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Solar Thermal Power Systems Project
Parabolic Dish Power Systems
Research and Advanced Development

Chemical Energy Storage Systems Screening and Preliminary Selection

August 1980

Prepared for
U.S. Department of Energy
Through an agreement with
National Aeronautics and Space Administration
by
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

Note: Temperature Cascading of chemical storage system

Prepared by the Jet Propulsion Laboratory, California Institute of Technology, for the U.S. Department of Energy through an agreement with the National Aeronautics and Space Administration.

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S. H. Kalfayan and H. E. Marsh

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FOREWORD

This report, one of two reports, describes the first part of a two-part study on chemical storage and transport of solar-derived thermal energy. Both topical reports were prepared in support of an overall study that is in the process of assessing the use of paraboloidal dish solar thermal systems for high temperature industrial applications. This effort is being conducted by the Advanced Systems Definition task of the Research and Advanced Development element of the Solar Thermal Power Systems Project at Jet Propulsion Laboratory (JPL).

The first part of the study (this report) focuses on: (1) identifying and collecting a comprehensive list of candidate reversible chemical reaction cycles; (2) screening these cycles to a (mostly qualitative) set of criteria (stressing exothermic temperatures of 700°K (800°F) or higher, and eliminating those creating operational problems involving transport of solid chemical components); and, (3) selecting a list of the best ten candidates, on the basis of reaction characteristics, for further evaluation. This further evaluation concentrates on the chemical engineering and cost analyses of the selected ten candidates, and is discussed in the second part of this study (the second report, "A Chemical Engineering and Cost Study of Energy Transport and Storage Systems Using Reversible Chemical Reactions," by J. M. Schredder at JPL).

ABSTRACT

The purpose of this study, which is one of a two-part study of chemical storage and transport of solar-derived thermal energy, was to select the ten best chemical reaction cycles for further chemical engineering and cost study. Ninety-two cycles, which are classed as simple reversible reactions, were screened according to a set of criteria, most of which were qualitative:

- Reversibility
- Exothermic Temperature, $\geq 700^{o}K$ ($800^{o}F$)
- Handling (relating to solid components)
- Energy Density, Cost, Toxicity, Corrosiveness

The selected ten reaction cycles are:

(1) Sulfur Dioxide Oxidation/Sulfur Trioxide Decomposition

(2) Methanation/Steam Reforming

(3) Carbon Monoxide Disproportionation/Carbon Dioxide Reduction

(4) Methane Synthesis/Decomposition

(5) Ammonium Hydrogen Sulfate Synthesis/Decomposition

(6) Hydrogen Chloride Oxidation/Chlorine Reduction

(7) Liquefiable Metal Cycles

(8) Ammonia Synthesis/Decomposition

(9) Water Gas Reaction

(10) Calcium Hydride Synthesis/Decomposition

After further study of these ten and two other cycles, it was concluded that cycles 2, 1, 8, and 5 (in order of preference) are the most likely candidates for early application because of existing experimental experience with them. Another conclusion was that cycle 7 deserves further study, including experimental investigation, because it is the only cycle that was found in this limited search that offers both all-fluid components and the possibility of very high exothermic temperatures (1650-$2800^{o}K$ or 2500-$4600^{o}F$).

The development of a more accurate assessment of cycle performances was initiated using computerized thermochemical calculations. Some of the data generated in this work were used in the companion chemical engineering and cost study.

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SECTION I

INTRODUCTION

The present study was undertaken to identify suitable chemical reactions that could be used in the chemical heat pipes, and more specifically, in the high-temperature chemical heat pipes (HTCHP), utilizing solar thermal energy. An exothermic reaction temperature of 700°K (800°F) was chosen to demarcate the HTCHP from LTCHP (low-temperature chemical heat pipes) (Ref. 1). The candidate reactions in this report meet this threshold temperature requirement.

A large number of chemical cycles were subjected to a screening process employing four criteria: reversibility, exothermic temperature, energy transmission (a function of handling complexity), and a collective criterion that includes energy storage density, cost, toxicity, and corrosiveness. Limited resources did not permit a wider search. Thus, the potential that may exist in multi-step cycles (mostly for water splitting) is not evaluated in this report.

In the process of selecting the candidate chemical cycles, extensive use was made of the list of reversible chemical reactions prepared by Rocket Research Corporation (RRC) and the literature information they had compiled (Ref. 2). To the RRC list of 85 reactions, we added seven more, one of which was included in the final list. The final selection of the ten candidates was made by using the plan of selection discussed below.

The remainder of this report consists of the Discussion and two Appendixes. The Discussion describes the selection process and the limited, comparative characterizations of the ten selected candidates. Appendix A is a set of brief descriptions of seven of the ten selected cycles. Appendix B is an assessment of the dependability of the values of critical cycle temperatures used in screening and is intended for use in further engineering studies.

There are two major differences between this study and that of RRC (Ref. 2). In this study, the lower limit of acceptable exothermic temperature is higher, 700°K (800°F) versus 450°K (350°F). In addition, heavier penalty is charged to the necessity for handling solid products in the cycles. In other respects, this section of the study (screening) corresponds in depth with the comparable part of the RRC study. However, the Jet Propulsion Laboratory (JPL) improved the quality of estimates of critical cycle temperatures and reversibility. These are described in Appendix B.

The general conclusion of this screening of cycles is the selection of ten potentially useful cycles. These, along with cycle characteristics, are given in Table 1. This selection was somewhat refined by the limited thermochemical study described in Appendix B. Here, it was concluded that only four cycles are good candidates for early application because they have undergone considerable experimental development work, whereas the others are all in the concept stage. The four cycles are: the Methanation/Steam

Reforming (No. 2 in Table 1); the Sulfur Dioxide/Sulfur Trioxide System (No. 1); the Ammonia/Nitrogen-Hydrogen System (No. 8); and the Ammonium Hydrogen Sulfate reaction (No. 5). An additional conclusion of Appendix B is that further exploration should be made into the feasibility of the only all-fluid, high-temperature cycle found in this study, Liquefiable Metal Cycles (No. 7).

Table 1, Selected Reversible Chemical Reactions for Energy Storage

REACTION NO.	REACTION EXO $\rightleftharpoons$ ENDO	TEMP. EXO. *(1)	TEMP. ENDO. *(2)	PRESSURE EXO. (atm.)	PRESSURE ENDO (atm.)	ENERGY DENS.*(3) Btu/ft^3/10^3 (kJ/kg)	COST $ MBtu	REVER-SIBILITY *(4)	TOXI-CITY *(4)	CORRO-SIVENESS *(4)	TYPE OF REACTION	CATALYST REQUIRED	ADVANTAGES	DISADVANTAGES
1	$SO_2(g) + 1/2\ O_2(g) \rightleftharpoons SO_3(g)$	800°K 527°C 981°F	1100°K 827°C 1521°F	10.0	1.0	21.0 (1236)	1.13	1.25	4.00	4.00	Gas-Gas	Yes (Pt,V_2O_5 NO)	Very good reversibility. All gas reaction makes energy transmission easy. Catalytically controllable reaction. Not expensive.	Reverse reaction not studied thoroughly. For high-temperature operation, cost of materials, construction will be high. SO_3 can solidify. Polymerization can be avoided by heating.
2	$3H_2(g) + CO(g) \rightleftharpoons CH_4(g) + H_2O(g)$	700°K 427°C 800°F	1100°K 827°C 1521°F	40.0	1.0	7.98 (6053)	0.26	2.00	3.75	1.25	Gas-Gas	Yes (Ni)	Well studied reaction, particularly the reverse, steam-reforming reaction. High equilibrium conversion. Simple energy transmission. Inexpensive.	Energy storage density per volume is low. High input and low output temperatures. High storage pressures. Some coking,which can be reduced by excess steam. Catalyst studies necessary.
3	$2CO(g) \rightleftharpoons CO_2(g) + C(s)$	1170°K 897°C 1646°F		10.0	1.0	14.20 (3076)	0.84	1.00	3.75	1.00	Gas-Solid	Yes Ni, Chromia?	Reversibility very high. High output (exothermic) temperature. Inexpensive reaction. No special materials of construction.	Presence of solid component creates handling problem. Catalyst studies necessary.
4	$C(s) + 2H_2(g) \rightleftharpoons CH_4(g)$	851°K 578°C 1073°F 1234°F		1.0 1.0 1.0 (5)	1.0	5.59 (4674)	0.73	2.00	1.00	1.00	Gas-Solid	Yes Ni?	Reversibility reported to be very high. High Energy Intensity per weight. Non-toxic and non-corrosive reaction. Fairly high Texo.	Presence of solid component causes handling problem. Carbon can be fed into reactor as water-slurry. Energy penalty for evaporation and removal of water. Catalyst studies necessary.
5	$NH_{3(g)} + H_2O_{(g)} + SO_{3(g)} \rightleftharpoons NH_4HSO_{4(s)}$	700°K 427°C 800°F	800°K 527°C 981°F		1.0	103.6 (2957)	0.21	2.75	3.75	4.75	Gas-Solid (Gas-Liq.)	No	Inexpensive. High energy storage density. Low melting point of NH_4HSO_4 makes it liquid at reaction temperatures. Reaction studied fairly well.	Problems with product separation, which are met by using "alkali sulfate and oxide" separation schemes. Reversibility is said to improve by such schemes. SO_3 dissociation possible at reaction temps.
6	$4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2$	786°K 513°C 955°F	900°K 627°C 1160°F	1.0	1.0	11.0 (643)	2.26	2.50	4.25	4.75	Gas-Gas	Yes ($CuCl_2$)	Energy transmission very good.The forward reaction studied extensively. Problems of corrosiveness supposed to be minimized in the Kellog process.	Special containment materials necessary. Medium reversibility.
7	$2Na(\ell) + H_2O(\ell) + 1/2\ O_2 \rightleftharpoons 2NaOH(\ell)$	1665°K 1392°C 2537°F	2000°K 1727°C 3140°F			(6600)		2.50?	3.50	3.50	Gas-Liq.	No	High Energy Storage density and high Texo. Fluid nature of reaction components makes energy transmission easy.	Reaction not studied thoroughly. Product separation problems.
8	$N_2 + 3H_2 \rightleftharpoons 2\ NH_3$	773°K 500°C 931°F	1023°K 750°C 1380°F	200	200	3.55 (2695)	0.78	1.00	3.00	2.75	Gas-Gas	Yes Iron Oxide (promoted)	Very good reversibility. Energy transmission excellent. Not expensive. Well studied reaction.	Forward reaction requires high pressures. Reaction slow at lower temperatures. At higher temperatures yield of NH_3 decreases. Generally, poor kinetics.
9	$CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g)$	863°K 590°C 1093°F 1048°F 1261°F	813°K 540°C 1003°F	1.0 0.5 10.0		6.72 (934)	3.51	2.00	3.75	1.25	Gas-Gas	Yes	This is the so-called water-gas shift. Handling complexity is minimum. No special containment materials problems.	High storage pressure. Reversibility medium. Energy density only fair. Methane and C are by-products.
10	$Ca(s) + H_2(g) \rightleftharpoons CaH_2(s)$	1150°K 877°C 1610°F	1350°K 1077°C 1970°F	10.0	1.0	25.0 (4483)	11.4	1.00	1.50	2.50	Gas-Solid	No	Excellent Reversibility. High Energy Storage density. Calcium in liquid form at reaction temperatures.	Solid component creates handling (energy transmission) problems. Not inexpensive. Thermal breakdown of CaH_2 not studied thoroughly.

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*(1) T_{EXO}

The temperature of the exothermic reaction in degrees Kelvin at about 90% conversion. It was calculated from ΔG, ΔH and C_p values obtainable from the literature by using well-known thermodynamic relationships.

*(2) T_{ENDO}

The temperature of the endothermic reaction in degrees Kelvin, calculated the same way as T_{EXO}.

*(3) Energy Density

The gravimetric Energy Density is equal to the ΔH of the reaction in kilojoules divided by the kilogram of reactants. The volumetric Energy Density is calculated from the gravimetric by dividing the latter by the average density of the reactants, and is reported as kJ/l, j/cm^3, Btu/ft^3, etc.

*(4) Reversibility, Toxicity and Corrosiveness of Reactions

Ratings from 1 to 5 were assigned to these properties, following the example of RRC. Very high reversibility was given a rating of 1.00, and an irreversible reaction was rated 5.00. Other ratings were assigned depending on how many by-products, and how much of each were formed. If the components of a reaction were non-toxic or non-corrosive, a rating of 1.00 was assigned. Reactions containing highly toxic or highly corrosive components were rated 5.00.

SECTION II

DISCUSSION

A. PLAN FOR THE SELECTION OF CANDIDATE REACTIONS

The ten reactions listed in Table 1 were selected by using the scheme shown in Figure 1. Screening criteria and other parameters are defined in Table 1.

The 92 reactions were first classified into the following groups according to the physical state of the components:

- Group I. Reactions Containing Solid Components:
  - Sub-group A. Reactions with three solid components at room temperature
  - Sub-group B. Reactions with two solid components at room temperature
  - Sub-group C. Reaction with one solid component at room temperature
- Group II. Reactions Containing All Gas Components.
- Group III. Reactions Containing Gas and Liquid Components.

The reactions falling under each group and sub-group are shown in Table 2.

The next step was to screen out reactions which had average or less-than-average reversibility. Here the rating used by Rocket Research Corporation (RRC) was adopted as being considered adequate for screening. A high rating of 1.00 was given to reactions that were clearly reversible without showing any side reactions. The lowest rating was 5.00, which indicated that side reactions were present and that they constituted a large percentage of the total reactions. A rating of 2.50 was the demarcation line. Reactions rated 2.50 or higher were discarded. Therefore, it may be seen in Table 2 that 12 out of 13 reactions with 3 solid components were eliminated. Nine out of 40 reactions with 2 solid components, 4 out of 19 with 1 solid component, 6 out of 16 with all gas components, and 1 out of 4 with gas and liquid components were also eliminated, giving a total of 32 discarded reactions. Two exceptions to this rule were made in the cases of the NH_4HSO_4 reaction and the oxidation of hydrogen chloride, rated 2.75 and 2.50, respectively by RRC, because it is believed the reversibility of these reactions can be improved by using different separation schemes or reaction conditions.

The screening of the surviving 60 reactions was carried out next by using the criterion of exothermic reaction temperature T_{EXO}. In screening, because of resource limitations, no special attempt was made to refine cycle

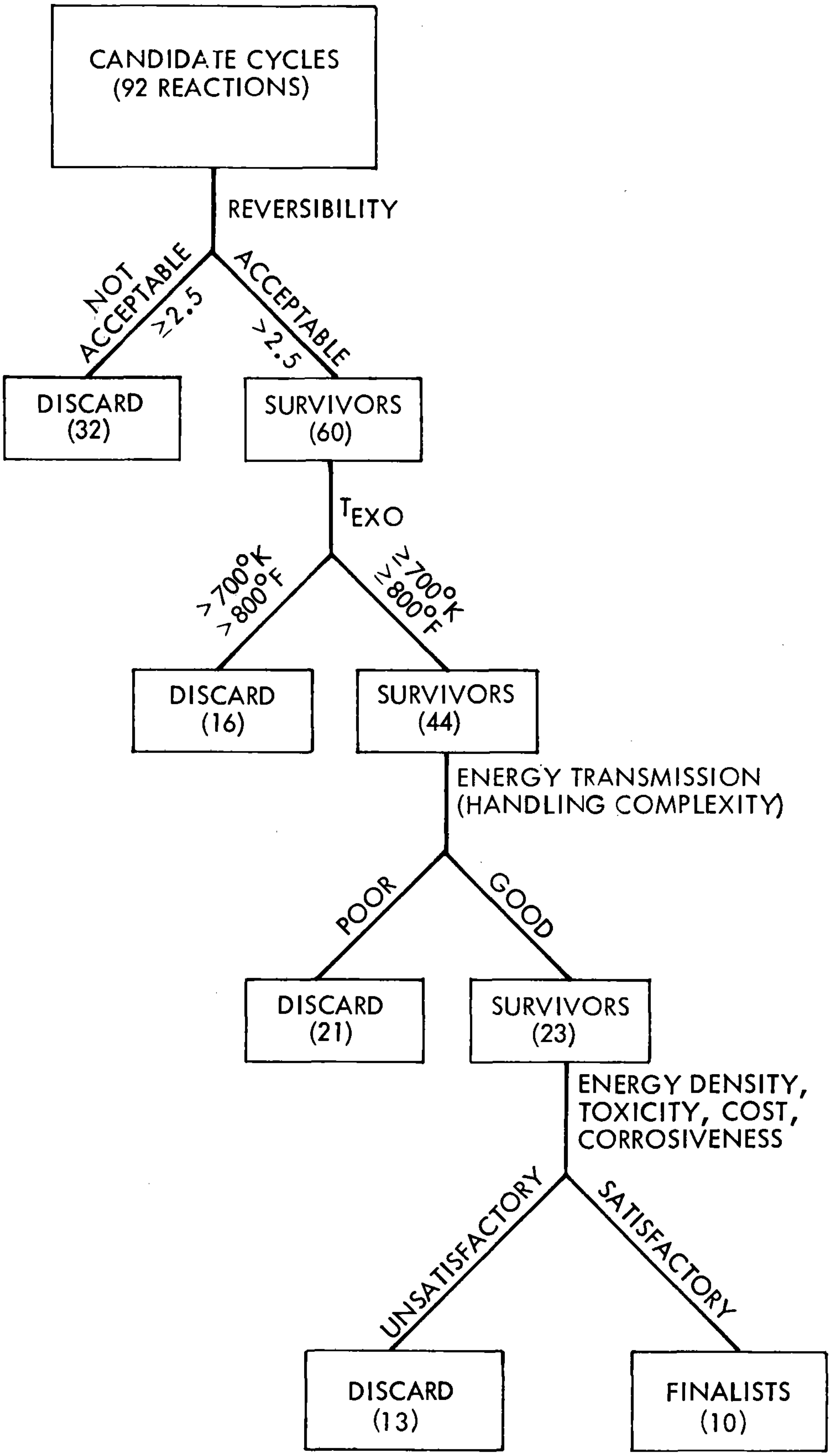

Figure 1. Selection Scheme For Chemical Energy Storage Systems

Table 2. Classification of Reversible Chemical Reactions According to their Physical State

I. REACTIONS CONTAINING SOLID COMPONENTS

A. REACTIONS WITH "THREE" SOLID COMPONENTS AT ROOM TEMPERATURE

Reversibility Rating			Solid(s)	Gas(g)
2.75	1.	$CH_{4(g)} + 4Na_{(s)} \rightleftharpoons C_{(s)} + 4NaH_{(s)}$	3s	1g
2.75	2.	$CH_{4(g)} + 4K_{(s)} \rightleftharpoons C_{(s)} + 4KH_{(s)}$	3s	1g
3.00	3.	$CH_{4(g)} + 2Li_2C_{2(s)} \rightleftharpoons 5C_{(s)} + 4LiH_{(s)}$	3s	1g
2.75	4.	$SiH_{4(g)} + 2Mg_{(s)} \rightleftharpoons Si_{(s)} + 2MgH_{2(s)}$	3s	1g
* 2.25	5.	$SiH_{4(g)} + 4Na_{(s)} \rightleftharpoons Si_{(s)} + 4NaH_{(s)}$	3s	1g
2.75	6.	$H_{2(g)} + Li_2C_{2(s)} \rightleftharpoons 2C_{(s)} + LiH_{(s)}$	3s	1g
2.50	7.	$2NO_{2(g)} + LI_2O_{(s)} \rightleftharpoons LiNO_{2(s)} + LiNO_{3(s)}$	3s	1g
3.25	8.	$2NO_{2(g)} + 2LiOH_{(s)} \rightleftharpoons LiNO_{2(s)} + LiNO_{3(s)} + H_2O_{(g)}$	3s	2g
3.75	9.	$2NO_{2(g)} + Li_2CO_{3(s)} \rightleftharpoons LiNO_{2(s)} + LiNO_{3(s)} + CO_{2(g)}$	3s	2g
3.25	10.	$2NO_{2(g)} + 2NaOH_{(s)} \rightleftharpoons NaNO_{2(s)} + N_aNO_{3(s)} + H_2O_{(g)}$	3s	2g
4.00	11.	$2NO_{2(g)} + Na_2CO_{3(s)} \rightleftharpoons NaNO_{2(s)} + NaNO_{3(s)} + CO_{2(g)}$	3s	2g
4.00	12.	$4NO_{2(g)} + 2Ca(OH)_{2(s)} \rightleftharpoons Ca(NO_3)_{2(s)} + Ca(NO_3)_{2(s)} + 2H_2O_{(g)}$	3s	2g
3.75	13.	$4NO_{2(g)} + 2CaCO_{3(s)} \rightleftharpoons Ca(NO_2)_{2(s)} + Ca(NO_3)_{2(s)} + 2CO_{2(g)}$	3s	2g

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*Signifies acceptable reversibility.

Table 2. Classification of Reversible Chemical Reactions According to their Physical State (Continuation 1)

B. REACTIONS WITH "TWO" SOLID COMPONENTS

Reversibility Rating			Solid(s)	Gas(g)
*1.5	1.	$H_2O_{(g)} + MgO_{(s)} \rightleftharpoons Mg(OH)_{2(s)}$	2s	1g
*1.5	2.	$H_2O_{(g)} + CaO_{(s)} \rightleftharpoons Ca(OH)_{2(s)}$	2s	1g
*2.25	3.	$H_2O_{(g)} + CuO_{(s)} \rightleftharpoons Cu(OH)_{2(s)}$	2s	1g
*1.75	4.	$SO_{3(g)} + LiO_{(s)} \rightleftharpoons Li_2SO_{4(s)}$	2s	1g
*1.75	5.	$SO_{3(g)} + NiO_{(s)} \rightleftharpoons NiSO_{4(s)}$	2s	1g
2.50	6.	$SO_{3(g)} + CuO_{(s)} \rightleftharpoons CuSO_{4(s)}$	2s	1g
*1.75	7.	$SO_{3(g)} + Cs_2O_{(s)} \rightleftharpoons Cs_2SO_{4(s)}$	2s	1g
*1.75	8.	$SO_{3(g)} + ZnO_{(s)} \rightleftharpoons ZnSO_{4(s)}$	2s	1g
*1.75	9.	$1\frac{1}{2}O_{2(g)} + Na_2O_{(s)} \rightleftharpoons NaO_{2(s)}$	2s	1g
*1.75	10.	$1\frac{1}{2}O_{2(g)} + K_2O_{(s)} \rightleftharpoons KO_{2(s)}$	2s	1g
*1.50	11.	$CO_{2(g)} + Li_2O_{(s)} \rightleftharpoons LiCO_{3(s)}$	2s	1g
*1.25	12.	$CO_{2(g)} + MgO_{(s)} \rightleftharpoons MgCO_{3(s)}$	2s	1g
*1.25	13.	$CO_{2(g)} + CaO_{(s)} \rightleftharpoons CaCO_{3(s)}$	2s	1g
*1.25	14.	$CO_{2(g)} + SrO_{(s)} \rightleftharpoons SrCO_{3(s)}$	2s	1g
*1.25	15.	$CO_{2(g)} + CdO_{(s)} \rightleftharpoons CdCO_{3(s)}$	2s	1g
*1.25	16.	$CO_{2(g)} + ZnO_{(s)} \rightleftharpoons ZnCO_{3(s)}$	2s	1g
*1.75	17.	$CO_{2(g)} + MnO_{(s)} \rightleftharpoons MnCO_{3(s)}$	2s	1g
*1.75	18.	$CO_{2(g)} + FeO_{(s)} \rightleftharpoons FeCO_{3(s)}$	2s	1g
*1.75	19.	$6H_2O_{(g)} + MgCl_{2(s)} \rightleftharpoons MgCl_2 \cdot 6H_2O_{(s)}$	2s	1g
*	20.	$4H_2O_{(g)} + 3Fe_{(s)} \rightleftharpoons Fe_3O_{4(s)} + H_{2(g)}$	2s	2g
2.50	21.	$2NH_{3(g)} + 6Na_{(s)} \rightleftharpoons N_{2(g)} + 6NaH_{(s)}$	2s	2g

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*Signifies acceptable reversibility.

Table 2. Classification of Reversible Chemical Reactions According to their Physical State (Continuation 2)

B. REACTIONS WITH "TWO" SOLID COMPONENTS (continued)

Reversibility Rating					Solid(s)	Gas(g)
2.50	22.	$2NH_{3(g)} + 6K_{(s)}$	$\rightleftharpoons$	$N_{2(g)} + 6KH_{(s)}$	2s	2g
	23.	$NH_{3(g)} + MgCl_{2(s)}$	$\rightleftharpoons$	$MgCl_2 \cdot NH_{3(s)}$	2s	1g
*1.50	24.	$NH_{3(g)} + FeCl_2 \cdot NH_{3(s)}$	$\rightleftharpoons$	$FeCl_2 \cdot 2NH_{3(s)}$	2s	1g
3.00	25.	$2NO_{2(g)} + \frac{1}{2}O_{2(g)} + Na_2O_{(s)}$	$\rightleftharpoons$	$2NaNO_{3(s)}$	2s	2g
2.75	26.	$2NO_{2(g)} + \frac{1}{2}O_{2(g)} + CaO_{(s)}$	$\rightleftharpoons$	$Ca(NO_3)_{2(s)}$	2s	2g
3.25	27.	$2NO_{2(g)} + \frac{1}{2}O_{2(g)} + BaO_{(s)}$	$\rightleftharpoons$	$Ba(NO_3)_{2(s)}$	2s	2g
*1.75	28.	$HF_{(g)} + NaF_{(s)}$	$\rightleftharpoons$	$NaHF_{2(g)}$	2s	1g
*1.50	29.	$HF_{(g)} + KF_{(s)}$	$\rightleftharpoons$	$KHF_{2(s)}$	2s	1g
*1.50	30.	$BF_{3(g)} + KF_{(s)}$	$\rightleftharpoons$	$KBF_{4(s)}$	2s	1g
*1.00	31.	$H_{2(g)} + 2Li_{(s)}$	$\rightleftharpoons$	$2LiH_{(s)}$	2s	1g
*1.00	32.	$H_{2(g)} + 2Na_{(s)}$	$\rightleftharpoons$	$2NaH_{(s)}$	2s	1g
*1.00	33.	$H_{2(g)} + 2K_{(s)}$	$\rightleftharpoons$	$2KH_{(s)}$	2s	1g
*1.00	34.	$H_{2(g)} + Mg_{(s)}$	$\rightleftharpoons$	$MgH_{2(s)}$	2s	1g
*1.00 √(10)	35.	$H_{2(g)} + Ca_{(s)}$	$\rightleftharpoons$	$CaH_{2(s)}$	2s	1g
*1.50	36.	$H_{2(g)} + Ti_{(s)}$	$\rightleftharpoons$	$TiH_{2(s)}$	2s	1g
2.75	37.	$H_{2(g)} + CaC_{2(s)}$	$\rightleftharpoons$	$Ca_{(s)} + 2CH_4$	2s	2g
2.50	38.	$3H_{2(g)} + 2Li_3N_{(s)}$	$\rightleftharpoons$	$6LiH_{(s)} + N_2$		
4.25	39.	$H_2O_{(g)} + CO_{2(g)} + Na_2S_{(s)}$	$\rightleftharpoons$	$Na_2CO_{3(s)} + H_2S_{(g)}$	2s	3g
*1.25	40.	$CS_{2(g)}$	$\rightleftharpoons$	$C_{(s)} + 2S_{(s)}$	2s	1g

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*Signifies acceptable reversibility

√Signifies selection in final 10. Number in parentheses refers to Table 1.

Table 2. Classification of Reversible Chemical Reactions According to their Physical State (Continuation 3)

C. REACTIONS WITH "ONE" SOLID COMPONENT AT ROOM TEMPERATURE

Reversibility Rating			Reactants		Products	Solid(s)	Gas(g)	Liquid(ℓ)
*2.25		1.	$NH_{3(g)} + HCl_{(g)}$	$\rightleftharpoons$	$NH_4Cl_{(s)}$	1s	2g	
*2.25		2.	$NH_{3(g)} + HBr_{(g)}$	$\rightleftharpoons$	$NH_4Br_{(s)}$	1s	2g	
*2.25		3.	$NH_{3(g)} + HI_{(g)}$	$\rightleftharpoons$	$NH_4I_{(s)}$	1s	2g	
*2.25		4.	$NH_{3(g)} + HF_{(g)}$	$\rightleftharpoons$	$NH_4F_{(s)}$	1s	2g	
*2.25	√(5)	5.	$NH_{3(g)} + SO_{3(g)} + H_2O_{(g)}$	$\rightleftharpoons$	$NH_4HSO_{4(s)}$	1s	3g	
*2.25		6.	$2NH_{3(g)} + SO_{3(g)} + H_2O_{(g)}$	$\rightleftharpoons$	$(NH_4)_2SO_{4(s)}$	1s	3g	
*2.25		7.	$2NH_{3(g)} + H_2SO_{4(\ell)}$	$\rightleftharpoons$	$(NH_4)_2SO_{4(s)}$	1s	1g	1ℓ
*2.00		8.	$NH_{3(g)} + H_3PO_{4(\ell)}$	$\rightleftharpoons$	$NH_4H_2PO_{4(s)}$	1s	1g	1ℓ
*2.00	√(4)	9.	$2H_{2(g)} + C_{(s)}$	$\rightleftharpoons$	$CH_{4(g)}$	1s	2g	
2.75		10.	$H_{2(g)}\ CO_{(g)}$	$\rightleftharpoons$	$C_{(s)} + 2H_2O_{(g)}$	1s	3g	
2.75		11.	$2H_{2(g)} + CO_{2(g)}$	$\rightleftharpoons$	$C_{(s)} + 2H_2O_{(g)}$	1s	3g	
		12.	$H_{2(g)} + 2Cs_{(\ell)}$	$\rightleftharpoons$	$2CsH_{(s)}$	1s	1g	1ℓ
2.75		13.	$2H_{2(g)} + CS_{2(g)}$	$\rightleftharpoons$	$2S_{(s)} + CH_{4(g)}$	1s	3g	
3.25		14.	$4HF_{(g)} + SiO_{2(s)}$	$\rightleftharpoons$	$SiF_{4(g)} + 2H_2O_{(g)}$	1s	3g	
*1.75		15.	$VCl_{2(s)} + \frac{1}{2}Cl_{2(g)}$	$\rightleftharpoons$	$VCl_{3(g)}$	1s	2g	
*1.25		16.	$C_{(s)} + 2Cl_{2(g)}$	$\rightleftharpoons$	$CCl_{4(\ell)}$	1s	1g	1ℓ
*1.75		17.	$CS_{2(g)} + 2H_2S_{(g)}$	$\rightleftharpoons$	$CH_{4(g)} + 4S_{(s)}$	1s	3g	
		18.	$2Cs_{(\ell)} + Br_{2(\ell)}$	$\rightleftharpoons$	$2CsBr_{(s)}$	1s		2ℓ
*1.00	√(13)	19.	$2CO_{(g)}$	$\rightleftharpoons$	$C_{(s)} + CO_{2(g)}$	1s	2g	

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*Signifies acceptable reversibility.

√Signifies selection in final 10. Number in parentheses refers to Table 1.

Table 2. Classification of Reversible Chemical Reactions According to their Physical State (Continuation 4)

II. REACTIONS CONTAINING ALL GAS COMPONENTS

Reversibility Rating			Reactants		Products	Solid(s)	Gas(g)	Liquid(ℓ)
*1.00	√(8)	1.	$3H_{2(g)} + N_{2(g)}$	$\rightleftharpoons$	$2NH_{3(g)}$		3g	
*2.00	√(2)	2.	$3H_{2(g)} + CO_{(g)}$	$\rightleftharpoons$	$CH_{4(g)} + H_2O_{(g)}$		4g	
2.50		3.	$2H_{2(g)} + CO_{(g)}$	$\rightleftharpoons$	$CH_3OH_{(g)}$		3g	
3.00		4.	$H_{2(g)} + C_2H_{4(g)}$	$\rightleftharpoons$	$C_2H_{6(g)}$		3g	
2.75		5.	$3H_{2(g)} + C_6H_6$	$\rightleftharpoons$	$C_6H_{12(g)}$		3g	
2.75		6.	$4H_{2(g)} + CS_{2(g)}$	$\rightleftharpoons$	$CH_{4(g)} + 2H_2S_{(g)}$		4g	
*1.25	√(1)	7.	$SO_{2(g)} + \frac{1}{2}O_{2(g)}$	$\rightleftharpoons$	$SO_{3(g)}$		3g	
3.00		8.	$3SO_{2(g)} + 2NO_{2(g)}$	$\rightleftharpoons$	$3SO_{3(g)} + N_2)_{(g)}$		4g	
*2.00		9.	$2NO_{(g)} + Cl_{2(g)}$	$\rightleftharpoons$	$2NOCl_{(g)}$		3g	
*2.00		10.	$2NO_{(g)} + O_{2(g)}$	$\rightleftharpoons$	$2NO_{2(g)}$		3g	
2.75		11.	$3NO_{(g)}$	$\rightleftharpoons$	$N_2O_{(g)} + NO_{2(g)}$		3g	
*2.00		12.	$2NO_{(g)} + CO_{(g)}$	$\rightleftharpoons$	$N_2O_{(g)} + CO_{2(g)}$		4g	
*2.00		13.	$CO_{(g)} + Cl_{2(g)}$	$\rightleftharpoons$	$COCl_{2(g)}$		3g	
*2.00	√(9)	14.	$CO_{(g)} + H_2O_{(g)}$	$\rightleftharpoons$	$CO_{2(g)} + H_{2(g)}$		4g	
2.50	√(6)	15.	$4HCl_{(g)} + O_{2(g)}$	$\rightleftharpoons$	$2Cl_{2(g)} + H_2O_{(g)}$		4g	
*2.00		16.	$N_{2(g)} + 3F_{2(g)}$	$\rightleftharpoons$	$2NF_{3(g)}$		3g	

III. REACTIONS CONTAINING GAS AND LIQUID COMPONENTS

Reversibility Rating			Reactants		Products	Solid(s)	Gas(g)	Liquid(ℓ)
*		1.	$2PCl_{3(\ell)} + O_{2(g)}$	$\rightleftharpoons$	$2POCl_{3(\ell)}$		1g	2ℓ
2.50		2.	$IF_{5(\ell)} + F_{2(g)}$	$\rightleftharpoons$	$IF_{7(\ell)}$		1g	2ℓ
*1.25		3.	$H_2O_{(g)} + SO_{3(g)}$	$\rightleftharpoons$	$H_2SO_{4(\ell)}$		2g	1ℓ
*2.00	√(7)	4.	$2Na_{(\ell)} + H_2O_{(\ell)} + \frac{1}{2}O_{2(g)}$	$\rightleftharpoons$	$2NaOH_{(\ell)}$		1g	3ℓ

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*Signifies acceptable reversibility.

√Signifies selection in final 10. Number in parentheses refers to Table 1.

temperature data. Values of T_{EXO} from RRC were used for some cycles. A few were calculated manually, assuming unique reactions, and others were obtained by using the Rocket Performance Program from NASA Lewis Research Center (Lewis Program). T_{EXO} values were not available for all 60 candidates. Sixteen reactions, however, had T_{EXO} values lower than 700°K (800°F) and were discarded. The surviving 44 reactions included those for which T_{EXO} values were not available. This situation did not prove to be difficult because in the next screening step many of the reactions without T_{EXO} values were eliminated. On the basis of good or poor energy transmission or handling complexity, 21 of these reactions were rated poor and discarded. Energy transmission was considered very poor when the reaction involved 2 or more solids, and poor when there was 1 solid component. The list of 23 survivors, however, included 7 reactions with 1 solid component and 2 reactions with 2 solid components. These exceptions were included because of the excellent reversibilities, and/or the availability of pertinent information about these reactions. This list is shown in Table 3.

The final screening was made by considering such properties as energy storage density, cost, toxicity, and corrosiveness and availabiliity of information. Here again, the RRC ratings were used. Thirteen more reactions could be screened out on the basis of these considerations, leaving the ten finalists listed in Table 1. Table 3 gives some of the reasons why these 13 reactions were not included among the final list.

A few of the reactions which were eliminated on the basis of toxicity or handling complexity, but which have high T_{EXO} values and satisfactory reversibility, are listed in Table 4 as "borderline" reactions. It was thought worthwhile to identify these reactions for possible further study.

B. TEN SELECTED CANDIDATE REACTIONS

Pertinent information about each of the ten reactions will be found in Table 1. The critical cycle reaction temperatures are reported in the Kelvin, Celsius and Fahrenheit scales. Energy densities are reported in volumetric and gravimetric units. The costs in dollars per MBtu's are RRC values, with the exception of the value given for reaction No. 8, which was arrived at by comparison to similar materials for which cost estimates are available. A cost estimate was not given for reaction No. 7, although it is suspected that it may be more than \$5/MBtu. The numerical toxicity and corrosiveness ratings were also taken from the RRC report. A rating of 1.00 means least, and a rating of 5.00 means most toxic or corrosive. Again, for reaction 7 (which is our own contribution) values reported were derived by comparison with similar materials.

Cycle reaction conditions (endothermic and exothermic reaction temperatures and pressures) listed in Table 1, come from a variety of sources. These sources are listed in Table 5. All of these values are approximations varying, one from another, in the degree to which they predict the true behavior of the cycles. Other screening criteria, reversibiity and energy storage density, are affected by this uncertainty. Also affected is the estimation of recoverable energy losses, which are considered in the second report of this study, "A Chemical Engineering Cost Study of Energy

Transport and Storage Systems Using Reversible Chemical Reactions" (Ref. 3). As Table 5 shows, partial refinement of cycle temperature data has been made in some cases by using some of the capabilities of thermochemical computer programs designed for Rocket Performance Program predictions. Much more should be done to produce more complete predictions of cycle performance. This was not possible on this program because of resource limitations. A more thorough discussion of thermochemical calculations and their significance is given in Appendix B.

Reactions other than those listed in Table 1, for which values of T_{EXO} were computed at JPL, or which were obtained from the RRC report, are given in Table 6. The values obtained from the latter report are identified by the letters RRC.

Most of the reactions in Table 1, namely the SO_2/SO_3 system, the methanation/steam reforming reaction, the ammonium hydrogen sulfate reaction, the oxidation of hydrogen chloride, the calcium/calcium hydride reaction, the NH_3/N_2-H_2, and the NaOH/Na systems are discussed in more detail in Appendix A.

The relationship of the exothermic reaction temperature, (T_{EXO}), to energy storage density for the reactions of Table 1, are shown in Figure 2. The high value obtained for reaction 7 was one reason for including it in the final list. The T_{EXO} values used for reactions 2 and 5 were not the ones listed in Table 1. The higher values obtained from the Lewis Program given in Table 3 were used.

Schematics for most of the chemical energy systems represented by the chemical equations of Table 1 are shown in Figures 3 through 9. Figures 5, 8 and 9 were taken from the RRC report (Ref. 2). Figures 3, 4 and 6 were adapted from that report.

Table 3. Reversible Chemical Reactions with Satisfactory T_{EXO} and Energy Transmission

No.	Reaction	T_{EXO}, ^{o}F (P_{EXO}, atm)	Reasons for not selecting the reactions involved
1.	$2Li_{(s)} + H_{2(g)} \rightleftharpoons 2LiH_{(s)}$	**	Lack of information
*2.	√(10) $Ca_{(s)} + H_{2(g)} \rightleftharpoons CaH_{2(s)}$	1610 (10 atm) RRC	Selected
*3.	√(5) $NH_{3(g)} + SO_{3(g)} + H_2O_{(g)} \rightleftharpoons NH_4HSO_{4(s)}$	1604 (1.0), 1622 (40), 800 RRC	Selected
4.	$2NH_{3(g)} + SO_{3(g)} + H_2O_{(g)} \rightleftharpoons (NH_4)_2SO_{4(s)}$	1667 (1.0) 1720 (40)	Less studied than previous reaction
5.	$2NH_{3(g)} + H_2SO_{4(\ell)} \rightleftharpoons (NH_4)_2SO_{4(s)}$	**	H_2SO_4 will decompose at T_{ENDO}
6.	$NH_{3(g)} + H_3PO_{4(\ell)} \rightleftharpoons NH_4H_2PO_{4(s)}$	**	Insufficient information about the reverse reaction
*7.	√(4) $C_{(s)} + H_{2(g)} \rightleftharpoons CH_{4(g)}$	1067 (1.0) 1234 (5.0)	Selected
8.	$2Cs_{(\ell)} + H_{2(g)} \rightleftharpoons 2CsH_{(g)}$	**	CsH decomposes at 572^{o}F
9.	$VCl_{2(s)} + \frac{1}{2}Cl_2 \rightleftharpoons VCl_{3(g)}$	**	Expensive, $218/MBtu
*10.	√(3) $2CO_{(g)} \rightleftharpoons C_{(s)} + CO_{2(g)}$	1646 (10)	Selected
11.	√(8) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$	550 (10), 660 (40) 981 (300) RRC	Poor kinetics. High pressures necessary for the forward reaction. Selected
*12.	√(2) $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$	1277 (1.0) 1505 (10) 1687 (40), 800 RRC	Selected
*13.	√(1) $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$	981 (10 atm)	Selected

*Selected

**T_{EXO} not determined. Probably over 800^{o}F.

√Signifies selection in final 10. Number in parentheses refers to Table 1.

Table 3. Reversible Chemical Reactions with Satisfactory T_{EXO} and Energy Transmission (Continuation 1)

No.	Reaction	T_{EXO}, °F (P_{EXO}, atm)	Reasons for not selecting the reactions involved
14.	$2NO_{(g)} + Cl_{2(g)} \rightleftharpoons 2NOCl_{(g)}$	2566 (1.0) 2790 (10)	High toxicity. Rated "borderline". Reverse reaction not studied well.
15.	$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$	3192 (1.0) 3198 (10)	Rated "borderline"
*16. +	$2NO_{(g)} + CO_{(g)} \rightleftharpoons N_2O_{(g)} + CO_{(g)}$	2240 (1.0)	At T_{EXO} shown N_2O not stable; gives $N_2 + \frac{1}{2}O_2$.
17.	$CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$	1261 (1.0) 1452 (10)	Highly toxic. Rated "borderline". Reverse reaction can be carried out electrochemically.
*18.√(9)	$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$	1048 (0.5) 1093 (1.0) 1261 (10)	Selected
*19.√(6)	$4HCl_{(g)} + O_{2(g)} \rightleftharpoons 2Cl_{2(g)} + 2H_2O_{(g)}$	955 (1.0) 1016 (5.0) 1041 (10), 800 RRC	Selected
20.	$N_{2(g)} + 3F_{2(g)} \rightleftharpoons 2NF_{3(g)}$	1167 (1.0) 1380 (10)	Expensive, \$164/MBtu
21.	$2PCl_{3(g)} + O_{2(g)} \rightleftharpoons 2POCl_{3(g)}$	**	Reversibility questionable
22.	$H_2O_{(g)} + SO_{3(g)} \rightleftharpoons H_2SO_{4(\ell)}$	1427 (1.0)	Commercially H_2SO_4 not manufactured as indicated. Decomposition of H_2SO_4 at T_{EXO}
*23.	$2Na_{(\ell)} + H_2O_{(\ell)} + \frac{1}{2}O_2 \rightleftharpoons 2NaOH_{(\ell)}$	2537 (0.01)	Selected

*Selected

**T_{EXO} not determined. Probably over 800°F.

√Signifies selection in final 10. Number in parentheses refers to Table 1.

+Selected in the beginning but later rejected. See Appendix B.

Table 4. "Borderline" Reactions

No.	Reaction	Reversibility	T_{EXO} ^{o}F	P_{EXO} (atm)
1.	$CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$	2.00	1260 1451	1.0 10.0
2.	$2NO_{(g)} + Cl_{2(g)} \rightleftharpoons 2NOCl_{(g)}$	2.00	2566 2790	1.0 10.0
3.	$2NO_{(g)} + O_{2(g)} \rightleftharpoons NO_{2(g)}$	2.00	3192 3198	1.0 10.0
4.	$CS_{2(g)} + 2H_2S_{(g)} \rightleftharpoons 4S_{(s)} + CH_{4(g)}$	1.75	841	1.0
5.	$ZnO_{(s)} + SO_{3(g)} \rightleftharpoons ZnSO_{4(s)}$	1.75	1449 RRC	1.0
6.	$CaO_{(s)} + CO_{2(g)} \rightleftharpoons CaCO_{3(s)}$	1.75	1340 RRC	0.1

Table 5. Sources of Critical Cycle Temperature Data Recorded in Table 1

No.	Reaction	T_{ENDO}	T_{EXO}
1.	$SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$	Lewis[1]	RRC[2]
2.	$3H_{2(g)} + CO_{(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$	RRC	RRC
3.	$2CO_{(g)} \rightleftharpoons CO_{2(g)} + C_{(s)}$	--	Lewis
4.	$C_{(s)} + 2H_{2(g)} \rightleftharpoons CH_{4(g)}$	--	Lewis
5.	$NH_{3(g)} + H_2O_{(g)} + SO_{3(g)} \rightleftharpoons NH_4HSO_{4(s)}$	RRC	RRC
6.	$4HCl_{(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)} + 2Cl_{2(g)}$	RRC	Lewis
7.	$2Na_{(\ell)} + H_2O_{(\ell)} + \frac{1}{2}O_{2(g)} \rightleftharpoons 2NaOH_{(\ell)}$	JPL	Lockheed[3]
8.	$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$	Williams[4]	Williams
9.	$CO_{(g)} + H_2O_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$	Lewis	Lewis
10.	$Ca_{(s)} + H_{2(g)} \rightleftharpoons CaH_{2(s)}$	RRC	RRC

1. Lewis = Rocket Performance Program from NASA Lewis Research Center
2. RRC = Rocket Research Corp. Report 77-R-559
3. Lockheed = Rocket Performance Program from Lockheed Propulsion Co.
4. Williams = Owen M. Williams, Australian National University, Personal Communication

Table 6. Other Reactions for which Exothermic Reaction Temperatures were Computed

No.	Reaction	T_{EXO}, ^{o}F	P_{EXO}, atm
1.	$N_2 + 3F_2 \rightleftharpoons 2NF_3$	1167 1379	1.0 10.0
2.	$2NO_2 + 3SO_2 \rightleftharpoons 3SO_3 + N_2O$	1401 1545	1.0 10.0
3.	$CO + Cl_2 \rightleftharpoons COCl_2$	1260 1451	1.0 10.0
4.	$Cl_2 + 2NO \rightleftharpoons 2NOCl$	2566 2790	1.0 10.0
5.	$C_2H_4 + H_2 \rightleftharpoons C_2H_6$	1272 1534	1.0 10.0
6.	$CO + 2H_2 \rightleftharpoons CH_3OH$	1291 1527 1700	1.0 10.0 40.0
7.	$3NO \rightleftharpoons N_2O + NO_2$	4254 4306	0.5 1.0
8.	$CO + H_2 \rightleftharpoons C_{(s)} + H_2O$	1336 1565 1732	1.0 10.0 40.0
9.	$2NO + O_2 \rightleftharpoons 2NO_2$	3192 3198	1.0 10.0
10.	$CO + 2NO \rightleftharpoons N_2O + CO_2$	2240	0.5
11.	$CS_2 + 2H_2 \rightleftharpoons 2S + CH_4$	1839 1945	10.0 40.0
12.	$SO_3 + H_2O \rightleftharpoons H_2SO_4$	722 812	1.0 5.0
13.	$CO_2 + 2H_2 \rightleftharpoons C_{(s)} + 2H_2O$	1136	10.0
14.	$CS_2 + 2H_2S \rightleftharpoons 4S_{(s)} + CH_4$	841	1.0

Table 6. Other Reactions for which Exothermic Reaction Temperatures were Computed (Continuation 1)

No.	Reaction	T_{EXO}, °F	P_{EXO}, atm
15.	$SO_3 + 2NH_3 + H_2O \rightleftharpoons (NH_4)_2SO_4$	1668 1720	1.0 40.0
16.	$CaO_{(s)} + H_2O \rightleftharpoons Ca(OH)_{2(s)}$	755 RRC	1.0
17.	$MgO_{(s)} + H_2O \rightleftharpoons Mg(OH)_2$	350 RRC	0.03
18.	$ZnO_{(s)} + SO_3 \rightleftharpoons ZnSO_4$	1149 RRC	1.0
19.	$K_2O + \frac{1}{2}O_2 \rightleftharpoons KO_2$	1160 RRC	0.08
20.	$CaO_{(s)} + CO_2 \rightleftharpoons CaCO_{3(s)}$	1340 RRC	0.1
21.	$MgO_{(s)} + CO_2 \rightleftharpoons MgCO_{3(s)}$	620 RRC	0.1?
22.	$HF + KF_{(s)} \rightleftharpoons KHF_{2(s)}$	620 RRC	1.0
23.	$2Na + H_2 \rightleftharpoons 2NaH$	620 RRC	0.034
24.	$MgCl_2 + NH_3 \rightleftharpoons MgCl_2 \cdot NH_3$	513 RRC	0.04
25.	$FeCl_2 \cdot NH_3 + NH_3 \rightleftharpoons FeCL_2 \cdot 2NH_3$	351 RRC	0.04
26.	$CS_2 \rightleftharpoons C_{(s)} + 2S_{(s)}$	621 RRC	1.00
27.	$C_{(s)} + 2Cl_2 \rightleftharpoons CCL_4$	521 RRC	1.00
28.	$C_6H_6 + 3H_2 \rightleftharpoons C_6H_{12}$	1341 RRC	30.0

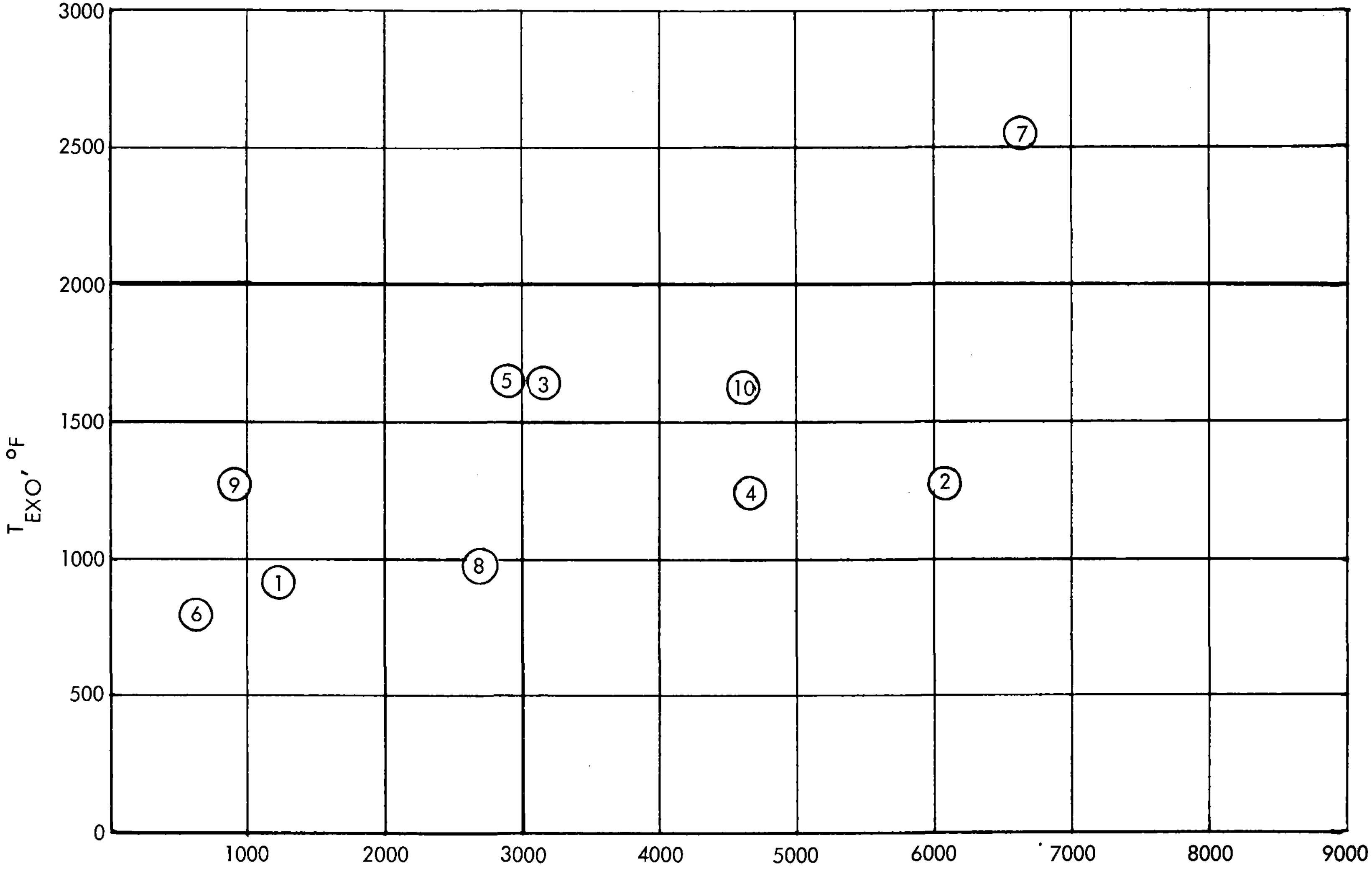

Figure 2. Relationship of T_{EXO} to Energy Storage Density for Reactions of Table 1

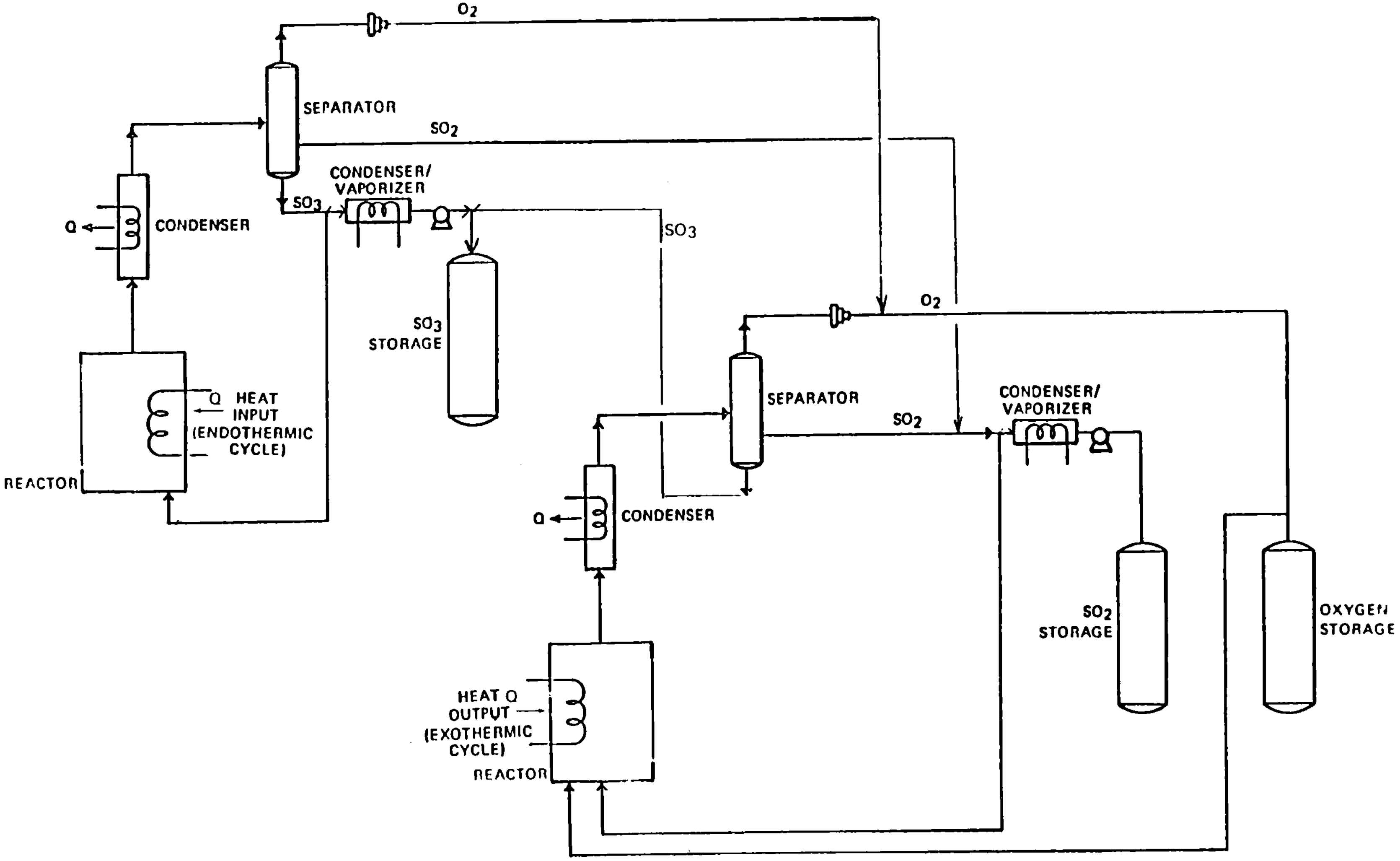

Figure 3. Sulfur Oxide Cycle, $SO_3 \rightleftharpoons SO_2 + \frac{1}{2}O_2$

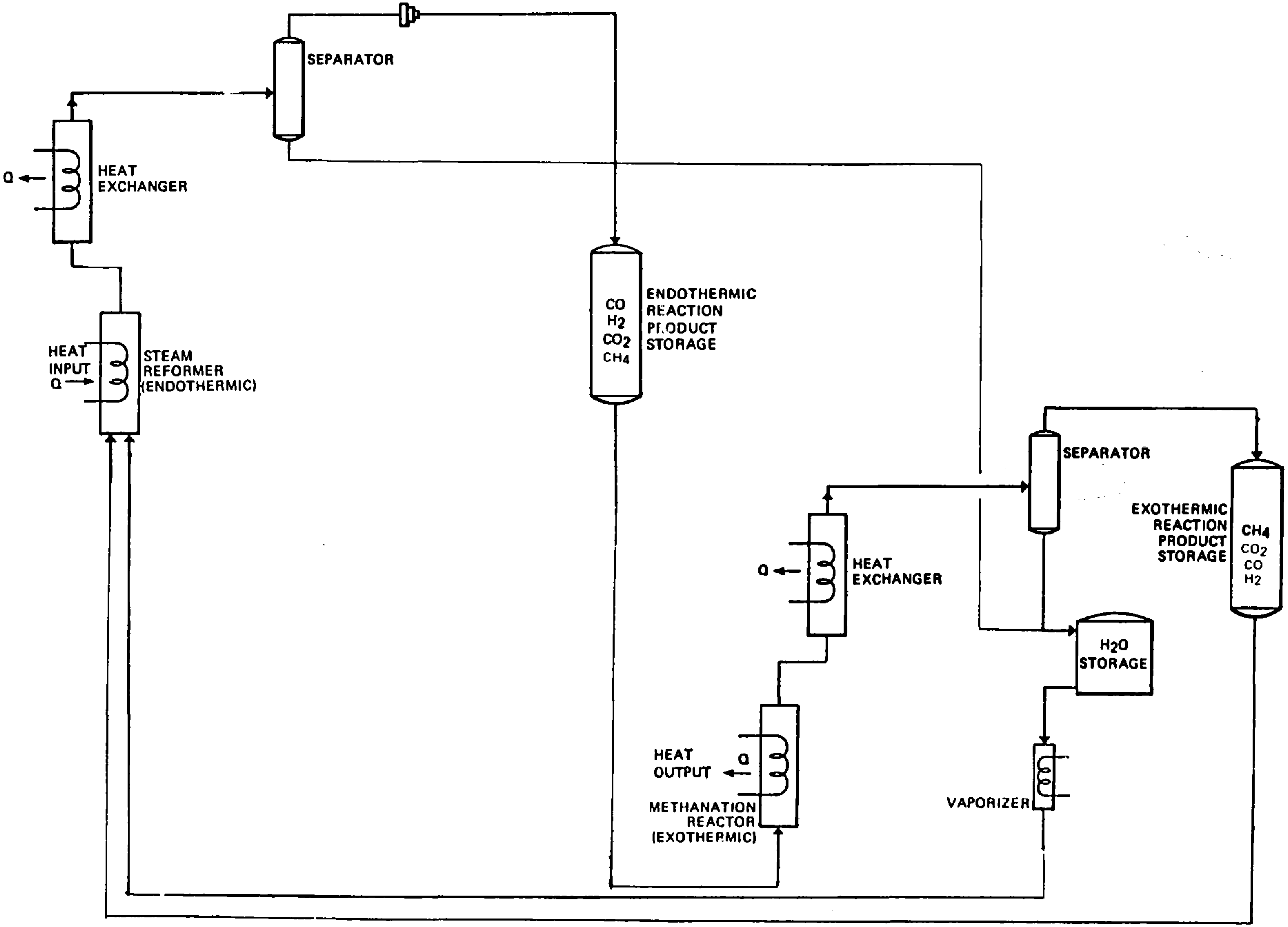

Figure 4. EVA-ADAM Cycle

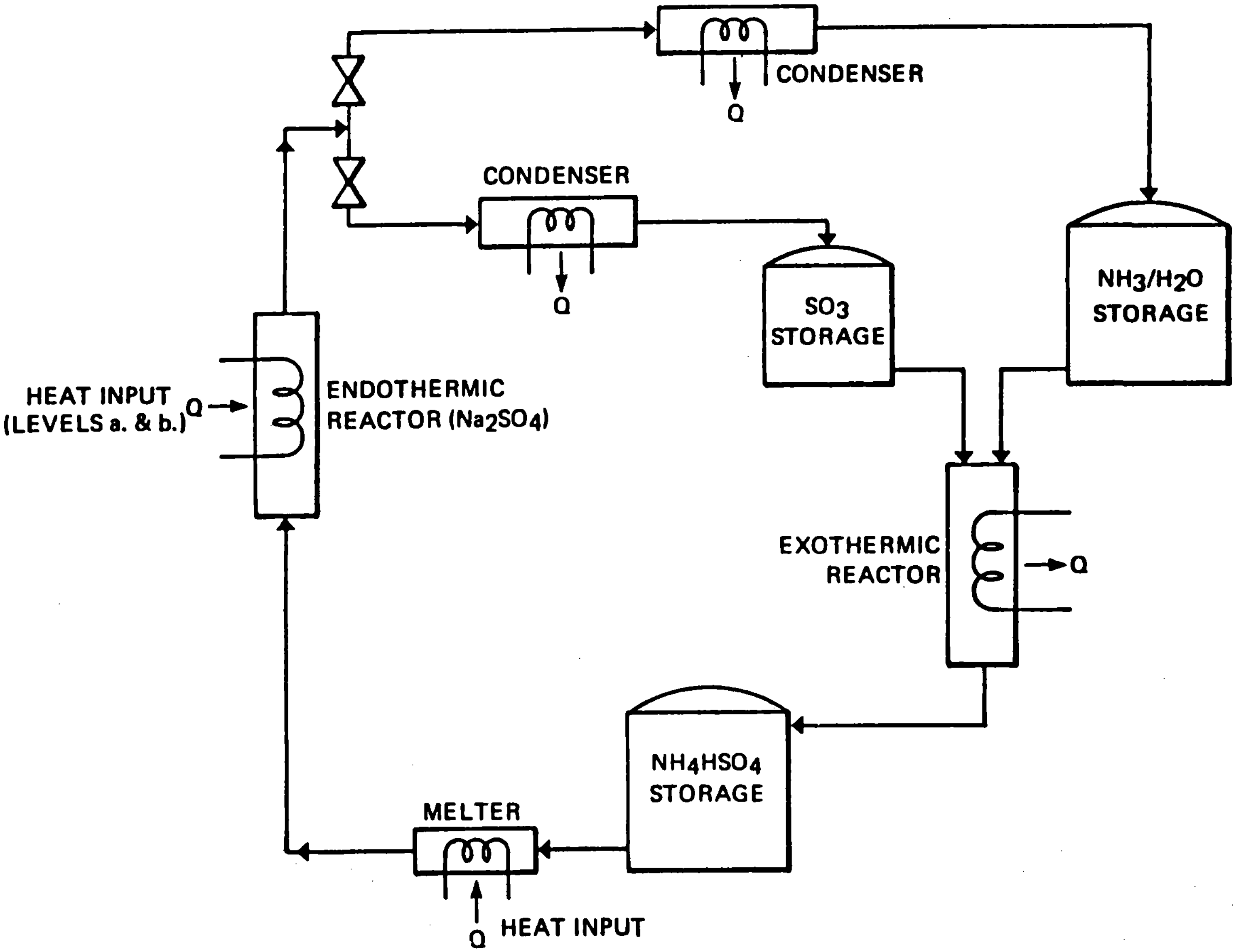

Figure 5. Simplified Schematic of Chemical Energy System Based on Ammonium Hydrogen Sulfate

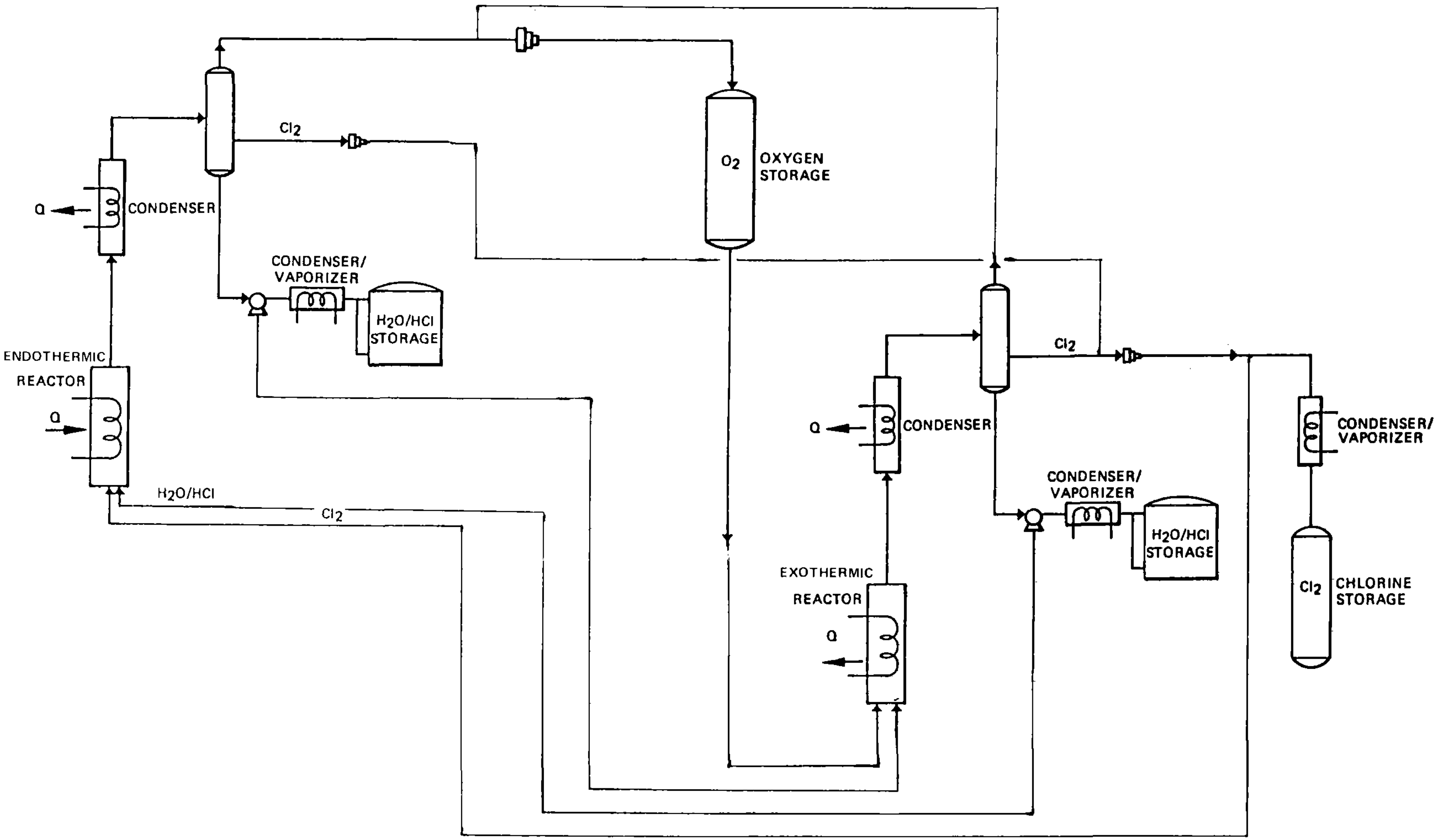

Figure 6. Oxidation of Hydrogen Chloride
$4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2$

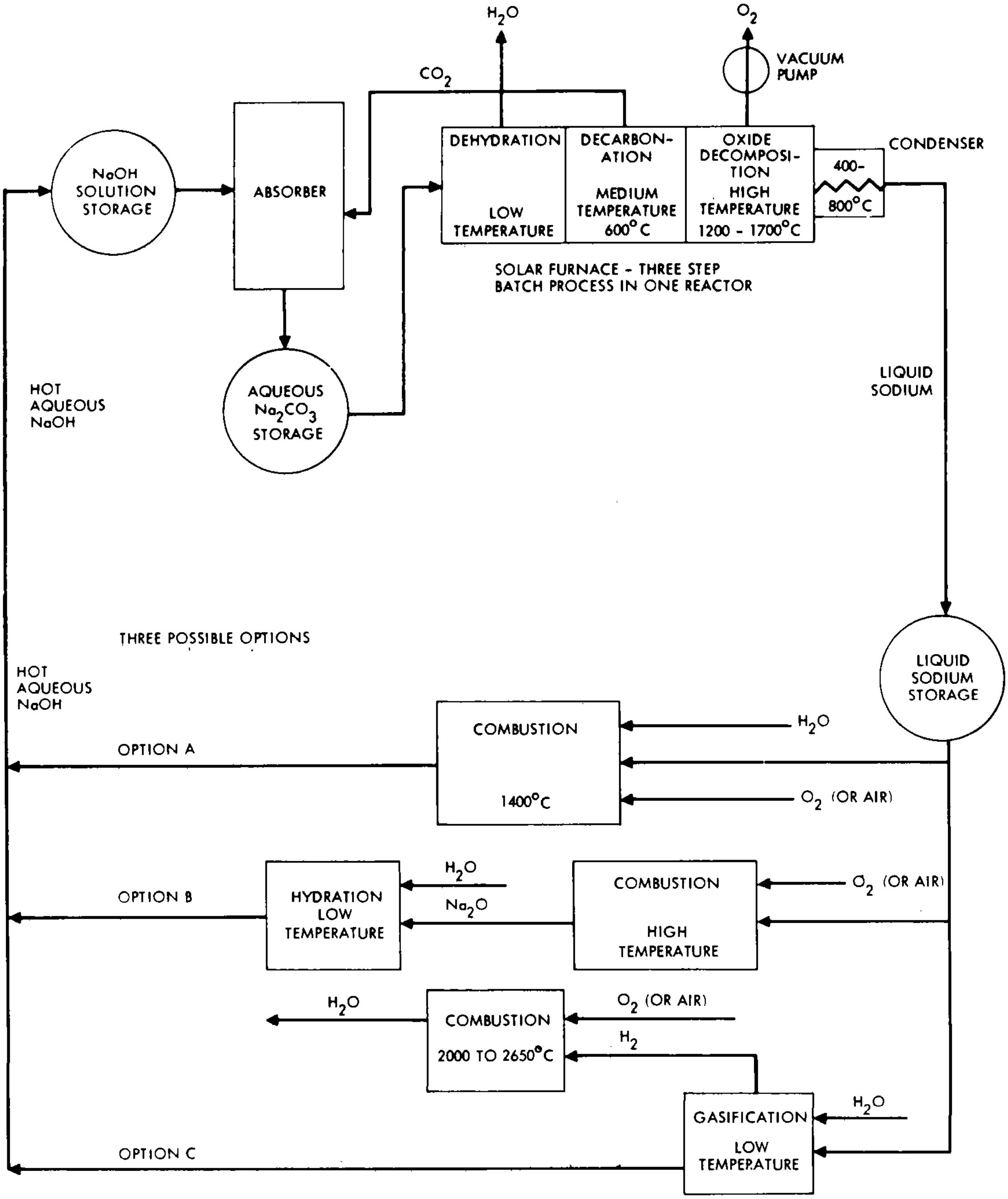

Figure 7. A Liquid Metal Cycle

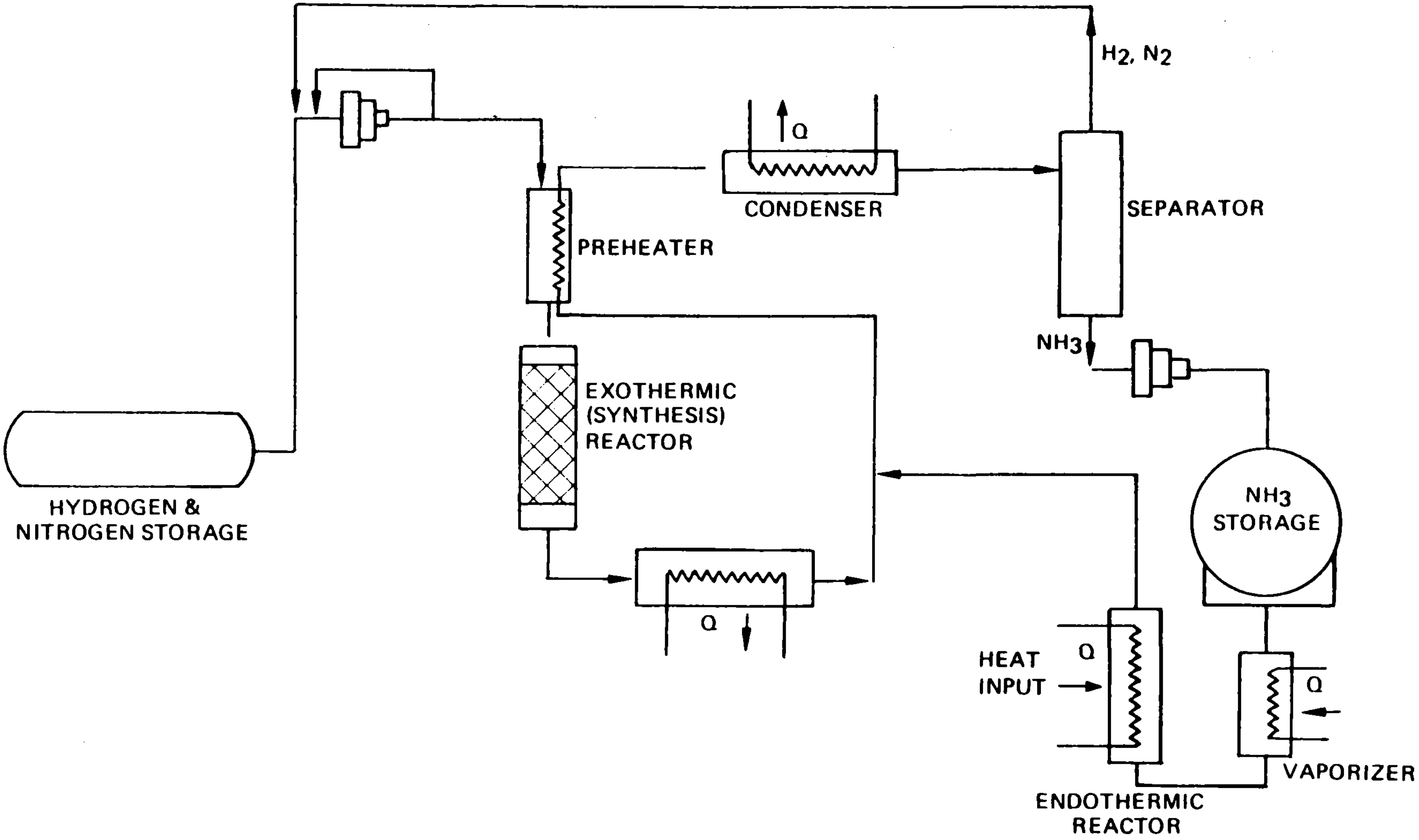

Figure 8. Simplified Schematic of Chemical Energy System Using Ammonia

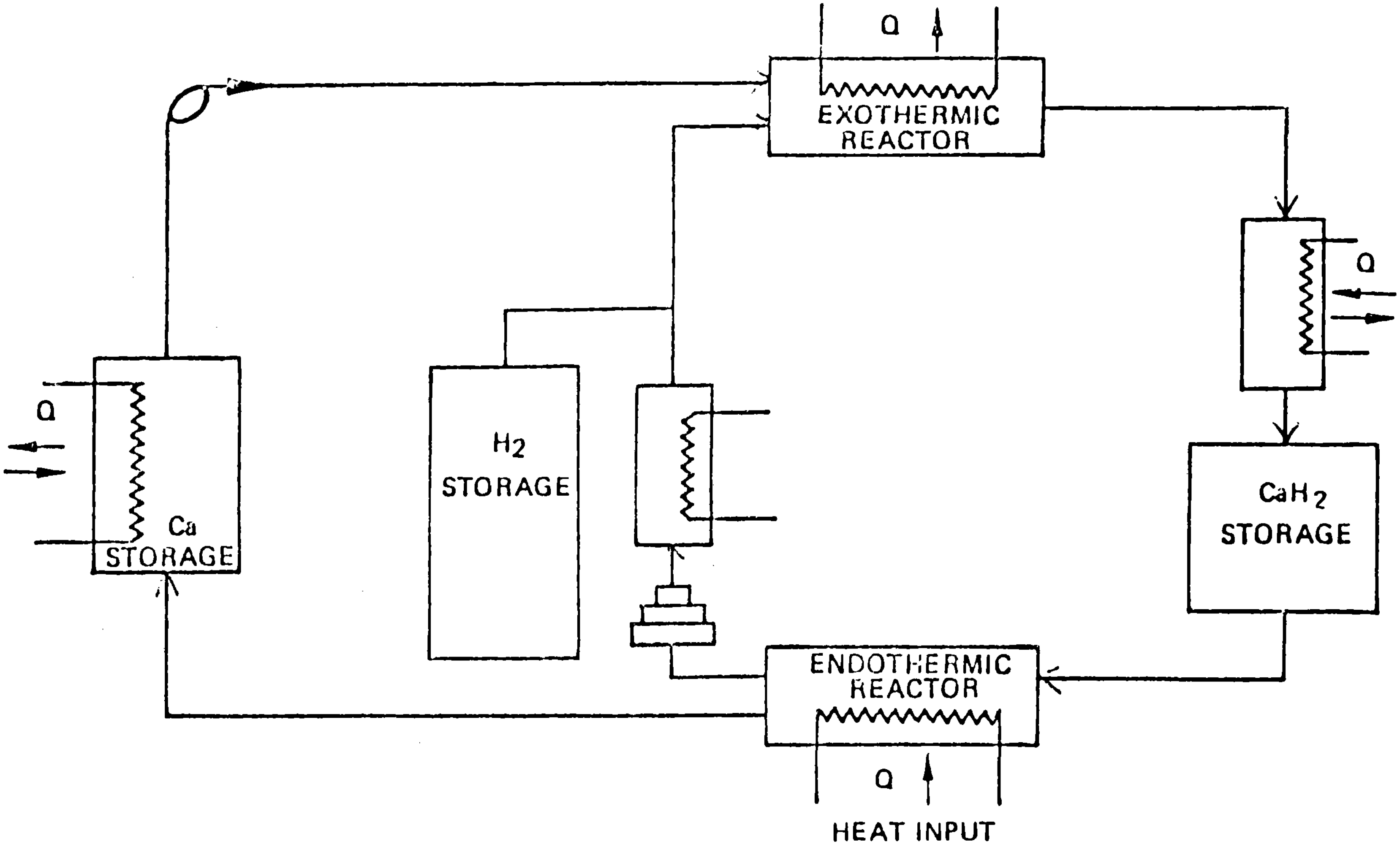

Figure 9. Simplified Schematic of Chemical Energy System Using Calcium Hydride

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APPENDIX A

SELECTED PROCESS DESCRIPTIONS *

Reaction
No.

*Out of the ten selected reactions (Table 1), reactions 1,2,5,6,7,8 and 10 are discussed in Appendix A.

APPENDIX A

1. THE SULFUR DIOXIDE/SULFUR TRIOXIDE SYSTEM

Equation: $SO_{2(g)} + 1/2\ O_{2(g)} \rightleftharpoons SO_{3(g)}$

Because of its industrial importance in the manufacture of sulfuric acid, the forward reaction has been studied thoroughly. The reverse reaction, the decomposition of SO_3, has had no industrial significance, and, therefore, very little is known about it.

Thermodynamically, the forward reaction is very favorable, but it is extremely slow in the absence of catalysts. Platinum sponge, vanadium pentoxide, V_2O_5, and nitric oxide are catalysts used in the so-called 'Contact' and 'Lead Chamber' processes. No catalyst studies have been made for the reverse reaction.

SO_3 is a fairly strong Lewis acid because of the affinity of sulfur for electrons. Gaseous SO_3 has a planar, triangular structure. The structure of solid SO_3 is very complex. Three well-defined phases have been identified. The γ-SO_3, which is formed by condensing SO_3 vapors at -80°C, is an ice-like solid melting at 16.8°C. It consists of cyclic trimers. The β-SO_3 is more stable and consists of helical chains of linked SO_4 tetrahedrons. The most stable form, α-SO_3, also consists of helical chains, but the chains are probably crosslinked into layers. Liquid β-SO_3 is a mixture of monomeric and trimeric SO_3. It can be readily polymerized by traces of water. Sulfur trioxide should be kept warm to minimize polymerization.

Both SO_2 and SO_3 can be stored in the condensed physical state, and because of this, the storage energy density of the system is relatively high. The dissociation of SO_3 is enhanced by low endothermic pressures, following Le Chatelier's principle. Thus, at 1517°F (825°C), the dissociation is 80% at 1 atmoshere and only 40% at 40 atmospheres (Ref. A-1). The dependence of the equilibrium constant, K, on temperature is shown in Figure A-1.

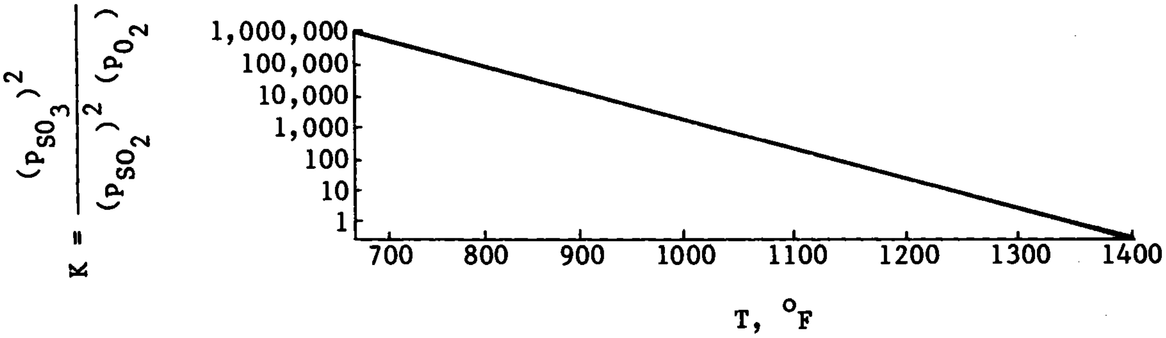

Figure A-1. Equilibrium Constant for $2SO_2 + O_2 \rightarrow 2SO_3$ (Ref. A-1)

Computer calculated equilibrium compositions are given in Appendix B.

2. THE METHANATION/STEAM REFORMING REACTION

Equation:

$$3H_{2(g)} + CO_{(g)} \underset{\text{Reforming}}{\overset{\text{Methanation}}{\rightleftharpoons}} CH_{4(g)} + H_2O_{(g)} \qquad (1)$$

This is a well studied reaction; however, only the reforming reaction is commercial. The equilibrium conversion is high compared to other reversible reactions, such as the SO_2/SO_3 system. It is possible to drive the reforming reaction to higher conversion by using excess steam in the feed. Excess steam, that is, more than the stoichiometric amount, also reduces coke (carbon) formation. The H_2O/CH_4 molar ratios used are from 2/1 to 4/1.

The above equation is idealized. Other chemical reactions and equilibria are also established, depending upon reaction conditions. The following two reactions are known to take place:

$$2CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_{4(g)} + CO_{2(g)} \qquad (2)$$

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)} \text{ (water-gas shift reaction)} \qquad (3)$$

It can be noticed that the linear addition of any two of the above three reactions, will give the third. At equilibrium, at any one temperature, the gaseous components present are: H_2, CO, Ch_4, H_2O and CO_2. Carbon dioxide, which does not appear in the methanation/steam reforming equation, is part of the equilibrium composition because of the equilibria represented by equations 2 and 3.

Some carbon producing reactions take place also. Examples are:

$$2CO \rightleftharpoons \underset{=}{C} + CO_2 \qquad (4)$$

$$CO + H_2 \rightleftharpoons \underset{=}{C} + H_2O \qquad (5)$$

$$CO_2 + 2H_2 \rightleftharpoons \underset{=}{C} + 2H_2O \qquad (6)$$

$$CH_4 \rightleftharpoons \underset{=}{C} + 2H_2 \qquad (7)$$

Use of excess steam will minimize carbon formation according to equations 5 and 6. Lower charging temperatures will minimize the cracking of methane to form carbon, as shown by equation 7, and operating at lower pressures will reduce carbonization, as pictured by equation 4. Prevention of coke or carbon formation is very important because the deposition of carbon on the nickel catalyst employed will deactivate it.

The selection of reaction conditions, in order to optimize the methanation/steam reforming reactions is a tricky task. Catalysis of both reactions seems to be satisfactorily worked out. Extending the catalyst life, however, is another problem. Besides deposition of carbon on the nickel catalyst, which can be reversed by burning off the carbon at higher temperatures, deactivation can be caused by trace amounts of H_2S which forms the stable NiS according to the following equation:

$$Ni + H_2S \longrightarrow NiS + H_2$$

Deactivation is also brought about by reaction with CO to form nickel carbide:

$$3Ni + 2CO \longrightarrow Ni_3C + CO_2.$$

The all-gas composition of the methanantion-reforming reaction makes it highly suitable for energy transmission, but the same fact lowers the energy storage density. Storage pressures are necessarily high. The dollar cost to produce one MBtu is $0.26, a relatively very low figure.

5. THE AMMONIUM HYDROGEN SULFATE REACTION

Equation: $NH_{3(g)} + SO_{3(g)} + H_2O_{(g)} \rightleftharpoons NH_4HSO_{4(s)}$ or

$$NH_{3(g)} + (SO_2 + 1/2\ O_2) + H_2O_{(g)} \rightleftharpoons NH_4HSO_{4(s)}$$

The high heat of reaction (334 kJ/mole) and the fact that the components of this reaction can be stored in condensed phases, leads to a high energy density value (103.6 Btu/ft^3/10^3), making it attractive as a candidate for chemical energy storage. The separation of the products of the endothermic reaction (i.e., NH_3, H_2O and SO_3) poses problems. Two chemical separation schemes are under consideration (Ref. A-2). In both schemes, NH_3 and H_2O are released at 750-930°F, and SO_3 is released at 1560-1830°F in a second reaction.

In the one scheme, NH_4HSO_4 is reacted with alkali metal sulfates. Sulfates of potassium, rubidium and cesium have been shown to work. The reaction can be represented as follows:

$$NH_4HSO_{4(\ell)} + M_2SO_{4(s)} \xrightarrow{750\text{-}930^\circ F} M_2S_2O_{7(s)} + NH_{3(g)} + H_2O_{(g)}.$$

The ammonia and gaseous water are separated from pyrosulfate. The latter is heated at above 1560°F to release SO_3 and yield back the original sulfate.

$$M_2S_2O_7 \longrightarrow M_2SO_4 + SO_3\uparrow.$$

In the other scheme NH_4HSO_4 is reacted with metal oxides. Preferred oxides are ZnO, CuO and MnO. The reaction is probably as follows:

$$NH_4HSO_{4(\ell)} + MO \xrightarrow{750^\circ F\ \text{plus}} MSO_4 + NH_3 + H_2O.$$

SO_3 is obtained by heating the metal sulfate. The original oxide is recovered at the same time.

$$MSO_{4(s)} \xrightarrow{1560^\circ F\ \text{plus}} MO_{(s)} + SO_{3(g)}.$$

Since its melting point is 296°F (147°C), NH_4HSO_4 is liquid at reaction temperatures.

6. THE OXIDATION OF HYDROGEN CHLORIDE

(The Deacon Process)

Equation: $$4HCl_{(g)} + O_{2(g)} \rightleftharpoons 2Cl_{2(g)} + 2H_2O_{(g)}$$

The all-gas nature of this reaction makes it attractive as a chemical storage system, because of easy energy transmission. However, it has its drawbacks. The reversibility of the reaction is not rated highly in the literature. Reasons are not given, but it is possible that in the presence of oxygen, chlorine will form oxides such as Cl_2O_3, ClO_2, Cl_2O_5, etc. The forward reaction has been studied to a large extent, because at one time this was the principle method of producing chlorine. The oxidation of HCl is accelerated by oxygen carriers, such as copper salts, which, for best results, should be supported on inert, porous substrates, such as pumice. Optimum operating temperatures are 800-890°F. Raising the temperature will increase the rate of reaction, but will decrease the HCl conversion. Above 750°F, the catalyst activity starts to decrease because of volatilization of $CuCl_2$. The corrosion rate of the equipment is also high at the operating temperatures. The latter phenomenon is said to be minimized in the M. W. Kellogg process, a modification of the Deacon process. This process uses a fluid bed to maintain a more uniform temperature. High conversions of HCl are reported. (Details of this process should be obtained.) Other modifications of the Deacon Process are the following: (a) The AIRCO process, which uses an improved copper-base catalyst with rare earth promoters in a special reversing flow reactor. The reaction is self-sustained and no external heat is necessary. Percent conversion is high; and, (b) the SHELL process, which uses a copper-base catalyst containing alkali metal chlorides, and chlorides of rare earth metals, such a yttrium, zirconium, thorium and uranium, supported on silica gel. Operating temperatures are 625-750°F, lower than the operating temperature of the Deacon Process (see Ref. A-3).

7. LIQUEFIABLE METAL CYCLES

Equation: $2Na_{(\ell)} + H_2O_{(\ell)} + 1/2\ O_{2(g)} \rightleftharpoons 2NaOH_{(\ell)}$

This equation is an idealized representation of a set of possible cycles being investigated at JPL, based on low-melting metals.

A computerized calculation of the adiabatic reaction of a composition with half of stoichiometric oxygen indicates that a temperature of about 1400°C would be reached, but that less than 70% of the sodium would be consumed. Increased oxygen content would improve both conversion and temperature. Two other options for the exothermic phase of this cycle are possible, each offering a higher temperature:

(1) $2Na_{(\ell)} + 1/2\ O_{2(g)} \rightarrow Na_2O_{(s)} + \text{Heat}$
$Na_2O_{(s)} + H_2O_{(\ell)} \rightarrow 2NaOH_{(\ell)} + \text{Heat}$

(2) $2Na_{(\ell)} + 2H_2O_{(\ell)} \rightarrow 2NaOH_{(\ell)} + H_2O_{(g)} + \text{Heat}$
$H_{2(g)} + 1/2\ O_{2(g)} \rightarrow H_2O_{(g)} + \text{Heat}$

The second reaction of option (2) has adiabatic flame temperatures ranging from 2000°C to 2650°C, depending on the gas mixture used.

The chief question concerning these cycles is: Can the thermal decomposition and subsequent isolation of the free metal be effected practically? Thermodynamics indicate that the endothermic reaction is a distinct possibility. However, because of the volatility of NaOH, and because of its very high stability, potential subcycles in which NaOH would be first convertd to a more tractable compound are being investigated.

Figure 7 shows the current conceptions of this cycle. Successful isolation of elemental sodium from the thermal decomposition of sodium carbonate was reported by T. Szarowics (Ref. A-6).

8. THE AMMONIA/NITROGEN-HYDROGEN SYSTEM

Equation:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

The forward reaction in the above equation represents the most important commercial method of producing ammonia.

The reverse reaction is also used industrially, as a source of hydrogen. Therefore, ammonia is already used as a means of storing hydrogen (and nitrogen). As a consequence of the industrial uses of both the forward and the reverse reaction, there is ample practical information about the NH_3/N_2-H_2 system.

The processes used today for the synthesis of NH_3 are modifications of the original Haber-Bosch process (Ref. A-7). Modifications consist mainly of differences in the source of N_2 and H_2, catalyst used, temperature and pressure conditions, and methods of recovering the product.

In the United States, the principal source of H_2 is the thermal reforming of natural gas (methane) with steam. Other sources are the decomposition of steam over coke to make water-gas, the partial oxidation of hydrocarbons, and the electrolysis of water.

Sources of nitrogen for the process are furnished by air, with enough air being used to supply the desired H_2/N_2 ratio; producer gas with water-gas; and liquefied air. Impurities such as oxides of carbon and compounds of sulfur are removed from the gases used in these processes.

The most extensively used catalyst is iron oxide. Promotors are always used with the catalyst. Double promotion with both acidic (or amphoteric) oxides and alkaline oxides increases the yields much more than the addition of acidic oxides alone. Examples of acidic and amphoteric oxides are SiO_2 and Al_2O_3, respectively, and an alkaline oxide that is used is K_2O.

The reaction of N_2 with H_2, even in the presence of catalysts, is sluggish and, in order to improve the kinetics, higher temperatures (400°C) and pressures (200-400 atmospheres) are used. Therefore, improvement in the reaction rate is done at the expense of product yield.

The compressor work required for the ammonia reaction is held to be a severe disadvantage in using this reaction for energy storage (Ref. A-8). According to O. M. Williams (Refs. A-8 and A-9), the problem of compressor work is resolved by carrying out all the steps of the system at the exothermic reaction pressure of 200-300 atmospheres.

It is claimed that a reactor designed for the dissociation reaction features a very efficient heat transfer system in which the hot exit stream of hydrogen and nitrogen is used to heat the entering stream of ammonia (Ref. A-8).

The cost of storing hydrogen and nitrogen in above-ground tanks will be very high. It has been proposed that underground storage in porous rock formations could be used.

10. THE CALCIUM HYDRIDE/CALCIUM SYSTEM

Equation: $Ca_{(s)} + H_{2(g)} \rightleftharpoons CaH_{2(s)}$

The fairly high heat of formation of CaH_2 (195 kJ/mole) (Ref. A-4) and the fact that two of the components in this system are in the condensed state and leads to a relatively high energy density. There are no side reactions in this highly reversible reaction. The melting point of metallic calcium is 1549°F, and since the reaction temperatures exceed this value, liquid calcium is involved. A 100% conversion of Ca to CaH_2 is reported at 570°F (Ref. A-5).

Solar-thermal energy could be utilized to melt the calcium and introduce it as a liquid into the reactor.

APPENDIX A

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APPENDIX B

CYCLE THERMAL PROPERTIES

APPENDIX B

CYCLE THERMAL PROPERTIES

A. OBJECTIVES

The primary purpose of Appendix B is to assess the quality of the cycle thermal property data presented in this report. A secondary purpose is to demonstrate the need for computerized thermochemical calculations to obtain better predictions of the behavior or performance of chemical energy storage cycles.

In the report, which deals with cycle screening and preliminary selection, one property, T_{EXO}, which is the predicted temperature of the exothermic reaction, is used as a screening criterion. The only other property data presented are T_{ENDO}, a temperature selected for preforming the endothermic reaction in the solar-thermal receiver/reactor, and the corresponding selected operating pressures, P_{EXO} and P_{ENDO}. Other thermal properties are implied, however, in two other criteria: reversibility and energy storage density.

Some of the capabilities offered by computerized thermochemical calculations will be illustrated by presentation and interpretation of some of the results we obtained using two thermochemical computer programs designed for predicting chemical rocket propellent performance.

B. GENERAL CONCLUSIONS

1. Cycle Selection

A summary of important information about the ten candidates selected by screening, including results of the analyses of this Appendix, is given in Table B-1. The following conclusions are drawn on the basis of a combination of screening and cycle thermal property analyses:

(1) If early application is top priority, select cycles which have significant work on them: In order, cycles 2, 1, 8, and 5.

(2) If top priority is high performance, determine the feasibility of cycle 7.

(3) The following cycles, in order, 10, 3 and 4, should be set aside, but not rejected, pending later inquiry into the applicability of existing technology for handling solids in flowing chemical processing systems.

(4) The following cycles, in order, X1, X2 and 9, should be set aside, but not rejected, pending more comprehensive thermochemical analyses.

(5) The remaining cycle, number 6, should be set aside pending further technical/economic analysis of its potential corrosion problem.

(6) The search for new candidates should continue. Previously rejected cycles should be re-examined in the light of increased understanding.

2. Computerized Thermochemistry

A plan for utilizing exisiting thermochemical computer programs for predicting the performance of chemical energy storage systems was generated. Part of the plan that was carried out applied to the cycles listed in Table B-1, and the usefulness of the selected program elements was demonstrated. The planned analyses of the same twelve cycles should be completed. Investigation should be made to determine the applicability of the existing programs to more comprehensive modeling of solar thermal fuels and chemicals processes, and storage cycles in particular.

Table B-1. Summary of Analyses of Computer Results

Reaction No. (per Table 1)	Reaction $\underset{ENDO}{\overset{EXO}{\rightleftharpoons}}$	Is Equation Unique?	Reversibility	T_{EXO} (°K)	ΔT (°C)	P_{EXO}/P_{ENDO} (atm)	CCE* (%)	Comments
1.	$SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$	Yes	OK	800	300	10/1	70	Under development
2.	$3H_{2(g)} + CO_{(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$	No	OK if extra H_2O is recycled	700	400	40/1	75	Under development
3.	$2CO_{(g)} \rightleftharpoons CO_{2(g)} + C_{(s)}$	Yes	Solid carbon must be transported	1170	350	10/1	EXO:32	T_{EXO} by computer T_{ENDO} estimated
4.	$C_{(s)} + 2H_{2(g)} \rightleftharpoons CH_{4(g)}$	Yes	Solid carbon; possibilities of tars	851	--	1/1	EXO:46	T_{EXO} by computer
5.	$NH_{3(g)} + H_2O_{(g)} + SO_{3(g)} \rightleftharpoons NH_4HSO_{4(s)}$	No	Solid exothermic product	700	100	--	--	Under development; computer error illustrated
6.	$4HCl_{(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)} + 2Cl_{2(g)}$	Yes	Probably OK	786	114	1/1	EXO:45	T_{EXO} by computer
7.	$2Na_{(\ell)} + H_2O_{(\ell)} + \frac{1}{2}O_{2(g)} \rightleftharpoons 2NaOH_{(\ell)}$	No	Question for experiment: Can free metal be separated from decomposition products	1665	335	1/0.5	--	Under investigation; Several potential cycle options; T_{EXO} by computer; T_{ENDO} by hand
8.	$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$	Yes	OK	773	250	200/200	26	Under development
9.	$CO_{(g)} + H_2O_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$	Wrong, see Details	Considerable carbon is predicted for this stoichiometry	956	344	10/10	30	Chemistry error illustrated
10.	$Ca_{(s)} + H_{2(g)} \rightleftharpoons CaH_{2(s)}$	Yes	OK	1150	200	10/1	--	No computer results
X1.	$2CO_{(g)} + 2H_{2(g)} \rightleftharpoons CO_{2(g)} + CH_{4(g)}$	No	Not known	773	--	2/?	--	Derived from Reaction 2
X2.	$CO_{(g)} + 2NO_{(g)} \rightleftharpoons CO_{2(g)} + N_2O_{(g)}$	Wrong						Chemistry error illustrated

*CCE = Cycle Capacity Estimate = % Conversion (EXO) + % Conversion (ENDO) - 100. Reaction 2 CCE is corrected for dilution.

C. DATA QUALITY

As stated in the text of the report, the values of critical cycle temperatures (T_{ENDO} and T_{EXO}) presented come from a variety of sources. The sources of data for the ten selected cycles are listed in Table 5. They vary in their dependability as indexes for predicting cycle behavior. Three general classes are identified. Even the best predictions are approximations of values that would be observed in operating cycles. The best class of thermal property estimates are those given for cycles which have been studied most intensively (Reactions 1, 2, 5, and 8 in Table 1). In these instances, reported values were furnished by the investigators, either directly or through the RRC report (Ref. 2). In most of these cases, theoretical results have been substantiated or corrected by experimental data. To the extent that they have been done, the computerized thermochemical calculations done at JPL are probably second in dependability, with some notable exceptions. More will be said about these later. The last class of estimates include hand calculations at JPL and most RRC values. The chief fault in this last class of data is the assumption that the given reaction equation is a complete, or unique, description of the relevant chemistry. These general conclusions about data quality are supported by details in part F of this Appendix.

D. CYCLES AND THEIR PROPERTIES

An ideal closed cycle would receive thermal energy in the solar thermal receiver/reactor, use some of that energy to run itself, and deliver the remainder at some required temperature and rate. The cycles of this report are (or, in some cases, are only perceived to be) reversible chemical reactions. In this appliction, a reversible reaction would be driven in the endothermic direction in the receiver/reactor and would be provided with the conditions to proceed spontaneously in the exothermic direction at the delivery end of the cycle. As illustrated in Figures 3 through 9, separations are made, when feasible, to improve cycle performance. Closure of the cycle is accomplished by transport in the loop of endothermic and exothermic products. If storage is included, its chief purpose is the integration of a continuous process at the exothermic end with a batch or discontinuous process at the endothermic end of the cycle.

As will be seen in the accompanying report on costs, an important performance characteristic of chemical energy storage/transport cycles is the overall thermal efficiency. Such factors as line losses, storage losses, compression requirements, and recoverable heat are very important in determining efficiency. So also are the cycle charcteristics which chiefly concern this section. However, these characteristics are improtant in their own right. They can be defined as follows:

(1) In the endothermic phase of the cycle, what conditions (P_{ENDO} and T_{ENDO}) are required to produce an acceptable endothermic product composition, and how much heat per unit mass is needed?

(2) How much heat is released in the exothermic phase, and at what temperature?

One important characteristic of cycles that is ignored in simple estimations is the dependence of the exothermic process performance upon the performance of the endothermic process including feasible separations. As will be seen in part F of this Appendix, the products of endothermic reactions contain not only those specie that the reaction equation states will be formed but two other sets of components. One set are the specie identified in the equation as the endothermic feed components, in varying but significant amounts. These are present because their consumption is limited by the equilibrium which is established at the specific chosen conditions of pressure and temperature. The other set of components are products of other reactions that also occur under those conditions. The whole mixture, identified endothermic products, identified endothermic feed, and specie not identified by the given reaction equation, is a result of a number of interdependent reactions all at equilibrium. This, of course, is the thermodynamic result, which assumes that enough time is allowed for equilibrium to be reached. Kinetic considerations are beyond the scope of this study.

Exothermic reactions do not go to completion, as shown in part F. As a consequence, less heat can be realized than the heat of reaction indicates. The extent to which endothermic reactions can be pushed depends upon pressure and temperature. Separations are not always feasible and are never perfect. In the practical sense, separation effectiveness must be balanced against cost. The product of endothermic reaction extent and separation effectiveness determines the composition of the exothermic feed. Further reduction in the heat that can be realized from the exothermic reaction results from the degree to which its feed composition varies from ideal.

Clearly, good estimates of the interdependent performances of the two phases of a cycle are necessary for the overall evaluation of the cycle's performance.

E. THERMOCHEMICAL CALCULATIONS

Calculations made for screening often have been too simple, generally erring in the optimistic direction. Assumptions are made that the given, single reaction expression represents the true chemistry, that reactions proceed to completion, and that perfect separations are made. In the calculations described below, the first two assumptions are not made, and error in the conservative direction is introduced by the assumption that no separations are included in the cycles.

Two basic kinds of calculation are required, one for the endothermic process and another for the exothermic process. It is not intended to discuss the mathematics of these calculations here. The object instead is to make clear the connection between the calculations and the processes. To illuminate that connection, one of the simpler cycles (No. 1, Table 1, SO_2/SO_3) will be used as an example.

The first part of the endothermic problem is as follows, using the SO_3 cycle without separations as an example: Given sulfur and oxygen in the molar ratio of one to three, what is the equilibrium composition at a given pressure and temperature? The solution is found by determining the relative concentrations (or partial pressures) of the relevant specie for which the change in free energy is zero at the given pressure, temperature and overall (elemental basis) composition. For example, as will be seen in part F, in a 1/3 S/O system at 10 atm and 800°K, the equilibrium composition would be $SO_2/O_2/SO_3$ = 0.05163/0.02582/0.92255. At 1 atm and 1100°K, those ratios would be 0.54709/0.27355/0.17936.

The second part of the endothermic problem, which is not treated quantitatively in this section of the report, is the detemination of the heat required. The answer to that depends on the molecular composition of the starting mixture and the beginning and final conditions. For example, if a mixture having the second set (above) of ratios ($SO_2/O_2/SO_3$) was brought, instantaneously and without reaction, from 1 atm and 298°K to 1100°K at the same pressure and then allowed to react, no change in composition would take place. The only heat involved would be the necessary increase in the sensible heat of the mixture; this heat would have to be furnished from the surroundings. If the starting mixture were richer in SO_3, more heat would be required to break the bonds necessary for the mixture to reach equilibrium composition. On the other hand, if the starting mixture were leaner in SO_3, less heat would be required because some of it would be supplied internally as the composition shifted toward equilibrium.

As will be seen in part F, the SO_3 cycle chosen for example is simple enough for the endothermic calculation to be done by hand. The given reaction is unique. (True, other reactions do occur, but not to any significant degree.) This is true also of Reaction 8, NH_3 decomposition/synthesis, and it appears to be so for several others. In many other cycles, however, a system of interdependent reactions must be considered. It is much more practical to handle this kind of problem with an appropriate thermochemical computer program. Two general factors have been identified so far which put a cycle into this category: high temperatures and systems containing carbon, hydrogen and oxygen together.

There are at least two approaches to the calculation of the exothermic phase of a cycle. The first, which gives a unique property for any given starting composition and starting temperature, is the adiabatic flame calculation. The unique property is the temperature achieved under these conditions. It is called the adiabatic flame temperature. In practice, this set of conditions represents the case in which the flame is allowed to develop fully before any energy is extracted, by transfer of heat or by expansion work. The second approach is applicable to processes in which the flame is generated and held in a catalyst bed, which is also part of the interface through which heat is transferred to the load. Reactions 1, 2 and 8 are examples. In this case, the flame temperature is not unique. It may be chosen. However, it cannot be higher than the adiabatic flame temperature for the same starting conditions.

The adiabatic flame calculation is straightforward, but it is not simple, even in the case of simple reaction systems, such as the SO_2/SO_3 system. The reason for this is that a balance between the sensible heat of the mixture (which is a function of the temperature) and the heat of reaction (which also is a function of temperature) must be determined iteratively. If a suitable thermochemical program is available, it is not practical to do this problem by hand. However, it is a rewarding exercise to do one or two simple cases. On the other hand, calculation of exothermic processes with simultaneous heat extraction can be done in a way similar to the endothermic case.

Returning to our SO_2/SO_3 example, the first set of composition data given earlier represent the results of the adiabatic flame calculation under a given set of conditions. Since T_{EXO} = 800°K at 10 atm was determined by RRC, JPL does not know the starting composition (stoichiometric SO_2 and O_2 plus an unknown amount of SO_3) or the starting temperature (298°K or something higher resulting from preheating).

It was planned, using available computer programs, to undertake the problem of interdependence of the endothermic and exothermic processes cited in part C. However, there was not sufficient time to complete the plan. With a given cycle, the plan was as follows:

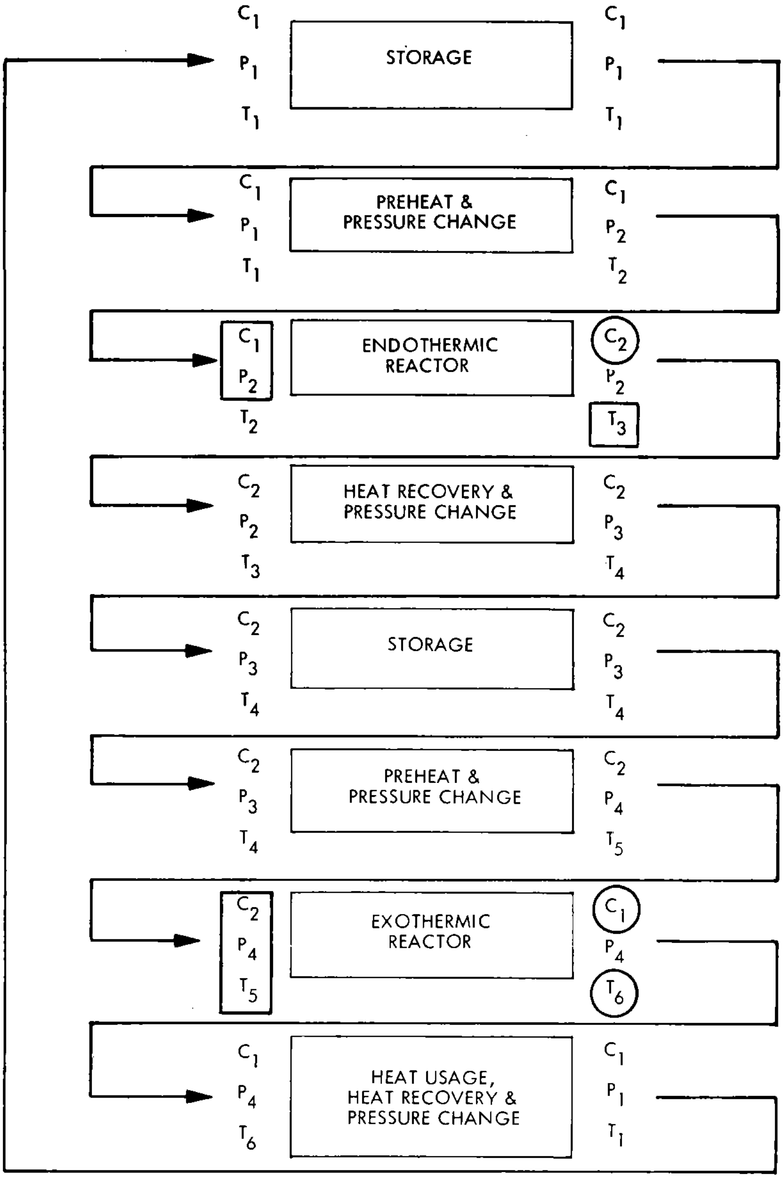
(1) Determine the equilibrium compositions for a series of pressure-temperature conditions. The selection of pressure-temperature combinations for these calculations is governed by at least two things: practical range for receiver/reactor operation and prior knowledge of the proposed cycle.

(2) Using some reasonable criteria (e.g., 70% conversion), select a group of the endothermic product compositions from the previous calculations.

(3) For each of the compositions selected in step (2), run the "adiabatic flame" calculation with selected given pressures and starting temperatures. Starting temperatures depend upon how much preheat is assumed. The pressure range should include the specific value representing the constant-pressure cycle option.

(4) The results of the above steps would represent the key parameters of a set of hypothetical cycles. Such a cycle, with losses absent, is illustrated in the diagram in Figure B-1. From this point on, the details of the plan had not been worked out. The aim, however, is to develop a standardized figure of merit with which to compare cycles and sets of conditions within cycles. Such a figure of merit should represent cycle performance more accurately than the cycle capacity estimate (CCE) used in part F and, at the same time, would be easier to calculate than the specific cycle efficiencies calculated elsewhere in this report. This future effort would attempt to include feasible separation with reasonable effectiveness values in the cycles.

The results of a number of thermochemical calculations are shown in the tables of part F of this Appendix, eight endothermic sets, and ten exothermic sets. The endothermic sets were done in accordance with step 1 of



LEGEND:

C = COMPOSITION P = PRESSURE T = TEMPERATURE

GIVEN KEY PARAMETERS (RECTANGLES):

ENDOTHERMIC	FEED COMPOSITION	C_1
	PROCESS PRESSURE	P_2
	PROCESS TEMPERATURE	T_3
EXOTHERMIC	FEED COMPOSITION	C_2
	PROCESS PRESSURE	P_4
	FEED TEMPERATURE	T_5

RESULTS (CIRCLES):

ENDOTHERMIC	PRODUCT COMPOSITION	C_2
EXOTHERMIC	PRODUCT COMPOSITION	C_1
	ADIABATIC REACTION TEMPERATURE	T_6

ALL OTHER PARAMETERS CAN BE ASSIGNED.

Figure B-1. Idealized Chemical Energy Storage Cycle (Compositions are "frozen" in all steps except in the two reactors) the above plan. Because they were run before the above plan had been generated, none of the exothermic sets qualify for use in step 3 for a number of reasons, the chief one being the lack of correspondence of given exothermic feed compositions with endothermic product compositions. Therefore, all the T_{EXO}'s in the tables of part F are higher than they would have been if they were calculated according to the plan.

The shortcomings of determining cycle thermal properties by simple calculations based on simple, given reaction equations have been discussed extensively. Part F of this Appendix demonstrates amply the improvements that can be made by the use of appropriate thermochemical computer programs. There are a number of problems, however, in dealing with such programs. To some extent problems arise because the programs were designed for another purpose. Results should not be taken on faith, but they should be reviewed critically. The results tabulated in part F for Reaction 5 are an example of one kind of serious problem. The compound representing the exothermic product in the given equation (NH_4HSO_4 in this case) did not appear as a product in the adiabatic flame calculation. The general chemical features of this reaction cycle have been substantiated by experimental work. Consequently, the absence of NH_4HSO_4 was interpreted as a computer mistake. The complete absence of this compound and its associated data from the program's data bank was confirmed to be the cause.

F. CYCLE STUDIES

This part of Appendix B discusses the analyses of what the thermochemical calculations (augmented by other knowledge) told us about the cycles. All but one of the ten selected cycle candidates (Table 1) plus two additional cycles are analyzed separately in the following pages. A summary of the results appears in Table B-1).

Although these analyses are limited by incomplete thermochemical calculation sets, enough data were available in some cases to allow reasonable estimations of cycle performance. The general scope of analysis is illustrated below by an annotated outline of the format followed:

REACTION IDENTIFICATION

GIVEN EQUATION

Given Conditions

The pressures and temperatures for the endothermic and exothermic processes, as cited in Table 1, are listed. The sources of these data are given in Table 5.

UNIQUENESS & REVERSIBILITY

The calculations excellently demonstrated the error of assuming that given reaction equations are unique in every case.

The computer role here was to identify reaction products which might separate from the cycling stream and interfere with reversibility.

CONVERSION

Where the data were available, the following characteristics were determined and/or assessed:

- Conversion
- Cycle Capacity Estimate (CCE)
- Comparison of Computed with Given Values
- Effects of Off-Stoichiometric Compositions
- Effect of Constant-Pressure Cycle Operation
- Effect of Increasing the Endothermic Process Temperature

Conversion and CCE are parameters that need some explanation. They are simple approximations intended to give qualitative impressions of cycle thermal efficiency.

- Conversion. For simple (unique-type) reactions, there is little problem. However, deciding the conversions in the more complex systems is difficult. The approach followed here was to select a key element, that is not in excess, then calculate from the computer results the fraction of that element which was in the reduced form (or the oxidized form). In each case, conversion is defined.

- CCE (Cycle Capacity Estimate). In a very rough sense, this is an index representing the fraction of ideally available energy per unit of reaction that a cycle operated under a given set of conditions will carry, assuming that there are no separations, perfect recoveries and no losses. The CCE assumes that the amount of the energy (in or out) of a reaction in one direction is proportional to the conversion. Thus, if C_F is the conversion in the forward direction, the C_R is the conversion in the reverse direction (in decimal), then CCE = $C_F + C_R - 1$.

REACTION 1

$$SO_2\,(g) + 1/2\,O_2\,(g) \overset{EXO}{\rightleftharpoons} SO_3\,(g)$$

Given Conditions:

ENDO: P = 1.0 atm T = 1100°K
EXO: P = 10.0 atm T = 800°K
ΔT = 300°C

UNIQUENESS & REVERSIBILITY

Computer results (Table B-2) show no significant side reactions. Sub-dew-point separations are possible but can be dealt with.

CONVERSION

Only endothermic process compositions were calculated by JPL computer (Table B-2). Conversion calculated for given conditions using computer data are as follows:

ENDO: 75% sulfur as SO_2
EXO: 95% sulfur as SO_3.

The latter was interpolated by Newton's method. Based on these conversions, Cycle Capacity Estimate (CCE), previously defined, is 70%. Conversions are increased slightly by adding extra oxygen; however, the increase is probably not enough to counter-balance the dilution effect. Elimination of the cost of compressor work by raising the endothermic process pressure to that of the exothermic process would be paid for by a loss of approximately 33% in CCE. The 75% endothermic conversion can be increased to over 90% by raising the temperature (94% at 1300°K, 98% at 1500°K) with accompanying increases in CCE.

Table B-2. Equilibria for Reaction 1
(Specie Concentrations in Mole Fractions)

S/O = 1/3, Moles

0.5000 atm

	700°K	900°K	1100°K	1300°K	1500°K
O_2	.01755	.14971	.28773	.32271	.32997
SO_2	.03509	.29940	.57545	.64541	.65993
SO_3	.94736	.55091	.13681	.03188	.01009

1.0000 atm

	700°K	900°K	1100°K	1300°K	1500°K
O_2	.01404	.12801	.27355	.31860	.32861
SO_2	.02805	.25600	.54709	.63718	.65721
SO_3	.95791	.61599	.17936	.04422	.01418

10.0000 atm

	700°K	900°K	1100°K	1300°K	1500°K
O_2	.00662	.07012	.20799	.29236	.31904
SO_2	.01322	.14022	.41597	.58471	.63807
SO_3	.98016	.78966	.37603	.12293	.04289

20.0000 atm

	700°K	900°K	1100°K	1300°K	1500°K
O_2	.00527	.05743	.18484	.27924	.31363
SO_2	.01052	.11484	.36966	.55848	.62724
SO_3	.98421	.82773	.44550	.16228	.05913

S/O = 1/3.05, Moles

0.5000 atm

	700°K	900°K	1100°K	1300°K	1500°K
O_2	.03622	.16384	.29943	.33382	.34096
SO_2	.02423	.28587	.56382	.63432	.64895
SO_3	.93956	.55029	.13675	.03186	.01008

1.0000 atm

	700°K	900°K	1100°K	1300°K	1500°K
O_2	.03321	.14257	.28549	.32977	.33962
SO_2	.01806	.24225	.53525	.67601	.64621
SO_3	.94873	.61518	.17926	.04420	.01417

10.0000 atm

	700°K	900°K	1100°K	1300°K	1500°K
O_2	.02751	.08600	.22107	.30398	.33021
SO_2	.00639	.12629	.40318	.57315	.62691
SO_3	.96609	.78770	.37575	.12287	.04287

20.0000 atm

	700°K	900°K	1100°K	1300°K	1500°K
O_2	.02664	.07370	.19833	.29109	.32489
SO_2	.00460	.10107	.35656	.54672	.61609
SO_3	.96875	.82523	.44512	.16219	.05910

S/O = 1/2.95, Moles

0.5000 atm

	700°K	900°K	1100°K	1300°K	1500°K
O_2	.00598	.13620	.27627	.31179	.31917
SO_2	.05929	.31353	.58699	.65634	.67074
SO_3	.93472	.55027	.13675	.03186	.01008

1.0000 atm

	700°K	900°K	1100°K	1300°K	1500°K
O_2	.00358	.11423	.26187	.30761	.31778
SO_2	.05460	.27062	.55887	.64818	.66804
SO_3	.94182	.61515	.17926	.04420	.01417

10.0000 atm

	700°K	900°K	1100°K	1300°K	1500°K
O_2	.00046	.05586	.19532	.28097	.30806
SO_2	.04851	.15666	.42894	.59616	.64906
SO_3	.95103	.78748	.37575	.12287	.04288

20.0000 atm

	700°K	900°K	1100°K	1300°K	1500°K
O_2	.00023	.04320	.17182	.26765	.30257
SO_2	.04806	.13195	.38307	.57016	.63833
SO_3	.95170	.82485	.44511	.16220	.05910

REACTION 2

$$3\ H_2\ (g) + CO\ (g) \overset{EXO}{\rightleftharpoons} CH_4\ (g) + H_2O\ (g)$$

Given Conditions:

ENDO: P = 1.0 atm T = 1100°K
EXO: P = 40.0 atm T = 700°K
ΔT: = 400°C

UNIQUENESS & REVERSIBILITY

The above reaction equation is not unique for this process (which is called EVA-ADAM). As Tables B-3, B-4, and B-5 show, significant CO_2 is formed, as well as solid carbon under certain conditions. Table B-6 shows, in addition, some ethylene. Other specie show up in even smaller amounts.

Significant solid carbon is the predicted product for the endothermic process when the stoichiometric composition for the above-cited reaction is assumed (Table B-3). This is avoided by those working with this process by the addition of extra water (Tables B-4 and B-5), thus eliminating a cause of irreversibility.

CONVERSION

Using the given conditions and computer data (Table B-4) for the more likely practical extra-water system, the following conversions are calculated:

ENDO: 90% carbon as non- CH_4
EXO: 96% carbon as CH_4.

In complex systems such as this, cycle capcity estimates (CCE) are likely to be even poorer than for simple systems. However, the above conversions show CCE = 75%, allowing for the dilution by extra water.

There is a large discrepancy, 493°C, between the given T_{EXO} and that reported in Table 1 of the text and that calculated by computer (Table B-6). There are two reasons for this difference:

(1) The computer calculation is for an adiabatic flame, while the given value was provided by those working with the system. They have, no doubt, accounted for the fact that the exothermic process will be run with simultaneous heat extraction.

(2) Table B-6 assumes the stoichiometric mixture, no extra water. Running the whole cycle at 40 atm would result in a loss of about 56% in CCE.

Table B-3. Equilibria for Reaction 2
(Specie Concentrations in Mole Fractions)

C/H/O = 1/6/1, Moles

1.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
C	.00000	.00000	.06331	.00122	.00000
CH_4	.48897	.39068	.11025	.01912	.00297
CO	.00000	.00343	.08634	.23429	.24806
CO_2	.00554	.05125	.04524	.00484	.00474
H_2	.02206	.21521	.56653	.72502	.74600
H_2O	.48343	.33943	.12832	.01540	.00249

10.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
C	.00000	.00000	.00000	.00000	.00000
CH_4	.49557	.45165	.32166	.12038	.02686
CO	.00000	.00056	.03105	.16397	.23237
CO_2	.00225	.02365	.05814	.02585	.00421
H_2	.00886	.09615	.32562	.59526	.71390
H_2O	.49332	.42800	.26352	.09453	.02265

40.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
C	.00000	.00000	.00000	.00000	.00000
CH_4	.49745	.47136	.38934	.23035	.08299
CO	.00000	.00020	.01151	.09465	.19610
CO_2	.00130	.01416	.04385	.04019	.01240
H_2	.00509	.05709	.20982	.44464	.63786
H_2O	.49615	.45720	.34549	.19017	.07062

100.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
C	.00000	.00000	.00000	.00000	.00000
CH_4	.49824	.47990	.42075	.29941	.14716
CO	.00000	.00001	.00578	.05759	.15589
CO_2	.10091	.00999	.03387	.04272	.02052
H_2	.00353	.04011	.15272	.34357	.54973
H_2O	.49732	.46990	.38688	.25670	.12668

Table B-4. Equilibria for Reaction 2 (Specie Concentrations in Mole Fractions)

C/H/O = 1/7/1.5, Moles

1.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
CH_4	.38984	.29868	.09542	.00236	.00005
CO	.00000	.00297	.10266	.19585	.20592
CO_2	.00574	.05341	.06661	.02511	.01633
H_2	.02267	.22226	.57423	.68784	.68291
H_2O	.58175	.42268	.16107	.08883	.09479

10.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
CH_4	.39595	.35525	.23734	.06619	.00451
CO	.00000	.00049	.02711	.14756	.20271
CO_2	.00235	.02446	.06334	.03796	.01705
H_2	.00908	.09903	.33443	.59431	.67616
H_2O	.59262	.52076	.33778	.15399	.09955

20.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
CH_4	.39694	.36551	.27073	.11071	.14710
CO	.00000	.00028	.01670	.11643	.19545
CO_2	.00180	.01897	.05520	.04435	.01865
H_2	.00688	.07644	.27064	.52649	.66080
H_2O	.59438	.53879	.38672	.20201	.11039

40.0000 atm

	500°K	700°K	900°K	1100K	1300°K
CH_4	.39770	.37353	.29842	.15917	.03757
CO	.00000	.00016	.01008	.08540	.17933
CO_2	.00138	.01464	.04644	.04846	.02207
H_2	.00521	.05874	.21573	.44984	.62611
H_2O	.59572	.55292	.42933	.25713	.13491

100.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
CH_4	.39842	.38144	.32708	.21952	.08894
CO	.00000	.00008	.00507	.05173	.14411
CO_2	.00097	.01033	.03553	.04861	.02874
H_2	.00359	.04126	.15705	.34940	.54715
H_2O	.59701	.56689	.47526	.33073	.19103

Table B-5. Equilibria for Reaction 2 (Specie Concentrations in Mole Fractions)

C/H/O = 1/10/3, Moles

1.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
CH_4	.20013	.17007	.03170	.00031	.00000
CO	.00000	.00111	.05738	.10200	.11480
CO_2	.00000	.02035	.06290	.04067	.02816
H_2	.19967	.27585	.57539	.61146	.59952
H_2O	.60020	.53261	.27263	.24553	.25756

10.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
CH_4	.20013	.19867	.12718	.01990	.00068
CO	.00000	.00004	.01382	.08726	.11420
CO_2	.00000	.00101	.03828	.04145	.02820
H_2	.19967	.20340	.37344	.57586	.59830
H_2O	.60020	.59689	.44729	.27553	.25858

20.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
CH_4	.20013	.19974	.15163	.04406	.00261
CO	.00000	.00000	.00748	.07024	.11270
CO_2	.00000	.00027	.02715	.04122	.02832
H_2	.19967	.20067	.31689	.53075	.59483
H_2O	.60020	.59932	.49654	.31373	.26150

40.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
CH_4	.20013	.20003	.17122	.07536	.00907
CO	.00000	.00000	.00369	.05030	.10780
CO_2	.00000	.00007	.01696	.03880	.02865
H_2	.19967	.19992	.27032	.47020	.58316
H_2O	.60020	.59998	.53781	.36533	.27132

100.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
CH_4	.20013	.20011	.18890	.11756	.03299
CO	.00000	.00000	.00117	.02763	.08999
CO_2	.00000	.00001	.00685	.03134	.02937
H_2	.19967	.19971	.22738	.38436	.53945
H_2O	.60020	.60016	.57570	.43911	.30819

Table B-6. Adiabatic Flame for Reaction 2

Entering Composition			
CO/H_2 = 1/3, Moles			
Starting Temperature			
298°K			
Reaction Pressure, atm	1	10	40
Adiabatic Flame Temp., °K	956	1092	1195
Final Composition, Mole Fractions			
$C_{(s)}$	.04404	.00000	.00000
CH_4	.06721	.12763	.15085
CO	.14272	.16022	.15082
CO_2	.03140	.02792	.02577
H_2	.63478	.58451	.54745
H_2O	.07985	.09972	.12510
C_2H_4	.00000	.00000	.00001

REACTION 3

$$2\ CO_{(g)} \overset{EXO}{\rightleftharpoons} CO_{2\ (g)} + C_{(s)}$$

Given Conditions:

ENDO: P = 1.0 atm T = 1500°K
EXO: P = 10.0 atm T = 1170°K
ΔT = 350°C

UNIQUENESS & REVERSIBILITY

Only the exothermic process was calculated for this cycle (Table B-7). Between ambient temperature and T_{EXO}, the results show the equation above to be unique. Other transitory specie can be expected at much higher temperatures.

The biggest problem with the reversibilty of reactions of this type is engineering, not chemical. If the solid component, carbon in this case, can be transported in the loop and properly contacted in the reactor, the cycle will be reversible.

CONVERSION

An exothermic conversion of 32% carbon as $C_{(s)}$ and CO_2 is calculated from the data in Table B-7. This, of course, assumes pure CO feed. We do not have data on the endothermic process. However, judging from the temperatures required for other gasification processes, one might expect reasonable conversion at 1500°K or higher.

Table B-7. Adiabatic Flame for Reaction 3

Entering Composition	
CO = 100%, Moles	
Starting Temperature	
298°K	
Reaction Pressure, atm	10
Adiabatic Flame Temp., °K	1170
Final Composition, Mole Fractions	
$C_{(s)}$	.16217
CO	.67566
CO_2	.16217

REACTION 4

$$\mathrm{C\ (s) + 2\ H_2\ (g)} \overset{\text{EXO}}{\rightleftharpoons} \mathrm{CH_4\ (g)}$$

Given Conditions:

ENDO: P = 1.0 atm T = ? °K
EXO: P = 1.0 atm T = 851°K
ΔT = ?

UNIQUENESS & REVERSIBILITY

At the temperatures shown in Table B-8, the above equation is unique for this process. However, at higher temperatures, other specie will become significant. For example, the product in the 5 atm pressure example contains 5.8×10^{-7} mole fraction of ethane.

The reversibility of this reaction is in question. The endothermic process is the pyrolysis (or cracking) of methane. Unless it is carried out under extreme conditions, the product will contain not only C and H_2, but a considerable variety of hydrocarbons, including tars. The presence of tars will add to the difficulty of cycling all components.

CONVERSION

The exothermic reaction at the given conditions (Table B-8) would proceed to a conversion of 46% carbon as CH_4. A pressure of 5 atm raises this value to 54%. These are for the ideal feed, containing zero CH_4.

Table B-8. Adiabatic Flame for Reaction 4

Entering Composition		
$H_2/C_{(s)}$ = 2/1, Moles		
Starting Temperature		
298°K		
Reaction Pressure, atm	1	5
Adiabatic Flame Temp., °K	851	941
Final Composition, Mole Fractions		
$C_{(s)}$	.26372	.24517
CH_4	.22537	.28233
H_2	.51090	.47250

REACTION 5

$$NH_3\ (g) + H_2O\ (g) + SO_3\ (g) \overset{EXO}{\rightleftharpoons} NH_4\ HSO_4\ (s)$$

Given Conditions:

ENDO: P = 1.0 atm T = 800°K
EXO: P = ? T = 700°K
ΔT = 100°C

UNIQUENESS & REVERSIBILITY

Table B-9 must not be considered as a reasonable prediction. It is included here chiefly as an example of the dependence of computerized thermochemical prediction quality upon adequate data. The computer data bank did not include the specie NH_4HSO_4 and $(NH_4)_2SO_4$. Being barred from considering these two products, the program evolved an unnatural process, for which the main reaction appears to be:

$$2NH_3 + 3SO_3 \rightleftharpoons 3H_2O + N_2 + 3SO_2$$

Even though the results of Table B-8 do not apply, they give evidence of a considerable number of specie that are likely to be present in the natural process. Certainly, the given equation is not unique.

Table B-9. Adiabatic Flame for Reaction 5

Entering Composition		
$SO_3/NH_3/H_2O$ = 1/1/1 Moles		
Starting Temperature		
298°K		
Reaction Pressure, atm	1	40
Adiabatic Flame Temp., °K	1147	1157
Final Composition, Mole Fractions		
H_2	.00438	.00156
H_2O	.62355	.61779
H_2S	.02037	.03129
N_2	.13256	.13304
SH	.00001	--
SO	.00006	.00002
SO_2	.20031	.20468
S_2	.01751	.00958
S_2O	.00126	.00203

REACTION 6

$$4\ HCl\ (g) + O_2\ (g) \overset{EXO}{\rightleftharpoons} 2H_2O\ (g) + 2\ Cl_2\ (g)$$

Given Conditions:

ENDO: P = 1.0 atm T = 900°K
EXO: P = 1.0 atm T = 786°K
ΔT = 114°C

UNIQUENESS & REVERSIBILITY

At the temperatures shown in Table B-10, the given equation is unique for this process. Other specie are calculated to be present, but in insignificant concentrations. The data do not reveal any special problem with reversibility, except the existence of very corrosive mixtures.

CONVERSION

Only exothermic processes were calculated (Table B-10). At the given conditions, conversion is 45% chlorine as Cl_2. This value is only mildly increased by higher pressure: 50% at 5 atm, and 52% at 10 atm.

Table B-10. Adiabatic Flame for Reaction 6

Entering Composition			
$O_2/HCl = 1/4$, Moles			
Starting Temperature			
298°K			
Reaction Pressure, atm	1	5	10
Adiabatic Flame Temp., °K	786	820	834
Final Composition, Mole Fractions			
Cl_2	.28458	.30761	.31766
HCl	.34417	.30731	.29123
H_2O	.28459	.30762	.31766
O_2	.08666	.07745	.07344

REACTION 7

$$2Na\ (\ell) + H_2O\ (\ell) + 1/2\ O_2\ (g) \overset{EXO}{\rightleftharpoons} NaOH\ (\ell)$$

Given Conditions:

ENDO: P = 0.5 atm T = 2000°K
EXO: P = 1.0 atm T = 1665°K, or higher
ΔT = 335°C

UNIQUENESS & REVERSIBILITY

This cycle, which is in the conceptual stage of development, is not intended to be run as a simple reversible reaction. As explained in Appendix A and illustrated in Figure 7, each of the endothermic and exothermic processes will probably consist of more than one step and/or sub-cycle. In the special case for which computer calculations were made (see Table B-11), a variety of specie besides those appearing in the given reaction equation are shown to be present. (Even more of lower concentration are predicted but not shown.) This is generally true for reactions occurring at higher temperatures. Simple equations are seldom unique for such reactions.

The key question of reversibility concerning this cycle is whether or not elemental metal can be effectively separated from products of thermal decomposition of its compound.

CONVERSION

Conversion in the endothermic phase of this cycle cannot be calculated yet. Its value will depend ultimately on the balance between the rates of metal vapor condensation and the rates of recombination that can be achieved by engineering design.

Conversion in the one set of exothermic calculations made (Table B-11) was, for 2.0 and 6.8 atm respectively, 66% and 69% of the sodium oxidized. The three exothermic process modes have not been studied thoroughly. However, it would appear that essentially 100% conversion can be obtained at little cost by the addition of more water and/or air.

Table B-11. Adiabatic Flame for Reaction 7

Entering Composition		
$O_2/H_2O/Na$ = 1/4/8, Moles		
Starting Temperature		
298°K		
Reaction Pressure, atm	2.04	6.80
Adiabatic Flame Temp., °K	1699	1864
Final Composition		
Gas Phase, Mole Fractions		
Na	.51732	.51700
NaOH	.20285	.18385
H_2O	.13723	.10770
H_2	.13017	.16837
Na_2	.00891	.01776
$(NaOH)_2$	.00177	.00127
NaH	.00171	.00394
H	.00004	.00009
Condensed Phase, Mole/Mole Gas		
$NaOH_{(\ell)}$	.85433	.74286

REACTION 8

$$N_2\ (g) + 3\ H_2\ (g) \overset{\text{EXO}}{\rightleftharpoons} 2\ NH_3\ (g)$$

Given Conditions:

ENDO: P = 200 atm T = 1023°K
EXO: P = 200 atm T = 773°K
ΔT = 250°C

UNIQUENESS & REVERSIBILITY

The computer calculations (Tables B-12 and 13) show the above reaction equation to be unique for all reaction conditions considered. The reversibility of this reaction (with the aid of catalyst) is well known.

CONVERSION

Graphic interpolation of data (from Table B-12) for the given conditions gives an estimate of 94% nitrogen as N_2 in the endothermic phase, and 32% nitrogen as NH_3 in the exothermic phase of this cycle. The CCE corresponding to these values is 26%. The data in Table B-12 are not applicable because of the low pressures and resulting low temperatures. A moderate increase in CCE, 26% to 31%, can be obtained by increasing pressure to 300 atm. The greatest improvement in efficiency could be obtained by lowering the temperature of the exothermic phase. This could be done in design by allowing greater heat extraction during reaction. This is not acceptable, however, because of the nearness of the calculated temperature to the lower limit of this study, 800°F.

Table B-12. Equilibria for Reaction 8 (Specie Concentrations in Mole Fractions)

N/H = 1/3, Moles

50.0000 atm

	200°K	400°K	600°K	800°K	1000°K
H_2	.00006	.07220	.51274	.71661	.74299
NH_3	.99988	.90370	.31632	.04450	.00933
N_2	.00006	.02410	.17094	.23889	.24768

100.0000 atm

	200°K	400°K	600°K	800°K	1000°K
H_2	.00004	.05181	.42460	.68839	.73625
NH_3	.99991	.93089	.43384	.08213	.01832
N_2	.00005	.01730	.14156	.22948	.24543

200.0000 atm

	200°K	400°K	600°K	800°K	1000°K
H_2	.00003	.03701	.33788	.64262	.72346
NH_3	.99993	.95061	.54946	.14315	.03537
N_2	.00004	.01237	.11265	.21423	.24117

300.0000 atm

	200°K	400°K	600°K	800°K	1000°K
H_2	.00002	.03036	.29111	.60652	.71150
NH_3	.99994	.95949	.61182	.19128	.05132
N_2	.00004	.01015	.09706	.20219	.23718

400.0000 atm

	200°K	400°K	600°K	800°K	1000°K
H_2	.00002	.02636	.26041	.57692	.70027
NH_3	.99994	.96482	.65276	.23075	.06628
N_2	.00004	.00882	.08683	.19233	.23344

Table B-13. Adiabatic Flame for Reaction 8

Entering Composition		
H_2/N_2 = 3/1, Moles		
Starting Temperature		
298°K		
Reaction Pressure, atm	10	40
Adiabatic Flame Temp., °K	563	622
Final Composition, Mole Fractions		
H_2	.60931	.57498
NH_3	.17937	.22484
N_2	.21132	.20019

REACTION 9

$$CO\ (g) + H_2O\ (g) \overset{\text{EXO}}{\rightleftharpoons} H_2\ (g) + CO_2\ (g)$$

Given Conditions:

ENDO: P = 10.0 atm T = 1300°K
EXO: P = 10.0 atm T = 956°K
ΔT = 344°C

UNIQUENESS & REVERSIBILITY

The above equation does not properly express the reactions that would take place if a composition corresponding to a stoichiometric mixture of the above was used in a cycle. (This is not to say that the equation is not applicable to the reaction in its well known usage, namely, the water-gas shift reaction.) The more likely equation representing a closed cycle inferred from the data in Table B-14, would be:

$$3\ CO + H_2O + H_2 \rightleftharpoons 2\ CO_2 + CH_4$$

It is judged from Tables B-14 and 15 that a cycle free of solid carbon, and therefore reversible, could be attained at a pressure of 10 atmospheres.

CONVERSION

From the above-cited data, the following conversions are estimated:

ENDO: 75% carbon as CO
EXO: 73% carbon as non-CO

A value of CCE computed from these values is 30%. Further calculations might reveal considerable improvement by raising the pressure.

An interesting circumstance can be seen by examining Tables B-15 and B-16. If one starts with each pair of reactants in the given equation separately and raises them to ignition temperatures, he can expect exothermic reactions from both mixtures, according to the calculation.

Table B-14. Equilibria for Reaction 9 (Specie Concentrations in Mole Fractions)

C/H/O = 1/2/2. Moles

1.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
C	.17263	.10859	.00000	.00000	.00000
CH_4	.05025	.06450	.01433	.00005	.00000
CO	.00002	.00912	.18117	.25039	.28476
CO_2	.32738	.38232	.31885	.24964	.21526
H_2	.00393	.08018	.27582	.24944	.21521
H_2O	.44578	.35529	.20983	.25049	.28477

10.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
C	.17314	.11591	.03810	.00000	.00000
CH_4	.05081	.07910	.06722	.00448	.00009
CO	.00000	.00287	.08035	.24482	.28467
CO_2	.32688	.38125	.38157	.25520	.21535
H_2	.00125	.02796	.14176	.24171	.21509
H_2O	.44791	.39290	.29099	.25378	.28482

20.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
C	.17321	.11685	.05207	.00000	.00000
CH_4	.05089	.08140	.07734	.01360	.00028
CO	.00000	.00203	.05708	.23320	.28440
CO_2	.32681	.38115	.39087	.26682	.21562
H_2	.00088	.02005	.10673	.22597	.21472
H_2O	.44820	.39852	.31590	.26041	.28497

40.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
C	.17326	.11749	.06177	.00000	.00000
CH_4	.05094	.08308	.08563	.03094	.00111
CO	.00000	.00143	.04051	.21051	.28333
CO_2	.32677	.38110	.39774	.28951	.21669
H_2	.00063	.01432	.07901	.19664	.21331
H_2O	.44840	.40258	.33533	.27239	.28556

100.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
C	.17330	.11806	.07021	.00000	.00000
CH_4	.05099	.08460	.09391	.06120	.00595
CO	.00000	.00090	.02571	.16888	.27703
CO_2	.32672	.38106	.40411	.33115	.22299
H_2	.00039	.00913	.05209	.14748	.20508
H_2O	.44859	.40623	.35396	.29129	.22894

Table. B-15. Adiabatic Flame for Reaction 9

Entering Composition			
H_2O/CO = 1/1, Moles			
Starting Temperature			
298°K			
Reaction Pressure, atm	.05	1	10
Adiabatic Flame Temp., °K	838	863	956
Final Composition, Mole Fractions			
CH_4	.02695	.03272	.05423
CO	.14742	.14897	.14924
CO_2	.35388	.35234	.35213
H_2	.27303	.25419	.18943
H_2O	.19872	.21178	.25497

Table B-16. Adiabatic Flame for Reaction 9

Entering Composition	
CO_2/H_2 = 1/1, Moles	
Starting Temperature	
298°K	
Reaction Pressure, atm	10
Adiabatic Flame Temp., °K	813
Final Composition, Mole Fractions	
$C_{(s)}$	.08117
CH_4	.08143
CO	.02320
CO_2	.38435
H_2	.08147
H_2O	.34838

REACTION XI

$$2\ CO + 2\ H_2 \overset{EXO}{\rightleftharpoons} CO_2 + CH_4$$

Given Conditions:

ENDO: P = 4-20 atm T = 1000 - 1150°K
EXO: P = ? T = 773°K
ΔT = 327 - 377

SPECIAL NOTE

This cycle came to our attention too late for it to be subjected to the screening process. It is a new approach being investigated both theoretically and experimentally at NRL. This cycle is modeled after the EVA-ADAM cycle, Reaction 2. Instead of reforming methane with water, this cycle uses carbon dioxide. The chief reason for this is to reduce the amount of water latent heat to be dealt with in the cycle.

UNIQUENESS & REVERSIBIILTY

As with Reactions 2 and 9 (which also contain compounds of carbon, hydrogen and oxygen) the given equation is not unique. The reversibility of this cycle is in doubt. For the endothermic phase of the cycle (methane reforming), additional CO_2 eliminates solid carbon. That is based on the assumption that the EVA-ADAM conditions would be used (1.0 atm. and 1100°K). However, if the exothermic phase (methanation) can be carried out at approximately 40 atm and 700°K, about 20% of the product moles are predicted to be carbon in the solid state when 4 extra moles of CO_2 are recycled. In fact, for any potentially practical set of exothermic conditions and for any composition in the range studied, the thermochemical program predicts a very large fraction of solid carbon. These conclusions are illustrated in Tables B-17 and 18 and Figure B-2.

Table B-17. Equilibria for Reaction X1
(Specie Concentrations in Mole Fractions)

C/H/O = 1/2/1, Moles

1.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
C	.38787	.34037	.23001	.03037	.00166
CH_4	.10963	.11175	.04266	.00834	.00192
CO	.00001	.00499	.13515	.45080	.49706
CO_2	.11215	.15467	.13486	.01885	.00130
H_2	.00499	.09079	.31951	.47177	.49578
H_2O	.38535	.29744	.13781	.01987	.00227

10.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
C	.38816	.34493	.29359	.13484	.01547
CH_4	.11104	.13837	.10727	.05054	.01696
CO	.000003	.00157	.04481	.28233	.47260
CO_2	.11186	.15353	.16162	.08285	.01195
H_2	.00159	.03184	.15346	.34691	.46254
H_2O	.38734	.32977	.23924	.10253	.02048

20.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
C	.38820	.34549	.30232	.17276	.02873
CH_4	.11124	.14254	.12380	.07278	.03012
CO	.000002	.00111	.03189	.22104	.44938
CO_2	.11182	.15343	.16581	.10622	.02191
H_2	.00113	.02284	.11585	.28786	.43291
H_2O	.38761	.33459	.26032	.13933	.03695

40.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
C	.38823	.34587	.30840	.20576	.05262
CH_4	.11137	.14558	.13732	.09601	.04955
CO	.000001	.00078	.02267	.16738	.41207
CO_2	.11180	.15337	.16896	.12688	.03768
H_2	.00080	.01632	.08590	.22907	.38827
H_2O	.38780	.33808	.27676	.17490	.06215

100.0000 atm

	500°K	700°K	900°K	1100°K	1300°K
C	.38825	.34620	.31369	.23949	.09198
CH_4	.11150	.14834	.15075	.12394	.08262
CO	.000001	.00049	.01441	.01121	.34067
CO_2	.11177	.15333	.17193	.14847	.06735
H_2	.00050	.01041	.05671	.16107	.31005
H_2O	.38797	.34122	.29251	.21496	.10729

Table B-18. Adiabatic Flame for Reaction X1

Entering Composition			
CO/H_2 = 1/1, Moles			
Starting Temperature			
298°K			
Reaction Pressure, atm	1	10	40
Adiabatic Flame Temp., °K	998	1125	1218
Final Composition, Mole Fractions			
$C_{(s)}$	.11167	.11112	.10660
CH_4	.01940	.04413	.06679
CO	.32106	.32192	.32472
CO_2	.06924	.06902	.07082
H_2	.41679	.36757	.32848
H_2O	.06184	.08624	.10258

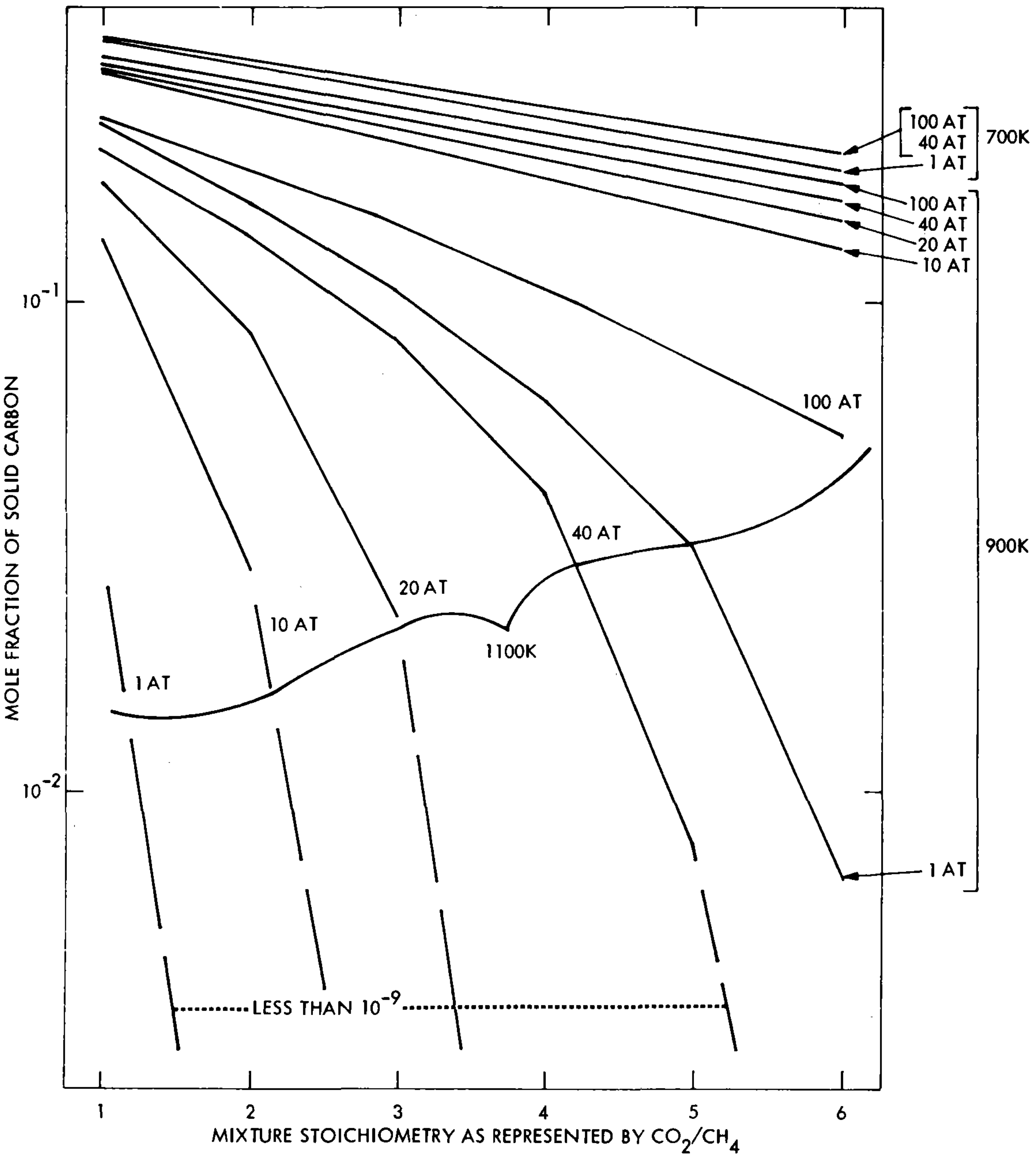


Figure B-2. Carbon Formation in Methanation/CO_2 Reforming

REACTION X2

$$\mathrm{CO}_{(g)} + 2\ \mathrm{NO}_{(g)} \overset{\mathrm{EXO}}{\rightleftharpoons} \mathrm{CO_2} + \mathrm{N_2O}$$

Given Conditions: None given.

SPECIAL NOTE:

This cycle is not real. It is included here primarily as an illustration of the ability of computerized thermochemical calculations to set things straight. As will be seen in Table B-19, one of the chief components, N_2O does not exist in significant amounts at the studied conditions even though its data were in the program. The reason for its absence is thermodynamic. This is a reaction being studied in the air pollution field, where temperatures are considerably lower, and N_2O is probably present.

It is possible that an attractive candidate cycle could be based on this system. We have not studied it, however.

Table B-19. Equilibria for Reaction X2 (Specie Concentrations in Mole Fractions)

C/N/O = 1/2/3, Moles

0.1000 atm

	1000°K	1500°K	2000°K	2500°K	3000°K
CO	.00000	.00001	.00367	.07692	.22870
CO_2	.40000	.39998	.39541	.30413	.09497
NO	.00002	.00092	.00560	.01658	.02921
N_2	.39999	.39954	.39628	.37226	.30905
O	.00000	.00000	.00093	.02084	.15300
O_2	.19999	.19954	.19810	.20977	.18509

0.5000 atm

	1000°K	1500°K	2000°K	2500°K	3000°K
CO	.00000	.00000	.00165	.04006	.17600
CO_2	.40000	.39999	.39793	.35010	.17424
NO	.00002	.00092	.00560	.01649	.03038
N_2	.39999	.39954	.39678	.38191	.33402
O	.00000	.00000	.00042	.00915	.07294
O_2	.19999	.19954	.19761	.20228	.21042

1.0000 atm

	1000°K	1500°K	2000°K	2500°K	3000°K
CO	.00000	.00000	.00117	.02958	.10495
CO_2	.40000	.39999	.39854	.36323	.21024
NO	.00002	.00092	.00560	.01644	.03296
N_2	.39999	.39954	.39690	.38458	.34325
O	.00000	.00000	.00029	.00643	.05180
O_2	.19999	.19954	.19748	.19974	.21222

10.0000 atm

	1000°K	1500°K	2000°K	2500°K	3000°K
CO	.00000	.00000	.00037	.01011	.07159
CO_2	.40000	.40000	.39954	.38798	.31090
NO	.00002	.00092	.00559	.01633	.03323
N_2	.39999	.39954	.39710	.38940	.36585
O	.00000	.00000	.00009	.00201	.01599
O_2	.19998	.19953	.19727	.19464	.20327

20.0000 atm

	1000°K	1500°K	2000°K	2500°K	3000°K
CO	.00000	.00000	.00026	.00723	.05462
CO_2	.40000	.40000	.39968	.39105	.33223
NO	.00002	.00092	.00560	.01631	.33112
N_2	.39999	.39953	.39712	.39010	.37025
O	.00000	.00000	.00007	.00142	.01120
O_2	.19998	.19952	.19723	.19383	.19850