



Thermochemical Energy Storage Systems - A Review

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THERMOCHEMICAL ENERGY STORAGE SYSTEMS - A REVIEW

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ABSTRACT

This report reviews the characteristics of thermochemical storage systems, analyzes the present state-of-the-art of the relevant technical disciplines, and presents some potential solar storage applications. The material has been prepared as an invited contribution to the Solar Energy Handbook, W. C. Dickinson and P. N. Cheremisinoff, eds., to be published by Marcel-Decker.

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THERMOCHEMICAL ENERGY STORAGE SYSTEMS - A REVIEW

I. Introduction

Thermal energy can be stored in three forms: (1) as sensible heat, (2) as latent heat of transitions, or (3) as chemical bond energy. In the third approach, energy, when available, is used to drive an energy-consuming (endothermic) reaction; and energy is withdrawn from storage by reversing the reaction, thus effecting the energy-releasing (exothermic) reaction. Since thermochemical energy storage technologies are presently at an embryonic stage of development, one cannot seriously consider such systems for current use.

The purpose of this report is to review the state-of-the-art of thermochemical technologies. Current research and development activities will be summarized, problem areas identified, and the future prospects of varied chemical systems and applications discussed.

Specifically excluded from consideration in the present discussion are electrochemical, photochemical, and radiochemical reactions. This chapter deals solely with reactions in which thermal energy is stored and released as a consequence of net changes in chemical bond energy; therefore the term "thermochemical" is used.

A. Characteristics of Thermochemical Energy Storage and Transport Systems

The characteristics which are unique to thermochemical systems when compared to sensible and latent heat systems, are:

High Energy Densities - Thermochemical storage systems have energy storage densities (based on either 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 heat 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, and potential environmental impact problems (e.g., those resulting from storing copious quantities of hot material) are avoided. On the other hand, 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, however, as it may be possible to recover it elsewhere in the chemical cycle.

Long-Term Storage - In ambient storage, long-term storage with little or no degradation is possible, thus making seasonal or extended storage applications feasible.

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

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

While these characteristics may be considered advantages for many applications, they must be weighed against the following potential drawbacks:

Furthest From State-of-the-Art - Thermochemical technologies are the least developed; and considerable amounts of time, money, and effort are required to develop thermochemical systems to commercialization.

System Complexity - Thermochemical systems will probably be quite complex when compared with sensible and latent heat systems. Not only will individual components be complex, but interactions between various components will be needed in order to achieve acceptable total system efficiencies.

B. Current State-of-the-Art Analysis

The technical disciplines important to the development of energy storage systems are given in Figure 1. Also listed for each discipline are

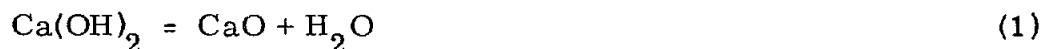
problem areas which are generally unresolved at this time and which must be solved if a thermochemical storage concept is to be developed successfully. A general discussion of the state of the art of these technical disciplines is given below to put thermochemical storage in the proper perspective relative to sensible and latent heat systems.

Chemistry - The heart of a thermochemical energy storage system is the reversible chemical reaction itself. Generally speaking, no such reaction is presently well enough 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, moreover, additional questions concerning catalyst lifetime, degradation, and poisoning must be addressed.

Heat Transfer - Equally important to the thermochemical energy storage system are the chemical reactors and process-stream heat exchangers. Generally speaking, design techniques are available for predicting system performance. What is lacking, however, is information regarding such things as the thermophysical and transport properties of the various constituents of the chemical system and the effects of catalyst performance, reaction kinetics, long-term cyclic operation, to name a few, on heat transfer. Small-scale experiments are required to verify theoretical predictions before large-scale systems are designed and constructed.

Materials - Material compatibility and corrosion problems can be significant, the degree depending upon the temperatures of the storage operation and the chemicals involved. Ambient storage, however, mitigates the material problems to the extent that the corrosive conditions may now 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, viz., the reactor and heat exchangers.

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



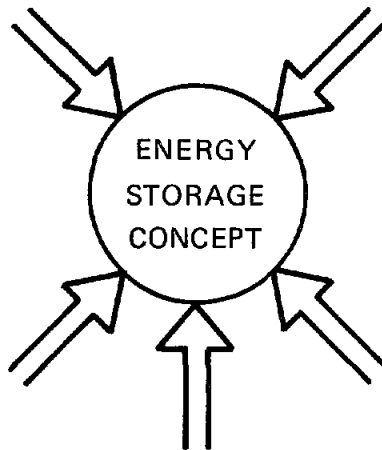
which has an attractively large heat of reaction of 1590 J/g. However, if one considers the fact that 594 J/g are lost in the condensation of

CHEMISTRY

- REACTION IDENTIFICATION
- REACTION RATES
- REVERSIBILITY
- SIDE REACTIONS
- CATALYST LIFETIME

CHEMICAL ENGINEERING

- FORMULATE OPERATIONAL CYCLES
- OPTIMIZE CYCLE EFFICIENCY



HEAT TRANSFER

- REACTOR/HEAT EXCHANGER DESIGN
- CATALYTIC REACTOR DESIGN
- VARIABLE CHEMICAL BED CHARACTERISTICS
- INEFFICIENT GAS/SOLID HEAT TRANSFER

SYSTEMS ANALYSIS

- TECHNICAL & ECONOMIC FEASIBILITY STUDIES
- COST/BENEFIT STUDIES
- IDENTIFY REQUIRED R & D

MATERIALS

- COMPATIBILITY
- CORROSION
- IMPURITY EFFECTS
- INEXPENSIVE MATERIALS OF CONSTRUCTION

Figure 1. Technical disciplines necessary to the development of energy storage systems.

H₂O and the sensible heats associated with H₂O and CaO, the net energy density is only 996 J/g. 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 also be optimized, and the recovery and re-use of potential rejected energies are necessities for the development of economically viable thermochemical energy storage and transport systems.

Systems Analysis - In addition to the fundamental investigations described above, systems analyses must be performed. These studies are required to establish the technical and economic feasibility of a proposed concept, to identify required research, and to establish the relative merits of the proposed system as compared with competing technologies. These studies must continue throughout the development process in order to filter in new information as it becomes available and to ensure that the concepts being developed will be technically and economically viable.

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 five technical disciplines shown on Figure 1 before one can accurately assess the potential of thermochemical techniques, let alone develop thermochemically based concepts to the point of commercialization. Current efforts (described in greater detail below) are directed at fairly specific problems in each discipline. Very little work is going on which can be considered systems development.

II. Background

A. Thermodynamics of Reactions

" . . . any reaction or change of state that appears with increasing temperature on an equilibrium temperature-composition phase diagram must necessarily occur with the absorption of heat and a positive entropy change. "1

This statement is as valid as the First and Second Laws of Thermodynamics. When applied to thermochemical reactions of interest for energy storage applications, it indicates that they must necessarily have positive enthalpy and entropy changes when written in the energy charge (endothermic) direction. Furthermore, the endothermic process will necessarily take place at a temperature greater than the exothermic process (unless one does additional work to the system).

Since thermodynamics forms the basis from which reactions are selected, it is appropriate to review briefly the relevant thermochemical quantities and examine their interdependence. For the sake of simplicity, assume standard states for all reactants and products, and $\Delta C_p = 0$ for the reaction. One can then define a temperature T_{eq}° as

$$T_{eq}^\circ = \Delta H_{298}^\circ / \Delta S_{298}^\circ \quad (2)$$

where ΔH_{298}° and ΔS_{298}° are the enthalpies and entropies of reaction at 298 K. If $T > T_{eq}^\circ$, the endothermic reaction proceeds; for $T < T_{eq}^\circ$, the exothermic reaction proceeds. The enthalpy is essentially fixed if one selects (1) the storage application and (2) the class of reaction. The former determines T_{eq}° , since the source and end-use temperatures are defined, and the latter fixes ΔS_{298}° , since entropy changes are essentially constant for a class of reactions. Therefore, while one generally seeks to maximize energy density, a realistic limit is set. Conversely, if one assumes a specific application (fixes T_{eq}°) and a desired energy density (fixes ΔH_{298}°), then the required ΔS_{298}° is fixed and one is restricted to a specific class of reactions. One also notes that given a class of reactions, as the storage temperature increases so does the theoretical energy storage density.

Inasmuch as the interplay between ΔH_{298}° , ΔS_{298}° , and T_{eq}° has been discussed, it is appropriate to explore factors which govern their magnitudes. The change in entropy depends mainly upon the phase characteristics of the reactants and products, and generalizations can be made relating the magnitude of the entropy change to the class of reaction. Some familiar examples are Trouton's rule (entropy of vaporization at the normal boiling point is ~ 92 J/K/mole) and Richard's rule (the entropy of fusion of metals is ~ 9.2 J/K/g. at.). The following reaction characteristics are associated with positive entropy production: net increase in number of molecules, net increase in molecular complexity, net increase in number of gaseous species, and an increase in number of liquid species. It is beyond the scope of this review to detail the methods used to estimate entropy changes, but a few quantitative remarks are useful to help orient the reader. When reactants and products are all solids, the entropy change will be within a few entropy units of zero. The greatest entropy change is associated with the production of gaseous species (e.g., a net increase of one diatomic gas molecule is associated with an entropy change of ~ 170 J/K/mole gas).

The magnitude of the enthalpy change depends primarily upon the molecular bond chemistry, and is a direct measure of the net change in bond energy. Also, T_{eq}° is a measure of bond energy; that is, the greater the energy, the higher is the temperature required to cause bonding re-arrangements.

The concept of a singular turning temperature T_{eq}° is a reasonable simplification when one considers reactions which do not involve gaseous species. However, if gaseous products are formed during the endothermic reaction, the magnitude of T_{eq}° is affected to the extent that the equilibrium constant K_{eq} depends on pressure

$$T_{eq} = \frac{\Delta H_{298}^\circ}{\Delta S_{298}^\circ + \ln K_{eq}(P)} \quad (3)$$

The magnitude of the effect of pressure is illustrated on Figure 2, where T_{eq} is plotted against pressure P for several candidate reaction systems.

Equations (2) and (3) lose their significance when reactions which involve both gaseous reactants and products are analyzed, in which case the reactions typically reverse directions gradually over a range of temperatures. As an illustration of the thermodynamics involved, consider the reaction



When we assume the system to be charged initially with n moles of SO_3 , if x moles of O_2 form, the amounts of SO_3 and SO_2 in a closed system at temperature T and total pressure P_T are $(n - 2x)$ and $2x$, respectively. The partial pressures of SO_3 , SO_2 , and O_2 are therefore given by:

$$P_{SO_3} = \frac{(n - 2x)}{(n + x)} P_T \quad (5)$$

$$P_{SO_2} = \frac{2x}{(n + x)} P_T \quad (6)$$

$$P_{O_2} = \frac{x}{(n + x)} P_T \quad (7)$$

The free energy of reaction (with gas ideality assumed) is given by

$$\Delta F_T = \Delta F_T^\circ + RT \ln (P_{SO_2}^2 P_{O_2} / P_{SO_3}^2) \quad (8)$$

and at equilibrium, $\Delta F_T = 0$. Substituting Equations (5), (6), and (7) into Equation (8), one derives an expression relating P_T , T , and x :

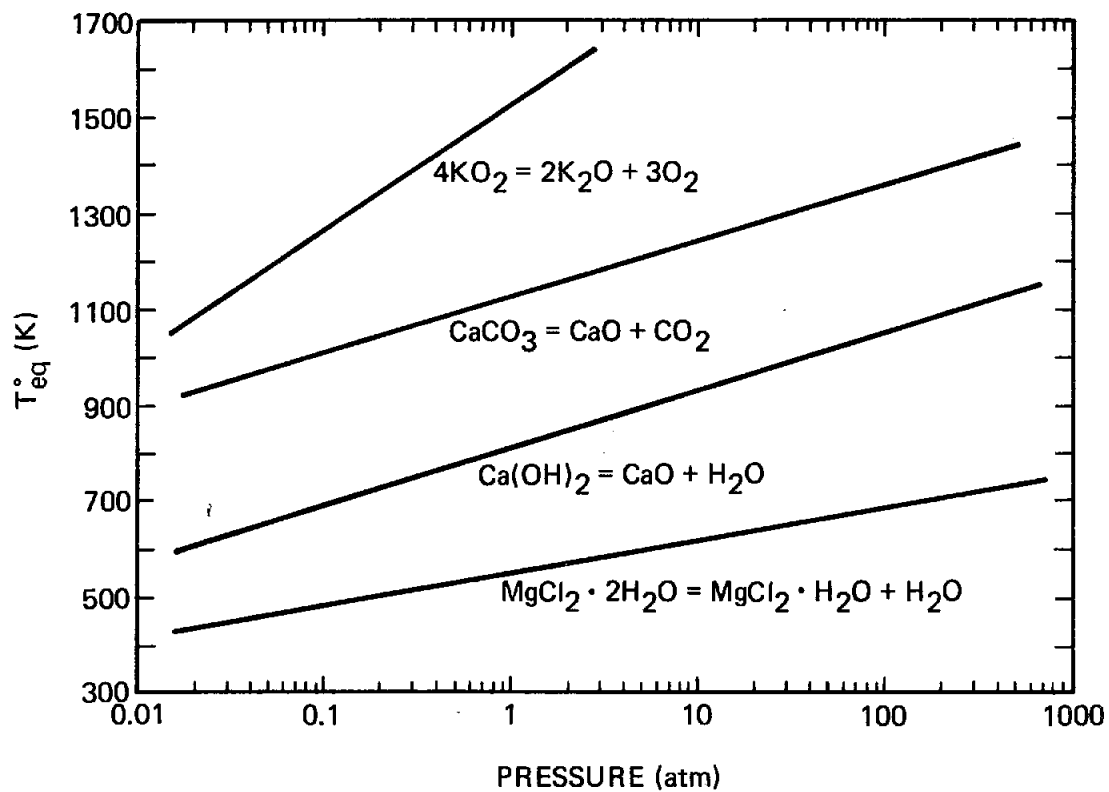


Figure 2. Dependence of turning temperature T_{eq}° on pressure for various candidate reactions.

$$\ln \frac{(n+x)(n-2x)^2}{4x^3} = \ln P_T + \frac{\Delta F_T^\circ}{RT} \quad (9)$$

The solution of Equation (9) is given in Figure 3, where x is represented as the degree of SO₃ dissociation. Note that the reaction 2SO₃ = 2SO₂ + O₂ reverses direction (fraction SO₃ converted varies from 0.1 to 0.9) over a temperature range of ~450 K. Furthermore, as the pressure increases, the curves are displaced to higher temperatures.

B. Candidate Reactions

Selection Criteria--When one is selecting a thermochemical reaction for use in a storage application, the criteria which must be considered include

Thermodynamic Requirements - Suitable values for ΔH and T, such that operational temperatures and desired energy densities are met.

Reversibility - Reactions must be reversible with no significant side reactions or changes in reaction rates with time.

Reaction Rates - The rates of the forward and reverse reactions must be rapid enough to satisfy energy input and output requirements.

Controllable - One must be able to turn reactions on and off as required.

Ease of Storage - The reactants and products must be conducive to simple and inexpensive storage.

Safe - The chemicals should not pose insurmountable safety hazards due to chemical corrosivity, toxicity, flammability, etc.

Inexpensive and Available - The chemicals must be readily available and reasonably inexpensive. Specific cost requirements, however, can only be determined by a detailed economic analysis for the specific application.

Classification of Reactions--Because the number of reversible chemical reactions is virtually endless, it is helpful to think within a systematic classification framework. One approach, which is adopted here, is to consider the way in which reactions are controlled. Given the endothermic reaction, how can one prevent energy degradation and loss through back reaction? Three methods can be used: (1) catalyzed reactions, (2) separation of products, and (3) thermal quenching.

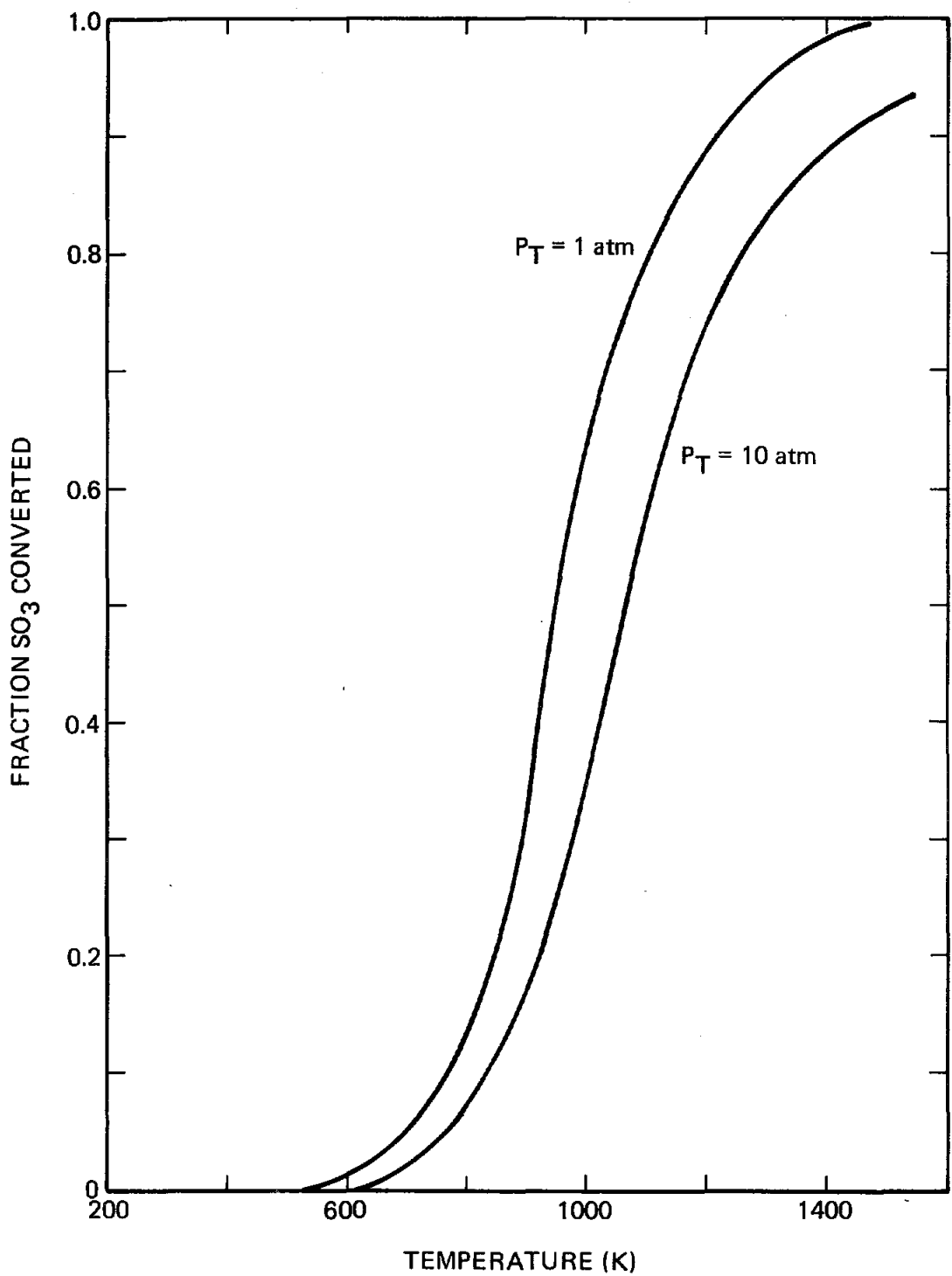


Figure 3. Equilibrium conversion of SO_3 .

Products of endothermic catalyzed reactions can be stored indefinitely in the absence of the appropriate catalyst for the reverse reaction. The recovery (discharge) of the stored energy can be effected by passing the chemicals over the catalyst in the exothermic reactor heat exchanger.

The back reaction of the products may also be prevented by physically separating them, and whereas homogeneous reactions do not lend themselves to easy separation, heterogeneous reactions do. The latter can be grouped according to the nature of the species in the reactor/heat exchanger component; thus gas/solid, gas/liquid, and liquid/solid reactions are possible. However, because of the entropy requirements discussed earlier, one is generally not interested in liquid/solid interactions.

It is also possible in theory to quench the products of the endothermic reaction to metastable states by rapid heat removal. The exothermic recombination of the products must be slow enough to allow quenching to ambient, and yet the kinetics must be fast enough to provide adequate energy discharge when required. This approach, however, is not realistic; it is discussed simply for the sake of completeness.

In summary, it is convenient to categorize candidate reactions into three groups:

1. Catalyzed reactions
2. Solid/gas decomposition reactions
3. Liquid/gas decomposition reactions

Potential Chemical Reactions--Several investigators have attempted to generate comprehensive lists of potential candidate reactions,²⁻⁵ some of which are listed in Tables I-III, where they are categorized by reaction class and ordered according to the T_{eq}° . No attempt is made here to critically assess the merits and drawbacks associated with each. These tables are by no means complete, and technically and economically viable reactions are no doubt missing. An asterisk is used to denote reactions which are currently under investigation for use in energy storage or transport applications.

TABLE I
POTENTIAL CANDIDATE REACTIONS (CATALYZED)

REACTION	T_{eq}° (K)
$C_2H_6(g) = C_2H_4(g) + H_2(g)$	1136
* $2SO_3(g) = 2SO_2(g) + O_2(g)$	1035
* $CH_4(g) + H_2O(g) = CO(g) + 3H_2(g)$	961
$CH_4(g) + CO_2(g) = 2CO(g) + 2H_2(g)$	961
$2H_2O(g) + 2Cl_2(g) = 4HCl(g) + O_2(g)$	896
$COCl_2(g) = CO(g) + Cl_2(g)$	801
$2NO_2(g) = 2NO(g) + O_2(g)$	778
* $C_6H_{12}(g) = C_6H_6(g) + 3H_2(g)$	568
$2NH_3(g) = N_2(g) + 3H_2(g)$	466
$CH_3OH(g) = CO(g) + 2H_2(g)$	415

*TECHNOLOGIES PERTINENT TO THIS REACTION ARE CURRENTLY UNDER DEVELOPMENT.

TABLE II
POTENTIAL CANDIDATE REACTIONS (GAS/SOLID)

REACTION ^(a)	T _{eq} ^o (K)
BaCO ₃ (s) = BaO(s) + CO ₂ (g)	1566
MgSO ₄ (s) = MgO(s) + SO ₃ (g)	1469
Li ₂ CO ₃ (s) = Li ₂ O(s) + CO ₂ (g)	1387
ZnSO ₄ (s) = ZnO(s) + SO ₃ (g)	1373
CaCO ₃ (s) = CaO(s) + CO ₂ (g)	1110
*M ^{II} (OH) ₂ (s) = M ^{II} O(s) + H ₂ O(g)	530–1000
MgCO ₃ (s) = MgO(s) + CO ₂ (g)	670
2LiH(s) = 2Li(l) + H ₂ (g)	645
MgH ₂ (s) = Mg(s) + H ₂ (g)	560
*NH ₄ X(s) = NH ₃ (g) + HX(g)	500–650
*MgCl ₂ · xNH ₃ (s) = MgCl ₂ · yNH ₃ (s) + (x–y)NH ₃ (g)	415–550
*CaCl ₂ · xNH ₃ (s) = CaCl ₂ · yNH ₃ (s) + (x–y)NH ₃ (g)	310–460
*RENi ₅ H ₆ (s) = RENi ₅ (s) + 3H ₂ (g)	215

* TECHNOLOGIES PERTINENT TO THIS REACTION ARE CURRENTLY UNDER DEVELOPMENT

(a) M^{II} = ALKALINE EARTH ELEMENT
X = HALOGEN
RE = RARE EARTH ELEMENT

TABLE III
POTENTIAL CANDIDATE REACTIONS (LIQUID/GAS)

REACTION	T_{eq}° (K)
$2\text{NaOH}(l) = \text{Na}_2\text{O}(s) + \text{H}_2\text{O}(g)$	1700
$2\text{LiOH}(l) = \text{Li}_2\text{O}(s) + \text{H}_2\text{O}(g)$	1000
$^*\text{NH}_4\text{HSO}_4(l) = \text{NH}_3(g) + \text{H}_2\text{O}(g) + \text{SO}_3(g)$	738
$\text{H}_2\text{SO}_4(l) = \text{H}_2\text{O}(g) + \text{SO}_3(g)$	615
$2\text{KO}_2(l) = \text{K}_2\text{O}_2(l) + \text{O}_2(g)$	515
$^*\text{H}_2\text{SO}_4(\text{dilute}) = \text{H}_2\text{SO}_4(\text{concen.}) + \text{H}_2\text{O}(g)$	—
$\text{NaOH}(\text{dilute}) = \text{NaOH}(\text{concen.}) + \text{H}_2\text{O}(g)$	—
$^*\text{NH}_4\text{Cl} \cdot 3\text{NH}_3(l) = \text{NH}_4\text{Cl}(s) + 3\text{NH}_3(g)$	~320

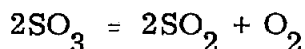
*TECHNOLOGIES PERTINENT TO THIS REACTION ARE CURRENTLY UNDER DEVELOPMENT.

III. Applications of Reversible Chemical Reactions

The previous sections have dealt with the potential advantages and state-of-the-art of reversible chemical reactions, and have discussed factors one must consider when selecting a chemical reaction for a particular application. This section will describe the principles of operation and the major physical characteristics of various storage systems which are based upon reversible chemical reactions. There are three major potential applications of reversible chemical reactions in solar energy systems: (1) thermal energy storage, (2) energy transport, and (3) heat pumping.

Conceptually, a thermal energy storage system may be represented as in Figure 4 which illustrates the use of a hypothetical reaction $AB = A + B$. 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 the operation to be repeated.

In reality, however, the thermal energy storage systems based upon reversible chemical reactions are far more complex than those depicted in the simple schematics of Figure 4. Figures 5 and 6 present one possible configuration for a system based upon the reaction



which is coupled with an energy source which provides 1173 K (900°C) helium.⁶ Figure 5 depicts the endothermic end of the storage system, and Figure 6, the exothermic end. As may be seen, this system consists of a number of reactors, condensers, vaporizers, heat exchangers, separation columns, compressors, and storage tanks. To maximize efficiency and cost effectiveness, great care must be taken in integrating the storage system with the rest of the energy conversion system.

The basic features of a chemical heat pipe are illustrated in Figure 7, with the hypothetical reaction $A + B = C + D$ used as an example. The chemical heat pipe may be used to transport solar thermal energy over long distances to an end user or to other parts of the solar energy system as is required in distributed systems. The components comprising the system are essentially identical to those described in Figure 4, with the storage tanks replaced by pipelines through which the reactants and products are transmitted and possibly stored. As with the thermal storage system discussed earlier, actual systems are far more complex, and again, great care must be taken to integrate the heat pipe into the total system.

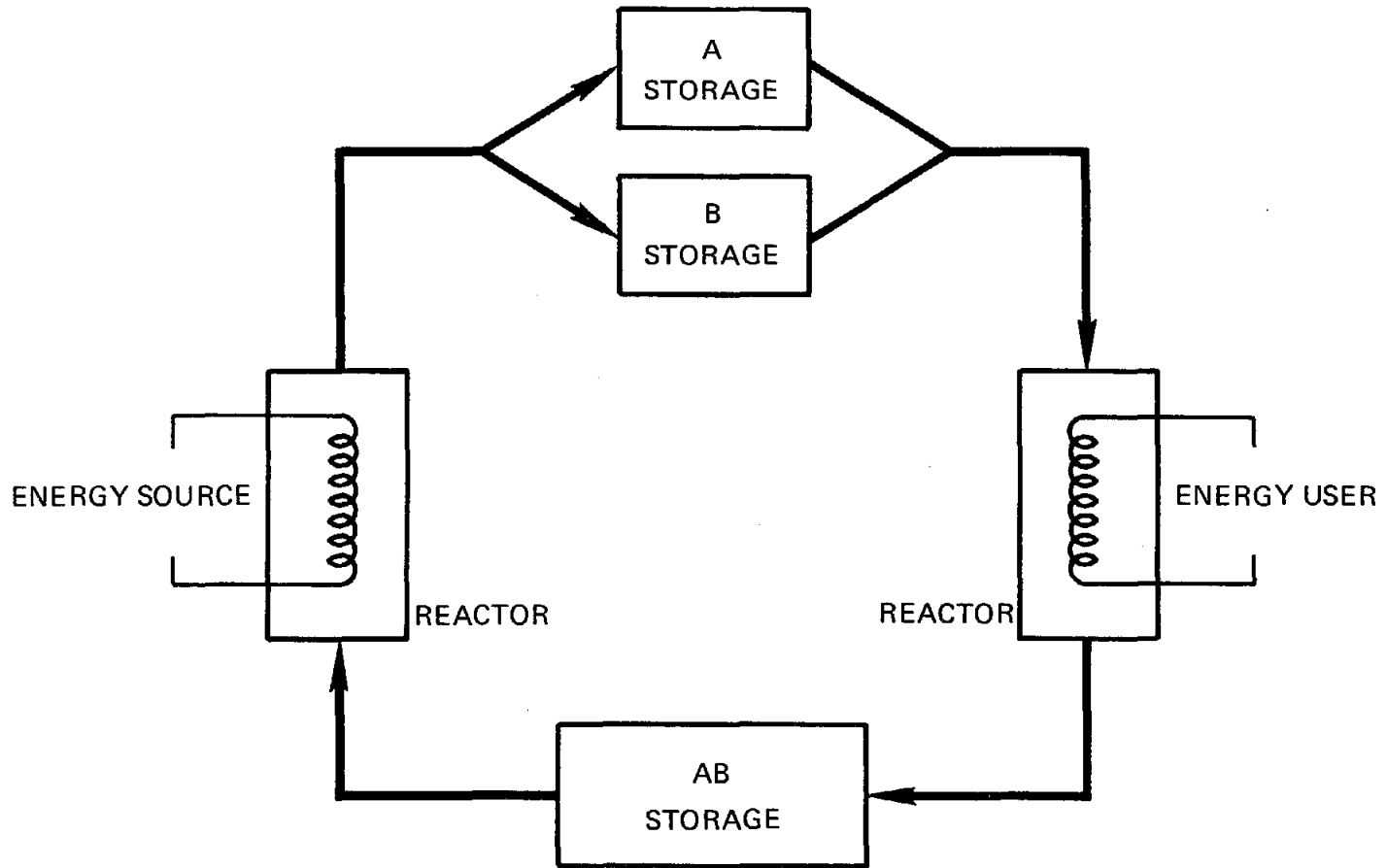


Figure 4. Thermochemical energy storage concept based on the reaction $AB = A + B$.

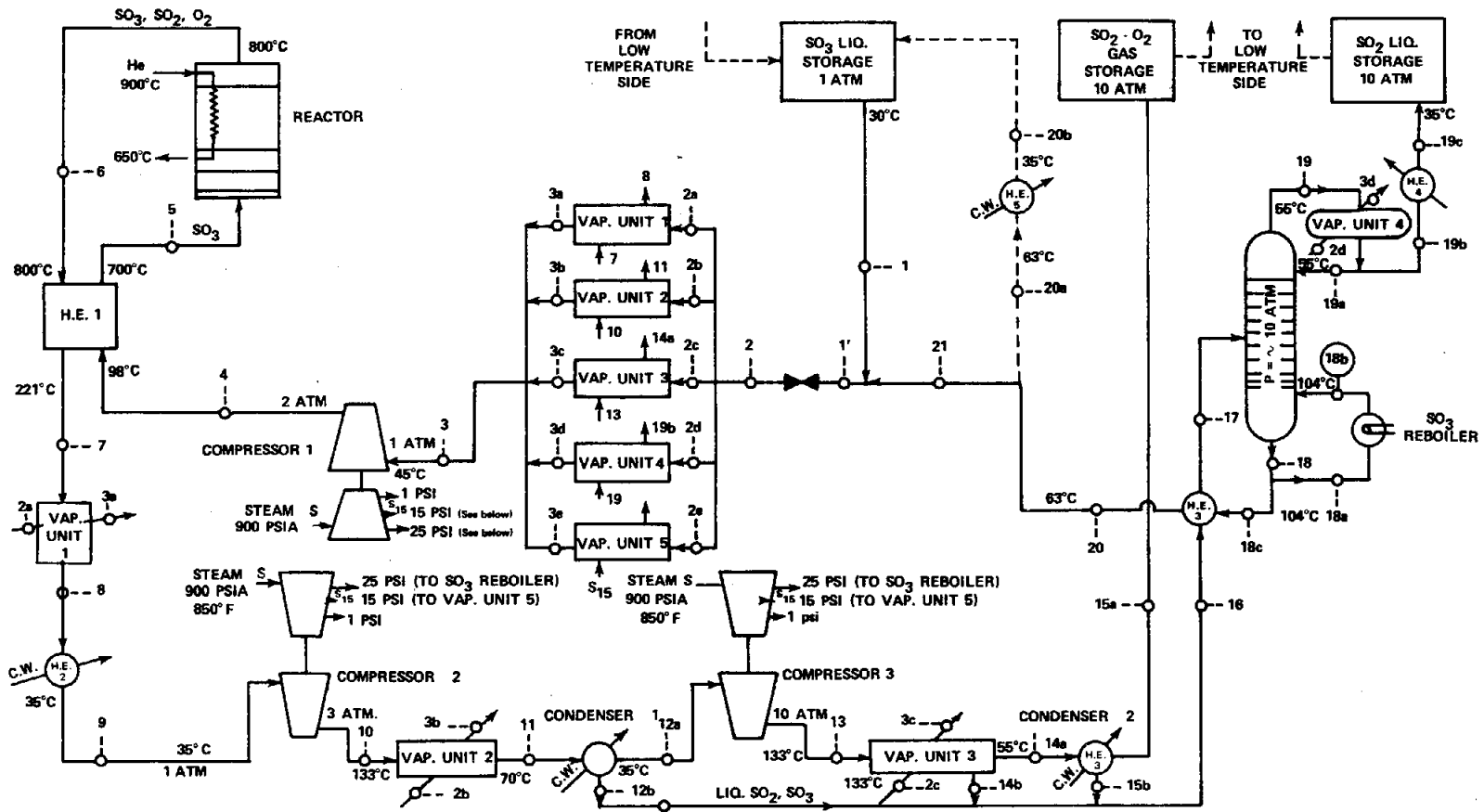


Figure 5. An endothermic reaction process diagram for a thermal energy storage system based on the SO_3/SO_2 reaction (Reference 6).

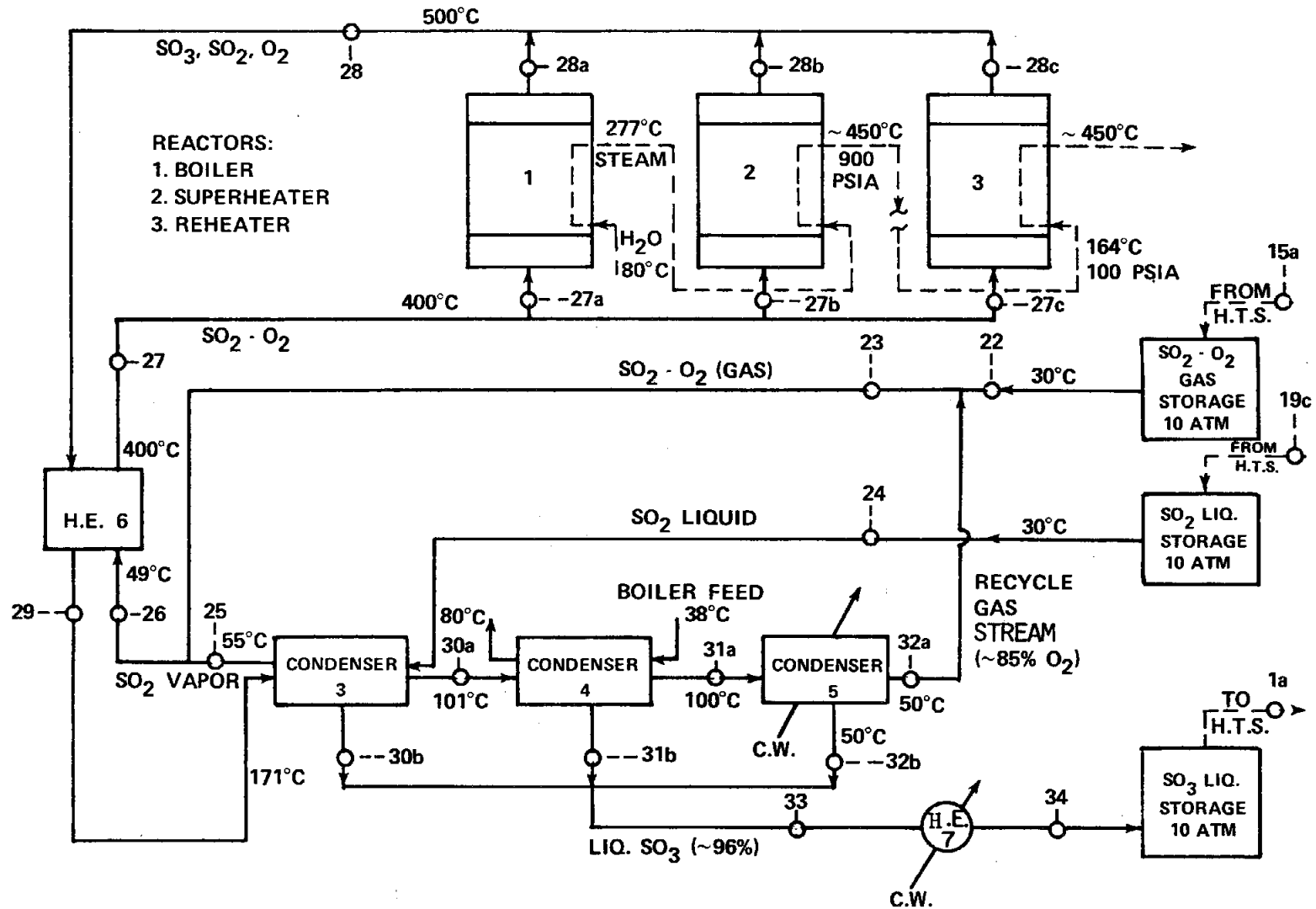


Figure 6. An exothermic reaction process diagram for a thermal energy storage system based on the SO₃/SO₂ reaction (Reference 6).

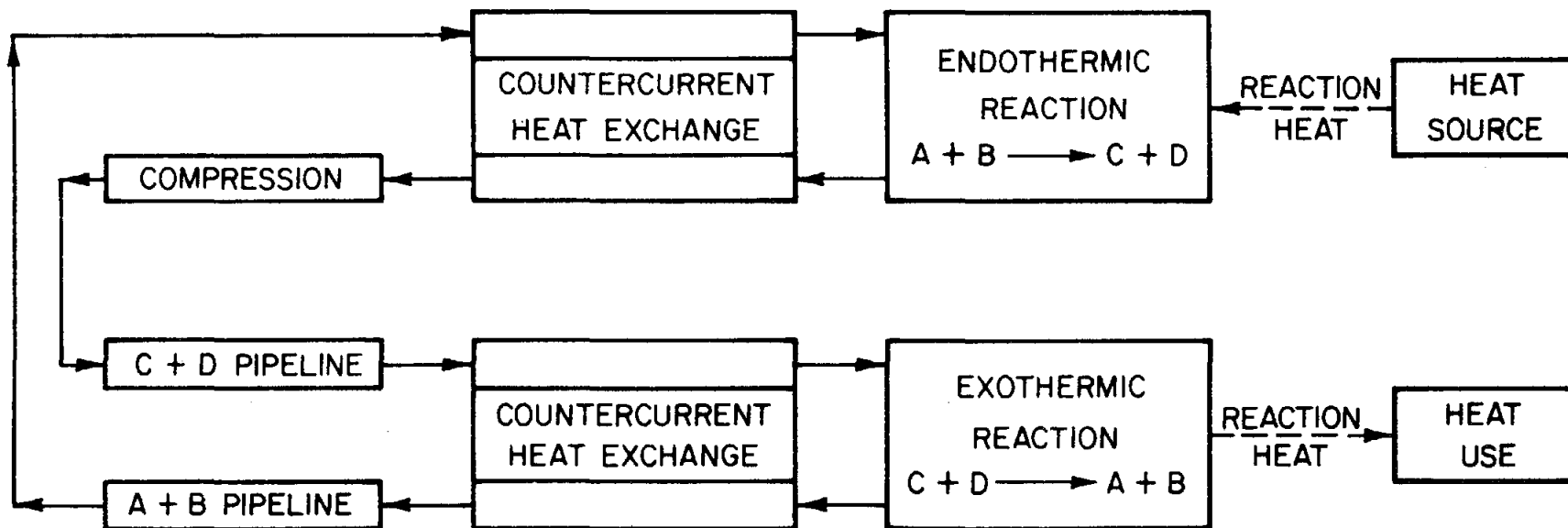


Figure 7. Closed-loop chemical heat pipe based on the reaction $A + B = C + D$.

The third major use of chemical reactions in solar applications is as a chemical heat pump. The chemical reactions required for such a storage system are represented illustratively by $AB = A + B(g)$ and $CB = C + B(g)$ [a special case is where the latter reaction is simply the vaporization of B, $B(l \text{ or } s) = B(g)$]. Further, these two reactions must have a common vapor species, $B(g)$ in this case. The reactions are selected so 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 so that their respective pressure/temperature relationships are compatible with the intended operating conditions. The components of a chemical heat pump system (high-temperature and low-temperature reactor heat exchangers, which may be fixed, moving, or fluidized beds, and a connecting pipeline) are illustrated in Figure 8. Also shown is the pressure/temperature relationship 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) and 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 8 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, shown on Figure 8 by the dashed arrow, 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.

One specific example of a chemical heat pump storage system currently under development is the sulfuric acid scheme,⁷ where AB is dilute sulfuric acid, A is concentrated sulfuric, B(g) is water vapor, and BC is condensed water. Figure 9 presents a photograph of a subscale (10^9 J) experiment which is currently under development and test. Shown on this photograph are the acid and water storage tanks, the reflux column to prevent acid carryover to the water tank, input/output heat exchangers, and the ducting for water vapor transport.

This brief discussion has presented some of the potential solar storage applications of reversible chemical reactions. The following section reviews the status of the various investigations underway which are concerned with developing and implementing these concepts.

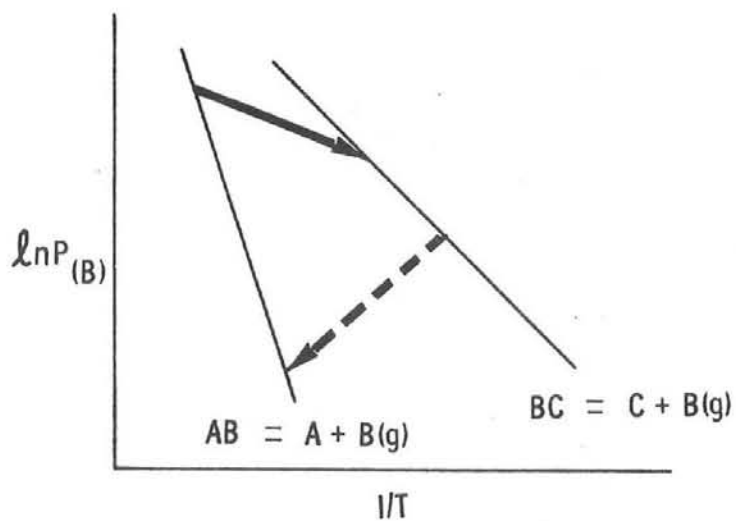
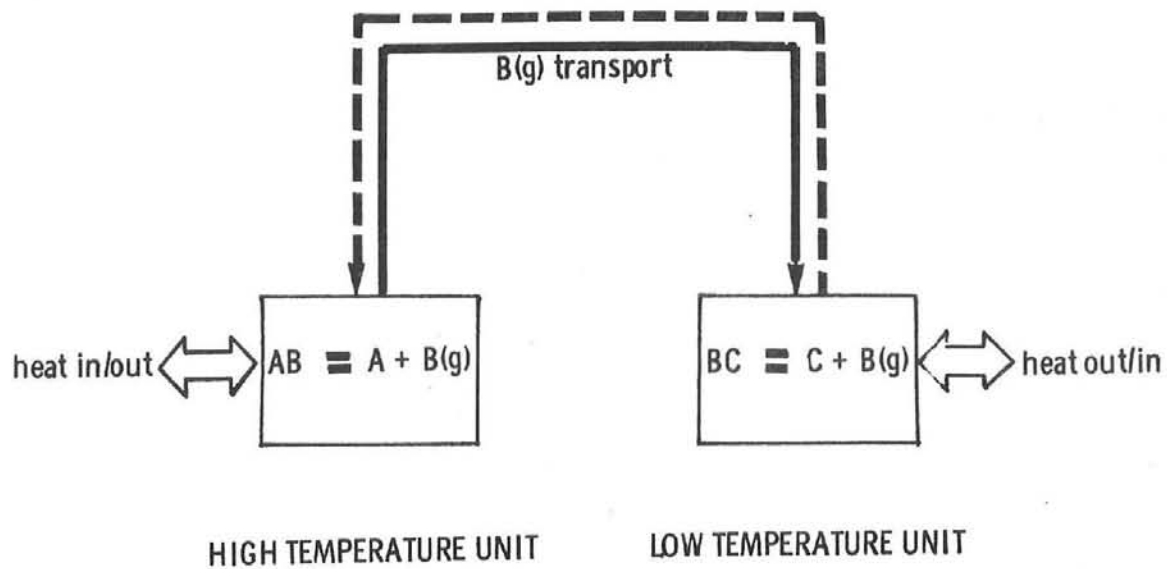


Figure 8. Chemical heat pump storage system based on the reactions $AB = A + B$ and $BC = B + C$.

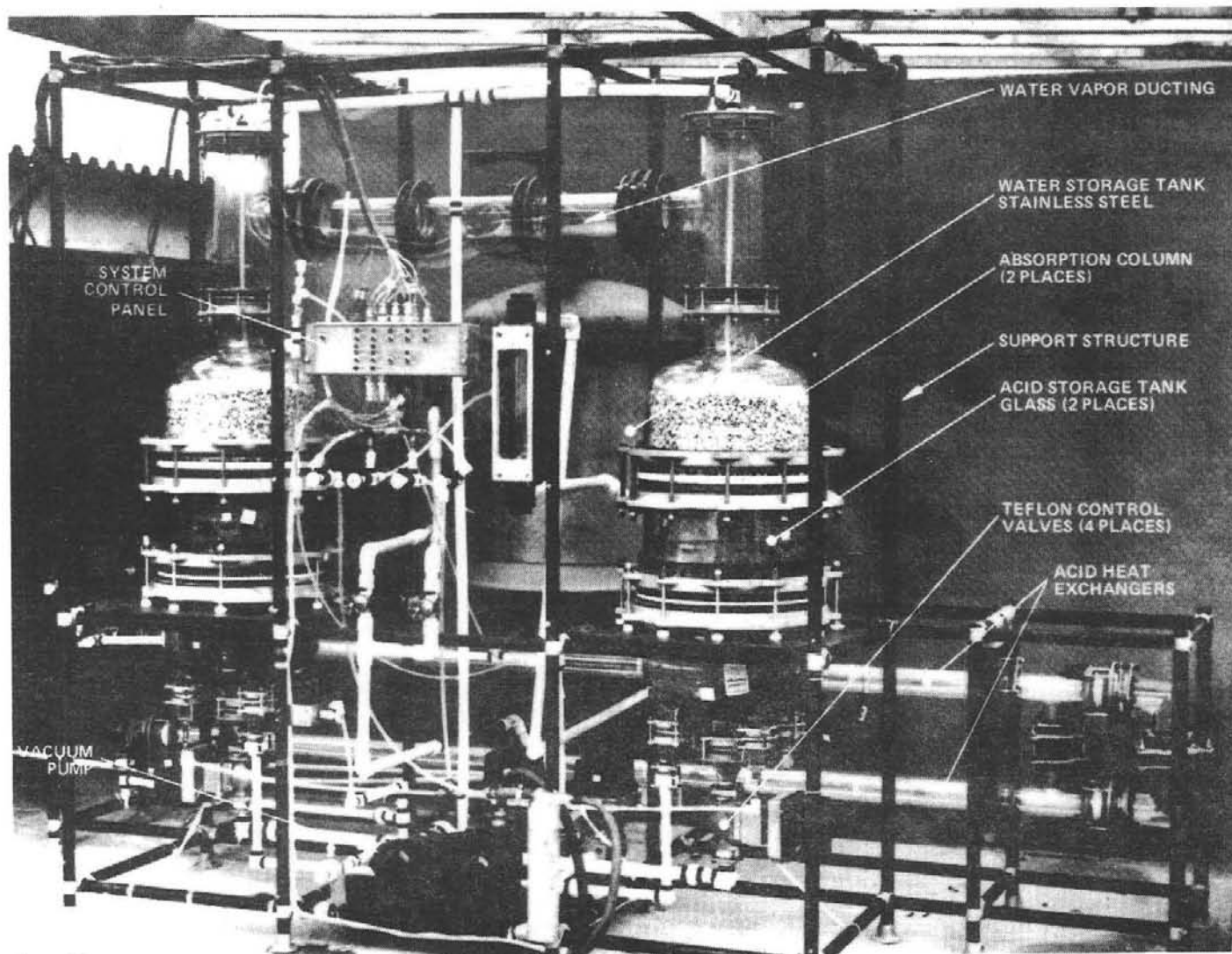


Figure 9. Sulfuric acid/water thermal energy storage system (Courtesy of the Rocket Research Company).

IV. Review of Current Activities

In this section we will briefly review all current research and development activities pertaining to thermochemical energy storage technologies relevant to solar applications which are known to the authors. System study activities will be discussed first, followed by technology development activities, and then by system development activities.

A. System Studies Activities

These activities are paper studies which explore the potential impact of thermochemical technologies in various solar applications.

Extended Storage for Solar Applications--A study is currently underway to evaluate the concept of chemical storage of solar energy on a total system basis.⁸ Technical considerations include selection of reactions or reaction sequences which may be useful for energy storage, evaluation of selected reactions on thermodynamic and kinetic bases, and preliminary design and modeling of energy storage subsystems based on these reactions. By means of a computer model of a solar-thermal power generation facility, the technical and economic feasibility of extending the solar-thermal conversion concept to include baseload power generation is being studied.

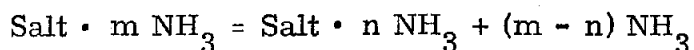
Advanced Storage Concepts for Solar Heating/Cooling--The DOE, Division of Solar Heating/Cooling has funded a study to determine the optimum role which advanced thermal storage subsystems can play in solar heating and cooling applications.⁹ To be considered are cold storage for air conditioning, cold-side storage in heat pump applications, hot storage for space heating and hot water, and air conditioning applications. The scope of advanced technologies to be considered will include thermochemical, phase change, and other advanced concepts. This study was initiated in September 1977, and at the time of this writing, conclusions were not yet available.

B. Technology Development Activities

Technology development refers to activities which are aimed at generating the basic data prerequisite to thermochemical storage system design, fabrication, and test. The bulk of the current effort is aimed at chemically characterizing potential chemical systems, although some work aimed at understanding fundamental heat-transfer characteristics is also underway. Technology development is distinguished from systems development (discussed in Section C) in that the former is "science"-oriented while the latter emphasizes "engineering" problems.

Hydrated Salts--Numerous salts form stable hydrates, but the $\text{MgCl}_2 \cdot n\text{H}_2\text{O}$ system has received the most attention to date, primarily because of its low cost and thermodynamic characteristics, which are matched with solar heating and cooling requirements. L. Greiner¹⁰ is attempting to design a chemical heat pump system based on $\text{MgCl}_2 \cdot n\text{H}_2\text{O}$ reactions. Preliminary experiments have suggested that chemical kinetics are sufficiently rapid; however, R. W. Carling¹¹ has given evidence of potential side reaction and irreversibility problems. More work is thus required to chemically characterize hydrated salt reactions before they can be seriously considered for storage applications. Uses are probably restricted to lower temperature applications, as hydrate salts are generally not stable at high temperatures.

Ammoniated Salts--Thermal energy storage and/or transport systems based on the generalized reaction



have been proposed by numerous investigators.¹²⁻¹⁷ The most promising solar-related application appears to be heating and cooling; higher-temperature applications do not appear feasible, since stable high-temperature salts are not known. The reaction kinetics for the dissociation and association of the following salts have been studied by the Martin Marietta Corporation staff:¹⁸ $\text{CaCl}_2 \cdot 8\text{NH}_3$, $\text{CaCl}_2 \cdot 4\text{NH}_3$, $\text{CaCl}_2 \cdot 2\text{NH}_3$, $\text{FeCl}_2 \cdot 6\text{NH}_3$, $\text{FeCl}_2 \cdot 2\text{NH}_3$, $\text{FeCl}_2 \cdot \text{NH}_3$, $\text{MgCl}_2 \cdot 6\text{NH}_3$, $\text{MgCl}_2 \cdot 2\text{NH}_3$, and $\text{MgCl}_2 \cdot \text{NH}_3$. Among these, the ferrous chloride ammoniate reactions did not behave reversibly, and undesirable side reactions took place. The calcium chloride salts behaved reversibly, and kinetic data for the reaction $\text{CaCl}_2 \cdot 8 \text{NH}_2 = \text{CaCl}_2 \cdot 4\text{NH}_3 + 4\text{NH}_3$ are shown in Figure 10. It is apparent that there is a significant amount of scatter in the data, suggesting potential problems if precise performance characteristics are required. The magnesium chloride salts too behaved reversibly and reproducibly; and as an example, the kinetic data pertaining to the reaction $\text{MgCl}_2 \cdot 6\text{NH}_3 = \text{MgCl}_2 \cdot 4\text{NH}_3 + 2\text{NH}_3$ are shown on Figure 11. The Martin Marietta program has advanced to a point where the characteristics of coupled reactions are being studied. A two-reactor system has been assembled, in which candidate salt pairs are being cycled; chemical behavior and energy balance data are being generated.

On the basis of the experimental work to date, it is clear that one cannot predict kinetic data from analogous reactions; each candidate reaction must be investigated on an individual basis. One must also be concerned with the presence of moisture, since it has been shown to significantly alter the kinetic characteristics of certain reactions,

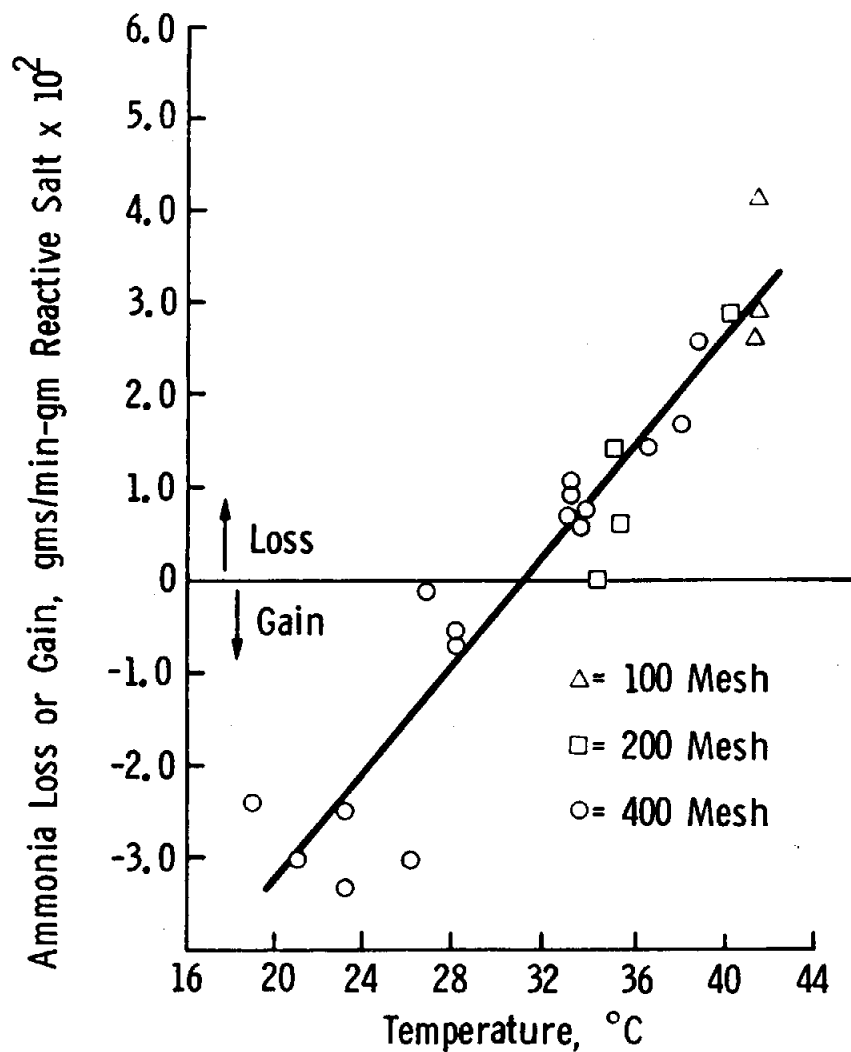
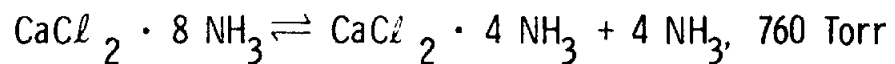


Figure 10. Forward and reverse reaction rate data for the reaction $\text{CaCl}_2 \cdot 8\text{NH}_3 = \text{CaCl}_2 \cdot 4\text{NH}_3 + 4\text{NH}_3$ (Reference 18).

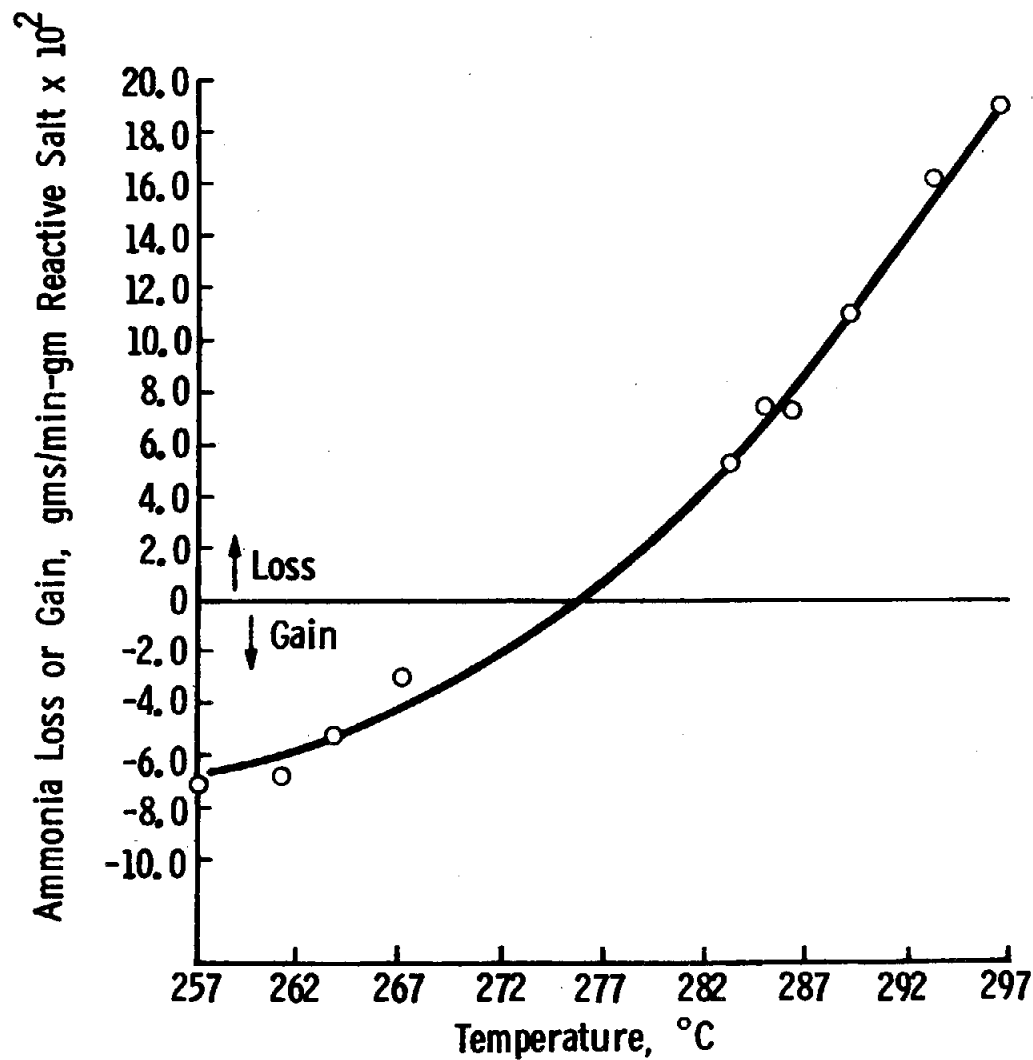
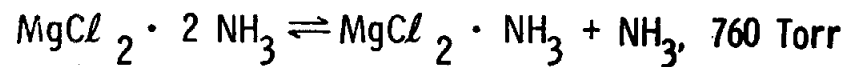
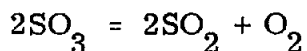


Figure 11. Forward and reverse reaction rate data for the reaction $\text{MgCl}_2 \cdot 2\text{NH}_3 = \text{MgCl}_2 \cdot \text{NH}_3 + \text{NH}_3$ (Reference 18).

magnesium chloride reactions, to be specific. Another potential problem which occurs during the initial ammoniation of a salt bed is sintering, which has been observed on occasion and results in an inert mass. This sintering effect is not well understood, and warrants further attention.

Methanolated Salts--Methanolated salts (salt \cdot n CH₃OH) are possible alternatives to hydrated salts and ammoniated salts. However, there is a paucity of data on methanolated salts. Not only are they ill characterized, but even their existence is not well established. P. Offenhartz and co-workers¹⁹ have initiated a study to identify potential salt systems and thermodynamically characterize them. The ultimate objective of their effort is to develop a methanolated salt heat pump based upon a single-substrate/methanol reaction for use in solar heating/cooling applications. Preliminary results indicate there are several potentially useful salts, viz., MgCl₂, CaBr₂ and FeBr₂; however, it is premature to draw conclusions at this stage.

SO₃ Decomposition--Several investigators have examined the use of the reaction



in storage^{6, 20-22} and transport²³ applications, and system design flow sheets for energy storage applications have been derived. To illustrate the complexity of the SO₂/SO₃ thermochemical system, the process flow diagrams developed by M. L. Bhakta⁶ are given in Figures 6 and 7 for the endothermic and exothermic ends of the system. A flow diagram has also been developed in which the endothermic and exothermic processes are carried out in the same reactor.²⁰

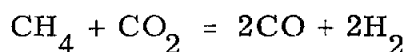
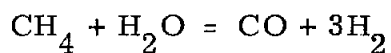
Two materials problems must be addressed before one can commit to the development of an SO₃/SO₂ energy storage system: (1) Are inexpensive and effective catalysts available for the high temperature endothermic reaction, and (2) Are materials of construction which can withstand the corrosive sulfidation/oxidation environment available? These two questions are currently being addressed by Schmidt²⁴ and Bradshaw.²⁵

Even if these materials problems were solved, it is not clear that a concerted development effort will materialize. Preliminary results indicate that the capital cost of an SO₃/SO₂ energy storage system may be excessively high.²² Therefore, strong justification (technical and economic) is needed for the continued development of the system.

Dilution/Concentration--Coupling solar energy to dilution/concentration reactions is not new. Concepts and devices based on the absorption-refrigeration cycle have long been proposed for intermittent solar refrigeration.²⁶ Various refrigerant-absorbent combinations have been studied, including ammonia-water, ammonia-lithium nitrate, water-lithium bromide, Freon 21-tetraethylene, glycoldimethyl ether, and ammonia-sodium thiocyanate.²⁷⁻³¹ However, work to date on the dilution/concentration reactions has generally not explored the potential of incorporating energy storage or heat pumping capabilities.

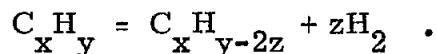
It is possible to store energy in aqueous solutions of acids (e.g., H_2SO_4) or bases (e.g., NaOH). By adding or distilling water from a solution, one is discharging or storing a quantity of energy equivalent to the enthalpy of dilution. The technical basis for such a process is well understood. Also, heats of solution are well known, and calculational procedures for predicting quantities of input and output energies under various operational conditions (e.g., initial and final concentration) are straightforward.^{32,33} Further, there are no reaction kinetic problems to contend with. Though enthalpies of dilution are not typically as large as enthalpies of decomposition, and one cannot expect enormous energy densities, concentration/dilution schemes offer the advantage of being all-liquid systems in the heat exchanger, thereby facilitating the rates of heat transfer in and out. Operational temperatures will in all probability be restricted to low temperatures because of potential materials corrosion problems.

Methane-Based Reactions--Several methane-based reactions have been proposed for use in energy storage applications; among them are



To drive both reactions, high-temperature energy sources (~900 K) are required. Both are catalytically controlled, and the pertinent chemical technology (reaction rates, side reactions, reversibility, catalyst selectivity, catalyst availability, etc.) is sufficiently developed to allow one to design and engineer a storage system based upon them. However, a cost-effective use of these reactions in a strict storage application has not been identified; moreover, such an application does not seem imminent. Storage would require the containment of gaseous reactants and products, and gas compression and storage are generally prohibitively expensive. Thus the use of methane-based reactions will most likely be restricted to energy transport applications.³⁴⁻³⁷

Organic Hydrogenation/Dehydrogenation Reactions--It is well known that numerous organic compounds can be catalytically decomposed and recombined according to the generalized reaction



The one reaction often cited is the dehydrogenation of cyclohexane to benzene.^{38, 39} These reactions are catalytic in both the exothermic and endothermic directions, and commercial technology generally exists with regards to catalyst availability, reaction conversion rates, catalyst performance, reaction selectivity, and so on.

It is, however, doubtful that existing technology is really pertinent to storage applications, since the requirements are completely different. Once-through conversion efficiencies, which are important in current industrial applications, are meaningless when one considers storage applications wherein the extent of the side reactions and conversion efficiencies in a cyclic operation are of concern. One must therefore build a new chemical data base which is relevant to thermal energy storage. For this purpose, current industrial technologies do form an excellent base from which to proceed.

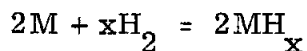
The fact that gaseous hydrogen must be compressed and stored is a major problem. The unfavorable economics associated with compressing and storing hydrogen suggest that this class of reactions should not be seriously considered if energy storage is the only application of interest; applications requiring the transport of energy may be feasible. The DOE, Division of Energy Storage Systems, under the technical management of Sandia, is contemplating several studies to address energy transport in chemical heat pipes using the benzene/cyclohexane reaction.^{40, 41}

Inorganic Hydroxides--The alkali and alkaline earth elements form hydroxides and oxides which can theoretically be dehydrated and hydrated, respectively.⁴² Only the $Mg(OH)_2/MgO$ and $Ca(OH)_2/CaO$ systems have been investigated to date,⁴³⁻⁴⁶ and preliminary studies indicate the rates of reaction (hydration and dehydration) to be sufficient for solar heat storage applications. Superheated steam is required to accomplish the hydration of both MgO and CaO . However, MgO was found to be inert in highly superheated steam, a result indicating that an upper temperature limitation to the exothermic reaction exists. The practical implication is that the efficiencies of $Mg(OH)_2/MgO$ -based systems are unacceptably low, since the exothermic (hydration) temperature will necessarily be significantly lower than the endothermic (dehydration) temperature.

CaO does not appear to be inert to highly superheated steam, and current activities are aimed at fully characterizing the $CaO/Ca(OH)_2$ reaction.^{40, 41} Although the optimum application for the $CaO/Ca(OH)_2$

reaction has yet to be defined, the high-temperature storage requirements of solar power generating systems make them leading candidates.

Hydride Decomposition--A large number of metals and alloys react reversibly with hydrogen thus:



where M is a metal or alloy. Numerous alloys have been studied in detail, for example, Fe-Ti alloys,⁴⁷ Mg-Ni alloys,⁴⁸ and AB₅ compounds,^{49, 50} where A is one or a mixture of rare earths and B is Ni or Co. It is reasonable to assume that one can obtain virtually any desired pressure-temperature relationship by varying the alloy composition. Predictive methods (e. g., correlating thermodynamic properties with average lattice hole size), which are on the verge of surfacing, will allow one to select suitable metal compositions with reasonable confidence.

Experimental evidence to date suggests that hydriding and dehydriding kinetics are rapid. Hysteresis effects have been observed between the absorption and desorption reactions, but the kinetics in either case are sufficiently rapid for most solar storage applications.⁵¹

Hydride reactions are being applied to vehicular propulsion^{52, 53} and to off-peak energy storage for hydrogen-oxygen fuel cell power generation.^{51, 54-55} However, the use of hydrides in thermal energy storage applications imposes different chemical and systems constraints. D. Gruen et al.^{56, 57} have been developing a hydride-based solar heat pump system (referred to as HYCSOS). After selecting the LaNi₅ and mischmetal Ni₅ hydrides, suitable chemical reaction characteristics were proven experimentally, and a subscale system is currently under test. Preliminary results indicate that operational goals will be met; however, the cost of such a system appears to be unacceptably high. Libowitz and Blank⁵⁸ have evaluated hydride-based storage systems relative to sensible and latent heat systems, and also conclude that system economics are unattractive.

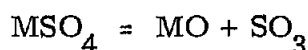
In summary, hydride systems, while apparently technically feasible, appear to suffer from poor economics due to costs associated with the chemicals, heat exchanger/reactor components, and hydrogen containment. In addition, questions concerning long term performance and stability are as yet unanswered.

Carbonates--Alkali metal and alkaline earth elements all form stable carbonates which decompose to form one mole of CO₂ gas per mole carbonate. Carbonate compounds are generally quite stable, and high-temperature sources are needed for energy storage applications. Carbonates generally require temperatures in excess of 1100 K.

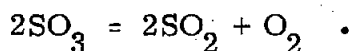
Numerous investigations have been performed to study the endothermic decomposition reactions,⁵⁹ but the only carbonate for which there is data pertinent to use in an energy storage concept is CaCO_3 .^{60,61} Thermal cycling did not alter the rate of the endothermic process, which was reasonably rapid in all instances; however, thermal cycling led to a continuous decrease in the exothermic reaction rate.

In summary, the carbonates have not received much attention to date, and clearly the chemical characteristics of such systems will have to be investigated in greater detail. However, as with most gas/solid type reactions, the major problems will probably not be chemical in nature, but will be associated with heat transfer design.

Sulfates--Upon heating, metal sulfates decompose, and the two reactions which must be considered simultaneously are⁶²



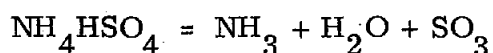
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The sulfates are very stable compounds and high temperature sources are required to drive them (generally > 1400 K). A suitable thermal energy source does not seem imminent, and therefore, no research has been directed at metal sulfate-based storage. Given the high-temperature requirements and the corrosive nature of sulfidizing/oxidizing environments, the outlook for sulfate based storage systems is not promising.

Oxide Decomposition--The decomposition of metal oxides has been proposed for energy storage⁶³ applications and the peroxides and superoxides of the alkali metals were suggested as prime candidates. To date, technical feasibility has yet to be demonstrated, and no projects are actively pursuing oxide decomposition concepts. In addition to the normal concerns such as reaction rates, storing gaseous oxygen, and gas/solid heat exchange, the oxides are extremely reactive to water and carbon dioxide, and great care must be taken to exclude them in an operational system.

Other Reactions--Wentworth and Chen,⁶⁴ and Prengle and Sun,⁶⁵ have discussed the use of the reaction



which operates around temperatures of 800 K. The attributes include extremely high energy densities, readily condensible gaseous products which facilitate storage, and liquid-phase heat exchange. Developmental work is

in progress,⁶⁶ and several major problems are identified. Among these are (1) in actual practice the reaction does not proceed as written, and efficient chemical steps must be found to effect the separation; and (2) sulfur/oxygen-containing salts are generally extremely corrosive to materials of construction.

The reaction $N_2 + 3H_2 = 2 NH_3$ has been proposed as an energy transport concept,⁶⁷ but its use solely in energy storage applications is probably limited because of the large costs associated with compressed gas storage and the high operational pressures of this system.

Heat Exchange Modeling and Experiments--Several activities are under way which are concerned with the problem of heat exchanger or reactor design. Springer, et al.⁶⁸ are performing a preliminary analysis of fixed-, moving-, and fluidized-bed reactors. Howerton^{40, 41, 69} and Prenger^{40, 41, 70} are developing a mathematical model for packed-beds and experimentally determining effective conductivities and solid/gas heat transfer coefficients at imbedded surfaces. Wentworth and co-workers⁷¹ are computing solar flux profiles for point focused collectors, and will use this information for reactor design. Offenhartz¹⁹ will be performing lab-scale experiments to obtain engineering design data for packed-bed systems.

C. System Development Activities

System development refers to activities which are "engineering" oriented. The activities range from single component design and evaluation, to total-system design. Very little work is ongoing in this area, because much of the thermochemical technology data base is just now being developed.

Several system development efforts are under way for chemical heat pump storage systems. A number of subscale systems have been designed and fabricated, and are currently being tested to generate operational and performance data. These systems include the sulfuric acid/water storage system,⁷ the HYCSOS system,^{56, 57} and the $CaCl_2 \cdot 6H_2O$ heat pump system.⁷² In addition, L. Greiner¹⁰ is currently testing and designing components integrated into a $MgCl_2 \cdot xH_2O$ chemical heat pump system. It is too early to report conclusive findings from these activities.

The paucity of data and activities reported in this system development section is an accurate reflection of the state-of-the-art of thermochemical systems.

V. Summary and Conclusions

Thermochemical systems possess several unique characteristics when compared to sensible and latent storage systems; these include: (1) high energy densities, (2) ambient temperature storage, (3) long-term storage, (4) transportability, and (5) low energy capacity related costs. The potential advantages must be weighed against the facts that thermochemical systems are furthest from state-of-the-art and, in general, are more complex than sensible or latent systems.

The potential applications of thermochemical reactions include: (1) thermal energy storage systems, (2) energy transport systems, and (3) heat pump and storage systems. The principles of each of these applications were discussed above.

Before the advantages and disadvantages of thermochemical storage systems can be quantified, technology development is required in the following areas:

1. Chemistry - Generally speaking, no such reaction is presently well enough 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, moreover, additional questions concerning catalyst lifetime, degradation, and poisoning must be addressed.
2. Heat Transfer - Equally important to the thermochemical energy storage system are the chemical reactors and process-stream heat exchangers. Generally speaking, design techniques are available for predicting system performance. What is lacking, however, is information regarding such things as the thermo-physical and transport properties of the various constituents of the chemical system and the effects of catalyst performance, reaction kinetics, long-term cyclic operation, to name a few, on heat transfer. Small-scale experiments are required to verify theoretical predictions before large-scale systems are designed and constructed.
3. Materials - Material compatibility and corrosion problems can be significant, the degree depending upon the temperatures of the storage operation and the chemicals involved. Ambient storage, however, mitigates the material problems to the extent that the corrosive conditions may now 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, viz., the reactor and heat exchangers.

4. Chemical Engineering - Almost all thermochemical reaction cycles for storage or transport applications contain steps which are potentially wasteful of energy and the net result is a much reduced effective energy density. Operational cycles must be optimized, and the recovery and re-use of potential rejected energies are necessities for the development of economically viable thermochemical energy storage and transport systems.
5. Systems Analysis - System studies are required to establish the technical and economic feasibility of a proposed concept, to identify required research, and to establish the relative merits of the proposed system as compared with competing technologies. These studies must continue throughout the development process in order to filter in new information as it becomes available and to ensure that the concepts being developed will be economically viable.

In summary, thermochemical technology is at a very early stage of development, and much is needed in the way of technology development before one can accurately assess the potential of thermochemical techniques, let alone develop thermochemically based concepts to the point of commercialization.

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