

Thermochemical Hydrogen Production by the Magnesium-Sulfur-Iodine Cycle

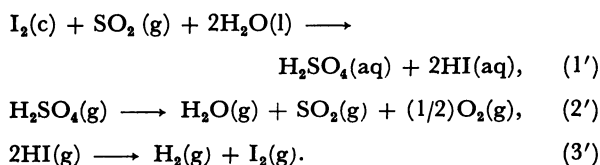
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A new thermochemical cycle, consisting of (i) redox reaction of sulfur dioxide and iodine with magnesium oxide in aqueous phase, (ii) hydrolysis of magnesium iodide, (iii) thermal decomposition of magnesium sulfate, and (iv) thermal dissociation of hydrogen iodide, is presented for hydrogen production. The key reactions (i) and (ii) are experimentally verified.

Among a number of thermochemical cycles so far proposed for hydrogen production, the sulfur-iodine cycle has been considered as one of the most promising. This cycle comprising (i) redox reaction of sulfur dioxide and iodine, (ii) thermal decomposition of sulfuric acid, and (iii) thermal dissociation of hydrogen iodide is expressed by the following sequence,



The key operation for the cycle consists in the separation process of the acid mixture (H_2SO_4 -HI) formed by Reaction 1' since simple distillation causes the reverse reaction resulting in evolution of I_2 and SO_2 . Thus, several proposals have been made on the separation: addition of excess iodine to form polyiodides (HI_x),¹⁾ use of nickel metal,²⁾ and electrolytic promotion³⁾ of Reaction 1'.

The present authors have examined an addition of a series of metal oxides (Fe_2O_3 , CoO , NiO , CuO , ZnO , PbO , MgO etc.), whose sulfates decompose at relatively low temperatures ($<1200^\circ\text{C}$), to the acid mixture. As a result of preliminary experiments, following points were obtained:

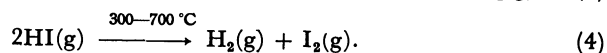
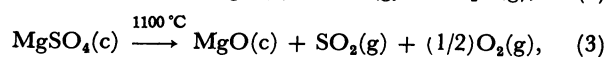
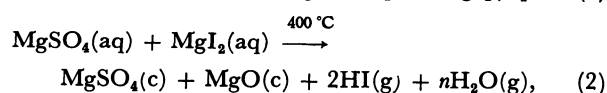
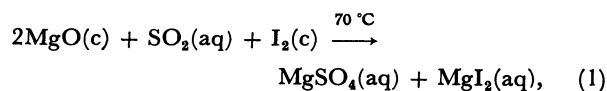
(i) Metal oxides are easily dissolved into the acid mixture by heating, however, the reverse reaction takes place as the solution gets concentrated when the amount of metal oxide is less than the equivalent to the acids.

(ii) Neither HI vapor nor H_2 is observed to be evolved directly from the solution.

(iii) For complete prevention of the reverse reaction, the amount of metal oxide should be equivalent to that of the acids. In other words, the formation of metal sulfate and iodide is considered to be inevitable.

Since a separation of the metal sulfate and iodide solution is another troublesome operation for the cycle, effects of the addition of metal oxide seemed unfavorable. However, the present authors noticed that it would be unnecessary to separate the sulfate and iodide in the case of magnesium oxide, because the temperature required for the thermal decomposition of MgSO_4 (1100°C) is far apart from that for the hydrolysis of MgI_2 (400°C). Such a temperature difference between these reactions was considered to have a possibility of allowing HI and SO_3 to be evolved separately.

Thus, a new thermochemical cycle using magnesium, sulfur, and iodine was designed as follows:⁴⁻⁶⁾



Each of the reactions was studied in this work. Experimental verifications were particularly focused on the key reactions 1 and 2.

Reaction Characteristics and Experimental Verification

Reaction 1 (Redox Reaction of SO_2 and I_2 with MgO in Aqueous Phase). Iodine powder 552 mg was added to 2 cm³ of approximately 6.8 wt% SO_2 aqueous solution in a beaker and the mixture was agitated until a colorless solution was obtained. Then, 174 mg of MgO powder, prepared by the decomposition of MgSO_4 , was added to the resulting mixed acid solution at 70°C with stirring. The magnesium oxide was easily dissolved to make a transparent solution after several minutes.

This mixed solution was subjected to EDTA chelate analysis, sulfate gravimetry, and thiosulfate iodometric titration for concentrations of Mg^{2+} , SO_4^{2-} , and I^- ions, respectively. Molar ratio $[\text{Mg}^{2+}] : [\text{SO}_4^{2-}] : [\text{I}^-] = 2.0 : 1.0 : 2.0$ was obtained. Thus, 100% yield and high reaction rate were verified for this reaction.

Reaction 2 (Hydrolysis of MgI_2 Hydrate). *X-Ray Analysis:* In order to grasp an outline of Reaction 2, an X-ray analysis was made on solid phases. A mixed solution of MgSO_4 and MgI_2 produced by Reaction 1, was heated in a quartz boat in an atmosphere of N_2 at 100, 200, 240, 300, 350, or 1100°C . Each of the solid residues was examined by X-ray analysis. Results are shown in Fig. 1. Since magnesium iodide and magnesium hydroxyiodides are extremely hygroscopic or easily oxidized in air, samples were kept in an N_2 atmosphere during measurement.

Based on the results shown in Fig. 1, changes in solid phases in course of Reaction 2 is expressed by

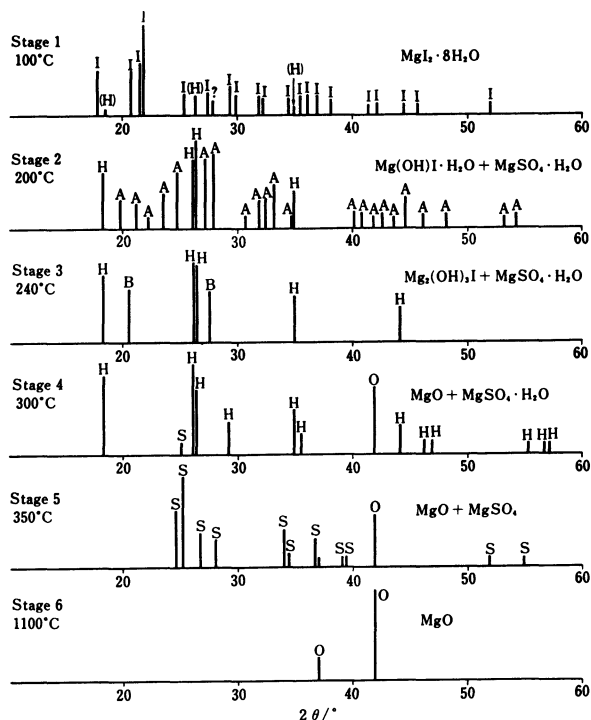
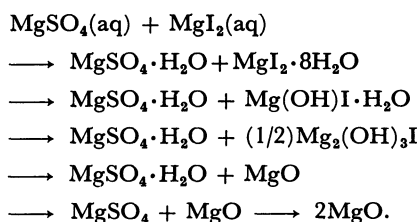


Fig. 1. Changes in X-ray diffraction patterns during heating of a mixed solution of MgI_2 and MgSO_4 (Cu $K\alpha$).

I: $\text{MgI}_2 \cdot 8\text{H}_2\text{O}$, H: $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, A: $\text{Mg}(\text{OH})\text{I} \cdot \text{H}_2\text{O}$
B: $\text{Mg}_2(\text{OH})_2\text{I}$, S: MgSO_4 , O: MgO .



Thus, the hydrolysis of $\text{MgI}_2 \cdot 8\text{H}_2\text{O}$ and the dehydration or thermal decomposition of $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ were found to separately proceed, as far as the result of X-ray analysis is concerned.

Thermal Analyses: A mixed solution of $\text{MgSO}_4 + \text{MgI}_2$ was also analyzed by TG and DTA from 25 to 1200 °C in a stream of argon at a heating rate of 200 °C/h. Results are shown in Fig. 2, where each arrow shows the theoretical weight calculated by using atomic weights for possible products. The plateaus observed at 130, 210, 260–300, and 350 °C correspond exactly to

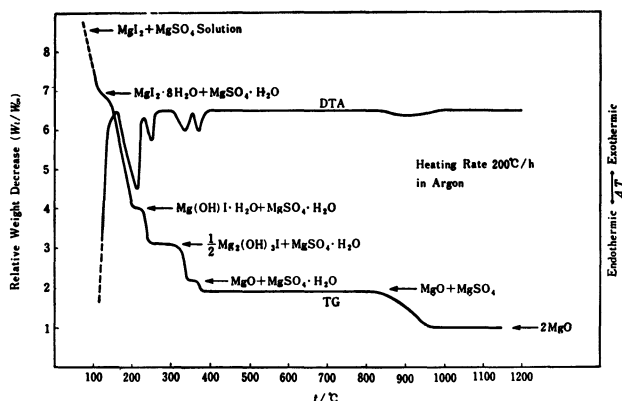


Fig. 2. TG and DTA curves for heating a mixed solution of MgI_2 and MgSO_4 .

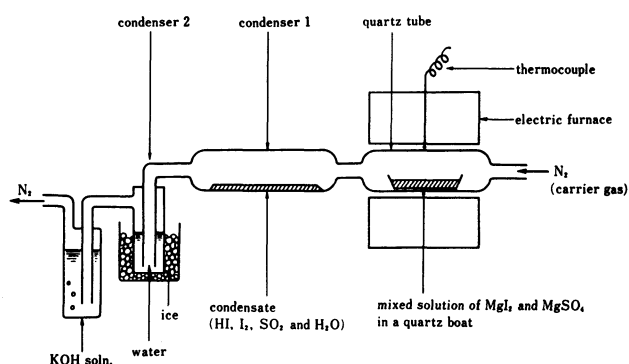


Fig. 3. Apparatus for hydrolysis of a mixed solution of MgI_2 and MgSO_4 .

$\text{MgSO}_4 \cdot \text{H}_2\text{O} + \text{MgI}_2 \cdot 8\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot \text{H}_2\text{O} + \text{Mg}(\text{OH})\text{I} \cdot \text{H}_2\text{O}$, $\text{MgSO}_4 \cdot \text{H}_2\text{O} + (1/2)\text{Mg}_2(\text{OH})_2\text{I}$, and $\text{MgSO}_4 \cdot \text{H}_2\text{O} + \text{MgO}$, respectively, while the one at 400–800 °C lies slightly lower than the calculated position for $\text{MgSO}_4 + \text{MgO}$, i.e., the weight decrease observed for the reaction at 350–400 °C is slightly larger than the theoretical.

At any rate, general tendency of the results of thermal analyses may be considered to be in good agreement with those of X-ray analysis. To clarify the details of the reactions in the range 300–400 °C, a further study resorting to chemical analyses was performed as described below.

Chemical Analysis: Products of Reaction 2 were chemically analyzed. As shown in Fig. 3, a mixed solution of MgSO_4 and MgI_2 in a quartz boat was

TABLE 1. RESULTS OF CHEMICAL ANALYSIS FOR HYDROLYSIS OF A MIXED SOLUTION OF MgI_2 AND MgSO_4 ^{a)}

Heating mode	No. 1 ^{b)}			No. 2 ^{c)}			
Species determined	Distillate (25—430 °C)	Residue	Total	Distillate 1 (25—300 °C)	Distillate 2 (300—430 °C)	Residue	Total
I ⁻	1.85 ^{d)}	0.02 ^{d)}	1.99	1.62 ^{d)}	0.24 ^{d)}	0.02 ^{d)}	1.99
I ₂	0.12	0		0.06	0.05	0	
SO ₄ ²⁻	0	1.91	2.01	0	0	1.92	2.01
SO ₃ ²⁻	0.04	0.06		0	0.06	0.03	
R ^{e)}	R=0.050			R=0.045			

a) The figures give quantities in mmol. b) Direct heating (see text). c) Two-step heating (see text).

d) Calculated by I_2 (I-/2). e) $R \equiv \text{SO}_3^{2-}/(\text{SO}_4^{2-} + \text{SO}_3^{2-})$.

heated in an N_2 atmosphere. Evolved vapors of I_2 , HI, and SO_2 were collected in condensers while a solid residue in a quartz boat was dissolved in HCl.

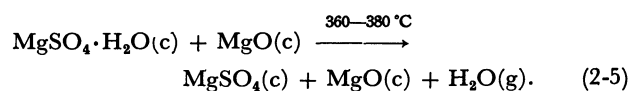
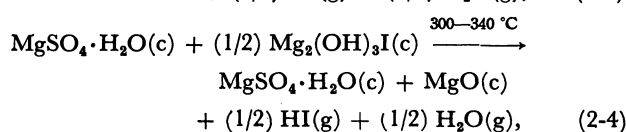
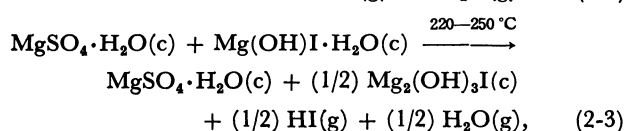
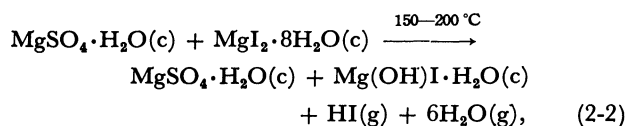
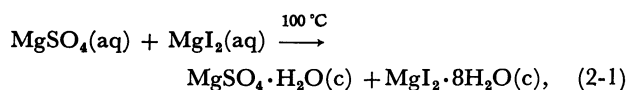
The amounts of I_2 and I^- and the total amount of SO_3^{2-} and SO_4^{2-} for each reaction product were determined by thiosulfate iodometric titration and sulfate gravimetry. The amount of SO_3^{2-} was determined by back-titration of excess free iodine after adding a measured amount of I_2 to the sample.

Results for the cases of direct heating up to 430 °C (designated No. 1) and of heating in two steps of 25→300 and 300→430 °C (designated No. 2) are shown in Table 1. For the case of No. 2, evolution of SO_2 was undetected in the range of 25–300 °C whereas considerable amounts of I_2 and SO_2 were generated at 300–430 °C. A slight amount of I_2 formation would be attributable to the thermal dissociation of HI, though, this I_2 formation is only assumed to result from the reverse reaction of Reaction 1 since the total amount of I_2 evolved is almost equal to that of SO_3^{2-} . The contribution of the reverse reaction was calculated to be $R=0.050$ for No. 1 and $R=0.045$ for No. 2, where R (reverse reaction factor) is defined by

$$R \equiv \frac{SO_3^{2-}}{SO_3^{2-} + SO_4^{2-}}. \quad (5)$$

Thus, it is concluded that 95% of each of HI and H_2SO_4 was successfully separated by the addition of MgO.

Discussions on Reaction 2: As results of X-ray, thermal, and chemical analyses, total reactions are conclusively expressed as follows:

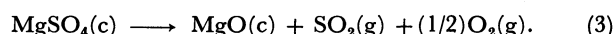


This reaction sequence is also supported excellently by the results of hydrolysis of pure $MgI_2 \cdot 6H_2O$ previously reported by the present authors.⁷⁾

The reverse reaction was observed to proceed at 300–430 °C within an extent of 5%; as least 95% of reactants was consumed in accordance with this sequence. A slight amount of some complex compound ($Mg-I-SO_4$) capable of causing the reverse reaction, though undetectable by X-ray analysis, might be present in the mixture of MgI_2 and $MgSO_4$ hydrates after drying the mixed solution.

Reaction 3 (Thermal Decomposition of $MgSO_4$).

Thermal decomposition of $MgSO_4$ is reported⁸⁾ to take place as follows:



The present experiments also confirmed the complete conversion of $MgSO_4$ into MgO at 1100 °C as shown in Figs. 1 and 2. Decomposition of SO_3 to SO_2 and O_2 is reported to proceed to almost 100% conversion at 1100 °C.⁹⁾

Reaction 4 (Thermal Dissociation of HI).

Thermal dissociation of HI is well known to occur according to

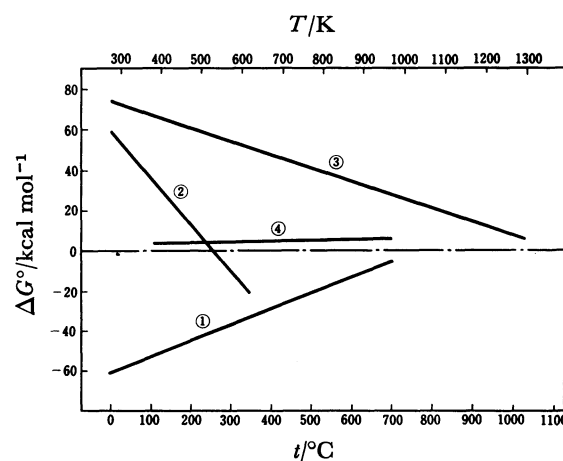


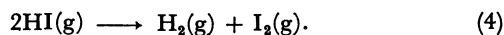
Fig. 4. Free energy change (ΔG°) vs. temperature plot for Reactions 1–4.

(1) $I_2(c) + SO_2(g) + 2MgO(c) + 6H_2O(l) \rightarrow MgI_2 \cdot 6H_2O(c) + MgSO_4(c)$, (2) $MgI_2 \cdot 6H_2O(c) \rightarrow MgO(c) + 2HI(g) + 5H_2O(g)$, (3) $MgSO_4(c) \rightarrow MgO(c) + SO_2(g) + (1/2)O_2(g)$, (4) $2HI(g) \rightarrow H_2(g) + I_2(g)$.

TABLE 2. ENTHALPY, ENTROPY, AND FREE ENERGY CHANGES (ΔH_{298}° , ΔS_{298}° , AND ΔG°) FOR REACTIONS 1–6^{a)}

Reaction	$\Delta H_{298}^\circ / \text{kcal mol}^{-1} \text{ b)}$	$\Delta S_{298}^\circ / \text{cal mol}^{-1} \text{ K}^{-1} \text{ b)}$	$\Delta G^\circ / \text{kcal mol}^{-1} \text{ b)}$
1	-83.5	-81.1	-59.3 at 298 K
2	+123.4	+233.5	-33.7 at 673 K
3	+92.5	+68.3	+0.6 at 1400 K
4	+2.3	-5.3	+5.6 at 700 K
5	-14.9	-34.4	-4.7 at 298 K
6	-51.5	-142.0	-9.5 at 298 K
Total	+68.3	+39.0	

a) (1) $I_2(c) + SO_2(g) + 2MgO(c) + 6H_2O(l) \rightarrow MgI_2 \cdot 6H_2O(c) + MgSO_4(c)$, (2) $MgI_2 \cdot 6H_2O(c) \rightarrow MgO(c) + 2HI(g) + 5H_2O(g)$, (3) $MgSO_4(c) \rightarrow MgO(c) + SO_2(g) + 1/2 O_2(g)$, (4) $2HI(g) \rightarrow H_2(g) + I_2(g)$, (5) $I_2(g) \rightarrow I_2(c)$, (6) $5H_2O(g) \rightarrow 5H_2O(l)$. b) 1 cal = 4.184 J.



The extent of conversion is reportedly 18–29% at 600–1000 K according to Bodenstein.¹⁰⁾

Thermodynamic Calculation

The enthalpy change (ΔH_{298}°), entropy change (ΔS_{298}°) and free energy change (ΔG°) for each of the processes involved in the present cycle were calculated based on the thermochemical data by Barin and Knacke¹¹⁾ and estimated values for $\text{MgI}_2 \cdot 6\text{H}_2\text{O}$.⁷⁾ The results are shown in Fig. 4 and Table 2.

Conclusion

1) A new thermochemical cycle for hydrogen production (Magnesium-Sulfur-Iodine cycle) was successfully presented on the basis of a combination of MgO and a sulfur-iodine scheme.

2) The feasibility of the two key reactions, (i) redox

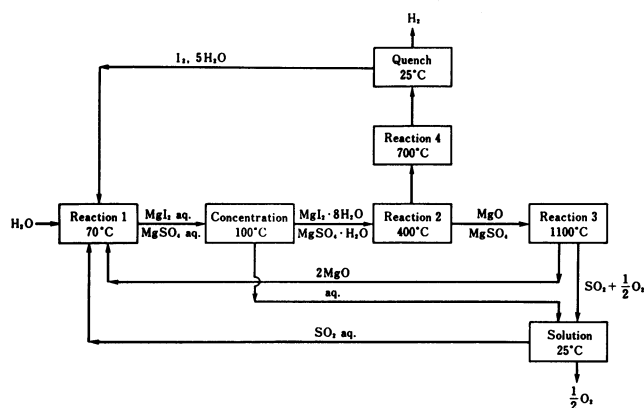


Fig. 5. Material flow in magnesium-sulfur-iodine cycle.

reaction of SO_2 and I_2 with MgO in aqueous phase and (ii) hydrolysis of MgI_2 hydrate, were experimentally verified. Conversion was found to be 100% for reaction (i) at 70 °C and 95% for reaction (ii) at 400 °C, respectively. Sufficiently high reaction rates were observed for both the reactions.

3) For this cycle it is unnecessary to separate the mixed solution of MgSO_4 and MgI_2 , that is, HI and SO_3 are separately evolved at different temperatures. Therefore, the material flow-sheet can be so simple, as shown in Fig. 5.

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