeared to be short as the reactants evolved heat on mixing at room temperature. Cooling of the equilibrium mixture from 98°C to 25°C produced  $\text{Bi}_2\text{O}_3 \cdot 3\text{SO}_3$ .

Additional experiments are being carried out to obtain equilibrium concentrations and rates of reactions for bismuth oxide made with ~50 wt% sulfuric acid solutions. Future work will involve the thermal decomposition of the precipitated sulfates and the accurate determination of equilibrium  $\text{SO}_3$  pressures at elevated temperatures.

A preliminary evaluation of the energy efficiency of the bismuth sulfate alternate to the hybrid sulfuric acid cycle has been completed. The hybrid cycle has been described in the literature.<sup>3</sup> A process sensitivity study<sup>4</sup> using a simplified flow sheet seen in Fig. 2 illustrated the action of process variables on the cycle's efficiency. Data taken from this study were used as a basis for comparison with the modified process involving an insoluble bismuth sulfate. The flow sheet for this latter case is seen in Fig. 3. The sulfuric acid stream leaving the electrolyzer was assumed to be at 50 wt% concentration in both cases. An equilibrium yield of 75% was calculated for sulfur trioxide decomposition at 1100 K based on published thermodynamic data (JANAF Tables).

Tables IV and V illustrate the potential benefits to be gained on adopting the bismuth sulfate method of solution concentration. 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, the hybrid process operating at an effluent acid concentration of 50 wt% showing a 36.1% efficiency as compared with the bismuth sulfate alternate having an efficiency of 47.8%.

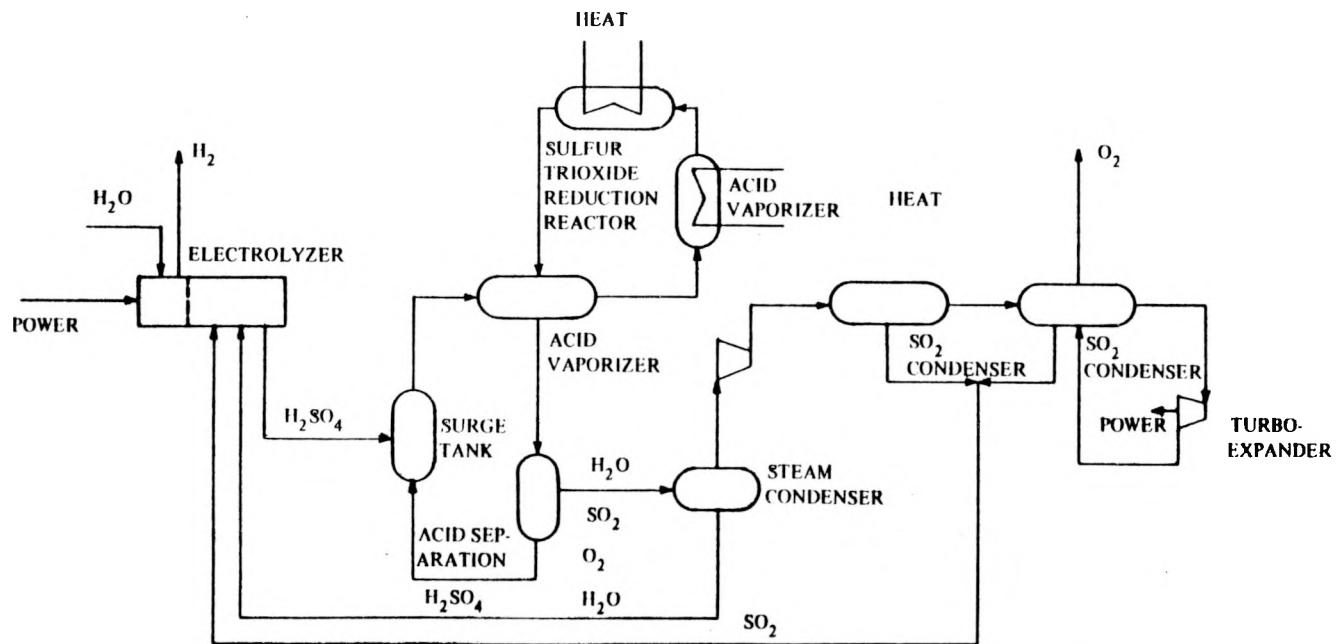


Fig. 2.  
Hybrid sulfuric acid cycle (simplified flow sheet).

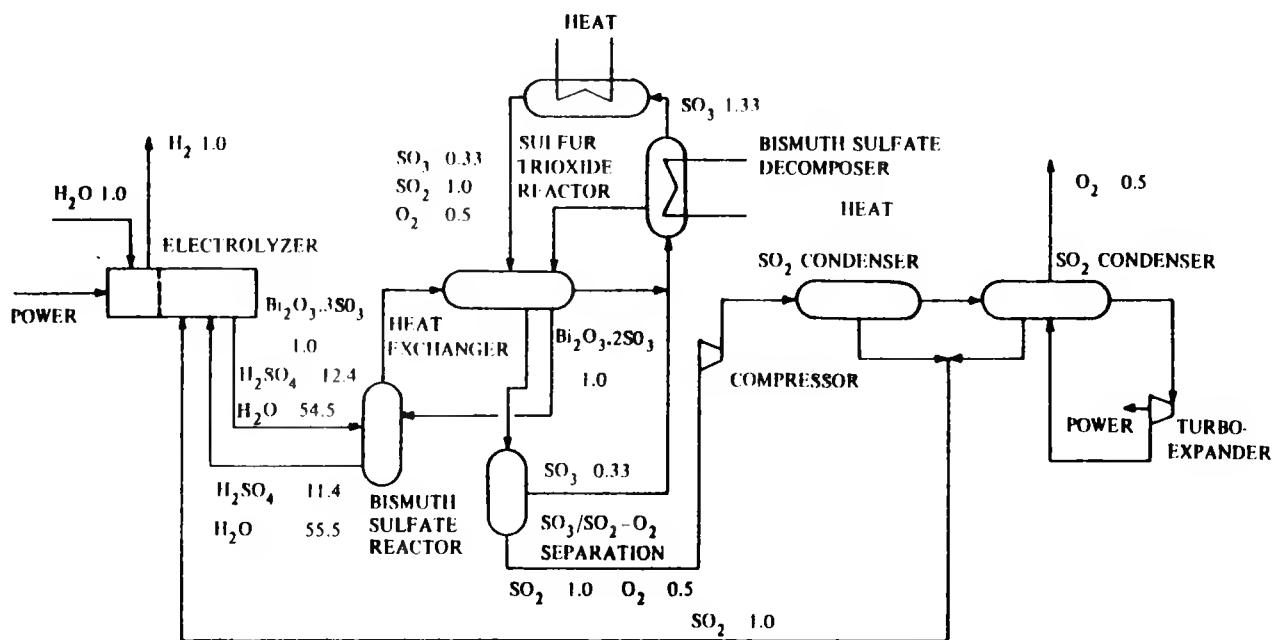


Fig. 3.  
Hybrid sulfuric acid cycle, bismuth sulfate modification.

**TABLE IV**  
**HEAT BALANCE FOR HYBRID SULFURIC ACID CYCLE**  
**(Units = kcal/mole H<sub>2</sub> Produced)**

Step	Power (Heat Eq.)	Heat Required	Heat Available
1. Electrolysis	10 (30)		10 <sup>a</sup>
2. Acid Vaporization		155	
3. Acid Heating		75	
4. Acid Decomposition		68	
5. Acid Cooling			73
6. Acid Condensation			96
7. Steam Condensation			63 <sup>a</sup>
8. SO <sub>3</sub> /SO <sub>2</sub> /O <sub>2</sub> Separation	10 (30)		
	<hr/>	<hr/>	<hr/>
	20 (60)	298	169 73 <sup>a</sup>

$$\text{Efficiency} = \frac{68.3}{60 + 298-169} = 0.361$$

<sup>a</sup>Heat unavailable for matching.

**TABLE V**  
**HEAT BALANCE FOR BISMUTH SULFATE MODIFIED**  
**HYBRID SULFURIC ACID CYCLE**  
**(Units = kcal/mole H<sub>2</sub> Produced)**

Step	Power (Heat Eq.)	Heat Required	Heat Available
1. Electrolysis	10 (30)		10 <sup>a</sup>
2. Bismuth Sulfate Formation			3.6 <sup>a</sup>
3. Bismuth Sulfate Decomposition		40-60 (estimated)	
4. SO <sub>3</sub> Decomposition		23	
5. SO <sub>3</sub> /SO <sub>2</sub> /O <sub>2</sub> Separation	10 (30)		
	<hr/>	<hr/>	<hr/>
	20 (60)	63-83	13-16 <sup>a</sup>

$$\text{Efficiency} = \frac{68.3}{143 \text{ (max)}} = 0.478$$

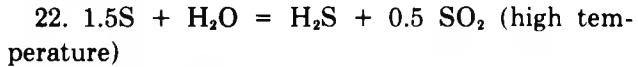
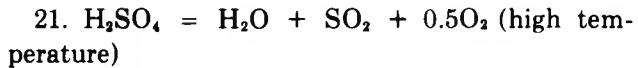
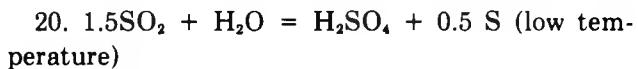
<sup>a</sup>Heat unavailable for matching.

Additional benefits are a decrease in corrosion due to the absence of aqueous sulfuric acid phase at elevated temperature and a lesser heat exchanger surface requirement. Process unknowns at present include the effect of a low concentration of bismuth ion on the electrolysis process and the relative difficulties of heating and transporting the solid bismuth sulfates at high temperatures (800 to 1100 K).

The obvious potentialities inherent in the use of insoluble metal sulfates clearly make this process a prime choice for further intensive investigation.

### LASL BASE-LINE CYCLE—ALTERNATE REACTIONS

The LASL base-line cycle has been described in the literature.<sup>5</sup> It consists of the following reaction sequence.



Investigations were carried out on reaction 20, the disproportionation of  $\text{SO}_2$  with water.

In prior periods, several heterogeneous catalysts (cobalt molybdate, both as-received and in the presulfided form, as well as hydrogen mordenite-type molecular sieves, both as-received and preloaded with cobalt) had been investigated without marked promise for successful application.

Small-scale screening experiments were conducted on such heterogeneous catalysts as palladium black, platinized asbestos, and 0.3% platinum on alumina pellets. A 6M  $\text{H}_2\text{SO}_4$  solution was used,  $\text{SO}_2$  being bubbled through the catalyst bed wet with this acid. No evidence of free sulfur formation was observed, even at a temperature of 373 K.

Much better success has been reported already in the use of homogeneous catalysis systems, especially iodine. However, the iodine system has serious drawbacks, namely, corrosion, the slowing of reac-

tion rate as the acid concentration increases, and difficulty in separation of the reaction products.

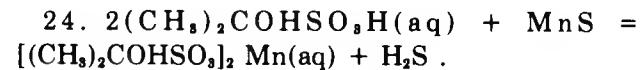
It was reported by Foerster and Gruner<sup>6</sup> that the reaction could be catalyzed by systems employing homogeneous catalysts such as sulfur, or the thiosulfate or dithionate ions, especially at 423 K.

Many experiments were conducted in this temperature range and higher, using tank pressure  $\text{SO}_2$  ( $\sim 3$  atm) in pressure vessels. The starting acid concentration for these was set at 6M  $\text{H}_2\text{SO}_4$ .

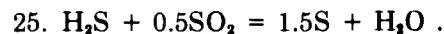
At this acid concentration, neither sulfur nor thiosulfate appeared to give any substantial yield of sulfur or increase in the  $\text{H}_2\text{SO}_4$  concentration. The trithionate ion has not been tried as yet, although no great improvement over the other two catalysts would be anticipated, based on Foerster and Gruner's work.

Other work involved tests of reaction schemes involving the substance  $\text{MnS}$  as an alternate to reaction 22 in the base-line cycle.

Dilute solutions of  $\alpha$ -hydroxy sulphylic acid were prepared to test the following proposed reaction.



Test evaluations carried out at room temperature showed that free  $\text{SO}_2$  was present even in dilute solution. Free  $\text{SO}_2$  reacted, in situ, with liberated  $\text{H}_2\text{S}$  according to the following reaction.



Relatively large amounts of the phase  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  in two of the tests may account for a fraction of the free S according to the following reaction sequence.



Quantitative tests of the  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ - $\text{MnS}$  and  $\text{HCOOH}$ - $\text{MnS}$  systems produced quantitative yields of  $\text{H}_2\text{S}$  at room temperatures. Dilution of the filtrate followed by treatment with  $\text{CO}_2$  failed to precipitate  $\text{MnCO}_3$ , although subsequent tests showed that the dilution was within the limit of detection for carbonate.

## FUTURE RESEARCH

In the combined DBES and DES programs, we will continue to test reactions in cycles that are potentially suitable for different heat-source temperatures that also appear reasonable from the point of view of thermochemistry. Certainly there are many attractive cycles that have not yet been identified and tested. However, from our laboratory experience, it is increasingly apparent that the most attractive cycles are usually impractical because of slow reaction rates for the low-temperature steps. One method of improving kinetics is to utilize solution chemistry for low-temperature steps. Previously, we have tried to avoid solution chemistry since solution-drying steps are generally recognized as being unattractive from the viewpoint of chemical engineering. Nevertheless, it is important to note that after 3 to 5 years of development in several countries, essentially all of the cycles that have actually been demonstrated experimentally contain solution-drying or solution-concentration steps. Therefore, we plan to examine more closely solution chemistry as a method for promoting otherwise attractive cycles. We also hope to identify and incorporate precipitation reactions in order to minimize solution-drying operations. We hope the use of solution reactions will also give added flexibility and lead to the discovery of cycles that are less corrosive.

We will again consider hybrid thermochemical-electrochemical cycles. The use of an electrochemical step can lead in many cases to simplification of the solution chemistry described above. However, our primary objective in studying hybrid systems is to synthesize cycles with low max-

imum temperatures for use with solar heat sources and/or cycles that avoid the use of corrosive chemicals.

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