SAND77-8034
Unlimited Release

Thermochemical Energy Storage and Transport

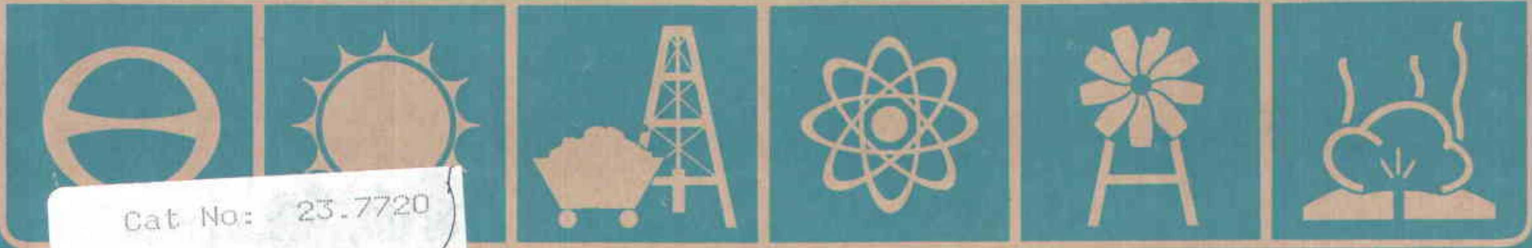
(Presented at the American Nuclear Society Meeting,
New York City, N.Y., June 1977)

R. W. Mar, T. T. Bramlette

Prepared by Sandia Laboratories, Albuquerque, New Mexico 87115
and Livermore, California 94550 for the United States Energy Research
and Development Administration under Contract AT (29-1) 789

Printed September 1977

Sandia Laboratories
energy report



SF 2900-QQ8(3-74)

Issued by Sandia Laboratories, operated for the United States Energy Research & Development Administration by Sandia Corporation.

SAND77-8034
Unlimited Release
Printed September 1977

THERMOCHEMICAL ENERGY STORAGE AND TRANSPORT

R. W. Mar
T. T. Bramlette
Exploratory Chemistry Division 8313
Sandia Laboratories

ABSTRACT

The objective of the Thermochemical Energy Storage and Transport Program is to develop, verify, and demonstrate the technology necessary to store and transport energy by reversible chemical reactions. Current emphasis is on such fundamental problems as chemical kinetics and heat transfer characterization.

TABLE OF CONTENTS

ILLUSTRATIONS

THERMOCHEMICAL ENERGY STORAGE AND TRANSPORT

Introduction

As part of the ERDA National Thermal Energy Storage Program* Sandia Laboratories has planned and is implementing a Thermochemical Energy Storage and Transport Program. The main objective of this Program is to develop, verify, and demonstrate the technology necessary to store and transport energy by reversible chemical reactions.

In general, the Program emphasis is currently on such fundamental problems as chemical kinetics and heat transfer characterization. Many fundamental questions must be addressed before the potential of thermochemical techniques can be accurately assessed. This paper reviews the use of thermochemical reactions for energy storage and transport and discusses the general Program structure, content, and thrust.

Thermal energy can be stored in three forms: (1) as sensible heat, (2) as latent heat of transitions, or (3) as chemical bond energy, i.e., through the use of reversible thermochemical reactions. The characteristics unique to the thermochemical approach are:

- High Energy Densities - Thermochemical storage systems have energy storage densities (based on mass or volume) ranging from about a factor of two to more than an order of magnitude greater than is possible with sensible and latent systems.

- Ambient Storage - Energy storage at ambient temperatures is possible for thermochemical systems, i.e., chemical reactants and products can be cooled to and stored at ambient temperatures. The ability to store at ambient temperatures and still discharge at high temperatures has obvious advantages: chemical interactions between the media and storage container materials are avoided, insulation requirements are eliminated, overall system heat losses are reduced,

---

*Managed by Charles J. Swet, Chemical and Thermal Energy Storage Branch, Division of Energy Storage Systems, Office of Conservation, ERDA.

and potential environmental impact problems (i.e., storing copious quantities of hot material) are avoided. However, there is a penalty associated with storage at ambient temperatures: sensible and possibly latent heats are rejected upon cooling the products to ambient. This reject heat may not necessarily be lost; it may be possible to use it elsewhere in the chemical cycle.

- Long-Term Storage - With ambient storage, long-term storage with little or no degradation is possible, which makes seasonal or extended storage applications feasible.

- Temperature Boosting - Pressure/volume work can be converted into thermal energy quite easily for certain thermochemical reactions. Therefore, it is possible, in theory, to discharge an energy storage system at temperatures greater than the charge temperature.

- Transportability - Chemical reactions can be selected such that the products and reactants are easily transported, e.g., as gases in a pipeline. Therefore, the endothermic and exothermic reactors can be physically separated by long distances.

- Low Energy-Capacity-Related Costs - The cost of an energy storage system can generally be divided into two categories: power costs and capacity costs. The power related costs are those associated with reactors, heat exchangers, etc.: capacity related costs are associated with raw materials costs, storage tank costs, etc., and are generally low for thermochemical systems.

The technical disciplines important to the development of energy storage systems are given in Figure 1. Also listed are probable problem areas in each of these technical disciplines which are generally unresolved at this time, and which must be solved if a storage concept is to be developed successfully. A brief discussion of the state-of-the-art of these technical disciplines serves to illustrate where the technical efforts in the Thermochemical Energy Storage and Transport Program will be directed.

- Chemistry - The heart of a thermochemical energy storage system is the reversible chemical reaction itself. Without exception, no reaction is well enough researched and understood to allow its immediate incorporation into a storage system. Consequently, a considerable amount of research and development is required to characterize any potentially useful reaction with respect to such parameters as reaction rates, side reactions, reversibility, cyclability, long-term performance, reproducibility, reliability, and impurity effects. For catalyzed reactions, additional questions concerning catalyst lifetime, degradation, and poisoning must be addressed.

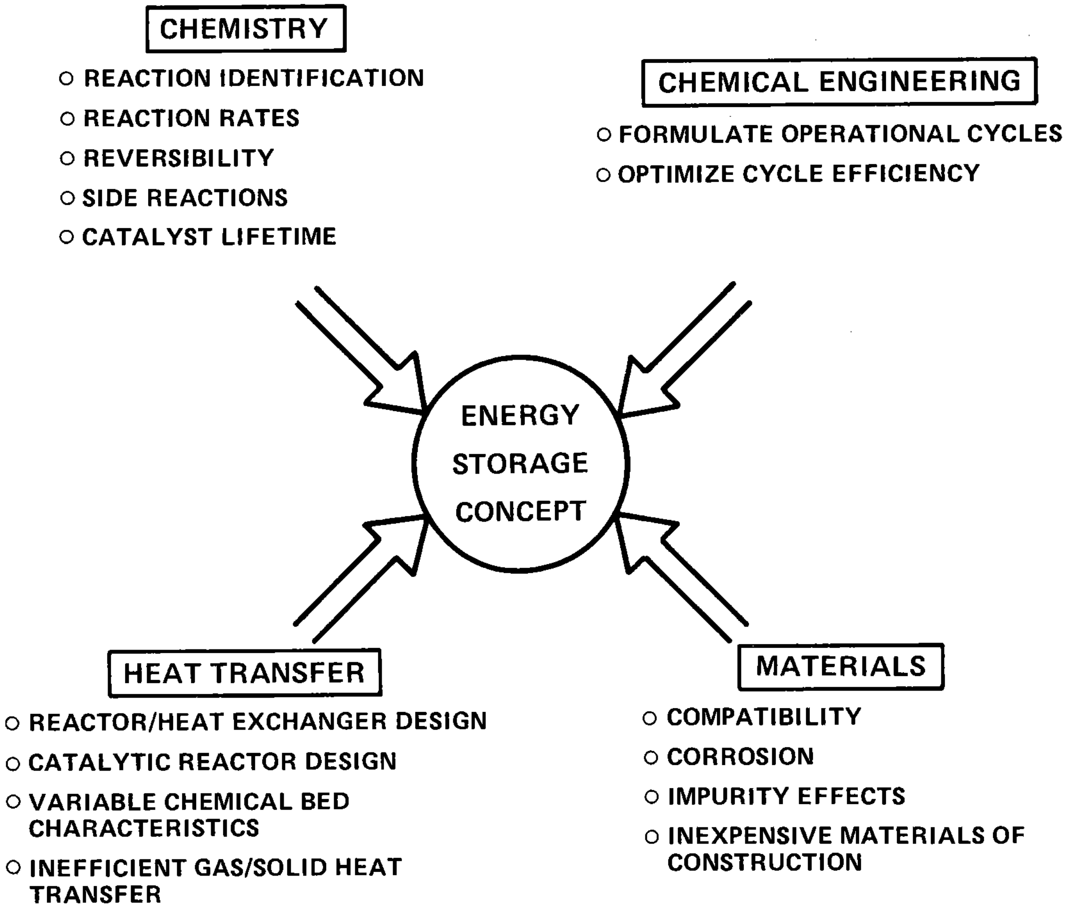


Figure 1. Technical Disciplines Necessary to the Development of Energy Storage Systems

- Heat Transfer - The heat transfer technology pertinent to thermochemical storage systems is largely undeveloped. Exothermic and endothermic reactors must be designed that allow for the complete control of reactions along with efficient heat removal or input. The heat transfer problems may or may not be formidable, depending upon the nature of the chemicals at the heat exchange surface. Heat exchange during liquid phase reactions can be accomplished efficiently. On the other hand, gas/solid reactions cannot be handled as easily due to inherent low heat transfer rates, variable bed characteristics, and bed density changes that occur upon reaction cycling. Catalytic reactors coupled to a heat exchange function are also not well developed.

- Materials - Material compatibility and corrosion problems can be significant depending upon the temperatures of the storage operation and the chemicals involved. Ambient storage mitigates the materials problems to the extent that the corrosive conditions may be confined to a fairly small portion of the total system. Unfortunately, the highest temperatures (and therefore the most corrosive environment) are generally found in the most complex and expensive components of the system: the reactor and heat exchanger.

- Chemical Engineering - Almost all thermochemical reaction cycles for storage or transport applications contain steps which are potentially wasteful of energy; the net result is a much reduced effective energy density. As an example, consider the reaction

  $$Ca(OH)_2 \rightarrow CaO + H_2O$$

  which has an attractively large heat of reaction of 380 cal/cm. However, if one considers the fact that 142 cal/gm are lost due to the condensation of H_2O and the sensible heats associated with H_2O and CaO, the net energy density is only 238 cal/gm. The solution, of course, is to use the heat of condensation and sensible heats for secondary purposes; therein lies one of the technical challenges that must be met if the thermochemical system is to be used to its best advantage. Operational cycles must be optimized. The recovery and re-use of potential rejected energies are necessities for the development of economically viable thermochemical energy storage and transport systems.

In summary, thermochemical technology is at a very early stage of development, and much is needed in the way of technology development in each of the four technical disciplines shown on Figure 2 before one can accurately assess the potential of thermochemical techniques, let alone develop thermochemical-based concepts to the point of commercialization.

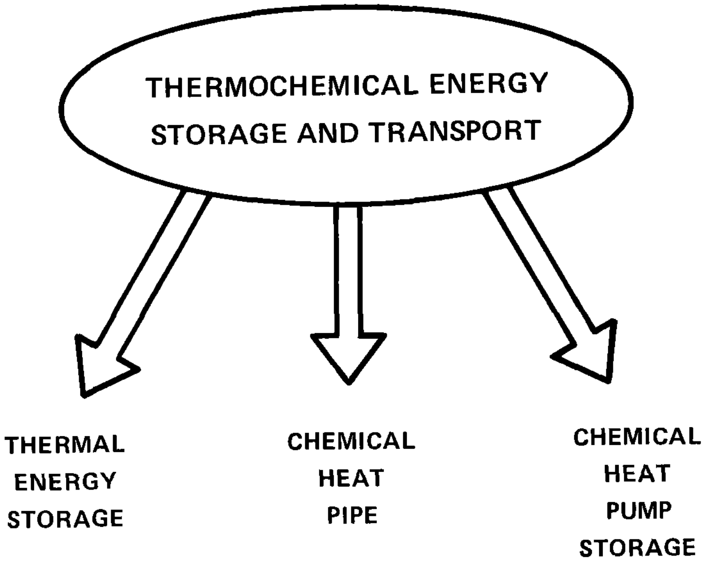


Figure 2. Three Application Concepts

Application Concepts for Thermochemical Reactions

In discussing the technical contents of the Thermochemical Energy Storage and Transport Program, it is convenient to categorize activities in terms of three application concepts: (1) thermal energy storage, (2) chemical heat pipes, and (3) chemical heat pumps (as illustrated in Figure 2).

Figure 3 illustrates the use of a hypothetical reaction $AB \rightleftarrows A+B$ in a thermal energy storage concept. The essential elements of the system are storage vessels for the reactant and product chemicals, and endothermic and exothermic heat exchanger reactors. During the energy storage step, AB is transported to the endothermic reactor where heat is provided from an energy source to decompose AB into A and B. The products are then physically separated and placed in storage tanks. During energy discharge, A and B are recombined in the exothermic reactor, where heat is withdrawn for use. The product of the exothermic reaction is then placed in storage, ready for repeated operation. A number of variations from the schematic shown in Figure 3 are possible, in fact probable. The exothermic and endothermic reactors may be combined into one component, and one may wish to combine the storage and heat exchange units. In addition, the inlet and outlet streams to and from a reactor would typically be equipped with heat exchangers to improve system efficiency.

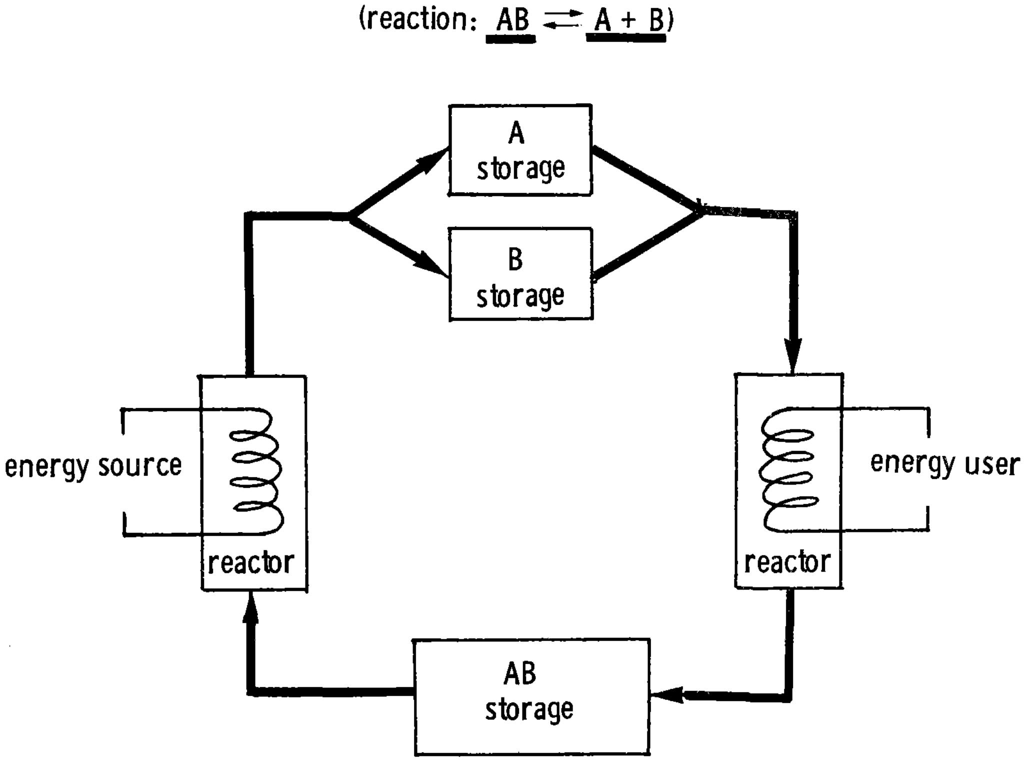


Figure 3. Thermochemical Energy Storage Concept

The basic features of a chemical heat pipe are illustrated in Figure 4, with the hypothetical reaction A+B ⇄ C+D used as an example. The components comprising the system are essentially identical to those described in Figure 3, with the storage tanks replaced by pipelines through which the reactants and products are transmitted.

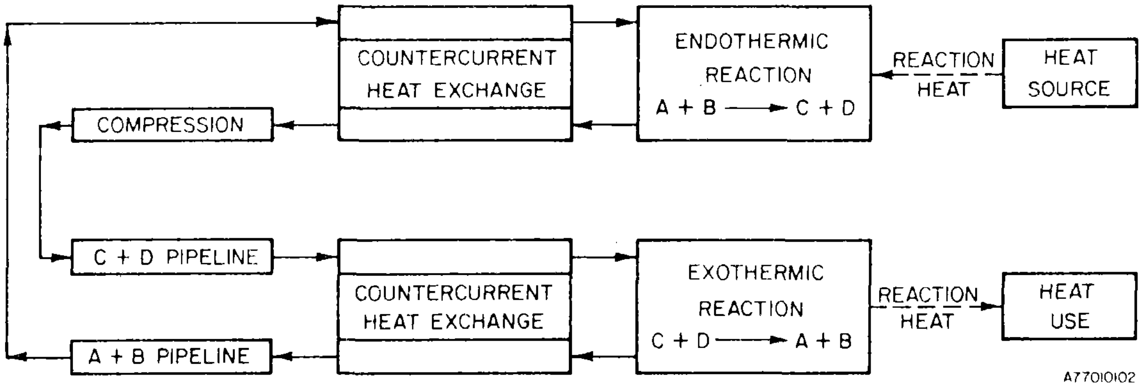


Figure 4. Closed-Loop Chemical Energy Pipeline

The chemical requirements for a chemical heat pump storage system are summarized in Figure 5. Two reactions are required, as represented by $AB \rightleftarrows A+B$ and $CB \rightleftarrows C+B$. Further, these two reactions must have a common vapor species, B(g) in this case. The reactions are selected such that there is a significant difference in enthalpy of reaction, for it is this difference which accounts for the storage feature of a chemical heat pump. The two reactions must be selected such that their respective pressure/temperature relationships are compatible with the intended use conditions. The components of a chemical heat pump system (high- and low-temperature reactor heat exchangers, and a connecting pipeline) are illustrated in Figure 6a. Figure 6b shows the pressure/temperature relationships for both the high-temperature and low-temperature reactions. During charge, energy is absorbed by the high-temperature unit, and AB is decomposed into A and B(g); the latter is transported to the low-temperature unit where it reacts with C to form BC. Heat is released at the low-temperature unit where it is either used or rejected. The charge sequence is shown on Figure 6b by the solid arrow. During energy discharge, energy is absorbed by the low-temperature unit, BC decomposes, and gaseous B is transported over to the high-temperature unit. There it combines exothermically with A to form AB. The discharge process is shown on Figure 6b by the dashed arrow. The discharge sequence may be used for either heating or cooling. For heating, energy is absorbed from the environment in the low-temperature reactor, and heat is rejected from the high-temperature component to the indoors. For cooling, heat is withdrawn from indoor air at the low-temperature reactor and rejected to the outdoor environment through the high-temperature component.

Requirement	Example
● coupled reactions	$AB \rightleftarrows A + B(g)$ $BC \rightleftarrows C + B(g)$
● common vapor transport species	B(g)
● different enthalpies of reaction	$\Delta H_{\substack{\text{decomp.}\\ AB}} > \Delta H_{\substack{\text{decomp.}\\ BC}}$
● suitable P-T curves for AB and BC	

Figure 5. Ingredients for a Chemical Heat Pump

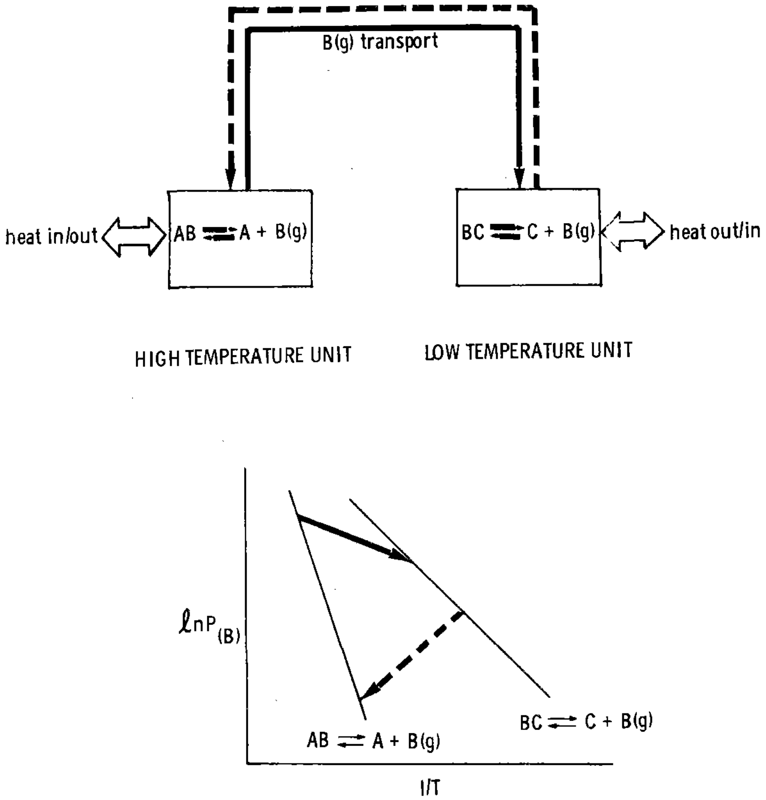


Figure 6. Chemical Heat Pump System

Program Contents

Reactions Investigated

Reactions currently under investigation in the Program are categorized according to reaction type in Figure 7. The thermal decomposition of inorganic hydroxides, hydrated salts, ammoniated salts, methanolated salts, and ammonium hydrogen sulfate are being investigated. Sulfuric acid concentration and dilution are also being pursued, as well as several catalyzed reactions including the decomposition of sulfur trioxide, methanation/reformation, and coal gasification. These reactions are displayed on a temperature scale in Figure 8. To help orient the reader, various energy sources are also displayed, placed at temperatures typically attainable from them. As one can see, the reactions under development span temperatures ranging from slightly above ambient to approximately 1100K. It is also apparent from Figure 8 that the reactions under development are potentially applicable to a wide variety of uses.

TYPE	REACTION
THERMAL DECOMPOSITION (GAS/SOLID)	○ $Ca(OH)_2 \rightleftharpoons CaO + H_2O$ ○ $MgCl_2 \cdot xNH_3 \rightleftharpoons MgCl_2 \cdot yNH_3 + (x-y)NH_3$ ○ $CaCl_2 \cdot xNH_3 \rightleftharpoons CaCl_2 \cdot yNH_3 + (x-y)NH_3$ ○ $MgCl_2 \cdot xH_2O \rightleftharpoons MgCl_2 \cdot yH_2O + (x-y)H_2O$ ○ SALT • MeOH $\rightleftharpoons$ SALT + MeOH
THERMAL DECOMPOSITION (LIQUID/GAS)	○ $NH_4HSO_4 \rightleftharpoons NH_3 + H_2O + SO_3$ ○ H_2SO_4(dilute) $\rightleftharpoons$ H_2SO_4(conc.) + H_2O
CATALYZED (GAS/GAS)	○ $2SO_3 \rightleftharpoons 2SO_2 + O_2$ ○ $CH_4 + H_2O \rightleftharpoons 3H_2 + CO$ ○ $\left\{\begin{matrix} C + H_2O \rightarrow CO + H_2 \\ CO + 3H_2 \rightarrow CH_4 + H_2O \end{matrix}\right\}$

Figure 7. Chemical Reactions Under Investigation

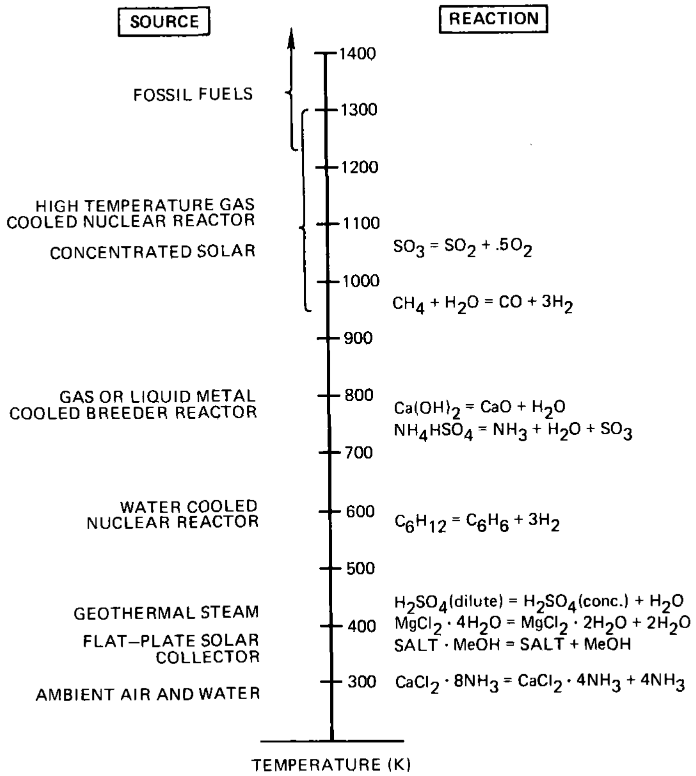


Figure 8. Temperature Ranges of Reactions Under Investigation

Applications Investigated

Numerous applications for the three technology concepts discussed (i.e., thermal energy storage, chemical heat pipe, and chemical heat pump) can be proposed; those applications we feel show the greatest potential are given in Table I. The specific applications being addressed in this Program are indicated by the double circle. The fact that an application is not being addressed in this Program does not imply that applicable and pertinent technologies are not being developed. Technologies developed for one specific application are generally applicable to numerous others.

TABLE I

POTENTIAL APPLICATIONS

Concept	Application
Thermochemical Storage	◎ Solar Thermal-Electric Power
	◎ Fossil Utilities - Improved Efficiency
	○ Peak Following Utilities - Nuclear, Fossil
	○ Industrial Waste Heat Recovery
Chemical Heat Pipes	◎ Industrial Process Heat - Nuclear, Fossil Energy Source
	○ Total Energy Systems
	○ Distributed Solar Systems
	○ District Building Heating
Heat Pumps	◎ Building Heat/Cooling - Solar

Energy storage is required to serve as a buffer between the energy source and power generation equipment; however, the real utility of thermochemical techniques may be in the extension of solar energy systems to load-following applications. The overall efficiency of conventional fossil utilities may be improved by the incorporation of energy storage systems. It may also be possible to extend non-solar energy sources, e.g., nuclear and fossil, to peak-following activities. Another application is the recovery and redistribution of waste reject heat.

Chemical pipes may be used to provide industrial process heat and energy for district heating from central energy sources that may be fossil, nuclear or solar based. The ability to transport low-grade thermal energy has obvious applications in total energy systems. Chemical heat pipes may also be used to provide the link between the distributed collectors and the central storage system in a distributed solar energy system.

The only application we envision for the chemical heat pump is solar building heating and cooling.

Illustrative Examples

The Thermochemical Energy Storage and Transport Program is comprised of numerous activities subcontracted with the private sector by Sandia and ERDA. Time does not permit a detailed discussion of all activities; the reader is referred to the Program Annual Operating Plan[1] for additional information. However, a few brief remarks regarding several of the ongoing studies serve to illustrate the nature of current problems being addressed.

Typical of the many projects comprising this program is Martin Marietta Corporation's project to develop an energy storage concept based on paired ammoniated salts. The concept is very similar to that illustrated in Figure 6 for the chemical heat pump. A high-temperature decomposition reaction is used for the storage and discharge of energy, and the decomposition product, ammonia, is stored as a low-temperature ammoniated salt. Of prime concern for the past year have been the chemical kinetics of various ammoniated salt decomposition reactions. One can use thermodynamics to point out potentially useful reactions for a given temperature range of operation, but in general, kinetic reversibility and cyclability are unknown, and can be characterized only by an experimental study.

Figure 9 shows kinetic data for the decomposition/recombination $FeCl_2 \cdot 6NH_3$. Two sets of data are given for different starting materials, anhydrous $FeCl_2$ and $FeCl_2 \cdot 4NH_3$. It is seen that the kinetics appear to be chemical source dependent. When using the tetrammoniate as the starting material, the chemical kinetics were slower than when starting with the anhydrous salt; in fact, it was not possible to initiate the recombination reaction at all until the reaction temperature was reduced to less than 40°F.

Kinetic data for the decomposition/recombination of $CaCl_2 \cdot 8NH_3$ are shown in Figure 10. As one can see, a significant amount of scatter is evident during the lower temperature recombination process, which suggests kinetic problems.

---

[1] Fiscal Year 1977 Annual Operating Plan for the Thermochemical Energy Storage and Transport Program of the National Thermal Energy Storage Program, Sandia report SAND77-8226, June 1977.

Courtesy of Martin Marietta Corporation

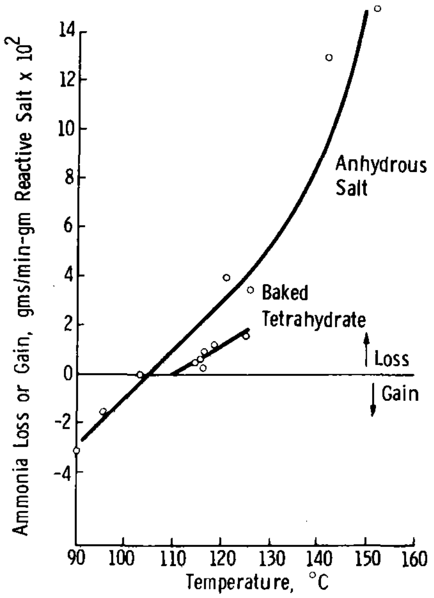


Figure 9. Rate Data, $FeCl_2 \cdot 6NH_3 \rightleftharpoons FeCl_2 \cdot 2NH_3 + 4NH_3$

Courtesy of Martin Marietta Corporation

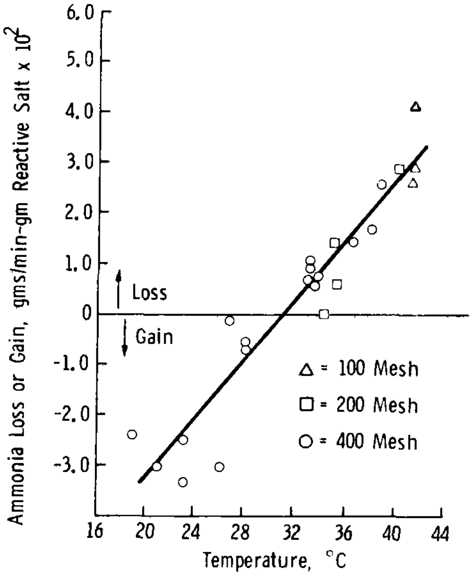


Figure 10. Rate Data, $CaCl_2 \cdot 8NH_3 \rightleftharpoons CaCl_2 \cdot 4NH_3 + 4NH_3$

To illustrate that not all salts are ill behaved, Figure 11 shows kinetic data for the decomposition of $MgCl_2 \cdot 2NH_3$; no kinetic hindrances are apparent.

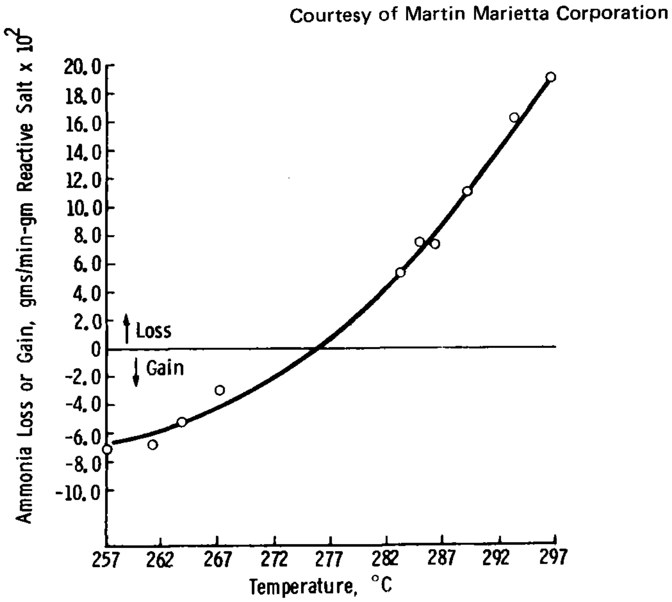


Figure 11. Rate Data, $MgCl_2 \cdot 2NH_3 \rightleftarrows MgCl_2 \cdot NH_3 + NH_3$

In summary, it is acknowledged that the kinetics of thermal decomposition reactions are largely unknown, and that they must be investigated experimentally. Further, one cannot extrapolate kinetic data from analogous reactions; each candidate reaction must be treated on an individual basis.

The sulfuric acid project of Rocket Research Company is an example of an activity which has progressed past the basic chemical characterization stage, and emphasis is currently in the design and engineering of a viable (technically and economically) system. The concept is simply the distillation of water from dilute sulfuric acid during energy charge, and the combination of water and concentrated sulfuric during discharge. To illustrate the extent of technical understanding, the predicted and experimental temperature rises observed in a recombination reactor are compared in Figure 12 for numerous experimental conditions. It is seen that temperature rises can be predicted to within 10°C; further, the heat transfer processes involve all liquid phases and are well understood. The emphasis of the sulfuric acid project is currently on identifying the most promising applications for the reaction, and on the engineering design of efficient system components such as the distillation reactor.

Courtesy of Rocket Research Corporation

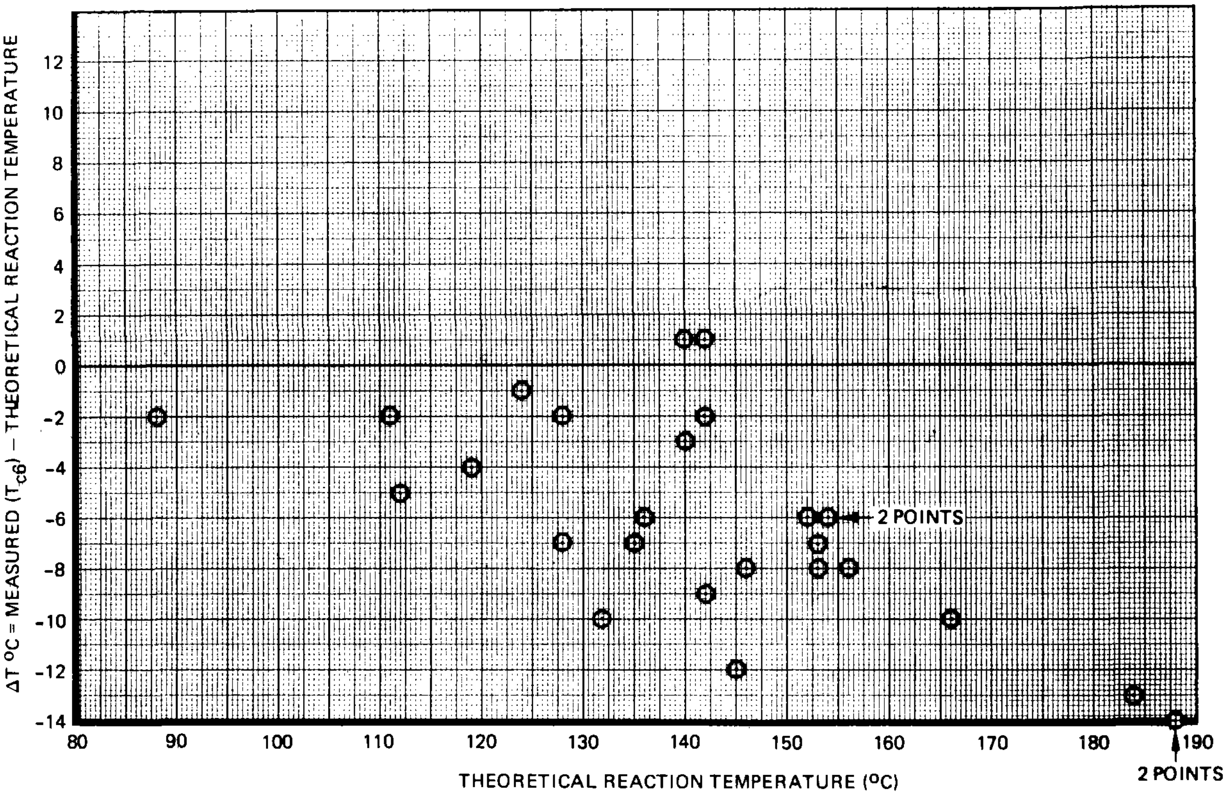


Figure 12. Deviation of T_{c6} From Theoretical as a Function of Theoretical Reaction Temperature

Summary

Thermochemical techniques are potentially useful in numerous energy storage and transport applications; a Program has been planned and implemented by Sandia Laboratories and the ERDA Chemical and Thermal Storage Branch to develop the pertinent technologies. In general, the Program emphasis is currently on fundamental problems such as chemical kinetics and heat transfer characterization. Many fundamental questions must be addressed before the potential of thermochemical techniques can be accurately assessed.

UNLIMITED RELEASE

INITIAL DISTRIBUTION

NASA-Lewis Research Center
Cleveland, Ohio
Attn: W. J. Masica

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830
Attn: H. W. Hoffman

US ERDA (6)
Chemical and Thermal Storage Branch
Washington, D.C. 20545
Attn: J. H. Swisher (1)
      C. J. Swet (5)

US ERDA
Albuquerque Operations Office
Special Programs Division
P. O. Box 5400
Albuquerque, NM 87115
Attn: D. K. Nowlin

A. Narath, 5000; Attn: J. H. Scott, 5700
G. E. Brandvold, 5710
J. A. Leonard, 5712
R. P. Stromberg, 5714
R. H. Braasch, 5715
D. G. Schueler, 5719
H. M. Stoller, 5730
R. K. Traeger, 5731
V. L. Dugan, 5740
S. G. Varnado, 5742
R. S. Claassen, 5800; Attn: R. G. Kepler, 5810
                            M. J. Davis, 5830
                            H. J. Saxton, 5840
R. L. Schwoebel, 5820
A. W. Mullendore, 5825; Attn: D. M. Haaland
T. B. Cook, Jr., 8000; Attn: A. N. Blackwell, 8010
                             C. H. DeSelm, 8200
                             W. C. Scrivner, 8400
L. Gutierrez, 8100
A. F. Baker, 8124; Attn: R. M. Green
R. C. Wayne, 8130
W. G. Wilson, 8131
A. C. Skinrood, 8132; Attn: L. G. Radosevich
G. W. Anderson, 8140

B. F. Murphey, 8300
D. M. Schuster, 8310 (5)
D. R. Adolphson, 8312
R. W. Mar, 8313 (20)
T. T. Bramlette, 8313 (20)
W. R. Hoover, 8314
L. A. West, 8315
T. S. Gold, 8320
P. J. Eicker, 8326
C. C. Hiller, 8326
J. L. Wirth, 8340
D. L. Hartley, 8350
Technical Publications and Art Division, 8265, for TIC (2)
F. J. Cupps, 8265/Technical Library Processes Division, 3141
Technical Library Processes Division, 3141 (2)
Library and Security Classification Division, 8266-2 (3)

Org.	Bldg.	Name	Rec'd by*	Org.	Bldg.	Name	Rec'd by*

*Recipient must initial on classified documents.