

A Study of the Thermochemical Hydrogen Preparation X. Estimation of the Thermal Efficiency of Sulfuric Acid Cycles

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The thermal efficiency of thermochemical water-splitting cycles which adopt decomposition of sulfuric acid as an oxygen generation step was estimated by analysis of the flow sheets. Mass and heat flow of cycles were assumed based on the experimental results and thermochemical data. The cycles are classified into two types; A) cycles in which an electrochemical reaction is involved; B) cycles in which the methanol synthesis process is involved. It is estimated that more than 500 kcal/mol-H₂ of heat is circulated into cycle, and about 270–460 kcal/mol-H₂ of them should be recovered in the process. The amount of heat that should be circulated in the process will be one of the essential factors which will decide the scale of heat exchanger. Assuming 75–100% of thermal regeneration ratio, higher thermal efficiency (42–74%) can be expected for A type cycles and lower thermal efficiency (30–44%) is expected for B type cycles. However, the scale of plant for A type cycles will be larger than that for B type cycles, because of the dimensional demerit of electrochemical reaction and large amount of heat that should be circulated in the process.

1 Introduction

The thermochemical hydrogen production process produces hydrogen utilizing the nuclear heat from the very high temperature gas-cooled reactor (VHTGR). The thermal efficiency defined by Funk and Reinstrom^{1,2)} is adopted in this paper. “*Q*” is the heat that is supplied from the heat source and “*W*₁” is the work which is required to operate the process and “*θ*”₁ is the efficiency of energy conversion from heat to work.

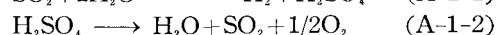
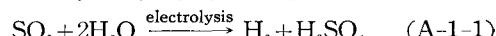
$$\eta_{\text{HHV}} = \Delta H_{298}^{\circ}(\text{H}_2\text{O, liq}) / (Q + W_1 / \theta_1) \quad (1)$$

Higher thermal efficiency is expected for the thermochemical hydrogen production process than that by the electrolysis of water utilizing electricity from the nuclear power station. The present thermal efficiency of the electrolysis of water is about 24% and more than 30% of efficiency is expected in future with the improvements in the electrolysis of water³⁾.

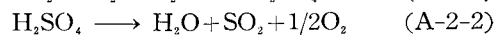
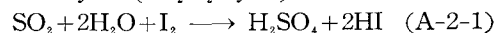
As previously stated⁴⁾, the sulfuric acid cycles

are thought to be promising. Prior to the development of continuous bench-scale experiment, it is necessary to estimate the thermal efficiency of candidate cycles whose chemical feasibility has been experimentally proved. The following sulfuric acid cycles are examined in this paper.

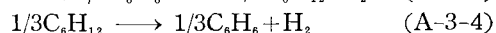
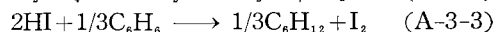
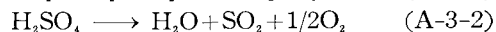
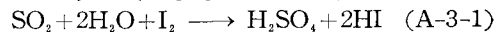
(1) A-1 cycle (SO₂-hybrid cycle)^{4~11)}



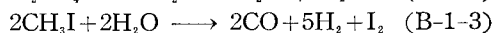
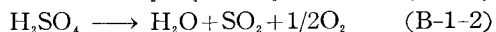
(2) A-2 cycle (SO₂-I₂ cycle)^{4~6, 12, 13)}



(3) A-3 cycle (SO₂-I₂-Benzene cycle)¹⁴⁾



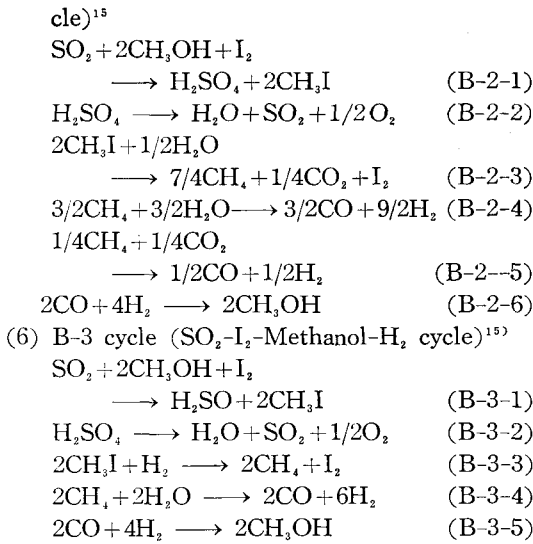
(4) B-1 cycle (SO₂-I₂-Methanol cycle)¹⁵⁾



(5) B-2 cycle (SO₂-I₂-Methanol modified cy-

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Key words: Sulfuric Acid Iodine Cycle, Sulfuric Acid Methanol Cycle, Water-Splitting, Hydrogen Production, Process Simulation



Abraham and Schreiner¹⁶⁾ estimated the thermal efficiency of several thermochemical cycles by utilizing T-S diagram. Funk and Reinstrom^{1,2)} and Funk and Knoche¹⁷⁾ proposed a method to estimate the thermal efficiency based on a flow sheet.

By T-S diagram, the least heat requirement of a quasi-static cycle can be easily calculated assuming a perfect thermal regeneration. However, this method is inadequate to elucidate the heat requirement of individual cycle since actual mass and heat flow can be displayed apparently in T-S diagram.

Thus, an estimation of thermal efficiency was performed by the flow sheet method. A mass flow sheet of each cycle was assumed based on the experimental results and the thermochemical data¹⁸⁻²¹⁾.

2 Mass and Heat Flow of Cycles

The estimated mass and heat flow of the cycles are shown in Figs.1~6. In these figures, R, H, and S mean the reactor, heat exchanger, and separator, respectively. The enthalpy of reaction (ΔH°_T), the Gibbs energy (ΔG°_T), the conversion ratio of reaction, the heat input for heating the reactants ($Q_r = H^{\circ}_T - H^{\circ}_{298}$), the heat output for cooling the products ($Q_p = H^{\circ}_T - H^{\circ}_{298}$), the difference of Q_r and Q_p ($\delta = Q_r - Q_p$), the enthalpy of each reaction step at 298K

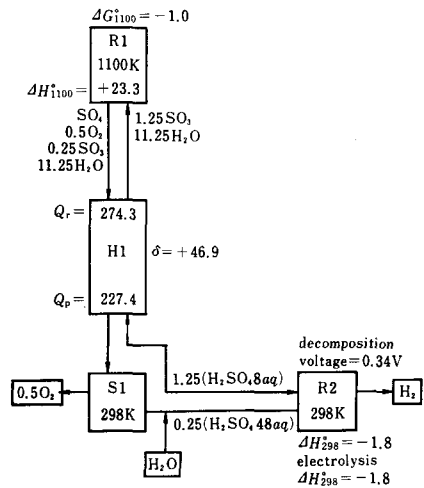


Fig. 1 The flow sheet of A-1 cycle (SO₂-hybrid)

Unit: kcal/mol-H₂

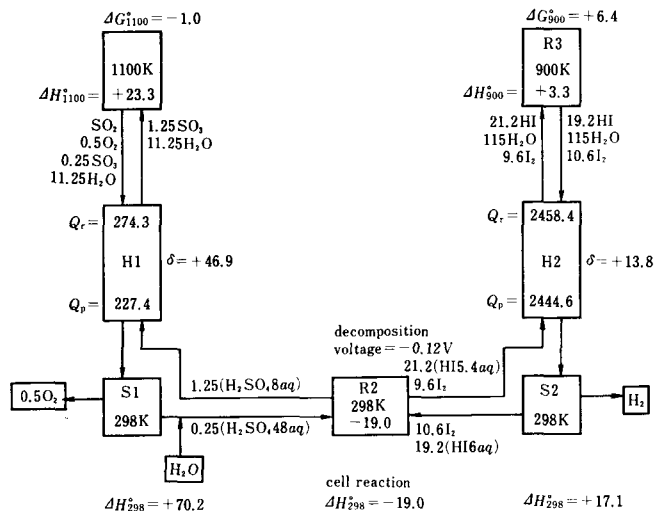


Fig. 2 The flow sheet of A-2 cycle (SO₂-I₂ cycle)

Unit: kcal/mol-H₂

(ΔH°_{298}), and the decomposition voltage of cell or electrolysis reactions are also shown in the figures.

The concentration of sulfuric acid was assumed to be 40 wt% and 73 wt% for A-1 to A-3 cycles^{4,6)} and B-1 to B-3 cycles¹⁵⁾, respectively. It was assumed that equilibrium is attained in the decomposition of SO₃ with 80% of conversion ratio⁵⁾.

The following assumptions were made in the construction of flow sheets.

1. A-1 cycle: R2 designates an electrolysis cell

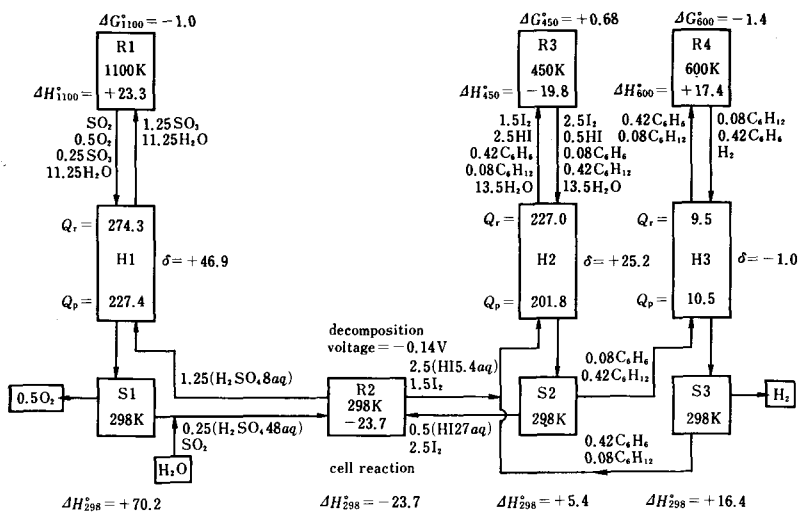


Fig. 3 The flow sheet of A-3 cycle (SO_2 - I_2 -benzene)
Unit: kcal/mol- H_2

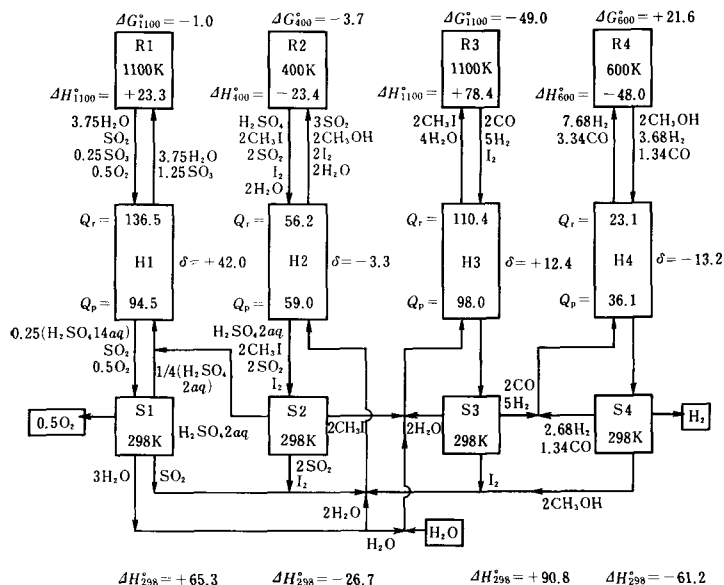


Fig. 4 The flow sheet of B-1 cycle (SO_2 - I_2 -methanol cycle)
Unit: kcal/mol- H_2

(Pt/Active carbon/ SO_2 , $\text{H}_2\text{SO}_{4\text{aq}}$ /diaphragm/ H_2 , H_2SO_4 /Pt). The decomposition voltage was assumed to be 0.34V^{12} .

- A-2 cycle: R2 designates a cell reaction (Pt/Active carbon/ SO_2 , $\text{H}_2\text{SO}_{4\text{aq}}$ /cation exchange membrane/ I_2 , HI_{aq} /Pt). Such a cell type reaction method was adopted in order to produce sulfuric acid and hydriodic acid separately¹². The decomposition voltage

was assumed to be -0.12V^{13} . Hydrogen is evolved by the decomposition of hydrogen iodide. The conversion of hydrogen iodide to hydrogen was assumed to be 9.4% under the existence of iodine and this is the equilibrium conversion ratio¹⁴.

- A-3 cycle: R2 designates the same cell reaction as in A-2 cycle. The decomposition voltage was assumed to be -0.14V^{13} . This value is slightly lower than that of A-2 cycle, because the I_2/HI ratio was increased from that of A-2 cycle. Hydrogen is evolved by the benzene-cyclohexane cycle. The conversion ratios of reaction A-3-3 and A-3-4 were assumed to be 80% . However, higher conversion ratios can be expected from the experimental results and the equilibrium conversion ratios¹⁴.

- B-1 cycle: Methyl iodide and sulfuric acid are produced in R2. The conversion of methanol was optimistically assumed to be 100% under excess SO_2 ¹⁵. The methanol synthesis process is utilized as a methanol recovery process (R4). The conversion ratio was assumed to be 60% (equilibrium) under 300 atm at 600 K . Hydrogen is evolved by the steam reforming reaction of methyl iodide. The experimental results showed that the direct steam reforming reaction of methyl iodide is a difficult process¹⁵, however it is expected that the further research on the catalyst will realize such

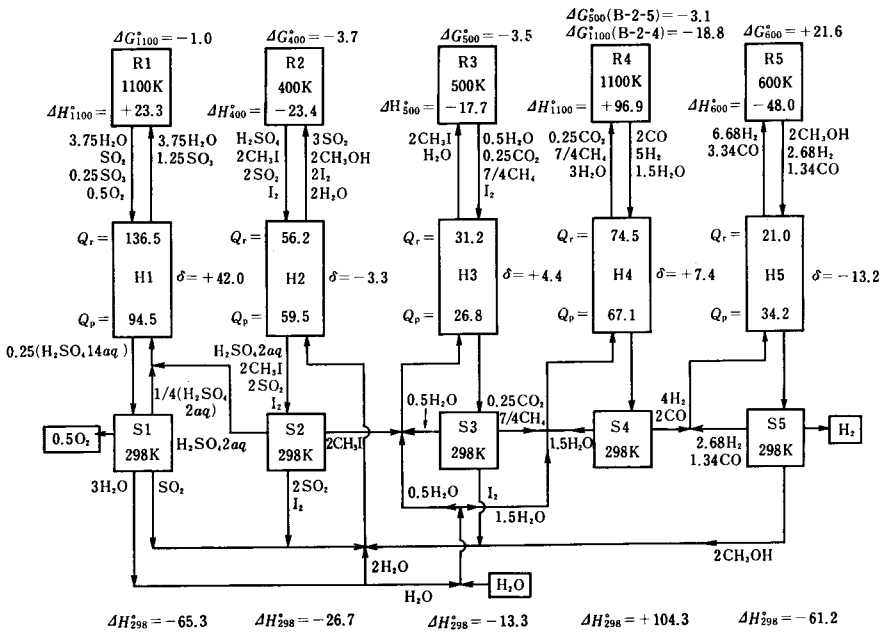


Fig. 5 The flow sheet of B-2 cycle (SO₂-I₂-methanol-modified)
Unit: kcal/mol-H₂

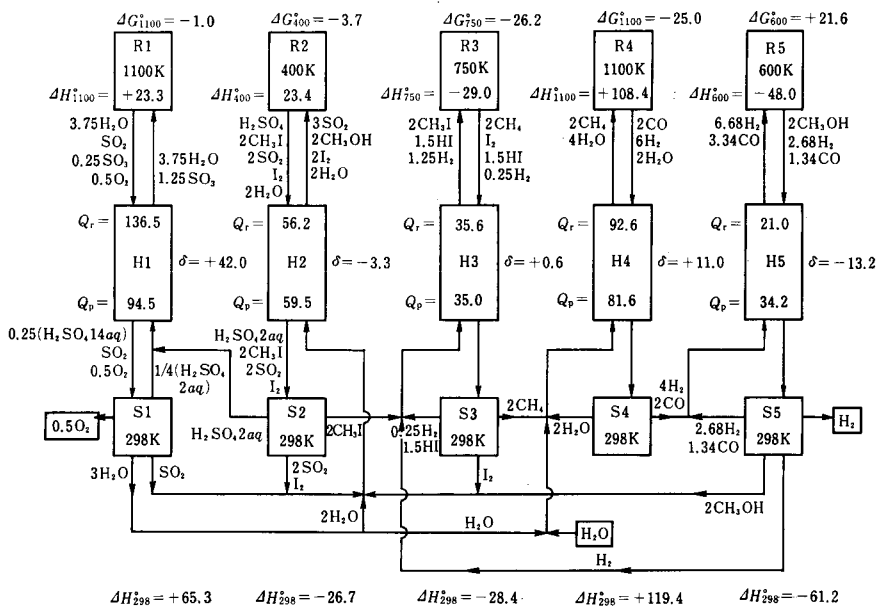


Fig. 6 The flow sheet of B-3 cycle (SO₂-I₂-methanol-H₂)

a process. The conversion of methyl iodide was assumed to be 100% with 2 fold excess of steam. The formation of hydrogen iodide was observed experimentally, however, in this flow sheet, it was neglected.

5. B-2 cycle: Except that a two step steam

reforming process of methyl iodide was adopted in this cycle (R4 and R5), the other processes are the same processes as in A-1 cycle. The conversions of methyl iodide and methane were also assumed to be 100% with 2 fold excess of steam.

6. B-3 cycle: Except that a hydrogenation process of methyl iodide was adopted in this cycle (R3)¹⁵⁾, the other processes are the same processes as in A-1 and A-2 cycles. The formation of hydrogen iodide and its recirculation were assumed in this cycle.

In order to estimate and to compare the thermal efficiency of the cycles, the heat flow in Figs. 1~6 are summarized in Table 1. Definitions of the parameters are given in the foot note. " Q_{exch} " implies the amount of heat which should be exchanged within the cycle, between the cycle and the VHTGR, or between the cycle and surroundings. This amount of heats should be adsorbed and exhausted by the endothermic and exothermic steps of the cycle. " $Q_{\text{rec}}^{\text{I}}$ " implies the maximum heat which can be recovered within the cycle. It is assumed that this heat is recovered within each reaction step, that is, Q_p of products is recovered in Q_r of reactants of the same reaction. This assumption may be reasonable, since the exothermic reactions proceed at low temperatures and the products cannot be used to preheat the reactants of the high temperature endothermic reactions. " $Q_{\text{rec}}^{\text{II}}$ " implies the amount of heat which can be recovered from the exothermic steps. The heat of reaction and Q_p of the exothermic step will be regenerated in heating the reactants and then, the excess heat can be recovered, for example as steam, and will be used for the shaft and separation works of the

cycle. Here, $Q_{\text{rec}}^{\text{II}}$ does not include the heat of the reactions which proceed at the temperature of the surroundings. " Q_{elec} " is the external electricity required in A cycles. If the overpotentials and the ohmic drops of the electrolysis and the cell reactions in A cycles are the same under the same current density, the additional electricity will be required for A-1-1 and A-2-1 reactions compared to A-3-1 reaction. This electricity is assumed to be the difference in the decomposition voltages. In Table 1, Q_{elec} is calculated assuming the conversion factor from heat to electricity is 40%. $Q_{\text{req}}^{\text{min}}$ implies the least heat requirement of the cycle, that is, the heat reequied when 100% thermal regeneration in each reaction step can be realized. Thus, this heat is equal to the sum of the reaction enthalpy at 298 K of the endothermic reaction steps. Q_{elec} is also included in $Q_{\text{req}}^{\text{min}}$.

Using $Q_{\text{req}}^{\text{min}}$ the maximum possible thermal efficiency, " η^{max} " can be estimated. In actual case, the amount of heat which is required by the cycle will be larger than $Q_{\text{req}}^{\text{min}}$. It is possible to estimate the heat requirement of the cycle if the ratio of thermal regeneration " R_i " can be assumed.

$$Q_{\text{reg}} = \sum^{\text{endo}} (\Delta H_{\text{T}}^{\circ} + Q_{\text{r}} - Q_{\text{p}} \times R_i) + Q_{\text{elec}} \quad (2)$$

$$Q_{\text{reg}}^{\text{min}} = \sum^{\text{endo}} (\Delta H_{\text{T}}^{\circ} + Q_{\text{r}} - Q_{\text{p}}) + Q_{\text{elec}} \\ = \sum^{\text{endo}} \Delta H_{298}^{\circ} + Q_{\text{elec}} \quad (3)$$

" $Q_{\text{H}_2\text{O}}$ " is the heat required to heat or cool

Table 1 The summary of heat flow and the expected thermal efficiency of cycles

Cycle	Q_{exch} kcal	$Q_{\text{rec}}^{\text{I}}$ kcal	$Q_{\text{rec}}^{\text{II}}$ kcal	Q_{elec} kcal	$Q_{\text{H}_2\text{O}}$ kcal	$Q_{\text{reg}}^{\text{min}}$ kcal	η^{max} %	$\eta_{R=0.75}$ %
A-1	297	227	0	55	199	125	55	76
A-2	2759	2672	0	2	2005	90	74	44
A-3	547	464	0	0	357	92	40	37
B-1	516	272	88	0	66	156	42	9
B-2	547	272	101	0	66	170	48	33
B-3	592	292	116	0	66	185	34	30

$\Delta H_{\text{T}}^{\circ}$; reaction enthalpy at TK. ΔH_{298}° ; reaction enthalpy at 298 K.

$Q_{\text{p}} = \sum^{\text{product}} (H_{\text{T}}^{\circ} - H_{298}^{\circ})$. $Q_{\text{r}} = \sum^{\text{reactant}} (H_{\text{T}}^{\circ} - H_{298}^{\circ})$. $Q_{\text{H}_2\text{O}}$; Q_{p} and Q_{r} of water. $Q_{\text{exch}} = \sum^{\text{endo}} (\Delta H_{\text{T}}^{\circ} + Q_{\text{r}}) + \sum^{\text{exo}} (\Delta H_{\text{T}}^{\circ} + Q_{\text{p}})$. $Q_{\text{rec}}^{\text{I}} = \sum^{\text{endo}} (Q_{\text{p}}) + \sum^{\text{exo}} (Q_{\text{r}})$. $Q_{\text{rec}}^{\text{II}} = \sum^{\text{exo}} (\Delta H_{\text{T}}^{\circ} + Q_{\text{p}} - Q_{\text{r}})$. $Q_{\text{reg}}^{\text{min}} = \sum^{\text{endo}} (\Delta H_{\text{T}}^{\circ} + Q_{\text{r}} - Q_{\text{p}} + Q_{\text{elec}}) = \sum^{\text{endo}} (\Delta H_{298}^{\circ}) + Q_{\text{elec}}$. $Q_{\text{elec}} = [(\text{Decomposition Voltage})_{\text{A-1 or A-2}} - (\text{Decomposition Voltage})_{\text{A-3}}] / 0.4$. $\eta^{\text{max}} = 68.3 / Q_{\text{reg}}^{\text{min}}$. $\eta_{R=0.75} = 68.3 / [\sum^{\text{endo}} (\Delta H_{\text{T}}^{\circ} + Q_{\text{r}} + Q_{\text{elec}} - Q_{\text{p}} \times R_i)]_{R_i=0.75}$.

the hydrated water of sulfuric acid and hydriodic acid. As can be seen from Table 1, very large portion of the Q_p and Q_r is the Q_{H_2O} , especially in A cycles.

3 Discussion

From the estimated values of Q_{exch} , it becomes clear that a large amount of heat should be circulated in the thermochemical hydrogen production process. The amount of heat should be circulated in a cycle will decide the scale of heat exchanger and then will be one of the essential factors to determine the cost of hydrogen. The estimated value of Q_{rec}^I for A-2 cycle is too large to be accepted from this standpoint. A-2 cycle can be improved by introducing a two step benzene-cyclohexane cycle instead of the direct decomposition of hydrogen iodide. It is concluded from these A-2 and A-3 cycles that it is essential to replace a reaction whose conversion is low by other two step reactions whose conversions are high enough. A-3 cycle will still need larger heat exchanger than B cycles. This is mainly due to the large Q_{H_2O} , as can be seen from Table 1. In order to reduce the Q_{rec}^I of A-3 cycle further, it is desirable to produce concentrated sulfuric acid and hydriodic acid. This will be possible by adding external electricity and by the improvement of the electrolysis cell. The amount of Q_{H_2O} will be also related to the thermal regeneration ratio R_i , since more than half of Q_{H_2O} is the heat of evaporation (condensation) of water, thus, in order to realize higher thermal regeneration ratio for such a low temperature heat, larger heat exchanger will be required. The estimated values of Q_{rec}^I and Q_{H_2O} indicate that smaller scale of heat exchanger and higher thermal regeneration ratio than those for A-3 cycle are expected for B cycles, although almost the same amount of heat should be circulated in A-3 and B cycles.

A very high thermal efficiency can be expected in A-3 cycle, if 100% thermal regeneration is realized. However, when the thermal regeneration ratio is 75%, the expected thermal efficiency will decrease to 48%. The expected maximum thermal efficiency for A-1 and B cycles are 55% and about 40%, respectively.

The expected thermal efficiency will decrease to 42% and 30–34% for A-1 cycle and B cycles, respectively, when the thermal regeneration ratio is 75%. Comparing A and B cycles, it becomes clear that the maximum thermal efficiency largely depends on the exhaust heat (Q_{rec}^II) from the cycles by the exothermic reactions. If this waste heat can be recovered, for example as electricity, the total efficiency of the VHTGR can be improved.

The thermochemical water-splitting cycle includes the separation and the transportation processes in addition to the reaction processes. In these flow sheets, it is assumed that the products of different phases can be separated spontaneously and that the additional work or heat to purify the separated products will be negligible. In the cycles studied here, no solid materials are used except for iodine. In the actual case, the iodine can be treated in a dissolved state in hydriodic acid. Thus, the work for the transportation of materials can be assumed to be negligible. However, in B cycles, an additional work to compress CO and hydrogen up to 300 atm is required in the methanol synthesis process. The theoretical work to compress n -mol of ideal gas from 1 atm to 300 atm at 298 K is calculated by eq. 4 and 10.2 kcal/mol-methanol is required.

$$W_{com} = nRT \ln P_2/P_1 = 3 \times 2 \times 298 \times 10^{-3} \times \ln 300 = 10.2 \quad (4)$$

In the industrial methanol synthesis plant including the steam reforming process to produce hydrogen and CO from natural gas, the waste heat from the process is recovered for the turbo-compressor and the amount of waste heat is estimated to be 40–70 kcal/mol-methanol from the published unit consumption figures^{22, 23}. From these considerations, it is concluded that the steam reforming and the methanol synthesis steps in B cycles will require large energy consumption. Moreover, in B cycles, hydrogen should be separated from CO. From the published data²⁴ on the industrial pressure swing adsorption (PSA) and the cryogenic separation processes, it is estimated that about 2.7 kcal/(mol-gas mixture) of electricity is required to separate hydrogen from CO, CH₄, etc. Using this data, it is estimated that B-1 and B-2

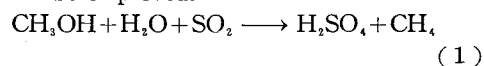
cycles will consume about 14 kcal of electricity to separate hydrogen from CO ($3.68\text{H}_2/1.34\text{CO}$ in S_4 and S_5) and that B-3 cycle will consume 23 kcal of electricity to separate hydrogen and hydrogen iodide from CO and CH_4 (0.25H_2 , $1.5\text{HI}/2\text{CH}_4$ in S_3 and $3.68\text{H}_2/1.34\text{CO}$ in S_5). Thus, in order to obtain higher thermal efficiency, an effective utilization of $Q_{\text{rec}}^{\text{H}}$ is desired for B cycles. This $Q_{\text{rec}}^{\text{H}}$ is low temperature heat (400--600K). It will be difficult to utilize such a low temperature heat effectively in the compression of CO and hydrogen and in the separation of hydrogen from the other gas.

The separation of SO_2 from O_2 is a common process in A and B cycles. This process will require not so much energy, since SO_2 can be liquified easily (bp. -10°C). The published data²⁵⁾ on the separation of acidic gas (CO_2 , COS , H_2S) from hydrogen, CO, etc by Rectisol process indicate that about 0.7 kcal of electricity and 1.2 kcal of steam per one mol of acidic gas are required. If the application of the Rectisol process for the separation of SO_2 is possible, the energy consumption for the purification of O_2 will be small compared to the other steps.

From the standpoint of the separation process, A cycles are better than B cycles. However, the demerit of A-2 and A-3 cycles also originates from the separation problem in A-2-1 reaction. In order to produce the hydriodic acid from sulfuric acid separately, the cell reaction is adopted, thus, it is inevitable that the large scale plant is required compared to B cycles because of dimensional demerit of electrolysis cell. The same is true for A-1 cycle. The addition of external electricity will be a method to increase the current density and then to reduce the scale of plant. Moreover, by this method it is possible to increase the concentration of acids and to reduce $Q_{\text{H}_2\text{O}}$ and then, to reduce the scale of heat exchanger. On the other hand η^{max} will decrease, for example by addition of 0.3V of external electricity, η^{max} of A-1, A-2, and A-3 cycles will decrease to 43, 54, and 54%, respectively.

From the standpoint of thermal efficiency, A-3 cycle seems to be the most promising cycle compared to the other cycles. B cycles are

attractive because of smaller scale of reactors and heat exchanger, however, the separation and shaft works will reduce the thermal efficiency to a lower level. There is a more essential method to improve the B cycles than effective utilization of $Q_{\text{rec}}^{\text{H}}$, if CH_4 can be produced directly by the following reaction 1, instead of reaction B-1-1, the whole cycle can be simplified and the expected thermal efficiency will be improved.



The preliminary experimental results¹⁵⁾ indicate that the reaction 1 is difficult to be carried out without side reactions, however, further research is still desirable in order to establish suitable thermochemical cycle.

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References:

- 1) J.E. Funk and R.M. Reinstrom, "System Study of Hydrogen Generation by Thermal Energy", US-AEC report TID-20441 (1964).
- 2) J.E. Funk and R.M. Reinstrom, *Ind. Eng. Chem. Process Des. Dev.* **5**, 336 (1966).
- 3) S. Srinivasan and F.J. Salzano, *Int. J. Hydrogen Energy* **2**, 53 (1977).
- 4) M. Dokiya, K. Fukuda, T. Kameyama, Y. Kotera and S. Asakura, *Denki Kagaku* **45**, 139 (1977).
- 5) M. Dokiya, T. Kameyama, K. Fukuda and Y. Kotera, *Bull. Chem. Soc. Japan* **50**, 2657 (1977).
- 6) M. Dokiya, K. Fukuda, T. Kameyama and S. Asakura, *Denki Kagaku* **46**, 465 (1978).
- 7) L.E. Brecher, S. Spewock and C.K. Warde, *Int. J. Hydrogen Energy* **2**, 7 (1977).
- 8) R. Carty, K. Cox, J. Funk, M. Soliman and W. Conger, *Int. J. Hydrogen Energy* **2**, 17 (1977).
- 9) F.H. Farbman, R.L. Ammon, C.C. Hardman and S. Spewock, "Proceedings of the 12th Intersociety Energy Conversion Engineering Conference", Vol. 1, 928, The American Nuclear Soc., La Grande, Ill., USA (1977).
- 10) Westinghouse Electric Corp., Astronuclear Laboratory, "Conceptual Design of an Integrated Nuclear-Hydrogen Production Plant Using the Sulfur Cycle Water Decomposition System", (NASA-CR-134976) (1976).
- 11) Westinghouse Electric Corp., "Papers on the Westinghouse Sulfur Decomposition System Presented at 1st World Hydrogen Energy Conference" (1976).
- 12) J.L. Russell, Jr., K.H. McCorkle, J.H. Norman, J.T. Porter II, T.S. Roemer, J.R. Schuster and R.S. Sharp, "Conference Proceedings of 1st World Hydrogen Energy Conference", Vol. 1, 1A-105, Univ. of Miami, FL., USA (1976).
- 13) J.R. Schuster, J.L. Russell, Jr., K.H. McCorkle, K.J. Mysels, J.H. Norman, D.R. O'keefe, R.S. Sharp, S.A. Stowell, P.W. Trester and D.G. Will-

- iamson, "Proceedings of the 12th Intersociety Energy Conversion Engineering Conference", Vol. 1, 920, The American Nuclear Soc., La Grande, Ill., USA (1977).
- 14) M. Dokiya, K. Fukuda and T. Kameyama, *Int. J. Hydrogen Energy*, to be published.
- 15) M. Dokiya, K. Fukuda and T. Kameyama, *Denki Kagaku* **47**, 150 (1979).
- 16) B.M. Abraham and F. Schreiner, *Ind. Eng. Chem. Fundam.* **13**, 305 (1974).
- 17) K.F. Knoche and J.E. Funk, *Int. J. Hydrogen Energy* **2**, 377 (1977).
- 18) D.D. Wagman, W.H. Evans, V.B. Parker, I. Hall, S.M. Bailey and R.H. Schumm, "Selected Values of Chemical Thermodynamic Properties", NBS-Technical Note 270-3 (1968).
- 19) D.R. Stull and H. Prophet ed. "JANAF Thermochemical Tables Second Ed.", NSRDS-NBS 37 (1971).
- 20) I. Barin and O. Knacke, "Thermochemical Properties of Inorganic Substances", Springer-Verlag Berlin (1973).
- 21) D.R. Stull, D.F. Westrum, Jr., and G.C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Jhon Wiley & Sons, Inc., New York (1969).
- 22) K. Konogi, *Kagaku to Kogyo* **31**, 24 (1978).
- 23) R. Yamazaki, *Kagaku Keizai* (5), 58 (1971).
- 24) H.A. Stewart and J.L. Heck, *Chem. Eng. Progr.* **65**, 78 (1969).
- 25) *Hydrocarbon Processing*, **52**, 99 (1973).



協会レポート

第9回 高温化学研究懇談会

本協会溶融塩委員会高温化学専門委員会と共催して昭和53年5月23日(火)13時30分より大阪大学工学部で、35名が参加して開催された。講演は下記の二件が塩川教授(阪大)の司会で行なわれた。

1. X線透過法による高温冶金反応の直接観察

大阪大学工学部 荻野和己
鉄鋼製錬プロセスのような高温融体の関与する複雑な反応過程を正しく解析するにはその実体の正確な把握が必要であることから、X線の透過能が各物質によって異なることを利用し、その透過像から反応過程を直接観察する試みが報告された。反応過程として 1) 溶鉄と溶融スラグとの反応によるCOガスの発生過程, 2) スラグによる溶鉄, 溶鋼の脱硫過程, 3) 酸素による溶鋼の脱炭過程などが取り上げられ、スライドおよび16mmフィルムにより紹介された。16mmフィルムによると気泡の発生過程などは非常によく観察できた。また、X線透過法を利用した表面張力および融解物の体積変化など物性測定についても報告があった。

2. 高温高圧下における無機合成反応

大阪大学産業科学研究所 小泉光恵
無機物質の合成についての今までの歩みが①物質の探索の時代から②材料のデザインの時代になりつつあることをダイヤモンド、立方晶BNおよびZnO-Bi₂O₃、バスタなど高温高圧下で合成される物質を例にとりあげて説明された。将来の無機物合成としては、材料の組織をミクロのオーダーで制御する方向に向かい、理論的な密度を有する多結晶体の合成が望まれていることが明らかになった。

講演後、小泉教授、島田助教授らの案内で産業科学研究所・合成無機材料部門および付属材料高圧センターの

ピストンシリンダー型高圧発生装置、熱間静水圧縮装置(HIP)などの見学が行なわれた。

第10回 高温化学研究懇談会

昭和53年10月20日(金)午前9時より、本協会秋季大会と共催して「高温電気化学—プラズマ化学を主体として」というテーマで青山学院大学理工学部で30名が参加して行なわれた。講演は松本 修教授(青山学院大理工学部)による「プラズマによる高温安定化合物の生成」と題するセッション・レクチャーを含めて7件あった。プラズマを用いる高温反応、低圧グロー放電およびマイクロ波放電など多方面にわたってプラズマを用いての研究が行なわれていることが報告された。なお、当日発表された講演題目は下記のものであった。

1. プラズマによる高温安定化合物の生成

(青山学院大) 松本 修, 小沼光晴, 神崎 愷

2. 高周波磁場結合型アークプラズマを利用する高温冶金反応

(東大) 西村博文, 石塚隆一, 明石和夫

3. 高周波グロー放電による金属の窒化および炭化

(青山学院大) 小沼光晴, 神崎 愷, 松本 修

4. 放電酸素中のイオン種の測定とO原子およびO₂生成機構

(上智大) 小駒益弘, 杉光英俊, 岡崎幸子
鈴木桃太郎

5. マイクロ波放電による直線上炭素分子の合成

(電通大) 坂田 朗, 中川直哉

6. 溶融アルカリ塩化物への四酸化三鉄の溶解

(山梨大) 児島弘直, 金子吉一

7. 溶融LiNO₃-NaNO₃系の内部易動度の濃度および温度依存性

(東工大) 楊肇 政, 高木隆三, 岡田 勲

(山梨大学工学部 児島弘直)