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HEAT STORAGE MATERIALS

By
C. E. Birchenall

December 1977

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Work Performed Under Contract No. EY-76-S-02-4042

College of Engineering
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Newark, Delaware

U. S. DEPARTMENT OF ENERGY

Division of Energy Storage Systems

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Heat Storage Materials

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Abstract

The range of usable alloys for high temperature heat storage was limited first on the basis of price and availability. Then published binary and ternary phase diagrams and a limited amount of thermal data were used to calculate maximum heat storage densities from a thermodynamic equation for the eutectic transformation. The latent heats of transformation were measured by differential scanning calorimetry or differential thermal analysis for the most promising alloys. Specific heats of the solid and liquid alloys were determined for all systems except $\text{Mg}_2\text{Si-Si}$. The measured heat storage densities, on both a mass and volume basis, were compared with those reported for other inorganic thermal energy storage media, which are mainly halides, hydroxides and carbonates. The alloy that melts at the lowest temperature ($\text{Mg/Mg}_2\text{Zn}$, 616K) is not outstanding relative to the other materials that transform in the same temperature range, and its temperature of transformation is too high to couple with water-cooled nuclear reactors (PWR and BWR, 505-544K). The highest temperature material ($\text{Mg}_2\text{Si/Si}$, 1206K) has good heat storage densities. It probably transforms at too high a temperature for use with advanced nuclear reactors, but it might be useful for solar thermal generation using an open Brayton cycle. In the intermediate temperature range, which is compatible with conventional fossil-fueled supercritical steam reactors (755-853K), four systems appear to surpass previously reported materials, (Al/Cu/Mg , 779; Al/Cu , 821; Al/Si/Mg , 833; Al/Si , 852).

The intermediate and high temperature alloys also may be useful for heat storage in connection with highway vehicle propulsion and the processing of cement, steel and nonferrous alloys. The specific heats of the alloys do not differ greatly from those of the salts, but their thermal conductivities are much better.

A new system has been developed to measure volume change during transformation and coefficients of thermal expansion of materials that have adequate ductility. X-ray absorption in a slab-shaped sample held in a refractory cell has been demonstrated on pure aluminum ($\Delta V/V_s = 0.079$) to be reproducible to within about 3 to 4 per cent and probably capable of easy improvement to about 1 to 2 per cent. A less precise measurement with an early version of the apparatus gave $\Delta V/V_s$ equal to 0.051 for the Al/Cu eutectic (compared with 0.075 for pure aluminum in that system).

Heat transfer and crystallization characteristics of a Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), borax, and thickening agent (an attapulgite clay) mixture have been studied. An apparatus to measure steady-state heat conduction was constructed and operated. Qualitatively the mixture has a thermal conductivity greater than water, but quantitative analysis of the data is not complete. The thickening agent modifies the growth morphology so that long needles of Glauber's salt are not produced. The clay fibers segregate to the grain boundaries during the first freezing cycle to form a set of microcells that remain during subsequent thawing-freezing cycles if the container is not shaken. Some macrosegrega-

tion of thickener takes place during the first cycle as fibers are pushed ahead of the advancing crystals. Using a vegetable dye to follow the solidification front, the rate of freezing was measured for different amounts of undercooling below the peritectic equilibrium temperature (31.4 C). Undercooling to 29°C did not start crystallization in the presence of borax. At 26° and 23°C the thickness of solid increased roughly as the square root of time, faster with greater undercooling, probably controlled by diffusion of heat from the advancing interface. At 26°C crystallization velocity was the same over 5 cycles. A mixture containing enough excess water to prevent precipitation of anhydrous sodium sulfate during the thawing cycle crystallizes more slowly than the standard mixtures.

Scope of the Work

The tasks undertaken in this study were to:

- 1: Carry out a literature survey on the properties of fusible metal alloys for use as TES (thermal energy storage) media in the temperature range above 400F.
- 2: Determine transformation heat of reaction and specific heats for selected binary metal alloys. Measure density changes at the transformation temperature for selected metal alloys.
- 3: Fully disclose the specific and detailed nature of the Glauber salt, nucleating agent and thickening agent discussed in the University of Delaware unsolicited proposal CS-U6-0098.
- 4: Determine the thermodynamic and transport properties of the salt mixture discussed in task 3.

Summary of Results

This part of the final report deals with the work done on tasks one and two and a part of the work done on tasks four in the College of Engineering. The whole of task three and the balance of the work on task four has been carried on in the Institute of Energy Conversion under the direction of Dr. Maria Telkes. She will submit the balance of the report as a separate item.

Tasks one and two are treated together as a single study of high temperature storage of heat utilizing metallic alloys mainly at eutectic composition. The systems to be investigated were limited on the basis of cost and availability of the elements to be included. Using the available binary and ternary phase diagrams, the heats of fusion of the elements and of a few intermetallic compounds, the transformation heats were estimated from an approximate thermodynamic model of the eutectic transformation. This preliminary estimate established the desirability of alloys that contain substantial amounts of aluminum and/or silicon for high heat storage per unit mass. Magnesium also is an acceptable ingredient. When storage is considered on a unit volume basis, copper and perhaps zinc appear to be useful as well.

Binary and a few ternary eutectics that stood out in the approximate calculations were melted from metals of good but commercial purity. Only in the case of silicon does it appear that impurities were present in sufficient concentration to affect the measured values. For measurements of heat of transformation that could be completed below 1000K the Perkin-Elmer DSC-2 (differential scanning calorimeter) was employed. All of the binary eutectics on the initial list and two ternary eutectics

were measured with excellent precision. Furthermore, in this range of temperature the DSC gave specific heats of liquid and mixed solid phases with reasonable precision. One alloy on the initial list, $\text{Mg}_2\text{Si-Si}$, had a transformation temperature above the operating limit of the DSC, so it was measured with lower precision on a DuPont DTA (differential thermal analyzer). Specific heats were not obtained with useful precision in that case.

Comparison of the heats of transformation and specific heats (the latter is likely to be a relatively minor contribution in many applications) of the alloys with those reported for other inorganic phase change materials in the same temperature range does not clearly identify the best material to use. Nevertheless, on the basis of heat storage capacity alone the alloys seem to enjoy an advantage from about 779 to 852K. Al/Cu/Mg (779), Al/Cu (821), Al/Si/Mg (833), and Al/Si (852) have high maximum mass and volumetric storage densities. The Mg/Si eutectic at 1206K has good storage density, although lower than the theoretical estimates. Magnesium loss during the high temperature measurements and the relatively low purity of the silicon may contribute to low values of heat storage and also transformation temperature. At 616K the Mg/Zn eutectic gave disappointing results, far below the initial estimates. If alloys are to be competitive in this range or lower, more complex mixtures are required.

The specific heats do not differ enough from those of the halides, hydroxides and carbonates to be noteworthy. The comparison is pertinent only where large temperature swings would

make the sensible heat compare in magnitude with the latent heat. The thermal conductivities favor the metals by an order of magnitude or two. This contribution affects the choice of heat exchanger surface area and the amount of containment material needed.

Volume change during transformation also should have major effects on system design. A new x-ray absorption technique was devised to measure this change directly with one sample instead of using the difference between solid and liquid densities, each measured independently, usually by different methods and on different samples. The crude apparatus built for demonstration suggested that, contrary to our initial expectations, the method should be sufficiently precise, if modified carefully, to enable thermal coefficients of expansion of both solids and liquids to be measured. After preliminary measurements on pure aluminum and the aluminum-copper eutectic, modifications were made to the system in several stages, the elimination of each source of error revealing another smaller but significant one that was masked. Although the refinements are not complete, the improved apparatus has been tested thoroughly on pure aluminum and seems to perform close to the projected level. The volume change measured for pure aluminum agrees with the previously published values that appear to have been determined most carefully. Additional improvements are possible, but the limitations henceforth should be determined mainly by the ability to prepare sound alloy samples.

I. Heat Storage in Alloys

by C. Ernest Birchenall and Alan F. Riochman

Introduction

Heat storage can be used in several ways to reduce the costs of operating energy generating, converting and distributing systems. When joined to a large-scale, central-station heat generator e. g. fossil-fueled or nuclear, the heat storage unit can level the operation of the heat generator, although the power conversion systems would still have to be sized to meet peak demands (peak shaving). Coupled with a solar input, the storage unit would buffer the mismatched interface between the intermittent source of heat and the cyclic demand on the converter (load leveling). Alternatively the application of many small-scale heat storage units at the sites where heat is to be used may be a way to level the load on both the heat generator and the power converter. Metallurgical heat treating furnaces should be easy to construct with a eutectic mixture regulating the temperature very precisely. Furnaces for baking and home heating also may be possible that would shift this part of the load to the off-peak hours in such a manner that these hours could be changed with the seasons. A central system with a solar heat source might benefit from the inclusion of a large-scale, central storage buffer and distributed small-scale storage capacity so that the converter can operate close to a fixed level.

Phase change materials (PCMs) have been used for decades (1) as

alternatives to the storage of low-temperature heat for comfort conditioning in water or rocks which use only their heat capacities. The possible advantages of such systems for high temperature storage have been recognized for years, but the systematic study of alloys instead of inorganic salts has been limited to very rough calculations on pure metals and a few binary alloys (2). This study undertakes an exploration of the characteristics that make some alloys better than others and includes experimental measurements on systems for which enough older data are available to make possible quantitative estimates of the heat storage densities.

Phase transformations that take place isothermally at some fixed temperature balance an entropy change which, when multiplied by temperature, exactly compensates an enthalpy, or sensible heat transfer change. The magnitude of this change is small for solid-solid transformations, but much larger for solid-liquid transformations. The further advantages that might seem to accrue from the transformation of a condensed phase to a gas, substantial as they are, are offset by the large system volumes that are required to handle the gases. In nearly all of the heat storage systems, regardless of type, the costs of the containing structures appear to be comparable with or exceed the costs of the storage materials.* Thus the heat storage density is critically important. Metals and alloys, because of their high thermal conductivities, offer an important advantage in that the ratio of heat exchanger area to storage volume can be much smaller for a fixed cycling time than it is for more poorly conducting materials.

*For example, the reports NASACR 135244 and 135245 by A. Ferrara, G. Yenetchi, R. Hoslett and R. Kosson, Grumman Aerospace Corporation, October 1977, show that the heat exchanger cost might be about six times the cost of the storage medium for a realistic design using some of the cheaper salt mixtures.

The thermodynamically irreversible losses in heat transfer are related to temperature gradients through which heat flow takes place, to the decrease in temperature between delivery to and extraction from the storage system. Isothermal phase change materials exhibit irreversibility internally only to the extent that they may undercool before nucleation of the low temperature phases or overheat before nucleation of the high temperature phases. Moreover, however, heat transfer to and from the interface separating the phases is through a gradient that can be smaller for materials with high thermal conductivity.

Although PCMs can store energy by overheating above the transformation temperature and offer some additional supply if undercooled below the transformation temperature, these contributions are proportionately small. In fact a sample calculation applied to the fusion of an average close-packed metal illustrates this point, and the general advantage of a PCM over a heat capacity storage system. The entropy of fusion of a normal fcc or hcp metal is shown to be about 10 joules per gram atom per kelvin in Fig. 1 (3). The molar heat capacities are not so uniform, but average about 30 joules per gram atom per kelvin. Fusion of a gram atom of such a metal at 800K yields 8 kJ, which could be stored in heat capacity only by a temperature rise of 270 kelvins. In practice the temperature rise is restricted by using much more storage material and a much larger container.

Any energy storage system which is to have a very large central unit or many smaller distributed units must use cheap,

Fig. 1) Entropies of fusion of some elements. Elements with unusual crystal structures and those that deviate markedly from the line that correlates other elements with the same crystal structure are identified by their chemical symbols. (Modified from Ref. 4.)

plentiful materials. The working substances and container materials must be chemically compatible over the range of operating temperatures, capable of easy fabrication and start up. This report is limited to heat storage materials, but even the experimental study of these materials on a laboratory scale requires that the inert container materials be used. The containment of the metals and alloys considered here appears to be no more difficult than the handling of the molten halides, hydroxides and carbonates being studies by others.

Most of the elements listed in Table 1 already are in widespread use for industrial purposes or are available in some adaptable alternative form. The prices of some of these elements varies widely, sometimes by more than a factor of two in a single year. The relative prices built into the molar price disadvantage factor (PDF) are uncertain in this sense. They have been based on price quotations from the Chemical Marketing Reporter. Yet the order is likely to remain nearly as given. Recognizing that the molar densities vary significantly and that the costs of the system will be affected by the size, a simple volume disadvantage factor (VDF) has been calculated. The overall disadvantage factor (DF) is the product of these two numbers. The elements are listed in Table 1 in the order of the disadvantage factor. It should be used only in a relative and very approximate way. Clearly aluminum and silicon are much more economical for these applications than antimony and tin. The table has been used as a guide to the choice of materials for study. However, a much more persuasive guide would have been the availability of reliable data.

Table 1

Relative molar prices and volumes of the
less expensive elements

<u>Element</u>	<u>PDF*</u>	<u>VDF⁺</u>	<u>DF = PDF x VDF ÷ 1.4</u>
S	0.17	2.2	0.26
Al	1	1.4	1
Si	1.3**	1.7	1.5
Zn	1.7	1.3	1.6
P	1.4	1.6	1.6
Na	0.72	3.3	1.7
Cu	3.2	1	2.3
Mg	1.8	2.0	2.5
Ca	1.2**	3.7	3.1
Pb	4.8	2.6	8.7
Sb	14.4	2.6	26
Cd	25.0	1.8	33
Sn	42.2	2.3	69
B	?	0.64	?

* Based on quotations from Chemical Marketing Reporter for June 20, 1977, the Wall Street Journal for June 23, 1977 and Data for April 1977 from "Wholesale Prices and Price Indexes", U. S. Dept. of Labor, Bureau of Labor Statistics.

** Not quoted directly. Generous estimate based on compounds that might be converted.

+ Room temperature ratios. Differences from thermal expansion will be less than changes from dissolution and the formation of intermediate phases.

Thermodynamics of Congruent and Eutectic Melting

Substances that have low vapor pressures obey the Clapeyron-Clausius equation precisely for vaporization from both solid and liquid phases.

$$\ln p = -\Delta H/RT + c \quad (1)$$

The low pressure vapors behave as ideal gases, so the molar free energies are given by

$$G - G^\circ = RT \ln p \quad (2)$$

if the gas at one atmosphere partial pressure is taken to be the reference state at which $G=G^\circ$. At the melting point T_m the vapor pressures and free energies of solid and liquid phases are equal.

$$\begin{aligned} p_l &= p_s \\ G_l &= G_s \\ \Delta G &= G_l - G_s = 0 \end{aligned} \quad (3)$$

However, at any other temperature

$$\begin{aligned} \Delta G &= RT \ln (p_l/p_s) \\ \Delta G &= RT \left(c_l - c_s - \frac{\Delta H_v}{RT} + \frac{\Delta H_s}{RT} \right) \end{aligned} \quad (4)$$

Let $\Delta H_s - \Delta H_v = L$, the latent heat of fusion.

From Eq. 1, $c_l - c_s = -L/RT_m$

Hence

$$\Delta G = L \left(1 - T/T_m \right) \quad (5)$$

Equation 5 shows that the driving force ΔG for transformation is proportional to the displacement from the equilibrium temperature T_m . If $T > T_m$, ΔG is negative, favoring melting. If $T < T_m$, ΔG is positive favoring the reverse transformation freezing. In the latter case undercooling to some extent is essential to supply excess driving force to nucleate solid; but the undercooling often is small in relatively impure melts owing to the presence of catalytic impurities or active container walls.

Equation 5 also shows that, in addition to the latent heat of the transformation being nearly independent of temperature, as implied by the fact that both condensed phases obey Eq. 1 with appropriate constant values of ΔH , the entropy change also is nearly independent of temperature;

$$\Delta S = - \left(\frac{\partial \Delta G}{\partial T} \right)_P = - L \frac{\partial}{\partial T} \left(1 - \frac{T}{T_m} \right) = L / T_m \quad (6)$$

These same considerations apply to the congruent melting of intermediate phases except that the pressures appearing in the Clapeyron-Clausius equation are partial pressures, the ΔH values are partial molar enthalpies of vaporization, and so on. The melting of an equilibrium mixture of solids to form a eutectic melt deserves more detailed treatment.

Table 2 is a collection of data pertinent to the melting of some elements that might be interesting in heat storage applications partly because of the considerations outlined in Table 1.

Table 2

Melting points, densities, latent heats and entropies
of fusion of selected elements

Element	Melting (or transformation) Temperature, K	Density ⁵ at T_m	Entropy of Fusion ⁶ J/g-atom-K	Latent Heat of Fusion ⁶		
				kJ/g-at	kJ/kg	kJ/m ³ × 10 ⁻⁶
Al	933.6	2.368	11.6	10.8	400	0.947
Ca	737 ($\alpha \rightarrow \beta$)		1.25	0.92	23	
	1123 ($\beta \rightarrow \epsilon$)	1.4	7.74	8.66	216	0.302
Cu	1357.7	7.938	9.62	13.1	206	1.64
Mg	922	1.59	9.71	8.95	368	0.585
Si	1683.2	2.525	30.0	50.6	1068	2.70
Zn	692.8	6.577	10.6	7.32	112	0.737

The free energy of mixing two substances A and B in proportions $1-x$ and x , respectively, to form a homogeneous solution is

$$\Delta G = RT [(1-x) \ln a_A + x \ln a_B] \quad (7)$$

where activity a can be written as the product of mole fraction x and activity coefficient γ . If Eq. 7 is written for the formation of a solid solution α from crystalline A and B or to form solid solution β , the results can be written

$$\Delta G^\alpha = RT [(1-x_\alpha) \ln a_A^\alpha + x_\alpha \ln a_B^\alpha] \quad (7a)$$

$$\Delta G^\beta = RT [(1-x_\beta) \ln a_A^\beta + x_\beta \ln a_B^\beta] \quad (7b)$$

If these solid solutions are to be in equilibrium with a liquid solution, it is desirable to fix the reference states so that they are the same for the liquid solution as they are for the solids α and β . Pure component A at its equilibrium melting temperature T_A has a latent heat of fusion L_A and a free energy of fusion equal to zero, hence the entropy of fusion S_A is given by

$$S_A = L_A / T_A \quad (6a)$$

At some other temperature T , the free energy of fusion is very nearly

$$G_A = H_A - TS_A = L_A \left(1 - \frac{T}{T_A}\right) = L_A \left(\frac{T_A - T}{T_A}\right) \quad (8)$$

because L_A and S_A are nearly unaffected by moderate changes in temperature. A similar result applies for component B. Together they may be used to write the equation for the free energy of solution of the eutectic liquid, of composition x_e , analogous to Eqs. 7a and 7b,

$$\Delta G^e = RT \left[(1-x_e) \ln a_A^e + x_e \ln a_B^e \right] + (1-x_e) L_A \left(\frac{T_A - T}{T_A} \right) + x_e L_B \left(\frac{T_B - T}{T_B} \right) \quad (7c)$$

where activities a_A^e and a_B^e are measured relative to pure liquids A and B. The final two terms change the overall reference states to the pure solids.

If A and B form an ordered intermetallic solid phase ϵ the heat of formation ΔH_ϵ of ϵ from the pure solids often can be approximated adequately by the free energy of formation ΔG_ϵ because the entropy change usually is very small. The B content in the compound is designated by x_ϵ . If the intermediate phase is not well-ordered and of narrow composition range an explicit entropy of mixing contribution may be required. Composition deviations that result from the introduction of point defects into essentially ionic or covalent structures require a more detailed treatment than that to be used here.

Consider the first of several cases. Two solid solutions α and β combine in the proportions (see Fig. 2)

$$f_\alpha = (x_\beta - x_e)/(x_\beta - x_\alpha) ; \quad f_\beta = (x_e - x_\alpha)/(x_\beta - x_\alpha) \quad (9)$$

as required by mass conservation, that is the lever rule, to

form the eutectic liquid. At the eutectic temperature T_e the free energy of transformation is zero.

$$\Delta G_e = 0 = \Delta G^e - f_\alpha \Delta G^\alpha - f_\beta \Delta G^\beta \quad (10)$$

Substituting from Eqs. 7a, b and c for ΔG^α , ΔG^β and ΔG^e ,

$$RT \left\{ (1-x_e) \ln a_A^e + x_e \ln a_B^e - \left(\frac{x_\beta - x_e}{x_\beta - x_\alpha} \right) \left[(1-x_\alpha) \ln a_A^\alpha + x_\alpha \ln a_B^\alpha \right] \right. \\ \left. - \left(\frac{x_e - x_\alpha}{x_\beta - x_\alpha} \right) \left[(1-x_\beta) \ln a_A^\beta + x_\beta \ln a_B^\beta \right] \right\} + (1-x_e) \frac{L_A}{T_A} (T_A - T) + x_e \frac{L_B}{T_B} (T_B - T) = 0 \quad (11)$$

The eutectic reaction has several characteristics in common with the melting of a pure substance. There is no net change in the average composition during the isothermal transformation at equilibrium, hence no tendency for macroscopic segregation.*

It is reasonable also to assume that the enthalpy and entropy changes of the component processes are insensitive to temperature. Although the expression written above for the equilibrium transformation is exact, its separation into entropy and enthalpy contributions can only be done approximately. Here it is assumed that the entropy contributions consist of the entropies of fusion of the pure components and the entropy for random mixing of these components in the liquid solution of eutectic composition less their entropies for random mixing in the solid solutions. These approximations are equivalent to treating all solutions as regular solutions.

*Limits of solid solubility are temperature dependent, often in a sensitive way, so severe undercooling before or after transformation may modify the course of the reaction to some extent.

Figure 2. Eutectic constructions for binary systems. (a) Eutectic liquid forms from two solid solutions. (b) Eutectic from one solid solution and one intermetallic phase. (c) Eutectic from two intermetallic phases.

$$\Delta S_e = -R \left\{ (1-x_e) \ln(1-x_e) + x_e \ln x_e - \left(\frac{x_\beta - x_e}{x_\beta - x_\alpha} \right) \left[(1-x_\alpha) \ln(1-x_\alpha) + x_\alpha \ln x_\alpha \right] - \left(\frac{x_e - x_\alpha}{x_\beta - x_\alpha} \right) \left[(1-x_\beta) \ln(1-x_\beta) + x_\beta \ln x_\beta \right] \right\} + (1-x_e) \frac{L_A}{T_A} + x_e \frac{L_B}{T_B} \quad (12)$$

By extension of this argument to greater numbers of components, the entropy change can be increased by mixing more and more components if they are present in nearly equal proportions. Although this development and the current supporting experimental work are directed mainly at binary, and a few ternary systems, it is intended to use that base to seek higher order eutectics that yield the benefits of increased entropy of mixing. The equation also shows that the largest contributions are provided by those elements that have the highest entropies of fusion. Fig. 1 shows that, among the inexpensive elements, silicon and aluminum deserve special attention.

With the entropy contributions identified, the enthalpy change at the eutectic temperature can be found in two ways (1) by multiplying ΔS_e by T_e and (2) by evaluating the remaining terms in the equation. Comparison of these numbers would be a direct check on the validity of the separation of contributions if the data were sufficiently precise. However, the comparisons also help to identify questionable data. The heat effect should be given by

$$\Delta H_e = (1-x_e) L_A + x_e L_B + RT \left\{ (1-x_e) \ln \gamma_A^e + x_e \ln \gamma_B^e - \left(\frac{x_\beta - x_e}{x_\beta - x_\alpha} \right) \left[(1-x_\alpha) \ln \gamma_A^\alpha + x_\alpha \ln \gamma_B^\alpha \right] - \left(\frac{x_e - x_\alpha}{x_\beta - x_\alpha} \right) \left[(1-x_\beta) \ln \gamma_A^\beta + x_\beta \ln \gamma_B^\beta \right] \right\} \quad (13)$$

At the same composition the activity coefficients ordinarily differ more strongly from unity for the solid phases than for the liquid phases, a tendency reinforced by the increasing deviation from unity with decreasing temperature. On the other hand, the most desirable liquids are more concentrated than the solid phases that react to form them, so the greater deviations from unity are likely to be displayed by the activity coefficients for the liquids. Unfortunately the experimental measurements seldom reach down to the eutectic temperatures and often are completely unavailable for the solid phases. In those cases, only rough extrapolations and judicious guesses can be used. Clearly it is desirable to have large latent heats of fusion for all components, combined with narrow ranges of solid solubility in which there are strong negative deviations from ideal solution behavior and a eutectic liquid that exhibits much weaker negative deviation.

Frequently a second case is found in which a solid solution α and an intermediate phase ϵ combine to form the eutectic. The combining proportions from Fig. 2 are:

$$f_{\alpha} = (x_{\epsilon} - x_e)/(x_{\epsilon} - x_{\alpha}) ; f_{\epsilon} = (x_e - x_{\alpha})/(x_{\epsilon} - x_{\alpha}) \quad (14)$$

Any entropy of random mixing in ϵ is neglected. The appropriate modifications are made readily in Eqs. 12 and 13:

$$\Delta S_e = -R \left\{ (1-x_e) \ln(1-x_e) + x_e \ln x_e - \left(\frac{x_{\epsilon} - x_e}{x_{\epsilon} - x_{\alpha}} \right) [(1-x_{\alpha}) \ln(1-x_{\alpha}) + x_{\alpha} \ln x_{\alpha}] \right\} \\ + (1-x_e) L_A/T_A + x_e L_B/T_B \quad (15)$$

$$\Delta H_e = (1-x_e)L_A + x_e L_B + \left(\frac{x_e - x_\alpha}{x_\epsilon - x_\alpha} \right) \Delta H_\epsilon + RT \left\{ (1-x_e) \ln \gamma_A^e + x_e \ln \gamma_B^e - \left(\frac{x_\epsilon - x_e}{x_\epsilon - x_\alpha} \right) \left[(1-x_\alpha) \ln \gamma_A^\alpha + x_\alpha \ln \gamma_B^\alpha \right] \right\} \quad (16)$$

Note that the activity coefficients for the components in the intermediate phase are replaced by the equivalent heat of formation, which is more likely to be tabulated.

The final case to be considered is that in which two ordered intermediate phases ϵ and ω combine to form a eutectic melt. The combining proportions are:

$$f_\epsilon = (x_\omega - x_e)/(x_\omega - x_\epsilon) \quad ; \quad f_\omega = (x_e - x_\epsilon)/(x_\omega - x_\epsilon) \quad (17)$$

The analogs of Eqs. 12 and 13 now become:

$$\Delta S_e = -R \left[(1-x_e) \ln(1-x_e) + x_e \ln x_e \right] + (1-x_e)L_A/T_A + x_e L_B/T_B \quad (18)$$

$$\Delta H_e = (1-x_e)L_A + x_e L_B + \left(\frac{x_\omega - x_e}{x_\omega - x_\epsilon} \right) \Delta H_\epsilon + \left(\frac{x_e - x_\epsilon}{x_\omega - x_\epsilon} \right) \Delta H_\omega + RT \left[(1-x_e) \ln \gamma_A^e + x_e \ln \gamma_B^e \right] \quad (19)$$

Some data on binary intermetallic phases that may be useful in these and later calculations of heat storage capacity are collected in Table 3.

The last case makes it clear by comparing Eqs. 18 and 19 that the separation of entropy and enthalpy of transformation cannot be exact, because Eq. 18 does not contain any explicit properties of ϵ and ω . They only need to form with sufficient

strength of binding to suppress substitutional disorder. Thus Eq. 19 seems likely to give a better estimate of the heat storage capabilities of such systems. In Eq. 19 and in Eq. 16 the heats of formation should be given positive values, as are L_A and L_B , representing heat absorbed during the decomposition of the compounds into the melt. In the calculations to follow, the values for estimated heat storage based on $T\Delta S_e$, that is on Eq. 12, 15 and 18, are designated as the first approximation, while the values based on ΔH_e as given in Eqs. 13, 16 and 19 are designated as second approximations and are given in parentheses in Table 4. The latter, however, are more sensitive to experimental errors in the tabulated data, so they are not necessarily more reliable than the first approximations. Our direct measurements can be compared with these calculated values, partly to look for errors in the tabulated data.

Table 3. Melting points, densities, latent heats, entropies of fusion and heats of formation of some congruently melting intermetallic phases.

Nominal Formula	Density kg/m ³ at 273K	T _m K	$\Delta H_f^{1,7}$ (298) kJ/g-atom	Entropy of Fusion J/g-at-K	Heat of Fusion (Experimental)		
					kJ/g-at*	kJ/kg	kJ/m ³ x 10 ⁻⁶
Al ₂ Ca		1352	-73.2	13.0	17.6 (13.0)	561	
Al ₂ Cu	4.34x10 ³	[864] ⁺	-13.3				
Al ₃ Mg ₂	2.23	726	-8.4				
CaCu ₅		1208	-6.1				
CaMg ₂		990	-13.4	16.6	16.4 (9.0)	554	
CaZn ₂		997		13.2	12.9 (9.4)	226	
Mg ₂ Si	1.99	1375	-26.4	20.7	28.5 (22.7)	1110	2.20
MgZn ₂	5.20	861	-17.6	16.5	14.2 (8.9)	275	1.4

* Values in parentheses are obtained by multiplying the weighted average of the entropies of fusion of the elements by the melting temperature T_m from column 3. This standard practice which neglects the heat of formation of the compound, the heat of solution of the liquid and the entropy of mixing of the liquid, consistently underestimates the heat of fusion as given by the values immediately above.

+ Undergoes peritectic decomposition.

Summary of Calculations and Measurements on Binary and Ternary Eutectic Alloys

Table 4 summarizes calculations for several systems for which tabulated data permit the use of Eqs. 15 (or 18) and 16 (or 19). In one case, Mg-Zn, the measured value lies far below the calculated values. The Al-Mg result also is seriously below predictions. Al-Cu gives very close agreement. Al-Cu-Mg is satisfactorily close to the predicted values and well above the earlier estimate.¹ Although the calculations based on tabulated data have been improved by a more realistic separation of Eq. 11 into entropic and enthalpic contributions, they still are not a satisfactory substitute for direct measurements on these eutectics that are made up of inexpensive metals and lie in an acceptable range of temperature.

Table 5 contains more approximate heat storage calculations for several binary alloys, mainly of calcium. Only the first approximation could be used, and entropy of mixing effects have been omitted for all solid phases, although such effects are likely to be small. Attention is directed to the Mg_2Si -Si eutectic which fulfills all of the conditions for high heat storage capacity. The measured heat storage capacity is below this estimate, probably because of ordering in the eutectic liquid. The eutectic temperature of 1220K is high, but the still excellent storage capacity might find application in steel heat treating furnaces and possibly as a ballast for a solar power tower. Naturally, additives will be sought to lower transformation temperature without serious loss in heat storage capacity.

Table 4. Entropies and enthalpies of eutectic transformations in selected binary and ternary systems

A-B	T_e K	$\rho_{\text{at } T_e}^0$ kg/m ³	x_a^*	x_e^*	x_c^*	$\Delta H_f^{1,2}$ kJ/g-at	Heat Storage calculated from Eq. 10(11)				Measured, DSC	
							kJ/g-at	kJ/m ³	kJ/kg	kJ/kg	kJ/kg	kJ/m ³
Mg-Zn	613		0.025	0.29	0.30 ⁺	12.6	8.96 (16.8)		247 464	134		
Al-Mg	722		0.19	0.375	0.38 ⁺	3.05	11.9 (12.4)		458 477	309		
Al-Cu	821 ^b	3258	0.025	0.175	0.333	13.3	12.0 (12.7)	1.17×10^6 1.24×10^6	359 380	347	4.3×10^6	
Mg-Cu	825		0.33 ^c (e)	0.42	0.67 (w)	5.58 (e) 10.5 (w)	12.6 (12.0)		309 294			
Al-Cu-Mg	781		x_e^*	Phase Proportions ^d		Heats of formation						
			0.668 Al 0.170 Cu 0.162 Mg	$f_1 = 0.354$ $f_{\text{CuMgAl}_2} = 0.620$ $f_{\text{CuAl}_2} = 0.026$		~ 1.5 8.0 13.25 ~ 3.6 (eutectic)		13.3 (13.1)	406 400	359		
Al-Mg-Si	832		0.822 Al 0.126 Si 0.051 Mg	$f_{\text{Mg}_2\text{Si}} = 0.067$ $f_{\text{Si}} = 0.094\text{Si}$ $f_a = 0.838$ $\left\{ \begin{array}{l} 0.981\text{Al} \\ 0.011\text{Si} \\ 0.0076\text{Mg} \end{array} \right.$		26.4 ~ 5.86 (eutectic)		14.8 (12.1)	549 449			

⁺ Structure not known, assumed to be ordered. Heat of formation estimated to be less than that of MgZn_2 (17.6 kJ/g.at).

A smaller ΔH_f or a disordered solid phase would lower the estimated heat storage in parentheses.

^b Melts congruently at Al_3Mg_2 and 724K.

^c The density measurements are described in a separate report by A. Harrison and C. E. Birchenall.

^d We measured 820.3K.

^e Mg_2Cu and MgCu_2 are ordered.

Table 5. Calculated heat storage capacities* for several binary metallic systems

A - B	T _e K	x _a ⁷	x _e ⁷	x _c ⁷	ΔH _c ^{3,7}	Heat Storage	
						kJ/g·at	kJ/kg
Si-Mg	1220	0	0.471	0.667	26.4	31.9	1212
Ca-Al	818	0	0.350	0.667	73.2	11.8	332
Ca-Zn	664	0	0.274	0.370	?	9.1	184
Ca-Mg	729	0	0.27	0.667		9.4	263
Mg-Ca	790	0	0.105	0.333		9.2	353
Ca-Cu	833	0.2	0.51	0.8		12.0	231

* The entropies of mixing and small solubilities in all solid phases have been neglected in calculating this table.

Fig. 3 compares the measured heat storage capacities for the selected binary and ternary alloys and for the intermetallic phase CaMg_2 on both mass and volume bases. The order of the alloys by the storage density per unit mass is not the same as the order per unit volume. Copper and zinc show up more favorably as components on the latter basis.

Fig. 3 Measured heat storage capacities of selected alloys.

Discussion

Definitive comparisons among the materials that have been proposed for high temperature storage are premature because the tabulated data may be uncertain and some critical data are completely missing. Preliminary comparisons are attempted with salts identified in the Dynatech Report⁹ to have merit because of unusually high storage density or a good temperature match to a particular application area. Lithium-containing compounds and fluorides stand out because of their low atomic numbers. The Philips¹⁰ studies have emphasized fluoride eutectics, and the Dynatech studies have emphasized lithium compounds and eutectics.

The relatively high cost of some of these materials, especially of lithium and lithium hydride, must be borne in mind. Also the salts usually require very careful drying to limit their corrosive attack on containers. Volume change measurements on transforming salts and salt eutectics are sparse. However, their volume changes for solid-liquid transformations are thought to be large; several values in excess of 20% are quoted in the Dynatech Report⁹. In contrast the alloy transformations appear to involve changes of less than 10%.

Where thermal conductivities of salts are given, they lie in the range 1 to 3 W/M·K, except that LiH has a value of 7. The solid metals have thermal conductivities of 40 to 400 W/M·K, and the alloys and liquid metals may drop to about half those values. Heat conductivity through metallic materials appears to be almost 10 to 100 times more favorable than through salts.

The Dynatech Report⁹ specified important temperature ranges to match the heat-generating sources in conventional utilities: water-cooled nuclear reactors (PWR and BWR), 505-544K; fossil-fueled supercritical steam reactor (FFR), 783-853K; high-temperature, gas-cooled, graphite-moderated nuclear reactor (HTGR), 977-1033K. For these cases the Dynatech group chose to study LiNO_3 (527K for PWR), 63LiOH/37LiCl eutectic (533K for BWR), LiOH (743K for FFR), and $\text{Na}_2\text{B}_4\text{O}_7$ (1015K for HTGR). However, $\text{Na}_2\text{B}_4\text{O}_7$ usually vitrified instead of crystallizing, an unfortunate (for these purposes) tendency shared with other borates, silicates and phosphates to make them unsuitable PCM's for heat storage. Thus lithium salts are the basis of all of the workable Dynatech materials.

Other large-scale applications may be possible in these and other temperature ranges. For example, central station, solar thermal power generation might be compatible with storage between 700 and 930 K for steam/Rankine and Brayton power conversion cycles. Intermediate scale industrial and transportation applications also may spread over a wide temperature range, including temperatures above 1600K for steel soaking pits. Small-scale storage applications at widely scattered temperatures, like intermediate scale applications, take place downstream from the power generator, and, if built around a heat-storage system, can play a role in the long term of leveling the load on the generating and distributing system. For that reason, although many of the data for non-metallic systems listed in Table 6 are taken directly from the Dynatech tabulations, Table 6 is not limited to the three

Table 6. Properties of some materials that store heat by phase change.

Material	Trans. Temp. K	Heat of Trans. kJ/kg	Density of Solid kg/m ³	Volumetric Heat Storage kJ/m ³	Heat Cap. kJ/kg·K sol/liq	Coeff. of Thermal Cond. w/m.K sol/liq	Cost \$/kg
Mg ₂ Si/Si	1206	774	(2000) ¹	1547 x 10 ³		26 / ₂₀	1.77
LiF	1121	1041	2655	2763	1.64 / _{2.52}	1.92	5.32
NaF/MgF ₂	1105	650	2192	1425	1.42 / _{1.38}	4.66	1.30
LiF/MgF ₂	1019	947	2630	2490	1.42 /		
NaF/CaF ₂ /MgF ₂	1018	574	2760	1580	1.17 /		
Li ₂ CO ₃	994	603	2104	1269	2.56 / _{2.56}		1.72
CaMg ₂	990	554	(1550) ¹	859		4 / ₂₀	1.62
MgCl ₂	988	454	2240	1010	0.75 /		.29
LiH	956	2582	790	2030	8.04 /	7 /	
Al	934	400	2370 ¹	1050	1.29 / ₂	204.2 /	.01
LiF/NaF/MgF ₂	923	860	2810	2417	1.42 / _{1.71}	1.15	1.30
Mg	922	368	1590 ¹	590		131 /	1.81
MgZn ₂	861	275	5200	1430			
Al/Si	852	515	(2250) ¹	1159	1.49 / ₂ 1.27 / ₂	180 / ₇₀	1.20
Al/Si/Mg	833	545	(2300) ¹	1254	1.39 / ₂ 1.21 / ₂	199 / ₇₀	1.25
Al/Cu	821	351	3258 ²	1144	1.11 / ₂ 1.11 / ₂	130 / ₈₀	1.22
Mg/Mg ₂ Ca	790	(343)	(1570) ¹	550			

Al/Cu/Mg	779	360	(3200) ¹	1152	1.09 ² / 1.18 ²	115/ 75	1.28
Li ₂ CO ₃ /Na ₂ CO ₃	769	368	2330	857		2.1/ 7	.77
LiOH	744	1100	1340 ¹	1470		2.8/ 7	4.34
Al/Mg	724 ²	310	2300 ¹	713 ²	1.73 ² / 1.62 ²	80/ 50	1.52
NaCl/MgCl ₂	723	429	2226	955	.93/ 1.01	.96/ 7	.18
NaCl/MgCl ₂ /KCl	713	326	2240	730			
LiOH/LiF	700	1163	1550	1800	2.14/ 7	2.6/ 7	
Zn	693	112	7140	800	.80/ 7		129
Li ₂ CO ₃ /K ₂ CO ₃ / Na ₂ CO ₃	670	275	2311	636	1.64/ 1.64	2.04/ 7	.33
KCl/NaCl/MgCl ₂	658	461	2252	1040 ²	0.96/ 1.04	.95/ 7	.19
Mg/Mg ₂ Zn	616	138	(4900) ¹	676	1.04/ 1.15	80/ 50	1.42
NaOH	593	160	2078	331	2.01/ 2.14	.92/ 7	.44
NaCl/NaNO ₃	570	109	2269	247	1.85/ 1.80	.61/ 7	.14
NaCl/Na ₂ CO ₃ /NaOH	555	316	2130	674	2.51/ 7		
LiCl/LiOHh	535	530	2120	1120	1.50/ 7	1.70	
Li	452	663	534	354			

1. Density estimated at the transformation temperature. Other densities are room temperature values.

2. Values measured in this work at transformation temperature.

This table combines values measured in this work and others extracted by tabulations from references 9, 12, 13 and a table also compiled from a variety of sources by Joseph P. Joyce of the NASA-Lewis Research Center.

ranges they emphasized nor to the salts they listed. Materials are listed according to transformation temperature. Values enclosed by parentheses are our calculated or estimated values. Those not so enclosed are either measured values or are taken directly from Dynatech tables. The density values with asterisks are for the solid at the transformation temperature. All other densities appear to be room temperature values, which gives corresponding volumetric heat storage values that are slightly too high. The solid heat capacities measured by DSC in this investigation are distinguished by superscript 2.

From Table 6 it appears that several metallic systems already identified have the best heat storage characteristics in the range to operate with fossil-fueled combustors. Al-Cu is in the middle of the range and MgZn_2 and Al-Cu-Mg lie at its extremes. Their heat storage capacities appear to be unmatched on a mass or volume basis. Heat conduction and containment should offer added advantages over other types of materials. In the HTGR and central-station, solar-thermal range the metallic materials must compete with fluoride mixtures unless the operating temperature is high enough to permit use of the magnesium-silicon eutectic or unless that transformation temperature can be lowered by further alloying. In the intermediate temperature range LiH has outstanding storage capability, but it is very reactive and expensive. Considering these factors, and the differences in thermal conductivity, price, and density, aluminum may be competitive in many cases.

A similar sort of comparison might be made between LiOH, one of the least expensive lithium compounds, and the Al-Mg eutectic.

LiOH/LiF and Zn may offer a choice, like LiOH and Al-Mg, to be determined by conduction and containment problems that are not definable without specifying an application. If metals are to play a role below the Mg/Mg₂Zn eutectic temperature, it must be for small-scale special applications that justify the use of relatively expensive metals or ternary or more complex systems must be identified that have higher storage capacity.

Thermal Conductivity of Pure Metals, Alloys and Intermetallic Compounds

The metals* under study for heat storage have thermal conductivities, K, between 120 and 400 W/M K at room temperature. K decreases approximately 10 to 20 per cent between room temperature and the melting point. A further decrease by approximately 50% occurs on melting. Silicon shows a much greater decrease on heating, from 48 to 25.7 W/M K between room temperature and 1200K. The data in Table 7 are abstracted from reference 11.

Specific data for alloys of interest are not available, but data for similar alloys are given in Table 8 to indicate representative trends. For example the addition of 10 to 20% Cu to Al reduces the thermal conductivity from 240 to 140 W/M K, where as the addition of 14% Mg reduces it to 85 W/M K, and 13% Si reduces it to 170 W/M K. In contrast to pure metals, the thermal conductivity of alloys increases, in the cases cited here and most others, on heating above room temperature.

Data for the thermal conductivities of the alloys in the li-

* Calcium is not tabulated.

Table 7 Thermal Conductivities of Pure Metals

<u>Metal</u>	<u>Temp. °K</u>	<u>K W.m.⁻¹K⁻¹</u> <u>x10⁻²</u>	<u>Pg (ref. 11)</u>
Al	300	2.37	6
"	933	2.11	"
"	933 (l)	0.91	"
Cu	300	3.98	81
"	1356	3.30	"
"	1356 (l)	1.66	"
Mg	300	1.56	207
"	923	1.45	"
"	923 (l)	0.79	"
Si	300	1.48	339
"	500	0.762	"
"	700	0.508	"
"	900	0.359	"
"	1200	0.257	"
Zn	300	1.21	461
"	692	1.00	"
"	692 (l)	0.50	"

Table 8 Thermal Conductivity of Alloys
and Intermetallics

<u>Alloy</u>	<u>Composition</u>	<u>Temp°K</u>	<u>K (SI)</u> <u>x10⁻²</u>	<u>Pg. (ref. 11)</u>
Al/Cu (17% Cu)	8% Cu	373	1.44	473
	10% Cu	326	1.61	
	12% Cu	373	1.42-1.60	
	14% Cu	353	1.55	
	20% Cu	326	1.46	
Al/Mg (36% Mg)	8% Mg	373	1.20, 1.26	479
	12% Mg	373	1.013	
	14% Mg	373	0.845	
	14% Mg	476	1.04	
	89% Mg	373	0.88	
Al/Si (13% Si)	13% Si	353	1.715	482
	"	473	1.757	
	"	573	1.799	
Mg/Si (56.5% Si)	1.5% Si	373	1.40	677
Mg ₂ Si		307	0.0793	1315
		504	0.0472	
		580	0.0398	

quid state are even more sparse. For the two systems reported, Pb-Sn (solder) and Sn-Cd undergo 50% and 60% reductions, respectively, on eutectic melting. However, the Pb-Bi eutectic alloy showed no significant change in thermal conductivity on melting.

Intermetallic compounds often have thermal conductivities more than an order of magnitude lower than the pure metals from which they form. Furthermore, these values may decrease rapidly with increasing temperature. Therefore, with a two-phase solid consisting of intermetallic phase dispersed in a metallic solid-solution matrix most of the heat flow would be through the solid-solution phase. Many intermetallic compounds melt to form metallic liquids. In those cases it would not be surprising to find that the thermal conductivity (without convection) of the liquid exceeds that of the solid.

These considerations have been used to estimate some of the thermal conductivity values for metals, alloys and intermetallic compounds in Table 6 . They should be recognized to be a poor substitute for directly measured values, but still reasonable estimates of the rate at which heat can be transferred in a heat storage system based on metals.

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II. Determination of Density Changes by X-ray Absorption by Andrew Harrison and C. Ernest Birchenall

1. Introduction

Thermal expansion coefficients and volume changes during transformation are measured readily by dilatometric methods when reactants and products both are liquid, both are solid, or when a discontinuous solid forms within a liquid phase. However, it is much more difficult to measure volume changes by dilatometry when a solid completely transforms to a liquid or the reverse. Previously, independent measurements of the solid and liquid densities at the melting point were required. The density of the solid is best determined by the extrapolation of thermal expansion measurements. The most accurate dilatometric and x-ray diffraction measurements on metals have been reported by Simmons and Balluffi (1). Density measurements of many liquid metals have been reported by Lucas (2) who used an Archimedean bob weight method.

An alternative method is presented in which density measurements during expansion and transformation are measured by the change in transmitted intensity of a monochromatic x-ray beam through a path of known length. The procedure is straightforward for the melting of a pure substance, a congruently melting phase or a eutectic mixture provided that the solid phases are uniformly dispersed on a fine scale.

The applicability of the method to the measurement of volume changes on transformation of some alloys that are

being considered as possible high temperature heat storage materials is discussed. The experimental method that has been developed is described, and the preliminary measurements on pure aluminum and on the copper-aluminum eutectic alloy are included.

2. Theory

The absorption of x-rays by any element is given by

$$I = I_0 \exp\left[-\frac{\mu}{\rho} \rho t\right] \quad (1)$$

where I = transmitted intensity, I_0 = incident intensity, $\frac{\mu}{\rho}$ = mass absorption coefficient, ρ = density and t = sample thickness or path length.

The mass absorption coefficient $\left(\frac{\mu}{\rho}\right)$ is a constant for a particular wavelength of x-ray radiation and for a particular absorbing element; it is independent of the chemical or physical state of the element. Consequently, for a metal alloy, the average mass absorption coefficient is given by the mass weighted average for all the constituents. If f_i is the mass fraction of component i in the alloy

$$\bar{\frac{\mu}{\rho}} = \sum_i f_i \left(\frac{\mu}{\rho}\right)_i \quad (2)$$

During congruent melting or eutectic transformation all components undergo the same proportionate change in spatial density even if some individual solid phases increase in density while others decrease, provided that no porosity develops. That is for each component:

$$\left(\frac{\rho_s - \rho_l}{\rho_s}\right)_{\text{component 1}} = \left(\frac{\rho_s - \rho_l}{\rho_s}\right)_{\text{component 2}} = \dots \quad (3)$$

Combining equations (1) and (2), and subtracting the logarithm of the intensity transmitted through the solid from that transmitted through the liquid

$$\ln(I_1/I_s) = t(\rho_s - \rho_l) \sum_i f_i \left(\frac{\mu}{\rho} \right)_i \quad (4)$$

This gives the density change on transformation in terms of the change in transmitted x-ray intensity. In practice to find the volume change on transformation requires that either the density of the solid or of the liquid at the melting point be known.

$$\frac{\Delta V_{\text{transf}}}{V_s} = \frac{1/\rho_l - 1/\rho_s}{1/\rho_s} = \frac{\rho_s - \rho_l}{\rho_l} \quad (5)$$

The solid density at the melting point can be obtained from the same experiment if the density of the alloy at room temperature is known and if the sample deforms on expansion so that it maintains the same thickness defined by the cell walls. Using an analog of equation (4) and including a correction for the thermal expansion of the cell from room temperature to the melting point

$$\ln(I_m/I_r) = \left\{ \rho_r t_r - \rho_m t_r [1 + k_c (T_m - T_r)] \right\} \sum_i f_i \left(\frac{\mu}{\rho} \right)_i \quad (6)$$

where the subscripts r and m denote room temperature and melting temperature, respectively, and k_c is the linear coefficient of thermal expansion of the cell material. From this measurement the volumetric coefficient of expansion and hence also the linear coefficient of expansion of the solid alloy can be determined. Naturally, the cell must not deform plastically.

Above the melting temperature, the volumetric expansion coefficient of the liquid metal can be obtained in a similar way.

Table 1 Mass absorption coefficients* for characteristic x-rays
(in cm² per gram):

	$\lambda =$	Cu K_{α} 1.542Å°	Mo K_{α} 0.711	W K_{α} 0.209
B		2.4	0.39	0.17
C		4.6	0.63	0.18
N		7.5	0.92	0.19
O		11.5	1.4	0.19
Mg		39	4.2	0.27
Al		48	5.2	0.29
Si		62	6.6	(0.33)
P		76	8.1	(0.37)
S		90	10	0.42
Ca		65	20	0.65
Cu		53	51	1.8
Zn		61	55	1.95
Pb		250	130	5.5

* These values are averaged from tables given by C. S. Barrett and T. B. Massalski "Structure of Metals", 3rd edition, McGraw-Hill, 1966.

Also by L. S. Birks, "Electron Probe Microanalysis" Interscience Publishers, Inc. 1963.

The values in parentheses were interpolated.

3. Selection of Materials and Conditions

Using the equations presented above and the tabulated mass absorption coefficients (Table 1) and densities, the feasibility of using this method for the determination of volume changes on transformation of the metals and metal alloys that are being considered as possible heat storage materials was investigated.

Absorption in the sample cell

The sample cell material must have a low absorption cross section to x-rays (i.e., low atomic number) and also have suitable refractory properties. Boron nitride, graphite and alumina were considered as candidate materials. Estimates of the reduction in transmitted intensity caused by absorption in the cell walls were based on the assumption that a 2mm thick wall would be about the minimum for mechanical stability. The transmitted intensity I_c through the cell walls is given by

$$I_c/I_o = \exp \left[\rho_c \left(\frac{\mu}{\rho} \right)_c t_c \right] \quad (7)$$

The fraction of the incident x-rays transmitted was calculated for Cu, Mo and W K_α radiation (Table 2) based on a total wall thickness of 4mm.

Table 2 Fraction of incident x-rays transmitted through 4mm of several low atomic number refractory materials

	Cu K_α	Mo K_α	W K_α
Graphite	0.016	0.567	0.850
Boron Nitride	0.012	0.555	0.850
Alumina	v.low	0.010	0.695

This calculation suggests that Cu K_{α} radiation should not be used. Mo K_{α} should be satisfactory with any of the three materials, including thicker cells.

Absorption in the sample

The sample thickness must be large enough that errors due to heterogeneities in the microstructure do not arise and so that any mismatch between the cell walls and the sample is negligible. On this basis the minimum sample thickness was taken to be 2mm. The maximum sample thickness is limited by the transmitted intensity which should be sufficiently high to give a statistically reliable count rate. Since the characteristics of the x-ray source and of the detector were unknown, this thickness was left as an unspecified parameter. However, as a first approximation, a transmitted intensity of $10^{-4} I_0$ was taken to be the minimum for useful measurements. Fortunately this was found to be a very conservative estimate and $<10^{-6} I_0$ was found to be acceptable even when the generator was operated at low power.

Table 3 lists the fraction of the incident radiation that is transmitted through the cell and specimen for six combinations of average mass absorption coefficient and density to cover the range of likely interest (compare Table 1). The intensity transmitted through the cell is taken to be $0.6 I_0$ and the sample thickness 3mm. Cases a, b and c are appropriate for Mo K_{α} radiation; cases d, e and f are appropriate for W K_{α} radiation.

Table 3 Fraction of transmitted radiation through the cell and and sample (3mm thick) when the cell absorbs $0.4I_0$.

	a	b	c	d	e	f
$(\frac{\mu}{\rho})_{ave}$	5	15	30	0.27	0.5	1.5
ρ	3	3	5	3	2	5
I/I_0	6.7×10^{-3}	7.4×10^{-5}	v. low	0.47	0.44	0.063

These calculations suggest that Mo K_{α} radiation would be suitable only for the light elements, eg Mg and Al, whereas W K_{α} radiation could be used with any of the elements. Another possibility is to use Ag K_{α} radiation which would give intermediate behavior but closer to Mo K_{α} .

A second consideration in the choice of monitoring radiation is that the lighter elements will give a smaller change in signal for a given change in density with hard radiation than with soft radiation. This can be seen from Eq. 4. Hence in order to get the maximum signal change, and with it the most accurate determination of the density change, the lowest energy radiation that will give sufficient transmitted intensity should be used. Table 4 gives the expected signal change $\frac{I_e}{I_s}$ for a 5% density change on transformation for the cases considered in Table 3.

Table 4 Transmitted intensity change for a 5% density change for the cases considered in Table 4.

	a	b	c	d	e	f
I_e/I_s	1.25	1.57	9.5	1.01	1.02	1.12

Hence W K_{α} would be useful only with heavier elements or if thicker samples were used.

4. Experimental

Description of Apparatus

The apparatus is shown schematically in Fig. (1). A graphite cell containing the test sample is located inside an electrical resistance furnace. The axis of the windows of the sample cell is aligned with a collimated x-ray beam, and the transmitted intensity is measured with a Ge detector and an energy dispersive pulse counting system.

Graphite was chosen as the cell material (in preference to BN) on the bases of cost, availability and ease of fabrication. It is critical that the sample fit tightly inside the cell, so the cell was designed to compress the sample on assembly. The cell (Fig. 2) consists of three plates of graphite (3.33 cm sq.) clamped firmly between two supporting stainless steel plates. The center plate has the same thickness as the sample and a recess slightly larger than the sample—to allow for thermal expansion. The two outer plates constitute the cell walls and are thinned in the center to 1.5mm to minimize absorption of the x-ray beam whilst still retaining structural stability.

The test samples are 1.9cm x 0.8cm x 0.25cm and are recessed to receive a thermocouple. The thickness is controlled accurately to better than 0.2% to ensure a tight fit inside the cell. Smaller sample sizes could be used if necessary, the main limitations on minimum size being the area of the sampling beam and the accuracy of the alignment. When large samples of material are available, it is practical to use a large beam area to minimize errors that could result from small scale heterogeneities in the test material and small changes in alignment of the system as it heats.

The metal alloy samples are examined metallographically to ensure that the phases are dispersed evenly and on a fine enough scale for the measurement to be representative. For example, the Cu-Al eutectic alloy measured in this study had an average interlamellar spacing of about 3×10^{-3} mm while the beam diameter as it passed through the sample had a diameter of about 7 mm. Consequently the density measured should have been a very good average.

The furnace (Fig. 3) was constructed by winding about 5m of No. 22 Nichrome resistance heating wire on the outside of an aluminum oxide tube of external diameter about 9cm. The tube has a spiral groove (2 turns per cm) on the outside in which the wire is cemented in position with electrical resistor cement. Two diametrically opposite holes (8mm dia) in the tube are the x-ray beam windows. A layer of 'Cerafelt' fibrous insulating wadding (2cm thick) is held in place with stainless steel tape. The furnace is purged with inert gas flowing at a rate of about one liter per minute to prevent oxidation of the sample and cell. The furnace stands on a Marinite base and a firebrick insert is used to raise the sample cell to the correct height. The heating is controlled by a variable output transformer, and the temperature inside the furnace is monitored using a Chromel-Alumel thermocouple which enters through the top of the furnace protected by an alumina sheath. The maximum temperature attainable by the furnace is near 1000°C, but the base and alignment track become hot when the furnace reaches 800°C.

A standard focus Mo x-ray tube is powered by a solid-state, high stability x-ray high voltage generator (Philips XRG-3000).

The radiation is filtered and attenuated by zirconium foils and collimated using a 3mm bore stainless steel tube.

A Ge solid state detector with a multichannel energy-dispersive analyzer provides adequate resolution of the K_{α} peak and integration of this or any other selected region of the spectrum. The electronics automatically compensate for dead time at high counting rates.

Procedure

A rectangular parallelepiped of the sample of known size is weighed accurately to determine the sample density at room temperature. The sample is placed in the cell, and the cell is located inside the furnace. Alignment is verified using a fluorescent screen. The generator output is adjusted so that the count rate is $>10^4/\text{sec}$, but so that the 'dead time' of the analyzer is less than 10%. The absorption cross-section of the alloy is determined by recording the reduction in transmitted intensity when samples of the alloy of known thickness are used to attenuate the beam, Eq. 1.

The count rate over 100 second intervals is checked for repeatability, and the temperature of the sample is recorded. The furnace is switched on and 100 sec. counts are recorded as the sample heats up. The temperature of the sample is recorded at the beginning and end of each count period. The heating is maintained at about 8K/min by manually increasing the furnace supply voltage as required to compensate for the increasing heat loss with temperature. Near the transformation temperature the heating rate

is reduced to enable a better determination of the intensity change on transformation. Measurements are continued above the melting temperature to determine the volumetric expansion coefficient of the liquid alloy. The maximum temperature that can be used is determined by the furnace limit ($\sim 1000^\circ\text{C}$), but the volatility of the sample, or by misalignment from overheating the base.

A calibration experiment in which no sample is used in the cell (but the x-rays are attenuated by an equivalent sample mounted outside the furnace) is also carried out. This permits a correction to be made to the expansion coefficients for changes in transmitted intensity that are not caused by density changes in the sample.

5. Results

1) Commercially Pure Aluminum

Based on the calculations presented in Section 3, aluminum was chosen as the test material with which to verify the feasibility of the method using the Mo x-ray source that was immediately available. This experiment approximates to case a) that was considered in Section 3. It was necessary to attenuate the radiation using 0.5mm of zirconium foil ($\sim$ by a factor of 200) to prevent saturation of the detector.

The plot of $\log_e I_t$ versus average temperature is shown in Fig. 5 for a typical experiment. Third-order polynomials were fitted to the expansion data for the solid and for the liquid. The values of $\log_e I_t$ at the transformation temperature for the solid and the liquid were determined from extrapolations of these

fitted curves. The results are summarized below (Table 5) and are seen to give very good agreement with the tabulated data.

Table 5 Measured and tabulated results for pure aluminum

	Temperature °C	Measured	Tabulated	Refs.
Density	20(s)	-	2698.9	3
in	660(s)	2565	2575	
kg/m ³	660(1)	2387	2368-2410	4
	760(1)	2355		
$\Delta V/V_S$		0.0745	0.0769	5
Linear exp. coeff(s) K ⁻¹		2.73×10^{-5}	3.0×10^{-5}	1
Vol. exp. coeff(l) K ⁻¹		1.36×10^{-4}	1.1×10^{-4}	4

NOTE: Tabulated values that are not referenced were calculated from the appropriate density and expansion data for which references are given.

ii) Copper/Aluminum Alloy

The Cu/Al eutectic alloy was the first to be prepared for heat storage measurements. For the reasons described in Section 3 this is an unfavorable alloy to monitor with Mo K_α radiation since it contains a substantial proportion (17 Atomic %) of Cu, which has a high absorption cross-section to that radiation. As anticipated, the K_α radiation was too strongly absorbed to be useful for the density change measurements. A narrow band of the higher energy continuum radiation (Fig. 4c) was selected using the energy dispersive analyzer, and this was used to monitor the density changes. This was found to work satisfactorily, and the

experimental results are summarized in Table 6.

Table 6 Summary of density change results on Cu/Al alloy

	Temperature °C	Measured	Tabulated*
Density	20(s)	3506	3570
in	548(s)	3424	3400
kg/m ³	548(l)	3258	3290
	748(l)	3186	3200
Lin. exp. coeff(s) K ⁻¹		1.5×10^{-5}	2.9×10^{-5}
Vol. exp. coeff(l) K ⁻¹		1.14×10^{-4}	
$\Delta V/V_s$		0.051	0.050

*See the summary by L. F. Mondolfo, Aluminum Alloys, Butterworths, London, 1976, pp. 255-6.

6. Discussion

i) The accuracy of the method

The calibration of the empty cell constituted the largest uncertainty in the method. The two principal contributing factors are the change in attenuation of the x-ray beam by the purge gas on expansion and the thinning of the cell walls through oxidation. Density changes in the cell wall caused by thermal expansion supply a negligible contribution to the calibration factor. Argon purge gas gave an unacceptably high calibration factor. Nitrogen and helium gave lower calibration factors that were found to be irreproducible. The uncertainty in the values of the expansion coefficients caused by heating of the purge gas is approximately $\pm 5\%$. The fractional volume change determination is only affected indirectly by this error, the resultant error in $\Delta V/V_s$ being less than $\pm 1\%$.

It should be possible to determine the absorption coefficient

to better than $\pm 1\%$ and the thickness of the sample even more precisely. The only other measurement which limits the accuracy of the method is the determination of the intensity change for the particular density changes of interest. The reproducibility of this factor has yet to be determined, but it is anticipated that a final accuracy of better than $\pm 5\%$ on the volume change of transformation should be obtained.

(ii) The applicability of the method

The method has been shown to be applicable to cases of low atomic number using Mo K_{α} radiation and, with minor modification, to metal alloy samples containing a substantial proportion of a heavier element. By using the appropriate radiation Mo, Ag or W K_{α} , and by choosing a sample of suitable thickness, virtually any material that melts below 1000°C can be studied. In some cases, a change of cell material or particular atmospheric control may be required. Difficulty would be encountered with samples that do not deform on expansion to maintain the same thickness as the cell, but otherwise the method should be generally applicable to the study of pure metals, metal alloys, salts, hydrocarbons, polymers or any other substance that can be machined or cast into a dense sample of suitable size.

(iii) Future developments

When alloys containing high atomic number elements are studied with Mo or Ag K_{α} radiation, the K_{α} peak is more strongly absorbed than the high energy continuum radiation (Fig. 4). The K_{α} intensity can be increased by increasing the generator output, but

this results in saturation of the detector by the continuum radiation. To utilize the K_{α} radiation and hence gain maximum precision on the intensity change measurement it would be necessary to isolate the K_{α} radiation from the continuum radiation using a monochromator. A graphite monochromator would suit this purpose best and could be incorporated with a small degree of modification to the existing system. For some of the alloys that contain a larger proportion of heavy elements it may prove necessary to use W K_{α} radiation unless thinner samples can be used satisfactorily. It is planned to change to a Ag tube in which the K_{α} rays can be excited by the power sources on hand and to select the characteristic radiation with minimum loss in intensity with a graphite monochromator.

7. Recent Modifications in the X-ray Dilatometry Experiment

Changes in transmitted intensity caused by density changes in the purge gas (on heating) have been minimized by converting the furnace to vacuum operation. The furnace is now mounted on an aluminum base and is covered by a stainless steel cover (Fig. 3). The vacuum seal between the base and cover is achieved using a Viton O-ring seal. Beryllium windows (5/8" dia. and 0.01" thick) are held between O-rings in standard Cajon fittings which are soldered to the cover. Vacuum and electrical connections are all made through the aluminum base. A vacuum of <5 torr is achieved using a small rotary vacuum pump. A maximum temperature of ~800C can be reached before conduction through the base makes the alignment bar uncomfortably hot.

On testing the vacuum furnace, without a sample cell, the transmitted intensity was found to decrease after a temperature of ~300C was reached. This was eventually traced to the degassing of the volatile binder from the fibrous insulation. A replacement insulating material did not overcome this problem, nor did repeated 'bake-outs' of the furnace at 800C. The fibrous insulation has now been replaced by two nested stainless steel heat shields which have been found to work satisfactorily.

The stability of the x-ray generator caused some concern but was found to be more than adequate providing that the water cooling jet in the x-ray tube remained totally unblocked. To this end the plumbing module was cleaned thoroughly and the tube

backflushed (by reversing the water connections) prior to each experiment.

Some increase in intensity is still observed on heating an empty cell, but this is now considerably reduced from the early experiments. A small irreversible contribution exists because of thinning of the graphite walls through oxidation. This contribution is very small (graphite has a low μ/ρ) but could be improved by improving the vacuum, using a scavenger (e.g. titanium) or by using a slow purge of inert gas. When harder radiation is used then this error will become even less significant.

The increase in intensity on heating was observed to increase as the collimator size was reduced, leading to the conclusion that the primary cause of the change is distortion of the alignment as the apparatus heats up. This conclusion is consistent with the observations that the increase in intensity occurs most rapidly at high temperatures and is almost totally reversible. The use of a 1/8" collimator, giving a beam diameter of $\sim 3/16$ -1/4" at the sample, gives approximately a 1% increase in count between room temperature and 660C for an empty cell. Some improvement may be achieved by water-cooling the aluminum base to prevent heating of the alignment bar. For the purpose of determining the volume change on transformation the use of the empty cell correction (which is $\sim 7\%$ of the signal change caused by solid expansion) will be adequate. The use of thicker samples, which is possible with the present Mo x-ray source and very desirable with the Ag source being prepared, will increase the signal/correction ratio and will be undertaken in the near future.

8. Results from the Vacuum Furnace

Tables 7 and 8 summarize the data and results obtained recently from vacuum furnace experiments.

Empty cell calibrations using a 3/32" bore collimator are observed to be much greater than, and to have an uncertainty equal to, the correction required when a 1/8" bore collimator is used. Future experiments therefore will be carried out using the 1/8" bore collimator whenever the sample size permits.

The volume change on transformation measurements for aluminum appear to be consistent, having an average value of 0.079. This is a little higher than the value (0.077) determined by Wray (5) from estimates of the best density measurements on the solid (1) and liquid (6). They are however significantly greater than the value of 0.070 reported by several workers (7).

The results for the solid expansion were not so reproducible. The data from experiments 47 and 54 showed irregularities in the plots of $\ln V$ v. T and also exhibit rather low values for the expansion coefficient. Sample 47 had been heated to $\sim 200^\circ\text{C}$ several times before carrying out the experiment, and sample 54 was slightly undersize. Consequently neither may have filled the cell completely at 20°C . The other three results are more consistent and are closer to the value determined from the work of Simmons and Balluffi (1) of $2.97 \times 10^{-5} \text{ K}^{-1}$ and that reported in the C.R.C. handbook $2.5 \times 10^{-5} \text{ K}^{-1}$ (4). In the other experiments the sample is marginally thicker ($\sim 0.0001''$) than the minimum thickness of the sample cell. A good fit can be assured by

Table 7 Summary of Data Using the Vacuum Furnace Assembly
Experiments 47-52 were done with a 3/32" collimator
and 53-57 were done with a 1/8" collimator.

Expt	ln I				Δ ln I		
	20°C	560(±)°C	660(±)°C	760	20-660	melting	660-760
47*	11.6330	11.7900	12.0290	12.0732	0.157	0.239	0.0442
48	11.8479	12.0571	12.3115	12.3725	0.2092	0.2544	0.0612
49	11.5715	11.6031	—	11.6252	0.0319	—	0.0218
50	11.6553	11.7166	—	—	0.057	—	—
51	11.6587	11.6564	—	11.7012	0.0277	—	0.0148
52	11.6616	11.7004	—	11.7137	0.0388	—	0.0133
53	11.6835	11.6950	—	11.6971	0.0085	—	0.0051
54**	11.9207	12.0243	12.2679	12.3033	0.119	0.2437	0.0354
55	11.9015	12.0737	12.3233	12.3162	0.1805	0.2496	0.0229
56	11.7720	11.7823		11.7843	0.0103		0.0020
57 #	11.8074	11.9670	12.2173	12.2546	0.1600	0.2503	0.0373

* Preheated to 200C, therefore the change from 20-660 C is too low.

** Undersized sample, " " " " " "

Density decreased rapidly just below the eutectic temperature.

Table 8 Summary of Results for Aluminum Using Vacuum Furnace Assembly

Expt.	Aln I (corr.)*			Densities** gms/cm ³			Ave. Linear coeff. Expn.	$\Delta V/V_0$	Ave. Liq. coeff. Expn. K ⁻¹
	20-660	Melting	660-760	660(s)	660(e)	760(e)	K ⁻¹ x 10 ⁻⁵		x10 ⁻⁴
47	0.1181	0.239	0.0276	2.5969	2.4154	2.3926	2.0 x	0.075	1.5
48	0.1703	0.2544	0.0446	2.5569	2.3637	2.3280	2.0	0.082	1.5
54	0.1036	0.2437	0.0319	2.603	2.4179	2.3918	1.9 x	0.077	1.5
55	0.1711	0.2496	0.0194	2.5563	2.3662	2.3480	2.9	0.060	0.5
57	0.1506	0.2503	0.0336	2.5718	2.3817	2.3505	2.6	0.060	1.3
Averages (48, 55, 57 only)				2.56	2.37	2.34	2.8	0.079	1.1
Corrections: Expts. 47, 48 (3/32" collimator)				20-660	0.0539 (Ave. of 4 expts.)		x Initial sample may not have filled the container		
				660-760	0.0166 (Ave. of 4 expts.)				
Expts. 54, 55, 57 (1/8" collimator)				20-660	0.0094 (Ave. of 2 expts.)				
				660-760	0.0035 (Ave. of 2 expts.)				

Other data used, $\rho_{20} = 2.6989 \text{ gr}/\text{cm}^3$; $\frac{1}{\rho} = 5.16 \text{ cm}^2/\text{grm}$ (measured experimentally)

Cell thickness (20°C) = 0.254cm; linear coeff. expⁿ graphite $7.56 \times 10^{-6} \text{ K}^{-1}$

manufacturing the samples, ~0.001 mm oversize, and then grinding them using fine grade emery paper to the desired thickness or by compressing the sample holder in a press. The use of thicker samples, as advocated earlier, also will reduce the error caused by any mismatch in the cell and sample thickness.

The expansion data for the liquid exhibit considerable scatter, although the average coefficient of expansion is the same as the literature value, $1.1 \times 10^{-4} \text{ K}^{-1}$. The expansion of the liquid was derived in each case from about 10 to 15 data points. This shortage of data contributes a large proportion of the uncertainty in the final result. The relatively large correction that is required (from the empty cell experiment) also makes this measurement unreliable.

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FIG. 1 SCHEMATIC DIAGRAM OF APPARATUS

FIG. 2
THE SAMPLE CELL

FIG. 3 VACUUM FURNACE ASSEMBLY

FIG. 4 EFFECT OF FILTERING Mo RADIATION WITH Zr SHOWING ALSO THE DIFFERENTIAL ABSORPTION OF K_{α} LINE BY A SAMPLE CONTAINING A HEAVY ELEMENT.

Low Temperature Storage

INTRODUCTION

This section of the report describes the work carried out under ERDA Contract No. E(11-1)-4042 in the College of Engineering at the University of Delaware to investigate the thermal and physical properties of the Glaubers salt heat storage mixture developed by Dr. M. Telkes(1,2). The work includes visual observations of the crystallization process, measurement of the crystallization rate and its dependence upon the degree of undercooling and measurements of the thermal conductivities of both the solid and the liquid mixture.

The mixture under investigation(3) consists of Glaubers salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) (88% by weight) a thixotropic thickening agent (an attapulgitic clay) (~2% by wt.) and borax (~3% by weight). The Glaubers salt is the phase change T.E.S. material. It partially melts in a peritectic transformation at 32°C (90°F) with a heat of transformation 250kJ/Kg (108 Btu/lb). The partial melting results in a saturated aqueous solution containing 36% by wt. of Na_2SO_4 and excess anhydrous sodium sulfate. The anhydrous sodium sulfate, being denser than the saturated solution, segregates out and is thus unable to recombine readily with the solution on cooling. This naturally reduces the heat storage capabilities of the salt. The thixotropic thickening material is added to produce a gel which inhibits settling of the anhydrous particles on melting, enabling their reconversion to Glaubers salt and the recovery of the stored heat of fusion. The borax crystals are added as a suitable nucleating agent (identified by Dr. Telkes) to minimize supercooling of the mixture. The borax is denser than the saturated

solution and is also supported by the gel on a finely dispersed scale.

The peritectic reaction which occurs on solidification is not fully understood and the development of a basic understanding of this and of the physical aspects of the behaviour of the gel will probably be a vital step in optimizing the performance of the mixture. However, for practical applications, this may prove to be superfluous if calorimetric tests show that the gel facilitates complete recovery of the heat of fusion and that deterioration does not progress after multiple successive melting and solidification cycles. The crystallization and thermal properties mutually determine the rate at which heat can be input to or recovered from the mixture and are important in the design and sizing of heat exchange and container systems. Some data are available for the crystallization from saturated solutions of Glaubers salt(4) and for the thermal conductivity of solutions of various compositions(5). We are concerned with how these are modified in the presence of the thickening agent. It will be shown that the solidification process is distinctly different in the thickened material, and it is obvious that even if the thermal conductivities of thickened and unthickened materials do not differ drastically, convective heat transfer in the thickened material will be considerably reduced.

Part III of the report describes the thermal conductivity measurement technique developed by Mr. A. S. K. Harding and Dr. Y. S. Lou; Part IV describes the crystal growth studies initiated by Dr. J. J. Kramer and continued by Dr. A. J. Harrison and Dr. Y. S. Lou.

III. Thermal Conductivity

3.1 INTRODUCTION

The inclusion of this thickener in the sodium sulphate decahydrate mix, to improve its performance as a thermal energy storage material, does raise questions on the actual behaviour of this modified material when used in any system. An analytical approach to answering some of the questions can be directed primarily to:

- a) Establishing the ability to suppress the directional deposition of the anhydrous sodium sulphate.
- b) Obtaining the thermophysical properties of the thickened material, and both the liquid and solid densities.
- c) Determining interface velocities for differing boundary conditions.
- d) Testing the material in a model test cell, to determine correlation with a corresponding mathematical model.

In all of the above experimentation, attention is being paid to observing the effects of cycling on its performance. This report does not include item (c), as this was undertaken by Dr. Andrew Harrison, and is presented in Part II of the report.

3.2 Experimental methods and observations

3.2.1 Visual observations: (i) - The mixes for heating and air-conditioning were placed in one-half gallon plastic containers and left to stand undisturbed for a year and eight months respectively. This was done primarily to find out whether aging, sedimentation, etc. has any effect on the thermophysical properties, and if overall it does cause drastic changes in the expected performance of the system. It has been observed that a clear solution does

separate out of the mixes. Definite weight proportions and composition of the solution have not been established, since the original intention has not been fulfilled and decanting the solution would have altered the initial composition. Another set has been prepared to make these measurements.

(ii) Visual observations of cooling and heating runs have been made to determine the pattern of crystallization and melting [Ref. Bailey, Kramer, and Harrison]. This was necessary in determining the form of the mathematical model that can be useful in the analysis. In many cases a distinct interface was distinguishable, though it was not easy to detect for thicknesses over 1/4 in. because of the opacity of the mixes. It was observed, as was expected, that ahead of the interface during solidification the concentration of the thickener progressively increased. This is suggesting that it may be necessary to include impurity as a parameter in the model analysis. However, this is not contemplated now as it would only complicate the work when a one-dimensional, finite domain, Stefan-type solution might provide a start in predicting the behaviour of the mixes.

(iii) It is difficult to make any conclusive observations from the cooling-heating cycles demonstrated so far by Bailey, Kramer and Harrison. The impairment of visual observation due to a cellular type pattern that develops on the plexiglass walls of their cells during and after the first cooling half cycle makes it difficult to detect whether some anhydrate settles at the bottom or not. Nevertheless, it is possible that with good insulation of the cell, a controlled environment, and knowledge

of the thermophysical properties (including the effect of aging and cycling), the extent of anhydrate settlement can be estimated by observation of successive interface growth rates for constant boundary conditions and the assumption that no preferential redistribution of the nucleating agent occurs.

3.2.2 Determination of the thermophysical properties:- (K_1 , Cp_1 , K_s , Cp_s and H_{1s})

K $\equiv$ Thermal conductivity; Cp $\equiv$ Heat capacity, H $\equiv$ Energy of phase transition. Subscripts 1 and s refer to the liquid and solid phases respectively.

Thermal Conductivity Measurement:- This has been done using the concentric cylinders configuration, adopting the comparative study method with water as the reference medium. To check the values of the cell constant, sodium chloride solution of 12.5% by weight solute to solvent strength was tested to determine its thermal conductivity.

The cell comprises an inner stainless steel tube (A) within which the main heater (M) is located, an end heater (E_1, E_2) on either side, two phenolic spacer pieces (S_1 & S_2), a Plexiglass tube set concentrically with the steel tube and spaced 0.25 in. apart, and an outside Plexiglass tube through which the cooling water is circulated (Diagram A1). The test section is 2.25 ± 0.002 in.i/d, $2.75 \pm .005$ in.o/d and 6 in.long. The total length of the cell is 24 in.; and it is boxed and insulated substantially with fibre glass insulation. Thermocouples, 12 per tube and 3 per column, are located on longitudinal axes 90° apart on the steel and Plexiglass tubes within the test section. The beads of these thermocouples are embedded to within 0.001 in. and

0.015 in. of coming through the steel and plexiglass tube surfaces respectively. This was done to avoid any contact between the thermocouple beads and the salt hydrate. Thermocouples are also located on the main and end heater elements, and in the spacer pieces at intervals of 0.25 in. to within 0.25 in. of their contact surfaces within the medium. These are used to determine how near to a steady state condition exists before data are taken. The temperature of the coolant is monitored at the inlet to and the outlet from the cell, and the temperature of the surroundings is also recorded. The temperature measurements are obtained using an ice-bath reference, through two 24-point switches on to a Leeds and Northrop type K-4 Potentiometer and an electronic null detector.

3.3 Heat capacity and heat of transition measurements:- The measurement of these quantities have been attempted using the Perkin-Elmer Differential Scanning Calorimeter (DSC 2). The first few results were not convincing but have led to plans for more experimentation with the instrument to determine the extent to which the test problems with this material can be obviated, if at all. Although the 86.5 mg of sample is large for usual DSC samples, yet doubts exist about how representative such samples are of the mixes. In consequence samples will be filled into the sample pans by using the mixes (a) when in solution and (b) solidified. The former is expected to approximate more closely the bulk material since the impurity effect of the thickener as well as its part in maintaining homogeneity and incomplete crystallization should still be present. The use of the solid material can, however, cause

problems since it is quite possible that the crystallization (purifying) process would have separated out some of the thickener, and deposition of the anhydrate may set in. It is expected the data will clarify some of the doubts.

3.4 Model test cell:- This is a rectangular cell with a test section 1 in. wide, 2 in. high and 6-1/2 in. long. It comprises two brass chiller plates B and B, two 1/16 in. Filon pieces into which the thermocouple probes are located. The rest is made out of Plexiglass and Styrofoam and glass tubes which lead the thermocouples, sixty in all, to the recording instrument. The thermocouples, once located, are insulated and sealed in the glass tubes to minimize any convective effects. They are placed in six rows, five in a row, on the bottom and top surfaces of the test section.

3.5 Results:- Numerical data are presently available for the thermal conductivity study. Obtaining these results involve setting the low side temperature and gradually increasing the energy input through the heaters. The temperature readings of the thermocouples embedded in the phenolic pieces are taken and the end heaters adjusted until there is little or no gradient in the pieces in the longitudinal direction. The cell is then left to run for a minimum of eight hours. A typical data sheet is as shown, and there are in all forty-five such sets.

3.5.1 Observation:- There is clear indication from the recorded data that the 89° mix has a higher thermal conductivity than water. It is hoped that when the program for reducing the information is

completely debugged, the figures will be made available. Further work on the materials is ongoing and conclusions will be available in the not too distant future.

A1

(11) TEST SECTION

INTERNAL DETAILS OF THERMAL CONDUCTIVITY CELL

SCALE 1:1	APPROVED BY	DRAWN BY
DATE		
		DRAWING NUMBER

THERMAL STORAGE TEST CELL ~ A CENTRAL TRANSVERSE SECTION.

FULL SCALE

A2.

SCHEMATIC OF THE THERMAL CONDUCTIVITY MEASUREMENT SET-UP

DATE

THERMOCOUPLE NO.

HEATER INPUT

	1	2	3	4	5	6	7	8	9	10	11	12	Left Guard	Main	Right Guard	
	13	14	15	16	17	18	19	20	21	22	23	24	Volts	AMP	Volts	AMP
Potentiometer	1.3955	1.4095	1.4006		1.4019	1.385	1.407	1.405	1.4009	1.4054	1.4089	1.405	1.35	0.104	1.98	0.55
Reading													DVM		DVM	DVM
MV	1.346	1.345	1.3457	1.347	1.344	1.3435		1.3471		1.347	1.3441	1.347				
Control Thermocouple																
Readings	1.315	1.3619		1.3619	1.3642			1.3785		1.366	1.3646				SET 2	
MV		1.3245	1.3262	0.9555	1.4085			1.3245	1.713	1.7415	1.764	1.402	cf (x) p IV (iii)			
Potentiometer	1.2325	1.2520	1.2385		1.2405	1.2215	1.2480	1.2455	1.2385	1.2460	1.2515	1.2445	1.55	0.120	6.08	0.675
Reading													DVM		DVM	DVM
MV	1.1590	1.1565	1.1575	1.1585	1.1550	1.1530		1.1585		1.1575	1.1545	1.1550				
Control Thermocouple																
Readings	1.2595	1.1865		1.1825	1.1855			1.2055		1.1865	1.1845				SET 2	
MV		1.1290	1.1300	0.9565	1.2560			1.1235	1.6990	1.7420	1.7730	1.2430	cf (xi) p V (ii)			
Potentiometer	1.2295	1.2475	1.2325		1.2368	1.2175	1.244	1.2413	1.2351	1.2422	1.2465	1.2409	1.45	0.113	5.74	0.6375
Reading													DVM		DVM	DVM
MV	1.1628	1.1612	1.161	1.1634	1.160	1.1585		1.168		1.1627	1.1595	1.1605				
Control Thermocouple																
Readings	1.2547	1.1890		1.1855	1.1882			1.2065		1.189	1.1875				SET 3	
MV		1.1367	1.1372	0.9424	1.2462			1.1324	1.6515	1.6905	1.7185	1.2403	cf (xii) p V (iii)			
Potentiometer	1.2122	1.222	1.2166		1.2165	1.2023	1.2199	1.2186	1.2165	1.2188	1.2212	1.219	1.30	0.101	4.09	0.45
Reading																0.17
MV	1.179	1.1785	1.1793	1.1798	1.1775	1.1776		1.1797		1.179	1.1768	1.1783				
Control Thermocouple																
Readings	1.2248	1.1914		1.1887	1.191			1.2035		1.1945	1.1927				SET 4	
MV		1.167	1.1675	0.934	1.221			1.1645	1.4293	1.4431	1.4607	1.2762	cf (xiii) p V (-)			

IV. Crystal Growth Studies

4.1 Crystal growth observations on an unthickened Glaubers salt solution

Glaubers salt crystallizes from a super-saturated solution as colorless, long, needle-shaped, monoclinic crystals which may be 2 cm or more in length. Using a cell of cylindrical cross-section and with radial heat flow, Glaubers salt crystals were observed to nucleate at a borax film around the periphery of the cell and to grow generally in the radial direction. However, a significant proportion of the crystals had their axes deviate as much as 60° from the radial direction. This suggests that the direction of growth is crystallographically controlled provided that a component of heat flow exists along the growth axis.

4.2 Crystal growth observations on thickened mixtures

In contrast to the unthickened mixtures the large monoclinic crystals are no longer observed but are replaced by a more homogeneous solidification. The presence of the greyish colored thickener makes visual observations very difficult and a suitably thin cell had to be constructed to enable observations to be made using transmitted light.

4.2.1 The crystallization cell

A cell (fig. 1) was designed to enable nearly unidirectional heat flow so that its use could be extended to the measurement of the crystallization rate. The cell has internal dimensions 3" x 2" x 1/4" and has 1/2" thick plexiglas walls to minimize heat losses through the sides. The 1/4" thickness is near the maximum that can be used if satisfactory observations are to be made using transmitted light. Further insulation of the cell walls is provided by an air

FIG. 1 SCHEMATIC DIAGRAM OF CRYSTALLIZATION CELL #1

gap between the wall and a second wall which is press fitted into position and sealed with vacuum grease. Filling apertures are located at both ends of the cell. The heat flow is controlled by brass chill plates on the top and bottom which are sealed by O-rings. The plates are thermostated by a flow of water through copper tubes, soldered to the chill plates, from constant temperature recirculating water baths. The plate temperatures are monitored using iron-constantan thermocouples.

4.2.2 Procedure

The cell is warmed and filled with the liquid mixture (which has been stored in a thermostated bath at 34C) using a jet suction pump to draw in the mixture. The filling tubes are sealed with rubber membranes to allow for expansion on solidification. The chill plates are maintained at a temperature just above the transition temperature (34C) for several hours to allow thermal equilibrium to be achieved. One or both of the chill plates are then cooled to a desired temperature. A microscope lamp with an infra-red filter, supplying back illumination for the cell, is switched on only when observations are being made to minimize distortion of the crystallization by heat from the lamp.

4.2.3 Observations

After cooling the chill plate there is usually a delay of 5-10 minutes before any solidification is observed. Following this delay, the initial crystallization occurs very rapidly and is probably associated with a rapid return to the equilibrium temperature after an initial supercooling. Steady growth of the 'crystallization' front, which is virtually linear (sometimes curved

because of end effects), then proceeds. The crystallization front is defined by the increased light transmission through the solidified material and by the dark band of segregated thickener that is observed to develop just ahead of the interface. In most cases, the top plate was maintained at 34°C and the bottom plate at some lower temperature. Solidification proceeded until some equilibrium position was reached near the top plate. When cooling was effected from top and bottom, simultaneously the two solidification fronts coalesced near the center line of the cell leaving a dark line of segregated thickener.

Fig. 2 shows the cell after equilibrium has been achieved in an experiment where cooling was effected from the bottom plate. The long needle-shaped crystals are replaced by a cellular-structured solid which is produced by microsegregation of the thickener into the crystal grain boundaries. The crystallite or cell size is in the early stages less than 0.5mm dia. but this increases as the solidification proceeds and as the rate slows down. The dark band at the top of the cell is the unsolidified mixture which now contains an increased proportion of thickener.

After solidification had been completed the cooling plate was increased to a temperature above 32°C to remelt the mixture. No apparent visual change occurred after several hours at 40°C since the mixture was found to retain its cellular structure in the melted state. The structure broke down very easily when probed through the filling port to yield a mixture which was homogeneous in appearance. It is probable that surface adhesion to the cell walls contributed to the stability of the structure, but on disassembly of the cell the structure appeared to be continuous

UNSOLIDIFIED
MIXTURE

TOP PLATE 34°C

'CELLULAR'
STRUCTURE

BOTTOM PLATE 26°C

(A) MIXTURE SOLIDIFIED

(34C)

(>40C)

(B) REMELTED

FIG.2 PHOTOGRAPHS OF THE CELL USING BACK-ILLUMINATION

throughout the cell. From the point of view of the stability of the mixture this result is very encouraging, but it showed that it would be impossible to make visual measurements of the melting rate.

On refreezing the mixture, very little change was observed in the appearance of the cell. The development of the solidification front could be observed in some cases because of the faint band of thickener that developed ahead of the interface. After the second cycle it was impossible to discern the position of the growing solid-liquid interface.

4.3 Measurement of the crystallization velocity

To determine whether the crystallization rate is controlled by the thermal diffusion rate or by the crystallization kinetics, it was studied as a function of the degree of undercooling. Information on the crystallization velocity is also important in the determination of the maximum thickness of salt mixture that can be used for a given practical set of heat retrieval conditions.

A series of preliminary measurements was made using cell #1 which was described in section 2.2.1. In each case the cell was first equilibrated at 34°C and then the top plate maintained at 34°C while the bottom plate was reduced to the required cooling temperature. Three nominal cooling temperatures 23, 26 and 29°C were investigated. Measurement of the interface position was recorded approximately every 2 minutes using a vernier travelling microscope.

Fig. 3 summarizes the results of these studies. The crystallization rate at 23°C was faster than that at 26°C. Crystallization could not be initiated by maintaining the bottom plate at 29°C.

The growth rate appears to be parabolic, the growth rate decreasing with increasing thickness of solid. These observations are consistent with a crystallization process that is controlled by the rate of thermal diffusion from the solidification front.

The observation that crystallization could not be initiated by a chill plate at 29°C (even after several hours) suggests that at least 3°C of supercooling is required even in the presence of the borax nucleating agent. For most practical applications this would not impose a serious limitation on the use of the salt mixture.

Fig. 3 also shows the effect on the crystallization rate of using a lower proportion of Na_2SO_4 in the mixture to give the equivalent of a thickened saturated solution. Crystallization occurs more slowly from the 36% mixture than from the 44% mixture. The reduction in rate may be caused by a lower interface temperature which results from the progressive reduction in concentration of the liquid mixture as crystallization proceeds.

4.3.1 Multiple heating and cooling cycles

The stability of the mixture under the effect of successive solidification and melting cycles is a prime factor in the determination of its suitability for practical applications. The cellular structure of the material (2.2.3) that is maintained on melting makes it difficult to observe multiple cycles. The addition of a small amount of green food dye enabled 5 freezing cycles to be observed because the dye was pushed ahead of the interface on each freezing cycle. The increase in optical density caused by the addition of the dye made the first solidification cycle harder to observe.

The results showing the effect of added dye and of multiple cycles are shown in fig. 4. There was no significant change in the crystallization rate over the first 5 cycles when cooled at 26°C.

4.3.2 Estimation of the ratio of the solid and liquid thermal conductivities

The equilibrium interface position was recorded for four cooling plate temperatures with the top plate maintained at -40°C. The ratio of the thermal conductivities of the solid and the liquid was then computed using the assumptions that linear temperature profiles existed and that the interface was at the transformation temp (31.7°C). Values for k_s/k_l of 1.11, 0.97, 1.00 and 1.04 were obtained. These results were somewhat surprising (c.f $k(\text{ice})/k(\text{water}) \sim 4.3$) and suggested that the temperature distribution within the mixture was being modified by conduction vertically through the thick plexiglas walls. To what extent this would affect the growth rate has not been determined.

4.3.3 Modified cell and vacuum technique

To minimize conduction through the cell walls a new thin walled cell was constructed which it is hoped will yield more quantitatively reliable crystal growth rate data. Heat loss by convection from the side walls is reduced by carrying out the experiment inside a vacuum chamber which is evacuated to ~ 100 microns. A cell wall thickness of $1/8"$ and a reduced cell height to $1-1/8"$ were required to prevent distortion of the cell through internal pressure. The sample thickness was increased from $1/4"$ to $3/8"$ to increase the sample/wall thickness ratio.

The plexiglas to brass seal was achieved using an epoxy

SOLID
THICKNESS
(MM)

FIG.5 DATA FROM THE THIN WALLED CELL

cement and the filling ports (which are threaded internally) are plugged with brass screws and sealed with silicone rubber. The cell is supported in the vacuum bell jar by the copper tubes which supply the thermostated water to the chill plates.

Only one set of data has been obtained with this system so far (fig. 5). This cannot be compared directly with the data from cell #1 because of the reduced cell height. However the new data lie between the data in fig. 3 as expected from the cooling temperature (24.3°C cf 23 and 26°C), and the parabolic shape is retained.

4.4 Simple analysis of the crystal growth rate data

We can represent the interface growth in the cell at any given time (t) by:

We have assumed that linear temperature profiles are maintained and will consider the heat flow to be unidirectional.

Let the interface velocity be v cm/sec. when the solid thickness is x . Then, for unit cross-sectional area:

$$\text{Rate of formation of solid} = v\rho_s \text{ gm/cm}^2/\text{sec.}$$

$$\text{Rate of heat release at interface} = v\rho_s \Delta H_c \text{ J/sec/cm}^2$$

(ρ_s = solid density and ΔH_c is the heat of fusion of the solid)

mixture in J/gm).

Heat flow through the solid $Q_s = \frac{k_s (T_m - T_b)}{x}$ J/sec/cm²

Heat flow through the liquid $Q_l = \frac{k_l (T_t - T_m)}{(h-x)}$ J/sec/cm²

If there is no heat flow through the side or end walls of the cell

$$Q_s = Q_{\text{cryst}} + Q_l$$

$$v \rho_s \Delta H_c = \frac{k_s (T_m - T_b)}{x} - \frac{k_l (T_t - T_m)}{(h-x)}$$

$$\Delta H_c = \frac{1}{v \rho_s} \left(\frac{k_s (T_m - T_b)}{x} - \frac{k_l (T_t - T_m)}{(h-x)} \right)$$

The data from 3 experiments using the 44% thickened Glaubers salt mixture were treated as shown above. The first two sets of data were those obtained from cell #1 (fig. 3) and the third set was from the modified thin-walled vacuum cell. Experimental heats of fusion (or crystallization) were obtained. The interface temperature was taken to be 31.7°C (89°F) and the density of the solid taken to be that of Glaubers salt (1.46 g/cm³).

The experimental data were fitted to 3rd order polynomial expansions (this gave a better fit than a 2nd order polynomial), and the solid thickness after 25, 50, 100 and 150 minutes was calculated from these. Data from the early part of the crystallization were not considered since the temperature profiles would not be fully developed in the early stages. Differentiation of the polynomial expansions permitted the corresponding velocities dx/dt to be calculated.

4.4.1 Results of analysis

Case #1 Cell #1, $h = 4.763\text{cm}$, $T_t = 34^\circ\text{C}$, $T_b = 26^\circ\text{C}$

$$x(\text{mm}) = 2.2827 + 0.15597t - 4.995 \times 10^{-4}t^2 + 7.8243 \times 10^{-7}t^3 \quad (t \text{ in min})$$

Case #2 Cell #1, $h = 4.763\text{cm}$, $T_t = 34^\circ\text{C}$, $T_b = 23.2^\circ\text{C}$

$$x(\text{mm}) = 2.45518 + 0.25929t - 1.349 \times 10^{-3}t^2 + 3.2329 \times 10^{-6}t^3 \quad (t \text{ in min})$$

Case #3 Cell #2, $h = 2.619\text{cm}$, $T_t = 34^\circ\text{C}$, $T_b = 24.25^\circ\text{C}$

$$x(\text{mm}) = 3.34357 + 0.22268t - 2.395 \times 10^{-3}t^2 + 1.2373 \times 10^{-5}t^3 \quad (t \text{ in min})$$

Time (mins)	ΔH (cal/grm)		
	Case #1	Case #2	Case #3
25	40.0	29.2	39.0
50	29.8	26.8	45.4
100	25.3	26.0	
150	25.3	23.6	

All the results show a lower experimental ΔH than the theoretical 55 cal/grm (reduced from the 60 cal/grm of pure G.S. by the addition of 'inert' thickener + borax). It is likely that the thermal conductivity of the solid will be higher than that of the liquid or saturated solution and this may be a partial explanation for the low measured value. If heat is lost through the cell walls this will increase the crystallization velocity and so reduce the calculated heat of fusion. The latter explanation is consistent with the higher ΔH values calculated from the data from the thin walled vacuum cell. The fact that the calculated ΔH values tend to decrease with increasing solid thickness for cases 1 and 2 has not been satisfactorily explained.

It must be emphasized that the calculated ΔH is not necessarily a measure of the total heat storage capability of the salt since we have not considered the unsolidified material nor the effect of any crystallization that occurs in the solid behind the interface; it is merely a device to analyze simply the process occurring in the

cell. The accurate determination of the thermal conductivity of the solid and the acquisition of a complete and consistent set of data from the thin walled cell will enable a more precise and meaningful analysis of the solidification of the mixture.

4.5 Conclusions

I) Solidification of the thickened mixture results in a cellular structure which is caused by microsegregation into the crystal grain boundaries.

II) The cellular structure is retained on melting and refreezing.

III) Some macrosegregation of the thickener occurs ahead of the growing interface. This appears to be significant only on the first cycle.

IV) The crystallization is limited by the rate of thermal diffusion from the growing interface.

V) The crystallization rate is the same for the first 5 cycles when a cooling temperature of 26°C is used.

VI) A thickened saturated solution of Glaubers salt (36%) crystallizes more slowly than the 44% mixture when cooled at -23°C.

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