NASA CONTRACTOR REPORT

NASA CR-61363

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PHASE CHANGE MATERIALS HANDBOOK

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September 1971

(NASA-CR-61363) PHASE CHANGE "ATERIALS N72-19956 HANDEOOK D.V. Hale, et al (Lockheed Missiles and Space Co.) Sep. 1971 200 p CSCL 20M G3/33 19660

Prepared for

NASA-GEORGE C. MARSHALL SPACE FLIGHT CENTER Marshall Space Flight Center, Alabama 35812 Ì

NASA CR-61363	GOVERNMENT ACCESSION NO.	3. RECIPIENT'S CATALOG NO.
TITLE AND SUBTIFLE		5. REPORT DATE September 1971
Phase Change Materials Handbo	ook	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)		8. PERFORMING ORGANIZATION REPOR
D. V. Hale, M. J. Hoover, and	l M. J. O'Neill	LMSC-HREC D225138
9. PERFORMING ORGANIZATION NAME AND ADDR	ESS	10. WORK UNIT NO.
Lockheed Missiles & Space Con	npany	
Huntsville Research & Engineer	ring Center	11. CONTRACT OF GRANT NO.
4800 Bradiord Drive, Huntsville	e, Alabama	NA58-45183
12. SPONSORING AGENCY NAME AND ADDRESS		13. TYPE OF REPORT & PERIOD COVE
National Aeronautics and Space	Administration	High Series Contractor
George C. Marshall Space Fligh	ht Center, Alabama 35812	Report
		14. SPONSORING AGENCY CODE
15. SUPPLEMENTARY NOTES	. .	
Laited by Barbara E. Richard,	Space Sciences Laboratory	, National Aeronautics
and Space Administration, Geor	rge C. Marshall Space Flig	ht Center, Alabama 35812
16 4B3TR4CT		
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PREFACE

The concept of using phase change materials (PCM) to maintain a constant temperature is at least as old as the ice box. Over the years many applications of this idea have emerged, including the need for energy storage and release in the spacecraft environment. Since 1964 Space Sciences Laboratory at Marshall Space Flight Center has been doing research and development to make the technique more applicable to the environment of space. For example, through inhouse work and contractual efforts many phase change materials have been defined over a wide temperature range and much data on their performance has been gathered. Information on packaging problems, the effects of bubble formation, supercooling and other design and performance considerations has been developed by this and other laboratories.

As the state of the art grew, the concept began to be applied by designers as a part of the overall thermal control of space vehicles. The increase in popularity of the technique indicated that an engineering handbook encompassing the entire work to date was desirable. In November, 1970, a contract was let with Lockheed Missiles & Space Company in Huntsville to prepare such a handbook.

The information contained in this document should enable the engineer to determine whether or not the use of PCM would be helpful in overcoming his particular thermal control problems; further, data necessary for design and development of a PCM thermal control package is also presented.

In anticipation of a possible second edition of this handbook, Space Sciences Laboratory would be especially interested in receiving questions, comments, and additional input. These can be directed to Barbara E. Richard, Marshall Space Flight Center, Space Sciences Laboratory, S&E-SSL-T, Marshall Space Flight Center, Ala., 35812, Phone: (205) 453-3090.

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FOREWORD

Lockheed Missiles & Space Company, Huntsville Research & Engineering Center presents this Handbook of Phase Change Materials to the National Aeronautics and Space Administration, George C. Marshall Space Flight Center (NASA-MSFC).

This work fulfills Task I: Phase Change Material Handbook Development, as set forth in Contract NAS8-25183, which is to compile a handbook from existing PCM property and design data. This handbook development program was sponsored by the George C. Marshall Space Flight Center, National Aeronautics and Space Administration, Huntsville, Alabama. Miss Barbara E. Richard is the Contracting Officer's Representative of the study.

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NOMENCLATURE

Α	area			
В	Marangoni number			
Btu	British thermal unit			
°C	degrees Celsius			
cal	calorie			
cm	centimeter			
Comp	component			
с _р	specific heat at constant pressure	2		
DTA	differential thermal analyzer			
E	energy			
emf	electromotive force			
°F	degrees Fahrenheit			
ft	foot			
gm	gram			
$h_{f}^{}, \Delta H_{f}^{}$	latent heat of fusion			
hr	hour			
J	joule			
k	thermal conductivity			
°К	degrees Kelvin			
kg	kilogram			
lb _m	pounds mass	Preceding	page	blank

m	mass, meter
mm	millimeter
N	newton
N _{pr}	Prandtl number
P	pressure
PCM	phase change material
Q	heat rate
R	Rayleigh number, thermal resistance
rad	radiator
Т	temperature
t	thickness
ΔΤ	temperature difference
TCS	thermal control system
v	volume
ΔV _{melt}	volume change during melting
w	watt
Greek	
α	thermal diffusivity
E	emissivity
∆ θ	time change
μ	dynamic visc osity
ν	kinematic viscosity ($\nu = \mu/\rho$)
ρ	mass density
σ	surface tension, Stefan-Boltzmann constant
<u>θT</u> ðX	partial derivative of temperature with respect to X-coordinate; i.e., temperature gradient in X-direction

Subscripts

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adh	adhesive
Al	aluminum
atm	atmospheric
avg	average
С	container
comp	component
ср	cold plate
eq	equivalent
F	filler
f	fusion
gen	generated
<i>l</i> , L	liquid phase
max	maximum
melt	at melting point
РСМ	phase change material
pulse	during heat generation pulse
RAD	radiation
rad	radiator
s, S	solid phase
T, tot	total

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Section 1 INTRODUCTION AND SUMMARY

The unique ability of phase change materials (PCM) to absorb and liberate large quantities of heat without appreciable temperature change will undoubtedly have numerous ramifications in the fields of spacecraft thermal control and energy storage. Although the major effort to date in PCM technology has been largely confined to preliminary theoretical and empirical research, actual PCM flight systems scheduled for use on the Lunar Roving Vehicle and Skylab attest to the practicality of the PCM technique. For the design engineer, however, there is still a large gap between research achievements and actual flight systems. The goal of this handbook is to provide the theory and data needed by the thermal design engineer to bridge this gap, within the limits of the current state of the art of PCM technology.

To accomplish this goal, information is included in this handbook relating to many aspects of PCM technology. The relationship between PCM and more conventional thermal control techniques is described and numerous space and terrestrial applications of PCM are discussed. Material properties of the most promising PCMs are provided in detail. The purpose and use of metallic filler materials in PCM composites are presented. Material compatibility considerations relevant to PCM design are also included.

The engineering considerations of PCM design are described in detail, especially those pertaining to the thermodynamic and heat transfer phenomena peculiar to PCM design. Methods of obtaining data not currently available are presented. The special problems encountered in the space environment are described. Computational tools useful to the designer are discussed.

In summary, each aspect of the PCM problem important to the design engineer is covered to the extent allowed by the scope of this effort and the state of the art.

Section 2

DEFINITION AND DISCUSSION OF PROPERTIES AND TERMS

The following definitions include terms used in this handbook which describe PCM behavior and PCM properties. The purpose of these definitions is to provide the designer with a handy reference for terms used in PCM technology.

<u>Amorphous</u>: Without definite form; not crystalline. Amorphous solids can be thought of as supercooled liquids. They do not have a sharp melting point like a crystalline solid. Glass is a typical amorphous solid.

<u>Autoignition Temperature</u>: The temperature at which a material will selfignite and sustain combustion in the absence of a spark or flame.

British Thermal Unit (Btu): The heat required to raise the temperature of one pound of water one degree Farenheit, at its maximum density (Ref. 1).

<u>Calorie (cal)</u>: The amount of heat necessary to raise 1 gram of water one degree Kelvin at 288[°]K. It is equivalent to 0.00396 Btu or 4.184 Joules (Ref. 2).

<u>Coefficient of Volume Expansion</u>: The ratio of the change in volume per degree Kelvin to the volume at 273° Kelvin.

<u>Corrosion</u>: The result of electrochemical or chemical reaction between a metal and its surroundings. Corrosion may be classified into eight forms: galvanic, uniform, concentration-cell, pitting, intergranular, stress, selective leaching and erosion. The kinetics of corrosion reactions deal with the effects of time, temperature, pressure, and surface conditions on the rate of corrosion. Surface films are used as barriers between the metal and its environment to prevent corrosion.

<u>Crystal</u>: A solid in which the atoms or molecules are arranged in a regularly spaced, repeating pattern. Most crystalline solids are made up of millions

of tiny single crystals called grains. Any single crystal, no matter how large is a grain. The crystals of a single substance all show the same geometrical structures; corresponding crystal faces have the same angles between them. Crystals vary greatly, depending upon the type and strength of the bonds between the constituent atoms, ions, or molecules. The crystal structure has been used as a basis for identification by X-ray, electron, and neutron diffraction methods. Crystals may be classified into geometrical types which include: simple cubic, body-centered cubic, face-centered cubic, tetragonal, orthorhombic, monoclinic, triclinic, and hexagonal (Refs. 1 and 5).

<u>Eutectic</u>: That mixture of two or more substances which has the lowest melting point. A eutectic compound has a sharp melting point, as does a pure compound. The composition stays the same in reversible freezing-melting cycles.

<u>Flammable</u>: That property of a material which permits it to oxidize rapidly and release heat of combustion when exposed to flame or fire, and allows continuous burning after the external ignition source is removed (Ref. 6).

<u>Flash Point</u>: The temperature at which a liquid or combustible vapor ignites and burns. The ensuing fire is transient and self-extinguishing. There are several common flash point tests and each yields a different value for the same substance.

<u>Freezing Point</u>: The temperature at which a material solidifies on cooling from a molten state. The freezing point is not always the same as the melting point.

<u>Heat Capacity at Constant Pressure</u> (C_p) : The quantity of heat required to raise a unit mass of homogeneous material one unit of temperature with pressure held constant. Heat capacity is expressed as energy per unit mass per unit change in temperature.

<u>Hygroscopic</u>: The property of a material which enables it to absorb and retain water from ambient air. The properties of a material can be drastically altered by absorbed water (Ref. 6).

<u>Melting Point</u>: The temperature at which liquefaction of a solid occurs. Alloys and impure materials have a melting range. The melting point is not always the same as the freezing point.

<u>Nucleation</u>: The formation of the first crystals capable of spontaneous growth into large crystals in an unstable liquid phase. These first particles, called nuclei, may be formed on solid particles already in the system (heterogeneous nucleation) such as dust, glass, or other foreign solids. Nuclei may be generated spontaneously from the liquid itself at the onset of freezing (homogeneous nucleation).

Oxidizing Agents: Generally sources of oxygen. Some materials are chemically constituted such that they can supply oxygen to a reaction, even in the absence of air.

<u>Phase Change:</u> The change of a material in one physically distinct and mechanically separable state (such as a definite solid state) to another distinct form (such as a liquid). Phase changes consist of four types: solid-solid, solid-vapor, solid-liquid, and liquid-vapor.

Polymorphism: The ability to exist in two or more crystalline forms.

<u>Prandtl Number</u> (N_{pr}) : The ratio of the fluid dynamic viscosity μ of a liquid to the quotient of its thermal conductivity k and heat capacity C_{p} .

$$N_{pr} = \mu / (k/C_p).$$

This property influences the heat-convecting ability of a fluid. Fluids such as liquid metals have low Prandtl numbers (N_{pr}) and are effective for convective heat transfer applications.

<u>Rayleigh Number (R)</u>: The ratio of gravity force to viscous force. The Rayleigh number is defined as (Ref. 7):

$$R = \frac{g\beta \frac{dT}{dY} d^4}{\nu \alpha}$$

- g = acceleration due to gravity
- β = coefficient of thermal expansion of the liquid

dT/dy = the vertical temperature gradient applied to the lower surface

- d = thickness of fluid layer
- v = kinematic viscosity
- α = thermal diffusivity.

<u>Solid Solution</u>: Thermodynamically and physically analogous to the common liquid solution except for the existence of a regular crystal lattice; a homogeneous crystalline phase composed of several distinct chemical species. Solid solutions are commonly found in mixtures of monatomic substances (silver and gold, potassium and rubidium). Extensive solid-solution formation can occur only when the molecules or atoms of the two substances are very similar in size and state. The constituents are distributed at random among the various lattice sites, and no long-range order exists (Ref. 1).

Surface Tension (σ): The force acting on the surface of a liquid tending to minimize the area of the surface. Surface forces govern such phenomena as the wetting or nonwetting of solids, capillary rise, and the curvature of freeliquid surfaces. Molecules on the surface of a liquid are only partly surrounded by other molecules and thus are drawn inward by neighboring molecules. This unbalanced force at the surface is opposed by a surface tension force which results in the tendency of the liquid to give a minimum surface area. Surface tension is a function of temperature: the surface tension of liquids decreases with rising temperature (Refs. 4 and 5).

<u>Supercooling</u>: The process of cooling a liquid below the solid-liquid equilibrium temperature without any formation of the solid phase. Supercooling when only one phase is present is called one-phase supercooling. Supercooling in the presence of both solid and liquid is two-phase supercooling. The amount of supercooling depends upon the particular material and the environment surrounding it. The best way to reduce supercooling is to ensure that all of the original crystalline material does not melt. Crystalline seeds present in the melt tend to nucleate the solid phase when heat is removed. Nucleating catalysts are available for some materials (Ref. 7).

Thermal Conductivity (k): The ability of a material to transmit heat due to a temperature gradient in the material. Thermal conductivity varies with the temperature and has the dimensions of heat rate per unit area and per unit of temperature gradient.

<u>Thermal Diffusivity (α)</u>: The time rate of temperature movement through a material. It is not a measure of amount of heat nor of heat transfer. A large value indicates the ability of a body to equalize temperature differences within itself. This combines a small value of heat capacity C_p , denoting little heat storage, with a large value of thermal conductivity k, indicating a high heat flux for a given temperature difference. Therefore thermal diffusivity is:

$$\alpha = \frac{\mathbf{k}}{\rho C_{\mathbf{p}}} \cdot$$

<u>Toxicity</u>: The ability of a material to produce injury on a susceptible site on or in the body. Toxicologic phenomena cannot always be predicted with accuracy or explained on the basis of physical or chemical laws. Toxicity hazard is the probability that injury may be caused by the manner in which the material is used. There are three routes through which materials may enter the blood stream: the skin, the gastrointestinal route, and the lungs. Absorbed poisons may be of temporary or permanent duration. Local injury is produced by exposure of toxic materials to the skin or mucous membranes (Ref. 3).

<u>Vapor Pressure</u>: The pressure exerted when a solid or liquid is in equilibrium with its own vapor. Vapor pressure is a function of absolute temperature.

Wetting Ability: The tendency of materials to adhere to containers. If the angle between a fluid interface and a solid wall, or the "contact angle," is less than 90 degrees, the fluid is said to wet the container. The lower the surface tension, the greater the wetting ability.

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Section 3 THERMAL CONTROL TECHNIQUES

Phase change materials represent only one of many types of thermal control techniques. The following discussion is intended to show where PCM fits in the overall family of thermal control techniques and to remind the reader of the alternate methods which should be considered for various thermal control problems.

Each component of a spacecraft, from a microelectronic circuit to a human occupant, will operate correctly only when maintained within a specific temperature range. The thermal control problem is to control the energy exchange between each component and its environment in a way which will keep its temperature within the operational range.

The various thermal control techniques can be categorized into three main groups: (1) passive; (2) semipassive; and (3) active. A passive thermal control system (TCS) maintains the component temperature within the desired range through geometrical and thermophysical considerations alone, and requires neither moving parts, nor moving fluids, nor power input. A semipassive TCS involves the transfer of heat from a hot source to a cold sink. The transfer of heat may be from a source hotter than the component to the component, or from the component to a colder sink, or a combination of both. A semipassive TCS requires power input, or moving fluids, or moving parts, or a combination of these devices. An active TCS involves the transfer of heat from a cold source to a hot sink. In general, the component is the cold source and heat is "pumped" from it to a warmer sink through power input, or moving fluids, or moving parts, or a combination of these devices.

The outline below lists some of the numerous thermal control techniques currently used in spacecraft, or planned for use in future spacecraft.

I. Passive

- A. Thermal Coatings
- B. Thermal Insulations
- C. Heat Sinks
- D. Phase Change Materials

II. Semipassive

- A. Heater-Pump-Radiator Fluid Systems
- B. Thermal Louvers
- C. Heat Pipes

III. Active

- A. Vapor Compression Heat Pumps
- B. Absorption Cycle Heat Pumps

Each of these TCS techniques will be briefly reviewed in the following subsections.

3.1 PASSIVE THERMAL CONTROL TECHNIQUES

3.1.1 Thermal Coatings

Thermal coatings are substances placed on the surface of the component whose temperature is to be controlled. The substances selected exhibit the necessary thermal radiation characteristics to maintain thermal equilibrium within the operational temperature range of the component. By far the most important application for thermal coatings is on the exterior surfaces of the spacecraft. An orbiting vehicle receives heat via radiation from the sun

and the planet, develops internal heat due to electronics and mechanical inefficiencies, and emits heat to deep space via radiation. By using a thermal coating with the correct absorptivity for solar and planetary radiation, and the correct emissivity for radiating to deep space, the spacecraft can achieve the proper heat balance to control the surface temperature within the desired range. Thermal coatings are used on other spacecraft components, such as the interior walls, to maintain heat transfer rates and temperatures at desired levels. Since thermal coatings involve no moving parts or power input, they are quite reliable for TCS applications. The major problem associated with thermal coating reliability is degradation of the coating due to prelaunch or space environmental conditions.

3.1.2 Thermal Insulations

Thermal insulations are materials placed between the component and a hot source or cold sink, which effectively resist the transmission of heat to or from the component. The most efficient of these thermal insulations under vacuum conditions are the multilayer insulation (MLI) composites. MLI composites consist of alternate layers of reflective shields (generally goldized or aluminized mylar plastic) and low thermal conductivity spacer materials. The reflective shields block radiation to or from the component, and the spacer materials and contact resistance between adjacent layers block the conduction of heat to or from the component. The composites have two major applications: (1) to insulate cryogenic storage tanks, thereby preventing wasteful boiloff of the stored cryogen; and (2) to block heat transmission from exterior surfaces to the interior of spacecraft, and to dampen internally the cyclical variation of temperature experienced by the outermost surfaces of the spacecraft due to revolution about the planet. These MLI composites and other thermal insulations are quite reliable, since they contain no moving parts or power supplies which could fail. The major problems associated with MLI reliability are prelaunch degradation, structural damage during the ascent phase of the mission due to the fragility of the composites, and penetration heat leaks caused by structural supports and plumbing.

3.1.3 Heat Sinks

Heat sinks are materials of large thermal capacity (mC_n) which are placed in thermal contact with the component whose temperature is to be controlled. As heat is absorbed or generated by the component, the severe temperature rise which would occur if the component were not in contact with the heat sink will be reduced, because the heat will be conducted into the sink whose thermal capacity allows only a small temperature rise. The sink, in turn, will dispose of this heat via conduction or radiation to some other part of its environment. Heat sinks are useful only for components which have cyclical variations or short operation periods in heat absorbed or internally generated. They lend their thermal mass to the component to dampen its temperature variations. Obviously, the heat sinks can serve the same function in reverse; i.e., they can prevent severe cooling during periods of low heat absorption or generation. The most extensively used application for heat sinks is temperature control of electronic packages which have cyclical variations in power dissipation. The thermal mass of the sink maintains the component within the operational temperature range. In this and similar applications, heat sinks are quite reliable. The major disadvantage in the use of sinks is their excessive weight, since they must be made of metal to have the large thermal conductivity and capacity required.

3.1.4 Phase Change Materials

Phase change materials are discussed throughout the remainder of this handbook.

3.2 SEMIPASSIVE THERMAL CONTROL TECHNIQUES

3.2.1 Heater-Pump-Radiator Fluid Systems

A heater-pump-radiator (HPR) fluid thermal control system is a dynamic system for the addition or removal of heat from a component to maintain its temperature within the operational range. In general, some form of tempera-

ture sensor or thermostat detects changes in the temperature of the component and signals the heater and pump to adjust input heat and fluid flow rate to maintain the temperature within the required range. Such a system relies on a radiator of temperature lower than the component to accept the heat from the fluid and radiate it to deep space. In principle, if heating only is needed for the entire mission, the radiator can be deleted. If cooling only is needed, the heater can be deleted. An example of an HPR thermal control system is a system which maintains the atmosphere within a manned spacecraft at a fixed temperature. The fluid heats or cools the atmosphere in some sort of heat exchanger in which the atmospheric gas and the fluid exchange heat. If the atmosphere needs cooling, the heater is not used and the coolant fluid decreases the temperature of the atmosphere in the heat exchanger. If the atmosphere needs heating, the heater supplies the additional heat needed. By using both the cooling power of the radiator and the heating power of the heater, the temperature of the atmosphere is maintained within a prescribed range. The reliability of such a system will, of course, depend on the successful operation of the pump and heater, which could be jeopardized by failure of either device or by a fluid leak in the loop.

Note for later comparisons that the HPR system requires a "cold-running" radiator, i.e., a radiator whose temperature is lower than the component temperature. Such a radiator could conceivably be an impossibility if the incident heat flux is so large that the heat balance on the radiator requires a higher radiator temperature. Generally, this is not the case; however, a "cold-running" radiator is still inefficient, since the efficiency of radiating heat increases with the fourth power of the radiator temperature.

3.2.2 Thermal Louvers

Thermal louvers are basically thermal coatings which have variable radiation characteristics. These characteristics are thermostatically varied to maintain the proper temperature of a component which is experiencing cyclical variation in absorbed or generated heat. Operation of the louver system can

best be explained by describing the usual application of a thermal louver TCS. Electronic packages having variable power dissipation are generally mounted to heat sinks, as described previously. At peak power levels it is desirable to discharge more heat from the sink than at low power levels. Heat can be discharged by attaching a louver assembly to the heat sink. A bimetallic actuator opens the louvers at higher temperatures, and closes them at cooler temperatures. When the louvers are open they expose a highly emissive surface to dump maximum quantities of radiant heat to some external structure or to deep space. When they are closed, the outer surface has a lower emissivity, and dumps a smaller quantity of heat. When properly designed for specific applications, the louver TCS is able to maintain the sink, and therefore the component, at the proper temperature with a high degree of reliability.

3.2.3 Heat Pipes

The heat pipe is a TCS which utilizes saturated vapor convection and condensation to transfer heat over large distances with small temperature differentials. An example of a heat pipe application will best illustrate the operation of this TCS. A spacecraft within view of the sun has one side exposed to the solar radiation and one side sheltered in the shadow of the spacecraft. This effect tends to elevate the temperatures on the bright side and reduce the temperatures on the dark side. To simplify the thermal control problem of the interior, it is desirable to minimize the temperature differences between the bright and dark sides. A heat pipe extended from the hot to the cold side can effect heat transfer to minimize the temperature difference. The heat pipe is hollow and contains a low-pressure fluid. The fluid evaporates at the warm end of the pipe, absorbing heat there. The pressure will be greater at the warm end due to the evaporation and the elevated temperature. The pressure gradient causes the vapor to convect to the colder end where it condenses, liberating heat. The condensed liquid returns to the warm end through capillary action along a wick contained in a portion of the pipe cross section. The total process causes heat to move from the warm to

the cold side. A properly designed heat pipe should be quite reliable as a TCS, if no leaks occur along the pipe.

3.3 ACTIVE THERMAL CONTROL TECHNIQUES

3.3.1 Vapor-Compression Heat Pumps

A vapor-compression heat pump operates in the standard thermodynamic refrigeration cycle. This cycle is essentially composed of four processes: (1) heat removal from the component by evaporation of fluid; (2) compression of the fluid to higher temperature and pressure; (3) heat dump to radiator by condensation of fluid; and (4) expansion of fluid through turbine or throttle valve to initial pressure and temperature. The heat pump is essentially different from the semipassive HPR fluid system in that the radiator may be operated at a temperature higher than the component temperature, thus increasing the radiator efficiency, allowing a decrease in radiator area and weight. The vapor-compression heat pump is very reliable, providing successful operation of all components. The performance of such a refrigerator is, of course, limited by the performance of a Carnot refrigerator operating between the same temperature extremes.

3.3.2 Absorption-Cycle Heat Pump

An absorption-cycle heat pump can be used as a superior replacement for the conventional vapor-compression heat pump, if the spacecraft has on board a high temperature source producing large quantities of waste heat. Such a source is envisioned for the space station in the form of a nuclear reactor. Basically, the absorption-cycle heat pump is equivalent to the vaporcompression heat pump, with the substitution of an absorbent fluid loop for the compressor. The absorbent fluid loop utilizes the waste heat from the high temperature source to reduce the pumping power below that required for the vapor-compression cycle. The absorption-cycle heat pump also utilizes a "hot-running" radiator, with the benefit in efficiency and the associated reduction in radiator weight and area. The absorption-cycle refrigerator should

perform the same function in cooling a component that the vapor-compression refrigerator performs, with savings in weight and radiator area. The reliability of such a TCS should be comparable to the reliability of the conventional heat pump.

Section 4 PHASE CHANGE MATERIAL APPLICATIONS

The use of phase change materials for thermal control is not a new concept; consider the ice box used to store perishable foods before efficient, inexpensive active refrigeration systems were developed. In recent years, however, research and development effort in PCM technology has resulted in novel PCM applications, for both terrestrial and space environments. Recent studies indicate that perhaps the most beneficial application of phase change materials will be in the space environment.

In the following discussion, PCM applications are divided into two categories: (1) PCM space applications, and (2) PCM terrestrial applications. Both actual and potential applications are included, and examples are provided.

4.1 PCM SPACE APPLICATIONS

The use of PCM in thermal control systems (TCS) and thermal energy storage systems (TES) in the space environment has received widespread interest in recent years. The general areas of PCM space applications are discussed separately below.

4.1.1 Electronic Component Thermal Control Systems

The numerous electrical components used on a spacecraft present challenging thermal control problems. High power dissipating components must be prevented from overheating, and the usual earthbound cold-plate/convection method is no longer available. Conversely, components that are only activated occasionally must be prevented from cooling below an operational temperature, and the lack of atmosphere precludes normal convective methods. Such components present an ideal application for PCM thermal control.

The simplest form of PCM-TCS for electronic components is for oneduty cycle components in launch or reentry vehicles. Although such components are used only once, they generate large quantities of heat which must be removed from the component to prevent overheating and subsequent failure. By utilizing PCM, such a component can be thermally protected as shown in Fig. 4-1. The generated heat is absorbed via latent heat of fusion by the PCM without an appreciable temperature rise of the component. Such a system is totally passive and very reliable.

A more general application of PCM-TCS for electronic components is for cyclically operating components; i.e., components which operate in repeating on-off cycles. Such a system is shown in Fig. 4-2. In this arrangement, when the component generates heat during the "on" portion of the cycle, the energy is stored via phase change in the PCM. During the "off" portion of the cycle, the heat of fusion energy is removed via radiator, heat pipe, thermal strap, etc., to refreeze the PCM in preparation for the next on portion of the cycle. The alternate melting and freezing of the PCM enables the component to operate very nearly isothermally at all times.

Three PCM thermal control systems were used on the Lunar Roving Vehicle (LRV) during the mission of Apollo 15. The first PCM system was attached to the Signal Processing Unit (SPU) and to batteries via thermal straps. During each LRV sortie, the heat produced by the SPU was absorbed through phase change in the PCM package. The thermal mass of the batteries offered additional heat storage capability. After the sortie, louvers were opened on a radiator which was also connected to the PCM package via thermal straps. The PCM was thus refrozen by dumping the latent heat of vaporization to space via radiation, thereby preparing the PCM package for the next sortie. The second PCM system was integrally bonded to the Drive Control Electronics (DCE). During a sortie, the heat dissipated within the DCE was absorbed by the PCM. After the sortie, the PCM was refrozen via a thermal strap-louvered radiator system. The third PCM system was integrally bonded to the Lunar Communications Relay Unit (LCRU). During a sortie, heat generated by the LCRU was stored within the PCM. After the sortie, insulation pads covering radiator surfaces on the LCRU


Fig. 4-1 - PCM Thermal Control System for One Duty Cycle Electronic Component on Launch or Reentry Vehicle



Fig. 4-2 - PCM Thermal Control System for Cyclically Operating Components

were manually removed to allow heat radiation to space to refreeze the PCM. Information on these three LRV-PCM systems was obtained from conversations with W.R. Humphries, Astronautics Laboratory, MSFC.

It can be seen from these discussions that the use of PCM for thermal control of spacecraft electronic components is a very general and useful technique.

4.1.2 Thermal Energy Storage Devices

The utility of storing and releasing energy via phase change was demonstrated for electronic components in the previous subsection. This concept can be extended to a larger scale for space missions which will present varying spacecraft thermal environments. For example, a satellite orbiting the earth encounters drastically different thermal environments cyclically as it passes in and out of the Earth's shadow. During such a mission, solar energy can be stored and released by a PCM package to dampen the otherwise large temperature changes that would be experienced during the orbit cycle. A specific example might be a crew compartment or refrigeration compartment which is required to remain nearly isothermal throughout the orbit. The compartment could be enveloped by a layer of PCM to absorb and release solar energy during the orbit to provide isothermal conditions at the melt temperature of the PCM.

Another example of variable spacecraft thermal environment is encountered by landing vehicles on atmosphereless planets or moons. The day/night cycle on such a cosmic body presents a thermal environment which changes radically during the rotation of the body. If the landing craft is enshrouded in PCM, the solar energy can be conserved from the day for use during the night, thus ensuring an operational inner environment for crew and/or components.

Another example of PCM thermal energy storage devices is shown in Fig. 4-3, in schematic form. The dissipative losses of energy in electronic components, which generally are treated as wasted energy, can be heat piped to a central PCM-TES for later use in thermal control or energy production. This recovery of usually wasted energy for conversion into reusable energy should be beneficial for long space voyages.



Fig. 4-3 - Central PCM Thermal Energy Storage System

The use of PCM systems to store energy isothermally for later release is seen to be an important and unique application of PCM in the space environment.

4.1.3 Electrical Power Devices

PCM's with high melt temperatures can be used in conjunction with electronic power-producing systems. Radiators used to collect solar energy can be packed with PCM to store the energy via phase change at the melt temperature. This stored energy can then be converted into electrical power by using the large temperature difference between the radiator and deep space in either thermionic or thermoelectric devices. If the power-producing devices are sized for the mean solar power received during the planetary orbit, production of electrical power can continue during the shadow portion of the orbit because of the capability of the PCM to store energy. With conventional photoelectric radiators, the power production ceases during the shadow portion of the orbit, and energy is stored in cells or batteries for use during the off portion of the cycle. The thermionic or thermoelectric concept, when fully developed, may offer significant increases in efficiency over the conventional concepts. Preliminary analytical and experimental studies reported in Ref. 1 indicate the feasibility of this PCM application, and materials have been found with suitable properties for such PCM systems.

4.1.4 Experimental Devices

Phase change material systems can be used in conjunction with space flight experiments. Many delicate experiments rely upon precisely calibrated instruments. PCM packages can be integrated into these instruments to maintain thermal stability and/or to ensure isothermal conditions during the experiment.

Another PCM application for flight experiments is shown in Fig. 4-4. The radiation properties of the surface are to be determined. By monitoring the package temperature, the $\Delta \theta$ melt can be determined and from this value the radiation heat rate to the package can be determined:

$$\dot{Q}_{RAD} = \frac{m_{PCM}h_f}{\Delta\theta_{melt}}$$

From this heat rate data, radiation properties can be obtained from the known surface area and other boundary conditions of the energy interchange. The radiometric property data thus obtained are found under isothermal conditions, which allow accurate corrections for heat losses and other sources of error.

4.1.5 Cargo Containers

PCM charged containers can be used to transport film, food, waste products, biological samples, etc., from space vehicle to vehicle. Such a system is planned for use on Skylab (SL-1) for transporting human waste from the Orbital Workshop (OWS) to the Command Module for return trip to earth. Such containers represent isothermal protection systems for perishable cargo.

4.1.6 Thermal Capacitors

PCM can be used to great advantage in fluid loop/radiator systems because of its unique isothermal heat storage capacity. One such application is currently sheduled for use on Skylab. The coolant fluid returning from the





external radiators experiences sizable temperature variations during the course of an orbit cycle. For efficient operation of the heat exchangers, through which the fluid passes, these temperature variations are too large. A thermal capacitor utilizing PCM can dampen these temperature variations by alternate melting and freezing, as illustrated in Fig. 4-5. Thus, the thermal capacitor is used to maintain the fluid entering the heat exchanger within an allowable temperature range.

Another thermal capacitance application for PCM is in the radiator itself. If the radiator is subject to cyclical heat removal requirements during the course of a mission, it must ordinarily be sized for the peak load for successful operation. If PCM is integrated into the radiator, the radiator can be sized for the mean heat removal requirement, since it can store the energy at peak load via phase change for later dumping to space by radiation. Significant savings in area and weight can be obtained with such a PCM radiator.

4.1.7 Delicate Instrument Thermal Control

For delicate, highly temperature-sensitive instruments, PCM can be used to maintain these instruments within extremely small temperature ranges. Guidance and control instruments, such as navigational gyroscopes, must often be controlled within bands of 0.5° K. In Ref. 2, PCM thermal control was studied for such instruments, and tremendous savings in weight and volume were predicted over conventional TCS.

4.1.8 Thermally Isolated Component Thermal Control

Components whose temperature must be controlled are often on booms, antennas, radiators, etc., which are physically far removed from the main spacecraft. Active thermal control is therefore often impossible or very difficult for such components. PCM packages can be used very effectively for thermal control of such components, thereby eliminating the need for coolant fluid lines, heat pipes, thermal straps, etc., between the main craft and the component. Large savings in weight and increased reliability can result from the use of PCM systems in such applications.



Fig. 4-5 - PCM Thermal Capacitor in Fluid Loop

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4.2 PCM TERRESTRIAL APPLICATIONS

The earthbound application of phase change materials is well known in such systems as refrigerated portable containers, ice boxes and chests, coldwall mugs, etc. However, more novel PCM applications have been considered and some of these are described in the following discussion.

4.2.1 Precise Thermal Control of Instruments

Temperature-sensitive instruments required to deliver highly accurate responses have been protected by PCM thermal control systems. Russian investigators have studied the feasibility of using PCM to precisely control the temperature of gravity meters which require a relative accuracy of 10^{-8} , as reported in Ref. 3. Initial analytical and empirical studies verified the feasibility of such a PCM application. In this and other related applications, the instrument to be controlled is surrounded by PCM in close thermal contact. Heat flow to or from the instrument is intercepted by the PCM and stored isothermally as latent heat of fusion. The instrument temperature remains constantly at the melt temperature of the PCM.

Another PCM technique for thermal control of instruments was reported in Ref. 4. In this novel technique, the volume change during melting was used to open or close a heat flow path to the instrument. This variable thermal impedance path was used to maintain the instrument at the desired temperature. This same investigator also designed a system which utilized the volume change during melting of the PCM to activate an active thermal control system for the small volume inside which the instrument was located.

4.2.2 Solar Energy Storage Devices

PCM can be used to store solar energy during daylight hours for use during the night period in thermal control or power production. A system using a lithium hydride PCM was successfully tested and reported in Ref. 5.

A more exotic application was reported in Ref. 6. A house was constructed with a large mass of Glauber's salt in the basement. Solar energy collected on the roof was transported via conduction to the basement and stored as latent heat of fusion in the PCM. During night periods and cloudy days, the PCM refroze, supplying heat for thermal control of the house, thereby precluding the need for active heating of the house. In the future, such systems could become more common as the cost of power rises and the worry over pollution at power plants increases.

4.2.3 Aircraft and Missile Component Thermal Control

The use of PCM for thermal control of aircraft and missile components has been investigated. In Ref. 7, pessimistic results were reported regarding the use of PCM to thermally protect aircraft electronics, but most of the problems were due to the low thermal conductivity of the PCM which could have been improved by the addition of fillers which are now being used.

Very optimistic results were reported in Ref. 8 regarding the use of PCM to thermally protect missile electronic components. An actual package was fabricated and successfully tested, proving the feasibility of PCM thermal control of an electronic missile transmitter.

4 2.4 Other Exotic PCM Terrestrial Applications

Other novel techniques utilizing PCM have been investigated for terrestrial application. In Ref. 9, cooking instruments such as skillets, pans, etc., were packed with PCM to maintain their temperatures at the correct levels for cooking selected foods. In Ref. 10, a system was described in which PCM was used in the process of water purification. Such applications may find widespread usage in the near future.

In summary, numerous space and terrestrial applications of phase change materials have been and continue to be investigated. The preceding discussion is not meant to include all possible applications, but merely to point out the variety of applications which are found in the literature.

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Section 5

PHASE CHANGE MATERIALS AND PROPERTY DATA

Thermal control by use of fusible materials is a new technology compared to other methods. Although few materials have actually been tested for PCM technology, over 500 have been reported as potential candidates in the reviewed literature. The 500 potential PCMs listed in the literature were selected exclusively on the basis of heat of fusion and melting temperature. This number of candidates is reduced substantially when other factors and properties are considered. For example, many organic nitrates have high heats of fusion and convenient melting temperatures, but they are so hazardous that they have been excluded from this handbook. There is no foreseen advantage to the use of any of hundreds of materials with hazardous or undesirable features, when there are safer or more reliable ones with equivalently high heats of fusion and the same melting temperatures. Glycerine, for example, has a reported freezing point of 290° K (63° F, 17° C), but many investigators have been unable to freeze it even when it is kept in liquid nitrogen for several days. Obviously, a candidate PCM must have reliable freezing behavior.

Volume changes are an important consideration also. Most materials shrink when they freeze, and the change in volume varies greatly among PCMs. Water, gallium, and gallium alloys expand on freezing. Some materials have high vapor pressures near their melting points, exerting excessive stress on containers.

A number of salt hydrates melt to form a lower hydrate and water. Reversible freezing does not take place with these. Yet a few of the same material type — salt hydrates — do melt "congruently," freeze reversibly, and are among the highest rated of all PCMs.

To aid the designer in selecting the ideal PCM for his purpose, PCMs are categorized and evaluated in detail in later paragraphs.

5.1 DESIRABLE PCM PERFORMANCE PROPERTIES

There is no perfect PCM material because no one material has all of the desirable properties to the degree that would be ideal. A PCM is expected to provide isothermal control for a specified time in a particular application. Obviously tradeoffs exist in selecting the most ideal PCM for a selected application.

Frequently unacceptable properties of PCMs can be corrected. For example, metallic fillers can be used to increase the thermal conductivity of poorly conducting PCMs. Nucleating catalysts may be found for materials which supercool to overcome this fairly common problem. Volume changes may be compensated for in a number of ingenious ways. If space limitations are more important than weight, a metallic PCM can provide the same heat of fusion on a volume basis as almost any PCM, and has the advantage of high thermal conductivity.

In general, the ideal PCM would have the following features:

- <u>High Heat of Fusion</u>: This property defines the available energy and may be important on a weight basis or a volume basis. Some PCMs are attractive either way.
- <u>Reversible Solid-to-Liquid Transition</u>: The composition of the solid and liquid phases should be the same.
- <u>High Thermal Conductivity</u>: This property is necessary to prevent thermal gradients. Fillers are used to improve system performance.
- <u>High Specific Heat and Density</u>.
- Long Term Reliability During Repeated Cycling.
- <u>Dependable Freezing Behavior</u>.
- Low Volume Change During Phase Transition.
- Low Vapor Pressure.

5.2 A FIRST SCREENING OF PCM CANDIDATES

Materials selected as potential PCM candidates are listed in Tables 5-1 through 5-7.* Each table corresponds to one type of PCM according to the following categories:

Table 5-1 - Paraffins Table 5-2 - Non-Paraffin Organics Table 5-3 - Salt Hydrates Table 5-4 - Metallics Table 5-5 - Fused Salt Eutectics Table 5-6 - Miscellaneous Table 5-7 - Solid-Solid

A description of each type is presented in following paragraphs. In most cases it is recommended that the general categories be considered first in designing a PCM package.

The most critical properties are listed in Tables 5-1 through 5-7* which include the melting point, density and latent heat of fusion on a weight and volume basis. All properties are given in the international system, the English system and the most widely used metric system. The materials listed are not specifically recommended, due to lack of test data related to PCM applications. However, literature searches have listed them because of their reasonable values of heat of fusion or convenient melting temperature. It is the designer's task to check materials under consideration for PCM performance capabilities, as well as for other properties of importance. A rating code is presented in the far right-hand column of the tables. The word "prime" in the rating indicates that the material was selected as a prime candidate and is presented in depth in this handbook. Data for prime candidates are presented in Tables 5-8 to 5-28. The numbers in the column rating PCMs which are not primes correspond to the code shown on the following page.

^{*}An index of Phase-Change Materials follows the appendixes. The tables are presented beginning on page 5-19.

1. <u>Insufficient Data</u>: Enough information is not readily available to merit an in-depth treatment, although some of these candidates may be quite attractive.

2. <u>Undesirable Freezing Behavior</u>: These materials have undesirable melting-freezing behaviors. This includes supercooling to a marked extent with no reported nucleating catalysts, or incongruent melting with lack of reversibility.

3. <u>Dangerous</u>: These materials are explosive, highly toxic, or extremely corrosive.

4. <u>Lack of Merit</u>: For present PCM applications these materials have low heats of fusion, are toxic, moderately dangerous, have extreme melting temperatures, or in most cases, a combination of several unattractive features.

As the technology progresses, improvements may be made, or additional information may become available to change the status of some of the materials. New material systems with highly desirable properties are expected to be discovered. However, further searching of the same literature for materials with high heats of fusion in the desired temperature range is not likely to prove fruitful. Many such reviews have already been made (Refs. 2, 5, 7, 8, 10, 18, 19 and 22). Prime candidates are discussed in Section 5.3.

A description of each of the seven types of PCM corresponding to Tables 5-1 through 5-7 follows:

5.2.1 Paraffins (Table 5-1)

The normal paraffins of type $C_n H_{2n+2}$ are a family of saturated hydrocarbons with very similar properties. All of the series below pentane ($C_5 H_{12}$) are gases at ordinary temperatures. Those between C_5 and C_{15} are liquids, and the rest are waxy solids.

Normal or straight chain paraffins usually melt at higher temperatures than branched chain structures. The chemical properties are governed by structural considerations. The normal straight chain and the symmetrically branched ones are the most stable (Ref. 32). The paraffins with even numbers of carbon atoms are more widely used than those with odd numbers of carbon atoms because they are more available, more economical, and generally have higher heats of fusion. The melting point tends to increase with molecular weight.

Paraffins are noted for extremely low thermal conductivities. They have insulating properties comparable to the best insulators. They are better insulators than rock wool, for example. The temperature of melted paraffin may rise to the boiling point, with solid adjacent to the boiling paraffin. Thermal gradients are inevitable unless corrective measures are taken. The use of metallic fillers is generally recommended. Aluminum honeycomb has been found to improve system performance (Ref. 19). The section on Engineering Design, page 8-1, describes the heat transfer considerations of filler design. Faraffins were among the first materials to be selected for PCM technology considerations. They are reliable, safe, noncorrosive, and predictable. On the other hand, they are moderately flammable and low thermal conductivity limits their effectiveness.

Paraffins have been observed to creep out of open pans due to their high wetting ability. Teflon coated containers cleaned with ethanol proved to minimize this problem.

Properties of Paraffins are as follows:

- 1. High heat of fusion per unit weight
- 2. Wide melting point selection (268 to 339° K (23 to 151° F, -5 to 66° C)
- 3. Flammable
- 4. Nontoxic
- 5. Noncorrosive
- 6. Chemically inert and stable below 773°K (932°F, 500°C); above this temperature, complex reactions occur such as dehydrogenation, cracking, aromatization, etc.

- 7. Negligible supercooling behavior
- 8. Low volume change on melting
- 9. Low vapor pressure in the melt
- 10. Density ranges from 700 to 770 kg/m³ (43.7 to 48.1 lb/ft³)
- 11. Low thermal conductivity (can be increased with fillers)
- 12. Many are commercially available at reasonable cost
- 13. High wetting ability
- 14. Predictable and dependable.

Four paraffins are listed as prime candidates that have been tested in actual PCM equipment. They are:

Tetradecane	$C_{14} H_{30}; \Delta H_{f} = 228 \text{ joules/kg (98 Btu/lb)}$
Hexadecane	$C_{16} H_{34}; \Delta H_{f} = 237 \text{ joules/kg (102 Btu/lb)}$
Octadecane	$C_{18} H_{38}; \Delta H_{f} = 244 \text{ joules/kg (105 Btu/lb)}$
Eicosane	$C_{20} H_{42}; \Delta H_{f} = 244 \text{ joules/kg (105 Btu/lb).}$

5.2.2 Non-Paraffin Organics (Table 5-2)

The non-paraffin organics are the most numerous of the PCM candidates. This category includes a wide variety of organic materials with highly varied properties. Each of these materials will have its own design parameters, unlike the paraffins which have very similar properties.

Organic materials should not be exposed to excessively high temperatures, flame, or strong oxidizing agents. Almost all organic materials are flammable. Exposure to high temperatures can cause decomposition, frequently accompanied by fumes of moderate-to-high toxicity. Caution should be exercised in handling organic materials of any type.

In one survey of over 500 organic materials, 113 melted between 303 and 473° K (86 to 392° F, 30 to 200° C). Their latent heats of fusion are usually from 4.2×10^4 to 2.5×10^5 joules/kg (20 to 100 Btu/lb; 10 to 60 cal/gm).

The thermal diffusivity of organics runs from very low values to values comparable to that of water, or even higher. The use of fillers to improve diffusivity is generally recommended (Tables 5-8 to 5-28). This category of PCM materials is too large to list properties applying to all of them. Factors to be considered in this general category are

- Most are flammable
- Some are toxic
- Many of the long-chain acids exhibit polymorphism (two or more crystalline forms)
- The flash point of many is low
- Impurities may greatly affect melting points
- Fillers are recommended to improve thermal conductivity
- Elevated temperatures will decompose many of them
- Many have convenient melting temperatures
- Solid-solid transitions are common
- Many have attractively high heats of fusion.

Ten prime PCM candidates are listed in this category and have been tested to varying degrees.

- Polyethylene Glycol 600; $\Delta H_f = 146 \times 10^3$ joules/kg (63 Btu/lb)
- Acetic Acid; $\Delta H_f = 187 \times 10^{3^{-1}}$ joules/kg (80.3 Btu/lb)
- Tristearin; $\Delta H_f = 191 \times 10^3$ joules/kg (82.1 Btu/lb)
- Myristic Acid; $\Delta H_f = 199 \times 10^3$ joules/kg (85.5 Btu/lb)
- Stearic Acid; $\Delta H_f = 199 \times 10^3$ joules/kg (85.5 Btu/lb) Elaidic Acid; $\Delta H_f = 218 \times 10^3$ joules/kg (93.7 Btu/lb) Acetamide; $\Delta H_f = 241 \times 10^3$ joules/kg (10⁴ Btu/lb)

- Methyl Fumarate; $\Delta H_f = 242 \times 10^3$ joules/kg (104 Btu/lb)
- Oxazoline Wax TS970; ΔH_{f} DTA estimated high
- Oxazoline Wax ES-254; $\Delta H_{f}DTA$ estimated high.

5.2.3 Salt Hydrates (Table 5-3)

Salt hydrates may be regarded as alloys of inorganic salts and water with a definite number of moles of water forming typical crystalline solids of general formula $AB \cdot nH_2O$.

Salt hydrates, with some exceptions, generally have incongruent melting points. A salt hydrate of type AB \cdot nH₂O will usually melt to form a new solid phase different from the original and containing fewer moles of water, i.e.,

 $AB \cdot nH_2O \longrightarrow AB \cdot mH_2O + (n-m)$ moles of H_2O , or to the anhydrous form: $AB \cdot nH_2O \longrightarrow AB + nH_2O$.

At the transition point of a salt hydrate having an incongruent melting temperature, three phases are in equilibrium: two solid phases and a liquid phase of a saturated solution of the salt. Because of incomplete solubility, the lower hydrate usually settles to the bottom of the container so that most of it is unavailable for recombination with water when the temperature is lowered. Incongruent melting results in lack of reversible melting and freezing. Salt hydrates which possess congruent melting points, on the other hand, melt like other pure compounds. The three prime candidates from this category all have excellent freezing characteristics.

Features of salt hydrates are as follows:

- High heat of fusion per unit weight and volume
- Small volume change upon melting
- The majority tested have incongruent melting points and subsequent lack of easy reversibility (exceptions: LiNO₃ · 3H₂O, Ba(OH)₂ · 8H₂O, and Na₂ HPO₄ · 12 H₂O)
- Relatively high thermal conductivity for non-metals
- Supercooling to a marked extent, which can be minimized with suitable nucleating agents
- Corrosive.

The prime candidates from this category are:

Sodium Hydrogen Phosphate Dodecahydrate; $\Delta H_f = 265 \times 10^3$ joules/kg (114 Btu/lb) Lithium Nitrate Trihydrate; $\Delta H_f = 296 \times 10^3$ joules/kg (128 Btu/lb) Barium Hydroxide Octahydrate; $\Delta H_f = 302 \times 103$ joules/kg (130 Btu/lb).

5.2.4 Metallics (Table 5-4)

This category includes the low melting metals and metal eutectics. These metallics have not yet been seriously considered for PCM technology because of weight penalties. However, when volume is a consideration, they are likely candidates because of the high heat of fusion per unit volume. They have high thermal conductivities, so fillers with added weight penalties are not required. Low melting alloys usually contain some of the elements with low melting points (Bi, In, Cd, Pb, Sn). The use of metallics poses a number of unusual engineering problems. The design properties are excellent, while construction and operating properties are less desirable according to Ref. 23. A major difference between the metallics and other PCMs is their high thermal conductivity, and low Prandtl numbers of the order of 0.001 to 0.1.

With some of these materials, the question of corrosion is a critical one. Gallium, for example, is one of the most reactive metals in its effect on common structural metals, such as aluminum. However, it is compatible with titanium. The use of inhibitors minimizes corrosion problems with some materials.

Features of metallics are as follows:

- Low heat of fusion per unit weight
- High heat of fusion per unit volume
- High thermal conductivity, fillers not required
- Low specific heat
- Relatively low vapor pressure.

[•]Cadmium, however, is not a routinely approved material for space applications apparently because of its relatively high vapor pressure. It can deposit on transistors and foul their operation. Cadmium is also relatively toxic for long exposures.

- Low volumetric expansion on melting
- High thermal stability
- Minimal hazardous behavior.

Prime candidates from this category are:

Cerrobend eutectic; $\Delta H_{f} = 32.6 \times 10^3$ joules/kg (14.0 Btu/lb) Gallium; $\Delta H_{f} = 80.3 \times 10^3$ joules/kg (34.4 Btu/lb).

5.2.5 Fused Salt Eutectic (Table 5-5)

A fused salt eutectic contains two or more inorganic salts which form a eutectic compound. A eutectic system has a sharp melting point, like a pure compound. In principle, there are many PCM possibilities in this category. Data on this type of PCM are generally lacking. Due to lack of information or unsatisfactory performance, there are presently no prime candidates from this category.

Some of the listed candidates contain nitrates because nitrates have lower melting points than the corresponding halides (chlorides, fluorides, bromides and iodides). While the data on nitrate-containing eutectics may look encouraging, heating nitrates is not generally recommended. Nitrates may explode when exposed to heat or flame, or when shocked, or by spontaneous reaction. Ammonium nitrate is able to detonate by itself under certain conditions (Ref. 14).

Aside from the nitrates, there are many other possibilities. There are several eutectic formulations which are patented. A few of these have the versatility of offering several melting temperatures according to specific weight ratios of the components. One series has magnesium sulfate, sodium sulfate, and water as components, with several melting points possible, according to the ratio of the components (Table 5-5). Aluminum chloride $(AfCl_3)$ is used as a component in eutectics because it appreciably lowers the melting points of other chlorides. It forms binary and ternary compounds and eutectics

with lithium chloride (LiC!) and sodium chloride (NaC!). When heated, aluminum chloride nearly doubles in volume on melting, although in eutectics the volume expansion is considerably lowered. Some of the A!C!₃ eutectics may have desirable properties as heat storage materials.

Systems containing lithium generally produce lower melting eutectics than analogous alkali and alkali-earth systems. They are also characterized by lower viscosity and high electrical conductivity (Ref. 15).

Features of Fused Salt Eutectics are as follows:

- Components can be varied with some eutectics to give a choice of values for the melting point and heat of fusion
- They offer a wide selection of possibilities
- The heat of fusion is generally high
- The presence of moisture during preparation influences the melting point*
- They are corrosive.

5.2.6 Miscellaneous (Table 5-6)

This category includes PCM materials which do not clearly fall into the other general categories. The Transit Heet series is a proprietary formulation of unknown composition, probably a eutectic combination of salt hydrates. Dowtherm A is an organic eutectic of diphenyl-diphenyl oxide, which is used as a heat transfer liquid. It has an objectionably strong odor, a low heat of fusion (97.9 x 10^3 joules/kg; 42.2 Btu/lb), and a convenient melting temperature range (Ref. 1).

A most important member is water. It should not be overlooked in favor of more exotic materials. Water has the highest heat capacity of any

The variations in melting temperatures reported by different investigators are due to the influence of moisture during preparation.

known ordinary substance. The heat of fusion per unit weight or volume is the highest of all the recommended PCM materials. It is free of many problems (toxicity, flammability, stability) which are important considerations in most other systems. It is stable, nontoxic, nonflammable, and its thermal conductivity is fairly high for a non-metal.

Aluminum chloride is an inorganic salt used extensively in the technology of organic chemistry, and its properties have been thoroughly studied. This highly hygroscopic material has many unusual properties. It doubles in volume on melting and forms eutectics with other chlorides which melt at a lower temperature than any of the components (Ref. 22). As a PCM, it has been considered as a component in eutectics, rather than used by itself.

The prime candidates from Category 6 are:

Water; $\Delta H_f = 333 \times 10^3$ joules/kg (143 Btu/lb) Transit Heet; $\Delta H_f = 230 \times 10^3$ to 301 x 10³ joules/kg (99 to 129 Btu/lb).

5.2.7 Solid-Solid Phase Change Materials (Table 5-7)

The possibilities for high enthalpies, low coefficients of thermal expansion, and minimal supercooling lead to the consideration of solid state transitions. Many organic materials undergo solid-solid transitions at a transition temperature below the melting point. Plastic crystals constitute a series of organic materials which have high transitional enthalpies. Ten with high latent heats of transition, comparable to heats of fusion of solid-liquid PCM candidates, are listed in Table 5-7. These enthalpies range from 184 to 301 joules/kilogram (79 - 130 Btu/lb, 44 - 72 cal/gm). The transition temperatures are from $341 - 457^{\circ}$ K ($154 - 363^{\circ}$ F, $68 - 184^{\circ}$ C).

Features of Plastic Crystals: (Refs. 7 and 8):

- They are soft, waxy solids that can be extruded under considerably less pressure than ordinary crystals
- They have unusually high vapor pressures for solids
- Volume changes are usually of the order of 10 to 50%
- Supercooling is not an inherent property of solid state transitions
- Transition temperatures are fairly high.

5.3 FINAL PCM CANDIDATES

PCMs that were not subject to one of the limitations mentioned in the rating code (page 5-4) are prime candidates and are presented in detail in Tables 5-8 through 5-28.

Twenty-one PCM candidates originally looked attractive from literature searches. Further screening of their properties indicated these merited testing. Although test data are limited, observations available at the present state of technology are noted.

These final candidates offer a choice of PCM types. All have reasonably high heats of fusion on a volume basis. All except the metallics have attractive heats of fusion on a weight basis.

Tables 5-8 to 5-28 present property data, test observations and behavioral characteristics. Where data were unavailable, a dash is inserted. All data are in international, engineering, and the metric system of units. Conversion to other systems of units can be made by using the conversion tables (Appendix A).

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<u>Order</u>

Each category of PCM is listed in order of melting points, from low melting points to high melting points.

Accuracy

The number of significant figures is dependent upon the accuracy of reported data, as it was found. In some cases, accurate figures were reported, but in other cases rough data are all that are available at the present time.

Density

Superscripts on values of density refer to the temperature in degrees Centigrade at which the density was measured. For example, the density of

tetradecane in Table 5-1 is reported as 0.756^{20} . This means the density is 0.756 grams per cubic centimeter at 20°C. In many cases, the temperature of the reported density was not given. In other cases it was not specified whether the given density is for the solid or liquid material.

Missing Data

When no data are listed, such data are not readily available. Data which could be found are reported. As further information becomes available, missing data can be filled in the spaces provided.

					Table 5-1 PARAFFID	4S								
		Me	lting Po	int	Latent H Per	eat of Fu Unit Mas	aion a		Density		Latent He Per U	at of Fuel nit Volum	5.	PCM
Jan 1		°K	ိင	۰F	Joules x 10 ⁻³ kg	cal/gm	Btu/lb	gm/cm ³	1b/ft ³	kg/m ³	<u>Joules</u> x 10 ⁻⁶ meter ³	cal/cm ³	Btu/ft ³	Rating *
n-Dodecane	C ₁₂ H ₂₆	261	-12	JL	4 4 1 1			0.750	46.8	750				-
n-Tridecane	C ₁₃ H ₂₈	267	- 6	12				0.756 ²⁰	47.2	756		1		1
n - Tetradecane	C14H30	278.7	5.5	41.9	228	54	98	0.771 ⁵⁵	48.1	171	173	41	4600	Prime
n - Pentadecane	C15H32	283	9	50	205	49	88	0.768 ²⁰	47.9	768	157	38	4200	I
n -Hexadecane	C16H34	289.9	16.7	62.1	237.1	56.67	102.0	0.774 ²⁰	48.3	774	184	43.9	4927	Prime
n-Heptadecane	C17H36	294.9	21.7	71.1	213	51	92	0.778 ²⁰	48.6	778	166	40	4500	-
n-Octadecane	C18H38	301.2	28.0	82.4	244	58	105	0.774 ²⁰	48.3	114	188	45	5030	Prime
n-Nonadecane	C19H40	305.2	32.0	89.6	1									-
n-Eicosane	C20H42	309.9	36.7	98.1	246	59	106	0.778 ²⁰	48.6	778	191	46	5150	Prime
n-Heneicosane	č21H44	313.4	40.2	104.4	200.	48	86	0.758 ²⁰	47.3	758	152	36	4100	-
n-Docosane	C22H46	317.2	44.0	2.111	249	60	107	0.763 ²⁰	47.6	763	190	46	5090	-
n-Tricosane	C23H48	320,7	47.5	117.5	232	56	100	0.764 ²⁰	47.7	764	177	43	4770	-
n-Pentacosane	C25H52	322.6	49.4	120.9				0.769	48.0	769				1
n-Tetracosane	C24H50	323.8	50.6	123.1				0.766 ²⁰	47.8	766			1	1
Paraffin Wax	8	327.6	54.4	129.9	146	35	63	0.88	55	880	128	31	3500	-
n-Hexacosane	C26H54	329.5	56.3	133.3	256	61	110	0.770	48.0	170	197	47	5280	
n-Heptacosane	c27 ^{H56}	332.0	58.8	137.8				0.773	48.2	773		-) 	1
n-Octacosane	C28H58	334.8	61.6	142.9	253	61	109	0.779 ^{61.1}	48.6	677	197	48	5300	-
n-Nonacosane	C29H60	336.6	63.4	146.1	240	57	103	:						1
n-Triacontane	C ₃₀ H ₆₂	338.6	65.4	149.7	251	60	108							-
n-Hentriacontane	C31 ^{H64}													1
n - Dot ricontane	C32H66	343	70	158		1		0.782 ^{70.3}	48.8	782				I
n - Tritriacontane	C ₃₃ H ₆₈	344.2	71.0	159.8		:	:					-		-
*(1) Insufficient Data; (2) Undesi	irable Freezing Behavior;	(3) Dang	erous; (4) Lack	of Merit.									

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Table 5-2 NON-PARAFFIN ORGANICS

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L			Mel	ting Poi	, T	Latent He	at of Fur	non		Density		Latent Heal	t of Fusio	e	
-	Name	Formula		Γ	T	T-loc						Tanta z			PCM Rating *
			۰ĸ	°°	°۴	ver × 10' 3	cal/gm	Btu/lb	gm/cm ³	16/ft ³	kg/m ³	Joules x 10 ^{-b}	cal/cm ³	Btu/ft ³	•
	Ethylene Glycol	носн ₂ сн ₂ он	260	- 13	6	146	35	63	1.113 ²⁵	69.48	1113	163	39.	4370	4
	Formic Acid	нсоон	281.0	7.8	46.0	247	59	106	1.2267 ¹⁵	76.580	1226.7	303	72.	8120	2,3
	Myristic Acid, Ethyl Ester	CH ₃ (CH ₂) ₁₂ COOC ₂ H ₅	284	11	52	184	44	62							1
	Acetic Acid	сн ₃ соон	289.9	16.7	62.1	187	44.7	80.3	1.05 ²⁰	65.6	1050	196	46.9	5260	Prime
	Glycerin	сн ₂ онснонсн ₂ он	291.1	17.9	64.2	198.7	47.5	85.3	1.260 ²⁰	78.66	1260	251	59.9	6720	2
	Lithium Chloride Ethanolate	LiC1 · 4C2H60	294	21	70	188	45	81							4
<u> </u>	Polyethylene Glycol 600	н(ос ₂ н ₂) пон	293- 298	20-	68- 77	146	35	63	1.1 ²⁰	69	1100	161	38.5	4320	Prime
-	d-Lactic Acid	CH ₃ (CH) ₂ COON	299	26	62	184	44	79	1.249 ¹⁵	77.98	1249	230	55	6170	1
	Diphenyloxide	(c ⁶ H ²) ² 0	301	28	28	:		-	1.073 ²⁰	66.99	1073				
	Methyl Palmitate	c ₁₇ H ₃₄ O ₂	302	29	84	205	49	88							_
	1-3 Methyl Pentacosane	C26H54	302	29	84	197	47	84	1						I
	Camphenilone	C ₉ H ₄₀	312	39	102	205	49	88				:			-
	Docasyl Bromide	C ₂₂ H ₄₅ Br	313	40	104	201	48	86							1
-	Caprylone	(CH ₃ (CH ₂) ₆) ₂ CO	313	40	104	259	52	110							
	Heptadecanone	C ₁₇ H ₃₄ O	314	41	106	201	48	86							1
	l -Cyclohexylooctadecane	C24 ^H 48	314	41	106	218	52	93							1
	4 - Heptadecanone	c17H340	314	41	106	197	47	84							1
	8-Heptadecanone	c ₁₇ H ₃₄ 0	315	42	108	102	48	86				-			1
	Cyanamide	HNCNH	317	44	111	209	50	90	1.08 ²⁰	67.4	1080	226	54	6050	-
	Methyl Eicosanate	C ₂₁ H ₄₂ O ₂	318	45	113	230	55	66		:				1	1
	Elaidic Acid	с _в н ₇ с ₉ н ₁₆ соон	320	47	117	218	52	93.7	0.851 ⁷⁹	53.1	851	185	44.3	4970	Prime
	3-Heptadecanone	C17H340	321	48	118	218	52	93							-
	2 -Heptadecanone	c17H340	321	48	118	218	52	93			;	:			1
	Camphene	C10 ^{H16}	323	50	122	238	57	102	0.842 ⁵⁴	52.6	842	201	48	5380	2
	Oxazoline Wax-ES-254		323	50	122						1 1 1			3 3 1	Prime
•	* (1) Insufficient Data: (2) Undes	irable Freesing Behavior;	(3) Dang	e rous; (4) Lack	of Merit.									

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Table 5-2 (Cont'd)

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			Me	iting Poi	Int	Latent He Per	unit Mae	sion s		Density		Latent He. Per Un	at of Fusio it Volume	g	PCM
	NAME	a muzo z	°K	ိင	۰F	Joules x 10 ⁻³ kg	cal/gm	Btu/lb	gm/cm ³	16/ft ³	kg/m ³	<u>Joules</u> x 10 ⁻⁶ meter ³	cal/cm ³	Btu/ft ³	Rating*
	9-Heptadecanone	c17H340	324	51	124	213	51	26			1	1			1
	Methyl Behenate	C ₂₄ H ₄₆ O ₂	325	52	126	234	56	101		1					-
	Ethyl Lignocerate	C26H5202	327	54	129	218	52	93							-
	Palmitic Acid	сн ₃ (сн ₂) ₁₄ соон	328	55	181	163	39	20	0.85	53	850	138	33	3700	4
	Hypophosphoric Acid	H4P206	328	55	131	213	51	26							1
	Chloroacetic Acid	сн ₂ сисоон	329	56	133	130	31.1	56.0	1.58 ²⁰	98.6	1580	205	49.1	5500	3.4
	Tristearin	(C ₁₇ H ₃₅ COO) ₃ C ₃ H ₅	329	56	133	190.8	45.60	82.10	0.862 ⁸⁰	53.8	862	164.4	39.30	4410	Prime
	Trimyristin	(C ₁₃ H ₂₇ COO) ₃ C ₃ H ₃	306- 330	33- 57	91- 135	201 213	48- 51	86- 92				6 1 1			1
	Myristic Acid	C14H28O2	331	58	136	199	47.5	85.5	0.858 ⁶⁰	53.6	858	168	40.1	4500	Prime
	Ethyl Cerotate	C28 ^{H5602}	333	99	140	226	54	26			1			1	1
5	Heptadecanoic Acid	C17H34O2	333.8	60.6	141.1	189	45.2	81.2					:		1
-23	Beeswax		335.0	61.8	143.2	177	42.3	76.0	0.95	59	950	168	40.2	4510	4
	Glycolic Acid	носн ₂ соон	336	63	145	109	26	47							4
	p-Chloroaniline	H ₂ NC ₆ H ₄ CI	342	. 69	156	156	37.2	66.8	1.213	75.73	1213	189	45.1	5060	4
	Stearic Acid	сн ³ (сн ²)1 ⁶ соон	342.6	69.4	156.9	199	47.6	85.5	0.847 ⁶⁹	52.9	847	169	40.3	4520	Prime
Pr	Oxazoline Wax-TS-970		347	74	165	* • • • •									Prime
וקם	Bromcamphor	C ₁₀ H ₁₅ O Br	350	77	171	174	41.6	74.7	1.449 ⁸¹	90.46	1449	252	60.3	6760	4
iha	Durene	C10H4	352.5	79.3	174.7	156	37.4	67.2	0.838 ²⁰	52.3	838	131	31,3	3510	4
nơ	Acetamide	c2H50N	354	81	178	241	57.7	104	1.159	72.36	1159	280	67	7510	Prime
n	Methyl Brombenzoate	C ₈ H ₂ O ₂ Br	354	81	178	126	30.2	54.2		1					4
۶ø	Dimethytartrate	(соосн ₃) ₂ снон	360	87	189	147	35.1	63.0	1.30 ⁴⁵	81.2	1300	191	45.6	5110	4
e '	Ethyl Lithium	Li C ₂ H ₅	368	95	203	389 (calc)	93(calc)	167¢calc)) 					e
bla	a Napthol	с ₁₀ н ₇₀ он	369	96	205	163	38,9	6.9	1.095 ^{98.7}	68.36	1095	178	42.6	4780	Ŧ
nk															
	* (1) Insufficient Data; (2) Unde.	sirable Freezing Behavio	; (3) Dan	gerous;	(4) Lack	of Merit.									

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Table 5-2 (Cont'd)

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		2	Me	lting Po	Int	Latent He Per	eat of Fu Unit Mai	leion 16		Density		Latent He Per Ur	at of Fusionity Volume	e	PCM
			м°	ာ	°۴	Joules × 10 ⁻³ kg	cal/gm	Btu/lb	gm/cm ³	1b/ft ³	kg/m ³	<u>Joules x</u> 10 ⁻⁶ meter ³	cal/cm ³	Btu/ft ³	Rating *
	-														
	Glutaric Acid	(CH ₂) ₃ (COOH) ₂	370.7	97.5	207.5	156	37.4	67.2	1.429	89.21	1429	223	53.4	2990	4
	p-Xylene Dichloride	C ₈ H ₈ C ₂	373	100	212	138.7	32.9	59.1	+ - - -	1 2 1	8				4
	Methyl Fumarate	(CH CO ₂ CH ₃) ₂	375	102	216	242	57.9	104	1.0452	65.250	1045.2	435	104	11660	Prime
	Catechol	с ⁶ н ⁴ (он) ²	377.5	104.3	219.7	207	49.4	88.7	1.37 ¹⁵	85.5	1370	283	67.7	1590	
	Resorcinol	с ₆ н ₄ (он) ₂	383	110	230										- 1
	Quinone	0:C6H40	388	115	239	171	40.9	73.5	1.318 ²⁰	82,28	1318	226	53.9	6040	2
	Acetanilide	с ^в н ⁹ ио	388	115	239	152	36.3	65.2	1.2.14	75.5	1210	184	43.9	4920	4
	Succinic Anhydride	(CH ₂ CO) ₂ O	392	119	246	204	48.7	87.5	1.104	68.92	1104	225	53.8	6030	-
	Benzoic Acid	c ⁶ II ₅ cooii	394.9	121.7	251.1	142.8	33.9	6.03	1.26615	79.03	1266	181	42.9	4813	4
	Stilbene	(C ₆ H ₅ CH) ₂	397	124	255	167	39.9	71.7	1.164	d 72.67	1164	194	46.4	5200	4
	Benzamide	c ₆ H ₅ CONH ₂	400.4	127.2	261.0	169.4	40.48	72.70	1.341	83.72	1341	227	54.28	6080	4
5-	Phenacetin	сн ₃ соинс ₆ н ₄ ос ₂ н ₅	410	137	279	136.70	32.68	58.69					-	:	4
25	a Glucose	с [°] н ¹⁵ о [°] . н ⁵ о	414	141	286	174	41.7	74.9	1.544	96.39	1544	269	64.4	7220	4
	Acetyl-p-toluidine	сн ₃ соинс ₆ н ₄ сн ₃	419	146	295	180	43.0	17.2							4
	Phenylhydrazone Benzaldehyde	C ₆ H ₅ CH ₂ N ₂ HC ₆ H ₅	428	155	311	134.8	32.21	57.85							3, 4
P	Salicylic Acid	нос ⁶ н ⁴ соон	432	159	318	199	47.6	85.5	1.443 ²⁰	90.09	1443	287	68.7	2700	7
re	Benzanilide	с°н ² соинс°н ²	434	161	322	162	38.8	69.7	;						4
ce	o-Mannitol	c6H1406	439	166	111	294	70.3	126.1	1.489 ²⁰	92.96	1489	438,1	104.7	11740	1
dir	Hydroquinone	C ₆ H ₄ (OH) ₂	445.6	172.4	342.3	258	61.7		1.35820	84,78	1358	351	83.8	9390	2
Ig	p-Aminobenzoic Acid	с ₆ н ₄ ин ₂ соон	460	187	369	153	36.5	65.6	:						4
pa				-											
ge															
bla															
nk															
	"(1) Insufficient Data; (2) Undesi	irable Freezing Behavior;	(3) Dang	erous; (4) Lack	of Merit.									

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Table 5-3 SALT HYDRATES

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;	-	Me	tting Po	ŧ	Latent He Per 1	at of Fu Unit Mas	ion		Density		Latent Hea Per Un	it of Fusio it Volume	5	PCM
Zanc	r ormula	м°	Ϋ́	۰F	Joules x 10 ⁻³	cal/gm	Btu/lb	*,4m/cm ³	1b/ft ³	kg/m ³	<u>Joules</u> x 10 ⁻⁶ meter ³ x 10 ⁻⁶	cal/cm ³	Btu/ft ³	Rating *
Sodium Hydrogen Arsenate Dodecahydrate	Na2HAsO4 · 12H2O	301	28	82		:		1.736	108.4	1736				2
Calcium Chloride Hexahydrate	CaCl ₂ · 6H ₂ O	302.6	29.4	84.9	170	40.7	73.1		1	3				1
Lithium Nitrate Trihydrate	Lino ₃ · 3H ₂ O	303.03	29.88	85.78	296	70.7	128	1.55 ^{solid}	96.8	1550	460	011	12330	Prime
Sodium Sulfate Decahydrate	$Na_2SO_4 \cdot 10H_2O$	305.6	32.4	90.3	253	60.5	109	1.46 ²⁰	91.2	1460	372	89	9980	2
Sodium Carbonate Decahydrate	Na ₂ CO ₃ · 10H ₂ Q	306	33	16	251	60	108	1.4416	89.9	1440	360	86	9640	2
Sodium Hydrogen Phosphate Dodecahydrate	Na ₂ HPO ₄ · 12H ₂ O	309	36 -	26	280	66.8	114	1.52 ²⁰	94.9	1520	427	102	11430	Prime
Ferric Chloride Hexahydrate	FeCL ₃ 6H ₂ O	310	37	66	226	54	16							-
Cobalt Sulfate Heptahydrate	CoSO4 · 7H2O	313.9	40.7	105,3	170	40.7	73.1				•			1
Ferric Nitrate Enneahydrate	Fe(NO ₃) ₃ · 9H ₂ O	320.4	47.2	117.0				1.684 ²⁰	105.1	1684				-
Magnesium Sulfate Heptahydrate	MgSO4 · 7H2O	321.6	48.4	1.9.1	202	48.2	86.6		:					-
Sodium Thiosulfate Pentahydrate	Na ₂ S ₂ O ₃ · 5H ₂ O	322	49	120	200	47.9	86	1.69 ^{solid}	106	1690	335	80	8970	1
Lithium Acetate Dihydrate	Lic ₂ H ₃ O ₂ · 2H ₂ O	331	28	136	251 -	06-09	108 -							-
Magnosium Chloride Tetrahydrate	MgCt ₂ · 4H ₂ O	331	58	136	178	42.5	76.3	:						_
Sodium Hydroxide Monohydrate	NaOH • H ₂ O	337.5	64.3	147.7	272	65	117	1.72	107	1720	473	113	12670	I
Barium Hydroxide Octahydrate	Ba(OH) ₂ · 8H ₂ O	351	78	172	301	72	129	2.18	136	2180	657	157	17600	Prime
Aluminum Potassium Sulfate Dodecahydrate	AIK(SO ₄) ₂ · 12H ₂ O	364	16	195.8	184	44	79) 		•	-
Magnesium Chloride Hcxahydrate	MgCI ₂ · 6H ₂ O	390	117	243	167	40	72	1.56	97.4	1560	268	64	170	-
Sodium Acetate Trihydrate	NaC2H3O2 · 3H2O	410	137	279	172	41	74	1.45	90.5	1450	247	59	6610	2
	,						<u> </u>				-			
⁴ (1) Insufficient Data; (2) Undes	iirable Freezing Behavior;	(3) Dang	erous;	4) Lack	of Merit.			2						

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Table 5-4 METALLICS

C STAR	Former	Me	lting Po	ant	Latent Her	eat of Fur Unit Mas	rion 8		Density		Latent Hei Per Ur	at of Fusionity Volume	5.	MOd
		°K	°c	°F	<u>Joules</u> x 10 ⁻³ kg	cal/gm	Btu/lb	gm/cm ³	lb/ft ³	kg/m ³	<u>Joules</u> x 10 ⁻⁶ meter ³	cal/cm ³	Btu/ft ³	Rating *
Gallium-Gallium Antimony Eutectic	Very small amounts of GaSb in Ga matrix	303.0	29.8	85.6		;	1				-			-
Gallium	Ga	303.2	30,0	86,0	80.3	19.2	34.4	5.90325	368.5	5,903	469	112	12,560	Prime
Cerrolow Eutectic	49 Bi + 21 Int	181	58	136	90.9	21.8	39.1	8.820	549	8,800	800	192	21 480	-
	18 Pb + 12 Sn													•
Bismuth-Cadmium-Indium Eutectic	33 Bi + 16 Cd + 51 In	334	61	142	25	9	Ξ	8-10	500- 620	8,000- 10,000	201-251	48- 60	5380- 6730	4
Cerrobend Eutectic	50.5 Bi + 26.7 Pb + 13.3 Sn + 10.0 Cd	343	20	158	32.6	7.78	14.0	9.4 ^{solid}	587	9,400	305	73	8180	Prime
Bismuth-Lead-Indlum Eutectic	52 Bi + 26 Pb + 22 In	343	. 70	158	29	2	13	8-10	500- 620	8,000- 10,000	234- 293	56- 70	6280- 7850	-
Bismuth-Indium Eutectic	34 Bi + 66 In	345	72	162	25	Ŷ		8-10	500- 620	8,000- 10,000	201- 251	48- 60	5380- 6730	4
Bismuth-Lead-Tin Eutectic	52.2 Bi + 32.0 Pb + 15.5 Sn	369	96	205			1	1	:				i	1
Bismuth-Lead Eutectic	55.5 Bi + 45.5 Pb	398	125	257			1	10.46	653,02	10,460	1			-
I'l meannrain nata, (e) unas	ILADIC F TECZING DCHAVIOL	(3) Uan	gerous;	(4) Lack	of Merit.									

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PCM	Rating*	-		-	-	-	-	-	
	Btu/ft ³								
t of Fusio it Volume	cal/cm ³								
Latent Hea Per Uni	<u>Joules</u> x 10 ⁻⁶								
	kg/m ³				· · · · · · · · · · · · · · · · · · ·			• .	
Density	1b/ft ³								
	gm/cm ³								
eion e	Btu/lb	101							
eat of Fu Unit Mae	cal/gm	56							
Latent H Per	Joules × 10 ⁻³ kg	234							k of Merit.
int	°F	39		52	\$	70-	75-	75	(4) Lac
elting Po	ပို	4		11	18	21- 24	21-24	21- 24	angerous
X	°,	277	···	284	591	294- 297	294-297	294-	or: (3) D
	8 muiso 4	31 Na ₂ SO ₄ 13 NaC <i>I</i>	16 KC <i>I</i> 40 H ₂ O	32 Na ₂ SO ₄ 14 Nac <i>i</i> 12 NH ₄ CI	42 H ₂ 0 37 Na ₂ SO ₄ 17 NaC <i>t</i> 46 H ₂ O	25 Na ₂ S ₄ 21 MgSO ₄ 54 H ₂ O	19 Na ₂ SO ₄ 17 MgSO ₄ 64 H ₂ O	21 Na ₂ SO ₄ 19 MgSO ₄ 60 H ₂ O	l desirable Freezing Behavi
,	ottan		11	111	1 1 1 1	ł 1	1 1	F 7 4	(1) Insufficient Data; (2) Uni

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Table 5-5

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	PCM	lating*	-			_							-			-						
		tu/ft ³				 							 						 			
	of Fusion Volume	al/cm ³ B				 						*	 						 			
	Latent Heat Per Unit	<u>Joules</u> x 10 ⁻⁶ ci		-															 			
		kg/m ³				 				-									·			
	Density	1b/ft ³																				
		gm/cm ³							·					·								
	sion 18	Btu/lb				101			-	90						92			 	_		
Cont'd)	leat of Fu Unit Mar	cal/gm				 56	-			20						5			 			
Table 5-5 (0	Latent F Per	Joules x 10 ⁻	1			234				209						213						k of Merit
	oint	۰F	126			 154				158			187			661			 			: (4) Lac
	elting Po	ပ	52			68				20			. 86			93			 			1 Angerous
	X	°K	325			 341				343			359			366			 			L or: (3) Da
	Fremula		20 Lino ₃	61 NH4NO3	19 Ag NO ₃	79 AICI3	17 NaCł	4 ZrCI2		66 AICI3	20 NaCI	14 KC#	24 Lino ₃	71 NH 4 NO ₃	5 NH4 CE	60 AICI	26 NaCI	14 KC#				sirable Freezing Behavi
	N		l	I	1	 1	1	1		1	i	1	1	1	I	l	,	I				(1) Insufficient Data; (2) Undes

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	PCM	3 Rating*		
ASC-HRI	lon e	Btu/ft		
ELN	at of Fue it Volum	cal/cm ³		
	Latent He Per Ur	<u>Joules</u> x 10 ⁻⁶		
		kg/m ³		
	Density	1b/ft ³		
		gm/cm ³		
	eion 1	Btu/lb	88 8	
(ont'd)	unit Ma	cal/gm	60 60	
Table 5-5 (C	Latent H Per	Joules x 10 ⁻³ kg		
	oint	°F.	5 88 5 1 6 6 7 1 7	of Merit
	elting P	ပ	9 1 4 5 3	4) Lack
	X	Å	6 4 1 5 0 5	erous; (
	Formula		66 AICI ₃ 34 NaCI 40 NaNO ₃ 53 KNO ₃ 53 KNO ₃	iirable Freczing; (3) Dang
	J		HTS (regiate red trademark of El du Point de Nemours Co Inc.)	(1) Insufficient Data; (2) Undes

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	r	8	1				
	PCM	Rating	Prime	4	4	Frime	
	5.	Btu/ft ³	8860	2800	17820	5600- 7200	
	at of Fusi ift Volume	cal/cm ³	62	25	159	89.2- 115.9	
	Latent Hei Per Ur	<u>Joules</u> x 10 ⁻⁶ meter 3	331	105	665	373- 489.9	
		kg/m ³	999.8	1060	2440	1600	
	Density	lb/ft ³	62.42	66.2	152	001	
		*gm/cm ³	8666.0 0	1.06 ²⁵	2.44 ²⁵	1.6	
	aion 18	Btu/Ib	143.1	42	117	99- 129	
EOUS	eat of Fu Unit Mar	cal/gm	69.61	23.4	65	55-	
MISCELLAN	Latent H Per	<u>Joules</u> × 10 ⁻³	333.4	6.79	272	230- 301	
	int	٩	32.0	54	378.3	-60- 450	
1	Melting Po	°c	0.0	12	192.4	-51- 232	
	Ŵ	×,	273.2	285	465.6	222- 505	(3) Des
	Formula		н ₂ о	26.5 C ₅ H ₅ C ₆ H ₅	0.5 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	222-	irable Freezing Rehavior
			Water	Dowtherm A	Aluminum Chloride	Transit Heet Series Fatented trademark of Royal Industries, Santa Ana, Calif.	* (1) Insufficient Data: (2) Under

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Table 5-7 SOLID-SOLID

	Ter Ter	ransitio nperatu	_ = 1	1 0	Latent Hei [Transiti	at on	Densi	ty	Molecular	Me	lting P	oint	Heat o	Fusion	
Name	м°	°c	٥F	<u>Joules</u> x 10 ⁻³ kg	cal/gm	Btu/lb	Kg/m ³	lb/ft ³	Weight	°,K	ပ	۰F	<u>Joules</u> x 10 ⁻³ kg	cal/gm	Btu/lb
Diaminopentaerythritol	341	68	154	184	44	62		1	1 2 2 2		:				
2-Amino-2-methyl-l, 3 Propanediol	351	82	172	264	63	113		4 6 6 8	105.14	3 52- 357	79- 84	174- 183.2	31.7	7.58	13.6
2-methyl-2-nitro-1, 3-propanediol	352	19	174	201	48	96	1	-	135.12	354- 357	81-	178- 183	32.0	7.65	13.7
Trimethylolethane	354	81	178	192	46	83	1160	72.42	• • • •						
2 -Hydroxymethyl-2-Methyl-1, 3 - Propanediol	354	8	178	192	46	83) 1 1		470	197	387	46	Ξ	20
Monoaminopentaerythritol	359	86	187	192	46	83		1 1 1 1			:				
Tris(hydroxymethyl) acetic acid	397	124	255	205	49	88		-					4 4		1
2-Amino-2-hydroxymethyl-1, 3-propanediol	404	131	268	285	68	122			121,14	411- 419	138- 146	280- 295	25	6.0	10.8
2. 2-bis(hydroxymethyl) propionic acid	425	152	306	289	69	124			134.13	425- 428	152-	305-	26.8	6.41	11.5
Pentacrythritol	457	184	363	301	72	129			136.15	531	258	496	37.2	8.90	16.0
													- 480 - 1000		

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5-39

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N-TETRADECANE

Ref. Name: n-Tetradecane Synonyms: -Formula: C₁₄H₃₀ Description: A colorless liquid, a paraffin Molecular Weight: 198.38 Density: 825 kg/m^3 (51.5 lb/ft³, 0.825 gm/cm³) Solid: 18 at 277° K (38°F, 4°C) Liquid: 771 kg/m^3 (48.1 lb/ft³, 0.771 gm/cm³) 18 at 283° K (50° F. 10° C) Thermal Conductivity: 0.150 W/m-°K (0.0865 Btu/hr-ft-°F, 18 $3.58 \times 10^{-4} \text{ cal/sec-cm-}^{\circ}\text{C}$ Specific Heat: 2070 J/kg-^oK (0.495 Btu/lb-^oF, 0.495 gm-cal/gm-^oC) at the melting point 18 Thermal Diffusivity: -Latent Heat: 226×10^3 J/kg (98 Btu/lb, 54 cal/gm)* 20 $172 \times 10^{6} \text{ J/m}^{3}$ (4600 Btu/ft³, 41 cal/cm³) Melting Temperature: 278.6° K (41.9°F, 5.5°C) 27 Boiling Temperature: 525.6°K (486.5°F, 252.5°C) 27 Coefficient of Thermal Expansion: -Volume Change on Melting: -Supercooling: - None observed <u>Surface Tension</u>: 27.43×10^{-3} N/m (15.66 x 10^{-5} lb/in, 27.43 dynes/cm) 30 at 283° K (50°F, 10°C) Viscosity: -Vapor Pressure: $133 \text{ N/m}^2 (0.02 \text{ lb/in}^2, 1 \text{ mm})$ 27 at 347.8° K (166.3°F, 74.6°C)

*Calculated using density of the liquid.

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<u>Cost</u>: \$15.90/500 grams

<u>Compatibility</u>: Noncorrosive to most structural materials

Hazard Characteristics:

Flash Point: -

Autoignition Temp: -

- Flammability: A fire hazard when exposed to flame or heat; can 14 react with oxidizing materials.
- Toxicity: Nontoxic. The effects of the vapor phase vary with the volatility for the paraffin series.
- <u>PCM Candidacy</u>: One of the paraffin series which has been selected by several investigators for tests in PCM hardware. Like all paraffins, it is nontoxic, noncorrosive, predictable, and has very low thermal conductivity.

Test Performance: Described in References

2, 17, 18 19and 24

N-HEXADECANE

Ref.

Synonyms: -

Formula: C16H34

Description: A colorless liquid; a paraffin

Molecular Weight: 226.45

Density:

Solid:
$$835 \text{ kg/m}^3 (52.1 \text{ lb/ft}^3, 0.835 \text{ gm/cm}^3)$$
 18
at $288^{\circ}\text{K} (59^{\circ}\text{F}, 15^{\circ}\text{C})$

Liquid:
$$776 \text{ kg/m}^3$$
 (48.4 lb/ft³, 0.776 gm/cm³ 18
at 289.8°K (62.1°F, 16.7°C)

Thermal Conductivity:
$$0.15 \text{ W/m}^{\circ}\text{K} (0.087 \text{ Btu/hr-ft-}^{\circ}\text{F}, 18$$

 $3.6 \times 10^{-4} \text{ cal/sec-cm-}^{\circ}\text{C})$
at 289.8°K (62.1°F, 16.7°C)

Thermal Diffusivity:
$$8.7 \times 10^{-8} \text{ m}^2/\text{sec} (3.4 \times 10^{-3} \text{ ft}^2/\text{hr}, 6$$

 $8.7 \times 10^{-4} \text{ cm}^2/\text{sec})$

Latent Heat:
$$237.1 \times 10^3$$
 J/kg (102.0 Btu/lb, 56.67 cal/gm) 30
200 x 10⁶ J/m³ (5360 Btu/ft³, 47.8 cal/cm³)*

Melting Temperature:
$$289.8^{\circ}$$
K (62.1°F, 16.7°C)

Boiling Temperature: -

Coefficient of Thermal Expansion: -

Volume Change on Melting: -

Supercooling: Negligible

Surface Tension:
$$27.47 \times 10^{-3}$$
 N/m (15.69 x 10^{-5} lb/in, 27.47 dynes/cm) 6
at 293°K (68°F, 20°C)

* Calculated using density of the liquid.

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6

Ref. <u>Viscosity</u>: $3454 \ge 10^{-11}$ N-sec/m² (0.720 $\ge 10^{-12}$ lb-sec/ft², 28 3.454×10^{-8} centipoise) at 293° K (68° F, 20° C) Vapor Pressure: $133 \text{ N/m}^2 (0.02 \text{ lb/in}^2, 1.0 \text{ mm})$ at 378.4° K (221.5°F. 105.3°C) Cost: \$16.50 per 100 grams Compatibility: Noncorrosive to most structural materials Hazard Characteristics: Flash Point: -Autoignition Temp: -Flammability: A fire hazard when exposed to flame or heat; 14 can react with oxidizing materials. Toxicity: Nontoxic. The effects of the vapor phase vary with 14 the volatility for the paraffin series. PCM Candidacy: One of the paraffin series which has been selected for tests in PCM hardware. It is nontoxic, non-corrosive, predictable, and is noted for its low thermal conductivity. Test Performance: Described in References

2,17,18 19 and 24 . !

N-OCTADECANE

Ref.

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<u>Name</u>: n-Octadecane

Synonyms: -

Formula: C₁₈H₃₈

Description: Colorless crystal; a paraffin

Molecular Weight: 254

Density:

Solid:
$$814 \text{ kg/m}^3$$
 (50.8 lb/ft³, 0.814 gm/cm³) 18
at 300°K (80°F, 27°C)

Liquid:
$$774 \text{ kg/m}^3$$
 (48.3 lb/ft³, 0.774 gm/cm³) 18
at 305°K (90°F, 32°C)

Thermal Conductivity:
$$0.15 \text{ W/m-}^{\circ}\text{K}$$
 (0.087 Btu/hr-ft- $^{\circ}\text{F}$,18 $3.6 \times 10^{-4} \text{ cal/sec-cm-}^{\circ}\text{C}$)at 301.2°K (82.4 $^{\circ}\text{F}$, 28.0 $^{\circ}\text{C}$)

Thermal Diffusivity: -

Latent Heat:
$$243 \times 10^3$$
 J/kg (105 Btu/lb, 58 cal/gm) 20
188 x 10⁶ J/m³ (5070 Btu/ft³, 45 cal/cm³)^{*}

Coefficient of Thermal Expansion: -

Volume Change on Melting: -

Supercooling: - Negligible

Surface Tension:
$$27.45 \times 10^{-3}$$
 N/m (15.67 x 10^{-5} lb/in., 27.45 dynes/cm) 30
at 303[°]K (86[°]F, 30[°]C)

Viscosity:
$$2.68 \times 10^{-3}$$
 N-sec/m² (5.60 x 10^{-5} lb-sec/ft², 2.68 centipoise) 28
at 313°K (104°F, 40°C)

Vapor Pressure:
$$133 \text{ N/m}^2$$
 (0.02 lb/in², 1 mm) 27
at 448.1[°]K (346.8[°]F, 174.9[°]C)

^{*}Calculated using density of the liquid.

<u>Cost</u>: \$6.00 per 100 grams

Compatibility: Noncorrosive to most structural materials

Hazard Characteristics:

Flash Point: -

Autoignition Temp: -

Flammability: A fire hazard when exposed to flame or heat; can react with oxidizing materials.

Toxicity: Nontoxic. The effects of the vapor phase vary with the volatility for the paraffin series.

14

<u>PCM Candidacy</u>: One of the paraffins which has been selected for tests in PCM hardware. It is nontoxic, noncorrosive, predictable, and is noted for its low thermal conductivity. Used on Lunar Rover.

Test Performance: Described in References

2, 9, 17, 18, 19 and 24

Table 5-11 N-EICOSANE

	Ref.
<u>Name</u> : n-Eicosane	
Syncnyms: -	
Formula: C ₂₀ H ₄₂	
Description: A white waxy solid, a paraffin	
Molecular Weight: 282.54	
Density: Solid: 856 kg/m ³ (53.4 lb/ft ³ , 0.856 gm/cm ³) at 308 ^o K (94 ^o F, 34 ^o C)	18
Liquid: 778 kg/m ³ (48.6 lb/ft ³ , 0.778 gm/cm ³) at 310 [°] K (98 [°] F, 37 [°] C)	18
Thermal Conductivity: $0.150 \text{ W/m}^{\circ}\text{K} (0.0865 \text{ Btu/hr-ft-}^{\circ}\text{F}, 3.58 \times 10^{-4} \text{ cal/sec-cm-}^{\circ}\text{C})$	18
Specific Heat:	
Solid: 2210 J/kg- [°] K (0.528 Btu/lb- [°] F, 0.528 gm-cal/gm- [°] C) at 310 [°] K (98 [°] F, 37 [°] C) Liquid: 2010 J/kg- [°] K (0.481 Btu/lb- [°] F, 0.481 gm-cal/gm- [°] C)	27
Thermal Diffusivity: -	
<u>Latent Heat</u> : 247×10^3 J/kg (106 Btu/lb, 59 cal/gm) 192 x 10 ⁶ J/m ³ (5150 Btu/ft ³ , 46 cal/cm ³)*	10
Melting Temperature: 309.8°K (98.1°F, 36.7°C)	27
Boiling Temperature: 478°K (401°F, 205°C)	27
<u>Coefficient of Thermal Expansion</u> : $0.0003^{\circ}K^{-1}$ ($0.0002^{\circ}F^{-1}$, $0.0003^{\circ}C^{-1}$)	9
Volume Change on Melting: -	
Supercooling: None observed	
<u>Surface Tension</u> : -	
<u>Viscosity</u> : $4290 \times 10^{-8} \text{ N-sec/m}^2$ (896.6 x $10^{-9} \text{ lb-sec/ft}^2$, 4290 x $10^{-5} \text{ centipoise}$) at 311.0°K (100.0°F, 37.8°C)	30

^{*}Calculated using density of the liquid.

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<u>Vapor Pressure</u>: $133 \text{ N/m}^2 (0.02 \text{ lb/in}^2, 1 \text{ mm})$ at 471.2° K (388.4°F, 198.0°C)

Cost: \$15.00 per 100 grams

<u>Compatibility</u>: Compatible with most structural materials, noncorrosive

Hazard Characteristics:

Flash Point:

Autoignition Temp: -

Flammability: When exposed to flame, high temperatures, or strong 14 oxidizing materials, a fire hazard is presented.

Toxicity: Generally nontoxic. The effects vary with the volatility for all paraffin hydrocarbons.

<u>PCM Candidacy</u>: A PCM from the paraffin series that has been tested in actual hardware. It is nontoxic, noncorrosive, and has very low thermal conductivity. It is considered to be reliable and predictable. Used on Lunar Rover.

Test Performance: Described in References

9, 11, 17, 18, 19, 24, and 40

POLYETHYLENE GLYCOL 600

	Ref.
<u>Name</u> : Polyethylene Glycol 600	
<u>Synonyms</u> : Carbowax	
Formula: H(OCH ₂ CH ₂) _n OH	
Description: Colorless viscous liquid; a non-paraffin organic	
Molecular Weight: 570-630	10
<u>Density</u> : Solid: - Liquid: 1100 kg/m ³ (69 lb/ft ³ , 1.1 gm/cm ³) $2 + 293^{\circ} K (68^{\circ} F = 20^{\circ} C)$	
$\frac{\text{Thermal Conductivity: 0.160 W/m-}^{\circ}K (0.0923 Btu/hr-ft-}^{\circ}F, 3.82 \times 10^{-4} \text{ cal/sec-cm-}^{\circ}C) \\ \text{at } 323^{\circ}K (122^{\circ}F, 50^{\circ}C)$	10
<u>Specific Heat:</u> Solid: 2250 J/kg- ^O K (0.54 Btu/lb- ^O F, 0.54 gm-cal/gm- ^O C) Liquid: -	10
Thermal Diffusivity: -	
<u>Latent Heat</u> : 146×10^3 J/kg (63 Btu/lb, 35 cal/gm) 161 x 10 ⁶ J/m ³ (4320 Btu/ft ³ , 38.5 cal/cm ³) [*]	10
<u>Melting Temperature</u> : 293-298°K (68-77°F, 20-25°C)	10
Boiling Temperature: -	
<u>Coefficient of Thermal Expansion</u> : $0.0075^{\circ}K^{-1}$ ($0.0042^{\circ}F^{-1}$, $0.0075^{\circ}C^{-1}$)	
Volume Change on Melting: -	
Supercooling: None observed	
<u>Surface Tension</u> : 44.3×10^{-3} N/m (25.4 x 10^{-5} lb/in, 44.5 dynes/cm)	9
<u>Viscosity</u> : 11.5×10^{-3} N-sec/m ² (24.1 x 10^{-5} lb-sec/ft ² ,	9
11.5 centipoise)	
at 293°K (68° F, 20°C)	

^{*}Calculated using the density of the liquid.

Ref.

Vapor Pressure:
$$690 \times 10^{-6} \text{ N/m}^2 (270 \times 10^{-6} \text{ lb/in}^2, 5.2 \times 10^{-6} \text{ mm}) 9$$

at 373° K (212°F, 100°C)

Cost: \$4.00 per kilogram for Baker grade

Compatibility: Compatible with aluminum

Hazard Characteristics:

Flash Point: 519[°]K, (475[°]F, 246[°]C) 9 Autoignition Temp: -

Flammability: Slight, when exposed to heat or flame can react with 14 oxidizing materials.

Toxicity: Non-toxic. Physically and chemically related to glycerine. 14

<u>PCM Candidacy</u>: Polyethylene glycol 600 exhibits excellent freezing 10 characteristics. It is nontoxic, has low volatility, and is compatible with a number of structural materials. The heat of fusion is not high, but other properties appear to be desirable.

Test Performance: Described in Ref. 9.

5-50

ACETIC ACID

Name: Acetic acid	
Synonyms: Vinegar acid, glacial acetic acid, ethanoic acid, methane carboxylic acid	
Formula: CH ₃ COOH	
<u>Description</u> : Clear, colorless liquid; pungent odor of vinegar; a non-paraffin organic	
Molecular Weight: 65.05	
Density:	
Solid: -	
Liquid: 1050 kg/m ³ (65.6 lb/ft ⁻ , 1.05 gm/cm ⁻)	10
at 293° K (68°F, 20°C)	
<u>Thermal Conductivity</u> : Liquid: $0.18 \text{ W/m-}^{\circ}\text{K} (0.104 \text{ Btu/hr-ft-}^{\circ}\text{F}, 0.00043 \text{ cal/sec-cm}^{\circ}\text{C})$	10
at 298° K (77°F, 25°C)	
Specific Heat:	10
Solid: 2040 J/kg- $^{\circ}$ K (0.487 Btu/lb- $^{\circ}$ F, 0.487 gm cal/gm- $^{\circ}$ C)	
Liquid: 1960 J/kg- [°] K (0.467 Btu/lb- [°] F, 0.468 gm cal/gm- [°] C)	
Thermal Diffusivity: $0.839 \times 10^{-7} \text{ m}^2/\text{sec}$	
$(3.25 \times 10^{-3} \text{ ft}^2/\text{hr}, \ 0.839 \times 10^{-3} \text{ cm}^2/\text{sec})$	34
<u>Latent Heat</u> : 187×10^3 J/kg (80.4 Btu/lb, 44.7 cal/gm)	10
$196 \ge 10^6 \text{ J/m}^3 (5.26 \ge 10^3 \text{ Btu/ft}^3, 46.9 \text{ cal/cm}^3)^*$	
Melting Temperature: 289.8°K (62.1°F, 16.7°C)	14
Boiling Temperature: 391.3°K (244.6°F, 118.1°C)	14
$Coefficient of Thermal Expansion: 1.071°K^{-1} (0.595°E^{-1} - 1.071°C^{-1})$	10
liquid at 298°K (68°F, 20°C)	
Volume Change on Melting: +15.6%	10
Supercooling: One phase supercooling of about 15°K (27°F, 15°C)	10
Surface Tension: 27.42×10^{-3} N/m (15.66 x 10^{-5} lb/in	28
27.42 dynes/cm)	
at 293°K (68°F, 20°C)	

*Calculated using density of the liquid.

Ref

Viscosity:
$$1.31 \times 10^{-3}$$
 N-sec/m² (0.274 x 10^{-4} lb-sec/ft², 28
1.31 centipoise) 28

at $288^{\circ}K$ (59°F, 15°C)

Cost: \$2.41 per pound, U.S.P. grade

\$3.60 per pound for Baker analyzed reagent

Compatibility:

<u>Metals</u> - Does not attack aluminum, stainless steel, silver and other precious metals, titanium, tantalum, and zirconium. It reacts with magnesium, nickel and nickel alloys, tin, copper and copper alloys, beryllium, chromium, and zinc, in varying degrees.

<u>Nonmetals</u> - Compatible with fluorocarbons (TFE, FEP) graphite, and glass-ceramics. Reacts with acrylics, rubbers, epoxys, nylon and phenolics.

Hazard Characteristics:

·Flash Point: 313° K (104° F, 40° C)

Autoignition Temp: 839[°]K (1050[°]F, 566[°]C)

Flammability: Moderate, when exposed to heat or flame; can react vigorously with oxidizing materials.

Toxicity: Caustic, irritating. When heated to decomposition it emits toxic fumes.

<u>PCM Candidacy</u>: Although a catalyst to overcome exhibited 15^oK onephase supercooling has not yet been reported, further effort may prove successful. The volume expansion on melting is fairly large (16%).

10

Ref.

10

Table 5-14 TRISTEARIN

Ref. Name: Tristearin Synonyms: -Formula: (C17H35CO2)3 C3H5 Description: White crystalline solid; a non-paraffin organic Molecular Weight: 891.46 **Density:** Solid: -Liquid: 862 kg/m^3 (53.8 lb/ft³, 0.862 gm/cm³) 10 at $353^{\circ}K$ (176°F. 80°C) Thermal Conductivity: -Specific Heat: -Thermal Diffusivity: -<u>Latent Heat:</u> 191 x 10³ J/kg (82.1 Btu/lb, 45.6 cal/gm) 164 x 10⁶ J/m³ (4410 Btu/ft³, 39.3 cal/cm³)* 10 Melting Temperature: 329°K (133°F, 56°C) 10 Boiling Temperature: -Coefficient of Thermal Expansion: -Volume Change on Melting: -10 Supercooling: None observed Surface Tension: -<u>Viscosity:</u> 18.50×10^{-3} N-sec/m² (3.870 x 10^{-4} lb-sec/ft², 18.50 centipoise) 28 at 348°K (167°F, 75°C) Vapor Pressure: 133 N/m² (0.02 lb/in², 1 mm) 28 at 378.4°K (221.5°F, 105.3°C) Cost: \$4.50 per 10 grams for Baker grade 10 Compatibility: Compatible with aluminum

*Calculated using density of the liquid.

Hazard Characteristics:

Flash Point: -

Autoignition Temp: -

Flammability: -

Toxicity: -

<u>PCM Candidacy:</u> No unusual freezing behavior is noted (Ref. 10), but polymorphism has been reported. Under certain conditions the following sequence can occur: Solid 1 --> Liquid 1 --> Solid II --> Liquid II. The transition of Liquid I to Solid II is exothermic.

MYRISTIC ACID

Ref.

Name: Myristic acid Synonyms: -Formula: CH₃(CH₂)₁₂ COOH Description: Fine, white crystals; a non-paraffin organic Molecular Weight: 228.37 **Density:** Solid: -Liquid: 858 kg/m^3 (53.6 lb/ft³, 0.858 gm/cm³) 10 at 333° K (140°F, 60°C) Thermal Conductivity: -Specific Heat: $1590 \text{ J/kg-}^{\circ}\text{K}$ (0.381 Btu/lb- $^{\circ}\text{F}$, 0.381 gm-cal/gm- $^{\circ}\text{C}$) Solid: 10 Liquid: 2260 J/kg-[°]K (0.539 Btu/lb-[°]F, 0.539 gm-cal/gm-[°]C) Thermal Diffusivity: -<u>Latent Heat:</u> $199 \times 10^{3} \text{ J/kg}$ (85.5 Btu/lb, 47.5 cal/gm) $168 \times 10^{6} \text{ J/m}^{3}$ (4500 Btu/ft³, 40.1 cal/cm³)* 10 Melting Temperature: 331°K (136°F, 58°C) 10 Boiling Temperature: 523.6°K (482.9°F, 250.5°C) 10 Coefficient of Thermal Expansion: -Volume Change on Melting: -Supercooling: None observed 10 Surface Tension: -Viscosity: -Vapor Pressure: 133 N/m² (0.02 lb/in², 1 mm) 28 at 415°K (288°F, 142°C) Cost: \$19.25 per 500 grams, Baker analyzed reagent

* Calculated based on density of the liquid.

<u>Compatibility</u>: Compatible with many structural materials 10 including aluminum

Hazard Characteristics:

Flash Point: -

Autoignition Temp: -

Flammability: -

Toxicity: Apparently low. This material occurs naturally 14 in coconut products.

<u>PCM Candidacy:</u> Exhibits good freezing behavior. No unusual behavior characteristics are reported.

STEARIC ACID

Name: Stearic acid Synonyms: Octadecanoic acid Formula: CH₃(CH₂)₁₆ COOH Description: White, amorphous solid, a saturated straight-chain fatty acid; non-paraffin organic Molecular Weight: 284.47 Density: Solid: Liquid: 847 kg/m^3 (52.9 lb/ft³, 0.847 gm/cm³) 10 at 342° K (156°F, 69°C) Thermal Conductivity: -Specific Heat: -Thermal Diffusivity: -<u>Latent Heat:</u> $199 \times 10^3 \text{ J/kg}$ (85.5 Btu/lb, 47.6 cal/gm) $169 \times 10^6 \text{ J/m}^3$ (4520 Btu/ft³, 40.3 cal/cm³)* Melting Temperature: 342.6° K (156.9°F, 69.4°C) 10 Boiling Temperature: 656°K (721°F, 383°C) 14 $\frac{\text{Coefficient of Thermal Expansion:}}{\text{Solid: 8100 x 10^{-7} oK^{-1} (4500 x 10^{-70} F^{-1}, 8100 x 10^{-7} oC^{-1})}$ 10 Volume Change on Melting: -Supercooling: None observed, no unusual freezing behavior 10 has been noted. Surface Tension: 39.3×10^{-3} N/m (22.4 x 10^{-5} lb/in, 39.3 dynes/cm) 28 at 358°K (185°F. 85°C) <u>Viscosity</u>: 11.6×10^{-3} N-sec/m² (2.42 x 10^{-4} lb-sec/ft², 11.6 centipoise) 28 at 343°K (158°F. 70°C) Vapor Pressure: 133 N/m² (0.02 lb/in², 1 mm) 28 at 585.8°K (344.7°F, 173.7°C)

*Calculated based on density of the liquid.

Ref.

Cost: \$12.50 per 300 grams for Baker analyzed reagent	
\$ 2.59 per pound for U.S.P. grade	
<u>Compatibility</u> : Compatible with many structural materials; exhibits container separation in pyrex	10
Hazard Characteristics:	14
Flash Point: 469 [°] K, (385 [°] F, 196 [°] C)	
Autoignition Temp: 668 [°] K (743 [°] F, 395 [°] C);	
Flammability: Slight when exposed to heat or flame. Heats spontaneously.	
Toxicity: Very slight, used in cosmetics.	
<u>PCM Candidacy</u> : The only unusual behavior exhibited by this candidate is compound-container separation with a pyrex container.	10

Table 5-17 ELAIDIC ACID

Ref.

<u>Name</u> : Elaidic acid	
Synonyms: Octadecanoic acid	
Formula: C ₈ H ₁₇ CH:CH(CH ₂) ₇ COOH	
Description: A non-paraffin organic	
Molecular Weight: 282.46	
Density: Solid: — Liquid: 851 kg/m ³ (53.1 lb/ft ³ , 0.851 gm/cm ³) at 352°K (174°F, 79°C)	10
Thermal Conductivity:	
Specific Heat:	
<u>Thermal Diffusivity:</u> —	
<u>Latent Heat</u> : 218×10^3 J/kg (93.7 Btu/lb, 52.1 cal/gm) 185×10^6 J/m ³ (4970 Btu/ft ³ , 44.3 cal/cm ³)*	10
<u>Melting Temperature</u> : 320 [°] K (117 [°] F, 47 [°] C)	22
Boiling Temperature: 561°K (550°F, 288°C)	10
Coefficient of Thermal Expansion: -	
Volume Change on Melting: -	
Supercooling: None observed	10
Surface Tension: -	
<u>Viscosity</u> : -	
<u>Vapor Pressure</u> : 133 N/m ² (0.02 lb/in ² , 1 mm) at 444.4 ^o K (340.3 ^o F, 171.3 ^o C)	28
Cost: \$12.50 per 25 grams for Baker grade	
Compatibility: Compatible with aluminum	10
•	

*Calculated based on density of the liquid.

Table 5-17 (Cont'd)

Hazard Characteristics:

Flash Point: -Autoignition Temp: -Flammability: -Toxicity: -

<u>PCM Candidacy</u>: An organic acid which is compatible with aluminum and 10 exhibits good freezing behavior.

Ref.

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Table 5-18 ACETAMIDE

	Ref.
Name: Acetamide	
Synonyms: Acetic acid amine, Ethanamide	
Formula: CH ₃ CONH ₂	
Description: White to slightly yellow, deliquescent, fine crystals; a non-paraffin organic	35
Molecular Weight: 59.07	
Density: Solid: 1159 kg/m ³ (72.36 lb/ft ³ , 1.159 gm/cm ³) at 293°K (68°F, 20°C) Liquid: 998.6 kg/m ³ (62.30 lb/ft ³ , 0.9986 gm/cm ³) at 358°K (185°F, 85°C)	10
Thermal Conductivity: -	
Specific Heat: -	
Thermal Diffusivity: $33 \times 10^{-7} \text{ m}^2/\text{sec} (0.13 \text{ ft}^2/\text{hr}, 33 \times 10^{-3} \text{ cm}^2/\text{sec})$	13
<u>Latent Heat:</u> 241 x 10 ³ J/kg (104 Btu/lb, 57.7 cal/gm) 280 x 10 ⁶ J/m ³ (7520 Btu/ft ³ , 67 cal/cm ³) [*]	5 10
Melting Temperature: 354°K (178°F, 81°C)	14
Boiling Temperature: 495°K (432°F, 222°C)	28
Coefficient of Thermal Expansion: -	
Volume Change on Melting: +8.15%	10
Supercooling: None observed	10
<u>Surface Tension:</u> 39.3×10^{-3} N/m (22.4 x 10^{-5} lb/in, 39.3 dynes/cm) at 358°K (185°F, 85°C)	33
<u>Viscosity:</u> 2.22 x 10^{-3} N-sec/m ² (4.64 x 10^{-4} lb-sec/ft ² , 2.22 centipoise) at 393°K (248°F, 120°C)	28

*Calculated using density of the solid.

Table 5-18 (Cont'd)

 Vapor Pressure:
 133 N/m² (0.02 lb/in², 1 mm)
 Ref.

 at 338°K (149°F, 65°C)
 28

Cost: \$5.56 per pound, Baker analyzed reagent

Compatibility: Compatible with aluminum

Hazard Characteristics:

Flash Point: -

Autoignition Temp: -

Flammability: -

Toxicity: When heated to decomposition, it reportedly emits toxic cyanide fumes (decomposition point unavailable)

<u>PCM Candidacy</u>: For an organic compound, acetamide has a high density, low volume of expansion on melting, good thermal diffusivity, and low volumetric expansion on melting. On a volume basis, the heat of fusion is relatively high. One investigator reports a high vapor pressure near the melting point. Acetamide sublimes profusely when heated.

5

14
METHYL FUMARATE

Ref.

Name: Methyl Fumarate Synonyms: -Formula: (CHCO₂CH₃)₂ Description: White crystalline solid; a non-paraffin organic Molecular Weight: 144.12 Density: Solid: Liquid: 1045.2 kg/m^3 (65.250 lb/ft³, 1.0452 gm/cm³) 30 at 378.6°K (221.9°F, 105.5°C) Thermal Conductivity: -Specific Heat: Solid: Liquid: -Thermal Diffusivity: -Latent Heat: 242×10^3 J/kg (104 Btu/lb, 57.9 cal/gm) 10 $435 \times 10^6 \text{ J/m}^3 (1.17 \times 10^4 \text{ Btu/ft}^3, 104 \text{ cal/cm}^3)^*$ Melting Temperature: 375°K (216°F, 102°C) 10 Boiling Temperature: 465°K (378°F, 192°C) 10 Coefficient of Thermal Expansion: -Volume Change on Melting: + 18 to 20% Supercooling: None observed 10 Surface Tension: 25.67×10^{-3} N/m (14.66 x 10^{-5} lb/in , 25.67 dyne/cm) 30 at 379°K (223°F, 106°C) Viscosity: -Vapor Pressure: -

Cost: \$17.60 per 100 grams for Baker grade

* Calculated based on density of the liquid.

Compatibility: ---

Hazard Characteristics:

Flash Point: ---

Autoignition Temp: —

Flammability: —

Toxicity: ---

<u>PCM Candidacy</u>: Vigorous convection has been observed when methyl fumarate melts. This convection may be largely the surface tension driven type. The volume change figure 18 to 20% is only approximate. This candidate sublimates profusely when heated. Ref.

Table 5-20

OXAZOLINE WAX - TS-970

	Ref.
Name: Oxazoline wax - TS-970	
Synonyms: -	
Formula: -	
Description: A commercial wax; non-paraffin organic	
Molecular Weight: 970	
Density: -	
Thermal Conductivity: Estimated quite low	10
Specific Heat: -	
Thermal Diffusivity: Estimated very low	10
Latent Heat: DTA estimated large	10
Melting Temperature: 347°K (165°F, 74°C)	10
Boiling Temperature: -	
Coefficient of Thermal Expansion: -	
Volume Change on Melting: -	
Supercooling: None observed	
Surface Tension: -	
<u>Viscosity:</u> –	
Vapor Pressure: -	
Volume Change on Melting: -	

<u>Cost:</u> –

10

.

10

10

<u>Compatibility</u>: Very inert and consequently compatible with many 10 materials. Exhibits container separation with quartz and pyrex.

Hazard Characteristics:

Flash Point: -

Autoignition Temp: -

Flammability: Probably flammable

Toxicity: -

<u>PCM Candidacy</u>: Similar to Oxazoline Wax ES-254. Although very little data are available on this candidate, it may be suitable for some applications.

5-66

Table 5-21

OXAZOLINE WAX - ES-254

	Ref.
Name: Oxazoline wax-ES-254	
Synonyms: -	
Formula: -	
Description: A commercial wax; non-paraffin organic	
Molecular Weight: 723	
Density: -	
Thermal Conductivity: Appears to be quite low	10
Specific Heat: -	
Thermal Diffusivity: Estimated very low	10
Latent Heat: DTA estimated large	10
<u>Melting Temperature</u> : 323°K (122°F, 50°C)	10
Boiling Temperature: -	
<u>Coefficient of Thermal Expansion</u> : —	
Volume Change on Melting: -	
Supercooling: $2-3^{\circ}K(4-5^{\circ}F, 2-3^{\circ}C)$	
Surface Tension: -	
Viscosity: -	
Vapor Pressure: -	
<u>Cost</u> : -	
<u>Compatibility</u> : Very inert and consequently compatible with many materials. Exhibits container separation with	10

quartz and pyrex.

,

Hazard Characteristics:

Flash Point: -

Autoignition Temp: -

Flammability: Probably flammable

Toxicity: -

<u>PCM Candidacy</u>: Container separation was exhibited with quartz and pyrex, and might be present with other containers. Differential thermal analysis indicates a high heat of fusion.

Table 5-22

SODIUM HYDROGEN PHOSPHATE DODECAHYDRATE

Ref. Name: Sodium Hydrogen Phosphate Dodecahydrate Synonyms: -Formula: Na2HPO4 • 12H2O Description: White crystals, 39.36% by weight anhydrous salt; a salt hydrate Molecular Weight: 138.01 Density: Solid: 1520 kg/m^3 (94.9 lb/ft³, 1.52 gm/cm³) 10 at 293° K (68°F, 20°C) Liquid: -Thermal Conductivity: Solid: $0.514 \text{ W/m}^{\circ}\text{K}$ (0.297 Btu/hr-ft- $^{\circ}\text{F}$, 1.23 x 10⁻³ cal/sec-10 $cm^{\circ}C$) at 305°K (90°F, 32°C) Liquid: 476 w/m- $^{\circ}$ K (275 Btu/hr-ft- $^{\circ}$ F, 1.14 cal/sec-cm $^{\circ}$ C at 322° K (120°F, 49°C) Specific Heat: Solid: 1690 J/kg- $^{\circ}$ K (0.404 Btu/lb- $^{\circ}$ F, 0.404 gm-cal/gm- $^{\circ}$ C) at 273.2° K (32.0°F, 0.0°C) Liquid: 1940 J/kg-[°]K (0.464 Btu/lb-[°]F, 0.464 gm-cal/gm-[°]C) at 323 $^{\circ}$ K (122 $^{\circ}$ F, 50 $^{\circ}$ C) Thermal Diffusivity: -Latent Heat: $280 \times 10^3 \text{ J/kg}$ (114 Btu/lb, 66.8 cal/gm) 10 $427 \times 10^6 \text{ J/m}^3 (1.14 \times 10^4 \text{ Btu/ft}^3, 102 \text{ cal/cm}^3)^*$ Melting Temperature: 309°K (97°F, 36°C) 10 Boiling Temperature: ---Coefficient of Thermal Expansion: Solid: $8.3 \times 10^{-5} \, {}^{\circ}\text{K}^{-1}$ (4.6 x $10^{-5} \, {}^{\circ}\text{F}^{-1}$, 8.3 x $10^{-5} \, {}^{\circ}\text{C}^{-1}$) Liquid: $43.5 \times 10^{-5} \text{ K}^{-1}$ (24.2 x $10^{-5} \text{ o} \text{ F}^{-1}$, 43.5 x $10^{-5} \text{ o} \text{ C}^{-1}$) Volume Change on Melting: +5.1% * Calculated based on density of the solid.

Supercooling: None observed

Surface Tension: -

Viscosity: ---

Vapor Pressure: ---

<u>Cost</u>: \$4.33 per pound for Baker analyzed reagent. Much less for unanalyzed reagent.

<u>Compatibility</u>: Corresive to aluminum. Corrosion of aluminum by basic salt hydrates can be eliminated in some cases by inhibitors such as sodium silicate (water glass).

10

Hazard Characteristics:

Flash Point: -

Autoignition Temp: -

Flammability: -

Toxicity: - Very alkaline. Contact should be avoided.

<u>PCM Candidacy</u>: A candidate from the salt hydrate category. It melts congruently with no separation into the lower hydrate and liquid. The use of inhibitors such as sodium silicate (water glass) should overcome corrosion problems.

Table 5-23

LITHIUM NITRATE TRIHYDRATE

Ref.

Name: Lithium Nitrate Trihydrate Synonyms: -Formula: LiNO3 • 3 H2O Description: Clear, colorless liquid or crystalline solid; a salt hydrate with 56.5% by weight of anhydrous salt Molecular Weight: 123.00 Density: 1550 kg/m^3 (96.8 lb/ft³, 1.55 gm/cm³) Solid: 10 Liquid: 1430 kg/m^3 (89.3 lb/ft³, 1.43 gm/cm³) Thermal Conductivity: -Specific Heat: -<u>Thermal Diffusivity</u>: $1.8 \times 10^{-7} \text{ m}^2/\text{sec} (7.0 \times 10^{-3} \text{ ft}^2/\text{hr}, 1.8 \times 10^{-3} \text{ cm}^2/\text{sec})$ 13 <u>Latent Heat</u>: 296 x 10^3 J/kg (128 Btu/lb, 70.7 cal/gm) 460 x 10^6 J/m³ (1.23 x 10^4 Btu/ft³, 110 cal/cm³* Melting Temperature: 303.03°K (85.78°F, 29.88°C) 10 Boiling Temperature: -Coefficient of Thermal Expansion: -Volume Change on Melting: +8% Supercooling: Without a catalyst, up to 30°K of supercooling can be 10 expected. An effective catalyst, Zn (OH) NO3 has been reported. Surface Tension: -Viscosity: -Vapor Pressure: -Calculated using density of the solid.

Cost: For anhydrous LiNO3 - \$8.38 per pound for Baker analyzed reagent. About \$6.00 per pound for unanalyzed grade. To obtain the hydrate, add approximately 0.8 gm of water to each gm of anhydrous LiNO₂.

<u>Compatibility</u>: Compatible with aluminum, quartz, and pyrex. Non-wetting effects have not been observed.

Hazard Characteristics:

Flash Point: -

Autoignition Temp: -

Flammability: -

Toxicity: -

PCM Candidacy: This salt hydrate melts congruently, has an attractively 10 high heat of fusion, and convenient melting temperature. It is compatible with many structural materials. An effective nucleating catalyst has been reported, which prevents supercooling. Because of coordinated water of hydration, $LiNO_3 \cdot 3H_2O$ does not exhibit

> hazardous behavior typical of anhydrous nitrates. Its properties as a PCM candidate appear to be highly desirable. However, the effects of thermal cycling and impurities on catalyst performance have not been experimentally evaluated.

BARIUM HYDROXIDE OCTAHYDRATE

Ref. Name: Barium hydroxide octahydrate Synonyms: -Formula: Ba(OH)₂ · 8H₂O Description: A salt hydrate with 54.31% by weight of anhydrous Molecular Weight: 315.51 Density: Solid: 2180 kg/m^3 (136 lb/ft³, 2.18 gm/cm³) 10 at 289°K (61°F, 16°C) Liquid: -Thermal Conductivity: -Specific Heat: Solid: $1170 \text{ J/kg}^{\circ} \text{K} (0.28 \text{ Btu/lb}^{\circ} \text{F}, 0.28 \text{ gm}\text{-cal/gm}^{\circ}\text{-C})$ 22 Liquid: -Thermal Diffusivity: -Latent Heat: 301 x 10³ J/kg (129 Btu/lb, 72 cal/gm) 22 $657 \times 10^6 \text{ J/m}^3 (1.76 \times 10^4 \text{ Btu/ft}^3, 157 \text{ cal/cm}^3)^*$ Melting Temperature: 351°K (172°F, 78°C) 22 Boiling Temperature: -Coefficient of Thermal Expansion: -Volume Change on Melting: -Supercooling: Negligible 22 Surface Tension: -Viscosity: -Vapor Pressure: -Cost: \$2.60 per pound, Baker analyzed reagent

Calculated using density of the solid.

Compatibility: Corrosive to aluminum	10
Hazard Characteristics:	
Flash Point:	
Autoignition Temp: —	
Flammability: —	
Toxicity: Very alkaline. Breathing dust or contact with skin is harmful.	14
<u>PCM Candidacy</u> : This salt hydrate melts congruently with negligible supercooling. It absorbs carbon dioxide from the air, which can be prevented with closed containers. It is corrosive to aluminum. There are no particular hazards or handling problems, with due precaution for	10, 14 22

human contact.

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Table 5-25

CERROBEND EUTECTIC

<u>Name</u> : Cerrobend eutectic	
Synonyms: -	
Formula: 50.5 Bismuth + 26.7 lead + 13.3 tin + 10.0 cadmium	10
Description: A low melting eutectic; a metallic PCM	
Molecular Weight: -	
<u>Density:</u> Solid: 9400 kg/m ³ (587 lb/ft ³ , 9.4 gm/cm ³)	10
<u>Thermal Conductivity:</u> 19 W/m- ^o K (11 Btu/hr-ft- ^o F, 0.045 cal/sec-cm- ^o C)	10
<u>Specific Heat:</u> Liquid: 167 J/kg- ⁰ K (0.04 Btu/lb- ⁰ F, 0.04 gm-cal/gm- ⁰ C) Solid: Same as liquid	10
Thermal Diffusivity: -	
<u>Latent Heat:</u> $32.6 \times 10^3 \text{ J/kg}$ (14.0 Btu/lb, 7.78 cal/gm) $305 \times 10^6 \text{ J/m}^3$ (8180 Btu/ft ³ , 73 cal/cm ³)*	10
Melting Temperature: 343°K (158°F, 70°C)	10
Boiling Temperature: -	
<u>Coefficient of Thermal Expansion:</u> $6.6 \times 10^{-5} {}^{\circ}\text{K}^{-1}$ (3.7 x 10 ⁻⁵ ${}^{\circ}\text{F}^{-1}$, 6.6 x 10 ⁻⁵ ${}^{\circ}\text{C}^{-1}$)	
Volume Change on Melting: +1.7%	10
Supercooling: Slight, about 1°K (2°F, 1°C)	
Surface Tension: -	
<u>Viscosity:</u> —	
Vapor Pressure: -	
<u>Cost</u> : \$6.45 per pound	10
Compatibility: Compatible with aluminum	10
*Calculated using density of the solid.	

⁵⁻⁷⁵

Hazard Characteristics:

Flash Point: ---

Autoignition Temp: ---

Flammability: ---

Toxicity: —

<u>PCM Candidacy</u>: Cerrobend has a very low heat of fusion on a weight basis, but a reasonably high one on a volume basis. Its thermal conductivity is much higher than that of other PCM candidates. For some applications Cerrobend will probably be superior when all trade-offs are considered. The relatively high vapor pressure of cadmium, however, should be considered, especially for space applications.

Table 5-26 GALLIUM

Ref.

^{*}Calculated using density of the solid.

Ref. Surface Tension: 735×10^{-3} N/m (420 x 10⁻⁵ lb/in. 735 dynes/cm) 21 at 303° K (86°F, 30°C) <u>Viscosity</u>: 1.612×10^{-3} N-sec/m² (3.37 x 10⁻⁵ lb-sec/ft². 26 1.612 centipoise) at 370.8°K (207.9°F. 97.7°C) Vapor Pressure: 133 N/m² (0.02 lb/in², 1 mm) 14 at 1622° K (2460°F, 1349°C) Cost: Moderately high depending on purity; about \$7.50 per gram <u>Compatibility</u>: Very corrosive to nearly all metals, especially 21, 23, 26 aluminum. Anodized aluminum is attacked. It is compatible with titanium, fused quartz, ceramics, titania, zirconia, beryllia, alumina, tungsten, graphite, and tantalum. Hazard Characteristics: Flash Point: -Autoignition Temp: -Flammability: -Toxicity: Incomplete information; appears to be nonpoisonous 14 PCM Candidacy: Gallium has high thermal conductivity, low vapor 2,23,26 pressure, a small volume change on freezing, and a high heat of fusion on a volume basis. It has excellent physical and chemical stability. It is one of few materials which expands on freezing. Gallium is extremely anisotropic; the directional variation in 26 electrical resistivity may be the greatest of any known metal. Gallium has an extremely wide liquid range; it melts at 29.78°C 14 and boils at 2,403°C. Its chemical properties are close to those of aluminum and indium. In general, gallium and gallium salts are considered to be nontoxic. It appears to have possibilities where a low melting, thermally stable liquid metal with high conductivity is desired.

<u>Gallium Alloys</u>: Many eutectic alloys are formed with gallium and other metals. The heat of fusion for these alloys is about 42 J/kg (10 calories per gram 18 Btu/lb) and the thermal conductivity is 50 times that of water. The densities are around 6 grams/mf (4 x 10^2 lb m/ft³, 6 x 10^3 kg/m³). Gallium forms triple eutectic alloys and tetradic eutectic

The melting points of some eutectic alloys of unreported compositions are:

alloys.

Gallium - Aluminum: 299°K (79°F, 26°C) Gallium - Zinc: 298°K (77°F, 25°C) Gallium - Tin: 293°K (68°F, 20°C) Gallium - Indium: 289.6°K (61.7°F, 16.5°C) Gallium - Aluminum - Zinc: 295.1°K (71.4°F, 21.9°C).

According to Ref. 2, some 87 alloys of gallium were prepared and investigated. The data on one of these are as follows:

95 Ga + 5 Zn, melting point 298°K (77°F, 25°C).

This Ga-Zn eutectic can be alloyed with 2 to 3% lithium, and 0.05 to 0.1% bismuth.

In general, the purity of the initial metals, and the accuracy of the 2,23,26 eutectic ratio between components, are of prime significance. It is possible to obtain a number of different control temperatures by selecting a particular alloy.

Table 5-27 WATER

Name: Water	Ref.
Ivallie. Water	
Synonyms: -	
Formula: H ₂ O	
Description: Clear, colorless liquid; a miscellaneous PCM	
Molecular Weight: 18.016	
Density:	
Solid: 916.8 kg/m ³ (57.24 lb/ft ³ , 0.9168 gm/cm ³) at 273.15 $^{\circ}$ K (32.00 $^{\circ}$ F, 0.00 $^{\circ}$ C)	28
Liquid: 999.8 kg/m ³ (62.42 lb/ft ³ , 0.9998 gm/cm ³) at 273.15 ^o K (32.00 ^o F, 0.00 ^o C)	
Thermal Conductivity:	34
Liquid: 0.567 W/m - $^{\circ}\text{K}$ (0.328 Btu/hr-ft- $^{\circ}\text{F}$, 1.40 x 10 ⁻³ cal/sec-cm- $^{\circ}\text{C}$) at 273.2 $^{\circ}\text{K}$ (32.0 $^{\circ}\text{F}$, 0.0 $^{\circ}\text{C}$)	
Solid: 2.2 W/m- [°] K (1.3 Btu/ft-hr- [°] F, 0.0054 cal/sec-cm- [°] C) at 273.2 [°] K (32.0 [°] F, 0.0 [°] C)	
Specific Heat:	
Solid: 2040 J/kg- [°] K (0.487 Btu/lb- [°] F, 0.487 gm-cal/gm- [°] C) Liquid: 4210 J/kg- [°] K (1.00 Btu/lb- [°] F, 1.00 gm-cal/gm- [°] C)	28
Thermal Diffusivity:	
Liquid: $1.35 \times 10^{-7} \text{m}^2/\text{sec} (5.23 \times 10^{-3} \text{ ft}^2/\text{hr}, 1.35 \times 10^{-3} \text{ cm}^2/\text{sec})$	3,34
Solid: 8.40 x 10^{-7} m ² /sec (3.26 x 10^{-2} ft ² /hr, 8.43 x 10^{-3} cm ² /sec)	
<u>Latent Heat:</u> 333.4×10^3 J/kg (143.1 Btu/lb, 79.69 cal-gm) 330×10^6 J/m ³ (8932 Btu/ft ³ , 79.67 cal/cm ³) [*]	28
Melting Temperature: 273.15°K (32.00°F, 0.00°C)	28
Boiling Temperature: 373.2°K (212.0°F, 100.0°C)	28
<u>Coefficient of Thermal Expansion:</u> Solid: $1125 \times 10^{-70} \text{K}^{-1} (625 \times 10^{-70} \text{F}^{-1}, 1125 \times 10^{-70} \text{C}^{-1})$	10

Preceding page blank *Calculated using density of the liquid. 5-81

Volume Expansion on Melting: -9.06%

Supercooling: Variable; depends upon impurities and rate of cooling 10

Surface Tension: 75.6 x
$$10^{-3}$$
 N/m (42.8 x 10^{-5} lb/in, 75.6 dynes/cm) 28
at 273.2°K (32.0° F, 18.0°C)

Viscosity:
$$1.79 \times 10^{-3} \text{ N/m}^2 (3.74 \times 10^{-5} \text{ lb-sec/ft}^2, 28$$

1.79 centipoise) at 273°K (32°F, 0°C)

Vapor Pressure:
$$610.4 \text{ N/m}^2$$
 (0.0886 lb/in², 4.579 mm) 28
at 273.2[°]K (32.0[°]F, 0.0[°]C)

Cost: Sold as distilled or deionized water

<u>Compatibility</u>: The liquid must be conditioned to remove corrosion-causing impurities.

<u>Metals</u>: Resistant in high purity (distilled or deionized) to aluminum and alloys, beryllium up to 500°F, copper and alloys, nickel, stainless steel, titanium and alloys, magnesium, tungsten, zinc up to 120°F, and zirconium and alloys. It will pit or tarnish carbon steels, cast irons, molybdenum, tantalum, tin, and wrought iron.

Nonmetallics: Compatible with graphite, hydrocarbon rubber, neoprene, nylon, polyethylene, polypropylene, polystyrene, acrylics, silicone rubber and urethane rubber. Long term service is not recommended with epoxy, phenolics, polyacrylic rubber, butyl rubber, or acetyl homopolymer.

Hazard Characteristics:

Flash Point: None

Autoignition Temp: None

Flammability: Completely nonflammable

Toxicity: None

<u>PCM Candidacy</u>: Water has one of the highest heat capacities of any substance known. It has the highest heat of fusion per unit weight and per unit volume of all PCMs to date. It is one of few materials which expands on freezing. The thermal conductivity and diffusivity are higher than that of most liquids.

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Table 5-28

TRANSIT HEET

Name: Transit Heet; Registered trademark of Royal Industries, Santa Ana, California, a series with different melting points Synonyms: -Formula: Proprietary formulation; probably inorganic hydrated salts Description: A miscellaneous PCM Molecular Weight: -<u>Density</u>: $1600 \text{ kg/m}^3 (100 \text{ lb/ft}^3, 1.6 \text{ gm/cm}^3)$ 9 Thermal Conductivity: -Specific Heat: Solid: 1760 J/kg-^oK (0.42 Btu/lb-^oF, 0.42 gm-cal/gm-^oC) 16 Liquid: 3400 J/kg-[°]K (0.8 Btu/lb-[°]F, 0.8 gm-cal/gm-[°]C) Thermal Diffusivity: -Latent Heat: 230×10^3 to 372×10^3 J/kg (99 to 160 Btu/lb, 16 55 to 89 cal/gm) 368×10^6 to 596 x 10^6 J/m³ (9900 to 16000 Btu/ft³, 88 to 142 cal/cm³) Melting Temperature: Available in a range: 222 to 505°K 16 $(-60 \text{ to } 450^{\circ} \text{F}, -51 \text{ to } 232^{\circ} \text{C})$ Boiling Temperature: -Coefficient of Thermal Expansion: -Volume Change on Melting: -Supercooling: -Surface Tension: -Viscosity: -Vapor Pressure: -PCM Candidancy: Available in a wide choice of melting temperatures, with a high heat of fusion per unit weight and volume. Presently used in shipping containers. Test Performance: Described in Refs. 9 and 16. 9.16

Ref.

^{*}Temperature and phase not reported.

Section 6

CONTAINER AND FILLER MATERIALS PROPERTIES AND COMPATIBILITIES

6.1 INTRODUCTION

In selecting container and filler materials, thermal and mechanical properties must be considered as discussed in Section 8. Compatibilities of PCM materials with their containers is an important consideration as well. Metals have been the universal choice for PCM containers and for fillers because of their high thermal conductivities, yet none of the PCM candidate materials have been rigorously tested for long-term compatibility with these aerospace metals. Generally the concern is corrosion of the container metal by the PCM itself or by some impurity in the PCM. Of course, some impurities have no effect on the compatibility of the basic materials and a few types of impurities even inhibit corrosion.

6.2 MATERIAL CORROSION

The primary mode of material corrosion of concern in PCM technology is chemical corrosion. Generally, PCMs of the salt hydrate, metallics, and fused-salt categories are the most corrosive.

Basically, two corrosive sources are potential problems; the PCM itself or an impurity therein. For example, $Ba(OH)_2 \cdot 8H_2O$ reacts strongly with aluminum precluding their use together. This process is defined by the chemical formula, $2 Al + Ba(OH)_2 \cdot 8 H_2O \rightarrow Ba Al(OH)_4]_2$ + $3 H_2 + 2 H_2O$, and is just one example of numerous incompatibilities of PCMs with container metals. Known cases of incompatibilities with the 22 prime PCM candidates are identified in Section 5 (Tables 5-8 through 5-28).

Corrosion by PCM impurities normally occurs when the contaminant is a metal ion such as Pb^{+2} and the base PCM material, such as water, acts as an electrolyte between the ion and the container metal (Ref. 1). The result is that the aluminum is removed from the container by ionization. This form of corrosion can occur for a large variety of combinations of container metals and contaminants. None are documented with regard to their severity in a PCM application. Furthermore, the concentration of the contaminants along with several other variables influences the extent of corrosion. For these reasons, specific details are not presented as to which combinations to avoid. References 7 and 8 present the limited information that is available. A general guideline, however, can be obtained from Table 6-1. Any metal listed in the table will react with any ion listed below it. For example, iron (Fe) metal will dissolve in a nickel (Ni) solution plating out nickel metal. There are exceptions to the general trend indicated in the table, however. Therefore design decisions regarding contaminants should not be based solely on the data in Table 6-1.

6.3 CORROSION INHIBITORS

A corrosion inhibitor is any substance used to reduce the corrosion rate of metals by materials. The first step for selecting a corrosion inhibitor for a specific system is a thorough study of the system itself. Inhibitors that are valuable for some applications can be harmful in others. Extrapolation from one system to another has caused considerable damage to many industrial systems. Although inhibitors for some corrosion problems can be similar to others, this similarity should be regarded as coincidence. The lengthy procedures required for the development of a good corrosion inhibitor explains why most inhibitors are developed by specialists in that field (Ref. 8).

There are two basic categories of inhibitors, as follows:

• Oxide films. Oxide films such as those formed on aluminum, titanium, and stainless steel form a protective layer which is

Element	Reaction
Beryllium	$Be^{2+} + 2e^{-} = Be$
Aluminum	$Al^{3+} + 3e^{-} = Al$
Titanium	$Ti^{2+} + 2e^{-} = Ti$
Manganese	$Mn^{2+} + 2e^{-} = Mn$
Vanadium	$v^{2+} + 2e^{-} = v$
Zinc	$Zn^{2+} + 2e^- = Zn$
Chromium	$Cr^{3+} + 3e^{-} = Cr$
Gallium	$Ga^{3+} + 3e^- = Ga$
Iron	$Fe^{2+}+2e^{-}=Fe$
Chromium	$Cr^{3+} + e^{-} = Cr^{2+}$
Titanium	$Ti^{3+} + e^{-} = Ti^{2+}$
Thallium	$T\ell^+ e^- = T\ell$
Vanadium	$v^{3+} + e^- = v^{2+}$
Nickel	$Ni^{2+} + 2e^- = Ni$
Tin	$\mathrm{Sn}^{2+} + 2\mathrm{e}^{-} = \mathrm{Sn}$
Lead	$Pb^{2+} + 2e^- = Pb$
Hydrogen	$2H^{+} + 2e^{-} = H_{2}$
Tin	$Sn^{4+} + 2e^- = Sn^{2+}$
Copper	$Cu^{2+} + e^{-} = Cu^{+}$
Copper	$Cu^{2+} + 2e^{-} = Cu$

Table 6-1POTENTIALS OF ELECTROCHEMICAL REACTIONS

6-3

inert to many PCMs. When corrosion resistance needs to be increased, the oxide coating is treated to make it thicker.

 Additives. Additives form protective surfaces which can be formed by compounds absorbed directly on the metal surface to provide physical protection against corrosive attack. These include long chain aliphatic acids and aqueous solutions of sodium bicarbonate and sodium phosphate. These inhibitors can be added in small amounts to the PCM to decrease corrosion. (A common use of this type are rust inhibitors for radiators, steam boilers, etc.). Although added to the bulk of the PCM, they adsorb onto the metal surface to form a continuous layer.

Corrosion prevention and control methods are becoming increasingly important. There are many possibilities for effective applications of inhibitors as new materials become important, and as long-term compatibility is required. Reference 8 provides some specific information. Some suggested inhibitors are listed for specific PCM/metals combinations in following paragraphs.

6.4 PCM CONTAINER AND FILLER METALS

Three metals are currently being used for PCM containers: aluminum, titanium, and stainless steel. These metals have high strength-to-weight ratios, are corrosion resistant, and have good thermal conductivities. All of them have been widely used in aerospace technology (Ref. 2). Although stainless steel is heavier than the others, it is more elastic and can thus accommodate PCM volume changes. Each of these metals has its own advantages and special characteristics. It is the designer's task to choose the metal or metal combination most suitable for a particular application. Other metals or metal alloys may be highly desirable and merit consideration.

6.4.1 Aluminum

Because of aluminum's low density, high thermal conductivity, and corrosion resistance, many PCM designers use it for containers and fillers. Pertinent properties of aluminum (Refs. 5, 6, and 10) are shown on the following page:

6-4

Thermal Conductivity: 72 W/m-°K, (135 Btu/hr-ft-°F, 0.52 cal/sec-cm-°C) at 273 to 373°K (32 to 212°F, 0 to 100°C) Density: 2.69 x 10³ kg/m³, (168 lb/ft³, 2.69 gm/cm³) at 293°K (68°F, 20°C) Specific Heat: 0.894 x 10³ J/kg-°K, (0.214 Btu/lb-°F, 0.214 cal/gm) Coefficient of Thermal Expansion: 23.86 x 10⁻⁶ °K⁻¹ (13.26 x 10⁻⁶ °F⁻¹, 23.86 x 10⁻⁶ °C⁻¹).

Aluminum is amphoteric: it will form compounds with PCMs which are strong acids or strong bases (alkali hydroxides). It forms salts with strong acids (chlorides, nitrates, and sulfates) and aluminates (AMO_2^{-1}) with bases (Ref. 10). However, materials which are compatible with aluminum are as follows with prime PCMs underlined (Refs. 1 and 11):

Acids:

<u>acetic</u>, <u>elaidic</u>, <u>myristic</u>, <u>stearic</u>, benzoic

Alcohols:

ethylene glycol

Dry Inorganic Salts: (does not include salt hydrates)

Miscellaneous Organics:

<u>acetamide</u>, <u>methyl fumarate</u>, <u>paraffins</u>, <u>polyethylene glycol</u>, tristearin, oxazoline w**a**xes,

most fused salt eutectics

Oxidizing PCMs:

Sulfur Compounds:

(only if protective aluminum oxide film is present)

most PCMs which are inorganic sulfides or organic sulfides

Water:

high purity: distilled or deionized water.

6-5

silicates

Inhibitors which may be useful for reducing corrosion of aluminum with various PCMs are:

- Soluble oils, alkyl arylsulforates, and amines for acids
- Silicates with a high ratio of silicate to soda for alkaline compounds
- Borates, silicates, nitrates, phosphates, and soluble oils for water
- Oxide coatings are extremely effective for most chemicals
- Coatings such as paint, electroplated metals, metal alloys of aluminum, teflon, glass, etc.

Further information can be obtained from Refs. 5 and 19.

Aluminum can be soldered, brazed, and welded. Soldering aluminum differs from soldering other common metals in several ways. The refractory oxide coating on aluminum requires special fluxes. With aluminum, resistance to corrosion depends much more on solder composition than it does for most other metals. Aluminum-to-aluminum joints are generally superior in strength to joints between aluminum and dissimilar metals (Ref. 3). Silver solders commonly used for joining other metals cannot be used for joining aluminum because none of them has a low enough melting range. The various types of solders and fluxes are described in Ref. 3.

6.4.2 Titanium

The interest in titanium is becoming more and more widespread. On a strength-to-weight basis, it is superior to all other structural materials (Refs. 12 and 15). It has outstanding corrosion resistance. It is one of the few metals that would be suitable for use with gallium and alloys of gallium since these PCMs are very aggressive to most metals, especially aluminum. This resistance is due to the formation of a protective film, promoted by oxygen or oxidizing agents (Ref. 13).

Methods for joining titanium are still in development. Suitable techniques for soldering, brazing, and welding have been reported (Ref. 12).

6-6

Pertinent properties obtained from Ref. 12 and 14 are as follows:

Thermal Conductivity: 4.8 to 6.14 W/m- $^{\circ}$ K (9.0 to 11.5 Btu/hr-ft- $^{\circ}$ F, 0.037 to 0.048 cal/sec-cm- $^{\circ}$ C) at 293 $^{\circ}$ K (68 $^{\circ}$ F, 20 $^{\circ}$ C) Density: 4.54 x 10 3 kg/m 3 , (283 lb/ft 3 4.54 gm/cm 3) Specific Heat: 519 J/kg- $^{\circ}$ K, (0.124 Btu/lb- $^{\circ}$ F, 0.124 gm-cal/gm- $^{\circ}$ C) Coefficient of Thermal Expansion: 9.0 x 10 $^{-6}$ $^{\circ}$ K⁻¹ (5.0 x 10 $^{-6}$ $^{\circ}$ F⁻¹ 9.0 x 10 $^{-6}$ $^{\circ}$ C⁻¹)

Note that the thermal conductivity is about 1/16 that of aluminum.

The following PCMs are compatible with titanium under ordinary service conditions. Prime PCMs are underlined:

Acids:	<u>acetic</u> , chloroacletic, <u>stearic</u> , lactic, salicylic, succinic acids
Salts:	Most inorganic and organic salts, magnesium sulfate, sodium chloride, sodium sulfate, potassium chloride
Miscellaneous:	Water, gallium, hydrogen sulfide,

Detailed data on titanium alloys, mechanical and physical properties and other valuable information can be found in Refs. 13, 16 and 17.

Recently a patent was granted for anodizing titanium which may have great significance in increasing the compatibility range of this metal (Refs. 20 and 21).

6.4.3 Stainless Steel

In PCM technology, stainless steels have been used for containers or parts of containers. Stainless steel bellows were used in containers because of their elasticity in adjusting to continual volume change caused by PCM melting and freezing (see Engineering Design, Section 8, page 8-40). The advantages of great strength, elasticity, and corrosion resistance have qualified this metal for some PCM applications (Refs. 1, 9, 17, and 18).

Stainless steels can be soft soldered and silver soldered. No problems such as sensitization, hardening, or tempering arise at the low temperatures involved in soldering. All stainless steels can be brazed, and no fluxes are required. Welding with few problems is common.

Corrosion resistance is a major consideration in the selection of a stainless steel alloy. Basically, corrosion resistance of all stainless steel depends upon its chromium content. Chromium as a pure metal is very active, but it occurs as an oxide in stainless steel, usually $FeO \cdot Cr_2O_3$. The reason stainless steel is so inert to many environments is due to the formation of this oxide (Ref. 4). Since the alloys vary so widely in corrosion resistance, it would be advisable to consult data for specific alloys. Generalizations are difficult to make, although all stainless steels are moderate to excellent in corrosion resistance.

A few physical properties are presented as follows:

Thermal Conductivity: 4.3 to 7.69 W/m- $^{\circ}$ K, (8.0 to 14.4 Btu/hr-ft- $^{\circ}$ F, 0.033 to 0.0596 cal/sec-cm- $^{\circ}$ C) at 293 $^{\circ}$ K (68 $^{\circ}$ F, 20 $^{\circ}$ C)

Density: 7530 to 8010 kg/m³, (470 to 500 lb/ft³, 7.53 to 8.01 gm/cm³) at 293[°]K (68[°]F, 20[°]C)

Specific Heat: 460 to 500 J/kg- $^{\circ}$ K (0.11 to 0.12 Btu/lb- $^{\circ}$ F, 0.11 to 0.12 gm-cal/gm- $^{\circ}$ C)

Coefficient of Thermal Expansion: 11×10^{-6} to $20.3 \times 10^{-6^{\circ}}$ K⁻¹ (6. 1×10^{-6} to $11.3 \times 10^{-6^{\circ}}$ F⁻¹, 11×10^{-6} to $20.3 \times 10^{-6^{\circ}}$ C⁻¹)

References - Section 6

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Section 7 PCM FILLERS AND COMPOSITES

The use of fillers with phase change materials offers distinct advantages, the primary one being the improvement of PCM thermal conductivity. Composite systems of metal fillers with PCM offer increased thermal conductivity and thereby improved system performance (Ref. 1). All PCMs, with the exception of the metallics, have low thermal conductivities, comparable to the best insulators (Ref. 2). The temperature at the heated surface of such a PCM may rise far above the melting point (even to the boiling point) with PCM solid still available but thermally isolated from the heated surface. System failure can result from undesirable thermal gradients, high vapor pressure, or a combination of factors. Low thermal conductivity in a PCM limits the flux rate that can be absorbed and the efficiency of the system.

When a filler is used, the penalty resulting from the displacement of some of the fusible material by metallic filler must be considered. This displacement substitutes the product of specific heat and temperature rise of the metal for the much larger heat of fusion of the PCM. The optimum configuration of metallic filler with PCM to improve system performance varies according to application. The section on Engineering Design, Section 8, pages 8-13 to 8-18, outlines a technique for determining the optimum percentage of filler.

Fillers can also serve to improve the structural integrity of the PCM package.

7.1 TYPES OF FILLERS

X

Fillers used with PCM in reported tests include:

• Aluminum in the following forms: powder, foam, wool, honeycomb

- Copper foam
- Alumina $(A \ell_2 O_3)$ as a foam and powder.

Powder-PCM composites gave no noticeable change in the thermal conductivity of lithium nitrate trihydrate filled with aluminum powder or with alumina (AI_2O_3) powder (Ref. 3). Aluminum wool gave some improvement in system performance, but significantly less than that indicated in the preliminary analysis of the weight of aluminum used (Ref. 1). The same was generally true of the copper and aluminum foams tested. The test results reported with different PCM's indicate that aluminum honeycomb offers the most system improvement compared to the others tested (Refs. 1, 3, and 4).

An important type of filler for which test data are lacking is aluminum fins. These are currently being used as fillers by several investigators, although test results have not yet been reported. Fins are used in preference to honeycomb in some cases because of the problems encountered with obtaining good contact between honeycomb and the cold plate. Fins are welded to the cold plate, whereas honeycomb is usually attached to the cold plate with epoxy, resulting in an undesirable contact resistance. One investigator is currently using fins as a filler for paraffin PCMs, with the fins packed as closely as possible (Ref. 5).

The type of metal filler selected should be considered from the standpoint of fabrication. Soldering, brazing, and welding are the preferred techniques for providing maximum thermal conductivity from the container plate through the filler. Metals used as fillers and containers are discussed in detail in Section 6, as to their properties and compatibilities with various PCMs.

7.2 FILLER OPTIMIZATION

A few obvious conclusions can be deduced from thermodynamic considerations to optimize the effects of fillers. The density of the filler ρ_F should be small for an optimum filler since total system weight is to be minimized. Thermal conductivity of the filler, k_F , should be large since the primary role of the filler is to enhance the conductivity through the PCM. The specific heat should be high since any heat stored as sensible heat in the filler offers an improvement in energy storage capacity. Detailed information is contained in Engineering Design, Section 8, on the following items:

- Amount of filler required for a particular application
- Effects of bond and contact thermal resistance between filler and cold plate
- Three-dimensional heat transfer effects within the filler.

References - Section 7

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Section 8 PCM ENGINEERING DESIGN CONSIDERATIONS

In the design of PCM thermal control systems for specific applications, several engineering considerations must be examined. In this section, the following topics will be investigated in detail: (1) thermodynamic considerations, (2) heat transfer considerations, (3) combined thermodynamic/heat transfer considerations and the function of fillers, (4) containment considerations, and (5) an engineering formalism which yields the proper design of a PCM thermal control system from the initial requirements. Because of the lack of general engineering design guidelines and data in the literature, the bulk of the guidelines and data presented in this section was developed during this study.

8.1 CHOICE OF PCM

In selecting a proper PCM for a specific application, the first criterion to be considered is the operational temperature range of the component to be protected. The PCM must have a melt temperature within this range, and to ensure that unintentional undercooling or overheating will not damage the component, the PCM melt temperature should be near the middle of the component's operational temperature range. Tables 5-1 through 5-7 present numerous PCM candidates in the order of melt temperature, which can be used efficiently to locate a PCM for a specific application. If more than one PCM is found with suitable melt temperatures, secondary comparisons should be made to eliminate all but the best PCM. The secondary comparisons that should be considered are presented on the following page in Table 8-1.

None of the PCM candidates may be superior in all categories, and engineering trade-offs must be made to select the best PCM for a specific application. If a prime candidate has the proper melt temperature, the detailed table for that material (Tables 5-8 through 5-28) should prove valuable. In general, the prime candidates should cause fewer design problems than their non-prime counterparts.

Table 8-1 SECONDARY COMPARISONS

PROPERTY OR CHARACTERISTIC	DESIRABLE VALUE OR TENDENCY
Heat of fusion	High
Thermal conductivity	High
Specific heat	High
Density	High
Volume change during melting	Low
Vapor pressure	Low
Melting/freezing behavior	Dependable and reversible
Availability	Readily available
Cost	Low
Compatibility	Compatible with container and filler materials
Toxicity	Nontoxic
Hazardous behavior	Not exhibited
Property data	Readily available and well documented
Surface tension	Low

.

8.2 THERMODYNAMIC CONSIDERATIONS

To design a PCM thermal protection system properly, the thermodynamic conservation relations for the system must be developed. Development of the relations will vary from application to application, but the general example discussed below illustrates the methodology to be used in developing the thermodynamic relations for any application.

Consider the thermal protection system shown in Fig. 8-1. An electrical component is thermally protected by the PCM package/radiator system. The component internally generates energy cyclically, as shown in Fig. 8-2. By design, the radiator will operate very close to the PCM melt temperature at all times and the radiant energy exchange will be very nearly constant, as shown in Fig. 8-2. Considering these to be the only energy exchanges to which the package is subject, the radiator sizing is easily determined as follows. For cyclical operation, the energy state of the system at time (1) must be the same as the energy state at time (2). This requires the total energy dissipated by the component during the cycle to equal the total energy radiated by the radiator. Therefore, during each complete cycle, the area under the $\dot{Q}_{generated}$ curve must equal the area under the $\dot{Q}_{radiated}$ curve in Fig. 8-2. In mathematical form

$$\sigma A_{rad} \in T^4_{melt} \Delta \theta_{1-2} = \dot{Q}_{pulse} \Delta \theta_{pulse}$$

assuming an absolute zero thermal radiation sink and no solar or planetary radiation incident upon the radiator surface. (For applications in which incident radiation is appreciable, the above equation must be adjusted such that the energy emitted minus the energy absorbed from incident radiation will equal the energy generated by the component during each complete cycle). For a particular application, PCM and radiator surface, T_{melt} , ϵ , $\Delta \theta_{1-2}$, \dot{Q}_{pulse} , and $\Delta \theta_{pulse}$ are fixed quantities. Therefore, the radiator area must be:



Fig. 8-1 - PCM/Radiator Thermal Control System



Fig. 8-2 - Energy Exchanges

$$A_{rad} = \frac{\dot{Q}_{pulse} \ \Delta \theta_{pulse}}{\sigma \ \epsilon \ T_{melt}^{4} \ \Delta \theta_{1-2}} = \dot{Q}_{gen}_{avg} \left[\frac{1}{\sigma \ \epsilon \ T_{melt}^{4}} \right]$$

Notice that this radiator is sized for the average power being dissipated by the component. A thermal control system utilizing only radiation to control the component temperature (no PCM involved) would require a radiator sized for \dot{Q}_{pulse} , making such a radiator larger in area by the ratio $\dot{Q}_{pulse}/\dot{Q}_{avg}$. This shows one of the advantages of a PCM system. In Fig. 8-3, the total energy stored in the PCM system is shown as a function of time. To store and release energy as heat-of-fusion energy without appreciable sensible heat storage and release, the quantity of PCM must be the following:

 $m_{PCM} = \frac{E_{max}}{h_f}$ (neglecting sensible heat storage)

where E_{max} is that shown in Fig. 8-3.

The simple thermodynamic considerations described above have accomplished three objectives: (1) the definition of the energy storage requirements of the PCM, (2) the determination of the required mass of PCM, and (3) the determination of the radiator size. In the next section, the actual mechanisms of energy transfer are discussed.

8.3 HEAT TRANSFER CONSIDERATIONS

Although the thermodynamic considerations are simple and straightforward, the heat transfer problems are perhaps the largest obstacles to be overcome in the design of PCM systems. As a general rule, the materials with relatively large heats of fusion have relatively low thermal conductivities. Therefore, for reasonable heat fluxes, a very steep temperature gradient is required to transfer the heat from component to PCM. This steep temperature gradient can result in a large temperature excursion of the component during the melting process.



Fig. 8-3 - Total Energy in PCM

Returning to the PCM/radiator example discussed previously, the heat fluxes at the cold plate and radiator can be used to determine the temperature distribution within the package as a function of time. An assumption that will be used in determining the temperature distributions is that a linear quasisteady state temperature distribution will be achieved quickly compared to the time required for the liquid/solid interface to move an appreciable distance. This assumption has been confirmed by computer thermal analysis conducted during this study. Deviations from this assumption would result in improved package performance if they did occur. This assumption means that the temperature distributions throughout the package can be assumed to be linear whenever constant value heat fluxes are being applied. The transient period can be neglected principally because C_p/h_f is such a small ratio that the transient period is negligible compared to the time required for appreciable interface movement.

At the point during the cycle (Fig. 8-3) at which total solidification occurs, the temperature distribution should be as shown in Fig. 8-4.



Fig. 8-4 - Temperature Distribution at Total Solidification

The heat has been removed from the radiator by radiation. The radiator temperature, in absolute degrees, is approximately equal to the PCM melt temperature. Therefore $\dot{Q}_{rad} \approx \sigma A_{rad} \epsilon T_{melt}^4 = const.$ The heat being radiated away at a constant rate is being supplied at a constant rate to the radiator by conduction. Therefore the slope of the temperature distribution at the radiator (and throughout the solid phase) must equal:

$$\left(\frac{\partial T}{\partial X}\right)_{s} = \frac{\sigma A_{rad} \epsilon T_{melt}^{4}}{k_{s} A_{cp}}$$

This slope has been constant throughout the solidification process and has been essentially linear throughout the solid phase during the entire process.

If properly designed, the component heat pulse should begin just as the solid boundary reaches the cold plate.

In Fig. 8-5, the temperature distribution is shown for the PCM after approximately 50% of the PCM has melted.



Fig. 8-5 - Temperature Distribution at 50% Melt

The slope of the solid temperature distribution remains the same as cited previously; however, the liquid phase now has a linear temperature distribution with the slope,

$$\left(\frac{\partial T}{\partial X}\right)_{\ell} = \frac{\dot{Q}_{pulse}}{k_{\ell} A_{cp}}$$

The rate of melting is easily calculated as

$$\dot{m} = \frac{Q_{pulse} - \dot{Q}_{rad}}{h_f}$$

Upon melt completion, the distribution will assume the shape shown in Fig. 8-6.



Fig. 8-6 - Temperature Distribution at Total Melt

The slope is still the $\left(\frac{\partial T}{\partial X}\right)_{\ell}$ cited previously.

Because the liquid phase thickness is maximum at total melt, the component temperature will be at its maximum value at this point, namely,

$$T_{comp_{max}} = T_{melt} + (t) \left(\frac{\partial T}{\partial X}\right)_{\ell}$$

If the system is optimally designed, the component heat generation will cease just as the liquid boundary reaches the radiator. Freezing will begin at the radiator surface and the freeze boundary will move toward the cold plate.

After 50% of the PCM has frozen, the temperature distribution will assume the shape shown in Fig. 8-7.



Fig. 8-7 - Temperature Distribution at 50% Solidification

The liquid will all be near the melt temperature and the solid will have the slope $\left(\frac{\partial T}{\partial X}\right)_{a}$ described earlier.

After the solidification has completed, the distribution will return to that given in Fig. 8-4. The cycle will then repeat itself.

Of primary importance to the design engineer is the maximum temperature the component will reach during the cycle. Recalling the relation developed previously,

$$T_{comp_{max}} = T_{melt} + (t) \left(\frac{\partial T}{\partial X}\right)_{\ell}$$
,

where

$$\left(\frac{\partial T}{\partial X}\right)_{\ell} = \frac{Q_{\text{pulse}}}{k_{\ell} A_{\text{cp}}}$$

Substitution yields:

$$T_{comp_{max}} = T_{melt} + \frac{Q_{pulse} t}{k_{l} A_{cp}}$$
.

If the component is to operate properly, this T_{comp}_{max} must be less than the maximum operational temperature of the component. However, if the best PCM for this operational temperature range has a relatively low thermal conductivity (as is usually the case), the following design barrier presents itself. From the thermodynamic discussions presented earlier,

$$m_{PCM} = \frac{E_{max}}{h_f} = \rho_{PCM} A_{cp} t$$

Solving for t yields:

$$t = \frac{E_{max}}{h_f^{\rho} PCM c_p}$$

Substituting for t in our relation for T yields:

$$T_{comp_{max}} = T_{melt} + \frac{\dot{Q}_{pulse} E_{max}}{k_l A_{cp}^2 h_f \rho_{PCM}}.$$

For a given application and given PCM for the desired temperature range, T_{melt} , \dot{Q}_{pulse} , E_{max} , k_{f} , A_{cp} , h_{f} , ρ_{PCM} are all fixed quantities. Therefore, T_{comp}_{max} is fixed and, if it exceeds the maximum operational temperature of the component, an apparent roadblock is presented to the designer. High-conductivity filler materials allow the designer to hurdle the barrier. They are discussed in the next subsection.

8.4 COMBINED THERMODYNAMIC/HEAT TRANSFER RELATIONS AND THE FUNCTION OF FILLERS

When the component temperature rise for a particular application exceeds the maximum operational temperature of the component, filler materials must be integrated into the PCM package to improve the thermal conductivity of the PCM. Different types of filler materials are described in detail in Section 6. The function of filler materials is to provide low thermal-resistance paths through the PCM, which raises the equivalent thermal conductivity of the PCM, and reduces the temperature gradient necessary to dissipate the imposed cold-plate heat load. The reduction in temperature gradient reduces the temperature excursion of the component.

The remainder of this subsection is devoted to the development of the combined thermodynamic/heat transfer relations for a PCM package withfiller materials uniformly distributed within. Two additional assumptions are made in the development of the relations: (1) Contact resistance between the filler material and the cold plate is assumed negligible, and (2) Three-dimensional heat transfer effects are neglected, based on the assumption that the filler materials are so closely spaced that these effects are negligible. The errors introduced by these assumptions are discussed later.

Five equations in five unknowns can be derived for the system in question (Fig. 8-8).



Fig. 8-8 - PCM Package with Filler

8.4.1 Conservation of Energy

After the maximum energy that must be stored by the PCM package, E_{max} , is determined, the following heat balance will hold.

$$E_{\max} = \rho_{PCM} A_{PCM} t h_{f} + \left[\rho_{F} A_{F} C_{p_{F}} + \rho_{PCM} A_{PCM} C_{p_{PCM}} \right] \frac{t}{2} \left(T_{comp_{max}} - T_{melt} \right). (1)$$

(Datum: E = 0 when filler and PCM are at T_{melt} throughout, and PCM is solid throughout)

This equation treats both the energy stored through latent heat of fusion and sensible heat stored within the liquid PCM and the filler material:

8.4.2 Temperature Range Constraint

$$\dot{Q}_{\text{pulse}} = \frac{k_{T} A_{T} \left(T_{\text{comp}} - T_{\text{melt}}\right)}{t} .$$
 (2)

1

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The equation establishes a relation between the total conductivity, area, thickness, and temperature excursion $(T_{comp_{max}} - T_{melt})$.

8.4.3 Additive Conductances Relation

For parallel conductances, the total equivalent conductance can be found from the following equation:

This relation neglects three-dimensional effects and contact resistances. The errors imposed by these neglections are discussed later.

8.4.4 Conservation of Mass

The design engineer will want to know the weight of the PCM, container, and filler. The mass balance shown on the next page will hold.

$$W_{T} = \left(\rho_{PCM}A_{PCM} + \rho_{F}A_{F}\right) t + \rho_{C}\left[2A_{T} + 4\sqrt{A_{T}} t\right] t_{C}.$$
 (4)

The radiator weight is neglected for two reasons: (1) the outer surface of the container could be coated to serve as a radiator, and (2) another method of heat removal might be used for other applications.

8.4.5 Additive Area Relation

The total area is the sum of the cross sectional areas of the PCM and filler. Thus,

$$A_{PCM} + A_{F} = A_{T} \quad . \tag{5}$$

For a given application, PCM, filler material, and container material, these simultaneous equations (1 through 5) can be solved to yield W_T , t, k_T , ^{A}PCM , and $^{\Delta}T_{excursion} = \begin{pmatrix} T_{comp_{max}} - T_{melt} \end{pmatrix}$ as functions of filler area, ^{A}F . A computer program was coded under this contract which solves the five equations and yields the parametric data discussed above. To obtain a quantitative idea of the functional relationships between the variables described above, a parametric study was conducted using aluminum as the filler and container material, using different power and energy requirements, using a cold plate area of 0.093 m² (1 ft²), and using a fictitious PCM which has typical properties of a prime candidate, as described in the table below.

FICTITIOUS PCM PROPERTIES		
Density	^р РСМ	$\frac{1602 \text{ kg/m}^3}{(100 \text{ lb}_m/\text{ft}^3)}$
Thermal Conductivity	k PCM	0.519 W/m- [°] K (0.3 Btu/hr-ft- [°] F)
Specific Heat	с _р рсм	1673.6 J/kg - ^o K (0.4 Btu/lb _m - ^o F)
Heat of Fusion	h _f	232,400 J/kg (100 Btu/lb _m)

The results of the parametric study are presented in Figs. 8-9 through 8-17 for different power and energy requirements.

The curves illustrate several interesting facts (Fig. 8-9). The intersections of the three curves with the y-axis represent the weight, thickness, and temperature excursion for a PCM package without filler. The thickness and weight are least for this condition, and addition of filler causes a monatonic increase in both quantities. However, the temperature excursion is highest at this condition, and decreases drastically with small additions of filler until a minimum point is reached around 50% filler.* Similarly, the intersections of the three curves with the $A_F/A_{tot} = 1.0$ vertical line represent the weight, thickness, and temperature excursion for a solid aluminum heat sink. At this condition, the weight and thickness reach their maximum values, showing the inferiority of a heat sink compared to a PCM package.

Curves of this type can easily be generated for a particular application, PCM, container, filler, and cold plate area. Such curves can then be used in the following manner by the designer. The designer will know the maximum temperature excursion his component can sustain. By going to the curve for temperature excursion, he can find the minimum filler area required to maintain the excursion below the maximum. From the other curves, the required minimum weight and thickness can be obtained. If the weight represents a savings over other thermal control techniques, more sophisticated analytical

^{*} Note that the temperature excursion curve in each of the Figs. 8-9 through 8-17 reaches a minimum value at $A_F = 0.5 A_T$. This will occur mathematically whenever the sensible heat storage of the package and the thermal conductivity of the PCM have negligible effects upon total energy storage and total heat transfer, respectively. Since the fictitious problem under consideration meets each of these criteria, the minimum values occur at $A_F = 0.5 A_T$. For most applications, the minimum temperature will occur near 0.5 A_T for the same reason. However, for applications in which sensible heat storage and/or PCM thermal conductivity become significant, the minimum value will not occur at 0.5 A_T .

and experimental design studies should be considered. If the weight or thickness is not competitive with other thermal control techniques, the PCM technique can be eliminated from further consideration.

The nine sets of curves in Figs. 8-9 through 8-17 show the effect of varying the heat rate and energy requirements parametrically. The computer code which can be used to obtain such curves for other applications is given in Section 11. It must be remembered that these data are based on a onedimensional idealization of the problem and, as such, are optimistic. However, nowhere in the literature was there found either data or methods for obtaining data which would give parametric estimates of thickness, weight, and temperature excursion for a general PCM application.

8.5 CONTACT RESISTANCE AND THREE-DIMENSIONAL EFFECTS

The errors introduced by contact resistance and three-dimensional conduction effects were neglected in the preceding analysis. These effects can be significant as the following discussion indicates.

Consider a filler material of aluminum honeycomb in a container 1 cm thick. The thermal conductivity of the PCM is so much less than that of aluminum that the total equivalent conductance through the PCM/honeycomb composite is approximately $k_{A\ell} A_{A\ell} / t$. If a relatively high conductivity metal-filled adhesive is used to bond the honeycomb to the cold plate, the thickness of adhesive between the honeycomb and cold plate will represent a thermal resistance between the honeycomb and cold plate. The resistance of the adhesive will be $t_{adh}/k_{adh} A_{adh} \approx t_{adh}/k_{adh} A_{A\ell}$. The total resistance through the package now becomes the sum of the two series resistances, namely

$$R_{eq} = \left(\frac{t_{adh}}{k_{adh}} + \frac{t}{k_{A\ell}}\right) = \frac{1}{A_{A\ell}}$$

Since k_{adh} will at best be only a few percent of $k_{A\ell'}$ perhaps 3%, an adhesive thickness of 3% t or 0.03 (lcm) = 0.3 mm will cause the resistance R_{eq} to be double the value obtained by neglecting the adhesive resistance. Since the heat entering the package must pass through both resistances, $\dot{Q} = \Delta T/R_{eq}$, doubling the R_{eq} will double the ΔT through the package, and consequently the temperature excursion of the component will be doubled. This effect is shown schematically in Fig. 8-18.

Besides the resistance due to the adhesive layer, there are the additional contact resistances between the adhesive and honeycomb and between the adhesive and cold plate. Also, bubbles can form in the adhesive upon curing, reducing the effective cross-sectional area of the heat path through the adhesive, and thereby increasing the resistance. All of the effects can obviously cause the component temperature to rise appreciably above the value predicted by the idealized one-dimensional analysis presented earlier. These effects indicate the need for a metal-to-metal contact which could be accomplished by some form of welding, soldering, or integral fabrication of filler and cold plate.

The effect of three-dimensional heat transfer upon temperature excursion was analyzed via computer thermal analysis. The results indicated that threedimensional conduction effects can cause the temperature excursion of the component to increase above the value predicted by the one-dimensional idealized predictions. However, the extensive analyses required to make general conclusions regarding three-dimensional conduction effects were beyond the scope of this study.



Fig. 8-9(a) - PCM Package Weight, Thickness, and Temperature Excursion as Functions of Filler Area $(E_1, Q_1, SI \text{ Units})$



Fig. 8-9(b) - PCM Package Weight, Thickness, and Temperature Excursion as Functions of Filler Area (E_1, Q_1 , English Units)



Fig. 8-10(a) - PCM Package Weight, Thickness, and Temperature Excursion as Functions of Filler Area (E_1, Q_2 , SI Units)



Fig. 8-10(b) - PCM Package Weight, Thickness, and Temperature Excursion as Functions of Filler Area (E₁,Q₂, English Units)



Fig. 8-11(a) - PCM Package Weight, Thickness, and Temperature Excursion as Functions of Filler Area (E₁, Q₃, SI Units)



Fig. 8-11(b) - PCM Package Weight, Thickness, and Temperature Excursion as Functions of Filler Area (E₁,Q₃, English Units)



Fig. 8-12(a) - PCM Package Weight, Thickness, and Temperature Excursion as Functions of Filler Area (E₂, Q₁, SI Units)



Fig. 8-12(b) - PCM Package Weight, Thickness, and Temperature Excursion as Functions of Filler Area (E₂,Q₁, English Units)



Fig. 8-13(a) - PCM Package Weight, Thickness, and Temperature Excursion as Functions of Filler Area (E₂, Q₂, SI Units)



Fig. 8-13(b) - PCM Package Weight, Thickness and Temperature Excursion as Functions of Filler Area (E₂, Q₂, English Units)



Fig. 8-14(a) - PCM Package Weight, Thickness, and Temperature Excursion as Functions of Filler Area (E_2, Q_3 , SI Units)



Fig. 8-14(b) - PCM Package Weight, Thickness, and Temperature Excursion as Functions of Filler Area (E₂, Q₃, English Units)



Fig. 8-15(a) - PCM Package Weight, Thickness, and Temperature Excursion as Functions of Filler Area (E₃, Q₁, SI Units)



Fig. 8-15(b) - PCM Package Weight, Thickness, and Temperature Excursion as Functions of Filler Area (E₃, Q₁, English Units)



Fig. 8-16(a) - PCM Package Weight, Thickness, and Temperature Excursion as Functions of Filler Area (E₃, Q₂, SI Units)



Fig. 8-16(b) - PCM Package Weight, Thickness, and Temperature Excursion as Functions of Filler Area (E₃, Q₂, English Units)



Fig. 8-17(a) - PCM Package Weight, Thickness, and Temperature Excursion as Functions of Filler Area (E₃, Q₃, SI Units)


Fig. 8-17(b) - PCM Package Weight, Thickness, and Temperature Excursion as Functions of Filler Area (E₃, Q₃, English Units)



Fig. 8-18 - Effect of a Small Adhesive Thermal Resistance

8.6 CONTAINMENT CONSIDERATIONS

The design of the container for a PCM package must be influenced by both structural and thermal considerations. Structurally, the package must be leak-proof for the liquid PCM and must be able to withstand all imposed static and dynamic loads. Thermally, the container must be integrated into the thermal protection package without degrading the system performance.

A major problem in the design of PCM containers is the accommodation of the change in volume upon melting and freezing of the contents. Several methods have been considered to deal with the phase transition volume change. One method is shown in Fig. 8-19. An elastic bellows between the cold plate and the opposite wall are prestressed in tension during the fill process. After filling is complete, the bellows exert a compressive load on the liquid PCM. When solidification occurs, the bellows further contract and still maintain a compressive load on the PCM.



Fig. 8-19 - Elastic Bellows Container

A bellows container using stainless steel as the bellows material was built and tested (Ref. 1). No filler material was used in the bellows container, but there is no apparent reason why a filler could not be attached to the cold plate in such a container. The major advantage of a bellows-type container is that no void or gas volume must be left in the container to provide room for PCM expansion upon melting. Since void or gas volume could cause a decrease in heat transfer within the container, the bellows container does have a distinct thermal advantage over other techniques. However, the nonrigidity of the container and the cyclical change in loading could cause structural or leak problems. This should be considered by the design engineer.

The more commonly used container is the rigid container which has void or gas volume for expansion of the PCM during melting. Rigid containers are currently planned for use on the Lunar Roving Vehicle and on the Skylab Cluster. Such a container is shown in Fig. 8-20.



Fig. 8-20 - Rigid PCM Container

The void region is shown at the top where it would be under terrestrial gravitation, but in free-fall environment this void volume will occupy different regions of the container as discussed in Section 10.

A significant problem in designing the rigid container is the sizing of the void volume. If the container were totally vacuum tight and evacuated prior to flight, theoretically the void volume required would merely be the volume change upon expansion of the PCM, namely,

Void Volume =
$$V_L - V_S = m_{PCM} \left(\frac{1}{\rho_L} - \frac{1}{\rho_S} \right)$$
.

However, gas will be in the void volume while the solid phase exists in the container, due to equilibrium vapor pressure formation above the solid phase and prelaunch molecular diffusion through the minute holes that will exist in joints and seams of the container. Regardless of the pressure of this gas above the solid phase, when complete liquefaction occurs, a large pressure will be set up within the container since there is no volume for the gas phase to occupy. Therefore, sufficient volume must be added to the container to maintain trapped gases at a reasonable pressure.

Some designers (Ref. 2) of rigid containers have taken the most conservative view that the pressure above the solid phase has reached atmospheric pressure due to leaks before launch. With the aid of Fig. 8-21, one can see from the ideal gas law at constant temperature that the relation between maximum pressure and total volume is

$$P_{max} = P_{atm} \left(\frac{V_{T} - V_{S}}{V_{T} - V_{L}} \right) = \left[\frac{V_{T} - \frac{m_{PCM}}{\rho_{S}}}{V_{T} - \frac{m_{PCM}}{\rho_{L}}} \right] \left(P_{atm} \right).$$





Fig. 8-21 - Volume Relationships for Rigid Containers

The container should therefore be designed to withstand the P_{max} structural loading associated with the final choice of V_T . If the PCM liquid will rise appreciably above the melt point at any time during planned operation, the thermal expansion of the liquid should also be considered in determining the total container volume.

The effects of the void or gas volumes within the container on heat transfer are hard to estimate quantitatively. However, it is apparent that such void spaces will decrease the conduction heat transfer below that for the idealized void-free models currently assumed for analysis, especially if voids were to form between the cold plate and PCM or between the filler and PCM. In general, the degradation due to voids should be least for materials with high wetting tendencies; i.e., those which cling to the solid metallic surfaces within the package. It is apparent from the previous discussion that materials with very small percentage volume changes during phase transition will cause the fewest thermal and structural problems to the designer engineer.

The bonding between any filler material present and the cold plate portion of the container is a problem area previously discussed. To prevent thermal resistance at the bond, it is recommended that metal-to-metal bonding be used. Soldering and brazing techniques can be used for a particular application if welding is not possible.

Obviously, the container material must not be incompatible with the PCM. The in-depth pages in Section 5 describe compatibility problems, if any, between the prime PCM candidate and metals which might be considered for container materials.

A slightly different packaging technique can be used to improve thermal performance of PCM systems which are to be used for one-duty-cycle components. Such components generate high amounts of heat for a period of time and then cease operation, never again to be activated. Such a component can be placed in thermal contact with a PCM package to keep it relatively isothermal for its short lifetime. The PCM package essentially absorbs, via phase change, all the energy generated by the component, and refreezing after the cycle is unnecessary. The container technique shown in Fig. 8-22 could be used for such an application.



Fig. 8-22 - One-Duty-Cycle PCM Container

The spring initially could be compressed so that throughout the melt process it would hold the solid firmly in contact with the cold plate. The liquid would pass to the bottom and the cold plate would remain virtually isothermal at the melt temperature without the addition of filler materials to the package. In Ref. 1, a similar technique was presented in which a pressurized bladder was used to perform the same function as the spring.

8.7 PCM ENGINEERING FORMALISM

To proceed quickly and efficiently in the design of a PCM thermal protection system, the designer should follow a formalism similar to the one outlined below.

- 1. Choose from Tables 5-1 through 5-7, in Section 5, the PCM with best properties, as described previously, which matches the temperature range of the component.
- 2. Perform thermodynamic analysis to: define thermal flux and storage requirements; determine most efficient heat dump for cyclical components; size radiators, thermal straps, heat pipes or other heat dump methods; and determine initial estimate of PCM quantity required.
- 3. Perform combined thermodynamic/heat transfer analysis to obtain weight, thickness, and temperature excursion as functions of filler amount. If the one-dimensional idealized model used in earlier analyses is sufficiently accurate, the computer code in Section 11 may be used to accomplish this task. Pick the minimum weight and thickness which will meet temperature excursion requirements.
- 4. Select a compatible container material and design container according to guidelines given earlier.
- 5. Conduct necessary thermal analysis to verify the performance of the PCM system.
- 6. Conduct necessary experimentation to prove performance and reliability of PCM system.

Reference - Section 8

- 1. Bentilla, E. W., et al, "Research and Development Study on Thermal Control by Use of Fusible Materials," Final Report of Contract NAS8-11163, Northrop Space Laboratories, NSL 65-16-1, April 1966, Hawthorne, Calif.
- 2. Humphries, W. R., Communication, NASA-MSFC, S&E-ASTN-PLA, March 1971.

Section 9 METHODS FOR OBTAINING PROPERTY DATA

Methods for obtaining physical properties vary widely. Among the factors to be considered are cost, accuracy, time, and suitability. Each method has its own particular set of features and most suitable applications.

Property data are abundant for materials such as heat transfer fluids which are used widely for industrial purposes. Studies for the most part have been made of materials in demand, leaving incomplete data on those not yet in demand. Most of the prime PCMs fall into the latter category. As demand for PCM properties increases, more property data will become available. Until such data are available, a PCM designer may have to test the PCMs of interest.

Some properties can be measured directly, such as melting point, density, surface tension, and viscosity. Simple methods are available for such properties, or methods for measuring them are easily devised. Properties such as heat capacity and latent heat are not measured directly, but are obtained by means of a transducer or by computations based on measurements of other variables. Specialized equipment is usually employed for such studies as heat capacity versus temperature.

The purpose of this section is to suggest some rapid methods for obtaining a particular property. References are listed for detailed information. Accuracy desired, applications, and cost are factors to be considered when choosing a method. Extreme accuracy may not be required or the variation of a property with temperature may be of interest only in a limited temperature range. Thus elaborate, complete studies may not be necessary.

9.1 MELTING AND FREEZING TEMPERATURES

The melting temperature is the temperature at which a solid material melts. Superheating a solid is rarely encountered, so, for all practical purposes, it is negligible. Melting points are generally determined by observing a small amount of the solid as the temperature is gradually elevated. The solid is usually placed in a small glass capillary tube which is then placed in a gradually heated oil bath. The temperature at which the solid melts is the melting temperature.

The melting point may not be the same as the freezing point. For many pure materials they are approximately the same. Differences arise because of supercooling or impurities effects. Melting points are generally reproducible, but freezing points are not necessarily reproducible. Freezing points may be easily determined by cooling the PCM with a temperature-measuring device (such as a thermometer or thermocouple) placed in the bulk of the PCM. When both solid and liquid are present and the temperature attains a constant value, this point is taken as the freezing temperature. The reader is referred to Ref. 1 for a review of the types of freezing behavior which may be encountered.

9.2 LATENT HEAT OF FUSION

The determination of heat of fusion is neither simple nor direct. It requires a temperature control system to bring the test material to its melting temperature. A method for measuring the amount of heat absorbed at this temperature is required and is usually complicated. Latent heat is derived from calculations of other variables or from specialized equipment.

A simple, inexpensive method consists of placing the test sample in an insulated refractory container with differential thermocouple junctions inside and outside the container. The container with a sample is placed in a furnace whose heating rate is controlled so that a constant temperature gradient is maintained across the container walls. The heat flow to the sample is

therefore almost constant, and the heat received by the sample in a given time is easily determined. The time the sample takes to go through a given temperature interval is proportional to the heat gained and is a measure of the heat capacity. The time of a temperature arrest is directly proportional to the latent heat (Ref. 2).

Heat flow to the test material depends on the constants of the container. For improved accuracy, the container should be calibrated with a standard in the temperature range of interest. The materials tested by this method all had considerably higher thermal conductivities than the container. The heat flow to the sample should not equal or exceed the rate at which it can be conducted through the sample. Samples with low thermal conductivity can present difficulties if this property is overlooked.

The Differential Scanning Calorimeter (DSC) is undoubtedly the best instrument for measuring heat of fusion. It is also useful for measuring specific heat (Ref. 3). It is accurate and makes use of the differential method against a known standard. Usually a number of heating rates are offered, and runs can be made in hermetically sealed pans with a choice of atmosphere. Some DSC's have the additional feature of low temperature auxiliary equipment using liquid nitrogen. Features of the DSC are:

- 1. Wide temperature range of operation (cryogenic to fairly high temperatures)
- 2. High accuracy
- 3. Choice of atmosphere (vacuum, nitrogen, oxygen, etc.)
- 4. Capability of measuring latent heat and specific heat
- 5. Inexpensive to operate
- 6. High initial cost.

9.3 HEAT CAPACITY

No simple, direct method exists for measuring heat capacity. Measurements are obtained by calculations based on measurements of other properties, or with sophisticated equipment. The DSC is a specialized instrument suitable for obtaining heat capacities. It subjects the test sample to a linear temperature program with the heat flow rate to the sample continuously measured (Ref. 3). This heat flow rate is proportional to the instantaneous specific heat.

The heat capacity of a substance depends on the variables that contribute to the thermodynamic state: temperature, pressure, electric and magnetic fields. Heat capacity increases with temperature. It is different for a material in the liquid phase and for the same material in the solid phase. Heat capacities can be calculated for solids and gases, but calculation of the heat capacity of a liquid is more complicated. Details of methods for determining heat capacity are given in the following:

Reference 2: a differential laboratory method
Reference 3: Differential Scanning Calorimeter method
Reference 4: heat capacities of liquids
Reference 5: computer method for four paraffins.

9.4 THERMAL DIFFUSIVITY

The thermal diffusivity is the time rate of temperature movement through a material. A large value indicates the ability of the material to equalize temperature differences within itself. The metallic PCMs have large values of thermal diffusivity while the non-metallic PCMs have low values. The paraffin PCMs have extremely low values of thermal diffusivity, so temperature gradients are not easily dissipated in paraffins.

The thermal diffusivity (α) of a PCM is determined by:

- Applying a constant heating rate (B) to one plate of a test cell containing PCM.
- Measuring the constant temperature difference (ΔT) between the heated and unheated plates of the test cell of known height (h).

The equation relating these quantities is:

$$\alpha = \frac{Bh^2}{2\Delta T} \cdot$$

A test cell can be made from a section of Plexiglass tubing with the open ends covered by aluminum foil. A small inlet should be drilled into the cell so that the cell can be filled with PCM. The PCM can be injected into the test cell with a hypodermic syringe. The cell should be well insulated to minimize heat leakage. A constant heating rate is applied to the top plate of the cell to avoid natural convection. A linear temperature programmer with a control thermocouple will provide a constant heating rate. Reference 6 describes in detail a simple method for measuring thermal diffusivity.

References - Section 9

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- O'Neill, M.J., "Measurements of Specific Heat Functions by Differential Scanning Calorimetry," <u>Analytical Chemistry</u>, Vol. 38, No. 10, September 1966.
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- 5. Bentilla, E.W., K.F. Sterrett, and L.E. Karre, Final Report for Contract NAS8-11163, Northrop Space Laboratories, Hawthorne, Calif., April 1966.
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Section 10 PCM IN THE SPACECRAFT ENVIRONMENT

Space conditions have been studied carefully and are still under investigation. Since this subject is so extensive and well documented, only those factors possibly influencing PCM performance are discussed.

Vacuum, radiation, magnetic fields, electric fields and zero-gravity are major factors influencing the design of spacecraft (Ref. 1). The question of the importance of these factors on PCM performance has not yet been studied. The application of PCM technology to spacecraft is so new that information in the literature relating to space performance is almost absent. Future studies will give useful data, whereas the present state of the technology leaves the PCM designer with earthbound performance on which to base design parameters.

Some generalizations from known facts are necessary to ascertain which factors are important and which are negligible in space conditions. Therefore, a look into basic forces known to affect PCM performance seems desirable. From the studies in 1-g, predictions have been made about certain aspects of the behavior of materials in zero-g. Until specific information is available, the designer is called upon to evaluate available facts.

10.1 FORCES AND CONVECTION

Gravity and intermolecular forces are the two main types of forces affecting the convective behavior of materials, and they have been studied extensively in 1-g. Under earthbound conditions the comparatively small effects of intermolecular forces (exhibited as surface-tension forces) are barely noticeable unless a very small amount of fluid is being considered. Typical effects

of gravity body forces are the shaping of liquids in containers, the rise of vapor bubbles in liquids, convection currents, and hydrostatic pressure. Although the surface-tension forces are small in comparison with gravity forces at 1-g, the effects are evident in capillary rise or depression, and the meniscus of liquids in contact with solids.

When a liquid is free from gravity effects, the intermolecular or surface-tension forces play a larger role in the heat transfer mechanics. Research concerning the behavior of fluids in zero-g has therefore involved the study of surface tension phenomena and their effects on fluid behavior. A convective motion driven by surface tension force has been suggested as a possibility in zero-g (Ref. 2). The presence of such a convective motion would conceivably affect the freezing-melting behavior of a PCM.

The question of how magnetic and electric forces affect melting and freezing in space remains to be answered. The application of extreme magnetic fields up to 18,000 gauss (1.8 tesla) produced no effect on the intermolecular force of surface tension. From this and similar studies, it can be assumed that the magnitudes of magnetic and electrical fields likely to be encountered in the space environment are not strong enough to influence the thermodynamic parameters of phase change to a significant degree.

Gravitational forces between molecules are comparatively weak relative to intermolecular or interatomic forces. For example, the gravitational energy between two CO₂ molecules is 1.1×10^{-44} erg, whereas the intermolecular attraction is 1.4×10^{-14} erg (Ref. 2). The thermodynamic parameter of fusion is directly related to intermolecular forces. The rate of freezing or melting is mainly determined by the difference in the equilibrium temperature and the interface temperature of the solid and liquid. With the same temperature gradient, the rate of freezing or melting should be the same in a nongravity field as in a gravity field. Although phase-change kinetics are not influenced directly by gravity fields, they are influenced indirectly through convection. The effects of convection possible in zero-g, however, are as yet not well known.

10.1.1 Bouyancy Convection

An analysis of cellular convective motion in a fluid layer heated from below was made by Rayleigh as the driving force for the convection. Rayleigh's theory considers buoyancy forces caused by density gradients in a gravity field. The Rayleigh number is the ratio of gravity force to viscous force, and the onset of convective motion occurs when a critical value R_c is reached. At this point the buoyancy force is large enough to overcome the viscous force. The Rayleigh number is given by:*

$$R = \frac{g\beta}{\nu} \frac{dT}{dy} d^4$$

g = acceleration due to gravity

 β = coefficient of expansion of the liquid

 $\frac{dT}{dy}$ = the vertical temperature gradient applied at the lower surface

- d = thickness of fluid
- ν = kinematic viscosity

 α = thermal diffusivity.

The boundary conditions cause variations in the Rayleigh number. The critical Rayleigh number, R_c , takes a value of about 600 for two free boundary surfaces, about 1100 for one rigid and one free boundary surface, and about 1700 for two rigid boundary surfaces (Ref. 2). When heat is produced internally in a fluid layer with one rigid wall below and a free surface above, the R_c takes a value of about 2770.

In all liquids instability sets in at the Rayleigh number 1700 ± 50 . For R less than 1700, no natural convection occurs (Ref. 3).

^{*} A sample calculation of a Rayleigh number is given in Appendix B.

For most liquids a critical thickness d_c of the fluid layer for instability is about 1 centimeter. For thicknesses less than d_c , surface tension should be more effective in producing instability than buoyancy (Section 10.1.2).

The criterion for instability under maximum reinforcement of the two forces, buoyancy and surface tension is

$$\frac{R}{R_c} + \frac{B}{B_c} \ge 1$$
 (Ref. 4)

where B_c is an expression for surface tension convection, described and defined in the following section. In the absence of gravity, R = 0 and the onset of cellular motion occurs as B exceeds B_c .

10.1.2 Surface Tension Convection

Fluid flow caused by surface tension gradients is called the Marangoni effect. If the free surface of a liquid experiences a temperature gradient, a surface tension gradient will result, since surface tension varies with the temperature (Ref. 5). The higher the temperature of a liquid, the lower the surface tension becomes. The liquid will flow along the free surface, from a region of low surface tension to one of high surface tension. This corresponds to flow from hot regions to cold regions. The liquid flow is fastest near the surface, and the depth of the turbulence depends on several hydrodynamic parameters.

The occurrence of "tear drops" in a wine glass is a common illustration of the Marangoni effect. The layer of liquid on the wetted glass wall has a higher surface tension than the bulk of liquid in the glass, due to the evaporation of alcohol and subsequent change of temperature and composition. As a result, liquid on the glass walls draws up more liquid from the bulk until a "tear" is formed. When the tear becomes large, it falls back into the liquid.

Studies are presently in progress to study this type of convection so that its importance can be ascertained, since any kind of convection affects the freezing-melting rate. Marangoni convection force can be evaluated from the Marangoni number, discussed in this section.

The presence of any free surface (such as voids or bubbles) in the PCM liquid phase is likely to give rise to Marangoni convection.

A Marangoni number has been given as 80 for the critical value ($B_c = 80$) at which cellular flow will begin. The Marangoni number B^* expresses the ratio of surface tension to viscous force. It is defined by (Ref. 5):

$$B = \frac{\frac{d\sigma}{dT} \frac{dT}{dy} d^2}{\rho_{\nu} \alpha}$$

where

 $\frac{d\sigma}{dT}$ = rate of change of surface tension with temperature

 $\frac{dT}{dv}$ = vertical temperature gradient

d = thickness of a horizontal layer of liquid

 ρ = density

 ψ = kinematic viscosity

 α = thermal diffusivity.

10.1.3 Bubbles Formation and Material Expansion

Because the presence of bubbles in zero-g causes different effects than their presence in 1-g, they are worth serious consideration. Ordinarily, bubbles rise to the top of a system in one-g, and they can be dealt with in a predictable way. In zero-g, however, their presence can seriously interfere with PCM performance. They may be dispersed throughout the PCM or they may congregate in one place. In some instances they may be desirable; in

^{*}A sample calculation of a Marangoni number is given in Appendix B.

other cases they may cause system failure. It is desirable to be aware of their possible formation and either remove them or plan to use them in a predictable way.

The effect of bubbles on all aspects of PCM operation is extremely complex. Certain generalizations seem reasonable at the present state of PCM technology. It seems likely that bubbles will affect PCM operation in some of the following ways:

- 1. The thermal conductivity will be altered. A recent flight experiment was notably affected by the formation of a bubble in a liquid, next to a heater which was to warm the liquid.
- 2. Bubbles in the liquid phase will cause stirring actions. In a zero-g field, they would migrate to the hot side because of surface-tension or Marangoni flow.
- 3. Small bubbles in the solid phase can take up some of the volume shrinkage, and thereby avoid the formation of large cavities.

There are several types of bubbles likely to occur during PCM performance in zero-g: PCM vapor bubbles, cavities or voids from volume shrinkage, and gas bubbles. These bubbles can be formed in three general ways:

- 1. Volume shrinkage from solidification can cause cavities or voids in a rigid container.
- 2. Vapor bubbles of PCM can arise within a liquid which is overheated.
- 3. Dissolved gas forms bubbles when it is rejected like any other solute during solidification; it is liberated from entrapment in the solid during melting.

The fact that most liquids shrink on freezing means that a cavity or void will be formed unless the container is collapsible. Chalmers (Ref. 6) suggested several ways (shown on the following page) that a solid with void may look in a container.



Types a, b, and e would obviously interfere with heat transfer.

1

Accurate prediction of bubble formation would require detailed examination of inertial and surface forces acting on the bubble.

The most persistent type of bubbles in PCMs are dissolved gases (Ref. 2). During solidification, dissolved gases can be rejected just as any other solute at the solid-liquid interface. During the reverse process of melting, bubbles previously overgrown by solid can be liberated. In a 1-g field, buoyancy forces would tend to localize bubbles; the bubbles would be more likely to float to the top and coalesce. In a zero-g field, bubbles are more likely to be trapped in the frozen solid than in a 1-g field.

A large amount of dissolved gas can be avoided by PCM preparation. The PCM in liquid form can be boiled under reduced pressure. Another method would be to purge the liquid with a less soluble gas. For example, the bubbles that form when water is frozen are largely dissolved oxygen. Since nitrogen is far less soluble than oxygen, a purging with nitrogen decreases the bubble formation considerably (Ref. 2).

A method that might be useful in the separation of liquid and vapor makes use of the dependence of surface tension on temperature. A vapor bubble in a liquid with temperature gradients will be warmer at one pole of the bubble than at the other. The liquid at the warmer interface of the bubble, where the surface tension is lower, will flow to the colder region where the surface tension is higher. The net result of this is a movement of the vapor bubble from cold to warmer regions (Ref. 2). This effect is not noticeable

at 1-g due to strong buoyancy effects, but it may be useful in zero-g conditions. The bubbles tend to congregate at the warm surface, thus becoming separate from the liquid.

10.2 SOLIDIFICATION IN SPACE ENVIRONMENT

A knowledge of the effects of zero-g on solidification would be most desirable. Since the technology of thermal control with PCM is relatively new, there are many questions yet to be answered. The basic mechanism of dynamic nucleation in any environment has yet to be uncovered, since it has only recently been recognized as a separate problem. The simulation of possible effects to be studied in zero-g appears to be virtually impossible in the laboratory.

It is entirely possible that the absence of gravity will have no significant effect on solidification. This possibility is based upon the fact that the intermolecular forces which are the primary forces involved in crystal growth are far greater than gravitational forces. Thus the effect of zero gravity on solidification may be unimportant. Factors which must be taken into account in the event they do affect solidification in zero-g are the possible formation of a distorted solid-liquid interface, void spaces forming in the PCM, and the absence of gravity-driven convection (Ref. 6). Any distortion of the interface could affect the way solidification occurs. The absence of gravity-driven convection will undoubtedly affect the interfacial temperature and the total growth rate of crystals.

Nucleation under ordinary conditions is a very complex phenomenon. Theoretical studies have been concentrated on phase kinetics rather than on rates of heat transport. General statements on interface morphology for a range of materials cannot be made because work in this area has been so specialized. Since many of these effects cannot be satisfactorily evaluated in the laboratory, flight data would be most desirable.

10.3 PENETRATING RADIATION IN PCM TECHNOLOGY

Particle radiation produces damage to materials mainly by (1) production of displaced and excited electrons (ionization), (2) displacement of atoms by direct collision, and (3) production of thermal spikes (Ref. 7).

Ionization effects are not significant in metals. Fusion thermal spikes are important for materials containing atoms for high atomic number ("heavy" metals) which are irradiated with massive particles.

Photons likely to be encountered which can cause damage consist of the following (Ref. 8).

- 1. Those of energies above 10^5 eV can cause atomic displacements
- 2. Those of energies above 12 to 25 eV can cause ionization
- 3. Those of larger wavelengths can cause electronic excitation.

Transient effects from radiation are manifested only when the material is in the radiation field. They are not observable when the material is removed from the field. Temporary effects are predominantly electrical in nature, and persist only a matter of minutes or hours. The material spontaneously relaxes back to its original state in a short time. The most probable effect on the material is the nucleation of crystals in supercooled liquid or bubbles in superheated liquid (Ref. 2). These phenomena are observed in bubble chambers or Wilson cloud chambers. Only one study specifically deals with the transient effects of radiation on the crystallization process (Ref. 9). However the dosage rates used were γ -radiation far above any to be encountered in space.

Many of the damage effects from radiation are permanent in the effect on engineering properties. However, one of the great advantages of PCM thermal control devices is their self-annealing ability to both temporary and

permanent damage (Ref. 2). Many permanent effects are annealable when the temperature is raised. Damage which is not annealable is primarily encountered with organic materials in which chemical bonds are broken. Fission can be neglected because high atomic number materials are not contemplated for PCMs.

Radiation effects on PCM behavior are believed to be insignificant for periods of about a year (Ref. 2). A summary of the dose rates for various space radiations in different depths of material is given in Ref. 8. A summary of particle fluxes and energies in space environments is given in Ref. 10. The dose rates in various space environments and doses producing appreciable changes in various materials are summarized in Ref. 8.

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Section 11 PCM COMPUTER PROGRAMS

In the literature, several computer codes are described which deal with various aspects of the PCM thermal control problem. In this section, the function of each computer tool is briefly described and reference is provided for the design engineer who desires additional information or access to the code. Also presented in this section is the code used to obtain parametric data for PCM package thickness, weight, and temperature excursion based on the one-dimensional idealized model described in Section 8. This code was developed during this study.

In Ref. 1, a finite-node, one-dimensional component/PCM/radiator temperature distribution prediction technique is described. A Runge-Kutta solution of the nodal heat balance equations is used to predict numerically the temperature distribution as a function of time. The melt interface location is also predicted as a function of time.

In Ref. 2, a finite difference computer method is described for prediction of temperature distribution and solid/liquid interface location as a function of time during the solidification process. Temperature-dependent properties, liquid subcooling, and graphical output are significant features of this program. A temperature versus time forcing function can be applied at one face in the model, and the thermal response throughout the network is predicted.

In Ref. 3, a modified transient thermal analyzer program is described which utilizes the finite difference technique to obtain temperatures and meltfront location as a function of time. A subroutine which handles latent heat calculations is incorporated into the main program. The program was used to analyze one-dimensional adiabatic PCM systems and radiating two-dimensional fins with attached PCM. Additional discussion of this computational tool is

provided in Ref. 4. The main program used in the analysis was the Lockheed SHARE Program for an IBM 7090 digital system.

In Ref. 5, the Lockheed SHARE Program for the IBM 7094 digital computer was used to obtain a finite difference solution to the temperature versus time distribution within a PCM package. This program is a finite time step transient thermal analyzer which utilizes the familiar electrical analogy to represent the thermal network. Additional discussion of the program is provided in Ref. 6.

In Ref. 7, the solidification process was analyzed by using a finite element computer program in which derivatives were approximated by Taylor Series. The program was specifically written for the PCM solidification problem and compared favorably with experimental data.

In Ref. 8, the usual finite difference solution was coded into a computer program for use in analyzing thermal energy storage devices containing PCM. Orbit simulation with the resultant periodic heat absorption was used as the forcing function and temperature distribution and melt-front location were predicted versus time.

In Ref. 9, the component/PCM/radiator system was analyzed via analog computer simulation. A one-dimensional network was assumed and runs were made using an electrical analogous network. Details of the method were not given.

During the current study, a digital computer program was coded to predict the total package thickness, weight, and component temperature excursion for a PCM thermal control package as functions of filler amount and thermal loading. The parametric data obtained from this program are based on a one-dimensional idealization of the general PCM problem. The theory used in the program is discussed in detail in Section 8. The program is coded for use on the IBM 7094, but can easily be converted to Univac 1108. The data shown in Figs. 8-9 through 8-17 were generated in less than one minute on the 7094. A listing of the program is given in Table 11-1. In Table 11-2, an explanation of program variable names

is provided, as are the proper units for these variables in International Units and British Engineering Units. If either unit system is followed for input variables, the output variables will also follow the same system, although the Hollerith units in the titles and headings will always show only International Units.

Also during this study, a transient thermal analysis was conducted for an aluminum honeycomb/octadecane PCM system to determine threedimensional effects on system performance. The Lockheed-Huntsville Thermal Analyzer, a finite difference program, was used in this analysis. This is a Lockheed-Huntsville developed program which is easily modified to handle the PCM problem. The heat of fusion was treated as a spike in the specific heat versus temperature curve as shown below.



At the melt temperature, a spike of height C_{p_f} and width ΔT_f is used with $C_{p_f} \Delta T_f = \Delta H_f$. Therefore a pseudo-sensible heat storage simulates the heat of fusion storage of energy. The ΔT_f was chosen to be extremely small so that the thermal effects occurred very near the melt temperature. Such a treatment of the heat of fusion seems to be the most simple and straightforward since it precludes coding modifications. The results of the analyses obtained with the two Lockheed-Huntsville computer programs are discussed in detail in Section 8.

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Table 11-1
PCM PACKAGE DESIGN OPTIMIZATION PROGRAM
\$JOB H210-L5208 (LMSC) .911000.00.12.140CE
SEXECUTE IBJOB
\$1BJOB
SIRFTC MAIN
C PCM PACKAGE DESIGN OPTIMIZATION PROGRAMONE DIMENSIONAL IDEALIZED MOD
C ALL INPUT AND OUTPUT VARIABLES ARE IN STANDARD INTERNATIONAL UNITS
DOUBLE PRECISION KP,KF,KT,RHOP,CPP,HFP,RHOF,CPF,RHOC,EMAX,Q,DELT,
1AT, A, B, C, AF, AP, T, WTOT
C READ PCM, FILLER, AND CONTAINER PROPERTIES
READ (5,1) RHOP, KP, CPP, HFP, RHOF, KF, CPF, RHOC
1 FORMAT (8E10.5)
C READ PROBLEM RESTRAINTS
2 READ (5.3) EMAX. Q.AT
IF (FMAX.LT. (1.0) GO TO 13
3 FORMAT (3E10.5)
C WRITE PROBLEM SUMMARY AND HEADING
WRITE (6+4)
4 FORMAT (1H1+35X+12HINPUT VALUES)
WRITE (6.5) EMAX.Q.AT
5 FORMAT (1H0,5HEMAX=,E12,5,2X,6HJOULES,5X,2HQ=,E12,5,2X,5HWATTS,5X,
13HAT=+E12+5+2X+13HSQUARE METERS)
WRITE (6.6)
6 FORMAT (1H0+25X+44HPROPERTIES OF THE PCM+ FILLER+ AND CONTAINER)
WRITE (6,7) RHOP, KP, CPP, HFP, RHOF, CPF, RHOC, KF
7 FORMAT (1H0.5HRHOP=.E12.5.2X.10HKG/CUBIC M.5X.3HKP=.E12.5.2X. 8HW/
1M-DEGK, 5X, 4HCPP=, E12, 5, 2X, 13HJOULE/KG-DEGK, //, 1X, 4HHFP=, E12, 5, 2X,
28HJOULE/KG,5X,5HRHOF=,E12,5,2X,10HKG/CUBIC M,5X,4HCPF=,E12,5,2X,
313HJOULE/KG-DEGK .//.1X.5HRHOC=.E12.5.2X.11 HKG/SQUARE M, 5X, 3HKF =,
4F12.5.2X.8HW/M-DFGK)
WRITE (6+8)

Table 11-1 (Cont'd)

t	B FORMAT (1H0,45X,22HPARAMETRIC OUTPUT DATA)
	WRITE (6,9)
¢	9 FORMAT (1H0,15X,2HAF,15X,2HAP,15X,2HKT,15X,1HT,15X,4HDELT,14X,4HWT
-	107./)
	WRITE (6.1C)
10	FORMAT (14X,6H(SQ-M),11X,6H(SQ-M),9X,10H(W/M-DEGK),10X,3H(M),13X,
с	16H(DEGK)+13X+4H(KG)) SOLVE THE SIMULTANEOUS EQUATIONS PARAMETRICALLY IN AF
-	DO 12 J=1+11
	AP=AT-AF
	KT=(KP*AP+KF*AF)/AT
	A=KT*AT/O
	B=RHOP*AP*HFP
•	C=(RHOF*AF*CPF+RHOP*AP*CPP)/2.0
	DELT=(-(A*B)+SQRT((A*B)**2+(4.0*A*C*EMAX)))/(2.0*A*C)
	T=A*DFLT
	WTOT=((RHOP*AP+RHOF*AF)*T)+((2.0*AT+4.0*T*SQRT(AT))*RHOC)
C .	WRITE ANSWERS
	WRITE (6,11) AF, AP, KT, T, DELT, WTOT
11	FORMAT (1H0+10X+E12+5+5X+E12+5+5X+E12+5+5X+E12+5+5X+E12+5+5X+E12+5
•	1)
	AF=AF+0•1*AT
12	CONTINUE
с	GO BACK FOR NEW CASE
	GO TO 2
<u> </u>	THERE ARE NO MORE CASES
13	
· · · · · · ·	
. 14	ANDREAL CITY (ISTRUM COMPLETED)
	STOP

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END

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•• ••••	Table 11-1 (Cont'd)
\$DATA	
1602.0 0.519	1673.6 232400.0 2712.89 224.93 920.48 3.445
360000+0 100+0	•093
360000.0 500.0	•093
360000+0 1000+0	•093
1800000.0 100.0	•093
1800000.0 500.0	•^93
1800000.0 1000.0	•093
3600000+0 100+0	•093
3600000+0 500+0	•093
3600000.0 1000.0	.093
-10.0	REPROV
ala a a	NOT '
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		TERS		JØULE/KG-DEGK	JØULE/KG-DEGK	•			M TØT (KG)	0.21261E 01	0.25258E 01	0.289726 01	0.33732E 01	0.40074E 01	0.48946E 01	0.62239E 01	0.84353E 01	0.12837E 02	0.25775E 02	0.207215 03
Table 11-1 (Concluded)	INPUT VALUES).10000E 03 WATTS AT= 0.93000E-01 SQUARE MEI	ES ØF THE PCM, FILLER, AND CØNTAINER	KP= 0.519002 00 W/M-DEGK CPP= 0.16736E 04	F= 0.92048E 03		DUT DATA	T DELT (M) (DEGK)	0.200885 02	0.53987E 00	0.30739E 00	0.23514E 00	0.20614E 00	0.19809E 00	0.20641E 00	0.23582E 00	0.30885E 00	0.54219E 00	0.38498E 01	
					KG/CURIC M CF	KF= 0.22493E 03 W/M-DEGK			0.96960E-02	0.11528E-01	0.12979E-01	0.14836E-01	0.17308E-01	0.20766E-01	0.25947E-01	0.34565E-01	0.51715E-01	0.10210E 00	0.80532E 00	
					2F= 0.27129E 04			PARAMETRIC ØUT	KT (W/M-DEGK)	C.51900E 00	C.22960E 02	0.45401E 02	C.67842E 02	C.93283E 02	0.11272 5 03	C.13517E 03	C.15761E 03	0.18005E 03	C.20249E 03	0.22493E 03
		J&ULES 2= (PRUPERTI	KG/CUBIC M	JUULE/KG RH(K6/SQUARE M			AP (SO-M)	0.930006-01	0.83760E-01	0.744006-01	· 0.65100E-01	0.55800E-01	0.46500E-01	0.37200É-01	0.279605-01	0.18600E-01	0.930C0E-02	0.34645E-09
	·	EMAX=_0.36000E_06		RHØP= 0.16020E 04	HFP= 0.23240F 06	RH2 C= 0. 34450E 01		-	аF (SQ-M)	0.00000E-38	0.9300JE-02	0.13600E-01	0.27900E-01	0.37200E-01	0.46500E-01	0.55800E-01	0.65100E-01	0.74400E-01	0-83700E-01	0.93000E-01
		ì			i					11	-8									

Table 11-2

EXPLANATION OF PROGRAM VARIABLE NAMES

Btu-hr-ft-^oF Btu/hr-ft-^oF Btu-hr-ft-^oF Btu/lb_ - ⁰F Engineering $Btu/lb_m - {}^{o}F$ British Btu/lbm Units $1\mathrm{b_m/ft}^3$ $1\mathrm{b_m/ft}^3$ $\mathrm{lb_m/ft}^2$ Btu/hr Btu ft² ft² ft² 면 ft International $W/m-^{O}K$ J/kg-⁰K W/m-^oK W/m-^oK J/kg-⁰K kg/m³ kg/m² kg/m³ Units J/kg ъ2 $^{\rm o}_{\rm K}$ ឨ ≽ E ٤ Program Variable RHOP RHOF RHOC EMAX Name DELT СРР CPF HFP КΤ КР КF \mathbf{AP} ΨT AF α (H , c_{ppcM} | ∆T_{max} ^k PCM i ^hf_{PCM} Usual Symbol APCM ρ_{PCM} E max $^{\rm C}{\rm p_F}$ ρ_ct ، ۲ \mathbf{A}_{T} \mathbf{A}_{F} Н $ho_{\rm F}$ ¥. ٠a Maximum Component Temperature Excursion Heat Rate from Component into PCM Package Total Energy Stored in PCM at Total Melt Total Equivalent Thermal Conductivity Total Package Cross-Sectional Area Container Density per Unit Area Filler Thermal Conductivity Filler Cross-Sectional Area PCM Thermal Conductivity PCM Cross-Sectional Area above Melt Temperature Variable Total Package Thickness PCM Heat of Fusion Filler Specific Heat PCM Specific Heat Filler Density PCM Density

 $^{1b}_{m}$

kg

WTOT

Ъ М

Total Package Weight

.
INDEX OF PHASE CHANGE MATERIALS

All phase change materials appearing in the handbook are listed alphabetically. Frequently used synonyms are also listed with the name of the primary material given to the right of each synonym.

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Sodium carbonate decahydrate	5-27
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Sodium hydroxide-monohydrate	5-27
Sodium sulfate decahydrate	5-27
Sodium thiosulfate pentahydrate	5-27
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Succinic acid anhydride (succinic anhydride)	5-25
Succinic anhydride	5-25

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Т	
Tetracosane	5-19
Tetradecane	5-19, 5-41, 5-42
Tetramethylbenzene (Durene)	5-23
Transit Heet (Inorganic hydrated salts)	5-37, 5-83
Tricosane	5-19
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5-37, 5-81, 5-82

5-25

W

Water

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p-Xylene dichloride

☆U.S. GOVEPNMENT PRINTING OFFICE: 1971-745378/4029

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Appendix A

TABLE OF CONVERSION FACTORS AND

TEMPERATURE CONVERSION EQUATIONS

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	CIBLE	Appendix A		
RO	DIIC.	TABLE OF CONVERSION FACTORS		
at REF	Property	To Convert From -	Τo	Multiply By -
40		Pound Mass/Foot ³ Pound Mass/Foot ³	Gram/Centimeter ³ Kilogram/Meter ³	1.602×10^{-2} 1.602 × 10 ¹
	Density	Gram/Centimeter ³ Gram/Centimeter ³ Kilogram/Meter ³	Pound Mass/Foot ³ Kilogram/Meter ³ Pound Mass/Foot ³	6.243×10^{1} 1.0×10^{3} 6.243×10^{-2}
		Kilogram/Meter ³	Gram/Centimeter ³	1.0×10^{-3}
		Btu/Pound Mass Btu/Pound Mass Calories/Gram	Calories/Gram Joules/Kilogram Btu/Pound Mass	5.567×10^{-4} 2.324 × 10 ³ 1.796
		Calories/Gram Joules/Kilogram	Joules/Kilogram Btu/Pound Mass	4.184×10^{3} 4.302×10^{-4} 2.395×10^{-4}
	Latent Heat of Fusion	Btu/Foot ³ Btu/Foot ³	Calories/Centimeter ³ Joules/Meter ³	$\frac{2.335 \times 10}{8.917 \times 10^{-3}}$ 3.731 x 10 ⁴
		Calories/Centimeter ³ Calories/Centimeter ³ Joules/Meter ³	Btu/Foot ³ Joules/Meter ³ Btu/Foot ³	1.121×10^{-5} 4.184 x 10 ⁻⁵ 2.680 x 10 ⁻⁵
		Joules/Meter ³	Calories/Centimeter	2.390 x 10 ⁻⁷
	Specific Heat	Btu/(Pound mass - ^o F) Btu/(Pound mass - ^o F) Gram Calories/(Gram - ^o C)	Gram Calories/(Gram-°C) Joules/(Kilogram- [°] K) Btu/(Pound mass- [°] F)	1.00 4.184 \times 10 ³ 1.00
		Gram Calories/(Gram-°C) Joules/(Kilogram- [°] K) Joules/(Kilogram- [°] K)	Joules/(Kilogram- [°] K) Btu/(Pound mass- [°] F) Gram Calories/(Gram- [°] C)	4.184×10^{-4} 2.390 x 10 ⁻⁴ 2.390 x 10 ⁻⁴
	· · · · · · · · · · · · · · · · · · ·	Pounds/Inch Pounds/Inch	Dynes/Centimeter Newtons/Meter	1.752×10^5 1.752×10^2
	Surface Tension	Dynes/Centimeter Dynes/Centimeter Newtons/Meter	Pounds/Inch Newtons/Meter Pounds/Inch	5.708×10^{-3} 1.0 x 10 ⁻³ 5.708 x 10 ⁻³
		Newtons/Meter	Dynes/Centimeter	1.0 x 10
		Btu/(Hr-Foot- ^o F) Btu/(Hr-Foot- ^o F)	Calories/(Sec-Centimeter-°C) Watts/(Meter-°K)	4.142×10^{-3} 1.730
	Thermal Conductivity	Calories/(Sec-Centimeter-C) Calories/(Sec-Centimeter-°C) Watts/(Meter-°K)	Btu/(Hr-Foot-F) Watts/(Meter- [°] K) Btu/(Hr-Foot- [°] F)	4.177×10^{-1} 5.780 x 10 ⁻¹
		watts/(Meter-"K) Foot ² /Hr Foot ² /Hr	Centimeter ² /Sec Meter ² /Sec	2.581×10^{-1} 2.581 x 10 ⁻⁵
	Thermal Diffusivity	Centimeter ² /Sec Centimeter ² /Sec Meter ² /Sec	Foot ² /Hr Meter ² /Sec Foot ² /Hr	3.875 1.0 x 10 ⁻⁴ 3.875 x 10 ⁴
		Meter ² /Sec	Centimeter ² /Sec	1.0 x 10 ⁴
	_	Pounds/Inch ² Pounds/Inch ² Millimeters of Mercury	Millimeters of Mercury Newton/Meter ² Pound/Inch ²	$5.171 \times 10^{\circ}$ 6.893×10^{3} 1.934×10^{-2}
	Fressure	Millimeters of Mercury Newtons/Meter ²	Newton/Meter ² Pound/Inch ² Millimeters of Mercury	1.333×10^{2} 1.451×10^{-4} 7.500×10^{-3}
		Pound-Sec/Foot ²	Centipoise	4.789 x 10 ⁴
1	Viscosity	Pound-Sec/Foot ² Centipoise Centipoise	Newton-Sec/Meter ² Pound-Sec/Foot ² Newton-Sec/Meter ²	4.789 x 10 ¹ 2.088 x 10 ⁻⁵ 1.0 x 10 ⁻³
		Newton-Sec/Meter ² Newton-Sec/Meter ²	Pound-Sec/Foot ² Centipoise	2.088 1.0 x 10 ³

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From	То	Equation
° _F	°c	$^{\circ}C = \frac{^{\circ}F - 32}{1.8}$
°F	°ĸ	${}^{O}K = \frac{5}{9} \left\{ {}^{O}F + 459.67 \right\}$
°c	°F	$^{\circ}$ F = 1.8 $^{\circ}$ C + 32
°c	°ĸ	^o K = ^o C + 273.15
°K	°F	$^{\circ}F = \frac{9}{5} ^{\circ}K - 459.67$
°K	°C	$^{\circ}C = ^{\circ}K - 273.15$

TEMPERATURE CONVERSION EQUATIONS

Appendix B

SAMPLE CALCULATION OF RAYLEIGH AND MARANGONI NUMBERS

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Appendix B

To illustrate how Rayleigh and Marangoni numbers are calculated, the following sample calculation is offered.

Krytox 143 AZ oil is a fluid currently used to study convection. A fluid layer of depth d is heated and the temperature difference ΔT is measured across the distance d.

Data used for the calculation are presented at the temperatures reported. The average temperature is approximately 100° F. Data were selected which were nearest the average temperature of 100° F.

The Rayleigh number R is defined by:

$$R = \frac{g\beta \frac{dT}{dy} d^4}{\nu \alpha}.$$

The Marangoni number B is defined by:

$$B = \frac{-\frac{d\sigma}{dT} \frac{dT}{dy} d^2}{\rho \nu \alpha}$$

Krytox 143 AZ oil Average temperature = 100°F

$$\nu = 18 \times 10^{-2} \text{ cm}^2/\text{sec (100°F)}$$

$$\rho = 1.86 \text{ gm/cm}^3 (75°F)$$

$$\beta = 11.0 \times 10^{-4} 1/^{\circ}\text{C (77-210°F)}$$

$$\sigma = 16.0 \text{ dyne/cm (78.8°F)}$$

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$$\frac{d\sigma}{dT} = -0.1 \text{ dyne/cm} - {}^{\circ}C (104^{\circ}F)$$

$$\alpha = 4.5 \times 10^{-4} \text{ cm}^{2}/\text{sec} (100^{\circ}F)$$

$$g = 980 \text{ cm/sec}^{2}$$

$$Pr = 400 (\text{dimensionless})$$

$$\frac{dT}{dy} = \Delta T/\text{d assuming a linear temperature gradient}$$

$$R = \frac{980 \times 11.0 \times 10^{-4} \Delta T \text{ d}^{3}}{18 \times 10^{-2} \times 4.5 \times 10^{-4}} = 1.33 \times 10^{4} \Delta T \text{ d}^{3}$$

$$B = \frac{-0.1 \Delta T d}{1.86 \times 18 \times 10^{-2} \times 45 \times 10^{-4}} = 6.64 \times 10^{2} \Delta T d.$$

Measurements are made for the variables ΔT (temperature gradient) and d (the thickness of fluid).

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