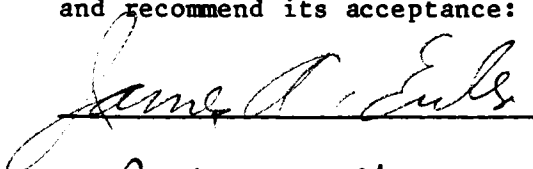
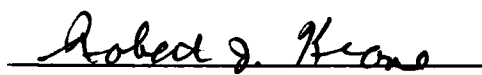


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AN INVESTIGATION OF THE THERMAL TRANSPORT PROPERTIES
OF OCTADECANE, A MATERIAL USED IN THERMAL
ENERGY STORAGE SYSTEMS

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Richard G. Irby

August 1985

To my family, especially Dad

ACKNOWLEDGMENTS

I would like to thank all of the people who assisted me in the course of this research. I am particularly indebted to my Major Professor, Dr. Roger Parsons, and thesis committee members, Drs. Robert Krane and James Euler. Their guidance, encouragement, and patience were essential to my work. However, any errors or omissions which may remain are entirely my responsibility.

I wish also to thank Drs. John R. Missimer and Edward Keshock of The University of Tennessee, Dr. Allen Solomon of the Oak Ridge National Laboratory, and Dr. Ralph Deal of Kalamazoo College for their encouragement and suggestions concerning the direction of this research. I wish to thank the administrative, technical, and clerical personnel of the Oak Ridge National Laboratory who helped me perform and report this research.

I would like to thank my friend, John Castleman, for his expressions of confidence.

ABSTRACT

An investigation of the thermal transport properties of solid octadecane is presented. A literature search revealed that few data concerning those properties have been published, and that those that have been published were not consistent. An experimental program was developed to determine the value of the material's thermal properties and to find an explanation for the inconsistencies in the published data. The program included three different types of experiments; a freezing experiment which produced the ratio of the thermal conductivity to the product of latent heat and density, a conduction experiment which produced values of thermal diffusivity, and a series of "line source" measurements of thermal conductivity. The results indicated that, for the sample used, the thermal properties did indeed vary in a systematic way, and that the results depended on sample preparation and the method of measurement.

The probable causes of the variations in the reported data are shown to be failures to account for (1) voids which form in the solid and (2) natural convection in the liquid during freezing.

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LIST OF SYMBOLS

A	coefficient of a fitted curve
a	radius of the wire probe used (in line source technique)
B	coefficient of a fitted curve
b	radius of the bounding cylinder (in line source technique)
c	specific heat
DC	digital conversion value
DVM	digital volt meter
E	fractional error
F	calibration factor
L	latent heat of fusion
l	thickness of a confined material or length of the wire probe used in the line source technique
LST	line source technique
q	heating rate for a line source, or heat transfer rate
R	resistor or resistance
S	switch
T	temperature
t	time
V	voltage
X	location of the phase front in a freezing experiment or in the Neumann solution
x	distance on a coordinate axis
x*	a transformation variable used in place of the independent variable, x, when the thermal diffusivity varies

Y	a curve fitting variable, $= \ln[T(x,t) - T_f(t)]$
α	thermal diffusivity
α_Ω	temperature coefficient of resistance
γ	Euler's constant ($=0.57716\dots$)
Δx	change in the value of the variable represented by x
λ	characteristic constant in the Neumann's solution
ρ	density
τ	a time constant in exponential decay of a temperature profile
Ω	electrical resistance
ω	a parameter used in the line source evaluation, ($=2 c_m \rho_m / c_w \rho_w$)

SUBSCRIPTS:

BR	bridge
c	calibration
e	effective
f	face
I	current measuring channel
i	initial
l	liquid, or linear (in line source technique)
m	melting, or test material (in line source technique)
n	dummy subscript
o	output
PCM	phase change material
r	reference

RTD	resistance temperature detector (the probe used in the line source technique)
s	solid or surface
VO	voltage measuring channel
w	wire (in line source technique)
Ω	resistance
1	low temperature phase
2	high temperature phase

I. INTRODUCTION

Octadecane is a member of the hydrocarbon family called alkanes or parafins which have been used in various devices or a medium for the storage of thermal energy. The performance of such devices is influenced by the thermal transport properties of the energy storage medium. There is considerable disagreement in the literature concerning these properties in octadecane. Table I.1 shows various values of thermal conductivity reported by researchers. The large variation in these values makes the predicted performance of thermal devices uncertain. The work reported here is an attempt to determine the nature of these properties and possibly to find the reason for the disagreements.

Thermal energy storage systems (TESS's) are devices which can temporarily store low grade thermal energy. Such devices have been widely used in space flight to store heat generated by electrical equipment until release to the environment is possible. Recent efforts in energy conservation have also focused on TESS's for their possible use in matching intermittent energy sources, such as solar energy or waste process heat, with intermittent demands, such as for batch processings needs as residential heating. Regardless of the specific application, the general function of a TESS is to absorb and store thermal energy for a period of time and then release it when desired.

Table I.1. Reported Values of Thermal Conductivity
for the Solid Phase of Octadecane

Source	Thermal Conductivity (W/M°C)
Pizzolato and and Farmer [22]	0.15
Bailey and Davila [1]	0.164
Powell and Challonar [23]	0.19
Bailey and Liao [2]	0.41
Griggs and Yarbrough [11]	0.35
Deal, Irby, Keshock and Soloman [9]	0.525, 0.56

The performance of a TESS depends on two factors, the amount of energy that can be stored and the rate at which energy can be absorbed or released. These factors are never totally independent and may be quite interrelated. As the amount of energy in a TESS approaches the extremes of its capacity the heat transfer is inhibited. The degree to which this occurs depends on the design and application of the TESS.

The capacity of a TESS is determined by the amount of storage material available and its ability to store energy. Some TESS's employ a thermal mass which absorbs energy in the form of sensible heat. The capacity of such a system would be determined by the size of the thermal mass, the specific heat and the average change in temperature experienced. Other TESS's store energy as latent heat of a material undergoing phase change. In such cases the capacity would depend on the latent heat of the phase change material, PCM, and the amount of the material.

The rate of energy storage in a TESS depends on the heat transfer process both internal and external to the thermal mass. The external mode of heat transfer may be radiation, conduction, convection or a combination of any, depending on the application. The same applies to the internal mode of heat transfer, though radiation is less often important. All of these natural heat transfer processes are driven by temperature differences, and depend on various material properties.

The interdependence of the capacity and storage rate of a TESS is readily seen. As the energy content of a sensible heat storage system approaches its extremes the heat transfer is driven by a smaller and smaller temperature difference. In latent heat storage systems the overall temperature difference may not change, but the energy must be transferred internally through more of the PCM as it changes phase. The internal heat transfer process may be of such a nature that the material properties of the PCM are of minor importance, but their influence can never be completely eliminated.

When a TESS uses a PCM for the energy storage medium the system may also be called a phase change device, which has been more generally defined by Humphries and Griggs [16] as a "component which is used to either thermally control a medium or store energy by utilizing a material which undergoes a phase change." Humphries and Griggs also list a number of applications of the devices and the important desirable properties of the phase change material. The most important properties listed are high heat of fusion and proper melting temperature. Other desirable characteristics indicate a need for rapid heat transfer, stability, affordability and a generally benign character. The alkanes, or parafins, are cited as prime candidates and it is stated that they are widely used. Various parafins listed by Hale, et al [13] have melting points from -12°C to 71.0°C and latent heats of fusion from 200 kJ/kg to 256 kJ/kg. Their wide range of melting temperature and their other properties indeed make them suitable for many applications.

Octadecane has a melting point of 28°C which is slightly above room temperature and makes it easy to study in the laboratory. It is also comparatively inexpensive and readily available from several suppliers. Because it is typical of many of the parafins, and is convenient, octadecane is often used in research. The findings of such research should be expected qualitatively to apply to other parafins. The experiments reported here were conducted with octadecane.

II. BACKGROUND

A survey of the literature revealed that while the thermal conductivity of liquid octadecane is well established, considerable disagreement exists over the value for the solid. The value of $0.15 \text{ W/m}^\circ\text{C}$ for liquid octadecane, or the equivalent has been published by several researchers [2, 13, 16, 22, 23, 27]. Table I.1 shows the values reported by various researchers for the thermal conductivity of solid octadecane. The values vary by a factor of over three.

Two of the values in Table I.1 can be discarded. The value of $0.15 \text{ W/m}^\circ\text{C}$ is discarded because the researchers apparently assume the solid and liquid values were the same. This was pointed out as an erroneous assumption by Humphries and Griggs [16], who were aware that published values varied. The origin of the value used by Bailey and Davila [7] is not known, and they apparently obtained it elsewhere for use in experimental predictions. The experimental results showed more rapid freezing than their calculations predicted which indicates the thermal conductivity is actually higher. The indicated value was not determined by them.

The work reported by Powell and Challonar [23] dealt with thin films. A steady state guarded-plate apparatus was used. They were primarily interested in the liquid thermal conductivity but included measurements from the solid. They explained a couple of high measurements ($0.20 \text{ W/m}^\circ\text{C}$) as being due to the existence of certain crystalline forms shortly after solidification. Their measurements are among the

lowest for the solid. The only explanation that can be suggested for the low results is that gas pockets may have formed during the freezing process. It has been found by this author that freezing parafins without the formation of voids requires extreme care.

Bailey and Davila [1] were reporting the use of a new technique for determining the precise location of the phase front during one-dimensional freezing experiments. The phase front locations found in their experiments [1], were used by Bailey and Liao [2], who determine the value of thermal conductivity required to force agreement of calculated and experimental results. Griggs and Yarbrough [11] used two steady state cylindrical thermal conductivity measuring devices to obtain values of 0.374 W/m²K to 0.317 W/m. Their technique was well developed but two of the temperatures, 30°C and 35°C, at which measurements were made are above the melting point of octadecane and are thus suspect.

The work of Deal, Irby, Keshock, and Solomon [9] led to the work reported here. Their work included two independent determinations of thermal conductivity. The first determination was made by comparing experimental results with results generated by a finite difference program, TES, developed by Solomon and Serbin [24]. The unique feature of the finite difference technique is that the state of each node is determined by the amount of energy associated with it. The energy of each node is advanced with the finite difference scheme. Temperature and other properties are specified as functions of the nodal

energy. The "measured" values of thermal conductivities were the values found by trial and error which, when used in TES, produced the best agreement with the experimental results. The researchers were surprised to find such a high value for the thermal conductivity of the solid. A very high conductivity indicated for the liquid ($6.2 \text{ W/m}^\circ\text{C}$) was due to a considerable heat transfer rate through natural convection to the walls of the test cell. This value was not presented as a conductivity measurement for the liquid.

The other measurement of thermal conductivity by the same researchers was made with a thermal comparator. This device produces a small voltage which indicates the interface temperature of a pointed probe when touched to the smooth surface of a sample. The thermal conductivity of the test sample is determined by comparing the indication produced by it with indication produced by samples with known conductivity. The results indicated even higher thermal conductivities. Unfortunately, the researcher did not take adequate precautions to avoid melting at the contact point. It is now believed by the researcher that melting did occur, and the energy absorbed by the melting process lowered the probe temperature so that a higher than actual thermal conductivity was indicated.

III. PURPOSE AND OBJECTIVES

The data so far reported indicate that there is a considerable uncertainty associated with the thermal properties of high purity alkanes. To help clarify this situation the experimental program reported here was carried out. The program included several independent experiments each of which would produce values of thermal properties. It was originally expected that the three experiments would produce results which would be in agreement and that the true and proper thermal conductivity would have been determined. This expectation was eventually discarded.

The experience of previous researchers indicated that the variation in thermal properties could be real and possibly be caused by the freezing process. Deal [9,10] had found that regardless of the steps taken to de-gas his apparatus, bubbles formed at the phase front during the melting process. He concluded that voids had formed in the solid during the freezing process. Thomas and Westwater [25] reported on the growth of crystal at the phase front in the freezing process for octadecane. Crystal structures were readily observed on the surface of the PCM container used in the experiments reported here. The arrangement of the crystals and voids could affect the indicated thermal properties.

This program was aimed primarily at the determination of thermal conductivity and its variation in octadecane. The experiments were also expected to reveal the influence of other properties on the phase

change process. They were conducted in a typical experimental phase change device and all were conducted on the same material. Three types of experiments were conducted.

The first experiment was an elementary phase change process. One-dimensional freezing occurs due to conduction of heat out of the PCM cell through one end which is held at constant temperature. The classical solution of the governing equation, derived by Neumann, requires only a few reasonable assumptions. This process is basic to phase change energy storage and produces a comparison of the thermal conductivity to the latent heat of the PCM. The procedure is similar to those used by previous investigators [2,9].

The second type of experiment was a one dimensional conduction experiment without phase change. The procedure is similar to that of the first experiment except that the initial condition is solid PCM and heat is removed from both ends held at constant temperature. The solution to the governing equation is a Fourier series and can be found in many mathematical texts. The heat is conducted in the same direction as in the phase change experiment so that the results should be comparable except that the measured property is thermal diffusivity, not conductivity. The solution used here involves a special transformation variable. Though it is elementary, no previous references to the technique have been found. This may be because the solution is an infinite series, a problem that was avoided here by a technique to be discussed in Section IV.

The third technique is called a line source technique (LST). This technique uses the temperature history of an electrically heated thin wire to indicate thermal conductivity. The classical solution to this problem was given by Carslaw and Jaeger [7]. The technique produces values of the thermal conductivity averaged through all directions radial to the thin wire. The measurement is very localized since only the region very near the wire is involved.

Comparison of the results of the three measurements is expected to provide insight which could not be achieved otherwise. The first measurement provides the value of thermal conductivity which is indicated by the phase change process. The second measurement through an analysis procedure to be discussed later, provides data on the variation of the thermal diffusivity in the solidified PCM. The third experiment provides a measurement of thermal conductivity at several locations in the PCM. The average of these measured values in the third experiment which were obtained without phase change will be compared with the results of the first measurement to determine if the measuring technique had any influence on the results. The results of the second and third experiments will be analyzed in an attempt to understand the possible variation of the thermal properties.

IV. THEORETICAL BASIS FOR MEASUREMENTS

The measurement techniques used here are based on the solutions to basic problems in heat transfer. These problems are governed by differential equations dictated by the physics of heat transfer. With the aid of various assumptions and the application of boundary conditions, the differential equations are solved to obtain mathematical expressions for temperature or other data important to the problem. These expressions may, in turn, be solved for the thermal properties necessary to describe the physics involved.

Physical experiments which simulate each of the basic problems were conducted and data were measured or calculated and recorded. These data were substituted into the mathematical expressions derived for each problem. The evaluation of these mathematical expressions for the value of the thermal property involved, constitutes a measurement of that thermal property.

A discussion of each of the basic problems used is given below:

IV.A. The Phase Change Problem

The problem of primary interest in this work is one that was solved by Neumann in the 1860's and later studied by Stefan. In various forms the problem and its analysis bear their names. Neumann's solution is for a fairly general problem depicted in Figure IV.A.1 and described as follows: A material which exhibits a change of phase at a temperature, T_m , occupies the semi-infinite space on one side of a

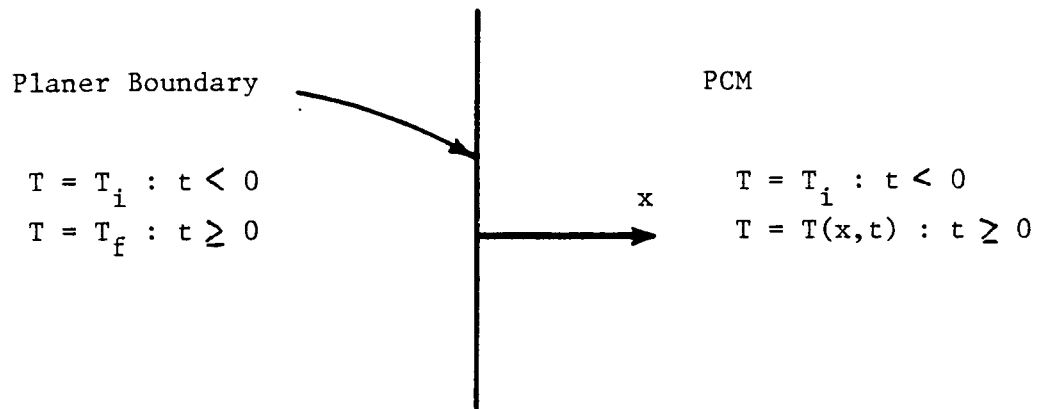


Figure IV.A.1. Physical Representation of the Stefan Problem

plane. Initially the temperature throughout the solid is T_i , greater than T_m . At time, $t_0 = 0$ the temperature of the plane boundary is instantaneously reduced to T_f less than T_m . Heat must be removed at the planer boundary to maintain T_f . Neumann's analysis provides the solution for the temperature in the region occupied by the materials, $x > 0$.

Details of the mathematical description, depicted in Figure IV.A.2, are as follows: It is assumed that the density, specific heat, thermal conductivity, and thermal diffusivity of the low temperature phase are ρ , c_1 , k_1 , α_1 , and of the high temperature phase are ρ , c_2 , k_2 , α_2 . After time, $t = 0$, there will exist both phases separated by the moving planer boundary or phase front at $x = X(t)$. Within the region of each phase the conduction equation applies.

$$\frac{\partial^2 T_1}{\partial x^2} - \frac{1}{\alpha_1} \frac{\partial T_1}{\partial t} = 0 \quad \text{if } x < X(t)$$

and

IV.A.1

$$\frac{\partial^2 T_2}{\partial x^2} - \frac{1}{\alpha_2} \frac{\partial T_2}{\partial t} = 0 \quad \text{if } x > X(t)$$

where T_1 and T_2 are the temperature functions for the low and high temperature regions. Boundary conditions which must be met are:

$$T_1 = T_f \text{ at } x = 0$$

IV.A.2

$$T_2 \rightarrow T_i \text{ as } x \rightarrow \infty$$

At the phase front two conditions must be met. The temperature defined by each function must be equal to the phase change temperature:

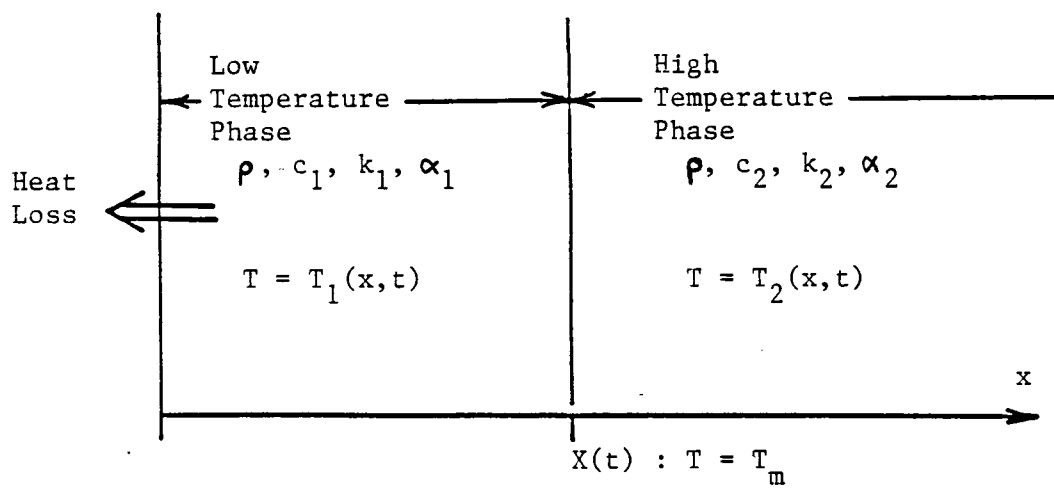


Figure IV.A.2. Mathematical Representation of the Stefan Problem

$$T_1(X) = T_2(X) = T_m$$

and the energy equation requires that:

$$k_1 \frac{\partial T_1}{\partial x} + k_2 \frac{\partial T_2}{\partial x} = L\rho \frac{dX}{dt} \text{ at } x = X(t) \quad \text{IV.A.3}$$

Neumann's solution provides a temperature function for each of the two regions:

$$T_1(x,t) = T_f + \frac{(T_m - T_f)}{\text{erf}(\lambda)} \text{erf} \frac{x}{2(\alpha_1 t)^{1/2}} \quad \text{IV.A.4}$$

for $0 < x < X(t)$ and:

$$T_2(x,t) = T_i - \frac{(T_i - T_m)}{\text{erfc} \left[\lambda \left(\frac{\alpha_1}{\alpha_2} \right)^{1/2} \right]} \text{erfc} \frac{x}{2(\alpha_2 t)^{1/2}} \quad \text{IV.A.5}$$

for $x > X(t)$, where λ is a constant determined from the equation:

$$\frac{k_1(T_m - T_f)}{\text{erf}(\lambda)} e^{-\lambda^2} - \frac{k_2(T_i - T_m)(\alpha_1/\alpha_2)^{1/2} e^{-\alpha_1 \lambda^2/\alpha_2}}{\text{erfc} [\lambda(\alpha_1/\alpha_2)^{1/2}]} = \lambda L \alpha_1 \rho \pi^{1/2} \quad \text{IV.A.6}$$

and $X(t)$ is a function which provides the location of the phase front and is

$$X(t) = 2\lambda (\alpha_1 t)^{1/2} . \quad \text{IV.A.7}$$

A typical temperature profile is shown in Figure IV.A.3.

Carslaw and Jaeger [7] also provide solutions for problems where the conditions have been changed slightly. If the initial temperature is changed to the melting temperature, i.e. $T_i = T_m$, the solution is

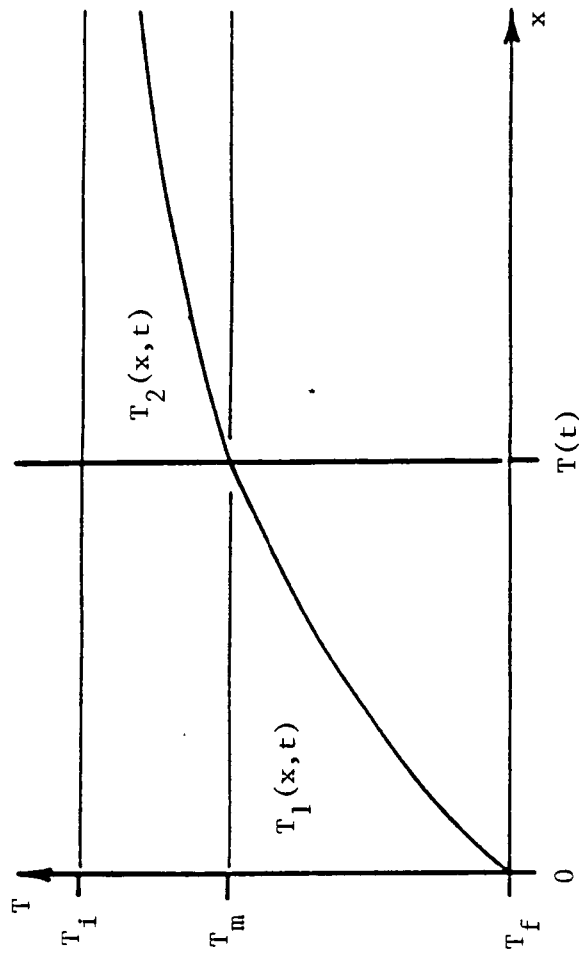


Figure IV.A.3. Typical Temperature Profile of Neumann's Solution for the Stefan Problem

simplified. The temperature function for the high temperature phase becomes a constant:

$$T_2 = T_i = T_m . \quad \text{IV.A.8}$$

and the equation which determines λ is simplified to:

$$\frac{k_1(T_m - T_f)}{\text{erf}(\lambda)} e^{-\lambda^2} = \lambda L \alpha_1 \sqrt{\pi} \quad \text{IV.A.9}$$

or

$$\lambda e^{\lambda^2} \text{erf} \lambda = \frac{k_1(T_m - T_f)}{L \alpha_1 \rho \sqrt{\pi}} \quad \text{IV.A.10}$$

The form of the temperature function for the low temperature phase and the function for the phase front location are not changed, but a new value of λ results.

It is also noted that when the left hand side of Equation IV.A.10 is small, then λ may be approximated by the equation

$$\lambda^2 = \frac{c_1(T_m - T_f)}{2L} \quad \text{IV.A.11}$$

This equation may also be obtained by an analysis which assumes a linear temperature profile in the low temperature phase. In this case, the sensible heat absorbed by the low temperature phase is neglected.

Most substances exhibit a change in density during phase change. This case is also treated by Carslaw and Jaeger [7]. This is done by defining the velocity with which the high temperature phase must move to make room for the expansion or takes up the space for the contraction. This modifies the conduction equation in the high temperature phase and thus its solution. The equation for λ is changed also. It should be apparent however that for the modified initial condition (i.e., $T_i = T_m$) the same simplified forms of the solution result as before.

Phenomenon associated with the liquid state were not taken into account in this discussion. What would be the liquid phase for a real PCM was referred to as the "high temperature" phase. When the initial state is liquid at a temperature substantially above the melting point, any real, finite dimensioned, phase change device will induce natural convection in the liquid. The importance of this phenomenon to the performance of the device depends on the design. For the experiments reported here the effects were minimized as much as possible and were not taken into account for any calculations.

IV.B. A Simple Transient Conduction Experiment To Measure Thermal Diffusivity

The arrangement of the experimental apparatus was convenient for a simple transient conduction experiment which could be analyzed to determine the thermal diffusivity of the solid PCM. The apparatus, which will be described more fully in Section V, included a cylindrical cell for the PCM with a diameter four times the height. The ends

of the cell were aluminum discs which were temperature controlled with circulating water coolant. The classical problem to be modelled is the decay of a temperature profile in a slab whose two surfaces are held at the same constant temperature. The design of the PCM cell was adequate to model the conditions of this problem.

As shown in Figure IV.B.1, the problem, which is discussed in both heat transfer and mathematics texts [7, 17, 18] is as follows: an infinite plane wall exists in the region $0 < x < L$. It is made of a material with the uniform properties of density (ρ), specific heat (c) and thermal conductivity (k). At time, $t = 0$, the temperature in the wall is defined as a function of x .

$$T(x,0) = f(x) \quad (\text{IV.B.1})$$

For time, $t > 0$, the temperatures of the surfaces are equal and constant.

$$T(0,t) = T(L,t) = T_s \quad \text{for } t > 0. \quad (\text{IV.B.2})$$

The governing equation is

$$k \frac{\partial^2 T}{\partial x^2} = \rho c \frac{\partial T}{\partial t}. \quad (\text{IV.B.3})$$

This equation is sometimes normalized by the transformations:

$$\bar{x} = \frac{x}{L}, \quad \bar{t} = \frac{\frac{k}{\rho c} t}{L^2} \quad \text{and} \quad \bar{T} = \frac{T - T_s}{T_r - T_s} \quad (\text{IV.B.4})$$

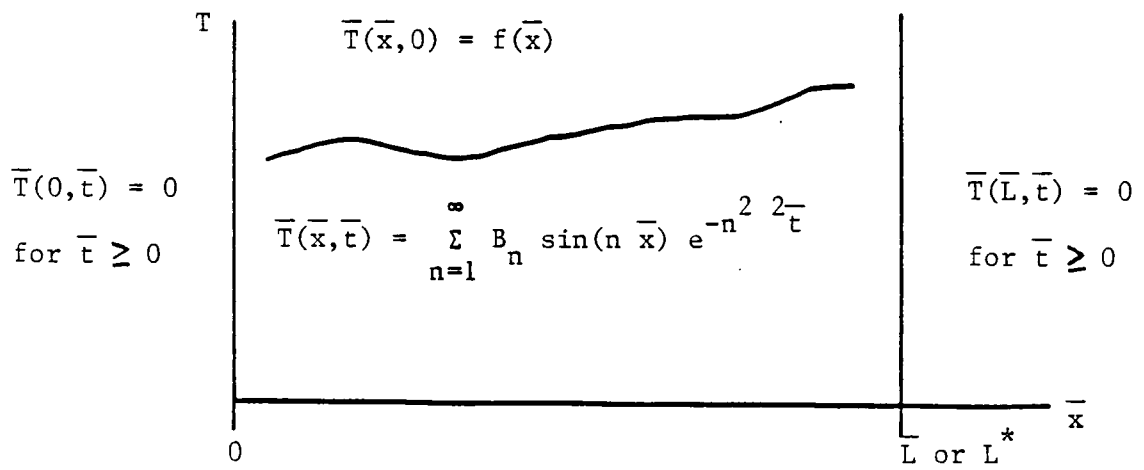


Figure IV.B.1. Representation of the Transient Conduction Problem

where T_r is a convenient reference temperature and the governing equation becomes:

$$\frac{\partial^2 \bar{T}}{\partial \bar{x}^2} = \frac{\partial \bar{T}}{\partial \bar{t}} \quad (\text{IV.B.5})$$

The solution may be found by the separation of variables technique and is found to be the Fourier series:

$$\bar{T}(\bar{x}, \bar{t}) = \sum_{n=1}^{\infty} B_n \sin(n\pi\bar{x}) e^{-n^2\pi^2\bar{t}} \quad (\text{IV.B.6})$$

where

$$B_n = 2 \int_0^1 f(\bar{x}) \sin n\pi\bar{x} d\bar{x} . \quad (\text{IV.B.7})$$

As was stated earlier, it was suspected that the thermal properties of the PCM, octadecane, would not be constant throughout the PCM cell. The freezing process is accompanied by a reduction in volume, and it was suspected that certain regions in the PCM cell would contain substantial voids and the effective value of thermal properties would be altered. It was believed to be reasonable that void fraction would be essentially constant across surfaces parallel to the faces of the cell. Therefore, it was assumed that the affected properties of density and thermal conductivity, would not vary radially. With these assumptions the original governing equation becomes:

$$k(x) \frac{\partial^2 T}{\partial x^2} = \rho(x) c \frac{\partial T}{\partial t} . \quad (\text{IV.B.8})$$

or

$$\alpha(x) \frac{\partial^2 T}{\partial x^2} = \frac{\partial T}{\partial t} . \quad (\text{IV.B.9})$$

Previous studies of octadecane have not taken into account the possible variability of effective thermal properties. Here a solution to conduction equation which takes into account his variability was desired. To do so a new transformation variable was defined:

$$x^* = \int_0^x \frac{1}{\sqrt{\alpha(s)}} ds , \quad (\text{IV.B.10})$$

To substitute this into the equation it is noted that:

$$\frac{\partial x^*}{\partial x} = \frac{1}{\sqrt{\alpha}} \quad (\text{IV.B.11})$$

and that the second derivative is expressed by:

$$\frac{\partial^2 T}{\partial x^2} = \frac{\partial}{\partial x} \left(\frac{\partial T}{\partial x} \right) \quad (\text{IV.B.12})$$

so that

$$\frac{\partial^2 T}{\partial x^2} = \frac{\partial^2 T}{\partial (x^*)^2} \left(\frac{\partial x^*}{\partial x} \right)^2 + \frac{\partial T}{\partial x^*} \frac{\partial}{\partial x} \left(\frac{\partial x^*}{\partial x} \right), \quad (\text{IV.B.13})$$

If the second term of the right hand member of the equation is neglected, the form and solution method of the equation is retained. This assumption is made here and will be evaluated in Section VII.B. With this assumption and substituting Equation V.B.11, IV.B.13 becomes

$$\frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha} \frac{\partial^2 T}{\partial (x^*)^2}. \quad (\text{IV.B.14})$$

Substituting this into the governing equation, IV.B.9, produces:

$$\frac{\partial^2 T}{\partial (x^*)^2} = \frac{\partial T}{\partial t} \quad (\text{IV.B.15})$$

The normalizing transformations can now be defined by:

$$\bar{x} = \frac{x^*}{L^*}, \quad \bar{t} = \frac{t}{(L^*)^2} \quad \text{and} \quad \bar{T} = \frac{T - T_s}{T_r - T_s}. \quad (\text{IV.B.16})$$

The normalized equation is the same as before:

$$\frac{\partial^2 \bar{T}}{\partial \bar{x}^2} = \frac{\partial \bar{T}}{\partial \bar{t}} \quad (\text{IV.B.17})$$

and has the same solution.

This experiment was used to determine the thermal diffusivity in the PCM after it had been solidified in the phase change experiment. The average thermal diffusivity through to the cell was determined by analyzing the decay of the temperature profile. It was also found to be possible to analyze the shape of the temperature profile as it decayed to determine the value of the transformation variable, x^* , at the locations of the thermocouples. Using this data and the locations of the thermocouples, the average value of thermal diffusivity was determined for the intervals between the thermocouples. This analysis is explained in Section VI.

IV.C. Basis for the Line Source Technique

The "line source" technique for measuring thermal conductivity is based on the solution of the conduction equation for a transient problem with boundary condition of a line source. Solutions to this problem under various conditions are discussed in detail by Carslaw and Jaeger [7]. This technique is also referred to as a "transient hot wire" method since electrically heated wires are usually used to simulate the line source. The technique have been used extensively by researchers, who have used it to measure thermal conductivity of solids [4], liquids [12, 14, 20], and gases [8, 15]. The technique has been adapted for use with electrically conducting liquids [6] and molten salts [19]. The technique has also been combined with natural convection correlations and adapted to measure thermal conductivity, specific heat and kinematic viscosity of fluids.

The transient conduction problem on which the line source technique is based, is described by essentially as follows: an infinite solid is initially at a constant temperature of 0. Starting at time, $t = 0$, heat is liberated along a line conveniently chosen to be the Z-axis. Heat is liberated along the line at a constant rate, of per unit of length per unit of time. The governing equation is:

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad \text{IV.C.1}$$

with the boundary conditions

$$T(r) \rightarrow 0 \text{ as } r \rightarrow \infty$$

IV.C.2

$$\frac{\partial T}{\partial r}(r) \rightarrow 0 \text{ as } r \rightarrow \infty$$

The solution given by Carslaw and Jaeger [7] is

$$T(r,t) = \frac{q}{4\pi k} \int_0^t e^{-(r^2)/4\alpha(t-t')} \frac{dt'}{t-t'} \quad \text{IV.C.3}$$

a variable transformation allows this to be rewritten as:

$$T(r,t) = -\frac{q}{4\pi k} \text{Ei} \left(-\frac{r^2}{4\alpha t} \right) \quad \text{IV.C.4}$$

where Ei is the exponential integral defined by

$$\text{Ei}(u) = \int_u^\infty \frac{e^{-\zeta}}{\zeta} d\zeta \quad \text{IV.C.5}$$

For small values of u :

$$Ei(-u) = \gamma + \ln u + \sum_{n=1}^{\infty} \frac{(-u)^n}{n \cdot n!} \quad \text{IV.C.6}$$

where γ ($= 0.57716\dots$) is Euler's constant [7].

Substituting this expression in II.C.4 produces:

$$T(r,t) = -\frac{q_1}{4\pi k} \left[\gamma + \ln \frac{r^2}{4\alpha t} + \sum_{n=1}^{\infty} \frac{\left(-\frac{r^2}{4\alpha t}\right)^n}{n \cdot n!} \right] \quad \text{IV.C.7}$$

$$= -\frac{q_1}{4\pi k} \left[\gamma + \ln \frac{r^2}{4\alpha} - \ln t + \sum_{n=1}^{\infty} \frac{\left(-\frac{r^2}{4\alpha t}\right)^n}{n \cdot n!} \right] \quad \text{IV.C.8}$$

The technique as used here requires that the partial derivative of the temperature with respect to the logarithm of time be evaluated. Taking this derivative of II.C.8 gives:

$$\frac{\partial T}{\partial \ln(t)} = -\frac{q_1}{4\pi k} \left[-1 - \sum_{n=1}^{\infty} \frac{\left(-\frac{r^2}{4\alpha t}\right)^n}{n!} \right] \quad \text{IV.C.9}$$

$$= \frac{q_1}{4\pi k} \left[1 + \sum_{n=1}^{\infty} \frac{\left(-\frac{r^2}{4\alpha t}\right)^n}{n!} \right]$$

The term in brackets is recognized as the series expression of the exponential:

$$1 + \sum_{n=1}^{\infty} \frac{\left(-\frac{r^2}{4\alpha t}\right)^n}{n!} = \exp \frac{r^2}{4\alpha t}$$

so that II.C.9 becomes

$$\frac{\partial T}{\partial \ln(t)} = \frac{q}{4\pi k} \exp \left(\frac{r^2}{4\alpha t} \right) \quad \text{IV.C.10}$$

If the term of the exponential is small enough this the partial derivative may be approximated by

$$\frac{\partial T}{\partial \ln(t)} = \frac{q}{4\pi k} \quad \text{IV.C.11}$$

Solving this for the thermal conductivity produces:

$$k = \frac{q}{4\pi} / \frac{\partial T}{\partial \ln(t)} \quad \text{IV.C.12}$$

Equation IV.C.12, will be used to determine the thermal conductivity of octadecane with the line source device described in Section V. The applicability of this equation is discussed in Appendix C, where it is shown that, for this device, Equation II.C.12 is applicable over a time period determined by:

$$1.8 < \log \frac{\alpha t}{a^2} < 3.5 \quad \text{IV.C.13}$$

where

α = thermal diffusivity of the test material

t = elapsed time

a = radius of line source RTD wire.

V. THE EXPERIMENTAL FACILITY

V.A. Overview

The experiments reported here were conducted in a computerized facility at the Oak Ridge National Laboratory. The core of the facility is a cell which contained the PCM, octadecane. The cell was designed to be able to simulate a variety of experiments in one dimensional conduction and with or without phase change. A coolant system provided the capability to vary the boundary conditions as necessary for each experiment. Instrumentation in the cell included thermocouples, which provided temperature profiles in the cell, and three RTD's which were used in the line source measurements of thermal conductivity. A special bridge circuit was provided for obtaining the thermal conductivity data.

The computer was equipped with an interface through which signals could be sent for control the coolant system or the RTD circuit and data could be received from the instrumentation. A schematic diagram of the facility is shown in Figure V.A.1. Individual components are described below.

V.B. The PCM Cell

The PCM cell, Figure V.B.1 had a chamber in the shape of a cylinder, 5.08 cm (2 in.) high and 20.32 cm (8 in.) in diameter, which was filled with the PCM, octadecane. The wall was made of a 0.32 cm (1/8 in.) thick flexible PVC sleeve and was insulated with about 3 cm of

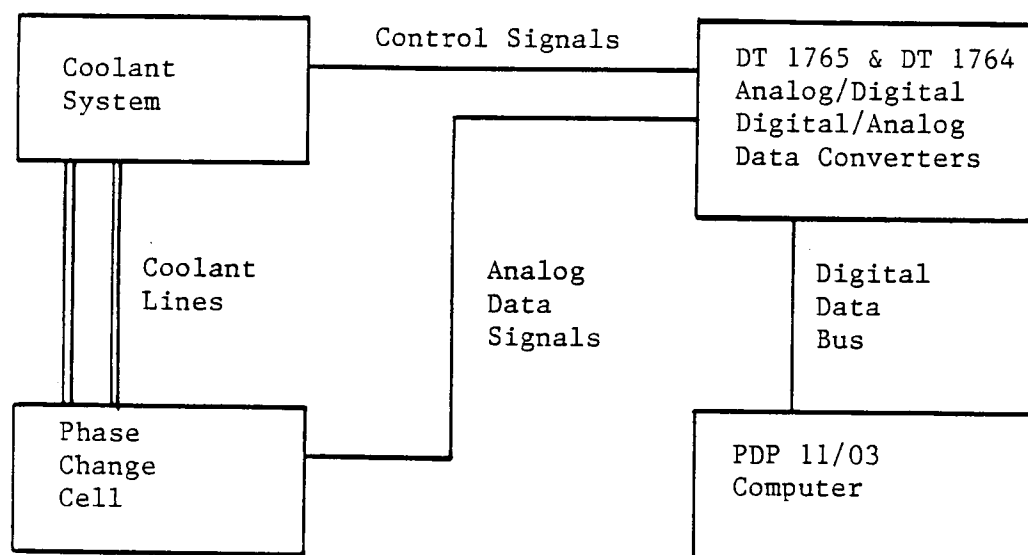


Figure V.A.1. Schematic of the Experiment Control and Data Acquisition System

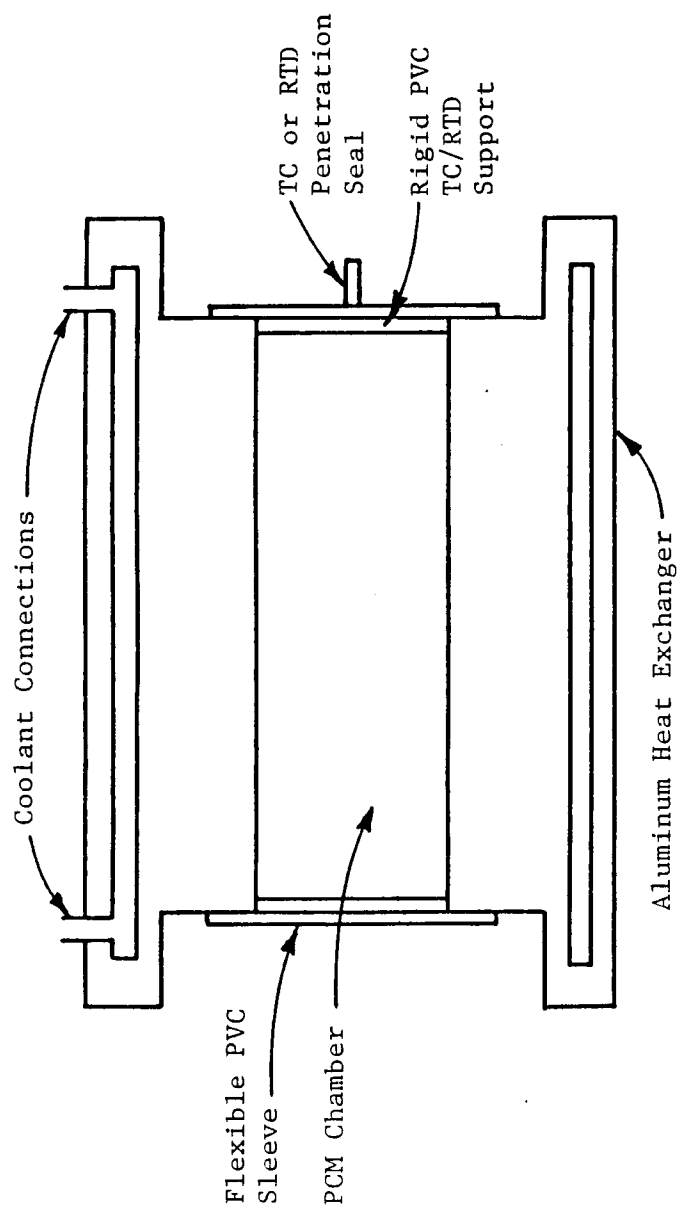


Figure V.B.1. The Phase Change Cell

fiberglass wool insulation. The faces of the cylinder were aluminum discs, to which the PVC sleeve was sealed with a barge hose clamps. Seven small gage thermocouples wires and three small platinum wire RTD's passed through the chamber near and parallel to a diameter. Plates which supported the aluminum discs were mounted in a frame which allowed for accurate adjustments of the cylinder height. The frame was supported on blocks used to level the cell. The overall design of the cell made it quite serviceable.

These wires were supported by two rectangular pieces of 0.48 cm (3/16 in.) rigid PVC located against the inside of the wall at the penetrations.

The flexibility of the sleeve allowed for the change in density of octadecane on freezing. The low conductivity of the PVC and the insulation reduced wall effects to a minimum. The supports and a small amount of tension placed on the thermocouples and RTD's by the penetration seals ensured accuracy in the location of measurements.

V.C Boundary Condition Control

The temperatures of the aluminum discs were controlled to provide the necessary boundary conditions of the cell. Each disc was an integral part of a heat exchanger machined from a solid piece of aluminum. The back side of each heat exchanger was sealed with an aluminum plate which provided the connections to the coolant system. The coolant system, Figure V.C.1, included a pump, hot and cold coolant

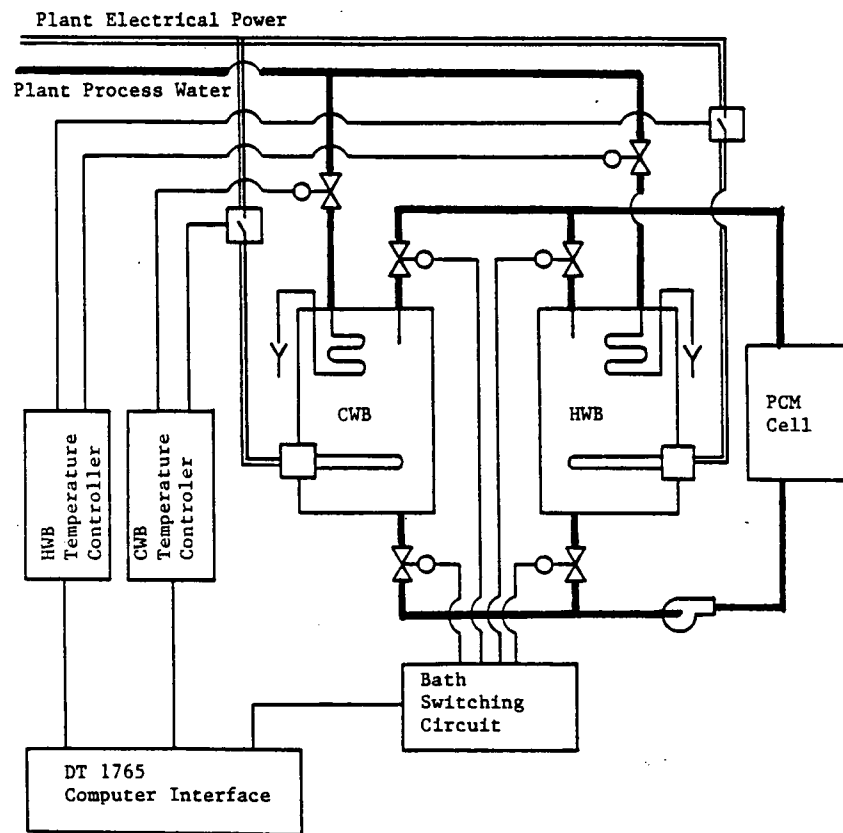


Figure V.C.1. Schematic of the Coolant System

sources or baths, each with a temperature control circuit, and circulating piping with cross connects and valves so that the coolant sources could be switched during experiments.

A channeled surface on the back side of the discs and a high coolant velocity ensured an adequate heat transfer rate from the coolant to the discs. The coolant system could be connected to one or both heat exchangers during an experiment. The coolant sources were switched during experiments by a circuit controlled with a computer generated signal. The temperature of each coolant bath was maintained by a circuit which controlled power to a heater element and raw cooling water to a coil in each bath. Each control circuit acted on two input signals: a voltage from a thermister circuit indicating both temperature and a computer controlled voltage indicating the required bath temperature. The disc temperatures could be varied by switching the source or by slowly varying a bath temperature. The system worked adequately for the experiments reported here.

Several deficiencies in the system were apparent, however. The volume of each of the baths, 208 l (55 gal) was intended to prevent any significant variation in the bath temperature even when switching coolant baths; the volume of the bath acted as a thermal capacitor. It worked well for such a purpose, but the volume and limited heating and cooling capacity prevented the bath temperature from following closely anything but a very slowly changing input signal. Experiments using this mode of operation were unsuccessful. Another problem

involved the mass of the PCM cell heat exchangers. This mass and the finite heat transfer rate were such that after a switch of coolant baths, several minutes were required before face temperature dropped to the required value. The bath temperature controllers also caused a problem. To prevent rapid switching of the heating and cooling elements, a dead band was designed into the controllers. This caused a variation in the temperature of coolant supplied to the cell heat exchangers of about 0.5°C (0.9°F). The effects of the thermal mass of the heat exchangers and the dead band of the temperature controllers were accounted for by modifying the analysis procedures.

V.D Instrumentation

The instrumentation on the PCM cell included nine thermocouples and three platinum wire RTD's. One thermocouple was placed in each of the discs in a hole drilled along a radius about 1.6 cm ($5/8$ in.) from the face of the disc. The other seven thermocouples were placed at 0.635 cm ($1/4$ in.) intervals in the cell. The three RTD's were placed at 1.27 cm ($1/2$ in.) intervals in the cell. The small diameters of the thermocouples, 0.25 mm (0.01 in.) and the platinum wires 0.2 mm (0.008 in.) ensured that the temperature profile was not disturbed and that error due to conduction along the wires was negligible. Details of the installation of the thermocouples and RTD's are shown in Figure V.D.1.

The thermocouples provided temperature profiles in the cell at regular intervals during experiments. Each cell thermocouple was

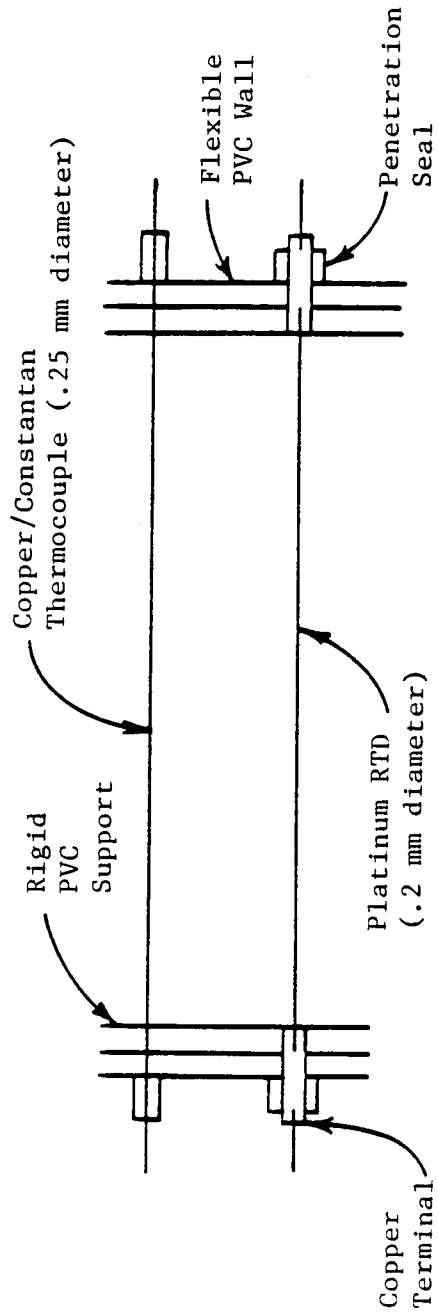


Figure V.D.1. Thermocouple and RTD Installation

connected to a reference thermocouple in an automatic bath controlled within several hundredths of a degree at a temperature slightly above freezing. The thermocouples voltage was read by the computer interface capable of reading from 0 to 10 millivolts with a resolution of about 2.5 microvolts. The system could therefore read temperatures from freezing to about 215°C ($\approx 420^{\circ}\text{F}$) with a resolution of about 0.05°C ($\approx 0.1^{\circ}\text{F}$). A calibration function in the form of a second order polynomial was generated for each thermocouple circuit. The function related temperature to the digital conversion received by the computer. This eliminated intermediate calibration steps and the possible introduction of error.

The resistance temperature detectors were used in the line source technique to measure thermal conductivity only. As such they were also used to simulate a line source, the heat being supplied by resistance heating. The experimental data required to make a determination of thermal conductivity include the linear heat rate and a history of RTD temperature for a short time after the heat rate is initiated.

A bridge circuit, Figure V.D.2, provided all the electrical signals to the interface. A constant voltage power supply was connected to terminals, 3 and 4. The relay switch, S_1 , was closed on a computer generated signal to initiate resistance heating. The voltage divider made of resistors, R_{VD1} , R_{VD2} , and R_{VD3} , provided a current indicating voltage, V_I , at terminals 5a and 6. This signal was also used to

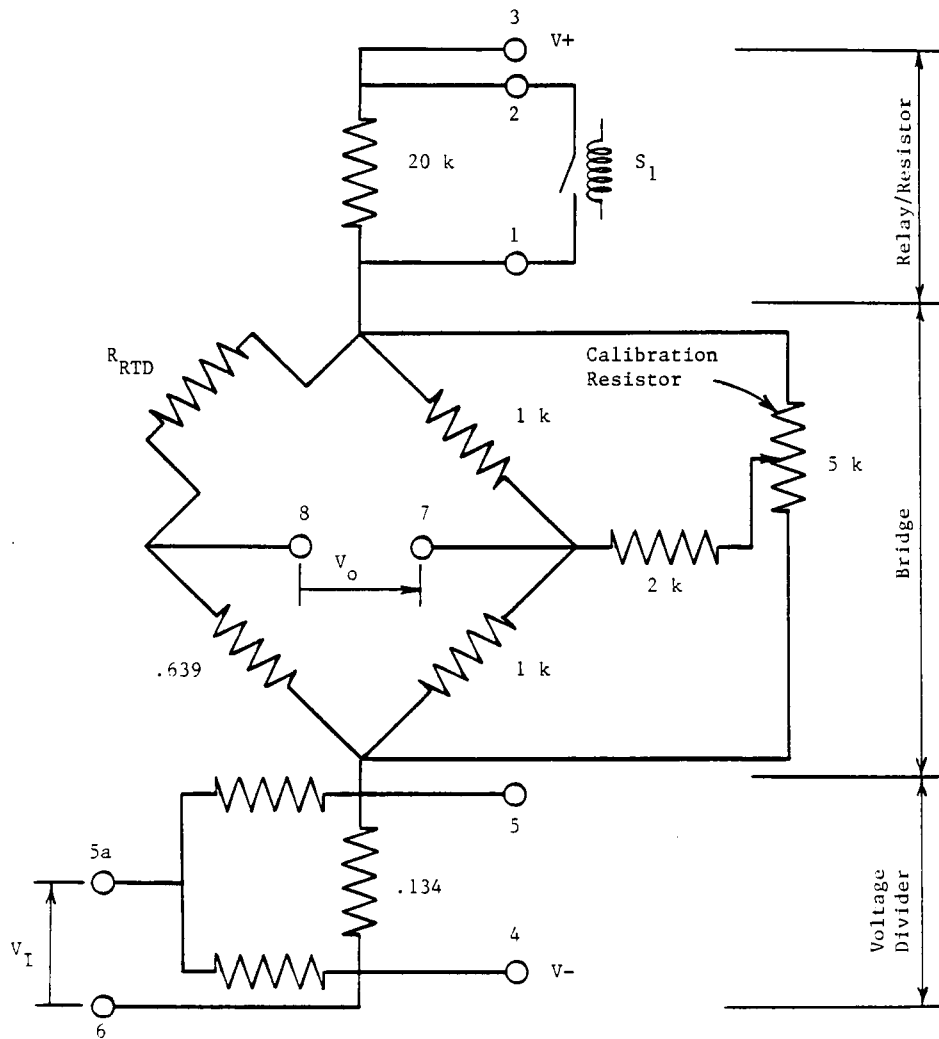


Figure V.D.2. Bridge Circuit for LST Data Acquisition

V_o = Temperature indication, V_I = Current indication

calculate the bridge voltage. The output voltage, V_o , was compared to the bridge voltage to determine the rise in resistance of the RTD.

The current in the RTD is approximately the same as the current in the voltage divider, I_{VD} , which was determined using Ohm's law:

$$I = V/R = V_{VD}/R_{VD}$$

$$I_{VD} = V_I \frac{R_{VD2} + R_{VD1}}{R_{VD2}} \frac{1}{R_{VD}} \quad \text{V.D.1}$$

where

$$R_{VD} = \frac{1}{\frac{1}{R_{VD3}} + \frac{1}{R_{VD1} + R_{VD2}}}$$

$$I_{VD} = F_1 \cdot V_I \quad \text{V.D.2}$$

where $F_1 = (R_{VD2} + R_{VD1})/(R_{VD2} \cdot R_{VD})$. The bridge voltage was determined by the equation:

$$V_{BR} = F_2 \cdot V_I \quad \text{V.D.3}$$

where F_2 was determined experimentally for each RTD at the time the bridge adjustments were made. With the circuit in the calibration mode (the switch, S_1 , is open), the voltage across terminals 5a and 6 and terminals 5 and 1 were measured with a digital voltmeter, DVM. These voltages were then used to calculate the factor, F_1 .

It is shown in Appendix C that the output voltage, V_o , varies proportionally with the resistance of the RTD over a small range. That is:

$$\frac{d V_o}{d R_{RTD}} = V_{BR} R_2 (R_2 + R_{RTD})^{-2} \quad V.D.4$$

The resistance of platinum wire is known to vary with temperature. Its temperature coefficient of resistance, α_Ω , is nearly constant at $0.00392^\circ\text{C}^{-1}$. The resistance follows the relation [15]:

$$R = R_r [1 + \alpha_\Omega (T_o - T_r)] \quad V.D.5$$

Taking the derivative with respect to temperature:

$$\frac{dR}{dT} = R_r \alpha_\Omega \quad V.D.6$$

This can not be related to the instantaneous resistance by solving Equation V.D.5 for the reference resistance and substituting:

$$\frac{dR}{dT} = \frac{R \alpha_\Omega}{1 + \alpha_\Omega (T - T_r)}$$

The output voltage varies with the RTD temperature as follows:

$$\begin{aligned} \frac{d V_o}{d T_{RTD}} &= \frac{d V_o}{d R_{RTD}} \cdot \frac{d R_{RTD}}{d T_{RTD}} \\ &= \frac{V_{BR} R_2}{(R_2 + R_{RTD})^2} \cdot \frac{R_{RTD} \alpha_\Omega}{1 + \alpha_\Omega (T - T_r)} \end{aligned} \quad V.D.7$$

Substituting Equation V.D.3 gives

$$\frac{d V_o}{d T_{RTD}} = \frac{F_2 V_I R_2}{(R_2 + R_{RTD})^2} \frac{R_{RTD} \alpha_\Omega}{[1 + \alpha_\Omega (T - T_r)]} \quad V.D.8$$

The circuit had to be "zeroed" for the slight differences in resistance of each of the RTD's. With the supply voltage applied to terminals 3 and 4 and the switch, S_1 , open, only a small voltage is applied to the bridge. In this condition, the variable resistor, R_c , is adjusted until the output voltage is only slightly positive. This ensures that when the switch, S_1 , is closed the output voltage will remain within the measurable range of 0 to millivolts.

Effects due to resistance heating of the other resistors were eliminated by design. Resistors, R_2 and R_{VD3} , are made of manganese which has a nearly constant resistance. The remaining resistors are of such size that little current is available for resistance heating.

V.E. Experiment Control and Data Acquisition

The system was run by a PDP-11/03 minicomputer. Two interface boards, a DT-1764 and DT-1765 were connected to the data bus of the computer. Special Fortran compatible instructions could be used in a program to communicate with the boards. The two boards had outside connections including a total of 40 channels capable of reading voltages in the range of 0 to 10 millivolts (suitable for copper-constantan thermocouples). Also, available on the boards were two digital to analog converters capable of producing voltages in the range of -10 to 10 volts. These were used to provide control voltages to two temperature controllers of the coolant baths. Four mode bits which were also on one of the boards produced voltages of either 0 or

5 volts. These were used to switch the valve alignment of the coolant systems, or during the "line source" measurements, to control the switch, S_1 . An internal clock with a resolution of $1/60$ second was available in the computer.

The temperature measurements during the phase change and transient conduction experiments were made by reading each of the TC channels 100 times and averaging the digital conversion. This average value was used in the calibration function to determine the indicated temperature. The nine thermocouples could be read in less than 10 seconds in this manner. A typical program used to execute an experiment is found allows the specification of the time interval between thermocouple readings, the control temperatures for the hot and cold water baths, and the switching times for the alignment valves. Also, specified is the name of the disk filed to receive the recorded data, cycles in the number of data on each file.

In the "line source" measurements the data acquisition system was used a little differently. The control program initially requires the input of several constants which characterize the bridge circuit and the calibration constants for the data acquisition channel. The program then signals for the relay, S_1 , to close and goes into a cycle of reading both the output voltage, V_o , and the current indicating voltage, V_I , and the time. It was found that about six of these cycles could be performed and recorded in $1/60$ of a second. A preset number of these cycles were recorded and then the relay was opened. The

remainder of the program performs an analysis of the data and prints the results. The analysis of the data is explained in Section VI.C.

In these experiments the two A/D channels were calibrated to the input voltage. The voltage to digital conversion for these boards was linear to within 1/2 of a digital increment, or 0.01% of full scale. Simple first order polynomials were considered to be adequate. These were generated from two data points near the opposite ends of the voltage range for each channel. The calibration equation used in the program was of the form:

$$V_n = A_n (DC_n) + B_n \quad \text{V.E.1}$$

where

V_n = measured voltage

A_n and B_n = calibration constants

DC_n = the digital conversion value

$n = I$ for the current channel or VO for the temperature channel.

VI. ANALYSIS PROCEDURES

VI.A. Analysis of the Phase Change Experiments

The purpose of this experiment was to extract a value of thermal conductivity which characterizes the freezing behavior of n-octadecane. To do this the value of some variable must be measured and compared with results of the mathematical solutions of Section IV.A. The primary variable that was recorded was the temperature at various points in the test section. There is some difficulty in this comparison because of the complexity of the mathematical solution. Researchers have found that a much easier and more reliable variable is the location of the phase front [1,9].

Researchers have used several methods for determining the location of the phase front including visual and ultrasonic methods [1]. The method used here was that used by Deal and Solomon [9] and depends on analyzing the temperature histories of each of the thermocouples in the test section. It can be seen by taking the derivatives with respect to time of Equations IV.A.4 and IV.A.5, that the rate of change of the temperature at a given point changes as the phase front passes. If the temperature of each thermocouple is plotted, the time of passing of the phase front may be determined by noting when this discontinuity occurs.

Simply noting when the temperature drops below the freezing point of the PCM is not a reliable indication of the passage of the phase front. The thermocouples sometimes get out of calibration which would

cause a false indication. The presence of the thermocouple can locally distort the freezing front and provide a false reading. Noise on the thermocouple circuit can cause the temperature indication to indicate freezing early or late. By using several data points on each side of the discontinuity, curves are developed for the temperature histories before and after the passing of the phase front. These two curves which are nearly straight lines in the vicinity can be extrapolated to their intersect which is at the time of passage.

Once the time at which the phase front passes a certain point in the PCM, this ordered pair of time and distance can be used in the Equation IV.A.7 to determine the constants. This is similar to the technique used by Deal and Solomon [9]. They used each ordered pair as a separate measurement of the thermal conductivity. Their results varied significantly. To improve the reliability of the method, here several of the ordered pairs were used together in the method of least squares to fit an equation similar in form to Equation IV.A.7.

A close examination of the experimental apparatus and method will indicate the proper form of the equation to be fit. Two experiments of this type were analyzed. One started with the liquid PCM just above the freezing point, but as close as practicable. In this case Equation IV.A.10, or IV.A.11 if applicable, could be used to determine the thermal conductivity once the data is obtained. In the other experiment the liquid was initially about 10°C higher than the melting temperature. In this case Equations IV.A.10 and IV.A.11 are not

applicable. Equation II.A.6 must be used, and a check must be made that the results are not affected by natural convection in the melt or by the finite nature of the test section.

In each of the two experiments the initial conditions of the test were established by connecting the cell heat exchanger to the high temperature water supply which was controlled at the proper temperature. At a prescribed time the heat exchanger was switched to the cold water supply at a much lower temperature. This was intended to simulate a step change in the temperature of the face of the PCM chamber. Unfortunately the thermal mass of the piping system and the heat exchangers along with the finite heat transfer coefficient of the coolant in the heat exchanger combined to produce a reduction in the face temperature which at best took several minutes.

The experiment has been shown not to model precisely the problem that Neumann analyzed. However, it is noted that after the effect of the thermal mass has died away and heat transfer rate through the PCM has reduced by the thickness of the solid PCM, the temperature profile in the PCM will closely approximate that of Neumann's calculation. All ordered pairs generated from data after this time could be used to determine the thermal conductivity.

There were some problems with the experiment however. First, the exact time at which the effective step change in temperature occurred is not known. Second, the finite heat transfer coefficient, the small but finite resistance of the aluminum, and any possible contact

resistance of the PCM combined to add to the "effective" thickness of the PCM. These effects may be taken into account by defining new variables as follows:

$$X_e = X' + x_0 \quad (\text{VI.A.1})$$

and

$$t_e = t' - t_0 \quad (\text{VI.A.2})$$

where x_0 is effective thickness of the added resistance to heat transfer, t_0 is the effective time of the "step change" in face temperature. The primes denote the recorded data from the experiment and subscript, e, denotes the effective value which should be used in Equation II.A.7 which becomes:

$$X' + x_0 = 2\lambda [\alpha_1 (t' - t_0)]^{1/2} \quad (\text{VI.A.3})$$

Solving this for t' produces:

$$t' = \frac{1}{4\lambda^2\alpha_1} (X')^2 + \frac{x_0}{2\lambda^2\alpha_1} X' + \frac{x_0^2}{4\lambda^2\alpha_1} + t_0 \quad (\text{VI.A.4})$$

Equation IV.A.4 is of the form of a second order polynomial and may be fitted to any three or more data points with the method of least squares. The equation is of the form:

$$t' = C_1(X')^2 + C_2(X') + C_3 \quad (\text{VI.A.5})$$

where:

$$C_1 = \frac{1}{4\lambda^2\alpha_1} \quad (\text{VI.A.6})$$

$$C_2 = \frac{x_0}{2 \lambda^2 \alpha_1} \quad (\text{VI.A.7})$$

$$C_3 = \frac{(x_0)^2}{4 \lambda^2 \alpha_1} + t_0 \quad (\text{VI.A.8})$$

This technique when applied to the phase change experiment without superheat worked well. When applied to the experiment with superheat, however, the results were not satisfactory. This was found to be caused by the effects of natural circulation and heat loss. The superheat has the effect of delaying the phase front progression, but the superheat dissipates due to the natural circulation and heat loss. So the superheat effects are pronounced early in the experiment but are negligible late in the experiment. The previously described analysis will thus produce artificially high values of the delay time and effective thickness of the end face, and high values of thermal conductivity.

To remedy the problem it was assumed that the added effective thickness for both experiments was the same. This eliminates one unknown, and changes the equation to be fitted to:

$$X_e = 2\lambda [\alpha_1 (t' - t_0)]^{1/2} \quad (\text{VI.A.9})$$

or solving for t'

$$t' = \frac{1}{4\lambda^2\alpha_1} (X_e)^2 + t_0 \quad (\text{VI.A.10})$$

where $X_e = X' + x_0$; x_0 is taken from the phase change experiment without phase change. The fitted equation is of the form:

$$t' = C_1 (X_e)^2 + C_2(X_e) + C_3 \quad (\text{VI.A.11})$$

where

$$C_1 = \frac{1}{4\lambda^2\alpha_1} \quad (\text{VI.A.12})$$

$$C_2 = 0 \quad (\text{forced}) \quad (\text{VI.A.13})$$

$$C_3 = t_0 \quad (\text{VI.A.14})$$

Details of the curve fitting are given in Appendix A. Regardless of which equation, VI.A.4 or VI.A.10, is used to fit the data, the first coefficient, C_1 , is used to evaluate the thermal conductivity. The constant, λ , is determined from the appropriate equation, IV.A.6, IV.A.10 or IV.A.11.

VI.B. Analysis of The Transient Conduction Experiment

The one-dimensional conduction experiment was performed in the Phase Change Cell after the phase change experiment without superheat. A effort was made to keep the PCM in the same state for this experiment. The conduction experiment was started by bringing the PCM to a relatively uniform temperature a few degrees below melting. The cell heat exchangers were then switched to the cold water supply and the resulting temperature histories of all the thermocouples were recorded as in the phase change experiment. The data was in the form of

temperatures measured the locations of this thermocouples and at regular intervals at time.

The analysis of the experiment depends on noting that the initial time used in the Fourier series solution discussed in Section IV.B may be selected at any time after the face temperature reaches a steady uniform value. Each of the terms in the Fourier series can then be calculated using the profile at the selected time as the initial condition. Since the higher frequency terms of the series decay rapidly, a single sinusoid may be assumed if a sufficient time delay is allowed. In Appendix B it is shown that for the experiment reported here, a time delay of 620 seconds is sufficient to reduce the error caused by neglecting the higher order terms to less than 0.1°C .

Once the delay time has passed, the temperature function can be expressed as:

$$T(x,t) = T_f + \overline{T}_0(x) \cdot \exp(-t/\tau) \quad (\text{VI.B.1})$$

where

T_f = face temperature

$\overline{T}_0$ = function which describes the temperature profile at the selected t_0

τ = a decay constant.

The relation of the decay constant to the physical properties of the material can be determined. Equating the exponential term in Equation VI.B.1 to that in Equation VI.B.6 produces

$$-t/\tau = -n^2 \pi^2 \overline{t} \quad (\text{VI.B.2})$$

in which $n = 1$ and for the modified solution $\bar{t} \equiv t/(L^*)^2$. Therefore:

$$\tau = \frac{L^*}{\pi}^2 \quad (\text{VI.B.4})$$

and

$$L^* = \int_0^L \frac{1}{\sqrt{\alpha}} dx = \pi \sqrt{\tau} \quad (\text{VI.B.5})$$

From the phase change cell description in Section V.A it should be apparent that part of the integral in Equation VI.B.5 is taken over the thickness of the aluminum plate. This contribution to the integral can easily be calculated and subtracted from the value of L^* found from Equation VI.B.5. The remainder is then the contribution to the integral of the interior portion of the cell which is determined by the properties of the PCM. The average value of the inverse of the square root of thermal diffusivity of the PCM can be found for any interval by:

$$\left(\frac{1}{\sqrt{\alpha}}\right)_{\text{ave}} = \frac{\Delta x_{\text{PCM}}^*}{\Delta x_{\text{PCM}}} \quad (\text{VI.B.6})$$

The effective value of the thermal diffusivity can be found by taking the inverse square of Equation VI.B.6:

$$\alpha_{\text{eff}} = \left(\frac{\Delta x_{\text{PCM}}^*}{\Delta x_{\text{PCM}}}\right)^2 \quad (\text{VI.B.7})$$

The time constant for each of the equivalent to seven thermocouple locations was determined by fitting the data to an equation Equation VI.B.1. A first order polynomial form of the equation is obtained by the substitution of a new variable defined as:

$$\bar{T}(x,t) = T(x,t) - T_f \quad (\text{VI.B.8})$$

and taking the logarithm of each side of the resulting equation. This produces:

$$\ln [\bar{T}(x,t)] = \ln [T_o(x)] - \frac{1}{\tau} \cdot t \quad (\text{VI.B.9})$$

If this equation is applied to each thermocouple location individually the result is a equation of the form:

$$Y_i(t) = A_i t + B_i \quad (\text{VI.B.10})$$

where

$$Y_i(t) = \text{a function defined by } \ln [T(x_i, t) - T_f]$$

$$A_i = -\frac{1}{\tau}, \text{ the negative inverse of the decay constant}$$

$$B_i = \ln [T(x_i, t_o) - T_f] \text{ the natural log of the difference of the thermocouple and face temperatures at the selected } t_o.$$

The equation may be fitted to the data by the method of least squares. Each thermocouple will provide a calculation of the time constant from which may be determined the value of thermal diffusivity.

An indication of the variation of thermal diffusivity through the cell may be obtained by analyzing the temperature values, $T_o(x)$, obtained during the data fitting process. If a good estimate of the

maximum temperature can be found, these temperatures can be used to determine the value of transformation variable, x^* , at the location of each thermocouple. Then the average value of the inverse of the square root of the thermal diffusivity may be determined for each interval between two thermocouples:

$$\frac{1}{\sqrt{\alpha}} = \frac{\Delta x^*}{\Delta x} \quad (\text{VI.B.11})$$

Since the temperature profile in the transformation variable, x^* , is a sinusoid with a period of, $2L^*$, the value of, x^* , may be determined from the equation:

$$x_i^* = \arcsin \left(\frac{\bar{T}_{o,i}}{\bar{T}_{o,\max}} \right) \frac{L^*}{\pi} \quad (\text{VI.B.12})$$

where $\bar{T}_{o,\max}$ = the maximum temperature difference in the cell.

To obtain a reasonable estimate of maximum temperature. In the cell, the thermocouple temperature data were analyzed. This required an assumption concerning the values of diffusivity in the intervals between the thermocouples, which is the data to be determined. By making an assumption about two, or possibly three intervals, however, the values of thermal diffusivity for all intervals could be determined. The assumptions need only concern the relative values of properties in intervals and not the actual value. The process involves making repeated modified guesses of the maximum temperature and testing to see if the appropriate assumption is true.

The phase change cell is divided into eight intervals by the seven thermocouple locations. These intervals can be numbered as in Figure VI.B.1. From looking at the temperature profiles in Appendix B it appears that the maximum temperature occurs in interval number 5. Several assumptions were tested each of which concerned two or three intervals and which included this interval. Tested assumptions included:

1. That the value of diffusivity in interval four was the average of those in intervals three and five.
2. That the value of diffusivity in interval five was the average of those in intervals four and six.
3. That the values of diffusivity in intervals four and five were equal, or
4. That the values of diffusivity in intervals five and six were equal.

Using the various assumptions generally had little effect on the values calculated for the outer intervals. The first two and last assumptions caused very drastic changes in the thermal diffusivity between the central cells, and were discarded. The third assumption was finally used and produced reasonable results. It should be noted however that the values of thermal diffusivity for intervals four and five should be assumed to be an average over the two cells and not over each individuality.

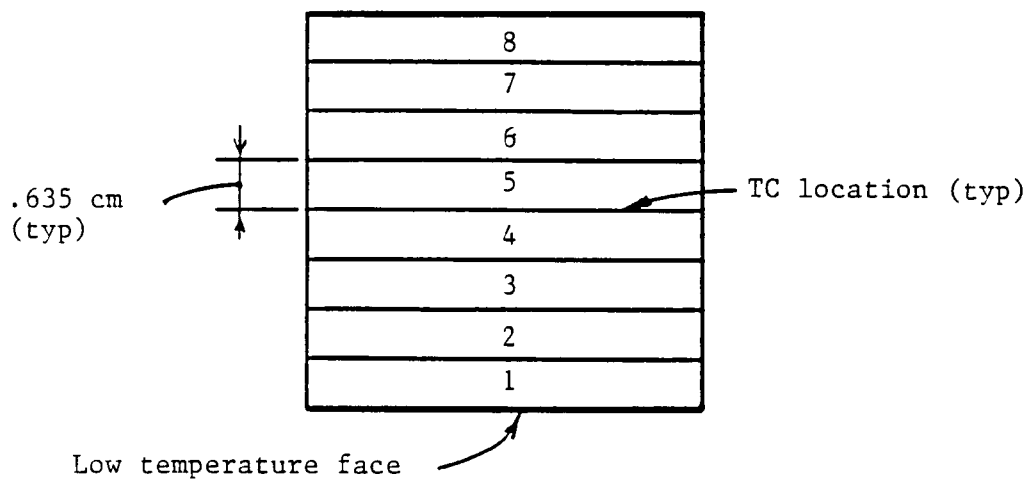


Figure VI.B.1. The Intervals of the PCM Cell Used for Calculating Thermal Diffusivity

These calculations were made with data obtained at various times after the beginning of the experiment. Each calculation was made with eleven data sets obtained in a sequence at 45 second intervals. The initial temperature profile was predicted for the time of the central data set. In this way time wise changes in the effective thermal diffusivity could be calculated.

VI.C. Analysis of The Line Source Experiments

Obtaining accurate values of thermal conductivity with the line source technique depends on calculating accurate values of the linear heat rate and the partial derivative of the temperature with respect to the logarithm of time. These two data were used in Equation IV.C.12. The raw data were a series of digital values grouped in set of three. Each consisted of digital conversions for the two signals produced by the bridge circuit discussed in Section V.D, and a digital value indicating the time.

The data were first manipulated to improve the accuracy of the time indications. It was in Section V.E that a series of approximately six data data sets could be obtained in each clock tick ($1/60$ s), so that each of these six sets had the same time indication. More accurate time indications were obtained by incrementing the time $1/6$ of a clock tick ($1/360$ s) for the second, third, fourth, fifth, and sixth data sets in each series.

The next step was to determine for each data set the time that had elapsed since the initial increase in the linear heat rate.

Because there was an unknown delay between the initiating signal and the energizing of the circuit, an estimate of the true initial time was needed. This was found by noting the current indication first data set in which exceeded a predetermined value, which was approximately half of the value of the current indication expected for a fully energized circuit. The time indication of this data set was then subtracted from the remaining time indications to obtain values of elapsed time. Values of the logarithm of time were then calculated and added to the data sets.

Equation IV.C.13 defines the limits of applicability of Equation IV.C.12. Using conservative estimates of the thermal diffusivity, the upper and lower time limits were calculated, and data which fell within these limits were used to calculate the two variables needed to evaluate Equation IV.C.12.

The linear heat rate, q_1 , was calculated by dividing the resistance heating by the length of the RTD:

$$q_1 = \frac{(I_{RTD})^2 R_{RTD}}{L_{RTD}} \quad (VI.C.3)$$

The current in the RTD is essentially the same as the current in the voltage divider circuit, which was determined using Equation V.D.2 so that Equation VI.C.3 becomes:

$$q_1 = \frac{(F_1 V_I)^2 R_{RTD}}{L_{RTD}} \quad (VI.C.4)$$

The current indicating voltage, V_I , was determined by Equation V.E.1 for the current channel. Making this substitution in VI.C.4 produces:

$$q_1 = \frac{(F_1)^2 [A_I (\overline{DC_I}) + B_I]^2 R_{RTD}}{L_{RTD}} \quad (VI.C.5)$$

where $\overline{DC_I}$ is the average of the current indications.

The derivations of the RTD temperature with respect to the logarithm of time is the product of three terms as can be shown by the chain rule:

$$\frac{d T_{RTD}}{d \ln(t)} = \frac{d T_{RTD}}{d V_o} \frac{d V_o}{d (DC_T)} \frac{d (DC_T)}{d \ln(t)} \quad (VI.C.6)$$

The first term on the right side is the derivative of the RTD temperature with respect to the output voltage, V_o , of the bridged circuit described in Section V.D. It was evaluated by taking the reciprocal of Equation V.D.8:

$$\frac{d T_{RTD}}{d V_o} = \frac{(R_2 + R_{RTD})^2 [1 + \alpha_\Omega (T - T_r)]}{F_2 V_I R_2 R_{RTD} \alpha_\Omega} \quad (VI.C.7)$$

The voltage, V_I can be determine using the averaged current indication, $\overline{DC_I}$, in Equation V.E.1. Substituting into VI.C.7 gives:

$$\frac{d T_{RTD}}{d V_o} = \frac{(R_2 + R_{RTD})^2 [1 + \alpha_\Omega (T - T_r)]}{F_2 [A_I (\overline{DC_I}) + B_I] R_2 R_{RTD} \alpha_\Omega} \quad (VI.C.8)$$

The second term is the derivative of the measured output voltage with respect to the digital conversion for the measurement channel. This was found by taking the derivative of Equation V.E.1 for that channel:

$$\frac{d V_o}{d (DC_T)} = A_{V_o} \quad (VI.C.9)$$

The third term is the derivative of the digital conversion with respect to the logarithm of time, which was determined by analyzing the experimental data.

Still observing the limits set by Equation IV.C.13, the method of least squares was used to generate a first order polynomial relating the output voltage indication to the logarithm of time:

$$DC_T (\ln t) = A_{DC,T} \cdot \ln(t) + B_{DC,T} \quad (VI.C.10)$$

Taking the derivative of this equation with respect to logarithm of time produces the required term:

$$\frac{d DC_T}{d \ln(t)} = A_{DC,T} \quad (VI.C.11)$$

Substituting Equations VI.C.11, VI.C.9, and VI.C.8 into Equation VI.C.6 produces:

$$\frac{d T_{RTD}}{d \ln(t)} = \frac{(R_2 + R_{RTD})^2 [1 + \alpha_\Omega (T - T_r)]}{F_2 [A_I (\overline{DC_I}) + B_I] R_2 R_{RTD} \alpha_\Omega} \cdot A_{V_o} \cdot A_{DC,T} \quad (VI.C.12)$$

Finally substituting Equations VI.C.12 and VI.C.5 into Equation IV.C.12 produces:

$$k = \frac{(F_1)^2 F_2 [A_I (\overline{DC_I}) + B_I]^3 (R_{RTD})^2 R_2 \alpha_\Omega}{4 \pi L_{RTD} (R_2 + R_{RTD})^2 [1 + \alpha_\Omega (T - T_r)] A_{V_o} A_{DC,T}} \quad (IV.C.13)$$

VII. RESULTS

VII.A. Results of the Phase Change Experiments

Two phase change experiments were performed and analyzed. The first was started with a temperature barely above the melting point so as to simulate no superheat in the melt. This allows the use of simpler equations for determination of the physical constants and nearly eliminates the effects of natural convection completely. The second experiment was performed with a superheat of about 10°C . This experiment was intended to determine the effect of natural convection on phase front progression if found. Both experiments were started with liquid n-octadecane at nearly uniform temperatures, and in each the face temperature was dropped to about 16°C below the freezing point.

The actual temperature data can be found in Appendix A. Plots of the temperature history for each of the two experiments are shown in Figures VII.A.1, and VII.A.2. From the plots were determined the data in Tables VII.A.1 and VII.A.2. The tables list the location of the phase front as a function of time. During the analysis it was found that the data fit well except for those of thermocouple 2. Thermocouple 2 was so close to the face, it is believed to have been affected by the slow drop in temperature of the face, as described in Appendix A.

The phase change experiment without superheat was analyzed first. The data were fit to an equation of the form of VI.A.5, with

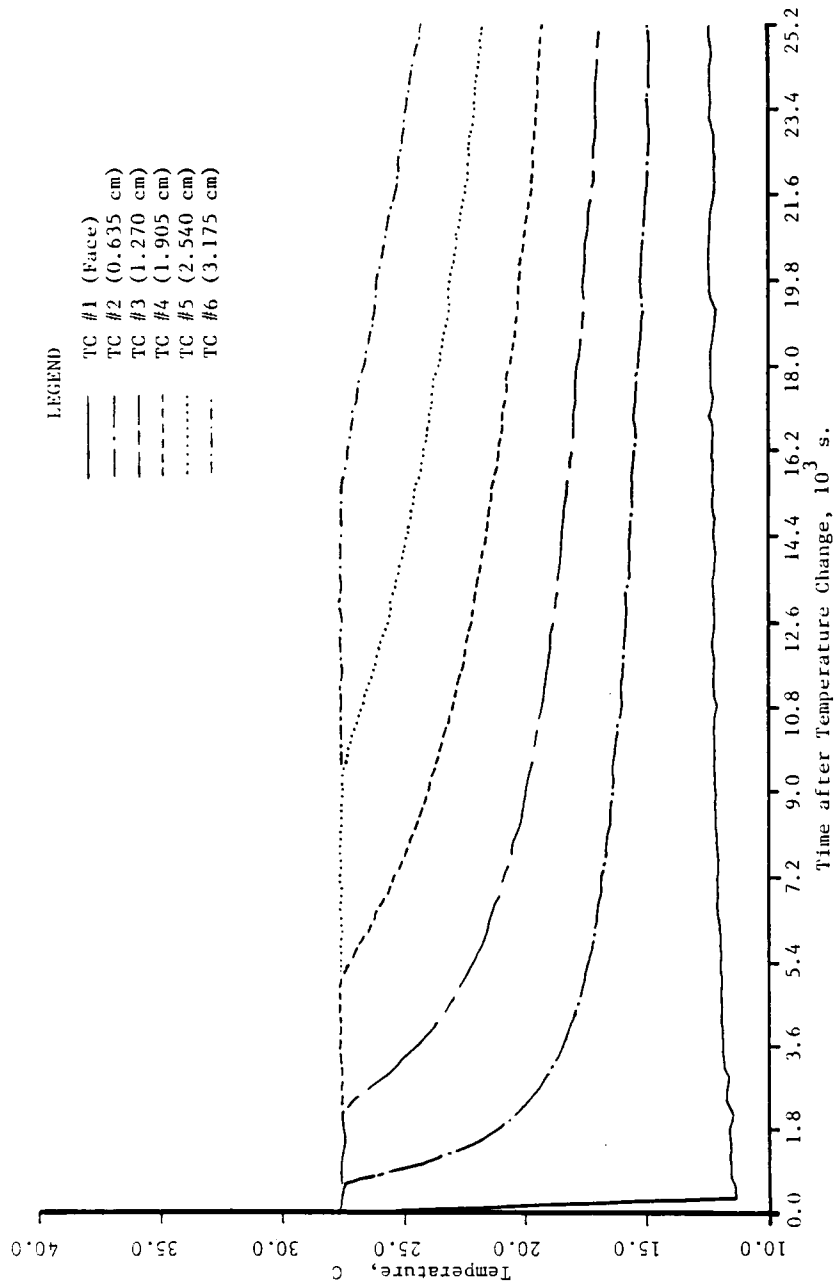


Figure VII.A.1. Thermocouple Data for the Phase Change Experiment Without Superheat

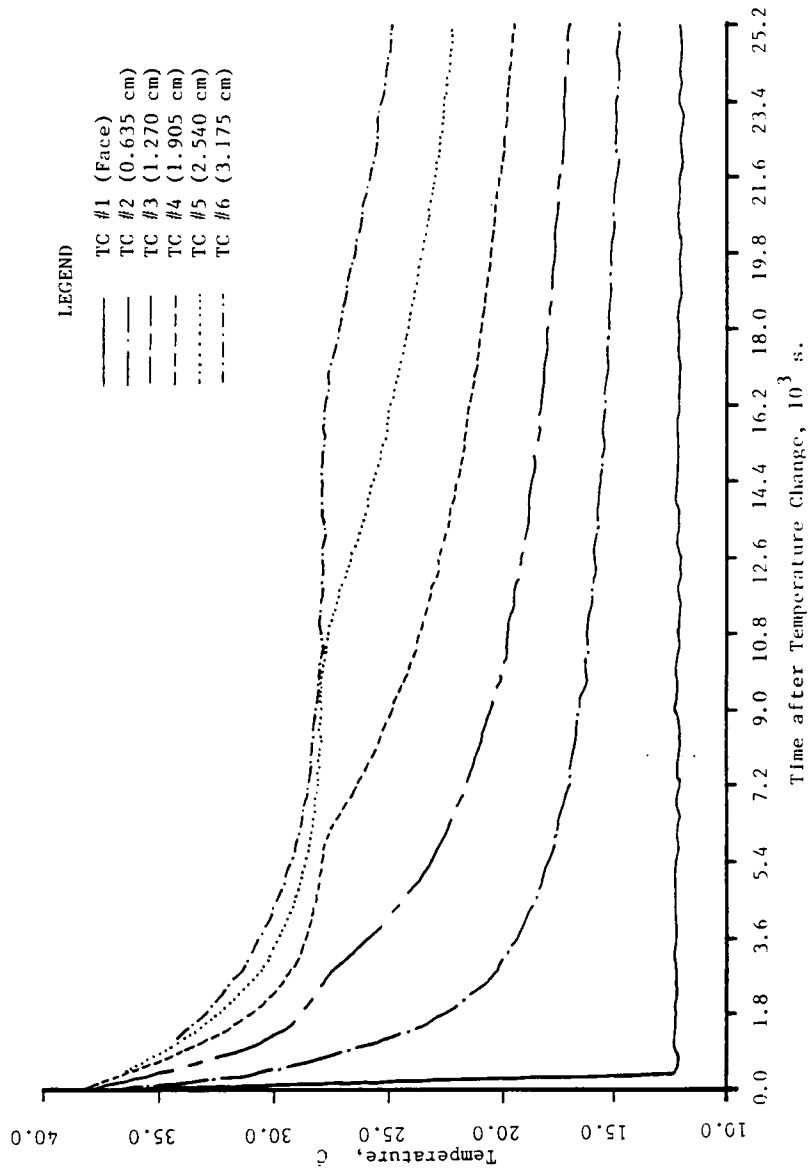


Figure VII.A.2. Thermocouple Data for the Phase Change Experiment With Superheat

Table VII.A.1. Phase Front Location vs Time
for the Phase Change Experiment
Without Superheat

Time (s)	Phase front location (m)	Thermocouple No.
2,295	0.0127	3
5,094	0.0190	4
9,450	0.0254	5
15,390	0.0318	6
21,600	0.0381	7

Table VII.A.2. Phase Front Location vs Time
for the Phase Change Experiment
With Superheat

Time (s)	Phase front	
	location (m)	Thermocouple No.
2,700	0.0127	3
6,030	0.0190	4
10,620	0.0254	5
16,200	0.0318	6
22,500	0.0381	7

the constant, λ , determined from Equation IV.A.11. Combining the Equation VI.A.6 for the coefficient, C_1 , with Equation IV.A.11, and solving for the thermal conductivity produces

$$k = \frac{\rho L}{2 (T_m - T_f) C_1} \quad (\text{VII.A.1})$$

The value of thermal conductivity which best fit the data was 0.43 W/m°C.

The analysis of the phase change experiment with superheat was more complicated. The thermal conductivity of the PVC walls of the cell was approximately times that of the PCM liquid. Conduction in the wall would cause the liquid near the wall to cool faster than liquid in the center of the cell. Natural convection would cause this cooler and denser liquid to flow toward the phase front. The warmer liquid would flow away from the phase front. Eventually the superheat of the liquid was dissipated.

A detailed analysis of this transient natural convection flow is beyond the scope of the work reported here. Without such analysis a reliable selection of the equations and data values to be used for determining the thermal conductivity cannot be made. The thermal conductivity cannot be made. The thermal conductivity was bracketed, however, using Equation IV.A.6 and making the assumptions that (1) the natural convection had no effect on the superheat and (2) the effect of superheat was completely eliminated by the natural convection. Solving Equation IV.A.6 for the thermal conductivity gives:

$$k_1 = \frac{\lambda L \alpha_1 \rho \sqrt{\pi} + k_2 (T_i - T_m) \sqrt{\alpha_1/\alpha_2} \left(\frac{\exp(-\alpha_1 \lambda^2/\alpha_2)}{\operatorname{erfc}(\lambda \sqrt{\alpha_1/\alpha_2})} \right)}{(T_m - T_f) \exp(-\lambda^2)/\operatorname{erf}(\lambda)} \quad (\text{VII.A.2})$$

If the full superheat is assumed (i.e. T_i = initial temperature of liquid), Equation VII.A.2 indicates a thermal conductivity of 0.46 W/m°C. If the superheat is assumed to be zero (i.e. $T_i = T_m$), the equation indicates a thermal conductivity of 0.42 W/m°C.

VII.B. Results of the Transient Conduction Experiment

The analysis of this experiment provided measurements of the thermal diffusivity of the PCM. Average values over the entire thickness of the PCM cell and over the smaller regions between the thermocouples were obtained. The measurement depended on an analysis of the decay of a sine wave temperature profile in the PCM. The decay curves of all thermocouples were analyzed at intervals of time and compared, to determine the thermal diffusivity as it may have varied both across the thickness of the PCM cell and in time.

The calculated values of thermal conductivity for each interval and time are listed in Appendix B. The data showed some variation that could not be explained by the variation of the thermal properties. A look at the raw data, temperature histories of the thermocouples, revealed that the last two sets of measurements should be discarded because the boundary condition was not held properly. The

very first set of measurements, which, analysis showed, were made at an acceptable time, were eliminated because they did not meet Chavenet's criteria. It was assumed that the proper boundary condition had not yet been obtained at this time in the experiment.

The remaining values of thermal diffusivity are given in Table VII.B.1. The data show a definite variation in the thermal diffusivity across the cell, but a variation in time cannot be determined from this data. The extreme variation of the values for the intervals 6, 7, and 8, (upper region of cell) led to the conclusion that the data for thermocouple 7, at 0.0381 m (between intervals 6 and 7), was suspect. It was recalled that this thermocouple is in the region that was last to freeze in the phase change experiment, and which, therefore, was likely to have high concentrations of voids. A void located near the thermocouple could disturb the pattern of heat flow changing the indicated temperature. In this case it was concluded that a void on the right hand side of the thermocouple caused an increase in the measured temperature. The calculated value of the transformation variable, x^* , at 0.0381 m was decreased. The end result was an increased calculated value for thermal diffusivity in interval 6 and a decrease for the interval 7.

Because of the apparent problem with the data of thermocouple 7, they were dropped from the analysis of this experiment. New values of thermal diffusivity were calculated for the combined intervals 6 and 7, from 0.03175 to 0.04445 meters, as listed in Table VII.B.2. With

Table VII.B.1. Thermal Diffusivity of Octadecane
from the Transient Conduction Experiment
(in $10^{-6} \text{ m}^2/\text{s}$)

Number	Interval (m)		Time (s)			
	From	To	2250	2700	3150	3600
1	0.00000	0.00635	0.277	0.287	0.305	0.271
2	0.00635	0.01270	0.244	0.262	0.262	0.246
3	0.01270	0.01905	0.184	0.207	0.216	0.195
4-5	0.01905	0.03175	0.131	0.155	0.169	0.166
6	0.03175	0.03810	0.192	0.218	0.230	0.214
7	0.03810	0.04445	0.107	0.115	0.116	0.108
8	0.04445	0.05080	0.239	0.243	0.255	0.242
	Effective					
All	0.0000	0.0508	0.174	0.193	0.212	0.191

Table VII.B.2. Revised Thermal
Diffusivity of Octadecane for
the Combined Intervals
6 and 7

Time (s)	Thermal diffusivity (10^{-6} m ² /s)
2250	0.140
2700	0.154
3150	0.159
3600	0.147

the substitution of this data the plots appear as in Figure VII.B.1. The variation in the thermal diffusivity appears to be much more reasonable than in the previous plot. The averaged values for each interval are listed in Table VII.B.3 and plotted in Figure VII.B.2.

It was concluded that the variation in the thermal diffusivity was caused by the formation of voids in the PCM. The effect of voids in a material on the apparent thermal diffusivity can be understood more clearly by noting that the thermal diffusivity, α , is the ratio of the thermal conductivity to the product of the density and specific heat:

$$\alpha = k/\rho c \quad \text{(VII.B.1)}$$

where:

k = thermal diffusivity

ρ = density and,

c = specific heat.

Noting also that no observable effect on the specific heat is expected, the effect may be understood by considering how the density and thermal conductivity could be changed by the presence of voids. These effects are more easily explained.

The added volume of the voids will decrease the apparent density of the solid PCM. The overall average of this effect is limited a decrease to the density of the liquid PCM. Locally this effect may be greater, however, due the possibility of the PCM flowing. It may be

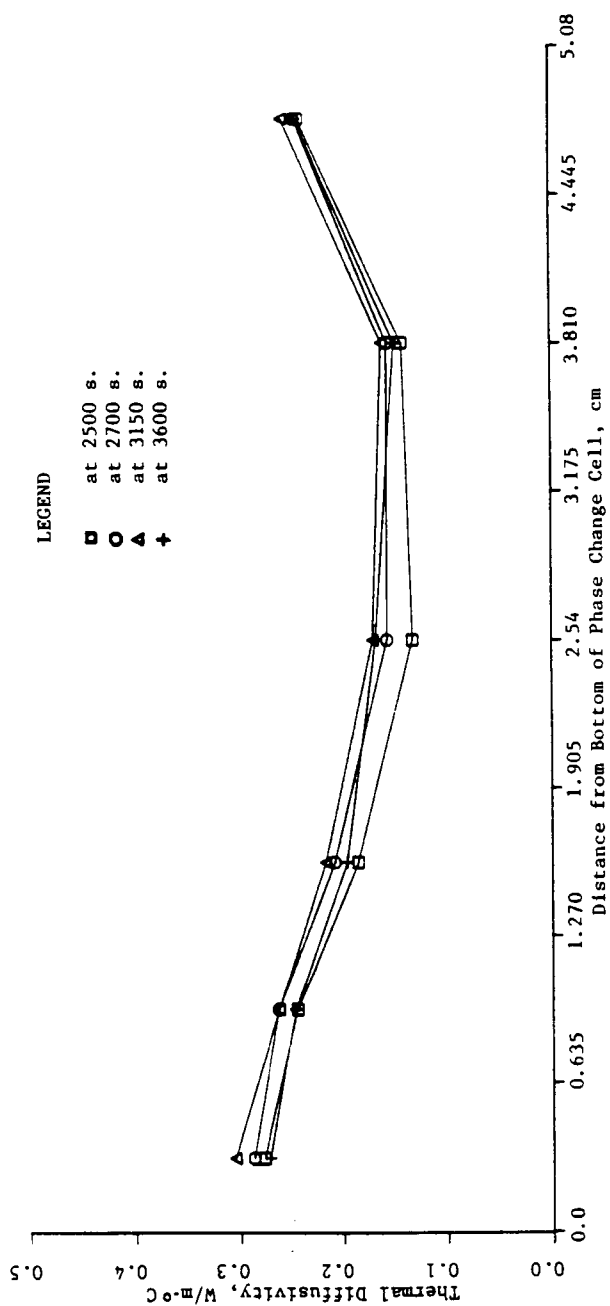


Figure VII.B.1. Effective Thermal Diffusivity of Octadecane in PCM Cell During the Transient Conduction Experiment

Table VII.B.3. Averaged Effective Thermal
Diffusivity of Octadecane in the
PCM Cell During the Transient
Conduction Experiment

Interval (m)		Thermal diffusivity ($10^{-6} \text{ m}^2/\text{s}$)
From	To	
0.00000	0.00635	0.284
0.00635	0.0127	0.253
0.01270	0.01905	0.200
0.01905	0.03175	0.154
0.03175	0.04445	0.150
0.04445	0.0508	0.245
0.00000	0.0508	0.192

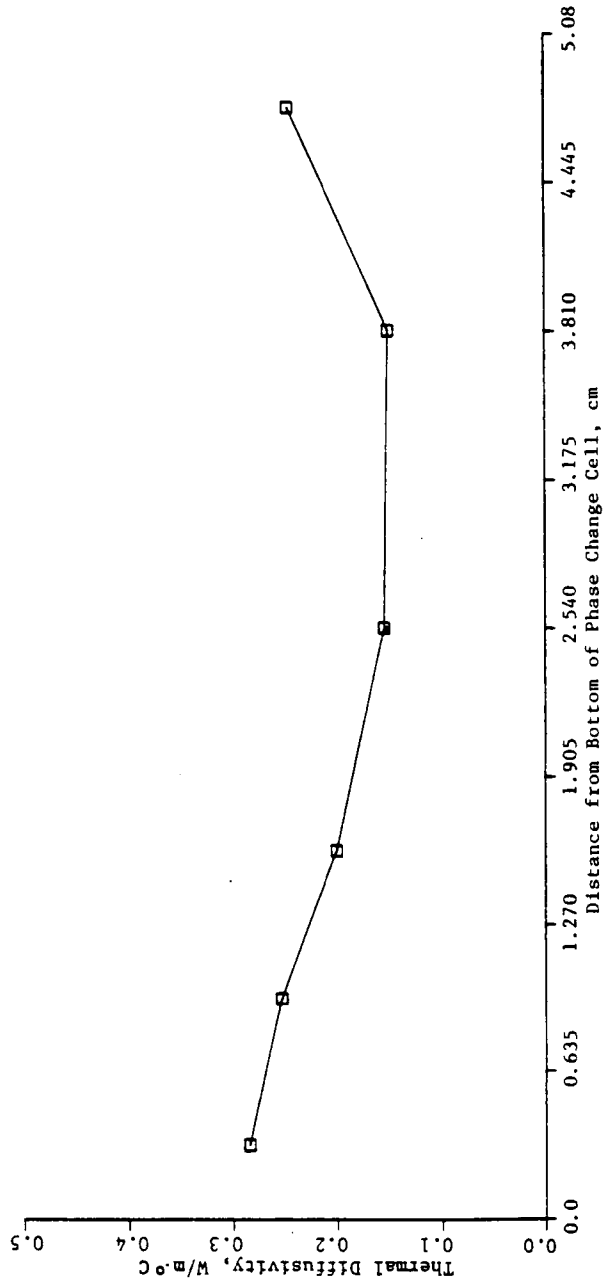


Figure VII.B.2. Averaged Effective Thermal Diffusivity of Octadecane in the PCM Cell During the Transient Conduction Experiment

expected that the earliest forming solid PCM will have the lowest void fraction.

The presence of voids in the PCM will also decrease the apparent thermal conductivity. The magnitude of the effect cannot easily be bounded, however, because it will depend not only on the occupied volume of the voids, but also on the arrangement of the voids. If the voids were neatly arranged so that the axial direction of heat flow was not much disturbed, the effect would be limited that caused by the reduction in area of heat flow from the apparent area. Since in steady state:

$$k = q/A \frac{dT}{dx} \quad (\text{VII.B.2})$$

a higher apparent area for heat flow will cause a decrease in the apparent thermal conductivity. In this "ideal case," the relationship of thermal conductivity to the apparent of effective area is:

$$\frac{k_{\text{eff}}}{k_s} = \frac{A_s}{A_{\text{eff}}} \quad (\text{VII.B.3})$$

Furthermore, if the length dimension in the direction of heat flow is not disturbed, the change in area is related to the change in density by:

$$\frac{\rho_{\text{eff}}}{\rho_s} = \frac{A_s}{A_{\text{eff}}} \quad (\text{VII.B.4})$$

Combining Equations VII.B.3 and VII.B.4 shows that, for the "ideal case:"

$$\frac{k_{eff}}{k_s} = \frac{\rho_{eff}}{\rho_s} \quad (VII.B.5)$$

so that substituting the effective properties into VII.B, would produce no change in the effective thermal diffusivity.

However, the voids do not arrange themselves "neatly" and the direction of heat flow must be modified by the irregularly spaced and irregularly shaped voids. The effective heat flow path is thus longer than the straight line distances between two points and the effective area may be decreased even more than as previously discussed. The effect will be to further decrease the apparent thermal conductivity.

The overall effect of the voids must be a reduction in the apparent thermal diffusivity. The increase in the apparent thermal diffusivity caused by the decrease of apparent density must be more than compensated for by the reduction in the thermal conductivity.

The minimum void density was expected in the interval from 0.000 m to 0.0064 m which is where the maximum thermal diffusivity was measured. This maximum value is the most appropriate measured value for the thermal diffusivity of the PCM. Using this maximum indicated thermal diffusivity, the density of the solid PCM and the specific heat,* conductivity of the solid PCM was determined to be 0.41 W/m°C.

The results shown in Figure VII.B.2 agree with the conclusions concerning the effect of voids and the probable distribution of voids

*The specific heat used here is the average of the three values given in Reference 1.

in the cell. The lowest values of measured thermal diffusivity are found slightly above the center of the cell. It was noted that in the phase change experiment in which the solid was prepared, freezing occurred primarily from the bottom upward. However, before the phase front had reached thermocouple 7, freezing had occurred in the upper region as well. The two phase fronts met in the interval from 0.03810 to 0.04445 meters. This is the region where a local void was assumed to have disturbed the temperature data of thermocouple 7, and where the lowest thermal diffusivity was indicated.

As noted in Section IV.B, the analysis used here depends on the assumption that:

$$\frac{\partial T}{\partial x^*} \cdot \frac{\partial}{\partial x} \left(\frac{\partial x^*}{\partial x} \right) \approx 0 \quad \text{VII.B.6}$$

A strict mathematical evaluation reveals that this is not a valid assumption near the ends of the test cell. However, it is believed that the influence of the term is minimal as is evident from the consistency of these results with others presented here.

VII.C. Results of the Line Source Thermal Conductivity Measurements

Measurements were made with three line source RTD's, placed at 0.0127 m (0.5 in.) intervals in the PCM cell to determine if a pattern could be established in the variation the thermal conductivity of the PCM, octadecane. Each of the RTD circuits was calibrated as described

in Section VI.C and Appendix C. They were then used to measure the thermal conductivity of the liquid and solid forms of the PCM. The solid form was prepared during a Phase Change experiment as described in Section VI.A. The results of these measurements are shown in Tables VII.C.1, VII.C.2 and VII.C.3.

The results show that this method is fairly reliable in that the standard deviation of the measurements was small for each circuit. There was, however, some error that was built into each circuit that was not removed by the calibration technique. This is seen by the different values of thermal conductivity measured for liquid state material. Since the liquid state thermal conductivity is well established at $0.15 \text{ W/m}^\circ\text{C}$, a final calibration factor was calculated for each RTD circuit which would produce the correct value of liquid thermal conductivity. These factors were then applied to the solid phase measurements to determine the thermal conductivity for solid octadecane. The results are shown in Table VII.C.4.

These measured values of thermal conductivity are very precise. A typical set of data obtained with the LSTs is shown in Figure VII.C.1. An uncertainty analysis on the uncorrected values of thermal conductivity indicated that the standard deviation of the mean for each set of measurements was less than 1.5% of the mean. However, since the source of the systematic error was unknown, it was also not known to be independent of temperature. The corrected thermal

Table VII.C.1. LST #1 Thermal Conductivity
Measurements of Octadecane
(Location 0.0127 m)

Measurement	State	Temperature (°C)	Thermal Conductivity (w/m°C)	Average Conductivity	Standard Deviation (%)
1	Liquid	31.4	0.166		
2	Liquid	31.2	0.168		
3	Liquid	28.4	0.167	0.167	0.8
4	Liquid	28.2	0.169		
5	Liquid	28.1	0.166		
6	Solid	21.5	0.451		
7	Solid	21.5	0.449		
8	Solid	21.5	0.453	0.451	0.4
9	Solid	21.4	0.450		

Table VII.C.2. LST #2 Thermal Conductivity
Measurements of Octadecane
(Location 0.0254 m)

Measurement	State	Temperature (°C)	Thermal Conductivity (w/m°C)	Average Conductivity (w/m°C)	Standard Deviation (%)
1	Liquid	31.0	0.168		
2	Liquid	30.8	0.170		
3	Liquid	30.6	0.167	0.168	0.7
4	Liquid	28.3	0.167		
5	Liquid	28.2	0.168		
6	Solid	21.6	0.440		
7	Solid	21.6	0.428		
8	Solid	21.6	0.427		
9	Solid	21.6	0.433	0.438	3.1
10	Solid	21.6	0.427		
11	Solid	21.6	0.457		
12	Solid	21.6	0.457		

Table VII.C.3. LST #3 Thermal Conductivity
Measurements of Octadecane
(Location 0.0381 m)

Measurement	State	Temperature (°C)	Thermal Conductivity (w/m°C)	Average Conductivity	Standard Deviation (%)
1	Liquid	30.4	0.156	0.156	1.9
2	Liquid	30.0	0.153		
3	Liquid	28.2	0.159		
4	Solid	21.7	0.410	0.404	1.9
5	Solid	21.7	0.397		
6	Solid	21.7	0.410		
7	Solid	21.7	0.397		

Table VII.C.4. Average and Adjusted Values
of Thermal Conductivity of Solid
and Liquid Octadecane

LST #	Measured		Adjusted	
	k _{liquid}	k _{solid}	k _{liquid}	k _{solid}
1	0.167	0.451	0.15	0.41
2	0.168	0.438	0.15	0.39
3	0.156	0.404	0.15	0.39

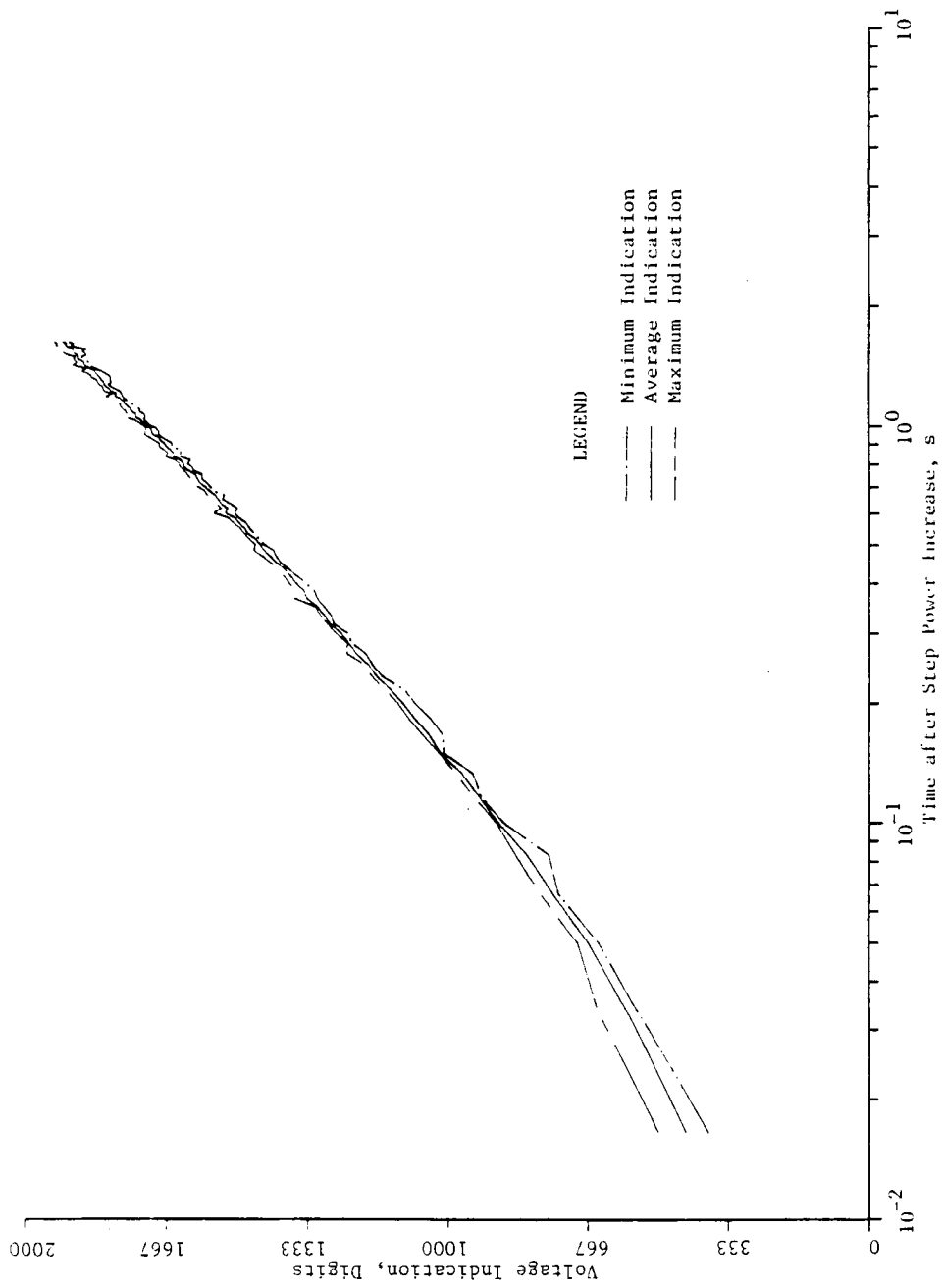


Figure VII.C.1. Sample of Line Source Data vs Time

conductivity measurements for the solid PCM are therefore slightly unreliable.

The data indicate a very slight trend in variation of the thermal conductivity. The value at 0.0127 m from the bottom face is higher than the measurements at 0.0254 m and 0.0381 m by about 2 1/2%. This is not very much of a variation but it is larger than one standard deviation of the corrected values.

VII.D. Discussion of ORNL/CSD-92

ORNL/CSD-92 [9] is an Oak Ridge National Laboratory technical paper titled *On the Solidification of N-Octadecane Paraffin Wax*. It reports results and analyses of phase change experiments similar to those reported here. In fact the work reported here is a continuation of the work reported in ORNL/CSD-92. Both sets of experiments used the same computer system with similar programs for data acquisition and experiment control. The biggest differences were in the design of the phase change cell, and in the initial conditions used for the phase change experiment. Also, in this more recent work, follow-up experiments were performed to determine the properties of the PCM in the state in which it was left by the experiment.

ORNL/CSD-92 reports on four phase change experiments. These experiments were performed in the phase change cell shown in Figure VII.D.1. The sides of this phase change cell were made of 0.0254 m thick plexiglass (methyl methacrylate). This material is reported to have a thermal conductivity of 0.2 W/m°C. It is seen from Figure

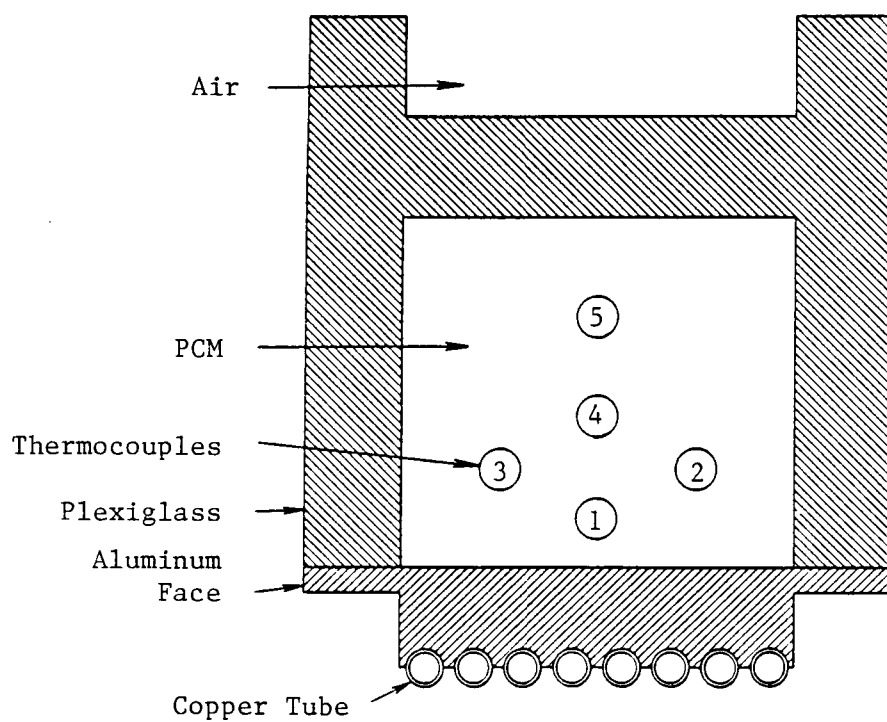


Figure VII.D.1. PCM Cell Used in Experiments Reported in ORNL/CSD-92
(after Figure 2 of Reference 9)

VII.D.1 that there is a more significant path for conduction in walls of this phase change cell than in the wall of the phase change cell shown in Figure V.B.1, page 32. The experiments of ORNL/CSD-92 were started with the liquid PCM at temperatures 10 to 26°C above the melting point.

Analysis of the experiments in ORNL/CSD-92 were in several forms. First, using 0.15 W/m°C for the thermal conductivity in an expression which was derived from Neumann's analysis, predicted phase front locations were compared with experimental observations. The predictions were 30 to 35% lower than experimental observations, indicating that the actual thermal conductivity was much higher than assumed. Next, an expression was derived for the thermal conductivity as a function of other PCM properties and experimentally observed data. Predicted thermal conductivities ranged from 0.516 to 0.648 W/m°C with an average of 0.59 W/m°C. Finally, a special finite difference computer code, called TES, was used to predict cooling curves for the experiments. The best fit of the predictions and the experimental data was obtained by assuming that the solid and liquid thermal conductivities were 0.525 and 6.5 W/m°C, respectively.

In evaluating the data of ORNL/CSD-92 the first calculations made were repeated using the thermal conductivity measured here in the phase change experiments. The expression for the phase front location used was

$$X(t) = \frac{2 k_x (T_m - T_f) t}{\rho L} \quad (\text{VII.D.1})$$

This equation may be obtained by combining Equations IV.A.7 and IV.A.11, and it neglects the effects of initial superheat and of the solid's specific heat. The value of thermal conductivity used was 0.41 W/m°C. The results, shown in Table VII.D.1 indicate that the measured thermal conductivity is more than sufficient to make up the reported inconsistency.

The remaining two analyses conducted in ORNL/CSD-92 attempt to take into account the sensible heat in both the liquid and solid. Neither, however, takes into account the effect of natural convection or conduction in the walls. Due to the initial superheat and high conductance of the walls of the test cell, the effect of natural convection is significant. Natural convection currents transfer heat to the walls fairly quickly and the walls conduct the heat to cooled face. By the nature of each of the analyses the superheat is assumed to be transferred by conduction through both the liquid and solid phases. The indicated conductivity is based on an artificially high heat transfer rate. The indicated thermal conductivities are therefore much higher than the actual values.

VII.E. Discussion of Results

Table VII.E.1 lists values for the thermal conductivity found by various methods and investigations for the PCM, octadecane. The lowest value is believed to be the result of the inappropriate assumption

Table VII.D.1. Comparison of ORNL/CSD-92
Data with Predictions

ORNL/CSD-92 EXP No.	$T_i - T_m$ (°C)	$T_m - T_f$ (°C)	t (s)	X_{obs} (m)	X_{pred} (m)	% error of X
1	10.5	9.5	4,200	0.0127	0.0129	+1.6
			16,800	0.0254	0.0257	+1.2
2	26.0	9.5	4,500	0.0127	0.0133	+4.7
			19,200	0.0254	0.0275	+8.3
3	22.0	9.5	4,800	0.0127	0.0137	+7.9
			18,000	0.0254	0.0266	+4.7
4	22.0	9.5	5,400	0.0127	0.0146	+15.0
			17,400	0.0254	0.0262	+3.1

X_{obs} = observed value,

X_{pred} = predicted value.

Table VII.E.1. Reported Values of Thermal Conductivity of Octadecane

Thermal Conductivity	Source	Type of Experiment
0.15	[22]	Unknown
0.164	[1]	Unknown
0.19	[23]	Steady-state one dimensional conduction
0.41	[2]	Conduction w/phase change
0.35	[11]	Steady-state radial conduction
0.525, 0.56	[9]	Conduction w/phase change
0.43 (0.42—0.46)	—	Conduction w/phase change
0.41 (0.18—0.45)	—	Transient one dimensional conduction (measured thermal diffusivity)
0.39, 0.41	—	Transient radial conduction (line source technique)

that the liquid and solid thermal conductivities are equal. Too little is known or is apparent concerning the second value to determine how it was obtained. The remaining values are well documented and the variations can be explained by the behavior of octadecane on freezing and the effects on the indicated values of the various methods. Powell and Challonar [23] used a guarded plate apparatus to measure the thermal conductivity of the PCM at thicknesses of 2 and 3 mm. Precautions were taken to eliminate air from the prepared sample, but apparently no precautions were taken to eliminate voids which could be filled with gaseous octadecane at low pressure. It is probable then that voids did form and reduced the heat transfer rate significantly. The indicated thermal conductivity is approximately half the true conductivity.

The values of $0.41 \text{ W/m}^\circ\text{C}$ found by Bailey and Liao [2] and $0.43 \text{ W/m}^\circ\text{C}$ found in the phase change experiment conducted here were determined from the experimentally determined ratio of the thermal conductivity to the product of the latent heat and density of the PCM. In both sets of experiments, very small voids could have formed in the solid PCM causing a reduction in the effective thermal conductivity and effective density of the PCM. As has been discussed, the reduction in the conductivity is probably slightly more severe than the reduction in density depending on the arrangement of the voids. If the effects were equal the indicated thermal conductivity would be the true value.

The values of for 0.525 and 0.56 W/m°C found by Deal and Solomon [9], and 0.46 W/m°C found in phase change experiment conducted here are higher than the true value because of effects of superheat and convection in the initial liquid state of the PCM. The value of 0.35 W/m°C found by Griggs and Yarbrough [11] appears to be a reasonable value for the effective thermal conductivity for the solid PCM with a moderate distribution of voids. It is in agreement with the values found in the one dimensional conduction experiment reported here, which were calculated from the experimentally determined thermal diffusivity. The uncertainty of the specific heat affects the calculated thermal conductivity. Using the maximum and minimum values of the indicated for each property results in a range of thermal conductivity values from 0.18 W/m°C to 0.45 W/m°C. The table value, of 0.41 W/m°C results from using the highest indicated thermal diffusivity and the average specific heat for octadecane from Reference 16.

The thermal conductivity measurements obtained with the line source technique are in the range expected, but do not show the strong variation expected to be caused by the distribution of voids. This may be caused by preferential freezing around the RTD or due to the averaging of the conductivity in all directions.

VIII. CONCLUSIONS

A variety of values have been reported for the thermal transport properties of the solid phase of the PCM, octadecane. The work reported here has shown the variation may at least partially be explained by the presence of voids and their effect on the measurement technique used. The presence of voids will decrease both the effective density and thermal conductivity with the thermal conductivity being more severely altered. There is some variation in reported values of the specific heat which cannot be explained by the effects of voids. These may be due to variations in the purity of the sample.

The objective of this work was to obtain the appropriate value of thermal conductivity for use in modeling phase change processes in thermal energy storage devices. The most appropriate value was found to be approximately $0.43 \text{ W/m}^\circ\text{C}$. Analyses should also account for wall effects and the effects of natural convection in the melt. Failure to do so has led to erroneous conclusions in past experiments.

This work also indicates a need for further study of the thermal properties of octadecane. Thermal conductivity measurements on a sample prepared under pressure sufficient to preclude the formation of voids would be valuable. More data on the specific heat is needed. Also, the effects of impurities and mixture ratios on the thermal properties of parafins and parafin mixtures would be helpful for design engineers.

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APPENDIXES

APPENDIX A

As was discussed in Section VI.A the analysis of the "Phase Change Experiment" data required two steps. First, the time at which the phase front passes the location of each thermocouple is determined. Then, these data are fitted to an equation of the form of Equation VI.A.4. The resulting constants are used to determine the thermal conductivity by substitution into either Equations IV.A.6, IV.A.10 or IV.A.11 as applicable.

Figure VII.A.1, page 62, and Figure VII.A.2, page 63, show the plotted results of two phase change experiments. The discontinuities in the temperature history are easily located. The data around the discontinuity in each curve was plotted also in a graph with a much expanded temperature scale. One of these plots is shown in Figure A.1. Such plots provided an even clearer indication of the time at which the phase front passed.

Table VII.A.1, page 64, and Table VII.A.2, page 65, show locations and times for the thermocouples in the two phase change experiments reported. These will be fitted by the "method of least squares" to an equation of the form:

$$t = C_1 \cdot (X')^2 + C_2(X') + C_3 \quad \text{A.1}$$

where

$$C_1 = \frac{1}{4\lambda^2\alpha_1} \quad \text{A.2a}$$

$$C_2 = \frac{x_o}{2\lambda^2\alpha_1} \quad \text{A.2b}$$

$$C_3 = \frac{x_o^2}{4\lambda^2\alpha_1} + t_o \quad \text{A.2c}$$

The "method of least squares" is a standard technique in data regression. It is found in numerous tests [15,17] where it is shown that the coefficients are found by solving the matrix equation:

$$\begin{array}{ccccccc} \Sigma(X')^4 & \Sigma(X')^3 & \Sigma(X')^2 & C_1 & = & \Sigma(X')^2 t' & \\ \Sigma(X')^3 & \Sigma(X')^2 & \Sigma(X') & C_2 & = & \Sigma X' t' & \text{A.3} \\ \Sigma(X')^2 & \Sigma(X') & N & C_3 & = & \Sigma t' & \end{array}$$

where Σ means $\sum_{i=1}^N$, N is the number of data pairs used. Table A.1 shows the final set of data for the phase change experiment without initial superheat. (The data for the No. 2 thermocouple was eliminated by applying Chauvenet's criterion for rejecting data. The variable used in the evaluation was $\frac{C_1(X')^2 + C_2(X')}{t' - C_3}$, where C_1 , C_2 , and C_3 are the coefficients in Equation A.1, determined when all data are used.)

Equation A.2a was substituted into Equation IV.A.11 and solved for the thermal conductivity, k :

$$k = \frac{\rho L}{2 \cdot C_1 \Delta T} \quad \text{A.4}$$

where the values and sources for the variables used are:

Table A.1. Data from Analysis
of the Phase Change Experiment
Without Superheat

$\Sigma (X')$	0.127 m^4
$\Sigma (X')^2$	$3.6290 \times 10^{-3} \text{ m}^3$
$\Sigma (X')^3$	$1.1266 \times 10^{-4} \text{ m}^2$
$\Sigma (X')^4$	$3.0973 \times 10^{-6} \text{ m}$
$\Sigma (X')^2(t')$	$55.184 \text{ m}^2 \cdot \text{s}$
$\Sigma (X')(t')$	$1677.8 \text{ m} \cdot \text{s}$
$\Sigma(t')$	53829 s
N	5
C_1	14871000 s/m^2
C_2	14693 s/m
C_3	-401 s
x_o	0.0005 m
t_o	-405 s
k_{PCM}	$0.43 \text{ w/m}^\circ\text{C}$

$$\rho = 810 \text{ kg/m}^3 \quad [1,25]$$

$$L = 243 \text{ kJ/kg}^\circ\text{C} \quad [1,25]$$

$$\Delta T = 15.5^\circ\text{C} \quad \text{experimental data}$$

$$C_1 = 14,870,000 \quad \text{experimental data}$$

The values of all the data are found in Table A.1.

Analysis of the phase change experiment with superheat was slightly different. The added resistance to heat transfer in the form of an equivalent thickness of solid n-octadecane was determined from the previous experiment. Therefore it could be used in the equation to be fitted to the data of this experiment. The equation to be fitted is of the form

$$t' = C_1(X_e)^2 + C_3$$

where

$$C_1 = \frac{1}{4\lambda^2\alpha}, \quad C_3 = t_0$$

For this equation the "method of least squares" requires that C_1 and C_3 be determined from the simultaneous equations:

$$C_1 \sum (X_e)^4 + C_3 \sum (X_e)^2 = \sum (X)^2 t'$$

$$C_1 \sum (X_e)^2 + C_3 \cdot N = \sum t'$$

where $X_e = X' + x_0$ as described in Section VI.A (Equation VI.A.1). The resulting data are shown in Table A.2.

The thermal conductivity indicated by this experiment can not be calculated directly. Equation IV.A.6 would be valid if the effect of

Table A.2. Data from Analysis
of the Phase Change Experiment
With Superheat

x_o	0.0005 m (from Table A.1)
$\Sigma (x)^2$	$3.6417 \times 10^{-3} \text{ m}^2$
$\Sigma (x)^4$	$3.7199 \times 10^{-6} \text{ m}^4$
$\Sigma (x)^2 t'$	$5.8646 \times 10^1 \text{ m}^4 \cdot \text{s}$
$\Sigma t'$	$5.8050 \times 10^4 \text{ s}$
N	5
C_1	15331000 s/m^2
C_3	444 s
t_o	444 s
k_{PCM}	0.42 w/m°C (neglecting superheat)
k_{PCM}	0.46 w/m°C (including superheat)

initial superheat were constant. As discussed in Section VII.A, it is seen that the initial superheat is eventually dissipated by natural convection and heat loss through sides and the end of the cell, so that the effect of the superheat is not constant. However, Equation IV.A.6 can be used to bracket the indicated thermal conductivity. If the effect of superheat is neglected, Equation IV.A.6 will produce a minimum indication, and if the superheat is assumed to have full effect, the equation produces a maximum indication. Since the effect of superheat is small, the two values should be close.

Equation IV.A.6 solved for the thermal conductivity, k_1 is:

$$k_1 = \frac{\lambda L \alpha_1 \rho \sqrt{\pi} + k_2 (T_i - T_m) \sqrt{\alpha_1 / \alpha_2} \frac{\exp(-\alpha_1 \lambda^2 / \alpha_2)}{\operatorname{erfc}(\lambda \sqrt{\alpha_1 / \alpha_2})}}{(T_m - T_f) \exp(-\lambda^2) / \operatorname{erf}(\lambda)}$$

The value and sources for the variables used are:

$$\lambda = 0.276, \text{ from analysis } [\lambda = (4 \cdot A \cdot \alpha_1)^{-1/2},$$

$$L = 243 \text{ KJ/kg; [1]}$$

$$\alpha_1 = 0.214 \times 10^{-6} \text{ m}^2/\text{s; from conduction experiment,}$$

$$\rho = 810 \text{ kg/m}^3; \text{ solid density, [1],}$$

$$k_2 = 0.15 \text{ W/m}^\circ\text{C; [1],}$$

$$\alpha_2 = 0.84 \times 10^{-7} \text{ m}^2/\text{s; [1],}$$

$$T_m - T_f = 15.4^\circ\text{C; experimental data,}$$

$$T_i - T_m = 10.7; \text{ experimental data (if using superheat),}$$

$$T_i - T_m = 0.0; \text{ experimental data (if neglecting superheat)}$$

The results are shown in Table A.2.

APPENDIX B

ERROR ANALYSIS OF THE CONDUCTION EXPERIMENT

WITHOUT PHASE CHANGE

The classical solution of the plane wall conduction problem given in Section IV.B is an infinite series. It would be quite difficult to obtain a value of thermal conductivity from the experiment performed here if all terms had to be included. Therefore only the first term of the series was considered. This required that the initial temperature profile be a single sinusoid with a period equal to the wall thickness. Such a temperature profile cannot exist in the steady state. To obtain this temperature profile, the test cell was first brought to a steady uniform temperature and then the face temperatures were dropped to the value used in the experiments. Time was then allowed so that all of the terms except the first decayed sufficiently to be negligible.

To determine this delay period the terms of the solution are calculated for the initial condition of a steady uniform temperature. These are found in Equation II.B.6:

$$\bar{T}_n = B_n \sin(n\pi\bar{x}) \exp(-n^2\pi^2 \bar{t}) \quad \text{B.1}$$

where from Equation II.B.7:

$$B_n = 2 \int_0^1 f_0(\bar{x}) \sin n\pi \bar{x} d\bar{x}$$

If the initial temperature is used for the reference temperature, T_r in Equation IV.8.4, then:

$$f_0(\bar{x}) = \text{constant} = 1$$

$$B_n = 2 \int_0^1 \sin(n\pi\bar{x}) d\bar{x} \quad \text{B.2a}$$

$$= \frac{-2}{n\pi} [(-1)^n - 1] \quad \text{B.2b}$$

It is seen that the even ordered terms are all zero. Letting $n = (2m - 1)$, a new series may be calculated with terms of the form:

$$\bar{T}_m = \frac{4}{(2m - 1)\pi} \sin[(2m - 1)\pi\bar{x}] \exp[-(2m - 1)^2 \pi^2 \bar{t}] \quad \text{B.3}$$

The error caused by neglecting each of these terms will be greatest when the sine function is equal to ± 1 . Thus the maximum absolute value of each term is expressed:

$$|\bar{T}_m|_{\max} = \frac{4}{(2m - 1)\pi} \exp[-(2m - 1)^2 \pi^2 \bar{t}] \quad \text{B.4}$$

It can be shown that the sum of higher order terms is less than the first term neglects so that only the second order term is to be checked.

$$|\bar{T}_2| = \frac{4}{3\pi} e^{-9\pi^2 \bar{t}} \quad \text{B.5}$$

It is desired that the error caused by neglecting this term be less than the uncertainty of the temperature measurement. To obtain this, the right hand member of the equation must be multiplied by the original temperature difference which is found in the data.

$$\begin{aligned}\Delta T_{O \text{ max}} &= 26.4^{\circ}\text{F} - 13.6^{\circ}\text{F} \\ &\approx 12.8^{\circ}\text{F}\end{aligned}$$

The error associated with the second term is

$$E_2 = 12.8 \frac{4}{3\pi} e^{-9\pi^2 \bar{t}} \quad \text{B.6}$$

where from IV.B.4

$$\bar{t} = \frac{\alpha t}{L^2}$$

Thus it is desired that

$$12.8 \frac{4}{3\pi} \exp -9\pi^2 \frac{\alpha t}{L^2} < E_{TC} \quad \text{B.7}$$

or

$$t > - \frac{L^2}{9\pi^2 \alpha} \ln \frac{E_{TC}}{12.8 \frac{4}{3\pi}}$$

Assuming the conservative values:

$$L = 0.0526 \text{ m}$$

$$\alpha = 0.2 \times 10^{-6} \text{ m}^2/\text{s}$$

and an uncertainty for the thermocouple data of 0.1°C , the required delay time is calculated to be:

$$t_{\text{delay}} = 620 \text{ s} .$$

The delay required for the decay of the higher order terms of the Fourier series should be added to the time required for the face temperature to drop from its initial temperature to a steady value. This

time was observed in early experiments to be about 3 minutes. Therefore, for conservatism a delay of about 1000 seconds was used. Data taken less than 1000 seconds after the switch of coolant baths was eliminated from the calculations.

The remaining data represent the decay of a single sinusoidal temperature profile in the test cell. The decay constant is a function of the thermal diffusivity and the thickness of the test cell. The profile is a sinusoidal function in the transformation variable, x^* , defined in Section IV.B. The distortion of the sinusoid in the normally define x-dimension will reveal the variation of the thermal diffusivity in test cell.

The use of a sinusoid for the initial temperature profile in the cell will change for form of the solution to Equation IV.B.5 only in the calculation of the coefficients, B_n . The initial temperature profile may be define as:

$$T_o(x) = f_o(x) = T_f + \Delta T_{\max,o} \sin \frac{\pi x^*}{L^*} \quad B.9$$

Letting, $T_r = T_f + \Delta T_{\max}$ and substituting in the normalizing variables of Equation IV.B.16. The coefficients in IV.B.4. Take on the form:

$$B_n = 2 \int_0^1 \sin(\pi \bar{x}) \sin(n\pi \bar{x}) d\bar{x} \quad B.10$$

so that:

$$B_1 = 1 \quad \text{B.11}$$

and:

$$B_n = 0 \quad \text{for } n > 2 \quad \text{B.12}$$

The total solution then is

$$\bar{T}(\bar{x}, \bar{t}) = \sin(\pi \bar{x}) \exp(-\pi^2 \bar{t}) \quad \text{B.13}$$

where, from Equation IV.B.16:

$$\bar{T}(\bar{x}, \bar{t}) = \frac{T(\bar{x}, \bar{t}) - T_f}{\Delta T_{\max, o}} \quad \text{B.14}$$

$$\bar{x} = \frac{x^*}{L^*} \quad \text{B.15}$$

and

$$\bar{t} = \frac{t}{(L^*)^2} \quad \text{B.16}$$

Each thermocouple should have a temperature history defined by an equation of the form of Equation VI.B.1.

$$T(x, t) = T_f + \bar{T}_o(x) \exp\left(-\frac{t}{\tau}\right)$$

The method of least squares was applied to the data by converting this to a first order polynomial form as discussed in Section IV.B. The polynomial form is Equation VI.B.10:

$$Y_n(t) = A_n t + B_n$$

where:

$$Y_n(t) = \ln[T(x_n, t) - T_f]$$

$$A_n = -1/\tau \text{ (The negative inverse of the time constant)}$$

$$B_n = \ln [T(x_n, 0) - T_f].$$

The data were in the form of temperature histories for each of the nine thermocouples one in each end face and seven in the PCM chamber). Separate temperature profiles and decay constants were calculated for sequences of eleven data sets. The eleven data sets in each group were taken at 45 second intervals. The temperature profiles were obtained by calculating the base temperature function, $[T(x_n, 0) - T_f]$, for each of the seven thermocouples at the same reference time, t_0 .

Table B.1 lists the calculated temperature profiles for each of the calculation times. The average logarithmic decay constant for all thermocouples was calculated for the same times. From these decay constants the value of L^* was calculated using Equation VI.B.4. These data are listed in Table B.2.

Table B.2. Logarithmic Decay
 Constants and L^* Values vs
 Time for the Transient
 Conduction Experiment

Calculation time (s)	Logarithmic Decay Constant (s)	L^* (s ^{1/2})
1800	1918	137.6
2250	1586	125.1
2700	1437	119.1
3150	1312	116.4
3600	1451	119.9
4050	1035	101.1
4500	1439	119.2

$$L^* = \int_0^L 1/\alpha^{1/2} dx$$

The values of the transformation variable, x^* , were then calculated using Equation VI.B.12. $\bar{T}_o$, max, the assumption that the effective thermal diffusivity in the intervals 4 and 5 were equal. The assumed temperatures and the values of x^* at each thermocouple are listed in Table B.3.

To obtain the value of x^* for the PCM chamber the contribution made by the aluminum face plates of the cell was calculated and subtracted appropriately (this value was calculated to be $1.7 \text{ s}^{1/2}$ for each face). With this taken into account the values of effective thermal diffusivity for each interval and for the entire PCM chamber were calculated. Values are listed in Table B.4 and plotted in Figure B.1.

As discussed in Section VII.B two pairs of intervals were combined each into one double size, 0.0127 m, interval. The intervals from 0.01905 m to 0.02540 m and from 0.02540 to 0.03175 were merged because the analysis was based on the assumption that the average thermal diffusivities in these two intervals were equal. The intervals from 0.03175 m to 0.03810 m and from 0.03810 m to 0.04445 m were merged because extreme variation in the thermal diffusivity in these two intervals indicated a fault in the data for the thermocouple at 0.03810 m. It was concluded that diffusivity calculated for the experimental time of 4050 seconds. The examination revealed that the face temperature had risen slightly during the interval and had thus distorted the calculations. The effect of this small fluctuation in

Table B.3. Assumed Maximum T_o and Calculated Values of x^* at Thermocouple Locations for the Transient Conduction Experiment

Time (sec)	$T_{o,max}$	x^* ($s^{1/2}$)					
		Thermocouple locations					
		0.00635	0.01270	0.01905	0.02540	0.03175	0.04445
1800	8.619	14.7	28.6	45.2	65.2	85.2	101.7
2250	6.515	13.8	26.6	41.4	58.9	76.5	91.0
2700	4.739	13.6	26.0	39.9	56.1	72.2	85.8
3150	3.324	13.2	25.6	39.3	54.8	70.2	83.5
3600	3.329	13.9	26.7	41.1	56.6	72.2	85.9
4050	1.585	11.6	22.7	34.8	47.7	61.2	72.5
4500	1.082	14.0	28.1	42.2	57.3	72.5	85.4
							105.9
							122.4
							110.4
							104.5
							102.1
							105.3
							89.2
							105.9

Table B.4. Thermal Diffusivity of Octadecane Calculated
for the Transient Conduction Experiment
(in $10^{-6} \text{ m}^2/\text{s}$)

Interval (m)		Time (s)							
From	To	1800	2250	2700	3150	3600	4050	4500	
0.00000	0.00635	0.241	0.277	0.287	0.305	0.271	0.411	0.267	
0.00635	0.01270	0.209	0.244	0.262	0.262	0.246	0.325	0.203	
0.01270	0.09050	0.145	0.184	0.207	0.216	0.195	0.276	0.203	
0.01905	0.03175	0.101	0.131	0.155	0.169	0.166	0.233	0.176	
0.03175	0.03810	0.149	0.192	0.218	0.230	0.214	0.312	0.240	
0.03810	0.04445	0.094	0.107	0.115	0.116	0.108	0.144	0.096	
0.04445	0.05080	0.224	0.239	0.243	0.255	0.242	0.393	0.303	
Effective									
0.00000	0.05080	0.143	0.174	0.193	0.212	0.191	0.271	0.193	

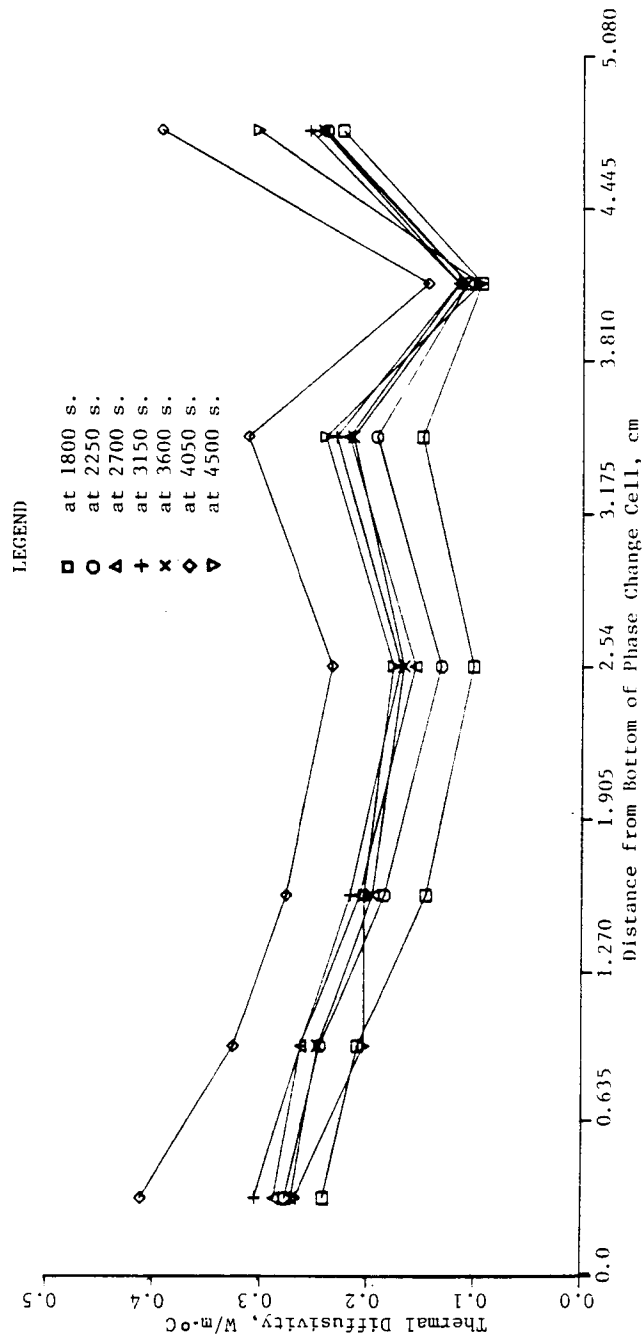


Figure B.1. Calculated Effective Thermal Diffusivity of Octadecane in the PCM Cell During the Transient Conduction Experiment

face temperature was amplified by the advanced decay of the sinusoidal temperature profile. The data for this profile and the last were judged not to adequate and were therefore drop from the calculation. The faulty data was caused by an abnormally large void near the thermocouple and in the interval from 0.03810 m to 0.04445 m.

Finally a statistical analysis was performed which eliminated the data for the experimental time of 1800 seconds. This analysis was performed on the ratio of the transformation variable, Δx^* , to the Δx , for each interval. The mean and standard deviation of the five data calculated for each interval were calculated. The results are listed in Table B.5.

It was found that half of the values calculated for the time of 1800 seconds did not meet Chauvenet's criterion. (For 5 data the deviation from the mean must be less than 1.65 times the standard deviations.) The remaining data for 1800 seconds was very close to not meeting the criterion and so all of these data were eliminated.

The remaining data were used to calculate the results listed in Section VII.B.

Table B.5. Statistical Analysis of the Data
from the Transient Conduction Experiment

Interval (m)		$\Delta x^* / \Delta x$ ($\sqrt{s/m}$)			$\Delta x^* / \Delta x$ Mean		Standard Deviation	$\Delta x^* / \Delta x$ Corrected Mean		Corrected Standard Deviation
From	To	1800	2250	2700	3150	3600				
0.00000	0.00635	2037	1900	1867	1811	1921	84	1875	48	
0.00635	0.01270	2187*	2024	1954	1954	2016	95	1987	38	
0.01270	0.01905	2626*	2331	2198	2152	2265	187	2237	78	
0.01905	0.03175	3147	2763	2540	2433	2454	298	2548	151	
0.03175	0.04445	2936*	2673	2548	2508	2608	169	2584	72	
0.04445	0.05080	2113	2046	2029	1980	2033	48	2022	29	

*Values were found not to meet Chavenet's criteria. All values calculated for 1800 seconds were eliminated from the final results.

APPENDIX C

ERROR ANALYSIS OF THE LINE SOURCE TECHNIQUE

As discussed in Section IV.C, the line source technique depends on the use of Equation IV.C.12 to predict the temperature of the platinum RTD. Equation IV.C.12 was developed for a theoretical infinitely long line source with a diameter of zero. Any real apparatus must have both finite length and finite diameter, and be placed in a medium with finite bounds. Besides the errors that might be introduced by the physical arrangement of the line source RTD in the test cell, there is the possibility of error due to the data acquisition system. These errors are discussed below.

The errors due to the finite diameters of the probe and of the test medium have been discussed by Horrocks and McLaughlin [14]. They present revised equations for the temperature at the radius of the probe for each case. For a finite wire diameter:

$$T(a,t) = \frac{q_1}{4\pi k_m} \ln(t) + \ln \frac{4\alpha_m}{a^2 \gamma} + \frac{a^2}{2\alpha_m t} + \frac{(w-2)a^2}{2w\alpha_m t} \ln \frac{4\alpha_m t}{a^2} \quad \text{C.1}$$

where:

a = radius of wire

$w = 2 c_m \rho_m / c_w \rho_w$

γ = Euler's constant (= 0.57716...)

For a medium bounded by a cylinder of radius, b :

$$T(a,t) = \frac{q_1}{4\pi k_m} \left[2 \ln\left(\frac{b}{a}\right) - 4 \sum_{n=1}^{\infty} \frac{\exp\{-\alpha_m t (x_n/b)^2\}}{\{2/\pi N_0(x_n)\}^2 - x_n^2 \frac{a}{b}} \right] \quad \text{C.2}$$

where

x_n = roots of the zero-order Bessel function

$N_0(x_n)$ = corresponding zero-order modified Bessel function.

These equations were plotted in a graph which was similar to Figure C.1. The graph uses the non-dimensional variables of $4\pi k_m T/q_1$ and $\ln(\alpha_m t/a^2)$. It is seen that the curve is the necessary straight line over a period which depends on the parameters: ω and b/a . For the application used here, ω is calculated with the following data:

For octadecane [1]:

$c \approx 1.88 \text{ KJ/Kg}^\circ\text{C}$ (0.45 BTU/lbm $^\circ\text{F}$) solid

$\approx 2.1 \text{ KJ/Kg}^\circ\text{C}$ (0.50 BTU/lbm $^\circ\text{F}$) liquid

$\rho \approx 860 \text{ Kg/m}^3$ (54 lbm/ft ^{3})

$\approx 790 \text{ Kg/m}^3$ (49 lbm/ft ^{3})

For platinum [21]:

$c = 0.142 \text{ KJ/Kg}^\circ\text{C}$ (0.034 BTU/lbm $^\circ\text{F}$)

$\rho = 21,500 \text{ Kg/m}^3$ (1340 lbm/ft ^{3})

$w = 2 \cdot \frac{(1.88)(860)}{(0.142)(21500)} = 1.06$ for solid

$= 2 \cdot \frac{(2.1)(790)}{(0.142)(21500)} = 1.09$ for liquid

For the parameter, b/a , in this application the radius, b , is assumed to be the distance to the nearest boundary from which was 0.0127 m

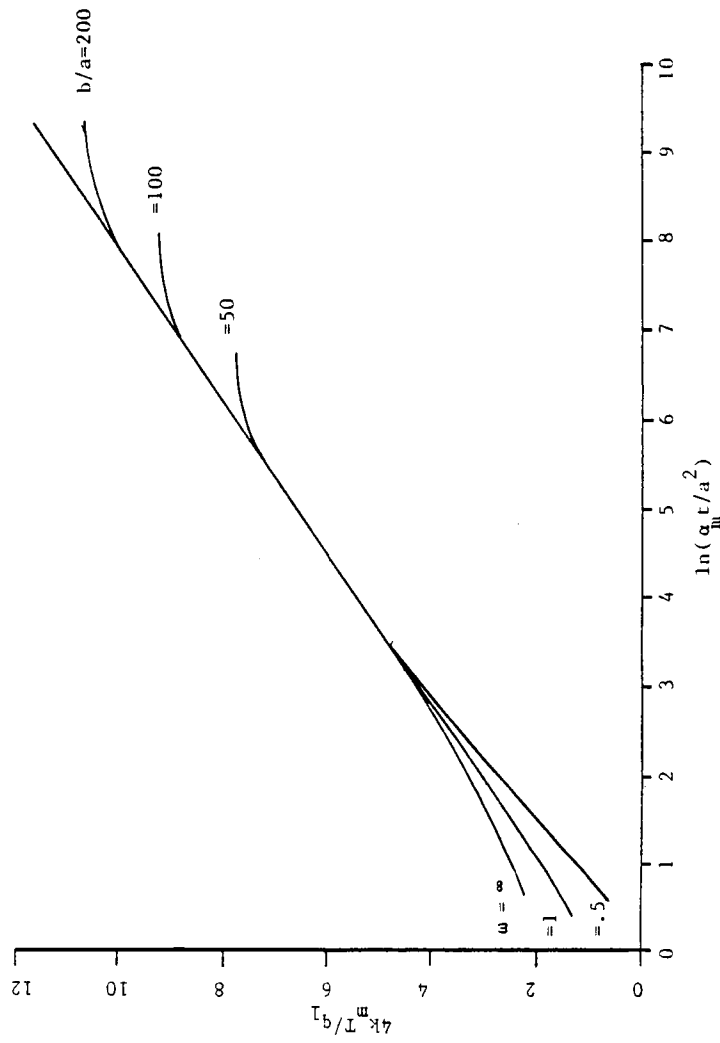


Figure C.1. Non-dimensionalized Plot of Temperature vs Logarithm of Time for a Finite Line Source Apparatus

(0.5 in.). The radius of the RTD were was 0.101×10^{-3} m (0.00398 in.). The parameter is:

$$b/a \approx 125$$

Observation of Figure C.1 reveals that Equation IV.C.12 is applicable for times such that:

$$1.5 < \ln \frac{\alpha t}{a^2} < 3.5 \quad \text{C.3}$$

Using a thermal diffusivity of 0.09×10^{-6} m²/s for the liquid [16] and a range of 0.14×10^{-6} to 0.26×10^{-6} m²/s for the solid (from the results of the transient conduction experiment), the time limits for the data were calculated as follows

$$0.5 \text{ s} < t < 3.7 \text{ s for the liquid} \quad \text{C.4}$$

$$0.15 \text{ s} < t < 1.3 \text{ s for the solid} \quad \text{C.5}$$

Data taken within these limits were used in the analysis.

The error introduced by the finite length of the line source RTD can be eliminated by a special circuit design which requires voltage taps along the RTD [19]. Such a design was not convenient for the application intended here, and instead, it will be demonstrated that the

error is negligible. This error is caused by two effects: (1) the distortion of the radial temperature field in the test material near the ends of the cell and (2) the loss of heat through conduction out of the ends of the RTD into the electrical leak.

Blackwell [5] showed that the effect of the distorted temperature field could be bounded by making the assumption that the temperature at the bounding planes at the ends of the probe was constant. A modified version of equation IV.C.12 results:

$$\frac{dT(x)}{d(\ln t)} = \frac{q_1}{4 \pi k_m} \operatorname{erf} \frac{x}{2 \sqrt{\alpha_m t}} \quad \text{C.6}$$

The fractional error caused by the distortions at both ends of the cell of length, L , can be approximated by:

$$E \approx 2 \frac{\int_0^L \frac{x}{2 \sqrt{\alpha_m t}} \operatorname{erfc} \frac{x}{2 \sqrt{\alpha_m t}} dx}{L} \quad \text{C.7}$$

or letting $x' = \frac{x}{2 \sqrt{\alpha_m t}}$

$$E \approx 2 \frac{\int_0^{L/2\sqrt{\alpha_m t}} \operatorname{erfc} x' dx'}{L/2\sqrt{\alpha_m t}} \quad \text{C.8}$$

Since the erfc function is continuously decreasing, E will be greater for smaller values of $\sqrt{\alpha_m t}$. The maximum allowed by Equation C.3 is

$$\begin{aligned}
 (\sqrt{\alpha_m t})_{\max} &= \sqrt{a^2 e^{3.5}} \\
 &= 5.8 \times 10^{-4} \text{ m}
 \end{aligned}$$

The length, L , of the RTD is approximately 0.194 m, so that:

$$L/2 \sqrt{\alpha_m t} = 166$$

Using this value the error, E is calculated to be:

$$E = 2 \frac{\int_0^{166} \text{erfc } x' dx'}{166} = \frac{(2) (0.563)}{166} = 0.0068$$

or about 0.68% of the measured value.

The error due to conduction along the RTD wire can be bounded by a method presented by Horrocks and McLaughlin [14]. This error is less than the temperature difference of a heat wire in steady state conduction whose ends are held at constant temperature. The fractional error at a distance, x , from the end, is evaluated by the equation

$$E(x) = \exp \left[-\frac{x}{a} \left(2 \frac{k_m}{k_w} \ln \frac{b}{a} \right)^{1/2} \right] \quad \text{C.9}$$

This fractional error must be averaged over the half length $L/2$, of the RTD wire. The following data were used in the calculation:

$$k_m = k_{\text{octadecane}} \approx 0.4 \text{ w/m}^\circ\text{C (from experiment)}$$

$$k_w = k_{\text{platinum}} \approx 69 \text{ w/m}^\circ\text{C [15]}$$

$$b = 0.0127 \text{ m}$$

$$a = 0.101 \times 10^{-13}$$

$$L = 0.194$$

The fractional error calculated is:

$$E \approx 0.0001$$

or about 0.01% of the theoretical value.

The errors so far discussed in this appendix have been those associated with the physics of the RTD itself. The following discussion concerns those errors which are associated with the data gathering technique:

It has been stated that the current in the RTD is essentially total current in the bridge. An analysis of the circuit shown in Figure V.D.2, page 39, shows that this is essentially true. The fraction of the total current in the RTD or left hand side (LHS) can easily be calculated. Two states must be checked to determine which causes the greatest current in the right hand side of the (RHS) bridge. If the variable resistor is adjusted to either limit the resistance in the RHS of the bridge is:

$$R_{RHS} = \frac{r}{\frac{1}{5000} + \frac{1}{1000 + \frac{1}{\frac{1}{1000} + \frac{1}{2000}}}} = 1250 \, \Omega$$

Thus the fraction of the bridge current in the RTD is

$$\begin{aligned} \frac{I_{RTD}}{I_{BR}} &= \frac{\frac{V_o}{1.299}}{\frac{V_o}{1.299} + \frac{V_o}{1250}} \\ &= \frac{\frac{1}{1.299}}{\frac{1}{1.299} + \frac{1}{1250}} \\ &= 0.9990 \end{aligned}$$

If the bridge is adjusted to the center of its range, then

$$\begin{aligned} R_{RHS} &= \frac{1}{\frac{1}{1000} + \frac{1}{2500}} \cdot 2 \\ &= 1428 \, \Omega \end{aligned}$$

$$\begin{aligned} \frac{I_{RTD}}{I_{BR}} &= \frac{\frac{1}{1.299}}{\frac{1}{1.299} + \frac{1}{1428}} \\ &= 0.9991 \end{aligned}$$

The resistance of the voltage divider circuit used to determine the current was measured with the system connected. Therefore the internal resistance of data interface board was taken into account.

The data for all of the measurements made with each of the line source RTD's, are listed in Tables C.1, C.2 and C.3.

Table C.1. Thermal Conductivity Measurement Data for LST #1

	Measurement Number								
	1	2	3	4	5	6	7	8	9
Temperature ($^{\circ}\text{C}$)	31.4	31.2	28.4	28.2	28.1	21.5	21.5	21.5	21.4
P_1	157.8	157.8	157.8	157.8	157.8	157.0	157.0	157.0	157.0
P_2	208.1	208.1	207.1	207.1	207.1	203.7	203.7	203.7	203.7
A_1 ($\mu\text{V}/\text{DC}$)	2.442	2.442	2.442	2.442	2.442	2.439	2.439	2.439	2.439
B_1 (μV)	0.331	0.331	0.331	0.331	0.331	0.359	0.359	0.359	0.359
A_{VO}	2.481	2.481	2.481	2.481	2.481	2.440	2.440	2.440	2.440
L_{RTD} (m)	0.194	0.194	0.194	0.194	0.194	0.194	0.194	0.194	0.194
R_{RTD} (ohms)	0.683	0.683	0.677	0.677	0.677	0.659	0.659	0.659	0.659
R_2 (ohms)	0.639	0.639	0.639	0.639	0.639	0.639	0.639	0.639	0.639
$\alpha_0/[1 + \alpha_0(T - T_F)]$ ($^{\circ}\text{C}^{-1}$)	0.00349	0.00349	0.00353	0.00353	0.00353	0.00362	0.00362	0.00362	0.00362
DC_1	2155.2	1828.2	1837.9	1838.6	1836.2	2876.1	2876.1	2403.3	3011.6
$d \text{ DC}_{VO}/d(\text{Lat})$	456.0	275.5	279.0	276.4	280.6	382.4	384.4	221.9	442.7
k ($\text{W}/\text{m}^{\circ}\text{C}$)	0.166	0.168	0.167	0.169	0.166	0.451	0.449	0.453	0.450
S.TIME (sec)	0.5	0.5	0.51	0.8	0.5	0.2	0.2	0.2	0.2
F.TIME (sec)	1.5	1.5	1.4	1.2	1.5	1.3	1.3	1.1	1.1

Table C.2. Thermal Conductivity Measurement Data for LST #2

	Measurement Number											
	1	2	3	4	5	6	7	8	9	10	11	12
Temperature ($^{\circ}\text{C}$)	31.0	30.8	30.6	28.3	28.2	21.6	21.6	21.6	21.6	21.6	21.6	21.6
F1	157.8	157.8	157.8	157.8	15.8	157.0	157.0	157.0	157.0	157.0	157.0	157.0
F2	210.0	208.1	208.1	208.5	208.5	205.45	203.7	203.7	203.7	203.7	203.7	203.7
A _I ($\mu\text{V}/\text{DC}$)	2.442	2.442	2.442	2.442	2.442	2.439	2.439	2.439	2.439	2.439	2.439	2.439
B _I (μV)	0.331	0.331	0.331	0.331	0.331	0.359	0.359	0.359	0.359	0.359	0.359	0.359
A _{VO} ($\mu\text{V}/\text{DC}$)	2.441	2.481	2.481	2.481	2.481	2.44	2.440	2.440	2.440	2.440	2.440	2.440
L _{RTD} (m)	0.197	0.194	0.194	0.194	0.194	0.194	0.194	0.194	0.194	0.194	0.194	0.194
R _{RTD} (ohms)	0.692	0.683	0.683	0.686	0.677	0.677	0.670	0.659	0.659	0.659	0.659	0.659
R ₂ (ohms)	0.639	0.639	0.639	0.639	0.639	0.639	0.639	0.639	0.639	0.639	0.639	0.639
α_{Ω}	0.00350	0.00350	0.00350	0.00353	0.00361	0.00361	0.00361	0.00361	0.00361	0.00361	0.00361	0.00361
$\frac{\text{d} \text{DC}_{\text{VO}}}{\text{d}T}$ ($^{\circ}\text{C}^{-1}$)	1820.0	1818.7	1818.5	1829.8	1829.1	2872.5	2874.9	2873.7	2378.5	2377.6	2562.9	2560.3
$\text{d} \text{DC}_{\text{VO}}/\text{d}(\text{Int})$	273.0	271.0	274.7	277.9	275.2	392.5	405.0	405.3	227.3	229.4	268.4	268.5
k ($\text{W}/\text{m}^{\circ}\text{C}$)	0.168	0.170	0.167	0.167	0.168	0.440	0.428	0.427	0.433	0.427	0.457	0.457
S.TIME (sec)	0.6	0.6	0.6	0.5	0.5	0.2	0.23	0.23	0.23	0.23	0.24	0.3
P.TIME (sec)	1.65	1.65	1.3	1.5	1.5	1.2	1.22	1.25	1.24	1.24	1.2	0.9

Table C.3. Thermal Conductivity Measurement Data for LST #3

	Measurement Number						
	1	2	3	4	5	6	7
Temperature ($^{\circ}\text{C}$)	30.4	30.4	28.2	21.7	21.7	21.7	21.7
F1	157.8	157.8	157.8	156.45	157.8	157.0	157.0
F2	203.2	208.1	208.6	208.3	207.1	207.1	203.7
A _I ($\mu\text{V}/\text{DC}$)	2.442	2.442	2.442	2.439	2.442	2.442	2.439
B _I (μV)	0.331	0.331	0.331	0.359	0.331	0.331	0.359
A _{VO} ($\mu\text{V}/\text{DC}$)	2.441	2.481	2.481	2.440	2.481	2.481	2.440
L _{RTD} (m)	0.201	0.194	0.194	0.200	0.194	0.494	0.194
R _{RTD} (ohms)	0.710	0.683	0.7046	0.689	0.677	0.677	0.659
R2 (ohms)	0.639	0.639	0.639	0.639	0.639	0.639	0.639
α_{Ω} ($^{\circ}\text{C}^{-1}$)	0.00350	0.00350	0.00355	0.00361	0.00361	0.00361	0.00361
$\overline{\text{DC}}_{\text{I}}$ (DC)	0.815	1813	1814.5	2358.7	2355.2	2509.2	2507.5
d DC _{VO} /d(lnt)	286.42	287.0	285.7	237.8	242.1	289.9	296.9
k (w/m $^{\circ}\text{C}$)	0.156	0.150	0.154	0.388	0.376	0.388	0.376
S.TIME (sec)	0.68	0.69	0.6	0.3	0.2	0.27	0.27
F.TIME (sec)	1.5	1.4	1.5	1.4	1.1	1.2	1.47

VITA

Richard G. Irby was born in Newport News, Virginia on November 22, 1950. He was raised in Yorktown, Virginia and was graduated from York High School in 1969. After high school, he briefly attended Virginia Polytechnic Institute and State University before serving two years active duty in The United States Navy.

After his military service, Mr. Irby attended the Newport News Shipbuilding Apprentice School. He was graduated with top academic honors in 1977, as a certified piping designer. He then moved to Knoxville, Tennessee, where he worked for Tennessee Valley Authority in their nuclear program and attended The University of Tennessee part time until December 1977. He obtained a Bachelor of Science degree from The University in December 1981, and entered The Graduate School of The University of Tennessee. Mr. Irby was re-employed by The Tennessee Valley Authority in July 1983 while continuing to work toward a Master's degree. He was awarded a Master of Science degree with a major in Mechanical Engineering in August 1985.