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<https://doi.org/10.15017/17547>

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出版情報：九州大学大学院総合理工学報告. 4 (1), pp.1-13, 1982-06-30. 九州大学大学院総合理工学研究科

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## Thermochemical Water-Splitting for Hydrogen Production by Antimony-Iodine Processes

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(原稿受理 昭和57年2月10日)

A new thermochemical water-splitting process named "Sb-I Process" was proposed on the basis of thermodynamic considerations and some preliminary experiments. The process consists of three reactions which eventually produce hydrogen from water via HI intermediate. Subsequent examinations, however, showed that this process embraced a difficulty in the separation of HI gas from the reaction system. To overcome this difficulty, the process was subjected to modification in two ways. First the electrolysis of the aqueous HI solution was combined with the original process to eliminate the HI separation step. The overall efficiency for this "Sb-I Hybrid Process" was estimated to be 33~37% when the recovery of heat was assumed to be 80%. The second modification was carried out by introducing calcium as an additional reaction medium. The resulting modified process, "Sb-I-Ca Process", consists of five reactions. It was found that all reaction- and separation-steps in this process could be conducted without serious difficulties. From a flow diagram made on the basis of the experimental results, the overall efficiency was estimated to be about 39% with an assumption of 80% heat recovery.

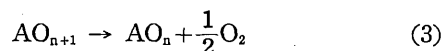
### 1. Proposal of Sb-I process

#### 1.1. Introduction

The thermochemical hydrogen production from water is very attractive in the search for new energy carriers to replace the fossil fuels<sup>1)</sup>. Many thermochemical water-splitting processes (cycles) have been reported in the literatures<sup>2)3)</sup>. However, no processes seem satisfactory enough to be commercially acceptable at present, although a hybrid sulfuric acid cycle<sup>4)</sup> and a sulfuric acid-hydrogen iodide cycle<sup>5)</sup> are now being developed in the U.S.A. and in Europe. We have proposed a new water splitting process named "Sb-I Process"<sup>6)</sup>, which was devised as follows.

#### 1.2. Process composition

First, we composed a general three-step process based on the considerations mentioned below.



(1): Water reaction.

(2): Hydrogen-producing reaction.

(3): Oxygen-producing reaction.

where  $AO_n$  and  $AO_{n+1}$  refer, respectively, to a lower oxide (or a metal) and the higher one, and B for a hydrogen acceptor. The considerations taken into account were;

a) From the viewpoint of overall efficiency, the process should be constructed of basic reactions as few as possible

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**Table 1** Candidates for  $AO_n-AO_{n+1}$  couple

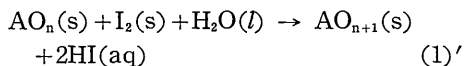
$\frac{1}{2}As_2O_3 - \frac{1}{2}As_2O_5$	BaO-BaO <sub>2</sub>	$\frac{1}{2}Bi_2O_3 - \frac{1}{2}Bi_2O_5$
Cd <sub>2</sub> O-2 CdO	3 CoO-Co <sub>3</sub> O <sub>4</sub>	Cu <sub>2</sub> O-2 CuO
3 PbO-Pb <sub>3</sub> O <sub>4</sub>	$\frac{1}{2}Pb_3O_4 - \frac{3}{2}PbO_2$	2 Mn <sub>3</sub> O <sub>4</sub> -3 Mn <sub>2</sub> O <sub>3</sub>
Mn <sub>2</sub> O <sub>3</sub> -2 MnO <sub>2</sub>	Hg-HgO	2 NiO-Ni <sub>2</sub> O <sub>3</sub>
Pb-PbO	Ag-Ag <sub>2</sub> O	$\frac{1}{2}Sb_2O_3 - \frac{1}{2}Sb_2O_5$

and the number of elements other than hydrogen and oxygen involved should be no more than two.

b) For the oxygen formation step, preferable is a thermal decomposition of a solid oxide, since such a reaction usually yields two easily separable products, the lower oxide and oxygen.

c) The oxidation of the lower oxide should be attained by the water reaction.

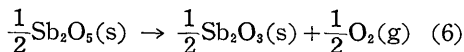
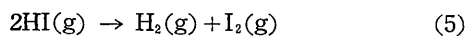
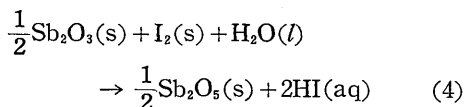
For the hydrogen acceptor B, iodine was chosen by considering the corrosive problem and the relative ease of the thermal decomposition of hydrogen iodide. As for  $AO_n-AO_{n+1}$  couples, a number of candidates in which the higher oxides can dissociate oxygen below 1300 K, a temperature attainable with high-temperature gas-cooled reactors<sup>8)</sup>, were screened from comprehensive chemistry books such as one by Gmelin<sup>9)</sup> as shown in **Table 1**. Among these systems, only four, i.e., 3CoO-Co<sub>3</sub>O<sub>4</sub>, Cu<sub>2</sub>O-2CuO,  $\frac{1}{2}As_2O_3 - \frac{1}{2}As_2O_5$ ,  $\frac{1}{2}Sb_2O_3 - \frac{1}{2}Sb_2O_5$ , were thermodynamically acceptable in the reaction (1)', being associated with the standard free energy change less than 10 kcal/mol for the reaction (1)' as shown in **Table 2**.



**Table 2** Thermodynamic data for reaction (1)'

$AO_n-AO_{n+1}$	$\Delta H_{298}^\circ$ (kcal/mol)	$\Delta G_{298}^\circ$ (kcal/mol)
$\frac{1}{2}As_2O_3 - \frac{1}{2}As_2O_5$	+10.6	+ 8.5
3 CoO-Co <sub>3</sub> O <sub>4</sub>	- 3.4	- 1.7
Cu <sub>2</sub> O-2 CuO	- 2.8	+ 6.2
$\frac{1}{2}Sb_2O_3 - \frac{1}{2}Sb_2O_5$	+10.5	+ 7.5

Further, preliminary experiments revealed that, of the four,  $\frac{1}{2}Sb_2O_3 - \frac{1}{2}Sb_2O_5$  couple was the most suitable; the other three systems were excluded because of such flaws as a slow reaction rate for 3CoO-Co<sub>3</sub>O<sub>4</sub>, occurrence of a side-reaction for Cu<sub>2</sub>O-2CuO, and harmfulness for  $\frac{1}{2}As_2O_3 - \frac{1}{2}As_2O_5$ . The "Sb-I Process" thus constructed is expressed as follows;



### 1.3. Preliminary examination of each step

In reaction (4) solid Sb<sub>2</sub>O<sub>5</sub> and aqueous HI solution are obtained by a con-

tact of solid  $\text{Sb}_2\text{O}_3$  and aqueous iodine solution at lower temperatures. This reaction is a well-known one<sup>9)</sup> which has been applied to the volumetric analysis of  $\text{Sb}^{3+}$ . The aqueous HI obtained here is distilled to get gaseous HI, which can be thermally decomposed to hydrogen and gaseous iodine in reaction (5) at higher temperatures. As to reaction (5), it is well established that hydrogen iodide is ca. 25 per cent dissociated at 800 K<sup>10)</sup>. The hydrogen generated will be separated from gaseous HI and iodine with a porous membrane. For the last reaction (6), published data<sup>11)</sup> show that  $\text{Sb}_2\text{O}_5$  when heated at about 1070 K transforms to  $\text{Sb}_2\text{O}_4$ , the complex oxide of trivalent and pentavalent antimony, and that  $\text{Sb}_2\text{O}_4$  further decomposes to  $\text{Sb}_2\text{O}_3$  above 1200 K. The produced  $\text{Sb}_2\text{O}_3$  is sublimed to be separated from the reaction system, and recycled back to reaction (4).

Each reaction of this process is thermodynamically acceptable as shown in Table 3. Thus we conclude that these three reactions can be successfully combined to compose a water splitting process.

Table 3 Thermodynamic data for the Sb-I process

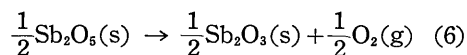
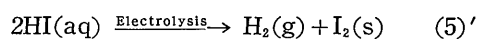
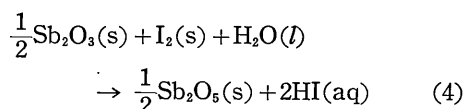
Step	K T	$\Delta H^\circ$ kcal/mol	$\Delta G^\circ$ kcal/mol
(4)	298	+10.5	+ 7.5
(5)	800	+ 3.1	+ 6.0
(6)	1250	+31.2	+ 1.1

## 2. Investigation of Sb-I hybrid process

### 2.1. Introduction

Although all reactions of the Sb-I process proposed in the previous section are feasible thermodynamically, it has turned out that the preparation of HI gas

from the aqueous solution after the first step consumes a considerable amount of thermal energy. In order to eliminate this difficulty, the electrolysis of the aqueous HI solution was introduced instead of the thermal decomposition of HI gas. The Sb-I hybrid process thus constructed is written as follows<sup>12)</sup>.



### 2.2. Examination of each step

#### (a) $\text{Sb}_2\text{O}_3/\text{I}_2/\text{H}_2\text{O}$ reaction

The first step reaction was carried out in a mixed solvent system of  $\text{CCl}_4$ - $\text{H}_2\text{O}$ . It was found that the produced HI could be extracted into the water phase while unreacted  $\text{I}_2$  remained in  $\text{CCl}_4$  phase. Thus the two components being easily separated. As shown in Fig. 1, a completion of the reaction required a long period when  $\text{I}_2$  was reacted with a stoichiometric amount of  $\text{Sb}_2\text{O}_3$ . However, the reaction period could be decreased significantly by adding excess  $\text{Sb}_2\text{O}_3$ : at  $\text{Sb}_2\text{O}_3/\text{I}_2=4$  the reaction was

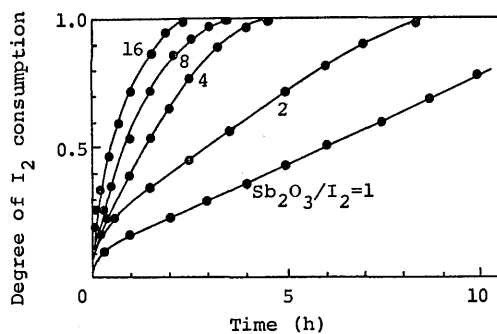


Fig. 1 Dependence of  $\text{I}_2$  consumption on time.

$\text{I}_2$ : 10.9 mol/m<sup>3</sup>,  $\text{CCl}_4$ : 50 cm<sup>3</sup>,  
 $\text{H}_2\text{O}$ : 50 cm<sup>3</sup>, Temp.: 298 K

completed in about 5 h. As for the concentration of produced HI, it was found that the HI concentration could not be increased more than 2 wt%; in case I<sub>2</sub> was added in excess of that composition, side reaction such as the formation of SbI<sub>3</sub> took place.

(b) Electrolysis of HI solution

As seen in Table 4<sup>(3)</sup>, the standard electrode potentials show that HI can be electrolyzed at a cell voltage only about one half as large as H<sub>2</sub>O is electrolyzed. The electrolysis of HI was actually examined by using ca. 2 wt% (0.1M) HI solution. The polarization curve in Fig. 2 indicate anode and cathode decomposition potentials of +0.28 and -0.32 V (vs. SCE), respectively, with a minimum anodic overpotential of ca. 0.05 V. The cell voltage at current density of 40 mA/cm<sup>2</sup> was 0.63 V, showing that no major overpotential was associated under the conditions.

Table 4 Standard electrode potential (V, 25°C)

$I_2 + 2e = 2I^-$	+0.536
$I_3^- + 2e = 3I^-$	+0.536
$O_2 + 4H^+ + 4e = 2H_2O(l)$	+1.229
$2H^+ + 2e = H_2$	±0.000

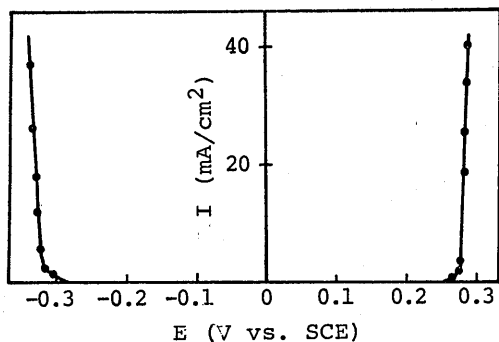


Fig. 2 I-E curve for 0.1 M HI solution at 288 K.

(c) Decomposition of Sb<sub>2</sub>O<sub>5</sub>

It is known that Sb<sub>2</sub>O<sub>5</sub> is thermally

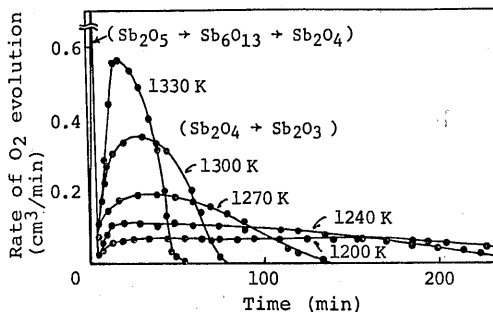


Fig. 3 Decomposition of Sb<sub>2</sub>O<sub>5</sub> to Sb<sub>2</sub>O<sub>3</sub> (N<sub>2</sub>: 40 cm<sup>3</sup>/min).

decomposed to Sb<sub>2</sub>O<sub>3</sub> through Sb<sub>6</sub>O<sub>13</sub> and Sb<sub>2</sub>O<sub>4</sub><sup>(4)</sup>. Fig. 3 shows the time courses of the rate of O<sub>2</sub> evolution in the decomposition of Sb<sub>2</sub>O<sub>5</sub> to Sb<sub>2</sub>O<sub>3</sub> at 1200 K and above. In the Sb<sub>2</sub>O<sub>5</sub> decomposition two maxima appeared in the rate of O<sub>2</sub> evolution, which corresponded to Sb<sub>2</sub>O<sub>5</sub> → Sb<sub>6</sub>O<sub>13</sub> → Sb<sub>2</sub>O<sub>4</sub> and Sb<sub>2</sub>O<sub>4</sub> → Sb<sub>2</sub>O<sub>3</sub>, respectively. The rate of the second decomposition Sb<sub>2</sub>O<sub>4</sub> → Sb<sub>2</sub>O<sub>3</sub> was small at 1200 K, but increased with a rise in temperature. The reaction went to completion in about 2 h at 1270 K.

2.3. Evaluation of Sb-I hybrid process

A flow diagram for the Sb-I hybrid process was constructed on the basis of the above mentioned results as shown in Fig. 4. The figures in the diagram represent the exothermal or endothermal heats (in unit of kcal) associated with respective steps.

The overall efficiency ( $\eta_{LHV}$ ) of the process was evaluated on the conditions: i) the starting charge ratio of Sb<sub>2</sub>O<sub>3</sub> to I<sub>2</sub> in the first step reaction is fixed at a=Sb<sub>2</sub>O<sub>3</sub>/I<sub>2</sub>=3, ii) the cell voltage for the HI electrolysis is 0.7 or 0.9 V, and iii) the efficiency of heat → electricity conversion is 40%. Fig. 5 shows  $\eta_{LHV}$  as a function of heat recovery. At 80% heat recovery  $\eta_{LHV}$  becomes 33~37%. It is seen that, at high heat reco-

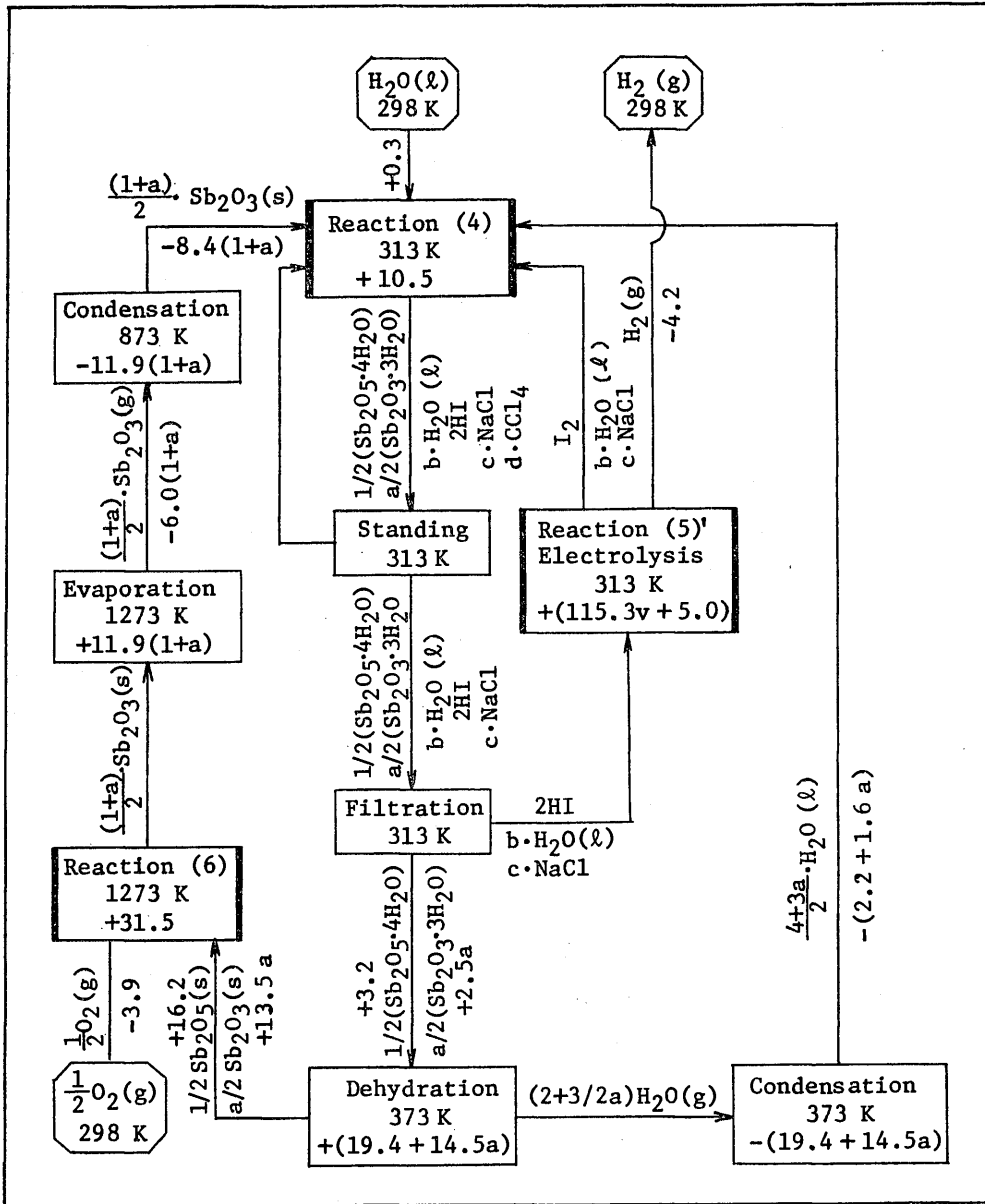


Fig. 4 Flow diagram of the Sb-hybrid process.

very,  $\eta_{LHV}$  for the process is considerably higher than the efficiency of conventional water electrolysis (20~25 %).

### 3. Proposal of Sb-I-Ca process

#### 3.1. Introduction

The Sb-I hybrid process proposed in

the previous section includes an electrolysis step which consumes an electric energy as large as 24.7 kcal/mol, or ca. 40 % of the absolute value of the standard free energy of formation of  $H_2O(l)$ . This means that the purity of thermochemical process is considerably

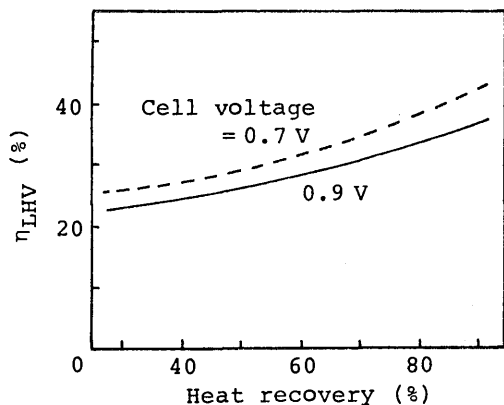
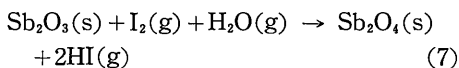


Fig. 5 Dependence of efficiency ( $\eta_{LHV}$ ) on heat recovery ( $Sb_2O_3/I_2=3$ ).

decreased in the process. This section deals with the purely thermochemical revision of the Sb-I process by use of calcium as an additional medium<sup>15)16)</sup>.

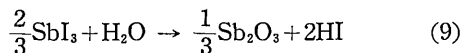
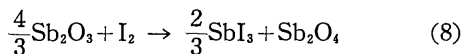
3.2. Process modification

In order to increase the reaction yield of the first step of the Sb-I process, it was attempted to replace the solid-liquid reaction at room temperature by the following solid-gas reaction at high temperature.



However, this reaction turned out to be

a thermodynamically unfavorable one with a positive  $\Delta G^\circ$ . In practice the predominant occurrence of reaction (8) was confirmed at 600 K. This suggests a possibility that reaction (7) may eventually achieved in two steps by combining reaction (8) with (9).



The  $\Delta G^\circ$  (kcal/mol) for reactions (8) and (9) are listed below.

T(K)	400	600	800	1000	1200
$\Delta G^\circ_{(8)}$	-1.90	+3.43	+7.68	+12.89	+20.76
$\Delta G^\circ_{(9)}$	+16.97	+12.57	+10.91	+9.29	+7.20

As seen from the list, reaction (9) becomes more favorable at high temperature. Experimental examinations, however, showed that reaction (9) hardly proceeded even at 1293 K. Then we tried further to decompose reaction (9) into two reactions by introducing an element M as a reaction medium as follows.

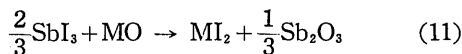
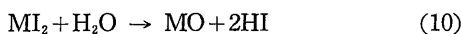


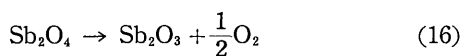
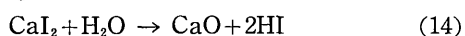
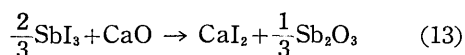
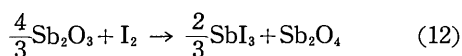
Table 5 Thermodynamic data for reactions (10) and (11)

Reaction		$\Delta H^\circ_{298}$ ( $\Delta H^\circ_{600}$ ) (kcal/mol)	$\Delta G^\circ_{298}$ ( $\Delta G^\circ_{600}$ ) (kcal/mol)
$MgI_2 + H_2O \rightarrow MgO + 2HI$ (10 a)		+14.20	+5.54
$\frac{3}{4}FeI_2 + H_2O \rightarrow \frac{1}{4}Fe_3O_4 + \frac{1}{4}H_2 + \frac{3}{2}HI$ (10 b)		+19.18	+14.56
$CaI_2 + H_2O \rightarrow CaO + 2HI$ (10 c)		+47.10	+38.64
$MgO + \frac{2}{3}SbI_3 \rightarrow MgI_2 + \frac{1}{3}Sb_2O_3$ (11 a)		+14.53 (+10.29)	+14.30 (+15.33)
$\frac{1}{4}Fe_3O_4 + \frac{2}{3}SbI_3 \rightarrow \frac{3}{4}FeI_2 + \frac{1}{4}I_2 + \frac{1}{3}Sb_2O_3$ (11 b)		+ 6.41 (+ 1.01)	+ 5.09 (+ 9.59)
$CaO + \frac{2}{3}SbI_3 \rightarrow CaI_2 + \frac{1}{3}Sb_2O_3$ (11 c)		-18.37 (-22.73)	-18.90 (-17.89)

As the candidate of element M were selected Mg, Fe, and Ca, on the basis that their iodides undergo hydrolysis easily. Thermodynamic data for reactions (10) and (11) are listed in Table 5. As far as reaction (10) is concerned, Mg seems to be most favorable element. However, Mg as well as Fe were inadequate for reaction (11): the yield of reaction (11) was 74.2% for Ca, while those were only 1.4% and 2.3% for Mg and Fe, respectively. After these examinations, we concluded that only Ca could be a candidate for M with its enough reactivities in both (10) and (11).

### 3.3. New modified process

Through the exploration mentioned above, a new modified process, "Sb-I-Ca Process", was constructed, which consists of the following five reactions.



It is seen that reactions (12), (13) and (14) are introduced in place of the first step reaction of the original Sb-I process. Fig. 6 shows  $\Delta G^\circ$  vs. temperature for the respective reactions. Each reaction except (14) has the temperature region, where  $\Delta G^\circ$  becomes less than 10 kcal/mol below 1300 K, assuring that it is thermodynamically acceptable as a constituent reaction of the process. While  $\Delta G^\circ$  of (14) remains still a large positive value at high temperature in the figure, it was verified experimentally that the reaction could take place at considerable ease.

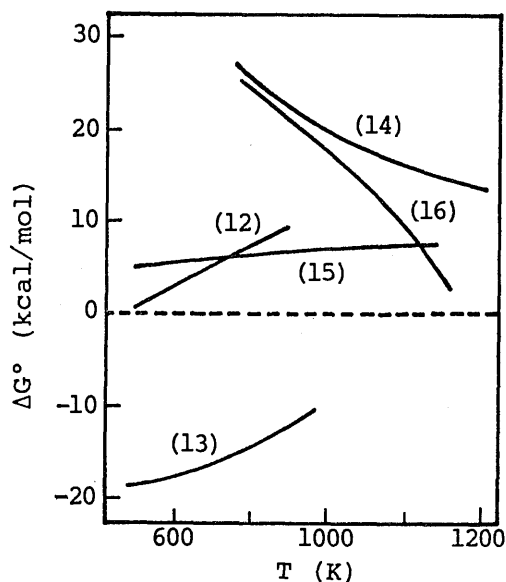


Fig. 6 Temperature dependence of  $\Delta G^\circ$  for each reaction of the Sb-I-Ca process.

## 4. Examination of Sb-I-Ca process

### 4.1. Feasibility of each step

#### (a) $\text{Sb}_2\text{O}_3/\text{I}_2$ reaction

The reaction between  $\text{Sb}_2\text{O}_3$  and  $\text{I}_2$  was studied as follows. An excess of gaseous  $\text{I}_2$  ( $\text{I}_2/\text{Sb}_2\text{O}_3 = 1.2 \sim 7.5$  equivalent ratios) was brought into contact with pulverized  $\text{Sb}_2\text{O}_3$  in the temperature range 550 ~ 750 K. The reaction was found to proceed scarcely at a temperature below 373 K, in spite of the favorable thermodynamic data:  $G_{298}^\circ = -2.7$  kcal/mol. The results in Fig. 7 show that the reaction is driven to completion in 2 h at 720 K when the number of  $\text{I}_2$  equivalent to  $\text{Sb}_2\text{O}_3$  is 3.0. The solid  $\text{Sb}_2\text{O}_4$  formed was easily separated from the gaseous mixture of the produced  $\text{SbI}_3$  and the excess  $\text{I}_2$ . Subsequently,  $\text{SbI}_3$  could be separated from gaseous  $\text{I}_2$  by liquefaction on cooling the mixture to a moderate temperature, e.g., 673 K. As shown in the flow diagram repre-



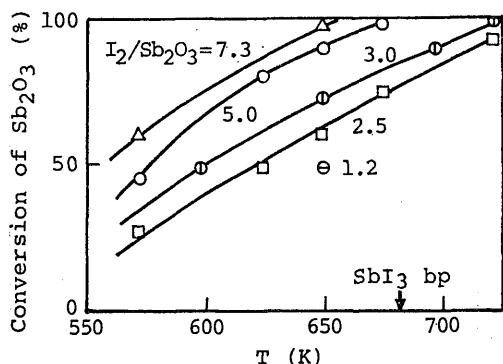


Fig. 7 Temperature dependence of  $Sb_2O_3$  conversion in reaction (12). Reaction time: 2 h

sented later, the separated products,  $Sb_2O_4$  and  $SbI_3$ , go to reactions (16) and (13), respectively; the gaseous  $I_2$  is recycled back to reaction (12).

(b)  $SbI_3/CaO$  reaction

The reaction between  $SbI_3$  and  $CaO$  is thermodynamically favorable at all temperatures:  $\Delta G^\circ \leq -10 \text{ kcal/mol}$ . This was in fact confirmed experimentally. The liquefied  $SbI_3$  was allowed to react with pulverized  $CaO$  in a sealed tube. The formation of the solid products,  $CaI_2$  and  $Sb_2O_3$  was confirmed by X-ray diffraction and chemical analysis. As Fig. 8 shows, the conversion of  $SbI_3$  increased with a rise in reaction temperature. The  $CaO$  conversion reached about 75% in 60 h at 633 K with the equivalent ratio  $CaO/SbI_3=1$  as shown in Table 6, but did not go further under the present experimental conditions. As  $CaO/SbI_3=4$ , the  $SbI_3$  conversion reached 100%. This means that no particular separation process for  $SbI_3$  is necessary after reaction (13) under these conditions. However, it is still necessary to separate the produced  $Sb_2O_3$  (solid) from the solid mixture of  $CaI_2$  and  $CaO$ , since the presence of  $Sb_2O_3$  harms the subsequent reactions

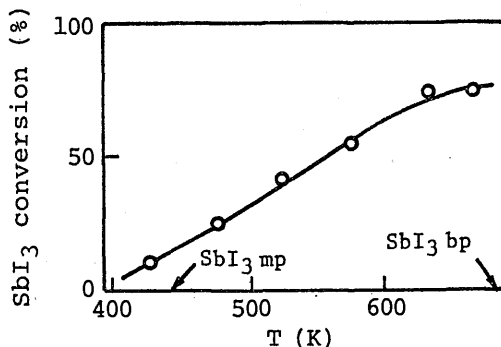


Fig. 8 Temperature dependence of  $SbI_3$  conversion in reaction (13).  $SbI_3/CaO=1$  (equiv. ratio), Reaction time: 6 h

Table 6 Conversion of reactants in reaction (13) under various conditions<sup>a)</sup>

$SbI_3/CaO$ <sup>b)</sup>	Time (h)	$SbI_3$ conv. (%)	$CaO$ conv. (%)
4/1	6	18.9	75.6
2/1	6	37.2	74.4
1/1	6	73.7	73.7
1/1	60	75.1	75.1
1/2	6	87.9	44.0
1/4	6	100.0	25.0

a) Reaction temp.: 633 K.

b) Equivalent ratio.

(14) and (15). Fortunately, the separation is relatively easy because their solubilities in water (100 g) greatly different, i.e., 215.7 g for  $CaI_2$  and  $8.45 \times 10^{-4}$  g for  $Sb_2O_3$  at 298 K.

(c)  $CaI_2/H_2O$  reaction and HI decomposition reaction

The hydrolysis of  $CaI_2$  and the decomposition of HI were experimented as follows. A carrier gas, He, was saturated with water vapor in the temperature range 298~348 K, and passed over molten  $CaI_2$  loaded in a porcelain boat at temperature above 973 K. The surface area of the melt was about  $5 \text{ cm}^2$  and the contact time was estimated as 15 s. The hydrolysis produces HI ac-

cording to reaction (14), but at the same time a part of the produced HI is further decomposed thermally to  $H_2$  and  $I_2$  according to reaction (15) under these conditions. Therefore, in order to determine the degree of reaction, all the effluent containing HI,  $I_2$ ,  $H_2$  and  $H_2O$  was absorbed in water and the respective amounts of  $I^-$  and  $I_2$  were analyzed by iodometry. Further, the quantities of  $H_2$  gas were determined by gas chromatography. The solid CaO produced was identified on the basis of X-ray diffraction pattern.

The results are depicted in Fig. 9. Though thermodynamic calculations indicated that the equilibrium conversion of  $H_2O$  was fairly low as shown by the broken lines, the experimental conversion was unexpectedly high at temperatures above the melting point of  $CaI_2$  (1052 K). At a He/ $H_2O$  mole ratio of 50, for instance, the  $H_2O$  conversion reached 60% at 1100 K while the calculation predicted only 7%. Although the inert

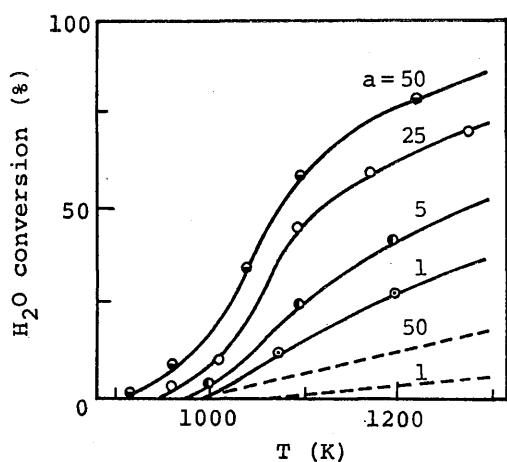


Fig. 9 Temperature dependence of  $H_2O$  conversion in reaction (14). Solid lines: this work, broken lines: calculated, a: number of He mole to  $H_2O$

gas affects the equilibrium conversion favorably, a conversion level of about 20% is still expected at 1173 K even in the absence of it ( $He/H_2O=0$ ).

On the assumption that a chemical equilibrium is attained, the equilibrium constant ( $K_p$ ) for reaction (14) was evaluated as a function of temperature as shown in Fig. 10. It is clear that there are great differences between the observed  $K_p$  and that estimated from the reported thermodynamic data<sup>17)20)</sup>; at 1100 K the observed  $K_p$  is larger by a factor of about 100. The observed value of  $\Delta G^\circ$  was 5.9 kcal/mol in contrast to 17.9 kcal of the estimated value based on the thermochemical data. Similarly, the observed and estimated values of  $\Delta H^\circ$  were 45 and 103 kcal/mol, respectively, at the temperature range 900~1000 K. Similar discrepancies between the observed and estimated equi-

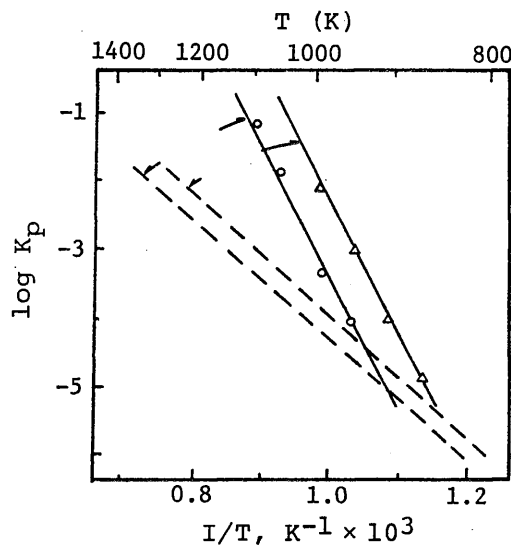


Fig. 10 Equilibrium constant for the hydrolysis of  $CaI_2$  and  $CaBr_2$ .

—○— : This work  
 —△— : C. Marchetti<sup>21)</sup>  
 - - - : calculated

librium constants have been reported for the hydrolysis of  $\text{CaBr}_2^{21)}$  as also presented in Fig. 10. These discrepancies may have been caused in part by the uncertainty of the thermodynamic data used, but more plausibly they may be attributed to the formation of a melt solution of  $\text{CaI}_2$  or  $\text{CaBr}_2$  with  $\text{CaO}$ , because the hydrolysis was carried out at temperatures above the melting points of the calcium halides. Anyway, it is clear that, owing to such an unexpectedly high reactivity, the high temperature hydrolysis of  $\text{CaI}_2$  is acceptable as a reaction step of the thermochemical process.

The extent of HI dissociation in reaction (15), which was determined from the analyses of  $\text{I}^-$  and  $\text{I}_2$  contained in the effluent as mentioned before, was found to be very close to the equilibrium value at higher temperatures: 26% at 1100 K, and 28% at 1200 K.

After reactions (14) and (15), the gaseous mixture consisting of  $\text{H}_2$ ,  $\text{I}_2$ , HI and  $\text{H}_2\text{O}$  is sent to a separation step, while the solid  $\text{CaO}$  is returned to reaction (13) to start the cycle over again. The separation step of the gaseous compounds was not studied in detail, but the following method is suggested. First,  $\text{I}_2$  is condensed from vapor phase by cooling it to a moderate temperature, e.g., 433 K (the condensation pressure of  $\text{I}_2 = 0.53$  atm). The liquefied  $\text{I}_2$  is evaporated and recycled to reaction (12). Next,  $\text{H}_2$  is separated from gaseous HI and  $\text{H}_2\text{O}$ ; the use of membranes such as ones made with palladium and ceramics may be conceived. The mixture of  $\text{H}_2\text{O}$  and HI is returned to reaction (14) without further separation.

(d) Decomposition of  $\text{Sb}_2\text{O}_4$

The decomposition of  $\text{Sb}_2\text{O}_4$  was found to begin at about 1170 K in a nitrogen gas stream as mentioned before. The volatile  $\text{Sb}_2\text{O}_3$  produced can be easily separable from the unreacted  $\text{Sb}_2\text{O}_4$ . The vapor phase is then cooled, and the  $\text{Sb}_2\text{O}_3$  solid separated from  $\text{O}_2$  is sent back to reaction (12).

The value of  $\Delta G^\circ_{1300}$  for this reaction was calculated to be 20.4 kcal/mol based upon the thermodynamic data<sup>17)</sup> published in 1973. This is too large a value considering the ease of the reaction as demonstrated above. The experiments above indicate  $\Delta G^\circ_{1300} = 3.7$  kcal, a value which has been proved to agree with that calculated from the thermodynamic data<sup>20)</sup> published in 1977.

#### 4.2. Evaluation of the Sb-I-Ca process

Based on the examinations just described, a schematic flow diagram of mass and heat was constructed for the Sb-I-Ca process as shown in Fig. 11. The diagram as a whole should contain five reaction steps [R-(12) to R-(16)], eight phase-transition steps and one gas-separation step. The operation temperature of each step was set as indicated in view of the results described. The mass and heat flow was expressed on the basis of 1 mole  $\text{H}_2$  production. On this basis, all the intermediate compounds should be taken in excess depending on the conversion levels of the respective reaction steps. Thus,  $\text{I}_2$ ,  $\text{CaO}$ ,  $\text{H}_2\text{O}$  and HI were used in excess by 2, 2, 16 and 6 mole, respectively, in R-(12) through R-(15). The conversion levels were assumed as follows: 100% (with respect to  $\text{Sb}_2\text{O}_3$ ) in R-(12), 100% ( $\text{SbI}_3$ ) in R-(13), 20% ( $\text{H}_2\text{O}$ ) and 100% ( $\text{CaI}_2$ ) in R-(14), 25% (HI) in R-(15), and 100% ( $\text{Sb}_2\text{O}_4$ ) in R-(16). The heat

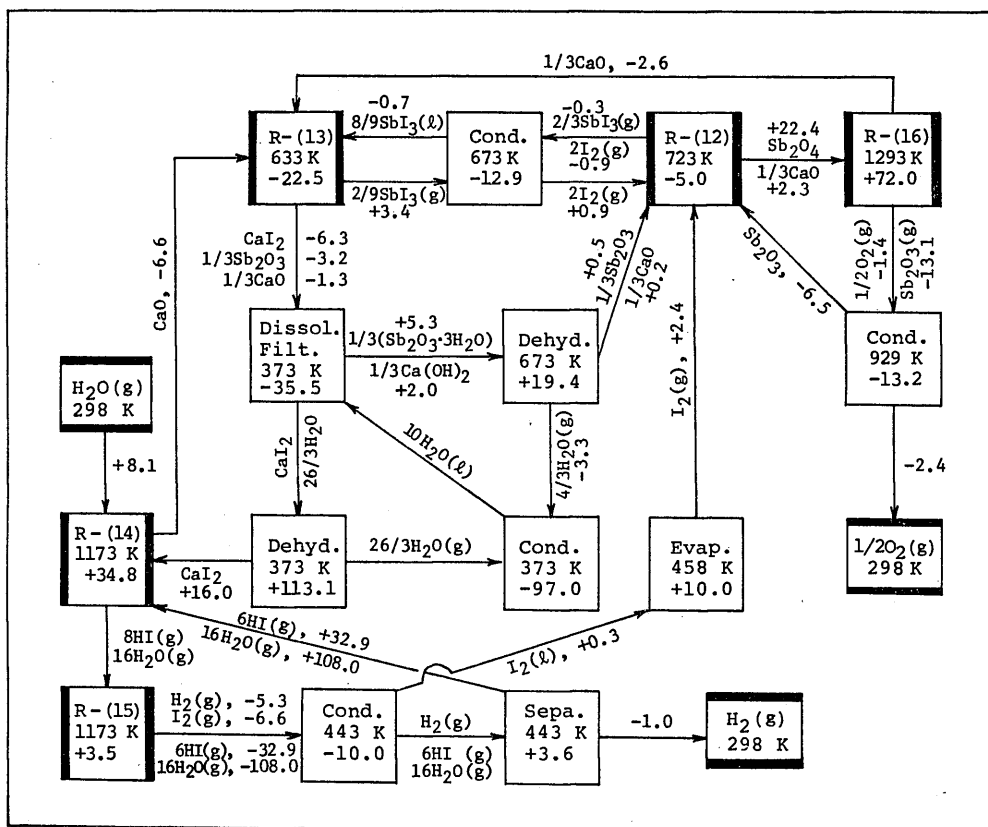


Fig. 11 Flow diagram of the Sb-I-Ca process.

R: Reaction, Cond.: Condensation, Dissol.: Dissolution, Filt.: Filtration, Dehyd.: Dehydration, Evap: Evaporation, Sepa.: Separation

liberated at each step was indicated by kcal on the same basis. The heat associated with heating or cooling of materials between the steps was calculated by use of heat capacities of the respective materials. The work ( $W_{\text{th}}$ ) for the gas separation of  $\text{H}_2$  was calculated on the assumption of an ideal solution.

$$W_{\text{th}} = -RT[N_a \ln X_a + (N_b + N_c) \ln(X_b + X_c)] \quad (17)$$

where  $N_a(X_a)$ ,  $N_b(X_b)$  and  $N_c(X_c)$  are number of moles (mole fractions) of  $\text{H}_2$ ,  $\text{HI}$  and  $\text{H}_2\text{O}$ , respectively. This gave +3.6 kcal as shown in the diagram. Power for transportation, crushing, and

mixing of reactants are neglected.

The overall thermal efficiency,  $\eta_{\text{LHV}}$  is defined<sup>22)</sup> as

$$\eta_{\text{LHV}} = \frac{-\Delta H_{298}^{\circ}(\text{H}_2\text{O}(\text{g})) \times 100}{\Sigma Q_+ + \epsilon_R \cdot \Sigma Q_- + W_{\text{th}}/\epsilon_S \cdot \epsilon_{\text{QW}}} \quad (18)$$

where  $\Sigma Q_+$  and  $\Sigma Q_-$  represent the sums of the heat associated with all endothermic and exothermic steps, respectively,  $\epsilon_R$  the efficiency of heat recovery,  $W_{\text{th}}$  the theoretical work of separation,  $\epsilon_S$  the efficiency of separation,  $\epsilon_{\text{QW}}$  the efficiency of conversion from heat to work. The heat for endothermic and exothermic steps are summarized in **Table 7**:  $\Sigma Q_+$  and  $\Sigma Q_-$  are cal-

Table 7 Heat balance for the Sb-I-Ca process

Step	Endothermic heats (kcal)	Exothermic heats (kcal)
Reactions (5) <sup>a)</sup>	+110.3	- 27.5
Phase changes and dissolution (8) <sup>a)</sup>	+142.5	-168.6
Heating and cooling operations (20) <sup>a)</sup>	+204.7	-202.4
Total	+457.5 ( $\Sigma Q_+$ )	-398.5 ( $\Sigma Q_-$ )

a) The figures in the ( ) indicate the total number of reactions, phase changes and operations involved.

culated to be +457.5 kcal and -398.5 kcal, respectively. As the table shows, a major part of  $\Sigma Q_+$  is responsible to the heat associated with the heating operations of reactants. This heat is therefore a major factor affecting  $\eta_{LHV}$  of this process. On assuming that  $\epsilon_s = 1.0$  and  $\epsilon_{QW} = 0.4$ ,  $\eta_{LHV}$  is shown as a function of  $\epsilon_R$  in Table 8. At  $\epsilon_R = 0.8$  the overall efficiency is about 39%, a value which is well competitive with that of the electrolytic hydrogen production.

However, the following reservations are to be mentioned. The first point is the length of some of the reaction times: 2 h for reaction (12) and 6 h for reaction (13), etc. These long reaction times would have two disadvantageous effects on the development of a "working" cycle, i.e., the reactions would have to be large and hence capital-cost intensive, and the inventory of intermediate chemicals would also be great. The second is a problem in transferring enormous amounts of heat at temperatures over 1000 K. These heat transfer steps would pose large engineering as well as capital-cost problems. The third point is hydrogen removal techniques with membranes which have not been successful economically up to data.

With these reservations being attached, the Sb-I-Ca process is evaluated to

Table 8 Total thermal efficiency ( $\eta_{LHV}$ ) for the Sb-I-Ca process

$\epsilon_R$	0.4	0.5	0.6	0.7	0.8	0.9
$\eta_{LHV}(\%)$	18.9	21.7	25.5	30.8	39.1	53.4

present a concept of new thermochemical cycles for water splitting though the commercialization involves several difficulties at present.

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