Final Report

on the

STORAGE OF SOLAR ENERGY FROM

A SOLAR CHEMICAL REACTOR

Report Prepared

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Governor's Energy Advisory Council Forecasting and Policy Analysis Division Austin, Texas under Contract No. (IAC-76-77-(1148)

March, 1977

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STORAGE OF SOLAR ENERGY FROM A SOLAR CHEMICAL REACTOR

ABSTRACT

Solar energy is of great potential benefit to the State of Texas in the satisfaction of energy requirements in such diverse end-use areas as agriculture, industry and the individual dwelling. Since solar energy is derived from an intermittent source, the maximum benefit from the solar energy can be realized from a system which provides for the storage of energy over periods when the source itself is not available.

Traditional methods of storing energy have centered on thermal storage using rocks, oil, water, phase changes, etc. These methods have generally proved to be both expensive and inefficient because of the low energy density and the need to store at the collection temperature. Alternatively, energy can be stored in chemical reactions. Generally, more energy can be stored in a chemical reaction and this leads to a higher energy density, i.e. more energy can be stored in a given volume of products. Furthermore, the products of the reaction usually can be stored at room temperature, thus eliminating the need for well insulated containers. The Solar Energy Laboratory at the University of Houston has already found a promising chemical storage system to function as an integral part of the Solar Thermal Tower at 1000°K, the design operating temperature of a full-scale tower producing electricity, by using a set of specifically desirable thermodynamic and physical reaction properties.

In this study, we have: 1) identified three additional areas for the application of solar energy, 2) modified the criteria for choosing chemical reactions for storage of solar energy to conform to these

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applications, 3) searched for chemical reactions based upon these criteria, and, 4) found the best reactions, to our knowledge, for each application. In addition to screening these reactions from a feasibility point of view, we have considered the economic and practical aspects of the reactions of choice. Only preliminary experimental work has been done on these reactions so that their success is not assured but these reactions are certainly the best that we have at present. The impact of one of these applications, solar heating and cooling, upon the energy use in the State of Texas has been evaluated. The reactions and applications are:

- 1. Solar Heating and Cooling with Slightly Concentrating Collectors NH_4HCO_3 (1) = $NH_3(g) + H_2O$ (1) + $CO_2(g)$
- 2. Solar Heating and Cooling with Moderately Concentrating Collectors $H_3PO_4 \cdot H_2O(1) = 1/2 H_4P_2O_7(1) + 3/2 H_2O(1)$

3. Solar Cooking and Agricultural Drying

$$(NH_4)_2SO_4(1) = 3/4 NH_4HSO_4(1) + 3/4NH_3(g) + 1/4 (NH_4)_2SO_4(1)$$

4. High Temperature "Synthetic Fuel" $NH_4PO_3(0) = NH_3(g) + 1/2 H_2O(g) + 1/4 P_4O_{10}(g)$ or $CaCO_3(s) = CaO(s) + CO_2(g)$

Problems of separation of the products of reaction at the temperature of the decomposition have been considered and a number of possible methods have been proposed. In addition, the problems of side reactions, reliability of thermodynamic data, and the stability of the products of the reaction over numerous cycles is certainly recognized and some possible experimental methods for studying these factors have been proposed.

THE STORAGE OF SOLAR ENERGY FROM A SOLAR-CHEMICAL REACTOR

INTRODUCTION

The only source of energy which is guaranteed to last as long as there is life on earth is solar energy. Indeed, practically all of the sources of energy on the earth today can be traced back to solar energy. There are two basic problems with the use of solar energy, the diffuse nature of the energy and the intermittent nature of the energy. Various solar collection systems have been devised to concentrate and collect the solar energy but the development of an efficient means of solar energy storage so that the supply of energy is continously available is still lacking.

A number of different types of storage systems have been propsed in the past and have been implemented. Indeed, the fossil fuels which we are currently using for energy represent a natural manner in which solar energy has been stored over the lifetime of the earth. The majority of energy storage systems constructed have been based upon physical changes such as storage in the heating of rocks or fluids, or phase transitions such as the melting of eutectic salts. These systems are generally very inefficient in that large masses or volumes of material are needed to store adequate amounts of energy. An alternative to these systems is the storage of energy in chemical compounds. Note that the natural system of fossil fuel is essentially a chemical system.

Last year in the solar energy laboratory program, we took this approach and set forth a number of desirable thermodynamic and physical properties for a chemical reaction which could be operated cyclically to store and retrieve energy which was collected in a solar tower so that electricity could be generated in a conventional Rankine cycle. On the basis of these criteria, we examined a number of possible chemical reactions and were able to find one, the decomposition of ammonium acid sulfate (AHS), which met these criteria. Further study of the AHS system and reduction to practice is being carried out.

During the course of our studies, we noted that there were many reactions which met certain of our specified criteria but not others and were, therefore, discarded for the specific application. However, these same reactions could be much better than the conventional methods of storage for other specific applications of solar energy.

Therefore, we have looked at other possible applications of solar energy and have specifically chosen three distinct areas for possible study. These are: 1) Solar Heating and Cooling, 2) Solar Cooking and Agricultural Drying, 3) High Temperature Generation of a "Synthetic Fuel" via solar energy at temperatures greater than about 1000°K. The first two systems are characterized by a relatively low temperature for the generation of heat. As a consequence, the decomposition reaction can take place at a much lower temperature. The latter system would be more sensitive to the energy per unit mass of the products. It appears that the latter system could also be applied to the conversion of "dirty" fuels to a "clean" form of energy. The collection devices for the first two systems are currently available and are constantly being improved. The collection system for the third system could be developed.

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The first step in our program was the modification of the criteria used to find the AHS system to correspond to the specific needs of these three examples. Many of the criteria are the same and especially crucial to the selection of suitable reactions is the concept of the turning temperature, $T^* = \frac{\Delta H^\circ}{\Delta S^\circ}$ which can be calculated from standard thermodynamic tables. The particular applications and collection systems essentially set upper and lower limts for this quantity so that reactions can be immediately classified. With the specific criteria for the exact application, we screened possible reactions. As a result of the screening, we found the best reactions suitable for exploitation.

The specific reactions and applications are:

- 1. Solar Heating and Cooling with Slightly Concentrating Collectors NH_4HCO_3 (1) = NH_3 (g) + H_2O (1) + CO_2 (g)
- 2. Solar Heating and Cooling with Moderately Concentrating Collectors $H_3PO_4 \cdot H_2O(1) = 1/2 H_4P_2O_7(1) + 3/2 H_2O(1)$
- 3. Solar Cooking and Agricultural Drying

 $(NH_4)_2SO_4$ (1) = 3/4 NH_4HSO_4 (1) + 3/4 NH_3 (g) + 1/4 $(NH_4)_2SO_4$ (1)

4. High Temperature "Synthetic Fuel"

 $NH_4PO_3 = NH_3(g) + 1/2 H_2O(g) + 1/4 P_4O_{10}(g)$ or

 $CaCO_3(s) = CaO(s) + CO_2(g)$

These reactions are technically feasible but in some cases the side reactions remain a major question and the problem of the separation of the products of the decomposition at that temperature is still unanswered. We have, however, investigated a number of general separation processes for gases at various temperatures. These include distillation, thermal diffusion, chromatography, gravity separation, membrane separations, and gas centrifuges. We have also developed and planned a number of experiments to obtain data to extend these basic recommendations to the point of practical application. These are the design of the high temperature vapor pressure measurement apparatus and the use of differential thermal analysis to verify the thermodynamic properties of the reactions. In addition, preliminary ideas for the modification of commercial thermal analysis equipment to test the stability of the reactants and products in repeated cycles have been proposed.

In the following sections, we will present a more thorough discussion of each of these areas.

CRITERIA FOR REACTIONS TO STORE CONCENTRATED SOLAR ENERGY

Before getting into the general criteria, it should be emphasized that the type of reactions considered in this study are uncatalyzed reactions, and, thus, the products must be separated at the temperature of the reaction in order to prevent back reaction. In addition, reactions involving solids were given a lower priority in this study. However, the thermodynamic and physical criteria are just as applicable to catalyzed and uncatalyzed reactions.

The major modification in the criteria given in this paper rests in the value of the turning temperature. Thus, it is necessary to define two new temperatures, T_c , the temperature of the collector, and T_u , the temperature of the use or application. These values are given in Table 1.

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ТΔ	21	5	1
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Application	Т _с	Tu
Solar Heating and Cooling Slightly Concentrating Collector	1 3 0 C	50 to 130 C
Solar Heating and Cooling Moderately Concentrating Collector	300 C	50 to 250 C
Solar Cooking and Agricultural Drying	350 C	100 to 350 C
High Temperature "Synthetic Fuel"	1000 C	400 to 1000 C

The first and second criteria are thus modified in terms of these temperatures to read:

- 1. The forward reaction for storing the energy should occur with a high yield at $\rm T_{\rm C}>T\star$
- 2. The reverse reaction for generation of heat should occur with a high yield at $T_u < T^*$ or using the thermodynamic relationship for the turning temperature, T*,

$$T \star = \frac{\Delta H^{\circ}}{\Delta S^{\circ}} \begin{cases} \Delta Cp = 0 \text{ (change in heat capacity)} \\ K = 1 \text{ (Thermodynamic equilibrium constant} \\ when K = 1, T = T^*) \end{cases}$$

- 3. Large ΔH° to maximize storage capacity.
- 4. Small molar volume (∇) of products (perferably liquids) to minimize storage volume.

maximum
$$\frac{\Delta H^{\circ}}{\overline{V}}$$

 Reaction should be completely reversible with no side reactions in order for the materials to be used for long periods of time.

- 6. Reactions should be fast enough so that the absorption of solar energy and regeneration of the heat can be carried out rapidly. This requires a low activation energy or a catalyst for the reaction.
- 7. For an uncatalyzed reaction the products must be readily separated prior to storage. For a catalyzed reaction the product mixture must be stable during the storage period.
- Preferably the compounds involved in the reactions can be handled with known technology not requiring sophisticated equipment.
- Preferably the compounds should not be highly reactive towards water or oxygen. Both water and oxygen are difficult to exclude completely from any closed system.
- 10. The compounds should be commercially available in the quantities needed and preferably at a low cost.

If a chemical reaction can satisfy these ten criteria, it should be considered as a viable candidate for solar thermal storage. In the present stage of our research, we have evaluated various thermal decomposition reactions, seeking reactions that best satisfy these ten criteria.

SPECIFIC REACTIONS FOR THE STORAGE OF SOLAR ENERGY FOR VARIOUS APPLICATIONS Solar Heating and Cooling

One of the major applications of solar energy today is the heating and cooling of buildings. This has been made possible through the use of flat bed or moderately concentrating collectors. The temperature of the collectors must be nominally 130°C for cooling by absorption airconditioning systems while the requirement for heating is nominally above ambient temperatures. For these applications, the storage of heat

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is in rocks, water, or other fluids. It is especially difficult to find a chemical reaction for storage in this temperature range since the heat of reaction decreases with the temperature of the decomposition. Yet, we have found one reaction which meets many of the ten criteria. This is the decomposition of ammonium bicarbonate according to the reaction:

> NH_4HCO_3 (1) = NH_3 (g) + CO_2 (g) + H_2O (1) $\begin{cases} t = 130^{\circ}C \\ p = 50 \text{ atm} \end{cases}$

At atmospheric pressure, the decomposition occurs at about 60-70°C but at a pressure of 50 atms, the reaction can be made to proceed at about 130° C. The ammonia and carbon dioxide can then be liquefied and stored after separation. A distillation scheme for separation has been reported in the literature and requires about 15-16 kcal/mole.² This leaves a net value of about 15-16 kcal/mole.³ If a more energy efficient process of separation can be found, the net energy for storage can be increased. Alternatively, the ammonia could be separated from the water and carbon dioxide by the formation of an alkali metal bicarbonate. This appears feasible but is not proven. The water and carbon dioxide is freed with solar energy at 150°C. It should be noted that the heat of vaporization of the liquid ammonia and the liquid carbon dioxide also can be used for refrigeration or cooling. However, the relatively high pressure required for this reaction is a distinct disadvantage for home usage. For example, the normal freon air-conditioning system operates at a pressure of about 10 atms. The rather complicated separation scheme is also a major disadvantage of this system, but it is necessary to prevent the reaction between NH_3 and CO_2 to give ammonium carbamate. The advantages of the reaction are that for this temperature range, it has a relatively high heat of reaction, the materials are readily available and harmless, a separation system is known, and the reactants and products can be stored as liquids.

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Another promising reaction for the heating and cooling application requires the use of moderately concentrating collectors since the decomposition temperature is in the range of 180° to 280° C. This involves the decomposition of phosporic acid (85%) into water and pyrophosphoric acid according to the reaction⁴

180°-280°C

 $H_{3}PO_{4} \cdot H_{2}O(1) = 1/2 H_{4}P_{2}O_{7}(1) + 3/2 H_{2}O(g)$

The separation process for this reaction is quite simple since the products are a gas and a liquid. The water will be condensed and the back reaction will involve a liquid, thus lowering the ΔH of the reaction by the heat of vaporization of water. This is one of the disadvantages of the system. The range of temperatures for the decomposition is due to the fact that a liquid product is formed. While this might appear to be a distinct disadvantage, it should be noted that this feature allows one to design for the middle or high portion of this range, and still have some decomposition and hence storage occurring at lower temperatures. In other words, the reaction will work even if the sun goes behind a cloud for a few minutes. This feature makes the reaction ideal for heating. One of the difficulties with the system is the rather low heat of reaction, 11-18 kcal/mole depending upon the decomposition temperature. In addition, the product, $H_4 P_2 O_7(1)$ must be stored hot in order to remain fluid. A major advantage is the availability and cost of phosphoric acid.

Solar Cooking and Agricultural Drying

Solar cooking is one of the simplest applications of solar energy but it must be generally accomplished with direct sunlight. That is,

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there is no convenient storage system for this application. Daniels⁵ stated the requirements for such a system as follows, "Solar cooking might be greatly advanced if it were possible to place a heat absorbing unit on the solar cooker for any two or three sunny hours of the day and then carry it into the kitchen and keep it in an insulated box to be used later. The problem of developing such a heat storing device has not yet been solved. The vessel must have sufficient heat storage in a volume small enough not to shadow an appreciable part of the solar collector and a weight small enough to be supported on the grill and easily lifted and carried. Its insulation must be sufficient to prevent serious loss of heat during exposure to the focused sunlight, but after enough heat has been accumulated it can be set in a fully insulated box or corner of the floor so the heat losses after removal from the cooker will be small. Finally, it must be capable of storing heat equivalents to 1 kwhr of heat or more at a temperature high enough to permit effective cooking later. It is desirable to regulate the rate at which the heat is made available for cooking with such stored heat."

Solar drying of hay and other crops has been practiced since the beginning of agriculture, but in the modern day farm, considerable energy is spent in heating air to dry crops in a controlled manner. If a storage system could give a temperature in the range of 350°C, it could be used profitably for both of these applications. Such a reaction is the partial decomposition of ammonium sulfate. Here again, the chemical is a major item of commerce and is relatively inexpensive. The reaction can be written as

 $(NH_4)_2SO_4$ (1) = 3/4 NH_4HSO_4 (1) + 3/4 $NH_3(g)$ + 1/4 $(NH_4)_2SO_4$ (1) The reaction cannot be driven to completion because of side reactions

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that take place at higher temperatures and because of the production of a liquid as the product. The pressure of the ammonia above the reaction mixture will only be about 0.5 atm at 340°C. Thus it will be necessary to compress the ammonia in order to liquefy it. The energy for the vaporization of the ammonia could come from room temperature and provide cooling. This reaction will also take place over a range of temperatures, and will have a convenient separation process. The heat of reaction is relatively high, 20-25 kcal/mole. The product should be stored at a temperature above the melting point of the NH₄HSO₄ (~150°C)

In order to eliminate the work of compressing the NH_3 from 0.5 atm to a liquid at 10 atm, the NH_3 can be reacted with a salt such as $CaCl_3$ at room temperature.⁷ The NH_3 is not held firmly to the $CaCl_2$ and it can be taken off at a pressure in excess of 0.5 atm by simply increasing the temperature slightly above room temperature. It is in this manner that the reverse reaction would be initiated. The liberated NH_3 would then react with the $NH_4HSO_4(1)$ to produce the desired heat at 100-350°C. High Temperature "Synthetic Fuel"

The discovery of a high temperature reaction which cculd be used to act as a "synthetic fuel" would be a distinct incentive for the development of higher temperature solar collectors. One possible reaction in this temperature range is the decomposition of ammonium metaphosphate⁸ as follows:

 $NH_4PO_3(1) = NH_3(g) + 1/2 H_2O(g) + 1/4 P_4O_{10}(g)$

The temperature for this decomposition is in the range of 700°C and is, thus, slightly lower than the desired temperature. The back reaction is known to occur at temperatures greater than 400°C and the heat of reaction

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is relatively high. Thus this reaction would be suitable for application from room temperature to the range of 600°C. There is a distinct problem with separation. There are no known techniques which could operate at temperatures around 700°C. One possibility is by gas density or diffusion or gas centrifuges, but these are not proven. There is also a possibility of decomposition of the ammonia at this high of a temperature.

The second reaction which can be used as a synthetic fuel is merely an example of a number of reactions of this type which were discussed in reference 1. The major disadvantage of the reaction is the formation of a solid from a solid, that is the reactant and product are both solids. This reaction is

 $CaCO_{3}(s) = CaO(s) + CO_{2}(g)$

If the reaction is carried out at about 50 atm then the carbon dioxide can be liquefied. The energy density for this reaction is quite good and there are no serious separation problems. In working with reversible reactions of solids, there is a tendency for the particle size of solid to increase due to crystallization. This has a deleterious effect since the reactive surface of the solid is decreased. To overcome this the solid is attached to an inert support such as silica.¹⁰ This presents the solids from recrystallization and retains the reactive surface area.

Two other potential chemical reactions for storage of solar energy were discussed at the Joint Conference 1976 of the American Section of ISES and the Solar Energy Society of Canada held recently in Winnipeg. These are:

Solar Heating and $\operatorname{Cooling}^9$

 H_2SO_4 (a H_2O) = $H_2SO_4((a-x)H_2O) + xH_2O(g)$

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and Solar Cooking and Agricultural Drying¹⁰

 $Ca(OH)_{2}$ (s) = CaO (s) + H₂O (g).

The first reaction operates in a temperature range of 180-320°C. It has a relatively good energy density, 60-110 kcal/liter and does not have a separation problem. It is quite analogous to the phosphoric acid reaction. The second reaction was also discussed in reference 1 and suffers the disadvantage of dealing with solids. The use of adsorbents improves the solid handling properties of the material but reduces the energy density.

At this point it is instructive to compare the various types of storage. In Table 2, the temperature of use, the temperature of collection and the temperature of storage are given for various materials.

Storage Medium	T u (°C)	т _s (°С)	T _c (°C)	∆H/V (kcal/lite	Comments r)
Sensible Heat Storag	<u>e</u>				
H ₂ 0 (1)	30-100	100	100	70	l atm Pressure
Pebbles, Ceramic	100-400	400	400	90	1/3 void
Iron	100-400	400	400	273	solid
Aluminum	100-400	400	400	194	solid
Pebbles, Ceramic	100-200	200	200	30	1/3 void
Iron	100-200	200	200	91	solid
Aluminum	100-200	200	200	65	solid
Latent Heat of Fusio	n Storage				
Heats of Fusion of Solids	MP	MP	MP	60-100	Inorganic MP 30-200°C
	MP	MP	MP	50- 60	Organic MP 30-200°C
Chemical Reaction St	orage				
NH4HCO3	30-120	30	130	400	Credit for NH ₃ Vaporization for cooling
H ₃ P0 ₄ •H ₂ 0	200	150	180-280	100-200	Lower value for lower temperature
H ₂ SO ₄ ·aH ₂ O	100-200	30	180-320	90-270	Lower value for lower temperature
(NH ₄) ₂ SO ₄	250	150	3 00-350	350	Energy to condense NH ₃ not subtracted
NH4HSO4	400	150	400-500	740	No credit for NH ₃ cooling
Ca(OH) ₂	400	30	500	470	H₂O stored as liquic ∆H°=16.4 kcal/mole
NH4P03	600	150	700	740	No Credit for NH ₃ Cooling
CaCO ₃	600 +	30	850	780	CO ₂ stored as liquic AH ⁶ =41.5 kcal/mole

The Comparison of Properties of Various Storage Processes

MP = melting point

The advantages of the chemical systems are the high heat storage per unit volume and the low temperatures of storage. The use of large volumes of metals such as iron or aluminum is precluded by heat transfer problems. This could be circumvented by using pebbles of this material but the storage volume would have to be increased. For these materials and for the heats of fusion, the temperature of storage is the temperature of collection. In addition, the temperature for use for the heats of fusion is the melting point. For comparison purposes, the $\Delta H^{\circ}/V$ is 10^4 kcal/liter for gasoline and about 10^3 kcal/liter for natural gas stored at 100 atm. Thus, the best chemical system is close to methane but about an order of magnitude lower than gasoline.

GAS PHASE SEPARATION PROCESSES

In a recent textbook on separation processes,¹¹ the following schemes for the separation of gases were listed: distillation, absorption, adsorption, gaseous diffusion, sweep diffusion, thermal diffusion, mass spectrometry, and gas permeation. These processes and the concept of large scale chromatography and gaseous centrifuges have been considered for use with thermal decomposition reactions. Mass Spectrometry can be easily eliminated on the basis of energy requirements.

The use of distillation, adsorption and absorption are quite common in the chemical industry. The major concern in these cases is the amount of energy required. A second factor is the temperature of the separation process. These systems are certainly applicable to the low temperature reactions but the high temperature reactions may cause some problems. In general, the separation factors in the reactions of interest are large enough to use these techniques.

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Two systems which are on the frontier of separation processes are the use of membranes and the use of large-scale chromatography. There is a definite temperature limitation based upon the stability of the membranes and the fact that the separation factor decreases as the temperature increases. In addition, multistage membrane separations are not energy efficient. The large-scale chromatographic technique is quite promising. The greatest problem is the newness of the equipment. There are also problems with obtaining column materials for high-temperature chromotography.

The separation of isotopes of uranium suggests two other methods of gas separation, thermal diffusion and gas centrifugation. Equipment exists for making this separation in which the separation factor is just slightly larger than unity so that these processes should be highly effective with compounds such as ammonia and sulfur trioxide where the separation factor is much greater than one. However, the energy and temperature questions are still present.

In the future, we will have to obtain much more information on each of these separation processes and try to determine the most energy efficient and practical methods to effect the necessary separation. On a more general scale, the energy requirements for separation may turn out to be the deciding factor in choosing a particular reaction for the storage of solar energy.

EXPERIMENTAL STUDIES

Although this project did not involve experimental work, we have obtained some data which has been useful in selecting the specific reactions recommended for the various applications. We have determined the vapor pressures of some of the reactants as a function of temperature

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and have obtained some thermal data which confirms the thermodynamic data. We have also planned a number of experiments to determine the stability of the reactions under cyclic conditions.

In the vapor pressure apparatus, a given amount of material is heated and the pressure of the gases given off is determined. Provisions for heating the sample to about 1000°C have been made. These measurements have led to the limitations placed upon the decomposition of ammonium sulfate since side reactions were noted at about 350°C. In addition, these studies have pointed out the difficulties in translating differential thermal analysis data to large scale decompositions.

In the differential thermal analysis experiment, a sample and a reference are heated at a constant rate and the difference between the temperature of the sample and the temperature of the reference is continuously recorded. The area of the curve is a measure of the heat of the reaction while the peak temperature is related to T* in certain cases. In any case, the temperature range of the decomposition is given by the data. We have obtained such data for the three lower temperature reactions of interest and this data essentially confirms the thermodynamic data given in the standard tables.

We have also made detailed plans to study the reactions of interest in sealed containers in a cyclic manner in order to determine if the reactions can be recycled without deomposition. The control module will be the same commercial unit that was used in the differential thermal analysis studies. The output will be continously recorded so that any loss in energy will be noted. With a sealed container, there will be no need to separate since the back reaction will be made to occur by simply lowering the temperature.

The results of the experimental work are shown in Figures 1 and 2.

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IMPACT OF ENERGY STORAGE

The impact which energy storage would have on the use of solar energy must be considered individually for each application. However, the same approach would be taken in each of the applications, only the demand rate over the period of a year would vary. In this report only the impact from the use of solar energy for heating and cooling will be considered.

The impact of energy storage should be considered from three standpoints: (1) storage for a 24-hour period to offset the nightime period, (2) storage for 2-3 days to offset cloudy periods, (3) storage during the fall and spring to offset the peak power demand for cooling in the summer months. Each of these will be discussed separately as it would apply to an apartment complex of ten units, each containing a living area of 1800 ft². Since the energy storage unit may be somewhat complex, it will probably find its immediate use in larger units such as apartment complexes. Furthermore, space is more critical in apartment complexes compared to individual homes. Consequently, the highest energy density found in chemical storage systems will be most important so that the volume of the storage material can be kept reasonably small. This also will be an important factor for heating and cooling other large facilities, such as office buildings.

The monthly demand rate for heating and cooling a 10-unit apartment complex containing 18,000 ft² in the Houston area is shown in Figure 3. Note that the peak demand occurs in the July and August months. The demand in this period is approximately 95 x 10^6 BTU/month, which corresponds to a daily peak demand = 3.17 x 10^6 BTU/day. The insolation rate varies

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tremendously from the winter months to the summer so that there is also a significant winter demand. The insolation rate curve depends upon the solar collector area. In Figure 3 the insolation curve has been adjusted in magnitude so that the annual demand equals the collection.

Our first consideration is energy storage for 24 hours to offset the nightime period. If we are to accommodate the peak demand of July and August, this corresponds to a storage of 3.17×10^6 BTU. If the storage efficiency were only 75% and the energy density 400 kcal/l (see Table 2) the volume of chemicals stored would be 93.6 ft³ = (4.5 ft)³. If the energy density were only 100 kcal/l the volume of storage would be 375 ft³ = (7.2 ft)³. Neither of these volumes seems to be prohibitive and chemical storage for a 24-hour period is very reasonable.

Energy storage by a conventional technique such as heating rods has an energy density of 30 kcal/l and this would require a volume of $1250 \text{ ft}^3 = (10.8 \text{ ft})^3$. This is reasonably large but again does not seem to be prohibitive as long as underground storage is possible. For an energy storage period of 24 hours, chemical storage would be more convenient than conventional techniques but its impact would not be great. For much larger facilities, say 10 times this demand, the impact would be more significant.

For a 3-day storage we simply increase the previous demand and storage volumes by a factor of three. Now the storage volume by conventional means becomes $3750 \text{ ft}^3 = (15.5 \text{ ft})^3$. This seems to be intolerable considering the confined space of an apartment complex. However, with a chemical system with an energy density of 400 kcal/l the storage volume would be 281 ft³ = (6.5 ft)³. This seems to be well within reason and a chemical storage system would permit 3-day storage and essentially a

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stand-alone system for heating and cooling.

Finally, we consider the use of a chemical storage system for annual storage for the peak demand in the summer and winter periods. In this case, the conventional storage is impractical since the material must be stored hot in insulated containers. This seems impractical for storage over a 4 to 7 month period where the heat loss would be intolerable. In order to use a chemical system for annual storage we consider the possibility of storing energy when the demand is less than the solar energy supplied. The heat integrated over these periods is then supplied to the periods where the demand exceeds the collected solar energy. In Figure 3 we have shown the rate of collected energy by the dashed curve. Note that the demand exceeds the supply in the periods of June to September and November to February, and it is for these periods that we must use the stored energy. By using the stored energy to supply the excess energy required for these peak periods, we can decrease the total area of the solar collectors, thus decreasing the cost of the solar system.

For the 10-unit apartment complex considered previously, the excess energy that must be stored for the February to June period is approximately 70 x 10^6 BTU. For a chemical storage system with an energy density of 400 kcal/l and a storage efficiency of 75%, the storage volume would be approximately 2,000 ft³ = (12.6 ft)³. This storage volume corresponds to the volume of a typical bedroom (16' x 16' x 8'). This does not seem to be unreasonable, considering the fact that energy is supplied for a year-round basis.

If the storage system were not used, the solar collectors would need to supply the peak demands of 9.5 x 10^7 BTU/month in July and

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 6.7×10^7 BTU in January. However, if the chemical storage system of energy density 400 kcal/l were used, the solar collectors need supply only 7.5 x 10^7 BTU/month in July and 3.7 x 10^7 in January (dashed line). This is a reduction of about 20% and 45% in solar collectors for these periods which would be a significant decrease in cost. Since the collectors would be oriented to increase the insolation rate in January at the expense of the insolation in July, the reduction would be on the order of 30%. It is not possible to evaluate precisely the dollar saving because it will depend upon the cost of the solar collectors and the cost of the storage system.

In conclusion we can see that a chemical storage system would make a significant impact on the use of solar energy for heating and cooling by making it a stand-alone system with a storage capacity of about 3 days. Furthermore, the storage system could make an impact on the cost of using solar energy by storing energy on an annual basis for use in peak summer and winter demands.

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Figure 1. Log Vapor Pressure of Ammonium Sulfate versus Reciprocal Temperature



Figure 2. DTA of Ammonium Bicarbonate, Phosphoric Acid and Ammonium Sulfate, Equimolar a month.



Figure 3. Monthly Heating and Cooling load for an 18,000 ft² Apartment Complex in the Houston area. Each apartment contains 3 bedrooms and 2 baths.

