MASTER

New Applications
of High-Temperature
Solar Energy
for the Production of
Transportable Fuels
and Chemicals
and for
Energy Storage

19 January 1979

THE AEROSPACE CORPORATION

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NEW APPLICATIONS OF HIGH-TEMPERATURE
SOLAR ENERGY
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ENERGY STORAGE

19 January 1979

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Prepared by
Energy Systems Directorate
Energy and Resources Division
THE AEROSPACE CORPORATION
Post Office Box 92957
Los Angeles, California 90009

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ACKNOWLEDGEMENT

The following persons contributed to the preparation of this report on new solar-energized, high-temperature processes which can be utilized to produce transportable fuels, chemicals, and metals.

Howard Webb directed the work reported herein. He also gathered data on energy statistics reported in Appendix A, and prepared the material dealing with recommended programmatic activities to further the development of a solar fuels and chemicals program.

Dr. L. Robbin Martin developed the carbon recovery cycle concept described in this report. He also contributed the material related to the traditional approaches used in the petroleum and metals industries. Dr. Martin was also responsible for gathering and organizing the material on recent literature and new concepts in the areas of hydrogen economy, water decomposition and electrolysis, and hydrogen cycles. Lastly, he described the research needed to overcome problems in the solar fuels and chemicals program, based on the concepts discussed in this report.

Dr. Ron Cohen prepared the material on energy storage, both in the areas of traditional approaches and new concepts.

Dr. Richard Rountree organized the report in its original draft form, including the preliminary editing of the inputs.

Ginny Jackson typed the first draft of this report.

Chriss Gamez prepared much of the illustrative material included in this report in addition to typing the report itself.

The report in its present form was prepared by Dr. L. R. Sitney.

CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENT.....	ii
EXECUTIVE SUMMARY.....	1
1. INTRODUCTION.....	1-1
1.1 BACKGROUND OF PROGRAM ACTIVITIES.....	1-3
1.2 KEY CONCEPTS.....	1-5
1.2.1 Loops.....	1-5
1.2.2 Thermodynamic Efficiency.....	1-6
1.3 APPLICABLE SOLAR THERMAL POWER TECHNOLOGY.....	1-7
1.3.1 High-Temperature Solar Thermal Test Facilities....	1-9
1.4 REPORT CONTENTS.....	1-11
2. LITERATURE REVIEW OF THERMOCHEMICAL CYCLES.....	2-1
2.1 FUELS AND OPEN-LOOP STORAGE.....	2-2
2.1.1 Hydrogen.....	2-4
2.1.2 Hydrogen Production.....	2-5
2.2 CLOSED-LOOP CHEMICAL ENERGY STORAGE SYSTEMS (CESS).....	2-15
2.2.1 Closed-Loop System Overview.....	2-16
2.2.2 Criteria for Selecting Closed-Loop Chemical Energy Storage Systems.....	2-17
2.2.3 Candidate Systems.....	2-20
2.2.4 Utilization of Solar Thermal Technology for Closed- Loop Systems.....	2-31
2.3 LITERATURE SURVEY FINDINGS.....	2-32
3. NEW IDEAS FOR TRANSPORTABLE FUELS.....	3-1
3.1 SOURCES OF CARBON DIOXIDE.....	3-1
3.1.1 Current CO ₂ Availability.....	3-1
3.1.2 Future CO ₂ Availability.....	3-2
3.2 REDUCTION OF CO ₂ WITH SOLAR ENERGY.....	3-4
3.3 POTENTIAL CARBON CYCLES.....	3-6

CONTENTS (Continued)

	<u>Page</u>
3.3.1 Overview.....	3-6
3.3.2 Detailed Description of Carbon Cycles.....	3-9
3.4 HIGH TEMPERATURE METAL VAPOR-GAS SEPARATOR.....	3-19
3.5 END USES OF CARBON MONOXIDE.....	3-20
3.6 RECOMMENDED PROGRAM EFFORTS.....	3-21
3.6.1 Summary of Problem Areas and Critical Evaluations.	3-22
3.6.2 Basis for a Near-Term Program.....	3-22
3.6.3 Program Planning Activities.....	3-23
4. HIGH-TEMPERATURE CHEMICAL CONCEPTS.....	4-1
4.1 FUELS AND OPEN-LOOP APPLICATIONS.....	4-1
4.1.1 Current Production of Fuels.....	4-1
4.1.2 Potential Fuels and Open-Loop Applications Using Hydrogen.....	4-2
4.2 METALS REDUCTION.....	4-4
4.2.1 Current Reduction Techniques.....	4-4
4.2.2 Potential Metals Reduction Applications.....	4-10
4.3 POTENTIAL CLOSED-LOOP APPLICATIONS.....	4-13
4.3.1 Dual System Energy Storage.....	4-13
4.3.2 Closed-Loop Benefits via Solar Technology.....	4-14
4.4 SUMMARY OF FINDINGS ON NEW CONCEPTS.....	4-15
5. GENERAL PROBLEM AREAS, INTERESTS, AND EVALUATIONS.....	5-1
5.1 GENERAL PROBLEM AREAS.....	5-1
5.1.1 Materials Compatibility.....	5-1
5.1.2 Separation of Products.....	5-2
5.1.3 Electrolytes and High-Temperature Electrodes.....	5-3
5.1.4 Selective Emission at High-Temperatures.....	5-4
5.1.5 Kinetics.....	5-5
5.1.6 Thermodynamics.....	5-5
5.1.7 Problem Areas Summary.....	5-6
5.2 SPECIAL INTERESTS AND CRITICAL EVALUATIONS.....	5-6
REFERENCES.....	R-1

CONTENTS (Continued)

	<u>Page</u>
APPENDIXES.....	A-1
A. ENERGY STATISTICS.....	A-1
A-1 ENERGY DISTRIBUTION RELATIONSHIPS.....	A-1
A-2 ENERGY CONSUMPTION IN THE INDUSTRIAL SECTOR.....	A-3
A-3 ENERGY USAGE IN THE TRANSPORTATION SECTOR.....	A-6
B. OPEN- AND CLOSED-LOOP CYCLE DATA.....	B-1
B-1 OPEN-LOOP DATA ON WATER DECOMPOSITION CYCLES.....	B-1
B.1.1 Listing of Cycles.....	B-1
B.1.2 Efficiency Calculations.....	B-1
B-2. CLOSED-LOOP DATA.....	B-25
B.2.1 System Enthalpy and Working Temperature.....	B-25
B.2.2 Candidate Systems for Closed-Loop Chemical Energy Storage Systems.....	B-37
B.2.3 Supplemental Thermodynamic and Energy Flow Data...	B-39

FIGURES

	<u>Page</u>
1 Carbon Cycle Concept.....	2
1-1 Conceptual Carbon Cycle Recovery Technique.....	1-2
1-2 A Summary of Properties of Typical Solar Concentrating Collectors	1-8
2-1 Computer Search Algorithms.....	2-2
2-2 Theoretical Hydrogen Electrolysis Voltages as a Function of Temperature.....	2-8
2-3 Direct Dissociation-Diffusive Separation.....	2-12
2-4 Schematic of Westinghouse System.....	2-14
2-5 Operational Methanol Cycle.....	2-23
2-6 Operational AHS Cycle.....	2-25
2-7 Schematic Diagram of Proposed NH ₃ System.....	2-28
2-8 Energy Transmission System ADAM + EVA.....	2-30
3-1 Extraction of Carbon Dioxide from Stack Gas.....	3-2
3-2 Carbon Dioxide Recovery Process.....	3-5
3-3 An Iron-Based Cycle.....	3-11
3-4 A Nickel-Based Cycle.....	3-13
3-5 A Cadmium-Based Cycle.....	3-15
3-6 A Zinc-Based Cycle.....	3-16
3-7 A Cobalt/Sulfur-Based Cycle.....	3-18
3-8 Solar Furnace Product Separation.....	3-19
4-1 Dual-System Closed-Loop Energy Storage Concept.....	4-14
A-1 Energy Consumption in the U.S. by Consuming Sector.....	A-1
A-2 U.S. Energy Demand Provided by Various Sources.....	A-2

FIGURES (Continued)

	<u>Page</u>
A-3 Energy Demand in the Industrial Sector.....	A-3
B-1 Simplified Flow Chart for Cycle No. 24.....	B-20
B-2 Simplified Flow Chart for Cycle No. 36.....	B-21
B-3 Simplified Flow Chart for Cycle No. 57.....	B-22
B-4 The Composition of Dissociating Water Vapor at Thermodynamic Equilibrium, $P = 1$ Atmosphere.....	B-36
B-5 Methanol Cycle Energy Analysis.....	B-42
B-6 Ammonium Hydrogen Sulfate Cycle Energy Analysis.....	B-44
B-7 Equilibrium Percentages of NH_3 in Stoichiometric Mixture of N_2 , H_2 , and NH_3 at Various Temperatures and Pressures.....	B-46
B-8 Basic Temperature-Enthalpy Diagram for the $\text{NH}_3\text{-N}_2\text{-H}_2$ System.....	B-46
B-9 Schematic of $\text{SO}_2\text{-SO}_3$ Solar Thermal Closed-Loop Energy Storage System.....	B-47
B-10 Equilibrium Fraction of $[\text{SO}_2] / [\text{SO}_2 + \text{SO}_3]$ as a Function of Temperature at Constant Total Pressure.....	B-47
B-11 Comparison of Dissociation Curves for COCl_2 , $\text{H}_2\text{O} + \text{CH}_4$, and SO_3 as Working Fluids for a Gas Dissociation Solar Power System.....	B-48
B-12 Equilibrium Conversion Relations for the $\text{CH}_4\text{-H}_2\text{O}$ System at Atmospheric Pressure.....	B-48

TABLES

	<u>Page</u>
I Potential Carbon Cycles.....	5
1-1 Solar Thermal Hardware Status.....	1-9
1-2 Approximate Specifications for Solar Thermal Test Facilities.....	1-10
2-1 Heat of Reaction Comparison.....	2-26
3-1 Potential Carbon Cycles.....	3-8
3-2 End Uses of Carbon Monoxide.....	3-21
A-1 Energy Requirements for Selected Metals in the United States in 1973.....	A-4
A-2 Energy Requirements for Selected Nonmetallic Materials for Primary Products in the United States in 1973.....	A-5
A-3 Energy Costs of Bringing Fossil Fuels to Market.....	A-5
A-4 Energy Used for Transportation in 1968.....	A-7
B-1 Compilation of Thermochemical Cycles for Hydrogen Production from Water.....	B-2
B-2 Compilation of Additional Thermochemical Cycles for Hydrogen Production from Water.....	B-9
B-3 Comparison of Cycle Efficiency Estimate Based on LHV.....	B-24
B-4 Reactions Proposed in Previous Investigations.....	B-29
B-5 Thermal Decomposition of Ammonium Salts.....	B-30
B-6 Thermal Decomposition of Group IA and IIA Hydroxides.....	B-31
B-7 Thermal Decomposition of Group IA and IIA Carbonates.....	B-32
B-8 Thermal Decomposition of Group IA and IIA Sulfates.....	B-33
B-9 Thermal Decomposition of Group IA and IIA Oxides.....	B-34
B-10 Energy Content of Candidate Chemical Energy Storage Reactions, Excluding Those Containing Solids.....	B-37

TABLES (Continued)

	<u>Page</u>
B-11 Energy Content of Candidate Chemical Energy Storage Reactions, Systems with Solid Constituents.....	B-38
B-12 Energy Density of Potential Chemical Energy Storage Systems.....	B-40
B-13 Methanol Reaction System: Reaction 1, Solar Input Reaction.....	B-41
B-14 Methanol Reaction System: Reaction 2, Output Heat Reaction.....	B-41
B-15 Ammonium Hydrogen Sulfate Reaction System: Reaction 1, Solar Input Reaction.....	B-42
B-16 Ammonium Hydrogen Sulfate Reaction System: Reaction 2, Solar Input Reaction.....	B-43
B-17 Ammonium Hydrogen Sulfate Reaction System: Reaction 3, Output Heat Reaction.....	B-43
B-18 Heat of Formation of Ammonia.....	B-44

EXECUTIVE SUMMARY

One of the goals of the Department of Energy (DOE) is the utilization of solar energy in the production of transportable fuels. Recent DOE-sponsored work at The Aerospace Corporation has identified a thermochemical carbon recovery technique which could benefit from the high temperatures produced with aid of solar energy. This technique utilizes new multistep chemical processes of high thermodynamic efficiency to produce carbon monoxide and hydrogen from which a variety of commercial organic chemicals, including fuels such as gasoline, can be synthesized. Figure 1 illustrates the wide variety of fuels and materials which can be produced from CO and H₂ through the use of the carbon recovery cycle. A near-term application of the processes would use carbon from fossil fuels in an open-loop system, rather than carbon from the closed-loop recovery system, to reduce the CO₂ to CO.

The DOE-sponsored study at Aerospace initially included the examination of markets for high temperature process heat applied to industrial processes, with solar energy used to produce this process heat in systems similar to those being developed for the generation of solar thermal electric power. Collaboration with the cement, petrochemical, and chemical industries resulted in the identification of a number of industrial process heat applications which were reported to the DOE in February 1978 (Reference 1).

This solar fuels and chemicals study was performed subsequent to the process heat study. It had as its objective the identification of new industrial processes for the production of transportable fuels and essential chemicals which could capitalize on the high temperatures achievable through solar thermal power technology. The primary accomplishment of this study has been the identification of new closed-loop thermochemical processes for the reduction of carbon dioxide to carbon monoxide, one of the two basic building blocks for the synthesis of transportable fuels and organic chemicals by the well-known Fischer-Tropsch process. In particular, carbon

Figure 1. Carbon Cycle Concept

monoxide will combine with hydrogen to form gasoline in this process when the proper iron or cobalt catalyst is used.

The solar fuels and chemicals study was limited to the examination of processes requiring temperatures in excess of 1000°K since lower temperature processes had already been examined in studies concerned with the application of waste heat from nuclear power plants to industrial processes. No work was performed on resource recovery techniques involving photovoltaic, photolytic, biomass, or battery processes and systems. Neither experimental work nor economic studies were performed on the carbon cycle techniques, and design and equipment aspects of the utilization of solar energy in the production of fuels and chemicals were not investigated.

In developing the carbon cycle processes, the primary activity included an extensive literature search and the thermodynamic evaluation of a number of candidate chemical cycles. In reviewing the existing chemical literature, slightly over four million abstracts were accessed, using a key word search by means of a computer. Approximately 330 publications were identified as having potential value. Each of these abstracts was reviewed and 104 of the technical articles were subsequently examined in detail. In addition, many of the authors were contacted for information on more recent publications. This comprehensive review, along with independent research by The Aerospace Corporation, provides the basis for this report and recommendations.

Although both hydrogen and carbon closed- and open-loop chemical cycles were studied, it was concluded that the carbon cycles offered sufficient additional potential to warrant concentrating on them in subsequent work. Among the reasons for this selection is the fact that, whereas over 98 percent of the energy used to reduce the CO_2 to CO is released in the combustion of CO to CO_2 , only about 75 percent of the energy required to reduce the H_2O to hydrogen is released when the hydrogen is burned due to the fact that water is formed as a vapor rather than in the liquid state. Thus, the overall efficiency is higher for the carbon cycle than for the hydrogen cycle.

Carbon monoxide, in addition to being used as a feedstock for the production of hydrogen and organic chemicals, is an excellent fuel and can be used to power existing fossil fuel power plants for the production of electric power and industrial process heat. Hydrogen can be produced from CO by means of the water-gas shift reaction:

Subsequently, hydrogen and carbon monoxide can be combined in the Fischer-Tropsch process over a number of specific catalysts to form methane, methanol, gasoline, higher alcohols, ethylene glycol, and numerous other organic chemicals which have a large commercial market.

Several commercial chemical processes exist currently with the capability of separating carbon dioxide, which comprises 12 to 18 percent of power plant stack gas, from the balance of the flue gas. In the near term, the CO_2 can be reduced to CO by coal or other carbonaceous materials. However, for the long term, it is desirable to develop a closed-loop carbon recovery cycle to reduce the CO_2 to CO and oxygen, using carbon produced in the cycle itself to accomplish this reduction. Five thermodynamically-allowed processes for the reduction of CO_2 (see Table 1) have been identified by The Aerospace Corporation and patents have been applied for. In addition, a patent application has been filed for a liquid metal gas separation process. Each of these five processes has a theoretical thermodynamic efficiency approaching 60 percent. One of the processes will theoretically occur at temperatures below 1400°K (2060°F) and can, therefore, take advantage of solar technology currently being developed for Brayton cycle solar thermal power plants.

In future activities, both experimental and theoretical work will be necessary to establish the full potential of the closed-loop carbon recovery cycles. The purpose of the experimental work is to demonstrate that at least one of the cycles, which has already been identified as thermodynamically feasible, will actually proceed at a reasonable rate at or

Table I. Potential Carbon Cycles

Cycle	Theoretical Efficiency (Percent)		
	Without Separation	With Separation*	
<u>Open-Loop Cycle Using External Carbon Source</u>			
$C + CO_2 = 2CO$ (1000°K)	98		
<u>Closed-Loop Cycles to Produce Carbon</u>			
<u>Direct Reduction of CO₂</u>			
$2Cd(l) + CO_2 = 2CdO + C$ (600°K) $2CdO = 2Cd(g) + O_2$ (1900°K)	}	56	46
$2Zn(g) + CO_2 = 2ZnO(s) + C$ (1300°K) $2ZnO = 2Zn(g) + O_2$ (2400°K)			
$2CoO + 2SO_2 + CO_2 = 2CoSO_4 + C$ (500°K) $2CoSO_4 = 2CoO + 2SO_2 + O_2$ (1400°K)	}	44	37
	}	60	(60)
<u>Secondary Reduction of CO₂ via CO</u>			
$C + CO_2 = 2CO$ (1000°K) $2CO + 4Fe_3O_4 = 6Fe_2O_3 + 2C$ (500°K) $6Fe_2O_3 = 4Fe_3O_4 + O_2$ (1800°K)	}	62	20
$C + CO_2 = 2CO$ (1000°K) $2Ni + 2CO = 2NiO + 2C$ (600°K) $2NiO(l) = 2Ni(l) + O_2$ (2850°K)	}	60	49

* Accounts for work required to separate products by suggested chemical process.

near the predicted temperature. The theoretical effort should attempt to identify additional thermodynamically allowable carbon and hydrogen cycles with higher efficiencies than those already identified. Work should also be initiated to develop catalysts to promote the reaction rate in the low-temperature rate limiting step in any potential closed-loop process, e.g., the third process given in Table 1. As soon as one of the processes has been shown to be feasible, including the demonstration of a commercially viable reaction rate, a conceptual design should be established for a plant to produce carbon monoxide from CO_2 by a closed-loop carbon recovery cycle. The design should include options for both an electric power plant burning CO and O_2 and a chemical plant to convert CO and H_2O to CO_2 and H_2 . The H_2 and additional CO can then be reacted over catalysts in the Fischer-Tropsch process to form the desired chemical(s), including gasoline. These plant designs are necessary to establish plant and process costs for the production of power and of chemicals by means of solar energy.

In addition to the fuels and chemicals work described previously, work was also carried out in the following areas:

- Review and presentation of data identifying the fuels and materials which are the most significant in the energy economy, and identification of promising relationships to solar technology.
- Examination of traditional methods of production for fuels and materials to determine potential energy savings.
- Summary of the literature on the hydrogen economy and the production and use of hydrogen for energy storage, transportation, conversion, and metals production.
- Presentation of new concepts for materials production and closed-loop energy storage capitalizing on the higher efficiencies and new processes possible through high temperature solar technology.

In the area of energy economy, a cursory review of the role of fuels and materials determined that fuels and materials are significant in this economy and indicated that the fuels and materials sector is compatible with temperatures achievable with the state of the art in solar technology.

For example, liquid fuels account for 44 percent of all energy projected to be consumed in the United States between 1970 and 1985; currently, these fuels account for about 95 percent of all transportation energy. Transportation energy (25 percent) together with industrial energy, including electrical power generation, account for approximately 70 percent of the Nation's total energy consumption. Production of fuels and materials accounts for about half of the industrial energy consumption with approximately half of this energy going into the production of iron and petroleum. Solar thermal power technology currently under development should allow temperatures of the order of 1400°K (2060°F) to be achieved in the solar receiver and to be used for the production of fuels and chemicals in the near term through open-loop cycles and in the far term through closed-loop carbon recovery cycles.

In discussing the production of fuels and materials, the primary emphasis has been placed on the existing techniques used to produce the fuels and metals and on indicating how solar thermal technology might be used to reduce the consumption of depletable energy that is currently being used in their production. For example, petroleum production uses approximately 10 percent of the energy in the oil to provide process heat in the refining step. This energy could conceivably be replaced by solar energy to save significant amounts of oil. In the metals reduction sector, solar energy could provide the high temperatures needed to reduce the ore to the metal, but it is not obvious that it would be feasible to produce aluminum or magnesium in commercial quantities through the use of solar energy.

The use of solar energy in connection with closed-loop energy storage systems has a high potential, but little consideration has been given to this application of solar energy in the past. A novel concept has been conceived by Aerospace consisting of a dual system for energy storage which features a gaseous medium ($\text{CO} + \text{H}_2$) for transmission and a condensed system (NaHF_2) for storage. While this system incurs the penalties of additional complexity and some loss of efficiency, it requires significantly

less storage volume than a gaseous system and should be capable of being constructed for a much lower capital investment.

Potential problem areas pertinent to solar-derived fuels and chemicals have been identified. These problems are primarily associated with the limited high temperature experience in industry and include materials compatibility, separation of reaction products, development of solid electrolytes and high-temperature electrodes, selective emission of receiver coatings at high temperature, and a lack of chemical kinetics data and high-temperature thermodynamic data. The kinetics and thermodynamic data are essential for the determination of the technical and economic feasibility of any new process. Research should be pursued to acquire the necessary data to demonstrate the feasibility of these new solar fuels and chemicals processes.

1. INTRODUCTION

A major goal of the DOE Division of Central Solar Technology (CST) is to utilize solar thermal power technology to reduce the consumption of petroleum in the United States. Commercial production of transportable fuels and/or petrochemicals from non-petroleum sources could lead to a significant decrease in petroleum imports. This report of work sponsored by CST at The Aerospace Corporation discusses these two applications as well as the production of metals and closed-loop energy storage.

Near term applications of solar thermal power technology will probably be limited to temperatures of the order of 1000°K (1340°F), whereas later applications may be at temperatures as high as 2000°K (3140°F). The advantages of the higher temperatures are improved theoretical process efficiencies and the ability to utilize chemical reactions, which do not occur at the lower temperatures, for the production of feedstocks for the synthesis of transportable fuels and organic chemicals.

In particular, this report describes and presents a conceptual configuration for a closed-loop carbon recovery concept which can take advantage of the high temperatures achievable with solar thermal power technology to produce carbon monoxide (CO) and hydrogen (H_2). The CO and H_2 , in turn, can then be reacted to produce a large variety of organic chemicals, including gasoline, by the well-known Fischer-Tropsch process. Figure 1-1 shows a conceptual representation of the carbon recovery technique, which uses existing processes for the extraction of carbon dioxide (CO_2) from power plant stack gas and for the reduction of the CO_2 to CO , as well as for the production of H_2 from water and CO , and for the production of organic chemicals from H_2 and CO . Research will be required only to establish the feasibility of the closed-loop carbon recovery technique and to integrate high-temperature solar thermal technology into the process, as indicated by the "boxed" area of the figure. However, an existing near-term, open-loop process can be used to reduce the CO_2 to CO until the carbon recovery technique is developed. Recommended steps to implement a Solar Fuels and Chemicals Program are presented in Section 3.6 of this report.

Figure 1-1. Conceptual Carbon Cycle Recovery Technique

Based on the work performed to date on this study, The Aerospace Corporation has applied for patents for five solar-energized thermochemical processes to reduce CO_2 waste gas to CO . The CO would then be used to produce a feedstock for subsequent synthesis of transportable fuels and organic chemicals by the Fischer-Tropsch process. The carbon recovery technique has the potential to provide large quantities of transportable fuels without depleting our limited petroleum supplies. The technique also will alleviate the environmental impact of current power plant operations by reducing the amount of CO_2 released into the atmosphere and the attendant "greenhouse" effect of CO_2 .

1.1 BACKGROUND OF PROGRAM ACTIVITIES

The advantages of higher efficiencies and new chemical reactions to produce transportable fuels and essential materials were identified for further study as part of the overall DOE program on solar thermal applications, which involves a number of different activities pertinent to this study.

A number of firms have been assisting DOE in its fuels and chemicals program. The overall activity includes: (1) identification of promising R&D areas and solar thermal applications, (2) development of industrial interest, and (3) development of preliminary program plans for the fuels and chemicals program. The Aerospace Corporation effort involved an examination of the entire industrial market with the intent of identifying candidate solar thermal systems for industrial processes. The investigation covered two areas: high temperature industrial process heat applications and the fuels and chemicals applications reported here.

The industrial process heat program plan was completed in early 1978 and reported to DOE (Reference 1). This plan presented the technical, economic, and programmatic bases to expand the current DOE solar industrial process heat program to include high-temperature process heat applications based on the use of solar thermal electric power system technology. The study results were derived in a coordinated effort with industrial firms dedicated to maintaining and advancing their technology and business posture

in the process heat market. The status of current and near-future solar thermal power technology, as presented in the process heat study, is summarized in Section 1.3 of this report.

The initial intent of this fuels and chemicals study was to examine the utilization of solar thermal technology for the production of these materials. It was hoped that economically attractive high-temperature processes could be identified which consisted of a single or, at most, only a few reaction steps which would utilize highly concentrated solar energy to provide the driving force. As the study progressed, emphasis shifted to the production of transportable fuels and essential materials, and to closed-loop storage, especially as these processes related to carbon cycling. It soon became evident that near-term applications were extremely important since existing industrial equipment and processes could be utilized to the greatest extent possible. As a result, carbon cycling, which involved the use of CO_2 from stack gases, appeared to be especially promising. A review of the chemical literature indicated that essentially no work had been done on closed-loop carbon recovery techniques although the reduction of CO_2 by carbon in open-loop systems at moderate temperatures was well known. Work was initiated to identify thermochemical cycles to decompose CO_2 to carbon at temperatures below 3400°K and the five carbon recovery cycles reported herein resulted from that effort.

An earlier in-house study (Reference 2) on the long distance transport of solar energy by means of a chemical heat pipe indicated that there were no serious technical barriers to the concept and that long distance transport of energy appeared to be feasible. This concept was found to be economically competitive with the conventional transport of electrical energy when the end use was thermal rather than electrical energy. This concept was considered to have potential, both to save petroleum and as a replacement for fuel.

Although little work has been carried out on thermochemical cycles for the production of carbon, the literature revealed that a significant effort was under way in the development of thermochemical cycles for the production of hydrogen, primarily from water. This hydrogen-oriented effort

stemmed from the interest in a hydrogen economy which would use hydrogen as the basic medium for energy storage, transportation, conversion, and metals reduction. Fortunately, much of the knowledge which has been developed in the search for high-temperature hydrogen cycles can be capitalized upon in the development of high-temperature thermochemical cycles for the recovery of carbon. Some of the hydrogen work is described in Section 2, while new ideas for the application of high-temperature solar energy are presented in Section 4.

1.2 KEY CONCEPTS

This section describes two key concepts used in the remainder of this report: "loops" and thermodynamic efficiency.

1.2.1 Loops

The idea of a "loop" is convenient in the discussions in this report which deal more with a secondary, i.e., chemical, rather than a primary energy source, i.e., the sun. The secondary chemical energy sources are simply recycled in a loop to deliver energy to the consumer in a more useful form, location, or time than the primary energy source. In such a process, a reversible chemical reaction absorbs thermal energy, Q , by converting a set of low-energy (i.e., low chemical potential) reactants, A and B , into high-energy storable chemical products, C and D . Subsequent reaction of the products into the original reactants, A and B , releases the absorbed energy, Q , as shown below:

In a closed-loop system, the reactants and products are cycled from the primary energy source to the user regeneration site without the addition or removal of material. In an open-loop system, the reactants are removed from the surroundings and the products are released to the surroundings, although not necessarily at the same location. In most of the open-loop systems, which are treated in both Section 2 and Section 4, more than two

reactions will be necessary in order to operate at somewhat lower temperatures in the energy-absorption step. Examples of a closed-loop system, e.g., the ADAM + EVA system, are provided in Section 2.2. In the ADAM + EVA system, the two reactions are:

An example of a multistep water decomposition reaction, also called a cyclic thermochemical decomposition, for open-loop use is:

It should be noted that the intermediate reactants, Cd and CdO, are not consumed in this process. Many of these processes are discussed in Appendix B.

1.2.2. Thermodynamic Efficiency

The thermodynamic efficiency which will be cited in this report is equivalent to the yield efficiency of the overall reaction, i.e., the energy liberated in the formation of the product (CO_2 or H_2O) divided by the sum of all the positive heat of reactions associated with the reactions involved in the cyclic thermochemical process. Thus,

$$\epsilon = \frac{\Delta H_f^\circ (\text{CO}_2)}{\sum \Delta H_r},$$

where only reactions with a positive heat of reaction, ΔH_r , are included in the summation. $\Delta H_f^0(\text{CO}_2) = -94.0$ kcal/mole. In the iron-based cycle for the decomposition of CO_2 into carbon and oxygen, the following steps and heats of reaction are involved:

$$\epsilon = \Delta H_f^0 / \sum \Delta H_r = 94.0 / 150.8 = 0.62$$

If a phase change is involved in the process, the heat of the phase change must be included in the $\sum \Delta H_r$.

1.3 APPLICABLE SOLAR THERMAL POWER TECHNOLOGY

Many solar thermal collector system configurations presently exist for obtaining large amounts of thermal energy at temperatures high enough to efficiently support the fuels and materials applications. An extensive review of the state of the art of solar collector systems was reported in The Aerospace Corporation study (Reference 1) of high-temperature industrial process application requirements, so only the highlights of that study will be presented here.

The summary of the expected performance of typical solar concentrating collectors is shown in Figure 1-2. Several of these medium- and high-temperature concepts (i.e., concentration ratio above 20) have been or are currently under development to satisfy solar thermal electric applications. Each of these systems requires implementation of the following functions: (1) collection of energy, (2) conversion of solar

energy to thermal energy, (3) thermal energy transport, (4) energy storage or a backup system to cover periods when insolation is not available, and (5) master control to regulate the supply to satisfy the demand. The hardware status of this solar technology is shown in Table 1-1 for temperatures above 600°K.

Figure 1-2. A Summary of Properties of Typical Solar Concentrating Collectors (Reference 81)

Table 1-1. Solar Thermal Hardware Status

Temperature Range	Collector Type	Development Status
High 600-1100°F Steam	Central Receiver Dish Distributed	Technology Available Large-Scale Experiments
Very High Up to 2000°F Hot Air	Central Receiver Dish Distributed	Technology under Development by EPRI
Over 2000°F	Central Receiver Dish Distributed	Requires Receiver Materials R&D

1.3.1 High-Temperature Solar Thermal Test Facilities

Table 1-2 lists the maximum operating temperatures and other specifications of solar thermal test facilities in the United States and France, using data from Reference 3. An additional row has been added to the reference data to show the maximum operating temperature divided by $2^{1/4}$, which is a crude estimate of the temperature at which the facility loses half of the energy through re-radiation, assuming that black body radiation is the only loss process.

It is clear that temperatures over 2000°K can readily be achieved, and that even temperatures over 3000°K are feasible with high concentration ratios. This temperature regime allows a large number of high temperature chemical reactions for cyclic decomposition schemes to proceed with their attendant higher efficiencies. Efficiency is important because, other things being equal, the cost of a fuel-producing plant will be inversely proportional to its efficiency. Therefore, it is important to

Table 1-2. Approximate Specifications for Solar Thermal Test Facilities

Characteristic	Test Facility			
	Sandia	Georgia Tech.	White Sands	Odeillo
Total Thermal Energy, kW _{th}	5,000	400	30	1,000
No. of Heliostats	222	550	356	63
Heliostat Size, m	6x6	1.1 diam	0.6x0.6	6x7.5
Total Heliostat Area, m ²	8,257	532	137	2,835
Test Area Diameter, m ⁽¹⁾	2-3	0.3-1.0	0.08-0.15	0.25-1.0
Peak Flux, W/cm ⁽²⁾	250	375	400	1,600
Maximum Temperature, °K ⁽³⁾	2,570	2,370	2,720	4,070
Maximum Temperature/2 ^{1/4} , °K ⁽⁴⁾	2,161	2,000	2,290	3,422
<p>(1) For center area receiving approximately 1/2 of total energy, and area capturing 95 percent or more of total energy.</p> <p>(2) Small area at center of beam.</p> <p>(3) Maximum temperature of black body at center of beam.</p> <p>(4) 50 percent efficiency temperature, if radiation is only loss process.</p>				

consider the advantage of high operating temperatures that may be available from solar furnaces, even if the materials and engineering problems are difficult. The optimum temperature should be determined by an analysis of the increased efficiency versus the more severe engineering problems associated with the higher temperatures.

The remainder of the report covers the three applications areas for solar thermal fuels and chemicals activities: production of transportable fuels and open-loop storage, production of essential materials, and closed-loop storage. Within each of the sections describing an application area, information is presented on the current method of operation for the application, where applicable, as well as on the solar thermal approach for the application.

Section 2 presents a review of the technical literature on the use of thermal energy for the production of fuels, which are a form of open- and closed-loop storage. Section 2 also includes a review of the so-called hydrogen economy, together with a summary of its relationship to solar technology. Section 3 describes The Aerospace Corporation's transportable fuels and chemicals effort, which covers both the accomplishments to date and recommended future DOE-sponsored activities. Some new ideas for the use of high-temperature solar thermal energy in the production of essential materials, the production of hydrogen, and closed-loop chemical energy storage are presented in Section 4. Two appendices are included to present additional data on energy usage in the United States (Appendix A) and on open- and closed-loop thermochemical cycles (Appendix B).

2. LITERATURE REVIEW OF THERMOCHEMICAL CYCLES

In this section, the scientific literature on new methods of using thermal energy for the production of fuels, which are a form of open- and closed-loop storage, has been reviewed from 1966 to the present. Since the earliest paper on the subject of thermochemical cycles was published by Funk and Reinstrom (Reference 4) in 1966, the literature search should be complete. The data bases which were searched included Chemical Abstracts and the National Technical Information Service (NTIS) abstracts. No ideas, other than process heat, were found for the production of materials.

The literature search was accomplished by computer, utilizing the DIALOG abstract search system available at the Lockheed Data Center in Sunnyvale, California. The system searches titles and/or abstracts for key words. The key words may be required to be related to one another in a Boolean algebraic formula in order to constrain the search by a logical method. Thus, there may be a requirement for a title or abstract to contain words "A" and "B" or "C", but not "D". In practice, it was found that it was necessary to search only the title of an article to determine that the article was pertinent. When a search is run, the computer informs the operator how many articles in the data base fit the formula. Information on each article which fits the key words can then be printed out on request.

Each data base was searched three times by the three algorithms shown in Figure 2-1. These key word combinations were devised by fitting all of a set of 20 papers of interest in this field, which had been found manually. The search identified 332 "fits" which were printed and read as abstracts. Of these, 104 complete papers were obtained and read. Of these, approximately 70 were significant enough to be referenced in this report. While it is possible to overlook important papers in this type of search, the probability appears lower than missing a paper in a manual search. Furthermore, by stating the algorithm, it is possible to define all papers to be included with a certainty not possible in a manual search.

Water <u>or</u> Thermochemical	<u>and</u> Decomposition <u>or</u> Hydrogen	<u>and</u> Cycle <u>or</u> Cycles
Solar <u>or</u> Storage	<u>and</u> Thermochemical <u>or</u> Chemical	<u>and</u> Energy <u>or</u> Heat
Water <u>or</u> Solar	<u>and</u> Hydrogen <u>or</u> Thermal	<u>and</u> Decomposition <u>or</u> Production

Figure 2-1. Computer Search Algorithms

2.1 FUELS AND OPEN-LOOP STORAGE

This section reviews the literature on hydrogen production from water by means of electrolysis, thermal decomposition, and a recent hybrid system. Constraints on the choice of chemical systems for fuels, the potential of hydrogen as a fuel, and the utilization of solar technology for the production of hydrogen are also summarized in this section.

The vast majority of chemical systems currently in use are of the open-loop type. Fuels are produced by continual input of reduced forms of carbon, and the combustion products are released to the environment. Since the combustion products need not be returned to a primary energy source for reprocessing, such systems are simple to use and are particularly convenient for moving vehicles. The requirement that the products be released into the environment severely limits the number of chemical elements which may be used in open-loop systems. The relative scarcity and high toxicity of many forms of most elements eliminate them from serious consideration as open-loop systems. In fact, these constraints limit the compounds of interest for such systems to those containing hydrogen, carbon, nitrogen, and oxygen.

Solar energy can be used to produce hydrogen, which can be used directly as a fuel, from water. The direct use of hydrogen is a subject of major importance, and will be discussed in subsequent paragraphs. It would be desirable to produce carbon-based fuels with the use of solar energy

since tremendous amounts of energy are now required to hydrogenate coal and to refine petroleum. Replacement of the combustion heat, presently used to produce fuels, with solar heat is an important possibility but, since this is regarded as process heat, it is outside the scope of this report (see Reference 1).

One interesting possibility would be the direct thermal dissociation of carbon dioxide:

The reaction temperature, i.e., the temperature at which the equilibrium constant for the reaction is unity, is approximately 3350°K. If a process could be discovered to extract carbon dioxide inexpensively from the atmosphere or from industrial waste gases, this reaction (if feasible) would represent an open-loop, carbon-based fuel cycle. This cycle would not require any input of carbon but only a source of heat, such as solar energy, to produce carbon monoxide, which could then be used as a feedstock for the production of other fuels, such as methanol or methane.

An example of a nitrogen-based fuel would be ammonia (NH₃) or hydrazine (N₂H₄). These materials might be produced from air and water with the aid of solar energy and, since they are easily liquefied, they are simple to store. Because of these factors, the possibility of nitrogen-based fuels should not be dismissed. In fact, ammonia has already been tested as a vehicle fuel (Reference 5) and was shown to be feasible. It must be kept in mind, however, that ammonia and especially hydrazine are highly toxic materials which could be too dangerous for use by the general public, and that the heating value of ammonia is rather poor.

Some authors have suggested open-loop fuels based on boron and hydrogen (boranes) or silicon and hydrogen (silanes). However, both classes of compounds have a toxicity which is too high for general use (References 6,7).

2.1.1 Hydrogen

Hydrogen has been accorded a special position in this report for several reasons: (1) it has received more attention than any other element in the literature on fuels from solar or nuclear energy sources; (2) it is the most environmentally benign fuel because its combustion produces no carbon compounds and only minimal nitrogen oxides (Reference 8); (3) it is uniquely flexible as a medium of energy storage and transport; and (4) the thermodynamic and technical problems of solar-energized hydrogen production are typical of many programs for solar chemical energy storage or materials production.

The virtues of hydrogen have been cited in many publications (e.g., References 9,10). The element is itself an important industrial material, being used for the production of ammonia, methanol, and synthetic fuels, as well as for ore reduction and in food processing (Reference 11). Inexpensive hydrogen could result in greatly expanded use as a fuel and in ore reduction (References 12,13). The combustion of hydrogen in vehicles produces little nitrogen oxide if the proper adjustments are made (References 14,15). Hydrogen fuel in internal combustion engines does produce some hydrogen peroxide in the exhaust, but this should not present a severe problem (Reference 16).

Hydrogen could probably also be distributed through the natural gas system for household use (Reference 17). Over very long distances, hydrogen is less expensive to transport than electricity (Reference 18). Hydrogen is also comparatively easy to convert into electricity, especially if pure oxygen is cogenerated. The two elements may be recombined at high pressure to produce very high-temperature steam or recombined in a fuel cell to produce electricity directly (Reference 19). Thus, hydrogen is an important closed-loop as well as an open-loop storage medium. A novel feature of hydrogen is that it might be employed in chimneyless home heating because water is the only combustion product; such heating would also supply humidity and would be as efficient as electric heating.

The principal disadvantages of hydrogen are the difficulty of storage and questions about its safety due to accidental ignition and explosion. Storage as a gas is very inefficient because of its low-energy density, and storage as a liquid requires extreme cryogenic conditions. There is considerable promise in the storage of hydrogen as a metal hydride, but such a system is inevitably more difficult to use than the simple liquid hydrocarbons currently in use (Reference 20). With regard to safety, some writers feel that the hazards of easy spark ignition and wide explosion limits are offset by the rapid dispersal of accidentally released hydrogen gas (References 21,22). It is difficult to compare the relative safety of hydrogen and presently used fuels in quantitative terms. There is also serious doubt at this time that hydrogen can be produced as cheaply as fossil fuels.

These technical and economic disadvantages are balanced to some degree by the problems facing fossil fuels: (1) increasing scarcity and cost, (2) atmospheric pollution from surface mining, and (3) the possibility of problems from CO₂ buildup in the atmosphere (Reference 23).

2.1.2 Hydrogen Production

Hydrogen can be produced from water by three principal reactions: (1) reaction of water with carbon, (2) electrolysis of water, or (3) thermal decomposition of water in single or multiple chemical steps. The first method consumes fossil fuels and, although it might benefit from process heat generated with solar energy, no further consideration is given to it in this report.

2.1.2.1 Electrolysis

The electrolysis of water is commercially viable, although somewhat more expensive than the coal reduction process. The efficiency of the process is limited by the efficiency of the generation of electricity and the efficiency of the electrolysis cells.

The present method for electrolyzing water is to pass the current through an aqueous solution of sodium or potassium hydroxide, with the concentration chosen for minimum resistance (20-30 percent). The cell reactions are:

The minimum necessary voltage for this process is given by the Nernst equation:

$$\Delta G = -nFE,$$

where

ΔG = standard free-energy change for the reaction

n = number of electrons per reaction

F = Faraday's constant

E = volts

This minimum voltage decreases as the temperature is raised, according to the relationship:

$$\Delta G = \Delta H - T\Delta S$$

The exact temperature dependence is complicated by the fact that both ΔH and ΔS are also slightly temperature-dependent. In practice, the actual cell voltage will be higher than this because of the overvoltage phenomenon. Overvoltage is a reflection of the nonidealities of the cell and the kinetic limitations of the process. Since raising the temperature lowers both the ideal voltage and the overvoltage, the optimum would be to operate at the highest possible temperature.

Practical operating electrical efficiencies of 70-78 percent have been achieved with liquid water electrolyzers. Kissel, et al, (References

24,25) report laboratory operating efficiencies of nearly 100 percent. The theoretical maximum is 120 percent, which would correspond to the cell actually absorbing ambient heat.

The efficiency of electric power generation is, therefore, the major limitation on electrolysis, since power generation usually involves a Rankine cycle steam turbine and generator. Such cycles operate below the Carnot efficiency and presently achieve working efficiencies of 30-40 percent. Thus, the overall efficiency for conversion of heat to hydrogen via electrolysis with present technology is also in the range of 30-40 percent. This efficiency is a standard against which thermal decomposition schemes for water may be compared and, in general, should be exceeded if some new scheme is to be a serious candidate. However, capital investment in any scheme is a major consideration and there is no general agreement about the comparative capital expense of thermal decomposition schemes and electrolysis plants.

Three important new ideas have been advanced in the literature for improving the efficiency of electrolysis: (1) high-pressure electrolysis, (2) high-temperature vapor phase electrolysis, and (3) hybrid electrolysis-thermal decomposition cycles. High-pressure electrolysis (Reference 26) is fairly simple to implement and takes advantage of the fact that the required theoretical electrolysis voltage increases only slightly as the back-pressures of hydrogen and oxygen are allowed to rise, whereas the overvoltage tends to decrease substantially. Therefore, product gases may be delivered at high pressure at slightly lower voltage, resulting in a substantial energy savings. On the other hand, high-pressure cells would have an increased capital cost.

High-temperature electrolysis has been discussed by Bockris (References 27,28). Electrolysis of steam with solid electrolytes at very high temperature takes advantage of the decrease in the standard free energy change for water decomposition with increasing temperature, as shown in Figure 2-2. By operating at high temperatures of the order of 1000°C , the

required voltage will drop considerably since thermal energy is essentially substituted for electrical energy with a consequent gain in efficiency.

Hybrid cycles also substitute thermal energy for electrical energy by combining thermal decomposition with electrolysis in a complex chemical cycle. These schemes will be discussed in Section 2.1.2.3.

Figure 2-2. Theoretical Hydrogen Electrolysis Voltages as a Function of Temperature

All of these new ideas are important because they reduce the use of electricity, the most inefficiently produced element in the process.

2.1.2.2 Thermal Decomposition Cycles

Water may be decomposed directly into hydrogen and oxygen at very high temperatures or it may be decomposed in a series of chemical reactions, or "steps", which may use heat at a lower temperature than would be required for the direct decomposition. The idea of multiple-step decomposition of water appears to have originated with Funk and Reinstrom in 1966 (Reference

3). Much interest was generated in such processes by the cycles suggested by DeBeni and Marchetti in 1970 (Reference 29). Since then, many different cycles have been suggested through a combination of imagination and computer searching. Bamberger and Richardson compiled a list of 72 water decomposition cycles in 1976 (Reference 30) and a supplemental list of 129 more cycles in 1978 (Reference 31). These are given in Tables B-1 and B-2 in Appendix B. Computer searches for cycles have been conducted at the Institute of Gas Technology (Reference 32), at General Atomics (References 33,34), and by others (Reference 35). Many of the cycles in the Bamberger and Richardson list are based on incomplete thermodynamic data and are not feasible.

Water decomposition cycles may be categorized by the number of reactions in the cycle. The direct decomposition of water is, therefore, "one-step". Funk and Reinstrom suggested the form of two types of two-step cycles:

An example of a three-step cycle is No. 43 in Table B-1, Appendix B, i.e.:

Examples of higher numbers of steps also are given in Appendix B.

Examples of flow charts for several cycles, which have been prepared by Wentorf and Hanneman (Reference 36), are also shown in Appendix B.

A number of interesting papers have been written on the thermodynamics of water decomposition cycles, beginning with the Funk and Reinstrom paper. The thermodynamic efficiency problem is discussed in Section 1.2.2 and Appendix B.1.2.

It is clear from thermodynamic efficiency considerations that there is much to be gained from operating with the highest temperature cycles. However, most of the cycles were designed with the idea of minimizing the maximum operating temperature, so that nuclear reactors could supply the necessary heat. It is possible that concentrated solar radiation could provide a higher operating temperature than had been envisioned at the time most of the cycles were devised. Therefore, it is reasonable to assume that more efficient, higher temperature cycles may have been overlooked. With the possibility of higher temperature operation, a twofold gain in efficiency is possible through higher Carnot efficiencies and fewer steps. Reduction of the number of steps not only improves the thermodynamic efficiency but also lowers the capital and operating costs of a thermal dissociation process. On the other hand, higher temperature will increase these costs so that a tradeoff needs to be made to determine the preferred temperature.

There is another important efficiency consideration. That is the question raised in Section 2.1.2.1 about whether electrolysis is likely to be more efficient than thermal dissociation as a means of producing hydrogen from water. This is a highly controversial issue, and as many papers can be found in favor of electrolysis (References 27,28,35,37,38,39,40) as can be found in favor of thermal dissociation (References 19,41,42,43,44). The controversy seems difficult to resolve at this early stage, but it is clear that high-temperature operation could change the picture considerably for the efficiency of thermal dissociation cycles.

An example of a high-temperature cycle which was considered by Glandt and Myers (Reference 40), but rejected because of the high temperatures required, is the cesium cycle (Cycle No. 21 in Table B-1, Appendix B):

Cycles of this sort should be reexamined since the last step, which requires a temperature of 1500°C , is feasible with a source of high-temperature solar heat.

An important new idea for the direct one-step dissociation of water, which is shown in Figure 2-3, appeared recently in a paper by Fletcher and Moen (Reference 45). The idea is to heat a fine grid to 2500°K with focused sunlight and then allow steam to diffuse through the grid. Because H and H_2 diffuse much more rapidly than the oxygen-containing species, a substantial separation can be effected. The attractive part of this scheme is that diffusive separation is not sensitive to the grid material and might work for the separation of other materials as well (see Section 4). However, even with this kind of separation, there is still a severe materials problem since the grid must not only remain strong at the operating temperature, but also it must be chemically stable to both oxidation and reduction at that temperature. The authors suggest iridium or thorium oxide for the grid material.

In evaluating and comparing all thermal decomposition schemes, it is essential to remember that, in addition to the efficiency considerations, there may also be problems with product separation or reaction kinetics.

At very high temperatures, the reaction rate problem is not likely to be severe but the separation problem may be critical, especially if all species are gaseous. In this latter case, the species must be separated by some sort of "active" membrane or diffusion while still hot, or else quenched very rapidly before recombination. These problems are very severe, and could be insuperable for many systems.

Figure 2-3. Direct Dissociation-Diffusive Separation

For low-temperature multi-step processes, reaction kinetics are often ignored, and may be quite serious, since some suggested reactions may simply not take place at any useful rate. Since low-temperature schemes usually involve several phases of matter, the separation problem is somewhat more hopeful but can still render a scheme useless. It has been pointed out

(Reference 37) that small losses or difficulties at each separation step can severely reduce the economic efficiency of such processes.

Some important papers on the practical problems of cycles are those of Pangborn (Reference 44) and Coen-Portisini and Imarisio (Reference 46).

2.1.2.3 Hybrid Systems

Several hybrid systems employing more than one process have been introduced in the literature.

The Westinghouse Corporation (Reference 47,48) has developed a hybrid cycle which employs both thermal decomposition and electrolysis steps. The reactions are:

The system is shown schematically in Figure 2-4. The virtue of this hybrid approach is that the electrical work required for the oxidation of aqueous sulfur dioxide is only 15 percent of that required to decompose water directly, thus greatly reducing the amount of electrical power and, hence, the total energy required. This system is perhaps the most carefully studied of all the schemes for decomposing water since careful analysis of the operating conditions has been made (References 49-52).

Chao and Cox (Reference 41) mention a hybrid cycle due to Hallet which involves the electrolysis of hydrogen chloride:

The thermal step requires a temperature of 1000°K . Unfortunately, they calculate an efficiency of only 28 percent for this cycle.

Figure 2-4. Schematic of Westinghouse System

Schuetz (Reference 53) has discussed another hybrid cycle based on the electrolysis of HBr , which also requires a temperature of 1000°K for the second thermal step:

2.1.2.4 Utilization of Solar Thermal Technology for Hydrogen Production

On the basis of this review of the literature on the hydrogen economy, it appears that solar energy supplied from highly concentrated

solar radiation at high temperature could benefit schemes for the thermochemical decomposition of water. In this regard, solar thermal energy has the potential for being superior to nuclear reactor heat, which is currently limited to a maximum temperature of about 1100°K . The virtue of highly focused solar radiation is that it can open up a new regime of higher temperature, thereby improving the energy efficiencies of thermochemical cycles and permitting new chemical reactions to be used in those cycles. Since cycles operating at a higher temperature tend to have a smaller number of reactions, practical efficiencies should be improved still further. On the other hand, a higher temperature will increase the severity of any materials problem.

2.2 CLOSED-LOOP CHEMICAL ENERGY STORAGE SYSTEMS (CESS)

Closed-loop chemical energy storage systems (defined in Section 1.2.1) are expected to play a vital role in the development of solar energy systems and power plants. The critical need with respect to solar thermal energy systems is the development of energy storage capabilities for the 10 to 18 hours per day that the demand for energy exceeds the solar thermal system's output. There is also a need to develop a capability to have several days' energy stockpiled to act as a reserve for periods of cloud cover. In addition, there is the need to extract the process heat developed at the source in the most efficient manner and to transmit the derived energy to the user. Because of their greater potential efficiency, chemical energy storage systems (CESS) are considered to be prime candidates to displace the steam extraction, long-distance electrical energy transmission systems that now dominate energy distribution from power plants, at least when heat only is required.

This section discusses CESS in terms of criteria for their selection. The closed-loop energy storage system relationship to solar technology is also summarized.

2.2.1 Closed-Loop System Overview

The potential applications of CESS are not limited to solar power plants. In fact, during the past decade, the development of CESS has been primarily directed toward nuclear power plant application, with emphasis on working under the conditions of the high-temperature gas cooled reactor and the German pebble bed reactor at 1200°K (Reference 54). Consideration has also been given toward extracting energy from light water reactors which operate at lower temperatures. The main reason that more work has not been done to develop CESS to operate at temperatures above 1500°K is that the nuclear power plant applications did not warrant it. This inhibition does not apply to solar thermal power plants.

One important consideration in favor of CESS is that the energy can be transmitted and stored in the form of reactive materials at ambient temperature. The ambient temperature feature is very important since the stockpiling of energy from day to day or from season to season could be accomplished without loss.

A great many chemical systems have been proposed as candidates for CESS. The degree to which they have been subjected to analysis varies greatly. In many potentially interesting systems, there are insufficient thermodynamic data available to permit a thorough evaluation at this time. Several systems, notably the ADAM + EVA system, have been developed to the commercial stage. This section will present an overview of the proposed systems, including the candidate lists of several authors. The advantages of systems containing all gases will be compared with those of systems containing condensed phases.

A principal approach to chemical energy storage has been to subject well-established commercial chemical synthesis processes to some degree of engineering analysis in order to identify good candidates for closed-loop CESS. The idea has been to adapt and modify processes for CESS use with a maximum direct carry-over of technology. The approach has been similar in efforts to develop closed-loop CESS for energy transmission.

In addition, there have been recent efforts to identify new candidates for CESS. This later effort has evolved through two steps: (1) establishing criteria by which ideal candidates can be identified, and (2) systematically evaluating the potential of a large number of reactions to see if they meet the criteria for "ideal systems".

2.2.2 Criteria for Selecting Closed-Loop Chemical Energy Storage Systems

Every effort should be made to stimulate the detailed analysis of new systems which could serve as CESS, using the best available thermodynamic and kinetic data, and to support research and development work on the most promising candidates. Criteria that will be useful in identifying and properly characterizing promising closed-loop CESS are suggested and discussed next.

2.2.2.1 System Enthalpy and Working Temperature

The first steps toward characterizing the potential of a given reaction (or series of reactions) to serve as a closed-loop CESS are to establish the temperature range over which it operates effectively and to characterize its heat of reaction per unit weight or unit volume under the conditions proposed for the minimum and maximum operating temperatures. In general, the heat absorbing temperature (high) and the heat releasing temperature (low) will be separated by different amounts for different systems, and this will determine the thermal efficiency of the system. This question is complex and is discussed in Appendix B.2.1. Two different methods of rating such systems are suggested in the Appendix: one based on the maximum and minimum working temperatures for a system, and another method based on the heat storage density available for two given working temperatures.

The data used in the JANAF tables (Reference 55), or some other source which embodies true temperature-dependent heat capacities (C_p^0), enthalpies (ΔH^0), entropies (ΔS^0), and Gibbs free energy (ΔG^0), should be used to derive these representative temperatures and reaction

heats. It is most important to recognize that, at high temperatures in particular, all equivalent reaction channels must be investigated to identify the species with the lowest Gibbs energy.

It is essential to tabulate values of ΔH per unit mass and per unit volume since this information is required to establish the masses of material needed to transport and to store a given amount of energy for the reaction of interest. This has a direct bearing on the ultimate cost of the reactants to be used, and on the size and cost of the transmission network and the storage facility. It is obvious that a reaction having all liquid reactants and products will have 10^3 to 10^4 times smaller storage and transmission line requirements at one atmosphere than one involving all gases if the molar heats of reaction are identical.

2.2.2.2 Further Criteria

In addition to the thermochemical criteria listed above, it is useful to draw attention to other properties of a proposed system to assist in the evaluation. The relative importance assigned to these criteria will depend upon the way the CESS is to be used (i.e., transmission or storage), the nature and size of the planned operation, and also upon how soon the system is to be employed. Wentworth and Chen (Reference 38) proposed a set of ten criteria for selecting CESS which were further elaborated on and developed in an OTA report (Reference 33). The criteria listed in the OTA report are repeated here for convenience:

- (1) The reaction should be nearly complete within the temperature range of available collectors. In practical terms, it would be desirable to have 95 percent completeness at temperatures below 1000°C.
- (2) The reverse reaction should be nearly complete at the temperature at which useful energy is to be extracted. If the reaction is to be used in connection with a conventional power plant, this temperature would be approximately 500°C; if a Stirling cycle or Brayton cycle device were to be used, the temperature should be closer to 800°C.

- (3) The reversible reaction should be able to release energy for the user at temperatures close to those required for the solar collector reaction. OTA states here that the collector temperature should be as low as possible to minimize material problems and to maximize collection efficiency.
- (4) The energy absorbed per unit volume of the products stored should be as large as possible to minimize the volume of storage. It would be most desirable to be able to store the reaction products in liquid form to reduce both the storage costs and the energy losses in pumping the stored material.
- (5) The reaction should be completely reversible and no side reactions should occur to produce contaminants in a closed-cycle system. These side reactions would tend to create products which would accumulate and eventually poison the system.
- (6) Reactions should be fast.
- (7) None of the reactions involved should require extensive development of new chemical techniques and should not require expensive or elaborate equipment. This is of paramount importance for on-site equipment not operated by trained personnel.
- (8) The reaction products should not react strongly with water or oxygen, since it would be difficult to seal the system against these materials.
- (9) The materials used should be inexpensive and should not require chemicals for which shortages are likely to develop.

In addition, Wentworth and Chen listed two additional criteria:

- (1) for an uncatalyzed reaction, the products must be readily separated prior to storage and
- (2) for a catalyzed reaction, the product mixture must be stable during the storage period.

The first three criteria in the list could be quantitatively analyzed in terms of Method B described in Appendix B.2.1. However, the thermodynamic advantages of higher temperature operation should also be kept in mind. Criterion 4 seems particularly important for energy storage systems, but might not necessarily eliminate gaseous reactions from

consideration in the transmission of energy from very high-temperature sources.

At this early stage, criteria 7, 8 and 9 should not be stressed to the point of excluding the investigation and the development of new systems. These last three criteria certainly are important for systems to be adopted in the near future. Wentworth and Chen's remaining two criteria, which relate to separation of reactants and stability in storage, also require further analysis. For example, the development of effective inhibitors might dramatically affect the suitability of a particular CESS.

2.2.3. Candidate Systems

At this early stage in the development of CESS, it is important to consider as wide a range of potential candidates as possible. The first step toward identifying such candidates could reasonably include the systematic analysis of the representative enthalpies and working temperatures of a wide range of reactions. Three such tabulations are listed in Appendix B.2.2, taken from works by Schmidt (Reference 56), Hildebrandt, and Wentworth and Chen (Reference 38). Two processes from this list are of particular interest because of their large ΔH /unit mass:

From the point of view of energy storage, the NaF system would offer the advantage that the reactants and products are in the condensed phase, with HF being readily stored as a liquid.

Other candidates are described in the following paragraphs.

2.2.3.1 Gaseous Systems

Gaseous systems also have special virtues. It has been shown that the transmission of thermal energy over long distances by the use of gaseous

reactants can be more economical than by electrical transmission. It is also reasonable to use gaseous reactants to extract energy from high-temperature solar towers. An enormous capital investment is required, however, to store very large quantities of energy in the form of separated gaseous reactants. Therefore, at this point, on-site energy storage systems containing condensed phases, even solids, can play a very useful role.

To date, six systems described in the literature have been subjected to detailed engineering analysis regarding their suitability for employment in closed-loop CESS. The results of these analyses are summarized in following paragraphs. One of those systems, ADAM + EVA, (see Section 2.2.3.6) is being installed in a network in Germany for large-scale energy transmission (Reference 54). It should be noted that four of these systems are direct adaptations of major chemical processes: methanol formation from CO and H₂, ammonia synthesis from N₂ and H₂, sulfuric acid production via SO₂ and oxidation to SO₃, and methane synthesis from CO and H₂ (used in ADAM + EVA). It should also be noted that these four processes are dependent upon catalysts so that the reactants can be stored together indefinitely in the absence of the catalysts. The ammonium hydrogen sulfate system (AHS) was developed specifically to serve as a closed-loop CESS and has several important advantages over the other systems that are mentioned. The H₂O, H₂, O₂ system is mentioned briefly for the sake of completeness, since it was discussed under open loops in Section 2.1.

2.2.3.2 The Methanol Reaction System

The first of the systems analyzed is the methanol reaction system:

The heat of reaction is approximately 25 kcal/mole at the reaction temperature of 420°K. However, the reaction temperature can be increased by going to higher system pressures.

The commercial synthesis of methanol from CO and H₂ is a well established process technology. Stiles (Reference 57) has recently written a comprehensive review of the history, development, and current status of the technology associated with the synthetic process reaction aimed at assessing the commercial potential of methanol as a fuel to replace fossil fuels.

Prengle and Sun (Reference 58) recognized that this fully developed and mature technology could be used in the near term for a CESS based upon the synthesis and decomposition of methanol. They carried out a preliminary engineering feasibility analysis of such a CESS and concluded that the cycle would operate with a heat efficiency of 87 percent, a work efficiency of 31 percent, and would require the circulation of 3.6 tons of methanol/MW-hr of electrical energy produced. It is their conclusion that it is feasible to develop a CESS based upon the methanol system.

One distinct advantage of this system is the fact that the CO and H₂ require a catalyst to react. Because of this, there is no need to separate the gases during transmission or storage. The return half of the cycle is simplified because methanol is a liquid. The system is, therefore, close to an optimum energy transmission system. It is less favorable as a large-scale energy storage system because the energy would be stored in high-pressure gases. More favorable cases, of course, would involve energy storage in liquids for which $\Delta H/\text{volume}$ would be quite large.

Detailed analyses by Prengle and Sun characterize the thermodynamics of the forward and reverse reactions as shown in Appendix B.2.3. Their representation of a solar cycle using methanol follows. In Figure 2-5, E refers to heat exchangers, R to reaction chambers, P to pumps, S to storage containers, and T to turbines.

The overall heat of reaction is 84 kcal/mole at the equilibrium temperature of 740°K.

In contrast to the other five systems discussed in this section, the ammonium hydrogen sulfate system (AHS) is not part of a well established commercial process. It has been chosen for potential study and development as a CESS because it has several very favorable characteristics: (1) a very large heat of reaction; (2) the potential of an output temperature high enough to be suitable for use in electrical power generation; (3) the products of NH_4HSO_4 decomposition, NH_3 , H_2O , and SO_3 , can all be transmitted and stored as liquids, which is an optimum situation; and (4) the reaction product, NH_4HSO_4 can be transmitted as a liquid at temperatures above 420°K. The one disadvantage of the system is that the ammonia solution and the SO_3 must be transmitted and stored separately. Fortunately, the decomposition process can be carried out in two steps so that there is no direct problem in separating the SO_3 from NH_3 .

Prengle and Sun (Reference 58) have also carried out a feasibility study of the AHS system. Their assessment of the AHS system is that it is the most attractive system examined to date as a possibility for an operational cycle. The cycle is superior to the methanol system for the reasons just stated. The reaction has a 62 percent heat efficiency, a 34 percent work efficiency, and requires 3.8 tons of AHS circulation per MW-hr of electrical energy output.

The detailed thermodynamics of the AHS system, as characterized by Prengle and Sun, are in Appendix B.2.3. Their proposed operational cycle is shown schematically in Figure 2-6, using the same symbols used in the methanol discussion. The corresponding AHS cycle energy analysis is also given in Appendix B.2.3. Prengle and Sun do not present an economic analysis of the system.

Figure 2-6. Operational AHS Cycle

2.2.3.4 The Ammonia System

This process is expressed as follows:

The heat of reaction is approximately 13 kcal/mole at the process temperature.

The commercial synthesis of NH_3 using reactant gases and catalysts at high pressure is one of the most thoroughly investigated and characterized of industrial technologies. P. O. Carden (Reference 59) has suggested that the dissociation and resynthesis of NH_3 could serve as an efficient CESS devoted to the transmission of energy rather than for on-site energy storage. He has carried out a detailed analysis of the engineering feasibility of the system which is presented, in part, below. One aspect of the NH_3 system that he stresses is that, although $\Delta H^\circ/\text{mole}$ for NH_3 is small compared to that associated with a number of other candidates,

$\Delta H/\text{gm}$ is comparable to that obtained with other candidates. This is illustrated in Table 2-1. Carden goes on to list the advantages of the NH_3 system over the $\text{SO}_3 = \text{SO}_2 + 1/2 \text{O}_2$ system proposed by Chubb and discussed later in this section.

Table 2-1. Heat of Reaction Comparison

Reaction	Heat of Reaction	
	kcal/mole	kcal/gm
$\text{SO}_3 = \text{SO}_2 + 1/2 \text{O}_2$	+23.6	0.29
$1/2 \text{H}_2\text{O} + 1/2 \text{CH}_4 = 1/2 \text{CO} + 3/2 \text{H}_2$	+26	1.44
$\text{COCl}_2 = \text{CO} + \text{Cl}_2$	+26	0.26
$2\text{NF}_3 = \text{N}_2 + 3\text{F}_2$	+31	0.43
$\text{CH}_4 + \text{CO}_2 = 2\text{CO} + 2\text{H}_2$	+59	0.98
$\text{CH}_3\text{OH} = 2\text{H}_2 + \text{CO}$	+25	0.78
$\text{NH}_3 = 1/2 \text{N}_2 + 3/2 \text{H}_2$	+13.5	0.79

Carden's stated advantages are repeated here for convenience. "In comparing the present system with the one proposed by Chubb (Reference 60), it is felt that the former offers the following advantages:

- (1) It is less hazardous, since any ammonia which might accidentally escape is lighter than air. On the other hand, both sulphur dioxide and sulphur trioxide are heavier than air and, at the same time, are extremely toxic and form corrosive products.
- (2) Approximately 50 times more energy is transferred per unit volume.
- (3) Pipes and some other components are smaller and less massive.

(4) There should be fewer potential difficulties with materials since the operating temperatures are lower and there is more flexibility in their final choice.

(5) The catalyst is likely to be less expensive.

An additional important advantage of this reaction, and a characteristic of most processes requiring catalysts as well, is that the reactants N_2 and H_2 can be transmitted and stored together at high pressure without the potential of reaction. Thus, only one high-pressure gas pipe is needed for the delivery system, and one high-pressure liquid carrying pipe for the NH_3 return.

Carden also addresses various aspects of the NH_3 system and provides an economic analysis of the proposed system. He concludes that the ammonia system should be given continued consideration as a CESS devoted to energy transmission. A schematic diagram of the proposed system from Reference 57 is reproduced in Figure 2-7. Carden presents a detailed and systematic thermodynamic analysis of the system, which is given in Appendix B.2.3.2. This information allows Carden to optimize the system design as a function of the currently available technology. He has analyzed the reaction kinetics as a function of temperature to further characterize the system and performed a careful engineering analysis of the proposed system, including an estimate of system costs. He concludes that there is every reason for the further study and development of the system.

2.2.3.5 The Sulfur Trioxide System

This process is expressed as follows:

The heat of reaction is approximately 24 kcal/mole at a reaction temperature of 1040°K.

1. Sun's rays.
2. One of many paraboloidal mirrors.
3. Focal absorber.
4. Mirror unit counter-flow heat-exchanger.
5. Gas carrying tubes from other mirror units.
6. Central plant catalytic synthesizer.
7. Central plant counter-flow heat-exchanger.
8. Central plant ammonia separator.
9. Gas circulating pump for synthesis loop.
10. System compressor.
11. Gas circulating pump for coradiation.
12. Gas coradiation tubing.
13. Heat output to engine.

Figure 2-7. Schematic Diagram of Proposed NH_3 System

The catalytic oxidation of SO_2 to SO_3 is a critical step in the production of H_2SO_4 . Because of the enormous industrial and commercial importance of H_2SO_4 , the technology associated with the oxidation of SO_2 is fully developed and mature. Chubb (References 60,61) has proposed the SO_3 system as a CESS. The potential advantages of the system include: (1) its high enthalpy of reaction; (2) the fact that it can be used to absorb energy at over 1000°K and regenerate it at $500\text{--}600^\circ\text{K}$, which are temperatures appropriate for solar collectors and electric energy generators; (3) the fact that the necessary technology is already on hand; and (4) the potential of SO_2 and O_2 to be piped and stored together in the absence of specific catalysts. The disadvantages of the system are mentioned by Carden and summarized above. The analysis of Chubb is primarily directed toward evaluating the engineering requirements of the solar power plant as a whole. Appendix B.2.3.3 presents a schematic outline of the proposed plant and also contains some thermochemical information on the $\text{SO}_3 = \text{SO}_2 + 1/2 \text{O}_2$ reaction.

Like the NH_3 system, the SO_3 system seems primarily intended as an energy transmission system. In some developments of this concept, the O_2 is removed from the system, allowing liquid SO_3 and liquid SO_2 to be the transmitted and stored materials. This necessitates an on-site source of pure O_2 and a very effective program for separating O_2 from SO_2 at the solar collector end of the system.

2.2.3.6 The ADAM + EVA System

This process is expressed as follows:

The heat of reaction is approximately 49 kcal/mole at a reaction temperature of 960°K.

The commercial synthesis of methane from CO and H_2 is a well established process. For the past several years, there has been extensive interest in developing a CESS based on this process. The original motivation (Reference 54) was the development of a system to transmit energy more efficiently than electrical power in order to utilize the energy output of nuclear reactors. The name EVA refers to the chemical reactor for producing CO and H_2 (Einzelspaltrohr-Versuchsanlage). ADAM refers to the downstream methanator end of the process. This system is being readied for full scale development in Germany. A schematic representation of the original system is shown in Figure 2-8.

To characterize these systems further, the dissociation fractions of the $\text{H}_2\text{O} + \text{CH}_4$ reaction are compared with those of the SO_3 reaction in Appendix B.2.3.4.

A more detailed discussion of the $\text{CH}_4 + \text{H}_2\text{O}$ reaction, as given by Hanneman, Vakil, and Wentorf (Reference 62), is shown in Appendix B.2.3. This system is primarily being developed as an energy transmission system.

Figure 2-8. Energy Transmission System ADAM + EVA

It is compatible with existing natural gas pipelines, giving it enormously increased commercial potential. The fact that the energy carriers, CO and H_2 , are gases limits the potential value of the system for energy storage.

As with the other systems which require a catalyst, the CO and H_2 can be piped together at very high pressures so that only one pipe is needed from the source to the user. It still seems to be an open question whether the H_2O generated at the station is to be returned to the solar energy generator in a closed cycle or if it is to be scrubbed and released to the atmosphere.

2.2.3.7 The H_2 , O_2 , H_2O System

This system was discussed in Section 2.1. Because it is environmentally benign, hydrogen may be used as an open-loop energy storage and transport medium, and schemes for hydrogen energy storage were presented in the section on open loops. As a closed-loop system, hydrogen does have certain virtues which will be mentioned here.

Any process which decomposes water cyclically also produces oxygen. If the hydrogen and oxygen are both stored, then the energy may be recovered with high efficiency in either fuel cells or high-temperature steam turbines. In fuel cells, the hydrogen and oxygen may be recombined to produce electricity directly with high efficiency. In turbines, the hydrogen and oxygen may be burned in specially designed burners to produce high-temperature, high-pressure steam. In any such combustion process, the temperatures which can be achieved with hydrogen are quite high, yielding high thermodynamic efficiencies for subsequent processes.

2.2.4 Utilization of Solar Thermal Technology for Closed-Loop Systems

The implementation of solar thermal power for any major use requires some form of energy storage in order to average out the intermittent input. As a rule, the larger the storage capacity, the better (not considering costs). While fuels are an excellent means of storage, there are cases in which the large number of possible closed-loop systems could be an advantage. For example, a tremendous number of different chemical systems are permissible since problems with high expense and environmental release are not as severe as they are in open systems. Also, some closed-loop systems are simpler to implement than hydrogen cycles, which tend to be complicated.

In view of these considerations, it is somewhat surprising that more closed-loop systems have not been suggested since the possibilities are almost limitless. High temperatures improve the efficiencies and the number of feasible chemical reactions in closed-loop systems as they do in open-loop systems. The efficiency problem is severe in the case of closed loops where work must be delivered at the consuming end. In this case, the work must be generated with a Carnot efficiency limited by the lower temperature in the CESS cycle, so high temperatures are doubly important. If heat at a specified temperature is required by an industrial process, then a CESS which matches this delivery temperature can be very simple and efficient.

2.3 LITERATURE SURVEY FINDINGS

Numerous ideas were found in the literature for using heat for the production of one fuel (hydrogen) and for several chemical energy storage techniques. However, no new ideas were found for using heat to produce metals or other energy-intensive materials, other than the simple application of process heat. With few exceptions, mating these processes to solar energy sources has not been considered. In only one case, i.e., the direct decomposition of water, has the use of very high-temperature solar energy been considered.

Nevertheless, high temperature from concentrated solar radiation is a fundamentally new capability with many potential advantages. Much of the technology and chemistry for fuels production, metal reduction, and chemical energy storage needs to be reviewed in the light of this new high-temperature capability.

3. NEW IDEAS FOR TRANSPORTABLE FUELS

This section presents the elements of a new concept for a carbon cycle recovery technique to produce transportable fuels. The elements of the concept are discussed in the following sequence:

- Sources of carbon dioxide
- Solar energy reduction of CO₂
- Potential carbon cycles
- Use of carbon monoxide as fuel and feedstock

The section also contains recommendations for future areas of DOE programmatic support for a solar fuels and chemicals program.

3.1 SOURCES OF CARBON DIOXIDE

It is highly desirable to obtain carbon dioxide from abundant, existing sources. This can be accomplished in both the near-term and far-term by the methods to be described in this section. In the initial applications of the processes suggested here, the most economical sources to use would be enriched sources of CO₂, such as industrial stack gases, CO₂ wells, fermentation operations, and calcining operations. However, if an economically viable commercial operation can be established to scrub the CO₂, the best long-term source of CO₂ would be the atmosphere.

3.1.1 Current CO₂ Availability

Carbon dioxide is readily available from such sources as power plant stack gases which contain from 12 to 18 percent of CO₂. The CO₂ is separable from the balance of the flue gases by several commercial processes currently used for the production of liquid CO₂ and dry ice. Optimal use of this source would tend to alleviate CO₂ pollution problems.

Representative of these commercial CO₂ extraction processes is the Girbotol amine process, which is in wide use for dry ice production. This process is illustrated in Figure 3-1 which shows a series of cleaning

and separation steps. Essentially the stack gas is absorbed into an amine solution, which serves to pass the CO₂-free gas out of the system and send the solution on to a series of pumps and heat exchangers. The CO₂ is subsequently stripped from the solution and passed on in a gaseous state. It is common to have additional purification stages in the process, e.g., scrubbing with an aqueous solution containing potassium permanganate to remove traces of hydrogen sulfide.

Figure 3-1. Extraction of Carbon Dioxide from Stack Gas

3.1.2 Future CO₂ Availability

New schemes are necessary to accomplish more efficient extraction of carbon dioxide in the future. Such schemes are pertinent, since the CO₂ content of the atmosphere is 0.033 percent and increasing at a measureable rate. Concentration of this CO₂ to one atmosphere pressure requires a Gibbs energy expenditure of:

$$\Delta G = -RT \ln P_{\text{CO}_2} = +4.75 \text{ kcal/mole}$$

Absorption of CO_2 by calcium oxide would require an energy penalty of 42 kcal/mole, thus reducing any efficiency by 45 percent. For MgO , the penalty is 28 kcal/mole, or 39 percent. Carbon dioxide at its atmospheric partial pressure will be picked up by aqueous solutions if the pH is greater than about 10. A convenient industrial process which is capable of collecting CO_2 from the atmosphere is again the Girbotol amine process, which would react aqueous monoethanolamine (MEA) or diethanolamine (DEA) with CO_2 to form carbamates (Reference 63). The solution decomposes at 400°K to release the CO_2 . The energy penalty for this process should be about 32 percent for MEA or 23 percent for DEA, but the process is very convenient because the system is liquid.

A potential problem for this scheme lies not in thermodynamics but in kinetics. The rate of heterogeneous absorption of CO_2 by the liquid is given in Reference 64 as:

$$\frac{d(\text{CO}_2)}{dt} = 1/4 n \bar{v} \phi A,$$

where: n = atmospheric concentration of CO_2
 $\bar{v}$ = average molecular velocity for CO_2
 ϕ = collision efficiency
 A = area of surface

This expression assumes no limitations due to diffusion or transport; however, this is reasonable for small values of ϕ , which contains all the kinetic information. A number of papers have been written on the rate of CO_2 absorption by alkaline and amine solutions (Reference 65). Unfortunately, the rate is rather low, corresponding to a collision efficiency of about 4×10^{-5} for MEA in water. This corresponds to about two metric tons per day (24 hr) per 10^4 m^2 of liquid surface, which is disappointingly slow. This rate corresponds to an energy input less than the average sunlight energy input. In spite of this, it is clear that a catalyst for raising the collision efficiency, or some effective scheme to

increase the area, might improve things considerably. A completely different approach based on solids, which are less convenient to handle but have high specific areas, might be faster.

Figure 3-2 depicts a conceptual system for the collection of atmospheric carbon dioxide. A "lake" of aqueous ethanol amine or other basic solution continuously picks up CO_2 from the air. Liquid from the lake is circulated to a low-temperature solar heater (400°K), which strips the concentrated CO_2 out of solution. This CO_2 is then delivered to the high-temperature facility where it is decomposed into carbon and oxygen by means of a multistep thermochemical cycle. At no penalty in theoretical efficiency, the carbon can then be heated with more CO_2 at temperatures above 1000°K to give carbon monoxide as a product, if this is more convenient.

3.2 REDUCTION OF CO_2 WITH SOLAR ENERGY

High-temperature solar energy from state of the art solar thermal systems can be used to reduce carbon dioxide. These systems are summarized in Section 1.3. One advantage of carbon dioxide reduction with solar energy is the higher theoretical efficiency discussed in the following paragraphs.

Carbon dioxide may be reduced with carbon to carbon monoxide at temperatures above 1000°K :

At 1000°K , $\Delta H = +40.8$ kcal, and $\Delta G = -1.1$ kcal.

Since the reaction is endothermic by 40.8 kcal, this energy must be supplied by an external source such as the sun. This energy can then be recovered when the carbon monoxide is burned because the heating value of two moles of CO is greater than the heating value of one mole of carbon by approximately 40 Kcal (the exact value varies with the temperature):

$$2\text{CO}: \Delta H_c = -133.54 \text{ kcal}$$

$$\text{C}: \Delta H_c = -93.97 \text{ kcal}$$

Figure 3-2. Carbon Dioxide Recovery Process

The efficiency of the cycle is 0.97, i.e., 39.6/40.8. In a similar comparison with hydrogen production, the efficiency is only 0.75 because of the energy lost in the vaporization of the water.

For the near term, an external source of carbon, such as coal or coal liquefaction char, could be used to reduce CO_2 to CO. For the long term, carbon produced by the carbon recovery technique described in Section 3.3 would ultimately be used as a means of conserving fossil energy resources. Solar energy used in this way extends the heating value of carbon by 43 percent (i.e., 134/94). This could be an attractive process with a cheap source of CO_2 . However, extraction of the CO_2 by the Girbotol process incurs an additional penalty of about 22 kcal/mole of CO_2 , which reduces the theoretical efficiency for producing fuel with sunlight from 97 percent down to 63 percent. Nevertheless, the convenience of CO and its potential use as a feedstock material still make the scheme worthwhile.

3.3 POTENTIAL CARBON CYCLES

To efficiently utilize carbon dioxide in the long term for producing carbon monoxide, it was necessary to identify a potential carbon dioxide reduction process where carbon required for the reduction can be produced by the process itself. The following paragraphs provide an overview and details of the cycles identified.

3.3.1 Overview

Carbon dioxide can be decomposed directly to carbon monoxide and oxygen at very high temperatures, or decomposed to carbon and oxygen at intermediate temperatures by means of cyclic decomposition processes completely analogous to those for decomposing water. The temperature for direct decomposition is extremely high:

Therefore, it is necessary to look for cyclic schemes for decomposing CO₂ at somewhat lower temperatures. This was suggested by S. Dorner and C. Keller in 1975 (Reference 66), but has not been followed up. The virtue of decomposing CO₂ with solar energy is that a feedstock is obtained for carbon-based fuels without depleting fossil fuels. Such fuels have all the advantages of the easy storage and high density of fossil fuels without many of the environmental problems associated with such fuels.

Before listing some suggested cycles for reducing carbon dioxide, it should be pointed out that all hydrogen and carbon cycles are connected by the well-known water-gas shift reaction:

Whichever route is ultimately taken will depend on the efficiencies and costs that can be achieved.

A number of cycles for decomposing carbon dioxide are summarized in Table 3-1; they are shown primarily to illustrate a range of possibilities. Additional cycles, which might be superior for practical use, might be derived by computer. These cycles obey stringent thermodynamic criteria, and great care has been exercised in the thermodynamic calculations. Details of the efficiency calculations are given in Section 1.2.2. The efficiencies quoted first are the thermal yield efficiencies, while the second efficiencies are those which take into account the separation work for a suggested chemical separation scheme. Efficiencies given in parentheses mean the separation work is small and has been neglected.

Details of the separation problems are given in Section 3.3.2 for the cycles of Table 3-1. These cycles have reasonable efficiencies, and look quite good when compared with the efficiencies of hydrogen cycles. Efficiencies given in the literature for water decomposition cycles are based by convention on the higher heating value of hydrogen, which is the enthalpy released when liquid water is the end product of combustion. Such

efficiencies are not realizable in most applications, not even in fuel cells, since steam is usually the end product. The full heating value of carbon is available at all practical temperatures and, therefore, should be compared with the lower heating value efficiencies of the hydrogen cycles for fair assessment.

Table 3-1. Potential Carbon Cycles*

Cycle	Theoretical Efficiency (Percent)	
	Without Separation	With Separation
<u>Open-Loop Cycle Using External Carbon Source</u>		
$C + CO_2 = 2CO$ (1000°K)	98	
<u>Closed-Loop Cycles to Produce Carbon</u>		
<u>Direct Reduction of CO₂</u>		
$2Cd(l) + CO_2 = 2CdO + C$ (600°K) $2CdO = 2Cd(g) + O_2$ (1900°K)	56	46
$2Zn(g) + CO_2 = 2ZnO(s) + C$ (1300°K) $2ZnO = 2Zn(g) + O_2$ (2400°K)		
$2CoO + 2SO_2 + CO_2 = 2CoSO_4 + C$ (500°K) $2CoSO_4 = 2CoO + 2SO_2 + O_2$ (1400°K)	60	(60)
<u>Secondary Reduction of CO₂ via CO</u>		
$C + CO_2 = 2CO$ (1000°K) $2CO + 4Fe_3O_4 = 6Fe_2O_3 + 2C$ (500°K) $6Fe_2O_3 = 4Fe_3O_4 + O_2$ (1800°K)	62	20
$C + CO_2 = 2CO$ (1000°K) $2Ni + 2CO = 2NiO + 2C$ (600°K) $2NiO(l) = 2Ni(l) + O_2$ (2850°K)		
	60	49

* Patent applications for these cycles have been filed by L. R. Martin through The Aerospace Corporation in February 1978.

Other cycles can be devised that are based on tin or alkali metals. However, the separation problems are very severe for these cycles and the efficiencies are poor.

3.3.2 Detailed Description of Carbon Cycles

In calculating the thermodynamics of these cycles, all Gibbs energies and enthalpies are from the JANAF Tables (Reference 55), where available; the remaining values are from four-term expressions for the heat capacity data in the Bureau of Mines Tables (Reference 67) and the A.E.C. Tables (Reference 68). No reactions are included which have positive Gibbs free-energy changes. While it is possible to have industrial processes based on positive free-energy changes, such processes require the application of work (usually in the form of pumping work) which equals the amount of free energy required (Reference 69). Since such work must usually be supplied by electrical energy, a great penalty in efficiency is taken for such processes.

Also, the problem of product separation has been addressed in all cases. Only in the case of the iron cycle (described in Section 3.3.2.1) is the problem not satisfactorily resolved, at least on paper.

The efficiencies are estimated from the expression:

$$\epsilon = \frac{\Delta H_f^{\circ}(\text{CO}_2)}{\sum \Delta H_r}, \quad (\text{all positive enthalpies})$$

where $\Delta H_f^{\circ}(\text{CO}_2) = -94.0 \text{ kcal.}$

For each cycle, an "as written" efficiency is quoted, which includes the enthalpies of all reactions shown and the enthalpies of any phase transitions encountered in going from one reaction to the next. This is the convention used in quoting hydrogen cycle efficiencies although sometimes the phase changes are not included in H_2 efficiencies. Next, an efficiency is quoted which includes the enthalpy required for chemical product

separation although, in some cases, this enthalpy may be obtained from exothermic reactions in the cycle. Not included are the enthalpies required to change the temperature of reactants, since this may be obtained ideally by heat exchange with the products. Therefore, the efficiencies quoted are "ideal" efficiencies, but they include all theoretical energy requirements.

3.3.2.1 An Iron-Based Cycle

Figure 3-3 shows an iron-based cycle with primary chemistry as follows:

The efficiency of this cycle as written is 62 percent, i.e., $94.0/(40.8 + 110.0)$. Product separation in the third step is no problem because Fe_3O_4 is a solid at the reaction temperature and the oxygen can simply be pumped off. The separation in the second step presents problems, although the Fe_2O_3 could be removed from the carbon by dissolving it in acid:

This reaction is easily reversed with steam, but the energy penalty for generating the steam is great and the final efficiency would be only 20 percent. Furthermore, the excess enthalpy from the second step is unable to compensate for this loss. Therefore, in order for the iron process to be practical, some other separation of ferric oxide and carbon must be found. Depending on the state of the reaction products, it might be possible to employ physical methods of separation such as those in ore refining

Figure 3-3. An Iron-Based Cycle

operations; i.e., electrostatic, electromagnetic, flotation, or density separations. Such techniques might also apply to the other metal oxide separations.

3.3.2.2 A Nickel-Based Cycle

Figure 3-4 shows a nickel-based cycle with primary chemistry as follows:

The efficiency of this cycle is 60 percent, including the heat necessary to melt the nickel oxide in the third step. As in the iron cycle, the separation of oxygen is facilitated in the third step by the fact that nickel is still in the liquid phase at $2850^\circ K$. Needless to say, the materials problems would be extremely severe for this reaction. The separation of NiO and C in the second reaction could be performed by dissolving the nickel oxide in an ammonia solution:

Reversal of this reaction involves an energy penalty (to 49 percent), but some heat for this is available in the second step. As in the other cases, a physical separation might be more efficient. Another potential problem is that it might be necessary to find a catalyst for the second reaction, since the rate might be slow. Also, the second reaction must be run above $500^\circ K$ to prevent the formation of nickel carbonyl.

Figure 3-4. A Nickel-Based Cycle

3.3.2.3 A Cadmium-Based Cycle

Figure 3-5 shows a cadmium-based cycle with primary chemistry as follows:

This cycle has an efficiency, as written, of 56 percent, which does not include losses due to separation work. The separation of the CdO and C products may be accomplished by dissolving the CdO in ammonium hydroxide:

Reversal of this reaction entails an additional penalty in enthalpy, reducing the efficiency to 46 percent, however, this heat might be available from the first reaction in the cycle. Separation of the gaseous cadmium and oxygen is more difficult, and is critical for cycles of this kind. A number of workers have suggested rapid quenching of the products, but quenching would throw away a great deal of high-temperature heat and seriously reduce the efficiency. A possible method of separation for this system and others like it is described in Section 3.4.

3.3.2.4 A Zinc-Based Cycle

Figure 3-6 shows a zinc-based cycle with primary chemistry as follows:

This cycle, as written, has an efficiency of 44 percent, not including separation losses. However, the first reaction releases a large quantity of

Figure 3-5. A Cadmium-Based Cycle

Figure 3-6. A Zinc-Based Cycle

high-temperature heat that could be used for separation of the ZnO and carbon with some heat left over for other purposes, thus improving the outlook for this apparently low efficiency process. As in the case of cadmium, the ZnO and C could be separated by dissolving the oxide in ammonium hydroxide:

This reaction is easily reversible for recovery of the zinc oxide (37 percent efficient). Zinc oxide could also be separated by dissolving it in hydrochloric acid, and then hydrolyzing with steam to recover the zinc, but this method would likely have a higher energy penalty than the ammonia method.

Separation of the zinc vapor and oxygen could be accomplished in the device described in Section 3.4.

3.3.2.5 A Cobalt/Sulfur-Based Cycle

Figure 3-7 shows a cobalt/sulfur-based cycle with primary chemistry as follows:

This cycle has an efficiency of 60 percent and, since cobalt sulfate is soluble in methanol, the separation problem is trivial for the first reaction. No substantial amounts of energy should be required for this separation. The second reaction is analogous to the reaction for the decomposition of sulfuric acid. This reaction has been thoroughly developed for several thermochemical hydrogen cycles and separation is no problem. The only serious problem for this cycle is whether the first reaction will

Figure 3-7. A Cobalt/Sulfur-Based Cycle

go at a reasonable rate at 500°K . Cobalt sulfate is also water soluble, but dehydrating the heptahydrate that is formed would reduce the efficiency of the cycle to 26 percent.

3.4 HIGH-TEMPERATURE METAL VAPOR-GAS SEPARATOR

A high-temperature separator for a gaseous metal and oxygen might be based on the heterogeneous kinetics of solution in a molten inert metal. A device for this is illustrated in Figure 3-8. In this device, focused solar radiation heats a refractory block containing a pool of molten metal that does not form a stable oxide. This pool could be gold, silver, platinum, palladium, or possibly other materials. It is highly likely that

Figure 3-8. Solar Furnace Product Separation

the rates of solution in this pool are very different for metal vapor and oxygen; therefore the vapor pumped off the other side of the pool would be highly enriched in one component or other. Note that this method does not depend on the solubilities per se, but on the heterogeneous solution rates. Nor does it depend on the diffusivity of the vapors in the metal, because the pool could be circulating. This approach has not been tested, but it could have wide application in problems of this sort. The heterogeneous rates are analogous to the rates for gases dissolving in water, which differ greatly for different gases (Reference 70). Evaporation of the metal in the pool should not be a problem, since the products can be cooled after separation and any condensed precious metal allowed to run back into the pool.

3.5 END USES OF CARBON MONOXIDE

Carbon monoxide is an excellent fuel and can be used to power existing fossil fuel plants for electric utilities and for industrial process heat. Alternately, the carbon monoxide can be employed as a feedstock for the production of hydrogen or organic chemicals utilizing existing commercial processes, as shown in Table 3-2. Hydrogen has long been produced by the simple water-gas shift reaction shown on page 3-7. Subsequently, the hydrogen and carbon monoxide can be combined over different catalysts by the Fischer-Tropsch and other processes to form a variety of chemicals. Thus, a nickel catalyst will produce methane (reaction 2) and an iron or cobalt catalyst can yield gasoline (reaction 4). Reactions such as this are presently used in South Africa's SASOL plant for the production of synthetic gasoline.

The remaining reactions in Table 3-2 are examples of other commercial processes which produce higher alcohols, ethylene glycol, and other organic chemicals. Each of these products has a large commercial market. The respective processes are well-developed commercially and the specific catalysts and optimal conditions for many different products are well known.

Table 3-2. End Uses of Carbon Monoxide

Reaction	Product(s)	Catalyst(s)
$\text{CO} + 2\text{H}_2$	Methanol	Zinc, copper, chromium, alumina, mixed oxide
$\text{CO} + 3\text{H}_2$	Methane, water	Nickel
$n\text{CO} + 2n\text{H}_2$	Higher alcohols, water	Mixed oxide + alkali manganese
$n\text{CO} + 2n\text{H}_2$	Straight chain hydrocarbon (gasoline), olefins, waxes, oxygenated hydrocarbon, water	Iron, cobalt
$n\text{CO} + 2n\text{H}_2$	Long, straight chain paraffins, water,	Ruthenium
$n\text{CO} + 2n\text{H}_2$	Long, straight chain alcohols, water	Ruthenium
$n\text{CO} + 2n\text{H}_2$	Ethylene glycol, other products	Rhodium
$\text{CO} + \text{H}_2$	Formaldehyde	Copper (not presently commercial)
$\text{CO} + \text{H}_2$	Formic acid	Aqueous acid

3.6 RECOMMENDED PROGRAM EFFORTS

An organized fuels and chemicals program is necessary to resolve potential problem areas, to accommodate both near-term and extended energy needs, and to implement suggestions made in this section and in Section 5.

Recommended program efforts are outlined in the following paragraphs. First, general problem areas and critical evaluations are summarized from the expanded discussions of these topics in Section 5. Then, a review of the pertinent elements of this program is presented to serve as a basis for a near-term solar fuels and chemicals program which could provide early benefits by using existing equipment. This is followed

by an overview of an implementation plan currently being initiated by The Aerospace Corporation.

3.6.1 Summary of Problem Areas and Critical Evaluations

Various problem areas must be overcome and critical evaluations made in order to develop a near-term transportable fuel program. In addition, searches should be continued for new, high efficiency high-temperature cycles. These considerations are addressed in some detail in Section 5, but are summarized here.

The following problem areas are of primary concern when planning the program.

- Materials compatibility
- Separation of products
- Solid electrolytes and high-temperature electrodes
- Selective emission of receiver coatings at high temperatures
- Lack of kinetic data
- Lack of thermodynamic data

Identification of promising cycles, including hybrid cycles, should include the following critical evaluations: (1) quality of thermodynamic data, (2) high-temperature data needed on specific compounds, and (3) kinetic data.

3.6.2 Basis for a Near-Term Program

A program with a high level of confidence should be defined and established to utilize existing industrial systems to provide near-term benefits. Such a program could concentrate on the transportable fuel area by extending techniques currently used to extract CO₂ from stack gases and to produce the hydrocarbon chain. Various results reported in this study can serve as basic building blocks for the program. Such a foundation involves the following considerations:

- Bountiful supplies of enriched carbon dioxide should be obtained initially from such sources as industrial stack gases utilizing existing or adapted CO₂ extraction processes.
- Open-loop cycles to reduce carbon dioxide to carbon monoxide should be the cornerstone of near-term activities.
- Research should be started to develop closed-loop cycles to decompose CO₂ to carbon and oxygen.
- Specific existing solar central receiver technology should be identified and related to each implementation scheme. Emphasis should be placed on high-temperature pipeline transport with requirements for thermal energy as an end usage.
- Candidate carbon cycles identified in this report should serve as a baseline for initial studies.
- High-temperature application of solar thermal power technology (i.e., 1000°K - 3000°K) should be developed to improve cycle efficiencies.
- Other implementation schemes to be investigated should include those identified in this report pertaining to collection of atmospheric carbon dioxide, hybrid/dual-cycle fuel transport, and methanol-producing equipment.

3.6.3 Program Planning Activities

A three-part solar fuels and chemicals planning program should be initiated on carbon-based cycles to address the problem areas and critical evaluation.

First, two types of research are required to support the development of a solar fuels and chemicals program. Applied research and technology development must be carried out to identify new hydrogen and carbon cycles. The most feasible versions would be identified on the basis of technical performance, economic feasibility, and environmental impact. In addition, basic research is needed to improve our knowledge of new high-temperature processes for several of the more attractive elements; i.e., Ni, Sn, Zn, Sb, As, Bi, Mn, where the oxide, carbide, and pertinent hydride reactions of these elements are unknown at temperatures above approximately 1645°K (2500°F).

Second, more detailed analysis should be conducted on the selected processes, including those identified in this report. A computer analysis should be made of the available high-temperature thermodynamics to identify potentially attractive new cycles with efficiencies even greater than those already identified here for carbon dioxide cycles and hydrogen cycles. Work should also be initiated on developing catalysts that can provide reaction kinetics necessary for the commercial viability of the carbon dioxide cycles already identified here.

Third, work should be initiated to conceptually configure a complete chemical plant for production of gasoline and organic chemicals. This will serve to establish the economic potential and to provide a solar chemical alternative to fossil, bioconversion, fusion, and fission energy sources.

4. HIGH-TEMPERATURE CHEMICAL CONCEPTS

This section presents some new concepts for the use of high-temperature solar energy in the production of essential materials and for closed-loop chemical energy storage, as well as for the production of hydrogen as a fuel and open-loop applications. Prior to discussing the new approaches for the use of high-temperature solar energy in each of these areas, the traditional approach, where applicable, will be discussed briefly. This approach is intended to provide some insight into the present consumption of energy in these areas in order to indicate whether significant improvements can be achieved through the use of solar thermal energy.

Most of the information on energy requirements quoted in this section may be found in "Mineral Facts and Problems" (Reference 11). However, since closed-loop storage is a new technology, no traditional approaches to this area exist.

4.1 FUELS AND OPEN-LOOP APPLICATIONS

Petroleum is our most important fuel and is a primary energy source. The discussion of petroleum in this section deals with the amount of energy consumed in its processing rather than with the energy content of the products.

4.1.1 Current Production of Fuels

Petroleum supplies approximately 44 percent of the total primary energy requirements of the United States, with more than half of this amount being used for transportation. The great virtue of petroleum, aside from its obvious convenience, is its high energy storage density; the heat of combustion of gasoline is 11.43 kcal/gm or 8.02 kcal/cc.

Producing and refining petroleum requires tremendous amounts of energy. This energy consumption amounts to about 22 percent of that used for materials and fuels production, or 4.6 percent of the total energy budget of the United States. More disturbing is the fact that more than

10 percent of the total petroleum used in this country must be used for the production and refining of more petroleum. Thus, use of petroleum has a built-in tax which must be considered when comparing it to other primary energy sources. However, there is also a large energy cost for the production of other primary energy sources. The energy cost of plastics produced from petroleum may approach half that of aluminum on a per-ton basis and exceeds that of aluminum in total national energy use.

In the case of petroleum, there is no "theoretical efficiency" analogous to the one used for comparing metal reductions in Section 4.2. It is useful, however, to remember the 10 percent energy penalty used in petroleum refining since this may be compared to analogous penalties in the production of other primary energy forms. The point to be made with respect to the production of carbon-based fuels is that any use of solar energy to supplant the energy required to produce petroleum would save up to 10 percent of the petroleum. Obviously, any process which could produce carbon-based liquid fuels from non-petroleum sources would be even more desirable in terms of extending petroleum supplies.

4.1.2 Potential Fuels and Open-Loop Applications Using Hydrogen

The most important idea in the recent technical literature for producing fuels from thermal energy is the use of thermochemical decomposition cycles for water, as pointed out in Section 2. It was also pointed out that the efficiency of many of these cycles is poor because the maximum operating temperature was constrained to 1100°K , the maximum temperature available from near-term nuclear reactors. This poor efficiency is a result of Carnot limitations for cyclic processes, as well as the fact that the number of steps per cycle must increase at low temperatures, thus increasing the complexity of decomposition schemes. Solar energy offers the prospect of higher delivery temperatures. The advantages of this capability will be pointed out in the following paragraphs.

4.1.2.1 High-Temperature Cycles for Hydrogen

The data presented in Section 1.3 on high-temperature solar thermal test facilities showed that temperatures above 3000°K are feasible with solar energy. It was also pointed out that high process efficiencies should be possible at these very high temperatures even though the engineering problems are magnified. Research groups which have generated thermochemical hydrogen decomposition cycles, with or without the aid of computer programs, should now seek new cycles with the upper temperature constraints removed since it is very probable that many new hydrogen cycles will be found at higher temperatures.

An example of a very high-temperature cycle is the following:

While high temperature in itself does not ensure that efficiencies will be high, it is much more likely that improved efficiencies will be found in a new round of searches at high temperatures. It should be pointed out here, as it was in Section 1.3, that the optimum temperature for a given process should be based on a trade-off between the improved efficiency and the more severe materials and engineering problems associated with the higher temperatures.

4.1.2.2 Open-Loop Benefits of Solar Thermal Technology

The high temperatures available from concentrated solar radiation make possible a large number of high-temperature chemical reactions and higher efficiencies for the production of hydrogen from water, as well as for the production of carbon-based fuels from carbon dioxide. The following three suggestions are made to take advantage of the higher temperatures provided by solar thermal power technology: (1) conduct searches for high-temperature hydrogen cycles, (2) search for additional high-temperature

cycles for the cyclic reduction of CO_2 to CO , and (3) examine the feasibility of reducing CO_2 with coal or other carbonaceous material as a near-term solar fuels and chemicals approach.

4.2 METALS REDUCTION

4.2.1 Current Reduction Techniques

4.2.1.1 Iron

The iron and steel industry is the single largest industrial consumer of energy. It uses approximately 25 percent of all energy used for materials and fuels production, or about 5 percent of the total U.S. demand. The preparation of iron ore for the blast furnace production of pig iron and for steel furnace production of molten steel, as well as the subsequent casting, rolling, and forging, are dominated by very high-temperature processes. More than 90 percent of the energy consumed in iron and steel production is required at temperatures above 1755°K (2700°F).

Coal, especially in the form of metallurgical coke, plays a central role in the production of iron and steel. Iron ore is reduced to iron in the blast furnace by reactions with carbon and carbon monoxide. The net reaction may be written as:

The heat of this reaction is 57.6 kcal at 1300°K . This reaction is heat-consuming (endothermic) so that additional heat from the reaction

must be supplied to the system. The heat of this reaction is -94.5 kcal at 1300°K . The minimum amount of carbon that must be consumed to produce one

mole of iron is 1.05 moles, 0.75 moles due to the first reaction and an additional 0.30 moles for the second process.

In practice, approximately two moles of carbon per mole of iron are required for the reduction. Thus, the chemical efficiency of the system is roughly 50 percent per carbon atom used. This is quite high since the theoretical requirement does not consider the fact that air is used instead of oxygen, that slag must be melted, or any other practical factors.

4.2.1.2 Aluminum

Aluminum is second only to iron in world production of metals. Its production consumes the third largest fraction of energy used for producing materials and fuels in the United States. Production of aluminum metal is expected to grow faster than the growth of the gross national product (GNP) because aluminum is replacing other metals, such as iron and copper, in various uses. However, the growth rate is not expected to be as high as it has been in the last decade.

Eighty-five percent of the country's aluminum ore is imported. The ore presently used is bauxite, which consists of gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) and boehmite or diaspore ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$). Bauxite is presently converted to pure alumina by the Bayer process, patented by Karl Bayer in 1888. In this process, the dried crude ore is dissolved in strong sodium hydroxide solution at elevated temperatures and pressures (100-300°C, 60-1000 psi):

or

This process leaves behind the major impurities, which are silica and iron oxide. The alumina is recovered by cooling the solution:

The caustic soda may then be reused.

The refined alumina is then reduced to aluminum by the well-known Hall process (1886). Some of the alumina is converted to synthetic cryolite:

Aluminum is then produced by a combined chemical-electrochemical reduction of the alumina dissolved in molten cryolite at 950°C. In operation, the solution is about 6 percent alumina. Aluminum is produced at the cathode:

The anode reaction includes oxidation of carbon, in which the anode material is consumed:

The commercial electrolysis cells have an efficiency of about 35 percent with the remainder of the electrical energy going to maintain the temperature of the cell.

Production of aluminum requires from 202 to 278 million Btu per short ton of aluminum. This amounts to a total fuel requirement of 8-11 tons of coal per ton of aluminum. The energy requirement for the electrolysis stage is 170-210 million Btu and amounts to 7-8.4 tons of coal per ton of aluminum.

It is possible, at temperatures in excess of 2400°K, to reduce alumina directly with carbon:

At 2400°K, $\Delta H = 282$ kcal and $\Delta G = -11$ kcal.

The required heat of reaction may, in principle, be partially supplied by the heat of combustion (198 kcal) of the carbon monoxide product.

The remaining 84 kcal of enthalpy may be supplied by the combustion of 0.885 moles of carbon. Therefore, the theoretical minimum amount of carbon required to reduce aluminum is 1.942 moles of carbon per mole of aluminum, or 0.863 tons of coal per ton of aluminum. Thus, the present overall efficiency amounts to 10 to 12 percent of the theoretical maximum for reducing pure alumina to aluminum.

Aluminum is used for the reduction of a number of other metals such as calcium, columbium, molybdenum, strontium and chromium. Calcium, in turn, is used to reduce scandium, thorium and uranium. While these other materials do not account for a very large part of the U.S. energy budget, they are clearly tied to aluminum in energy requirements and are, therefore, very energy-intensive materials.

4.2.1.3 Magnesium

Production of magnesium in the United States consumes only about 4 percent as much energy as aluminum production, because the tonnage is much less. Nevertheless, the specific energy required is quite high, about 358 million Btu per ton, and there is a possibility for considerable energy savings if different methods of production could be found. Since magnesium is obtained from seawater, it is available in unlimited supply and it is conceivable that use of magnesium could expand as a substitute for less available metals.

Seawater contains 0.13 percent magnesium by weight and, in a process developed by Dow Chemical, it is mixed with calcium hydroxide to precipitate the solid magnesium hydroxide:

The filtered hydroxide is then dissolved in hydrochloric acid and the resulting magnesium chloride is dried, then fused at 700°C, and finally electrolyzed in graphite cells into molten magnesium and chlorine gas:

The electrolysis cells require 8 to 9 kilowatt-hours per pound of magnesium, which corresponds to 29 to 33 percent efficiency for the use of electrical energy. If electricity is generated with 30 percent efficiency, then the conversion of energy to magnesium is about 9 to 10 percent efficient.

It is possible to reduce magnesium directly with carbon by the Hansgirg Process at temperatures in excess of 2100°K:

At 2200°K, $\Delta H = 145$ kcal and $\Delta G = -5$ kcal.

The necessary enthalpy may be partially supplied by combustion of the carbon monoxide product and the rest supplied by the combustion of an additional 0.880 moles of carbon. Thus, the theoretical minimum amount of carbon required is 1.880 moles per mole of magnesium, or 0.94 tons of carbon per ton of magnesium. The present energy requirement corresponds to 12 to 13 percent efficiency on this basis.

Magnesium is used for the reduction of several other materials, including titanium, zirconium, hafnium, and beryllium.

4.2.1.4 Copper

Production and refining of copper requires about 2 percent of the energy used in the United States for materials and fuels, or about 0.4 percent of the total energy budget. It, therefore, consumes more energy than all other metals but aluminum and iron. Production of copper is expected to grow at a rate approximately equal to that of the GNP. Electrical applications will grow at a faster rate than the GNP, but substitutions of aluminum for high-tension lines and the use of satellites for communications will tend to reduce the growth somewhat.

Copper is found in ores as the sulfide or oxide. Sulfide ores are concentrated by flotation and reduced to metal in three steps: roasting, reverberatory smelting, and converting. Oxide ores of copper are reduced to the metal by a different set of processes. These ores are leached with sulfuric acid to dissolve the copper, and the copper sulfate is then electrolyzed directly to reduce the copper.

After the copper ores are concentrated, cementation copper or blister copper may then be further refined by electrolysis or fire-refining. Electrolytic refining produces a very high grade of copper. In practice, the electrolytic refining cells operate at about 0.250 volts and 90-95 percent current efficiency. The electricity required for this operation is about 0.73 million Btu per ton, or an energy cost of about 2.4 million Btu per ton.

Fire-refining is a high-temperature oxidation, followed by a reduction. Fire-refined copper is of high quality, but is not as good for electrical purposes as electrolytic copper. Also, valuable impurity metals are somewhat easier to recover in the electrolytic refining process.

Copper ores are of an increasingly poor grade, and the energy expended in concentration of the copper ore is a large fraction of the total energy cost. Therefore, it is difficult to make substantial changes in the energy cost by changing the methods of winning and refining the metal from concentrated ore.

4.2.1.5 Observations on Current Metal Production Techniques

Iron is currently reduced with surprisingly high efficiency and, even though the amount of energy required by the industry is large, it is unlikely that new technology would be substantially more efficient. In the case of electrolytically-reduced metals, the situation is different. Roughly speaking, both the generation of electricity and the electrolysis cells are 30 percent efficient, resulting in an overall 10 percent efficiency for metals production for aluminum and magnesium. Here, it would seem that substantial improvement is possible. Also, it is conceivable that

some new chemical process could be based on lower grade ores, such as aluminosilicates, which would improve the import-export advantage of aluminum.

4.2.2 Potential Metals Reduction Applications

Very little discussion appears in the literature about the possibility of using solar energy for the production of energy-intensive materials. The only material that is mentioned is oxygen, which is co-produced in the water decomposition cycles. Other energy-intensive materials are those which must be calcined, such as cement and quick-lime. Use of solar energy to do this may be worthwhile but, since this is an obvious process heat application, it is outside the scope of this report. Metals are the other main energy-intensive materials, and two new ideas are suggested for the use of solar energy in reducing metals from the refined ores: (1) high-temperature reductions with carbon that are not feasible at low temperatures and (2) cyclic decomposition processes for metals analogous to the hydrogen cycles.

4.2.2.1 High-Temperature Reduction

The temperatures available from focused solar radiation are so much higher than those presently used in industrial processes that a number of chemical reduction schemes, which are not thermodynamically allowable at lower temperatures and which have been nearly forgotten, should be reexamined for feasibility. Two examples are:

These processes must be carefully controlled to avoid carbide formation, but they have actually been used to produce aluminum and magnesium. (this is known as the Hansgirg Process for magnesium). While such processes clearly

require a source of carbon, they should require substantially less energy than the presently used electrolytic techniques (See Section 4.2.1). There may well be other such possibilities, and these should be examined.

4.2.2.2 Direct Cycles for Metals

An idea that was not seen in the literature is that thermal decomposition cycles could be used to produce materials other than hydrogen or carbon. The availability of very high temperatures from focused solar radiation greatly improves the prospects for the simplicity and efficiency of such schemes, just as it does for hydrogen.

As an example, consider cycle No. 21 in Table B-1, Appendix B. The three last steps in the cycle are:

These steps form a cycle for winning an alkali metal from its hydroxide, a process which must now be done electrolytically. This cycle should also work for the more economically important metals, e.g., sodium and potassium, at still higher temperatures (about 2500°K). Other such cycles might be devised which could be used to reduce other metals that presently require large amounts of carbon or energy for their reduction. Iron production is one of the largest national energy demands, since large amounts of carbon are required for reduction and heating of the ore. Iron may also be reduced with hydrogen (Reference 71) and any hydrogen cycle is, therefore, also an implied iron production cycle. However, the point of these remarks is that a more direct cycle might be developed specifically for the reduction of iron ore or any other important metal.

Certain oxides might be directly dissociated, for example:

In some of these very high-temperature schemes, all of the species may be gaseous and separation may be difficult. Nevertheless, a diffusive separation such as that suggested in Section 2.1.2.2 for H_2 and O_2 or the heterogeneous dissolution scheme described in Section 3.4 might work. Fast quenching of the products has been suggested by others, but this wastes high-temperature energy and decreases the thermal efficiency.

Since such a broad spectrum of possibilities presents itself, a great deal of research on new cycles and on the new materials problems is called for. In addition to the direct savings in energy, cyclic reduction of metals might have applications in lunar mining, since solar energy is abundant on the moon, but other materials are likely to be scarce.

4.2.2.3 Metals Reduction Benefits via Solar Technology

The advantages of high-temperature solar energy for metals reduction are essentially the same as those for hydrogen reduction. The high temperatures make possible new reactions and higher efficiencies than are presently available. In particular, metals that must now be reduced electrolytically at very low efficiency might be reduced with carbon directly or via cyclic decomposition schemes, using solar energy and high efficiency.

4.3 POTENTIAL CLOSED-LOOP APPLICATIONS

Very few closed-loop energy storage systems have appeared in the literature, especially considering the large number of possibilities available. Here, as in the other areas of this report, a reexamination of the possibilities would seem worthwhile. Similar advantages of simplicity, efficiency, and new chemical processes accrue at high temperature, with the added significance that the Carnot temperature-related efficiency of the end use must also be taken into account. The constraints on closed-loop systems are not as great as those on open-loop systems and, therefore, there should be many new possibilities. Well-developed criteria for closed-loop storage would enable searches to be made by computer.

4.3.1 Dual System Energy Storage

A salient problem with chemical energy storage systems is that the most convenient systems for transportation are the gaseous ones, whereas the systems with the best storage density are liquid or solid phase. It is possible to have a hybrid system that couples the most desirable qualities of vapor and condensed phases together. This new hybrid system concept is shown in Figure 4-1.

The novel aspect of the system is the use of a low density, conveniently transportable chemical energy storage system to deliver the energy from a primary energy source to the storage site, and the use of a high-density chemical energy storage system to store the energy. Energy would be supplied to the user site in the form of a gaseous (or perhaps liquid) CESS such as the ADAM + EVA system. During the period that user energy demand is low or energy supply is high, the excess energy is drawn off by the high-density system, e.g., the sodium bifluoride system:

The liquid HF is stored until the energy is needed at the user site.

Figure 4-1. Dual-System Closed-Loop Energy Storage Concept

This system introduces the penalties of additional complexity, and loss of efficiency, but saves greatly on storage volume which could be an enormous capital investment for gaseous storage systems. It would be interesting to see a systems study of the trade-offs involved.

4.3.2 Closed-Loop Benefits via Solar Technology

As in the other two areas, high temperature offers advantages of simplicity, efficiency, and new chemical processes for closed-loop storage systems. In addition, the Carnot temperature-related efficiency problem at the user site is alleviated by higher temperature storage systems. Some form of energy storage will almost certainly be required for the widespread use of solar energy and the field of closed-loop storage is almost unexplored.

In the fuels and open-loop storage area, a search is suggested for higher temperature cycles for the decomposition of water, and searches for a new kind of cycle: the cyclic decomposition of carbon dioxide.

In the materials production area, new processes are suggested for the direct reduction of metals now obtained electrolytically. Such processes could only become practical at the very high temperatures offered by solar thermal energy facilities. Searches are also suggested for cycles that decompose metal ores into reduced metal and oxygen or sulfur. Some direct processes for the decomposition of metal oxides at high temperature have been indicated.

Relative to closed-loop systems, a new hybrid approach is suggested that combines the best features of gaseous and solid storage. In all of these areas, solar energy at very high temperatures offers the advantages of simplicity, efficiency, and new chemical processes. The number of opportunities is so large that many options should be examined before deciding on specific systems for development.

5. GENERAL PROBLEM AREAS, INTERESTS, EVALUATION

This section discusses some general problems which face many schemes for the utilization of high-temperature solar energy. The most important feature of utilizing solar thermal energy for chemical applications is the possibility of operation at temperatures very much higher than nuclear reactor temperatures. This feature greatly expands the number of chemical cycles which may be considered and also permits cycles of higher theoretical efficiency. Unfortunately, such high temperatures also bring new engineering and materials problems as well as more limited industrial operational experience in the regime over 1100°K . In addition to the high-temperature engineering problems, there are gaps in high-temperature thermodynamics needed for cyclic thermochemical processes as well as a lack of kinetics data. These problem areas are discussed in this section, as well as some areas of special interest and critical evaluations which should be made.

5.1 GENERAL PROBLEM AREAS

The following six primary problem areas must be overcome to utilize high-temperature solar energy successfully:

- Materials Compatibility
- Separation of Products
- Solid Electrolytes and High Temperature Electrodes
- Selective Emission at High Temperatures
- Kinetics
- Thermodynamics

5.1.1 Materials Compatibility

Assuming that all of the thermodynamic problems have been worked out for a given chemical reaction cycle, there will always remain the problem of chemical compatibility of the various species in the cycle with

the walls of the container. The container must not only retain useful strength and have a low vapor pressure at the operating temperature, but also must be inert to chemical reaction with all species present.

The basic compatibility problem at high operating temperatures is that chemical kinetics may no longer be counted upon to protect the walls. In other words, the acceleration of chemical reaction rates at elevated temperatures allows all possible reactions to occur rapidly, and the only permitted container materials are those which have no thermodynamically allowed reactions with any of the species present. This problem is most apparent in the one-step dissociation of water or carbon dioxide, where the temperatures must exceed 2000°K, and the system must withstand both oxidizing and reducing environments at the same time.

Even the thermodynamic criterion for materials compatibility may not be stringent enough in cases where liquids are involved. This is because of the notorious ability of molten metals to dissolve many materials at high temperature, whether or not chemical reaction is allowed.

Therefore, although high-temperature data are available in the JANAF Tables (Reference 55) for many systems, there is still a need for thermodynamic data on the less common refractory materials, for example, hafnium and lanthanum compounds. There will also be a need for data on high-temperature solubilities for specific systems which involve liquid state materials at such temperatures.

5.1.2 Separation of Products

In all chemical cycles for energy storage, transport, or materials production, there is a common problem of product separation at the upper operating temperatures, so that energy may be stored or materials extracted for use. At lower and intermediate temperatures, this problem is often solved by a separation of phases, i.e., a gas may be pumped off from a solid or liquid. An interesting example of this is the CESS involving ammonium hydrogen sulfate (See Section 2.2.3.3). In this system, two successive phase separations at different temperatures enable the separation of the

gaseous products, with ammonia and water eliminated in the first step and with SO_3 eliminated in the second step, at a different temperature and pressure. In other systems, such as the ADAM + EVA system, the use of catalysts makes it unnecessary to separate the two gaseous products.

As the operating temperature is increased, however, reaction rates become fast even without catalysts and all phases become gaseous, making the separation problem much more difficult. Again, the problem is most obvious in one-step dissociations at very high temperatures. If the products are not separated while hot, they will rapidly recombine as the temperature is lowered. One approach to this problem, which was mentioned earlier (Reference 45), is to separate the products by diffusion, a technique which is particularly well suited to hydrogen. In other systems it may be possible to quench the products rapidly enough to prevent recombination; for example, heterogeneous cooling on a cold surface might be used. This idea has not been examined in the literature. The problem with quenching is that much high-temperature heat is wasted which might otherwise be exchanged with incoming reactants.

There is an apparent hope in the literature that selective membranes can be found for the separation of products, analogous to the well-known palladium membrane for separating hydrogen. Unfortunately, such conveniences seem to be rare, and it is not clear how to search systematically for such membranes.

In Section 3.4, a noble metal pool concept was suggested to separate gaseous products on the basis of differences in their heterogeneous dissolution rates. It is important to search for and to be open to other new basic ideas in high-temperature separation of products.

5.1.3. Electrolytes and High-Temperature Electrodes

It was pointed out in Section 2.1.2.1 that the theoretical voltage and the overvoltage for the electrolysis of water decline steadily as the temperature is raised. This is generally true of electrolytic separations and could be exploited for a number of other systems. Solar heat used in

this way is, in effect, three times as effective as heat used to generate electricity because of the inefficiency of electric power generation. The virtue of electrolysis is that product separation is automatic. The problem is that the necessary solid electrolytes and electrodes for gas phase high-temperature electrolysis have not been perfected, although much work is in progress. Here again, the highest temperatures offer the highest efficiencies, but less is known about high-temperature electrolytes.

The electrodes are a problem also, because they must be porous in some applications, but corrosion-resistant and good conductors with low overvoltage. These multiple requirements have led to the use of very exotic materials such as doped rare-earth oxides. More work is needed to obtain electrolytes and electrodes that can operate at optimum conditions.

5.1.4. Selective Emission at High-Temperatures

It is likely that the temperatures which may be exploited in the various chemical systems will be higher than any considered for solar thermal power generation. At such temperatures, the amount of energy re-radiated by the light-absorbing components can quickly become the main loss of efficiency (Reference 45). Much attention has been paid in the literature to selective emission coatings for low-temperature uses of solar energy, such as water heating (Reference 80). These coatings are black in the visible region of the spectrum out to wavelengths of 1 micron, and are "white" at wavelengths longer than this. Thus, much less energy is wasted in re-radiation in the infrared. The problem is much more difficult at higher temperatures because substances tend to become more like blackbodies as the temperature is raised. Nevertheless, some improvement is possible since the effect is already exploited in "gas mantles", for example. Clearly, spectroscopic data would be useful to identify the best refractory materials.

Another approach to this problem is to refocus the emitted infrared radiation back on the absorber (black, in this case) with mirrors which are transparent to visible light and reflecting for infrared. This approach has

been suggested in the literature and has been employed in some laboratory furnaces. Feasibility of this approach for high-temperature solar applications should be examined further.

5.1.5. Kinetics

Kinetic data are lacking for reactions in many of the proposed cycles, particularly for heterogeneous reactions. Many systems may prove to be impractical on this basis since the proposed reactions may simply not happen at a practical rate. A classic laboratory example of this is the "non-reaction" of traditional dry cleaning fluid, carbon tetrachloride, with water:

for which $\Delta H = -13.3$ kcal and $\Delta G = -56.4$ kcal.

These free energy and enthalpy changes mean that the equilibrium lies far to the right, and that the products should form explosively, reaching a final temperature of 1100°K . In fact, nothing happens at all because the kinetics are imperceptibly slow at room temperature. This is an object lesson in the importance of kinetics. Sometimes catalysts can be found to solve this problem, but not in all cases.

It may not be useful to take kinetic data if a cycle does not meet some minimum efficiency criteria. On the other hand, laboratory kinetic data are essential before proceeding to a pilot plant stage.

5.1.6. Thermodynamics

Thermodynamic data are essential for determining the feasibility of reactions and for finding new cycles. While much good high-temperature data are available in the JANAF Tables (Reference 55), many important systems are missing. In particular, the important amphoteric elements tin and zinc are not included, and the acidic oxide elements antimony, arsenic, and bismuth

are not included. Manganese and nickel are also not included. These elements have many useful chemical properties and should add to the number and flexibility of all dissociation cycles.

Additional data are available in the Bureau of Mines series (Reference 67) and in the Atomic Energy Commission report (Reference 68). Most of the old data, while of high quality, were not taken at as high a temperature as desirable (to 3000°K).

Better data would add to the value of computer searches for thermochemical cycles. Thermodynamic data are also needed to determine material compatibilities for structural materials at high temperatures.

5.1.7. Problem Areas Summary

The six problem areas just mentioned are broadly defined areas of research, and all have overlapping benefits to the various solar applications suggested in this report. Data in these areas are essential for determining the feasibility, efficiency, economics, and engineering practicality of any new process.

5.2 SPECIAL INTERESTS AND CRITICAL EVALUATIONS

Special interests involve developing a near-term transportable fuel program with continuing searches for high-temperature cycles, and determining more precise efficiencies for those cycles. Plans for such a program implementation were discussed briefly in Section 3.6.

The following list summarizes general areas in which further work should be carried out.

- Search for high-temperature cycles for hydrogen
- Assign more precise efficiencies to feasible cycles
- Search for high-temperature metal reduction processes
- Search for new metal and carbon cycles
- Search for new closed-loop storage systems
- Conduct dual-system studies
- Investigate hybrid electrolytic cycles

These items will offset the shortcomings of previous searches which have, for the most part, been limited to temperatures available from nuclear reactors. Accomplishment of such new searches will supplement any proposed cycles available from solar energy applications. High-temperature cycles are virtually non-existent except for those documented in this report. Of key interest are new cycles involving the reduction of metals and carbon cycles involving the reduction of carbon dioxide to carbon monoxide and/or carbon.

Identification of promising cycles, including hybrid cycles, should include the following critical evaluations:

- Quality of thermodynamic data
- High-temperature data needed on specific compounds
- Kinetic data

Potentially attractive high-temperature cycles, based on limited, suspect, or low-temperature data, will serve to identify high-temperature data needed on specific compounds. Data are known to be lacking for compounds of tin, zinc, antimony, arsenic, bismuth, manganese, and nickel which possess chemical properties that suggest their utilization in the high-temperature cycles. Other considerations to be taken into account include the separation of products and materials compatibility.

Kinetic data are lacking for reactions in many of the proposed cycles, particularly for the heterogeneous reactions involved in the low temperature, rate-limiting steps. While many systems may prove to be impractical on this basis, kinetic data are not essential if a cycle does not meet some minimum efficiency criterion. In contrast, laboratory kinetic data are essential before proceeding to a pilot plant stage. Laboratory kinetic data should be obtained for systems which show promise of exceeding efficiencies of established processes.

Other important research areas involve the high-temperature emissive properties of materials and identification of potentially attractive materials for use as solid electrolytes and high-temperature electrodes.

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APPENDIX A. ENERGY STATISTICS

This Appendix presents data on the energy role of fuels and materials in terms of:

- Energy distribution in the United States
- Relationship of major energy-consuming processes to overall industrial consumption
- Consumption of energy for the transportation of fuels and materials

A.1 ENERGY DISTRIBUTION RELATIONSHIPS

Energy used in the production and transport of fuels and materials comprises a significant fraction of the overall energy budget. This is apparent from an examination of the fraction of the energy budget attributed to the industrial and transportation sectors currently and in the future, as shown in Figure A-1. Only the utility sector consumes more energy than the industrial or transportation sector.

Figure A-1. Energy Consumption in the U.S. by Consuming Sector (Reference A-1)

The transportation sector, which is based almost entirely on oil, accounted for approximately 25 percent of the total energy consumed in the United States in 1970. The industrial sector, including electrical energy generated by the utilities, consumes at least 40 percent of the energy in-use budget, depending on whether the non-energy sector (e.g., petrochemicals) is added to the industrial portion. This 40 percent includes energy used in the production of fuels and materials.

The increase in energy consumption by user sector during the period 1971-1990, is shown in Figure A-1. The percentage of the total energy which is consumed by each sector decreases for all sectors except the utility sector. The amount of energy provided during this time period by each source of energy is shown in Figure A-2. The total amount of energy produced by each type of source also increases during this period, but the fraction of energy provided by petroleum and natural gas decreases noticeably, primarily because of the increased percentage of energy provided by nuclear sources.

Figure A-2. U.S. Energy Demand Provided by Various Sources (Reference A-1)

An additional point to be noted with respect to Figure A-2 is the dominant role of petroleum as a source of energy. Petroleum provided 44 percent of the energy consumed in 1971 and is expected to supply 41 percent of the energy consumed in 1990. This is a key point, since the finite supply of petroleum is expected to diminish in the 21st century and will require replacement by an alternative source of transportable fuels and petrochemical feedstocks.

A.2 ENERGY CONSUMPTION IN THE INDUSTRIAL SECTOR

Figure A-3 shows the primary energy-consuming areas within the industrial sector and the relationship of energy consumed in the production of fuels and materials to other industrial energy usages. Production of fuels and materials accounts for approximately half of the industrial energy usage which, in turn, amounts to about 40 percent of the total energy consumption of the United States. Production of iron and petroleum accounts for almost half of the energy used in the production of fuels and materials. Production of aluminum, copper, and magnesium in addition to iron and steel accounts for about 95 percent of all the energy used for metals production in the United States.

Figure A-3. Energy Demand in the Industrial Sector

Table A-1 (Reference A-2) shows the amount of energy required to produce various metals, while Table A-2 (Reference A-2) indicates the energy requirements for a number of the major non-metallic materials.

Table A-1. Energy Requirements for Selected Metals in the United States in 1973

Commodity	Product	Energy Required	
		Per Net Ton Product (10^4 Btu's)	Total (10^{12} Btu's)
Iron and steel	Steel slabs	24	3350
	Gray iron castings	34	366
	Carbon steel castings	42	54
Aluminum	Ingot	244	1170*
Zinc	Ingot	65	92
Lead	Ingot	27	23.9
Copper	Cement copper	87	14.9
	Refined copper	112	221
Chromium	High-carbon ferroalloy	61	15.8
	Low-carbon ferroalloy	129	19.5
Magnesium	Metal	358	42.0
Manganese	Ferromanganese	49.5	33.0
	Blast furnace	46	17
	Electric furnace	52	16
Titanium	Metal	408	8.2
Uranium	Uranium oxide		
	Acid circuit	776	2.1
	Alkaline circuit	1123	2.1
	Resin-in-pulp	795	2.3

* In practice, 40 percent of aluminum electrical energy in the United States is derived from hydroelectric plants. The figure 244×10^4 Btu/ton in Reference A-2 is reduced to 204×10^4 Btu/ton in calculating total U.S. use of 1.17 quads.

Table A-2. Energy Requirements for Selected Nonmetallic Materials for Primary Products in the United States in 1973

Commodity	Product	Energy Required	
		Per Net Ton Product (10 ⁴ Btu's)	Total (10 ¹² Btu's)
Calcium	Quicklime	8.5	182
Cement	Portland cement	7.6	688
Ceramics	Common brick	3.5	62
Glass	Glass containers	17.4	216
Refractories	Basic brick	27	18.2
	Fireclay brick	4.2	6.9
Clays	Kaolin	2.8	14.3
Gypsum	Other clays	0.1-5.3	16.7
	Calcined gypsum	1.5	19
Sand and gravel	Sand and gravel	0.056	53
			1276.1

Table A-3 (Reference A-1) shows the energy costs of bringing fossil fuels to market. These energy penalties are significant since they include energy expended for extraction, petroleum refining, and transport of the fuel to market. It should be noted that the petroleum industry consumes approximately 17 percent of the energy it produces in the process of bringing its product to market.

Table A-3. Energy Costs of Bringing Fossil Fuels to Market

Commodity	Energy Used	
	Percent	Btu's Per 10 ⁴ Btu's
Coal	3	30,000
Petroleum	6	60,000
Petroleum refining	11	110,000
Natural gas	7	70,000

A.3

ENERGY USAGE IN THE TRANSPORTATION SECTOR

Energy usage in the transportation sector is important because approximately 25 percent of this energy is required for the production of fuels and materials used in transportation. The ability to generate and transport energy through a solar fuels and chemicals program could be a major contributor to the relaxation of the United States dependence upon foreign sources of petroleum.

The distribution of energy consumed in the transportation sector in 1968 is given in Table A-4. Energy consumption has increased since that time but the relative percentages of usage by subsector have remained essentially the same. As pointed out above, secondary transportation activities account for about 25 percent of the energy consumed for transportation.

Prior to the opening of the Alaskan pipeline, energy consumption attributed to pipeline transport amounted to just over one percent of the total energy consumption for transportation. Studies have been conducted to determine more efficient methods of transporting energy by pipeline. A recent Aerospace Corporation study (Reference 2) compared energy transportation costs over a 100 mile distance by chemical heat pipe with the costs of hydrogen and natural gas transport by pipeline and with the transmission costs of an equivalent amount of electrical energy. This study indicated that, for the transport of comparable electrical generation capability, the heat pipe costs approximately three times as much as conventional electricity transport. If thermal energy were desired by the user, the cost of energy transport by pipeline would be slightly less for the heat pipe.

Table A-4. Energy Used for Transportation in 1968

Sector	Use	Energy Consumption 10 ¹⁵ Btu
Primary Transport (propulsion)	Automobile	7.60
	Truck and bus	3.06
	Jet	1.63
	Railroads	0.72
	Marine	0.55
	All other propulsion	<u>1.59</u>
	Subtotal	15.15
Secondary Transport (related activities)	Fuel refining, asphalt and road oil energy	2.42
	Primary metals used in transport manufacture	1.02
	Manufacturing	0.53
	Other activities	<u>1.05</u>
	Subtotal	5.02
TOTAL		20.17

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APPENDIX B. OPEN- AND CLOSED-LOOP CYCLE DATA

B.1 OPEN-LOOP DATA ON WATER DECOMPOSITION CYCLES

B.1.1 Listing of Cycles

The original Bamberger and Richardson list of 72 water decomposition cycles (Reference 30^{*}) is presented in Table B-1. An additional 129 reactions published by Bamberger (Reference 31) are given in Table B-2. Flow charts prepared by Wentorf and Hanneman (Reference 36) for cycles 24, 36, and 57 in Table B-1 are shown in Figures B-1, B-2, and B-3, respectively.

B.1.2 Efficiency Calculations

A number of interesting papers have been written on the thermodynamics of water decomposition cycles, beginning with the Funk and Reinstrom paper (Reference 4). In this paper, it was pointed out that no two-step processes were known to exist for operating temperatures below 1100°C. This is still the case. In a later paper by Abraham and Schreiner (Reference 72), it was concluded that three steps are the minimum number theoretically possible for a maximum operating temperature of 1000°K and that the number of necessary steps must increase as the temperature falls. In a recent paper by Glandt and Myers (Reference 40), it is suggested that no three-step processes are likely to exist below 1100°K, and that a six- or seven-step minimum might exist. This latter conclusion seems to be too pessimistic since cycles which violate this prediction appear in Table B-1.

The energy efficiency of multi-step water decomposition cycles is given by the Second Law of Thermodynamics and may not exceed the Carnot efficiency:

$$\epsilon = \frac{T_h - T_l}{T_h}$$

* Reference numbers are those given in the previous Reference Section.

Table B-1. Compilation of Thermochemical Cycles
for Hydrogen Production from Water

Cycle number	Elements	Maximum temperature, K	Number of reactions	Cycles	Reference*
1	Ag, Ag (Br, Sb)	800	4	$2\text{Ag} + 2\text{HBr} = 2\text{AgBr} + \text{H}_2$ $2\text{AgBr} + 2\text{NaOH} = 2\text{NaBr} + 2\text{Ag} + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$ $2\text{NaBr} + \frac{1}{2}\text{Sb}_2\text{O}_3 + \text{H}_2\text{O} = 2\text{NaOH} + \frac{2}{3}\text{SbBr}_3$ $\frac{2}{3}\text{SbBr}_3 + \text{H}_2\text{O} = \frac{1}{3}\text{Sb}_2\text{O}_3 + 2\text{HBr}$	1
2	Bi, Cl		3	$2\text{BiCl}_2 + 2\text{HCl} = 2\text{BiCl}_3 + \text{H}_2$ $2\text{BiCl}_3 = 2\text{BiCl}_2 + \text{Cl}_2$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$	1
3	Bi, S (Ca, Fe)	1400	7	$\text{H}_2\text{S} + \frac{2}{3}\text{Bi} = \frac{1}{3}\text{Bi}_2\text{S}_3 + \text{H}_2$ $\frac{1}{3}\text{Bi}_2\text{S}_3 = \frac{2}{3}\text{Bi} + \text{S}$ $\frac{1}{4}\text{CaS} + \text{S} + \text{H}_2\text{O} = \frac{1}{4}\text{CaSO}_4 + \text{H}_2\text{S}$ $\frac{1}{4}\text{CaSO}_4 + \frac{1}{2}\text{S} = \frac{1}{4}\text{CaS} + \frac{1}{2}\text{SO}_2$ $\text{Fe}_2\text{O}_3 + \frac{3}{2}\text{SO}_2 = 2\text{FeSO}_4 + \frac{1}{2}\text{S}$ $2\text{FeSO}_4 = \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$ $\text{SO}_3 = \text{SO}_2 + \frac{1}{2}\text{O}_2$	2
4	Bi, S (Ca, Zn)	1400	6	$\text{H}_2\text{S} + \frac{2}{3}\text{Bi} = \frac{1}{3}\text{Bi}_2\text{S}_3 + \text{H}_2$ $\frac{1}{3}\text{Bi}_2\text{S}_3 = \frac{2}{3}\text{Bi} + \text{S}$ $\frac{1}{4}\text{CaS} + \text{S} + \text{H}_2\text{O} = \frac{1}{4}\text{CaSO}_4 + \text{H}_2\text{S}$ $\frac{1}{4}\text{CaSO}_4 + \frac{1}{2}\text{S} = \frac{1}{4}\text{CaS} + \frac{1}{2}\text{SO}_2$ $\text{ZnO} + \frac{3}{2}\text{SO}_2 = \text{ZnSO}_4 + \frac{1}{2}\text{S}$ $\text{ZnSO}_4 = \text{ZnO} + \text{SO}_2 + \frac{1}{2}\text{O}_2$	2
5	Bi, S (Ca, Zn)	1400	7	$\text{H}_2\text{S} + \frac{2}{3}\text{Bi} = \frac{1}{3}\text{Bi}_2\text{S}_3 + \text{H}_2$ $\frac{1}{3}\text{Bi}_2\text{S}_3 = \frac{2}{3}\text{Bi} + \text{S}$ $\frac{1}{2}\text{CaSO}_4 + \text{S} = \frac{1}{2}\text{CaS} + \text{SO}_2$ $\frac{1}{2}\text{CaS} + 2\text{S} + 2\text{H}_2\text{O} = \frac{1}{2}\text{CaSO}_4 + 2\text{H}_2\text{S}$ $\text{ZnO} + \text{H}_2\text{S} = \text{ZnS} + \text{H}_2\text{O}$ $\text{ZnS} + 2\text{SO}_2 = \text{ZnSO}_4 + 2\text{S}$ $\text{ZnSO}_4 = \text{ZnO} + \text{SO}_2 + \frac{1}{2}\text{O}_2$	2
6	Bi, S (Mg)	1400	4	$\text{H}_2\text{S} + \frac{2}{3}\text{Bi} = \frac{1}{3}\text{Bi}_2\text{S}_3 + \text{H}_2$ $\frac{1}{3}\text{Bi}_2\text{S}_3 = \frac{2}{3}\text{Bi} + \text{S}$ $\text{MgO} + \text{SO}_2 + \text{H}_2\text{O} + \text{S} = \text{MgSO}_4 + \text{H}_2\text{S}$ $\text{MgSO}_4 = \text{MgO} + \text{SO}_2 + \frac{1}{2}\text{O}_2$	2
7	C, As	1000	5	$\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$ $\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$ $\text{CH}_3\text{OH} + \text{As}_2\text{O}_4 = \text{CH}_4 + \text{As}_2\text{O}_3$ $\frac{1}{2}\text{As}_2\text{O}_3 = \frac{1}{2}\text{As}_2\text{O}_5 + \frac{1}{2}\text{O}_2$ $\frac{1}{2}\text{As}_2\text{O}_5 + \frac{1}{2}\text{As}_2\text{O}_3 = \text{As}_2\text{O}_4$	3
8	C, Co	1200	3	$\text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2$ $\text{CO} + 3\text{CoO} = \text{C} + \text{Co}_3\text{O}_4$ $\text{Co}_3\text{O}_4 = 3\text{CoO} + \frac{1}{2}\text{O}_2$	4
9	C, Fe	1700	3	$\text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2$ $\text{CO} + 2\text{Fe}_3\text{O}_4 = \text{C} + 3\text{Fe}_2\text{O}_3$ $3\text{Fe}_2\text{O}_3 = 2\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{O}_2$	5
10	C, Mn	1250	3	$\text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2$ $\text{CO} + 2\text{Mn}_3\text{O}_4 = \text{C} + 3\text{Mn}_2\text{O}_3$ $3\text{Mn}_2\text{O}_3 = 2\text{Mn}_3\text{O}_4 + \frac{1}{2}\text{O}_2$	4
11	C, Mn (Na)	1100	[4]	$\text{CO} + 3\text{CO}_2 + 8\text{NaOH} = 4\text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O} + \text{H}_2$ $[4\text{Na}_2\text{CO}_3 + \text{Mn}_2\text{O}_3 = 2(\text{MnO}_2 \cdot 2\text{Na}_2\text{O}) + 3\text{CO}_2 + \text{CO}]$ $2(\text{MnO}_2 \cdot 2\text{Na}_2\text{O}) + (x+8)\text{H}_2\text{O} = 2\text{Mn}(\text{OH})_4 + 8\text{NaOH} \cdot x\text{H}_2\text{O}$ $2\text{Mn}(\text{OH})_4 = \text{Mn}_2\text{O}_3 + 4\text{H}_2\text{O} + \frac{1}{2}\text{O}_2$	6

Table B-1 (Continued)

Cycle number	Elements	Maximum temperature, K	Number of reactions	Cycles	Reference*
12	Cd, Cd	1500	[2]	$\text{Cd} + \text{H}_2\text{O} = \text{CdO} + \text{H}_2$ $[\text{CdO} = \text{Cd} + \frac{1}{2}\text{O}_2]$	7
13	Cd, S	1300	4	$\text{H}_2\text{O} + \text{Cd} = \text{CdO} + \text{H}_2$ $\frac{2}{3}\text{CdO} + \frac{1}{3}\text{SO}_2 = \text{CdSO}_4 + \frac{1}{3}\text{CdS}$ $\text{CdSO}_4 = \text{CdO} + \text{SO}_2 + \frac{1}{2}\text{O}_2$ $\frac{2}{3}\text{CdO} + \frac{1}{3}\text{CdS} = \frac{1}{3}\text{SO}_2 + \text{Cd}$	2
14	Cd, S	1300	5	$\text{H}_2\text{S} + \text{Cd} = \text{CdS} + \text{H}_2$ $\frac{2}{3}\text{CdO} + \frac{1}{3}\text{CdS} = \text{Cd} + \frac{1}{3}\text{SO}_2$ $\frac{1}{3}\text{CdO} + \frac{2}{3}\text{CdS} + \frac{1}{6}\text{SO}_2 = \text{CdSO}_4 + \frac{2}{3}\text{S}$ $\text{H}_2\text{O} + \frac{3}{2}\text{S} = \text{H}_2\text{S} + \frac{1}{2}\text{SO}_2$ $\text{CdSO}_4 = \text{CdO} + \text{SO}_2 + \frac{1}{2}\text{O}_2$	2
15	Cl, Cl	1000	1 + 1**	$2\text{HCl} = \text{Cl}_2 + \text{H}_2$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$	8
16	Cr, Cl	1000	[3]	$2\text{CrCl}_2 + 2\text{HCl} = 2\text{CrCl}_3 + \text{H}_2$ $[2\text{CrCl}_3 = 2\text{CrCl}_2 + \text{Cl}_2]$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$	9
17	Cr, Cl (Fe)	1100	[4]	$2\text{CrCl}_2 + 2\text{HCl} = 2\text{CrCl}_3 + \text{H}_2$ $[2\text{CrCl}_3 + 2\text{FeCl}_2 = 2\text{CrCl}_2 + 2\text{FeCl}_3]$ $2\text{FeCl}_3 = 2\text{FeCl}_2 + \text{Cl}_2$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$	10
18	Cr, Cl (Cu, Fe)	1100	[5]	$2\text{CrCl}_2 + 2\text{HCl} = 2\text{CrCl}_3 + \text{H}_2$ $[2\text{CrCl}_3 + 2\text{FeCl}_2 = 2\text{CrCl}_2 + 2\text{FeCl}_3]$ $2\text{FeCl}_3 + 2\text{CuCl} = 2\text{FeCl}_2 + 2\text{CuCl}_2$ $2\text{CuCl}_2 = 2\text{CuCl} + \text{Cl}_2$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$	10
19	Cr, Cr (Ba)	1200	3	$\text{Cr}_2\text{O}_3 + 4\text{Ba}(\text{OH})_2 = 2\text{Ba}_2\text{CrO}_4 + 3\text{H}_2\text{O} + \text{H}_2$ $2\text{BaCrO}_4 + \text{Ba}(\text{OH})_2 = \text{Ba}_3(\text{CrO}_4)_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$ $2\text{Ba}_2\text{CrO}_4 + \text{Ba}_3(\text{CrO}_4)_2 + 5\text{H}_2\text{O} = \text{Cr}_2\text{O}_3 + 2\text{BaCrO}_4 + 5\text{Ba}(\text{OH})_2$	11
20	Cr, S (Br)	1100	[4]	$2\text{CrBr}_2 + 2\text{HBr} = 2\text{CrBr}_3 + \text{H}_2$ $[2\text{CrBr}_3 = 2\text{CrBr}_2 + \text{Br}_2]$ $\text{Br}_2 + \text{SO}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{HBr}$ $\text{H}_2\text{SO}_4 = \text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$	12
21	Cs, Cs	1500	4	$2\text{Cs} + 2\text{H}_2\text{O} = 2\text{CsOH} + \text{H}_2$ $2\text{CsOH} + \frac{3}{2}\text{O}_2 = \text{H}_2\text{O} + 2\text{CsO}_2$ $2\text{CsO}_2 = \text{Cs}_2\text{O} + \frac{3}{2}\text{O}_2$ $\text{Cs}_2\text{O} = 2\text{Cs} + \frac{1}{2}\text{O}_2$	13
22	Cs, Hg	750	4	$2\text{CsHg}_{(x-4)/2} + 2\text{H}_2\text{O} = 2\text{CsOH} + (x-4)\text{Hg} + \text{H}_2$ $2\text{CsOH} + \frac{3}{2}\text{O}_2 = 2\text{CsO}_2 + \text{H}_2\text{O}$ $2\text{CsO}_2 + x\text{Hg} = 4\text{HgO} + 2\text{CsHg}_{(x-4)/2}$ $4\text{HgO} = 4\text{Hg} + 2\text{O}_2$	14
23	Cu, Cl	1000	[3]	$[2\text{CuCl} + 2\text{HCl} = 2\text{CuCl}_2 + \text{H}_2]$ $2\text{CuCl}_2 = 2\text{CuCl} + \text{Cl}_2$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$	8
24	Cu, Cl (Mg)	900	5	$2\text{Cu} + 2\text{HCl} = 2\text{CuCl} + \text{H}_2$ $4\text{CuCl} = 2\text{CuCl}_2 + 2\text{Cu}$ $2\text{CuCl}_2 = 2\text{CuCl} + \text{Cl}_2$ $\text{Cl}_2 + \text{Mg}(\text{OH})_2 = \text{MgCl}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$ $\text{MgCl}_2 + 2\text{H}_2\text{O} = \text{Mg}(\text{OH})_2 + 2\text{HCl}$	15

Table B-1 (Continued)

Cycle number	Elements	Maximum temperature, K	Number of reactions	Cycles	Reference*
25	Cu, Cu (Br, Ca)	1200	4	$\text{Cu}_2\text{O} + 4\text{HBr} = 2\text{CuBr}_2 + \text{H}_2\text{O} + \text{H}_2$ $2\text{CuBr}_2 + 2\text{Ca(OH)}_2 = 2\text{CuO} + 2\text{CaBr}_2 + 2\text{H}_2\text{O}$ $2\text{CaBr}_2 + 4\text{H}_2\text{O} = 2\text{Ca(OH)}_2 + 4\text{HBr}$ $2\text{CuO} = \text{Cu}_2\text{O} + \frac{1}{2}\text{O}_2$	10
26	Cu, Cu (Br, S)	1350	5 + 1**	$\text{Cu} + 4\text{HBr} = \text{H}_2\text{CuBr}_4 + \text{H}_2$ $\text{H}_2\text{CuBr}_4 + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + 4\text{HBr}$ $2\text{CuSO}_4 = 2\text{CuO} + 2\text{SO}_3$ $2\text{CuO} = \text{Cu}_2\text{O} + \frac{1}{2}\text{O}_2$ $2\text{SO}_3 + 2\text{H}_2\text{O} = 2\text{H}_2\text{SO}_4$ $\text{Cu}_2\text{O} + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + \text{Cu} + \text{H}_2\text{O}$	12
27	Cu, S (Br) (A = complexing agent)	1100	6	$2\text{Cu} + 2\text{HBr} = 2\text{CuBr} + \text{H}_2$ $4\text{CuBr} + 2\text{A} = 2\text{Cu} + 2\text{CuBr}_2 \cdot \text{A}$ $2\text{CuBr}_2 \cdot \text{A} = 2\text{CuBr}_2 + 2\text{A}$ $2\text{CuBr}_2 = 2\text{CuBr} + \text{Br}_2$ $\text{Br}_2 + \text{SO}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{HBr}$ $\text{H}_2\text{SO}_4 = \text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$	12
28	Eu, Cl	1000	4	$2\text{EuCl}_2 + 2\text{HCl} + 12\text{H}_2\text{O} = 2\text{EuCl}_3 \cdot 6\text{H}_2\text{O} + \text{H}_2$ $2\text{EuCl}_3 \cdot 6\text{H}_2\text{O} = 2\text{EuCl}_3 + 12\text{H}_2\text{O}$ $2\text{EuCl}_3 = 2\text{EuCl}_2 + \text{Cl}_2$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$	16
29	Fe, C	1200	4 + 1***	$\frac{1}{2}\text{Fe} + \frac{1}{2}\text{H}_2\text{O} = \frac{1}{2}\text{FeO} + \frac{1}{2}\text{H}_2$ $\frac{3}{2}\text{FeO} + \frac{1}{2}\text{H}_2\text{O} = \frac{1}{2}\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{H}_2$ $\frac{1}{2}\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{CO} = \frac{3}{2}\text{FeO} + \frac{1}{2}\text{CO}_2$ $\frac{1}{2}\text{FeO} + \frac{1}{2}\text{CO} = \frac{1}{2}\text{Fe} + \frac{1}{2}\text{CO}_2$ $\text{***CO}_2 = \text{CO} + \frac{1}{2}\text{O}_2$	17
30	Fe, Cl	1100	5	$3\text{FeCl}_2 + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$ $\text{Fe}_3\text{O}_4 + \frac{1}{4}\text{O}_2 = \frac{3}{2}\text{Fe}_2\text{O}_3$ $\frac{3}{2}\text{Fe}_2\text{O}_3 + 9\text{HCl} = 3\text{FeCl}_3 + \frac{9}{2}\text{H}_2\text{O}$ $3\text{FeCl}_3 = 3\text{FeCl}_2 + \frac{3}{2}\text{Cl}_2$ $\frac{3}{2}\text{Cl}_2 + \frac{3}{2}\text{H}_2\text{O} = 3\text{HCl} + \frac{3}{4}\text{O}_2$	18
31	Fe, Cl	1100	4	$3\text{FeCl}_2 + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$ $\text{Fe}_3\text{O}_4 + 8\text{HCl} = \text{FeCl}_2 + 2\text{FeCl}_3 + 4\text{H}_2\text{O}$ $2\text{FeCl}_3 = 2\text{FeCl}_2 + \text{Cl}_2$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$	19
32	Fe, Cl	1000	[3]	$12\text{FeCl}_2 + 2\text{HCl} = 2\text{FeCl}_3 + \text{H}_2$ $2\text{FeCl}_3 = 2\text{FeCl}_2 + \text{Cl}_2$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$	8
33	Fe, Cl	820	3	$3\text{FeCl}_2 + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$ $\text{Fe}_3\text{O}_4 + 6\text{HCl} + \frac{3}{2}\text{Cl}_2 = 3\text{FeCl}_3 + 3\text{H}_2\text{O} + \frac{1}{2}\text{O}_2$ $3\text{FeCl}_3 = 3\text{FeCl}_2 + \frac{3}{2}\text{Cl}_2$	10
34	Fe, Cl	1300	5	$3\text{FeCl}_2 + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$ $\text{Fe}_3\text{O}_4 + \frac{1}{4}\text{O}_2 = \frac{3}{2}\text{Fe}_2\text{O}_3$ $\frac{3}{2}\text{Fe}_2\text{O}_3 + \frac{3}{2}\text{Cl}_2 = 3\text{FeCl}_3 + \frac{3}{4}\text{O}_2$ $3\text{FeCl}_3 = 3\text{FeCl}_2 + \frac{3}{2}\text{Cl}_2$ $6\text{HCl} + \frac{3}{2}\text{O}_2 = 3\text{Cl}_2 + 3\text{H}_2\text{O}$	18

Table B-1 (Continued)

Cycle number	Elements	Maximum temperature, K	Number of reactions	Cycles	Reference*
35	Fe, Cl	1300	5	$3\text{FeCl}_2 + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$ $\text{Fe}_3\text{O}_4 + \frac{1}{4}\text{O}_2 = \frac{3}{2}\text{Fe}_2\text{O}_3$ $\text{Fe}_2\text{O}_3 + 6\text{HCl} = 2\text{FeCl}_3 + 3\text{H}_2\text{O}$ $\frac{1}{2}\text{Fe}_2\text{O}_3 + \frac{3}{2}\text{Cl}_2 = \text{FeCl}_3 + \frac{3}{4}\text{O}_2$ $3\text{FeCl}_3 = 3\text{FeCl}_2 + \frac{3}{2}\text{Cl}_2$	18
36	Fe, Cl (Mg)	1000	5	$3\text{FeCl}_2 + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$ $\text{Fe}_3\text{O}_4 + 8\text{HCl} = \text{FeCl}_2 + 2\text{FeCl}_3 + 4\text{H}_2\text{O}$ $2\text{FeCl}_3 = 2\text{FeCl}_2 + \text{Cl}_2$ $\text{Cl}_2 + \text{Mg}(\text{OH})_2 = \text{MgCl}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$ $\text{MgCl}_2 + 2\text{H}_2\text{O} = \text{Mg}(\text{OH})_2 + 2\text{HCl}$	15
37	Fe, S		3	$3\text{FeO} + \text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + \text{H}_2$ $\text{Fe}_3\text{O}_4 + 3\text{FeSO}_4 = 3\text{Fe}_2\text{O}_3 + 3\text{SO}_2 + \frac{1}{2}\text{O}_2$ $3\text{Fe}_2\text{O}_3 + 3\text{SO}_2 = 3\text{FeSO}_4 + 3\text{FeO}$	20†
38	Fe, S	1300	5	$\text{Fe}_2\text{O}_3 + 4\text{H}_2\text{S} = 2\text{FeS}_2 + 3\text{H}_2\text{O} + \text{H}_2$ $2\text{FeS}_2 + 4\text{SO}_2 = 2\text{FeSO}_4 + 6\text{S}$ $4\text{H}_2\text{O} + 6\text{S} = 4\text{H}_2\text{S} + 2\text{SO}_2$ $2\text{FeSO}_4 = \text{Fe}_2\text{O}_3 + \text{SO}_3 + \text{SO}_2$ $\text{SO}_3 = \text{SO}_2 + \frac{1}{2}\text{O}_2$	2
39	Hg, Cl		[3]	$2\text{HgCl} + 2\text{HCl} = 2\text{HgCl}_2 + \text{H}_2$ $[2\text{HgCl}_2 = 2\text{HgCl} + \text{Cl}_2]$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$	1
40	Hg, Hg	520	[2]	$[\text{Hg} + \text{H}_2\text{O} = \text{HgO} + \text{H}_2]$ $\text{HgO} = \text{Hg} + \frac{1}{2}\text{O}_2$	21
41	Hg, Hg (Br, C, Ca)	1200	5	$\text{Hg} + 2\text{HBr} = \text{HgBr}_2 + \text{H}_2$ $\text{HgBr}_2 + \text{CaO} + x\text{H}_2\text{O} = \text{CaBr}_2 \cdot x\text{H}_2\text{O} + \text{HgO}$ $\text{CaBr}_2 \cdot x\text{H}_2\text{O} + \text{H}_2\text{O} + \text{CO}_2 = \text{CaCO}_3 + x\text{H}_2\text{O} + 2\text{HBr}$ $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$ $\text{HgO} = \text{Hg} + \frac{1}{2}\text{O}_2$	10
42	Hg, Hg (Br, Ca)	1000	4	$\text{Hg} + 2\text{HBr} = \text{HgBr}_2 + \text{H}_2$ $\text{HgBr}_2 + \text{Ca}(\text{OH})_2 = \text{CaBr}_2 + \text{HgO} + \text{H}_2\text{O}$ $\text{CaBr}_2 + 2\text{H}_2\text{O} = \text{Ca}(\text{CH})_2 + 2\text{HBr}$ $\text{HgO} = \text{Hg} + \frac{1}{2}\text{O}_2$	10
43	Hg, Hg (Br, Sr)	1100	3	$\text{Hg} + 2\text{HBr} = \text{HgBr}_2 + \text{H}_2$ $\text{HgBr}_2 + \text{SrO} = \text{SrBr}_2 + \text{Hg} + \frac{1}{2}\text{O}_2$ $\text{SrBr}_2 + \text{H}_2\text{O} = \text{SrO} + 2\text{HBr}$	10
44	Hg, Hg (Br, Tl)	1100	4	$\text{Hg} + 2\text{HBr} = \text{HgBr}_2 + \text{H}_2$ $\text{HgBr}_2 + 2\text{TlOH} = 2\text{TlBr} + \text{HgO} + \text{H}_2\text{O}$ $2\text{TlBr} + 2\text{H}_2\text{O} = 2\text{TlOH} + 2\text{HBr}$ $\text{HgO} = \text{Hg} + \frac{1}{2}\text{O}_2$	1
45	I, Cu	1300	[3]	$2\text{HI} = \text{I}_2 + \text{H}_2$ $\text{I}_2 + \text{Cu} + \text{H}_2\text{O} = 2\text{HI} + \text{CuO}$ $[\text{CuO} = \text{Cu} + \frac{1}{2}\text{O}_2]$	20†
46	I, Fe (S)	700	2 + 1†	$2\text{HI} = \text{I}_2 + \text{H}_2$ $\text{I}_2 + 2\text{FeSO}_4 + 2\text{H}_2\text{O} = 2\text{Fe}(\text{OH})\text{SO}_4 + 2\text{HI}$ $2\text{Fe}(\text{OH})\text{SO}_4 = 2\text{FeSO}_4 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$	22

Table B-1 (Continued)

Cycle number	Elements	Maximum temperature, K	Number of reactions	Cycles	Reference*
47	I, I (Ca)	1100	4	$2\text{HI} = \text{I}_2 + \text{H}_2$ $\text{I}_2 + \text{CaO} = \frac{1}{6}\text{Ca}(\text{IO}_3)_2 + \frac{5}{6}\text{CaI}_2$ $\text{CaI}_2 + \text{H}_2\text{O} = \text{CaO} + 2\text{HI}$ $\frac{1}{6}\text{Ca}(\text{IO}_3)_2 = \frac{1}{6}\text{CaI}_2 + \frac{1}{2}\text{O}_2$	23‡
48	I, N (K)	900	5	$2\text{NH}_4\text{I} = 2\text{NH}_3 + \text{I}_2 + \text{H}_2$ $\text{I}_2 + 2\text{KNO}_3 = 2\text{KI} + 2\text{NO}_2 + \text{O}_2$ $2\text{NO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 = 2\text{HNO}_3$ $2\text{HNO}_3 + 2\text{NH}_3 = 2\text{NH}_4\text{NO}_3$ $2\text{NH}_4\text{NO}_3 + 2\text{KI} = 2\text{KNO}_3 + 2\text{NH}_4\text{I}$	24
49	I, N (Li)	750	[3]	$2\text{HI} = \text{I}_2 + \text{H}_2$ $\{\text{I}_2 + \text{LiNO}_2 + \text{H}_2\text{O} = \text{LiNO}_3 + 2\text{HI}\}$ $\text{LiNO}_3 = \text{LiNO}_2 + \frac{1}{2}\text{O}_2$	25
50	I, S	1300	3	$2\text{HI} = \text{I}_2 + \text{H}_2$ $\text{I}_2 + \text{SO}_2 + \text{H}_2\text{O} = 2\text{HI} + \text{SO}_3$ $\text{SO}_3 = \text{SO}_2 + \frac{1}{2}\text{O}_2$	20‡
51	I, S (N, Na)	1300	6	$2\text{NH}_4\text{I} = 2\text{NH}_3 + \text{I}_2 + \text{H}_2$ $\text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O} + 4\text{NH}_3 = 2\text{NH}_4\text{I} + (\text{NH}_4)_2\text{SO}_4$ $(\text{NH}_4)_2\text{SO}_4 + \text{Na}_2\text{SO}_4 = 2\text{NaHSO}_4 + 2\text{NH}_3$ $2\text{NaHSO}_4 = \text{Na}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O}$ $\text{Na}_2\text{S}_2\text{O}_7 = \text{Na}_2\text{SO}_4 + \text{SO}_3$ $\text{SO}_3 = \text{SO}_2 + \frac{1}{2}\text{O}_2$	26
52	K, K	1000	3	$2\text{KOH} + 2\text{K} = 2\text{K}_2\text{O} + \text{H}_2$ $2\text{K}_2\text{O} = \text{K}_2\text{O}_2 + 2\text{K}$ $\text{K}_2\text{O}_2 + \text{H}_2\text{O} = 2\text{KOH} + \frac{1}{2}\text{O}_2$	27
53	Mn, Mn (C, Li)	1100	4	$2\text{Mn}_3\text{O}_4 + 3\text{Li}_2\text{CO}_3 + \text{H}_2\text{O} = 6\text{LiMnO}_2 + 3\text{CO}_2 + \text{H}_2$ $6\text{LiMnO}_2 + 6\text{CO}_2 + 3\text{H}_2\text{O} = 6\text{LiHCO}_3 + 3\text{Mn}_2\text{O}_3$ $3\text{Mn}_2\text{O}_3 = 2\text{Mn}_3\text{O}_4 + \frac{1}{2}\text{O}_2$ $6\text{LiHCO}_3 = 3\text{Li}_2\text{CO}_3 + 3\text{CO}_2 + 3\text{H}_2\text{O}$	12
54	Mn, Mn (Cl)	1100	[3]	$\{3\text{MnCl}_2 + 4\text{H}_2\text{O} = \text{Mn}_3\text{O}_4 + 6\text{HCl} + \text{H}_2\}$ $\frac{3}{2}\text{Mn}_3\text{O}_4 + 6\text{HCl} = 3\text{MnCl}_2 + \frac{3}{2}\text{MnO}_2 + 3\text{H}_2\text{O}$ $\frac{3}{2}\text{MnO}_2 = \frac{1}{2}\text{Mn}_3\text{O}_4 + \frac{1}{2}\text{O}_2$	10
55	Mn, Mn (Li)	1100	3	$2\text{Mn}_3\text{O}_4 + 6\text{LiOH} = 6\text{LiMnO}_2 + 2\text{H}_2\text{O} + \text{H}_2$ $6\text{LiMnO}_2 + 3\text{H}_2\text{O} = 3\text{Mn}_2\text{O}_3 + 6\text{LiOH}$ $3\text{Mn}_2\text{O}_3 = 2\text{Mn}_3\text{O}_4 + \frac{1}{2}\text{O}_2$	12
56	Mn, Mn (Na)	1100	[3]	$\{\text{Mn}_2\text{O}_3 + 4\text{NaOH} = 2\text{Na}_2\text{O} \cdot \text{MnO}_2 + \text{H}_2\text{O} + \text{H}_2\}$ $2\text{Na}_2\text{O} \cdot \text{MnO}_2 + (x+2)\text{H}_2\text{O} = 4\text{NaOH} \cdot x\text{H}_2\text{O} + 2\text{MnO}_2$ $2\text{MnO}_2 = \text{Mn}_2\text{O}_3 + \frac{1}{2}\text{O}_2$	10
57	Ni, I (K, Li)	1000	6	$\text{Ni} + 2\text{HI} = \text{NiI}_2 + \text{H}_2$ $\text{NiI}_2 = \text{Ni} + \text{I}_2$ $\text{I}_2 + 2\text{LiOH} = \frac{5}{3}\text{LiI} + \frac{1}{3}\text{LiIO}_3 + \text{H}_2\text{O}$ $\frac{1}{3}\text{LiIO}_3 + \frac{1}{3}\text{KI} = \frac{1}{3}\text{KIO}_3 + \frac{1}{3}\text{LiI}$ $2\text{LiI} + 2\text{H}_2\text{O} = 2\text{HI} + 2\text{LiOH}$ $\frac{1}{3}\text{KIO}_3 = \frac{1}{3}\text{KI} + \frac{1}{2}\text{O}_2$	15
58	S, Cl (Fe)	1100	4	$\text{H}_2\text{S} = \text{S} + \text{H}_2$ $\text{S} + 2\text{HCl} + 2\text{FeCl}_2 = \text{H}_2\text{S} + 2\text{FeCl}_3$ $2\text{FeCl}_3 = 2\text{FeCl}_2 + \text{Cl}_2$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$	10

Table B-1 (Continued)

Cycle number	Elements	Maximum temperature, K	Number of reactions	Cycles	Reference*
59	S, S	1300	1 + 1**	$^{**}SO_2 + 2H_2O = H_2SO_4 + H_2$ $H_2SO_4 = H_2O + SO_2 + \frac{1}{2}O_2$	12
60	S, S (Ba, Fe)	1400	5	$\frac{1}{4}BaS + H_2O = \frac{1}{4}BaSO_4 + H_2$ $\frac{1}{4}BaSO_4 + \frac{1}{2}S = \frac{1}{4}BaS + \frac{1}{2}SO_2$ $Fe_2O_3 + \frac{3}{2}SO_2 = 2FeSO_4 + \frac{1}{2}S$ $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$ $SO_3 = SO_2 + \frac{1}{2}O_2$	2
61	S, S (Ba, Zn)	1400	4	$\frac{1}{4}BaS + H_2O = \frac{1}{4}BaSO_4 + H_2$ $\frac{1}{4}BaSO_4 + \frac{1}{2}S = \frac{1}{4}BaS + \frac{1}{2}SO_2$ $ZnO + \frac{3}{2}SO_2 = ZnSO_4 + \frac{1}{2}S$ $ZnSO_4 = ZnO + SO_2 + \frac{1}{2}O_2$	2
62	S, S (Fe)	1300	5	$H_2S = H_2 + S$ $H_2O + \frac{3}{2}S = H_2S + \frac{1}{2}SO_2$ $Fe_2O_3 + \frac{3}{2}SO_2 = 2FeSO_4 + \frac{1}{2}S$ $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$ $SO_3 = SO_2 + \frac{1}{2}O_2$	2
63	S, S (Mg)	1400	3	$H_2S = S + H_2$ $S + SO_2 + MgO + H_2O = MgSO_4 + H_2S$ $MgSO_4 = MgO + SO_2 + \frac{1}{2}O_2$	28
64	S, S (Zn)	1300	4	$H_2S = H_2 + S$ $H_2O + \frac{3}{2}S = H_2S + \frac{1}{2}SO_2$ $ZnO + \frac{3}{2}SO_2 = ZnSO_4 + \frac{1}{2}S$ $ZnSO_4 = ZnO + SO_2 + \frac{1}{2}O_2$	2
65	S, S (Zn)	1300	5	$H_2S = H_2 + S$ $2H_2O + 3S = 2H_2S + SO_2$ $ZnS + 2SO_2 = ZnSO_4 + 2S$ $ZnSO_4 = ZnO + SO_2 + \frac{1}{2}O_2$ $ZnO + H_2S = ZnS + H_2O$	2
66	Se, S (Zn)	1000	5	$H_2Se = Se + H_2$ $Se + SO_2 + 2ZnO = ZnSe + ZnSO_4$ $ZnSe + H_2SO_4 = ZnSO_4 + H_2Se$ $2ZnSO_4 = 2ZnO + SO_2 + SO_3 + \frac{1}{2}O_2$ $SO_3 + H_2O = H_2SO_4$	29
67	Se, V (K)	1000	5	$H_2Se = Se + H_2$ $\frac{3}{2}Se + 2KOH = K_2Se + \frac{1}{2}SeO_2 + H_2O$ $K_2Se + 2H_2O = 2KOH + H_2Se$ $\frac{1}{2}SeO_2 + V_2O_4 = V_2O_5 + \frac{1}{2}Se$ $V_2O_5 = V_2O_4 + \frac{1}{2}O_2$	3
68	Sn, Sn	2000	[3]	$\frac{1}{2}Sn + H_2O = \frac{1}{2}SnO_2 + H_2$ $[SnO_2 = SnO + \frac{1}{2}O_2]$ $SnO = \frac{1}{2}SnO_2 + \frac{1}{2}Sn$	30
69	Ta, Cl	1300	3	$2TaCl_2 + 2HCl = 2TaCl_3 + H_2$ $2TaCl_3 = 2TaCl_2 + Cl_2$ $Cl_2 + H_2O = 2HCl + \frac{1}{2}O_2$	31
70	V, Cl	1000	4	$2VCl_2 + 2HCl = 2VCl_3 + H_2$ $4VCl_3 = 2VCl_4 + 2VCl_2$ $2VCl_4 = 2VCl_3 + Cl_2$ $Cl_2 + H_2O = 2HCl + \frac{1}{2}O_2$	31

Table B-1 (Continued)

Cycle number	Elements	Maximum temperature, K	Number of reactions	Cycles	Reference*
71	V, Cl	1100	4	$2\text{VOCl} + 2\text{HCl} = 2\text{VOCl}_2 + \text{H}_2$ $4\text{VOCl}_2 = 2\text{VOCl} + 2\text{VOCl}_3$ $2\text{VOCl}_3 = 2\text{VOCl}_2 + \text{Cl}_2$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$	10
72	U, U (Sr)	900	3	$\text{Sr}_2\text{UO}_4 + 2\text{Sr}(\text{OH})_2 = (\text{SrO})_3 \cdot \text{SrUO}_4 + \text{H}_2\text{O} + \text{H}_2$ $(\text{SrO})_3 \cdot \text{SrUO}_4 + 2\text{H}_2\text{O} = \text{SrO} \cdot \text{SrUO}_4 + 2\text{Sr}(\text{OH})_2$ $\text{SrO} \cdot \text{SrUO}_4 = \text{Sr}_2\text{UO}_4 + \frac{1}{2}\text{O}_2$	12

* Reference number refers to references at end of Table

† Original reference not available

** Electrolysis

*** Radiolysis

† Photolysis

[] around the number of reactions or around a reaction indicate, respectively, a non-viable cycle or a reaction with a large positive free energy

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Table B-2. Compilation of Additional Thermochemical Cycles for Hydrogen Production from Water

Cycle number	Elements	Maximum temperature, K	Number of reactions	Cycles	Reference (Number refers to references following table)
1	As, S (Cd)	≤ 1 000	5	$\frac{2}{3}\text{AsH}_3 = \frac{2}{3}\text{As} + \text{H}_2$ $2\text{CdO} + \frac{2}{3}\text{As} + \text{SO}_2 = \frac{1}{3}\text{Cd}_3\text{As}_2 + \text{CdSO}_4$ $2\text{CdSO}_4 = 2\text{CdO} + \text{SO}_2 + \text{SO}_3 + \frac{1}{2}\text{O}_2$ $\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$ $\frac{1}{3}\text{Cd}_3\text{As}_2 + \text{H}_2\text{SO}_4 = \text{CdSO}_4 + \frac{2}{3}\text{AsH}_3$	1
2	As, S (Co)	≤ 1 000	5	See Cycle 1	1
3	As, S (Fe)	≤ 1 000	5	See Cycle 1	1
4	As, S (Mn)	≤ 1 000	5	See Cycle 1	1
5	As, S (Ni)	≤ 1 000	5	See Cycle 1	1
6	As, S (Zn)	≤ 1 000	5	See Cycle 1	1
7	Bi, S (Cd)	≤ 1 000	5	See Cycle 1	1
8	Bi, S (Co)	≤ 1 000	5	See Cycle 1	1
9	Bi, S (Fe)	≤ 1 000	5	See Cycle 1	1
10	Bi, S (Mn)	≤ 1 000	5	See Cycle 1	1
11	Bi, S (Ni)	≤ 1 000	5	See Cycle 1	1
12	Bi, S (Zn)	≤ 1 000	5	See Cycle 1	1
13	Br, S	1 120	2 + 1*	$*2\text{HBr} = \text{Br}_2 + \text{H}_2$ $\text{Br}_2 + \text{SO}_2 + \text{H}_2\text{O} = 2\text{HBr} + \text{H}_2\text{SO}_4$ $\text{H}_2\text{SO}_4 = \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2}\text{O}_2$	2
14	C, Cl	≤ 1 300	5	$\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ $2\text{FeCl}_2 + \text{CO}_2 = \frac{1}{3}\text{Fe}_2\text{O}_3 + \frac{2}{3}\text{Fe}_2\text{Cl}_6 + \text{CO}$ $\text{Fe}_2\text{Cl}_6 = 2\text{FeCl}_2 + \text{Cl}_2$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$ $\frac{1}{3}\text{Fe}_2\text{O}_3 + 2\text{HCl} = \frac{2}{3}\text{FeCl}_3 + \text{H}_2\text{O}$	3

Table B-2 (Continued)

Cycle number	Elements	Maximum temperature, K	Number of reactions	Cycles	Reference (Number refers to references following table)
15	C, Cl (Fe)	$\leq 1\ 300$	4	$\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ $\text{FeCl}_2 + \text{CO}_2 = \text{FeO} + \text{Cl}_2 + \text{CO}$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$ $\text{FeO} + 2\text{HCl} = \text{FeCl}_2 + \text{H}_2\text{O}$	3
16	C, Cl (Mn)	$\leq 1\ 300$	4	See Cycle 15	3, 4
17	C, Cl (Mn)	$\leq 1\ 300$	5	$\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ $\frac{2}{3}\text{Mn}_2\text{O}_3 + \frac{4}{3}\text{HCl} = \frac{2}{3}\text{MnO}_2 + \frac{2}{3}\text{MnCl}_2 + \frac{2}{3}\text{H}_2\text{O}$ $\frac{2}{3}\text{MnO}_2 = \frac{1}{3}\text{Mn}_2\text{O}_3 + \frac{1}{6}\text{O}_2$ $\frac{2}{3}\text{MnCl}_2 + \text{CO}_2 = \frac{1}{3}\text{Mn}_2\text{O}_3 + \text{CO} + \frac{2}{3}\text{Cl}_2$ $\frac{2}{3}\text{Cl}_2 + \frac{2}{3}\text{H}_2\text{O} = \frac{4}{3}\text{HCl} + \frac{1}{3}\text{O}_2$	3
18	C, S		3	$\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ $\text{CO}_2 + \text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{CO}$ $\text{H}_2\text{SO}_4 = \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2}\text{O}_2$	5
19	C, S (Al)	$< 1\ 200$	4	$\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$ $\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$ $\text{CH}_3\text{OH} + \text{SO}_2 + \frac{1}{3}\text{Al}_2\text{O}_3 = \frac{1}{3}\text{Al}_2(\text{SO}_4)_3 + \text{CH}_4$ $\frac{1}{3}\text{Al}_2(\text{SO}_4)_3 = \frac{1}{3}\text{Al}_2\text{O}_3 + \text{SO}_2 + \frac{1}{2}\text{O}_2$	6
20	C, S (Co)	$< 1\ 200$	4	See Cycle 19	6
21	C, S (Cu)	$< 1\ 200$	4	See Cycle 19	6
22	C, S (Mn)	$< 1\ 200$	4	See Cycle 19	6
23	C, S (Ni)	$< 1\ 200$	4	See Cycle 19	6
24	C, S (Sn)	$< 1\ 200$	4	See Cycle 19	6
25	C, S (Zn)	$< 1\ 200$	4	See Cycle 19	6
26	C, S	1 200	5	$\frac{1}{3}\text{CO} + \frac{2}{3}\text{H}_2 + \frac{1}{3}\text{H}_2\text{O} = \frac{1}{3}\text{CO}_2 + \text{H}_2$ $\frac{1}{3}\text{CO}_2 + \frac{2}{3}\text{H}_2\text{O} + \text{CH}_4 = \frac{4}{3}\text{CO} + \frac{8}{3}\text{H}_2$ $\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$ $\text{H}_2\text{O} + \text{SO}_2 + \text{CH}_3\text{OH} = \text{H}_2\text{SO}_4 + \text{CH}_4$ $\text{H}_2\text{SO}_4 = \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2}\text{O}_2$	7, 8
27	C, S (Fe)		5	$\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ $\text{CO}_2 + \text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{CO}$ $\text{H}_2\text{SO}_4 + \frac{1}{3}\text{Fe}_2\text{O}_3 = \frac{1}{3}\text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$ $\frac{1}{3}\text{Fe}_2(\text{SO}_4)_3 = \frac{1}{3}\text{Fe}_2\text{O}_3 + \text{SO}_3$ $\text{SO}_3 = \text{SO}_2 + \frac{1}{2}\text{O}_2$ (See also Cycle 18)	9
28	Cd, Cd	1 500	2 + 1*	$^*\text{Cd} + 2\text{H}_2\text{O} = \text{Cd}(\text{OH})_2 + \text{H}_2$ $\text{Cd}(\text{OH})_2 = \text{CdO} + \text{H}_2\text{O}$ $\text{CdO} = \text{Cd} + \frac{1}{2}\text{O}_2$	10

Table B-2 (Continued)

Cycle number	Elements	Maximum temperature, K	Number of reactions	Cycles	Reference (Number refers to references following table)
29	Cd, I (Ga, Pb)	1 100	6	$\text{Cd} + \text{H}_2\text{O} = \text{CdO} + \text{H}_2$ $\frac{6}{5}\text{CdO} + \frac{6}{5}\text{I}_2 = \frac{1}{5}\text{Cd}(\text{IO}_3)_2 + \text{CdI}_2$ $\frac{1}{5}\text{Cd}(\text{IO}_3)_2 = \frac{1}{5}\text{CdO} + \frac{1}{5}\text{I}_2 + \frac{1}{2}\text{O}_2$ $\text{CdI}_2 + \text{Pb} = \text{PbI}_2 + \text{Cd}$ $\text{PbI}_2 + \frac{2}{3}\text{Ga} = \frac{2}{3}\text{GaI}_2 + \text{Pb}$ $\frac{2}{3}\text{GaI}_3 = \frac{2}{3}\text{Ga} + \text{I}_2$	11
30	Ce, Cl		4	$2\text{CeOCl} + 2\text{H}_2\text{O} = 2\text{CeO}_2 + 2\text{HCl} + \text{H}_2$ $2\text{CeO}_2 + 8\text{HCl} = 2\text{CeCl}_3 + 4\text{H}_2\text{O} + \text{Cl}_2$ $2\text{CeCl}_3 + 2\text{H}_2\text{O} = 2\text{CeOCl} + 4\text{HCl}$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$	12, 13
31	Ce, Cl		3	$2\text{CeCl}_3 \times \text{H}_2\text{O} + (4 - 2x)\text{H}_2\text{O} = 2\text{CeO}_2 + 6\text{HCl} + \text{H}_2$ $2\text{CeO}_2 + 8\text{HCl} = 2\text{CeCl}_3 \times \text{H}_2\text{O} + (4 - 2x)\text{H}_2\text{O} + \text{Cl}_2$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$	13
32	Ce, Cl (C)		5	$\text{Ce}_2(\text{CO}_3)_3 + \text{H}_2\text{O} = 2\text{CeO}_2 + 3\text{CO}_2 + \text{H}_2$ $2\text{CeO}_2 + 8\text{HCl} = 2\text{CeCl}_3 + 4\text{H}_2\text{O} + \text{Cl}_2$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$ $2\text{CeCl}_3 + 3\text{H}_2\text{O} = 3\text{CeOCl} + 6\text{HCl}$ $3\text{CeOCl} + 3\text{CO}_2 = \text{Ce}_2(\text{CO}_3)_3 + \text{CeCl}_3$	12
33	Ce, S (Br)		4	$2\text{CeBr}_3 \times \text{H}_2\text{O} + (4 - 2x)\text{H}_2\text{O} = 2\text{CeO}_2 + 6\text{HBr} + \text{H}_2$ $2\text{CeO}_2 + 8\text{HBr} = 2\text{CeBr}_3 \times \text{H}_2\text{O} + (4 - 2x)\text{H}_2\text{O} + \text{Br}_2$ $\text{Br}_2 + \text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{HBr}$ $\text{H}_2\text{SO}_4 = \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2}\text{O}_2$	13
34	Cr, Co (Br)	1 320	5	$2\text{CrBr}_2 + 2\text{HBr} = 2\text{CrBr}_3 + \text{H}_2$ $2\text{CrBr}_3 = 2\text{CrBr}_2 + \text{Br}_2$ $4\text{CoO} + \text{Br}_2 = \text{CoBr}_2 + \text{Co}_3\text{O}_4$ $\text{Co}_3\text{O}_4 = 3\text{CoO} + \frac{1}{2}\text{O}_2$ $\text{CoBr}_2 + \text{H}_2\text{O} = \text{CoO} + 2\text{HBr}$	14
35	Cr, Cr (K)	1 200	3	$\frac{1}{2}\text{Cr}_2\text{O}_3 + 3\text{KOH} = \text{K}_3\text{CrO}_4 + \frac{1}{2}\text{H}_2\text{O} + \text{H}_2$ $3\text{K}_3\text{CrO}_4 + \frac{5}{2}\text{H}_2\text{O} = \frac{1}{2}\text{Cr}_2\text{O}_3 + 2\text{K}_2\text{CrO}_4 + 5\text{KOH}$ $2\text{K}_2\text{CrO}_4 + 2\text{KOH} = 2\text{K}_3\text{CrO}_4 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$	15
36	Cr, Cr (Sr)	1 300	3	$\text{Cr}_2\text{O}_3 + 4\text{Sr}(\text{OH})_2 = 2\text{Sr}_2\text{CrO}_4 + 3\text{H}_2\text{O} + \text{H}_2$ $2\text{SrCrO}_4 + \frac{4}{3}\text{Sr}(\text{OH})_2 = \frac{2}{3}\text{Sr}_5(\text{CrO}_4)_3\text{OH} + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$ $2\text{Sr}_2\text{CrO}_4 + \frac{2}{3}\text{Sr}_5(\text{CrO}_4)_3\text{OH} + 5\text{H}_2\text{O} = \text{Cr}_2\text{O}_3 + 2\text{SrCrO}_4 + \frac{16}{3}\text{Sr}(\text{OH})_2$	16
37	Cr, Mn (Br)	1 400	5	$2\text{CrBr}_2 + 2\text{HBr} = 2\text{CrBr}_3 + \text{H}_2$ $2\text{CrBr}_3 = 2\text{CrBr}_2 + \text{Br}_2$ $2\text{MnO} + \text{Br}_2 = \text{MnBr}_2 + \text{MnO}_2$ $\text{MnO}_2 = \text{MnO} + \frac{1}{2}\text{O}_2$ $\text{MnBr}_2 + \text{H}_2\text{O} = \text{MnO} + 2\text{HBr}$	14
38	Cu, Cl (Mg)	900	4	$2\text{CuCl} + 2\text{HCl} = 2\text{CuCl}_2 + \text{H}_2$ $2\text{CuCl}_2 = 2\text{CuCl} + \text{Cl}_2$ $\text{Cl}_2 + \text{MgO} = \text{MgCl}_2 + \frac{1}{2}\text{O}_2$ $\text{MgCl}_2 + \text{H}_2\text{O} = \text{MgO} + 2\text{HCl}$	17

Table B-2 (Continued)

Cycle number	Elements	Maximum temperature, K	Number of reactions	Cycles	Reference (Number refers to references following table)
39	Cu, Cu (Cl, N, S)	1 340	6	$2\text{Cu} + 2\text{NH}_4\text{Cl} = 2\text{CuCl} + 2\text{NH}_3 + \text{H}_2$ $2\text{CuCl} + 2\text{NH}_3 + \text{H}_2\text{O} = \text{Cu}_2\text{O} + 2\text{NH}_4\text{Cl}$ $2\text{Cu}_2\text{O} + 2\text{H}_2\text{SO}_4 = 2\text{Cu} + 2\text{CuSO}_4 + 2\text{H}_2\text{O}$ $2\text{CuSO}_4 = 2\text{CuO} + 2\text{SO}_3$ $2\text{CuO} = \text{Cu}_2\text{O} + \frac{1}{2}\text{O}_2$ $2\text{H}_2\text{O} + 2\text{SO}_3 = 2\text{H}_2\text{SO}_4$	18
40	Cu, S (Br, Mg)		6	$2\text{Cu} + 2\text{HBr} = 2\text{CuBr} + \text{H}_2$ $2\text{CuBr} + \text{MgO} = \text{MgBr}_2 + \text{Cu}_2\text{O}$ $\text{MgBr}_2 + \text{H}_2\text{O} = \text{MgO} + 2\text{HBr}$ $\frac{1}{2}\text{S} + \text{Cu}_2\text{O} = 2\text{Cu} + \frac{1}{2}\text{SO}_2$ $\frac{3}{2}\text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \frac{1}{2}\text{S}$ $\text{H}_2\text{SO}_4 = \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2}\text{O}_2$	12
41	Cu, S (Cl, Mg)		6	$2\text{Cu} + 2\text{HCl} = 2\text{CuCl} + \text{H}_2$ $2\text{CuCl} + \text{MgO} = \text{MgCl}_2 + \text{Cu}_2\text{O}$ $\text{MgCl}_2 + \text{H}_2\text{O} = \text{MgO} + 2\text{HCl}$ $\text{Cu}_2\text{O} + \frac{1}{2}\text{S} = 2\text{Cu} + \frac{1}{2}\text{SO}_2$ $\frac{3}{2}\text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \frac{1}{2}\text{S}$ $\text{H}_2\text{SO}_4 = \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2}\text{O}_2$	19
42	Eu, Cl (Co)	1 200	4	$2\text{EuCl}_2 + 2\text{HCl} = 2\text{EuCl}_3 + \text{H}_2$ $2\text{EuCl}_3 = 2\text{EuCl}_2 + \text{Cl}_2$ $\text{CoO} + \text{Cl}_2 = \text{CoCl}_2 + \frac{1}{2}\text{O}_2$ $\text{CoCl}_2 + \text{H}_2\text{O} = \text{CoO} + 2\text{HCl}$	14
43	Eu, Cl (Mg)	1 120	4	See Cycle 42	14
44	Eu, Cl (Ni)	1 120	4	See Cycle 42	14
45	Eu, Cl (Y)	1 120	4	$2\text{EuCl}_2 + 2\text{HCl} = 2\text{EuCl}_3 + \text{H}_2$ $2\text{EuCl}_3 = 2\text{EuCl}_2 + \text{Cl}_2$ $\frac{1}{3}\text{Y}_2\text{O}_3 + \text{Cl}_2 = \frac{2}{3}\text{YCl}_3 + \frac{1}{2}\text{O}_2$ $\frac{2}{3}\text{YCl}_3 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{3}\text{Y}_2\text{O}_3$	14
46	Eu, I (Sr)	1 300	3	$2\text{EuO} + \text{H}_2\text{O} = \text{Eu}_2\text{O}_3 + \text{H}_2$ $\text{Eu}_2\text{O}_3 + \text{SrI}_2 = 2\text{EuO} + \text{I}_2 + \text{SrO}$ $\text{I}_2 + \text{SrO} = \text{SrI}_2 + \frac{1}{2}\text{O}_2$	20
47	Fe, Br		3	$3\text{FeBr}_2 + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 6\text{HBr} + \text{H}_2$ $\text{Fe}_3\text{O}_4 + 8\text{HBr} = 3\text{FeBr}_2 + 4\text{H}_2\text{O} + \text{Br}_2$ $\text{H}_2\text{O} + \text{Br}_2 = 2\text{HBr} + \frac{1}{2}\text{O}_2$	21
48	Fe, Cl	$\leq 1\,300$	4	$3\text{FeCl}_2 + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 8\text{HCl} + \text{H}_2$ $\text{Fe}_3\text{O}_4 + \frac{9}{2}\text{Cl}_2 = 3\text{FeCl}_3 + 2\text{O}_2$ $3\text{FeCl}_3 = 3\text{FeCl}_2 + \frac{3}{2}\text{Cl}_2$ $6\text{HCl} + \frac{3}{2}\text{O}_2 = 3\text{H}_2\text{O} + 3\text{Cl}_2$	22
49	Fe, Cl		4	$3\text{FeCl}_2 + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$ $\text{Fe}_3\text{O}_4 + 8\text{HCl} = \text{FeCl}_2 + 2\text{FeCl}_3 + 4\text{H}_2\text{O}$ $2\text{FeCl}_3 = 2\text{FeCl}_2 + \text{Cl}_2$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$	22, 23

Table B-2 (Continued)

Cycle number	Elements	Maximum temperature, K	Number of reactions	Cycles	Reference (Number refers to references following table)
50	Fe, Cl	< 1 300	5	$3\text{FeCl}_2 + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$ $\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{Cl}_2 = \frac{1}{3}\text{FeCl}_3 + \frac{4}{3}\text{Fe}_2\text{O}_3$ $\frac{4}{3}\text{Fe}_2\text{O}_3 + 8\text{HCl} = \frac{8}{3}\text{FeCl}_3 + 4\text{H}_2\text{O}$ $3\text{FeCl}_3 = 3\text{FeCl}_2 + \frac{3}{2}\text{Cl}_2$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$	23
51	Fe, Cl	~ 1 300	5	$3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$ $\text{Fe}_3\text{O}_4 + 8\text{HCl} = 2\text{FeCl}_3 + \text{FeCl}_2 + 4\text{H}_2\text{O}$ $2\text{FeCl}_3 = 2\text{FeCl}_2 + \text{Cl}_2$ $3\text{FeCl}_2 + 3\text{H}_2 = 3\text{Fe} + 6\text{HCl}$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$	22
52	Fe, Cl	1 300	5	$3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$ $\text{Fe}_3\text{O}_4 + 8\text{HCl} + \frac{1}{2}\text{Cl}_2 = 3\text{FeCl}_3 + 4\text{H}_2\text{O}$ $3\text{FeCl}_3 = 3\text{FeCl}_2 + \frac{3}{2}\text{Cl}_2$ $3\text{FeCl}_2 + 3\text{H}_2 = 3\text{Fe} + 6\text{HCl}$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$	24
53	Fe, Cl	1 300	5	$3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$ $\text{Fe}_3\text{O}_4 + \frac{9}{2}\text{Cl}_2 = 3\text{FeCl}_3 + 2\text{O}_2$ $3\text{FeCl}_3 = 3\text{FeCl}_2 + \frac{3}{2}\text{Cl}_2$ $3\text{FeCl}_2 + 3\text{H}_2 = 3\text{Fe} + 6\text{HCl}$ $6\text{HCl} + \frac{3}{2}\text{O}_2 = 3\text{H}_2\text{O} + 3\text{Cl}_2$	22, 25
54	Fe, Cl	1 200	4	$3\text{FeO} + \text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + \text{H}_2$ $\text{Fe}_3\text{O}_4 + 8\text{HCl} = 3\text{FeCl}_2 + \text{Cl}_2 + 4\text{H}_2\text{O}$ $3\text{FeCl}_2 + 3\text{H}_2\text{O} = 3\text{FeO} + 6\text{HCl}$ $\text{H}_2\text{O} + \text{Cl}_2 = 2\text{HCl} + \frac{1}{2}\text{O}_2$	26
55	Fe, Cl	1 100	4	$3\text{FeCl}_2 + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$ $\text{Fe}_3\text{O}_4 + 8\text{HCl} = 2\text{FeCl}_3 + \text{FeCl}_2 + 4\text{H}_2\text{O}$ $2\text{FeCl}_3 = 2\text{FeCl}_2 + \text{Cl}_2$ $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$	27
56	Fe, Cl (C, Cu, Mg)	1 100	8	$3\text{FeCl}_2 + 4\text{H}_2\text{O} + \frac{1}{4}\text{O}_2 = \frac{3}{2}\text{Fe}_2\text{O}_3 + 6\text{HCl} + \text{H}_2$ $\frac{3}{2}\text{Fe}_2\text{O}_3 + 9\text{HCl} = 3\text{FeCl}_3 + \frac{9}{2}\text{H}_2\text{O}$ $3\text{FeCl}_3 + \frac{3}{2}\text{CO} = 3\text{FeCl}_2 + \frac{3}{2}\text{COCl}_2$ $\frac{3}{2}\text{COCl}_2 + \text{CuCl} = 3\text{CuCl}_2 + \frac{3}{2}\text{CO}$ $3\text{CuCl}_2 = 3\text{CuCl} + \frac{3}{2}\text{Cl}_2$ $\frac{3}{2}\text{Cl}_2 + 3\text{Mg(OH)Cl} = 3\text{MgCl}_2 + \frac{3}{2}\text{H}_2\text{O} + \frac{3}{4}\text{O}_2$ $6\text{HCl} + 6\text{Mg(OH)Cl} = 6\text{MgCl}_2 + 6\text{H}_2\text{O}$ $9\text{MgCl}_2 + 9\text{H}_2\text{O} = 9\text{Mg(OH)Cl} + 9\text{HCl}$	28
57	Fe, Cl (Mg)	923	6	$3\text{FeCl}_2 + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$ $\text{Fe}_3\text{O}_4 + 8\text{HCl} = \text{FeCl}_2 + 2\text{FeCl}_3 + 4\text{H}_2\text{O}$ $2\text{FeCl}_3 = \text{Fe}_2\text{Cl}_6$ $\text{Fe}_2\text{Cl}_6 = 2\text{FeCl}_2 + \text{Cl}_2$ $\text{Cl}_2 + \text{MgO} = \text{MgCl}_2 + \frac{1}{2}\text{O}_2$ $\text{H}_2\text{O} + \text{MgCl}_2 = \text{MgO} + 2\text{HCl}$	29
58	Fe, Fe (Cl)	1 600	3	$3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$ $\text{Fe}_3\text{O}_4 + 6\text{HCl} = 3\text{FeCl}_2 + 3\text{H}_2\text{O} + \frac{1}{2}\text{O}_2$ $3\text{FeCl}_2 + 3\text{H}_2 = 3\text{Fe} + 6\text{HCl}$	30

Table B-2 (Continued)

Cycle number	Elements	Maximum temperature, K	Number of reactions	Cycles	Reference (Number refers to references following table)
59	Fe, Fe (Cl)	1 300	3	$\frac{3}{2}\text{FeO} + \frac{3}{2}\text{Fe} + \frac{15}{6}\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + \frac{15}{6}\text{H}_2$ $\text{Fe}_3\text{O}_4 + 6\text{HCl} = 3\text{FeCl}_2 + 3\text{H}_2\text{O} + \frac{1}{2}\text{O}_2$ $3\text{FeCl}_2 + \frac{3}{2}\text{H}_2\text{O} + \frac{3}{2}\text{H}_2 = \frac{3}{2}\text{FeO} + \frac{3}{2}\text{Fe} + 6\text{HCl}$	31
60	Fe, Fe (K)	1 700	3	$2\text{Fe}_3\text{O}_4 + 6\text{KOH} = 6\text{KFeO}_2 + 2\text{H}_2\text{O} + \text{H}_2$ $6\text{KFeO}_2 + 3\text{H}_2\text{O} = 6\text{KOH} + 3\text{Fe}_2\text{O}_3$ $3\text{Fe}_2\text{O}_3 = 2\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{O}_2$	32
61	Fe, Fe (Na)	1 700	3	See Cycle 60	32
62	Fe, S	1 200	4	$\frac{1}{2}\text{Fe}_3\text{O}_4 + \frac{3}{2}\text{SO}_2 + \text{H}_2\text{O} = \frac{3}{2}\text{FeSO}_4 + \text{H}_2$ $\frac{3}{2}\text{FeSO}_4 = \frac{3}{4}\text{Fe}_2\text{O}_3 + \frac{3}{4}\text{SO}_2 + \frac{3}{4}\text{SO}_3$ $\frac{3}{4}\text{Fe}_2\text{O}_3 + \frac{1}{4}\text{SO}_2 = \frac{1}{4}\text{Fe}_3\text{O}_4 + \frac{1}{4}\text{SO}_3$ $\text{SO}_3 = \text{SO}_2 + \frac{1}{2}\text{O}_2$	25, 33
63	Fe, S (C)	1 200	5	$\frac{3}{2}\text{FeS} + \text{H}_2\text{O} = \frac{1}{4}\text{Fe}_3\text{O}_4 + \frac{3}{4}\text{FeS}_2 + \text{H}_2$ $\frac{3}{4}\text{FeS}_2 + \frac{1}{4}\text{S}_2 + \frac{1}{4}\text{Fe}_3\text{O}_4 = \frac{3}{2}\text{FeS} + \frac{1}{2}\text{SO}_2$ $\frac{3}{2}\text{SO}_2 + \text{H}_2\text{O} + \text{CH}_3\text{OH} = \text{CH}_3\text{HSO}_4 + \frac{1}{2}\text{S} + \text{H}_2\text{O}$ $\text{CH}_3\text{HSO}_4 + \text{H}_2\text{O} = \text{CH}_3\text{OH} + \text{H}_2\text{SO}_4$ $\text{H}_2\text{SO}_4 = \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2}\text{O}_2$	7
64	Fe, S (Cl)		7	$\frac{3}{4}\text{FeCl}_2 + \text{H}_2\text{O} = \frac{1}{4}\text{Fe}_3\text{O}_4 + \frac{3}{2}\text{HCl} + \frac{1}{4}\text{H}_2$ $\frac{3}{4}\text{FeS} + \frac{3}{4}\text{H}_2\text{S} = \text{FeS}_2 + \frac{3}{4}\text{H}_2$ $\frac{3}{4}\text{FeS}_2 = \frac{3}{4}\text{FeS} + \frac{3}{4}\text{S}$ $\frac{3}{4}\text{FeS} + \frac{3}{2}\text{HCl} = \frac{3}{4}\text{FeCl}_2 + \frac{3}{4}\text{H}_2\text{S}$ $\frac{1}{4}\text{Fe}_3\text{O}_4 + \frac{5}{4}\text{S} = \frac{3}{4}\text{FeS} + \frac{1}{2}\text{SO}_2$ $\frac{3}{2}\text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \frac{1}{2}\text{S}$ $\text{H}_2\text{SO}_4 = \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2}\text{O}_2$	19
65	Ge, Co (S)	1 100	3 or 4	$\text{Ge} + \text{H}_2\text{O} = \text{GeO} + \text{H}_2$ $\text{GeO} + \text{SO}_2 = \text{Ge} + \text{SO}_3$ or $(\text{GeO} + 3\text{CoO} = \text{Ge} + \text{Co}_3\text{O}_4)$ $\text{SO}_3 + 3\text{CoO} = \text{SO}_2 + \text{Co}_3\text{O}_4$ $(\text{Co}_3\text{O}_4 = 3\text{CoO} + \frac{1}{2}\text{O}_2)$	34
66	Ge, Cu (S)	< 1 300		See Cycle 65	34
67	Ge, Pb (S)	< 1 300		See Cycle 65	34
68	Hg, Hg (C, I, K, N)	900	4	$2\text{NH}_4\text{I} + \text{Hg} = 2\text{NH}_3 + \text{HgI}_2 + \text{H}_2$ $\text{HgI}_2 + \text{K}_2\text{CO}_3 = 2\text{KI} + \text{Hg} + \text{CO}_2 + \frac{1}{2}\text{O}_2$ $2\text{H}_2\text{O} + 2\text{NH}_3 + 2\text{CO}_2 + 2\text{KI} = 2\text{KHCO}_3 + 2\text{NH}_4\text{I}$ $2\text{KHCO}_3 = \text{K}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$	35
69	I, Br (Ni, S)	1 200	6	$2\text{HI} = \text{I}_2 + \text{H}_2$ $\text{H}_2\text{S} + \text{I}_2 = 2\text{HI} + \frac{1}{2}\text{S}_2$ $\text{NiBr}_2 + \frac{1}{2}\text{S}_2 = \text{NiS} + \text{Br}_2$ $\text{NiS} + 2\text{HBr} = \text{H}_2\text{S} + \text{NiBr}_2$ $\text{NiBr}_2 + \text{H}_2\text{O} = \text{NiO} + 2\text{HBr}$ $\text{NiO} + \text{Br}_2 = \text{NiBr}_2 + \frac{1}{2}\text{O}_2$	36

Table B-2 (Continued)

Cycle number	Elements	Maximum temperature, K	Number of reactions	Cycles	References (Number refers to references following table)
70	I, Fe (S)		1 ¹ + 2*	*2HI = I ₂ + H ₂ 1 ¹ 2FeSO ₄ + I ₂ + H ₂ SO ₄ = Fe ₂ (SO ₄) ₃ + 2HI *Fe ₂ (SO ₄) ₃ + H ₂ O = 2FeSO ₄ + H ₂ SO ₄ + 1/2O ₂	37
71	I, Fe (S)		1 + 1 ¹ + 1*	See Cycle 70	37
72	I, I	700	3	2HI = I ₂ + H ₂ 6/5I ₂ + 6/5H ₂ O = 2HI + 2/5HIO ₃ 2/5HIO ₃ = 1/5H ₂ O + 1/5I ₂ + 1/2O ₂	38
73	I, I (Ba, C, N)	1 100	3	2NH ₄ I = 2NH ₃ + I ₂ + H ₂ BaCO ₃ + I ₂ = BaI ₂ + CO ₂ + 1/2O ₂ BaI ₂ + 2NH ₃ + CO ₂ + H ₂ O = BaCO ₃ + 2NH ₄ I	39
74	I, I (Ba, C, Fe, N)	1 100	5	3/2HI = 3/4I ₂ + 3/4H ₂ 3/4FeI ₂ + H ₂ O = 1/4Fe ₃ O ₄ + 3/2HI + 1/4H ₂ 2NH ₄ I + 1/4Fe ₃ O ₄ = 3/4FeI ₂ + 2NH ₃ + H ₂ O + 1/4I ₂ BaI ₂ + 2NH ₃ + CO ₂ + H ₂ O = BaCO ₃ + 2NH ₄ I BaCO ₃ + I ₂ = BaI ₂ + CO ₂ + 1/2O ₂	39
75	I, I (Ba, C, Mg, N)	1 100	5	See Cycle 74	39
76	I, I (C, N, Na)	900	6	2NH ₄ I = 2NH ₃ + I ₂ + H ₂ 2NH ₃ + H ₂ O = 2NH ₄ OH 2NaI + 2NH ₄ OH + 2CO ₂ = 2NaHCO ₃ + 2NH ₄ I 2NaHCO ₃ = Na ₂ CO ₃ + H ₂ O + CO ₂ Na ₂ CO ₃ + I ₂ = 1/3NaIO ₃ + 5/3NaI + CO ₂ 1/3NaIO ₃ = 1/3NaI + 1/2O ₂	7
77	I, S	1 100	3	2HI = I ₂ + H ₂ 2H ₂ O + SO ₂ + I ₂ = H ₂ SO ₄ + 2HI H ₂ SO ₄ = H ₂ O + SO ₂ + 1/2O ₂	40
78	I, S (C)	1 100	4	2HI = I ₂ + H ₂ C ₂ H ₆ O + I ₂ + H ₂ SO ₃ = 2CH ₃ I + H ₂ SO ₄ 2CH ₃ I + H ₂ O = C ₂ H ₆ O + 2HI H ₂ SO ₄ = H ₂ O + SO ₂ + 1/2O ₂	7
79	Ni, I (C)	700	6	Ni + 2H ₂ O = Ni(OH) ₂ + H ₂ Ni(OH) ₂ = NiO + H ₂ O 6/5NiO + 6/5I ₂ = 1/5Ni(IO ₃) ₂ + NiI ₂ 1/5Ni(IO ₃) ₂ = 1/5NiO + 1/5I ₂ + 1/2O ₂ NiI ₂ + 4CO = Ni(CO) ₄ + I ₂ Ni(CO) ₄ = Ni + 4CO	11
80	Ni, I (N, Na)	1 100	4	2NH ₄ I + Ni = NiI ₂ + 2NH ₃ + H ₂ NiI ₂ = Ni + I ₂ I ₂ + Na ₂ CO ₃ = 2NaI + CO ₂ + 1/2O ₂ 2NaI + 2NH ₃ + CO ₂ + H ₂ O = Na ₂ CO ₃ + 2NH ₄ I	41
81	P, S		5	H ₃ PO ₃ + H ₂ O = H ₃ PO ₄ + H ₂ H ₃ PO ₄ + 1/2S = 1/4P ₄ O ₆ + 1/2SO ₂ + 3/2H ₂ O 1/4P ₄ O ₆ + 3/2H ₂ O = H ₃ PO ₃ 3/2SO ₂ + H ₂ O = H ₂ SO ₄ + 1/2S H ₂ SO ₄ = H ₂ O + SO ₂ + 1/2O ₂	19

Table B-2 (Continued)

Cycle number	Elements	Maximum temperature, K	Number of reactions	Cycles	Reference (Number refers to references following table)
82	S, S		4	$H_2S = S + H_2$ $\frac{3}{2}S + H_2O = H_2S + \frac{1}{2}SO_2$ $\frac{3}{2}SO_2 + H_2O = H_2SO_4 + \frac{1}{2}S$ $H_2SO_4 = H_2O + SO_2 + \frac{1}{2}O_2$	19
83	S, S (C, Ca)	1 150	6	$H_2S = S + H_2$ $\frac{3}{2}S + CaO = CaS + \frac{1}{2}SO_2$ $CaS + H_2O + CO_2 = CaCO_3 + H_2S$ $CaCO_3 = CaO + CO_2$ $\frac{3}{2}SO_2 + H_2O = H_2SO_4 + \frac{1}{2}S$ $H_2SO_4 = H_2O + SO_2 + \frac{1}{2}O_2$	42
84	S, S (Ca, Zn)	1 150	6	$H_2S = S + H_2$ $\frac{1}{2}CaS + 2H_2O + 2S = 2H_2S + \frac{1}{2}CaSO_4$ $\frac{1}{2}CaSO_4 + S = SO_2 + \frac{1}{2}CaS$ $ZnS + 2SO_2 = ZnSO_4 + 2S$ $ZnSO_4 + 0.143SO_3 = ZnO + SO_2 + \frac{1}{2}O_2 + 0.143SO_3$ $H_2S + ZnO = ZnS + H_2O$	43
85	S, S (Cd)	$\leq 1\ 300$	2	$SO_2 + H_2O + CdO = CdSO_4 + H_2$ $CdSO_4 = CdO + SO_2 + \frac{1}{2}O_2$	44
86	S, S (Co)	$\leq 1\ 300$	2	See Cycle 85	44
87	S, S (Co)	1 200	2	$\frac{3}{2}SO_2 + H_2O + \frac{1}{2}Co_3O_4 = \frac{3}{2}CoSO_4 + H_2$ $\frac{3}{2}CoSO_4 = \frac{1}{2}Co_3O_4 + \frac{3}{2}SO_2 + \frac{1}{2}O_2$	44
88	S, S (Fe)	$\leq 1\ 300$	2	See Cycles 85 and 87	44
89	S, S (Fe)	1 200	3	$Fe_2O_3 + 2SO_2 + H_2O = 2FeSO_4 + H_2$ $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$ $SO_3 = SO_2 + \frac{1}{2}O_2$	45
90	S, S (La)	1 150	6	$H_2S = S + H_2$ $\frac{5}{2}S + La_2O_3 = La_2O_2S_2 + \frac{1}{2}SO_2$ $La_2O_2S_2 + H_2O + 3CO_2 = La_2(CO_3)_3 + S + H_2S$ $La_2(CO_3)_3 = La_2O_3 + 3CO_2$ $\frac{3}{2}SO_2 + H_2O = H_2SO_4 + \frac{1}{2}S$ $H_2SO_4 = H_2O + SO_2 + \frac{1}{2}O_2$	42
91	S, S (Mn)	$\sim 1\ 250$	2	See Cycles 85 and 87	44
92	S, S (C, Mn)	1 100	5	$H_2S = S + H_2$ $\frac{3}{2}S + MnCO_3 = MnS + CO_2 + \frac{1}{2}SO_2$ $MnS + H_2O + CO_2 = MnCO_3 + H_2S$ $\frac{3}{2}SO_2 + H_2O = H_2SO_4 + \frac{1}{2}S$ $H_2SO_4 = H_2O + SO_2 + \frac{1}{2}O_2$	42
93	S, S (Ni)	$\leq 1\ 300$	2	See Cycle 85	44

Table B-2 (Continued)

Cycle number	Elements	Maximum temperature, K	Number of reactions	Cycles	References (Number refers to references following table)
94	S, S (Zn)	< 1 300	2	See Cycle 85	44
95	S, S (Zn)	1 144	4	$H_2S = \frac{1}{2}S_2 + H_2$ $\frac{1}{8}S_8 = \frac{1}{4}S_2$ $\frac{3}{2}SO_2 + ZnO = \frac{1}{2}S + ZnSO_4$ $ZnSO_4 + 0.143SO_3 = ZnO + SO_2 + \frac{1}{2}O_2 + 0.143SO_3$ $\frac{3}{4}S_2 + H_2O = H_2S + \frac{1}{2}SO_2$	43
96	Sb, S (Cd)	< 1 000	5	See Cycle 1	1
97	Sb, S (Co)	< 1 000	5	See Cycle 1	1
98	Sb, S (Fe)	< 1 000	5	See Cycle 1	1
99	Sb, S (Mn)	< 1 000	5	See Cycle 1	1
100	Sb, S (Ni)	< 1 000	5	See Cycle 1	1
101	Sb, S (Zn)	< 1 000	5	See Cycle 1	1
102	Se, As (K)	1 000	5	$H_2Se = Se + H_2$ $\frac{3}{2}Se + 2KOH = K_2Se + \frac{1}{2}SeO_2 + H_2O$ $\frac{1}{2}As_2O_3 + \frac{1}{2}SeO_2 = \frac{1}{2}As_2O_5 + \frac{1}{2}Se$ $\frac{1}{2}As_2O_5 = \frac{1}{2}As_2O_3 + \frac{1}{2}O_2$ $K_2Se + 2H_2O = 2KOH + H_2Se$	46
103	Se, S (Cd)	< 1 000	5	See Cycle 1	1
104	Se, S (Co)	< 1 000	5	See Cycle 1	1
105	Se, S (Cu)	1 100	6	$H_2Se = Se + H_2$ $CuO + \frac{3}{2}Se = CuSe + \frac{1}{2}SeO_2$ $\frac{1}{2}SeO_2 + \frac{1}{2}H_2O = \frac{1}{2}H_2SeO_3$ $\frac{1}{2}H_2SeO_3 + SO_2 + \frac{1}{2}H_2O = \frac{1}{2}Se + H_2SO_4$ $CuSe + H_2SO_4 = CuSO_4 + H_2Se$ $CuSO_4 = CuO + SO_2 + \frac{1}{2}O_2$	46
106	Se, S (Fe)		5	See Cycle 1	1
107	Se, S (K)	1 000	6	$H_2Se = Se + H_2$ $\frac{3}{2}Se + 2KOH = K_2Se + \frac{1}{2}SeO_2 + H_2O$ $K_2Se + 2H_2O = 2KOH + H_2Se$ $\frac{1}{2}SeO_2 + H_2O + SO_2 = \frac{1}{2}Se + H_2SO_4$ $H_2SO_4 = H_2O + SO_3$ $SO_3 = SO_2 + \frac{1}{2}O_2$	46
108	Se, S (Mn)	< 1 000	5	See Cycle 1	1

Table B-2 (Continued)

Cycle number	Elements	Maximum temperature, K	Number of reactions	Cycles	References (Number refers to references following table)
109	Se, S (Ni)	< 1 000	5	See Cycle 1	1
110	Se, S (Zn)	< 1 000	5	See Cycle 1	1
111	Se, S (Zn)	1 200	5	$H_2Se = Se + H_2$ $Se + 2ZnO + SO_2 = ZnSe + ZnSO_4$ $ZnSe + 2HCl = ZnCl_2 + H_2Se$ $ZnCl_2 + H_2O = ZnO + 2HCl$ $ZnSO_4 = ZnO + SO_2 + \frac{1}{2}O_2$	47
112	Se, Se (Mg, V)	1 000	7	$H_2Se = Se + H_2$ $\frac{4}{3}Se + \frac{2}{3}Mg(OH)_2 = \frac{2}{3}H_2Se + \frac{1}{3}MgSe + \frac{1}{3}MgSeO_4$ $\frac{1}{3}MgSeO_4 = \frac{1}{3}MgO + \frac{1}{3}SeO_2 + \frac{1}{6}O_2$ $\frac{1}{3}MgO + \frac{1}{3}H_2O = \frac{1}{3}Mg(OH)_2$ $\frac{1}{3}MgSe + \frac{2}{3}H_2O = \frac{1}{3}Mg(OH)_2 + \frac{1}{3}H_2Se$ $\frac{2}{3}V_2O_4 + \frac{1}{3}SeO_2 = \frac{2}{3}V_2O_5 + \frac{1}{3}Se$ $\frac{2}{3}V_2O_5 = \frac{2}{3}V_2O_4 + \frac{1}{3}O_2$	46
113	Sm, Cl (Co)	2 000	4	See Cycle 42	14
114	Sm, Cl (Mg)	2 000	4	See Cycle 42	14
115	Sm, Cl (Ni)	2 000	4	See Cycle 42	14
116	Sm, Cl (Y)	2 000	4	See Cycle 42	14
117	Te, S (Cd)	< 1 000	5	See Cycle 1	1
118	Te, S (Co)	< 1 000	5	See Cycle 1	1
119	Te, S (Fe)	< 1 000	5	See Cycle 1	1
120	Te, S (Mn)	< 1 000	5	See Cycle 1	1
121	Te, S (Ni)	< 1 000	5	See Cycle 1	1
122	Te, S (Zn)	< 1 000	5	See Cycle 1	1
123	U, U (C)		3	$U_3O_8 + H_2O + 3CO_2 = 3(UO_2CO_3) + H_2$ $3(UO_2CO_3) = 3UO_3 + 3CO_2$ $3UO_3 = U_3O_8 + \frac{1}{2}O_2$	48
124	V, Co (Br)	1 320	5	See Cycle 34	14
125	V, Mn (Br)	1 400	5	See Cycle 37	14

Table B-2 (Continued)

Cycle number	Elements	Maximum temperature, K	Number of reactions	Cycles	References (Number refers to references following table)
126	Yb, Cl (Co)	1 320	4	See Cycle 42	14
127	Yb, Cl (Mg)	1 320	4	See Cycle 42	14
128	Yb, Cl (Ni)	1 320	4	See Cycle 42	14
129	Yb, Cl (Y)	1 320	4	See Cycle 42	14

* — electrolysis † — photolysis

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Figure B-1. Simplified Flow Chart for Cycle No. 24

Figure B-2. Simplified Flow Chart for Cycle No. 36

Figure B-3. Simplified Flow Chart for Cycle No. 57

Numerous papers have been written on the thermodynamics of these cycles, e.g., References 41,69,73,74,75,76,77, and 78. A number of authors use the efficiency:

$$\epsilon = \frac{\Delta H^{\circ}}{\Delta G^{\circ}} \cdot \frac{T_h - T_l}{T_h}$$

where $\Delta H^{\circ} = -68.315$ kcal/mole and $\Delta G^{\circ} = -56.687$ kcal/mole for $H_2O(l)$. Clearly, it is very important to understand which type of factor is being used when comparing the efficiencies of various cycles and when comparing the cycles to electrolysis.

Two papers on the efficiencies of these cycles should be mentioned here. One is that of Abraham and Schreiner (Reference 72), in which it is pointed out that additional loss of efficiency is introduced if heat is absorbed at lower temperatures than the maximum in intermediate steps. They analyze three iron chloride cycles and find theoretical efficiencies not exceeding 45 percent. The other paper is that of Funk, Conger, and Carty (Reference 76) which takes the low-temperature heat into account and also accounts for the separation work which must be done in many cycles. Funk has pointed out in several papers that many cycles have reaction steps with positive free energy changes. Such steps require separative work, e.g., pumping, equal to the unfavorable free energy change, and this work must be obtained from some additional heat source with the usual losses in efficiency. His analysis includes such factors, as well as the work required to separate ideal gases in systems with otherwise favorable equilibria. The efficiency calculations of these and other authors are compared in Table B-3. Not surprisingly, the agreement between different authors is not very good because of the different factors taken into account. The agreement is strikingly poor for cycle number 70 and may be a misprint. In compiling Table B-3, the results of various groups have been converted to the lower heating value (LHV) of hydrogen by dividing by 1.2, where appropriate.

Table B-3. Comparison of Cycle Efficiency Estimates Based on LHV

Cycle		Cycle Efficiency					
Name	No.	Carnot	Abraham (Ref. 72)	Pangborn (Ref. 32)	Pangborn (Ref. 74)	Chao (Ref. 41)	Funk (Ref. 76)
De Beni	9	83			58		63
IGT L-1	12	80			55		
IGT J-1	16	74			38		
Cesium	21	83				41	
CuCl	23	70				23	
Beulah	24	67			23		
Mark 7	30	73			30		
C(+5-1)	31	73	44				
FeCl	32	70					22
Mark 9	33	68	44	34	34	45	
Agnes	36	65	41		24		
Mark 1	42	71			33	49	
GM	70	70		12		15	60
IGT C-5	77	76		48	48		
IGT A-2	78	77		26			

B.2 CLOSED-LOOP DATA

B.2.1 System Enthalpy and Working Temperature

The first step toward characterizing the potential of a given reaction, or series of reactions coupled into a system, to serve as a closed-loop energy storage system (CESS) is twofold: (1) establish the temperature range over which it operates effectively and (2) characterize its heat of reaction per unit weight or unit volume under the conditions proposed for the minimum and maximum operating temperatures. Two methods are proposed for thermochemical characterization: (1) Method A, which is directed toward establishing rankings in the working temperature range by minimum and maximum system temperature and (2) Method B, which is directed toward establishing a ranking of systems designed to service a particular collector operating at temperature T_1 and user energy regenerator operating at temperature T_2 .

B.2.1.1 Thermochemical Characterization by Method A

In the reaction,

$T_{\max}$ is defined as the temperature at which 95 mole percent of the system is in the form of the products $C + D$ at system pressure, $P_{\max}$, and $T_{\min}$ is defined as the temperature at which 95 mole percent of the system is in the form of reactants $A + B$ at system pressure, $P_{\min}$. The value of the molar heat of reaction, $\Delta H(T_{\max}, P_{\max})$, would be evaluated at $T_{\max}$ and $P_{\max}$. The effective heat of reaction per unit mass would be, in the simplest case,

$$0.95 \Delta H(T_{\max}, P_{\max}) / \text{molecular weight of reactants}.$$

The effective heat of reaction per unit volume could be defined either at $P_{\max}$ or the pressure at which the reagents are stored, depending upon the situation.

The value of $T_{\max}$ would be evaluated by determining the temperature at which the equilibrium constant, K , has the following value:

$$K = \frac{\alpha^2}{(a - \alpha)(b - \alpha)},$$

where a and b are the initial concentrations of reactants A and B in the system. For stoichiometric quantities of a and b ,

$$\frac{2}{a + b} = 0.95.$$

A similar approach can be used to determine $T_{\min}$.

The temperatures can be used to represent the nominal working limits of the system with $T_{\max}$ representing the solar collector temperature and $T_{\min}$ representing the temperature of the user energy regenerator.

It is recommended that Method A be used as the primary method for characterizing candidate high-temperature CESS.

B.2.1.2 Thermochemical Characterization by Method B

Assume that a particular solar collector and user regeneration system is defined with the former operating at temperature T_1 and pressure P_1 , and the latter at temperature T_2 and pressure P_2 . Under these conditions, given a set of system operating conditions and initial stoichiometry, the equilibrium composition of the chemical system is fully defined at T_1 , P_1 and T_2 , P_2 . Here, the effective heat of reaction at T_1 , P_1 is defined in terms of the gain in the concentration of products C and D, Δc and Δd , and the loss in the concentrations of reactants A and B, Δa and Δb :

$$\Delta H(T_1, P_1)_{\text{eff}} = \Delta c \cdot \Delta H_{f_C}(T_1, P_1) + \Delta d \cdot \Delta H_{f_D}(T_1, P_1) - \Delta a \cdot \Delta H_{f_A}(T_1, P_1) - \Delta b \cdot \Delta H_{f_B}(T_1, P_1)$$

In this equation, $\Delta H_{f,i}$ represents the molar heat of formation of species i at temperature T and pressure P . The values of Δa , Δb , Δc , and Δd would be determined by evaluating α for the same reaction:

as in Method A, except that the equilibrium constant, K , is a function of the temperature, i.e., $K(T)$. In this case, the value of T_1 determines the value of $K(T_1)$. The values of $\Delta H(T_1, P_1)_{\text{eff}}$ per unit volume and per unit mass could then be calculated directly. Method B would be the natural approach toward ranking systems with regard to a particular solar collector and user regenerator system.

B.2.1.3 Other Methods of Characterizing System Thermodynamics

Wentworth and Chen (Reference 38) have defined a "turning temperature", T^* , as a way to screen for chemical reactions which have a potential to regenerate high-temperature heat and which, therefore, would be candidates for a high-temperature CESS. The definition of T^* is:

$$T^* = \frac{\Delta H_{298}}{\Delta S_{298}},$$

where the change in the heat capacity at constant pressure, ΔC_p , is equal to zero and the equilibrium constant for the reaction is unity. This relationship for T^* is derived from the limited thermodynamic relationship between the standard heat of reaction ($\Delta H_{T_r}^0$) at a reference temperature T_r , the standard entropy of reaction ($\Delta S_{T_r}^0$) at the reference temperature, the difference between the heat capacities of the reactants and products, ΔC_p , and the equilibrium constant for the reaction, K . This relationship appears as:

$$T^* = \frac{\Delta H_{T_r}^0 + \int_{T_r}^T \Delta C_p dT}{\Delta S_{T_r}^0 + \int_{T_r}^T \Delta C_p dT/T - R \ln K}$$

Under the condition that $\Delta C_p = 0$, the values of ΔH_T and ΔS_T are independent of temperature so that ΔH_T and ΔS_T can be replaced by the ΔH_{T_r} and ΔS_{T_r} . T_r is any temperature at which ΔH and ΔS are evaluated. Under the constraint that $\Delta C_p = 0$, the turning temperature is defined by Wentworth and Chen as the temperature at which the equilibrium constant, K , has a value of unity. They have used 298°K as the common reference temperature for screening purposes, and their results are presented in Tables B-4 through B-9.

Table B-4 shows catalyzed reactions proposed by other investigators and is given for comparison purposes only. Table B-4 also presents data on the production and storage of hydrogen from water for comparison. Tables B-5 through B-9 contain data on various classes of uncatalyzed chemical reactions which can be considered for storage of chemical energy.

The purpose of T^* screening is to identify the temperature at which the equilibrium mixture of reactants and products "turns" from being reactant-dominated to products-dominated. This method is also used by other authors.

There are two basic flaws in the T^* method of screening, which are most critical in the high-temperature range of interest in this report. The first flaw is that the preceding integral relationship for T^* is not general, but holds only if there is no change in phase or change in state between the reference temperature and T^* for any of the reactants or products. This applies to changes of phase, such as solid-liquid or liquid-gas, and to molecular dissociation if the equilibrium state of the element at T^* is not that found at 298°K. The second flaw is that the approximation $\Delta C_p = 0$ is not useful for many systems of interest. These issues are discussed below, using the $H_2O = H_2 + 1/2 O_2$ reaction as an example, where it is shown that the T^* method can lead to errors of 2000° in "turning temperature".

The simple dissociation of water is actually difficult to characterize, as shown below, but many authors write the reaction:

Table B-4. Reactions Proposed in Previous Investigations

<u>Catalyzed Reactions</u>	$\Delta H^\circ (\text{kcal})^a$	$\Delta S^\circ (\frac{\text{cal}}{\text{deg}})^a$	$T^* = \frac{\Delta H^\circ}{\Delta S^\circ}$	$\frac{\Delta H^\circ (\text{kcal})}{V (\frac{\text{L}}{\text{mol}})}$	<u>comments and conditions</u>
$\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$	49.	51.	960	50	gas storage at 100 atm and 25°C
$\text{CH}_4(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g}) + 2\text{H}_2(\text{g})$	59.	61.5	960	60	gas storage at 100 atm and 25°C
$\text{SO}_3(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + 1/2\text{O}_2(\text{g})$	23.5	22.7	1,040	110	SO ₂ as liquid 1/2O ₂ as gas at 100 atm and 25°C
$\text{CH}_3\text{OH}(\text{g}) \rightleftharpoons 2\text{H}_2(\text{g}) + \text{CO}(\text{g})$	22.	53.	420	42	back reaction at 300 atm and 327°C to CH ₃ OH (l)
<u>H₂ Storage</u>					
$\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g})$	57.8	10.6	5,450	240	storage of H ₂ (g) only at 100 atm and 25°C

^aData taken from "Handbook of Chemistry and Physics" 51st Edition, 1970-1971, p. D-61

Table B-5. Thermal Decomposition of Ammonium Salts

	ΔH° (kcal)	ΔS° (cal/deg)	$T^* = \frac{\Delta H^\circ}{\Delta S^\circ}$	$\frac{\Delta H^\circ}{V} \left(\frac{\text{kcal}}{\text{L}} \right)$	comments and conditions
$\dagger \text{NH}_4\text{HSO}_4(\text{L}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{g}) + \text{SO}_3(\text{g})$	80.4 ^b	108.9 ^b	740.	740	products stored as liquids; $\Delta H^\circ=60$ for liquid storage
$\text{NH}_4\text{F}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HF}(\text{g})$	35.07 ^c	70.28 ^c	499.	512	products stored as liquids; $\Delta H^\circ=21.6$ for liquid storage
$\dagger \text{NH}_4\text{Cl}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$	42.1	68.0	618.	570	products stored as liquids; $\Delta H^\circ=30$ for liquid storage
$\dagger \text{NH}_4\text{Br}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HBr}(\text{g})$	45.01	66.	677.	640	products stored as liquids; $\Delta H^\circ=33$ for liquid storage
$\text{NH}_4\text{I}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HI}(\text{g})$	43.45	67.	649.	460	products stored as liquids; $\Delta H^\circ=31$ for liquid storage

$\dagger$ Candidates for solar energy storage based on T^* and $\Delta H^\circ/V$ criteria.

^a ΔH° and ΔS° for NH_4HSO_4 reaction are at 417°K. All other data at 298°K.

^bC. Howard Schomate and B. F. Naylor, Journal Amer. Chem. Soc., 67, 73 (1945).

^cData for Ammonium Halides taken from "Chemical Thermodynamics", F. T. Wall, W. H. Freeman, San Francisco, 1974, p. 462.

Table B-6. Thermal Decomposition of Group IA and IIA Hydroxides

	$\Delta H^\circ (\text{kcal})$	$\Delta S^\circ (\text{cal/deg})$	$T^* = \frac{\Delta H^\circ}{\Delta S^\circ}$	$\frac{\Delta H^\circ}{T^*} (\frac{\text{kcal}}{^\circ\text{K}})$	comments and conditions
$\text{Mg(OH)}_2(\text{s}) \rightleftharpoons \text{MgO}(\text{s}) + \text{H}_2\text{O}(\text{g})$	19.36 ^b	36.45 ^b	531.	330.	H ₂ O stored as liquid; $\Delta H^\circ = 9.6$
$\dagger \text{Ca(OH)}_2(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{g})$	26.09 ^b	34.68 ^b	752.	470.	H ₂ O stored as liquid; $\Delta H^\circ = 16.4$
$\dagger \text{Sr(OH)}_2(\text{s}) \rightleftharpoons \text{SrO}(\text{s}) + \text{H}_2\text{O}(\text{g})$	30.3 ^c	(35.6)	(852)	510.	H ₂ O stored as liquid; $\Delta H^\circ = 20.6$
$\dagger \text{Ba(OH)}_2(\text{s}) \rightleftharpoons \text{BaO}(\text{s}) + \text{H}_2\text{O}(\text{g})$	35.7 ^b	(35.6)	(1,000)	580.	H ₂ O stored as liquid; $\Delta H^\circ = 26.0$
$\dagger^a \text{LiOH}(\text{l}) \rightleftharpoons 1/2\text{Li}_2\text{O}(\text{s}) + 1/2\text{H}_2\text{O}(\text{g})$	13.55 ^b	13.49 ^b	1,004.	530.	H ₂ O stored as liquid; $\Delta H^\circ = 8.7$
$\dagger^a \text{NaOH}(\text{l}) \rightleftharpoons 1/2\text{Na}_2\text{O}(\text{s}) + 1/2\text{H}_2\text{O}(\text{g})$	21.16 ^c	12.48 ^c	1,696	720.	H ₂ O stored as liquid; $\Delta H^\circ = 16.3$
$\dagger^a \text{KOH}(\text{l}) \rightleftharpoons 1/2\text{K}_2\text{O}(\text{s}) + 1/2\text{H}_2\text{O}(\text{g})$	27.50 ^b	11.82 ^b	2,327	760.	H ₂ O stored as liquid; $\Delta H^\circ = 21.6$
$\dagger^a \text{RbOH}(\text{l}) \rightleftharpoons 1/2\text{Rb}_2\text{O}(\text{s}) + 1/2\text{H}_2\text{O}(\text{g})$	28.6 ^b	(12.6)	(2,270)	700.	H ₂ O stored as liquid; $\Delta H^\circ = 23.7$
$\dagger^a \text{CsOH}(\text{l}) \rightleftharpoons 1/2\text{Cs}_2\text{O}(\text{s}) + 1/2\text{H}_2\text{O}(\text{g})$	28.4 ^b	(12.6)	(2,254)	560.	H ₂ O stored as liquid; $\Delta H^\circ = 23.5$

[†]Candidates for solar energy storage based on T^* and $\Delta H^\circ/\bar{v}$ criteria.

^aThe values of ΔH° and ΔS° are at the melting point of the hydroxide which are 462°C for LiOH, 326°C for NaOH, and 360°C for KOH.

^bData from "Chemical Thermodynamics", F. T. Wall, W. H. Freeman, San Francisco, 1974, p. 462.

^cData from "Handbook of Chemistry and Physics", 51st Ed., 1970-1971, p. D-61, p. B 240.

Table B-7. Thermal Decomposition of Group IA and IIA Carbonates

	$\Delta H^\circ (\text{kcal})$	$\Delta S^\circ (\text{cal/deg})$	$T^* = \frac{\Delta H^\circ}{\Delta S^\circ}$	$\frac{\Delta H^\circ (\text{kcal})}{v}$	comments and conditions
$\text{MgCO}_3(\text{s}) \rightleftharpoons \text{MgO}(\text{s}) + \text{CO}_2(\text{g})$	28 ^b	41.8 ^b	670.	560	CO ₂ stored as liquid; $\Delta H^\circ = 26.8$
$\dagger \text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	42.62 ^c	38.36 ^c	1,110.	780	CO ₂ stored as liquid; $\Delta H^\circ = 41.5$
^a $\text{SrCO}_3(\text{s}) \rightleftharpoons \text{SrO}(\text{s}) + \text{CO}_2(\text{g})$	56.45 ^c	40.86 ^c	1,380.	950	CO ₂ stored as liquid; $\Delta H^\circ = 55.3$
$\text{BaCO}_3(\text{s}) \rightleftharpoons \text{BaO}(\text{s}) + \text{CO}_2(\text{g})$	64.35 ^c	41.1 ^c	1,570.	1,000	CO ₂ stored as liquid; $\Delta H^\circ = 63.2$
^a $\text{Li}_2\text{CO}_3(\text{s}) \rightleftharpoons \text{Li}_2\text{O}(\text{s}) + \text{CO}_2(\text{g})$	53.4 ^b	38.5 ^b	1,390.	1,020	CO ₂ stored as liquid; $\Delta H^\circ = 52.2$
$\text{Na}_2\text{CO}_3(\text{s}) \rightleftharpoons \text{Na}_2\text{O}(\text{s}) + \text{CO}_2(\text{g})$	76.81 ^c	35.29 ^c	2,710.	1,200	CO ₂ stored as liquid; $\Delta H^\circ = 75.7$
$\text{K}_2\text{CO}_3(\text{s}) \rightleftharpoons \text{K}_2\text{O}(\text{s}) + \text{CO}_2(\text{g})$	94.05 ^c	36.4 ^c	2,585	1,210	CO ₂ stored as liquid; $\Delta H^\circ = 93.0$
$\text{Rb}_2\text{CO}_3(\text{s}) \rightleftharpoons \text{Rb}_2\text{O}(\text{s}) + \text{CO}_2(\text{g})$	96.65 ^b	(36.7)	(2,634)	1,100	CO ₂ stored as liquid; $\Delta H^\circ = 95.1$
$\text{Cs}_2\text{CO}_3(\text{s}) \rightleftharpoons \text{Cs}_2\text{O}(\text{s}) + \text{CO}_2(\text{g})$	97.45 ^b	(36.7)	(2,655)	1,110	CO ₂ stored as liquid; $\Delta H^\circ = 96.0$

[†]Candidate for solar energy storage based on T^* and $\Delta H^\circ/v$ criteria.

^aCandidate for solar energy storage if $t \approx 1100^\circ\text{C}$ can be attained in the solar concentrator

^bData from "Handbook of Chemistry and Physics", 51st Ed, 1970-1971, p.D-61.

^cData from "Chemical Thermodynamics", F. T. Wall, W. H. Freeman, San Francisco, 1974 p. 462.

Table B-8. Thermal Decomposition of Group IA and IIA Sulfates

	$\Delta H^\circ(\text{kcal})$	$\Delta S^\circ(\text{cal/deg})$	$T^* = \frac{\Delta H^\circ}{\Delta S^\circ}$	$\frac{\Delta H^\circ(\text{kcal})}{V} \left(\frac{\text{cal}}{\text{l}} \right)$	comments and conditions
^a $\text{MgSO}_4(\text{s}) \rightleftharpoons \text{MgO}(\text{s}) + \text{SO}_3(\text{g})$	67.24 ^b	45.78 ^b	1,470.	1,080.	SO_3 stored as liquid; $\Delta H^\circ = 57.0$
$\text{CaSO}_4(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{SO}_3(\text{g})$	96.18 ^b	44.84 ^b	2,145.	—	
$\text{SrSO}_4(\text{s}) \rightleftharpoons \text{SrO}(\text{s}) + \text{SO}_3(\text{g})$	109.75 ^b	44.84 ^b	2,450.	—	
$\text{BaSO}_4(\text{s}) \rightleftharpoons \text{BaO}(\text{s}) + \text{SO}_3(\text{g})$	123.45 ^b	46.47 ^b	2,660.	—	
$\text{Li}_2\text{SO}_4(\text{s}) \rightleftharpoons \text{Li}_2\text{O}(\text{s}) + \text{SO}_3(\text{g})$	105.98 ^b	(42.9)	(2,470)	—	
$\text{Na}_2\text{SO}_4(\text{s}) \rightleftharpoons \text{Na}_2\text{O}(\text{s}) + \text{SO}_3(\text{g})$	137.05 ^b	42.91 ^b	3,190.	—	
$\text{K}_2\text{SO}_4(\text{s}) \rightleftharpoons \text{K}_2\text{O}(\text{s}) + \text{SO}_3(\text{g})$	161.41 ^c	41.74 ^c	3,867.	—	
$\text{Rb}_2\text{SO}_4(\text{s}) \rightleftharpoons \text{Rb}_2\text{O}(\text{s}) + \text{SO}_3(\text{g})$	167.15 ^b	(42.9)	(3,900)	—	
$\text{Cs}_2\text{SO}_4(\text{s}) \rightleftharpoons \text{Cs}_2\text{O}(\text{s}) + \text{SO}_3(\text{g})$	169.03 ^b	(42.9)	(3,940)	—	

^a Candidate for solar energy storage if $t = 1200^\circ\text{C}$ can be attained in the solar concentrator.

^b Data from "Handbook of Chemistry and Physics", 51st Ed., 1970-1971, p. D-61.

^c Data from "Chemical Thermodynamics", F. T. Wall, W. H. Freeman, San Francisco, 1974, p. 462.

Table B-9. Thermal Decomposition of Group IA and IIA Oxides

	$\Delta H^\circ (\text{kcal})$	$\Delta S^\circ (\text{cal/deg})$	$T^* = \frac{\Delta H^\circ}{\Delta S^\circ}$	$\frac{\Delta H^\circ (\text{kcal})}{\bar{v}}$	comments and conditions
$\text{MgO}_{(s)} \rightleftharpoons \text{Mg}_{(g)} + 1/2\text{O}_{2(g)}$	179.71 ^b	53.56 ^b	3,360.	---	
$\text{CaO}_{(s)} \rightleftharpoons \text{Ca}_{(g)} + 1/2\text{O}_{2(g)}$	197.83 ^b	51.99 ^b	3,800.	---	
$\text{SrO}_{(s)} \rightleftharpoons \text{Sr}_{(g)} + 1/2\text{O}_{2(g)}$	180.3 ^b	50.83 ^b	3,550.	---	
$\text{BaO}_{(s)} \rightleftharpoons \text{Ba}_{(g)} + 1/2\text{O}_{2(g)}$	174.26 ^b	48.37 ^b	3,600.	---	
$\text{Li}_2\text{O}_{(s)} \rightleftharpoons 2\text{Li}_{(g)} + 1/2\text{O}_{2(g)}$	216.54 ^c	81.72 ^c	2,650.	---	
$\text{Na}_2\text{O}_{(s)} \rightleftharpoons 2\text{Na}_{(g)} + 1/2\text{O}_{2(g)}$	151.36 ^b	80.54 ^b	1,880.	---	
$\text{K}_2\text{O}_{(s)} \rightleftharpoons 2\text{K}_{(g)} + 1/2\text{O}_{2(g)}$	129.92 ^c	78.6 ^c	1,652.	---	
^a $\text{Rb}_2\text{O}_{(s)} \rightleftharpoons 2\text{Rb}_{(g)} + 1/2\text{O}_{2(g)}$	119.92 ^b	(80.28)	(1,494)	680	store Rb(l) only; $\Delta H^\circ = 79$; O ₂ discharged to atmosphere
^a $\text{Cs}_2\text{O}_{(s)} \rightleftharpoons 2\text{Cs}_{(g)} + 1/2\text{O}_{2(g)}$	(115.)	(80.28)	(1,432)	525	store Cs(l) only; $\Delta H^\circ = 75$; O ₂ discharged to atmosphere

^a Candidate for solar energy storage if $t = 1200^\circ\text{C}$ can be attained in the solar concentrator.

^b Data from "Handbook of Chemistry and Physics", 51st Ed., 1970-1971, p. D-61.

^c Data from "Chemical Thermodynamics", F. T. Wall, W. E. Freeman, San Francisco, 1974, p. 462.

and then estimate the temperature at which the Gibbs free energy change is equal to zero, i.e., the temperature, T^* , at which the equilibrium constant is unity. The crudest approximation for this temperature is obtained from the ratio of the enthalpy change (ΔH) and the entropy change (ΔS) at 298°K:

$$T^* = \frac{\Delta H_{298}^{\circ}}{\Delta S_{298}^{\circ}}$$

This relation assumes that there is no difference between the heat capacities of the reactants and the products, i.e., the $\Delta C_p = 0$, which is a very poor assumption at high temperatures. This method gives a dissociation temperature for water vapor of 5456°K, which is a gross overestimate, but which appears in several papers.

A somewhat better approximation is to analyze the JANAF Thermochemical Tables (Reference 55) for the temperature at which the standard free energy of formation of water is equal to zero. This gives $T^* = 4320^{\circ}\text{K}$, a value which is still incorrect due to the method by which the JANAF Tables are compiled. The reason for this is that the reaction:

is not the reaction which occurs at such high temperatures. The actual reaction involves the dissociation of the hydrogen and oxygen molecules into atoms at temperatures above 3800°K. A still better procedure, therefore, is to choose the reaction with the lowest free energy products, and to find the temperature at which the free energy change for the reaction is zero. Thus, for the reaction:

the free energy change is zero at 3895°K. Another reaction occurs at a slightly lower temperature of 3880°K:

The only known general method of treating this problem is to employ computer programs which predict the concentrations of all species which can exist in the system as a function of temperature and pressure. An example of this, taken from a paper by Nakamura (Reference 79) is shown in Figure B-4. As the figure shows, the high temperatures quoted above are still misleading because, at lower partial pressure than one atmosphere, there may be appreciable product formation at still lower temperatures.

Figure B-4. The Composition of Dissociating Water Vapor at Thermodynamic Equilibrium, $P = 1$ Atmosphere

The T^* method is simple to use and requires the least amount of thermodynamic data to implement. However, as shown above, it is basically unreliable and may lead to the wrong decision regarding the suitability of particular systems for a high-temperature CESS.

B.2.2 Candidate Systems for Closed-Loop Chemical Energy Storage Systems

Two other sets of candidate systems supplement those presented by Wentworth and Chen in Tables B-4 through B-9. In Tables B-10 and B-11, Schmidt (Reference 56) lists $T_{\max}$ and $T_{\min}$ in a manner suggestive of Method A by considering 90 percent points in the forward and reverse reactions. Unfortunately, the thermodynamic analysis was not carried out to completion, resulting in some of the listed temperatures being unreliable. Table B-12 (from a private communication of A. Hildebrandt of the University of Houston) contains T^* based upon $\Delta G^0 = 0$, as listed in the JANAF Tables, but again without any consideration of the actual state of the

Table B-10. Energy Content of Candidate Chemical Energy Storage Reactions, Excluding Those Containing Solids

Reaction exothermic ↔ endothermic	Reaction Enthalpy at 298°K (77°F)		Temperature (°K) at which	
	Ws/g	Btu/lb	90% Formed	90% Dissociated
$\text{CO}(\text{G}) + 3\text{H}_2(\text{G}) \rightleftharpoons \text{CH}_4(\text{G}) + \text{H}_2\text{O}(\text{L})$	7,345	3,160	—	—
$\text{CO}(\text{G}) + 3\text{H}_2(\text{G}) \rightleftharpoons \text{CH}_4(\text{G}) + \text{H}_2\text{O}(\text{G})$	6,053	2,604	754	1,466
$\text{C}_2\text{H}_4(\text{G}) + \text{H}_2(\text{G}) \rightleftharpoons \text{C}_2\text{H}_6(\text{G})$	4,561	1,962	841	1,205
$2\text{CO}(\text{G}) + 2\text{H}_2(\text{G}) \rightleftharpoons \text{CH}_4(\text{G}) + \text{CO}_2(\text{G})$	4,118	1,772	778	1,152
$\text{CO}(\text{G}) + 2\text{H}_2(\text{G}) \rightleftharpoons \text{CH}_3\text{OH}(\text{L})$	3,996	1,718	345	434
$\text{N}_2(\text{G}) + 3\text{H}_2(\text{G}) \rightleftharpoons 2\text{NH}_3(\text{L})$	3,861	1,661	—	—
$\text{N}_2(\text{G}) + 3\text{H}_2(\text{G}) \rightleftharpoons 2\text{NH}_3(\text{G})$	2,695	1,159	346	528
$2\text{NO}(\text{G}) + \text{O}_2(\text{G}) \rightleftharpoons \text{N}_2\text{O}_4(\text{L})$	1,750	753	549	930
$\text{SO}_2(\text{G}) + \text{Air} \rightleftharpoons \text{SO}_3(\text{G})^*$	1,544	644	806	1,270
$\text{SO}_2(\text{L}) + 1/2\text{O}_2(\text{G}) \rightleftharpoons \text{SO}_3(\text{L})$	1,517	652	792	1,235
$\text{SO}_2(\text{G}) + 1/2\text{O}_2(\text{G}) \rightleftharpoons \text{SO}_3(\text{G})$	1,235	531	792	1,235
$\text{NO}(\text{G}) + 1/2\text{O}_2(\text{G}) \rightleftharpoons \text{NO}_2(\text{G})$	1,243	535	549	930
$\text{CO}(\text{G}) + \text{Cl}_2(\text{L}) \rightleftharpoons \text{COCl}_2(\text{L})$	1,172	504	628	881
$\text{NO}_2(\text{G}) + \text{NO}_2(\text{G}) \rightleftharpoons \text{N}_2\text{O}_4(\text{L})$	932	401	288	381
$\text{SO}_3(\text{L}) + \text{H}_2\text{O}(\text{L}) \rightleftharpoons \text{H}_2\text{SO}_4(\text{L})$	885	381	535	723
$\text{SO}_2(\text{G}) + \text{Air} \rightleftharpoons \text{SO}_3(\text{G})$	727	313	806	1,270
$\text{NO}(\text{G}) + 1/2\text{Cl}_2(\text{L}) \rightleftharpoons \text{NOCl}(\text{L})$	695	299	425	819
$\text{H}_2\text{O}(\text{L}) + \text{H}_2\text{SO}_4(\text{L}) \rightleftharpoons \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}(\text{L})$	230	99	—	—
For comparison:				
$\text{H}_2(\text{G}) + 1/2\text{O}_2(\text{G}) \rightleftharpoons \text{H}_2\text{O}(\text{G})$	13,423	5,775	2,830	5,600

*Based on SO_2 weight only. Air open cycle.

Table B-11. Energy Content of Candidate Chemical Energy Storage
Reactions, Systems With Solid Constituents

Reaction exothermic ⇌ endothermic	Reaction Enthalpy at 298°K (77°F)		Temperature at which P _{Diss.} =		
	Ws/g	Btu/lb	0.1 bar	1 bar	P _{Cond.}
Li (S) + 1/2 H ₂ (G) ⇌ Li H (S)	11,403	4,906	1,181	1,223	—
Na F (S) + (HF) _n (L) ⇌ Na HF ₂ (S)	4,442	1,911			
Li ₂ O (S) + CO ₂ (G) ⇌ Li ₂ CO ₃ (S)	3,029	1,303			
Na ₂ O (S) + CO ₂ (G) ⇌ Na ₂ CO ₃ (S)	3,014	1,296		2,445	
Mg (S) + H ₂ (G) ⇌ Mg H ₂ (S)	2,893	1,245	~500	560	—
Ca O (S) + SO ₃ (L) ⇌ Ca SO ₄ (S)	2,539	1,092			
Ca O (S) + CO ₂ (G) ⇌ Ca CO ₃ (S)	1,776	764	1,028	1,171	
Mg O (S) + CO ₂ (G) ⇌ Mg CO ₃ (S)	1,387	597		670	
Ba O (S) + CO ₂ (G) ⇌ Ba CO ₃ (S)	1,353	582		1,473	
Ni Cl ₂ (S) + 6 NH ₃ (L) ⇌ [Ni (NH ₃) ₆] Cl ₂ (S)	1,301	560			
NH ₃ (L) + H ₂ SO ₄ (L) ⇌ NH ₄ HSO ₄ (S)	1,256	540	—	—	—
KF (S) + (HF) _n (L) ⇌ KHF ₂ (S)	1,031	444			
Ca O (S) + H ₂ O (L) ⇌ Ca (OH) ₂ (S)	880	378	722	820	676
Mg O (S) + H ₂ O (L) ⇌ Mg (OH) ₂ (S)	644	277	614	649	598
Ba O (S) + H ₂ O (L) ⇌ Ba (OH) ₂ (S)	598	257	1,052	1,271	961
Fe Cl ₂ (S) + 6 NH ₃ (L) ⇌ [Fe (NH ₃) ₆] Cl ₂ (S)	302	129			
Ca Cl ₂ (S) + 6 NH ₃ (L) ⇌ [Ca (NH ₃) ₆] Cl ₂ (S)	210	90			

system at high temperature. In their work, Wentworth and Chen use $T^* = \Delta H^0 / \Delta S^0$, an approach which should be used only for qualitative purposes. In short, all these tables are, at best, qualitative guides for the relative merits of various CESS.

The tabulation of Schmidt is divided into two sections: Table B-10 lists CESS that include gases and liquids while Table B-11 involves solids. The heat of reaction data in both tables contain a useful ranking in terms of ΔH /unit weight. Unfortunately, the system pressures, which could be as high as 300 atm or more, are not listed so that it is not possible to rank ΔH /unit volume for these reactions. From the point of view of energy storage, the value of ΔH /unit volume is essential. As mentioned above, the values of the 90 percent and 10 percent temperature are not reliable in all cases. The temperature data listed in Table B-11 are interesting in that

Table B-12. Energy Density of Potential Chemical Energy Storage Systems

Reaction	$\Delta H/m$, kcal/g	$\Delta H/v$, kcal/cc	Reaction Temp, °K
$H_2O \rightleftharpoons H_2 + 1/2 O_2$	3.80	0.05	4,400
$CO_2 \rightleftharpoons CO + 1/2 O_2$	1.54	0.11	3,300
$C + H_2O \rightleftharpoons CO + H_2$	1.05	0.10	1,100
$Na_2O + CO_2 \rightleftharpoons Na_2CO_3$	(0.73)	(1.56)	1,100
$SO_3 \rightleftharpoons SO_2 + 1/2 O_2$	0.36	0.69	1,000
$C + CO_2 \rightleftharpoons 2 CO$	0.74	0.09	960
$H_2O + CH_4 \rightleftharpoons CO + 3 H_2$	1.45	0.05	950
$CH_4 + CO_2 \rightleftharpoons 2 CO + 2 H_2$	0.98	0.07	950
$CaCO_3 \rightleftharpoons CaO + CO_2$	0.42	1.02	828
$COCl_2 \rightleftharpoons CO + Cl_2$	0.14	0.03	790
$NO_2 \rightleftharpoons NO + 1/2 O_2$	0.30	0.05	760
$Ca(OH)_2 \rightleftharpoons CaO + H_2O$	0.21	0.46	750
$Na_2S_2O_7 + H_2O \rightleftharpoons 2NaHSO_4$	(0.68)	(1.80)	733
$KHF_2 \rightleftharpoons KF + HF$	0.24	0.41	700
$H_2SO_4 \rightleftharpoons SO_3 + H_2O$	0.21	0.39	630
$CaH_2 \rightleftharpoons Ca + H_2$	(1.07)	(0.20)	600
$NaNO_2 + 1/2 O_2 \rightleftharpoons NaNO_3$	(0.87)	(0.43)	593
$Mg(OH)_2 \rightleftharpoons MgO + H_2O$	0.15	0.36	520
$(NH_4)_2SO_4 \rightleftharpoons 2NH_3 + H_2SO_4$	(0.50)	(0.68)	508
$KVSO_4 \cdot 12 H_2O \rightleftharpoons KVSO_4 + 12 H_2O$	---	---	503
$Ni(OH)_2 \rightleftharpoons NiO + H_2O$	(0.02)	(0.12)	503
$MgH_2 \rightleftharpoons Mg + H_2$	0.71	(0.14)	500
$KNaC_4H_4O_6 \cdot 4 H_2O \rightleftharpoons KNaC_4H_4O_6 + 4 H_2O$	---	---	488
$H_2SO_4 \cdot H_2O \rightleftharpoons H_2SO_4 + H_2O$	0.29	0.53	480
$MgSO_3 \cdot 6 H_2O \rightleftharpoons MgSO_3 + 6 H_2O$	(0.11)	(0.16)	473
$CaCl_2 \cdot 2 H_2O \rightleftharpoons CaCl_2 + 2 H_2O$	(0.06)	(0.10)	473
$NiCl_2 \cdot 6NH_3 \rightleftharpoons NiCl_2 \cdot 2NH_3 + 4NH_3$	0.25	(0.70)	448
<u>Comparison</u>			
Hitec (400-600°F)	0.04	0.08	478-589
(KCl + MgCl ₂) Fusion	0.09	0.16	760
NaCl Fusion	0.12	0.24	1,000
NaOH Fusion	0.05	0.11	591
Hitec (900-1000°F)	0.02	0.04	758-811

Private Communication from A. Hildebrandt (Univ. of Houston) to H. Webb
(Aerospace Corporation)

() Preliminary Data

the system operating temperatures are listed for two representative working pressures, 0.1 and 1 bar.

The list in Table B-12 does contain both $\Delta H/\text{unit mass}$ and $\Delta H/\text{unit volume}$ data. Unfortunately, since the system pressure is not listed, it is difficult to take full advantage of such a ranking. However, such a list does draw attention to the difference in the energy density of systems containing condensed phases. As mentioned earlier, the representative temperatures listed are not reliable in all cases.

Wentworth and Chen have carried out a systematic analysis of the thermochemistry and the process conditions of a large number of candidate CESS, as listed in Tables B-4 through B-9. Their analysis contains generally useful information for the molar heat and entropy of reaction and for the $\Delta H/\text{unit volume}$ with the system pressure tabulated. Their listing of $T^* = \Delta H^0 / \Delta S^0$ is only of qualitative use, as mentioned earlier, and their main source of thermodynamic data is a secondary reference. Nevertheless, the importance and usefulness of their listing should not be minimized since it provides an excellent starting point for more detailed analysis.

B.2.3 Supplemental Thermodynamic and Energy Flow Data

The following data have been excerpted from various authors to aid in understanding the various systems and reactions.

B.2.3.1 Prengle and Sun Data

Prengle and Sun (Reference 58) provide data for the methanol and ammonium hydrogen sulfate (AHS) systems. Tables B-13 and B-14 present data for the thermodynamics of the reactions in the methanol system. Figure B-5 shows their energy flow analysis for that system. Tables B-15 through B-17 present thermodynamics data for the three reactions in the AHS system. Figure B-6 shows the corresponding energy flow analysis for that system.

Table B-13. Methanol Reaction System:
Reaction 1, Solar Input Reaction

Reaction 1. Solar Input Reaction						
$\text{CH}_3\text{OH}(\text{g}) \xrightarrow{\text{cat.}} \text{CO}(\text{g}) + 2\text{H}_2(\text{g})$						
$\Delta H^\circ = 1.752 \times 10^4 + 17.84T - 13.59 \times 10^{-3}T^2$						
$\Delta F^\circ = 1.752 \times 10^4 - 17.84T \ln T + 13.59 \times 10^{-3}T^2 + 58.96T$						
$K_a = K_y K_v (P/f^\circ)^2; \left(\frac{K_a}{K_v}\right) \left(\frac{f^\circ}{P}\right)^2 = \frac{4\xi^2}{(1-\xi)(1+2\xi)^2}$						
ξ = fraction conversion of methanol.						
$T(^{\circ}\text{K})$	ΔF°	$K_a = e^{-(\Delta F^\circ/RT)}$	P_{atm}	K_v	ξ	ΔH°
600	-10.684	7.8×10^3	1	1	≈ 1	
600	-10.684	7.8×10^3	300	2.51	0.46	
800	-22.02	1.037×10^6	300	1.25	0.96	23.28
900	-27.63	5.1214×10^6	300	1.15	0.992	
950	-30.41	9.9×10^6	300	1.10	0.996	22.47
	(kcal/mole)					(kcal/mole)

Table B-14. Methanol Reaction System:
Reaction 2, Output Heat Reaction

Reaction 2. Output Heat Reaction						
$\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \xrightarrow{\text{cat.}} \text{CH}_3\text{OH}(\text{g})$						
$\Delta H^\circ = -1.752 \times 10^4 - 17.84T + 13.59 \times 10^{-3}T^2$						
$\Delta F^\circ = -1.752 \times 10^4 + 17.84T \ln T - 13.59 \times 10^{-3}T^2 - 58.96T$						
$K_a = K_y \cdot K_v (P/f^\circ)^{-2}; \frac{K_a}{K_v} \left(\frac{f^\circ}{P}\right)^{-2} = \frac{\xi(3-2\xi)^2}{(1-\xi)(2-2\xi)^2}$						
ξ = fraction conversion of carbon monoxide.						
$T(^{\circ}\text{K})$	ΔF°	$K_a = e^{-(\Delta F^\circ/RT)}$	P_{atm}	K_v	ξ	
600	1.0684×10^4	1.28×10^{-4}	1	1	≈ 0	
600	1.0684×10^4	1.28×10^{-4}	300	0.398	0.76	
700	1.636×10^4	7.794×10^{-6}	300	0.636	0.3

Figure B-5. Methanol Cycle Energy Analysis

Table B-15. Ammonium Hydrogen Sulfate Reaction System:
Reaction 1, Solar Input Reaction

Reaction 1. Solar Input Reaction					
$\text{NH}_4\text{HSO}_4(\text{l}) + \text{Na}_2\text{SO}_4(\text{l}) \rightarrow \text{Na}_2\text{S}_2\text{O}_7(\text{l}) + \text{H}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{g}) + \text{NH}_3(\text{g})$					
$\Delta H^\circ = 12.07T - 30 \times 10^{-3}T^2 + 3.521 \times 10^5T^{-1} + 3.819 \times 10^4$					
$\Delta F^\circ = -12.07T \ln T + 30 \times 10^{-3}T^2 + 1.761 \times 10^5T^{-1} + 3.819 \times 10^4 - 9.432T$					
$K_a = a_{\text{H}_2\text{O}} \cdot a_{\text{NH}_3} = (\nu_{\text{H}_2\text{O}} \cdot \nu_{\text{NH}_3}) \left(\frac{1}{4} \right) (P/f^\circ)^2$					
If, $\nu_{\text{H}_2\text{O}} \cdot \nu_{\text{NH}_3} \approx 1$, $P \approx 2K_a^{1/2}$					
$T(^{\circ}\text{K})$	ΔF°	$K_a = e^{-(\Delta F^\circ/RT)}$	P_{atm}	$\nu_{\text{H}_2\text{O}} \cdot \nu_{\text{NH}_3}$	ΔH°
417	9530	0	0	1	
550	509	0.63	1.59	1	
600	-2702	2.27	3	1	
650	-5810	89.87	18.96	1	
700	-8811	563.8	48	0.98	
-773	-1.3×10^4	4725	142	0.94	3.005×10^4

Table B-16. Ammonium Hydrogen Sulfate Reaction System:
Reaction 2, Solar Input Reaction

Reaction 2. Solar Input Reaction

$$\Delta H^\circ = 3.81 \times 10^4 \text{ cal/mole} \quad \log K_a = 8.527 - 8.326 \times 10^3/T$$

$$\Delta F^\circ = 3.81 \times 10^4 - 39.02T$$

$$K_a = a_{\text{SO}_2} = \nu_{\text{SO}_2} \left(\frac{P}{f^\circ} \right)$$

$$\text{If } \nu_{\text{SO}_2} \approx 1; P \approx K_a$$

$T(^{\circ}\text{K})$	K_a	ν_{SO_2}	P_{atm}
600	0	1	0
800	1.317×10^{-2}	1	1.317×10^{-2}
1000	1.588	1	1.588
1173	26.85	1	26.85
1273	96.95	0.99	98
1308	145	0.98	148

Table B-17. Ammonium Hydrogen Sulfate Reaction System:
Reaction 3, Output Heat Reaction

Reaction 3. Output Heat Reaction

$$\Delta H^\circ = -12.07T + 30 \times 10^{-3}T^2 - 3.521 \times 10^5 T^{-1} - 7.6289 \times 10^4$$

$$\Delta F^\circ = 12.07T \ln T - 30 \times 10^{-3}T^2 - 1.761 \times 10^5 T^{-1} - 7.6289 \times 10^4 + 48.45T$$

$$0170 \quad K_a = (a_{\text{NH}_3} \cdot a_{\text{H}_2\text{O}} \cdot a_{\text{SO}_2})^{-1} = \left(\frac{1}{3} \right)^{-3} K_v^{-1} \left(\frac{P}{f^\circ} \right)^{-3}$$

0173

$$0174 \quad P = 3 \left(\frac{f^\circ}{K_a K_v} \right)^{1/3}; \quad \text{If } K_v = 1, P = 3 K_a^{-1/3}$$

$T(^{\circ}\text{K})$	ΔF°	$K_a = e^{-(\Delta F^\circ/RT)}$	P_{atm}	K_v	ΔH°
400	-3.32×10^4	1.42×10^{18}	0	1	
600	-1.2×10^4	2.32×10^4	0.105	1	
680	-3943	18.5	1.134	1	
→690	-2957	8.64	1.46	1	-7.084×10^4
800	7.597×10^3	8.4×10^{-3}	14.8	1	-6.7185×10^4

Figure B-6. Ammonium Hydrogen Sulfate Cycle Energy Analysis

B.2.3.2 Carden's Analysis

Carden (Reference 59) performed an analysis of the ammonia system, which is summarized by the following table and figures. Table B-18 gives the heat of formation of ammonia as a function of pressure and temperature.

Table B-18. Heat of Formation of Ammonia

Temperature (°C)	0	300	500	600	700
Pressure atm					
1	10.63†	11.99	12.66	12.89	13.04
100	—	12.43	12.92	—	13.23
300	—	13.32	13.45	—	13.61
600	—	14.66	14.24	—	14.19

†Ammonia in the gaseous phase.

The equilibrium percentages of NH_3 as a function of temperature and pressure are given in Figure B-7. Figure B-8 shows the complete temperature-enthalpy diagram for the $\text{NH}_3\text{-N}_2\text{-H}_2$ system, with the NH_3 data on the left and the idealized data for a stoichiometric mixture of N_2 and H_2 on the right. The horizontal separation of the two sets of curves represents the heat of reaction which is a function of both temperature and pressure. The shaded area represents the region of two-phase equilibrium for ammonia. The dashed lines show the track taken during dissociation (starting from the left and at a pressure of 300 atm) and during synthesis (starting from the right and for an NH_3 partial pressure of about 50 atm).

B.2.3.3 Chubb's Analysis

Chubb (Reference 60) has proposed the SO_3 system for closed-loop energy storage. His SO_3 plant is shown as a schematic outline in Figure B-9, and some pertinent thermochemical information is presented in Figure B-10.

B.2.3.4 Other Literature Data

Comparison of Chubb's reaction for SO_3 dissociation with other reactions for the dissociation of COCl_2 and $\text{H}_2\text{O} + \text{CH}_4$ is shown in Figure B-11 (Reference 60). Although not shown in the figure, the dissociation curve for NF_3 closely matches that for $\text{H}_2\text{O} + \text{CH}_4$. More thermodynamics of the $\text{H}_2\text{O} + \text{CH}_4$ reaction is given by Hanneman (Reference 62) in Figure B-12 for $\text{CH}_4/\text{H}_2\text{O}$ ratios of 1:3 and 3:1.

Figure B-7. Equilibrium Percentages of NH_3 in Stoichiometric Mixtures of N_2 , H_2 , and NH_3 at Various Temperatures and Pressures

Figure B-8. Basic Temperature-Enthalpy Diagram for the NH_3 - N_2 - H_2 System

Figure B-9. Schematic of SO₂-SO₃ Solar Thermal Closed-Loop Energy Storage System

Figure B-10. Equilibrium Fraction of $[SO_2] / [SO_2 + SO_3]$ as a Function of Temperature at Constant Total Pressure

Figure B-11. Comparison of Dissociation Curves for COCl_2 , $\text{H}_2\text{O} + \text{CH}_4$, and SO_3 as Working Fluids for a Gas Dissociation Solar Power System

Figure B-12. Equilibrium Conversion Relations for the CH_4 - H_2O System at Atmospheric Pressure