A NOTE ON SYNTHESIS OF THERMOCHEMICAL CYCLES FOR REDUCING CARBON DIOXIDE

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Introduction

It is widely known that the content of carbon dioxide is increasing in the earth’s atmosphere. The earth is becoming warmer by the so-called “greenhouse effect” caused by carbon dioxide emitted mainly from fossil fuel combustion. Carbon monoxide can be one of the major raw materials for “C1-chemistry” in the very near future. If a practical process to convert carbon dioxide to monoxide is established, the burden material can be raised to a new chemical feedstock as well as an energy resource.

Direct dissociation of carbon dioxide occurs at temperatures higher than 3350 K. A thermochemical cycle is therefore needed to overcome the free energy of dissociation at lower temperatures. Bamberger and Robinson have proposed a reaction cycle composed of cerium oxide and sodium phosphate. The cycle is so complex that it consists of six succeeding reactions. Martin has attempted to use solar energy for reducing carbon dioxide. The process comprises the reduction of carbon dioxide by metals and the decomposition of the resultant metal oxides into metals and oxygen at extremely high temperatures. The reaction sequences have been chosen on the basis of thermodynamic data only, without reaction kinetic information. Therefore, the feasibility of the proposed cycles may be very poor.

In this paper, thermochemical cycles for reducing carbon dioxide to carbon monoxide are synthesized in a systematic way by making use of directed graphs, and the feasibility of these cycles is discussed from the standpoint of chemical thermodynamics and chemical reaction kinetics.

1. Synthesis of Chemical Reaction Cycle

A chemical reaction described by the following reaction formula may be represented by a directed graph as illustrated in Fig. 1,

\[ AB + CD = AD + BC \] (1)
where A, B, C and D, are groups of atoms including stoichiometric coefficients. In Fig. 1, a node represents a chemical reaction and reaction condition (for example temperature and pressure), a number in a node indicates reaction number, and an arc indicates reactant or product including stoichiometric coefficient.

In the case where Reaction (1) does not occur at a moderate or considerably high rate due to either its positive change in free energy or its very slow kinetics, Reaction (1) must be divided into two reactions, Reactions (2) and (3). These two reactions have a common group of atoms, Z, for overcoming the barriers of thermodynamics and kinetics.

\[
\text{AB} + \text{CZ} = \text{BC} + \text{AZ} \quad (2)
\]

\[
\text{AZ} + \text{CD} = \text{AD} + \text{CZ} \quad (3)
\]

Group Z recycles in the chemical reaction cycle, \( 2 \rightarrow 3 \rightarrow 2 \), and Reactions (2) and (3) take place under conditions of different temperatures and pressures. Figure 2 illustrates a reaction cycle which consists of two reactions, as an example of the simplest reaction cycle. In a like manner, Reaction (2) can be divided into two reactions, Reactions (4) and (5), containing a common group Y as shown in Fig. 3.

\[
\text{AB} + \text{YZ} = \text{AZ} + \text{BY} \quad (4)
\]

\[
\text{BY} + \text{CZ} = \text{YZ} + \text{BC} \quad (5)
\]

All of the reaction cycles shown in Figs. 2 and 3, as a whole, represent Reaction (1).

In a directed graph, if two nodes are connected by only one arc, two reactions can be combined, as shown in Fig. 4, resulting in one reaction, which has three reactants and three products.

\[
\text{AB} + \text{DY} = \text{AD} + \text{BY} \quad (6)
\]

\[
\text{YZ} + \text{CD} = \text{DY} + \text{CZ} \quad (7)
\]

\[
\text{AB} + \text{CD} + \text{YZ} = \text{AD} + \text{BY} + \text{CZ} \quad (8)
\]

The sum of Reactions (6) and (7) is, thus, represented by Reaction (8).

### 2. Thermochemical Cycles for Reducing CO\(_2\)

The reaction cycle for reducing carbon dioxide into carbon monoxide and oxygen can be synthesized in a systematic way by making use of the above-mentioned procedure. For the selection of reaction sequence in a closed cycle, the following restrictions are considered:

(i) The elements used in the reactions are available in large quantities and highly toxic elements such as arsenic, cadmium, and mercury should not be involved.

(ii) The thermochemical reaction cycle is composed of several reactions, each of which proceeds within practical temperature limits and is not accompanied by any side reaction.

(iii) The cycle must involve reactions which take in CO\(_2\) and generate CO and O\(_2\).

Many inorganic chemical reactions have been investigated and several possible reactions, as shown in Table 1, are selected on the basis of information of reaction kinetics. At first, Reaction (9) is divided into two reactions.

\[
\text{CO}_2 = \text{CO} + \frac{1}{2} \text{O}_2 \quad (9)
\]

If Reaction (B-2) is selected from Table 1, Reaction (10) is necessarily adopted to form a closed cycle.

\[
\frac{1}{2} \text{SnO}_2 = \frac{1}{2} \text{Sn} + \frac{1}{2} \text{O}_2 \quad (10)
\]

The oxidation of tin by CO\(_2\) is known as a reversible reaction, but the decomposition of SnO\(_2\) into tin and oxygen is accompanied by a positive change in the standard free energy and is unlikely to occur even at extremely high temperatures. Reaction (10) then is divided into Reactions (C-4) and (11).
Table 1. Some examples of possible reactions

(A) Reactions taking in CO₂

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ + 2NaOH = Na₂CO₃ + H₂O</td>
<td>(A-1)</td>
</tr>
<tr>
<td>CO₂ + 2KOH = K₂CO₃ + H₂O</td>
<td>(A-2)</td>
</tr>
<tr>
<td>CO₂ + Mg(OH)₂ = MgCO₃ + H₂O</td>
<td>(A-3)</td>
</tr>
<tr>
<td>CO₂ + Ca(OH)₂ = CaCO₃ + H₂O</td>
<td>(A-4)</td>
</tr>
</tbody>
</table>

(B) Reactions generating CO

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>COCl₂ = Cl₂ + CO</td>
<td>(B-1)</td>
</tr>
<tr>
<td>Sn + 2CO₂ = SnO₂ + 2CO</td>
<td>(B-2)</td>
</tr>
<tr>
<td>S + 2CO₂ = SO₂ + 2CO</td>
<td>(B-3)</td>
</tr>
<tr>
<td>Ni(CO)₄ = Ni + 4CO</td>
<td>(B-4)</td>
</tr>
</tbody>
</table>

(C) Reactions generating O₂

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₃ = SO₂ + ½O₂</td>
<td>(C-1)</td>
</tr>
<tr>
<td>Ag₂O = 2Ag + ½O₂</td>
<td>(C-2)</td>
</tr>
<tr>
<td>2CuO = Cu₂O + ½O₂</td>
<td>(C-3)</td>
</tr>
<tr>
<td>SnO₂ = SnO + ½O₂</td>
<td>(C-4)</td>
</tr>
<tr>
<td>AgNO₃ = Ag + NO₂ + ½O₂</td>
<td>(C-5)</td>
</tr>
</tbody>
</table>

\[
\text{SnO} = \frac{1}{2} \text{Sn} + \frac{1}{2} \text{SnO}_2 \quad (11)
\]

These reactions are known to occur at 2000 K and 1000 K, respectively. Therefore, all the reactions in a tin-based cycle shown in Fig. 5 are proved to occur with considerably high rates at temperatures below 2000 K.

If Reaction (B-3) in Table 1 is chosen, the other is Reaction (12) to close a reaction cycle.

\[
\text{SO}_2 = \text{S} + \text{O}_2 \quad (12)
\]

The reduction of SO₂ to sulfur and oxygen is associated with a positive change in the standard free energy and a further division of Reaction (12) is impossible.

Selection of Reaction (C-1) in Table 1 leads to introduction of Reaction (13), which is thermodynamically unfavorable.

\[
\text{CO}_2 + \text{SO}_2 = \text{SO}_3 + \text{CO} \quad (13)
\]

Reaction (13) can be divided into Reactions (14) and (15).

\[
\text{CO}_2 + \text{CuSO}_4 = \text{SO}_3 + \text{CuCO}_3 \quad (14)
\]

\[
\text{CuCO}_3 + \text{SO}_2 = \text{CuSO}_4 + \text{CO} \quad (15)
\]

According to thermodynamic data, Reaction (15) is spontaneous and formation of carbon monoxide will be favoured. Unfortunately, Reaction (14) has no possibility. Thus, Reaction (14) is divided into Reactions (16) and (17) as illustrated in Fig. 6.

\[
\text{CO}_2 + \text{CuO} = \text{CuCO}_3 \quad (16)
\]

\[
\text{CuSO}_4 = \text{CuO} + \text{SO}_3 \quad (17)
\]

It is known that the chemical equilibrium state of the former is favorable at relatively low temperatures and the latter occurs at temperatures below 1000 K.

3. Discussion

All the reactions in a tin-based cycle have been proved to have moderate or considerably high reaction rates. Thus, a tin-based cycle seems promising, but its overall thermal efficiency is problematical owing to the recycle of SnO₂ and very high reaction temperatures.

A sulfate-based cycle, Reactions (C-1), (15), (16) and (17), can be modified as shown in Fig. 6 because of difficulties of CuCO₃ isolation. Then the cycle composed of Reactions (C-1), (17) and (18) is synthesized.
Reactions (C-1) and (17) have been established and Reaction (18) is thermodynamically favorable. In this cycle, other metals, such as manganese and magnesium, may be substituted for copper.

In consequence, one of the most promising cycles may be a sulfate-based cycle consisting of Reactions (C-1), (17) and (18). This cycle has the following features:

(i) It uses only carbon dioxide and heat energy at temperatures below 1000 K.

(ii) The change in the standard Gibbs free energy for each constituent reaction is less than 40 kJ/mol.

(iii) As it consists of both endothermic and exothermic reactions, a high thermal efficiency is attainable.

(iv) The reactions in the cycle are for the most part gas-solid reactions. Therefore, the reaction products can easily be separated, but a technique for separating gaseous components at high temperatures will be required.

Conclusions

An evolutional method for synthesizing chemical reaction cycles is proposed in which chemical reactions are represented with a directed graph. A search for reaction sequence is carried out for the reduction of carbon dioxide to monoxide.

As a result, a tin-based cycle and a sulfate-cycle are selected and the latter can be a promising cycle.

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Literature Cited