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"Sb-I-Ca PROCESS" FOR THERMOCHEMICAL HYDROGEN PRODUCTION

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A new thermochemical water-splitting process named "Sb-I-Ca Process" is proposed with relevant thermochemical data and preliminary experimental results. The process consists of basic steps of five reactions and three phase-transitions, each of which proceeds to an acceptable extent. The overall efficiency is estimated to be ca.50 % with an assumption of 70 % heat recovery.

The production of hydrogen from water by thermochemical processes is very attractive in the search for new energy carriers to replace the fossil fuels.1) So many thermochemical water-splitting processes have recently been reported in the literature.2) Nevertheless, at present no process seems to be satisfactory enough to be commercially acceptable. Previously the authors proposed a process named "Sb-I Process".3) Subsequent examinations, however, showed that the process embraced a serious difficulty in the separation of HI from the reaction medium.4) To avoid this difficulty a hybrid process which introduced electrolysis of the aqueous HI solution was proposed previously.4) In this work, we have attempted to modify the initially proposed process purely thermochemically by introducing calcium compounds as additional reaction media. The modified process, "Sb-I-Ca Process", consists of the following reaction (1)-(5) and phase transitions (6)-(8).

$$\left\{\begin{array}{lclcll}
4/3\mathrm{Sb_2O_3(s)} & + & \mathrm{I_2(g)} & \longrightarrow & 2/3\mathrm{SbI_3(g)} + \mathrm{Sb_2O_4(s)} & (1)\\
2/3\mathrm{SbI_3}(\ell) & + & \mathrm{CaO(s)} & \longrightarrow & \mathrm{CaI_2(s)} + 1/3\mathrm{Sb_2O_3(s)} & (2)\\
\mathrm{CaI_2}(\ell) & + & \mathrm{H_2O(g)} & \longrightarrow & \mathrm{CaO(s)} + 2\mathrm{HI(g)} & (3)\\
2\mathrm{HI(g)} & & & \longrightarrow & \mathrm{H_2(g)} + \mathrm{I_2(g)} & (4)\\
\mathrm{Sb_2O_4(s)} & & & \longrightarrow & \mathrm{Sb_2O_3(g)} + 1/2\mathrm{O_2(g)} & (5)
\end{array}\right.$$

$$\left\{\begin{array}{lcll}
2/3\mathrm{SbI_3(g)} & \longrightarrow & 2/3\mathrm{SbI_3}(\ell) & (6)\\
\mathrm{CaI_2(s)} & \longrightarrow & \mathrm{CaI_2}(\ell) & (7)\\
\mathrm{Sb_2O_3(g)} & \longrightarrow & \mathrm{Sb_2O_3(s)} & (8)
\end{array}\right.$$

where (s), (ℓ), and (g) refer, respectively, to solid, liquid, and gaseous states.

As shown in Table 1, each step of this process is thermodynamically acceptable except reaction (3), which was found to be also acceptable in practice as shown later. The reaction temperatures required are not exceeding 1300 K, which is said to be an upper limit available with high-temperature, gas-cooled reactors.5)

In the first reaction (1), gaseous iodine is brought into contact with powdered antimony trioxide. Experiments showed that with iodine in excess amounts

Table 1. Thermodynamic data6) for the "Sb-I-Ca Process" (1kcal=4.184 kJ)

Step	Temp K	Energies(kcal) for steps as written ΔH°	ΔG°
(1)	723	- 5.0	+ 6.5
(2)	653	-22.5	-17.3
(3)	1173	+34.8	+16.6
(4)	1173	+ 3.5	+ 7.3
(5)	1293	+71.8	+ 3.8
(6)	673	- 9.7	± 0.0
(7)	1052	+10.0	± 0.0
(8)	929	-22.1	± 0.0

($I_2/Sb_2O_3=3$) this reaction proceeded to completion in about 2 h at 723 K. The solid antimony tetroxide was easily separated from gaseous compounds. The gaseous antimony iodide is liquefied at 673 K in the step (6) and the excess iodine is sent back to the first reaction. In the second reaction (2), the liquefied antimony iodide reacts with pulverized calcium oxide to give solid calcium iodide and solid antimony trioxide. With the equivalent amounts of antimony iodide and calcium oxide, 6 h was required to convert 75 % of calcium oxide at 633 K, but further conversion could not be attained under the present experimental conditions. The formation of the solid products, calcium iodide and antimony trioxide, was confirmed by X-ray diffraction and chemical analysis. These solid products are easily separable by the difference in vapor pressure, (0.14 mmHg for calcium iodide and 70.8 mmHg for antimony trioxide at 1173 K6)). The reaction of liquefied calcium iodide with water vapor [reaction (3)] was found experimentally to proceed smoothly in spite of the unfavorable thermodynamic data. The water conversion in this reaction reached 60 % at 1173 K in a helium gas stream. As to the reaction (4), it is well established that hydrogen iodide dissociates to an extent of 30 % at 1173 K.7) The hydrogen generated can be separated from hydrogen iodide and iodine with a porous membrance. For the last reaction (5), we observed that antimony tetroxide decomposed to antimony trioxide within 2 h at 1293 K in a nitrogen gas stream. Thus, it is concluded that these eight steps can be successfully combined into a new water-splitting process.

From a flow sheet made on the basis of the above experimental results, an overall efficiency (η_{LHV}) of this new process was estimated to be ca.50 % when the recovery of heat was assumed to be 70 %.

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