THERMAL CONDUCTIVITY OF LOW CONDUCTIVITY SOLIDS - A TRANSIENT METHOD USING SPHERICAL GEOMETRY

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By

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SCOPE AND CONTENTS: A transient method of measuring the thermal conductivity of homogeneous low conductivity materials, especially suitable for polymeric solids, has been investigated. The method, based on transient conduction with spherical geometry, consists essentially of measuring the transient temperature in a test sphere placed in a highly convective field provided by a mixing bath or a jet flow. The measured temperature-time curve is matched with the corresponding dimensionless series solution to determine the diffusivity and the conductivity-temperature relationship from a single experiment.

This method is adequate in the case of polymeric materials, but is limited to the determination of a reliable average value in the temperature range considered, when the temperature coefficients of conductivity and specific heat are of opposite signs as is the case for most crystalline materials. This limitation can be overcome by using a finite-difference

model to predict the dimensionless temperature-time curve. The model, considers variable physical properties, is completely general, and allows the determination of the conductivity-temperature curve from a single experiment. However, a lengthy trial-and-error procedure is required with this more general model.

Naphthalene, naphthol β , paraffin wax, bismuth, ice ammonium nitrate and Lucite were the materials tested. These materials have conductivity values in the range 5.0 to 0.08 B . T. U./(hr.-ft.-^{o}F.). The percent standard deviations of thermal conductivity were never larger than $\pm$12% and as low as 1.5%. The measured values are comparable to the most reliable ones found in the literature. For example, the values determined for naphthalene, naphthol β and ice differ from literature values by 2.5%, 3.5% and 1.5%, respectively.

In the application of the proposed transient method with spherical geometry, the equipment used to measure thermal conductivity is very simple. The measurements are extremely fast and conductivity values can be determined to within $\pm$5%.

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1. INTRODUCTION

The present method of measuring thermal conductivity of solids evolved from a preliminary investigation of the prilling process. The prilling process involves the spraying of molten droplets into a cold gas stream. As the droplets fall, freezing occurs and the solid particles are collected at the base of the prilling tower. Heat is transferred in the gas phase by forced and natural convection. For the design of a prilling tower it would be desirable to have a mathematical model for predicting the rate of heat transfer and solidification. Such a mathematical model would predict local temperatures and the position of the freezing front as a function of time.

Preliminary attempts to develop such a model would require periodic experimental measurements to test its accuracy. A critical test would be the measurement and prediction of local temperature with time. It was therefore apparent that a technique would be required to measure local temperatures as a function of time in solids of low conductivity.

A literature search indicated that there is no information available concerning the error involved in measuring a local temperature in a spherical solid of low conductivity. It was therefore decided to experimentally determine the errors involved in such measurements.

To this end, a search of the literature was made to find a suitable standard whose thermal conductivity and other properties were well established. Naphthalene met these requirements and was chosen. An exact mathematical model for heat conduction with spherical symmetry and known Biot number was used to interpret the experimental data. The experimental approach was to fix a thermocouple at a known position in a naphthalene sphere. At time zero, the sphere was immersed in a stirred liquid and the temperature response was recorded. The heat transfer coefficient for the stirred liquid was measured by repeating the above experiment with a copper sphere. The accuracy of the temperature measurement in the naphthalene sphere was estimated by comparing the measured temperature with the predicted temperature using the exact model. Initial experiments with naphthalene indicated that the error could be kept to a reasonable level by suitably locating the thermocouple.

The literature search for conductivity data revealed that very little data were available and many of these were inconsistent. With this in mind and the success of the naphthalene experiments, it became apparent that a useful method for the measurement of the conductivity of such materials might be developed using a transient method with spherical geometry. It was decided to pursue this idea further and make the development of this method the subject of this thesis.

2. LITERATURE SURVEY

2.1 Sources of Information

In the search for physical properties and details about the existing methods for measuring the thermal conductivity, the following reference books were used extensively:

(a) International Critical Tables

(b) Comprehensive Treatise on Inorganic and Theoretical Chemistry, Mellor

(c) Retrieval Guide to Thermophysical Properties Research Literature, Y. S. Touloukian, Purdue Univ.

(d) Handbook of Thermophysical Properties of Solid Materials (5 volumes), McMillan Company, N. Y. 1961 A. Goldsmith, T. E. Waterman and H. J. Hirschorn, Armour Research Foundation

(e) Chemical Abstracts

(f) Properties of Materials at Low Temperature (Phase 1). A Compendium, General Editor, Victor J. Johnson, National Bureau of Standards, Cryogenic Engineering Laboratory, Pergamon Press 1961

(g) Encyclopedia of Chemical Technology, Thorpe

(h) Handbook of Chemistry and Physics, 36th. edition, 1954-1955, Chemical Rubber Publishing Co.

(i) Chemical Engineers Handbook, Perry, 4th edition.

2.2 Physical Properties of the Solids

The following is a list of materials studied in this investigation followed by a brief outline of their interesting properties. Property details can be found in the Appendices.

(a) Naphthalene - Naphthalene is a crystalline solid with isotropic and homogeneous structure. Many data for specific heat and thermal conductivity exist in the literature. These properties vary linearly with temperature; the specific heat values increase with temperature while the conductivity decreases. The data for naphthalene are numerous and appear reliable.

(b) Naphthol β - Naphthol β is a crystalline material slightly soluble in water (0.074 part per 100 parts). A reliable relationship exists for the variation of the specific heat in the temperature range 60°C. to 122°C. No values can be found for temperatures below 60°C. For an extensive temperature range, consistent conductivity values are available. The available data indicate that the conductivity decreases with temperature and specific heat increases with temperature.

(c) Paraffin Wax - A great number of different paraffin waxes are available and the density and conductivity values are necessarily a little scattered. However, a linear relationship exists for the conductivity variation with temperature in the case of amorphous paraffin wax. The conductivity decreases if the temperature increases. Only one value for the specific heat could be found.

(d) Bismuth - Bismuth has often a coarse crystalline structure and the conductivity is dependent upon the direction of heat conduction with respect to the crystal trigonal axis.

Among the metals, bismuth is one with very low conductivity. However, its value is still much larger than the ones for insulating materials or plastics. The density and specific heat properties are well known. The specific heat varies very little with temperature. The conductivity values are relatively scattered and reliable data for conductivity versus temperature does not seem to exist. Indications are that the conductivity decreases with an increase of temperature.

(e) Ammonium nitrate - It is a crystalline material very soluble in water and which undergoes five crystal structure transformations in the temperature range 169.6°C. to -16°C. The specific gravity changes at the same time by a noticeable amount. Density and linear specific heat variation with temperature are well known and values are consistent. Only one value of thermal conductivity has been proposed in the literature and this value is not representative and certainly much in error. This point of error will be discussed in detail in Section 5.4.7.

(f) Ice - Ice is crystalline, has a very compact structure and is usually isotropic. Density and specific heat values of good reliability exist. On the other hand, the available conductivity values are scattered but a few sources indicate more consistent values. The specific heat increases linearly with temperature but the conductivity decreases when the temperature increases.

(g) Poly (Methyl Methacrylate) - One of the commercial names is Lucite. This polymer is amorphous (or glassy) and its properties are representative of the ones for this class of materials. Its molecular weight is in the order of 100,000 and it is a low conductivity material. Relatively, the density and specific heat data are consistent. As for many such materials, the fabrication of the samples affect the physical properties and consequently the conductivity values are scattered. The specific heat and the conductivity increases linearly in the temperature range studied (0^{o}C. to 75^{o}C.).

2.3 Heat Conduction in Solids

Jakob (J1) reports that heat conduction is due to longitudinal oscillations in solid non-conductors of electricity, and to the motion of electrons in metals. From a phenomenological point of view, it means the exchange of heat between contiguous bodies or parts of a body which are at different temperatures. The heat may be thought of as the kinetic energy of motion (translational, rotational or vibrational) of ions or molecules.

2.4 Fundamental Equation of Heat Conduction

The basic law of heat conduction originates from Biot and is generally called Fourier's Law (J1). It is expressed as

$$q = - kA \frac{dT}{dx} \tag{1}$$

where q is the heat flow rate, A the heat transfer area and $\frac{dT}{dx}$ the gradient of temperature in the body. The proportionality constant k is the thermal conductivity. For isotropic materials k is independent of direction. Carslaw and Jaeger (C2) explain that strictly speaking, the conductivity depends upon temperature. However, when the range of temperature is small, the change in k may be neglected, and in the ordinary mathematical theory it is assumed that the conductivity does not vary with temperature. This assumption is also used in mathematical models which are employed to determine thermal conductivity from measured temperature variations in some test specimen.

2.5 Principles of Conductivity Measurement Methods

To keep the variation of the physical properties with temperature negligible, the temperature differentials used in the methods have to be as low as possible. Two types of heat flow situations are generally used for estimating the conductivity:

(a) steady-state heat flow

(b) unsteady-state heat conduction

The most popular geometries are:

(a) rectangular (slab or block)

(b) cylindrical

(c) spherical

Kingery and McQuarrie (K6) have summarized the concepts:

(a) Steady-state heat conduction - In static methods, the sample is allowed to come to a steady state and the temperature distribution measured to determine the thermal conductivity k by an integrated form of equation (1).

(b) Unsteady-state heat conduction - In dynamic methods the temperature is varied suddenly or periodically for one portion of the sample and the temperature change with time is measured to determine the diffusivity $k/C_p\rho$ by a form of the energy equation

$$\nabla^2 T = \frac{C_p \rho}{k} \frac{dT}{dt} \tag{1A}$$

To derive equation (1A), k must be assumed constant.

In both types of methods, various specimen shapes may be used but the initial and boundary conditions necessary to solve the mathematical relationships have to exist. In general, the greatest difficulty in thermal conductivity measurement is obtaining heat flow which coincides with that assumed in the mathematical model.

2.5.1 Heat flow with rectangular and cylindrical geometries (Steady and unsteady methods)

Rectangular geometry - For the case of a rectangular sample, the heat flow through the sample must be in one direction from one plane to the other, the temperature of each plane being known. The guarded-hot-plate apparatus is the most popular, though expensive, and it is used for all sort of materials. This method will be discussed in more detail in Appendix 1 (Section A1.3.1).

Cylindrical geometry - The cylinder is used in two ways. In a first method, heat is conducted radially and in the second one the heat conduction is unidimensional and longitudinal.

2.5.2 Problems due to the geometries

Guard methods - In the rectangular and the cylindrical samples, the heat conduction can exist in more than one direction. A method generally employed to insure that heat flows in a desired path is to provide heat guards to maintain the isothermals in the specimen and prevent extraneous heat flow. Different techniques for doing it and methods used for particular cases are reported in Appendix 1 (Section A.1.3.1). However, these guard methods are never perfect and can only hope to reduce extraneous heat flow to negligible proportion. Very careful design and measurements are necessary.

Infinite sample - A method of insuring correct heat flow without the use of heat guards is to employ a specimen which completely surrounds the heat source. This may consist of an infinite cylinder or slab, surrounding an infinite heat source. Shapes approximating an infinite cylinder or slab are satisfactory, if only the center section is employed (in a manner equivalent to heat guards). But they are sometimes difficult to fabricate.

Advantage of the spherical geometry - A method for avoiding guards is the use of a hollow sphere with internal heat generation. The sphere arrangement has two special advantages (J1):

(1) The heat is conducted through the material to be tested in the required direction (radially), without any loss.

(2) The thermal conductivity at different temperatures can be found by a single experiment, if thermocouples are arranged at more than two radial positions. This last point

applies to the case of steady state.

The symmetry of heat conduction is easily obtained in a spherical body.

2.5.3 Problems associated with steady-state methods

A few particular problems exist with the use of steady-state methods, specially for the case of low conductivity materials as plastic and other solid polymers, etc.

(a) It is necessary to evaluate the heat flux and two temperatures. Usually elaborate techniques and apparatus are required.

(b) With low conductivity materials, samples large enough to permit direct measurement of the internal temperature gradient have a thermal resistance so large that the heat flow is small, thus involving a lengthy measurement or the temperature drop is excessive (J2).

(c) If the required sample is too big, it may be difficult to get homogeneity.

(d) With an apparatus such as the guarded-hot-plate, reliable data are difficult to obtain with a small sample. Thin samples which are normally used tend to warp (J2). It is often difficult to get smooth and regular surfaces over a large area. Good thermal contact is then difficult to achieve.

(e) The time to reach steady state can be very long and is usually of the order of hours.

2.5.4 Advantage of the unsteady-state methods

Generally, their advantage is that a short time is sufficient for an experiment. Further, heat losses and gains have less influence on the result the faster the temperature changes. It should also be noted that the temperature change at only one point in the tested body has to be recorded. The major problems are:

(i) the accurate measurement of local temperature as a function of time

(ii) the satisfaction experimentally of suitable boundary conditions

2.5.5 Unsteady-state techniques with spherical geometry

Without extraneous heat loss, the heat conduction in a sphere is radial if the boundary conditions have radial symmetry.

It has been mentioned that transient methods are recommended as rapid methods for determining the thermal conductivity of low conductivity material. It appears that Ayrton and Perry (A2) were the only workers to use a transient method with spherical geometry to measure the thermal conductivity of a low conductivity materials. They measured the temperature at the center of a stone sphere as a function of time. The mathematical solution used is discussed in Carslaw and Jaeger (C2). The sphere is allowed to cool down by convection in a medium at constant temperature. The measurements are taken only after a certain time. The series converges rapidly and then, only the first term remains important thus giving a simple mathematical form. Ayrton and Perry investigated only stone. Carslaw and Jaeger (C2) suggested that theoretically the measurement of heat transferred from a sphere suddenly introduced in a well-stirred fluid (assuming the temperature of the fluid contained in a calorimeter being the same as the surface temperature of the sphere) could be used to determine the diffusivity and the conductivity. The variation of the fluid temperature would be the measured value. Experimentally, with relatively small spheres, the change could be difficult to measure. Methods using the temperature change in the sphere are preferable.

2.5.6 Prediction of thermal conductivity variation with temperature by a single transient heat conduction experiment and using the appropriate mathematical model

In the methods discussed above, assumptions of constant conductivity and specific heat are made. Small temperature ranges must be used and the whole range of temperatures of interest is covered by carrying out a series of experiments at different temperature levels. Recently, Dowty (D3) proposed solutions to the transient heat conduction equation with variable thermal conductivity. A finite-difference method was used to generate solutions for problems of one and two dimenstions. The one-dimensional solution was verified experimentally using a slab.

In their proposed transient technique for estimating the diffusivity and thermal conductivity of low conductivity materials, Chung and Jackson (C5) used a cylinder and from measured curves of log temperature versus time they calculated conductivity values. If the conductivity is constant with temperature, the curve should be a straight line. However, there was a slight curvature and they assumed it was caused by a temperature effect. They suggest that the calculations could be refined by taking the slope of the tangent to the curve at a given point to evaluate the diffusivity. Thus the conductivity variation with temperature could be predicted by doing a single experiment.

Nagler (N1) tried to measure conductivity variation with temperature from a single experiment. His mathematical model predicts the time-temperature curves for one-dimensional heat conduction. For the finite-difference solution, linear relationships for conductivity and specific heat must be provided. A two-constant iteration procedure is used until the right conductivity relationship is determined. A least-squares technique is used for matching the time-temperature curves with linear thermal conductivities. The computer time used was considered excessive.

The literature survey has shown that there has been only one investigation of the transient method with spherical geometry to determine the thermal conductivity of a low conductivity material. It has been mentioned in the Introduction and it will now be reiterated that preliminary experiments have indicated that the error in measuring the local temperature in a sphere of low conductivity as a function of time is not excessive. It was felt that the transient method with spherical geometry deserved further investigation. The further development of this method is the subject of this thesis.

In the following section the theory which is used to develop the transient method with spherical geometry is presented.

3. THEORY AND DEVELOPMENT OF METHOD

The method proposed for measuring conductivity of low conductivity solids is based on the prediction and measurement of local temperatures in a sphere for transient conduction with radial symmetry. Two methods are available for predicting local temperatures under these conditions. These include a solution for constant properties (G7) and a finite-difference solution which was developed in this investigation. The solution for the constant-property case and a brief development of the finite-difference model follow.

3.1 Constant-Property Solution

Gröber (G7) presents a solution to the heat conduction in a solid sphere of radius a, initially at uniform temperature T_i which cools in a medium whose temperature T_∞ is constant and uniform. Both the heat transfer coefficient h at the surface of the sphere and the properties of the material of the sphere k, Cp, and ρ, are constant. The series solution predicts the temperature distribution within the sphere as a function of time. For every Biot number, particular temperature profiles can be predicted. When the Biot number $\frac{hr}{k}$ becomes large enough, a unique solution exists and this corresponds physically to the case of constant surface temperature. More details are given in Appendix 2.

3.2 Variable-Property Solution

The model assumes radial symmetry, constant density, uniform initial temperature of the sphere and uniform constant temperature of the fluid cooling or heating the solid. Linear relationships express the variation of conductivity and specific heat with temperature. However relationships of higher order can also be used without any particular difficulty. The equation to be solved is

$$\rho \, Cp \frac{\partial T}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(k r^2 \frac{\partial T}{\partial r} \right) \quad (2)$$

Since k is temperature dependent it cannot be taken out of the partial derivative term. No analytical solution to equation (2) was found in the literature and a finite-difference model was therefore developed. Equation (2) is made dimensionless to obtain more general solutions. Time is made dimensionless using the relationship expressed by equation (3)

$$\tau = \frac{k0 \; t}{Cp0 \, \rho \, a^2} \quad (3)$$

where k and Cp are expressed as:

$$k = k0 + k1\,T \quad (4)$$

$$Cp = Cp0 + Cp1T \quad (5)$$

The dimensionless radius and temperature are respectively

$$R = \frac{r}{a} \quad \text{and} \quad \Theta = \frac{T_i - T}{T_i - T_\infty}$$

Introducing the following symbols

$$Td = (T_{\infty} - T_i) \tag{6}$$

$$Cp2 = \frac{Cp1\ T_i}{Cp0} \tag{7}$$

$$Cp3 = \frac{Cp1\ Td}{Cp0} \tag{8}$$

$$k2 = \frac{k1\ T_i}{k0} \tag{9}$$

$$k3 = \frac{k1\ Td}{k0} \tag{10}$$

equation (2) becomes:

$$\frac{\partial \theta}{\partial \tau} = \frac{(1 + k2 + k3\ \theta)}{(1 + Cp2 + Cp3\ \theta)} \frac{\partial^2 \theta}{\partial R^2} + \frac{2}{R} \frac{(1 + k2 + k3\ \theta)}{(1 + Cp2 + Cp3\ \theta)} \frac{\partial \theta}{\partial R} + \frac{k3}{(1 + Cp2 + Cp3\ \theta)} \left(\frac{\partial \theta}{\partial R}\right)^2 \tag{11}$$

An explicit finite-difference technique can be used to solve equation (11). The derivatives in equation (11) were replaced by finite-difference expressions using Taylor's series expansions up to the second order. The differentials $\partial \tau$, $\partial \theta$, ∂R become the differences $\Delta \tau$, $\Delta \theta$ and ΔR. The resulting finite-difference equation takes the form

$$\begin{aligned}\theta(I,2) = {} & A1\ (I) \times \theta\ (I,1) \\ & + A2\ (I) \times \theta\ (I + 1,\ 1) \\ & + A3\ (I) \times \theta\ (I - 1,\ 1) \\ & + A4\ (I) \times\ \theta^2(I + 1,\ 1) + \theta^2(I - 1,\ 1) \\ & - 2\ \theta(I + 1,\ 1) \times \theta\ (I - 1,\ 1)\end{aligned} \qquad (12)$$

with

$$A1\ (I) = 1.0 - \frac{2\ \Delta\tau}{(\Delta R)^2}\ \frac{(1 + k2 + k3\ \theta(I,\ 1)}{(1 + Cp2 + Cp3\ \theta(I,\ 1)} \qquad (13)$$

$$A2\ (I) = \frac{(1 + k2 + k3\ \theta(I,\ 1))}{(1 + Cp2 + Cp3\ \theta(I,\ 1))}\ \frac{\Delta\tau}{\Delta R}\left[\frac{1}{R(I)} + \frac{1}{\Delta R}\right] \qquad (14)$$

$$A3\ (I) = \frac{(1 + k2 + k3\ \theta(I,\ 1))}{(1 + Cp2 + Cp3\ \theta(I,\ 1))}\ \frac{\Delta\tau}{\Delta R}\left[\frac{1}{\Delta R} - \frac{1}{R(I)}\right] \qquad (15)$$

$$A4\ (I) = \frac{k3\ \ \Delta\tau}{4\ \ (\Delta R)^2\ (1 + Cp2 + Cp3\ \theta(I,\ 1))} \qquad (16)$$

I stands for the radial mesh points and 1 and 2 for the time increment. The method computation is straight forward. If the temperatures are known at time 1 for all mesh points along the radius, the temperature can be estimated at time 2 (time 1 + $\Delta\tau$) and for all points, by using equation (12) and the appropriate coefficients (13 to 16).

The accuracy of the finite-difference solution was tested by varying the appropriate step sizes and by comparing predicted temperatures with those from an analytical solution for constant properties. A summary of these tests are tabulated in Tables 1 and 2.

TABLE 1

DIMENSIONLESS TEMPERATURE θ - TIME CURVES WITH VARIATION OF THE TIME STEP

From finite-difference model with:

* $k = 0.1388 - 0.0022T$ (°C) (B.T.U./hr.-ft.-°F.)

$Cp = 0.6939$ B.T.U./(lb.-°F.) or (cal./gr.-°C)

$a = 0.021$ ft.

$h = 2100$ B.T.U./(hr.-sq.ft.-°F)

$T_i = 48.2$°C.

$T_\infty = 7.0$

$\Delta R = 0.05$

	$\Delta\tau = 0.00001$		$\Delta\tau = 0.000005$	
τ	R = 0.8	R = 0.9	R = 0.8	R = 0.9
	θ	θ	θ	θ
0.010	0.040	0.438	0.040	0.438
0.020	0.231	0.641	0.231	0.641
0.030	0.396	0.729	0.396	0.729
0.040	0.504	0.779	0.504	0.779
0.050	0.579	0.813	0.579	0.813
0.060	0.635	0.838	0.635	0.838

* The British system of units was adopted except for temperature which is in °C. The consistent units ft., lb., hr., are always used unless otherwise specified (see Nomenclature).

TABLE 2

COMPARISON OF THE SERIES SOLUTION WITH FINITE-DIFFERENCE SOLUTIONS FOR RADIAL MESH OF 21 AND 41 POINTS RESPECTIVELY WHEN RADIAL SYMMETRY EXISTS

$\Delta\tau = 0.00001$, [illegible]

Constant physical properties

	R = 0.0			R = 0.8		
τ	Series θ	ΔR=.05 θ	ΔR=.025 θ	Series θ	ΔR=.05 θ	ΔR=.025 θ
0.10	0	0	0	0.194	0.198	0.169
0.020	0	0	0	0.308	0.309	0.308
0.030	0.002	0.002	0.002	0.515	0.512	0.515
0.04	0.011	0.012	0.011	0.597	0.594	0.597
0.045	0.020		0.021	0.629		0.629
0.050	0.033	0.037		0.657	0.654	

These tests indicate that the finite-difference model is sufficiently accurate for the purpose of interpreting experimental data using the transient method with spherical geometry. A time increment equal to 0.00001 and a radial increment of 0.05 have been used for all further calculations using the finite-difference method.

3.3 Transient Heat Flow with Negligible Internal Resistance

For the application of the constant-property and variable-property models a knowledge of the heat transfer coefficient for the continuous phase is required. The development which follows will lead to a suitable method for experimentally determining this heat transfer coefficient.

According to Kreith (K7), when the thermal conductivity of a system is very high, the internal resistance is so small that the temperature within the system is substantially uniform at any instant. This simplification is justified when the external thermal resistance controls the heat transfer process. The error introduced by the simplification can be neglected when the Biot number ($Bi = \frac{hr}{k}$) is < 0.3. Assuming that the physical properties are constant, the heat transfer coefficient h is uniform around the sphere and the temperature is uniform in the sphere, a simple energy balance gives:

$$- C_p \rho V \, dT = h A (T - T_\infty) \, dt \qquad (17)$$

Solving equation (17) with boundary condition that at $t = 0$, $T = T_i$, equation (18) is obtained:

$$\ln \frac{T - T_\infty}{T_i - T_\infty} = \frac{h A}{C_p \rho V} t \qquad (18)$$

A plot of $\frac{T - T_\infty}{T_i - T_\infty}$ versus time on semi-log graph paper gives a straight line with a slope equal to $\frac{h A}{C_p \rho V}$. If an experiment can be set up to meet the prescribed conditions for the derivation of equation (17), an easy method of measuring the heat transfer coefficient around a sphere is obvious. The transient temperature is measured during cooling or heating of a high conductivity sphere (of copper for example) in a convective medium. These data permit the construction of the type of curve mentioned above. The slope of the expected straight line is measured and from it the heat transfer coefficient is calculated.

3.4 Development of the Method

The method for measuring the thermal conductivity of a poor conductor using spherical geometry and a transient measurement can be summarized in the following manner. The transient temperature of a sphere placed suddenly in a highly convective medium is measured and recorded continuously. For the same physical conditions, the series or the finite-difference solution predicts the dimensionless temperature change with time. The matching of the measured and predicted curves gives the diffusivity and the conductivity values by applying the relationship $\tau = \dfrac{k\ t}{C_p \rho\ a^2}$.

3.4.1 Convective medium

The solution to the conduction equation indicates that when the heat transfer coefficient h and the Biot number are large enough, the predicted temperature becomes independent of these parameters and there is uniform heat transfer around the sphere. These conditions exist for spheres as small as 0.5"D. and with conductivity less than 0.25 if h is 2000 or larger. The measurement of the transient temperature of a high conductivity sphere (copper for example) used in conjunction with the model presented in Section 3.3 indicates the average h existing in the chosen convective medium. A well-stirred liquid in a bath or a turbulent jet flow impinging on the sphere provides the required h.

3.4.2 Transient temperature-time curve

A thermocouple is positioned accurately in the sphere of material to be tested. At time zero, the sphere is placed in the chosen highly convective field and the temperature change is recorded. From these data, the dimensionless temperature-actual time curve is estimated. The series or the finite-difference solution is used to predict the dimensionless form of the temperature-time curve.

3.4.3 Thermal conductivity determination

The conductivity can be determined by assuming the conductivity-temperature relationship and through a trial-and-error procedure match the measured and predicted curves (finite-difference model). This method can determine accurately the variation of conductivity with temperature from a single transient measurement. However, a very simple approach exists and it requires only the use of the unique temperature-time curve predicted by the series solution for the case of high Biot number (> 300).

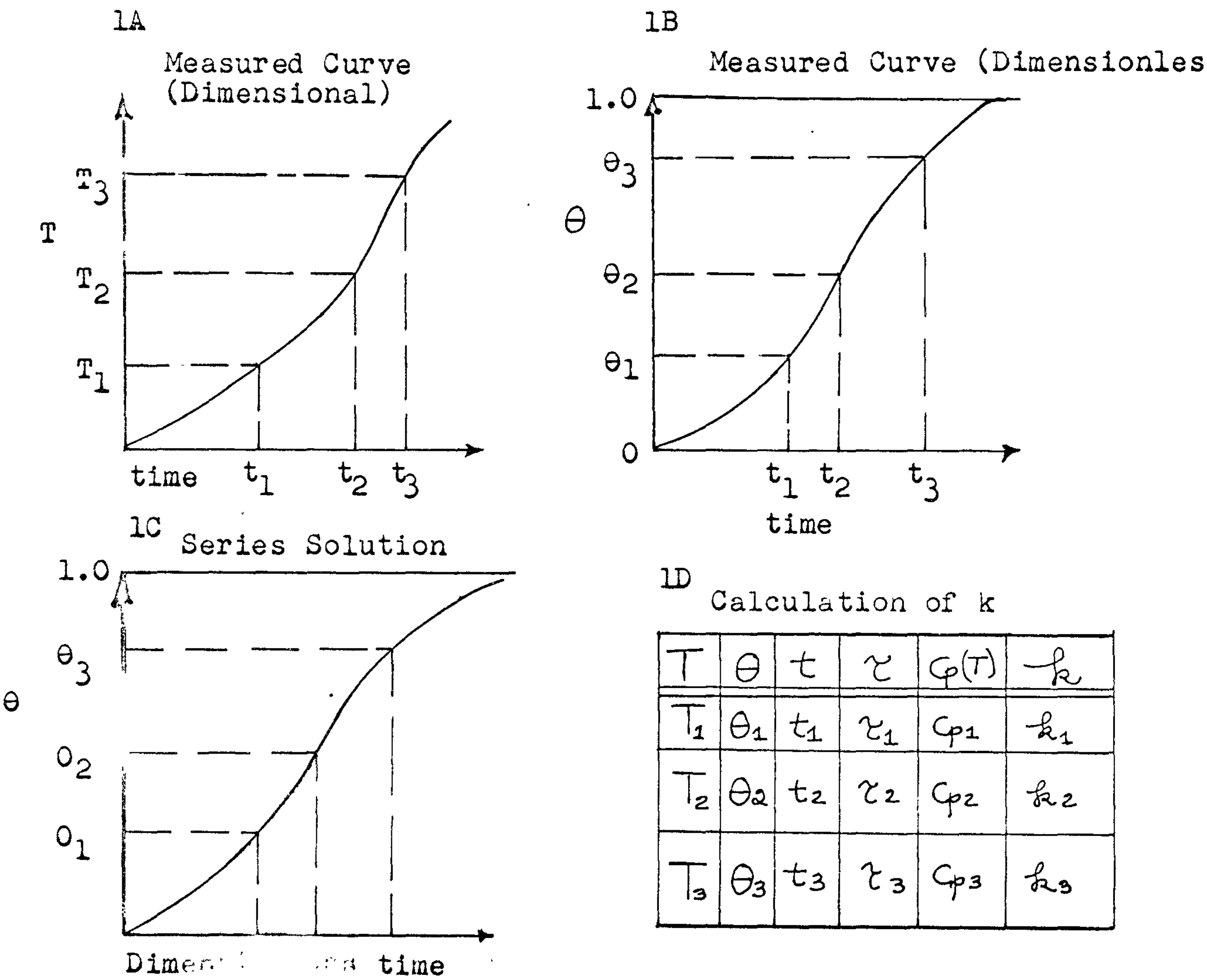
From the dimensionless predicted curves, time value corresponding to different temperatures are estimated. The measured curve gives the real time corresponding to the temperatures. By matching dimensionless and actual time values and using at every point the physical properties corresponding to dimensional temperatures, the conductivity data are determined. The matching is done by using the relationship

$$\tau = \frac{k\ t}{Cp\,\rho\,a^2} \quad \text{or} \quad k\ (T) = \frac{Cp(T)\,\rho\,a^2\ \tau}{t}$$

The conductivity determination scheme is illustrated in Figure 1.

FIGURE 1

STEPS IN DETERMINING THERMAL CONDUCTIVITY



T	θ	t	τ	Cp(T)	k
T_1	θ_1	t_1	τ_1	Cp_1	k_1
T_2	θ_2	t_2	τ_2	Cp_2	k_2
T_3	θ_3	t_3	τ_3	Cp_3	k_3

3.4.4 Working range and discussion

The transient cooling or heating experiment gives dimensionless temperature-time curves which are asymptotic to the temperature limits at $\theta = 0$ and 1.0 and have an "S" shape. In the θ value range 0 to 0.2 and 0.85 to 1.0, a small change in temperature corresponds to a large change of τ. Consequently, these portions of the curves are not suitable for determining conductivity values (see Section 5.2.2). The method requires a knowledge of specific heat data if the thermal conductivity is to be measured. On the other hand, if the conductivity is known the method can be used to determine the specific heat. By this method, variation of conductivity with temperature is determined but it is obvious that a more restricted approach of determining conductivity at the average temperature is possible.

When the conductivity has been determined, a simple comparison of this value with the one corresponding to the Biot number (satisfactory range: > 150) used to predict the dimensionless temperature-time curve will indicate whether or not the conductivity value is in the assumed range. If not, a trial-and-error procedure can still lead to the determination of conductivity values within an accuracy limited only by experimental errors. The conductivity is assumed and a Biot number estimated. Using the corresponding series solution curve, k values are determined. These new values are better and can be used for estimating a new Biot number. Thus the trial-and-error procedure is established (see Section 5.4.6.1 and Appendix 13).

4. APPARATUS AND EXPERIMENTAL PROCEDURES

4.1 Equipment

An enumeration of pieces of equipment used and their main characteristics follows:

4.1.1 Spheres

The spheres used were:

- Bronze spheres 0.5" and 1.0"D. from commercial suppliers.
- Cast Lucite spheres 0.5 and 0.625"D. from commercial suppliers.
- Naphthalene, naphthol β, bismuth, ice, ammonium nitrate, paraffin wax and Poly (methyl methacrylate) or Lucite molded 0.5"D. spheres.
- 2"D. naphthalene hemisphere contained in a 0.015" hemispherical copper plate.

Thermocouples were imbedded in these spheres which were fixed to supports. The supports were either 0.245"D. glass or 0.097"D. stainless steel 20" long tubes.

4.1.2 Thermocouples

Chromel-alumel thermocouples with fiberglass-teflon insulation were imbedded in the test spheres. The junction was spot-welded (0.010") and the wire diameter was 0.003" and in one case 0.008".

4.1.3 Bath

Two baths were used, one for bringing the sphere to its initial uniform temperature and the other containing the highly convective medium. The latter was a 4000 cc. insulated beaker fitted with a laboratory stirrer. The former was either a 4000 cc. Dewar flask for low temperatures or any large bath with a Haake thermocontrol unit when temperatures > 10°C. were required. Haake units were used to control temperatures of fluids to within ±0.1°C. The fluid used was normally water but pentane was used at low temperature and hydrocarbon oil (Varsol) with test spheres soluble in water.

4.1.4 Recorder

The transient temperatures in the test spheres were measured by a thermocouple and continuously recorded. For very fast temperature changes, a Honeywell 906 Visicorder was used.

This photographic type of oscillograph offers direct writing convenience combined with high sensitivity. The trace velocity exceeds 10,000 inches per second (equivalent to 2000 cycles per second sine wave at 1.6 inch peak-to-peak amplitude). Its scale is linear and so is the millivolt-temperature curve for chromel-alumel thermocouples in the range -40 to +75°C. Therefore, a linear scale is determined by simply establishing two points of the scale. An ordinary single point Honeywell recorder was also used occasionally.

4.1.5 Jet flow and nozzle

Jet flow has been created by using a 0.25" D. nozzle giving an outlet fluid velocity of 870 feet per minute and a total flow rate of 0.3 cu. ft./min. in an open atmosphere.

4.1.6 Diagram

Schematic diagrams shown in Figures 2 and 3 show the arrangement of the equipment.

4.2 Experimental Procedures

4.2.1

This section will provide a brief description of the experimental procedure used. The experimental investigation consisted of three main parts. These are:

(a) choosing and evaluating a convective medium

(b) fabricating spheres of the test material

(c) measuring and recording the temperature response when test speciments are placed in a convective medium and interpreting the data to obtain thermal conductivity values.

4.2.2 Determination of the heat transfer coefficient h

Bath volume, type and speed of stirrer, fluid, sphere diameters, temperature control of fluid methods are not characteristics of the method. However, the method requires that the sphere be placed in a uniform and known convective medium. As mentioned in the theory section, at high h values for a sphere of low conductivity, the heat transfers with radial symmetry. Hence, it is only necessary to determine, for the spheres to be tested, physical conditions which provide the desired Biot number. The three methods investigated were:

(a) Nucleate boiling

FIGURE 2

APPARATUS FOR MEASURING HEAT CONDUCTION IN SPHERES

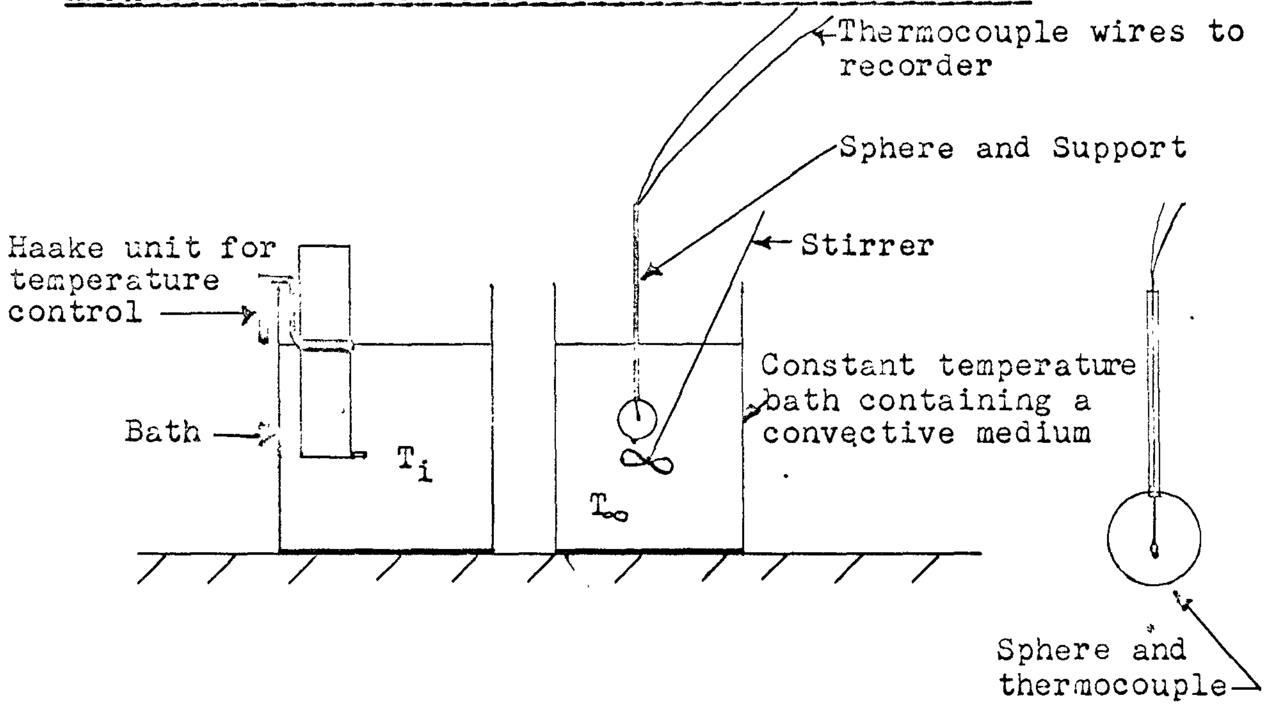


FIGURE 3

APPARATUS FOR MEASURING HEAT CONDUCTION IN HEMISPHERES

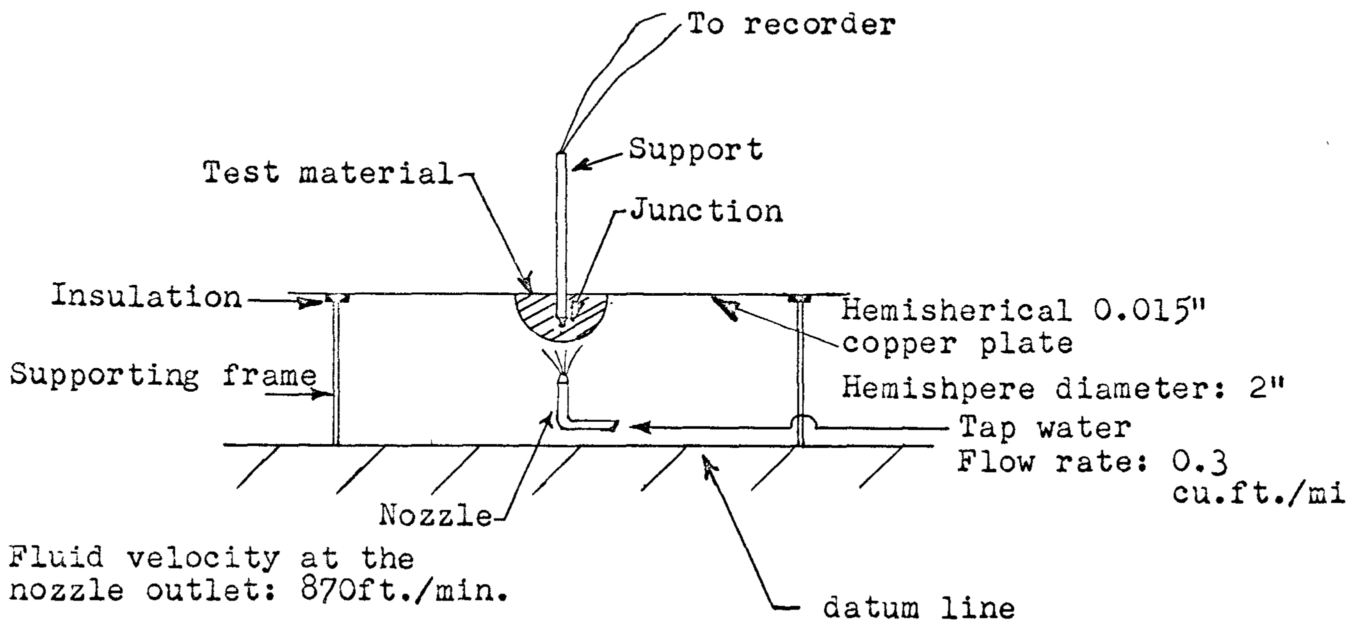
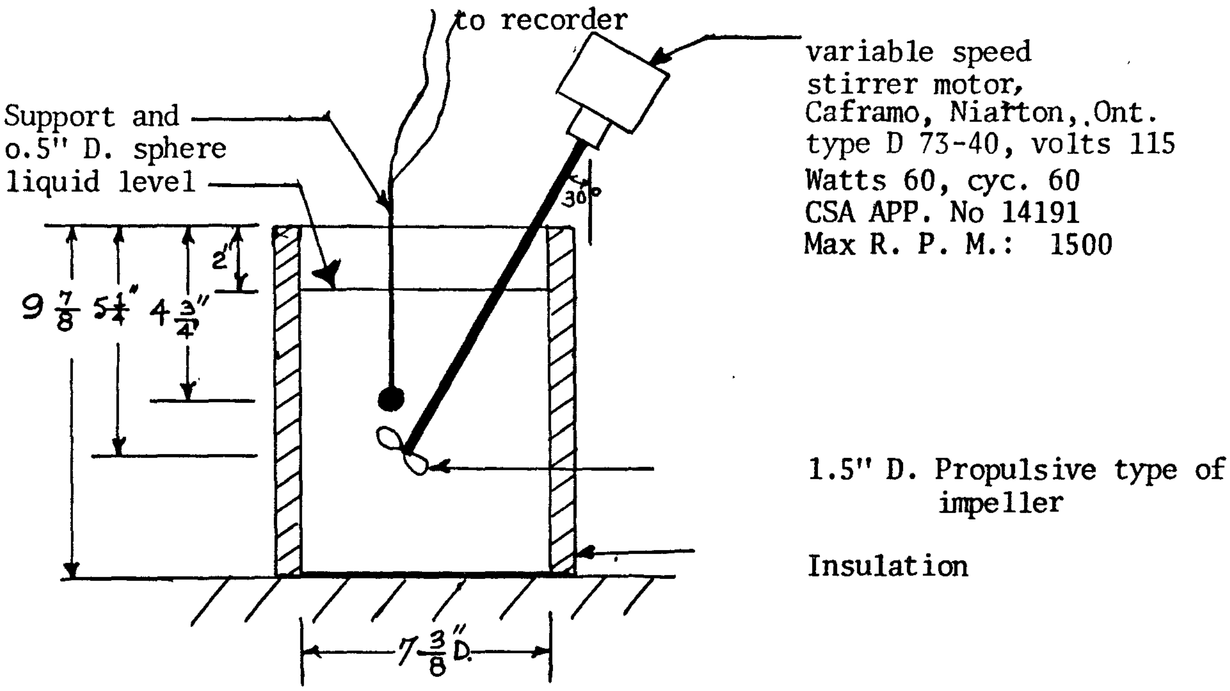


Fig. 2 (continued)



STIRRING: BATH, SPHERE AND STIRRER

SPHERE AND THERMOCOUPLE

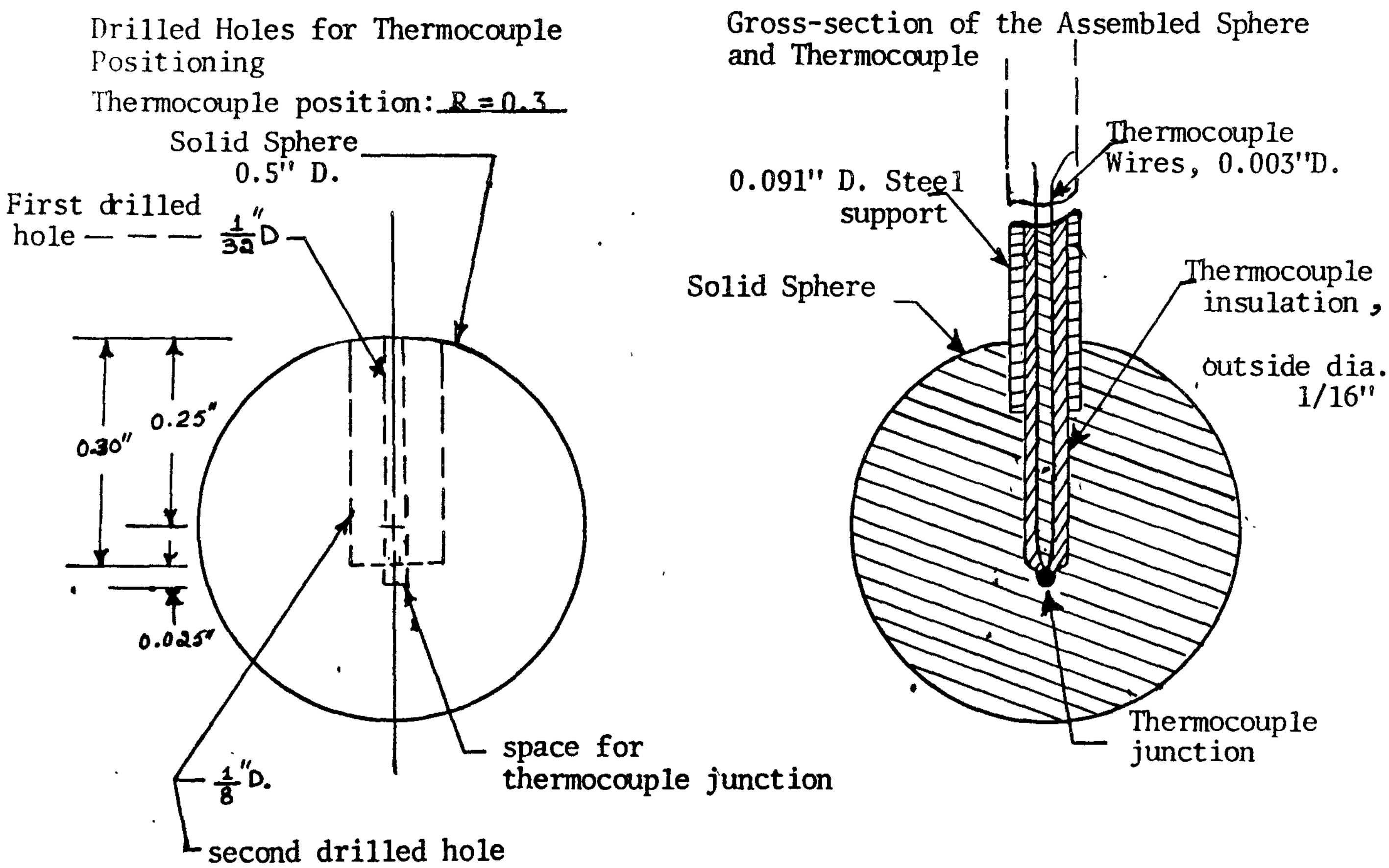
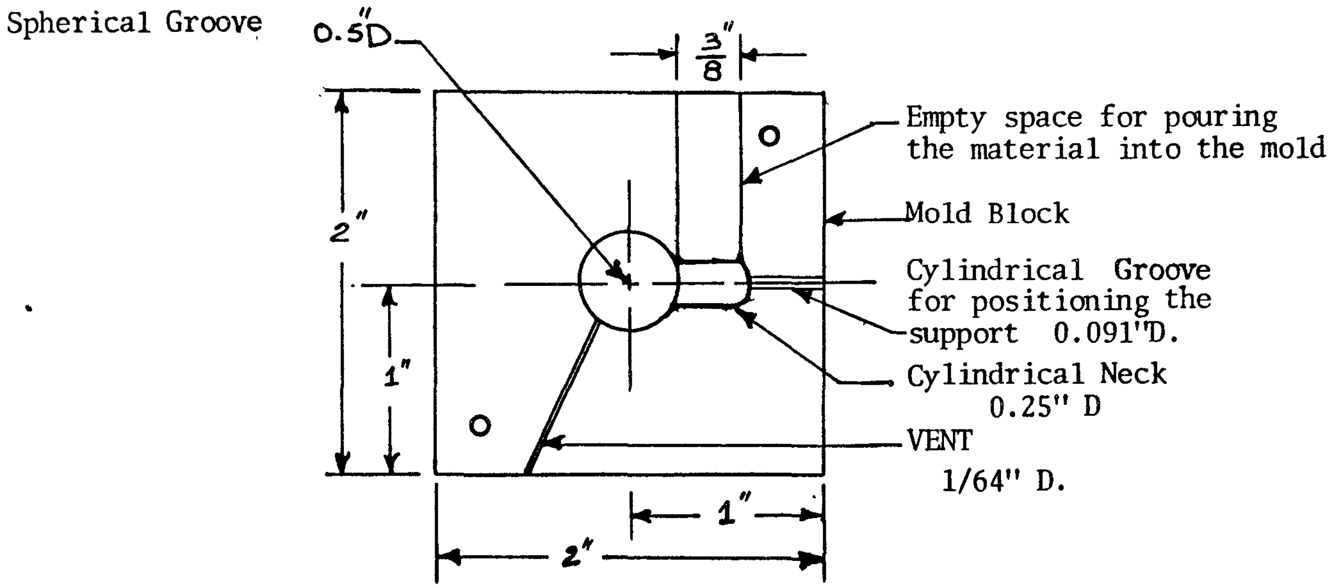
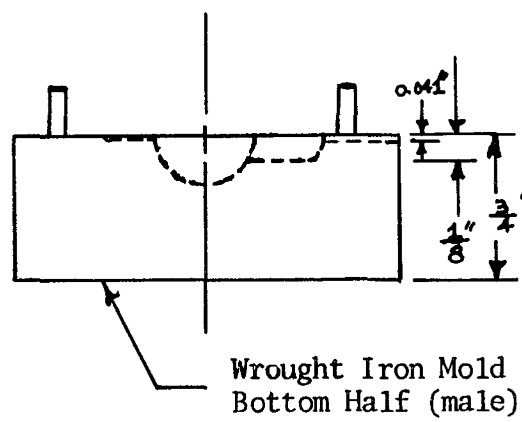


Fig. 2 (continued)

MOLD DETAILS





(b) Mixing

(c) Jet flow

(a) Nucleate boiling - When nucleate boiling exists at the surface of a body, the heat transfer coefficient can be very high. Experiments were made to produce boiling by plunging hot bronze spheres into cold baths of pentane or water. No nucleate boiling occurred because the sphere heat content and temperature were too low. This method showed no promise and further work was discontinued.

(b) Mixing - A well-stirred fluid in a bath is the second medium which has been investigated with 1"D. and 0.5"D. commercial bronze spheres. Heat transfer coefficients were measured and it was found that such a simple experimental set-up provides the desired heat transfer. Because it is simple and convenient, a stirred fluid was used in all cases to create the convective medium necessary in the determination of conductivity with spheres.

(c) Jet flow - A highly turbulent jet flow is another medium which has been considered. Heat transfer experiments were performed to determine whether a jet of water impinging on a sphere of low conductivity would provide a heat transfer coefficient of suitable magnitude. The results were compared with those found using the stirred fluid and it was concluded that a turbulent jet provided an adequate Biot number.

4.2.2.1 Temperature measurement

The bronze sphere with a thermocouple imbedded in and fixed to a support is first kept in a constant temperature bath at T_i until its temperature becomes uniform and constant. The other constant temperature bath is kept at temperature T_∞ and the fluid is continuously stirred. At time zero, the sphere is quickly moved and placed over the impeller blades in the bath at temperature T_∞. Simultaneously, the motor driving the recording chart paper is started. However, in the case of the bronze sphere the temperature change is so sudden and the heat transfer takes place in such a short time (< 3 sec.), that it is better to have the driving motor on before moving the sphere. The point where there is a sudden change in the slope of the recorded curve indicates zero time for the experiment. A typical run with a 0.5"D. Lucite sphere requires approximately 150 seconds. The time necessary to move the sphere from one bath to the other is less than 0.5 seconds. The transient temperature profile is recorded continuously until 90 to 95% of the possible temperature change has taken place. When possible, the experiment is repeated many times with the sphere to establish average values.

Cooling or heating experiments can be done although the cooling type is more convenient with the crude equipment used in the present work.

Thus the temperature-time history is recorded.

4.2.2.2 Interpretation of data

The temperature-time record is plotted on semi-log graph paper and the slope of the straight line obtained gives the average heat transfer coefficient as indicated in Section 3.3. The slope is equal to $\frac{hA}{C_p \rho V}$. Heat transfer coefficients of 1900 and more were measured and this allowed the use of spheres having a diameter of 0.45" and at least up to 0.625"D.

4.2.3 Sphere fabrication

Two types of spheres were used:

(a) Cast spheres supplied commercially

(b) Molded spheres made for this investigation

4.2.3.1 Cast spheres

If ready-made spheres are used, the thermocouples are positioned carefully in a drilled hole and the empty space is filled with an appropriate filler. With Lucite spheres for example, the hole is first filled with the monomer (methyl methacrylate) and a solution of benzoyl peroxide in dimethyl-phthalate. The drilled hole passes through the center of the sphere and is at least equal in length to the sphere radius. The first drilled hole has a diameter slightly larger than that of the thermocouple junction. A second hole of slightly larger diameter than the insulated wires is drilled along the same radius, but to a smaller depth. Thus the junction can be positioned at the bottom of the smaller hole and the accuracy of this positioning is within the junction size. The thermocouple with a bare junction is pushed carefully into the hole down to the bottom. Care is taken in filling the hole to avoid entrainment of air bubbles which might cause thermal resistance at the junction and poor contact. Torborg and Janssen (J2) reported that they had to take the same precaution while making epoxy cylinders.

The thermocouple junction is placed at the center or near the center of the test sphere (normally $R < 0.5$) because the temperature gradients are smaller than near the surface and therefore, positioning errors are much less critical (see Section 5.2.6).

4.2.3.2 Molded spheres

Two symmetrical molds were used to form 0.5"D. spheres. One of these had the particularity of forming a sphere with a cylindrical neck of 0.25" x.25". The function of the neck was to reduce heat conduction along the support from the sphere. It avoids the direct contact between the support and the sphere. The internal halves of the molds were grooved to reproduce one half of the sphere and the support, and were allowing an easy way of positioning the support and thermocouple. The material to be tested was poured into the mold cavity very slowly to avoid moving the junction. At that stage, the material was liquid and it was important to make sure that the mold was completely filled.

Naphthalene, naphthol β , ammonium nitrate, paraffin wax and bismuth liquid materials were allowed to cool down slowly. A thin film of sprayed teflon or mineral oil on the internal wall of the mold facilitated the liberation of spheres.

Ice spheres were made by freezing water and Lucite ones by polymerizing the monomer directly in the mold.

After the test spheres are fabricated and the proper convective medium is chosen, the conductivity determination becomes the next step.

4.2.4 Conductivity determination

Transient temperature change in the sphere of material to be tested is measured continuously after having placed the test sphere in a highly convective medium. Stirring was used to provide adequate mixing and the experimental procedure is the same as described in Section 4.2.2.1. The recorded signals are translated into temperature-time curves. Several repeats are made to check reproducibility and to provide an average temperature-time record for a particular sphere. If necessary, the readings are corrected for the calibration deviation.

Dimensionless temperatures are calculated and then interpreted in terms of a predicted temperature-time curve corresponding to the position of the thermocouple junction. The conductivity values at different temperatures are determined as described in Section 3.4.3. Corresponding to temperatures in the range studied, values of and t are determined and k calculated from

$$k(T) = \frac{Cp\ (T)\ \rho\ a^2}{t}$$

A linear regression of the data gives the conductivity-temperature relationship for the material tested.

4.3 Summary of the Work and Related Aspects Considered

A summary is given here of the work done, the reasons for doing it and of the investigations and aspects considered. The results section which follows discusses these points.

(a) Exploratory work to determine a suitable convective medium.

(1) Nucleate boiling - unsuccessful

(2) Jet flow - suitable

(3) Mixing - suitable and convenient to use

(b) Transient conduction with spheres.

(1) Spheres of naphthalene, naphthol β , bismuth, paraffin wax and ice were used to determine the temperature measurement accuracy and to verify that it is possible to determine the conductivity of low conductivity materials by the proposed transient method using spheres.

(2) Spheres of ammonium nitrate were tested because of their connection with the prilling operation.

(3) Spheres of Lucite were studied in the greatest detail.

(c) Variables considered.

In conjunction with the different conduction experiments, a few aspects have been studied:

(1) Influence of the support and prediction of its influence by using the finite-difference solution with angular conduction.

(2) Reproducibility of the measured profiles for the same sphere.

(3) Difference between results with cooling or heating experiments and influence on the k values determined.

(4) Positioning error.

(5) Influence of the difference (T_i - T_∞) and of the temperature level on the k values determined.

(6) Influence of the thermocouple size. Comparison between 0.008 and 0.003"D. thermocouples.

(d) Error introduced in determining k values by using the series solution profile.

(e) Possibility of using a hemisphere instead of a sphere as the geometry for the tested body.

5. RESULTS AND DISCUSSION

5.1 Determination of h

Preliminary experiments to produce boiling to obtain large h values were unsuccessful and further work was discontinued. Results with mixing and jet flow were successful and these are now reported.

5.1.1 Mixing flow

The largest values for h were obtained by positioning the impeller 4 in. below the surface of the liquid and the sphere immediately above the impeller. Accurate positioning was not important. Heat transfer coefficients of 1900 or more were determined for such a convective field with a bronze sphere of 0.5"D. With a 1"D. sphere, the h value is only 2/3 of the values obtained with the 0.5"D. sphere. This indicated that an upper limit existed to the size of sphere which could be used for such a study. The temperature-time records when plotted on semi-log graph paper gave straight lines except for a short initial period. This deviation is negligible. From 20 runs, an average h of 2050 was obtained (see Appendix 4).

5.1.2 Jet flow

No direct determination of heat transfer coefficients with jet flow have been made. However, experiments with the same sphere and temperature conditions using both, mixing and jet flow, indicated that the heat transfer is the same and therefore h for jet flow must have been approximately equal to 2000. It might have been much greater than 2000, but the heat transfer rate under these convective conditions is very insensitive to the value of h. A unique curve describes the temperature change. The relationship $Nu = 0.6\ Re^{\frac{1}{2}}\ Pr^{1/3}$ predicts an approximative h value of 2750. Table 3 presents a comparison between data obtained from mixing and jet flow. The agreement is excellent.

TABLE 3

TEMPERATURE PROFILES FOR 0.5"D. LUCITE SPHERE S-126

time, sec.	Θ-Mixing Flow	Θ-Jet Flow
0	1.00	1.00
15	0.993	0.991
30	0.875	0.865
40	0.728	0.719
50	0.575	0.578
65	0.399	0.401
75	0.304	0.312

5.2 Variables and Other Aspects Considered

5.2.1

Many different conditions existed in the experiments and sphere details which have or might have had a certain influence on the determination of conductivity coefficients. These points will be reported and discussed briefly in this section. They will help to answer some of the objections and questions which might be raised about the determined conductivity values.

5.2.2 Limited range of the temperature profiles

Because of their "S" shape, the curves θ-time are very sensitive to temperature errors in the ranges $\theta = 0$ to 0.2 and 0.85 to 1.0. This explains why their use has to be generally restricted to the range $\theta = 0.2$ to 0.85. Table 4 illustrates this point by a hypothetical case.

TABLE 4

EFFECT OF TEMPERATURE ERROR AT DIFFERENT TEMPERATURE LEVELS

Hypothetical case: $T_i = 50^{\circ}C$.

$T_\infty = 0^{\circ}C$.

Assumed temperature error: $1^{\circ}C$.

Assumed actual temperatures: 45 and $25^{\circ}C$.

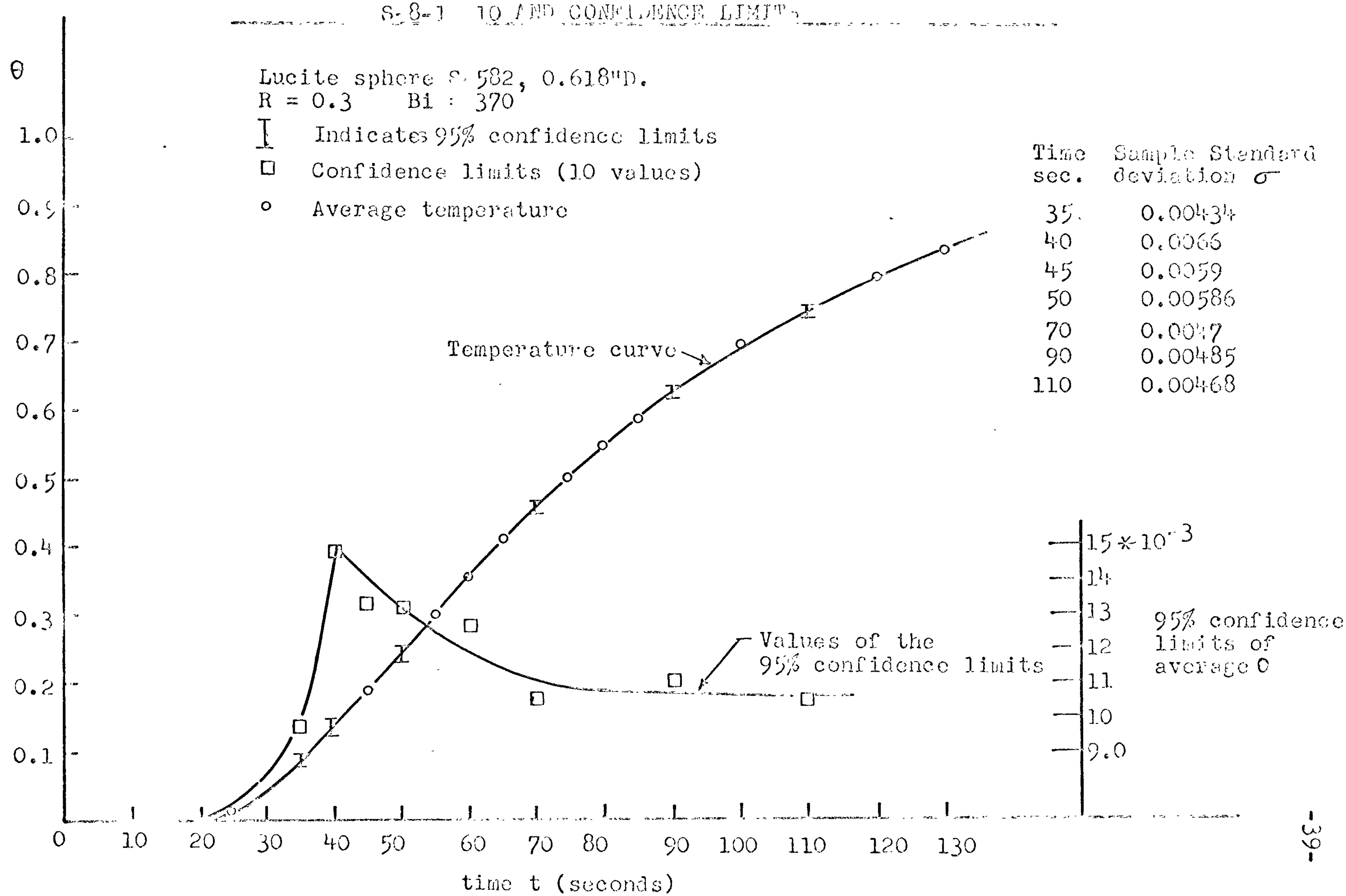
Biot = 500 and R = 0.0

Actual Temp. $T^{\circ}C$.	Measured Temp. $T^{\circ}C$.	θ actual	θ measured	% error for T	% error for θ	τ actual	τ measured	% error on k
45	46	0.1	0.08	2.2	20	0.066	0.0625	5.4
25	26	0.5	0.48	4	4	0.140	0.136	2.9

5.2.3 Reproducibility

For the same sphere and for experiments done in similar conditions, measured dimensionless temperature-time curves are reproduced very well and the individual points from a series of curves do not vary from average curve values by more than 4% between $\theta = 0.15$ and 0.85. Figure 2A shows typical results from

FIGURE 2A: AVERAGE TEMPERATURE-TIME CURVE FROM CONDUCTION EXPERIMENT S-8-1 10 AND CONFIDENCE LIMITS



Time sec.	Sample Standard deviation σ
35	0.00434
40	0.0066
45	0.0059
50	0.00586
70	0.0047
90	0.00485
110	0.00468

a Lucite sphere and the average curve for 10 measurements made in similar conditions. Confidence limits indicate that for the same sphere, measurements are well reproduced. At $\theta = 0$, the sample variance is automatically zero and the same thing happens when θ becomes 1.0. The confidence limits-time curve is increasing rapidly when temperature starts changing in the sphere and the gradient is high. A high value is reached and then, the values of the confidence limits decrease and finally level off when temperature gradient decreases.

5.2.4 Cooling and heating experiments

Most experiments consisted in cooling the spheres but some heating ones were done with ice, naphthalene, Lucite and naphthol. No particular trend in measured conductivity values which might be attributed to the type of heat transfer experiments was noticed. Furthermore, for the same sphere, cooling and heating produced comparable dimensionless profiles and conductivity values. This is illustrated in Table 5 for a Lucite sphere.

5.2.5 Influence of the ($T_i - T_\infty$) difference and the temperature level

These two variables seem to have no particular influence on the dimensionless temperature profiles and on the determined conductivity values. As should be expected, when a small temperature difference ($T_i - T_\infty$) exists, the variation of conductivity values with temperature is small. The variation of the specific heat with temperature has a most important effect in that respect. Table 6 gives an example of typical results.

TABLE 6

DIMENSIONLESS TEMPERATURES AND k VALUES MEASURED BY COOLING AND HEATING THE SAME SPHERE

R = 0.3

Bi = 370

Sphere S-585 (0.620"D.)				
Experiments	S-24-1, 4		S-24-5, 7	
T_i	71.9		2.8	
T_∞	9		54.8	
time (Sec.)	Cooling		Heating	
	θ		θ	
35	0.103		0.108	
65	0.394		0.408	
110	0.712		0.717	
130	0.796		0.795	
	T	k	T	k
	23.0	0.0901	24.0	0.0879
	30.4	0.0915	30.8	0.0915
	41.4	0.0952	40.2	0.0953

TABLE 6

CONDUCTIVITY DETERMINATIONS FOR DIFFERENT ($T_i - T_\infty$) VALUES AND TEMPERATURE LEVELS

(a) Sphere S-582 (Lucite)
Thermocouple position: R = 0.3

Experiments	S-8-1, 10		O-2-5, 8		O-2-1, 4		S-29-9, 12	
T_i	68.7		34.7		26.85		26.6	
T_∞	7.6		10.2		18.25		20.3	
ΔT	61.1		24.5		8.6		6.3	
	T	k	T	k	T	k	T	k
	26.3	0.0962	26.65	0.0934	26.2	0.0872	25.3	0.0981
	18.75	0.0988	24.28	0.0930	24.11	0.0902	24.17	0.0938
			22.0	0.0944	22.55	0.0909	23.6	0.0940
			20.3	0.0938	20.3	0.0908		
			19.4	0.0938	19.8	0.0893		

(b) Sphere S-583 (Lucite)
R = 0.6

Experiments	S-18-1, 6		S-23-1, 2		S-29-1, 4		S-29-5, 8	
T_i	71.2		71.8		36.1		26.6	
T_∞	14.1		12		8.7		18.8	
ΔT	57.4		59.8		27.4		7.8	
	T	k	T	k	T	k	T	k
	29	0.0985	29.2	0.104	29.2	0.109		
	27.6	0.0981	27.8	0.103	27.15	0.108		
	26.4	0.0967	26.2	0.103	25.4	0.106	25.6	0.102
	24.6	0.0948	24.7	0.103	23.8	0.105	23.8	0.0961
	22.7	0.0595			22.35	0.104	22.3	0.0931
					21.25	0.102	21.1	0.0925

5.2.6 Positioning error

Differences between temperature-time curves predicted by series solution are much less important for positions near the center than for positions near the surface. These profiles are used to determine conduc[illegible]. This means that for a similar error in the assumed position, the errors introduced into the conductivity determinations are much larger if the thermocouple junction is measuring temperature changes near the surface. Therefore, to minimize the positioning error it is necessary to place the junction as close as possible to the center of the sphere. In the present series of experiments, the positioning error is considered to be less than the junction size that is to say, less than 0.012 to 0.015". Therefore, the junction position is within R $\pm$ 0.04. Table 7 presents the different errors caused on the determination of k values for same position error but at different level of R. The optimum position is at R = 0.0.

5.2.7 Influence of the thermocouple size on temperature measurements

An attempt was made to estimate the influence of the thermocouple size. Thermocouples, 0.003"D. and 0.008"D. were tested in cast Lucite spheres of the same diameter and the temperature profiles compared. At a high temperature difference ($T_i - T_\infty$) of approximately 60°C., the sphere with the larger thermocouple indicated a faster temperature change at the be-

TABLE 7

PERCENTAGE DIFFERENCES OF DETERMINED k VALUES CAUSED BY ASSUMING THE WRONG POSITION

Sphere Experiments	S-120 (Lucite) D-18-1, 5			
	T	k	k	%
		R = 0.0	R = 0.1	difference
	47.2	0.0890	0.0863	4.2
	27.3	0.0865	0.0848	2.0
	16.9	0.0855	0.0850	0.6
		k R = 0.0	k R = 0.2	
	47.2	0.0890	0.0832	6.5
	27.3	0.0865	0.0830	4.0
	16.9	0.0855	0.0846	1.0
Sphere Experiments	S-585 (Lucite) S-24-1, 4			
		k R = 0.3	k R = 0.4	
	56.8	0.0926	0.0798	13.8
	41.4	0.0952	0.0845	11.2
	30.4	0.0915	0.0832	9.1
	23.0	0.0901	0.0837	7.1
Sphere Experiments	S-583 (Lucite) S-18-1, 6			
		k R = 0.6	k R = 0.77	
	54.4	0.1184	0.0747	63
	44.0	0.1046	0.0574	55
	30.2	0.1001	0.0446	44.6
	25.4	0.0955	0.0349	36.6

ginning and a slower one in the latter part of the experiments. (Results are given in Appendix 7). When $(T_i - T_\infty)$ is less than $10^oC.$, the dimensionless temperature is always slightly greater in the sphere with the larger thermocouple. This seems to indicate that heat is conducted out along the wire of larger diameter at a faster rate. Perhaps the size difference of the junctions and thermal contact variation cause this difference. On the other hand, this explanation does not hold for the behaviour at high $(T_i - T_\infty)$ values. An explanation of this behaviour is not available. Measured temperature-time curves using thermocouples of 0.008"D. and 0.003"D. were insignificantly different. To ensure suitable accuracy, all experiments were performed with a 0.003"D. thermocouple. Fine thermocouples have small heat capacity which allows a better response. Also, the possible conduction error is minimized and the small junction allows more precise point measurements.

5.2.8 Influence of the sphere support

The cross-sectional areas of the glass and stainless steel supports used are respectively equivalent to 6 and 1% of a 0.5"D. sphere surface. It might be expected that the presence of a support decreases the turbulence around the sphere and consequently the heat transfer coefficient, or that because of the missing area for convective heat transfer, the measured curves are affected. The use of glass and stainless steel supports and of spheres with necks to prevent possible conduction along the supports did not seem to be responsible for any particular difference. If any, it was within the experimental variations.

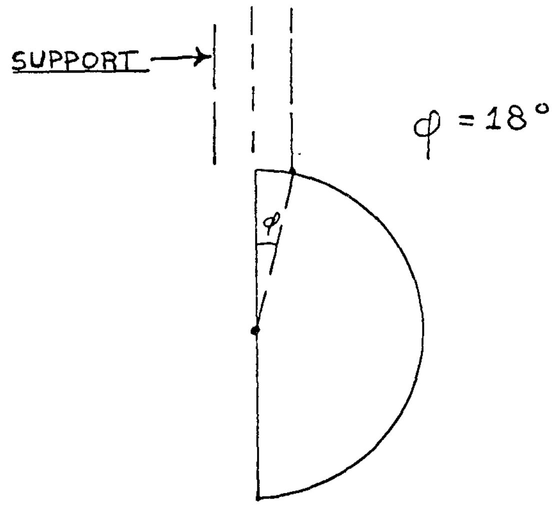
It is possible to predict their effects by mathematical solutions. By using the finite-difference model presented in Section 3.2, but assuming constant physical properties and considering axial symmetry, temperature-time curves can be predicted for the case of angular variation of the heat transfer coefficient. The computation was done using 21 radial and 31 angular mesh points. The details are given in Appendix 8. Generally speaking, these computations with non-symmetrical heat transfer coefficients indicate that because of the low conduction rates within spheres of low conductivity, the energy conditions in one half of the sphere do not affect very much the ones in the other half. They also show that when the heat transfer coefficients are high (> 1900), their variations around the sphere surface do not affect the temperature conditions inside.

Using a heat transfer coefficient of zero on the sphere surface in contact with the support and a variable coefficient over the remaining surface (see Table 8), finite-difference solutions indicated that the temperature variation with time in the half portion of the sphere opposite to the support did not change significantly from the case of heat transfer with radial symmetry ($h > 1900$). This explains why the support influence is negligible if the thermocouple junction is positioned in the half of the sphere opposite to the support. Table 8 shows the heat transfer coefficients used for the computation.

TABLE 8

VARIABLE HEAT TRANSFER COEFFICIENTS AROUND THE SPHERE USED TO SIMULATE THE INFLUENCE OF SUPPORT

ANGLE degrees	h
0	0
6	0
12	0
18	0
24	10
30	25
36	50
42	100
48	500
54	1000
60 to 180	2000



5.2.9 Temperature measurement accuracy

The determination of temperature measurement accuracy requires the comparison of measured profiles with predicted solutions. This comparison assumes that the necessary physical properties for predicting are known and that corresponding similar conditions can be reproduced experimentally. In making spheres many causes of error can be introduced. A few include porosity, non-homogeneity, imperfect sphericity. They are such that they can easily affect the sphere temperature history. Their importance is difficult to evaluate. Therefore, the measurements might be accurate though different from the predicted values. The actual temperature inaccuracies can be caused by, among other things, thermal resistance at the thermocouple junction, by conduction in the wires and by the thermocouple response to transient temperature changes. The above discussion indicates why it has been impossible to determine exactly the temperature measurement accuracy. But it is possible to estimate the total temperature errors and to determine a maximum temperature error.

Temperature measurements obtained from the naphthalene sphere deviate less than 10% from the predicted values even at 15°C. temperature level. A few data are presented in Table 9.

TABLE 9

TEMPERATURE ERROR IN NAPHTHALENE SPHERE

Measured temperature T°C.	Predicted temperature T°C.	% deviation
49.2	50.1	1.9
43.2	46.0	6.5
36.2	39.0	7.1
31.1	32.5	4.4
16.9	15.5	9.2

Although relatively important, the deviation from predicted values for naphthalene is still within an acceptable engineering accuracy. This fact and the better accuracy obtained for the conductivity values were the prime movers to extend the project of investigating the transient method proposed in this work.

Results with spheres of other materials, naphthol and ice for example, indicate comparable and even better accuracy than the ones with naphthalene spheres. Afterwards, the numerous data measured with Lucite spheres were used to assess the temperature measurement accuracy. An average value of approximately 0.0972 for Lucite conductivity in the range 0 to 75°C. was obtained. The conductivity values determined vary from this average by less than 12%. The many data available, their reliability and a comparison with the values proposed in the literature give confidence in the results obtained (see Section 5.4.8).

If a conductivity value of 0.1165 is assumed as the correct one for Lucite, temperature-time curves can be predicted. By comparing the measured curves with the predicted ones, hypothetical temperature errors can be calculated. The errors are hypothetical because the correctness of 0.1165 is only an assumption. Such a comparison was made (see Appendix 9). The largest percentage temperature errors for each sphere were used to evaluate the effect of conductivity errors on these temperature errors. Also, the conductivity value for each sphere differing most from 0.0972 was used to estimate the above conductivity errors. These conductivity errors were expressed in percentages based on 0.0972. The ratios of these percentages and the temperature percentage errors were then calculated. These ratios are always larger than one and usually rather close to 2.0. A ratio of one means that when the determined conductivity differs from .1165 by 10%, the temperature error estimation is 10%.

However, the ratios are around 2 or more and the values 0.1165 differs from 0.0972 by 20%. Thus a temperature error of approximately 10% exists when the conductivity error is 20%. The determined conductivity values vary from 0.0972 by less than 12%. Therefore, using the above reasoning, the overall error in temperature measurement with Lucite spheres is estimated to be less than 6%.

It is clear from the above discussions that the temperature measurements have an accuracy of at least 10% and most probably 5%. This is acceptable for most engineering purposes. This conclusion about the accuracy of temperature measurement is substantiated by experiments with the four materials naphthalene, naphthol β , ice, and Lucite.

5.3 Solutions for Cases of Temperature Dependent Physical Properties

5.3.1

By the appropriate finite-difference method, temperature profiles can be predicted for the case of materials having conductivity and specific heat varying with temperature. Predicted profiles for naphthalene, naphthol or ice, when compared to the actual ones allowed the determination of temperature measurement errors. But hypothetical cases can be set up and used to determine theoretically how much error is introduced by the use of series solution temperature-time curves for estimating conductivity coefficients from experimental data. This is explained in the next section.

5.3.2 Comparison between finite-difference and series solutions

Cases corresponding to real or hypothetical cases have been investigated. Temperature-time curves were predicted by using the finite-difference method and proposed conductivity and specific heat-temperature relationships. From dimensionless time values, actual time ones were estimated, through $t = Cp0 \rho a^2 \tau / k0$. Thus a hypothetical profile θ-actual time was determined and could be used in the same way as similar ones from experiments, to determine the conductivity values using the series solution temperature-time curves (see Section 3.4.3). At that point, the predicted and originally proposed values were compared and the difference existing attributed to the use of series solution curves. It also reflects the inaccuracies and the scatter introduced by personal errors in the curve reading. From these investigations it results that:

(a) When the ratio k/Cp remains constant over the temperature range, the use of series solution introduces no error. It is normal because then, the diffusivity term is essentially constant.

(b) When the ratio k/Cp varies but both, k and Cp increases with temperature, the finite-difference and series solutions are very similar and the values predicted by the series model are negligibly varying from actual ones. This holds true for a good range since variations of k/Cp up to 30% introduced no significant deviation (see Table A.10.2 in Appendix 10).

(c) When the ratio k/Cp varies with temperature but the temperature coefficients of k and Cp are of opposite sign, the series solution dimensionless temperature-time curve is different from the one predicted by the finite-difference model. Usually, the specific heat increases while the conductivity decreases with temperature as it is the case for most crystalline material (J1). Some computed cases are presented in Tables 10, 11, 12, 13, 14, 15. Conductivity values used in the finite-difference model are the proposed ones (k_p) and the ones determined by use of series solution temperature-time curves (Biot = 460 and a = 0.5") are called k_c. Figure 2B makes the comparison easier.

Discussion: - Cases 1, 2, 3 and 4 indicate that the deviations are not significantly affected by the temperature level, the temperature difference ($T_i - T_\infty$), by the level of values k/Cp and by the fact of considering cooling or heating. The variation of k/Cp in the range 50 to 20°C. is either 14% or 5%. These ratios are of the order of 0.5 or 0.2 and absolute ($T_i - T_\infty$) values range from 10 to 50°C. These observations do not differ from what has been found experimentally.

TABLES 10 TO 15

COMPARISON BETWEEN VALUES DETERMINED BY USING SERIES SOLUTION AND VALUES USED IN THE FINITE-DIFFERENCE MODEL WITH VARIATION OF PHYSICAL PROPERTIES

TABLE 10

CASE 1 (NAPHTHOL)

$R = 0.0$

$T_i = 66^{\circ}C.$

$T_{\infty} = 27^{\circ}C.$

$k_p = 0.147 - 0.000075\ T$

$Cp = 0.252 + 0.00128\ T$

$k_c = 0.1288 + 0.00026\ T$

at $50^{\circ}C$, $k/Cp = 0.455$

at $20^{\circ}C.$, $k/Cp = 0.524$

Variation of 14% based on the average value

T	k_p	k_c	% difference
63.2	0.1422	0.1466	+ 3.1
61.8	0.1424	0.1460	
56.7	0.1428	0.1423	
51.3	0.1432	0.1409	
46.5	0.1435	0.1415	
42.4	0.1438	0.1412	- 1.8

TABLE 11

CASE 2 (NAPHTHOL)

T_i = - 30°C.

T_∞ = + 20°C.

k_c = 0.1540 + 0.000184 T

T	k_p	k_c	% difference
- 24.8	0.1489	0.1515	+ 1.8
- 21.5	0.1486	0.1480	- 0.4
- 12.8	0.1480	0.1508	
- 7.6	0.1476	0.1534	
- 1.2	0.1471	0.1540	+ 4.7

TABLE 12

CASE 3 (NAPHTHOL)

T_i = + 20°C.

T_∞ = + 30°C.

k_c = 0.1453 + 0.000074 T

T	k_p	k_c	% difference
20.2	0.1455	0.1490	+ 2.4
20.5	0.1456	0.1462	+ 0.4
22.3	0.1453	0.1440	- 0.9
23.3	0.1452	0.1463	
24.2	0.1452	0.1486	+ 2.3
24.7	0.1451	0.1477	

TABLE 13

CASE 4 (SIMILAR TO PARAFFIN WAX)

$R = 0.0$

$T_i = 48.2$

$T_\infty = 7.0$

$k_p = 0.1388 - 0.00022\ T$

$Cp = 0.6939 + 0.00001\ T$

$k_c = 0.1374 - 0.000097\ T$

at 50°C., $k/Cp = 0.184$

at 20°C., $k/Cp = 0.194$

Variation of 5.25 %

T	k_p	k_c	% difference
47.0	0.1285	0.1342	+ 4.4
39.6	0.1301	0.1312	
30.4	0.1321	0.1350	+ 2.2
26.5	0.1330	0.1351	+ 1.6

TABLE 14

CASE 5 (SIMILAR TO NAPHTHALENE)

$R = 0.5$

$T_i = 50.2$

$T_\infty = 8.7$

$k_p = 0.22 - 0.00073\ T$

$Cp = 0.332 + 0.00111\ T$

$k_c = 0.2250 - 0.00061\ T$

at 50°C., $k/Cp = 0.47$

at 20°C., $k/Cp = 0.60$

Variation of 24%

T	k_p	k_c	% difference
48.9	0.1836	.1925	+ 4.8
48.6	0.1845	.1960	+ 6.2
46.5	0.1860	.1968	
44.1	0.1878	.2020	
41.6	0.1896	.2000	
39.1	0.1915	.1990	+ 3.9

TABLE 15

CASE 6 (SEVERE CONDITIONS)

$R = 0.9$

$T_i = 70$

$T_\infty = 10$

$k_p = 0.5 - 0.00065\ T$

$Cp = 0.3 + 0.001\ T$

$k_c = 0.396 + 0.0013\ T$

at 50°C., k/Cp = 1.32

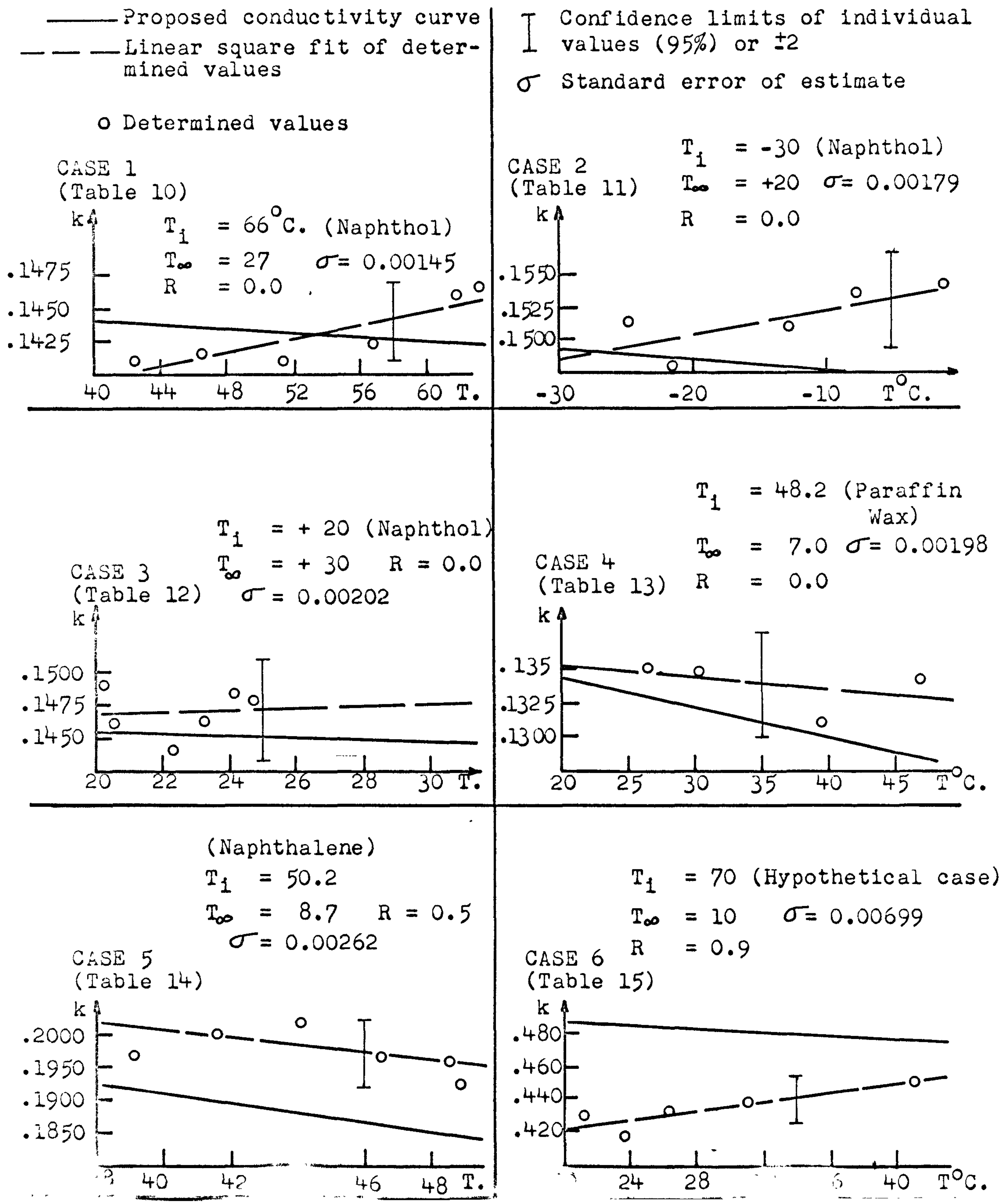
at 20°C., k/Cp = 1.52 Variation of 14%

T	k_p	k_c	% difference
41.0	0.473	0.450	- 5.0
31.0	0.480	0.438	- 8.9
26.2	0.483	0.433	- 10.4
23.6	0.485	0.417	- 14.0
21.2	0.486	0.430	- 11.5

In Case 5, the k/Cp variation is more important (24%) and the deviations are slightly larger and range from 4 to 6%. For the first four cases, the absolute deviations are all smaller than 4.8% and closer to 2%. Case 6 corresponds to a severe case because position R = 0.9 is considered. The difference of determined conductivity values with proposed ones is then up to 14%, thus showing that more errors can be expected when measuring the transient temperature near the surface. All

FIGURE 2 B

COMPARISON BETWEEN PROPOSED CONDUCTIVITY-TEMPERATURE CURVES AND DETERMINED ONES USING SERIES SOLUTION TEMPERATURE-TIME CURVES FOR BIOT NUMBER OF 460 AND SPHERE RADIUS OF 0.5".



cases, except Case 5, give determined conductivity-temperature curves which are slightly concave. The general trend is towards conductivity values increasing with temperature when really the actual values are decreasing. These inversed slopes were also obtained in experimental work as it will be seen later. In Case 5, R = 0.5 and then the variation of determined k values with temperature is similar to the actual one. A proposed explanation for this better behaviour is the fact that position R = 0.5 is more representative of the average of transient temperature and energy conditions within the sphere. It appears that position 0.5 gives more accurate slopes for the conductivity-temperature curves when the ratio k/Cp varies with temperature and k and Cp vary in opposite directions.

The use of series solution temperature-time curves gives a good average k value and errors in the whole range of values can be kept below 6% when the measurements corresponding to positions between R = 0 and 0.5 are considered. This was tested for variations of k/Cp up to 30%. However, slopes of determined conductivity-temperature curves can be opposite to actual ones and these determined curves also differ by their non-perfect linearity. Figure 2 illustrates these results.

5.4 Conductivity Determination - Results and Discussion

5.4.1 Introduction

Seven different materials were used in the determination of conductivity by the proposed method based on transient temperature measurements and use of series solution temperature-time curves. Naphthalene, naphthol β, ice, paraffin wax and bismuth were more or less used to check experimentally the method. A good deal of reliable data exist in the literature for these materials. Because no reliable conductivity data were known for ammonium nitrate, it became interesting to investigate it. The bulk of the work was done with Lucite spheres whose physical conditions and details of construction varied extensively. Therefore, Lucite data are very useful for determining the reproducibility of the method. Lucite is also interesting because it is a representative solid polymer and has the same thermal characteristics as many plastics, for example epoxies, all being low conductivity materials. Measured conductivity values will be presented for each sphere and compared to reliable literature data. Only essential data will be presented and more details can be found in the Appendices 11 to 14.

5.4.2 Naphthalene

There are many reliable data for the physical properties of naphthalene in literature. These data and the measured properties are presented in Table 15A and 15B. The measured density indicates that the 0.5"D. sphere used was slightly porous, but an examination of the structure revealed a relatively homogeneous body. A linear regression of the eleven points considered, which were always picked up in a relatively random way along the temperature-time curves, gave the measured conductivity-temperature relationship (k_c). The 95% confidence limits for individual observation are $\pm$0.0078 or 3.8% of 0.2017, the conductivity at the average temperature of the range considered. The deviations from a straight line are small and the determined linear relationship gives values differing by less than 2.5% from the literature data. Naphthalene provides an interesting check. The agreement between determined and available conductivity values is very good and it is illustrated in Figure 3A.

TABLE 15A

PHYSICAL PROPERTIES OF NAPHTHALENE

		References
Specific gravity	1.145	P2, P3
	1.065 $\pm$ 0.005	* measured
Specific heat	$Cp = 0.281 + 0.00111\ T$	P2
Conductivity	$k = 0.22 - 0.00073\ T$	I1
k/Cp at 50°C.	0.47	
k/Cp at 20°C.	0.60	

* The expression "measured" indicates values obtained experimentally during the present investigation.

TABLE 15B

NAPHTHALENE CONDUCTIVITY DETERMINED BY USING SERIES SOLUTION TEMPERATURE - TIME CURVES

Experiments D-11-3, 6

$R = 0.0$ specific gravity 1.065 ± 0.005

$T_i = 50.3$

$T_\infty = 8.7$

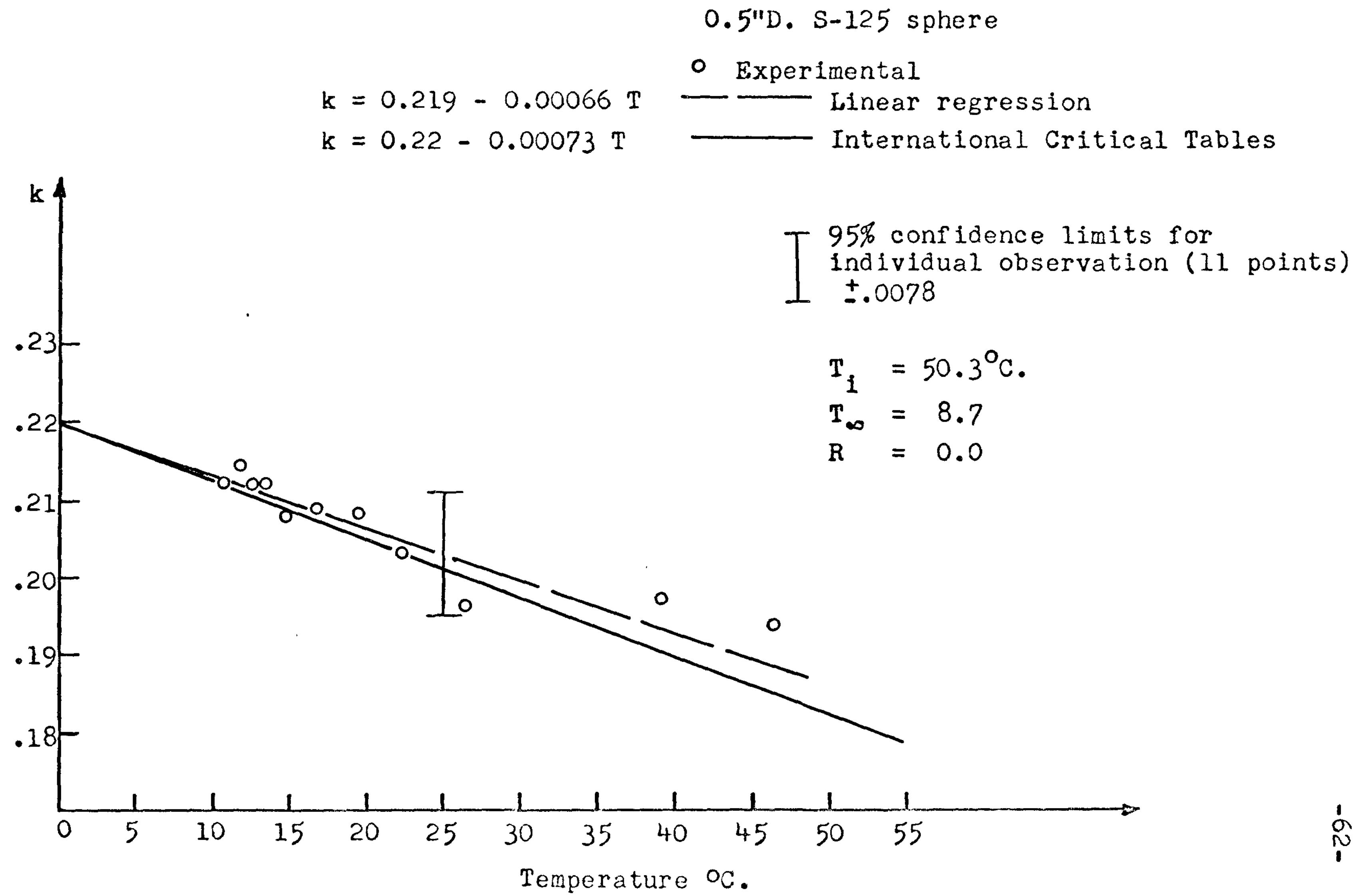
$k_p = 0.22 - 0.00073\ T$ (I1)

$k_c = 0.219 - 0.00066\ T$ (linear regression)

θ	T	k
0.092	46.4	0.192
0.264	39.15	0.198
0.577	26.4	0.196
0.669	22.4	0.203
0.745	19.4	0.208
0.805	16.7	0.209
0.855	14.7	0.208
0.891	13.35	0.212
0.916	12.5	0.212
0.936	11.5	0.214
0.953	10.7	0.212

FIGURE 3A NAPHTHALENE

Conductivity vs. temperature



5.4.3 Naphthol β

Naphthol β is a crystalline material and the three spheres tested had a structure which was slightly non-isotropic and non-homogeneous. Radial orientation of crystals and a few small pores were noticed. The physical properties for naphthol β are well known and given in Table 16.

TABLE 16

PHYSICAL PROPERTIES OF NAPHTHOL β

Specific gravity	1.217 1.17 ± 0.01	K3 (REF.) measured
Cp	Cp = 0.252 + 0.00128 T (60° to 122°C.)	P2
k_p	k = 0.1470 - 0.000075 T (60° to 122°C.)	I1
k/Cp at 50°C.	0.455	
k/Cp at 20°C.	0.524	
% variation of ratio k/Cp	14%	

The specific heat relationship is proposed for a limited range (60° to 122°C.). It was impossible to operate in that range because surface material started to be carried away by stirred fluid or to dissolve at around 70°C. The linear relationship for specific heat was assumed to hold in the lower temperature range considered in the present work. The measured conductivities are tabulated in Table 17.

TABLE 17

NAPHTHOL β CONDUCTIVITY VALUES DETERMINED BY USING THE SERIES SOLUTION CURVE

3 spheres of 0.5"D.

R = 0.0

Experiments	F-22-5, 6, 7			F-23-2			F-25-1		
T_i	-32.7			80.0			66.65		
T_∞	21.6			22.15			23.0		
ΔT	54.3			57.85			43.65		
	θ	T	k	θ	T	k	θ	T	k
	0.194	-22.15	0.141	0.153	71.1	0.148	0.140	60.6	0.137
	0.333	-14.6	0.144	0.268	64.45	0.145	0.238	56.3	0.133
	0.458	- 7.8	0.146	0.380	57.95	0.144	0.359	51.0	0.136
	0.566	- 1.9	0.147	0.488	51.75	0.143	0.465	46.4	0.135
	0.654	+ 2.85	0.147	0.585	46.15	0.143	0.560	42.2	0.133
	0.726	6.75	0.152	0.658	41.9	0.139	0.634	39.0	0.131
	0.788	10.1	0.154	0.726	37.95	0.139	0.704	35.9	0.132
	0.838	12.8	0.158	0.780	34.95	0.139	0.756	33.7	0.131
	0.871	14.6	0.158	0.824	32.3	0.139	0.805	31.5	0.132
				0.853	30.6	0.138	0.844	29.8	0.134
				0.878	29.2	0.135	0.875	28.5	0.134

Table 18 gives the least-squares linear fit of these data.

TABLE 18

LEAST-SQUARES LINEAR RELATIONSHIP FOR CONDUCTIVITY-TEMPERATURE AND COMPARISON WITH THEORETICAL CASES FROM FINITE-DIFFERENCE AND SERIES SOLUTION

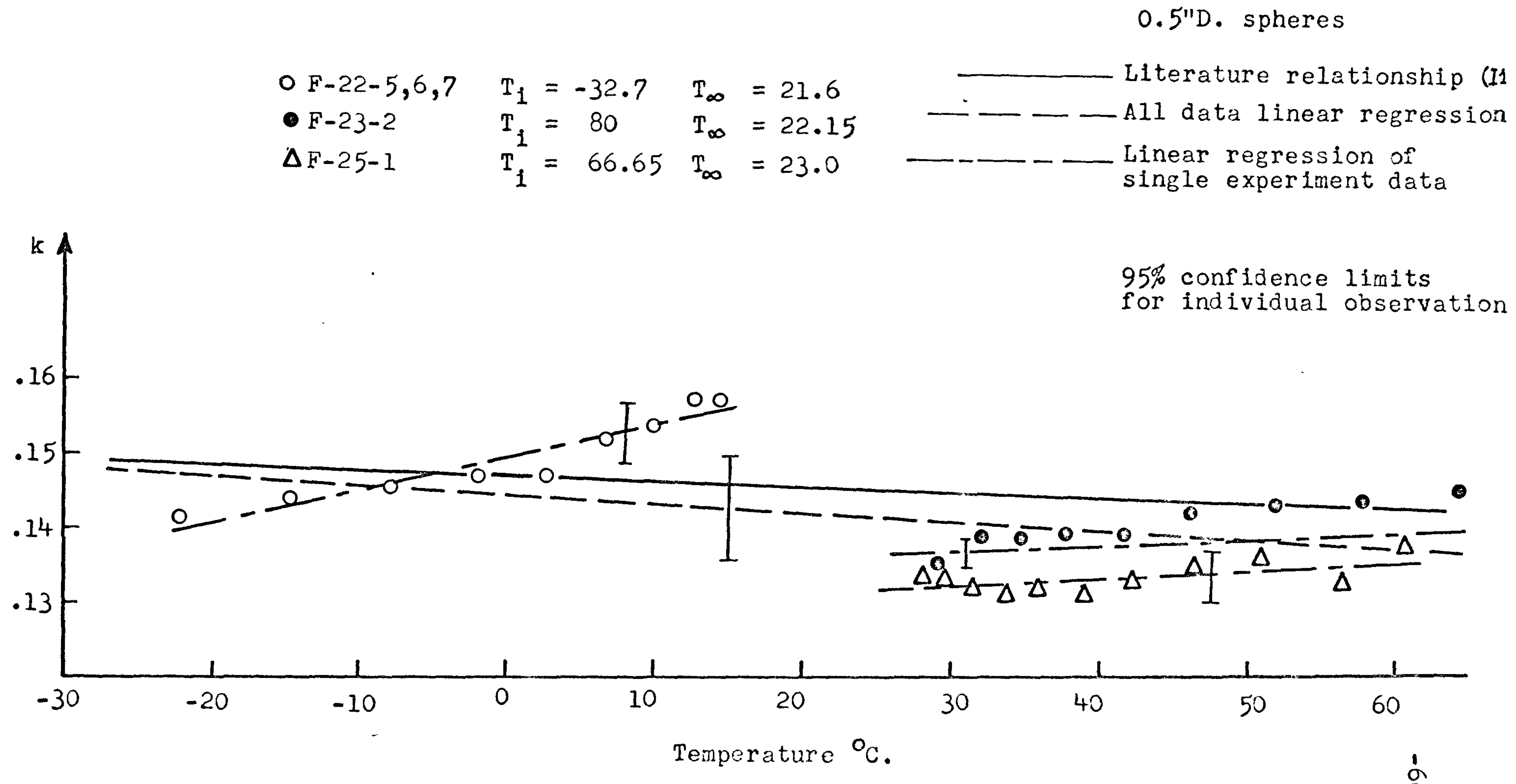
The results for Cases 1 and 2 are given in Section 5.3.2.

Case or Experiment	Number of Points	Standard Error of estimate	95% limits of individual observation	Determined relationship for k
F-22-5, 7	9	0.00213	±0.0043	0.149 + .00044 T
Case 2	5	0.00179	±0.0035	0.154 + 0.00018 T
F-23-2	11	0.0009	±0.0018	0.129 + 0.00026 T
F-25-1	11	0.00172	±0.0034	0.129 + 0.000096 T
Case 1	6	0.00145	±0.0029	0.129 + 0.00026 T
Combination of all experimental points	31	0.00714	±0.014	0.144 - 0.00012 T

Figure 4 illustrates the results. The variation of k/Cp with temperature is important (48%) because a range of -30 to +70°C. has been tested by using three different spheres. Table 18 indicates that the linear least-squares regressions of data from individual experiments give linear conductivity-temperature curves which have positive slopes. The standard errors of estimate are similar to the ones determined for comparable theoretical

FIGURE 4: NAPHTHOL β

Conductivity vs. Temperature



cases. These cases, based on hypothetical predicted values and finite-difference and series solutions, were presented in Section 5.3.2. The similarity of behaviour indicates that using series solution has the same effect in experimental cases as in theoretical ones. It means also that the scatter caused by error in reading graphs and doing calculations is the same in both cases. Theoretical and experimental cases give very similar values; therefore, this is an indication that the measurements are relatively accurate. The 95% confidence limits for all available points considered together are reasonable and vary by less than 10% from the average value. The linear regression gives a curve with a negative slope. This curve is only slightly different (<3.5%) from the one proposed by International Critical Tables (I1). It happens because two ranges of temperature were used and that values determined from experiments F-23 and F-25 are lower than expected. These lower values are possibly caused by the uniform loss of surface material at higher temperature as mentioned before. Experiment F-22 results indicate that the average value falls on the curve from literature and that many such average values could be used to determine accurately the complete conductivity-temperature curve.

5.4.4 Paraffin wax

5.4.4.1

Many different types of paraffin waxes exist and the variation of their properties is relatively important. This makes any comparison difficult. The literature indicates much scatter though International Critical Tables propose a best curve fit for data from many workers. The material was investigated to assess the generality of the method.

The spheres had an amorphous structure but the central part seemed porous and it was observed that the thermal contact was poor.

The available and measured physical properties except conductivities, are presented in Table 19. The conductivity values can be found in Table 20.

TABLE 19

PHYSICAL PROPERTIES OF PARAFFIN WAXES

		Reference
Specific gravity	0.92, 0.89, 0.87 to 0.94	I1
	0.87 to 0.91	Kern K3
	0.891 to 0.907 for 59°C. M.P. paraffin wax spheres Adopted value: 0.9	Measured
Specific heat	0.6939	K3

TABLE 20

CONDUCTIVITY k OF PARAFFIN WAX FROM LITERATURE

M.P. °C. (Melting point)	Specific gravity	Temperature °C.	k	References
		0	0.1662	I1
66	0.92	23	0.1547	I1
84		21 to 57	0.1136	I1
	0.87 to 0.94	18 to 25	0.1503	I1
	0.89	30	0.1325	I1
54		-56	0.1529	L3
		-37	0.1482	
		-21	0.1466	
		- 7	0.1438	
		+10	0.1403	
General survey on amorphous paraffin wax		-180 to +30	0.1388-0.00022T	I1

k/Cp ratio: at 50°C., k/Cp = 0.1845
at 0°C., k/Cp = 0.2
variation of 8%

5.4.4.2 Conductivity determination results

Table 21 gives the results for the four different spheres of paraffin wax tested.

TABLE 21

CONDUCTIVITY OF PARAFFIN WAX

Spheres diameter: 0.498" ± 0.002

Melting point: 59°C.

Thermocouple position: R = 0.0

A new sphere was used in every experiment

Specific gravity: 0.9

Experiment duration: ≈ 150 seconds

Exp.	F-15-1		F-15-3		F-15-4		F-15-5	
T_i	48.2		48.2		48.2		48.2	
T_∞	7.0		8.6		11.3		12.7	
ΔT	41.2		39.6		37.9		35.5	
	T	k	T	k	T	k	T	k
	43.1	0.109	43.55	0.0928	44.5	0.0888	44.6	0.0888
	39.65	0.104	39.05	0.0978	40.5	0.0946	41.1	0.0924
	34.7	0.0982	34.15	0.0968	34.9	0.0978	34.75	0.103
	30.2	0.0961	30.25	0.0936	30.45	0.0914	30.75	0.0985
	25.65	0.0962	24.9	0.0922	25.65	0.0912	26.45	0.0962
	22.65	0.0977	21.35	0.0976	21.4	0.0983		
	19.60	0.102	19.8	0.101				
	15.1	0.110	15.75	0.110				
			14.5	0.116				

Table 22 gives the least-squares linear fits of the data.

TABLE 22

LEAST-SQUARES LINEAR RELATIONSHIPS FOR

CONDUCTIVITY-TEMPERATURE DATA OF PARAFFIN WAX

Experiment	Number of Points	Standard error of estimate	95% limits for individual observation	Determined relationship for k
F-15-1	8	0.00594	±0.012	0.100 + 0.00005 T
F-15-3	9	0.00609	±0.0122	0.115 - 0.00056 T
F-15-4	6	0.0039	±0.0078	0.997 - 0.00018 T
F-15-5	5	0.0036	±0.0073	0.113 - 0.00048 T
Combination of all experimental points	28	0.0059	±0.0102	0.109 - 0.00034 T

The variation of k/Cp with temperature is indicated as 8% from 0 to 50°C. However, only one value of specific heat has been found and its accuracy is doubtful. Its variation with temperature is not known and if it was so, the slope of linear relationships might be affected one way or the other because $k(T) = \frac{Cp(T) \rho a^2}{t}$ is used.

The central portion of the spheres, where the junctions were positioned, was softer than the remaining body. The 0.01" long end of the supports imbedded in the spheres had a tendency to slide out after the second or third experiment was completed with the same sphere. These facts indicate that the contact between wax and metal was poor. The poor thermal contact explains to a large extent the low conductivity values obtained. The difference with the bulk of literature values could not be explained only on the basis of difference in the properties of the compared materials.

The points were linearly regressed to remove any human bias. But the points are very scattered and the data for experiments F-15-4 and F-15-5 have a student T values smaller than the ones proposed by distribution of T tables. This means that the probability of getting 95% of the points within the limits proposed is not really existing for these data. The determined slope of the conductivity-temperature curve for all points combined together is similar to the ones from curves proposed in the literature. But it is impossible to conclude from these data which ones are reliable.

This partial success does not mean that it is impossible to get good data with paraffin wax spheres. At least, these experiments indicate that the reproducibility is possible as shown by the standard error estimates, the 95% confidence limits and the determined k values. They also point out how essential good thermal contact is. Figure 5 illustrates the results.

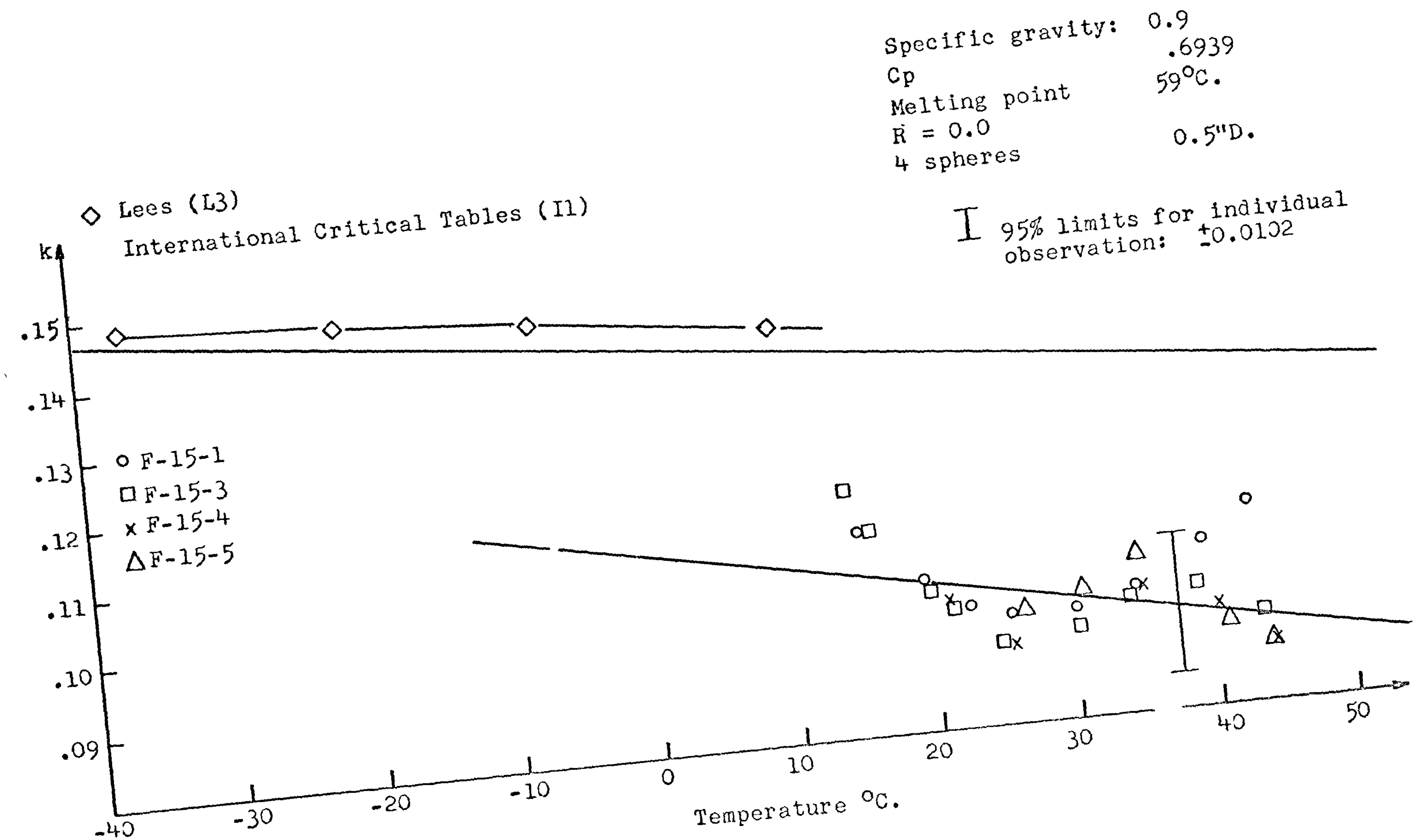
5.4.5 <u>Bismuth</u>

5.4.5.1

This metal has a low conductivity and can give a crystalline

FIGURE 5: PARAFFIN WAX

Conductivity versus temperature



structure as was observed by crystallographic examination. This structure had a certain amount of non-isotropy which could be held responsible for part of the deviation measured in the data. Also, the junction position could not be checked after the experiments were finished and the positioning had to be assumed perfect.

Although a low conductivity metal, bismuth has a high conductivity if compared to Lucite (>forty fold) and the heat transfer in the 0.5"D. sphere took place in less than 2.5 seconds. Time end-effects (moving the sphere, starting the recorder, etc.) become important and the possible time variation ($\approx \pm 0.2$ sec.) can affect very much the determined data in the early period of the heat transfer experiments. Therefore, bismuth results will indicate the experimental performance when severe conditions are used.

In the temperature range 0 to 75°C., the Biot number varies from 10.0 to 8.53 that is to say, by 8%, if based on the average value. These figures assume that the conductivity data proposed by Kern (K3) are the most reliable and vary linearly with temperature. The variation does not affect the conductivity determination at the average temperature if the series solution curve corresponding to the average Biot number is used. Table 23 shows the variation introduced in the determination of conductivity by using different Biot numbers. The figures indicate that the variation is larger if $R = 0.8$. Because the junction is at $R = 0.5$ and that only data between $\theta = 0.2$ and 0.85 are normally used, the relative error introduced by using the average value Bi = 9.25 is small and always less than ±1.5%. This error is negligible.

TABLE 23

VARIATION OF THE DETERMINED CONDUCTIVITY VALUES WITH BIOT NUMBER

0.5"D. bismuth sphere
Heat transfer coefficient: 2000
From (K3): at 17°C., k = 4.7
at 3.9°C., k = 3.9
Biot number variation: at 0°C., Bi = 10.0
at 75°C., Bi = 8.53

Average value = 9.25

	R = 0.0			R = 0.8		
	Bi=9.25	Bi=10.0	% variations of determined k	Bi=9.25	Bi=10.0	% variations of determined k
0.040	0.0608	0.060	1.32			
0.082				0.01028	0.010	2.8
0.204	0.101	0.100	1.0			
0.283				0.0259	0.025	3.65
0.545	0.18215	0.180	1.2	0.0623	0.060	3.7
0.695	0.23385	0.231	1.22	0.10454	0.100	4.35

Table 24 contains some of the most representative data for bismuth. It is worth noticing that the general trend for conductivity values is towards having them decreasing with temperature increase.

TABLE 24

PHYSICAL PROPERTIES OF BISMUTH

(a) Specific gravity (K3): 9.8

(b) Specific heat (K3): at $0^{o}C.$, Cp = 0.0294
at $100^{o}C.$, Cp = 0.0304
(Linearity of Cp is assumed for the calculations)

(c) Conductivity:* ⊥ or 11 indicates that the heat transfer is perpendicular or parallel to the trigonal axis of a bismuth single crystal. P indicates a polycrystalline structure.

ref.	K1			B1			K2		P1	T2	W4	K3	L4
*Cond.	P	⊥	11	P	⊥	11	⊥	11	P	P	P	P	P
$T^{o}C.$													
-173											4.05		
0													
17							3.845					4.7	
20								3.825					
25	4.71	4.56	3.51										
27											4.05		
30									3.87				
80									3.77				
100									3.63	4.35		3.9	
Not specified				4.64	5.44	4.07			4.11				4.11

k/Cp variation: at 75°C., k/Cp = 138.4
at 0°C., k/Cp = 166
Variation of 18%

5.4.5.2 <u>Conductivity determination results</u>

Two series of experiments were done with the bismuth sphere. Results are presented in Table 25.

TABLE 25

CONDUCTIVITY OF BISMUTH

Sphere diameter: 0.501"
Biot number used for the series solution: 9.25
Junction position: R = 0.5

Experiments 0-8-1, 5			JA-24-1, 5		
T_i	71		73.6		
T_∞	10.4		3.9		
θ	T°C.	k	θ	T	k
0.2	58.9	4.39	0.187	60.6	4.21
0.3	52.8	4.23	0.321	51.3	3.96
0.4	46.75	4.03	0.446	42.6	4.01
0.5	40.65	4.03	0.556	34.85	4.06
0.6	34.6	4.08	0.646	28.55	4.01
0.7	28.5	4.05	0.717	23.7	3.97
0.8	22.4	4.10	0.774	19.7	4.01
0.9	16.4	4.12	0.822	16.35	4.08
			0.857	13.9	4.06

Table 26 gives the linear regressions of the points.

TABLE 26

LEAST-SQUARES FITS OF THE DATA AND DETERMINED

CONDUCTIVITY-TEMPERATURE RELATIONSHIPS FOR BISMUTH

Experiments	Number of Points	Standard error of estimate	95% limits for individual observation	k-T relationship
0-8-1, 5	8	0.109	±0.22	3.95 + 0.0048 T
JA-24-1, 5	9	0.075	±0.15	3.92 + 0.0015 T
All data combined	17	0.097	±0.185	3.96 + 0.0033 T

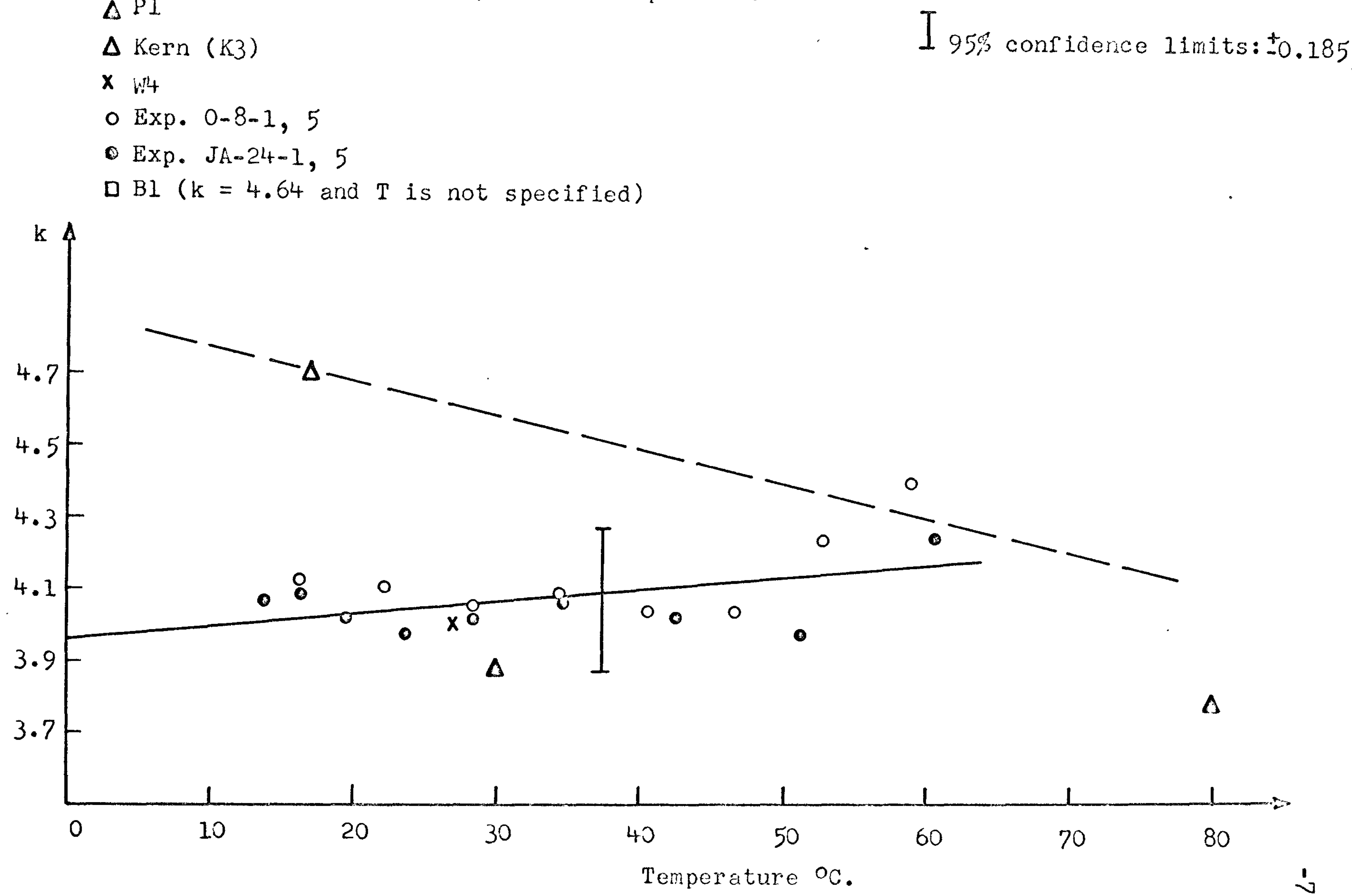
The results are illustrated in Figure 6.

Indeterminate errors caused for example by curve readings, initial time and dimensionless time determination or other operator's bias are always existing in the determination of conductivity values. They would be more important in the case of bismuth. However, the standard error of estimate values are quite similar for the two sets of experiments. The values obtained give a conductivity-temperature linear relationship with a positive slope and they are distributed along a concave shape curve. Because k and Cp vary oppositely with temperature, these behaviours can be caused by the use of series solution for determining k as demonstrated in Section 5.3.2.

The average value of k determined is lower than the

FIGURE 6: BISMUTH

Conductivity versus temperature



values from Kern (K3) but some other authors propose values in the same range. Moreover, this average value (≈ 4.1) is only 9% different from Kern's value. Thus, even in severe experimental conditions, everything indicates that satisfactory values were obtained for the conductivity of bismuth.

5.4.6 Ice

5.4.6.1

There are few available conductivity values for ice and they are scattered. However, the value 1.3 seems the most widely adopted one. The temperature-time curve predicted by the series solution and corresponding to the Biot number determined from k = 1.3, was used to estimate the conductivity values. As in the case of bismuth, the Biot number is smaller than 150 and actually for the 0.5"D. ice sphere, it is 32 when h = 2000 and k adopted is 1.3. Strictly speaking, the Biot number varies and so are the predicted temperature-time curves, but again as in the case of bismuth, the effect of the variation on the determined k values has to be considered negligible. This assumption is justified by calculations which are presented in Appendix 13.

These calculations indicate that the determined values of k are consistent with the assumed values only when a k value of 1.3 is used to calculate the Biot number. For example, when the assumed value of k is 1.21, the determined values of k range from 1.29 to 1.25. On the other hand, when 1.3 is assumed and used to estimate the Biot number, the determined values are between 1.32 and 1.29.

The comparison between the assumed k value used for determining the Biot number and the values determined by using the predicted temperature-time curve corresponding to that Biot number, gives a method of determining the conductivity range of an unknown material. Also, it allows the determination of an average conductivity value when the Biot number is such that the predicted temperature-time curve is dependent upon it.

5.4.6.2 Physical properties of ice

Table 28 presents the available data on physical properties of ice. Figure 7 gives the specific-heat temperature curve used.

TABLE 28

PHYSICAL PROPERTIES OF ICE

(a) Density: Kern (K3), 57.5 at 0°C.
Kreith (K7), 57.0
Perry (P2), 57.2
(P3), 57.2
Adopted value (not measured), 57.3

(b) Specific heat: Kreith (K7), Cp = 0.46
Reference (P3)

°C.	Cp	°C.	Cp
-100	0.329	-14.8	0.4668
- 78	0.463	-14.6	0.4782
- 60	0.392	-11.0	0.4861
- 38.3	0.4346	- 8.1	0.4896
- 34.3	0.4411	- 4.3	0.4989
- 30.6	0.4488	- 4.5	0.4984
- 31.8	0.4454	- 4.9	0.4932
- 23.7	0.4599	- 2.6	0.5003
- 24.5	0.4605	- 2.2	0.5018
- 20.8	0.4668		

From (J3)

°C.	Cp
- 73.16	0.3755
- 53.16	0.4110
- 33.16	0.445
- 13.16	0.481
- 3.16	0.498
0	0.5025

(c) Conductivity: Newman (N2), 1.372
Mitchell (M8), 1.21
Kreith (K7), 1.28 at 0°C.
Perry (P2), 1.3
Kern (K3), 1.3 at 0°C.
(P3), 0.943 and 0.532
Lees (L3),

T°C.	k	T°C.	k
-197	1.828	-90	1.380
-189	1.701	-82	1.368
-187	1.624	-69	1.360
-183	1.58	-59	1.336
-180	1.56	-50	1.320
-179	1.558	-41	1.287
-170	1.522	-27	1.242
-133	1.432	-16	1.260
-109	1.419		
-100	1.393		

5.4.6.3 Conductivity determination results

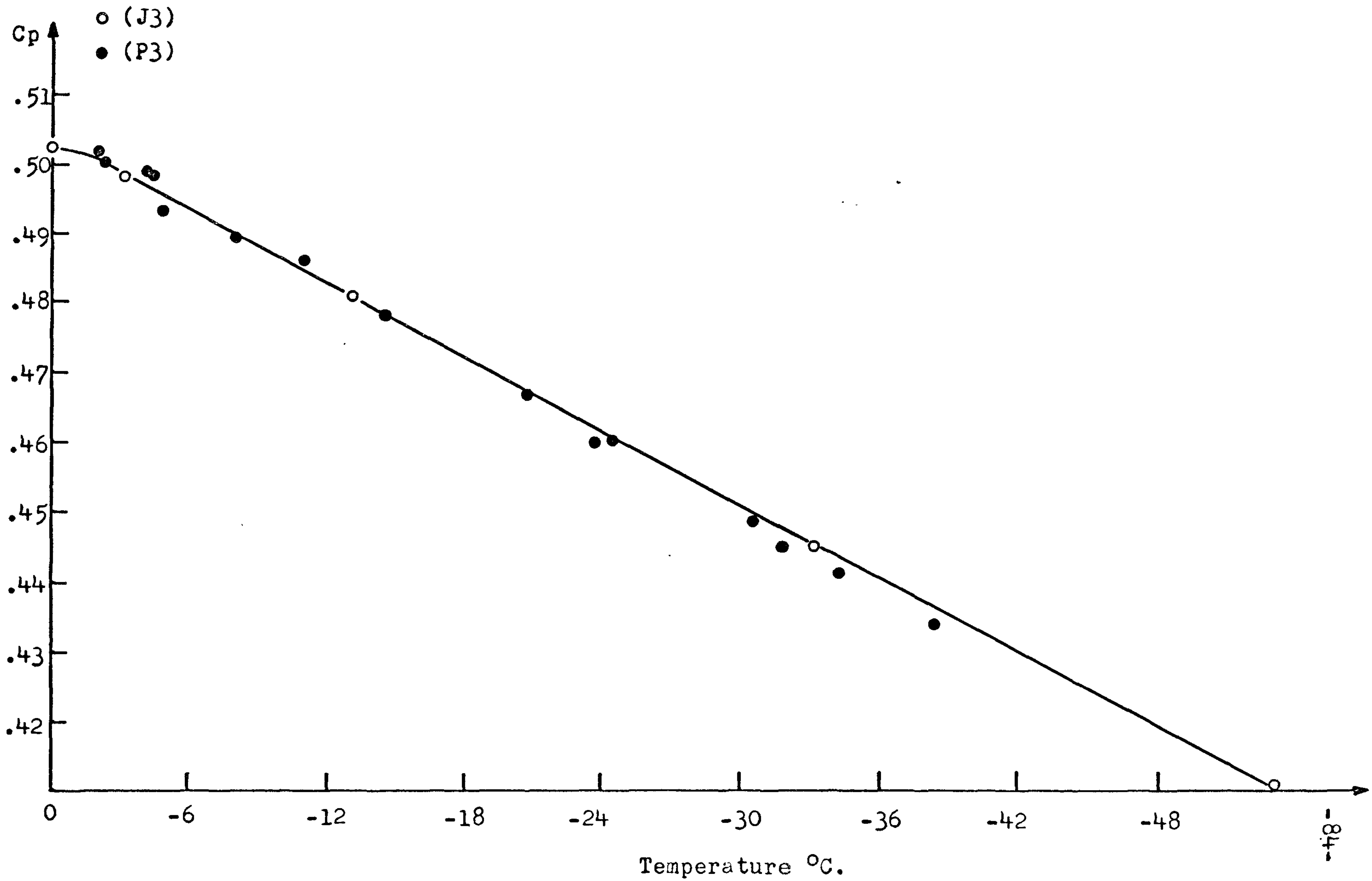
Only one sphere of ice was tested. The results are given in Table 29 and also are illustrated for comparison with literature data in Figure 8.

The linear regression of the 10 points gave a standard error of estimate σ of 0.0097 and 95% confidence limits of $\pm$0.019 for individual observation. The conductivity-temperature relationship is: $k = 1.293 - 0.00057\,T$. The value of 0.019 is only 1.5% of 1.3. The slope obtained is similar to the one expected for ice but the fact of calculating more points in one temperature range or a different curve reading accuracy might have changed slightly the slope, because the variation of the values is small.

The sphere seemed homogeneous, and the contact between

FIGURE 7: ICE

Specific heat versus temperature



the thermocouple and the material appeared very good. The average conductivity value determined is very similar to the ones proposed by other authors and therefore, experiments with ice were very satisfactory.

TABLE 29

CONDUCTIVITY OF ICE

Density: 57.3

Sphere diameter: 0.5"

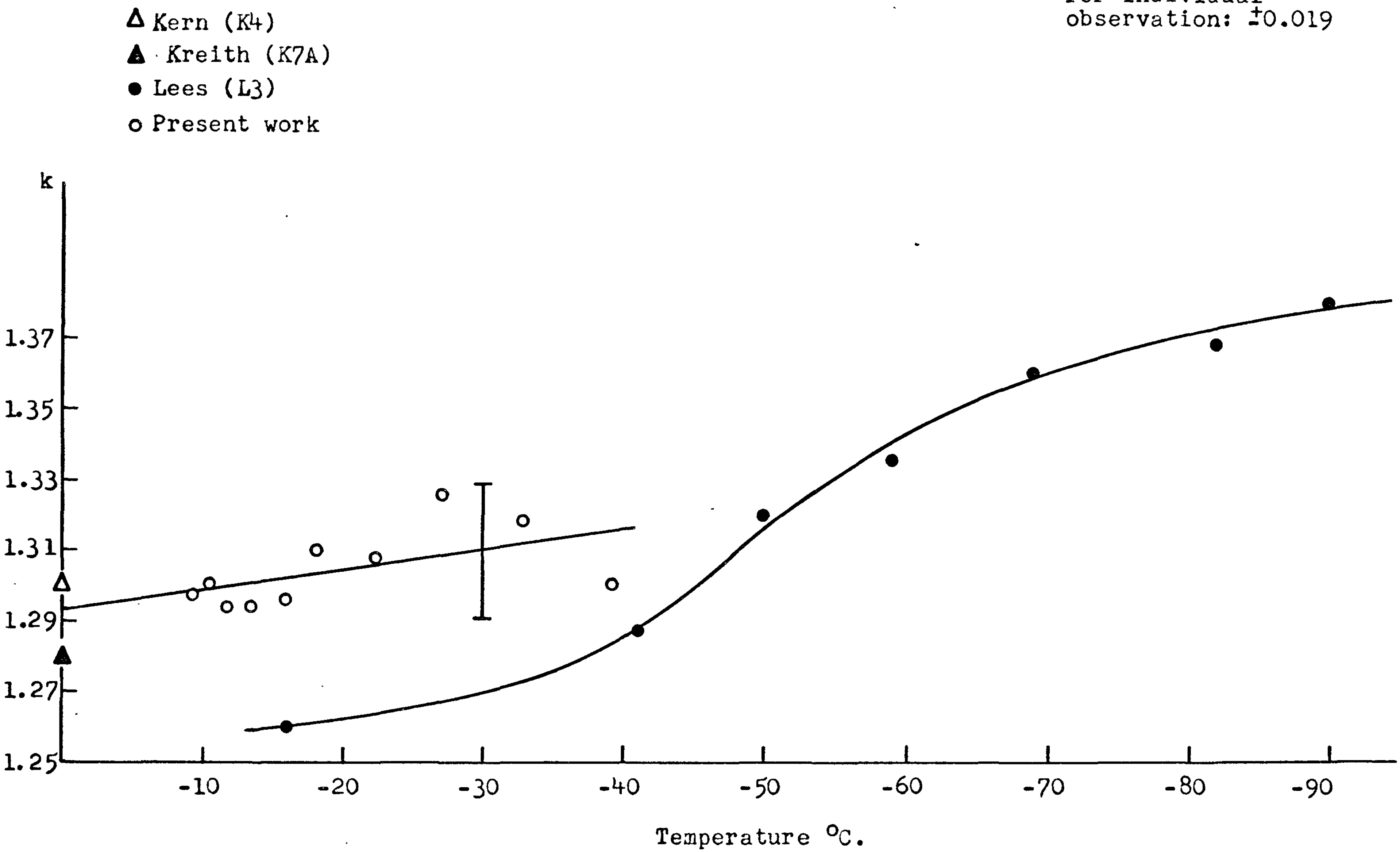
Actual length of one transient temperature measurement: ≈ 15 sec.

Thermocouple position: R = 0.0

Experiments	JA-29-13, 21	
T_i	-43.8	
T_∞	- 5.85	
ΔT	-37.95	
θ	T °C.	k
0.117	-39.35	1.30
0.288	-32.85	1.32
0.443	-27.0	1.33
0.568	-22.4	1.31
0.666	-18.5	1.31
0.740	-15.7	1.30
0.798	-13.5	1.29
0.845	-11.7	1.29
0.880	-10.4	1.30
0.907	- 9.4	1.30

FIGURE 8: ICE

Conductivity versus temperature



5.4.7 Ammonium nitrate (NH_4NO_3)

5.4.7.1

Ammonium nitrate has many crystalline forms and corresponding densities. A specific heat-temperature relationship has been proposed. It appears that only one value of conductivity has been determined by Golubev (G6). By mentioning that the specific gravity of Golubev's specimen was between 0.68 and 0.76 instead of being in the order of 1.66, Mellor (M6) claims that a considerable volume of air must have been trapped within the material. This means that the proposed conductivity value is not reliable.

In spite of the fact that the material has some of its properties varying widely with temperature and that consequently, the molded spheres had a tendency, under internal stresses developing during the fabrication and experiments, to crack severely, it was attempted to determine a more reliable value of k. Ammonium nitrate is a widely used material and often is prilled.

5.4.7.2 Physical properties

Physical properties of ammonium nitrate are listed in reference (E2).

Table 30 presents the pertinent ones.

TABLE 30

PHYSICAL PROPERTIES OF AMMONIUM NITRATE

(a) Crystalline characteristics and specific gravity.

Form	Crystal system	Specific gravity	Temperature range °C.
Liquid			above 169.6
Epsilon	Regular (cubic) (isometric)	1.594 at 130 $\pm 5^{\circ}$	125.2 to 169.6
Delta	Rhombohedral or tetragonal	1.666 at 93 $\pm 5^{\circ}$	84.2 to 125.2
Gamma	Orthorhombic	1.661 at 40 $\pm 1^{\circ}$	32.1 to 84.2
Beta	Orthorhombic	1.725 at 25°	-16 to 32.1
Alpha	Tetragonal	1.710 at -25 ± 5	-18 to -16

(b) Measured specific gravity: from molded 0.5"D. spheres at 25°C. and without thermocouples imbedded 1.66 $\pm$ 0.01

(c) Specific heat relationship: $Cp = 0.40 + 0.00028T$

(d) Thermal conductivity: Golubev(G6) proposes 0.1375 for the temperature range 0 to 100°C.

5.4.7.3 Conductivity determination results

Unfortunately, because of the experimental difficulties encountered, only one sphere could be tested satisfactorily. The results are presented in Table 31 and illustrated in Figure 9.

TABLE 31

CONDUCTIVITY OF AMMONIUM NITRATE

Specific gravity: 1.66 $\pm$ 0.01

Thermocouple position: R = 0.0

Melting point of the material: 169.6°C.

Approximative length of one transient temperature measurement: 65 seconds

Experiment	F-8-4	
T_i	65.75	
T_∞	5.0	
ΔT	60.75	
θ	T°C	k
0.078	61.	0.409
0.257	50.1	0.413
0.454	38.2	0.435
0.608	28.8	0.432
0.680	24.45	0.407
0.726	21.6	0.379
0.773	18.8	0.364
0.812	16.4	0.351
0.861	13.5	0.356

By linear regression, it was determined that: $k = 0.355 + 0.0013T$

Based on seven degrees of freedom, the 95% limits for individual observation are $\pm$0.026.

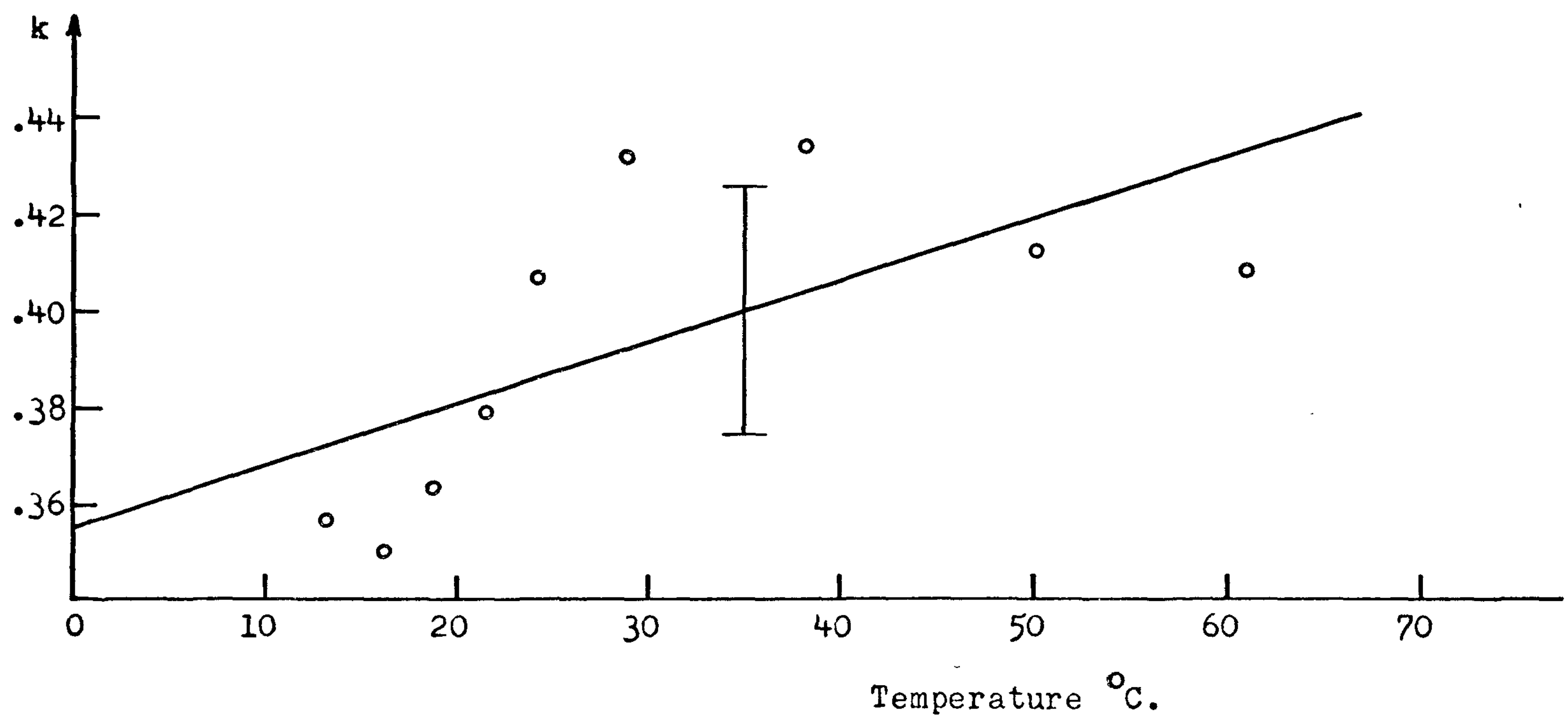
FIGURE 9: AMMONIUM NITRATE

Conductivity versus temperature

Specific gravity: 1.66

95% confidence limits for individual observation: ±0.026

Golubev (0 to 100°C.): 0.1375



The points are relatively scattered along the curve determined by linear least-squares fit. Two points fall outside the 95% confidence limits. More care in curve reading might remove some of the scatter but the experimental conditions were severe and very reliable results can hardly be expected. However the absolute value 0.026 for the limits is only 6.5% of the average k value 0.40. It is felt that the conductivity value 0.40 ± 0.03 in the temperature range 5 to 65°C. is much better than the value proposed by Golubev. More experiments would be necessary to assess the actual accuracy of the determined values.

5.4.8 Poly (methyl methacrylate) or Lucite

5.4.8.1

Lucite has been investigated extensively because it has the typical characteristics of solid polymers, the plastics for example, which are low conductivity materials. These materials are widely used and present many difficulties for their conductivity measurement by the standard methods. This was discussed in Section 2.5. Cherkasova (C3) concluded that the conductivity of amorphous polymers generally increases with temperature as a result of segmental mobility. Jakob (J1) also says that the amorphous or so-called glassy substances have the behaviour just mentioned above. They are therefore ideal for the method proposed in this work (see Section 5.3.2).

The molecular weight of Lucite (C3) reported is in the order of 100,000. Lucite is one of the polymers for which it is easier to get conductivity values because more workers used it for testing the measurement methods they had developed for low conductivity materials and because it is a popular construction material. A few relatively consistent series of data were found in the literature. But Nagler (N1) claims that care must be taken in using literature data, since differences in processing techniques may vary the thermal conductivity of a particular polymer by as much as 10%. Chung (C5) reports that the deviation of data from the mean was in the order of 1%. He also mentioned that a comparison with the values reported in the literature was inconclusive, because properties of mill-run materials vary considerably. Experimental results and a range of values are reported by manufacturers (T1). The conductivity values vary from 0.0919 to 0.138.

Many variables existed within the tested Lucite spheres. Among them are the type of supports, the sphere diameter, the method of fabrication, the thermocouple position and size, the occasional presence of bubbles and the quality of the thermal contact between the material and the junction, the homogeneity of the material and the surface uniformity. As a matter of fact, some spheres had some scratches, flat spots and other imperfection at the surface. It was particularly true for the molded spheres. Therefore, the results should give an idea of the reproducibility of the proposed method because all possible cases and sources of error are considered. Thus the method will be tested for severe conditions. The results will also be compared with the ones existing in the literature to determine their overall accuracy. They also permitted an answer to be given to many points as the effect of cooling or heating, etc.

Because of the too great number of Lucite spheres tested and the details of these sph , the experimental conditions and the determined conductivity valu are only shown in Appendix 14. In this section, there will be presented only the relationships obtained by linear regression and graphs.

5.4.8.2 Physical properties of Lucite

The specific gravity was measured and when possible, with a sphere without support and thermocouple. A value was adopted and used for all calculations.

The specific heat-temperature data are reliable and the ones from Reference G5 give a smooth non-linear curve which was used in the calculations.

The specific gravity and specific heat values are given in Table 3.2. The conductivity values are presented in Table 33. Also are indicated the determination methods and the accuracy of the values when known. It should help to compare the proposed method with the ones investigated in the literature.

TABLE 32

PHYSICAL PROPERTIES OF LUCITE

(a) Specific gravity

Case	Specific gravity	Reference
	1.1835	G5
	1.19	G5
	1.18-1.19	D4
Samples measured by NBS	1.175	C5
Molded sphere S-123 (thermocouple and support being positioned)	1.205	measured
Molded sphere S-126 (in same condition as S-123)	1.178	measured
Cast sphere of 0.625"D. from the lot received from suppliers	1.163	measured
1.1"D. cast sphere	1.18	measured
Value adopted for the calculations	1.18 ± 0.02	

(b) Specific heat:

Reference (D4): Cp = 0.35
N.B.S. (C5): Cp = 0.334 (10.5 to 89°C.) (average, 33.3°C.)

(G5)

T°C.	Cp
2	0.29
13	0.30
27	0.314
42	0.328
52	0.342
62	0.358
74	0.375
77	0.380

TABI

CONDUCTIVII

Reference	G5	L6	1	W7	B6	T1
	Guarded-plate	Compara Rods ARMCO		Guarded-plate		
T. range			0 to			
Accuracy						
T	k	k		k	k	k
0			125			
20				0.1030 &		
25			130	0.1150		
27					0.0990	
29	0.089					
33.3						
35						
37		0.089				
40		0.088				
50			138		0.0990	
52		0.088				
63	0.091					
75			160		0.0918	
83						
83					0.0900	
102					0.1042	
127					0.1038	
135						
143					0.1025	
Others						0.0919-0.138**

*Almost constan with temr
**Range of existing values

5.4.8.3 Conductivity determination results

Table 33A gives the results of the linear regressions of values determined for every sphere and a least-squares fit of all the points combined together.

TABLE 33A

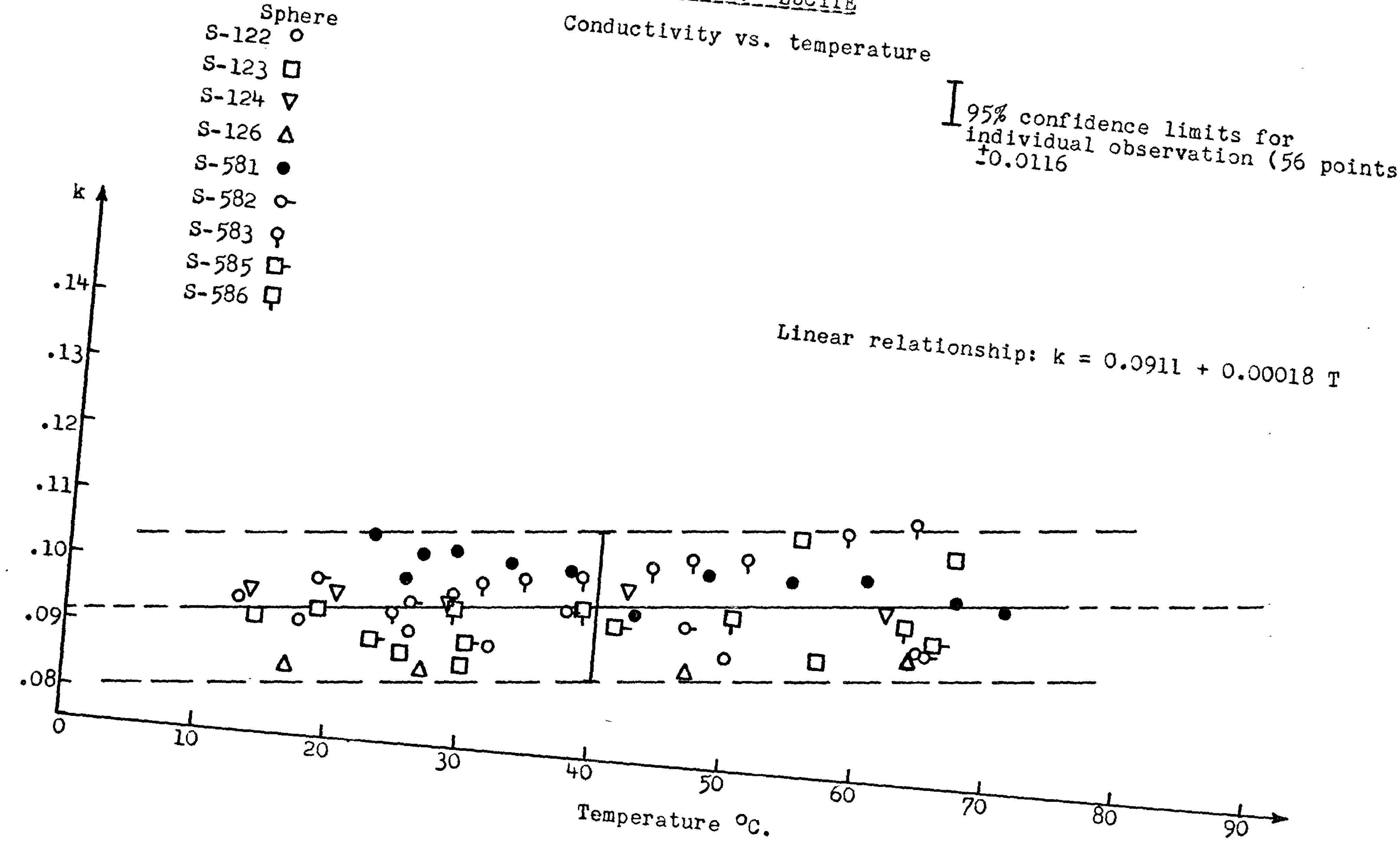
LINEAR REGRESSION RESULTS AND CORRESPONDING CONDUCTIVITY-TEMPERATURE RELATIONSHIPS

Sphere	Thermo-couple position R	Total number of points	Variance of estimate	95% limits for individual observation	Linear conductivity temperature relationships for k
S-122	0.6	5	0.57728×10^{-5}	0.0048	0.0931+0.00000694T
S-123	0.5	7	0.2951×10^{-4}	0.0108	0.0822+0.000444T
S-124	0.4	5	0.12464×10^{-5}	0.0022	0.0949+0.0000945T
S-126	0.0	4	0.98331×10^{-6}	0.0020	0.0821+0.000168T
S-581	0.3	11	0.63229×10^{-5}	0.0050	0.1015+0.0000276T
S-582	0.3	5	0.78737×10^{-6}	0.0018	0.0993-0.00007T
S-583	0.6	10	0.62694×10^{-6}	0.0016	0.0844+0.00046T
S-585	0.3	5	0.34639×10^{-5}	0.0038	0.0882+0.000112T
S-586	0.4	4	0.13082×10^{-6}	0.0007	0.0940+0.0000788T
All values combined		56	0.33928×10^{-4}	0.0116	0.0911+0.00018T

Figure 10 illustrates the curve obtained by doing a linear regression of all the points considered together and also the points themselves. Figure 11 contains the determined curve, the limits of the experimental values and the available literature

FIGURE 10: LUCITE

Conductivity vs. temperature



values.

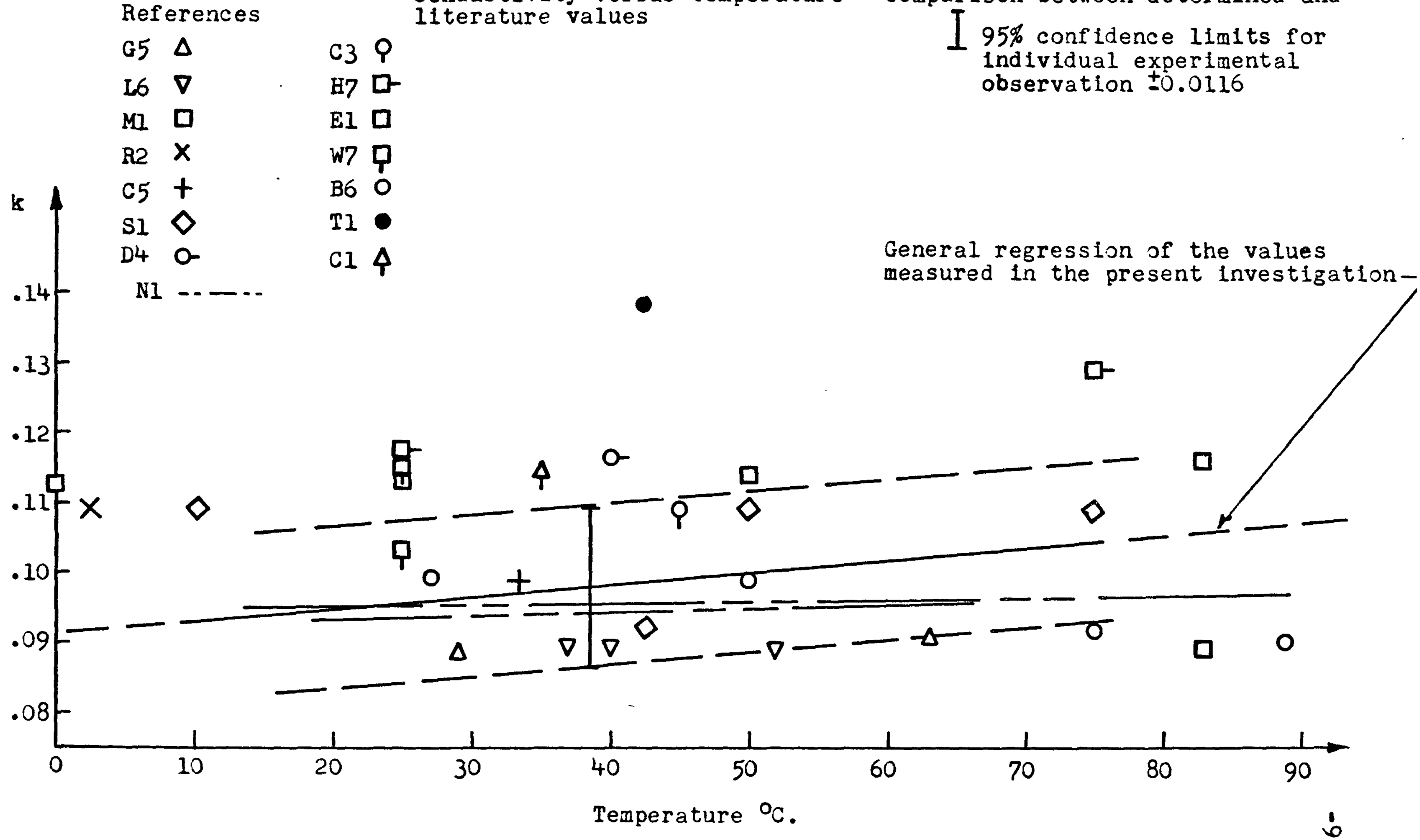
Results for nine spheres were obtained. Linear regressions of the results for every sphere were made. As predicted by Jakob (J1) and Cherkasova (C3), the determined relationships indicate that conductivity increases with temperature. Only results of sphere S-582 give a negative slope. This behaviour can be attributed to the material structure or other physical conditions which might have been peculiar in sphere S-582. It can also have been caused by experimental errors. Reference (B6) reports values decreasing with temperature. References S1 and L6 propose values almost constant but decreasing very slightly with temperature. The 95% confidence limits for all cases except one, are less than $\pm 5\%$ of the mean values and down to less than 1% in a few cases. The results for sphere S-123 are such that the variance of estimate σ^2 is important. The slope is much steeper than in other cases. There is no particular reason of discarding results from spheres S-123 and the same applies to S-582, because there is no way of explaining the actual cause of these more important deviations from a straight line. The experimental errors, the interpretation of curves and the behaviour of the material of the sphere are probably all responsible to a certain degree for the scatter. However these values are still within the general confidence limits (see Figure 10). The concept of general confidence limits will be presented below.

There is scatter in data and the values from the re-

FIGURE 11

LUCITE

Conductivity versus temperature - comparison between determined and literature values



gressions vary. It is normal considering that they come from many different spheres which were fabricated differently. It is in line with the 40% variation reported in References N1, C5 and T1. They indicate that the variation between samples can be important and Figure 11 showing the literature values for Lucite illustrates this point very well. In view of the discussion presented above, it seemed that it was impossible to conclude that one set of points was more representative of Lucite than the next one. Therefore, it was decided to consider all sets of values together and to make a general regression. Thus the most severe way of considering the data is adopted and it will indicate the overall reproducibility and accuracy of the fabricating and experimental methods and of measurements.

When considered together, the points correspond to random conditions. The general regression gives for Lucite $k = 0.0911 + 0.0018T$ and the 95% confidence limits for individual experimental observation are ± 0.0116. It is 12% of the mean value. Figure 11 shows that the determined curve is well passing through the values available from the literature.

Some authors as Nagler (N1) just claim they feel the values they have determined are comparable with other authors. In some cases accuracy of 2 or 3% is claimed and substantiated by comparison with literature values. However, often only the favourable ones are presented. Figure 11 indicates that the scatter is rather important among the literature values. If considered as a whole, they show more variation than the data obtained from Lucite spheres.

By using the guarded-hot-plate method, the National Bureau of Standards determined a value of 0.0992 at 33.3°C. and estimated the error as 3%. The present work proposes 0.0972 which is 2% different from the N.B.S. value. The measured values have a variation of ±12% while most curves from individual Lucite spheres have points varying from the mean value by less than 5%. The determined data show less scatter than the literature ones. This means that the method used is suitable to determine conductivity-temperature curves in the case of low conductivity solid materials such as plastics. Keeping in mind what has been said above about the difficulty of getting reproducible samples, it can be said that the results compare well with literature values and are satisfactory. The ±12% deviation is acceptable for many engineering purposes. A consistent fabrication method and the use of the same physical conditions for all spheres would probably keep the deviations at a ±5% level.

5.5 Hemisphere Geometry for Determining Conductivity

In discussing the finite-difference solution for conduction in spheres, it was mentioned (see Section 5.2.8) that computation indicated that for low conductivity materials and high h values, what happens in one part of the sphere does not affect much what happens in the opposite portion. If the heat transfer is radially symmetrical in the sphere, there is no heat conducted angularly. If hemispheres are considered and by imagination are taken apart from each other, and if the heat losses along the flat surfaces are assumed negligible, theoretically the heat transfer occurring at the surface and within these hemispheres is the same as in the complete sphere. This is true if the convective field is the same in both cases.

It is not always easy to make spherical test samples. But it is certainly easy in most cases to put the material to be tested in a thin metal hemisphere. If the thermal contact between the material and the metal plate is good, the latter should not affect the heat transfer in the low conductivity hemisphere. The idea of using an hemisphere to obtain temperature-time curve and to match it with the same type of curve as predicted for a sphere, has been checked experimentally with naphthalene. The characteristics of the hemisphere and of the jet flow used to create the convective field have been given in Sections 4.1.1 and 4.1.5, respectively. The schematic diagram of the experimental set-up can be found in Figure 3. A good listing of naphthalene properties is given in Section 5.4.2. The experimental data are presented in Appendix 11 (Section A.11.2) and a summary of the results appear in Table 34.

TABLE 34

DETERMINATION OF NAPHTHALENE CONDUCTIVITY

USING AN HEMISPHERICAL TEST SAMPLE

Specific gravity 1.13 (1.145, P2)

$k_p = 0.22 - 0.00073\ T$ (T1)

$R = 0.5$

$T_i = 25.9$

$T_\infty = 53$

T	k_c	k_p
28.9	0.234	0.1984
31.55	0.237	0.1965
35.6	0.244	0.1938
37.8	0.252	0.1918

Linear relationship obtained by regression of 15 values:

$$k_c = 0.195 + 0.0014\ T$$

The 95% confidence limits for individual values are ± 0.003

The data give a very good linear relationship and the deviation 0.003 is in any case less than 1.6% of the mean value. The determined curve has a positive slope. Because of the crude experiment made, no formal discussion about this error is really justified. Only a consideration of the values themselves is necessary. The difference between the literature and determined values goes from 18% to 30%. It might be mentioned that the too high values can be explained by the fact that the flat face of the hemisphere was not insulated at all, although it was protected against the fluid running over. The copper plate was very poorly insulated and heat could be conducted along the metallic support. The extraneous heat transfer affected the recorded temperature history and the result is an indication of more heat transfer than it should be.

The determined values show a large error, but they are good enough to indicate that it is possible to use an hemisphere instead of a sphere. It would certainly be interesting to explore more the hemisphere geometry.

It is felt that this geometry used with the transient method developed for spheres is promising and would probably give a satisfactory engineering accuracy in the determination of low conductivity materials conductivity.

6. GENERAL DISCUSSION

An experimental method based on transient conduction with spherical geometry has been proposed for the measurement of thermal conductivity of low conductivity solids. An analytical series solution for transient conduction with radial symmetry and constant properties has been used to interpret temperature-time measurements. The method is direct but the use of series solutions introduces deviations when the conductivity and the specific heat are varying oppositely with temperature. This has been checked by doing a theoretical investigation using a finite-difference model for variable-property materials. This model accounted for linear variations in thermal and specific heat with temperature. It can be used to determine the conductivity-temperature curve from a single experiment. However, a trial-and-error procedure is required. A linear relationship is first assumed and then a temperature-time curve is calculated using the model. The data are compared with experimental results to determine a new conductivity-temperature curve. The procedure is repeated until the assumed and determined curves are matched. The use of the finite-difference model has not been investigated very much because it requires long computer time. Restrictions exist in the use of the series solution, but it is satisfactory for determining the conductivity-temperature curve from a single experiment, when the diffusivity is constant and when k and Cp vary similarly with temperature. When the temperature coefficients of conductivity and specific heat are opposite in sign, at least a good average value for the temperature range considered can be obtained. These observations are substantiated by the results obtained for the measurement of the conductivities of seven materials including, naphthalene, naphthol β, paraffin wax, ice, bismuth, ammonium nitrate and Lucite.

For both, the series and the finite-difference model, radial symmetry has been assumed. Such a situation has been obtained in practice by using a highly convective field created either by mixing in a bath or by jet flow. The mixing which requires the easiest experimental set-up was chosen. The high h values obtained also provide a situation where the predicted temperature-time curves are independent of Biot number.

It should be emphasized that the transient temperature measurement is very fast (< 150 seconds) and that the apparatus used during this investigation is very simple. The advantages of transient methods have been noted by several investigators. However, only Ayrton and Perry (A2) have actually attempted to use a transient method with spherical geometry. They studied only one material, stone. They noted that most probably radial symmetry did not exist. The experience obtained in the present investigation allows one to express the opinion that inadequate mixing in the continuous phase was responsible for this difficulty. The method proposed in the present investigation provides adequate mixing and overcomes the difficulty mentioned above. The present method has also one further advantage in that the variation of conductivity with temperature can be estimated easily from a single experiment.

An assessment of the error involved in measuring a local temperature in a rigid sphere of low conductivity under transient conduction has been made. The temperature level, the temperature difference ($T_i - T_\infty$), the support size, the use of cooling or heating experiments, and the thermocouple size were some of the variables considered. Various diameters of spherical test specimens were used. The experimental set-up allowed the use of spheres having diameters of 0.45 to 0.625 inch. A preliminary study using hemispherical geometry has also been made.

The results were compared with literature data and in many cases are very similar. The largest variations ($\pm$12%) from the mean values were obtained by considering all data for Lucite spheres in a general linear regression. However, by using a transient method with cylindrical geometry, Janssen and Torborg (J2) obtained an accuracy of 6 to 13% for their results for epoxy plastics. It appears that the results obtained in the present investigation are as accurate as the ones obtained with more elaborate methods. It might therefore be concluded that the proposed method of determining conductivity might find many engineering applications.

7. CONCLUSIONS

An experimental method for measuring the thermal conductivity of homogeneous low-conductivity solids has been developed. The method is based on transient conduction with spherical geometry and is very appropriate for polymeric materials. Conductivities of naphthalene, naphthol β, paraffin wax, bismuth, ice, ammonium nitrate, and Lucite have been measured to evaluate the proposed method. The conductivity-temperature data were linearly regressed and compared with literature data. The results obtained gave 95% confidence limits for individual observation which, when expressed in % of the mean value (value corresponding to the average temperature over the temperature range considered), are: naphthalene - $\pm$3.8% naphthol β - $\pm$10%, paraffin wax - $\pm$10%, bismuth - $\pm$4.6%, ice - $\pm$1.5%, ammonium nitrate - $\pm$6.5% and Lucite - $\pm$12%. The largest differences between the linear regression values and the ones proposed by International Critical Tables are: 2.5%, 3.5%, and 1.5% for naphthalene, naphthol β, and ice, respectively. The values for paraffin wax are 30% lower than values reported in the literature. This deviation is attributed to poor thermal contact. Measured conductivities for bismuth differ by 8% from those given by Kern, but are very similar to values measured by some other authors. No reliable conductivity value could be found in the literature for ammonium nitrate to compare with the values determined in the present investigation. The measured conductivity for Lucite differs by only 2% from the value determined by the National Bureau of Standards using the guarded-hot-plate method.

The temperature accuracy has been evaluated and it is concluded that the temperature measurements are in error by less than 5%.

The proposed transient method is satisfactory for the determination of thermal conductivity of low conductivity materials. The applicability of the method has been established for the conductivity range 5.0 - 0.08 B.T.U./(hr.-ft.-^{o}F.). % standard deviations not larger than ±12% were observed for the measured values and normally, deviations of ±5% can be expected.

Some interesting conclusions concerning the details of the proposed method will now be given. A finite-difference model has been developed to account for property variations with temperature. Because of the long computer time required with this method, the series solution was used to interpret most of the experimental data. There are no restrictions on the use of the series solution when the thermal diffusivity is constant or when conductivity and specific heat vary similarly with temperature (variation of diffusivity of up to 30% is tolerable). It should be emphasized that the conductivity-temperature relationship is thus measured from a single temperature-time measurement at one point in the test specimen.

When the temperature coefficients of conductivity and specific heat are of opposite sign, a reliable average conductivity is obtained using the series solution. Working at a number of temperature levels will provide the conductivity-temperature relationship. A very general, but probably more costly alternative is to use the finite-difference model.

The temperature measurement method is very fast (< 150 seconds) and the equipment is very simple. High h values were required for the convective field to establish radial symmetry of heat conduction in the spheres. Heat transfer coefficients of 1900 and larger were obtained with the mixing bath used. The average h value determined was 2045. The Biot numbers were greater than 300 except for the case of bismuth and ice, where they were 9.25 and 32, respectively. Biot numbers greater than 300 insured that the predicted temperature-time curves were independent of the variation of these Biot numbers.

8. RECOMMENDATIONS

(1) The investigation on the influence of the use of the series solution for determining conductivity-temperature curves in the cases where k and Cp vary inversely with temperature should be extended.

(2) Consistent experiments with Lucite should be made. More care in fabrication and the use of similar conditions should give a better accuracy.

(3) More polymeric materials should be tested and specially ones having conductivity values lower than those for Lucite.

(4) The use of a jet flow would allow bigger sphere diameters. This and the use of a hemispherical geometry are promising and worthy of more investigation.

9. NOMENCLATURE

A	Area normal to heat flow	sq. ft.
a	solid sphere outside radius	foot
Bi	Biot number	h r/k
Cp	specific heat (also cal./gr.-^{o}C)	B.T.U./(lb.-^{o}F)
Cp0, Cp1, Cp2, Cp3	coefficients used in specific heat-temperature relationships and for finite-difference solutions	
D	diameter	foot
Fo	Fourier modulus	$\alpha t/a^2$
h	heat transfer coefficient for the liquid phase	B.T.U./hr.-sq.ft.-^{o}F)
I	indicates grid radial positions	
J	indicates grid angular positions	
k	thermal conductivity	B.T.U./(hr.-ft.-^{o}F)
k0, k1, k2, k3	coefficients used in conductivity-temperature relationships and for finite-difference solutions	
Nu	Nusselt number	$h\,D/k_f$
Pr	Prandtl number	$Cp\,\mu/k_f$
q	rate of heat flow	B.T.U./hr.
Re	Reynolds number	$v\,D\,\rho/\mu$
r	radius	ft.
R	dimensionless radius	r/a
t	time	hour

T	temperature	$^{o}C.$
Td	temperature difference $(T_{\infty} - T_i)$	
v	fluid velocity	ft./hr.
V	volume	cu. ft.
x	distance in rectangular coordinates	ft.
	thermal diffusivity $k/C_p\rho$	sq.ft./hr.
ΔT	temperature difference $(T_i - T_{\infty})$	
ΔR	radial increment in finite-difference models	
$\Delta \varphi$	angular increment in finite-difference models	
$\Delta \tau$	time increment in finite-difference models	
μ	absolute viscosity	lb_m/ft.-hr.
σ	standard error of estimate	
ρ	density	lb./cu.ft.
τ	dimensionless time	$k/C_p\rho\ a^2$
θ	dimensionless temperature	$T_i - T/T_i - T$
$\Delta \theta$	finite temperature difference	

<u>Superscripts</u>

"	inch
'	feet

<u>Subscripts</u>

c	determined value
f	fluid

i	initial
p	proposed value
∞	fluid in bath at a distance far removed from the solid body

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APPENDIX 1

A.1 LITERATURE SURVEY

A.1.1 Introduction

The thermal conductivity of materials is an important characteristic and much work has been done to find accurate methods of determining it. Usually, the methods are different for solids, liquids or gases. The present work deals only with solids and particularly low conductivity or insulating materials. Indeed, the problems can be quite different depending upon whether a high or low conductivity material is tested.

The general concepts of the most important methods will be presented. Also will be discussed some of the experimental work and investigations on methods of determining thermal conductivity. It will become obvious that the transient method with spherical geometry investigated in this work is the simplest and that its reproducibility is comparable to the most sophisticated methods for determining conductivity of low conductivity materials.

A.1.2 Concepts of the experimental methods for the determination of thermal conductivity

Carslaw and Jaeger (C2) give a general discussion about the type of methods available. They mention first that: "The thermal properties of any material occur in various combinations which may be regarded as characteristic of, and measured by, different experimental situations". "These are: (a) the conductivity k which is measured by steady-state experiments; (b) the heat capacity per unit volume $C_p\rho$ which is measured by calorimetry; (c) the quantity $(k\rho C_p)^{\frac{1}{2}}$ which is measured by some simple steady periodic experiments; (d) the diffusivity which is measured by the simplest variable state experiments. In fact, most variable state experiments, in principle, allow both k and α to be determined". The method investigated in this work falls in the latter section.

They classify the commoner methods as steady-state, periodic heating, and variable-state methods. They subdivide them again into methods suitable for poor conductors and for metals.

Jakob (J1) discusses also extensively many methods of measuring conductivities.

A.1.2.1 Steady-state methods: Metals

Jaeger (C2) also says that: "Metal is usually in the form of a rod whose ends are kept at different temperatures. The semi-infinite rod and the rod of finite length can be used".

A.1.2.2 Steady-state methods: Poor conductors

Kingery(K6) states that: "In static methods, the sample is allowed to come to a steady state and the temperature distribution measured to determine the thermal conductivity, k, by an integrated form of the equation"

$$q = - k A \frac{dT}{dx} \qquad (1)$$

Jaeger (C2) mentions that: "The usual method consists of keeping the two faces of a slab at different temperature and of measuring the heat flow". "Alternatively the material may be used in the form of a hollow cylinder or a hollow sphere".

A.1.2.3 Periodic-heating methods

According to Jaeger (C2): "In these methods the conditions at the ends of a rod or slab are varied with period T; when steady conditions have been established the temperatures at certain points are studied. A similar method is used to find the diffusivity of soil from the temperature fluctuations caused by solar heating".

A.1.2.4 Variable-state methods

Quoting Kingery (K6): "In dynamic methods the temperature is varied suddenly for one position of the sample and the temperature change with time is measured to determine the thermal diffusivity $k/Cp\rho$ by a form of the energy equation"

$$\nabla^2 T = \frac{Cp\rho}{k} \frac{dT}{dt} \qquad (1A)$$

Naturally, various specimen shapes may be used.

A.1.2.5 Problems associated with sample geometry

Kingery (K6) in his discussion considers different aspects associated with the sample geometry. He says that: "The greatest difficulty in thermal conductivity measurement is obtaining heat flow which coincides exactly with that assumed in deriving the mathematical relationship. In electrical conductors, the difference between the best and the worst conductors is a factor of about 10^{15}, and essentially all the flow can be obtained through the better conductor". "In the case of thermal conductors, the difference between the best and the poorest conductors is only a factor of about 10^{3}, and it becomes extremely difficult to get all the heat to flow through the test specimen as desired".

"A method generally employed to insure that heat flows in a desired path is to provide heat guards to maintain the isothermals in the specimen and prevent extraneous heat flow". "These guard methods are never perfect and can only hope to reduce extraneous heat flow to negligible proportions". Jakob (J1) reports that: "The plane-plate method is the simplest and therefore most frequently applied method; however, it meets with some remarkable difficulties". "One of them is the loss of heat at the edges of the plate which of course is relatively larger than the loss at the ends of cylindric devices". "With cylindrical geometry, the radial method is better because the diameter, being much smaller than the length of the cylinder, much smaller temperature differences may be used than with the longitudinal method".

Kingery (K6) continues by saying that: "Equivalent results obtained by various investigators for the same materials indicate that guard methods can be successfully applied if the apparatus is carefully designed and measurements are made with great care". "However, errors introduced can be considerable and have been considerable for much of the materials reported in the literature". "Some references are given and these authors conclude that the differences reported are due to the methods, even though any one method has fairly good reproducibility". "To obtain satisfactory guarding for absolute measurements, quite large samples are required". "This proposes a difficulty in the study of high purity essentially nonporous ceramic materials, since large specimens may be difficult to fabricate to desired specifications". The difficulty of fabricating large homogeneous samples exists also in the case of many other low conductivity materials.

From Kingery (K6): "A method of insuring correct heat flow without the use of heat guards is to employ a specimen which completely surrounds the heat source". "This may consist of an infinite cylinder or slab, surrounding an infinite heat source, or it may consist of a hollow sphere or spheroid. Shapes approximating an infinite cylinder or slab are satisfactory, if only the center section is employed (in a manner equivalent to heat guards), but they can be difficult to fabricate". Janssen and Torborg (J2) mention for example, that: "The epoxies are hard and it is very difficult to maintain a smooth, flat surface over a large area". "Also, thin samples tend to warp when exposed to temperature gradients and these effects produce very unpredictable conditions at the surface of samples". Kingery (K6) also mentions that a spherical shape is satisfactory. But, he concludes that the temperature measurements are more difficult because of the highly curved isothermals existing in a sphere. He proposes rather a prolate spheroid shape and claims it makes possible the development of a conductivity measurement method being very advantageous for ceramic samples of small size (2 cm.).

However, Jakob (J1) mentions that theoretically the spherical form is the best. The heat from a heater located at the center is conducted through the material in the radial direction without any losses. Jakob discusses the advantages and disadvantages of different geometry. No real general rule can be established. The type of material tested imposes limitations and each situation has to be considered differently.

A.1.3 Methods of Determining Thermal Conductivity of Solids

A.1.3.1 Steady-state methods

The guarded-plate method is the most frequently used one for determining thermal conductivity. One face of the sample is heated and the other one is kept at a lower temperature. Thus, the sample is submitted to a heat source and a heat sink. The guarding on the lateral faces is obtained by a ring heater or simply by insulating material. Jakob (J1) gives a discussion of the method. He mentions the difficulty of obtaining uniform thermal contact between the heating plate and the surface of the sample. Methods of overcoming the problem as spreading powder between the plates to fill gaps are also discussed. The difficulty of measuring the temperature at the surfaces of the sample is another problem he reports. Jakob mentions many variations of the single-plate system and their use in particular situations. It becomes clear from his discussion that the experimental approach can vary widely depending on what type of material and what range of temperature is considered For example, when large rectangular samples are not available, samples having a cylindrical geometry are used. At low temperature, the apparatus is placed in a Dewar vessel. But in any case, the heat transfer rate and two temperatures have to be measured and steady state has to be established. Also the samples have to be relatively large. Jakob mentions for example discs of 4 to 5 in. diameter, and Lang (L2) proposes test specimens of 18 in. square for his method.

The guarded-plate method is the standard one adopted by ASTM. It is called the ASTM Method C177. Lang (L2) considers that the method is expensive, requires skilled operators for conducting the tests and maintaining the equipment. Jakob (J1) presents a few diagrams of the devices he discusses. They indicate the complexity of the equipment required. Lang (L2) proposes the use of a simple heat flow meter placed at the center of a large square plate. He claims that by the use of a constant temperature heat source and sink, stable readings are obtained quickly. In determining conductivity of bismuth, Paskaev (P1) obtained an accuracy of 5%. Recently McMaster (M4) measured the thermal conductivity of dry and partially saturated fiber beds. His guarded-hot-plate apparatus had the hot plate above and the cold plate below. A "standard" Plexiglass disc positioned below the fiber bed was used to measure the heat flux in the test sample. The sample and the Plexiglass disc were sandwiched between the hot and cold plates. This method of measuring the heat flux is relatively easy, but still requires the standardization of the Plexiglass disc.

To avoid the problem of large sample and guarding, Krempasky (K8) developed a method based on the concept of a point-like source. The source is placed inside the sample which has to have dimensions only 3-5 times greater than the distance between the heat source and the thermoelement. The accuracy of the method depends only upon the accuracy of the distance measurement, according to the author. However, he assumes no heat loss to the surroundings. In developing a method for measuring the thermal conductivity of nonmetallic solids, Hall (H1) gives much care to the fabrication of the heating unit to get a good thermal contact and uniform heat flux. White (W3) has a complicated apparatus for low temperature determination. He pays much attention to the control of temperature by the use of a differential thermocouple. For asbestos, paper wood, leaves, Fiberglass and other laminates, Gier (G1) used an apparatus consisting of a cooled upper plate, a thin nichrome ribbon heater, a null-heat meter and a lower platen which can be either heated or cooled. Because of the dual purpose lower plate, the apparatus is very convenient for operation near room temperature.

Woodside William (W6) and Wilson (W7) make an analysis of errors due to edge heat loss in guarded-hot-plates. Laubitz (L3A) gives a method which can be used at high temperatures. The apparatus has guards and is cylindrical. A maximum error of 3% is claimed. In the determination of thermal conductivity of poly (methyl methacrylate) by a guarded-hot-plate apparatus, Shoulberg (S1) obtained points within ±2% from the mean values.

A.1.3.1.1 Internal heat generation

The steady-state methods mentioned above, but Krempasky's (K8), had external heat sources. But as mentioned in Jakob (J1) the heat source can be placed at the interior of the sample. Again the heat flux and two temperatures have to be measured and the steady state can be very long to reach, often a question of hours and even days when low conductivity materials are tested. Jakob discusses the use of spherical, cylindrical and wide hot-plate arrangements for thermal conductivity tests.

A method proposed by Banaev (B2) and using radial heat flow gives error estimated as ±3-5%. In Davidson's (D1) apparatus, heat flow is provided by current through a rod-shaped sample and is measured by a flow calorimeter. The Cenco-Fitch method also uses a flow calorimeter to measure the heat flow through the test sample. For the determination of Al_2O_3 conductivity, Kingery (K4) used spherical and cylindrical envelope methods. Manwitz (M1) used radial heat flow in cylinder to predict the conductivity of poly (methyl methacrylate). Radial heat flow in a cylinder was also used by Janssen (J2) to determine the conductivity of epoxy plastics. The over-all error in the steady-state measurements was estimated as being about 5%. This last method is similar to the one proposed by Burr (B11) for measuring the conductivity of coke. The estimated error in this case is ±5%.

A heat source in an infinite medium can be used to measure conductivity. De Vries (D2) extended the theory and discussed the characteristics of the cylindrical probe he developed. The apparatus is specially designed to test soils. Prolate spheroid geometry can also be used. The development of an expression for this special case and experiments using a prolate spheroidal envelope method have been made by Milton and Loeb and proposed by Kingery (K6). The shape allows the fabrication of small samples and easy temperature measurements because there are flat isothermals in the central portion.

A.1.3.1.2 Other steady-state methods

A few more steady-state methods exist. The most interesting are probably the so-called comparative methods and the methods with a test rod sandwiched between two rods.

Weeks (W1) used a constant heat flow method. The test specimens can be either square or cylindrical. They are small and only 1.75 inch. long. Two Armco Fe rods of known conductivity are used as heat source and sink. Their temperature is measured. The apparatus is first calibrated with Armco Fe sample of known conductivity being sandwiched between the two other rods. A very good accuracy is claimed. Knowing that surface temperature is difficult to measure, it is surprising that the sample surface temperature accuracy is estimated as $\pm 0.1^{\circ}C$.

A comparative method used by Francl (K5) allowed an easy determination of thermal conductivities. This simple method consists of comparing known and unknown conductivity samples placed in the same condition. However this method is dangerous because the diffusivity values of various samples can vary and cause much error. The comparative method developed by Clark (C6) is simple and consists of bringing two spheres into contact with the sample.

For poor conductors, Zierfuss (Z1) suggests to use a small sample (about 10 cu. cm.) and to bring it into contact with a hot copper bar. The temperature at the interface is measured and allows the determination of the thermal conductivity of the sample. Poor thermal contact and heat losses should be expected for such a case. The claimed accuracy is 5%.

A.1.3.2 Appraisal of steady and unsteady-state methods

With steady-state methods, the equipment is elaborated because the heat flux, and two temperatures have to be measured and controlled. Complicated methods are necessary to avoid the heat losses in apparatus. Usually the sample are relatively large and the time to reach steady state can be extremely long if low conductivity materials are tested. As mentioned by

Janssen (J2), the samples large enough to permit direct measurement of the internal temperature gradient have a large thermal resistance. Therefore, the heat flow is small and difficult to measure or a large temperature drop has to be used. A large temperature drop is a disadvantage. The conductivity may vary with temperature and it is better to have an average temperature really representative of the temperature range considered. This is obtained by using small temperature differences. The tested material might be heat sensitive and then, small temperature drop has to be used.

The unsteady-state methods overcome most of the difficulties reported for the steady-state methods. As mentioned by Jakob (J1), α is a kinematic quantity and therefore no heat-energy measurements are required. Generally a short time is sufficient for doing an experiment. Thus, heat losses and gains have less importance. The thermal disturbance in the sample is minimized and usually small temperature changes are sufficient. Also the equipment is usually simpler than the one used in steady-state methods. It can be extremely simple as in the case of the method proposed in this work. Small test samples can often be used and in most cases, the deviations obtained with transient methods are comparable with the ones in steady-state methods. Jaeger (C2) also mentions that some methods may be used "in situ" and allow determination of conductivity without bringing the sample to the laboratory. It is most desirable for soils and rocks. Many methods also allow the determination of α and k from the same experiment.

The disadvantages most frequently mentioned in literature are for example, the difficulty of measuring with sufficient accuracy the temperature which varies with time and the necessity of defining and satisfying the boundary conditions such that the experimental conditions agree with the ones used for developing the mathematical expressions. Jaeger (C2) points out that the contact resistance at a boundary is more difficult to evaluate and to correct, and that it may have more influence on the results than in steady-state methods.

A.1.3.3 Unsteady-state methods

Jakob (J1) reviews some of the early works on unsteady-state methods. Jaeger (C2) mentions the method developed by Ayrton (A2) who used a spherical geometry. His work will be discussed in more detail later. Only relatively recent works will be mentioned in this section.

To overcome the problems of measuring heat flux and the need for specimens of appreciable size and thickness, Chung and Jackson (C5) developed a method using radial heat flow. The speciments are rods of 1"D. and 8 inches long. The specimen is first heated by steam and then, suddenly cooled by circulating cold fluid in the jacket surrounding it. The logarithm of temperature is plotted against time. The mathematical solution predicts a straight line. The slope of the curve is a measure of the diffusivity and indirectly the conductivity can be determined. The experiment is taking place in approximately 30 minutes. The greatest variation from the mean reported is 1%. They assume that a large heat transfer coefficient exists. One advantage of the method is that it is not necessary to know the exact location of the thermocouple. The cooling lines for various positions in the specimen are parallel and thus, only the slope of the log temperature-time curve is needed. However, they noticed a curvature in that curve. They think it is caused by a temperature effect. Indeed, the equation is based on the assumption of constant physical properties, whereas actually they are a function of the temperature. They suggest to refine the calculations by taking the slope of the tangent to the curve at a given point to evaluate the diffusivity for a more limited average temperature. A similar approach was used in the present work.

Two variable-state methods have been developed by Harmathy (H3). He claims that they offer the advantage of producing negligible thermal disturbance in the specimen during measurement, and that the preparation of specimens is easy. The first method is based on the fact that the initial temperature rise, when a sample is brought into contact with a constant flux plane heat source, in a certain region of a finite solid is similar to the temperature rise in an infinite solid. Thus the measured temperature records are compared to the predicted values and a curve-fitting method allows the determination of all thermal properties of the solid. In the second method, a hot or cold pulse is applied to a plane surface of the specimen. At some distance in the specimen, a maximum temperature change is obtained. This can be predicted by a mathematical solution. Such a solution is used in conjunction with the experimental measurements to determine the diffusivity. This method is not so easy to use because a steady heat flux has to be provided. The authors mention that the heating foil resistivity is not really constant and they indicate that it is a main source of error.

Two recent references deal with some analytical aspects of the transient heat conduction. Beck (B5) proposes a way of optimizing the design of transient experiments for determinations of thermal conductivity. Aspects as the relative dimensions of the test specimen and the location of the measuring device are considered. A general analytical procedure for describing the transient temperature distribution within materials whose thermal conductivity vary with temperature has been developed by Hadi (H4). Many interesting types of boundary conditions were investigated. Experimental verifications were carried out only with a wall geometry. Burgstahler (B10) has studied the transient heat conduction in composite systems for n dimensions. Nagler (N1) has also developed a solution for transient heat conduction with variable physical properties. By a curve-fitting technique and doing a single experiment for each material, he determined the linear thermal conductivity relations for many low conductivity materials including poly (methyl methacrylate). It seems that there is now an increasing interest in the literature to consider the variation of physical properties with temperature in the development of solutions for transient heat conduction. This has been investigated in the present work.

The apparatus developed by Goldfein (G4) has a heat source placed on the top of the specimen. The specimen rests on a heat sink. The transient temperature is measured and from the slope of the temperature-time curve, the conductivity can be determined. Transient conduction in slabs and hollow cylinder is the base for Beatty's method (B3). Monatsber (M9) used transient conduction in plates and periodic temperature change. Beatty (B4) proposed a method for laminates. A copper plate is sandwiched between two layers of the materials and its temperature history is related to the conductivity of the test material. The test samples are heated by steam. They report higher values than the ones obtained with the guarded-plate method and they estimated the accuracy to be 8%. Beatty and co-authors mention that nobody has reported unsteady-state methods prior to 1950. It is a rather surprising statement.

A fast method has been proposed by McLaren (M3). The method is crude and gives only a relative thermal conductivity value. Temperature indicating crayons are put into contact with samples of known and unknown conductivity. The same heat flux is applied to all samples. The heat is conducted through the samples and the time when the crayons start to melt is an indication of the conductivity values.

A transient heat flow apparatus using a cylinder method is proposed by Hooper (H8). It consists of an electrically heated probe. The model is based on the concept of a linear heat source in an infinite body. The experiments take place in 10 minutes and specimens such as soils can be tested without disturbing the natural conditions. But it is mentioned elsewhere that temperature changes before introducing the probe into the sample should be avoided. Temperature changes affect the moisture conditions in wet samples. The problem exists but is considered less important in this case than in the case of the hot-plate method. The instrument is very precise and a reproducibility of 0.5% is reported for dry samples. Woodside (W5) and Goforth (G3) developed also probe methods and claim respectively an accuracy of 1 and 4%. Woodside considers his apparatus as ideal for measurement of thermal conductivity of dry and moist materials. Goforth is more interested in small samples.

For determining the conductivity of epoxy plastics, Janssen (J2) proposed a transient technique which consists of exposing a semi-infinite slab to a sudden temperature change and observing the temperature rise at a point in the slab with respect to time. The specimen has to be insulated and the heating is insured by a steam box in contact with one end of the sample. As the other apparatus mentioned above, Janssen's apparatus is relatively more elaborate than the one used for the present investigation. Janssen estimated his conductivity values to be within 10% of the true value.

A.1.3.3.1 Unsteady-state method with spherical geometry

Ayrton and Perry (A2) used a spherical geometry in the development of a transient method for measuring the thermal conductivity of low conductivity stones. This is the only work which has been found on the use of a spherical geometry without internal heat source in transient methods. Their method consists of bringing the sphere with a thermocouple imbedded at the center to a uniform temperature. At time zero, a rapid cold water stream starts flowing around the sphere which is in a bath. The temperature is recorded continuously.

The mathematical expression for this case is a series which converges rapidly (see Jaeger (C2), page 238). After a sufficient time only the first term is important and a simple solution is obtained. In the case of Ayrton, the sphere diameters were ranging usually from 5 cm. to 14 cm. and the time required to justify the simplification mentioned above was ranging from 600 to 1200 seconds. The mathematical expression is such that the use of two different temperature readings allows the determination of the conductivity. Then, the heat transfer coefficient can be determined.

Ayrton and Perry show that for similar spheres, the determined heat transfer coefficients are different by a factor of 2. They consider that the considerable difference is due to a certain extent to the difference in the stone and in the surface conditions, one being smoother than the other. They also discuss the fact that they feel the external temperature is not really constant as assumed for the model. They suggest that better results would be obtained by using greater precaution to ensure perfect uniformity of the outside temperature. The suggested methods are to make the water-bath larger and the stream of cold water more rapid. An estimation of their heat transfer coefficients and Biot numbers has been done. It indicates that h ranges between 18 and 36 and the Biot numbers between 2 and 4. It is obvious that in their experiments, the uniformity of the fluid temperature around the sphere can be suspected because the Biot numbers are so small.

In the present investigation, much higher heat transfer coefficients and Biot numbers were used to insure constant and uniform heat transfer at the surface of the sphere. Thus, the boundary conditions are reliable.

APPENDIX 2

A.2 SERIES SOLUTION FOR TRANSIENT CONDUCTION OF HEAT IN A SOLID SPHERE

The differential equation (1A) in spherical coordinates, for radial symmetry and constant physical properties, has the following form:

$$\frac{\partial T}{\partial t} = \alpha \left[\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right] \tag{19}$$

The boundary conditions are:

$$\left[\frac{\partial T}{\partial r} \right]_{r=a} = - \frac{h}{k} \left(T - T_\infty \right)_{r=a} \tag{20}$$

The solution is given in Page 56 of Grober's text book (G7), and will not be repeated here. However, in the course of the present investigation, the series solutions were calculated for the actual cases to avoid interpolation of the values from the graphs presented in the various textbooks.

A.2.1 Computation

The computation consists of two steps:

(a) The determination of the roots of equation

$$(1 - Bi) \sin V - V \cos V = 0 \tag{21}$$

(b) Using the roots V_k, summation of series (22) to obtain the dimensionless temperatures as a function of time and for different radial positions and Biot numbers.

$$\theta = \frac{T_i - T}{T_i - T_\infty} = 1 - \sum_{k=1}^{\infty} \frac{2(\sin V_k - V_k \cos V_k)}{V_k - \sin V_k \cos V_k} e^{-V_k^2 \tau} \frac{\sin (V_k R)}{V_k R} \qquad (22)$$

The computation has been done by using a program written for the McMaster University 7040 I. B. M. computer. The Reguli-Falsi technique has been used for root finding and the specified precision was 0.00005. Two hundred roots were calculated but never more than 15 were used. Tables A.2.1 gives the roots of equation 21. It is a more complete table than the one presented by Grober.

Table A.2.2 gives dimensionless temperature-time curves corresponding to different Biot numbers. It is important to notice that the differences between values for Bi = 0.2 and 0.4 are large. The differences between curves when Bi is greater than 50 are much smaller. The differences between values corresponding to Bi = 462 and 10^8 are negligible. For one particular location, the temperature-time curve is unique for Biot numbers greater than 300.

TABLE A.2.1

ROOTS OF THE EQUATION

$(1 - Bi) \sin V - V \cos V = 0$

Biot number	V_1	V_2	V_3	V_4	V_5	V_6	V_7	V_8	V_9	V_{10}
0	0.0	4.493	7.725	10.904	14.066	17.221	20.731	23.519	26.666	29.812
0.001	0.055	4.494	7.725	10.904	14.066	17.221	20.371	23.519	26.666	29.812
0.002	0.077	4.494	7.726	10.904	14.066	17.221	20.371	23.520	26.666	29.812
0.005	0.122	4.494	7.726	10.905	14.066	17.221	20.372	23.520	26.666	29.812
0.01	0.173	4.496	7.727	10.905	14.067	17.221	20.372	23.520	26.666	29.812
0.02	0.244	4.498	7.728	10.906	14.068	17.222	20.372	23.520	26.667	29.812
0.05	0.385	4.504	7.732	10.909	14.070	17.222	20.374	23.522	26.668	29.813
0.1	0.542	4.516	7.738	10.913	14.073	17.227	20.376	23.524	26.670	29.815
0.2	0.759	4.538	7.751	10.922	14.080	17.232	20.381	23.528	26.674	29.818
0.5	1.666	4.604	7.790	10.950	14.102	17.250	20.396	23.541	26.685	29.828
1.0	$\pi/2$	$3\pi/2$	$5\pi/2$	$7\pi/2$	$9\pi/2$	$11\pi/2$	$13\pi/2$	$15\pi/2$	$17\pi/2$	$19\pi/2$
2.0	2.030	4.913	7.979	11.086	14.207	17.336	20.469	23.604	26.741	29.879
5.0	2.570	5.354	8.303	11.335	14.408	17.503	20.612	23.729	26.581	29.978
10.0	2.836	5.717	8.659	11.658	14.687	17.748	20.828	23.922	27.025	30.135
20.0	2.986	5.978	8.983	12.003	15.038	18.089	21.152	24.227	27.311	30.404
50.0	3.079	6.158	9.238	12.320	15.403	18.489	21.576	24.666	27.759	30.854
∞	π	2π	3π	4π	5π	6π	7π	8π	9π	10π

TABLE A.2.2

DIMENSIONLESS TEMPERATURE-TIME CURVES FOR

DIFFERENT BIOT NUMBERS AT R = 0

Bi	0.2	0.4	1.0	9.25	50	172.6	462	10^8
τ	θ	θ	θ	θ	θ	θ	θ	θ
0.005	0	0	0	0	0	0	0	0
0.040	0.0002	0.0003	0.0008	0.0047	0.0088	0.0102	0.0106	0.0109
0.060	0.0017	0.0033	0.0078	0.0387	0.0621	0.0685	0.0703	0.0714
0.080	0.0055	0.0108	0.0248	0.1088	0.1583	0.1701	0.1733	0.1753
0.10	0.0116	0.0224	0.0507	0.1991	0.2707	0.2862	0.2904	0.2929
0.20	0.0577	0.1083	0.2277	0.6094	0.7012	0.7166	0.7206	0.7229
0.30	0.1093	0.1998	0.3932	0.8218	0.8838	0.8929	0.8951	0.8965
0.40	0.1590	0.2835	0.5255	0.9192	0.9548	0.9596	0.9607	0.9614
0.50	0.2061	0.3586	0.6292	0.9634	0.9826	0.9847	0.9853	0.9856
0.60	0.2506	0.4259	0.7103	0.9834	0.9932	0.9943	0.9945	0.9946
0.80	0.3322	0.5400	0.8231	0.9966	0.9990	0.9992	0.9992	0.9993
1.00	0.4049	0.6315	0.8920	0.9993	0.9998	0.9999	0.9999	0.9999
1.50	0.5540	0.7883	0.9686	0.9999	1.0	1.0	1.0	1.0

APPENDIX 3

A.3 FINITE-DIFFERENCE SOLUTION FOR TRANSIENT CONDUCTION OF HEAT IN A SOLID SPHERE

The sphere of radius a, is initially at a uniform temperature T_i. It cools in a medium whose temperature T_∞ is constant and uniform. The heat transfer coefficient at the surface of the sphere is h. The temperature distribution within the sphere as a function of time is required.

In spherical coordinates, equation 1A has the form of equation (23) when there is axial symmetry:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(k\, r^2 \frac{\partial T}{\partial r}\right) + \frac{1}{r^2 \sin\varphi}\frac{\partial}{\partial \varphi}\left(k \sin\varphi \frac{\partial T}{\partial \varphi}\right)$$

$$= \rho\, Cp \frac{\partial T}{\partial t} \tag{23}$$

The boundary condition is expressed by equation (20)

$$\left[\frac{\partial T}{\partial r}\right]_{r=a} = -\frac{h}{k}\left(T - T_\infty\right)_{r=a} \tag{20}$$

The initial condition is:

T at time zero is uniform and equal to T_i in the region $0 < r < a$.

If the physical properties k, Cp and ρ are constant, equation (23) can be simplified. Two cases will be presented.

The first one deals with the solution of equation (23) when the physical properties are constant. In the second case, the physical properties vary with temperature, but radial symmetry is assumed. The finite-difference method of solving applies to both cases. However, they are considered individually to avoid confusion of the details particular to each case.

A.3.1 Constant Physical Properties

After the appropriate simplifications and transformation into a dimensionless form by using:

$$\tau = \frac{kt}{Cp \rho a^2}, \quad R = \frac{r}{a} \quad \text{and} \quad \theta = \frac{T_1 - T}{T_1 - T_\infty} \tag{24}$$

the equation (23) becomes:

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial R^2} + \frac{2}{R}\frac{\partial \theta}{\partial R} + \frac{1}{R^2}\frac{\partial^2 \theta}{\partial \varphi^2} + \frac{1}{R^2}\, \mathrm{ctg}\,\varphi \frac{\partial \theta}{\partial \varphi} \tag{25}$$

A.3.1.1 Finite-difference form

To express equation (25) in finite-differences, Taylor's series expansion must be used. The forward expansion is:

$$f_2 = f_1 + \left(\frac{\partial f_1}{\partial h_1}\right)\frac{\Delta h}{1!} + \left(\frac{\partial^2 f_1}{\partial h_1^2}\right)\frac{\Delta h^2}{2!} + \left(\frac{\partial^3 f_1}{\partial h_1^3}\right)\frac{(\Delta h)^3}{3!} + \cdots \tag{26}$$

The value h is the independent variable and f is the function ($f = f(h)$). The grid is shown in Figure A.3.1. The grid corresponding to spherical coordinates is also given. The backward expansion gives:

$$f_2' = f_1 - \left[\frac{\partial f_1}{\partial h_1}\right]\frac{\Delta h}{1!} + \left[\frac{\partial^2 f_1}{\partial h_1^2}\right]\frac{(\Delta h)^2}{2!} - \left[\frac{\partial^3 f_1}{\partial h_1^3}\right]\frac{(\Delta h)^3}{3!} + \cdots \quad (27)$$

The terms of third order and of higher order are neglected. Thus, the first order derivative is for example:

$$\frac{f_2 - f_2'}{2\Delta h} = \frac{\partial f_1}{\partial h_1} \quad (28)$$

or in spherical coordinates:

$$\frac{\partial f_1}{\partial \varphi_1} = \frac{f_2 - f_2'}{2\Delta\varphi} \quad (29)$$

FIGURE A.3.1

GRID FOR TAYLOR'S SERIES EXPANSION

Rectangular coordinates

Spherical coordinates

By using Taylor's series expanions and combining them in the proper way, the terms of equation (25) can be expressed in finite-difference form as shown below.

The grid spacing used is such that I stands for radial positions, J for the angular positions and 1 and 2 indicates the time increment.

Then: $$\frac{\partial \theta}{\partial \tau} = \frac{\theta(I,J,2) - \theta(I,J,1)}{\Delta \tau} \tag{30}$$

The central differences give:

$$\frac{2}{R}\frac{\partial\theta}{\partial R} = \frac{2}{R}\;\frac{\theta(I+1,J,1) - \theta(I-1,J,1)}{2\Delta R} \tag{31}$$

Also

$$\frac{\partial^2 \theta}{\partial R^2} = \frac{\theta(I+1,J,1) - 2\,\theta(I,J,1) + \theta(I,J-1,1)}{(\Delta R)^2} \tag{32}$$

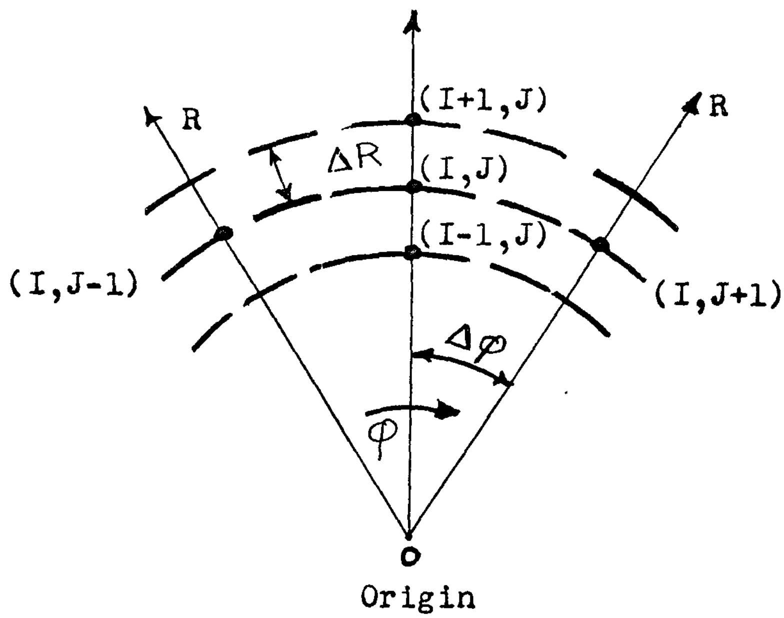
$$\frac{Ctg.\varphi}{R^2}\frac{\partial\theta}{\partial\varphi} = \frac{Ctg.\varphi}{R^2}\left(\frac{\theta(I,J+1,1) - \theta(I,J-1,1)}{2\Delta\varphi}\right) \tag{33}$$

$$\frac{1}{R^2}\frac{\partial^2\theta}{\partial\varphi^2} = \frac{1}{R^2}\left(\frac{\theta(I,J+1,1) - 2\,\theta(I,J,1) + \theta(I,J-1,1)}{(\Delta\varphi)^2}\right) \tag{34}$$

The grid is illustrated in Figure A.3.2.

FIGURE A.3.2

GRID SPACING FOR SPHERICAL COORDINATES



The finite-difference form of equation (25) is:

$$\theta(I,J,2) = A1(I)\ \theta(I,J,1) + A2(I)\ \theta(I+1,J,1) + A3(I)\ \theta(I-1,J,1) + A4(I)\ \theta(I,J+1,1) + A5(I)\ \theta(I,J-1,1) \tag{35}$$

The coefficients are:

$$A1(I) = 1 - \frac{2\,\Delta\tau}{R^2(I)\,(\Delta\varphi)^2} - \frac{2\,\Delta\tau}{(\Delta R)^2} \tag{36}$$

$$A2(I) = \frac{\Delta\tau}{(\Delta R)^2} + \frac{\Delta\tau}{R(I)\,\Delta R} \tag{37}$$

$$A3(I) = \frac{\Delta\tau}{(\Delta R)^2} - \frac{\Delta\tau}{R(I)\,\Delta R} \qquad (38)$$

$$A4(I) = \frac{\Delta\tau}{\Delta\varphi}\,\frac{ctg.\varphi}{2\,R^2} + \frac{\Delta\tau}{R(I)(\Delta\varphi)^2} \qquad (39)$$

$$A5(I) = \frac{\Delta\tau}{R^2(I)(\Delta\varphi)^2} - \frac{\Delta\tau}{\Delta\varphi}\,\frac{ctg.\varphi}{2\,R^2(I)} \qquad (39A)$$

The boundary condition expressed by equation (20) becomes:

$$\theta(I,J,2) = \frac{h(J)*a*\Delta R}{h(J)*a*R+k} + \frac{k*\theta(I-1,J,2)}{h(J)*a*\Delta R} \qquad (40)$$

I corresponds to the surface grid points. When there is radial symmetry, the terms introduced by the two last terms of equation (25) disappear.

For computation, 31 angular points were used between 0 and 180 degrees. For testing the accuracy of the finite-difference technique, 21 and 41 radial positions were used. For testing, radial symmetry was assumed. A grid of 20 radial increments is satisfactory as shown in Table 2 of Section 3.2. Table 1 shows that a time increment of 0.00001 is acceptable.

A.3.1.2 <u>Computation technique</u>

The finite-difference equation has been solved by an explicit method which can be drawn directly from the form of equation (35). At time zero, all values $\theta(I,J,1)$ are equal to 0. However, the surface positions have θ values of 1. The coefficients A1, A2, A3, A4 and A5 are known. The temperatures at time 2 (time 1 + $\Delta\tau$) are calculated for each point of the grid except the surface ones, by using equation (35) and the appropriate temperatures for time 1. The surface temperatures are calculated by using equation (40). Then the temperatures at time 2 can be assigned with the time position 1. By repeating the procedure given above, the complete temperature history is predicted.

The computation method is simple, accurate but time consuming because only a small $\Delta\tau$ can be used. Instability appeared when $\Delta\tau$ of 0.00005 was tried. For example, on the I. B. M. 7040, approximately nine minutes were required to compute the values from $\tau = 0$ to $\tau = 0.4$ with a time interval of 0.00001 and 40 radial increments or $\Delta R = 0.05$.

A.3.2 Variable Physical Properties and Radial Symmetry

When there is radial symmetry, equation (1A) has the form:

$$\rho \, Cp \frac{\partial T}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r}\left(k \, r^2 \frac{\partial T}{\partial r}\right) \tag{2}$$

Equation (21) is made dimensionless by using the relationships expressed by equation (3), and the expressions for dimensionless radius and temperatures.

$$\tau = \frac{k0 \; t}{Cp0 \, \rho \, a^2} \tag{3}$$

$$\theta = \frac{T_i - T}{T_i - T_\infty} \quad \text{and } R = \frac{r}{a}$$

The variation of the specific heat and conductivity with temperature is given by equations (4) and (5).

$$k = k0 + k1*T \tag{4}$$

$$Cp = Cp0 + Cp1*T \tag{5}$$

The symbols expressed by equations (6), (7), (8), (9) and (10) are also used to simplify the developed form of equation (2).

$$Td = (T_\infty - T_i) \tag{6}$$

$$Cp = \frac{Cp1\ T_i}{Cp0} \tag{7}$$

$$Cp3 = \frac{Cp1\ Td}{Cp0} \tag{8}$$

$$k2 = \frac{k1\ T_i}{k0} \tag{9}$$

$$k3 = \frac{k1\ Td}{k0} \tag{10}$$

The dimensionless form of equation (2) becomes the equation (11) after the appropriate sutstitutions are made.

$$\frac{\partial \theta}{\partial \tau} = \frac{(1 + k2 + k3\ \theta)}{(1 + Cp2 + Cp3\ \theta)} \frac{\partial^2 \theta}{\partial R^2}$$

$$+ \frac{2}{R} \frac{(1 + k2 + k3\ \theta)}{(1 + Cp2 + Cp3\ \theta)} \frac{\partial \theta}{\partial R}$$

$$+ \frac{k3}{(1 + Cp2 + Cp3\ \theta)} \left(\frac{\partial \theta}{\partial R} \right)^2 \qquad (11)$$

As demonstrated in Section A.3.1.1 for equation (25) a finite-difference form of equation (11) can be developed. This is the equation:

$$\begin{aligned} \theta(I,2) = {} & A1(I)\ \theta(I,1) + A2(I)\ \theta(I+1,\ 1) \\ & + A3(I)\ \theta(I-1,1) \\ & + A4(I) \left[\theta^2(I+1,1) + \theta^2(I-1,1) \right. \\ & \left. - 2\ \theta(I+1,1)\ \theta(I-1,1) \right] \end{aligned} \qquad (12)$$

The coefficients are:

$$A1(I) = \left[1.0 - \frac{2\ \Delta\tau}{(\Delta R)^2} \frac{(1 + k2 + k3\ \theta(I,1))}{(1 + Cp2 + Cp3\ \theta(I,1))} \right] \qquad (13)$$

$$A2(I) = \left[\frac{1 + k2 + k3\ \theta(I,1)}{1 + Cp2 + Cp3\ \theta(I,1)} \right] \frac{\Delta\tau}{\Delta R} \left[\frac{1}{R(I)} + \frac{1}{\Delta R} \right] \qquad (14)$$

$$A3(I) = \left[\frac{1 + k2 + k3\ \theta(I,1)}{1 + Cp2 + Cp3\ \theta(I,1)} \right] \frac{\Delta\tau}{\Delta R} \left[\frac{1}{\Delta R} - \frac{1}{R(I)} \right] \qquad (15)$$

$$A4(I) = \frac{k3*\Delta\tau}{4(\Delta R)^2\ (1 + Cp2 + Cp3\ \theta(I,1))} \qquad (16)$$

The finite-difference expression for the boundary condition is:

$$\theta(NRINC,2) = \frac{k0\left[k2 + k3\ \theta(NRINC,1)\right]\ \theta(NRINC-1,\ 2)}{h\ a\ \Delta R + k0\left[k2 + k3\ \theta(NRINC,1)\right]}$$

$$+ \frac{h\ a\ \Delta R}{h\ a\ \Delta R + k0(k2 + k3\ \theta(NRINC,1))} \qquad (41)$$

The initial conditions are:

at time zero ($\tau = 0$), $\theta = 0$ for $0 < R < 1.0$

at $R = 1.0$, $\theta = 1.0$

The method of computation is essentially the same as the one described in Section (A.3.1.2). The only difference is that the coefficients are temperature dependent and must be calculated for each position and time considered. Table A.3.1 shows how the finite-difference solution gives values similar to the ones from series solution when constant properties and radial symmetry are assumed. This is a good indication that the computation should be satisfactory for the case of variable properties.

TABLE A.3.1

COMPARISON BETWEEN SERIES AND FINITE-DIFFERENCE SOLUTIONS

In series solution, the Biot number = 462

In the finite-difference model

$k0 = 0.1165$ $\quad k1 = 0$

$Cp0 = 0.332$ $\quad Cp1 = 0$

$h = 2100$ $\quad T_i = 66$

$a = 0.0208$ $\quad T_\infty = 27$

R	0.0		0.5	
τ	θ series solution	θ finite-difference	θ series solution	θ finite-difference
0	0	0	0	0
0.02	0	0	0.024	0.026
0.04	0.011	0.013	0.152	0.153
0.06	0.070	0.074	0.295	0.295
0.08	0.173	0.177	0.419	0.419
0.10	0.290	0.293	0.522	0.522
0.15	0.548	0.548	0.708	0.707
0.20	0.721	0.746	0.821	0.820

APPENDIX 4

A.4 DETERMINATION OF HEAT TRANSFER COEFFICIENTS

The heat transfer coefficients were measured using the method based on equations (17) and (18) presented in Section (3.3) and described in Section (4.2.2). Table A.4.1 gives some of the curves which were plotted on semi-log graph paper to measure the heat transfer coefficients in the mixing bath.

TABLE A.4.1

TEMPERATURE-TIME CURVES FOR HEAT TRANSFER COEFFICIENT DETERMINATION

Sphere diameter: 0.5"D.

Experiment	A-25-19	A-26-8	A-26-9
ΔT	59.8	55.1	55
time (minute)	$\frac{T - T_\infty}{T_i - T_\infty}$	$\frac{T - T_\infty}{T_i - T_\infty}$	$\frac{T - T_\infty}{T_i - T_\infty}$
0.0	1.00	1.00	1.00
0.1	0.959	0.883	0.853
0.2	0.848	0.735	0.705
0.3	0.725	0.604	0.605
0.4	0.623	0.515	0.515
0.5	0.519	0.399	0.427
0.6	0.436	0.341	0.369
0.7	0.356	0.281	0.310
0.8	0.301	0.238	0.251
0.9	0.259	0.208	0.222
1.0	0.218	0.178	0.178
1.1	0.178	0.150	0.156
1.2	0.150	0.120	0.134
1.3	0.1[illegible]	0.105	0.119
1.4	0.1[illegible]		0.104

When plotted, the data give straight lines but with a slight curvature at initial time. These deviations are negligible even if they can change the h values by 100. The h values are large enough, so that the existing variations cannot affect the predicted temperature-time curves used in this investigation.

Table A.4.2 presents the h values measured. An average value of 2045 was obtained for h and the average temperatures T_i and T_∞ were respectively 72.7°C. and 12°C.

TABLE A.4.2

HEAT TRANSFER COEFFICIENTS FOR THE CONVECTIVE MEDIUM

The h values were measured at the surface of a 0.5"D. sphere

Experiment	h	Experiment	h
A-25-11	1892	A-25-21	2000
A-25-12	2064	A-26-1	2000
A-25-13	1880	A-26-2	2000
A-25-14	2000	A-26-3	2073
A-25-15	1962	A-26-4	2085
A-25-16	1925	A-26-5	2220
A-25-17	2064	A-26-6	2225
A-25-18	1923	A-26-7	2175
A-25-19	2040	A-26-8	2175
A-25-20	2020	A-26-9	2095

APPENDIX 5

A.5 CALIBRATION OF THERMOCOUPLES

The supplier guarantees the chromel-alumel thermocouples for a maximum deviation of 2 to 3°C. from the values proposed in the standard conversion tables. Actually, much less deviation from the chromel-alumel standard conversion table values was observed. The thermocouples were calibrated in position and deviations not greater than 0.5°C. were measured.

The dimensionless temperatures were compared and used for calculations in this investigation. Therefore, the calibration corrections did not affect much the temperature-time curves and even less the determined conductivity values.

The calibrations were done with the thermocouples in position in the spheres. The sphere and its thermocouple were kept in a temperature controlled bath long enough to insure uniform and constant temperature throughout the entire assembly. The bath was controlled within ±0.05°C. by a Haake unit and the bath temperature was measured with precision Anschutz thermometers allowing accurate readings (±0.05°C.) through 0.2°C. smallest scale divisions.

When using the Visicorder, no calibrations were required. In the temperature range -40 to +40°C., the standard conversion tables show that there is a linear relationship between the electrical potential developing at the junction and the temperature. In the range investigated, that is to say -40 to +75°C.

the deviation from the linearity is negligible. Moreover, the Visicorder has a linear scale. Therefore, with the Visicorder there is only need for determining accurately two points of the scale. Thus, a linear scale is set up and the temperature is determined easily by a direct reading on the recording paper.

APPENDIX 6

A.6 REPRODUCIBILITY OF THE TEMPERATURE-TIME CURVES FOR A SAME SPHERE

In Section (5.2.3) a discussion was given and Figure 2A shows that in the same conditions and with a same sphere, the measured temperature-time curves do not deviate appreciably from the average curve. In the case chosen as example, the maximum deviation was in the order of 0.015 at $\theta = 0.138$. Table A.6.1 gives the data used for calculating the results presented in Figure 2. The data given in Table A.6.2 indicate that there is also very good agreement between the average curves for three different series of experiments made with sphere S-582.

TABLE A.6.1

TEMPERATURE-TIME CURVES FOR A SAME SPHERE

Sphere S-582, 0.625"D. (Lucite)
R = 0.3
Bi = 370
Experiments S-8-1, 10

Experiment S-8-	1	2	3	4	5	6	7	8	9	10
time (sec)	θ	θ	θ	θ	θ	θ	θ	θ	θ	θ
35	.087	.080	.094	.095	.090	.083	0.090	.089	0.091	0.089
40	.137	.127	.144	.148	.140	.128	.139	.132	.145	.138
50	.244	.230	.250	.151	.249	.240	.245	.243	.247	.248
70	0.463	.454	.462	.469	.465	.453	.460	.462	.465	.459
90	.627	.619	.631	.634	.638	.625	.628	.628	.631	.620
110	.749	.743	.748	.736	.754	.744	.750	.744	.750	.748

TABLE A.6.2

COMPARISON OF AVERAGE TEMPERATURE-TIME

CURVES FOR A SAME SPHERE

Sphere S-582, 0.625"D. (Lucite)

R = 0.3

Bi = 370

Experiments	S-8-1, 10	S-11-1, 6	S-13-1, 13
T_i	68.65	72.4	71.85
T_∞	7.6	5.25	10.7
ΔT	61.05	67.15	61.15
time (sec.)	θ	θ	θ
0	0	0	0
25	0.015		
35	0.089		
40	0.138	0.140	0.141
50	0.245	0.251	0.246
60	0.359	0.364	0.355
70	0.461	0.466	0.457
80	0.548	0.558	0.547
90	0.629	0.633	0.625
100	0.694	0.699	0.689
110	0.747	0.756	0.743
120	0.796	0.803	0.789

APPENDIX 7

A.7 INFLUENCE OF THERMOCOUPLE SIZE ON TEMPERATURE MEASUREMENTS

The influence of the thermocouple size on temperature measurements is discussed in Section (5.2.7). Two thermocouple sizes were used and the experimental investigations did not permit to evaluate with certainty if there is any actual difference due to the thermocouple size. The data are given in Table A.7.1.

TABLE A.7.1

TEMPERATURE-TIME CURVES FOR DETERMINING THE INFLUENCE OF THE THERMOCOUPLE SIZE ON THE TEMPERATURE MEASUREMENTS

Sphere S-582, (Lucite), R = 0.3, 0.003"D. thermocouple

Sphere S-585, (Lucite), R = 0.3, 0.008"D. thermocouple wire

Experiments	S-8-1, 10	S-24-1, 4	S-29-13, 16	O-25-1, 8
Sphere	S-582	S-585	S-582	S-585
T_i	68.7	71.8	26.85	26.6
T_∞	7.6	9.0	18.25	21.2
ΔT	61.1	62.8	8.6	5.4
time (sec.)	θ	θ	θ	θ
30	0.044	0.058	0.076	0.084
40	0.138	0.141	0.159	0.193
50	0.191	0.240	0.260	0.301
60	0.303	0.337	0.367	0.399
70	0.461	0.436	0.452	0.482
80	0.548	0.523	0.540	0.571
90	0.629	0.597	0.607	0.647
100	0.694	0.659	0.665	0.698
110	0.747	0.712	0.719	
120	0.796	0.756		
130	0.837	0.796		

APPENDIX 8

A.8 INFLUENCE OF THE SUPPORT

The effect of the sphere support on the measured temperature-time curves has been estimated by using the finite-difference model and considering only axial symmetry. The heat transfer coefficient on the sphere surface in contact with the support was assumed to be zero and a variable coefficient was assumed over the remaining surface. Table 8 gives the h values profile used for the computation. The results indicate that there are negligible differences, for the half portion of the sphere opposite to the one in contact with the support, between the temperature-time curves based on variable heat transfer coefficients and the ones predicted for radial symmetry. The data for one position in the sphere are given in Table (A.8.1) to illustrate these results.

TABLE A.8.1

COMPARISON OF TEMPERATURE-TIME CURVES FOR RADIAL AND AXIAL SYMMETRY OF THE HEAT TRANSFER COEFFICIENTS-INFLUENCE OF THE SPHERE SUPPORT

Sphere radius, 0.0258 ft.

Thermal conductivity, 0.1165

Heat transfer coefficient for radial symmetry (series solution), 2100

Mesh for the finite-difference model, 21 radial points
31 angular points

Position, R = 0.3
Angle = 180°

τ	— Variable h — (finite-difference solution) θ	radial symmetry of h (series solution) θ
0.03	0.015	0.014
0.04	0.046	0.044
0.05	0.090	0.088
0.06	0.143	0.142
0.07	0.201	0.201
0.08	0.260	0.261
0.09	0.317	0.320
0.10	0.372	0.377
0.15	0.597	0.609

APPENDIX 9

A.9 ESTIMATION OF TEMPERATURE MEASUREMENT ERRORS FOR THE LUCITE SPHERE CASE

Because the exact values for the conductivity of Lucite are not known, there is no direct method of estimating the error of the temperature measurements made with Lucite spheres. An evaluation of the error is however possible and is given in some detail below.

For the sake of evaluating the error, a value of k = 0.1165 was assumed as the correct one for Lucite. The average conductivity value measured for Lucite is 0.0972 and the values are deviating from this average by less than ±12%. Using the value k = 0.1165, the temperature-time curves predicted by series solution were compared to the measured ones. However, the measured conductivity values for Lucite are different from 0.1165. A comparison with the values available in the literature (see Figure 11) indicates that the results obtained are reliable. Therefore, it is obvious that the comparison should show differences between the predicted and the measured curves. Such differences existed and hypothetical percentage errors of the measured temperature values were calculated for each Lucite sphere. An example is given in Table A.9.1.

TABLE A.9.1

TEMPERATURE ERROR FOR A LUCITE SPHERE

Sphere S-122 (Lucite)

R = 0.6

τ	T predicted	T measured	% temperature error based on predicted T
0.029	61.4	64.3	4.7
0.058	46.15	51.0	10.5
0.116	28.5	32.1	12.6
0.173	19.2	21.4	11.5
0.231	13.9	14.6	5.0
0.289	11.0	11.4	3.6

Maximum errors were considered for each sphere. It is important to remember that the conductivity values determined for each sphere using the series solutions and the method presented in Section (3.4.3) are varying within certain ranges. In the case of each sphere, there is one k value deviating the most from k = 0.0972. These values were considered and the differences between 0.1165 and these values were calculated. Then they were expressed as percentage differences based on 0.0972. The idea is to establish a relationship in the case of Lucite spheres, between the percent conductivity differences and the maximum temperature errors. So, ratios of these values were calculated. Table A.9.2 gives for each sphere the range of conductivity values, the maximum error and the largest conductivity deviation from k = 0.0972. Table A.9.3 presents the ratios mentioned above.

TABLE A.9.2

MAXIMUM TEMPERATURE ERRORS FOR LUCITE SPHERES

Sphere	range of k	Maximum temperature error, %	Largest deviation of k values from 0.0972
S-122	0.0906-0.0951	12.6	- 6.8%
S-124	0.0967-0.1006	9.4	+ 3.5%
S-126	0.0855-0.0936	18	-12 %
S-581	0.0971-0.106	4	+ 9 %
S-582	0.0948-0.0988	12.6	+ 2.5%
S-585	0.0901-0.0963	17.0	- 7.3
S-586	0.0960-0.0989	10	+ 1.75

As shown in Table A.9.3, the ratios obtained are not constant but they are all close to 2 or larger. This fact indicates that, in the case of Lucite spheres, when the assumed conductivity deviated from 0.0972 by 20%, temperature errors of 10% or smaller were estimated. Actually, the measured values deviate from 0.0972 by less than 12%. From the above reasoning, it can be concluded that the errors for the temperature measurements in Lucite spheres are smaller than 6%.

TABLE A.9.3

RATIOS FOR ESTIMATING THE TEMPERATURE MEASUREMENT ERRORS FOR LUCITE SPHERES

Sphere	Difference between k = 0.1165 and the measured k value most different from 0.0972, % (based on 0.0972)	Maximum temperature error assuming k of Lucite = 0.1165 %	Ratios of the percentages
S-122	26	12.6	2.1
S-124	16.5	9.4	1.76
S-126	32.0	18	1.8
S-581	11.0	4	2.75
S-582	22.5	12.6	1.8
S-585	27.3	17.0	1.6
S-586	18.0	10.0	1.8

APPENDIX 10

A.10 RESULTS FROM THE FINITE-DIFFERENCE SOLUTION WITH VARIABLE PHYSICAL PROPERTIES

A finite-difference model was used during the present investigation. It has been presented in Section (3.2) and more details can be found in Appendix (3). The model can give solutions for heat conduction in spherical solids when the physical properties are varying with temperature. The model can be used as the series solution, for determining the conductivity of solids. It is even more general than the series solution because it considers the variation of the properties. However, it requires long computer time and was not investigated extensively. For the determination of conductivity-temperature curves from a single experiment, the model has been used only with naphthol β.

The experimental errors were such that the use of the finite-difference model did not give easily much better results than the ones from the series solution (see Appendix 12). However, the model has been used to predict the temperature-time curves which were used in conjunction with the series solution and the proposed method of determining conductivity (see Section 3.4.3 and 5.3.2), to determine the deviation introduced by the use of a series solution for predicting conductivity-temperature curves. The theoretical cases investigated are given in Section (5.3). Table A.10.1 shows the complete calculations for Case 1.

TABLE A.10.1

COMPARISON BETWEEN THE CONDUCTIVITY-TEMPERATURE CURVE USED IN THE FINITE-DIFFERENCE MODEL AND THE ONE DETERMINED BY THE SERIES SOLUTION

Data used in the finite-difference model

$R = 0.0$

$Cp\,\rho\, a^2 = 113.5$

$k_p = 0.147 - 0.000075\ T$

$Cp = 0.252 + 0.00128\ T$

$k_c = 0.147$ $\qquad$ $k1 = -0.000075$

$Cp0 = 0.252$ $\qquad$ $Cp1 = 0.00128$

$T_i = 66^oC.$ $\qquad$ $T_\infty = 27^oC.$

$$\text{time (sec.)} = \frac{113.5\ Cp0\ \tau}{ko}$$

For the series solution, Bi = 462 and $k = \dfrac{113.5\ Cp\ \tau}{t\ (sec.)}$

Curve predicted by the finite-difference model — Values determined by the used of the series solution (k_c)

θ	time sec.	T	Cp	τ	k_c	k_p
.071	15.6	63.2	.333	.0605	.1466	.1422
.107	17.5	61.8	.331	.0680	.1460	.1424
.238	23.4	56.7	.324	.0905	.1423	.1428
.376	29.2	51.3	.318	.114	.1409	.1432
.501	35.0	46.5	.312	.140	.1415	.1435
.606	40.9	42.4	.306	.166	.1412	.1438

The finite-difference model indicated also that when the ratio k/Cp is constant, or when this ratio varies but k and Cp vary similarly with temperature, the series solution predicts temperature-time curves being the same or very similar to the ones predicted with the finite-difference model. This means that when these conditions exist, the variations of physical properties with temperature have negligible effect on the series solution which is derived by assuming constant physical properties and therefore, the series solution allows the determination of reliable conductivity-temperature curves from a single experiment. For the conditions described above, curves predicted by the series and the finite-difference models are compared and their good agreement is illustrated by an example given in Table A.10.2.

TABLE A.10.2

COMPARISON BETWEEN TEMPERATURE-TIME CURVES PREDICTED BY SERIES SOLUTION AND BY FINITE-DIFFERENCE MODEL WITH VARIABLE PHYSICAL PROPERTIES

a = 0.0208	k0 = 0.22	Cp0 = .332
T_i = 66°C.	k1 = 0.000073	Cp1 = .00111
T_∞ = 27°C.	h = 2100	Bi = 462
k/Cp = 0.765 at 50°C.	k/Cp = 0.776 at 20°C.	

	R = 0.0		R = 0.5	
	series solution	finite-difference	series solution	finite-difference
τ	θ	θ	θ	θ
0	0	0	0	0
0.04	0.011	0.012	0.152	0.144
0.05	0.033	0.034	0.225	0.214
0.06	0.070	0.069	0.295	0.281
0.07	0.118	0.115	0.360	0.344
0.08	0.173	0.167	0.419	0.402
0.09	0.232	0.222	0.473	0.455
0.10	0.290	0.279	0.523	0.504
0.15	0.547	0.531	0.708	0.692
0.20	0.720	0.706	0.821	0.809

APPENDIX 11

A.11 DATA FOR DETERMINING THE CONDUCTIVITY OF NAPHTHALENE, BISMUTH, PARAFFIN WAX AND AMMONIUM NITRATE

The tables in Appendix 11 give the details of the data obtained for the following materials: naphthalene, bismuth, paraffin wax and ammonium nitrate.

TABLE A.11.1

CONDUCTIVITY OF NAPHTHALENE - MEASUREMENTS WITH A SPHERE

Sphere S-125, R = 0, D = 0.5'

Experiments D-11-3, 6

T_i = 50.3

T_∞ = 8.7

time sec.	θ	T	k
12.9	0.092	46.4	0.192
18.4	0.264	39.15	0.198
31.2	0.577	26.4	0.196
35.0	0.669	22.4	0.203
39.0	0.745	19.4	0.208
44.2	0.805	16.7	0.209
50.1	0.855	14.7	0.208
53.8	0.891	13.35	0.212
59.1	0.916	12.5	0.212
63.4	0.936	11.5	0.214
69.0	0.953	10.7	0.212

TABLE A.11.2

CONDUCTIVITY OF NAPHTHALENE - MEASUREMENTS WITH AN HEMISPHERE

R = 0.5

Experiment M-7-1

T_i = 25.9

T_∞ = 53

time (sec.)	θ	°C.	k
50	0.032	26.8	0.241
60	0.054	27.4	0.236
70	0.081	28.1	0.233
80	0.110	28.85	0.234
90	0.142	29.75	0.236
100	0.176	30.65	0.236
110	0.208	31.55	0.237
120	0.242	32.45	0.240
130	0.275	33.35	0.246
140	0.303	34.10	0.246
150	0.330	34.8	0.246
160	0.356	35.6	0.244
170	0.385	36.3	0.246
180	0.410	37.05	0.250
190	0.439	37.80	0.252

TABLE A.11.3

CONDUCTIVITY OF BISMUTH

Bi = 9.25

R = 0.5

Experiments	0-8-1, 5			JA-24-1, 5			
T_i	71.0			73.6			
T_∞	10.4			3.9			
time (sec.)	θ	T	k	time (sec.)	θ	T	k
0.35	0.2	58.9	4.39	0.4	0.187	60.6	4.21
0.55	0.3	52.8	4.23	0.6	0.321	51.3	3.96
0.76	0.4	46.8	4.03	0.8	0.446	42.6	4.01
0.88	0.5	40.65	4.03	1.0	0.556	34.85	4.06
1.08	0.6	34.6	4.08	1.2	0.646	28.55	4.01
1.33	0.7	28.5	4.05	1.4	0.717	23.7	3.97
1.72	0.8	22.4	4.10	1.6	0.774	19.7	4.01
2.34	0.9	16.4	4.12	1.8	0.822	16.35	4.08
				2.0	0.857	13.9	4.06

TABLE A.11.4

CONDUCTIVITY OF PARAFFIN WAX

R = 0,   A new sphere was used in every experiment

Experiment	F-15-1			F-15-3			F-15-4			F-15-5		
T_i	48.2			48.2			48.2			48.2		
T_∞	7.0			8.6			11.3			12.7		
ΔT	41.2			39.6			37.9			35.5		
time (sec.)	θ	T	k	θ	T	k	θ	T	k	θ	T	k
40	0.124	43.1	0.109	0.060	45.4	0.0872	0.060	46	0.0873	0.060	46.1	0.0873
45	0.161	41.6	0.105	0.118	43.55	0.0928	0.100	44.5	0.0888	0.101	44.6	0.0880
50	0.208	39.65	0.104	0.171	41.4	0.0956	0.152	42.6	0.0920	0.132	43.5	0.0865
55	0.255	37.7	0.104	0.231	39.05	0.0978	0.209	40.5	0.0946	0.200	41.1	0.0924
65	0.328	34.7	0.106	0.321	35.5	0.0983	0.319	36.45	0.0978	0.325	36.7	0.0993
70	0.364	33.2	0.106	0.355	34.15	0.0968	0.360	34.9	0.0978	0.389	34.75	0.103
80	0.437	30.2	0.0961	0.421	31.50	0.0945	0.423	32.6	0.0954	0.458	31.95	0.101
85	0.474	28.65	0.0961	0.453	30.25	0.0936	0.451	31.55	0.0932	0.491	30.75	0.0985
90	0.489	27.15	0.0962	0.484	29.05	0.0922	0.481	30.45	0.0914	0.524	29.6	0.0975
95	0.548	25.65	0.0962	0.515	27.8	0.0911	0.510	29.4	0.0904	0.554	28.55	0.0968
105	0.620	22.65	0.0977	0.589	24.9	0.0922	0.576	26.9	0.0910	0.613	26.45	0.0962
115	0.695	19.6	0.102	0.678	21.35	0.0976	0.644	24.45	0.0926			
120	0.730	18.1	0.104	0.718	19.8	0.101	0.686	22.90	0.0947			
130	0.804	15.1	0.110	0.788	17.0	0.107						
135				0.820	15.75	0.110						
140				0.850	14.5	0.116						

TABLE A.11.5

CONDUCTIVITY OF AMMONIUM NITRATE

One sphere, 0.5"D.

R = 0.0

Experiment	F-8-4		
T_i	65.75		
T_∞	5.0		
ΔT	60.75°C.		
time (sec.)	θ	T	k
10	0.078	61	0.409
15	0.257	50.1	0.413
20	0.454	38.2	0.435
25	0.608	28.8	0.431
30	0.680	24.45	0.407
35	0.7265	21.60	0.379
40	0.7728	18.6	0.364
45	0.8115	16.45	0.351
50	0.8607	13.45	0.3565

APPENDIX 12

A.12 CONDUCTIVITY OF NAPHTHOL β - DETERMINATION USING THE SERIES AND FINITE-DIFFERENCE METHODS

The Tables A.12.1, A.12.2, and A.12.3 give the data obtained experimentally from three spheres and the conductivity results determined by using the series solutions. Also are given the k0 values determined by using the finite-difference model with the linear relationships proposed by International Critical Tables (I1). The relationships are:

$$k = 0.147 - 0.000075\ T$$

$$k = k0 - k1.T$$

and

$$Cp = 0.252 + 0.00128\ T$$

$$Cp = Cp0 + Cp1T$$

Theoretically, the determined k0 values ($k0 = \frac{\rho a^2\ Cp0\ \tau}{t\ (sec.)}$) should be constant. However, the experimental errors are such that they are varying, although very little. Their variation pattern is very similar to the variation of the conductivity values determined with the series solution. Measurements done by using k = 0.142 - 0.000075 T in the finite-difference model did not introduce any significant change in the k0 values determined. The finite-difference model gives good results but for the cases where the conductivity is not known, the computation could be relatively long.

TABLE A.12.1

CONDUCTIVITY OF NAPHTHOL β - EXPERIMENTS F-22-5, 6, 7

R = 0.0

T_i = -32.7

T_∞ = 21.6

Model	Series			Finite-difference
time (sec.)	θ	T	k	kO
15	0.194	-22.15	.141	0.142
20	0.333	-14.6	.144	0.144
25	0.458	- 7.8	.146	0.146
30	0.566	- 1.9	.147	0.147
35	0.654	+ 2.85	.147	
40	0.726	6.75	.152	
45	0.788	10.1	.154	
50	0.838	12.8	.158	
55	0.871	14.6	.158	

TABLE A.12.2

CONDUCTIVITY OF NAPHTHOL β - EXPERIMENT F-23-2

R = 0.0

T_i = 80.0

T_∞ = 22.15

Model	Series			Finite-difference
time (sec.)	θ	T	k	kO
20	0.153	71.1	0.148	.146
25	0.268	64.45	0.145	.146
30	0.380	57.95	0.144	.144
35	0.488	51.75	0.143	.144
40	0.585	46.15	0.142	.144
45	0.658	41.9	0.139	
50	0.726	37.95	0.139	
55	0.780	34.95	0.139	
60	0.824	32.3	0.139	
65	0.853	30.6	0.138	
70	0.878	29.2	0.135	

TABLE A.12.3

CONDUCTIVITY OF NAPHTHOL β

Experiment F-25-1

R = 0.0

T_i = 66.65

T_∞ = 23.0

Model time (sec.)	Series θ	Series T	Series k	Finite-difference kO
20	.140	60.6	.137	.137
25	.238	56.3	.133	.133
30	.359	51.0	.136	.136
35	.465	46.4	.135	.135
40	.560	42.2	.133	.134
45	.634	39.0	.131	
50	.704	35.9	.132	
55	.756	33.7	.131	
60	.805	31.5	.132	
65	.844	29.8	.134	
70	.875	28.5	.134	

APPENDIX 13

A.13 CONDUCTIVITY OF ICE - TRIAL-AND-ERROR PROCEDURE FOR LOW BIOT NUMBERS

The range of conductivity values for ice is such that the Biot numbers existing in the present investigations are smaller than 50. This means that the temperature-time curves predicted by the series solution and used for determining the conductivity, are dependent on the Biot numbers. The data presented in Table A.13.1 show that even if a single temperature-time curve is used (Bi = 32.0), reliable conductivity values are obtained.

The table also gives values determined using temperature-time curves corresponding to different Biot numbers. A conductivity value is first assumed and a Biot number calculated. Then, the conductivity values are determined. A comparison between the assumed and calculated values indicates whether or not the assumption was right. As illustrated, a trial-and-error procedure can be established and lead to the determination of reliable values. This trial-and-error method should be most useful when the conductivity value of the test material is completely unknown. The conductivity range can be estimated first and after, the determination of the conductivity values can be done.

TABLE A.13.1

RESULTS FOR A TRIAL-AND-ERROR PROCEDURE USED IN THE DETERMINATION OF ICE CONDUCTIVITY

Sphere, 0.498 ± 0.001"D.

R = 0.0

Experiments JA-29-13, 21

Heat transfer coefficient, 2000

T_i = -43.8, T_∞ = -5.85

trial			1	2	3	4
assumed k			4.5	0.833	1.21	1.30
Bi			9.25	50	34.45	32.0
time (sec.)	θ	T	k	k	k	k
2.2	0.117	-39.35	1.45	1.22	1.28	1.30
3.2	0.288	-32.85	1.52	1.30	1.29	1.32
4.2	0.443	-27.0	1.54	1.30	1.29	1.33
5.2	0.568	-22.4	1.50	1.27	1.28	1.31
6.2	0.666	-18.5	1.50	1.27	1.25	1.31
7.2	0.740	-15.7	1.49	1.27	1.29	1.30
8.2	0.798	-13.5	1.50	1.27	1.28	1.29
9.2	0.845	-11.7	1.50	1.26	1.29	1.29
10.2	0.880	-10.4	1.51	1.29	1.29	1.30
11.2	0.907	- 9.4	1.50	1.26	1.28	1.30

APPENDIX 14

A.14 EXPERIMENTAL CONDITIONS AND RESULTS FOR LUCITE SPHERES

Table A.14.1 gives the construction details and other characteristics of the Lucite spheres used in this investigation. Table A.14.2 contains the results obtained with the different spheres and the experimental conditions.

TABLE A.14.1

CONSTRUCTION DETAILS OF LUCITE SPHERES

P indicates a sphere fabricated by polymerizing methyl methacrylate in a mold.

C indicates a cast sphere from the supplier

All spheres have 0.003 inch chromel-alumel thermocouples except sphere S-585 with 0.008"D. wires.

S indicates a stainless steel support 0.097"D.

G indicates a glass support 0.245"D.

N indicates a sphere with a 0.25" x.25" cylindrical neck.

Sphere	Diameter (inch±0.003)	Fabrication method	Support	Neck
S-122	0.498	P	S	-
S-123	0.499	P	S	-
S-124	0.495	P	S	-
S-126	0.495	P	S	N
S-581	0.617	C	S	-
S-582	0.618	C	S	-
S-583	0.620	C	G	-
S-585	0.618	C	G	-
S-586	0.615	C	S	-

TABLE A.14.2

RESULTS FROM LUCITE SPHERES

Sphere	S-122	
Experiments	0-22-1, 5	
T_i	71	
T_∞	7.2	
R	0.6	
θ	T	k
.104	64.35	0.0951
.313	51.0	0.0917
.608	32.0	0.0906
.705	26.0	0.0920
.836	17.6	0.0931
.912	12.9	0.0950

Sphere	S-123	
Experiments	N-4-1, 5	
T_i	70.8	
T_∞	8.8	
R	0.5	
θ	T	k
.0655	66.7	.110
.254	55.0	.111
.422	44.6	.104
.657	30.0	.0876
.736	25.2	.0883
.848	18.2	.0940
.909	14.4	.0926

Sphere	S-124	
Experiments	N-13-1, 5	
T_i	70.85	
T_∞	9.7	
R	0.4	
θ	T	k
.144	62.1	.101
.465	42.45	.100
.691	28.65	.0965
.824	20.45	.0970
.901	15.85	.0967

Sphere	S-126	
Experiments	D-18-1, 5	
T_i	70.8	
T_∞	8.1	
R	0.0	
θ	T	k
.110	64	.0936
.376	47.2	.0890
.695	27.3	.0865
.859	16.9	.0855

Sphere	S-581	
Experiments	A-25-1, 10	
T_i	71.8	
T_∞	13.8	
R	0.3	
θ	T	k
.017	70.9	.102
.083	67.1	.103
.184	60.3	.105
.294	54.8	.104
.405	48.4	.104
.501	42.9	.0971
.586	37.9	.103
.663	33.4	.104
.733	29.4	.104
.783	26.5	.0993
.805	25.3	.106
.845	22.9	

Sphere	S-582	
Experiments	S-8-1, 10	
T_i	68.7	
T_∞	7.6	
R	0.3	
θ	T	k
.057	65.0	.0948
.359	46.7	.0960
.506	37.7	.0970
.694	26.3	.0962
.818	18.8	.0988

Sphere	S-583	
Experiments	S-18-1, 6	
T_i	71.2	
T_∞	14.1	
R	0.6	
θ	T	k
.128	63.9	.114
.220	58.6	.112
.364	51.2	.107
.422	47.1	.106
.476	44.0	.105
.565	38.9	.102
.638	34.7	.101
.696	31.4	.100
.740	29.0	.0985
.819	24.6	.0948

Sphere	S-585	
Experiments	S-24-1, 4	
T_i	71.8	
T_∞	9	
R	0.3	
θ	T	k
.103	65.4	.0962
.240	56.8	.0926
.485	41.4	.0952
.659	30.4	.0915
.774	23.0	.0901

Sphere	S-586	
Experiments	N-20-1, 5	
T_i	70.8	
T_∞	10.8	
R	0.4	
θ	T	k
.122	63.5	0.0989
.337	50.6	0.0980
.530	39.1	0.0975
.701	28.8	0.0960