

# SYNTHESIS OF CHEMICAL REACTION CYCLES EFFECTIVE IN SAVING ENERGY

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An evolutionary method of synthesizing chemical reaction cycles effective in saving energy is developed. The stoichiometry of reactions, the thermodynamics of chemical equilibrium and the chemical reaction rates are considered in the method. By the searching procedure presented here, several novel industrial chemical processes, in which chemical reactions can be carried out at lower temperatures, and a chemical heat pump system which upgrades thermal energy to a higher temperature are synthesized on the basis of linguistic descriptions of reaction rates in the literature.

## Introduction

In chemical processes, a great deal of thermal energy is consumed to maintain chemical reactors at high temperatures, since many reactions with a positive change in Gibbs standard free energy require a high reaction temperature. It is, therefore, very significant in saving energy to carry out chemical reactions at lower temperatures.

In this study, reaction integration, such as reaction coupling and staging reactions, is applied to make the overall chemical reactions proceed at lower temperatures. An evolutionary method to synthesize chemical reaction cycles effective in saving energy is derived and novel industrial chemical processes are proposed.

The factors that must be considered in the synthesis of chemical reaction cycles are the stoichiometry of reactions, the thermodynamic equilibrium, and the reaction rate. The methods previously proposed<sup>6,11,15,17,21)</sup> were derived on the basis of stoichiometric relations and the changes in Gibbs standard free energy. The procedure presented here, however, takes the linguistic descriptions of chemical reaction rates into account in addition to those two factors.

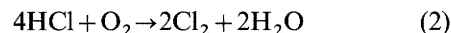
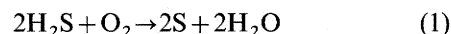
## 1. Reaction Coupling and Staging Reactions

### 1.1 Principle of reaction coupling

A reaction with a large positive change in Gibbs standard free energy,  $\Delta G^0$ , requires a very high reaction temperature. To cope with this problem, a

reaction with a highly negative  $\Delta G^0$  is coupled with a reaction which has a large positive  $\Delta G^0$ . Then the overall reaction, the sum of these coupled reactions, may proceed at a lower temperature<sup>22)</sup>. Lower reaction temperature saves thermal energy.

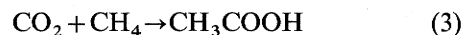
For example, in the Claus process and the Deacon process, the oxidation of hydrogen is coupled with the decomposition of hydrogen sulfide and hydrogen chloride, respectively. The decomposition of  $\text{H}_2\text{S}$  to  $\text{H}_2$  and  $\text{S}$  or  $\text{HCl}$  to  $\text{H}_2$  and  $\text{Cl}_2$  is thermodynamically favorable only at very high temperatures (above 2000 K), while the reaction of  $\text{H}_2$ , one of the product species of the decomposition reactions, with  $\text{O}_2$  is favorable at lower temperatures. The overall reaction, the sum of these coupled reactions, has a negative  $\Delta G^0$  and, therefore, favorable equilibrium conversion at about 700 K, as follows:



### 1.2 Method of staging reactions

Another method to overcome a positive Gibbs free energy change is staging reactions<sup>22)</sup>. A reaction process is divided into several stages and at each stage a reaction is carried out under a different condition.

For example, one mole of acetic acid can be made from one mole of carbon dioxide and one mole of methane according to the following stoichiometric equation.



Having a large positive value of standard free energy change, this reaction is unfavorable over a wide range

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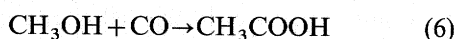
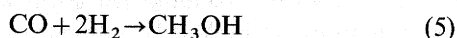
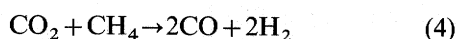
**Table 1.** Types of Reaction Division based on Reaction Coupling

I) $P+Q \rightarrow R+S$ +) $R+U \rightarrow V+W$ ----- $P+Q+U \rightarrow S+V+W$ $V+W \rightarrow R+U$	
II) $P+Q \rightarrow R+S$ +) $R+U \rightarrow V+P$ ----- $Q+U \rightarrow S+V$ $P+V \rightarrow R+U$	
III) $P+Q \rightarrow R+S$ +) $R+S \rightarrow U+V$ ----- $P+Q \rightarrow U+V$ $U+V \rightarrow R+S$	
IV) $P+Q \rightarrow R+S$ +) $R+S \rightarrow P+U$ ----- $Q \rightarrow U$ $P+U \rightarrow R+S$	
V) $P+Q \rightarrow R+S$ +) $R+U \rightarrow P+Q$ ----- $U \rightarrow S$ $P+Q \rightarrow R+U$	

**Table 2.** Types of Reaction Division based on Staging Reactions

I) $P+Q \rightarrow R+S$ -) $V+U \rightarrow W+R$ ----- $P+Q+W \rightarrow S+V+U$	
II) $P+Q \rightarrow R+S$ -) $P+U \rightarrow V+R$ ----- $Q+V \rightarrow S+U$	
III) $P+Q \rightarrow R+S$ -) $U+V \rightarrow R+S$ ----- $P+Q \rightarrow U+V$	
IV) $P+Q \rightarrow R+S$ -) $U+Q \rightarrow R+S$ ----- $P \rightarrow U$	
V) $P+Q \rightarrow R+S$ -) $P+Q \rightarrow R+U$ ----- $U \rightarrow S$	

of temperatures. Then it is divided into the following three stages.



The first reaction, methane reforming by carbon dioxide, proceeds to an equilibrium conversion over a nickel catalyst in the range of 850 K to 1100 K<sup>12</sup>. The second reaction, methanol synthesis, and the third, methanol carbonylation, have been carried out on a commercial scale. Thus, by making use of the reaction of carbon dioxide with methane, the production of acetic acid from carbon dioxide and methane in three stages is feasible and every reaction occurs at a temperature below 1000 K.

## 2. Reaction Cycles

### 2.1 Synthesis of reaction cycles

A network of chemical reactions can be described by a directed graph consisting of nodes which represent chemical reactions and arcs which indicate species of reactants and products including stoichiometric coefficients<sup>13</sup>. In an open cycle, arcs entering

and leaving the network show the feeds and the products of the process, and other arcs recycle in the network. In a closed cycle, all arcs recycle in the network and no arc goes out of the cycle.

Synthesis of chemical reaction cycles starts at a simplest closed one which consists of one reaction and its reverse reaction. One reaction in the cycle is divided into two reactions which occur at lower temperatures than the reaction temperature of the original one, based on the principles of reaction coupling and staging reactions. Types of reaction division are illustrated in **Tables 1** and **2** by chemical reaction equations and directed graphs. In reaction division based on the principle of reaction coupling, a reaction (e.g.  $R+U \rightarrow V+W$ ) is coupled with the original one (e.g.  $P+Q \rightarrow R+S$ ), and then the reverse reaction of the former one (e.g.  $V+W \rightarrow R+U$ ) must be added in the cycle. In staging reactions, the original reaction (e.g.  $P+Q \rightarrow R+S$ ) is divided into two reactions (e.g.  $U+V \rightarrow R+W$  and  $P+Q+W \rightarrow S+U+V$ ). One of them, the complementary reaction, can be derived by subtraction of the other reaction from the original one.

Tables 1 and 2 show that in the case when an original reaction, Reaction (ORG), is divided into two resultant reactions, Reaction (RR1) and Reaction

(RR2), at least one reactant or product species of Reaction (ORG) must be contained in the reactants of Reaction (RR1) or in the products of Reaction (RR2). In a directed graph, one node which indicates Reaction (ORG) is divided into two nodes, Reaction (RR1) and Reaction (RR2), which must be connected by at least one forward arc.

A reaction which has been proved experimentally to occur at a reasonable rate is called a known reaction. One reaction, which has one or more species of products in common with those of the original reaction and occurs at a temperature lower than that of the original reaction, is selected from the list of known reactions and the original reaction is subtracted by this known reaction. If the residual reaction is found in the list of known reactions and occurs at a temperature lower than that of the original reaction, then the reaction is divided into two known reactions. If not, the residual reaction must be divided in the same way as before. Until the cycle consists of known reactions, the selection of known reactions will be continued.

## 2.2 Preparation of list of known reactions

In the synthesis of reaction cycles, to take the reaction rates into account, a list of known reactions, which are confirmed as to their occurrence at reasonable rates, is prepared by making use of the information about chemical reaction rates. In the literature on chemical reactions, the rates are generally described by language, not by equations. The following linguistic descriptions of chemical reactions are considered to suggest that the reactions proceed at reasonable rates. These reactions have been selected as known reactions from the literature.

- , A reacts (readily, vigorously, violently or completely) with B to form (give) R, —
- , the usual (an excellent) method for (of) preparing R is (by) the reaction  $A + B \rightarrow R$ , —
- , the reaction takes place in the presence of C, —
- , the reaction can occur photochemically and is catalyzed by C, —
- , by heating A with B, R is formed according to the reaction  $A + B \rightarrow R$ , —

Reactions described by the following expressions are not considered to be known reactions.

- , A is slightly dissociated into B and C, —
- , A slowly reacts with B, —
- , the reaction does not proceed fast enough, —

About 2000 inorganic chemical reactions, the occurrence of which is confirmed, are selected from textbooks<sup>1,3,4,5,9,14,19,20</sup>, handbooks<sup>2,10,16,23,25</sup>, encyclopedias<sup>7,8,18,24</sup> and other literature. As the reactions in the list of known reactions are selected on the basis of information about reaction rates, the list is different considerably from one based on the change in free energy calculated from chemical thermo-

dynamic data. The former contains a few reactions, which have a positive change in Gibbs standard free energy calculated from the thermodynamic data, and excludes reactions which are not proved to occur experimentally in spite of negative changes in standard free energy. The reverse reaction of Reaction (2) is favorable thermodynamically above 700 K, but it has a large activation energy, so that the reaction of  $\text{Cl}_2$  and  $\text{H}_2\text{O}$ , at a high temperature does not produce HCl nor  $\text{O}_2$ , but rather HCl and HOCl. In the list of known reactions, there are many reactions for which the change in free energy cannot be calculated because the thermodynamic data are not available or a state of reactant or product species in the reaction is not specified. As sulfur has various states,  $S_x$ , where  $x$  is equal to 1–8 but is not specified, the change in Gibbs standard free energy for reactions which contain sulfur as a reactant or a product cannot be calculated accurately. The free energy of aqueous solutions is very complicated and data only for limited systems has been published, but many reactions which produce precipitation in aqueous solutions are contained in the list of known reactions.

## 2.3 Construction of data base

As a practical means of searching for candidate reactions, a chemical reaction data base is constructed based on the basis of the list of known reactions, as follows.

- (i) Preparation of an original reaction data base (ORDB)

Chemical equations of the known reactions with serial numbers are described in the ordinary way and are put in order of serial number. Addition of new reactions is possible.

Consistency of stoichiometric coefficients in chemical equations is checked by comparing the numbers of atoms contained on the right- and left-hand sides of the equation and correction is made if necessary.

Duplicate reactions in the list are deleted.

- (ii) Translation to an intermediate reaction data base (IRDB)

More information about each known reaction such as reaction temperature, heat of reaction and catalyst to be used is added to ORDB.

- (iii) Inversion of IRDB to an inverted data base (IVDB)

The known reactions in IROB are divided into groups. Every group consists of the reactions in which a given species is contained as a reactant or as a product. Consequently, a candidate reaction containing a specified species can be selected from IVDB very quickly.

## 2.4 Procedures for synthesis

Based on the inverted data base (IVDB), reaction cycles are synthesised by the following procedures.

- (i) Selection of candidate reactions from IVDB is

performed by a logical product of two attributes, product species and reaction temperature. A reaction that contains among its products one of the product species (the common species) in the original reaction, Reaction (OGR), and proceeds at a temperature lower than that of Reaction (OGR), is selected as a candidate reaction, Reaction (RR1).

(ii) Reaction (OGR) is subtracted by Reaction (RR1) to derive Reaction (RR2). Before the subtraction, the stoichiometric coefficients of the common species in the two reactions are converted to be equal.

(iii) If Reaction (RR2) is found in IVDB and occurs at a temperature lower than that of Reaction (OGR), the synthesis of chemical reaction cycle is completed. If not, Reaction (OGR) is replaced by Reaction (RR2) and procedures (i), (ii) and (iii) are repeated.

(iv) After the synthesis of chemical reaction cycle is finished, the feasibility of the cycle is evaluated from the viewpoints of separation of reaction products, reaction pressure, catalyst to be used, heat of reaction and so on.

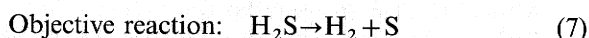
### 3. Development of Novel Processes

#### 3.1 Synthesis of open cycles

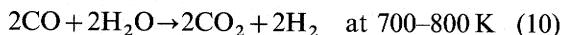
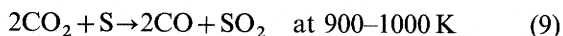
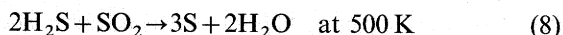
In the synthesis of an open cycle, the combination of an objective reaction and its reverse reaction is a starting cycle. In the cycle, the objective reaction is divided into two reactions by the method shown in the preceding section. Reactants and products of the objective reaction are the same as those of the reaction cycle, even if reactions in the cycle are divided.

Some examples of synthesized open cycles which have a possibility of developing into novel industrial chemical processes, are as follows:

##### i) Decomposition of hydrogen sulfide



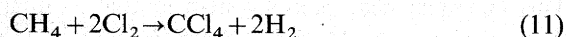
Open cycle:



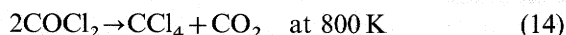
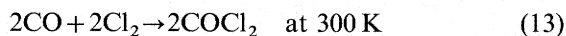
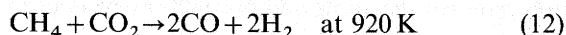
The objective reaction is thermodynamically favorable only at temperatures above 2000 K, but every reaction in the synthesized open cycle can be carried out at a satisfactory rate at a temperature lower than 1000 K. In the Claus process, which employs Reaction (8),  $\text{H}_2\text{S}$  is decomposed into S and  $\text{H}_2\text{O}$ . This cycle produces S and  $\text{H}_2$  which can be reused in the desulfurization process.

##### ii) Production of carbon tetrachloride

Objective reaction:



Open cycle:



Carbon tetrachloride is manufactured commercially by chlorination of methane, which produces not only  $\text{CCl}_4$  but also  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{HCl}$ . In the chlorination a large amount of chlorine is consumed in producing pollution-causing  $\text{HCl}$ , and separation of these by-products by distillation requires a great deal of energy. The synthesized cycle can produce mainly  $\text{CCl}_4$  and  $\text{H}_2$ , not  $\text{H}_2\text{O}$ .

#### 3.2 Synthesis of closed cycles

The chemical heat pump system is a closed cycle consisting of three reactions: two exothermic reactions at a high temperature,  $T_H$ , and at a lower temperature,  $T_L$ , and an endothermic reaction at a temperature,  $T_M$ , between  $T_H$  and  $T_L$ . The system has the function of upgrading thermal energy at  $T_M$  to  $T_H$  and serves to recover and utilize of waste heat exhausted from chemical processes.

A starting cycle consists of an exothermic reaction, which proceeds at  $T_H$ , and its reverse one, which occurs at temperatures above  $T_H$ . Then the reverse reaction must be divided into two or more reactions which take place below  $T_H$ . The synthesis of chemical heat pump systems is performed as follows:

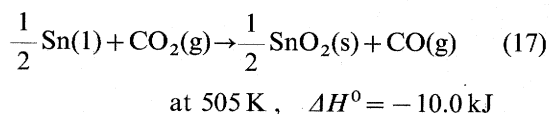
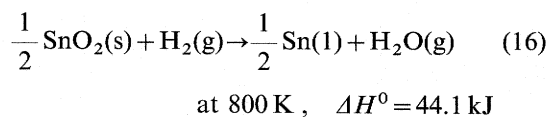
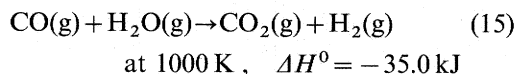
(i) An exothermic reaction which occurs at  $T_H$  is selected from the list of known reactions.

(ii) To divide the reverse reaction of the exothermic one in (i), an endothermic reaction of which the reaction temperature is lower than  $T_H$  is selected from the list of known reactions.

(iii) The endothermic reaction in (ii) is subtracted from the reverse reaction of the exothermic one in (i).

(iv) If the residual reaction of (iii) is an exothermic reaction which takes place at  $T_L$ , then the synthesis is completed. If not, the procedures from (i) to (iv) are continued until three known reactions in the cycle are found.

An example of the results is illustrated as follows:



This chemical heat pump system is able to upgrade thermal energy of 44.1 kJ at 800 K to that of 35.0 kJ at 1000 K. To utilize the system in practice, separation processes for reactants and products at every chemical reaction stage must be established.

## Conclusion

An evolutionary method of synthesizing chemical reaction cycles is developed. The searching procedure is based on thermodynamic principles, that is, the principles of reaction coupling and staging reactions. The stoichiometric relations are satisfied by addition and subtraction of reaction equations or division of one node into two nodes in a directed graph in which arcs indicate both chemical species and stoichiometry coefficients. Selection of candidate reactions from a list of known reactions assures the occurrence of reactions under a given condition because the known reactions have been proved experimentally to take place at a reasonable rate. By the present searching procedures, several novel processes are proposed which have a possibility of developing into industrial processes.

## Acknowledgement

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## Nomenclature

$\Delta G^0$	= Change in Gibbs standard free energy of reaction	[kJ]
$\Delta H^0$	= Change in standard enthalpy of reaction	[kJ]

## Literature Cited

- 1) Chambers, C. and A. K. Holliday: "Modern Inorganic Chemistry, An Intermediate Text", Butterworth & Co., Ltd., London (1975).
- 2) Chemical Society of Japan ed.: "Shinjikkenkagakuchoza (New Course of Experimental Chemistry)", Vols. 8-I, II, III, Maruzen Co., Ltd., Tokyo (1976).
- 3) Chitani, T.: "Shimpan Mukikagaku (Inorganic Chemistry, New Edition)", Vols. 1, 2, 3, Sangyotosho, Co., Ltd., Tokyo (1959, 1960).
- 4) Cotton, F. A. and G. W. Wilkinson: "Advanced Inorganic

- Chemistry, A Comprehensive Text", 2nd ed., John Wiley and Sons, Inc., New York (1972).
- 5) Duffy, J. A.: "General Inorganic Chemistry", 2nd ed., Longman Group Ltd., London (1966).
- 6) Fujii, S., H. Kameyama, K. Yoshida and D. Kunii: *J. Chem. Eng. Japan*, **10**, 224 (1977).
- 7) Grayson, M. ed.: "Kirk-Othmer Concise Encyclopedia of Chemical Technology", John Wiley and Sons Inc., New York (1985).
- 8) Grayson, M. ed.: "Kirk-Othmer Encyclopedia of Chemical Technology" 3rd ed., Vols. 1-24, John Wiley and Sons Inc., New York (1978-1984).
- 9) Ishikawa, S. and M. Igarashi: "Mukikagakusoron (Concise Inorganic Chemistry)", 5th ed., Baifukan Co., Ltd., Tokyo (1966).
- 10) Iwasaki, I. and Y. Oyagi ed.: "Mukikagakuzensho (Complete Book of Inorganic Chemistry)", Vol. XII-1-1, Maruzen Co., Ltd., Tokyo (1963).
- 11) Kameyama, H., K. Yoshida and D. Kunii: *The Chem. Eng. J.*, **11**, 223 (1976).
- 12) Kunugita, E., T. Hashitsume, Xing-wen Tao and Yuan-chen Wan: Proc. World Congress III of Chem. Eng., Tokyo, Vol. 1, p. 346 (1986).
- 13) Kunugita, E., E. Takatsuki and T. Ikeda: *J. Chem. Eng. Japan*, **17**, 336 (1984).
- 14) Lee, J. D.: "A New Concise Inorganic Chemistry", 3rd ed., Van Nostrand Reinhold Co., Ltd., Berkshire (1977).
- 15) Lauerhass, L. and D. F. Rudd: *Chem. Eng. Sci.*, **36**, 803 (1981).
- 16) Matsuura, S. ed.: "Mukikagakuzensho (Complete Book of Inorganic Chemistry)", Vol. VIII-1, Maruzen Co., Ltd., Tokyo (1962).
- 17) May, D., and D. F. Rudd: *Chem. Eng. Sci.*, **31**, 59 (1976).
- 18) Mizushima, S. ed.: "Kagaku Daijiten (Encyclopedia Chimica)", Vols. 1-10, Kyoritsu-shuppan Co., Ltd., Tokyo (1960-1964).
- 19) Murakami, Y.: "Mukikagaku (Inorganic Chemistry)", Sankyoshuppan Co., Ltd., Tokyo (1981).
- 20) Okabe, T.: "Mukipurosesukagaku (Inorganic Process Chemistry)", Maruzen Co., Ltd., Tokyo (1981).
- 21) Okai, H. and M. Ishida: *J. Chem. Eng. Japan*, **15**, 51 (1982).
- 22) Resnick, W.: "Process Analysis and Design for Chemical Engineers", McGraw-Hill Book Co., New York (1981).
- 23) Shibata, Y. and K. Yamazaki ed.: "Mukikagakuzensho (Complete Book of Inorganic Chemistry)", Vol. III new ed., Maruzen Co., Ltd., Tokyo (1958).
- 24) Tamamushi, B. ed.: "Rikagaku-jiten (Encyclopedia of Science and Chemistry)" 3rd revised ed., Iwanamishoten, Tokyo (1981).
- 25) Trontman-Dickenson, A. F. ed.: "Comprehensive Inorganic Chemistry", Vols. 1, 2, 3, Pergamon Press Ltd., Oxford (1973).