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SPACE THERMAL CONTROL BY FREEZING AND MELTING

SECOND INTERIM REPORT

SPACE THERMAL CONTROL STUDY

HREC-1123-2
LMSC/HREC D148619

LOCKHEED MISSILES & SPACE COMPANY
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May 1969

Contract NAS8-21123

by

P. G. Grodzka

APPROVED BY: J. S. Farrior
J. S. Farrior
Resident Director

FOREWORD

This report presents the results of an experimental study which had as its objective the definition and evaluation of specific new materials that can be used as phase change thermal control materials. The work reported essentially fulfills Tasks II, III and IV set forth in the original contract, NAS8-21123, and in the first modification to the original contract. These tasks are:

- Task II

  Define and evaluate specific new materials that can be used as phase change thermal control materials not to include the well-known paraffin family of compounds (n-octadecane, n-hexadecane, eicosane, octacosane, etc.). These materials are to be selected and evaluated to the following guidelines:

  - At least four materials (not including rejects) must be defined and evaluated for future use as phase change thermal control materials.
  - The four materials to be defined and evaluated must have equilibrium temperatures (melting points) between 270°K and 370°K. While the precise equilibrium temperature is not stated, a priori, it is required that the four equilibrium temperatures be dispersed nearly equally from 270°K to 370°K.
  - A maximum supercooling of 3°K below equilibrium temperature is required. Definition of "nuclei seeds," trace impurities which prevent excessive supercooling, is required.
  - Heats of fusion (or more generally heats of transition) must be greater than 56 cal/gm (100 Btu/lb).
  - Each material must be non-hazardous for manned space flight, i.e., they must be non-explosive, non-toxic, non-corrosive, and stable. Materials will be considered for use from 50°K below to 50°K above the equilibrium temperature.
  - Low volumetric change with temperature is required. A maximum of 5% thermal expansion is highly desired over the range of 50°K above and below the equilibrium temperature. Thermal expansion above 15% is not acceptable.

- TASK I

  Perform meaningful theoretical studies (including laboratory studies which are necessary to support the theoretical studies) on the scientific aspects involved with the use of phase change materials in the boundary conditions of space. (This study will not be directed toward defining specific applications of phase change materials in space.) Specific considerations will include the study of solidification crystallization, and nucleation as affected by the space conditions of weightlessness, void formation due to thermal contractions and other means, high energy radiation (which penetrates the phase change material container), and other boundary conditions. These studies should be appropriate for all types of potential materials. The term "nucleation" is used here to mean "the initiation of a new phase within a given phase."

This study program is sponsored by the George C. Marshall Space Flight Center, National Aeronautics and Space Administration, Huntsville, Alabama. Mr. T.C. Bannister, is the director of the study. Dr. P.G. Grodzka, Research Specialist, Thermal Control Systems Group, Lockheed Missiles & Space Company, Huntsville Research & Engineering Center, Huntsville, Alabama is the principal investigator. This report was prepared by Dr. Grodzka.

SUMMARY

A number of potential PCMs* are defined and evaluated. Of 27 materials experimentally evaluated, 16, covering a range of melting points from 16° to 102°C, are selected as being potential PCMs. Four that are designated as prime candidates are:

Lithium nitrate trihydrate with zinc-hydroxy nitrate catalyst (melting point, 30°C)

Acetamide (melting point, 81°C)

Methyl fumarate (melting point, 102°C)

Myristic acid (melting point, 58°C)

Also reported in the second part of the study are the results of a nucleation catalyst search. Of two new nucleation catalysts reported, the nature of one is fairly well established. The nature of the other is still unknown.

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*Abbreviation for Phase Change Material.

CONTENTS

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (Continued)

Section 1
INTRODUCTION

In the first part of the study (Reference 1) a thorough understanding of the role of heat transfer and phase kinetics in efficient phase change material (PCM) operation was developed. The purpose of the second part of the study is to define and evaluate specific new materials as candidate PCMs, in accordance with Tasks II, III, IV, V and VI. (See Foreword.)

Before materials can be evaluated as potential PCMs, it is necessary to state the criteria against which the materials are to be measured. The criteria should be such that they can be translated into meaningful experimental tests. In the present study, the translation of the understanding of the role of heat transfer and phase kinetics in efficient PCM operation into meaningful experimental tests required some research and development. Two experimental designs, both based on melting-freezing curves, evolved. The first design provides a way to screen out materials which would be unacceptable as PCMs. The first design also provides a way to qualitatively estimate the probable effectiveness of a given material as a PCM. The second scheme, once fully developed, will easily provide detailed information on freezing-melting characteristics. The second scheme should also be capable of easily providing quantitative estimates of thermal diffusivity in both the solid and liquid phases.

The theoretical bases of the two experimental methods is presented in the following sections. Also presented are the results of a materials evaluation study. Material evaluations are based on actual freezing-melting data (obtained by using mainly the first experimental method) and on considered judgement of other properties obtained in the literature.

Section 2

EXPERIMENTAL SELECTION AND EVALUATION OF NEW PCM MATERIALS

2.1 FIRST MATERIALS SELECTED FOR SCREENING

Two of the most important criteria which potential PCMs must meet in the present study are low melting temperature (in the range of 270 to 370°K) and high heat of fusion (in the range of 56 cal/gm). The initial designation of such materials can only be approached empirically. As far as is known, present theories of melting cannot easily predict materials with low melting temperatures and high heats of fusion. An empirical correlation is reported (Reference 2) which is based on insights obtained from the theories. This correlation provides a means of estimating heats of fusion from a knowledge of the molecular structure and melting point. The general validity of the correlation, however, remains to be evaluated.

It was felt that enough actual heat of fusion data could be found in the literature to give a good representation of a variety of materials. For materials selected on an intuitive basis and for which no heat of fusion data were found, the Fisher Model 360 Differential Thermal Analyzer was used to obtain a qualitative estimate. (The principles of Differential Thermal Analysis (DTA) are briefly presented in Appendix A.) In addition to heats of fusion and melting temperatures, the literature search provided data on many of the other thermal and physical properties of interest.

In the course of the literature search for candidate PCMs it became evident that in many cases reported melting points and heats of fusion could not be taken at face value. Many of these values refer to transition points, not true fusion. To appreciate the distinction it is necessary to consider the phase diagrams of the materials involved. Aspects of phase diagrams pertinent to the present study are given in Appendix B.

The results of a literature search for materials which can classify as candidate PCMs and which are readily available are given in Table 1. Sources from which the listed thermal and physical properties were obtained are designated by capital letters in the table. The key to these letter is given as follows:

A. Handbook of Chemistry and Physics, C. D. Hodgman, R. C. Weast and S. M. Selby, eds., 42nd Edition, The Chemical Rubber Publishing Co., Cleveland, O., 1960.

B. Handbook of Chemistry, N. A. Lange, Editor, McGraw-Hill, New York, 1961.

C. International Critical Tables, Vol. V, E. W. Washburn, ed., McGraw-Hill, New York, 1929.

D. Aravamudan, G. and S. Ramaseshan, Can. J. Chem., Vol. 39, 1961, p. 256.

E. Inorganic and Theoretical Chemistry, J. W. Mellor, Vol. 2., Longmans, Green and Co., New York, 1922, p. 853.

F. Inorganic and Theoretical Chemistry, J. W. Mellor, Vol. 14, Longmans, Green and Co., New York, 1935, p. 381.

G. Gallium and Gallium Compounds, Alcoa Company Brochure.

H. "Development of High Capacity Heat Storage Materials," Cryo-Therm, Inc., Mass. Inst. Tech., Instrumentation Lab, R-380, July 1962.

I. Ubbelohde, A. R., Melting and Crystal Structure, Claredon Press, Oxford, 1965.

J. Dowtherm Heat Transfer Fluids, The Dow Chemical Co., 1967.

K. NP Technical Data Sheet, NP Series TDS No. 3, Commercial Solvents Corp., January 1961.

L. Data Sheet, Catalog No. 914, Arapahoe Chemicals, Inc., 1962.

M. Cerro Alloy Physical Data, Bulletin J2-10-64-5M-BK, Cerro Sales Corp.

N. Chemical Formulary, Vol. II, H. Bennett, ed., Chemical Publishing Co., Inc., N. Y., 1935, p. 336.

O. Greenfield, I. G. and R. L. Smith, "Gallium-Antimony System," J. Metals, February 1955, pp. 351-352.

P. Timmermans, J., Physico-Chemical Constants of Binary Systems, Interscience Publishers, Inc., New York, 1959, p. 1159.

Q. Bentilla, E. W., K. F. Sterrett and L. E. Karre, "Research and Development Study on Thermal Control by Use of Fusible Materials," Final Report NSL 65-16-1, Northrop Space Laboratories, April1966.

R. Bannister, T., NASA/MSFC, private communication, 1968.

S. Fixler, S. Z., J. Spacecraft, Vol. 3, No. 9, September 1966, p. 1364.

T. International Critical Tables, Vol. IV, McGraw-Hill, New York, 1928.

U. Kay-Kries Chemicals Brochure, Organic Intermediates, 1967/1968.

V. Melpar Company, telephone communication

W. Mellor, J. W., Inorganic and Theoretical Chemistry, Vol. III Longmans, Green & Co., New York, 1922, p. 676.

The grade and source of supply of the materials listed in Table 1 are as follows:

Baker Analyzed Reagent

Sodium Sulfate
Disodium Hydrogen Phosphate Dodecahydrate
Silver Nitrate
Ferric Nitrate Enneahydrate
Potassium Nitrate
Ammonium Nitrate
Barium Hydroxide Octahydrate
Tin
Lead
Disodium Hydrogen Arsenate Dodecahydrate

Table 1

FIRST SELECTION OF PCM CANDIDATES

(Reference designated by capital letter below and to the right of given value. Key to references on pp. 3 - 4. Notes at end of Table on p. 10.)

	Chemical Formula	Molecular Weight	Melting Temp. °C (Note 1)	ΔH_f cal/gm	Density gm/ml	Percent Vol. Exp. on Melting (Note 2)	ΔH_f cal/ml (solid)	ΔH_f Btu/lb	Thermal Conductivity (Note 3)	Specific Heat $\frac{\text{g-cal}}{\text{g °C}}$	Volume Thermal Expansion Coefficient $^\circ C^{-1}$	Boiling Point °C (Note 4)	Further Information (Note 5)
SALT HYDRATE COMPOUNDS													
Lithium Nitrate Trihydrate	$LiNO_3 \cdot 3H_2O$	123.00	29.88c A	70.7 B	solid 1.55 D liquid ~ 1.43 B	8	110	128 H					56.11 . . .
Sodium Phosphate Dodecahydrate	$Na_2HPO_4 \cdot 12H_2O$	138.01	36i A	66.8 A	solid 1.52 20°C A	5.1 E	102	114 H	solid 1.31 24°C 1.23 32°C liquid 1.20 39°C 1.14 49°C C	solid 0.404 0°C liquid 0.464 50°C B	solid ~8.31x10^{-5} liquid ~43.5x10^{-5} E		39.36 +
Sodium Carbonate Decahydrate	$Na_2CO_3 \cdot 10H_2O$	286.16	~33i A	60 H	solid 1.44 16°C A		86	108 H					37.04
Sodium Sulfate Decahydrate	$Na_2SO_4 \cdot 10H_2O$	322.22	31i A	51.3 A	solid 1.464 20°C A		75.1	109 H					44.08
Sodium Arsenate Dodecahydrate	$Na_2HAsO_4 \cdot 12H_2O$	402.10	28i A		solid 1.736-59 20°C A								46.23 +
Barium Hydroxide Octahydrate	$Ba(OH)_2 \cdot 8H_2O$	315.51	78c A	72 H	solid 2.18 16°C A		157 H	130 H				103 W	54.31 +
Ferric Nitrate Enneahydrate	$Fe(NO_3)_3 \cdot 9H_2O$	404.02	47.2 A		solid 1.684 20°C A							125 F	39.86 0.2234C_P (50.5°C) . . . F
Lithium Acetate Dihydrate	$LiC_2H_3O_2 \cdot 2H_2O$	102.2	58 A	60-90 H									64.68

Table 1 Contd.

	Chemical Formula	Molecular Weight	Melting Temp. °C (Note 1)	ΔH_f cal/gm	Density gm/ml	Percent Vol. Exp. on Melting (Note 2)	ΔH_f cal/ml (solid)	ΔH_f Btu/lb	Thermal Conductivity (Note 3)	Specific Heat $\frac{g\text{-}cal}{g\ ^oC}$	Volume Thermal Expansion Coefficient $^oC^{-1}$	Boiling Point °C (Note 4)	Further Information (Note 5)
METALS, METAL EUTECTICS													
Ga-GaSb Eutectic	Very small amts. of GaSb in Ga matrix		29.8 O										
Gallium	Ga	69.72	29.8 A	19.2 A	solid 5.904 liquid 6.095 G	-3.2 G	112 G			solid 0.080 liquid 0.095 G	solid 5.8×10^{-5} liquid 12.0×10^{-5} G	2403 G	1.612 C_p (97.7°C) + G
Cerrobend Eutectic	50.5Bi 26.7 Pb 13.3 Sn 10.0 Cd M		70	7.78	solid 9.4	1.7	73	14	solid 45	solid 0.04	solid 6.6×10^{-5}		
Eutectic	52.2 Bi 32.0 Pb 15.5 Sn			96 N									
Cerrolow 136 Eutectic	49Bi 18 Pb 12 Sn 21 In M			58	solid 4.44 liquid 8.8 20°C		1.35	39.1	solid 8	liquid 0.03	solid 6.9×10^{-5}		
FUSED SALT EUTECTICS													
	24 $LiNO_3$ 71 NH_4NO_3 5 NH_4Cl			86 H									
	20 $LiNO_3$ 61 NH_4NO_3 19 $AgNO_3$			52 H									
NON-PARAFFIN ORGANIC COMPOUNDS													
Glycerol	$C_3H_5(OH)_3$	92.09	18 A	47.5 A	solid 1.334 18°C liquid 1.262 18°C I	5.7	63.2	85.5	liquid 0.613 48°C B	solid 0.330 0°C liquid 0.540 0°C B	liquid 0.505 20°C B	290 A	1490C_p 20°C A

Table 1 Contd.

	Chemical Formula	Molecular Weight	Melting Temp. °C (Note 1)	ΔH_f cal/gm	Density gm/ml	Percent Vol. Exp. on Melting (Note 2)	ΔH_f cal/ml (solid)	ΔH_f Btu/lb	Thermal Conductivity (Note 3)	Specific Heat $\frac{g\text{-cal}}{g\ ^\circ C}$	Volume Thermal Expansion Coefficient $^\circ C^{-1}$	Boiling Point °C (Note 5)	Further Information (Note 5)
Non-Paraffin Organic Compounds Contd.													
Acetic Acid	CH_3COOH	60.05	16.6 A	44.7 A	liquid 1.05 20°C C	$15.6\rho_s$ T	46.9	80.4	liquid 0.43 25°C B	solid 0.487 0° liquid 0.468 0° B	liquid 1.071 20°C B	118.1 A	... $1.30C_p$ 18°C A
Chloroacetic Acid	$ClCH_2COOH$	94.50	α61.2 β56 γ50 A	31.1 35.1 A	solid 1.58 20°C A	$10.7\rho_s$ T	α49.1 β55.5	α56.0 β63.2		solid 0.363 60°C B		189 A	
Methyl Fumarate	$(CHCO_2CH_3)_2$	144.12	102 A	57.9 A			104					192 A	
Acetamide	CH_3CONH_2	59.07	81 (69.4) A	58 H	solid 1.159 20°C liquid 0.9986 85°C C	$8.15\rho_s$ T	67	104				222 A	
Cyanamide	$CN\cdot NH_2$	44	42.9 A	49.8 A	solid 1.08 20°C A		53.8	98.6		solid 0.547 20°C B		140^{19} d A	
Elaidic Acid	$C_8H_{17}CH{:}CH(CH_2)_7COOH$	282.46	47 A	52.1 A	liquid 0.851 79°C A		44.3	93.7				288^{100} A	
Myristic Acid	$CH_3(CH_2)_{12}COOH$	228.37	58 A	47.5 A	liquid 0.858 60°C A		40.1	85.5		solid 0.381 0°C liquid 0.539 56 - 100°C B		250.5^{100} A	
Stearic Acid	$CH_3(CH_2)_{16}COOH$	284.47	69.4 A	47.6 A	liquid 0.847 69°C A		40.3	85.7			solid 8100×10^{-7} 33.8-45°C B	383 A	$11.6C_p$ 70°C

Table 1 Contd.

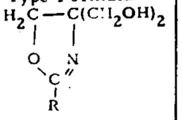
	Chemical Formula	Molecular Weight	Melting Temp. °C (Note 1)	ΔH_f cal/gm	Density gm/ml	Percent Vol. Exp. on Melting (Note 2)	ΔH_f cal/ml (solid)	ΔH_f Btu/lb	Thermal Conductivity (Note 3)	Specific Heat $\frac{g\text{-cal}}{g\ ^\circ C}$	Volume Thermal Expansion Coefficient $^\circ C^{-1}$	Boiling Point °C (Note 4)	Further Information (Note 5)
Non-Paraffin Organic Compound Contd. Tristearin	$(C_{17}H_{35}CO_2)_3$ C_3H_5	891.46	56 A	45.6 A	liquid 0.862 80°C A		39.3	82.1					$18.5C_p$ 75°C A
Quinone (see Note 6)	$O:C_6H_4:O$	108.09	115 A	40.9 A	solid 1.318 20°C A							Subl. A	
Quinol (see Note 6)	$p\text{-}C_6H_4(OH)_2$	110.11	170.5 A	58.8	solid 1.358 20°C A							286.2 A	
Resorcinol (See note 6)	$m\text{-}C_6H_4(OH)_2$	110.11	110 A	46.2 A	solid 1.285 15°C A							276.5 A	
Pyrocatechol (see Note 6)	$O\text{-}C_6H_4(OH)_2$	110.11	105 A	49.4 A	solid 1.371 15°C A							240 A	
Resorcinol-Pyrocathecol Eutectic	1:1	110	70°C P										
Diphenyloxide (see Note 6)	$(C_6H_5)_2O$	170.2	28 A	DTA Est. Small	solid 1.073 20°C A							259 A	
Diphenyl (see Note 6)	$C_6H_5C_6H_5$	154.20	69.71 A	26.1	solid 1.180 A		30.8	47.0				254-5 A	
Dowtherm A (Dow Chemical Company)	26.5% Diphenyl 73.5% Diphenyloxide J		12.0	23.4	liquid 1.071 12°C	7.10 (-6.63 on freezing)	25.1	42.2	liquid 0.325 60°C	liquid 0.374 12°C		257.7 (123.9 flash point)	$3.9C_p$ 25°C
Oxazoline Waxes (Commercial Solvents Corp.)	Type Formula  R Stearic Acid												

Table 1 Contd.

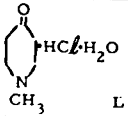
	Chemical Formula	Molecular Weight	Melting Temp. °C (Note 1)	ΔH_f cal/gm	Density gm/ml	Percent Vol. Exp. on Melting (Note 2)	ΔH_f cal/ml (solid)	ΔH_f Btu/lb	Thermal Conductivity (Note 3)	Specific Heat $\frac{\text{g-cal}}{\text{g } ^\circ\text{C}}$	Volume Thermal Expansion Coefficient $^\circ C^{-1}$	Boiling Point °C (Note 4)	Further Information (Note 5)
Non-Paraffin Organic Compounds Contd. Oxazoline Waxes (Commercial Solvents Corp.)	ES-254 K	723	37	DTA Est. large									
Conts.	TS-254 K	968	63	DTA Est. medium									
	TS-254A K	656	50	DTA Est. medium									
	TS-254AA K	398	93	DTA Est. medium									
	TS-970 K	937	74	DTA Est. large									
1-Methyl-4-Piperidone-HCl·H_2O (Arapahoe Chem Co.)	 L	167.64	94-95	DTA Est. v. large									
Polyethylene Glycol 600 (Carbowax)		570-630	20-25	35 S	liquid 1.1 20°C S		38.5	63 S	liquid 0.382 50°C S	solid 0.54 S		(246 flash point) S	
Tristearyl Orthoformate	$CH[O(CH_2)_{17}CH_3]_3$ U												

Table 1 Contd.

	Chemical Formula	Molecular Weight	Melting Temp. °C (Note 1)	ΔH_f cal/gm	Density gm/ml	Percent Vol Exp. on Melting (Note 2)	ΔH_f cal-ml (solid)	ΔH_f Btu/lb	Thermal Conductivity (Note 3)	Specific Heat $\frac{\text{g-cal}}{\text{g }^\circ\text{C}}$	Volume Thermal Expansion Coefficient $^\circ C^{-1}$	Boiling Point °C (Note 4)	Further Information (Note 5)
COMPARISON MATERIALS Transit Heet Series	Proprietary Formulation of Inorganic Hydrated Salts 60 V		16					95		solid 0.42 liquid 0.8			
	65 V		18					80		solid 0.45			
	86 V		30					132					
	89 V		32					108					
	97 V		36					113					
Paraffins Octadecane	$C_{18}H_{38}$		28 Q					105 Q		solid 0.4 liquid 0.6 R			. . .
Eicosane	$C_{20}H_{42}$		37 Q					106 Q		solid 0.6 liquid 0.6 R			. . .
Other Water	H_2O	18	0	79.71 A		-9.06		144	solid 5.7 liquid 1.29 4.1°C B	solid 0.492 0° C liquid 1.0 15°C B	solid 1125×10^{-7} B	100	. . .

NOTES:

1. The designation c and i mean congruent and incongruent melting points. See Appendix B for further explanation.
2. The designation ρ_s means density of the solid.
3. Unit of thermal conductivities is $\frac{\text{gm - cal}}{\text{sec cm}^2\ ^\circ\text{C/cm}} \times 10^3$
4. Superscripts indicate pressure in mm. of mercury
5. Values with no units are percent anhydrous salt in the hydrate. Values with the unit C_p (centipoise) are melt viscosity. The designations + and . . . indicate that the compound is very corrosive to aluminum (+) or very mildly to not at all corrosive to aluminum (. . .) .
6. Compounds referred to this note are not in themselves PCM candidates. Rather, various combinations yielding eutectics are the possible PCMs.

Bismuth
Monochloroacetic Acid
Resorcinol

Baker Grade (J. T. Baker Chemical Co.)

Myristic Acid
Dimethyl Fumarate
p-Benzoquinone
Hydroquinone
Elaidic Acid
Pyrocathecol
Phenyl Ether
Polyethylene Glycol 600

Baker USP Grade

Stearic Acid

Baker Practical Grade

Cyanamide
Biphenyl

B&A Reagent (Baker and Adamson Chemical Co.)

Lithium Nitrate
Acetic Acid

Fisher Certified (Fisher Scientific Co.)

Sodium Carbonate
Ammonium Chloride

Fisher Purified

Lithium Acetate Dihydrate

Eastman Technical (Eastman Organic Chemicals)

Acetamide

Commercial Solvents Corp.

Oxazoline Waxes (Unknown purity)

TS-970
TS-254
TS-254A
TS-254AA
ES-254

Kay-Fries Chemicals Inc.

Tristearyl Orthoformate (Unknown purity)

Arapahoe Chemicals

1-Methyl-4-Piperidone Hydrochloride
Hydrate (Unknown purity)

The Dow Chemical Co.

Dowtherm A (Unknown purity)

Alcoa

Gallium of unknown purity

As a result of DTA analysis, many of the first materials chosen on an intuitive basis were eliminated. The fused salt eutectics, for example, showed DTA endotherms which indicated low heats of fusion. In addition, the DTA showed that the solid phase composition was determined by the conditions of freezing. Very inhomogeneous solid phases were often obtained by uncontrolled freezing. Segregation was also detected by DTA for the eutectic 52.5 Bi, 32 Pb and 15.5 Sn. Because other materials appeared more promising, the noted materials were not investigated further.

2.2 EXPERIMENTAL EVALUATION OF PCMs

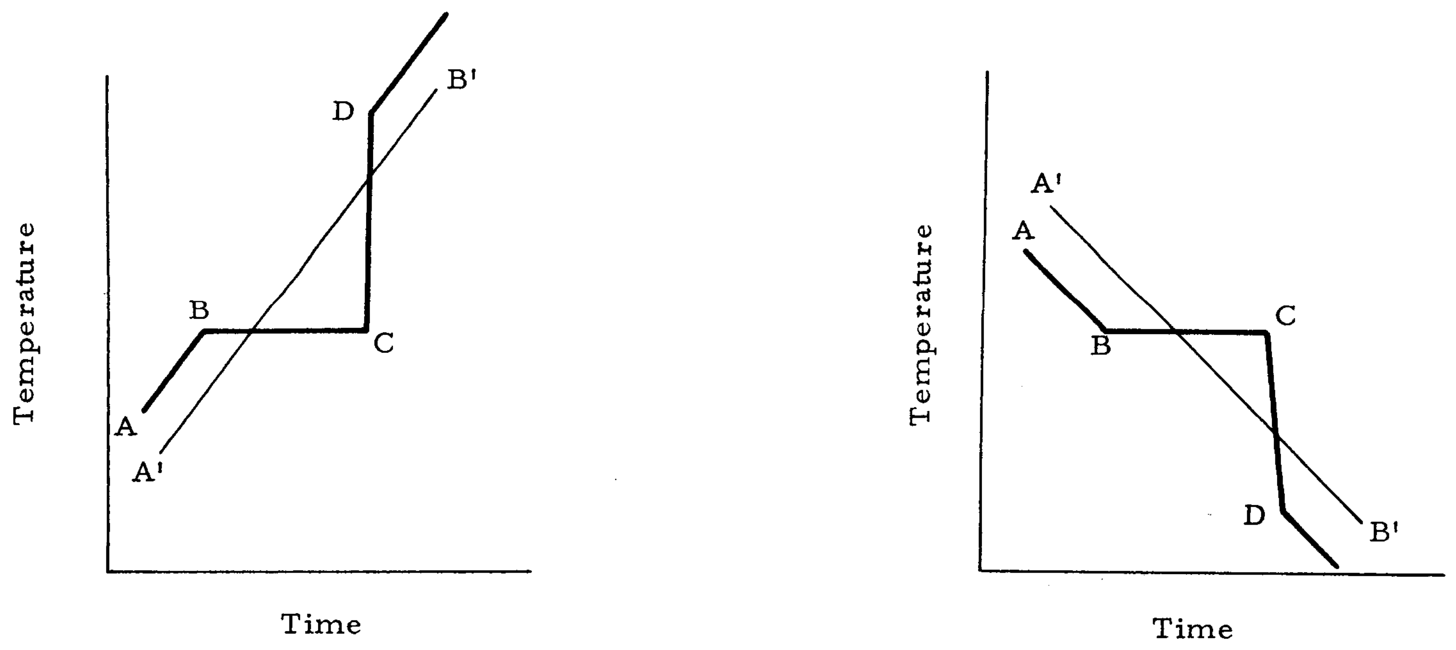
2.2.1 Interpretation of Freezing and Melting Curves

The screening and evaluation tests of potential PCMs carried out in the present study are based on freezing and melting curves. These curves are obtained by noting the temperature registered by a thermometer, or a thermocouple, located in the center of an unstirred PCM sample while the PCM sample is being heated or cooled. The interpretation of these curves in regard to the fulfillment of stated material criteria requires explanation.

Consider first of all the type of melting and freezing curves which would be obtained with an ideal PCM. An ideal PCM would have the following thermal and phase change properties:

- Large thermal diffusivity in both solid and liquid phases
- Thermal diffusivity of liquid and solid phases the same
- Composition of liquid and solid phases the same
- Heat-controlled phase change kinetics
- No one-phase supercooling
- Perfect contact between PCM and container walls
- No reaction between PCM and container.

Figure 1 can be deducted for a material of the preceding properties. Lines A'B' represent the heating and cooling curves of a reference material. The reference material, alumina sand in the present case, is heated or cooled under the same conditions as the PCM. The reference material, however, does not undergo phase change in the temperature region of interest. Curves ABCD are the melting and freezing curves of the PCM. At Point B on the


Melting Curve of Ideal PCM

Freezing Curve of Ideal PCM

Figure 1 - Ideal PCM Melting and Freezing Curves

melting curve ideal PCM begins to melt. On the freezing curve ideal PCM begins to freeze at Point B. In both cases the temperature at Point B is the melting temperature. The melting temperature is held until Point C is reached. Point C on both curves indicates that the phase transformation is complete. The liquid or the solid temperature now rapidly adjusts to that of the surroundings.

Actual materials, of course, will deviate from this ideal behavior to varying extents depending on material nature, rates of heating and cooling, and degree and kinds of impurities. Actually the parameters of material nature and rates of heating and cooling are interdependent. All pure materials would show ideal behavior if the rates of cooling or heating were suitably slow. In many cases a suitably slow rate is so slow that it is impractical.

With relatively rapid rates of cooling a pure, single-component material may show some of the following types of curves.

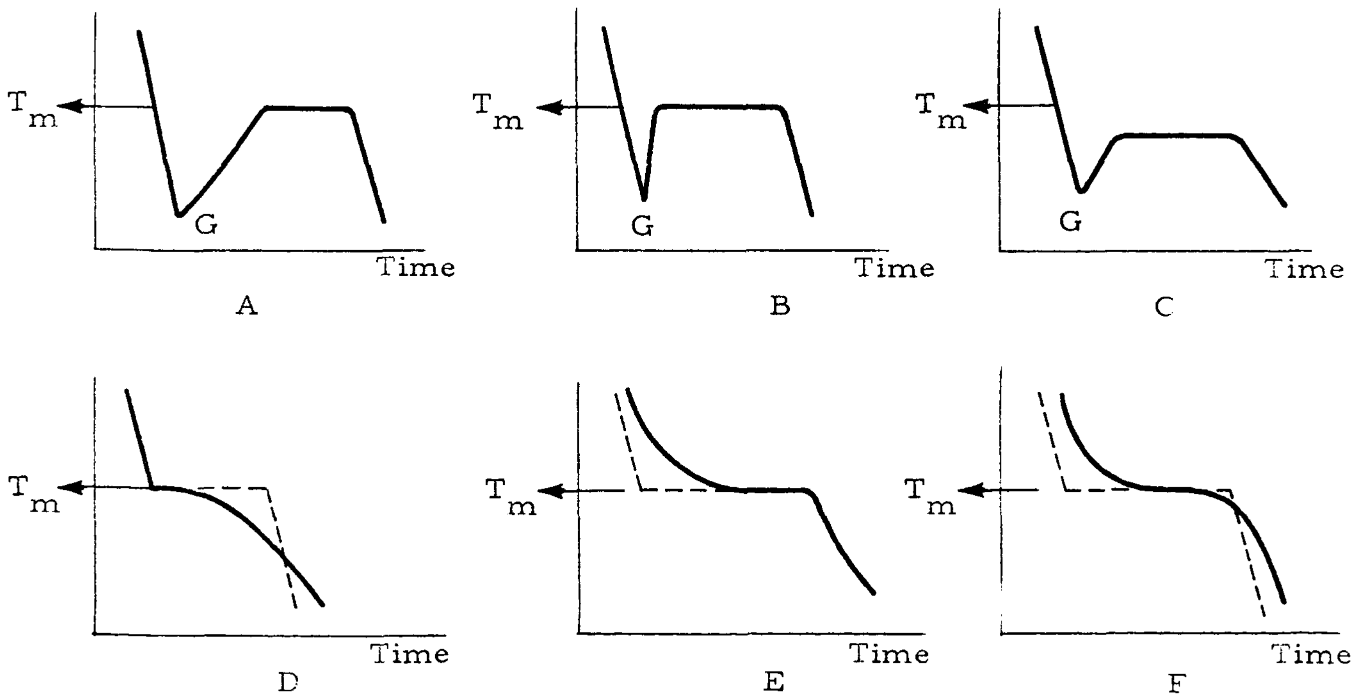


Figure 2 - Possible Types of Freezing Curves (Dashed Curves Represent Ideal Freezing)

These curves can be interpreted on the basis of extent of one-phase supercooling, two-phase supercooling, convection, and low thermal diffusivity. For example, Point G on Curves A, B and C represents the point in time of maximum one-phase supercooling. At this point nucleation occurs and the temperature thereafter rises and levels off at approximately T_m. Assuming that crystallization begins at the wall of the container, the rate of temperature rise from Point G can be taken as an indication of the thermal diffusivity of the liquid phase. In Curve A it is low and in Curve B it is high.

Curve C illustrates both one- and two-phase supercooling, (Reference 3). After nucleation the temperature does not rise to T_m but levels off at some value below T_m. This plateau represents a steady state phenomenon. Heat is being withdrawn as fast as it is being liberated. The rate of heat generation, however, is slow compared to the rate of heat transport. In other words, the process is "kinetic-controlled."

In Curve D, one-phase supercooling does not occur. At the beginning of the plateau the temperature is maintained at T_m, but then begins to fall before solidification is complete. This temperature decrease before solidification is complete can be interpreted as the result either of two-phase supercooling (because of rapid rate of heat removal towards the end of the solidification) or of the small amount of crystallizing material. Toward the end of a solidification the amount of heat being liberated by crystallizing material is so small, compared to what is being withdrawn, that it has little effect on the temperature sensor. The decision as to the major effect would depend on a consideration of the size and location of the temperature sensor. Severe departures from T_m early in the plateau would, of course, indicate two-phase supercooling. Also, as pointed out in Reference 4, convection can play a role in maintaining the temperature at T_m early on the plateau. Convection, however, is less effective as solidification proceeds.

Distorted shapes such as shown in Curves E and F are the result of low thermal diffusivity. In Curve E, T_m is reached later than in the ideal case because of low thermal diffusivity in the liquid phase (Convection is assumed as neglibible). In Curve F, resumption of steady-state cooling after complete solidification is delayed considerably because of low solid thermal diffusivity.

In the case of melting curves (pure, one-component materials), only low thermal diffusivities need be considered for superheating is rarely encountered. It would be expected that low thermal diffusivities would lead to the following distorted shape:

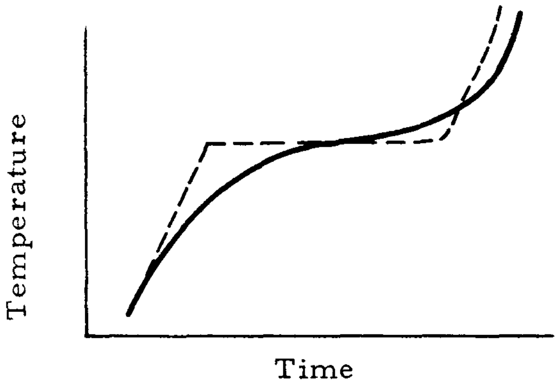


Figure 3 - Melting Curve of Material with Low Thermal Diffusivity

At a higher heating rate the curve would be even more distorted.

Another source of deviant melting-freezing curves is impurities. Generally speaking, the concentration of impurities increases in the liquid phase as crystallization proceeds. Consequently, the melting temperature is progressively lowered. The effect of increasing amounts of impurity on freezing curves is aptly illustrated in Figure 4.

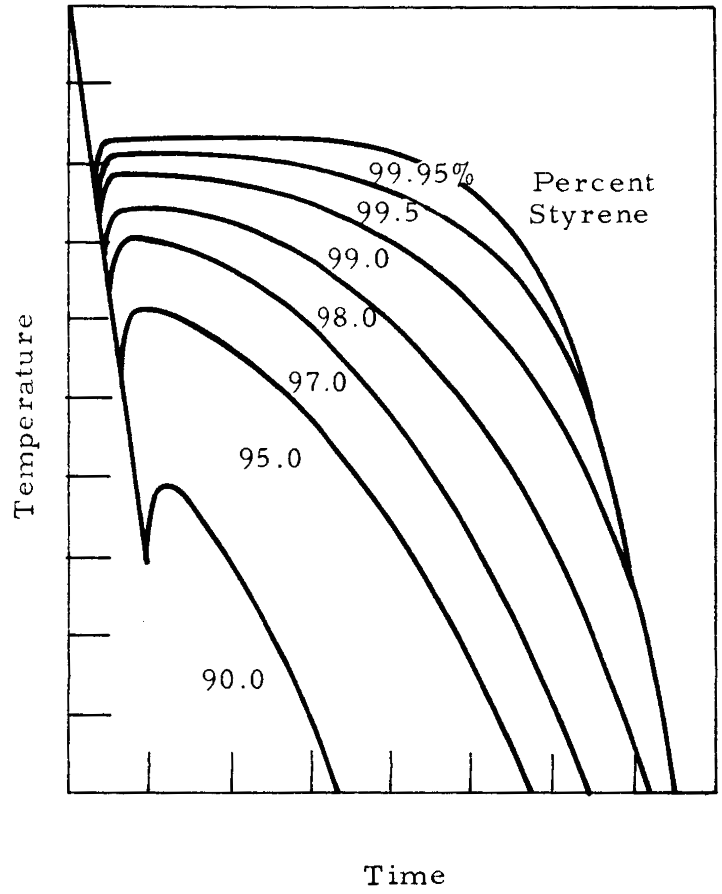


Figure 4 - Superimposed Freezing Curves of Styrene Diluted with Ethylbenzene (Reference 5)

The effect of impurities on the melting curves is illustrated in Figure 5.

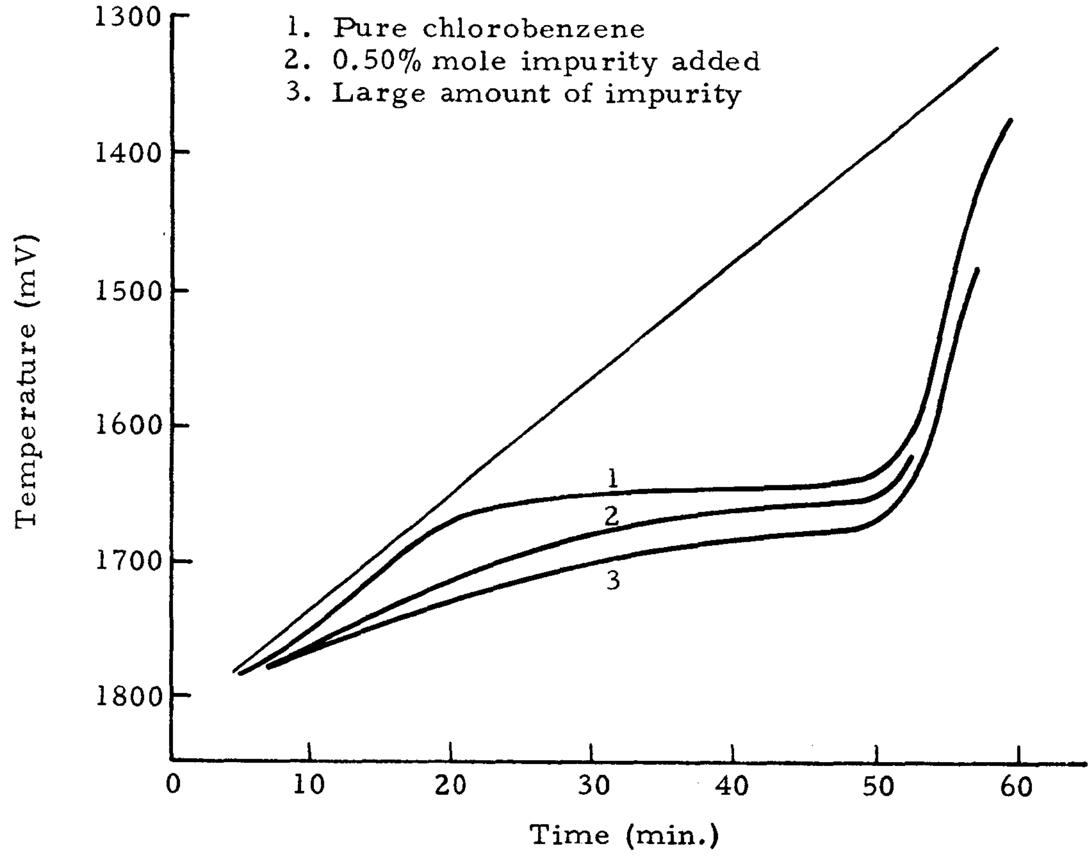


Figure 5 - Heating Curves (Reference 6)

The use of freezing and melting curves for determining the purity of materials is well established, and a sizeable body of literature on the subject exists (See Reference 7). Obviously, the subject of melting and freezing curves has many more aspects than can be discussed here. The preceding brief discussion, however, should serve to indicate the main general principles which guided the experimental evaluation of potential PCM materials.

2.2.2 First Screening Tests

The first screening tests of some 27 candidate PCMs were purposely crude. The experimental procedure consisted of placing PCM sample in a small flask or plastic container, melting the PCM, inserting a thermometer or thermocouple, and then placing the PCM container in a stirred ice bath. The temperature was observed as a function of time. Thermometers used were of the total-immersion types. Exposed stem corrections were not applied in the first screening.

The first screening tests served to screen out materials which showed extreme one- or two-phase supercooling. On the basis of the shapes of the freezing curves, it was possible to rate qualitatively the materials tested as potential PCMs. The first screening tests also served to provide a basis for devising the simple but more searching materials screening scheme described in Section 2.2.3.

The shapes of the freezing curves obtained in the first screening ran the gambit of behaviors that were considered possible. In addition, some unexpected types of shapes were observed. Considering the crudity of the experimental apparatus employed in this first screening, the relatively small departures from ideality exhibited by many of the compounds is surprising. Especially impressive was the small amount of two-phase supercooling exhibited by such high temperature melting compounds as $Ba(OH)_2 \cdot 8\,H_2O$, Cerrolow 136 Eutectic, stearic acid, and others. The magnitudes of the thermal heads during the freezing of these compounds under ice bath cooling was large (in the range of 58° to $78^\circ C$). The rate of cooling, therefore, was rather extreme.

The major class of materials eliminated in the first screening was a number of low melting eutectic combinations between the various hydroquinones and quinone – hydroquinone. The one eutectic combination tried, 1-1 pyrocatechol and resorcinol, showed such extreme one- and two-phase supercooling that further combinations were not tried.

Also eliminated in the first screening were the majority of salt hydrates which have incongruent melting points. These included sodium arsenate dodecahyrate, sodium sulfate decahydrate, and sodium carbonate decahydrate. The chief reson for eliminating these compounds was the lack of easy reversibility of the transition reaction. For sodium sulfate and sodium cardonate decahydrates, the addition of fillers or gels presumably would keep insoluble, lower hydrates suspended and thereby improve the reversibility. In one such experiment with sodium sulfate decahydrate, the addition of chopped glass fibers did improve the shape of the freezing curve. The improvement, however, was not marked. About the only advantage that sodium sulfate and sodium carbonate decahydrates offer over lithium nitrate is one of cost. Sodium sulfate decahydrate is commonly known as Glauber's salt and sodium carbonate decahydrate is common washing soda. For home heating purposes where large, tonnage quanities are being considered, it might be worthwhile to try to modify the properties of these two salts. Lithium nitrate is moderately expensive (presently $1.55 to $1.25 per pound, depending on amount bought) but not enough so as to eliminate its consideration.

The lack of reversibility of the fusion reaction of sodium arsenate dodecahydrate is easily understood when the solubility data is consulted (Reference 8). Sodium arsenate dodecahydrate has a transition point at 22°C where it transforms into liquid and the heptahydrate. Actually, the same condition should occur with sodium phosphate dodecahydrate. The transition in this case occurs at about 35°C. With the phosphate, however, the phase diagram shows that the compounds transition point is not far removed from being almost a congruent melting point (Reference 9). In present observations of the melting and freezing of sodium phosphate dodecahydrate no incongruent type behavior was noted, i.e., no separation of salt into liquid and lower hydrate was observed on melting or freezing. This observation confirms a similar observation reported by Telks (Reference 10, p. 50).

The results of the first screening tests are presented in Table 2. A rather subjective rating scale as a PCM (0 to 10, 0 poorest to 10 best) was set up for the materials that were tested A rating of seven or above was judged, again rather subjectively, as sufficient to qualifying a material for further tests. By this standard, some 16 of the materials tested survived the first screening.

2.2.3 Development of Experimental Plan for Detailed PCM Evaluation

The first screening tests, although adequate as a basis for selection of candidate PCMs, provided only very limited information on freezing-melting characteristics. As mentioned previously, an ice bath represents a rather extreme cooling environment for some of the higher melting temperature materials. Further information is also desirable on the effects of variables such as impurity kind and concentration, thermal cycling, container size and material, effect of fillers of various kinds, etc. The devising of an experimental scheme whereby the effects of all these variables can be easily assessed necessitated some preliminary experimentation.

Preliminary Experimentation: The first consideration in devising a more searching experimental evaluation is whether or not a particular material should be purified. As discussed in Section 2.2.1, the effects of too high a heating or cooling rate and of impurities can be very similar. It is desirable, therefore, to have a simple test which would indicate the presence of undesirable impurities.

The possibility of using differential thermal analysis (DTA) was explored briefly because DTA equipment was already on hand. Also, the literature on the subject indicates that DTA can be used not only to ascertain the

Table 2
RESULTS OF FIRST SCREENING OF CANDIDATE PCMs

	Chemical Formula	Reported Melting Temperature °C	Interpretation of Freezing Curve	Nucleation Supercooling Under Ice Bath Cooling	Freezing Behavior, Rating Scale 0 - 10 (poorest to best)	Further Notes
HYDRATED SALTS						
Lithium Nitrate Trihydrate	$LiNO_3 . 3H_2O$	29.8	Heat Controlled at beginning; kinetic controlled at end	Not observable with wire screen catalyst	9	
Barium Hydroxide Octahydrate	$Ba(OH)_2 . 8H_2O$	78	Heat controlled at beginning; kinetic controlled at end	Not observable	7	Easily contaminated by atmospheric CO_2. Forms $Ba(CO_3)_2$. Also, very corrosive to Al.
Disodium Phosphate Dodecahydrate	$Na_2HPO_4 . 12H_2O$	36.1	Heat controlled at beginning; kinetic controlled over sizable portion toward end	Not observable	8	Corrosive to Al Corrosion of Al be basic salt hydrates can be eliminated in some cases by inhibitors such as sodium silicate
Disodium Arsenate Dodecahydrate	$Na_2HAsO_4 . 12H_2O$	28	Formation of $Na_2HAsO_4 . 7H_2O$ instead of $Na_2HAsO_4 . 12H_2O$		1	
Sodium Carbonate Decahydrate	$Na_2CO_3 . 10H_2O$	33	Slight kinetic control throughout	$>5^\circ C$	6	Corrosive to Al
Sodium Sulfate Decahydrate	$Na_2SO_4 . 10H_2O$	31	Moderate amount of kinetic control	Not observable with Borax Catalyst	5	Performance improves with addition of fillers
Ferric Nitrate Enneahydrate	$Fe(NO_3)_3 . 9H_2O$	47.2	Large amount of kinetic control	$>28.7^\circ C$	1	
Lithium Acetate Dihydrate	$LiC_2H_3O_2 . 2H_2O$	58	None	$58^\circ C$	0	Very viscous melt. Extreme two-phase supercooling probable
METALS						
Gallium	Ga	29.8	Small amount of kinetic control throughout	Variable from 12 - 30°C	6	Very expensive
Ga-GaSb Eutectic		29.8	Major portion heat controlled	Variable from 2 - 11°C when solid GaSb particles present	7	Freezing behavior slightly better than just plain Ga

Table 2 Continued

	Chemical Formula	Reported Melting Temperature °C	Interpretation of Freezing Curve	Nucleation Supercooling Under Ice Bath Cooling	Freezing Behavior, Rating Scale 0 - 10 (poorest to best)	Further Notes
Metals Contd.						
Cerrolow 136 Eutectic	49Bi 18Pb 12Sn 21In	58	Heat control throughout	1°C	6	Heat of fusion too low, but freezing behavior excellent.
Cerrobend 158 Eutectic	50.0Bi 26.7Pb 13.3Sn 10.0Cd	70	Slight amount of two phase supercooling	None observable	8	Heat of fusion low, but high material density makes it a PCM candidate
ORGANIC MATERIALS						
Acetic Acid	CH_3COOH	16	Heat control through most of freezing	15°C	7	Crushed metals appear to have catalysis effect.
Choloracetic Acid	$ClCH_2COOH$	α61.2 β56.0 γ50.0	Small to moderate amount of kinetic control throughout	None observable	8	Very strong acid. Corrosive behavior to Al.
Methyl Fumarate	$(CH\ CO_2CH_3)_2$	102	Because of high melting temperature cooling environment room temp. Freezing shows small amount of kinetic control	None observable	7	Vigorous convection noted in melt. Compound appears to have peculiar surface tension properties
Acetamide	CH_3CONH_2	81 (69.4)	Heat control through most of freezing	None observable	9	
Cyanamide	$CN\cdot NH_2$	42.9	Small amount of kinetic control throughout	None observable	6	Very hydroscopic. Performance probably would have been better with purer sample. Disadvantage – low thermal decomposition temp.
Elaidic Acid	$C_8H_{17}CH{:}CH(CH_2)_7COOH$	47	Fair amount of kinetic control throughout	None observable	7	Sample quite impure.
Myristic Acid	$CH_3(CH_2)_{12}COOH$	58	Small amount of kinetic control throughout	None observable	8	
Stearic Acid	$CH_3(CH_2)_{16}COOH$	69.4	Small amount of kinetic control throughout	None observable	8	Stearic acid separates from glass on freezing.
Tristearin	$(C_{17}H_{35}CO_2)_3\ C_3H_5$	54.5 70.8	Fair amount of kinetic control throughout	None observable	7	
Glycerol	$C_3H_5(OH)_3$	18			1	Extremely difficult to freeze initially. Once frozen, however, refreezing no problem. Caused by memory effects.

Table 2 Continued

	Chemical Formula	Reported Melting Temperature °C	Interpretation of Freezing Curve	Nucleation Supercooling Under Ice Bath Cooling	Freezing Behavior, Rating Scale 0 - 10 (poorest to best)	Further Notes
Organic Materials Contd.						
Polyethylene Glycol 600 (carbowax)	$HO(CH_2CH_2O)_x$ CH_2CH_2OH	20-25	Small amount of kinetic control throughout	None observable	7	
1 Methyl – 4 Piperidone Hydrochloride Hydrate		94-95	Large amount of kinetic control throughout	None observable	2	
Oxazoline Wax TS970		74	Small amount of kinetic control throughout	2 - 3°C	8	Very inert compound sample – commercial product
Oxazoline Wax ES254		37	Small amount of kinetic control throughout	None observable	8	Very inert compound sample — commercial product. Freezing point higher than reported melting temperature.
Resorcinol-Pyrocathecol Eutectic		70	None		0	

purity of a material (Reference 11) but also to determine, qualitatively, thermal and kinetic properties (Reference 12). The use of DTA equipment was attempted but was soon abandoned because of equipment limitations. The simple Fisher Model 360 DTA was obtained mainly for a rough qualitative estimate of heats of fusion. It cannot easily be adapted to the rather specialized measurements that are required. The chief drawback of the equipment is the impossibility of positioning thermocouples so that they will remain centered and fixed during melting or freezing cycles. Another major obstacle is the necessity of constructing a chamber which can cool samples at a constant rate.

The consideration, however, of applying DTA to the characterization of melting and freezing behavior of a large number of diverse materials, along with the knowledge of freezing-melting curves gained in the first screening tests, did prove profitable. It led to an experimental scheme whereby a large number of diverse materials can be easily and quickly evaluated with a maximum yield of information. By some simple modifications of the Fisher DTA apparatus, it was possible to obtain melting and freezing curves at known heating and cooling rates. In the case of heating it was possible to utilize the capability of the Fisher DTA apparatus to maintain the heating rates at constant values.

Final Experimental Design: The experimental setup can be represented as shown in Figure 6.

When the apparatus is used for melting curves, the entire sample block is put into a furnace whose heating is controlled by the control thermocouple. The rate of heating can be set at from $0.5^{\circ}C/min$ up to $25^{\circ}C/min$. The highest heating rate actually used, however, was only $10^{\circ}C/min$.

Different, constant cooling rates, unfortunately, could not be attained with the apparatus. Moderate known cooling rates, however, were achieved by suspending the sample block over liquid nitrogen contained in a thermos

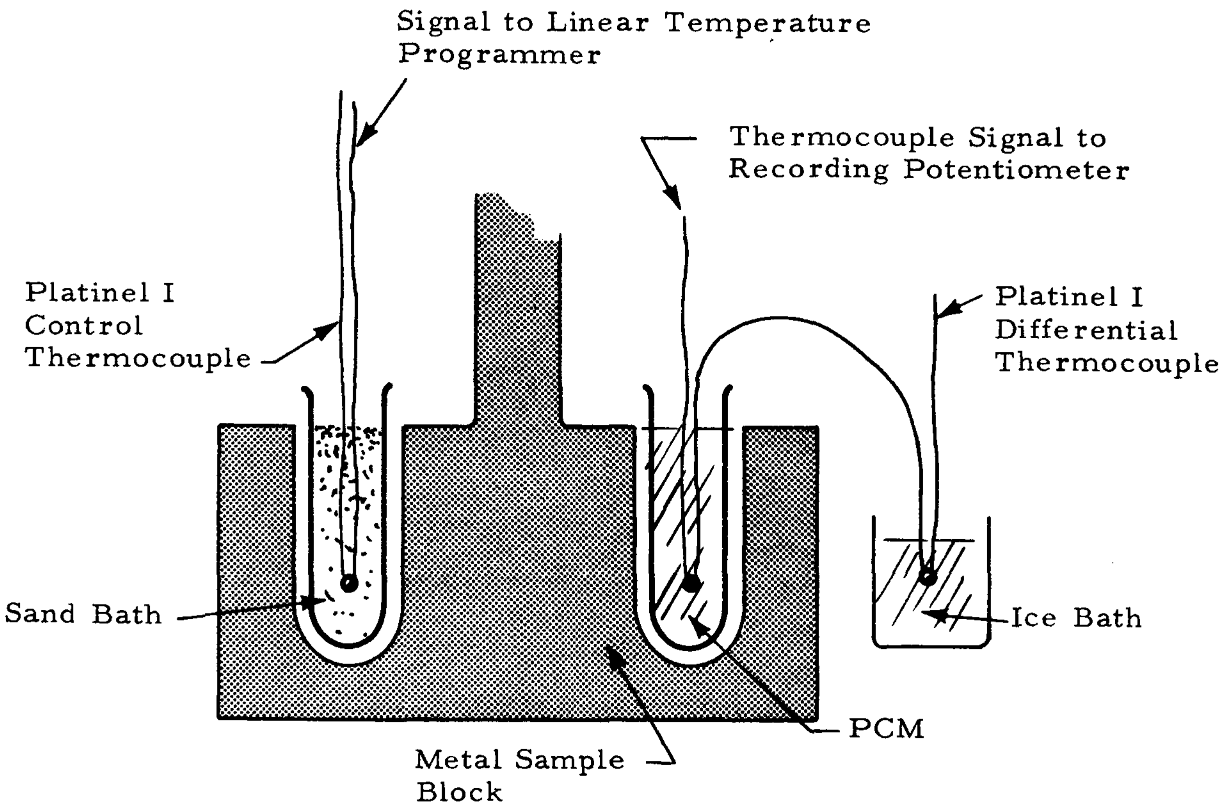


Figure 6 - Schematic Representation of Experimental Means Used to Obtain Melting and Freezing Curves

bottle. A cupped metal shield was used to damp out convective currents of vaporous nitrogen. The cooling arrangement is shown below in Figure 7:

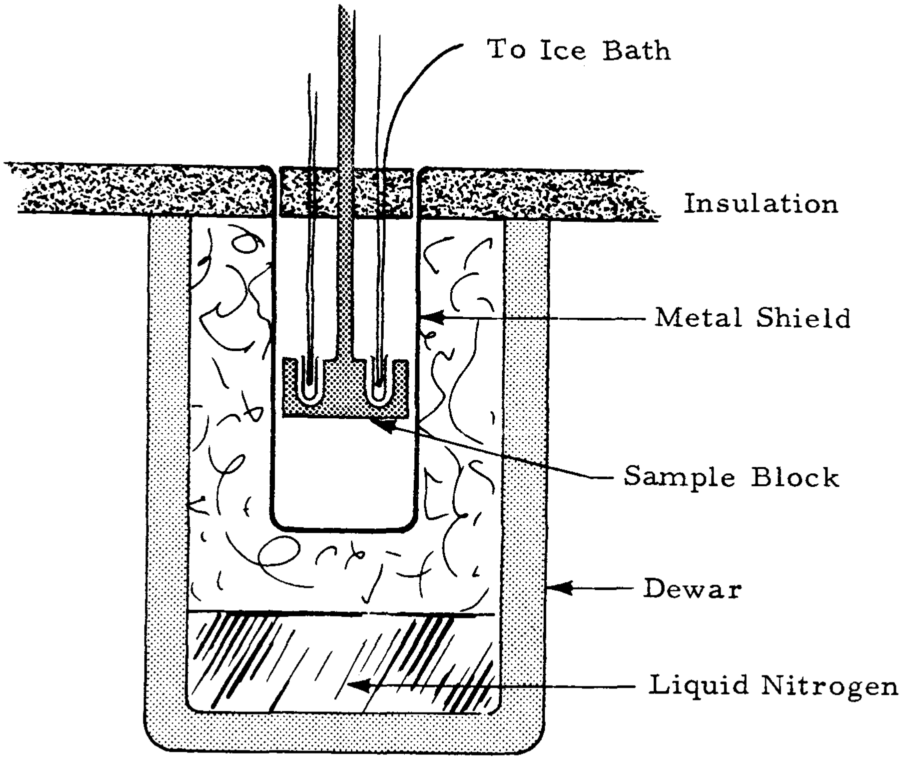


Figure 7 - Schematic of Experimental Arrangement to Obtain Cooling

By using another sample block, larger size samples could be run in the apparatus. The thermocouples were kept approximately centered and fixed through melting and freezing by slipping small plastic guards around the ceramic tube of the thermocouples. Although this expedient did lessen the wandering of the thermocouples, the problem was not solved. In addition another problem arose with the thermocouples. If both terminals of the differential thermocouple were immersed directly in an ice bath, a zero emf output was obtained. If one terminal was immersed in an ice bath and the other immersed in sample which in turn was immersed in an ice bath an emf corresponding to 2° to $3^{\circ}C$

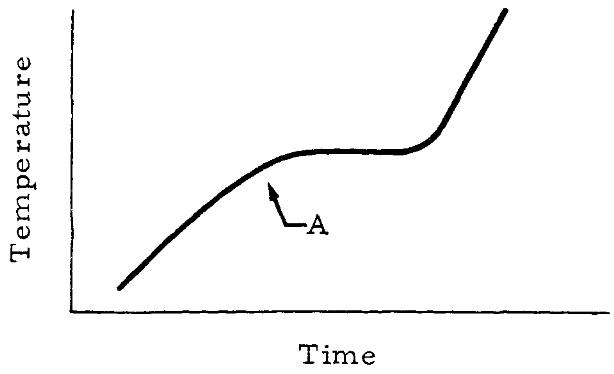
was consistently observed. It is inferred, therefore, that the thermocouples can act as heat sinks. What error this introduced in the melting-freezing curve was not ascertained. It is felt, however, that the shape of the curves was little affected.

With the preceding experimental setup, melting and freezing curves could be easily obtained. The size and kind of container, sample size, and heating rate, all could be varied. Also, the effect of thermal cycling could be checked easily.

The preceding apparatus, equipped with truly immobile thermocouples, should be capable of providing a quantitative estimate of the thermal diffusivity of the solid near the melting point. At steady state heating the temperature difference between the center of the sample and the surface of the sample is given by (Reference 13)

$$\Delta\theta = \frac{\beta a^2}{4k}$$

where $\Delta\theta$ is the temperature difference, β the constant heating rate, a the tube radius, and k the thermal diffusivity. From a melting curve it should be possible to determine $\Delta\theta$. This would be done by noting the temperature where the curve deviates from linearity. This point is designated as Point A on the following curve:



At Point A the surface of the sample can be assumed to have reached the melting temperature, while the temperature of the center of the sample can be read directly off the curve. Knowing the constant heating rate and the tube radius, the thermal diffusivity can easily be calculated.

Scheme of Evaluation Tests: A testing plan which was arrived at after careful consideration of the objectives of the present study and the physical interpretation of melting-freezing curves is presented in Chart 1. With this scheme it is felt that a material can be evaluated exhaustively as a potential PCM material within five to twelve experiments.

Results of PCM Evaluations Employing Refined Techniques: The curves obtained with the preceding apparatus for the test case of water and for some of the more promising PCM candidates from the first screening tests establish the validity of the principles applied. These curves, moreover, provide additional information on the effects of thermal cycling and catalyst performance. Adherence to the test plan presented in Chart 1 or rigorous interpretation of the data, however, was unwarrented in view of the previously mentioned unresolved equipment problems. Rather than try to resolve the present equipment problems, a more promising approach is described in Recommendations (Section 3). In the following paragraphs a summary of the meaningful results obtained by the refined experimental method is presented. The results are presented by material tested.

- H_2O

The most surprising observation was a $10^{\circ}C$ one-phase supercooling which occurred during a freezing run of water contained in a small quartz tube. A supercooling of this magnitude certainly was not expected, considering that the amount of water was relatively substantial, 0.19 mg, and no extraordinary effort was made to purify the water. The only purification procedure

Experiment	Conditions	Purpose	Possible Results	Meaning of Result	Further Experiments Indicated
① Melting curve	• Slowest heating rate • Small quartz tube	Check influence of impurities	a. No plateau or plateau short and below T_m b. "Ideal" curve c. Unexpected curve	a. Undesirable impurities b. Not undesirable impurities c. ?	a. Purify and repeat ① b. Go on to ② c. (1a)
(1a) Melting curves of: Fast frozen material Slow frozen material	• Same as ①	Pin down nature of unexpected behavior	a. Both curves have same shape b. Curves have different shape	a. Impurities not cause of unexpected behavior b. Impurities probably responsible	a. ? b. Purify and repeat ①
② Freezing curve	• Medium cooling rate • Small quartz tube	Check further on impurities; check freezing behavior	a. No plateau b. 1-phase supercooling c. 2-phase supercooling	a. Undesirable impurities b. Obvious c. Kinetic-controlled heat transfer	a. Purify and repeat ① b. Seek nucleation catalyst c. ⑤
③ Melting curves	• Different heating rates • Small quartz tube	Indication of thermal conduction	a. Curves identical shape b. Curves different shape c. Unexpected shape	a. Good thermal conductor indicated b. Poor thermal conductor c. ?	a. ④ c. ?
④ Melting curves	• Large pyrex tube • Different heating rates	Further indication of thermal conduction and convection	a. Curves identical shape b. Curves different shape c. Unexpected curve shape	a. Excellent conductor or convection b. Poor conductor c. ?	
⑤ Freezing curve	• Large pyrex tube • Medium cooling rate	Check further on phase kinetics	a. 2-phase supercooling b. "Ideal"	a. Poor kinetics indicated b. Good kinetics	
⑥ Melting curve	• Metal tube • Different heating rates	Check material compatibility with metal, especially wetting behavior	a. Material does not wet b. Material wets c. Other behavior	a. Poor thermally b. Good thermally	

CHART 1 - EXPERIMENTAL TEST PLAN FOR EVALUATING POTENTIAL PCM MATERIALS performed was one pass through a common deionizing resin. Certainly some impurities were introduced during manipulation of the sample into the test tube and apparatus. The surprising amount of water supercooling emphasizes that the rate of cooling is an important and too often neglected parameter of nucleation.

Other aspects of the freezing-melting curves of water are straightforward. No two-phase supercooling was evident. Also, the shapes of the curves as a function of heating rate indicate a sizeable thermal diffusivity. The value obtained for thermal diffusivity from water melting curves by the method outlined on page 29 was off by an order of 10 from the reported value: 0.048 ft^2/hr reported for ice, (Reference 14) $\approx$ 0.002 ft^2/hr obtained. This large deviation is not too surprising considering the difficulties with keeping the thermocouples fixed.

- $LiNO_3 \cdot 3H_2O$

In all of the freezing-melting curves obtained, no indication of complications arising from two-phase supercooling or superheating (if this is possible) was observed. The compound does show one-phase supercooling, but this can be overcome by the addition of catalyst (See Section 2.3). Melting curves of $LiNO_3 \cdot 3H_2O$ with added catalyst show about the same shapes as those without catalyst. The presence of catalyst in $LiNO_3 \cdot 3H_2O$, therefore, does not introduce any significant impurity effects.

Thermal cycling has not shown any effect on freezing-melting curves of $LiNO_3 \cdot 3H_2O$ with added catalyst. If the melt is maintained at temperatures far above the melting point for lengthy periods, however, the catalyst effectiveness is impaired. But after the melt is maintained at room temperature for some days, the effectiveness appears to be recovered.

The presence of dissolved gases does not adversely affect the freezing or melting behavior of $LiNO_3 \cdot 3H_2O$. In fact, were they not visually observed, the presence of bubbles would not readily be deduced from the freezing-melting curves. The bubbles, however, are very persistent and difficult to remove from the melt.

In all of the containers tested (quartz, pyrex and aluminum) $LiNO_3 \cdot 3H_2O$ showed excellent compatibility. No reaction or non-wetting effects were noted.

The shapes of the curves indicate that the thermal diffusivities of the solid and liquid phases approximate those of water.

- Na_2HPO_4 $12H_2O$

The melt without added catalyst showed variable one-phase supercooling. Two-phase supercooling was not observed. The shapes of the curves indicate that any impurities present exert negligible effect on the melting-freezing behavior. Also, as in the case of $LiNO_3 \cdot 3H_2O$, shape of the curves indicates that the thermal diffusivities of the solid and liquid phases approximate those of water.

- Oxazoline Wax TS-970

The melting-freezing curves of this compound are anomalous because of compound-container separation when the melt freezes, very low thermal conductivity, and apparently undesirable impurities.

The melting curve of the compound in a quartz tube shows a region where the temperature rise suddenly accelerates. This acceleration is interpreted as the result of a sudden contact between container wall and melt. After the sudden temperature rise, the temperature resumes a steady rise. The rate of this temperature rise, however, is fairly steep. It would appear, therefore, that undesirable impurities are present. In a larger pyrex tube, the melting curve shows no sudden temperature acceleration, although the whole curve has an odd shape. In this case a small area of compound-container contact remains after melt freezing. A continuous heat path, therefore, is always maintained.

The freezing curves of the compound show a variety of shapes depending on the container. All of the curves, however, show some amount of one- and two-phase supercooling. The worst case was about 21°C of one-phase supercooling. The amount of two-phase supercooling was only about 4° to 5°C even in the case of ice-bath cooling.

- Acetic Acid

Although some 10°C of one-phase supercooling was observed, no significant amount of two-phase supercooling was evident. The shape characteristics of the curves indicate that most probably the effect of impurities is slight, but that the thermal diffusivity is low.

2.3 CATALYST DEFINITION

2.3.1 Discussion

As indicated in Reference 1 a large element of luck is involved in finding a suitable nucleation catalyst for any given material. Only one theory is known which can somewhat guide the experimenter in his search for a suitable catalyst. This theory, mentioned earlier in Reference 1, designates as potent nucleation catalysts materials that have low-index planes in which the atomic arrangement is similar to that in certain low-index planes of the forming crystals. The problem with applying this theory is that a rather specialized knowledge of X-ray crystallography and its complex nomenclature is required.

The present study settled for searching out materials that have the same crystal structure as candidate PCM and possess lattice constants which closely match those of candidate PCMs. Even this approach is not without problems. For one, lattice parameters for a number of potential PCMs are either not listed in readily available sources or are not available. Secondly, a great number of the materials turned up are quite exotic and are not readily available. Their preparation would require a major effort. Finally, a great number of materials have to be rejected because of their solubility in PCM melt. A great number of materials also were tried as catalyts on hunch. One hunch — stressed metals — proved profitable for it led to a class of compounds called basic oxides which appear to have great possibilities as non-reactive nucleation catalysts.

The actual testing of materials for catalytic activity was also beset with problems. Some materials would work beautifully one day through any number of thermal cycles, only to show no activity the next day. With some catalytic activity would reappear after a time. In spite of all these difficulties a couple of apparently reliable catalysts for two of the most promising PCM materials were turned up in the present study. The results of the catalyst search for various PCM candidates are presented next. The presentation is organized by PCM material.

2.3.2 Results

$\underline{LiNO_3 \cdot 3H_2O}$: Without catalyst, $LiNO_3 \cdot 3H_2O$ will supercool about 30°C before crystallization begins. After a great number of materials were tried the discovery was made that some freshly stressed metal worked as nucleation catalysts at undercoolings of about 3° to 4°C. Unfortunately, most of the metals tried lost their catalytic activity after a day or so. Zinc metal, however, was remarkable for its persistent catalytic activity. The persistence of the catalytic effect with zinc led to the hypothesis that the active catalyst is a reaction product between zinc and $LiNO_3 \cdot 3H_2O$ melt. The first possibility considered was $Zn(OH)C\ell$. The beta modification of $Zn(OH)C\ell$ is reported to be orthorhombic with the following lattice parameters (Reference 15):

$$a_o = 5.86\text{A}, \qquad b_o = 6.58\text{A}, \qquad c_o = 11.33\text{A}$$

Lithium nitrate trihydrate is also orthorhombic. The lattice parameters are reported to be (Reference 16)

$$a_o = 6.82\text{A}, \qquad b_o = 12.78\text{A}, \qquad c_o = 6.05\text{A}$$

On the basis of the "mismatch" theory of nucleation, therefore, the compound $Zn(OH)C\ell$ would appear to be a promising candidate as a nucleation catalyst.

Unfortunately, a method of preparing crystalline β-$Zn(OH)C\ell$ was not found until recently. Material made by boiling down a solution of $ZnC\ell_2$ (Reference 17) did not show any catalytic activity. Either β-$Zn(OH)C\ell$ was not made by boiling down an aqueous solution of $ZnC\ell_2$ or β-$Zn(OH)C\ell$ is not a catalyst for lithium nitrate trihydrate.

In searching the literature for a method to prepare β-$Zn(OH)C\ell$, a method of preparing $Zn(NO_3)_2 \cdot 2\,Zn(OH)_2$ (Reference 18) was found. The method involves pyrolysis of $Zn(NO_3)_2 \cdot 6\,H_2O$. Material made by heating $Zn(NO_3)_2 \cdot 6\,H_2O$ on a hot plate in an open crucible has shown remarkable catalytic activity. It has invariably nucleated lithium nitrate trihydrate melt with only 1^o to 3^oC supercooling. Furthermore, it has retained its catalytic activity through any number of thermal cycles, provided that the melt was not heated too hot. If the melt was heated to about 100^oC and maintained at this temperature for a while, the catalyst lost its activity temporarily. On standing for a day or so, the activity was restored. The reason for the loss of activity after heating the melt excessively is not known.

From the experimental evidence, it is concluded that a basic oxide of zinc, most probably $Zn(NO_3)\cdot 2\ Zn(OH)_2$, is a nucleation catalyst for lithium nitrate trihydrate. Also, the catalyst will retain its activity through thermal cycling if the melt is not heated excessively.

$Na_2HPO_4\cdot 12\ H_2O$: The melt of this compound showed variable one-phase supercooling. The amount of one-phase supercooling appears to have some relation to the rate of cooling, but the relation was not explored further. A large number of materials were tried with negative results. Finally, it was noted that a melt of $Na_2HPO_4\cdot 12\ H_2O$ which had reacted a short while with a piece of tinned-iron metal crystallized through a number of thermal cycles with about 7° to 8°C supercooling. It is hypothesized that the compound causing the catalytic activity is a reaction product between iron and phosphate melt. Treatment of $Na_2HPO_4\cdot 12\ H_2O$ with pure tin did not result in catalytic activity.

The isomorphous compound $Na_2HAsO_4\cdot 12\ H_2O$ was found to be an excellent nucleation catalyst for supercooled $Na_2HPO_4\cdot 12\ H_2O$, as expected. The arsenate compound, however, melts at a lower temperature than the phosphate melt so that it is not a practical catalyst for the present application.

Gallium: A sample of gallium of unknown purity would always supercool by about 30°C before crystallizing. When a piece of antimony was added to gallium and portions of the liquid tested, variable supercooling was observed, depending on size of sample. The larger sized sample showed less supercooling.

After the preceding tests were carried out, a paper in the literature on the phase diagram of the system GaSb was found (Reference 19). This paper reported that gallium and the compound GaSb form a low melting (29.8°C) eutectic which undercools in gallium-rich mixtures. It would thus appear that GaSb is not a catalyst for gallium.

Acetic Acid: A great many materials were tried as catalysts for acetic acid with inconclusive results. Activated charcoal did show initial catalytic activity, but this activity disappeared after a few thermal cycles.

Glycerol: A great many materials were tried as catalysts for glycerol, but none showed the catalytic activity required. Glycerol, in fact, never was frozen in the present study. Even when a sample of glycerol was kept at liquid nitrogen temperature for three days and then subsequently warmed up to 0°C in a refrigerator, no crystallization resulted.

It is suspected that glycerol once nucleated will probably exhibit severe two-phase supercooling. The attempt to crystallize glycerol, however, was made because of an interesting conversation with Dr. H. Eyring, University of Utah. Dr. Eyring recalled the experience of scientists at Berkeley with glycerol. Once glycerol had been frozen no further trouble refreezing it was encountered. Glycerol apparently retains a "memory."

2.3.3 Conclusions

A basic oxide of zinc, most probably $Zn(NO_3)_2 \cdot 2\,Zn(OH)_2$, consistently nucleates lithium nitrate trihydrate within a 1° to 3°C supercooling range. The catalyst remains active through thermal cycling provided that the melt is not heated excessively.

An unknown reaction product between sodium phosphate and iron metal consistently nucleates sodium phosphate dodecahydrate within a 7° to 8°C supercooling range. This catalyst also retains its activity through thermal cycling.

2.4 FINAL EVALUATION OF PCM CANDIDATES

In Sections 2.1 through 2.3 the results of a literature search and of experimental studies of the melting-freezing characteristics of a number of potential PCMs are presented. These results are now considered in conjunction with other pertinent information and considerations so that four "best" materials can be designated as prime candidates as required in Task II (See Foreword). The quotes are used around the word "best" because the criteria set in Task II are quite general. For more specifically defined applications, more rigid criteria will undoubtedly be defined. In that case, it is possible that some of the materials designated "second-best" in the present study may turn out to be "best." It is obvious, however, that no one material is so perfect for all applications that further improvement of some of its properties is not warranted. A "best" PCM material for a specific application, in fact, cannot be designated unequivocally until all pertinent tradeoffs are evaluated.

In the first screening test, 16 materials received a rating of seven or above, thus qualifying them as candidate PCMs. These 16 materials are:

$LiNO_3 \cdot 3H_2O$

$Ba(OH)_2 \cdot 8H_2O$

$Na_2HPO_4 \cdot 12H_2O$

Ga - GaSb, eutectic

CH_3COOH, Acetic Acid

$C\ell CH_2COOH$, Chloroacetic Acid

$(CHCO_2CH_3)_2$, Methyl Fumarate

CH_3CONH_2, Acetamide

$C_8H_{17}CH{:}\,CH(CH_2)_7COOH$, Elaidic Acid

$CH_3(CH_2)_{12}COOH$, Myristic Acid

$CH_3(CH_2)_{16}COOH$, Stearic Acid

$(C_{17}H_{35}CO_2)_3C_3H_5$, Tristearin

$HO(CH_2CH_2O)_xCH_2CH_2OH$, Polyethylene Glycol 600

Oxazoline Wax TS970

Oxazoline Wax ES254

Cerrobend Alloy

If the criterion of non-reactivity with aluminum is set, the list above is reduced to 12. The candidate compounds barium hydroxide octahydrate, sodium phosphate dodecahydrate, gallium and chloroacetic acid are all corrosive to aluminum. In the case of sodium phosphate dodecahydrate, aluminum metal can probably be protected from corrosion by the addition of sodium silicate (water glass) to the melt. However, because the melting point of $Na_2HPO_4 \cdot 12H_2O$, 36°C, is so near that of $LiNO_3 \cdot 3H_2O$, 30°C, there does not appear to be any compelling reason for further considering $Na2HPO_4 \cdot 12H_2O$.

The next materials which came off second-best in an intra-comparison are the oxzaoline waxes, polyethylene glycol, stearic acid and tristearin.

The PCM-container separation observed with the oxazoline waxes in quartz and pyrex containers might also present a problem in aluminum containers. The point was not investigated further because other puzzling and unresolved features of oxazoline wax phase change behavior would have to be investigated further before a final evaluation could be made. In particular, although the DTA indicates a high heat of fusion, the wax-container separation complicates the thermogram to the degree than an equivocal statement about the value of heat of fusion is not possible. Also, the indicated low thermal diffusivity and presence of undesirable impurities make the oxazoline waxes a poor second in comparison to the other remaining 14 materials.

The compound stearic acid is eliminated from consideration as a prime candidate for two reasons. First, compound-container separation during freezing was observed for the case of a pyrex container. Also, although no unexpected freezing behavior was noted in the present study, reference is made in the literature to an irreversible polymorphic conversion (Reference 12, p. 179). Unfortunately, the original Russian reference (Reference 20) is not readily available. What the irreversible polymorphism means in terms of PCM performance awaits further study.

Tristearin also is eliminated from further consideration as a prime candidate because of a reported polymorphism (Reference 21). Under certain conditions the following sequence can occur:

> Solid I → Liquid I → Solid I → Liquid II; the transition Liquid I to Solid II is exothermic, having a heat of transition of -12.4 cal/gm.

Again, as with stearic acid, no unusual freezing behavior was actually noted.

Polyethylene glycol 600 exhibited good freezing characteristics. Its heat of fusion, however, is one of the lowest of the remaining compounds left in the list.

At this point the list of candidates for designation as prime candidates numbers seven. These seven materials are:

$LiNO_3 \cdot 3H_2O$	
CH_3COOH	Acetic Acid
$(CHCO_2CH_3)_2$	Methyl Fumarate
CH_3CONH_2	Acetamide
$C_8H_{17}CH{:}CH(CH_2)_7COOH$	Elaidic Acid

$CH_3(CH_2)_{12}COOH$ Myristic Acid

Cerrobend Alloy

The final selection of four prime candidates is based on rather subtle and intuitive considerations. Cerrobend, for example, has a very low heat of fusion on a gram basis — 7.78 cal/gm. On a volume basis, however, the value is a respectable 73 cal/ml. Because the other compounds have a much higher heat of fusion, however, Cerrobend is eliminated, even though its thermal diffusivity is undoubtedly much higher than that of the other compounds. For some applications Cerrobend will probably be superior to the other six compounds when all tradeoffs are considered.

Acetic acid is eliminated as a prime candidate mainly because a nucleation catalyst was not found in the present study to overcome the exhibited 16°C one-phase supercooling. Although a catalyst was not found in the present study, further effort will undoubtedly be successful. A secondary reason for disqualifying acetic acid as a prime candidate is that its volume expansion on melting is quite large (approximately 16%). One of the material criteria set forth in Task II is that thermal expansion above 15% is not acceptable.

The final elimination is elaidic acid on the intuitive and therefore nebulous grounds that the longer chain organic acids are more prone to polymorphic transitions than the shorter chain acids. No report, however, has been found in the literature of any polymorphism.

The volume expansion on melting for two of the four prime candidates was checked crudely by noting the volume of melt, allowing it to crystallize, and then noting the volume of the solid. Control over temperature or crystal form was not undertaken.

Lithium nitrate trihydrate and myristic acid show an approximate 8% increase in volume on melting. Acetamide is reported to also have an approximate 8% volume expansion on melting (See Table 1). The liquid density of methyl fumarate was determined to be about 1.0% gm/mℓ and the volume change on melting a rather high 18 to 20%. The volume change figure 18 to 20% is very approximate because methyl fumarate wet is pyrex container so well that it remained clinging to the walls when it crystallized. It was extremely difficult to estimate, therefore, the volume of the solid.

2.5 CONCLUSIONS

The four prime PCM candidates designated in the present study are:

- $LiNO_3 \cdot 3H_2O$ with added zinc hydroxy nitrate nucleation catalyst
- Acetamide
- Methyl Fumarate
- Myristic Acid

The order in which the compounds are presented represents a predicted effectiveness as PCMs. The order also represents to some degree the confidence with which the recommendation is made. Lithium nitrate trihydrate, because of its convenient melting point, was used as a test case in most of the development work. More data, therefore, was generated on it than on the other compounds.

Acetamide rates second place because of its relatively, for an organic compound, high density and low volume expansion on melting. On a volume basis the heat of fusion is a relatively high 67 cal/mℓ.

Methyl fumarate is ranked third because of its high expansion on melting. The observed 18 to 20% is above the limits set (15%) in Task II. This high volume expansion, however, may not be enough to disqualify methyl fumarate as a PCM especially when the properties of other PCM candidates are considered. For example, the paraffins have a low enough thermal diffusivity so that packing with metal foams has been considered. Packing with metal foams would increase not only the weight but also the volume of the PCM system. Very vigorous convection, on the other hand, has been observed in methyl fumarate melts. This convection may be largely the surface tension driven kind because the compound does appear to have unusual surface tension properties. If all of the tradeoffs are considered, therefore, it may turn out that methyl fumarate performs as well or better than a paraffin in a system which has the same internal container volume but with a considerable weight saving.

Myristic acid is placed fourth because of its low density and a feeling that it may exhibit polymorphism.

Section 3

RECOMMENDATIONS

A number of promising PCM candidates were singled out in the present study, but as indicated in Conclusions (Section 2.5), no one material was deemed so ideal that it could not stand improvement. The improvement most needed for many of the most promising PCM candidates is increased thermal diffusivity. The most promising way to increase thermal diffusivity in a given material is to add fillers. The addition of fillers, however, may alter the freezing-melting characteristics of the material. Thus, a means of easily checking the freezing-melting behavior of a potential PCM before and after filler addition is needed.

The development work in the present study on a refined experimental PCM evaluation provides the basis for a method of easily checking the melting-freezing behavior of a number of PCM-filler combinations.

It is recommended, however, that rather than try to adapt the sample container assembly of a Fisher Model 360 DTA apparatus, other commercial DTA apparatuses be surveyed for features which would make the instrument easily adaptable to determination of melting-freezing curves and measurement of thermal diffusivity. Should a suitable commercial instrument not be located, a sample chamber could be specially contructed.

The list of twenty-seven materials screened experimentally in the present study includes a fairly exhaustive variety of material classes — ionic salts, metals, organic esters, amides, acids, etc. The scope of the present study, however, did not permit extensive work on searching out, preparing, and testing any more than one or two representatives of each class. On the basis of the present work it is felt that materials from two of the classes should be examined more closely. In particular, less complicated organic hydrates than 1-methyl-4-piperidone hydrochloride hydrate should be sought. This organic compound showed a very large heat of fusion, but unfortunately also a very large degree of one-phase supercooling. Presumably, a simpler organic structure would result in more favorable freezing characteristics. Also, the fused salt eutectics should be looked at more closely. The material segregation problems observed in the present study might be avoided with binary eutectic combinations rather than the tertiary eutectic tried in the present study. One intriguing possibility is the combination of alkali nitrates with urea.

Section 4
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Appendix A

QUALITATIVE ESTIMATES OF HEATS OF FUSION BY DIFFERENTIAL THERMAL ANALYSIS (DTA)

In Differential Thermal Analysis (DTA) the temperature difference between a small sized sample and an equal amount of reference material is monitored as both are heated at a constant rate The temperature sensing device is a differential thermocouple, the ends of which are usually inserted directly into the sample and reference materials. The sample undergoes melting or other phase changes when heated, but the reference does not. The reference acts simply like a heat capacity. The sample phase change is accompanied by heat liberation or absorption. When sample and reference materials are heated the temperature difference between them is zero until a temperature is reached when the sample begins to undergo phase change or chemical reaction. At this point the sample temperature will begin to lag or exceed the reference material temperature. The temperature difference between sample and reference will increase until the phase change is complete. The temperature difference then rapidly returns to zero. A typical record of ΔT (temperature difference) vs T (temperature of sample surroundings) for fusion and then reaction is shown in Figure A-1.

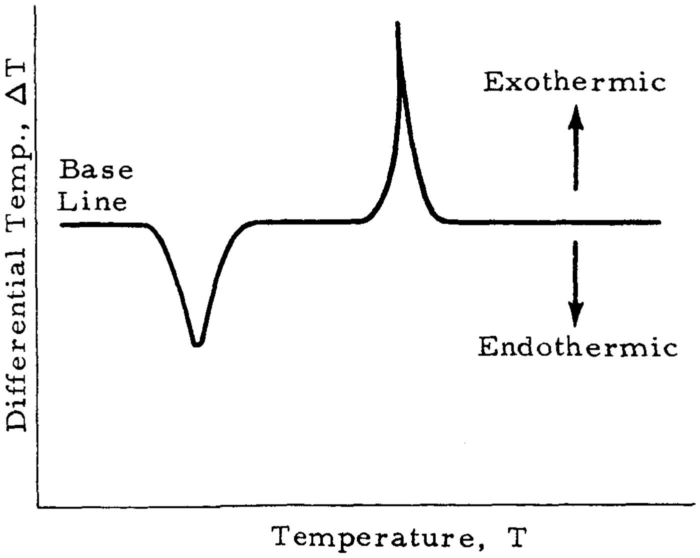

Figure A-1 - Typical Differential Thermal Analysis Curve (from Reference A.1)

Theoretically, the heat of reaction or phase change can be determined from the areas encompassed by the peaks. In practice quantitative DTA data is not easily obtained. Strict control of many operational variables such as sample size, sample form, choice of reference material, thermocouple placement, etc., is required.

The Fisher Model 360 DTA was used in the present study for determining qualitatively heats of fusion where the data were not found in the literature. The experimental procedure consisted of placing and melting the sample in a small quartz crucible. One end of a differential thermocouple was inserted directly into the melt; the other end of the thermocouple was placed in reference material (alumina sand). The sample was allowed to solidify around the thermocouple. The sample and reference were then heated in a furnace whose rate was controlled by a control thermocouple.

With the described experimental procedure only very qualitative data can be expected. Figures A-2 and A-6 are illustrative of the type of curves obtained. The major sources of error inherent in the procedure used are: starting from room temperature, the heating rates did not become constant until the temperature reached some 50 - 60°C; separation of solid sample from crucible wall led to what appeared to be exothermic peaks on the DTA thermograms in some cases (see Figure A-6); the appreciable volume expansion in some cases on melting made it difficult to keep the thermocouples adequately covered when the sample solidified; finally, positioning the thermocouples so that they would remain fixed through melting and solidification was not achieved adequately.

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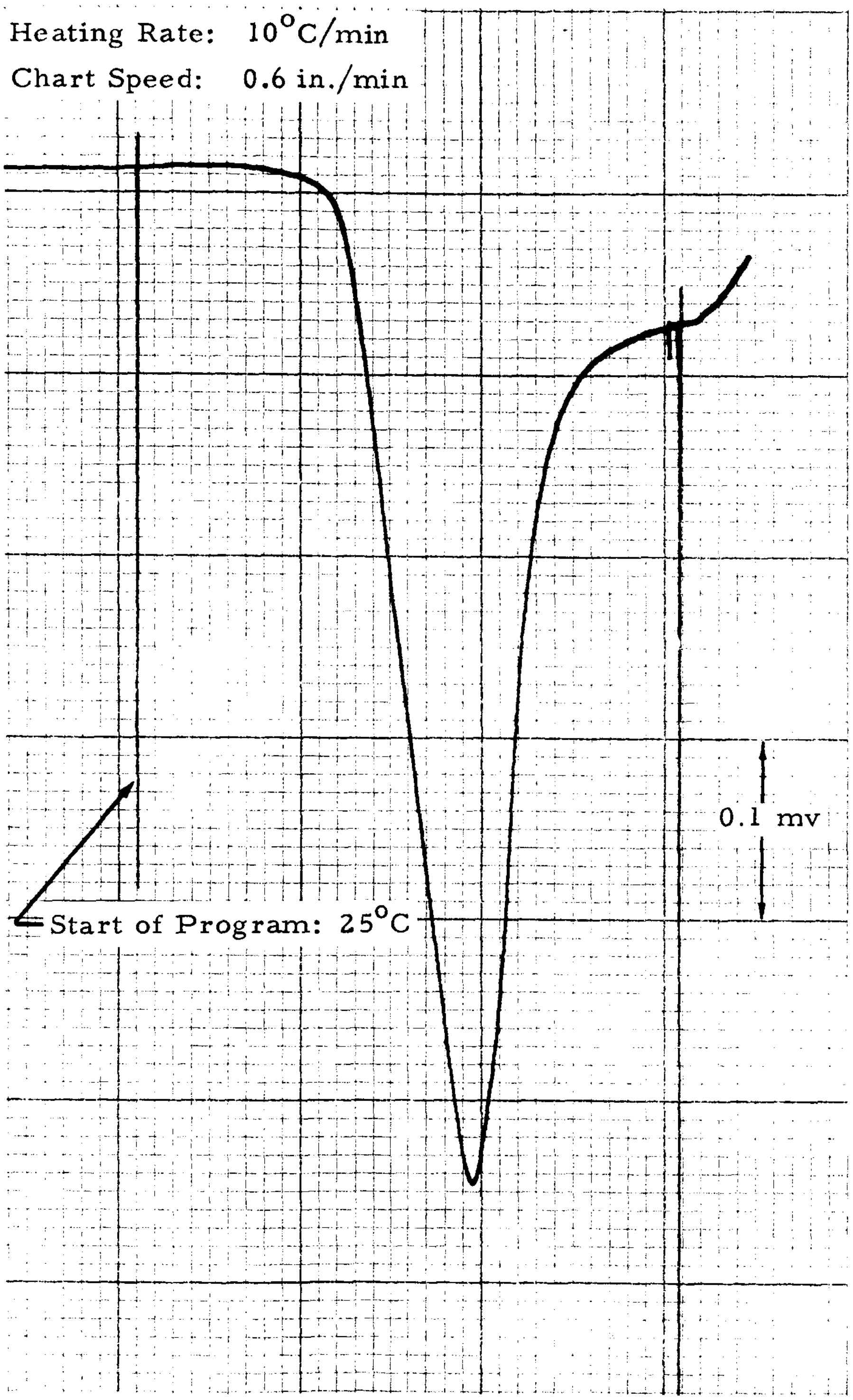


Figure A-2 - DTA Thermogram of Fused 88.2 mg $Na_2HPO_4 \cdot 12H_2O$

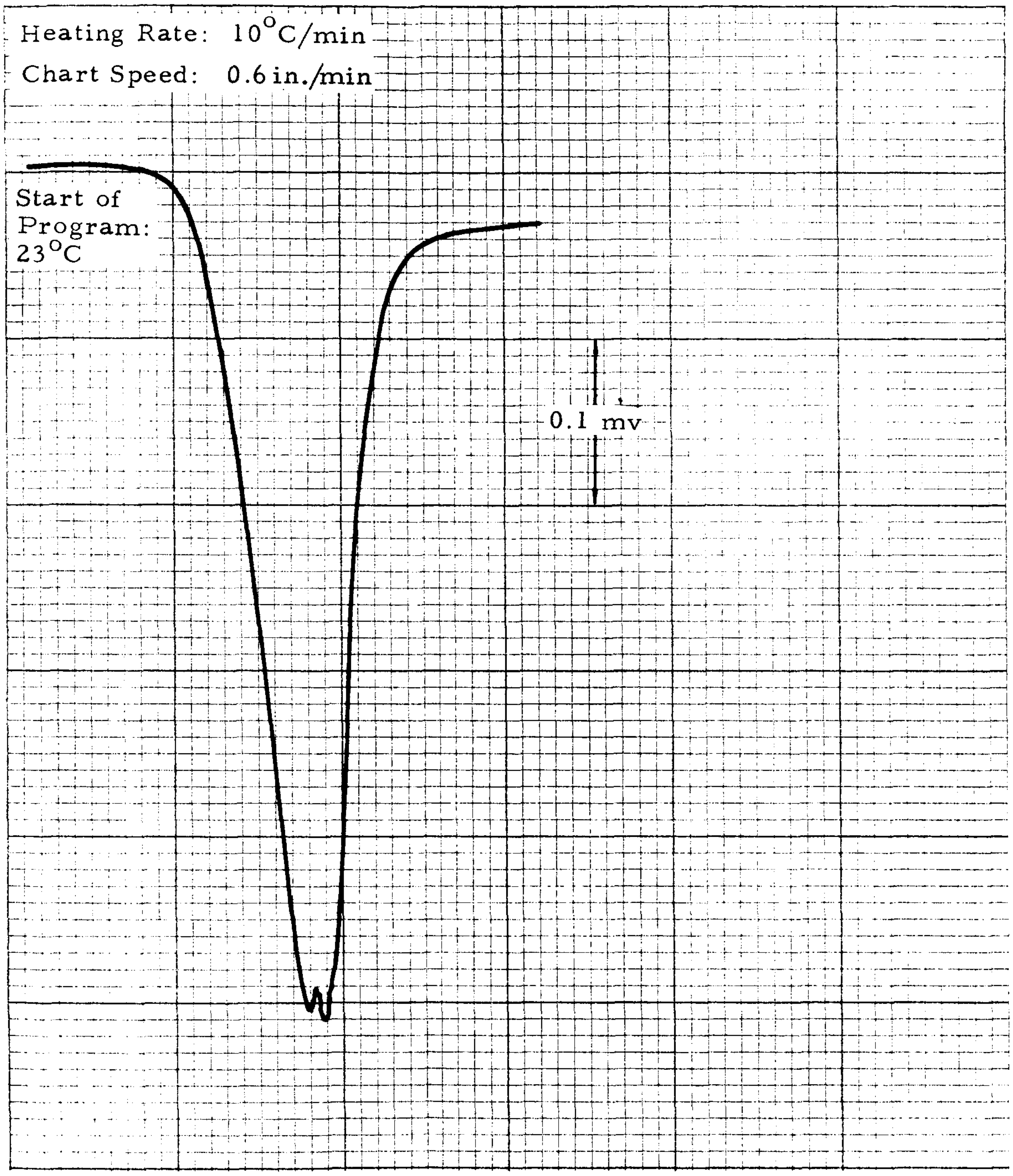


Figure A-3 - DTA Thermogram of 65.3 mg $LiNO_3 \cdot 3H_2O$ Reported Melting Point - 29.9°C

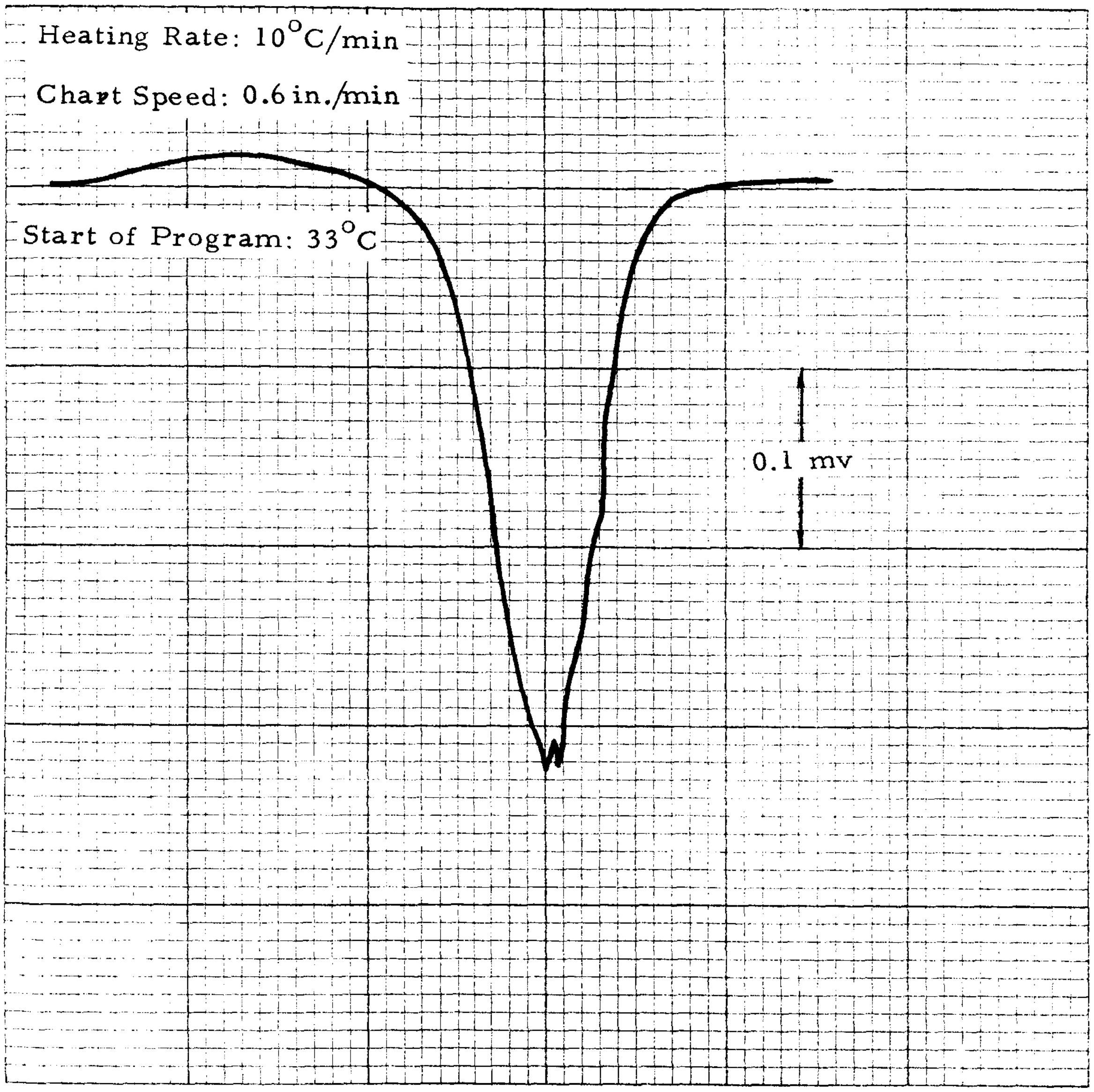


Figure A-4 - DTA Thermogram of 74.1 mg Acetamide Reported Melting Point - 81°C

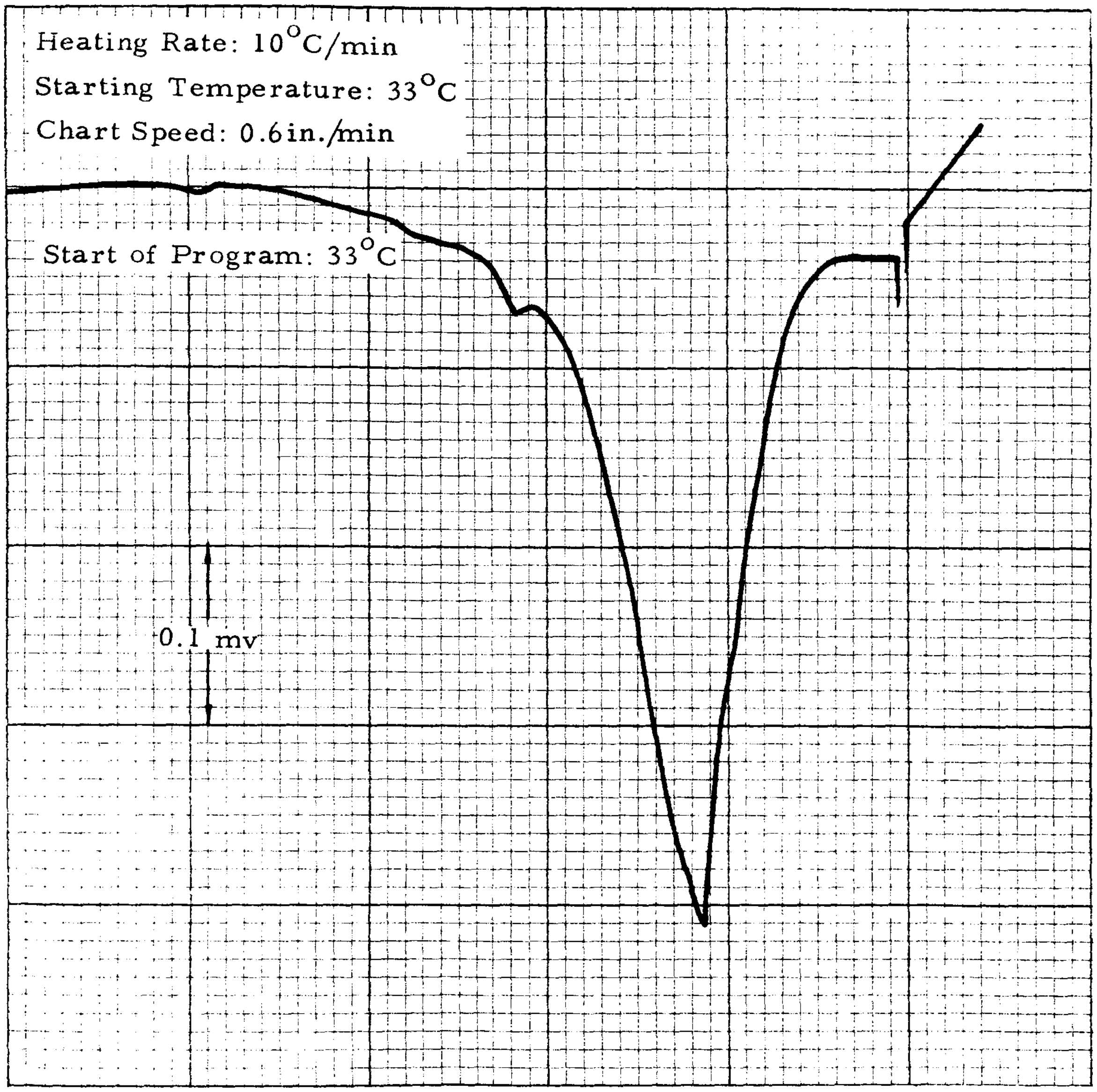


Figure A-5 - DTA Thermogram of 73 mg Dimethyl Fumarate Reported Melting Temperature - 102°C

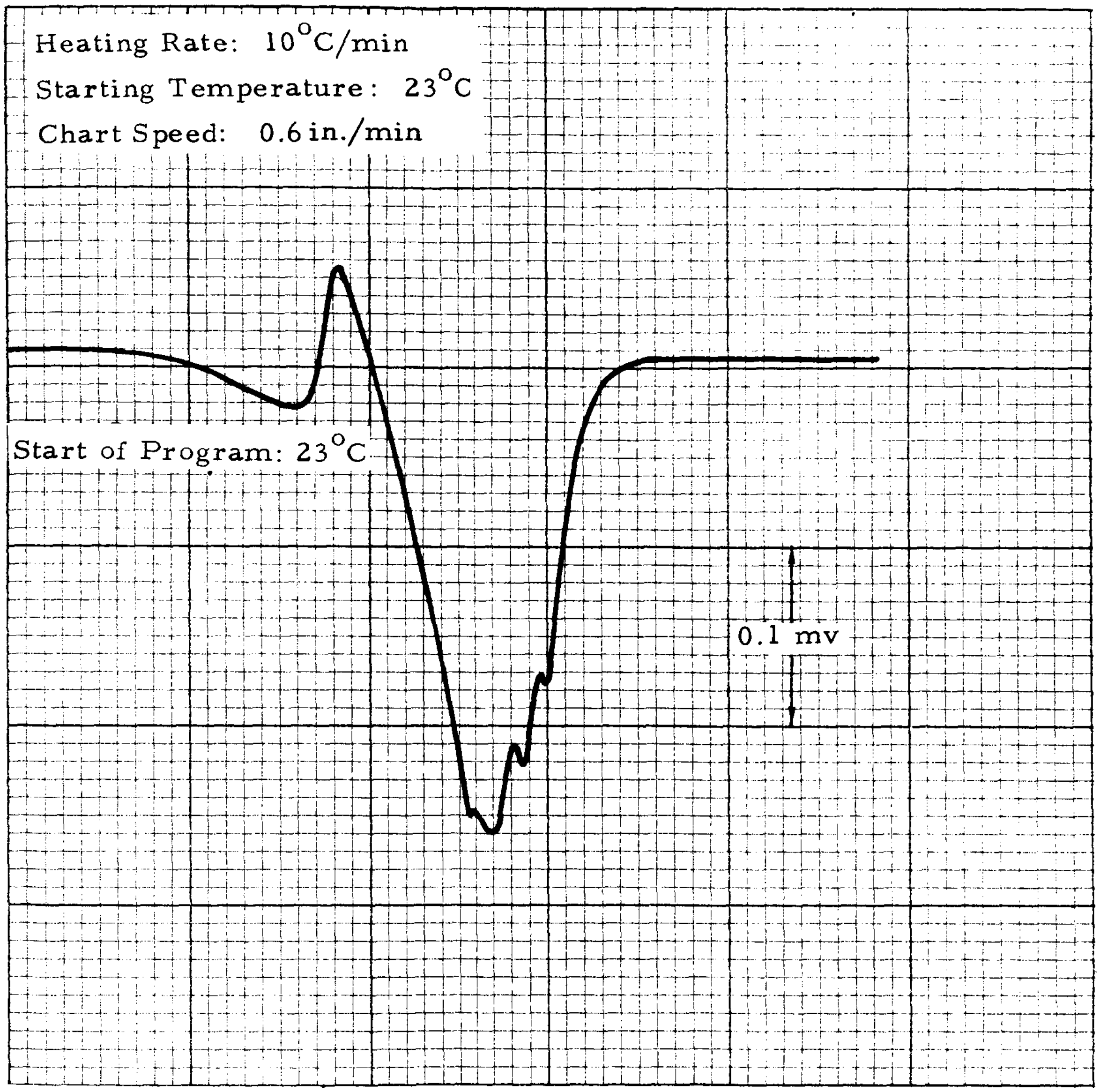


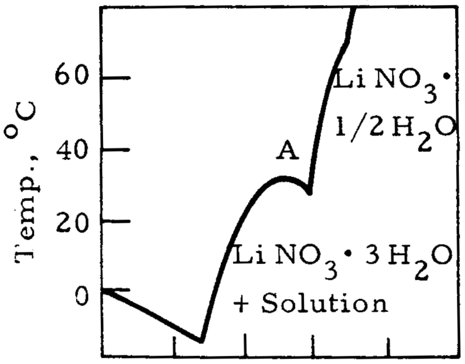
Figure A-6 - DTA Thermogram of 73 mg TS-970 Oxazoline Wax
Reported Melting Point - 74°C

Appendix B

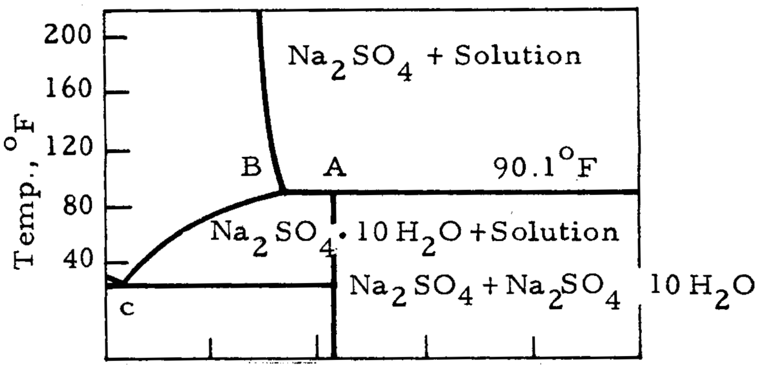
TYPES OF PHYSICAL DIAGRAMS IMPORTANT IN PHASE CHANGE MATERIAL SELECTION

B.1 CONGRUENT AND INCONGRUENT MELTING POINTS

In the case of the class of compounds consituting the salt hydrates, the melting points can be either congruent or incongruent. A consideration of the phase diagrams of $Na_2SO_4 \cdot LiNO_3$ and $10\,H_2O \cdot 3\,H_2O$ illustrates the differences.



(Reference B.1)



(Reference B.2)

In both diagrams the Point A corresponds to the percentage of salt in the salt hydrate compound. In the case of $LiNO_3 \cdot 3H_2O$ this Point A coincides with the maximum in the curve. Point A, therefore, represents the melting point of the compound $LiNO_3 \cdot 3\,H_2O$.

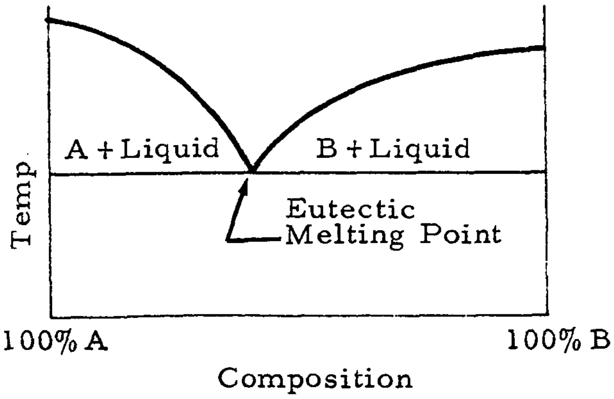
In the case of $Na_2SO_4 \cdot 10H_2O$, Point A does not coincide with any maximum. If a gram molecular weight of the compound $Na_2SO_4 \cdot 10H_2O$ (322.22 gm) were heated to 90.1°F, a clear solution would not be obtained. Rather a solution and 3.22 gm anhydrous Na_2SO_4 would result. If such a mixture were cooled very slowly and with constant agitation, solid $Na_2SO_4 \cdot 10H_2O$ would crystallize and the temperature would remain nearly constant until all of the melt solidifies.

In a gravity field the anhydrous Na_2SO_4 formed on melting $Na_2SO_4 \cdot 10H_2O$ would sink to the bottom. On cooling the mixture the settled anhydrous Na_2SO_4 becomes coated with $Na_2SO_4 \cdot 10H_2O$ and thereby becomes effectively removed from the solution. The solution left continues to deposit $Na_2SO_4 \cdot 10H_2O$, but the temperature does not remain constant. Rather it varies along the line B-C.

In a 0-g field, the crystallization would be closer to equilibrium crystallization. In an 0-g field the solid particles of anhydrous Na_2SO_4 would remain suspended. A more nearly equilibrium condition would then be realized.

B.2 EUTECTICS

The phase diagram of a two-component system which forms a eutectic is shown as follows:



The composition of the eutectic consists of separate crystals of A and B. Ideally, a eutectic would melt and freeze like a pure, one-component material. In reality a number of non-equilibrium effects can be expected.

APPENDIX B REFERENCES

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