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CONFERENCE ON THERMAL CONDUCTIVITY

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NINTH CONFERENCE ON THERMAL CONDUCTIVITY

HOWARD R. SHANKS, Editor

Containing papers presented October 6, 7 and 8, 1969 at
Iowa State University, Ames, Iowa

Jointly sponsored by
AMES LABORATORY, USAEC
U. S. OFFICE OF NAVAL RESEARCH
IOWA STATE UNIVERSITY

MARCH 1970

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Acknowledgements

I wish to thank the session chairmen for an excellent job of conducting their individual sessions and for their assistance in keeping the Conference on schedule. Particular thanks go to the Office of Naval Research and Dr. R. G. Morris for their help in the arrangement of travel for a number of participants from abroad. The Ames Laboratory and Iowa State University contributed valuable financial support to the Conference. G. C. Danielson, P. H. Sidles, R. L. Anderson and other members of Crystal Physics Group III of the Ames Laboratory provided a great deal of assistance with pre-conference arrangements and with the logistics of the Conference. I would also like to thank Dorthy Danielson, Eloise Anderson and Laura Shanks for providing the Ladies Program.

Preface

The annual Conference on Thermal Conductivity is the outgrowth of an informal conference first held by Battelle Memorial Institute in 1961. Each year since 1961 a different laboratory has volunteered to host the next conference. The sponsors and the chairman of the conferences are listed below.

Sponsoring Organization	Chairman	Date
Battelle Memorial Institute	C. F. Lucks	Oct. 1961
National Research Council (Canada)	M. J. Laubitz	Oct. 1962
Oak Ridge National Laboratory	D. L. McElroy	Oct. 1963
Naval Radiological Defense Laboratory	R. L. Rudkin	Oct. 1964
University of Denver	J. D. Plunkett	Oct. 1965
Air Force Materials Laboratory	M. L. Minges & G. L. Denman	Oct. 1966
National Bureau of Standards	D. R. Flynn & B. A. Peavy	Nov. 1967
T.P.R.C., Purdue University	C. Y. Ho & R. E. Taylor	Oct. 1968
Ames Laboratory, I.S.U. ONR	H. R. Shanks	Oct. 1969

The early conferences were primarily concerned with the methods of measurement and the development of standards. In recent years the nature of the conferences have changed. The conferences have taken on a definite international flavor with participants from England, Germany, France, Italy, India, Japan and Australia in addition to the United States and Canadian participation. The level of experimental sophistication has increased considerably. The number of papers which present results obtained at low temperatures ($T < 77$ K) and in magnetic fields has increased. A greater emphasis on the analysis and interpretation of experimental results has also been observed.

The Tenth Conference on Thermal Conductivity will be held during September, 1970 under the sponsorship of Arthur D. Little, Inc. and Dynatech Corp. R. P. Tye and A. E. Wechsler will serve as Co-chairman.

Howard R. Shanks
December, 1969

Abstract

The Ninth Conference on Thermal Conductivity was held at Iowa State University on October 6 - 8, 1969. The Conference was sponsored jointly by Iowa State University, the Ames Laboratory of the United States Atomic Energy Commission and the United States Office of Naval Research. This volume contains the texts of many of the papers that were presented at the Conference and some which were scheduled for presentation but because of travel problems were not presented. In addition, abstracts of the papers which were presented orally at the Conference but for which full texts are not available for publication are also included. In all 52 papers and 27 abstracts are included in this volume, contributed by authors from 9 countries: Canada, France, Germany, India, Italy, Japan, Union of Soviet Socialist Republics, the United Kingdom, and the United States of America. Topics covered include descriptions of methods for the measurement of thermal conductivity, thermal diffusivity and thermal contact conductance, experimental data on a variety of materials, theoretical developments and correlations between experimental and theoretical results. Data on solids, liquids and gases from cryogenic to very high temperatures are included.

Key Words: Conductance, conductivity, contact conductance, contact resistance, electrical conductivity, electrical resistivity, Lorenz function, resistivity, temperature, thermal conductivity, thermal diffusivity, thermal resistivity, thermophysical properties.

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Low Temperature Measurements I

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MAGNETIC FIELD DEPENDENT PHONON SCATTERING BY Mn^{3+} IONS IN Al_2O_3 .

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ABSTRACT

The paper describes measurements of the thermal conductivity and thermal magnetoresistance of a specimen of Mn-doped Al_2O_3 in the temperature range $0.5 - 4.2^\circ\text{K}$. The measurements confirm earlier data by de Goer (1969) in the range $1.4 - 4.2^\circ\text{K}$ showing the presence of resonant scattering at around 8 cm^{-1} presumably by Mn^{3+} ions and suggests that there may be an additional weak resonance at around 2 cm^{-1} . There are large magnetoresistance effects attributed to additional scattering between Zeeman levels first reported by Zadworny (1967). The anisotropy of a peak in the magnetoresistance as the field is moved with respect to the c-axis is much less than that expected from scattering between the levels of the ground state doublet of the undistorted site which is some evidence for a Jahn-Teller effect. A similar result was reported earlier for the isoelectronic Cr^{2+} ion (Challis, McConachie and Williams 1968). From the temperature dependence of the position of this peak at an angle of about 73° to the c-axis it is possible to place an upper limit on g of 4.3 (assuming the splitting = $g\beta H$). It is hoped to lower this limit by measurements at lower temperatures.

1. INTRODUCTION

In this paper we report measurements of the thermal conductivity of Mn-doped Al_2O_3 in the temperature range $0.5 - 4.2^\circ\text{K}$ and in fields from 0 - 21 kOe. The work forms part of a programme to study the properties of the d^4 ions Cr^{2+} and Mn^{3+} in sites of various symmetries. These ions are of particular relevance in that their ground state in both cubic and trigonal fields is an orbital doublet which is split only weakly by spin-orbit interaction into a set of levels spanning an energy range comparable with that of thermal phonons dominant at helium temperatures. It appears that a small concentration of these ions greatly reduces the thermal conduction in this temperature range, (e.g. Challis and Williams 1965, de Goer and Dreyfus 1967) indicating that the ions are strongly coupled to the phonon system. It seems probable that a model of a static crystal field with the symmetry of an undistorted site is inappropriate for these ions and that there is in fact a Jahn-Teller distortion present. This makes the analysis of the data more difficult but also perhaps of special interest. It has not yet been found possible to study the ground state of these ions using e.s.r. although they have been studied using acoustic paramagnetic resonance (Cr^{2+} in MgO: Marshall and Rampton 1968, Pointon and Taylor 1969; Cr^{2+} in Al_2O_3 : Guermeur et al. 1967, Anderson, Brabin-Smith and Rampton private communication).

The thermal conductivity of Cr and Mn doped Al_2O_3 was first studied in depth by the Grenoble group (Cr and Mn- Al_2O_3 : de Goer and Dreyfus 1967, de Goer 1969; Mn- Al_2O_3 : Zadworny 1967). It is clear from their work that the zero field conductivity at low temperatures is greatly reduced by Cr^{2+} ions produced by γ -irradiation and by ions assumed to be Mn^{3+} . Their results are interpreted in terms of resonance scattering at wave numbers ~ 6 and 70 cm^{-1} (Cr^{2+}) and 8 and 35 cm^{-1} (Mn^{3+}). Work in Nottingham on Cr- Al_2O_3 has been mostly in the temperature range $0.5 - 4.2^\circ\text{K}$. The measurements of the zero field conductivity of irradiated Cr- Al_2O_3 show that the presence of resonance scattering at a lower frequency cannot yet be ruled out although if it does

exist it is clearly appreciably weaker than the higher frequency scattering. We have also made a rather detailed investigation of the magnetoresistance. A part of this work has been given in conference reports (Challis, McConachie and Williams 1968) and the work will be published in detail at a later stage. An interesting exploratory investigation by Zadworny showed that large magnetoresistance effects occurred in $\text{Mn-Al}_2\text{O}_3$ and in the present work we have examined these in more detail.

2. SPECIMAN DETAILS AND EXPERIMENTAL METHOD.

The specimen which contained ~ 60 p.p.m. Mn by weight was kindly loaned by Mme de Goer and is labelled Mn 1 in the papers of Zadworny (1967) and de Goer (1969). The measurements were made with the field normal to the specimen axis which makes an angle of 59 and 61° ($\pm 2^\circ$) with the a and c axes respectively. Thus a direct comparison with measurements on ruby which were made with the field in the a , c and Y -planes is not possible although the field plane is nearer the Y -plane (containing the a and c axes) than to the other two principal planes. We have called the projections of the a and c directions onto the field plane the a' and c' directions respectively and the angle between them is approximately 71° . The measurement technique is described elsewhere (Challis, McConachie and Williams 1969); the magnetoresistance is plotted continuously on an x-y recorder.

3. RESULTS

The conductivity of the specimen between 0.5 and 4.2°K is shown in Figure 1 together with de Goer's values measured two years earlier. The conductivity at 4°K is about 0.1 of that of a pure Al_2O_3 specimen of the same dimensions (de Goer 1969). This is presumed to be the result of scattering by Mn^{3+} ions and the good agreement between the present data and that of de Goer demonstrates the expected stability of these ions in Al_2O_3 . A plot of K/T^3 (Figure 2) which is proportional to a phonon mean free path suggests the possible existence of a weak resonant scattering process at a wave number $\sim (3.8\text{k/hc}) \times 0.7$ i.e. $\sim 2\text{ cm}^{-1}$ in addition to that at $\sim 8\text{ cm}^{-1}$ noted earlier.

Figure 3 shows the thermal resistance at 1.05°K and in a field of 13.2 kOe as a function of the angle from the minimum which coincides to within experimental error with the a' direction. A further minimum occurs at an angle 61° away i.e. only about 10° from the c' direction. This general behaviour is quite similar to that observed with the field in the Y plane of $\text{Cr}^{2+}-\text{Al}_2\text{O}_3$ (Challis et al. to be published) where the minimum in the c -direction is lower than that in the a -direction. The anisotropy can also be seen in the magnetoresistance plots shown in Figure 4. The fields at which the first peak occurs when it is still reasonably well resolved vary from about 7.7 kOe at 61° from a' to 9.7 kOe at 3° from a' . The angles from the c -axis in each case are 31° and 71° respectively so that if this peak arises from transitions within the ground state doublet of the static field case with $g_{11} = 8$ and $g = 0$ with respect to the c -axis (Iow and Weger 1960), the ratio of these fields should be $(\cos 31^\circ / \cos 71^\circ) \sim 2.6$ and not $(9.7/7.7) \sim 1.3$. Clearly the measurements do not support the theoretical model. A similar conclusion follows from the work on Cr^{2+} where the small anisotropy is even more striking (Challis, McConachie and Williams 1968).

In figure 5 we show magnetoresistance data along the a' direction at various temperatures. The field H_{MAX} at which the first peak occurs increases with temperature and this is shown more clearly in Figure 6. The significance of the dependence of H_{MAX} on temperature is that if the splitting of the scattering doublet varies linearly with field, this dependence is proportional to the variation of the dominant phonon frequency with temperature. If only boundary scattering is present in zero field, this should be a linear dependence and the g -value of the doublet should be $\sim 56.6 (H_{\text{MAX}}/T)^{-1}$. But, if as believed, there is resonant scattering in addition, the dominant phonon frequency can be nearly temperature invariant (Challis, McConachie and Williams

1969). The data in Figure 6 suggest that the H_{MAX} against T plot is approaching the linear dependence at the lowest temperatures. From this we can deduce that for this direction $g \lesssim 4.3$ and that the effect of resonant scattering is becoming small in comparison with boundary scattering as is also known from the zero field data. A roughly similar g-value limit has been estimated for Cr^{2+} (Challis et al. to be published) but even at 0.4°K, the dependence was far from linear showing that the effect of resonant scattering relative to that of boundary scattering was greater in this case.

This could reflect a greater total scattering cross-section from Cr^{2+} than from Mn^{3+} but it is also consistent with the higher value of the resonant frequency for Mn^{3+} determined by de Goer (1969).

ACKNOWLEDGEMENTS

We are very grateful to Mr. W. B. Roys for his help in determining the orientation of the specimen, and to Mme de Goer for providing us with the specimen. One of us (R.G.W.) wishes to acknowledge with gratitude the receipt of an S.R.C. studentship held during the course of the work.

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FIGURE 1 - The thermal conductivity of Mn 1
 ● - Present data ▲ - de Goer

FIGURE 2 - K/T^3 of Mn 1. The mark A indicates the boundary scattering value calculated using the parameters given by de Goer (1969). Symbols as in Figure 1.

FIGURE 3 - The thermal resistivity ratio W_H/W_0 at 1.05°K and in 13.2 kOe as a function of field angle from the a' direction in the plane normal to the specimen.

FIGURE 4 - The magnetoresistance W_H/W_0 at 1.14°K at various field angles from the a' direction in the plane normal to the specimen. Measurements were also made at -99° , -49° and -3° but have been omitted for clarity. The plots at -99° and -49° were very close to those at -74° and 41° respectively.

FIGURE 5 - The magnetoresistance ratio W_H/W_0 for fields in the a' direction at various temperatures.

FIGURE 6 - The field H_{MAX} at which the low field peak occurs in Figure 5 plotted against temperature.

Note: 1 mW unit = $0.1 \text{ Wm}^{-1} \text{ K}^{-1}$

MAGNETO-THERMAL CONDUCTIVITY OF n-TYPE GERMANIUM
AT LOW TEMPERATURES*

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The thermal conductivity of high purity and of doped n-type Ge has been measured between 1.3 and 4.2 K, in magnetic inductions, B, up to 80 kG. The magnetic field is always parallel to the heat flow. The fractional change in the thermal conductivity due to the magnetic field is found to depend on the temperature, the type and concentration of impurities, and the orientation of the field relative to the crystallographic directions of the sample. In all cases the thermal conductivity is due to phonons.

For undoped Ge (with electron concentration of $6 \times 10^{13} \text{ cm}^{-3}$ at room temperature) the magnetic field is found to have no effect on the thermal conductivity, which is limited by boundary scattering, in agreement with expectations.

For Sb-doped Ge in which electrons are localized around the donor impurities (donor concentration $N_D \approx 1.5 \times 10^{16} \text{ cm}^{-3}$) the thermal conductivity decreases monotonically as B increases when $B \parallel [100]$. When $B \parallel [111]$ the thermal conductivity goes through a minimum as B increases from zero to the maximum value attainable. For P-doped Ge in which there is appreciable overlap between the wave functions of electrons centered on adjacent donors ($N_D = 1.7 \times 10^{17} \text{ cm}^{-3}$) the thermal conductivity increases monotonically as B increases for $B \parallel [100]$. The fractional changes in the thermal conductivity are larger the lower the temperature, but are generally smaller than about 30% in the temperature region investigated.

Most of the results for the doped material may be understood qualitatively as due to the magnetic field reducing slightly the extent of the impurity wave functions. When the magnetic field is not parallel to $[100]$ interpretation of our results is more difficult since the composition of the wave functions is also altered by the field.

Measurements will be made on additional crystals, and more detailed comparison with available theory will be attempted, to support the present model.

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THE PHYSICAL PROPERTIES OF Ni_3Fe FROM 80 TO 400 K*

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ABSTRACT. Thermal conductivity, λ , electrical resistivity, ρ , and Seebeck coefficient, s , measurements have been made from 80 to 400 K on a Ni_3Fe alloy (74.77 at. % Ni and 25.23 at. % Fe) in both a disordered and a highly ordered state. As indicated by a high residual resistivity of 3 $\mu\text{ohm-cm}$, the ordered sample is not perfect, and this causes a broad peak in λ at a fairly high temperature. The effect of lattice disorder is to lower λ and s and increase ρ . Although λ and ρ for the two states differ by about 50%, the Wiedemann-Franz ratio ($\lambda\rho/T$) is the same to within the combined uncertainty of the measurements. This ratio is near the Sommerfeld value, L_0 , from 180 to 400 K, and the positive deviation from L_0 below 180 indicates a significant, although not necessarily equal, lattice component to λ in both states.

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**Speaker

Thermal Conductivity of Silicon in the Boundary Scattering Regime*

by

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Thermal conductivity measurements have been made on high-purity single crystals of silicon with both rough-lapped and polished surfaces in the temperature range 1 to 4 K, where the boundary scattering of phonons is dominant. Rough-surfaced crystals cut with the rod-axis in the [111] and [110] directions gave results in good agreement with the theory for completely diffuse surface scattering. However, for a rod axis in the [100] direction there appears to be an appreciable fraction of specular reflection of the phonons. The effect depends only on the heat flux direction and not on the orientation of the rod surfaces that are exposed. Measurements on rods with cross-sections of differing rectangular geometry indicate the Casimir length ℓ_c to be given by the harmonic mean of the cross-sectional dimensions rather than a geometric mean, as is commonly used. By extension, ℓ_c is then equal to $4A/P$, where A = area, P = perimeter, and thus coincides with the mean free path for Knudsen flow of a gas. With polishing of the rod surfaces, the fraction of phonons reflecting specularly increases, and can be brought to over 90 percent at the lowest temperatures. The size-effect variation of the conductivity under such conditions is in excellent agreement with the theory.

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INTRODUCTION

Measurements of the thermal conductivity of high purity single crystals of silicon have been made in the temperature range 1-4 K. At these low temperatures, the transport of heat is by phonons as the silicon is an electrical insulator, and the heat transport is limited mostly by the scattering of phonons at the crystal surface. The thermal conductivity then does not have a unique value for the material, but depends upon the crystal dimensions. This "size-effect" of the thermal conductivity was first observed experimentally by deHaas and Biermasz¹ and an appropriate theoretical explanation was developed by Casimir².

In the Casimir model, phonon collisions with the crystal surface were assumed to result in diffuse scattering, in which the phonons are considered to be absorbed by the surface and then re-emitted with an energy distribution dependent upon the local temperature. If the crystal is isotropic, with the phonon velocities $v_i(\hat{r})$ independent of direction, the thermal conductivity for an infinitely long sample of cross-sectional radius R is

$$\kappa_{\text{iso}} = \frac{\pi^4 k^4}{15 h^3} \sum_{i=1}^3 v_i^{-2} \frac{4\pi}{3} (2R) \quad (1)$$

The specific heat at low temperatures is

$$C_{\text{iso}} = 4\pi^3 \frac{\pi^4 k^4}{15 h^3} 4\pi \sum_{i=1}^3 v_i^{-3} \quad (2)$$

Thus, by defining an average phonon velocity as

$$\langle v \rangle = \sum_{i=1}^3 v_i^{-2} / \sum_{i=1}^3 v_i^{-3} \quad (3)$$

the thermal conductivity can be expressed in the form familiar in gas kinetic theory:

$$K_{\text{iso}} = 1/3 C_{\text{iso}} \langle v \rangle \ell \quad (4)$$

with

$$\ell = \ell_c \equiv 2R. \quad (5)$$

ℓ is the phonon mean free path, and Eq. 5 is its definition. ℓ_c is termed the Casimir length, and indicates the special value of ℓ for an infinitely long crystal with perfectly diffuse walls.

Berman, Simon and Ziman³ extended this theory in two respects. Firstly, for a finite length crystal, phonons can originate at and reflect from the crystal ends, so that the conductivity is no longer simply proportional to the crystal diameter, but is dependent upon the ratio of the crystal radius to length. Secondly, some of the phonons striking the crystal surface might reflect specularly, increasing the phonon free path and hence the conductivity. The conductivity is then dependent upon a "surface roughness" factor f , which is a measure of the diffuseness of scattering and varies between $f = 1$ for perfectly diffuse scattering and $f = 0$ for perfectly specular reflection. The model continues to predict a T^3 dependence for the conductivity.

Berman, Simon and Ziman³ made measurements on diamond with ground surfaces as a test of their theory, and the conductivity showed a $T^{2.8}$ dependence and agreed reasonably well with the curve for $f = 0.60$. A later study by Berman, Foster and Ziman⁴ on rough surfaced single crystals of sapphire revealed a T^3 dependence for the conductivity, and agreement of the magnitude

within 10% of that given by the theory for $f = 1.0$. Since then, a variety of measurements have been made on dielectric materials over a wide temperature range that includes the boundary scattering regime^{5,6}, and particular attention has been given to the boundary scattering regime by Seward⁷ and Thacher⁸.

Analysis of the Data

For crystals which are anisotropic, such as silicon, the derivation of the thermal conductivity requires the evaluation of an integral over all angles of an expression containing the phonon velocities. This cannot be readily evaluated, since no simple expression for the velocities as functions of direction exist. We have, therefore, approximated the conductivity for a sample with a rod axis in the $\hat{n}$ direction as

$$K(\hat{n}) = 4\pi^3 \frac{\pi^4 k^4}{15 h^3} \sum_{i=1}^3 [v(\hat{n})]^{-2} \frac{4\pi}{3} (2R) \quad (6)$$

where the sum is over the acoustic phonon velocities for the $\hat{n}$ direction. We may write the specific heat of an anisotropic crystal as

$$C = 4\pi^3 \frac{\pi^4 k^4}{15 h^3} 4\pi \sum_{i=1}^3 \langle v_i^{-3} \rangle \quad (7)$$

and note that the sum is over the direction-averaged velocities and is the same for all rod directions. The "kinetic theory" form for the conductivity is then obtained if we define the average phonon velocity as

$$\langle v_1 \rangle = \sum_{i=1}^3 [v_i(\hat{n})]^{-2} / \sum_{i=1}^3 \langle v_i^{-3} \rangle \quad (8)$$

Another approach, admittedly somewhat arbitrary, is to take:

$$\langle v_2 \rangle = \sum_{i=1}^3 [v_i(\hat{n})]^{-2} / \sum_{i=1}^3 [v_i(\hat{n})]^{-3} \quad (9)$$

This, in effect, takes the specific heat to be that of phonons travelling in the $\hat{n}$ direction. The averages of Eqs. (8) and (9) are given in Table I. Also included are the velocities of the longitudinal and the two transverse acoustic modes, respectively.

Another problem in the analysis of the data results from the geometrical shape of the samples. In most cases, these were nearly square in cross-section with widths w_1 , and w_2 , while the Casimir expression applies to a circular cross-section of radius R . Following Casimir, it has been customary to define an effective radius R_e by

$$\pi R_e^2 = w_1 w_2 \quad (10)$$

and to take

$$\ell_c = 2R = 1.12 \sqrt{w_1 w_2} \quad (11)$$

We find, however, that the surface scattering can be better represented by taking ℓ_c proportional to an harmonic mean rather than a geometric mean dimension, and thus throughout use

$$\ell_c = w_{hm} = 2[w_1^{-1} + w_2^{-1}]^{-1} \quad (12)$$

For both rectangular and circular cross-section, ℓ_c is then equal to $4A/P$, where A = area and P = perimeter, and thus coincides with the mean free path for Knudsen flow of a gas⁹. The validity of Eq. (12) will be discussed later. For purposes of comparing the results with the Berman, Simon and Ziman theory, we also take the shape factor to be $(\ell_c/2L)$ in place of (R/L) , where L is the total length of the sample.

Experimental Methods and Results

The details of the experimental apparatus, which is of fairly standard design, are discussed elsewhere^{10,11}. The thermometers are of the germanium resistance type, manufactured by Texas Instruments, Inc.¹², and were calibrated against the helium vapor pressure using the 1958 He⁴ scale. Thermal contact of thermometers to the sample is made with indium-faced clamps, lightly coated with Apiezon vacuum grease. Measurements of thermal contact resistances of this type showed that the thermometers were within 0.05 millidegrees of the crystal temperature at their point of attachment. Typically, the thermometers were separated by a distance of 2 to 3 cm. It is estimated that the measurements of the conductivity have an overall accuracy of 5%.

Typical samples had widths from 0.5 to 2 mm and were 30 to 40 mm in length. "Rough" surfaces were prepared by lapping with either 600 grit silicon carbide or 20 μ , 10 μ or 5 μ aluminum oxide powder. Smooth surfaces were prepared by 6 μ and then 1 μ diamond polishing, using an oil lubricant. Very smooth surfaces were obtained by further polishing the best 1 μ diamond surfaces with Lustrox¹³, which combines mechanical and chemical polishing. Much practice was needed to develop optimum polishing technique. The very smoothest surfaces had surface structure beyond the resolution of the replica technique for electron microscope examination. Samples were prepared for electron diffraction examination, which was kindly done by Dr. G. F. Tufts of General Telephone and Electronics Laboratories, Inc., Bayside, New York. Although the results were somewhat variable, the best samples showed a high degree of perfection as evidenced by well-defined spots and Kikuchi lines.

Samples were cut from three different crystals, which shall be designated A, B and C. Crystal A was grown in the [111] direction, and had a room-temperature resistivity of 1.95 ohm-meters. From it samples of square cross-section were cut with the rod axis of the samples in the [111] direction, and with the exposed rod faces in the {110} and {112} directions. The dependence of the conductivity upon the crystal width is illustrated in Fig. 1, and the results are summarized in Table II. The qualitative features of the theory are borne out, as the measured conductivity increases roughly as T^3 and with the sample width. However, the exponent in the temperature-dependence tends to be slightly less than cubic especially for the samples lapped with the finer grits. The behavior can be attributed to a slight temperature dependence of the mean free path. This could in principle result from either some specularly in the surface scattering or some contribution from bulk scattering. However, none of these effects appears to be present. At the lower temperatures, where specularly would be more likely owing to the longer average phonon wavelength, the "measured" mean free path is very close to the Casimir value when $\langle v \rangle_2$ and Eq. (12) are used to compute ℓ and ℓ_c , respectively. The use of $\langle v \rangle_1$ and/or Eq. (11) would make $\ell/\ell_c < 1$. This would be possible only if there were appreciable bulk scattering. But then ℓ/ℓ_c should be strongly size dependent, whereas it is observed to be almost constant over the 7.5 to 1 range of $(\ell_c/2L)$ values investigated. The size-dependence predicted by the Berman, Simon and Ziman theory for perfectly diffuse scattering is slight, and is illustrated in Fig. 2. The size dependence does appear to be present, but it is difficult to verify. Included also is a sample of hexagonal cross-section, which has all exposed faces of the {110} type. Good agreement with other [111] rod results

was obtained, showing that the rough $\{110\}$ and $\{11\bar{2}\}$ surfaces scatter phonons equally well. It is worthy of note that even though the cross-section is somewhat close to circular, the agreement was improved by taking ℓ_c as $4A/P$.

Crystals B and C were grown in the $[100]$ direction, and had room temperature resistivities of 5.00 and 30.0 ohm-meters, respectively. One sample from crystal C was cut with the rod axis in the $[111]$ direction, with rod faces $\{110\}$ and $\{11\bar{2}\}$, and gave results entirely in agreement with crystal A. Since this crystal is apparently more pure, it provides further argument against any effect of bulk scattering.

Several samples with a $[100]$ rod axis were cut from crystals B and C, some with $\{100\}$ and some with $\{110\}$ faces exposed, and the results are summarized in Table III. The temperature dependence for most of these samples lies closer to $T^{2.9}$ than $T^{3.0}$, but this probably results from lapping with too fine a grit. There is no essential difference in the value of ℓ/ℓ_c between samples from crystals B and C, or between samples with different exposed faces. However, as shown in Fig. 2, the values of ℓ/ℓ_c for the $[100]$ rods lie distinctly higher than the $[111]$ rods, with the diffuseness f about 0.77 for the $[100]$ rods, and about 1.0 for the $[111]$ rods. The sample cut with the $[111]$ rod axis from crystal C rules out the possibility that some difference in the crystals is responsible. The effect, therefore, must be an orientational one. It is of a peculiar nature, however, since the rod axis, not the surface normal, is the significant direction. This is borne out most clearly by a comparison to the hexagonal-shaped rod, which had a $[111]$ rod axis and $\{110\}$ faces. Its conductivity is quite different from the $[100]$ rod axis samples with $\{110\}$ faces.

One run made on a sample cut from crystal C with a $[110]$ rod axis and pairs of $\{100\}$ and $\{110\}$ faces. The value of ℓ/ℓ_c agreed with the $[111]$ rods even though the faces are the same as those on the $[100]$ rods (Fig. 2). This further confirms the significance of the rod axis orientation.

The actual conductivity of a sample with a $[100]$ rod axis is about double that of a comparable $[111]$ rod sample. If $\langle v \rangle_2$ were used to compute the mean free path ℓ , the spread between the values of ℓ/ℓ_c between the $[111]$ and $[100]$ rods would increase over that obtained with $\langle v \rangle_2$. This raises the question of whether some other more accurate formula for $\langle v \rangle$ would fully account for the higher $[100]$ conductivity. The mode velocities in Table I disclose that this is most unlikely; the transverse modes, which account for about eighty percent of the conductivity, are simply too nearly isotropic to permit such a range of variation. Thus, the conclusion seems inescapable that acoustic phonons travelling in directions $[100]$ are reflected with appreciable specularity even from rough surfaces.

The samples discussed heretofore were all nearly square in cross-section. In order to substantiate the use of the harmonic mean (Eq. (12)) for the Casimir length, four samples of rectangular cross-section were run whose ratios of widths varied from 4/1 to 9/1. All these samples were cut from crystal A, with the rod axis in the $[111]$ direction and the face of greater width in the $\{110\}$ direction. All faces were lapped with either 20 μ or 10 μ , Al_2O_3 lapping compound, so that we could confidently assume completely diffuse scattering. Comparison of the measured value of ℓ with w_{HM} and $\sqrt{w_1 w_2}$ is given in Table IV, and it is seen that the use of w_{HM} is appropriate.

However, most unexpectedly, the log plot of the conductivity versus the temperature for these rectangular samples turned out not to be linear below 1.7 K, as illustrated in Fig. 3. Two checks were made on this effect: first, the conductivity of a sample of square cross-section was again measured, and

found to follow a simple power law over the entire range, thus ruling out any possible change in thermometry. Secondly, Run 99 (Table IV) is a repeat of the sample of Run 93, except that the distance between the thermometer clamps was changed from 2.66 to 1.43 cm. No difference was found in the measured value of the conductivity, so that the effect is not a result of special changes in the temperature distribution at the ends of the samples. The departure from a single power law is about 20% at 1.3 K.

Some results for samples polished with 1 μ diamond and with Lustrox are shown in Fig. 4. Of the two Lustrox-polished samples, Run 70 is a fairly typical one and Run 63 is one of the two very smoothest surfaces obtained. The temperature dependence is much less than T^3 , indicating that the phonon mean free path ℓ is now strongly temperature dependent. This is undoubtedly a consequence of the temperature dependence of the phonon wavelength distribution since one would expect phonons to be scattered specularly whenever the surface imperfections are roughly smaller in size than their wavelength. It is also seen that for the smooth surfaces the log plot of the thermal conductivity versus the temperature is no longer linear, the deviation becoming more severe as the smoothness improves.

The values of ℓ/ℓ_c for samples with 1 μ diamond polishes scatter about the curves of constant diffuseness f in the theory of Berman, Simon and Ziman, with values of f between 0.5 and 0.4 typical. The scatter probably reflects surface variations from the 1 μ polishing, since optical examination of the surfaces revealed a wide range of surface textures. Therefore, it is difficult to make meaningful comparisons between samples of different rod axes or rod faces, although the value of ℓ/ℓ_c obtained for the sample with the [111] rod axis is somewhat lower than the samples with a [100] rod axis, as was true of the rough surfaces.

The results obtained with surfaces polished with Lustrox was dependent upon polishing technique. With poorer technique, the surfaces when observed through an optical microscope using Nomarski (interference contrast) illumination had a pebbled texture with many grooves resulting from poor diamond polishing technique, and often were pitted from too long an exposure to the Lustrox. Generally the conductivity of these poorer surfaces increased from that of the diamond polished surfaces, although for one sample the conductivity was essentially unchanged.

Seven samples with "good" Lustrox surfaces showed reasonable consistency in the smoothness of the surface as determined by the conductivity. This is shown in Fig. 5, where the values of ℓ/ℓ_c at 3K and 1.5K are plotted on the curves of Berman, Simon and Ziman. The values of ℓ/ℓ_c at 3K do not lie quite parallel to the curves of constant diffuseness, but at 1.5K they lie almost on the $f = 0.10$ curve. (It will be noted that the conductivity is highly sensitive to f for small f values, and therefore that considerable variation about constant f curves is to be expected). All points are for samples with a [100] rod axis with the exception of one of the lower points, which is for a [111] rod axis. Five of these samples had widths of about 0.9 mm, one had a width of 1.80 mm, and the remaining one a width of 0.467 mm.

The results in Fig. 5 are for different samples, and it is possible that the variation in the conductivities is not a result of the size-effect but rather a result of differences in surface polishing. Therefore, a single sample from the above group was progressively shortened in length to increase the value of (ℓ/L) . The results are shown in Fig. 6, and give entirely satisfactory agreement with the theory.

Two samples of very smooth surfaces were produced, with values of ℓ/ℓ_c at 1.5 K about 30% above the $f = 1.10$ curve of the theory. On examination with the optical microscope, both these surfaces and those surfaces characterized as "good" (from Fig. 5) were almost featureless. Thus, the smoothness of a surface cannot be characterized sufficiently well by optical examination so that meaningful comparison between different rod axes or rod faces can be made.

The downward curvature illustrated in Fig. 4 for the log plot of the conductivity versus the temperature gives the appearance of the conductivity returning to a T^3 dependence. For the "good" Lustrox surfaces, a limit to the increase in the free mean path is reached at about 1.5 K. Since the mean free path is then reaching some temperature-independent value, the question is raised as to what the remaining scattering mechanism might be, and whether it is connected with the bulk or the surface. The fact that two surfaces smoother than the "good" Lustrox-polished ones could be prepared suggest the mechanism is still a surface effect. It would be very desirable to extend these measurements below 1.3 K, to determine if the conductivity does maintain a T^3 dependence for the smooth surfaces.

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Table I. Sound velocities in silicon at low temperatures (10^5 cm/sec.)

	<u>[100]</u>	<u>[111]</u>	<u>[110]</u>
v_{ℓ}	8.47	9.42	9.18
v_{t_1}	5.86	5.11	5.86
v_{t_2}	5.86	5.11	4.68
$\langle v \rangle_1$	5.00	6.11	6.00
$\langle v \rangle_2$	6.22	5.42	5.41

Note: (v_{ℓ} , v_{t_1} , and v_{t_2} are the velocities of the longitudinal and the two transverse acoustic modes respectively; $\langle v \rangle_1$ and $\langle v \rangle_2$ are the averages as given by Eqs. (13) and (14) respectively).

Table II. Summary of results for rough-surfaced samples with [111] rod axis.

<u>Run</u>	<u>Sample</u>	<u>Lap</u>	<u>ℓ_c, cm</u>	<u>$\ell_c/2L$</u>	<u>$\frac{d \log \kappa}{d \log T}$</u>	<u>(ℓ/ℓ_c)</u>	
						<u>3 K</u>	<u>1.5 K</u>
20 and 21	Al-1a	10 μ	0.217	.053	2.95	0.96	0.97
43	Al-5a	10 μ	0.100	.0156	3.00	1.09	1.09
44	Al-6a	10 μ	0.052	.0071	2.90	0.99	1.07
47	Al-7a	10 μ	0.055	.0110	2.96	1.00	1.04
48	Al-8a	10 μ	0.064	.0077	2.96	1.03	1.08
51	Al-10a	5 μ	0.286	.0339	2.70	0.85	1.02
83	Al-13a	5 μ	0.199	.0236	2.88	0.93	0.96
97	Al-15a	#600 SiC	0.087	.0112	2.93	0.88	0.91
85	Cl-1a	#600 SiC	0.095	.0197	2.94	0.98	1.02

Note: Lapping Compound is Al₂O₃, unless otherwise specified.

Table III. Summary of results for rough-surfaced samples with [100] rod axis.

<u>Run</u>	<u>Sample</u>	<u>Lap</u>	<u>ℓ_c, cm</u>	<u>$\ell_c/2L$</u>	<u>$\frac{d \log \kappa}{d \log T}$</u>	<u>ℓ/ℓ_c</u>	
						<u>3 K</u>	<u>1.5 K</u>
57	B2-2-2a	10 μ	.082	0.0109	2.90	1.50	1.60
72	C2-2-3a	5 μ	.071	0.0080	2.92	1.58	1.70
75	C2-3-3a	5 μ	.071	0.0105	2.90	1.57	1.69
76	B2-3-5a	5 μ	.082	0.0099	2.88	1.54	1.70
78	C2-3-5a	5 μ	.195	0.0241	2.84	1.35	1.49
84	B2-3-5b	#600 SiC	.069	0.0082	2.96	1.49	1.53
94	C2-3-3c	10 μ & Annealed	.071	0.0140	2.94	1.47	1.51

Note: Lapping Compound in Al₂O₃, unless otherwise specified.

Table IV. Summary of results for samples of rectangular cross-section.

Run	w_1/w_2	$\ell(3\text{ K})(\text{cm})$	$\sqrt{w_1 w_2}(\text{cm})$	$w_{\text{HM}}(\text{cm})$
40	3.9	.121	.144	.117
86	6.5	.0840	.177	.0790
98	7.3	.0968	.146	.0963
93 and 99	9.2	.0818	.118	.0709

Fig. 1. Thermal conductivity of square rough-surfaced [111] rods. Curves are labelled with rod widths in millimeters.

Fig. 2. Comparison of thermal conductivities of rough-surfaced rods with BSZ theory.

Fig. 3. Thermal conductivity of a rectangular rough-surfaced [111] rod, of width ratio 9:1 (Run No. 93 in Table IV).

Fig. 4. Thermal conductivity of various polished samples.

Fig. 5. Comparison of thermal conductivities of Lustrox-polished rods with BSZ theory.

Fig. 6. Comparison of thermal conductivity of a single Lustrox-polished rod with BSZ theory. Rod was polished once and then progressively shortened.

LOW TEMPERATURE ANISOTROPIC THERMAL
CONDUCTIVITY OF CADMIUM SELENIDE

By

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ABSTRACT

The thermal conductivity of cadmium selenide single crystals has been measured from 6 to 100 K. Both undoped and high resistivity (selenium compensated) samples were tested, with measurements made both parallel and perpendicular to the "c" axis.

The experimentation was performed using a doubly guarded unidirectional steady state thermal conductivity apparatus.

The results show that heat-treatment under selenium vapor has no effect on the thermal conductivity in this temperature range. Above 30 K no anisotropic effects were noticed, while below this temperature the ratio $\lambda_{||} / \lambda_{\perp}$ varies from 1.2 to 1.8 on the high resistivity specimens. This anisotropy is attributed to angularly dependent defect formation and is not considered basic to the lattice structure.

An attempt was made to fit the data using the Callaway theory. It was found that the combination of isotope, boundary, and phonon-phonon scattering alone will not account for the observed thermal conductivity. Varying the parameters in the theory would not allow all regions of the thermal conductivity curve to be simultaneously fitted to the data. It is concluded that impurity scattering and electron-phonon scattering, which were not included in the theory, could account for the observed thermal conductivity.

INTRODUCTION

Cadmium selenide is a II-VI compound semi-conductor that exhibits both the wurtzite and zinc blende structures, but the cubic form is metastable. The lattice parameters have been measured by Devlin, et al. (1), Khansevarov (2), Litwin (3), and Stuckes and Farrell (4), Elastic piezoelastic, and dielectric constants have been measured by Berlincourt, et al (5). The specific heat has recently been measured from 55 to 300 K by Demidenko (6). Kendall (7) has studied the electrical conductivity both perpendicular and parallel to the "c" axis in hexagonal CdSe from 77 to 300 K. The energy gap has been reported to be 1.72 ev at 300 K (8, 9) and 1.83 ev at 77 K (7). Anisotropic sound velocities of CdSe have been measured by Ioffe and Ioffe (9), who also measured the thermal conductivity of polycrystalline samples at 300 K. The photoelectric properties have been measured by Bube and MacDonald (10), Stupp (11), Langer, et al (12), and Tang (13). This paper reports measurements of the thermal conductivity of single crystal CdSe from 6 to 100 K which has not previously been reported. Measurements were made both perpendicular and parallel to the "c" axis on undoped crystals and crystals heat-treated under selenium to achieve high electrical resistivity.

EXPERIMENTAL PROCEDURE

The samples were single crystals purchased from Semi-elements, Inc. of Saxonburg, Pennsylvania. They were all n-type. Spectrographic analysis indicates a purity higher than .9999. Samples were purchased with the "c" axis perpendicular and the "c" axis parallel to the long axis. These crystals were approximately 5 mm square by 40 mm long. They were supplied with a 5 micron finish. The nominal electrical resistivity was reported to be 1 ohm-cm on the undoped samples, and $>10^6$ ohm-cm in the dark on the heat-treated samples.

The thermal conductivity measurements were made in a unidirectional, steady state guarded calorimeter of conventional design. The power input to

the sample was calculated from voltage and current measurements taken from a heater at one end of the specimen. The temperature gradient was determined from a combination of germanium resistance thermometers and a copper-constantan differential thermocouple. The resistance thermometers were used below 40 K and the differential thermocouple was used above 40 K. These thermometers were attached to the specimen with small indium faced copper clamps. Details of the apparatus design including uncertainty estimates are presented in Reference (14). Uncertainties in the data ranged from 3 to 9 percent, depending upon the temperature and measurement sensitivity, and are represented as uncertainty brackets on the data points in Figures 1 and 2.

RESULTS

The data on the samples with the "c" axis parallel to the temperature gradient are shown in Figure 1. The undoped sample shows a lower conductivity than the heat treated one. The undoped sample was slightly damaged before measurement, and in addition no spectrographic analysis had been performed upon it. It is thought that some surface defect induced strains or some unaccounted-for impurities may be responsible for the lower thermal conductivity found. The data on the crystals with the "c" axis perpendicular to the temperature gradient are shown in Figure 2. It is seen that heat treatment had no effect on the thermal conductivity. This indicates that lattice conductivity is the dominant mode at these temperatures.

The high resistivity samples exhibit anisotropy in the thermal conductivity below 30 K, but the data are nearly identical above this temperature. The lattice constants and elastic constants indicate that CdSe is weakly hexagonal, so that anisotropy in the properties which depend upon them is expected to be small. The present results are similar to those observed by Vook (15) on his unirradiated CdS samples. Cadmium selenide seems to exhibit some anisotropic defect formation below 30 K. The observed anisotropy is not considered to be basic to the lattice structure of a pure crystal. All the samples exhibited a dip in the thermal conductivity at 20 K.

This phenomena has been observed on other crystals before and is usually attributed to an impurity (11, 17).

DISCUSSION

An attempt was made to fit the data using the Callaway theory (18). The correction term for normal phonon-phonon processes was neglected in this attempt. Under this approximation the thermal conductivity is expressed by

$$\lambda(T) = \frac{k}{2\pi^2 c} \left(\frac{kT}{\hbar}\right)^3 \int_0^{\theta/T} \frac{\tau_T x^4 e^x dx}{(e^x - 1)^2} \quad (1)$$

where

$$\tau_T^{-1} = \frac{c}{LF} + A\omega^4 + (B_u e^{-\theta/aT} + B_n) \omega^2 T^3 \quad (2)$$

the first term in Equation (2) is the boundary scattering term due to Casimir (19), where $L = 1.12 \sqrt{l_1 l_2}$ where l_1, l_2 is the crosssectional area of the sample. The factor F is a correction for finite sample length and non-diffuse reflection of phonons at the boundaries taken from Berman (20). The term $A\omega^4$ represents point defects. Initially A was calculated from Klemen's expression for isotope scattering (21), as modified for compounds by Holland (16). The $\omega^2 T^3$ term is Herring's (22) form of the relaxation time dependence for phonon-phonon scattering. The B_u term denotes Umklapp processes and the B_n term denotes normal processes. The "a" in the exponential term is a parameter characteristic of dispersion in the frequency spectrum (16).

Equation (1) was numerically integrated on an IBM 360 computer. The theoretical value of the Casimir length L was 5.715 mm. The value for the isotope scattering parameter A was $5.72 \times 10^{-43} \text{ sec}^{-3}$. B_u and B_n were calculated from Equation (36) of Callaway's original paper (18), which indicated initial values of $1.0 \times 10^{-21} \text{ sec deg}^{-3}$. An average sound velocity of $2.05 \times 10^5 \text{ cm/sec}$, taken from Reference (9), was used, resulting in an average Debye temperature of 185 K. The dispersion parameter "a" was initially set equal to 3.

The results are shown on the solid curve in Figure 1. Clearly these results do not fit the data. The value of A based on mass difference scattering due to isotopes is too small. The fit is also poor in the boundary scattering and high temperature regions.

The parameters were varied to fit the data on the $c_{\perp}$ specimens, using the measured sound speed of 1.52×10^5 cm/sec perpendicular to the "c" axis, with the Debye cutoff temperature adjusted accordingly. The fitted curve is shown on Figure 2.

The fit is poor in the boundary scattering region. Using the correction (the F factor) for finite sample length from Reference (20) would not reduce the curve sufficiently to fit the data. Reducing L to fit the data in the low temperature region flattened the curve in the region of the maximum. No readjustment of the other parameters would fit all regions simultaneously. It is thought that another scattering mechanism, perhaps electron-phonon scattering, is present in these samples. However, no attempt was made to include this type of scattering in the relaxation time expression.

SUMMARY

The thermal conductivity of CdSe has been measured from 6 to 100 K. Over this range the thermal conduction is entirely lattice conduction. Anisotropy observed below 30 K is attributed to angularly dependent defect formation, and not to the basic lattice structure. An attempt to fit the data from the Callaway theory was only partially successful.

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Figure 1. THERMAL CONDUCTIVITY OF CADMIUM SELENIDE
PARALLEL TO THE "c" AXIS

Figure 2. THERMAL CONDUCTIVITY OF CADMIUM SELENIDE
PERPENDICULAR TO THE "c" AXIS

PHONON SCATTERING IN DISORDERED ALLOYS OF GaSb-InSb at 300°K

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ABSTRACT :

Measurements have been made of the thermal conductivity of alloys of GaSb-InSb at 300°K and over the whole range of concentration. In general the data are in good agreement with those of Woolley and Briggs (1964) and Kudman, Ekstrom and Seidel (1967) but lie well above those of Zeinalov and Aliev (1967) in the middle of the concentration range. An approximate fit to the data can be obtained using a Debye model if N-process scattering is included but it is not possible to conclude whether longitudinal or transverse modes predominate and it is suggested that this is also the case for all previous work on semiconductor alloys. It is further noted that the additional thermal resistance in the alloys is approximately proportional to the reciprocal relaxation time for defect scattering up to much higher defect concentrations than would be the case for a Debye model. This could indicate that conduction is by phonons in a narrow frequency range as in the model by Holland (1963).

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LATTICE THERMAL CONDUCTIVITY OF COPPER GERMANIUM CHALCOGENIDES

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ABSTRACT - Effects of an annealing at 700°C for 20 days on the lattice thermal conductivity of Cu_2GeSe_3 were studied. It is found that there is no remarkable change of the absolute value as well as the $T^{-0.7}$ dependency on the temperature of the lattice thermal conductivity by annealing, while the Hall mobility of the holes increases by two orders. The lattice thermal conductivity of Cu_2GeS_3 having the cubic structure was found to vary as T^{-1} with temperature while the one having distorted structure varies as $T^{-0.6}$. The lattice thermal conductivity of AgBiSe_2 and GeTe both of which have distorted structure, was found to vary less rapidly than T^{-1} with temperature. It is suggested that the deviation from the T^{-1} law of the lattice thermal conductivity is associated with the distorted crystal structures. The phonon scattering mechanism accompanied by the electronic transition between closely separated impurity levels as suggested by Spitzer et al. for Cd_3As_2 may be a dominant one in these crystals. The lattice thermal conductivity of Cu_2SnSe_3 - Cu_2GeSe_3 system, particularly for the alloys close to Cu_2SnSe_3 , were measured between 100 and 300 K and the results are also explained by the model used for Cu_2GeSe_3 .

I. INTRODUCTION

In a previous paper it was reported that the lattice thermal conductivity, λ_p , of Cu_2GeX_3 ($X=\text{S}, \text{Se}$) varies with temperature as $T^{-0.7 \sim -0.8}$, while that of Cu_2SnX_3 varies as T^{-1} in the temperature range from 50 K to 300 K. [1] (Fig.1). We suggested that the $T^{-0.7 \sim -0.8}$ dependency of Cu_2GeX_3 was due to the distortion of its crystal structure from cubic symmetry which the structure of Cu_2SnX_3 has. In order to ascertain the plausibility of this suggestion, the following investigations were carried out:

(1) Effects of the annealing on the temperature dependency of λ_p of Cu_2GeSe_3 . - If the $T^{-0.7}$ dependency of λ_p of Cu_2GeSe_3 is due to some stress generated in course of the crystallization, annealing should reveal the T^{-1} dependency of λ_p .

(2) Measurement of λ_p of the high temperature form of Cu_2GeS_3 . - It is known that Cu_2GeS_3 has a distorted structure at room temperature, while it transforms to the cubic structure above 670°C [2]. If the $T^{-0.8}$ dependency observed on Cu_2GeS_3 is due to its distorted structure, the λ_p of the high temperature form should show the T^{-1} dependency.

Figure 1. Temperature dependencies of the lattice thermal conductivity for Cu_2SnX_3 and Cu_2GeX_3 ($\text{X} = \text{S}, \text{Se}$).

(3) Measurement of λ_p of the another substances having distorted structure. - AgBiSe_2 has a cubic structure above 287°C , while it has a phase of distorted structure which is rhombohedral between 120°C and 287°C [3]. GeTe has a NaCl type structure above 700 K, while below this temperature it shows a rhombohedral distortion of the NaCl lattice [4]. It is interesting to study the temperature dependency of λ_p of these substances.

(4) Measurement of λ_p of Cu_2SnSe_3 - Cu_2GeSe_3 alloys. - In a previous work [1], the thermal conductivity of Cu_2SnSe_3 - Cu_2GeSe_3 alloys containing 20, 40, 60 and 80 % Cu_2GeSe_3 respectively were measured between 100 K and 300 K. It was found that all of these alloys had the similar values and the temperature dependency of λ_p to those of Cu_2GeSe_3 . As it is also interesting to study a transition from the T^{-1} dependency of λ_p for Cu_2SnSe_3 to the $T^{-0.7}$ dependency for Cu_2GeSe_3 , the thermal conductivity of the alloy system Cu_2SnSe_3 - Cu_2GeSe_3 in a composition range between 0 and 20 % of Cu_2GeSe_3 were measured between 50 K and 300 K.

II. EXPERIMENTAL PROCEDURES AND RESULTS

The method of the measurements of the thermal conductivity is the same as used in a previous work [1]. Annealing of Cu_2GeSe_3 was carried out at a desired temperature controled within $\pm 5^\circ\text{C}$. Preparation of Cu_2GeSe_3 having cubic structure was carried out by lowering it's melt to an ambient temperature of 800°C and then keeping this temperature for about 24 hours before quenching. AgBiSe_2 having distorted structure was also prepared by the similar method. Preparation of GeTe having a distorted structure was carried out by usual Bridgman method. Temperature dependency of λ_p and the Hall mobility, μ_H , of Cu_2GeSe_3 before and after annealing at 700°C for 20 days were shown in figure 2. It can be seen that there is no remarkable change both of the absolute value and the temperature dependency of λ_p by the annealing, while μ_H increases by about a two orders. This fact indicates that the $T^{-0.7}$ dependency of λ_p is not due to some stress generated in course of the crystallization.

Figure 3 shows the variation of λ_p with temperature of the quenched crystal of Cu_2GeSe_3 having cubic structure. For comparison, λ_p for the unquenched crystal having distorted structure is also shown in the same figure. It can be seen that λ_p of the cubic crystal varies with temperature as T^{-1} . Figure 4 shows the temperature variation of λ_p of the crystals having distorted structure of AgBiSe_2 and GeTe . It can be seen that λ_p varies less rapidly than as T^{-1} in these crystals. Result for GeTe quantitatively agrees with that reported by Ure [5]. These results indicate that the deviation from the T^{-1} dependency of λ_p is due to the distorted crystal structures.

Figure 5 shows λ_p of Cu_2SnSe_3 - Cu_2GeSe_3 system as a function of compositions. The calculated curve by the Klemens-Drabble's theory on the phonon scattering by mass difference is shown by dotted line [6]. Figure 6 shows again the data for figure 5 in a limited range of compositions between 0 and 1 %. In this figure power m for the T^{-m} dependency of λ_p is also plotted as a function of the compositions. It is noted that the reduction of the absolute value of λ_p and it's power m for the T^{-m} dependency of Cu_2SnSe_3 to the corresponding values for Cu_2GeSe_3 occurs when only 1 % Cu_2GeSe_3 is added.

III. DISCUSSIONS

Possible mechanisms which reduce the rate of variation of λ_p with temperature will be reviewed in the following.

Figure 2. Temperature dependencies of the lattice thermal conductivity and the Hall mobility of Cu_2GeSe_3 before and after annealing.

Figure 3. Temperature dependencies of the lattice thermal conductivity for cubic- and tetragonal- Cu_2GeS_3 .

(1) Contribution of the bipolar diffusion of carriers to the thermal conductivity. — Hashimoto [7] found that the thermal conductivity of Bi_2Se_3 varies less rapidly than T^{-1} in the temperature range 100 K to 250 K. He explained the result by the electronic contribution due to bi-polar diffusion of carriers to the thermal conductivity.

(2) Quantum transfer of energy between neighboring atoms. — Certain semiconductors, for instance, AgSbTe_2 [8] and Ga_2Se_3 [9], have thermal conductivities no more than 0.4 to 0.6 $\text{W m}^{-1} \text{K}^{-1}$ and vary less rapidly than as T^{-1} . Ioffe [9] suggested that, for materials with such low thermal conductivities, there is temperature-independent heat conduction mechanism due to a quantum exchange of the vibrating energy between neighboring atoms.

(3) Phonon scattering by imperfections arranged in line. — According to the theory of thermal conductivity in solids at low temperatures developed by Klemens [10], temperature-independent thermal conductivity should be observed when phonons are scattered by imperfections arranged in lines for instance, a core of the edge dislocations.

(4) Phonon scattering containing a electronic transition between impurity levels having small energy difference. — The lattice thermal conductivity of Cd_3As_2 was found by Spitzer et al. [11] to be nearly independent of the temperature between about 200 K and 400 K. They suggested that there were closely separated energy levels associated with the lattice defects and that phonons having nearly the same energy as the energy difference between

Figure 4. Temperature dependencies of the lattice thermal conductivity for AgBiSe_2 and GeTe .

these levels were scattered through the electronic transition between these levels.

Next problem is to consider which mechanism can explain the temperature dependency of λ_p in Cu_2GeX_3 and the other substances having distorted structure.

Mechanism (1) makes appreciable contribution to thermal conductivity when the separate contribution of electrons and holes to the electrical conductivity are comparable in magnitude [12]. However, the concentration of holes in our specimen is very large ($\sim 10^{26} \text{ m}^{-3}$) and the contribution of electrons to the electrical conductivity can be neglected in the temperature range studied. This can also be seen in the temperature variations of the electrical conductivity and the Hall coefficient [13].

Mechanism (2) requires a phonon mean free path, l , to be comparable with the lattice spacing, d . However, λ_p of Cu_2GeX_3 is not so small and a rough estimation leads to a value of $l \sim 10 d$ at 300 K.

If the mechanism (3) is assumed to be a dominant one, T^3 dependency of λ_p at lower temperatures in Cu_2GeSe_3 , which may be attributed to the phonon scattering by strain field due to dislocations, could not be explained (see figure 1). It may be possible that temperature variation will be enhanced by some stress near the dislocations.

In order that the mechanism (4) is a dominant one, very closely separated energy levels are necessary to be present in the band structure. The electrical conductivity and the Hall coefficient were measured between 100 and 300 K on the three specimens of as-grown, annealed at 200°C and annealed at

Figure 5. Lattice thermal conductivity of Cu_2SnSe_3 - Cu_2GeSe_3 system as a function of the compositions. The dotted curve is a calculated one by the Klemens-Drabble's theory.

700°C, respectively. In order to explain the temperature dependency of the Hall coefficient and the Hall mobility of these specimens, it was found that two acceptor levels separated in energy by 0.013 eV must be assumed[13]. These acceptors are probably associated with the different kind of Se vacancies. Consequently, the phonon scattering mechanism (4) may be important in Cu_2GeSe_3 because 0.013 eV is the phonon energy at about 150 K. By annealing, the lower levels appear to be annihilated and the upper levels to be generated. If the lower levels more effectively scatter the holes than the upper levels, μ_H should be increased by annealing while λ_p should be insensitive to the annealing because the transition probability is proportional to

Figure 6. Lattice thermal conductivity and its power m for the T^{-m} dependency for Cu_2SnSe_3 - Cu_2GeSe_3 system as a function of the compositions from 0 to 1.0 % of Cu_2GeSe_3 .

the product of the number of occupied lower levels and that of the unoccupied upper levels.

Distortion of the cubic structure in Cu_2GeSe_3 may be attributed to an ordering of copper and germanium atoms in the lattice[14]. The electronic state of the Se vacancy should be different in unit cells having ordered arrangement of the atoms from in the cells having random arrangement of the atoms which are contained in the ordered distorted lattice. Such circumstances are probably similar for other materials having distorted structures.

Cu_2SnSe_3 - Cu_2GeSe_3 alloys can be considered as mixture of the ordered lattices and the disordered lattices. It is probable that the alloys containing 1 % Cu_2GeSe_3 are in the same situation as that of Cu_2GeSe_3 . It is also probable that the transition probability between the acceptor levels associated with the ordered and the disordered lattices has nearly the same value over the alloy system.

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Gases

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CALCULATION OF COMPRESSIBILITY FACTORS
FOR ARGON, NITROGEN AND METHANE

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ABSTRACT

The isothermal compression, up to nearly half the liquid densities, of argon, nitrogen and methane at three different temperatures ranging from 0 to 150° C are investigated by using the cell method originally developed by Lennard-Jones and Devonshire. A two-potential model is adopted in the evaluation of the classical partition function to partially take into account the contributions arising from the correlations of molecular motions. The Lennard-Jones 12-6 potential and the Kihara hard core model are used respectively for the calculation of the energy of the geometrically symmetric lattice and the energy of augmentation arising from molecular motions. The potential parameters used in the calculations are those derived from fitting the second virial coefficient of dilute gases. The resulting calculated isotherms are compared with experimental measurements; agreement obtained is favorably good for the range of density considered.

The Kihara hard core model with parameters determined for dilute gases is found to be ineffective at very high densities. This agrees with the conclusion derived from the Monte Carlo and molecular dynamics calculations that the Lennard-Jones 12-6 potential is tolerably good in representing the effective pair potential at liquid densities.

I. INTRODUCTION

The classical theories for imperfect gases or dense fluids, i.e., the theory of cluster expansions^(1,2) and the hierarchy of integral equations for the radial distribution function and the higher order correlation functions,^(3,4) are well understood. Indeed, these theories are powerful in sustaining mathematical rigor in describing the dynamics of molecules to all orders of direct and indirect interactions. In the direct application to real fluids of the theory of cluster expansions, however, only a few low order virial coefficients can be evaluated exactly due to the fact that intolerable and ever-increasing mathematical complexities are encountered as one attempts to handle a cluster of a larger number of molecules simultaneously interacting with one another; thus, only dilute systems can be treated with satisfactory austerity. On the other hand, the hierarchy of an infinite number of integral equations must be appropriately truncated in order to practically solve for the radial distribution function which is ultimately essential for the evaluation of the thermodynamic properties of fluids. The Yvon-Born-Green equation, which uses the superposition approximation, has been solved for the case of argon with the adoption of a "realistic" Lennard-Jones (6-12) potential; the numerical calculations involved are of considerable magnitude; nevertheless, due to the nature of the superposition approximation, the results obtained agree only qualitatively with experimental measurements at high densities. More refined approximation methods, such as the hyper-netted-chain equation [3] and the Percus-Yevick equation [5], yield results superior to those from the superposition approximation, at least for argon; yet the agreement with experiments is still qualitative in nature in spite of the large amount

of numerical calculations that must be performed for the multiple integrals involved. These calculations are extremely time-consuming, even with the use of a modern high-speed computer. A refinement of the hyper-netted-chain and Percus-Yevick equations to take into account the triplet potentials has recently been given by Rushbrook and Silbert [6] and by Rowlinson [7]; no numerical results have yet been made available.

The cell method, developed by Lennard-Jones and Devonshire [8] for imperfect gases, is of fundamental importance in the theory of fluids. This method is simple in procedure and easy to use in performing numerical calculations. Although it has the drawback, clearly inherited from the approximate manner in the evaluation of the classical partition function, of being not valid for dilute gases, and although presently existing calculations using a Lennard-Jones 12-6 potential indicated that it appeared to describe the state of solids or of "expanded solids" rather than fluids, it, nevertheless, has been very useful in interpreting the thermodynamic properties of dense fluids and fluid mixtures. A critical and detailed examination of the cell method has been given by Barker [9]. Through numerical computations, this paper shows that the Lennard-Jones and Devonshire formulation of the cell model can be modified to yield compressibility factors for nonpolar and nearly spherical molecules comparable with experimental measurements for a limited range in density. The results for argon, nitrogen and methane are in reasonable agreement with experimental data. The reason for choosing these three fluids is that extensive experimental measurements at high densities are readily available for comparison.

II. THE CELL METHOD

Detailed description of the cell method has been given elsewhere [8,9,10]. Its derivation is briefly reviewed here for the purpose of clarity.

Consider a system of N identical molecules. The classical canonical partition function for such a system is given by

$$Z = \frac{1}{N! h^{3N}} \int \dots \int e^{-H(\vec{q}; \vec{p})/kT} d\vec{q} d\vec{p} \quad (1)$$

where $(\vec{q}; \vec{p}) = (\vec{q}_1, \vec{q}_2, \dots, \vec{q}_N; \vec{p}_1, \vec{p}_2, \dots, \vec{p}_N)$ are the coordinates and momenta of the N molecules, $d\vec{q} d\vec{p}$ is the volume element in the neighborhood of $(\vec{q}; \vec{p})$ T is the absolute temperature, k is the Boltzmann constant and h is Planck's constant; the Hamiltonian of the N -molecule system is assumed to have the form

$$H(\vec{q}; \vec{p}) = \sum_i \frac{p_i^2}{2m} + U(\vec{q}) \quad (2)$$

in which m is the mass of a molecule, U is the potential energy of the entire system which is assumed to depend only upon the coordinates of the molecules. Integrating over the momenta in Eq. (1) yields

$$Z = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} Q \quad (3)$$

where Q , the so called configuration integral, is given by

$$Q = \int \dots \int e^{-U(\vec{q})/kT} d\vec{q} \quad (4)$$

In the cell method approximation, the coordinate space of the system is divided in an appropriate symmetrical manner into N equal cells, one for each molecule; and, in the limit of high densities, the motion of a

molecule is confined to within its own cell in the field of force due to all the other molecules in the neighboring cells. If the energy per molecule is w when every molecule is at the center of its cell, the potential energy, in excess of w , of a molecule at a distance r from the center of its own cell, is the sum of the contributions, averaged over the surface of a sphere of radius r centered at the cell center, from all the other molecules when they are fixed at the centers of their respective cells, and the contributions arising from the correlations of molecular motions in different cells [9]. Denoting this excessive potential energy by $u(r)$, the configuration integral then has the form

$$Q = N! e^{-Nw/kT} \left[4\pi \int_0^R e^{-u(r)/kT} r^2 dr \right]^N \quad (5)$$

where R is the radius of a sphere having a volume equal to that of a cell; the factor $N!$ accounts for the fact that all N cells are equally available for all molecules. The partition function is then*

$$Z = \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} e^{-Nw/kT} \left[4\pi \int_0^R e^{-u(r)/kT} r^2 dr \right]^N \quad (6)$$

and the pressure is given by the usual thermodynamic relation

$$\frac{pv}{kT} = \frac{v}{N} \left(\frac{\partial \ln Z}{\partial v} \right)_T \quad (7)$$

in which p is the pressure and v is the volume per molecule,

* For the general case the partition function has the form $Z' = \frac{1}{\sigma^N} Z$, with Z given by Eq. (6). However, if σ is volume-independent, which is assumed in most cases [11], the pressure given by Eq. (7) will not be affected.

or the cell volume which is here implicitly related to the radius R appearing in the evaluation of Z .

III. THE POTENTIAL ENERGY WITHIN A CELL

Following Lennard-Jones, the coordinate space of the system is divided in such a manner that the centers of the cells form a face-centered cubic lattice. Let a denote the distance between nearest neighbors. Then the cell volume is given by

$$a^3 = \sqrt{2}V \quad (8)$$

and the radius of the spherical volume available for a molecule to move about is

$$R = \frac{1}{\sqrt{2}} \left(\frac{3}{2\pi} \right)^{1/3} a \quad (9)$$

To a molecule at the center of its cell, there are 12 neighbors arranged on a sphere of radius a , 6 on a sphere of radius $a\sqrt{2}$ and 24 on a sphere of radius $a\sqrt{3}$. In the evaluation of the potential energy of a molecule, only its neighbors on the three nearest shells will be considered; the contributions to the potential energy due to other distant neighbors are small enough to be neglected in practically all cases.

It is assumed, as in most practically useful theories of fluids, that the contributions to the configurational energy arising from direct many-body interactions are included in an "effective" pair potential, and thus the potential energy of a fluid is pairwise additive in terms of the effective pair potential. Clearly, the energies $u(r)$ and w are related to the effective pair potentials between two molecules.

The potential energy of a system of identical molecules is

$$U = \sum'_{i \neq j} \phi(r_{ij}) \quad (10)$$

where $\sum'$ indicates summation over all $i, j \leq N$, the number of molecules or cells except $i=j$, $\phi(r_{ij})$ is the effective pair potential between

molecules i and j separated at a distance r_{ij} from each other. Denote by the subscripts io and jo the cell centers of the two molecules, then one has the identity

$$\begin{aligned} \phi(r_{ij}) = & \phi(r_{iojo}) + [\phi(r_{ij}) - \phi(r_{iojo})] + [\phi(r_{jio}) - \phi(r_{iojo})] \\ & + \{[\phi(r_{ij}) - \phi(r_{ij})] - [\phi(r_{jio}) - \phi(r_{iojo})]\} \end{aligned} \quad (11)$$

where the brace represents the contribution arising from the correlations of molecular motions. The potential energy of the system can thus be written in the form

$$\begin{aligned} U = Nw + \sum_i \sum_{j \neq i} & \{ [\phi(r_{ij}) - \phi(r_{iojo})] \\ & + 1/2 [\phi(r_{ij}) - \phi(r_{ij})] - 1/2 [\phi(r_{jio}) - \phi(r_{iojo})] \} \\ = Nw + 1/2 \sum_i \sum_{j \neq i} & \{ [\phi(r_{ij}) + \phi(r_{ij})] - [\phi(r_{jio}) + \phi(r_{iojo})] \} \end{aligned} \quad (12)$$

where

$$w = \frac{1}{2N} \sum_i \phi(r_{iojo}) \quad (13)$$

is the "lattice energy" per molecule when all molecules are at their cell centers.

In order to make further practical progress within the realm of the cell method, it is necessary to calculate, or estimate, the correlation correction due to the motions of the molecules as expressed in Eq. (11). The direct complete evaluation of this correction is extremely difficult, if not impossible, due to mathematical difficulties [9] and the lack of an adequate effective pair potential which would effectively account for the many-body interactions for all molecular configurations. It appears plausible, although arbitrary from the point of view of mathe-

mathematical rigor, to "smear" the cells of the j molecules, referring to a certain i molecule, with certain probability distribution for the evaluation of the correlation correction term. Thus one may write

$$U = Nw + 1/2 \sum_i \sum_{j \neq i} \{ [\psi_{ij}(|\vec{r}_i|) + \bar{\psi}_{ij}(|\vec{r}_i|)] \quad (14)$$

$$- [\psi_{ij}(0) + \bar{\psi}_{ij}(0)] \}$$

where

$$\psi_{ij}(|\vec{r}_i|) = \phi(r_{ijo}) \quad (15)$$

and $\bar{\psi}_{ij}(|\vec{r}_i|)$ is the effective potential smeared over the j -cells. Comparing Eq. (14) with Eq. (15) or (6), it is seen that the excessive potential energy $u(r)$ arises from the change in $1/2[\psi_{ij}(|\vec{r}|) + \bar{\psi}_{ij}(|\vec{r}|)]$ when a molecule moves from its cell center to the position $\vec{r}$ with all the other molecules "smeared" throughout their individual cell volumes. The smearing scheme outlined above, however, is neither mathematically rigorous nor is it easy to perform due to the complicated distribution of molecules in the cells. But what it does suggest is to inquire into the question whether it be possible to find an "equivalent" effective pair potential in terms of the distance between $\vec{r}$ and the cell center of another molecule in concern such that the cell method will yield results comparable to experimental measurements. In this sense of approximation, therefore, it seems conceivable to adopt a two-potential model: one for the "lattice energy" of the hypothetical solid when all molecules are at their cell centers and another for the energy augmentation given by the brace in Eq. (14). The present work shows the comparison between the experimental compressibility factors for argon, nitrogen and methane and those calculated by using this approximation.

The effective pair potential by no means can be made to represent the true potential energy of a many-body system because there exists

many-body forces which are not pairwise additive. From the assumption of pairwise additivity, however, statistical mechanical calculations do yield results which agree, quantitatively at low densities and at least qualitatively at moderate and high densities, with experimental observations. The use of an effective pair potential, wherever possible, is obviously for the purpose of avoiding mathematical complications arising from many-body interactions. Although many fluids and fluid mixtures have been investigated with the use of the Lennard-Jones 12-6 potential, it is now known that this potential is not adequately effective for fluids at low and moderate densities because it fails in predicting the temperature dependence of the thermodynamic properties [12,13] (paradoxically, however, the Lennard-Jones 12-6 potential with parameters determined at low densities is quite good as an effective pair potential at high, especially at near-liquid, densities; see Discussion).

For a molecule moving in the field of other molecules, as in the case of a gas, Kihara [14] has developed from the consideration of the geometry of convex molecules a core model for the effective pair potential which has been successfully applied in the evaluation of the second virial and Joule-Thomson coefficients of gases [15,16].

The smearing scheme mentioned above is equivalent to finding a potential effective for the cell method in terms of the distances between the position of the molecule under consideration (the *i*-molecule) and the average, weighted by the intermolecular energy, positions of its neighbors (the *j*-molecules). Since the Kihara core model has proved to be successful in describing the behavior of a gas of which the molecules are chaotic in thermal motion, it seems to indicate that this model embodies somewhat of the many-body correlations. Therefore it is believed that the core

model should be adopted for the evaluation of the excess potential energy $u(r)$. The Kihara potential has the form

$$\phi(s) = 4\varepsilon_K \left[\left(\frac{1-\gamma}{s/\sigma_K-\gamma} \right)^{12} - \left(\frac{1-\gamma}{s/\sigma_K-\gamma} \right)^6 \right] \quad (16)$$

where γ is the measure of the size of the hard core, s is the distance between two molecules, ε_K is the depth of the potential and $\phi_K(\sigma_K) = 0$. We make the assumption, as a very first approximation, that the neighboring molecules (the j -molecules) on the average occupy the origins of their respective cells.

Consider a molecule at a distance r from the center of its cell and one of its neighbors on the n^{th} shell ($n = 1, 2, 3$) as shown in Fig. 1. The distance between the two molecules is

$$y_n = a(n\zeta^2 - 2\sqrt{n}\zeta\cos\theta)^{1/2} \quad (17)$$

$$\zeta = r/a \quad (18)$$

and the potential energy of interaction is then

$$\phi_{Kn}(\zeta) = 4\varepsilon_K \left[\left(\frac{1-\gamma}{y_n/\sigma_K-\gamma} \right)^{12} - \left(\frac{1-\gamma}{y_n/\sigma_K-\gamma} \right)^6 \right] \quad (19)$$

Introduce the notations

$$\rho = 2^{1/6}(1-\gamma)\sigma_K \quad (20)$$

$$\beta = 2^{-1/3}\gamma/(1-\gamma) \quad (21)$$

$$v_K^* = v/\rho^3 \quad (22)$$

where v again is the volume of a cell, ρ is the distance between the surface of the hard core and the point at which $\phi_K = \varepsilon_K$, a minimum. Eq. (19) in terms of v_K^* becomes to take the form

$$\phi_{Kn}(\zeta) = \frac{\epsilon_K}{4v_K^{*4}} \left[(n+\zeta^2 - 2\sqrt{n}\zeta \cos \theta)^{1/2} - \beta/v_K^{*1/3} \right]^{-12} - \frac{\epsilon_K}{v_K^{*2}} \left[(n+\zeta^2 - 2\sqrt{n}\zeta \cos \theta)^{1/2} - \beta/v_K^{*1/3} \right]^{-6} \quad (23)$$

Integrating ϕ_{Kn} over the spherical surface of radius $r = \zeta a$ and dividing through by 4π , it is readily obtained that the contribution to the average potential energy of a molecule at a distance $r = \zeta a$ from the center of its own cell due to a molecule on the n^{th} shell is

$$\begin{aligned} \bar{\phi}_{Kn}(\zeta) &= \frac{\epsilon_K}{880v_K^{*4}} \left[\frac{1}{\sqrt{n}\zeta} \left\{ \left(\sqrt{n}-\zeta - \frac{\beta}{v_K^{*1/3}} \right)^{-11} \left[11(\sqrt{n}-\zeta) - \frac{\beta}{v_K^{*1/3}} \right] \right. \right. \\ &\quad \left. \left. - \left(\sqrt{n}+\zeta - \frac{\beta}{v_K^{*1/3}} \right)^{-11} \left[11(\sqrt{n}+\zeta) - \frac{\beta}{v_K^{*1/3}} \right] \right\} \right] \\ &\quad - \frac{\epsilon_K}{40v_K^{*2}} \left[\frac{1}{\sqrt{n}\zeta} \left\{ \left(\sqrt{n}-\zeta - \frac{\beta}{v_K^{*1/3}} \right)^{-5} \left[5(\sqrt{n}-\zeta) - \frac{\beta}{v_K^{*1/3}} \right] \right. \right. \\ &\quad \left. \left. - \left(\sqrt{n}+\zeta - \frac{\beta}{v_K^{*1/3}} \right)^{-5} \left[5(\sqrt{n}+\zeta) - \frac{\beta}{v_K^{*1/3}} \right] \right\} \right] \end{aligned} \quad (24)$$

Let N_n be the number of molecules on the n^{th} shell, i.e., $N_1 = 12$, $N_2 = 6$, $N_3 = 24$. The total average potential energy of interaction is given by

$$\Phi_K(\zeta) = \sum_{n=1}^3 N_n \bar{\phi}_{Kn}(\zeta) \quad (25)$$

and the total average potential energy in excess of w takes the form

$$u(\zeta) = \phi_K(\zeta) - \lim_{\zeta \rightarrow 0} \phi_K(\zeta) \quad (26)$$

$$= \sum_{n=1}^3 N_n [\bar{\phi}_{Kn}(\zeta) - \phi_{Kn}(0)]$$

where

$$\begin{aligned} \phi_{Kn}(0) &= \lim_{\zeta \rightarrow 0} \bar{\phi}_{Kn}(\zeta) \\ &= \frac{\epsilon_K}{4v_K^{*4}} \left(\sqrt{n} - \frac{\beta}{v_K^{*1/3}} \right)^{-12} - \frac{\epsilon_K}{v_K^{*2}} \left(\sqrt{n} - \frac{\beta}{v_K^{*1/3}} \right)^{-6} \end{aligned} \quad (27)$$

A spherically or nearly spherically symmetric nonpolar molecule in the crystalline state, as suggested by Kihara [14], has nonuniform but possibly symmetric charge distributions due to the fixed geometry of the lattice structure. Thus a molecule in the crystalline state has electric multipoles which usually need not be considered in the gaseous state. This, in addition to the many-body interactions, probably partially explains the paradox that a Kihara pair potential workable for the second virial and Joule-Thomson coefficients fails to yield a correct value for the cohesive energy of solid argon and other inert gas molecular crystals [12,13]. The potential energy of interaction per molecule when all molecules are at the centers of their cells, as implied by the mechanical procedures in the development of the cell model, should be approximated by the cohesive energy of a "crystal" at the corresponding lattice spacing. Rossi and Danon [11] have shown that for crystalline molecular solids of inert gas molecules the Lennard-Jones 12-6 potential can be used as a good effective pair potential to yield reasonable results for the cohesive energy. It therefore appears

adequate, a priori from evidences made available in the literature, that the Lennard-Jones potential be used for the evaluation of w . This potential has the form

$$\phi_{LJ}(s) = 4\epsilon_{LJ} \left[\left(\frac{\sigma_{LJ}}{s} \right)^{12} - \left(\frac{\sigma_{LJ}}{s} \right)^6 \right] \quad (28)$$

where s is the distance between two molecules and ϵ_{LJ} and σ_{LJ} are constant parameters. Summing over the pair potentials given by Eq. (28) between a molecule and its neighbors on the three nearest shells yields, upon dividing by a factor of 2 for the purpose of averaging.

$$w = 6\epsilon_{LJ} \left(\frac{94257}{93275} \frac{1}{v_{LJ}^{*4}} - \frac{491}{216} \frac{1}{v_{LJ}^{*2}} \right) \quad (29)$$

$$v_{LJ}^{*} = v/\sigma_{LJ}^3 = \frac{1}{\sqrt{2}} \left(\frac{a}{\sigma_{LJ}} \right)^3 \quad (30)$$

A comparison between the Kihara and Lennard-Jones potential for nitrogen is shown in Fig. 2; the potential parameters are given in Table I.

IV. THE EQUATION OF STATE

It is convenient to introduce a reduced temperature and a free volume defined by

$$T^* = kT/\epsilon_K \quad (31)$$

$$\begin{aligned} v_f^* &= \frac{4\pi}{\sigma_K^3} \int_0^R e^{-u(r)/kT} r^2 dr \\ &= 4\pi\sqrt{2} v_K^* \int_0^{\frac{1}{\sqrt{2}} \left(\frac{3}{2\pi} \right)^{1/3}} e^{-u(\zeta)/\epsilon_K T^*} \zeta^2 d\zeta \end{aligned} \quad (32)$$

where the relations $\zeta = r/a$ and $a^3 = \sqrt{2}v$ have been used. The partition function given by Eq. (6) is then

$$Z = \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} v_f^{*N} \sigma_K^{3N} e^{-Nw/\epsilon_K T^*} \quad (33)$$

and the compressibility factor is given by

$$\begin{aligned} \frac{pv}{kT} &= \frac{v_K^*}{N} \left(\frac{\partial \ln Z}{\partial v_K^*} \right)_{T^*} \\ &= v_K^* \left[\frac{1}{v_f^*} \left(\frac{\partial v_f^*}{\partial v_K^*} \right)_{T^*} - \frac{1}{\epsilon_K T^*} \frac{dw}{dv_K^*} \right] \end{aligned} \quad (34)$$

In the above equation, v_f^* is defined in Eq. (32),

$$\left(\frac{\partial v_f^*}{\partial v_K^*} \right)_{T^*} = \frac{v_f^*}{v_K^*} - 4\pi\sqrt{2} \frac{v_K^*}{\epsilon_K T^*} \int_0^{\frac{1}{\sqrt{2}} \left(\frac{3}{2\pi} \right)^{1/3}} \frac{du(\zeta)}{dv_K^*} e^{-u(\zeta)/\epsilon_K T^*} \zeta^2 d\zeta \quad (35)$$

$$\frac{du(\zeta)}{dv_K^*} = \sum_{n=1}^3 N_n \left[\frac{d\bar{\phi}_n(\zeta)}{dv_K^*} - \frac{d\phi_n(0)}{dv_K^*} \right] \quad (36)$$

$$\begin{aligned} \frac{d\bar{\phi}_n(\zeta)}{dv_K^*} &= - \frac{\epsilon_K}{220v_K^{*5}} \left[\frac{1}{\sqrt{n}\zeta} \left\{ \left(\sqrt{n}-\zeta - \frac{\beta}{v_K^{*1/3}} \right) \left[11(n-\zeta) - \frac{\beta}{v_K^{*1/3}} \right] \right. \right. \\ &\quad \left. \left. - \left(\sqrt{n}+\zeta - \frac{\beta}{v_K^{*1/3}} \right) \left[11(\sqrt{n}+\zeta) - \frac{\beta}{v_K^{*1/3}} \right] \right\} \right] \\ &\quad - \frac{\beta\epsilon_K}{264v_K^{*16/3}} \left[\frac{1}{\sqrt{n}\zeta} \left\{ \left(\sqrt{n}-\zeta - \frac{\beta}{v_K^{*1/3}} \right) \left[12(\sqrt{n}-\zeta) - \frac{\beta}{v_K^{*1/3}} \right] \right. \right. \\ &\quad \left. \left. - \left(\sqrt{n}+\zeta - \frac{\beta}{v_K^{*1/3}} \right) \left[12(\sqrt{n}+\zeta) - \frac{\beta}{v_K^{*1/3}} \right] \right\} \right] \\ &\quad + \frac{\epsilon_K}{20v_K^{*3}} \left[\frac{1}{\sqrt{n}\zeta} \left\{ \left(\sqrt{n}-\zeta - \frac{\beta}{v_K^{*1/3}} \right) \left[5(\sqrt{n}-\zeta) - \frac{\beta}{v_K^{*1/3}} \right] \right. \right. \end{aligned}$$

$$\begin{aligned}
& - \left(\sqrt{n} + \zeta - \frac{\beta}{v_K^{*1/3}} \right)^{-5} \left[5 \left(\sqrt{n} + \zeta \right) - \frac{\beta}{v_K^{*1/3}} \right] \}] \\
& - \frac{\beta \epsilon_K}{30 v_K^{*10/3}} \left[\frac{1}{\sqrt{n} \zeta} \left\{ \left(\sqrt{n} - \zeta - \frac{\beta}{v_K^{*1/3}} \right)^{-6} \left[6 \left(\sqrt{n} - \zeta \right) - \frac{\beta}{v_K^{*1/3}} \right] \right. \right. \right. \\
& \left. \left. \left. - \left(\sqrt{n} + \zeta - \frac{\beta}{v_K^{*1/3}} \right)^{-6} \left[6 \left(\sqrt{n} + \zeta \right) - \frac{\beta}{v_K^{*1/3}} \right] \right\} \right]
\end{aligned}$$

$$\frac{d\phi_n(0)}{dv_K^*} = \frac{\epsilon_K n \left[-1 + 2 v_K^{*2} \left(\sqrt{n} - \beta/v_K^{*1/3} \right)^6 \right]}{v_K^{*5} \left(\sqrt{n} - \beta/v_K^{*1/3} \right)^{13}} \quad (38)$$

and the derivative of w with respect to v_K^* is given by

$$\frac{dw}{dv_K^*} = 12 \epsilon_{LJ} \left(\frac{\sigma_{LJ}}{\rho} \right)^6 v_K^{*-3} \left[- \frac{188514}{93275} \left(\frac{LJ}{\rho} \right)^6 v_K^{*-2} + \frac{491}{216} \right] \quad (39)$$

V. RESULTS

Three gases have been studied, argon, nitrogen and methane. Eq. (34) was used for the calculation of the compressibility factors. The potential parameters used are given in Table I.

TABLE I. Potential parameters

Gas	ϵ_K/k (°K)	γ	σ_K ° (Å)	ϵ_{LJ}/k (°K)	σ_{LJ} ° (Å)
A	147.2	0.111	3.314	117.7	3.504
N ₂	139.2	0.200	3.526	95.9	3.710
CH ₄	204.3	0.167	3.620	148.9	3.783

The Kihara potential parameters were those reported by Shirwood and Prausnitz [15], and the Lennard-Jones potential parameters are selected from reported values available in the literature such that the resulting calculated compressibility factors compare most favorably with experimental measurements. Both sets of parameters listed in Table I were determined from second virial coefficient data, presumably at low densities. By using different Lennard-Jones parameters, the computed isotherms have been found to deviate only slightly from those reported here.

Eq. (34) was carefully programmed to fit for the use of a computer and the numerical computation was facilitated by the Computer Center at The West Virginia Institute of Technology. In carrying out the integrals involved in the evaluation of v_f^* and $(\partial v_f^* / \partial v_K^*)$, given by Eqs. (32) and (35), a ζ -increment of the size $\frac{1}{2} \left(\frac{3}{2\pi} \right)^{1/3} / 60$ was used. No significant changes had been found in the values of the integrals when half of the above increment size was used. Thus it assures that there is no significant accumulative error in the numerical computation.

Fig. 3 shows the comparison between the computed and experimental compressibility factors for argon at three different temperatures. Both

the Lennard-Jones and Kihara parameters used were reported by Sherwood and Prausnitz [15]. The experimental data are those reported by Michels et al. [17]. The agreement is satisfactory, to within 10% or less, for all three temperatures except at very high densities. Also compared in Fig. 3 are the values computed by Wentorf et al. [18] from the Lennard-Jones potential. The inadequacy of the use of the Lennard-Jones potential in the cell method for the description of gases at high densities is clearly demonstrated.

The results for nitrogen are shown in Fig. 4. The Lennard-Jones parameters are those reported by Holborn and Otto [19], and the experimental points are by Michels et al. [20]. Again, the compressibility factors calculated by Wentorf et al. are plotted for comparison. And, again, the present work shows satisfactory results except at very high densities.

The computed compressibility factors for methane at three different temperatures are shown in Fig. 5. Comparison with experimental measurements, reported by Sage and Lacey [21], is made in Fig. 6, where pv/kT is plotted against the reduced pressure $P_r = P/P_c$ for various values of the reduced temperature $T_r = T/T_c$ with P_c and T_c being the pressure and temperature at the critical point. The cell method is inaccurate for gases at low densities, and there is no clear criterion as to how high the density should be in order for this method to be applicable with reasonable prediction. Fig. 6 shows that the applicability of the cell method also depends on the temperature. The calculated compressibility factors are consistently higher than the experimental data at high densities; however, the agreement is satisfactorily within 5.5% up to $P_r = 15$.

VI. DISCUSSION

The cell method is expected to yield results the more reasonable the higher the density. This is because of the fact that the higher the density the more probable that a molecule is imprisoned or trapped by its immediate neighbors. However, it was observed in comparison of the results of the present work with experimental measurements that the computed compressibility factors are consistently higher than the experimentally deduced data at very high densities, even though the deviation is not intolerable. This discrepancy demands some explanation. The Kihara potential parameters used in the present calculations are those derived from fitting the second virial coefficients of dilute gases. There is strong evidence that the Kihara potential determined for dilute gases can not represent correctly the effective pair potential at high densities [22]. Both the Monte Carlo calculations of McDonald and Singer [23] and the molecular dynamics calculations of Verlet [24] have provided quasi-experimental data showing that the Lennard-Jones 12-6 potential, while being incorrect for gaseous argon, is in fact tolerably good in representing the effective pair potential for liquid argon. The Kihara potential reduces to the Lennard-Jones form when $\gamma = 0$. Since the Kihara potential is more successful than the Lennard-Jones potential in describing dilute gases, it may be conjectured here that the former, if used as an effective pair potential for the entire range in density, must have density dependent parameters to account for the effect of many-body interactions which is the more significant the denser the fluid. To demonstrate the effect of the core size on the calculated compressibility factors, a set of trial computations was made with a smaller value for γ . The γ -value was so reduced

that $\rho = 2^{1/6}(1 - \gamma)\sigma_K$ remained constant, thus, making the repulsive part less steep and the bowl of the potential broader. The results of the trial calculations at high densities of the three gases investigated are shown in the respective figures. The necessity of a density dependent core size in the Kihara model is clearly demonstrated. The other parameters, i.e., ϵ and σ , must also vary accordingly with density in order that the Kihara potential can be used to represent the effective pair potential at high densities. At extremely high densities (possibly near the density of solid), the correlations between the motions of molecules should be small and the molecular configurations become solid-like, the Kihara potential thus should approach the form of the Lennard-Jones potential. This probably partially explains why the cell method in conjunction with the Lennard-Jones pair potential seemed to have described solids or "expanded solids" rather than normal fluids.

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FIGURE 1. Coordinates for the evaluation of $u(r)$.

FIGURE 2. Comparison of Lennard-Jones and Kihara potentials for nitrogen. The parameters are given in Table I.

FIGURE 3. Compression of argon. The solid curves are the calculated results of Eq. (34). The long broken curves are calculated by Wentorf et. al. and the short broken curves are for $\gamma = 0.095$. The experimental points are due to Michels et. al.

FIGURE 4. Compression of nitrogen. The solid curves are the calculated results of Eq. (34). The long broken curves are calculated by Wentorf et. al. and the short broken curves are for $\gamma = 0.185$. The experimental points are due to Michels et. al.

FIGURE 5. Calculated compressibility factors for methane.

FIGURE 6. Compression of methane. The solid curves are the calculated results of Eq. (34). The broken curves are for $\gamma = 0.160$. The experimental points are due to Sage et. al.

The Thermal Conductivity of High Temperature Gases and Their
Determination From Experiments With Electric Arc Discharges

By

Uwe Bauder

The "cascade arc technique" for the measurement of plasma transport properties up to 26,000°K and the mathematical evaluation method of the measured data is described.

Results are reported for hydrogen and nitrogen at 1 atm obtained by MAECKER under contract with this laboratory, together with the first results of an in-house program concerned with the determination of the properties of argon at high pressures up to 1000 atm.

In both cases the arc discharge is operated under steady state conditions. Because of its cylindrical symmetry and its well defined boundary conditions, the "cascade arc" is particularly well suited for transport property measurements. In addition, very high power densities and corresponding high temperatures and degrees of ionization may be obtained.

The thermal and electrical conductivities of optically thin plasma as well as its radiation source strength as a function of gas temperature and pressure may be determined from the following measurements in the cascade arc: (1) voltage/current characteristics of the arc column, $E, I(T, p)$; (2) total radiation $P(T, p)$; and (3) temperature distribution $T(r)$ across the column. A new and more accurate method was developed for the determination of the arc characteristics. The total radiation is measured with thermocouples. The temperature distribution is spectroscopically determined from absolute and relative total line and continuum radiation intensities by side-on and end-on observations.

With these experimental data, numerical integration of the energy equation of the arc column yields the transport properties of the particular plasma under study.

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The thermal conductivity coefficients of carbon dioxide
at high temperature and high pressure

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Abstract -

This paper describes the measurements of the thermal conductivity coefficients of carbon dioxide, in the temperature interval 25°C to 688°C, between the pressure of 1 bar and 1200 bars.

In the previous paper (1) (2) technique and results of the thermal conductivity measurements at high temperature and high pressure have been described. Particularly, values of the thermal conductivity coefficients of argon and helium have been reported in reference (3), of methane and ethane in reference (4).

A concentric cylinder method was used with a gap between the cylinders of 0.2mm in the temperature interval 25°C to 525°C and of 0.4mm in the temperature interval 400°C to 688°C.

The most important corrections which lead to the true value of the thermal conductivity are described. The accuracy of the tabulated data is estimated to be 2.5 per cent in the temperature range from 25°C to 400°C and at all pressures.

A comparison of the results shows a reasonable agreement with most of the published data. In the critical region an anomalous increase of the thermal conductivity was observed but the apparatus used was not really adequate in this region.

Key words

carbon dioxide, convection, high pressure, high temperature, radiation, thermal conductivity.

I- Introduction

The coefficient of thermal conductivity of carbon dioxide is of great interest to the design engineers of heat exchangers of nuclear reactors.

Carbon dioxide has been found very interesting in the range of medium temperatures, (limitation in temperature being due, as it is well known to the onset of corrosion), for its thermal properties (because its thermal conductivity and its specific heat are important), for its chemical properties (stability), and for its nuclear properties (stability to the radiation, absence of induced radioactivity transparency to the neutrons) and also for economical reasons. The practical limits of its range of use are 100 bars and 700°C.

The thermal conductivity coefficients of carbon dioxide have been measured by several workers. The most pertinent references at atmospheric pres-

sure, within the range of temperature of our present measurements being : Archer (5), Cheung (6) , Franck (7), Geier and Schäfer (8), de Haas and Westenberg (9) Johnston and Grilly (10), Keyes (11) (12), Rothman (13), Rothman and Bromley (14), Salceanu and Bojin (15), Schäfer (16), Sherratt and Griffiths (17), Stops (18), Timrot and Vargaftik (19), Vargaftik and Oleshchok (20), Vines (21).

Even if the maximum error is less than 2%, according to the various authors, in reality data obtained by the same method vary sometimes by 10 to 12%. This fact complicates the compilation of critical tables. In several experimental papers are given only the measured values (and sometimes plotted values) of the thermal conductivity coefficients; the basic primary data like the geometrical size of the cell, the temperature drop in the layer, the pressure, are often lacking; so it is very difficult to analyse these papers and determine if it is necessary the proper correction. It has been shown by Vukalovich and Altounin (22), that the discrepancies between the results on carbon dioxide, of different authors are the consequence of an insufficiently rigorous allowance for the temperature discontinuity. This is done by means of well-known formula for the temperature discontinuity :

$$\Delta T = \Delta T(\text{gas}) + B(1/P) \quad (1)$$

where ΔT is the temperature drop between the outer surface of the internal cylinder and the inner surface of the external cylinder.

$\Delta T(\text{gas})$ is the temperature drop in the gas layer.

B is a quantity which depends on the physical properties of the gas and the material of the cylinder, as well as on the geometrical parameters of the instrument.

P is the pressure.

It must be observed that at high temperature the radiation correction is very important (several per cent of the heat transfer by conduction) and very difficult to determine with accuracy even by a differential method; therefore it can seriously alter the heat transfer by conduction.

The effect of pressure on the thermal conductivity of carbon dioxide has been carried out in a large range of temperature and pressure. The most important experimental works are presented in table I. The data of Oskolkova (27) and of Stolyarov et al. (30) deal with the higher temperatures, the maximum being 200°C. The data of Guildner (34), those of Michels, Sengers and Van der Gulik (35), and those of Sellschopp (24) when plotted as isotherms of the conductivity versus the density show a maximum of the conductivity near the critical point (72.85 atm, 31.2°C). It should be mentioned that other high pressure data did not show an anomaly in the critical region (36). However, actually preference is for Michels' data which are considered to be particularly accurate.

II- Method of measurement

Two vertical coaxial cylinder cells were used in these measurements. The first with a gap of 0.2mm from 25°C to 525°C, the second with a gap of

Table I

Experimental works on thermal conductivity coefficients
of carbon dioxide at high pressure.

Year	Authors	Temperature range (T°C)	Pressure range (bar)	Method	Ref.
1934	Kardos	32.5- 35			
1934	Sellschopp	11.5- 40.7	1.1- 90.3	Conc. cyl.	24
1941	Cooper	0. - 40.9	1. - 75.	Hot wire	25
1946	Golubev	31.7- 99.8	50. -500	Hot wire	26
1948	Oskolkova	18.5-199.3	20. -300	Hot wire	27
1949	Borovik	10. - 40.	50. - 90		28
1949	Timrot, Oskolkova				29
1950	Stolyarov, Ipatiev Teodorovitch	37. -194.	20. -200	Hot wire	30
1951	Lenoir, Comings	41.1- 67.2	2.2-208	Conc. cyl.	31
1952	Shingarev	-45. -+91.	1. -200	Hot wire	32
1952	Keyes	0.7- 50.	13.9- 62.6	Conc. cyl.	33
1958 1962	Guildner	3.6- 75.2	2.2-300.	Conc. cyl.	34
1962	Michels, Sengers Van der Gulik	25. - 75.	1.-2140.	Par. plates	35
1963	Amirkhanov, Adamov	20. - 31.	57.- 74.	Par. plates	36
1968	Kuentzmann	35. - 84.	1. - 61	Conc. cyl.	37

0.4mm from 400 to 688°C.

The steady-state heat flow by conduction between two isothermal cylinders (1) (31) (33) (34) can be written applying Fourier's law as :

$$Q = \lambda K \Delta T \quad (2)$$

where

Q is the radial heat flow transmitted by conduction .

λ is the thermal conductivity of the medium between the isothermal cylinders .

K is the geometric constant of the cell .

ΔT is the temperature difference between the emitting and receiving cylinder .

The heat transfer by conduction, the geometric constant and the temperature difference must know to determine the thermal conductivity. The geometric constant of the cell is equal to $\frac{\ln(r_2/r_1)}{2\pi l}$ for infinite cylinders, and can be calculate using r_2 and r_1 the diameters of the receiving and emitting cylinders and l the length of the emitting cylinder. We have made a very accurate determination of the geometric constant by measuring the electrical capacity of the cell at room temperature (cf ref. 38).

III- Corrections

The total heat Q absorbed by the heating element can be accurately determine by measuring the voltage across the heater and the current passing through it. Unfortunately all of this heat is not transferred by conduction through the gas layer. At least three other heat transfer paths are possible, they are :

1) by conduction along the wires and all plugs used to hold and position the inner cylinder (Q_p).

2) by radiation across the gap (Q_r)

3) by free convection (Q_c)

Most of these corrections are difficult to apply. Therefore, in order to achieve reliable measurements, we have used a cell for which the smallest number of corrections are necessary. The method and procedure used to find these correction are thoroughly treated in reference (1) and (38).

1) Correction for the "parallel heat" transfer

These correction take into account the heat transfer by the insulating plugs and lead in wires and a part of the heat transmitted by radiation. Several proposal have been made to cancel or estimate these losses.

A classical method uses guard rings. But the advantages of this method are more apparent than real. The temperature control of the guard ring increases the time for reaching the equilibrium states and the temperature uniformization between guard rings and emitter involves a complexe and

bulky controlling system. Some indiscernible temperature fluctuations due to the guard heating can produce some perturbations of the amount of heat generated by the emitter or of the receiver temperature. For these reasons we preferred not to use guard rings.

Some authors have determined the parallel heat transfer by differential measurements in a high vacuum. But the experience shows that the temperature field under vacuum is different of the temperature field under a gaseous atmosphere, mainly because the thermal resistance silver quartz of the centering plug is not negligible in the parallel heat transfer, and is modified under vacuum.

The parallel heat transfer (corresponding to a parallel conduction λ_p) corrects the apparent value of the thermal conductivity coefficient of the fluid. A simple calculation does not permit to evaluate the parallel conduction. We have shown that the parallel heat losses are negligible by the leads and take place only by the insulating plugs and that the thermal resistance of the contact silver-insulating plug is not negligible. The parallel heat conduction has been found approximately constant with the temperature, the pressure and the nature of the gas. Therefore, we have determined this correction by estimating the difference between the measured values and the well-known thermal conductivity of argon at 25°C and 1 atm (39) ($\lambda = 17.4 \times 10^{-3} \text{ Wm}^{-1}$).

2) Radiant heat transfer

Heat transfer by simultaneous conduction, convection and radiation in absorbing and scattering media has been evaluated by several authors. While the formulation of heat transfer by conduction and convection leads to differential equations, the radiation leads to integral equation. A determination of the heat fluxes in an enclosure containing an absorbing and scattering medium requires the solution of a system of coupled conservation equations, namely the differential equation of motion, the integro-differential equation of energy and an integral equation describing the intensity at each location in the medium.

The complexity of this problem has lead several authors to adopt approximations. In general, convection is supposed negligible. In this case the energy transfer is obtained as the solution of a complicated non linear integro-differential equation. There are no general solutions available for this integro-differential equation and only a few studies on highly simplified problems have been reported.

The heat transfer by radiation in a partly transparent liquid disc capable of emitting and absorbing radiation has been calculated for steady state conditions by Fritz and Poltz (40). The disc is limited by two infinite, isothermal, parallel plates which emit, absorb and reflect thermal radiation. The formulation of Poltz has been generalized by Kohler who takes into account the variation of the absorption coefficient and the refraction index of the liquid, and of the emissivities of plates, with the wave-length (41).

The influence of radiant heat transfer on the thermal conductivity determination in test gases able of emitting and absorbing radiation has been evaluated by Leidenfrost. These first calculations were based on the gray gas

assumption (42). Furthermore, the temperature distribution within the test fluid was assumed linear, due only to conduction and not influenced by radiation. Recently Leidenfrost (43) has presented a more complete solution for the following system : the heat transfer takes place between two infinitely large parallel plates. The walls of the test cell are assumed to be isothermal, diffuse absorber and emitter of thermal radiation and to have constant radiation properties except for their variation with wavelength. The fluid is supposed to be an isotropic, homogenous gas which can absorb and emit thermal radiation. Results are obtained for a gray gas based on the Planck mean absorption coefficient. The author shows that the ratio of radiant to total heat transfer as a function of location is not uniform but increases from the wall to the middle of the layer. The radiation-conduction interaction alters the linear temperature profile that would be due to conduction alone. The ratio of radiant to total heat transfer is approximately the same for the gray and the non-gray gas in the immediate neighborhood of the hot wall and can be used to evaluate the radiation.

We have tried to estimate the heat transfer by radiation at room temperature in our cell by changing the emissivity of the wall. We observed that the thermal conductivity coefficient was practically non affected; we conclude that the influence of radiation is negligible at room temperature.

At high temperature we evaluated the heat transfer by radiation by the Stefan-Boltzmann relation :

$$Q_r = 4 \epsilon_a \sigma_s S \Delta T T_M^3 \quad (3)$$

if ΔT is small in comparison of the absolute temperature T_M

where ϵ_a = emissivity of silver
 S = mean emissive area
 σ_s = Stefan-Boltzmann constant

This approximation assumes that the whole energy stored by the gas is reemitted, that is to say that the gas is not absorbing.

The factor due to the cylindrical geometry is supposed to have no effect on the heat transfer by radiation. This assuming is justified when the ratio of the width of the interval to the diameter of the internal cylinder is small. In changing ΔT by KQ/λ in the relation (3) one obtains :

$$\frac{Q_r}{Q} = \left(\frac{4 \epsilon_a \sigma_s S T_M^3}{\lambda} \right) K \quad (4)$$

This relation confirms a qualitative conclusion : the ratio of the heat transfer by radiation to the heat transfer by conduction is smaller when the constant of the cell is lower, or when the gas layer is thinner.

The apparent thermal conductivity which corresponds to the total heat emitted W is equal to :

$$\lambda_{ap} = K \frac{W}{\Delta T} = K \frac{Q + Q_r}{\Delta T} = \lambda + 4 K \epsilon_a \sigma_s S T_M^3 \quad (5)$$

with

$$\alpha_r = 4 \epsilon_a \sigma S T_M^3 \quad (6)$$

one obtains

$$\lambda_{ap} = \lambda + \alpha_r K \quad (7)$$

If we make measurements in two different cells having constants K_1 and K_2 corresponding to gaps of 0.2mm and 0.4mm respectively, so $K_2 = 2 K_1$

At the same temperature and at the same pressure we deduce from :

$$\lambda_{ap1} = \lambda + \alpha_r K_1 \quad (8)$$

and

$$\lambda_{ap2} = \lambda + \alpha_r K_2 = \lambda + 2 \alpha_r K_1 \quad (9)$$

the relation

$$\lambda_{ap2} - \lambda_{ap1} = \alpha_r K_1 \quad (10)$$

So, we have a possibility to know the heat transfer by radiation in making two measurements in two different cells at the same temperature. This comparison has been made at 450°C for a transparent gas : argon, and an absorbing gas : carbon dioxide.

The absorption coefficient is defined as :

$$\kappa = \frac{1}{e} \ln \frac{I_0}{I'} \quad (11)$$

where e = thickness of the gas

I_0 and I' : intensity of the input and output radiations. The variation of the heat transfer due to the absorption which is a function of the reciprocal width will be also take into account in the difference of the apparent thermal conductivities.

At 450°C we have obtained the following values for $\alpha_r K_1$ expressed in $Wm^{-1} °C^{-1}$.

Table II

Variation of the	λ in $Wm^{-1} °C^{-1}$ coefficient at 450°C versus the density					
Density kg/m^3		1	100	200	300	400
Argon		0.9	1.1	0.8	0.8	1.1
CO ₂		0.6	0.9	0.8	0.9	1.4

The value of $\alpha_r K_1$ is less than the accuracy of our data, so it is difficult to make conclude on the variation of this coefficient with the test gas or the density; therefore assume that $\alpha_r K_1$ is the same for the gases

studied at a given temperature. According to table II this coefficient is about $0.8 \text{ Wm}^{-1} \text{ }^{\circ}\text{C}^{-1}$ at 450°C . This is in fair agreement with the value obtained from formula (3), in taking $\epsilon_a = 0.04$ and $S = 80 \text{ cm}^2$. This comparison has not been made above 500°C because then the structural modification in the silver of which is made the cell and which changes the cell constant for a gap as small as 0.2 mm and modifies also the emissivity. From 550°C to 688°C , we have made only one set of measurement in a cell having a gap of 0.4 mm and calculated the heat transfer by radiation with the formula (3) and $\epsilon_a = 0.04$.

At moderate temperatures, O_r is small and the correction factor does not exceed some parts in one thousand. Yet when the temperature increases the correction factor rapidly increases also, and at 688°C the radiation heat transport amounts to about 3% of the conduction heat transport. The accuracy in the determination of ϵ_a is essential over the whole temperature range. As the error due to the uncertainty of ϵ_a is large, the main error at high temperature on the thermal conductivity coefficient is due to the uncertainty of the radiation correction.

3) Correction for free convection

The correction for free convection can be avoided by selecting thin layers of test fluids (here 0.2 mm), measuring accross small temperature differences and maintaining a uniform temperature profile throughout the test chamber.

Convection is an energy transport associated with an average motion of the fluid and proportional to the temperature gradient in the fluid. Conduction is an energy transport connected with the molecular exchange of energy associated with the random motion of the molecules and independent of the temperature gradient. Thus the presence of convection can be detected by the variation of the temperature difference. If the measured thermal conductivity is not explicitly dependent on this variation, convection must be insignificant.

In general, this method is not valid in the critical region, because a variation of the temperature difference changes the steady-state of the fluid (temperature and/or density) and the corresponding thermal conductivity coefficient is different.

From a dimensional analysis of the equations governing free convection, it can be concluded that for small temperature differences, the contribution of convection to the total heat flow through a gas layer is determined by a dimensionless parameter, the Rayleigh number R_a (The Rayleigh number is equal to the product of Prandtl and Grashof numbers) It is defined as :

$$R_a = \frac{g \alpha \rho^2 C_p \Delta T}{\lambda \eta} \quad (12)$$

where g = gravitation constant

$$\alpha = - \frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P = \text{expansion coefficient}$$

ρ = density

C_p = specific heat at constant pressure

ΔT = applied temperature difference

e = thickness of the considered gas layer

λ = thermal conductivity coefficient

η = viscosity coefficient

Because both α and C_p become infinite at the critical point the probability of convection becomes extremely high. The use of the Rayleigh number assumes that the physical properties are constant in the fluid layer with temperature and density. In fact, the latter assumption is no longer applicable in the critical region for a vertical cylindrical layer because the gravity produces a stratification in density. In presence of this density gradient the Rayleigh number varies with position in the fluid.

For a Newtonian fluid, the free convection exists even for small values of R_a , its estimation is only a problem of accuracy of the measurement of these small values of R_a . The conditions of development of the free convection in a fluid layer between coaxial cylinder have been studied by Kraussold (44), who has found that the heat transfer by free convection is appreciable for $R \gg 1000$ and that the amount of the transmitted heat was the same for a vertical or a horizontal cell.

From more fundamental considerations of the convection, based on the work of Batchelor (45) it can be shown that for the annulus between two infinite cylinders, the ratio of heat transferred by convection to heat transferred by conduction is

$$\frac{Q_c}{Q} = \frac{Ra K}{720} \times 2 \pi r \quad (13)$$

where r = mean radius of the fluid layer.

We can remark that for a Rayleigh number of 1000, about 0.5% of the heat is transferred by convection in our cell, this result is confirmed by Kraussold's measurements.

4) Correction on the temperature difference and the cell constant

If we consider the temperature difference, the adsorption of gases on the wall can have some effect but both corrections must be made. Since the thermocouples are located at a small distance from the surface, the true value of the temperature difference ΔT is not the same as that measured by the thermocouples. Another correction is needed if the temperature of the fluid in contact with the wall is not at the same temperature as the wall. This correction is referred to as the accommodation coefficient and it is often found by plotting the reciprocal pressure ($1/P$) versus the reciprocal thermal conductivity at a given temperature and extrapolating this curve to the point where ($1/P$) equals zero.

The corrections on the cell constant are due to the effect of temperature and pressure.

IV - Estimation of the accuracy

The carbon dioxide gas used in these experiments was supplied by " Oxhy - drique Française" and was stated to have a purity of 99.9% . The high pressure is obtained by thermal compression so the purity of the gas was preserved throughout the measurements.

An estimate of the absolute accuracy of the thermal conductivity values reported here is not easy due to the involved nature of the measurements. In order to obtain the highest degree of accuracy possible, all minor errors, all factors affecting the accuracy have been considered and discussed in the reference (1).

The accidental errors estimated by the deviation between experimental points and plotted curves, are about 0.15%.

The systematic errors involve :

- the error due to the impurities which is negligible.
- the error on the measurement of the pressure (0.15%)
- the error on the measurement of the temperature (0.1%)
- the error on the cell constant (0.25%)
- the error on the effective power. transmitted by conduction which varies from 1.3% at 400°C to 3% at 700°C (the error on the heat transfer by radiation increases with the absolute temperature)
- the error on the temperature difference (0.6%)

After consideration of all factors, the accuracy of the thermal conductivity values measured and reported in this work are believed to be 2.5% or better up to 400°C at all the pressures. Above this temperature, the errors regularly increase and are about 4.5% at 688°C.

V - Experimental data

The thermal conductivity coefficient of carbon dioxide has been measured from 25°C to 688°C, in a pressure range from 1 to 1200 bars. The results of these measurements are tabulated in Tables III and IV. These tables give the following informations : the average temperature, the pressure, the temperature difference as measured by the thermocouples, the thermal conductivity coefficient after all corrections.

On figure 1, experimental data at 1 bar are plotted against temperature and compared with the previously reported experimentally measured values. The largest density of points show a mean scattering of $\pm 2.5\%$ up to 600°C . If we consider the accuracy of the pressure and of our measurements, the agreement is satisfactory.

The thermal conductivity coefficient versus density at a constant temperature is plotted graphically on figure 2. This figure shows that the same general shape of the thermal conductivity curve versus density is obtained in

this work as in by Michels et al (35), including a maximum in the critical region. This maximum is observed up to the isotherm 130°C. Nevertheless the fact that the same general shape is reported by two different methods leads to suspect that some maximum truly exists, but we must clearly state that our apparatus was not intended to be used near the critical point and therefore no conclusion on the real value of the thermal conductivity coefficients in the vicinity of this point can be drawn from our results. Above 200°C, the curves have been obtained by an interpolation of the experimental data for average temperatures, with the following relation :

$$\lambda(\rho, T_m) - \lambda(\rho, T_e) = a(T_m - T_e) = \lambda(0, T_m) - \lambda(0, T_e) \quad (14)$$

where

T_m = average temperature

T_e = experimental temperature

ρ = density

a = coefficient of temperature

This interpolation is valid above 200°C, because all the curves can be deduced by a translation along the thermal conductivity axis. The densities have been calculated with the tables of Vukalovich and Altounin (22) up to 600 bars and of Kennedy (46) above.

The deviations of the experimental of Michels et al. from our data, in terms of the density are in most cases approximately 1%, as it is shown figure 3.

IV- Critical region

In the critical region, accurate measurements of the thermal conductivity are difficult, because complication arise in obtaining a steady non equilibrium state.

For the study of the behavior of the thermal conductivity in the critical region, it is necessary to know the values of the appropriate thermodynamic parameters at which this property is measured; i.e., temperature and density. But as the thermal conductivity measurements require the introduction of a temperature gradient, the density varies rapidly with the location in the thermal conductivity cell. So, one knows only an average density which can be significantly different of the local density at which the thermal conductivity is determined.

Another, major difficulty is caused by the high probability of convection. We have seen that the Rayleigh number increases so much that the convection easily becomes the dominating effect near the critical point. Thus, some authors have concluded that any pronounced anomaly of the thermal conductivity is due to the convection (47).

For this last years the behavior of the thermal conductivity in the

critical region has been the subject of active discussions.

A number of authors state that the thermal conductivity does not show an extra increase in the critical region. Timrot and Oskolkova (29) reported that the thermal conductivity of carbon did not show any anomaly in the critical region, but it seems that their measurements were carried out too far away from the critical point. Vargaftik (47) referring to experiments performed by Shingarev (32) with carbon dioxide, has stated that the thermal conductivity contrary to the specific heat possesses no maximum in the supercritical region, the influence of the convection being excluded. The discussion of Vargaftik indicates that these conclusions were drawn after corrections for convection were applied by extrapolation the apparent values of the thermal conductivity coefficient observed with finite temperature differences to zero temperature difference. Very careful thermal conductivity measurements of carbon dioxide were carried out by Amirkhanov and Adamov (36) using both a horizontal plate method and a vertical concentric cylinder method. With the parallel plate apparatus a series of measurements were performed near coexistence line. With the smaller plate distance the data turned out to be independent of ΔT which guarantees absence of convection; the authors did not observe the existence of an anomaly.

Kardos (23) was the first to measure the thermal conductivity of carbon dioxide in the critical region, he has found an enormous increase of the heat transfer, but his measurements had been affected by convection.

Sellschop (24) has found an anomalous increase of the heat transfer in the critical region, but attributes the whole effect to the influence of convection.

Guildner (34) has reported a rapid increase of the thermal conductivity of carbon dioxide as the critical point is approached. He used a vertical cylindrical gas layer with a thickness of 0.68 mm. In his conductivity cell, energy transfer due to convection could not be avoided, even at the smallest temperature differences used, so that λ was determined by measurements made for various temperature differences ΔT and extrapolating to $\Delta T = 0$. It should be realized that when ΔT is varied at constant pressure, the average density of the gas change, because the heating of the internal cylinder raises the temperature of the two cylinders. Consequently the average conductivity in the gas layer changes as a function of ΔT ; therefore one should regard the data of Guildner as requiring further experimental checks.

Michels, Van der Gulik, Sengers (35) have obtained apparently convection free measurements of the thermal conductivity of carbon dioxide in the critical region, using a parallel plate method. Convection was avoided by using a relatively small distance between the plates ($d = 0.4$) and small temperature differences (ΔT varied from 0.03°C to 0.25°C). Absence of convection was demonstrated by verifying that the measurements were independent of the Rayleigh number. At 75°C and 40°C , there is a satisfactory agreement with the data of Guildner, confirming the anomaly of 30% at 40°C . Closer to the critical temperature the anomalous increase is considerably smaller than that reported by Guildner.

Recently a new experimental technique to study transport processes has been developed in which basically one takes a system in equilibrium and studies the time decay of the thermal fluctuations, namely by observing the spectrum of light scattered through the fluid (48). Although the theoretical basis already existed for a few decades experimental realization of this method has become very promising with the availability of lasers as light sources. In addition to the Brillouin lines the spectrum contains an unshifted central or Rayleigh line. The time decay of the temperature fluctuations at constant pressure is determined by the thermal diffusivity

The Rayleigh line width Δw_R is proportional to the thermal diffusivity

$$\Delta w_R \propto \frac{\lambda}{\rho C_p} \quad (15)$$

The thermodynamic theory of fluctuations predicts that the ratio of the intensity of the Rayleigh line I_R to the intensity $2 I_B$ of the two Brillouin lines is related to the specific heat ratio C_p/C_v according to the Landau. Placzek ratio

$$\frac{I_R}{2 I_B} = \frac{C_p - C_v}{C_v} \quad (16)$$

Since C_p diverges much faster than C_v , most of the variation of this ratio in the critical region is proportional to C_p . By comparing the line width Δw_R of the Rayleigh line with C_p ; one can test the existence of an anomaly of the thermal conductivity. Preliminary data seem to indicate that this critical exponent for the thermal conductivity may be of the same order of magnitude as that for $\sqrt{C_p}$ (49) (50).

We have planned to study in details the thermal conductivity near the critical point of carbon dioxide with a special cell. At the present time this project which needed considerable modifications of our experimental apparatus, has not been achieved. However, with the coaxial cylinder cell having a gap of 0.2mm, we have tried to do some measurements. To correct the data of the heat transfer by convection we have used the relation (13). These data which are less accurate than Michel's data are not published. Our data confirm the presence of a maximum of thermal conductivity near the critical density. The resultant deformation of isotherms can be still perceive up to 100°C above the critical temperature.

Thermodynamic anomalies near the gas liquid critical point have been claimed to be more correctly described by the Ising model theory of the ferromagnet and the lattice gas than by Van der Waals type theories (51). Part of the lattice gas symmetries are shown to be retained in the real gas if the same variables are used. The critical anomalies of the Ising model as well as of real systems are currently described by assuming asymptotic power law behavior in the vicinity of the critical point. Thus, the compressibility K_T diverges as $|T - T_c|^{-1.35}$ at $\rho = \rho_c$, and in addition it is known that C_v diverge as $\ln |T - T_c|$ or slightly faster, the relation

$$C_p = C_v + TV \left(\frac{\partial P}{\partial T} \right)^2 K_T \quad (17)$$

then implies that C_p diverges as K_T i.e. C_p diverge as $|T - T_c|^{-1.35}$
 As the measurement of the Rayleigh line width shows that the thermal conductivity varies as $\sqrt{C_p}$, then :

$$\lambda \propto |T - T_c|^{-0.675} \quad (18)$$

On figure 4 is represented the variation of the logarithm of the excess of thermal conductivity versus the logarithm of $(T - T_c)$ along an isochore corresponding to 240 Amagat. The slope of the straight line fitting our results is -0,68, in good agreement with measurements of ref. (52) obtained from Rayleigh line width.

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TABLE III

Thermal conductivity coefficients of carbon dioxide

(Gap of the cell 0.2 mm)

T °C	P x 10 ⁻⁵ N m ⁻²	ΔT °C	λ x 10 ³ W m ⁻¹ °C ⁻¹	T °C	P x 10 ⁻⁵ N m ⁻²	ΔT °C	λ x 10 ³ W m ⁻¹ °C ⁻¹
20.5	55.8	2.55	29.8	52.0	111.5	1.68	60.5
21.5	56.9	2.11	30.0	52.2	108.9	3.15	56.6
22.1	1041	1.72	177.5	52.4	837	2.18	144.3
22.3	950	1.77	172.4	52.9	121.6	2.75	65.3
22.4	26.5	3.29	18.5	53.2	81.1	2.91	32.6
22.4	824	1.84	165.7	53.5	101.3	3.63	48.2
22.5	55.1	3.43	27.4	53.5	760	2.26	138.7
22.5	740	1.91	159.6	53.5	105.2	3.34	53.0
22.6	4.5	3.64	16.5	53.6	709	2.32	134.5
22.7	627	2.01	151.1	53.8	622	2.43	128.1
22.8	3.8	3.65	16.5	54.1	182.4	3.46	81.3
22.9	510	2.14	142.1	54.1	202.6	3.33	84.9
23.1	412	2.27	133.8	54.2	152.0	3.78	73.1
23.2	308	2.45	123.6	54.3	59.4	3.63	25.1
23.3	211	2.69	112.4	54.3	604	2.45	126.8
28.7	307	1.66	118.9	54.4	91.2	4.41	38.9
29.9	556	2.28	139.7	54.5	507	3.40	120.1
30.3	710	2.14	149.9	54.6	50.6	3.80	23.7
30.7	811	2.06	155.1	54.6	450	3.54	115.1
30.9	20	3.24	18.3	54.6	456	2.61	118.8
31.2	1007	1.92	167.5	54.7	40.5	4.04	22.0
31.5	507	2.38	134.0	54.8	405	3.67	110.5
32.9	131	1.66	90.3	54.8	407	2.82	109.3
33.0	162	1.55	96.1	54.9	354.5	3.85	105.0
33.0	188	1.49	100.3	55.0	20.2	4.35	20.1
33.0	195	1.46	101.9	55.0	304.0	4.07	99.0
33.8	23.4	3.40	19.0	55.0	304.0	3.12	97.9
34.6	8.3	3.64	17.6	55.2	10.1	4.48	19.3
35.0	1	3.73	17.1	55.2	253.3	4.37	91.9
35.4	1	3.72	17.2	55.3	1	4.59	18.7
36.5	177	3.23	95.5	55.3	81.1	5.22	31.9
37.6	404	2.58	121.2	56.7	60.8	6.39	24.7
38.1	305	2.82	110.7	57.1	49.3	6.43	23.4
38.5	201	3.21	96.5	65.9	86.1	2.97	31.2
40.5	808	2.14	148.5	66.1	81.1	3.13	29.5
40.5	912	2.05	155.0	66.1	121.6	3.52	49.2
40.5	1014	1.99	160.8	66.3	70.9	3.36	27.1
40.5	1114	1.93	166.0	66.6	60.8	3.55	25.3
40.6	607	2.34	134.9	66.6	111.5	4.01	42.4
40.6	709	2.23	142.4	66.9	50.7	3.76	23.6
40.7	405	1.66	118.8	66.9	106.4	4.27	39.4
40.7	507	2.48	127.0	66.9	151.9	4.36	62.1
48.8	1110	1.94	162.7	67.0	40.5	3.93	22.4
48.9	578	2.41	129.3	67.1	101.3	4.54	36.8
50.2	1004	2.02	155.7	67.1	507	3.58	112.2
50.8	986	2.04	154.8	67.2	131.7	5.00	53.5
51.4	931	2.09	150.8	67.3	20.3	4.19	20.7
51.5	912	2.11	149.5	67.3	456	3.73	107.7

T °C	P x 10 ⁻⁵ N m ⁻²	ΔT °C	λ x 10 ³ W m ⁻¹ °C ⁻¹	T °C	P x 10 ⁻⁵ N m ⁻²	ΔT °C	λ x 10 ³ W m ⁻¹ °C ⁻¹
67.5	10.1	4.30	20.1	96.0	101	2.84	31.3
67.5	96.3	4.79	34.5	96.0	454	2.89	92.1
67.5	405	3.91	102.4	96.1	91	2.98	29.6
67.6	1	4.41	19.4	96.1	608	3.82	105.3
67.6	354	4.11	96.9	96.2	182	3.22	51.3
67.8	91.2	5.01	32.7	96.2	407	3.40	87.2
67.9	304	4.39	90.4	96.3	79	3.16	27.7
68.1	253.3	4.76	83.0	96.3	507	4.13	96.9
68.5	202.7	5.31	73.7	96.4	71	3.27	26.6
68.6	182.4	5.60	69.7	96.5	61	3.38	25.5
75.9	1014	2.14	142.2	96.6	51	3.49	24.6
76.1	912	2.24	135.9	96.6	304	3.54	74.0
76.4	862	2.28	133.2	96.7	41	3.59	23.7
76.6	912	2.25	135.1	96.7	152	3.77	43.1
77.5	811	2.35	129.1	96.8	30	3.68	23.0
78.1	507	2.59	106.5	96.8	142	3.97	40.6
78.3	202.6	2.65	66.4	96.9	20	3.76	22.4
78.3	709	2.48	121.8	97.0	10	3.84	21.8
78.5	70.9	3.32	26.6	97.1	1	3.93	21.3
78.5	182.4	2.83	61.5	97.1	132	4.24	37.8
78.7	101.3	2.78	33.2	97.1	253	3.94	65.8
78.7	454	2.72	101.0	97.3	122	4.47	35.6
78.7	608	2.64	113.6	97.5	203	4.57	55.8
78.8	60.7	3.51	24.9	99.3	416	4.56	96.4
78.8	152.0	3.30	51.9	102.2	1013	3.11	130.3
78.8	404	2.86	95.7	102.8	912	3.26	123.9
78.9	91.2	2.98	30.6	103.3	800	3.45	116.4
79.0	353	3.04	89.7	104.2	594	3.95	100.8
79.1	40.5	3.77	22.8	129.1	122	2.60	33.5
79.2	141.9	3.57	47.6	129.1	132	2.52	34.7
79.3	10.1	4.09	20.6	129.3	111	2.68	32.4
79.3	30.4	3.89	21.9	129.4	141	2.42	36.2
79.3	131.7	3.82	44.0	129.5	91	2.87	30.0
79.3	303.9	3.25	83.4	129.7	101	2.75	31.1
79.3	490	2.88	103.4	129.9	71	2.99	28.2
79.5	81.0	3.23	28.2	129.9	81	2.94	28.8
79.7	1	4.20	20.1	129.9	501	3.02	84.0
79.8	253.3	3.57	74.3	130.0	61	3.07	27.4
79.9	60.7	3.54	25.0	130.1	203	3.40	46.2
79.9	121.6	4.18	39.8	130.1	460	3.16	80.0
80.2	50.6	3.68	24.0	130.2	41	3.20	26.0
80.2	111.5	4.56	36.1	130.2	51	3.14	26.7
80.5	20.2	4.02	21.4	130.3	30	3.26	25.4
81.0	101.3	2.24	31.5	130.3	182	2.64	42.8
89.7	304	2.77	77.3	130.3	404	3.39	74.1
89.7	405	2.40	90.3	130.3	507	2.48	83.3
90.9	1013	3.02	135.4	130.4	1	3.43	23.9
91.9	912	3.17	129.0	130.4	10	3.37	24.5
92.5	808	3.36	121.7	130.4	20	3.32	24.9
93.0	1013	3.05	134.8	130.5	355	3.65	68.3
93.0	1020	3.04	135.2	130.7	152	4.07	37.9
93.2	703	3.55	144.1	130.8	304	4.00	61.8
95.8	111	2.68	33.5	131.0	941	2.04	116.9
95.8	503	2.75	96.9	131.2	253	4.51	54.2

T °C	P x 10 ⁻⁵ N m ⁻²	ΔT °C	λ x 10 ³ W m ⁻¹ °C ⁻¹	T °C	P x 10 ⁻⁵ N m ⁻²	ΔT °C	λ x 10 ³ W m ⁻¹ °C ⁻¹
131.2	608	2.25	92.3	205.2	523	1.48	68.8
131.7	807	2.21	107.7	205.3	199	2.36	42.3
132.0	709	2.09	99.9	206.7	608	2.41	75.9
132.2	154	2.23	37.8	206.7	715	2.20	83.3
132.2	673	2.42	98.0	206.8	813	2.06	89.3
132.3	312	2.22	62.3	207.1	914	1.93	95.3
132.4	57	1.90	27.2	207.2	1026	1.82	101.4
132.6	811	1.95	107.3	207.5	1132	1.73	106.9
132.7	1	2.10	24.3	207.9	1257	1.65	112.5
132.7	208	2.94	46.4	208.7	102	2.29	35.0
132.7	575	2.64	89.7	208.8	92	2.32	34.4
133.1	92	2.74	30.3	209.0	82	2.35	33.9
133.1	482	2.91	81.0	209.1	303	2.87	51.1
133.2	912	1.84	113.8	209.2	71	2.38	33.3
135.2	1095	1.92	123.8	209.2	253	3.11	46.7
135.2	1185	1.85	128.9	209.3	61	2.41	32.8
135.2	1278	1.79	133.2	209.4	30	2.49	31.6
139.1	408	3.26	71.7	209.4	41	2.46	32.0
139.4	304	3.88	59.1	209.4	51	2.43	32.5
181.6	203	1.99	42.4	209.5	20	2.51	31.3
182.3	91	2.49	32.8	209.5	203	3.39	42.4
182.3	101	2.45	33.4	209.7	182	3.51	40.7
182.4	71	2.58	31.5	209.9	151	3.69	38.4
182.4	81	2.54	32.1	210.0	141	3.75	37.7
182.5	30	2.73	29.5	210.1	121	2.88	36.3
182.5	41	2.69	30.0	210.1	132	3.81	37.1
182.5	51	2.65	30.5	210.2	113	2.92	35.9
182.5	60	2.62	30.9	210.3	455	3.59	64.1
182.8	10	2.78	28.7	210.5	355	4.08	55.7
182.8	20	2.76	29.0	228.5	50	2.21	34.3
182.9	1	2.83	28.2	229.1	87	2.15	36.2
183.3	182	3.63	40.3	229.3	353	2.62	54.8
183.8	142	3.93	36.7	229.5	303	2.81	50.7
183.8	150	3.87	37.3	229.7	252	3.02	46.7
183.9	131	4.01	35.8	229.9	1000	1.79	96.0
184.0	122	4.09	35.1	229.9	1001	1.78	96.6
184.1	112	4.15	34.4	229.9	1013	1.77	96.9
191.3	43	2.66	30.6	230.0	203	3.25	43.0
191.4	1013	1.90	103.2	230.0	506	3.39	66.3
191.6	912	2.00	97.4	230.1	182	3.35	41.5
191.9	1	2.77	29.2	230.1	932	1.83	93.4
191.9	811	2.13	91.4	230.2	455	3.58	62.7
192.4	709	2.29	84.3	230.2	876	1.90	89.7
192.8	608	2.48	77.3	230.3	152	3.50	39.5
193.1	507	3.73	69.6	230.3	421	3.72	60.1
193.5	406	3.08	61.1	230.4	142	3.55	38.9
194.2	304	3.58	51.7	230.4	407	2.78	59.1
195.1	203	4.29	42.0	230.4	811	1.98	85.7
197.1	101	5.14	34.0	230.4	912	1.88	91.1
204.8	89	1.89	34.4	230.5	709	2.12	79.6
204.9	55	1.99	32.6	230.7	132	3.61	38.2
205.1	310	1.94	51.9	230.8	122	3.65	37.7
205.1	409	1.68	60.5	230.8	507	2.52	65.7

T °C	P x 10 ⁻⁵ N m ⁻²	ΔT °C	λ x 10 ³ W m ⁻¹ °C ⁻¹	T °C	P x 10 ⁻⁵ N m ⁻²	ΔT °C	λ x 10 ³ W m ⁻¹ °C ⁻¹
230.8	594	2.32	72.0	274.3	354	2.50	55.1
231.1	111	3.71	37.2	274.4	304	2.65	51.8
231.2	101	3.76	36.6	274.6	253	2.80	48.6
231.3	91	3.80	36.2	274.8	203	2.97	45.6
231.3	405	2.80	58.4	276.7	142	3.15	42.4
231.4	81	3.84	35.7	276.7	152	3.12	42.9
231.6	71	3.88	35.2	276.7	181	3.04	44.2
231.8	62	3.92	34.8	276.8	122	3.22	41.4
231.9	51	3.97	34.4	276.8	132	3.18	42.0
232.0	41	4.00	34.1	277.0	101	3.28	40.5
232.1	30	4.04	33.7	277.3	51	3.42	38.5
232.2	10	4.11	32.9	277.4	30	3.48	37.9
232.2	20	4.07	33.3	277.4	41	3.45	38.2
232.2	87	4.26	36.4	277.5	20	3.50	37.6
232.5	199	3.69	42.7	277.6	1	3.58	36.6
254.4	152	3.30	41.3	277.6	10	3.53	37.3
254.5	182	3.18	43.1	288.1	182	2.92	45.4
254.5	203	3.10	44.3	288.3	142	3.03	43.4
254.5	505	2.18	65.7	288.3	152	3.00	43.9
254.8	405	2.42	58.6	288.4	101	3.14	41.6
254.9	304	2.73	51.2	288.4	121	3.08	42.5
255.0	454	2.30	62.0	288.5	81	3.20	40.8
251.1	252	2.91	47.7	288.6	20	3.36	38.6
255.5	122	3.42	39.7	288.6	30	3.24	39.0
255.5	131	3.39	40.1	288.6	52	3.28	39.7
255.5	141	3.35	40.5	288.6	62	3.24	40.2
255.6	91	3.53	38.3	288.8	1	3.44	37.6
255.6	101	3.49	38.7	297.3	37	2.43	39.7
255.6	111	3.46	39.1	297.3	983	1.60	89.4
255.7	81	3.57	37.8	297.4	669	1.93	73.4
255.8	71	3.60	37.4	297.4	782	1.80	79.2
255.9	51	3.67	36.6	297.4	881	1.70	84.1
255.9	61	3.64	37.0	297.4	1073	1.53	93.4
256.0	352	2.96	54.7	297.4	1077	1.52	93.8
256.1	41	3.70	36.2	297.4	1187	1.46	98.4
256.2	30	3.74	35.9	297.5	1	2.51	38.6
256.3	10	3.80	35.2	297.6	560	2.10	67.2
256.3	20	3.78	35.5	297.8	461	2.29	61.4
256.4	1	3.85	34.8	298.0	174	2.16	44.9
269.3	56	2.70	37.8	298.1	100	2.31	41.8
270.2	203	2.23	44.5	298.2	65	2.39	40.3
270.4	1013	2.40	92.6	298.2	357	2.54	55.1
270.5	912	2.53	87.7	298.6	263	2.79	49.8
270.6	1	2.86	35.5	301.2	406	2.24	59.9
270.7	811	2.69	81.9	301.2	456	2.14	62.8
270.8	101	2.75	39.9	301.2	505	2.06	65.4
271.2	709	2.87	76.3	301.4	354	2.35	56.8
271.5	608	3.10	70.4	301.7	253	2.58	51.1
271.8	507	3.37	64.0	301.7	304	2.45	54.0
272.3	414	2.68	58.1	301.8	196	2.73	48.1
274.0	509	2.15	65.1	301.9	203	2.71	48.5
274.1	455	2.26	61.6	372.2	400	1.87	58.6
274.2	405	2.37	58.4	372.3	297	2.02	54.1

T °C	P x 10 ⁵ N m ⁻²	ΔT °C	λ x 10 ³ W m ⁻¹ °C ⁻¹	T °C	P x 10 ⁵ N m ⁻²	ΔT °C	λ x 10 ³ W m ⁻¹ °C ⁻¹
372.4	193	2.18	50.1	451.0	41	2.00	51.0
372.5	871	1.93	79.9	451.0	63	1.98	51.7
372.6	91	2.33	46.6	451.0	610	1.95	70.2
372.6	775	2.03	75.6	451.1	1	2.03	50.3
372.7	952	1.85	83.5	451.1	505	2.06	66.2
372.8	60	2.38	45.6	451.2	407	2.18	62.5
372.9	31	2.42	44.9	451.4	304	2.30	58.9
372.9	653	2.17	70.6	473.2	1202	1.40	92.0
373.0	4	2.46	43.9	473.7	977	1.51	85.0
373.0	1020	1.79	86.3	474.6	824	1.61	79.6
373.5	1069	1.75	88.4	476.0	708	1.69	75.6
373.6	1147	1.71	91.0	477.2	612	1.76	72.2
373.8	1119	1.72	90.2	478.5	503	1.85	68.4
401.3	96	1.85	48.7	479.6	404	1.95	65.1
401.4	1	1.94	46.2	480.6	290	2.05	61.3
401.4	35	1.91	47.1	481.3	190	1.04	58.1
401.5	816	1.80	76.9	499.8	1098	1.66	89.4
401.5	949	1.69	82.2	501.9	900	1.79	82.2
401.6	706	1.91	72.5	502.0	30	1.81	55.1
401.6	1071	1.60	87.0	502.1	798	1.85	79.6
401.7	605	2.01	68.7	502.2	969	1.66	85.5
401.8	507	2.13	64.6	502.2	1094	1.61	88.5
401.8	1169	1.54	90.8	502.2	1198	1.56	91.5
402.1	507	2.28	64.6	502.4	193	1.45	59.1
402.4	1275	1.49	94.5	502.4	600	1.93	73.0
408.9	941	1.43	82.3	502.4	677	1.95	75.3
408.9	1005	1.39	84.7	502.5	691	1.87	75.2
409.0	827	1.51	77.7	502.5	1216	1.54	92.6
409.0	1077	1.35	87.7	502.6	530	2.09	70.2
409.1	711	1.60	73.1	502.7	500	2.03	69.1
409.2	612	1.69	69.0	502.8	400	2.13	65.7
409.3	509	1.80	64.6	502.9	295	2.23	62.4
409.5	403	1.92	60.3	527.6	1026	1.51	87.1
410.5	26	2.40	47.4	527.7	929	1.56	83.8
410.5	56	2.37	48.1	527.8	818	1.63	80.2
410.6	1	2.42	46.9	528.0	702	1.71	76.4
449.8	1000	1.62	84.8	528.1	609	1.77	73.5
450.3	822	1.75	78.1	528.3	508	1.86	70.2
450.8	122	1.93	53.0	528.5	401	1.94	66.8
450.8	203	1.86	55.6	528.8	184	2.14	60.5
450.8	719	1.85	74.2	529.0	90	2.21	58.4
450.9	719	1.85	74.2	529.1	52	2.23	54.8
				529.2	12	2.25	57.3

TABLE IV

Thermal conductivity coefficients of carbon dioxide
(Gap of the cell 0.4 mm)

T °C	$P \times 10^{-5}$ N m ⁻²	ΔT °C	$\lambda \times 10^3$ W m ⁻¹ °C ⁻¹	T °C	$P \times 10^{-5}$ N m ⁻²	ΔT °C	$\lambda \times 10^3$ W m ⁻¹ °C ⁻¹
407.3	572	1.63	68.0	556.9	912	1.21	85.7
407.4	507	1.69	65.1	557.2	1060	1.15	90.4
407.4	403	1.80	60.9	598.5	69	0.88	63.1
407.5	305	1.91	56.8	599.4	1047	1.32	92.0
407.9	206	2.03	53.2	600.0	69	0.88	63.4
408.2	107	2.15	49.7	600.4	931	1.38	88.0
408.3	10	2.25	47.1	601.0	798	1.44	83.6
450.8	507	1.66	66.6	601.8	629	1.53	78.3
450.8	590	1.58	69.8	672.3	531	1.22	79.3
450.8	807	1.42	79.8	677.5	816	1.11	87.2
450.9	405	1.76	62.7	677.5	919	1.08	90.0
451.0	303	1.85	59.0	677.6	714	1.14	84.6
451.2	196	1.96	55.3	677.6	519	1.20	80.0
451.3	97	2.05	52.5	677.6	1041	1.05	93.4
451.5	3	2.14	49.9	677.7	1048	1.05	93.4
451.5	15	2.13	50.3	677.8	608	1.18	81.7
556.2	10	1.66	59.5	677.9	76	1.37	68.9
556.3	79	1.65	60.2	677.9	507	1.21	79.4
556.5	401	1.46	69.0	678.0	398	1.25	76.6
556.6	506	1.41	72.4	687.3	333	1.24	75.9
556.8	604	1.35	75.6	687.7	199	1.29	72.9
556.8	710	1.29	79.4	687.9	51	1.31	71.0
556.8	816	1.24	82.7

Figure 1 -

Percentage deviation for the thermal conductivity coefficients of carbon dioxide at atmospheric pressure between the measurements of several authors (λ_a) and a mean curve fitting our experimental points.

Figure 2 -

Isotherms of thermal conductivity of carbon dioxide versus the density

Figure 3-

Percentage deviation versus the density between the thermal conductivity data of carbon dioxide measured by Michels e.a , by Guildner, and ours data.

Figure 4-

Excess of thermal conductivity ($\lambda - \lambda_c$) versus the excess of temperature ($T - T_c$) along the isochore corresponding to 240 Amagat (critical density = 236 Amagat) - (λ_c has been determined in plotting the excess of thermal conductivity versus density for isotherms above 200°C).

THERMAL CONDUCTIVITY OF BINARY GAS SYSTEMS AND WASSILJEW COEFFICIENTS

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ABSTRACT

The critically evaluated thermal conductivity data on eighty binary gas systems of Touloukian, Liley and Saxena are examined and Wassiljewa coefficients determined according to three different procedures corresponding to each experimental mixture at the temperature of measurement. The best set for each method is then selected at each temperature but for the entire composition range on the basis of three types of deviations between the calculated and experimental conductivity values viz., average, root mean square, and maximum. These three selected sets of Wassiljewa coefficients are next used to compute thermal conductivity values at nineteen equally spaced round compositions of the mixture and compared with the corresponding recommended thermal conductivity values of Touloukian et al. Calculation and consideration of the three deviations between the calculated and recommended conductivity values leads to the selection of the best probable set of Wassiljewa coefficients for each system at the temperature of measurement. These are reported here as a possible aid in the correlation and prediction of thermal conductivity and even viscosity and diffusion coefficients of multicomponent mixtures and in those regimes where no measurements exist at present.

INTRODUCTION

The general scarcity of thermal conductivity data on gases is much felt¹ as the search is extended to multicomponent systems and the temperature of interest increases from a couple of hundred degrees absolute to a thousand degrees absolute and above. The participation of rotational and vibrational modes of a polyatomic molecule in the process of energy transport has added a still unresolved complexity to the theoretical description of this property, Hirschfelder, Curtiss and Bird². The lack of experimental data and the absence of a rigorous theory for thermal conductivity has led to the development of a number of approximate, semitheoretical and even empirical procedures for the estimation of thermal conductivity of gases and their multicomponent mixtures. These methods have been recently reviewed by Touloukian, Liley and Saxena³. These authors³ have also evaluated most of the available thermal conductivity data on pure, binary and multicomponent gas systems and recommended the most probable values at round temperatures for pure gases, and at round compositions at the temperature of measurement for binary mixtures. In this paper we examine on the basis of these experimental data on eighty binary systems³ some of the semitheoretical procedures suggested for the computation of thermal conductivity with a view to establish a technique for the estimation of conductivity values over the whole range of composition and up to moderately high temperatures. It is not possible

to explicitly specify the limit for this temperature extrapolation and it will have to be judiciously prescribed for the individual system depending upon its molecular complexity, thermal and chemical stability, and further the estimation uncertainty will steadily increase with temperature.

At the eighth conference on thermal conductivity, this author⁴ presented the initial phase of this program in relation to ten binary systems of five stable rare gases. The computational aspect of this program is rather exhausting and a fairly painstaking subsequent analysis of the computer runs enables the final results to be tabulated with remarkable brevity. Fairly detailed account of the various calculation procedures for thermal conductivity based on the Wassiljewa form for thermal conductivity are available^{3,4} so that a straightforward introduction of the working expressions will be sufficient. It is hoped that this tabulated information will help in the correlation and prediction of thermal conductivity of multicomponent mixtures up to reasonably high temperatures as well as of viscosity and diffusion coefficients to a limited extent.

CALCULATION AND DISCUSSION

The Wassiljewa⁵ expression for the thermal conductivity of a binary mixture, k_{mix} , in terms of the conductivity values of its constituents k_1 and k_2 , their mole fractions x_1 and x_2 respectively in the mixture and Wassiljewa coefficients ϕ_{12} and ϕ_{21} , is

$$k_{mix} = \frac{k_1}{1 + \phi_{12}(x_2/x_1)} + \frac{k_2}{1 + \phi_{21}(x_1/x_2)} \quad (1)$$

The subscripts 1 and 2, used in conjunction with k , x , and ϕ , consistently refer in this paper to the heavier and lighter components of the mixture respectively. This notation is arbitrary and is for convenience because the expressions are always symmetrical and the two subscripts are interchangeable. Many expressions for ϕ_{ij} have been derived and suggested from time to time, but the ones used here for numerical calculations are based on the following three relations for the ratio of ϕ_{12} to ϕ_{21} ,

$$\frac{\phi_{12}}{\phi_{21}} = \frac{k_1}{k_2} \quad , \quad (2)$$

$$\frac{\phi_{12}}{\phi_{21}} = \frac{k_1}{k_2} \frac{59M_2^2 + 88M_1M_2 + 150M_1^2}{150M_2^2 + 88M_1M_2 + 59M_1^2} \quad (3)$$

and

$$\frac{\phi_{12}}{\phi_{21}} = \frac{k_1}{k_2} \left(\frac{M_1}{M_2} \right)^{0.15} \quad (4)$$

To a limited extent, each of the above relations in conjunction with one experimental value of the mixture conductivity and of the related pure components have been used for the computation of ϕ_{12} and ϕ_{21} . Thus, relations (2), (3) and (4) were initially proposed by Mason and von Ubisch⁶, Gambhir and Saxena⁷, and Saxena and Gambhir⁸ respectively. The calculations in each case were confined to mixtures of monatomic rare gases only.

Saxena⁴ computed ϕ_{12} and ϕ_{21} according to the above mentioned three methods for the available data on thermal conductivity of rare gas mixtures at each of the temperatures and compositions of the data point. In this way for each temperature as many sets of ϕ_{ij} were obtained as the experimental compositions of the gas mixture, Table 1 of reference 4. Next each of these ϕ_{ij} sets were used

to generate the k_{mix} values over the whole range of composition but for those values at which measurements were present and that particular ϕ_{ij} set was selected which gave the best agreement between the experimental and calculated conductivity values. The criterion of selection was based on the calculation of three types of deviations between the experimental and computed conductivity values viz., average (L_1), root mean square (L_2), and maximum (L_3). Using this set of ϕ_{ij} values of k_{mix} were also computed at the nineteen round compositions, 0.05-0.05-0.95, and compared with the recommended values of Touloukian, Liley and Saxena³. The degree of agreement for this case was again indicated in terms of the three deviations L_1 , L_2 , and L_3 , Table 2 of reference 4. The incentive behind such a huge numerical approach to pick and assess a ϕ_{ij} set is to be able to know for sure its competence over the whole composition range. This is important for in many cases only a few representative thermal conductivity data points are available in the whole composition range. The two sets of three deviations throw light on a number of points and for those cases where the experimental data do not depart appreciably from the smooth curve and Wassiljewa form is an accurate representation, these will be in good agreement with each other. Saxena⁴ reported the best ϕ_{ij} set for all the three methods and for each method both the sets of deviations. Here we have further condensed the reported information in as much as only the best ϕ_{ij} set out of the three is reported and only the second set of three deviations, and have further extended the scope of these calculations to additional seventy gas systems involving polyatomic and polar gases in addition to monatomic gases.

It was discovered that an error in the computer program changed the form of Eq. (4) to the following:

$$\frac{\phi_{12}}{\phi_{21}} = \frac{k_1}{k_2} [M_1 M_2]^{0.15} \quad (4a)$$

Consequently in reference 4 and here, the third method is based on Eq. (4a) instead of (4). The calculations of ϕ_{ij} according to these three methods and their subsequent scrutiny indicated that the third method is somewhat superior for mixtures involving polar gases and also when the two gases of the binary system are considerably different in their molecular weights. Of the systems considered here, the latter category included He-Kr, He-Xe, He-CO₂, H₂-Ar, H₂-Ne, H₂-Kr, H₂-Xe, H₂-N₂, H₂-O₂, D₂-Kr and D₂-Xe. The first and second methods proved appropriate with almost equal frequency among the remaining binary systems.

In the light of above comments it is simple to follow the entries of the table. In column 3 are the actual temperatures at which conductivity measurements have been performed and the actual references are indicated in the last column. The best ϕ_{12} and ϕ_{21} values are listed in columns 4 and 5 and the next three columns give the various deviations between the experimental and calculated conductivity values using the best ϕ_{ij} . N in the table stands for the number of experimental data points actually reported, though our deviations are always based on the nineteen recommended³ k_{mix} values except where an * appears on temperature. In such cases deviations are based on the actual experimental points only, N. It will be noted that the various L values are almost invariably within the limits of uncertainty in thermal conductivity data and consequently this may be taken as a very valid and comprehensive evidence in favor of the appropriateness of Wassiljewa form to represent thermal conductivity data over the entire composition range. The success of this form for mixtures involving complicated polyatomic and polar gases is particularly interesting though it is understandable in view of the several recent theoretical and experimental studies⁹⁻¹⁵.

In the earlier study⁴ on rare gas systems it was found that there is no systematic variation of ϕ_{ij} with composition and further almost infinite number

of coupled choices for ϕ_{12} and ϕ_{21} will reproduce k_{mix} data within an assigned magnitude for uncertainty in the latter. This has been amply discussed by a number of authors, see for example Huck and Thornton¹⁶. A similar situation was found in this work and to save space we do not report here the computed sets of ϕ_{ij} values at all of the experimental compositions. The set reported in the table may be taken as equally good for any value of the composition over the entire range. A similar situation exists in connection with the temperature variation of ϕ_{ij} . However, in the table are reported the ϕ_{ij} values at the temperatures where conductivity data exist and numerical calculations have been performed. It is not felt advisable to average out the ϕ_{12} and ϕ_{21} values in an effort to find a single set for the whole temperature range, because different conductivity data involve varying experimental uncertainties and these are reflected in the ϕ_{ij} values. A better alternative is to pick up the best set from the table once one has ascertained the temperature of his interest and a reliable estimate will be possible depending upon and limited by the accuracy of k_{mix} data used for the computation of ϕ_{ij} . Some judgment will therefore be needed in a few cases in using results of the table and this may not always be difficult. In preparing the table it was felt that until a unique set of thermal conductivity data as a function of temperature and composition may become available for each system, it will be appropriate to consider the raw data as such and in their entirety. It is also recommended to use the constants of the table in computing the thermal conductivity of multicomponent mixtures and at higher temperatures where experimental data may not be available according to the procedures discussed by Saxena and Gandhi¹⁷, and Saxena⁴, etc. It is also possible to compute viscosity and diffusion coefficients based on the knowledge of ϕ_{ij} reported here and procedures outlined by Saxena and Gambhir¹⁸, Gandhi and Saxena¹⁹, and Gupta and Saxena²⁰. It is remarkable to realize how much information is imbedded in the Sutherland-Wassiljewa form and in these ϕ_{ij} constants. Availability of the accurate and elaborate experimental data will help considerably in establishing these predictive procedures for the three transport properties of mixtures.

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Wassiljew coefficients, ϕ_{ij} , and other related information concerning thermal conductivity data, k , on eighty binary gas systems.

System Number	Gas Pair	Temp °K	ϕ_{12}	ϕ_{21}	L_1	L_2	L_I	N	References for k
1.	Ar+He	273.2	0.3244	2.820	0.9	1.3	2.7	4	[a]
		291.2	0.2921	2.500	2.1	2.5	5.7	11	[b]
		295.0	0.3134	2.870	1.2	1.5	2.4	11	[c]
		297.0*	0.3375	2.853	7.5	8.6	11.7	3	[d]
		302.2	0.3271	2.766	1.1	2.0	7.8	4	[e]
		308.2	0.3402	2.788	0.8	0.9	1.6	3	[f]
		311.2	0.3319	2.844	0.8	0.9	1.7	5	[g]
		323.2	0.3342	2.718	0.6	0.9	1.9	3	[f]
		343.2	0.3359	2.706	0.8	0.9	1.4	3	[f]
		363.2	0.3439	2.739	1.2	1.4	2.4	3	[f]
		373.2	0.3424	2.389	0.5	0.5	1.0	3	[h]
		589.2	0.3793	2.907	0.5	0.6	1.0	3	[h]
2.	Ar+Ne	793.2	0.3184	2.564	0.8	1.3	5.1	4	[e]
		273.2	0.6850	1.736	2.8	3.1	4.3	3	[i]
		291.2	0.5699	1.590	0.3	0.4	0.7	12	[b]
		302.2	0.6007	1.712	0.4	0.6	1.2	4	[e]
		311.2	0.6223	1.681	0.3	0.3	0.6	12	[j]
		313.2	0.5861	1.628	1.0	1.1	1.8	4	[k]
		338.2	0.6209	1.656	0.1	0.2	0.3	4	[k]
		363.2	0.6104	1.617	0.3	0.4	0.7	4	[k]
3.	Kr+Ar	793.2	0.6390	1.650	1.0	1.3	2.5	4	[e]
		291.2	0.7931	1.500	1.0	1.1	1.8	12	[l]
		302.2	0.7208	1.348	0.2	0.3	0.5	3	[e]
		308.2	0.7622	1.458	0.8	0.9	1.4	3	[f]
		311.2	0.7957	1.489	0.3	0.4	0.6	6	[j]
		323.2	0.7776	1.456	0.7	1.0	1.8	3	[f]
		343.2	0.7636	1.426	0.7	0.9	1.4	3	[f]
		363.2	0.7626	1.436	0.2	0.2	0.5	3	[f]
4.	Xe+Ar	793.2	0.8015	1.372	0.4	0.5	0.9	3	[e]
		291.2	0.3875	2.233	0.4	0.5	0.9	12	[m]
		302.2	0.3887	2.161	1.3	1.4	1.9	3	[e]
		311.2	0.3731	2.214	0.3	0.4	0.7	6	[g]
		313.2	0.3555	2.031	1.4	1.8	2.9	2	[n]
		338.2	0.3375	1.922	2.2	2.8	4.4	2	[n]
		366.2	0.3371	1.763	0.4	0.5	0.8	4	[n]
5.	Ne+He	793.2	0.4059	2.031	0.7	0.8	1.4	3	[e]
		273.2	0.3460	2.189	0.2	0.2	0.5	3	[o]
		291.2	0.2939	1.856	0.3	0.4	0.5	7	[b]
		302.2	0.3454	2.154	1.0	1.1	2.0	4	[e]
		303.2	0.3588	2.195	0.6	0.6	0.8	3	[p]
		323.2	0.3513	2.178	0.6	0.8	1.6	3	[p]
		343.2	0.3459	2.162	0.5	0.6	1.2	3	[p]
		363.2	0.3408	2.124	0.8	1.0	2.1	3	[p]
		793.2	0.3114	2.002	0.6	0.8	1.4	4	[e]

6.	Kr+He	291.2	0.4345	2.939	1.4	2.0	4.1	12	[l]
		302.2	0.4594	3.037	0.8	0.9	1.6	8	[e]
		308.2	0.4506	2.953	0.7	1.0	1.9	4	[f]
		323.2	0.4641	2.954	0.5	0.6	1.1	4	[f]
		343.2	0.4648	2.922	0.8	1.0	1.9	4	[f]
		363.2	0.4651	2.916	1.1	1.5	2.8	4	[f]
		793.2	0.4842	2.790	1.3	1.6	3.4	6	[e]
7.	Xe+He	291.3	0.3513	3.702	2.2	2.9	6.7	10	[m]
		302.2	0.3729	3.748	1.6	1.8	2.9	4	[e]
		303.2	0.3231	2.390	1.3	1.6	3.5	4	[p]
		311.2	0.3459	3.758	1.1	1.4	3.4	6	[g]
		323.2	0.3276	3.245	1.8	2.2	4.1	4	[p]
		343.2	0.3329	3.231	1.8	2.2	4.8	4	[p]
		363.2	0.3346	3.201	1.8	2.3	4.8	3	[p]
8.	Kr+Ne	793.2	0.4146	3.570	1.5	1.7	3.2	4	[e]
		291.2	0.4376	2.307	1.3	1.9	4.5	12	[l]
		302.2	0.4367	2.328	0.8	0.9	1.5	3	[e]
		311.2	0.4408	2.229	1.3	1.5	2.2	7	[j]
		313.2	0.4504	2.239	0.6	0.8	1.7	4	[k]
		338.2	0.4596	2.265	0.3	0.4	1.0	4	[k]
		363.2	0.4611	2.198	0.4	0.5	1.2	4	[k]
9.	Xe+Kr	793.2	0.4745	2.097	1.3	1.7	3.2	3	[e]
		291.2	0.7981	1.330	0.3	0.4	0.7	9	[m]
		302.2	0.8183	1.328	1.0	1.4	3.2	5	[e]
		313.2	0.7756	1.294	0.1	0.2	0.3	4	[k]
		338.2	0.7910	1.300	0.1	0.2	0.6	4	[k]
		363.2	0.7770	1.250	0.2	0.2	0.4	4	[k]
		793.2	0.8080	1.292	2.2	2.9	5.1	5	[e]
10.	Xe+Ne	291.2	0.3241	2.848	1.6	1.8	2.8	9	[m]
		302.2	0.3364	2.910	0.8	1.0	2.0	3	[e]
		303.2	0.3004	2.588	0.8	0.9	1.6	3	[p]
		323.2	0.3049	2.569	0.4	0.5	1.0	3	[p]
		343.2	0.3084	2.527	0.9	1.0	1.7	3	[p]
		363.2	0.3108	2.517	1.4	1.6	2.5	3	[p]
		793.2	0.3568	2.521	0.5	0.8	2.0	3	[e]
11.	Ar+CO ₂	593.2	1.054	0.8457	0.1	0.1	0.1	1	[h]
12.	Ar+D ₂	308.2	0.3215	2.378	1.9	2.2	3.5	4	[q]
		323.2*	0.3220	2.364	2.1	2.5	4.0	4	[q]
		343.2	0.3192	2.324	2.1	2.5	4.2	4	[q]
		363.2	0.3196	2.303	1.9	2.4	4.4	4	[q]
13.	Ar+H ₂	273.2	0.4138	2.219	1.6	1.8	2.7	5	[r]
		296	0.3837	2.204	2.1	2.4	3.6	4	[c]
		311.2	0.4431	2.333	3.2	3.5	4.9	4	[s]
		313.2	0.4233	2.165	1.1	1.3	2.6	3	[t]
		338.2	0.4166	2.168	0.8	1.0	2.2	3	[t]
		366.2	0.4137	2.081	1.7	2.2	4.3	3	[t]
14.	Ar+CH ₄	811.0	0.9200	0.982	0.4	0.5	1.3	1	[h]
15.	Ar+N ₂	90.2*	0.7279	1.487	1.5	1.7	2.8	10	[u]
		258.3*	0.6947	1.271	1.4	1.5	2.6	8	[u]
		273.2	0.7186	1.308	0.1	0.1	0.2	4	[v]
		293.3*	0.8300	1.577	2.2	2.5	4.9	8	[u]
		311.2	0.7606	1.312	1.2	1.4	2.1	5	[s]
		313.2	0.6883	1.234	0.7	0.8	1.3	3	[t]
		338.2	0.6958	1.294	0.7	0.7	1.4	3	[t]
		366.2	0.7041	1.295	1.2	1.4	2.1	3	[t]
		393.2*	0.8300	1.434	1.2	2.0	4.9	8	[u]
		473.2	0.8327	1.448	4.4	4.8	6.5	7	[u]
		593.2	0.7328	1.326	0.4	0.5	1.2	1	[h]
		90.2*	0.8418	1.466	2.7	3.2	6.3	8	[u]
		258.3*	0.6809	1.152	1.2	1.8	4.1	7	[u]
16.	Ar+O ₂	293.3*	0.7742	1.290	1.0	1.3	2.9	8	[u]
		311.2	0.8357	1.421	0.2	0.2	0.4	5	[s]
		313.2	0.7579	1.318	1.4	1.4	2.0	3	[t]
		338.2	0.7115	1.228	0.7	0.8	1.1	3	[t]
		393.2*	0.8361	1.434	2.9	3.8	8.4	7	[u]
		473.2*	0.8969	1.589	0.9	1.1	1.9	7	[u]

17.	Ar+C ₃ H ₈	591.2	1.079	0.5593	0.3	0.3	0.4	1	[h]
		811.2	0.9684	0.3680	2.5	2.7	4.0	1	[h]
18.	He+Air	328.3	0.8229	2.348	0.8	1.1	2.1	5	[w]
19.	He+n-C ₄ H ₈	328.4	0.2304	4.733	1.6	1.7	2.5	4	[w]
20.	He+CO ₂	273.2	0.6285	2.834	0.7	0.9	1.6	3	[o]
		590.2	1.077	3.017	3.8	4.6	8.2	1	[h]
21.	He+C ₃ H ₆	328.4	0.4301	3.823	0.6	0.7	1.2	6	[w]
22.	He+D ₂	303.2	1.269	0.9300	2.0	2.4	4.3	3	[x]
		323.2	1.245	0.9088	1.5	1.8	3.2	3	[x]
		343.2	1.239	0.9031	0.8	0.9	1.4	3	[x]
		363.2	1.230	0.8961	1.1	1.4	2.4	3	[x]
23.	He+C ₂ H ₆	328.4	0.2504	3.621	0.7	1.0	2.5	4	[w]
24.	He+C ₂ H ₄	328.4	0.2360	3.532	0.6	0.7	1.2	4	[w]
25.	He+H ₂	90.2	1.361	0.8566	2.6	3.6	8.0	9	[y]
		258.3	1.217	1.019	2.3	2.1	7.5	8	[y]
		273.3	1.214	1.030	0.7	1.7	6.2	8	[y]
		293.3	1.195	1.006	1.1	2.1	7.8	8	[y]
		303.2	1.127	0.9800	0.9	1.0	1.6	6	[z]
		303.3	1.196	1.049	0.1	0.2	0.3	5	[w]
		318.2	1.146	1.000	0.7	1.0	2.2	6	[z]
		328.2	1.178	1.034	0.3	0.4	0.7	7	[w]
		353.4	1.183	1.047	0.3	0.3	0.4	6	[w]
		378.3	1.166	1.030	0.4	0.5	0.8	6	[w]
		393.3	1.296	1.108	2.9	3.2	4.3	5	[y]
		398.2	1.192	1.056	0.8	0.9	1.5	6	[w]
		474.3	1.238	1.053	1.3	1.4	1.8	5	[y]
26.	He+CH ₄	589.2	1.176	1.726	1.3	1.6	2.8	3	[h]
27.	He+N ₂	273.2	0.8551	2.425	2.9	4.0	13.1	3	[o]
		303.2	0.8129	2.380	2.3	3.3	12.1	6	[aa]
		318.2	0.8383	2.436	0.9	1.1	2.2	6	[aa]
		377.2	0.8245	2.302	1.8	3.3	12.5	3	[h]
		589.2	0.9060	2.333	1.0	1.2	2.6	3	[h]
28.	He+O ₂	303.2	0.2393	3.024	0.6	0.8	2.0	6	[bb]
		318.2	0.2350	2.963	0.9	1.0	1.9	6	[bb]
29.	He+C ₃ H ₈	328.4	0.2482	4.446	0.4	0.6	1.1	4	[w]
30.	He+C ₃ H ₆	328.4	0.4785	3.812	0.3	0.4	0.7	3	[w]
31.	Kr+D ₂	308.2	0.4319	2.551	2.5	3.0	5.0	4	[q]
		323.2	0.4282	2.458	2.4	2.7	4.5	4	[q]
		343.2	0.4202	2.385	2.0	2.2	3.3	4	[q]
		363.2	0.4118	2.334	2.2	2.4	3.7	4	[q]
32.	Kr+H ₂	303.2	0.3000	2.705	1.7	2.0	3.0	6	[z]
		313.2	0.2779	2.384	3.1	3.5	5.9	3	[n]
		318.2	0.2835	2.507	1.5	2.1	4.3	6	[z]
		338.2	0.2931	2.442	1.6	2.0	3.7	3	[n]
		366.2	0.2825	2.333	1.3	1.5	2.7	3	[n]
33.	Kr+N ₂	303.2	1.484	1.232	0.3	0.4	0.6	7	[aa]
		318.2	1.342	1.143	2.7	3.6	8.3	6	[aa]
34.	Kr+O ₂	303.2	1.405	1.234	1.5	1.7	2.8	6	[bb]
		318.2	1.472	1.296	1.5	1.7	3.7	5	[bb]
35.	Ne+CO ₂	273.2	0.5553	1.772	3.0	3.2	4.5	4	[o]
36.	Ne+D ₂	303.2	0.6019	1.637	0.7	0.9	2.0	4	[x]
		323.2	0.6040	1.640	0.8	0.9	1.8	4	[x]
		343.2	0.6075	1.665	0.7	0.8	1.5	4	[x]
		363.2	0.6167	1.687	0.6	0.8	1.8	4	[x]
37.	Ne+H ₂	303.2	0.7722	1.641	1.5	1.9	3.3	6	[z]
		313.2	0.6981	1.471	1.2	1.5	2.5	3	[n]
		318.2	0.7420	1.590	0.8	1.0	1.5	6	[z]
		338.2	0.6924	1.441	0.6	0.8	1.8	3	[n]
		366.2	0.6903	1.433	0.9	1.0	1.6	3	[n]
		368.2	0.8169	1.735	3.5	4.2	6.5	2	[n]
		408.2	0.8115	1.752	5.2	5.9	8.6	2	[n]
		448.2	0.6600	1.399	1.6	1.8	2.6	2	[n]

38.	Ne+N ₂	303.2	0.6710	1.557	1.4	1.5	2.3	6	[aa]
		313.2	0.6815	1.535	0.8	0.8	1.3	3	[n]
		318.2	0.6918	1.582	1.0	1.2	2.1	6	[aa]
		338.2	0.7077	1.588	0.4	0.5	0.7	3	[n]
		366.2	0.7028	1.542	0.2	0.4	1.7	3	[n]
		368.2	0.8909	2.031	2.8	3.1	4.4	2	[n]
		408.2	0.7597	1.677	0.3	0.4	0.7	2	[n]
		448.2	0.7584	1.637	1.0	1.3	2.3	2	[n]
39.	Ne+O ₂	303.2	0.6329	1.499	0.2	0.3	0.5	5	[bb]
		313.2	0.6277	1.456	0.4	0.5	0.8	3	[n]
		318.2	0.6682	1.583	0.3	0.3	0.5	6	[bb]
		338.2	0.6179	1.483	0.5	0.6	1.0	3	[n]
		366.2	0.6383	1.507	0.3	0.4	0.7	3	[n]
		368.2	0.8152	1.872	7.2	7.7	10.4	3	[n]
		408.2	0.6940	1.594	0.5	0.7	1.3	3	[n]
		448.2	0.7149	1.596	0.3	0.4	0.6	3	[n]
40.	Xe+D ₂	311.2	0.2968	2.498	0.4	0.5	0.9	4	[cc]
		313.2	0.2907	2.583	1.8	2.0	3.6	3	[n]
		338.2	0.2836	2.547	1.2	1.8	4.2	3	[n]
		366.2	0.3045	2.370	1.8	2.3	4.7	4	[cc]
		366.2	0.3004	2.481	0.8	0.9	1.7	3	[n]
41.	Xe+H ₂	303.2	0.1925	2.854	2.4	2.6	3.8	6	[z]
		313.2	0.2118	2.818	5.4	6.3	11.0	3	[n]
		318.2	0.1847	2.709	1.6	1.9	3.4	6	[z]
		338.2	0.1947	2.637	3.4	3.8	7.1	2	[n]
		366.2	0.2034	2.541	2.9	3.7	7.3	3	[n]
42.	Xe+N ₂	303.2	0.4300	2.095	0.6	0.6	1.1	6	[aa]
		318.2	0.4161	1.994	0.7	0.9	1.8	6	[aa]
43.	Xe+O ₂	303.2	0.3984	1.983	0.9	1.2	2.5	6	[bb]
		318.2	0.4082	2.021	1.5	1.9	2.9	6	[bb]
44.	C ₂ H ₂ +Air	293.2	0.8708	1.069	0.7	1.2	4.2	5	[dd]
		338.2	0.8897	1.013	0.6	0.9	2.7	4	[dd]
45.	CO+Air	291.2	1.620	0.6237	0.1	0.1	0.1	4	[dd]
46.	CH ₄ +Air	295.2	0.7523	1.269	0.0	0.0	0.1	4	[dd]
47.	C ₆ H ₆ +C ₆ H ₁₄	360.9*	1.085	0.8799	0.5	0.6	0.7	3	[ee]
		398.2*	1.076	0.8930	0.7	0.9	1.3	3	[ee]
48.	CO ₂ +C ₂ H ₄	591.2	0.7287	1.155	0.2	0.2	0.4	1	[h]
49.	CO ₂ +H ₂	258.3*	0.1079	3.061	0.9	1.1	1.6	4	[ff]
		273.2	0.1077	2.941	1.2	1.5	2.6	9	[r]
		273.2	0.0987	2.950	1.2	1.4	2.4	7	[v]
		273.3*	0.1126	3.136	0.8	1.2	2.1	4	[ff]
		293.3*	0.1115	3.067	0.5	0.5	0.7	4	[ff]
		296.0	0.1219	3.168	2.4	2.7	4.4	4	[c]
		298.0	0.1185	3.091	4.0	4.5	6.7	5	[gg]
		353.3*	0.1247	3.102	0.1	0.1	0.2	4	[ff]
		393.3*	0.1450	3.165	1.5	1.5	1.9	4	[ff]
		433.3*	0.1548	3.180	2.0	2.2	2.9	4	[ff]
		473.3*	0.1650	3.195	2.9	3.5	4.4	4	[ff]
50.	CO ₂ +N ₂	273.2	0.6253	1.392	1.6	1.8	3.1	3	[o]
		323.2	0.7037	1.408	0.4	0.4	0.6	3	[hh]
		423.2	0.7244	1.256	0.2	0.3	0.4	3	[hh]
		523.2	0.7816	1.202	0.1	0.1	0.2	3	[hh]
		623.2	0.7976	1.106	0.2	0.2	0.3	3	[hh]
		642.2	0.8287	1.162	0.4	0.4	0.7	3	[ii]
		645.2	0.8179	1.148	0.5	0.6	0.8	4	[ii]
		648.2	0.8088	1.122	0.8	0.8	1.4	4	[ii]
		745.2	0.8239	1.903	0.4	0.6	1.2	1	[ii]
		842.2	0.8270	1.042	1.1	1.4	2.9	3	[ii]
		846.2	0.8236	1.040	0.9	1.2	2.3	3	[ii]
		950.2	0.8210	1.016	0.8	0.9	1.8	1	[ii]
		961.2	0.8316	1.021	0.6	0.8	1.5	3	[ii]
		1047.2	0.8466	1.029	0.4	0.5	0.7	1	[ii]
51.	CO ₂ +O ₂	370.0	0.9714	1.162	0.2	0.2	0.3	4	[h]

52.	$\text{CO}_2 + \text{C}_3 + \text{H}_8$	369.0	1.127	0.9256	0.3	0.3	0.5	3	[h]
53.	$\text{CO} + \text{H}_2$	273.2	0.1433	2.589	3.2	3.4	4.3	5	[r]
54.	$\text{D}_2 + \text{H}_2$	273.2	0.7151	1.442	0.2	0.2	0.5	5	[jj]
		313.2	0.7621	1.528	0.1	0.1	0.3	3	[n]
		338.2	0.7755	1.567	0.5	0.5	0.9	3	[n]
		366.2	0.7337	1.486	1.3	1.4	2.1	3	[n]
		368.2	0.7537	1.538	0.8	1.0	1.7	4	[n]
		408.2	0.7700	1.598	0.6	0.7	1.2	4	[n]
		448.2	0.7270	1.466	0.9	1.1	1.7	4	[n]
55.	$\text{D}_2 + \text{N}_2$	313.2	0.3951	1.990	1.9	2.2	3.8	2	[kk]
		338.2	0.4141	2.044	1.3	1.4	2.1	2	[kk]
		366.2	0.4119	1.967	1.0	1.1	2.0	2	[kk]
		368.2	0.4017	2.027	0.8	1.0	2.1	2	[n]
		408.2	0.4112	2.007	0.8	0.9	1.4	2	[n]
		448.2	0.4025	1.941	1.5	1.6	2.4	2	[n]
56.	$\text{C}_2\text{H}_4 + \text{H}_2$	298.2	0.5117	2.317	1.3	1.5	2.4	5	[gg]
57.	$\text{C}_2\text{H}_4 + \text{CH}_4$	590.0	0.9559	1.271	0.2	0.3	0.8	1	[h]
58.	$\text{C}_2\text{H}_4 + \text{N}_2$	591.0	1.408	0.7427	0.4	0.6	2.1	2	[h]
59.	$\text{H}_2 + \text{N}_2$	258.3*	0.5613	2.162	0.4	0.6	1.1	4	[ff]
		273.3*	0.5824	2.216	0.8	0.9	1.2	4	[ff]
		273.2	0.6484	2.601	3.5	4.2	6.9	5	[r]
		293.3*	0.5725	2.145	1.7	1.8	2.1	4	[ff]
		298.5	0.5545	2.056	1.0	1.2	2.4	9	[ll]
		313.2	0.5194	1.926	1.5	1.7	2.9	3	[kk]
		338.2	0.5383	1.966	1.8	2.0	2.9	3	[kk]
		348.0	0.5542	2.147	1.0	1.2	2.1	5	[ll]
		353.3*	0.5357	2.136	0.8	1.3	2.2	4	[ff]
		366.2	0.5383	1.922	0.9	1.0	1.6	3	[kk]
		368.2	0.5274	1.995	1.8	2.1	3.8	3	[n]
		372.3	0.5560	2.039	1.7	2.0	3.4	5	[ll]
		393.3*	0.5385	2.074	1.0	1.3	2.1	4	[ff]
		408.2	0.5368	1.998	1.7	1.9	3.2	3	[n]
		422.5	0.5554	2.012	0.6	0.7	1.2	8	[ll]
		433.3*	0.5334	2.038	1.7	2.1	2.8	4	[ff]
		448.2	0.5507	1.968	0.8	0.9	1.4	3	[n]
		473.3*	0.5585	2.120	0.4	0.4	0.6	4	[ff]
60.	$\text{H}_2 + \text{N}_2\text{O}$	273.2	0.1120	2.897	1.4	1.5	2.0	5	[r]
61.	$\text{H}_2 + \text{O}_2$	295.2	0.5551	1.987	1.0	1.3	2.6	11	[mm]
		313.2	0.5592	1.939	1.3	1.8	5.5	3	[kk]
		338.2	0.5370	1.916	0.7	0.8	1.3	3	[kk]
		366.2	0.5368	1.873	0.5	0.5	0.8	3	[kk]
62.	$\text{CH}_4 + \text{C}_3\text{H}_8$	368	1.665	1.015	1.2	1.3	1.8	3	[h]
63.	$\text{N}_2 + \text{O}_2$	313.2	1.733	0.5962	0.6	0.6	1.0	3	[kk]
		338.2	1.661	0.5970	0.4	0.4	0.6	3	[kk]
		366.2	1.661	0.5972	0.1	0.1	0.1	3	[kk]
		368.2	1.605	0.5402	0.7	0.8	1.2	3	[n]
		408.2	1.556	0.5413	0.5	0.6	1.3	3	[n]
		448.2	1.641	0.5676	0.3	0.3	0.5	3	[n]
		592.2	1.570	0.6290	0.1	0.1	0.1	1	[h]
64.	$\text{N}_2 + \text{C}_3\text{H}_8$	591.2	0.9428	0.8998	0.6	1.3	5.7	1	[h]
		811.2	0.9611	0.6576	1.2	1.3	1.9	1	[h]
65.	$\text{C}_3\text{H}_6\text{O} + \text{C}_6\text{H}_6$	349.9*	0.8083	1.044	0.4	0.5	0.7	3	[ee]
		376.0*	0.8236	1.038	0.1	0.1	0.1	3	[ee]
		398.3*	0.8344	1.048	0.3	0.4	0.5	3	[ee]
66.	$\text{NH}_3 + \text{Air}$	293.2	1.367	0.4940	0.5	0.5	0.9	4	[dd]
		353.2	1.345	0.5573	0.2	0.2	0.4	4	[dd]
67.	$\text{NH}_3 + \text{CO}$	295.2	1.414	0.5422	0.5	0.6	1.0	4	[dd]
68.	$\text{NH}_3 + \text{C}_2\text{H}_4$	298.2	0.8330	0.9948	0.4	0.7	2.0	3	[gg]
69.	$\text{NH}_3 + \text{H}_2$	298.5	0.4253	1.810	0.7	0.8	1.3	10	[ll]
		299	0.3778	1.528	0.6	0.7	1.2	4	[c]
		348.0	0.3982	1.553	1.3	1.7	3.2	5	[ll]
		372.3	0.4615	1.776	1.9	2.3	4.6	5	[ll]
		422.5	0.4724	1.686	1.2	1.4	2.6	5	[ll]

70.	$\text{NH}_3 + \text{N}_2$	298.5	0.7696	0.9692	0.5	0.6	0.9	9	[11]
		300	0.3743	0.5122	2.6	4.3	12.2	4	[c]
		348.0	0.6452	0.8716	1.4	1.8	3.7	6	[11]
		372.3	0.7221	0.9950	1.5	1.6	2.3	4	[11]
		422.5	0.7505	1.101	0.8	0.9	1.4	3	[11]
71.	$\text{C}_2\text{H}_6\text{O} + \text{Ar}$	367.0	1.139	1.059	0.4	0.5	1.3	3	[h]
72.	$\text{C}_2\text{H}_6\text{O} + \text{C}_3\text{H}_8$	368.0	1.051	0.9987	0.8	1.0	1.6	2	[h]
		591.0	1.049	0.9531	0.1	0.1	0.1	1	[h]
73.	$\text{CH}_4\text{O} + \text{Ar}$	351.2*	1.582	0.5215	0.1	0.1	0.1	3	[ee]
		373.2*	1.566	0.5485	0.1	0.2	0.2	3	[ee]
74.	$\text{CH}_4\text{O} + \text{C}_6\text{H}_{14}$	351.2*	0.6161	1.152	0.3	0.3	0.4	3	[ee]
		371.6*	0.6322	1.169	0.2	0.2	0.3	3	[ee]
		394.6*	0.6636	1.210	1.4	1.4	1.4	2	[ee]
75.	$\text{C}_2\text{H}_4\text{O}_2 + \text{C}_3\text{H}_8$	372.0	1.182	0.7668	0	0	0.1	1	[h]
76.	$\text{H}_2\text{O} + \text{Air}$	353.2	0.8727	0.6659	0.8	0.9	1.4	5	[dd]
77.	$\text{H}_2\text{O} + \text{CO}_2$	338.2*	1.364	0.5275	0.4	0.4	0.5	3	[nn]
		603.2*	1.322	0.5506	0.3	0.3	0.4	3	[nn]
78.	$\text{H}_2\text{O} + \text{N}_2$	338.2*	1.444	0.4183	1.1	1.3	1.9	3	[nn]
		603.2*	1.252	0.4948	1.1	1.1	1.3	3	[nn]
79.	$\text{CHCl}_3 + \text{C}_4\text{H}_{10}\text{O}$	332.5*	1.436	0.7839	2.0	2.3	3.1	3	[ee]
		347.2*	1.446	0.8060	0.7	0.7	0.9	3	[ee]
		377.8*	1.421	0.8137	0.0	1.0	1.3	3	[ee]
80.	$\text{C}_2\text{H}_6\text{O} + \text{C}_2\text{H}_4\text{O}$	374.0	0.7866	1.318	0.2	0.2	0.4	3	[h]

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COMPARISON OF EXPERIMENTAL DATA ON THE THERMAL
CONDUCTIVITY OF SOME GASES WITH THEORY

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Summary:

In this paper we attempt to give a survey of the present status of our knowledge of the theory of thermal conductivity of dilute gases.

For monatomic gases, the Chapman - Enskog equation is compared with experimental data on argon and helium. The approximate formulas for computing the thermal conductivity of polyatomic gases developed by Eucken, Hirschfelder, Mason and Monchick has been compared with the data on nitrogen, carbon dioxide, hydrogen, methane and ethane. The Mason and Monchick formulas are found to be the most accurate.

We also discuss the question of how these transport coefficients vary when a gas initially at atmospheric pressure is subjected to high pressures. An assessment is made of some methods used to predict the transport coefficients of a compressed gas ; the relation between experiment and the Enskog theory is discussed for argon and helium. A virial expansion with a logarithmic term is applied to describe the thermal conductivity of argon.

Key words -

Thermal conductivity - kinetic theory - logarithmic expansion
density dependence - correlation.

Introduction

During the last few years in our laboratory, we have developed experimental results for the thermal conductivity coefficient of compressed gases at high temperature. With the aim of testing the experimental data of argon, helium, hydrogen, nitrogen, carbon dioxide, methane, ethane, water and heavy water, we have compared them with the predictions of various theories.

If the gaseous pressure is sufficiently low, the thermal conductivity coefficient decreases first slowly, and afterwards proportionally to the pressure. This important decreasing of the thermal conductivity coefficient is observed when the mean-free-path of the particles is greater than or comparable to the dimensions of the gaseous layer.

In the usual experimental conditions proper to the study of the thermal conductivity of the dilute gases, i.e. corresponding to the pressure range about 0.1 to 2 bar, the thermal conductivity coefficient of almost all the studied gases is independent of the pressure. The mean-free-path of the particles is small with respect to the thickness of the gaseous layer, but still great with respect to the diameter of the particles.

In the range of study of the dense gases, an increase of pressure leads to an increase of the concentration of particles. Thus, a particle cannot travel large distances without being influenced by the others; the thermal conductivity increases with the density.

We have to examine only these two last cases.

I - DILUTE GASES -

A - Monatomic gases

The theory of transport phenomena in low density gases made up of spherical molecules, without structure, is formally complete (1), (2). The Chapman - Enskog treatment of the Boltzmann equation leads to expressions for the thermal conductivity coefficients in terms of collision integrals which are functions of the intermolecular potential. This expression is :

$$\lambda_0 = \frac{0.0832495 \sqrt{T/M} f_\lambda(T^*)}{\sigma^2 \Omega(2.2)^*(T^*)} \quad \text{W m}^{-1} \text{ } ^\circ\text{C}^{-1} \quad (1)$$

where M = molecular weight

T = absolute temperature

σ = a distance parameter which may be regarded as a measure of the molecular diameter.

$\Omega^{(2,2)*}(T^*)$ = the reduced collision integrals.

This last is determined as a function of reduced temperature T^* , with $T^* = T / (\epsilon / k)$. Here, ϵ represents the minimum energy of attraction between the molecules and k is Boltzmann's constant.

f_λ = a correction factor which accounts for the higher mathematical approximations to λ_0 . It is a slowly varying function of T which seldom differs from unity by more than about 0.5 %. This term can be omitted from equation (1) without significant error.

The essential computational problem is the evaluation of the reduced collision integrals, which are calculated from the intermolecular potential functions. Much of the available quantitative information about the intermolecular potential function has been obtained by fitting the statistical mechanical expressions to the experimental data. For this purpose, the statistical mechanical expressions are usually evaluated by means of an empirical form of the potential, involving a number of adjustable parameters. These adjustable parameters are then evaluated by fitting the resulting functions to the experimental data. Hence the ability to use equation (1), to correlate and predict experimental data rests on a proper choice of the model function.

In the past, one has usually relied on intuition to make this choice. Recently, Hanley and Klein, and Hanley and Childs, have clarified the overall relation of model functions, theoretical expressions and experiment (3) (4). Potential functions have been derived and classified in terms of families. If $V(r)$ is the interaction potential of two molecules separated by a distance r , and ϵ is the maximum energy of attraction, or energy minimum, the potentials of some well known families can be written as follows :

- The m - 6 family

$$V(r) = \epsilon \left[\left(\frac{\sigma}{r} \right)^m - \left(\frac{\sigma}{r} \right)^6 \right] / \left[\left(\frac{6}{m} \right)^{\frac{6}{m-6}} - \left(\frac{6}{m} \right)^{\frac{m}{m-6}} \right] \quad (2)$$

where the distance parameter σ is equal to the distance separating the molecules when $V(r) = 0$. The family parameter, m , depicts the repulsive part of the interaction. When $m = 12$, we have the famous 12-6 or Lennard - Jones potential.

- The Kihara family -

$$V(r) = 4 \epsilon \left[\left(\frac{\sigma - a}{r - a} \right)^{12} - \left(\frac{\sigma - a}{r - a} \right)^6 \right] \quad r > a$$

$$V(r) = \infty \quad r < a \quad (3)$$

where a is the hard core diameter of the molecule, σ is again the value of r for which $V(r) = 0$. The reduced parameter γ defined by $\gamma = a/\sigma$ is the parameter characteristic of the family.

- The Exp-6 family -

$$V(r) = \frac{\epsilon}{1 - 6/\alpha} \left[\frac{6}{\alpha} \exp \left\{ \alpha \left(1 - \frac{r}{r_m} \right) \right\} - \left(\frac{r_m}{r} \right)^6 \right] \quad (4)$$

where r_m is the value of r at the energy minimum and α is the family parameter which represents the steepness of the repulsive part of the function.

-The Morse family -

$$V(r) = \epsilon \left\{ \exp \left[- \frac{2c}{\sigma} (r - r_m) \right] - 2 \exp \left[- \frac{c}{\sigma} (r - r_m) \right] \right\} \quad (5)$$

where r_m is again the value of r at the minimum and the family parameter c is related to the curvature of $V(r)$ at $r = r_m$.

An examination of the fit of the viscosity coefficient and of the second virial coefficient to the expressions obtained from the above potentials for different gases have lead to the conclusion that no single form of the potential is clearly superior to the others (4) (5). As the thermal conductivity data are not so accurate as that concerning these two properties, one ought not to expect to make a choice here between these different potentials.

If one can properly fit experimental thermal conductivity data to equation (1), then one must be able to represent experimental viscosity data by the equation deduced from the kinetic theory :

$$\eta_s \times 10^7 = \frac{26.693 \sqrt{MT} f_\eta(T^*)}{\sigma^2 \Omega^{(2.2)*}(T^*)} \quad \text{kg m}^{-1} \text{ } ^\circ\text{C}^{-1} \quad (6)$$

without altering the correlation, the reverse calculus is also valid. Therefore, we determined theoretical thermal conductivity coefficients for argon and helium using the potential function and parameters found suitable for the viscosity data. These values were compared to our experimental values. Figure 1 shows the deviation curve for argon. The thermal conductivity curve of argon has been calculated by the Exp - 6 function with $\alpha = 15$, i.e. fit on the basis of the Di Pippo and Guevara data on viscosity (6). This figure clearly indicates that the correlation of λ_0 is satisfactory, allowing for the accuracy of our thermal conductivity data. In Table I is given the percentage deviation for helium between experimental data and a thermal conductivity curve calculated with a Lennard-Jones potential whose parameters provide a good fit to experimental viscosity data (5).

TABLE I

T	30	130	210	299	376	402	505
λ_{exp}	154.4	189.2	216.0	244.4	266.6	274.4	304.4
λ_{cal}	155.7	190.9	216.2	242.6	264.0	271.0	297.6
$\lambda_{\text{cal}}/\lambda_{\text{exp}}$	0.8	0.9	0.1	- 0.7	- 1	- 1.23	- 2.2

An examination of calculated thermal conductivity values with other potential functions leads to the conclusion that no single form of the potential function is clearly superior to the others.

Kinetic theory predicts that the thermal conductivity coefficient of a dilute monatomic gas is linearly related to the viscosity coefficient by the expression :

$$\lambda_0 = f C_v \eta_0 / M \quad (7)$$

where C_v is the specific heat at constant volume ($c_v = \frac{3}{2}R$) and

f is a constant. This constant is called the Eucken factor and is very close to 2.50. In figure 2 are shown the variation, at atmospheric pressure, of the Eucken factors of argon and helium versus the temperature. The viscosity coefficients have been taken from the paper of Di Pippo (5).

We have seen that the viscosity measured by Di Pippo and Guevara leads to calculated values of the thermal conductivity coefficients of argon and helium which is in good agreement with our experimental data. We will see that this conclusion is not restricted to these two gases.

It must be noted that there is a disagreement between two sets of experimental viscosity data for several gases (6). The disagreement is depicted for the case of argon in figure 3. One set (open circles) represents data points which are generally accepted as correct and which are used to compute the tables available. These data are mainly from the work of Trautz (7) and Vasilesco (8). The other set (closed circles) are points from the work of Di Pippo and Kestin (5) and from recent work by a group at Los Alamos (9). It is obvious that the discrepancy is important.

B - Polyatomic gases -

The Chapman - Enskog theory developed for monatomic gases describes poorly the thermal conductivity of polyatomic gases, since it does not allow for the influence of the internal degrees of freedom of molecules and their contribution to energy transfer. But, since the viscosity depends relatively little on the presence of internal degrees of freedom, then the relation (5) may be applied to polyatomic molecules with success, provided that the molecules are not too non-spherical. Hence it is suitable to discuss the thermal conductivity in terms of the viscosity and the Eucken factor (relation (7)).

1) The approximate formulae.

In 1913 Eucken (10) determined the first expression for the thermal conductivity of a polyatomic gas.

The Eucken factor, f , was written as a sum of terms which give separately the transfer of the translational energy and the transfer of the energy of the internal degrees of freedom :

$$f = \frac{\lambda_0 M}{\eta_0 C_v} = f_{tr} \frac{C_{v,tr}}{C_v} + f_{int} \frac{C_{v,int}}{C_v} \quad (8)$$

Here C_v is the total constant volume heat capacity, which is the sum of C_v the heat capacities due to the translational and internal modes.

$$C_v = C_{v,tr} + C_{v,int} \quad (9)$$

The partial Eucken factors, f_{tr} and f_{int} are defined similarly to f .

$$f_{tr} = \frac{\lambda_{e,tr} M}{\eta_0 C_{v,tr}} \quad (10)$$

$$f_{int} = \frac{\lambda_{e,int} M}{\eta_0 C_{v,int}} \quad (11)$$

Assuming that there is only slight interaction between the translational and internal degrees of freedom, by analogy with monatomic gases f_{tr} can be taken equal to 2.5. By simple mean free path arguments, f_{int} can be assigned a value of 1; this leads to the well-known expression for the Eucken factor:

$$f = 1 + \frac{9R}{4C_v} \quad (12)$$

Later, Hirschfelder (11), by considering a molecule in each quantum state as a separate chemical species and applying methods used in calculations on chemically reacting mixtures, suggested that

$$f_{int} = \frac{\rho D_{11}}{\eta} \quad (13)$$

where ρ is the gas density and D_{11} , the coefficient of self-diffusion. Then from Eq (8) Hirschfelder obtained the expression.

$$f = \frac{15}{4} \frac{R}{C_v} + \left(1 - \frac{3R}{2C_v} \right) \frac{\rho D_{11}}{\eta_0} \quad (14)$$

Starting from the formal semiclassical kinetic theory of polyatomic gas of Wang, Chang and Uhlenbeck (12) and Taxman (13) and systematically including terms which take into account in elastic collisions, Mason and Monchick (14) (15) (16) derived the final expressions for the partial Eucken factors:

$$f_{tr} = \frac{5}{2} \left[1 - \left(\frac{2C_{v,int}}{C_{v,tr}} \frac{1}{\pi Z} \right) \frac{A}{B} \right] \quad (15)$$

$$f_{int} = \frac{\rho D_{int}}{\eta} \left[1 + \frac{2}{\pi Z} \frac{A}{B} \right] \quad (16)$$

where

$$A = \frac{5}{2} - \frac{\rho D_{int}}{\eta_0} \quad (17)$$

and
$$B = 1 + \frac{2}{\pi Z} \left(\frac{5}{3} \frac{C_{v,int}}{R} + \frac{\rho D_{int}}{\eta_0} \right) \quad (18)$$

Here Z is the number of collisions necessary for establishment of equilibrium between the internal degrees of freedom and the translational motion.

These general expressions can be extended to several internal energy modes. If the internal energy modes are uncoupled, one defines a separate heat capacity (C_k), relaxation number (Z_k) and diffusion coefficient for energy (D_k) for each internal mode.

$$C_{v,int} = \sum_k C_k \quad (19)$$

$$\frac{C_{v,int}}{D_{int}} = \sum_k \frac{C_k}{D_k} \quad (20)$$

$$\frac{C_{v,int}}{Z} = \sum_k \frac{C_k}{Z_k} \quad (21)$$

In general it is the rotational modes or the rotational and vibrational modes, which are considered to contribute to the internal energy flux.

One assumes in general that for non-polar molecules the diffusion coefficient for internal energy transfer D_{int} is equal to the self-diffusion coefficient. A separate approximation is to retain only first order terms in Z . These two assumptions give:

$$f = \frac{\lambda_0 M}{\eta_0 C_v} = \left[\frac{15R}{4 C_v} + \left(1 - \frac{3R}{2 C_v} \right) \frac{\rho D_{11}}{\eta_0} \right] - \frac{2}{\pi C_v} \left(\frac{5}{2} - \frac{\rho D_{11}}{\eta_0} \right) \sum \frac{C_k}{Z_k} \quad (22)$$

It is easy to see that the first term in Eq. (22) is equivalent to the Hirschfelder expression (Eq. (14)), which fixes the upper limit of variation of f . Recently Saxena, Saksena and Gambhir (17) have proposed the following expressions based upon intuitive arguments rather than a rigorous kinetic theory, for the partial Eucken factors :

$$f_{tr} = \frac{5}{2} \left[1 - \frac{C_{v,int}}{C_v} \left\{ 1 - \exp \left(- \frac{C_v}{Z C_{v,tr}} \right) \right\} \right] \quad (23)$$

and

$$f_{int} = \frac{\rho D_{int}}{\eta_0} \left[1 - \frac{C_{v,tr}}{C_v} \left\{ 1 - \exp \left(- \frac{C_v}{Z C_{v,tr}} \right) \right\} \right] \quad (24)$$

The main characteristic of the various Eucken factor formulations presented is that each was developed without reference to a molecular model. Consequently, these expression should describe all polyatomic molecules and even models of real molecules.

In contrast, a classical treatment of gases consisting of rigid non spherical molecules has been developed by Dahler and colleagues. These authors consider in particular the effect of the coupling term of the linear and angular momenta of the molecules on the transport properties of a gas of rough spheres (18) (19) loaded spheres (20) and of spherocylinders (21).

2) Comparison with experimental data.

In small rigid polyatomic molecules, only collision numbers associated with the rotational relaxation are small enough to affect thermal conductivity significantly; hence Z_{vib} can be neglected. The theoretical expression of Z_{rot} is complicated and a strict theory has been developed only for very simple models (22) (23), however, Z_{rot} can be obtained from measurements of acoustical properties.

The dimensionless number $\rho D_{11}/\eta_0$ has been evaluated from the relations of self-diffusion and viscosity obtained by Chapman - Enskog.

$$\frac{\rho D_{11}}{\eta_0} = \frac{6}{5} \frac{\Omega^{(2.2)*}(T^*)}{\Omega^{(1.1)*}(T^*)} \quad (25)$$

The ratio of reduced integral collisions, $\Omega^{(2.2)*}(T^*)/\Omega^{(1.1)*}(T^*)$ varies slowly with the temperature, but it is very close to 1.1. for the more realistic potentials.

2.1. Nitrogen

On the figure 4 has been plotted the experimental data for N_2 and two theoretical estimates for the Eucken factors. The experimental viscosity coefficients are taken from the data of Di Pippo and Kestin (5). The experimental thermal conductivity coefficients are given in Table II.

TABLE II

T °C	27.4	28.9	134.8	146	185	200.2	203.7	227
$\lambda W m^{-1} \text{ } ^\circ C^{-1}$	25.8	26.0	32.7	33.7	36.3	37.3	37.5	39.0
T °C	300	375	401.5	451.7	501	528	556	669
$\lambda W m^{-1} \text{ } ^\circ C^{-1}$	43.5	48.3	49.8	53.3	55.5	57.0	59.2	66.9

The solid curve is obtained using the Hirschfelder formula (Equation (14)). The dashed curve represents the Mason-Monchick approximation (Equation (22)). For this calculation, the vibrational relaxation number, Z_{vib} , was assumed infinite, and the temperature variation of the rotational relaxation number was obtained from Parker's formula :

$$Z_{rot} = Z_{rot}^{\infty} \left[1 + \frac{\pi^{3/2}}{2} \left(\frac{\epsilon}{kT} \right)^{1/2} + \left(\frac{\pi^2}{4} + \pi \right) \frac{\epsilon}{kT} \right]^{-1} \quad (26)$$

Here Z_{rot}^{∞} is the limiting value of Z_{rot} obtained at high temperature, ϵ is the maximum energy of attraction between the two molecules and k is Boltzmann's constant. Z_{rot} and ϵ/k used in equation (26) were those given in reference (14).

2.2. Carbon dioxide

The thermal conductivity data of carbon dioxide are presented in figure 5 in terms of the Eucken factor as a function of temperature. The viscosity data are taken from Di Pippo (5). The solid curve represents the Hirschfelder formula (Equation 14)) the light dashed curve the Mason - Monchick formula (Equations (15) (16)).

Z_{rot} is calculated as in the reference (14). The heavy dashed curve is gotten using a much better approximation of D_{rot} ; proposed by Sandler (25). This author has shown that D_{rot} is not adequately approximated by the self-diffusion for Z less than 2.5 (such is the case for carbon dioxide where $Z_{rot} = 2.0$ at 300 °K). The model calculations indicate that a much better approximation for linear diatomic molecules is :

$$\frac{D_{rot}}{D_{11}} = 1 + \frac{0.27}{Z} - \frac{0.44}{Z^2} - \frac{0.90}{Z^3} \quad (27)$$

when this expression is used in the Mason - Monchick formulas, the

calculated values of the thermal conductivity are in exact agreement with the spherocylinder model calculations (21).

2.3. Hydrogen, Methane, Ethane

The Eucken factors of these three gases are represented in figures 6, 7, 8. Viscosity data are taken from the International Tables. For these gases, the Z_{rot} are higher, and we can hope for a better agreement with Hirschfelder data. So, until the experimental precision is improved and a better knowledge of the various constants occurring in the complicated theories is obtained, it seems sufficient to confine the interpretation of experimental data to the simple theory of Hirschfelder alone. For example, the oscillating - disk viscometers tend to yield higher values than capillary - flow viscometers ; the deviation which is about 3 % at 500 °C, corresponds approximately to the Eucken factor deviation between experimental data and the Hirschfelder equation.

C) Density dependence of the transport coefficients

1. Empirical relations

1.1. Excess values of the transport coefficient.

One consider often :

$$\Delta \lambda = \lambda(\rho, T) - \lambda_0(0, T) \quad (28)$$

the excess of thermal conductivity, where $\lambda_0(0, T)$ is the thermal conductivity in the low density limit corresponding to dilute gas at the same temperature. We have found that the thermal conductivity isotherms versus density are parallel to a good approximation ; it follows that the excess thermal conductivity $\Delta \lambda$ is independent of the temperature. This is illustrated in figures 9 - 13, where the excess thermal conductivities of respectively argon, helium, nitrogen, carbon dioxide and ethane are plotted as a function of density. It should be noted that this excess of thermal conductivity is not rigorously independent of the temperature, in particular, it does not take into account the anomaly of thermal conductivity in the critical region (26). When a large range of temperature is covered, discrepancies to the empirical relation have been observed (27).

Instead of considering the excess values of the transport coefficients as a function of density, it has been suggested by Golubev (28) (for the viscosity) that it is advantageous to consider them as a function of $\left(\frac{dP}{dT}\right)_\rho$. Such a relation has been studied by

Lennert and Thodos to obtain linear relations for the viscosity of argon, krypton, xenon (29). An extension to the thermal conductivity seems logical. The expression $\left(\frac{dP}{dT}\right)_\rho$ is calculated for each gas

with the corresponding equation of state. The figures 14 for argon

15 for helium, 16 for nitrogen, 17 for methane, 18 for ethane show that the representation of the thermal conductivity excess in terms of $(\partial P / \partial T)_\rho$ in logarithmic coordinates, leads to a linear relation between points, outside the critical region.

The resulting relation is expressed analytically by :

$$\Delta \lambda \times 10^3 = a \left(\frac{\partial P}{\partial T} \right)_\rho^b \quad (29)$$

The coefficients a and b are given for different gases in Table III.

TABLE III

GAS	a	b	Temperature range
Argon	10.28	0,95	25 < T °C < 200
	11.28	1	200 < T °C < 700
Helium	15.2	1	30 < T °C < 500
Nitrogen	13.2	0,95	25 < T °C < 528
Methane	18.2	0,95	30 < T °C < 450
Ethane	18.2	0.93	35 < T °C < 450

The coefficients a and b are not absolute, they depend the choice of equation of state as it is shown for argon for which $(\partial P / \partial T)_\rho$ has been calculate with two series of coefficients (30). The equation (29) can be used to extrapolate thermal conductivity to higher pressure.

1.2. Corresponding states

Under certain conditions, the law of corresponding states can be applied to the transport coefficients. In its elementary form, the law of corresponding states is only applicable to the inert cases. A method using molecular parameters as reduction parameters has been applied successfully by Trappeniens and co-workers to the viscosity of inert gases (31)

Another possible formulation of the corresponding states principle is to use the critical parameter λ_c as a reduction parameter. In this method, one considers the ratio λ / λ_c as a function of the reduced state variables:

P / P_c and T / T_c or ρ / ρ_c and T / T_c .

But as there are strong indications that the thermal conductivity becomes infinite at the critical point, the use of the value of the thermal conductivity at the critical point as a reduction parameter is meaningless. Therefore, we have used a pseudo-critical thermal conductivity obtained by extrapolation from data outside the critical region, using the excess values of thermal conductivity :

$$\lambda_c = \lambda_0(0, T_c) + \Delta \lambda(\rho_c, T) \quad (30)$$

where $\Delta \lambda$ is taken at a temperature T at least one hundred degrees higher than T_c . In figure 19 is represented the reduced excess of thermal conductivity versus the reduced density for different gases. If the agreement is relatively satisfactory up to the critical density, the discrepancy is important thereafter. This discrepancy can be due to the fact that the principle of corresponding states does not take into account the different internal molecular degrees of freedom to which polyatomic gases are sensitive.

II - Dense gases -

A - Theory of Enskog

An important development of the general theory of transport coefficients of a dense gas has been made by Enskog, from the generalized Boltzmann equation, for a gas of rigid spherical molecules. According to the theory of Enskog, the thermal conductivity coefficient at density ρ is represented by :

$$\lambda = \lambda_0 b \rho \left[\frac{1}{b \rho X} + 1.2 + 0.755 b \rho X \right] \quad (31)$$

where : λ_0 is the thermal conductivity coefficient of the fluid in the dilute state at the temperature considered

: $b = 2\pi\sigma^3/3$ is the covolume, with σ the diameter and m the mass of a molecule.

X is the value of the equilibrium radial distribution function at a distance σ from the centre of an individual molecule.

The theory of Enskog must be strictly applied to a gas of rigid spheres. Although the molecules of a real gas cannot be considered as rigid spheres, nevertheless the theory of Enskog has been widely used to interpret experimental thermal conductivity coefficients, mainly for lack of a simple expression for the density dependence of the thermal conductivity for more realistic molecules.

The most logical procedure is to compare the effect of density on the thermal conductivity coefficients of a real gas with that of a gas of rigid spheres having the same dilute gas value. This is achieved by calculating an effective value of the covolume b using the effective diameter σ utilized in the equation (1). The parameter X can be obtained from the virial expansion of rigid spheres.

$$X = 1 + 0.6250 b\rho + 0.28695(b\rho)^2 + 0.115(b\rho)^3 + 0.1103(b\rho)^4 + 0.0386(b\rho)^5 + 0.0127(b\rho)^6 + 0.004(b\rho)^7 + \dots \quad (32)$$

According to Eq. (31), the ratio λ/λ_0 for rigid spheres is a temperature independent function of the reduced density $b\rho$. Using this fitting, the thermal conductivity of argon and helium are compared with the Enskog theory in figure 20. It is seen that the discrepancy is important and that the Enskog theory fails completely for helium.

Another method has been described by several authors (32), using for b and X effective values deduced from the p - v - T of each gas. Then $b\rho X$ can be deduced from the equation of state for rigid spheres applied to the real gas.

$$b\rho X = \frac{PV}{RT} - 1 \quad (33)$$

Since for rigid spheres the external pressure P is identical to the thermal pressure $T\left(\frac{\partial P}{\partial T}\right)_\rho$

$$b\rho X = \frac{1}{R\rho} \left(\frac{\partial P}{\partial T}\right)_\rho - 1 \quad (34)$$

$\left(\frac{\partial P}{\partial T}\right)_\rho$ can be obtained from the compressibility isotherms or from the equation of state. In addition an effective value of the covolume can be calculated at low density, where X should approach unity. This is because at low density the modified Boltzmann equation of Enskog must reduce to the ordinary Boltzmann equation for the dilute gas. It follows that b is related to the second virial coefficient :

$$b = \frac{1}{R} \frac{dB}{dT} \quad (35)$$

obtained by substitution of the virial expansion :

$PV = RT + B\rho$ in Eq. (34). If we use an equation of state to calculate $b\rho^X$, the extrapolation of $\frac{b\rho^X}{\rho} = bX$ to $X = 0$, where

$X = 1$, gives the value of b at the temperature T .

Other choices of the parameter b can also be used at high density. The theory of Enskog predicts that, at constant temperature, λ/ρ assumes a minimum value as a function of ρ . This behavior is confirmed experimentally. Some authors calculate the product $\lambda_0 b$ from the experimental minimum value of λ/ρ at the temperature considered (2) (27).

This method has been applied to argon and helium. As it is shown in figure 2 the agreement is better for argon with the Enskog theory ; but the disagreement remains obvious for helium.

This although for one monatomic gas, reasonable agreement between the theory of Enskog and experiment has been obtained, it is better to use the empirical methods described in preceding section, for the prediction of thermal conductivity of dense gases.

P - Density expansion of the thermal conductivity coefficients.

In the case of dense gases, the statistical mechanical theory has attempted to take into account the effect of multiple collisions. Thus a virial expansion has been developed for the pressure.

$$PV = RT + B\rho + C\rho^2 \quad (36)$$

where the coefficients B, C , account for the effect of double, triple collisions. A similar development for the transport coefficients as a power series in the density has been obtained by Choh and Uhlenbeck (33) by solving the equation of Boltzmann in accordance with the method of Bogolubov (34). In particular, they obtained expressions for the first density correction and showed that these contained contributions from both collisional-transfer effects and three-body collisions.

We have seen that the excess thermal conductivity could be expanded in a power series in the density ρ , with coefficients independent of the temperature.

$$\Delta\lambda = \lambda(\rho, T) - \lambda(0, T) = \lambda_1\rho + \lambda_2\rho^2 + \lambda_3\rho^3 \quad (37)$$

However the values of the coefficients depend on the density range over which the equation is fitted to the data, as well as of the number of terms of the polynomial. The resulting equation can only be considered as an interpolation formula representing the experi-

mental data. The empirical coefficients cannot be identified with virial coefficients.

1. First coefficient .

Since the virial coefficients must be independent of the density and since at a low density, one can truncate the series at the first coefficient $\lambda_0(0,T)$, this coefficient can be predicted from the Chapman - Enskog theory (Equation (1)).

2. Second coefficient .

The Chapman - Enskog theory relates the dilute gas value to binary collision integrals. The theoretical prediction of the second coefficient λ_1 , involves the evaluation of triple - collision integrals. These integrals have been only calculated for a gas of rigid spheres (35) (36).

In consequence of the difficulties encountered in the estimation of the triple-collision integrals for a more realistic potential, several approximate methods have been carried out to evaluate this coefficient.

The first approximation is the Enskog equation for rigid spheres that we have already seen. Hoffman and Curtiss used a generalization of the Enskog development to take into account a part of the contribution from three-body interactions (37) and have calculated the second coefficient λ_1 for a Lennard-Jones potential (38). This calculation is only valid at high temperature in which the effect of the attractive portion of potential and bound pairs of molecules is small.

It seems that at lower temperature, or at higher pressure, it is necessary to take into account the dimerization effect. The bases of the molecular association have been described by Hirschfelder (39), Stogryn and Hirschfelder (40) have made calculation for the thermal conductivity; they consider monomer-dimer collisions but limit their definition of dimers to bound and metastable pairs. They use an expansion in the pressure rather than the density and they determine the coefficient $\beta = \left[\lambda^{-1} \left(\frac{\partial \lambda}{\partial P} \right) \right]_{P=0}$.

Recently Kim, Flym and Ross have made a similar analysis (41). The contribution of three-body collisions to λ_1 is approximated by two-body collisions between a monomer and a dimer, the latter being defined to include bound, metastable and orbiting pairs. Collisional transfer in binary collision is not taken into account as in the work of Stogryn and Hirschfelder.

For a comparison of these theories with experimental results, the second virial coefficient has been reduced to B_{λ}^* , by

$$\lambda_1 = 11.32 \sigma \left(\frac{\epsilon}{k} \right)^{\frac{1}{2}} M^{-\frac{3}{2}} B_{\lambda}^* \times 10^5 \text{ cal cm}^2 \text{ g}^{-1} \text{ sec}^{-1} \text{ K}^{-1} \quad (38)$$

Figure 22. shows that the agreement between these approximate theories leaves much to be desired, in particular at high reduced temperature. However, at lower temperature the agreement between the theories and the experimental results is satisfactory.

(It must be noted that the coefficients for helium and hydrogen have been obtained by extrapolation of the data at higher pressure).

C - Third coefficient.

A detailed inspection of the quadruple collision integrals determining the third coefficient becomes infinite. The divergence was found by estimating the probability of relevant collision events (42) (43) (44) and subsequently confirmed by explicit evaluation of a corresponding term for a two dimensional model gas (45) (46). It turns out that the leading term in λ_2 is proportional to $\ln L$, where L is a free path length which goes to infinity in the limit $\rho \rightarrow 0$, hence the divergence. It was conjectured that in a convergent theory, L should be of the order of the mean-free-path which is in first approximation at low density, inversely proportional to the density. It was suggested that λ_2 should be replaced by $\lambda_2 \ln \rho + \lambda_3$, so that

$$\lambda = \lambda_0 + \lambda_1 \rho + \lambda_2 \rho^2 \ln \rho + \lambda_3 \rho^2 + \dots \quad (39)$$

We consider the question of whether the experimental data can be represented by an equation of the form (39), as predicted by the theory, better than the expression (37).

As an example, we consider the thermal conductivity of argon at 25 °C in terms of the density.

If we wish a density expansion to correspond to a virial expansion, we must specify the following criterium : at a given temperature, the virial coefficients λ_0 , λ_1 , λ_2 should be independent of the density interval.

Successively we consider : the linear equation, the quadratic equation, the cubic equation given by expression (37) and the

equation given by expression (39). We determine the coefficients λ_0 , λ_1 , λ_2 , λ_3 from a least squares fit to all the data adding one point to each time. The results obtained are represented on the figures 23, 24, 25. The examination of this figure shows that only the equation including the logarithmic term gives constant coefficients λ_0 , λ_1 , λ_2 , in all the density range. We conclude that the theoretical expression is consistent with the experimental data. The percentage deviation between experimental data and calculated data is given in figure₃26; the agreement is satisfactory up to the density of 700 Kg m⁻³. A fit of the data with an equation including a logarithmic term has been considered similarly for the thermal conductivity coefficient of neon (47).

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Fig. 1 - Percentage deviation for dilute argon between our experimental thermal conductivity coefficient and the coefficient calculated from equation (1) using a potential function with parameters suitable for a good fit of the viscosity data of Di Pippo and Guevara. (Exp. 6 function where $\alpha = 15$; $\sigma = 3.65 \text{ \AA}$; $\epsilon/k = 156.5 \text{ }^\circ\text{K}$).

Fig. 2 - Variation of the Eucken factor $f = \frac{\lambda_e M}{\eta_b C_v}$ versus the temperature at atmospheric pressure for argon and helium

Fig. 3 - Experimental viscosity coefficients of dilute argon fitted with Eq. 7 using the 40.6 function with $\sigma = 3,15 \text{ \AA}$, $\epsilon / k = 224.1 \text{ } ^\circ\text{K}$

Fig. 4 - The experimental and calculated values for the total Eucken factor f for nitrogen as a function of temperature. Here the solid curve represents the Hirschfelder approximation, the dashed curve is obtained from Mason - Monchick formula (Eq.(22)).

Fig. 5 - The experimental and calculated values for the total Eucken factor f for carbon dioxide as a function of temperature. The solid curve represents the Hirschfelder approximation, the light dashed curve is obtained from the Mason - Monchick formulas (Eq.(15) (16)) and the heavy dashed curve results from the approximation of D_{rot} by equation (27).

Fig. 6 - Eucken factor for hydrogen - The solid curve represents Hirschfelder formulae (Eq. (14)).

Fig. 7 - Eucken factor for methane - The legend is the same as in Fig. 6.

Fig. 8 - Eucken factor for ethane - The legend is the same as in Fig. 6.

Fig. 9 - The excess thermal conductivity $\Delta \lambda$ of argon as a function of density

Fig.10 - The excess thermal conductivity $\Delta \lambda$ of helium as a function of density

Fig.11 - The excess thermal conductivity $\Delta \lambda$ of nitrogen as a function of density

Fig. 12 - The excess thermal conductivity $\Delta\lambda$ of carbon dioxide as a function of density

Fig. 13 - The excess thermal conductivity $\Delta\lambda$ of ethane as a function of density.

Fig. 14 - The excess thermal conductivity $\Delta \lambda$ of argon as a function of $(\partial P / \partial T)_\rho$

Fig. 15 - The excess thermal conductivity $\Delta \lambda$ of helium as a function of $(\partial P / \partial T)_\rho$

Fig. 16 - The excess thermal conductivity $\Delta \lambda$ of nitrogen as a function of $(\partial P / \partial T)_g$.

Fig. 17 - The excess thermal conductivity $\Delta \lambda$ of methane as a function of $(\partial P / \partial T)_g$.

Fig. 18 - The excess thermal conductivity $\Delta \lambda$ of ethane as a function of $(\partial P / \partial T)_{\rho}$

Fig. 19 - The reduced excess of thermal conductivity versus density for different gases.

Fig. 20 - Experimental thermal conductivity of argon and helium compared with the theory of Enskog. (b is obtained from λ_0)

Fig. 21 - Experimental thermal conductivity of argon compared with the theory of Enskog. (b is obtained from p-v-t data).

Fig. 22 - Variation of the reduced second virial coefficient B^* of the thermal conductivity versus the reciprocal reduced temperature and comparison with the theories of Enskog ; Hoffman and Curtiss ; Stogryn and Hirschfelder and Kim, Flynn and Ross.

Fig. 23 - Variation of the first virial coefficient of the thermal conductivity of argon λ_0 versus density ρ , at 25 °C.

Fig. 24 - Variation of the second virial coefficient of the thermal conductivity of argon λ_1 , versus density at 25 °C.

Fig. 25 - Variation of the third virial coefficient of the thermal conductivity of argon λ_2 , versus density at 25 °C.

Fig. 26 - Percentage deviation between the experimental values of the thermal conductivity of argon at 25 °C, in terms of the density and the calculated values by the equation :

$$\lambda = \lambda_0 + \lambda_1 \rho + \lambda_2 \rho^2 \ln \rho$$

where :

$$\lambda_0 = 17.4 \cdot 10^{-3} ; \lambda_1 = 2.60 \cdot 10^{-5} ; \lambda_2 = 0.1164 \cdot 10^{-7}$$

EXPERIMENTAL DETERMINATION OF ARGON PLASMA TRANSPORT PROPERTIES

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ABSTRACT - Measurements of the plasma transport properties of argon at atmospheric pressure are presented. The properties included in the study are electrical and thermal conductivity, radiation source strength, and viscosity as functions of the plasma temperature. The plasma source used for this study consists of a one-meter long, one-inch diameter, wall-stabilized, pulsed discharge with laminar, developed, axial flow at small Mach numbers. Data are collected by utilizing probe and optical diagnostics. The diagnostic techniques enable the plasma transport properties to be calculated using fewer assumptions than conventional methods (1).

KEY WORDS - Argon plasma, transport properties, radiation source strength, electrical conductivity, thermal conductivity, viscosity, plasma diagnostics, arc discharge, radiation absorption.

I. INTRODUCTION

The transport properties of high temperature argon have been calculated by a number of investigators (2-4). In addition, a more limited number of experimentally determined values are available (5-8). A comparison of the above results shows that serious discrepancies exist. Thus, these results should be carefully evaluated to determine the most reliable data for engineering usage.

The most important factor in evaluating experimentally determined properties is the source. It must be pure, stable, and in local thermodynamic equilibrium. If flow exists, it must be laminar, axial, and essentially developed so that axial convection and conduction losses can be neglected. The

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only discharge which appears to meet these stringent requirements is the wall stabilized arc. For these reasons, considerable effort was spent developing the wall stabilized source used for this study.

The diagnostic techniques used to investigate the source and collect data for the determination of properties must also be critically evaluated. This requires that sufficient details be made available in the reported results. The diagnostic techniques used for the present study are either explained in sufficient detail or suitable references are given. They include the measurement of the internal distributions of current density, total radiation, temperature, and stagnation pressure as well as voltage gradient, total current, static pressure gradient and total mass flow rate.

The last important consideration is the method used to reduce the measured data to transport properties (1). In this paper, the properties are obtained in a direct way so that the errors may be investigated. This allows changes to be made in the experimental procedures in order to reduce the significant errors in the measurements.

The results of the present investigation include thermal and electrical conductivity, total radiative source strength and viscosity as a function of plasma temperature. These data are evaluated and compared with the results of other researchers.

II. APPROACH

1. Introduction

The approach employed to measure transport properties was discussed in a previous paper (1). In summary, this method utilizes a plasma source which has a large region at constant temperature. This region includes and is symmetric about the cylindrical axis of the arc heated source. The discharge is wall stabilized and has a developed axial laminar flow at small Mach numbers. Because this symmetric source has a large diameter, a combination of radiometric and probe measurements may be used to diagnose its internal state. These data, combined with the equations which physically describe the discharge, are used in a direct way to obtain transport properties as a function of plasma temperature.

2. Facility

The plasma flow facility consists of: (1) a one-meter long, wall stabilized electric arc; (2) 1 megawatt d-c supply; (3) an automatic control system; (4) a system to store gases and measure flow rates; (5) diagnostic equipment such as probes, spectrometers, radiometers, and lasers. The basic arc column consists of 90 copper segments. Each segment is 1 cm thick with a 1-inch diameter bore and a 3-inch outer diameter. The segments are insulated from each other by a phenolic ring which is shielded from the arc radiation. The separation between segments is approximately 0.003 inches. This discharge may be pulsed for approximately two seconds without cooling the segments. Optical measurements are facilitated by mounting the arc vertically on a slide mechanism and the entire assembly is mounted on a hydraulic scissors table. This arrangement allows the discharge to be aligned with the

optical instrumentation.

A traversing mechanism is used with several water-cooled probes. The mechanism immerses the probes in the arc for approximately 20 milliseconds. Fig (1) shows the arc discharge tube and the probe traversing mechanism.

Figure 1. Wall-Stabilized Electric Arc Apparatus

The arc is started by placing a pneumatically-driven, uncooled anode in contact with the cathode tip. A resistor is connected in series with this anode to limit the starting current. The uncooled anode is withdrawn in 50 milliseconds and the arc attaches to the main anodes as the starter passes them. Shortly after initiating the discharge, addition power supplies are actuated until the desired current level is achieved.

A motor driven automatic controller is used to sequence the events during the operation. At preset time intervals, starting, addition of power, triggering of data acquisition systems and shutdown occur.

3. Basic Equations

In the discharge region, where approximate developed conditions exist, the plasma may be described by the following equations (9):

Momentum

$$(1 - v_z^2/c^2) \frac{dP}{dz} = \frac{1}{r} \frac{\partial}{\partial r} \left[r \mu \frac{\partial v_z}{\partial r} \right] \quad (1)$$

$$\frac{v_z}{\alpha} \frac{\partial \phi}{\partial z} = \frac{\partial^2 \phi}{\partial r^2} + \frac{1}{r} \frac{\partial \phi}{\partial r} + \frac{\partial^2 \phi}{\partial z^2} + \sigma E^2 + P_A - P_R \quad (2)$$

$$\phi = \int_{T_w}^T \lambda(T) dT \quad (3)$$

Ohm's Law

$$j_z = \sigma E_z \quad (4)$$

Radiative Transport

$$\frac{dI_v}{ds} = \epsilon_v - \alpha_v I_v \quad (5)$$

$$P_R = \int_0^\infty \epsilon_v dv$$

$$P_A = \int_{4\pi} \int_0^\infty \alpha_v I_v dv d\omega \quad (6)$$

Kirchoff's Law

$$\epsilon_v = \alpha_v B_v(T) \quad (7)$$

Because the flow velocity in the experiments is small compared to the speed of sound, the term v_z^2/c^2 may be neglected in Eq (1). In addition, the terms representing axial convection and conduction need not be included in Eq (2) for the experimental conditions. If absorption plays an unimportant role in the radiant energy transport, then the set of equations can be solved by computer program using the temperature dependent transport properties and boundary conditions as input data for a given voltage gradient (10). The calculated curves in this report are based on the above assumptions and Emmons' measured transport properties (5). If the absorbed power, P_A , must be included, an approximate solution may be obtained if the detailed radiative data are known as a function of frequency as well as temperature (11).

4. Working Equations

The electrical conductivity is determined by substituting the measured axial current density and voltage gradient in Ohm's law. This gives

$$\sigma(T_c) = j_z(0)/E_z \quad (8)$$

As the arc current is varied, T_c changes. Thus $\sigma(T_c)$ may be determined as a function of temperature.

In the constant temperature region near the axis, the energy transport by conduction may be neglected. For this case, the energy equation becomes

$$j_z \cdot E_z = P_R - P_A = P_E \quad (9)$$

Thus, the values of P_E are determined for various centerline temperatures.

If P_A is small, then P_R is obtained for the total wavelength range of importance as a function of plasma temperature.

The energy equation may be integrated two times to obtain the heat flux potential relative to the arc axis (1). This yields

$$\phi(r_b) - \phi(0) = \int_0^{r_b} \frac{1}{r_a} \left\{ \int_0^{r_a} [\sigma(r) E_z^2 - P_E(r)] r dr \right\} dr_a \quad (10)$$

Because the temperature distribution is known, the previously determined values of $\sigma(T)$ and $P_E(T)$ from Eqs (8) and (9) may be used in Eq (10) to determine $\phi(r_b) - \phi(0)$. However, the value of P_A may change as the integration progresses down the temperature profile. Thus, if P_A is significant, the integration should be terminated after a limited temperature drop and a temperature profile having a lower centerline temperature used to extend the calculation. $\phi(r_b) - \phi(0)$ is plotted as a function of temperature and the derivative of this curve yields, according to Eq (3),

$$\lambda = \frac{d}{dT} [\phi(r_b) - \phi(0)] = \frac{d}{dT} [\phi(r_b)] \quad (11)$$

Thus, no assumptions about the analytical form of λ are required.

For the flow conditions studied, Eq (1) may be integrated over the constant temperature region to yield (1)

$$\mu(T_c) = \mu(r) = \frac{r^2}{4[v_z(r) - v_z(0)]} \frac{dP}{dz} \quad (12)$$

Thus, the viscosity can be determined from measurements of static pressure gradient and the velocity profile.

III. DIAGNOSTIC METHODS

1. Plasma Temperature

As outlined in Ref (1), the temperature distribution of the plasma source is determined from the measured radial distribution of the continuum source strength in a line-free region of the spectrum. This is achieved by first measuring the absolute lateral intensity profile with a spectrometer and a standard source. These data are then reduced to radial distributions by employing a computer program developed by H. Olsen et al.(12). From these data, the radial temperature is obtained by employing the measured continuum source strength as a function of temperature as determined by H. Olsen (13). Lateral scans are obtained by either sweeping the image of the arc slit over the entrance slit of the spectrometer or by moving the plasma source across the optical axis in steps of 0.01 inch or less. For each step, the arc is pulsed for approximately one second. The first method gives good results for the centerline temperature while the second method is preferred in order to obtain more accurate results in the conduction dominated region of the plasma near the arc wall. A series of measured profiles

for various arc currents is shown in Fig (2), and Fig (3) shows a comparison of measured and computed centerline temperatures as a function of arc current.

Figure 2. Temperature Profiles for Various Arc Currents

2. Current Density

Current density distributions are determined by measuring the internal magnetic field strength of the discharge. The magnetic field data are obtained with a 1/8-inch diameter Hall-effect probe (14). Traverses through the discharge are achieved by utilizing the probe traversing mechanism. The measured data are corrected for plasma disturbance and finite probe size and are reduced to current density by employing electromagnetic theory. Values for current density at the arc axis as a function of total arc current are shown in Fig (3).

3. Voltage Gradient

The axial voltage gradient (E_z) is measured as a function of arc current by immersing two tungsten probes in the plasma with the traversing mechanism (1). In addition, E_z is determined by measuring the rate at which energy is transferred to the wall per unit length (Q). For the developed region (neglecting radiative errors due to the finite length of the discharge),

$\dot{Q}$ is equal to the power input to the discharge per unit length. Thus,

$$E_z = \dot{Q} / I_t$$

where I_t is the total arc current. In order to check these values, the total arc voltage and length are used to estimate E_z . This value should be greater because the measured total voltage includes electrode drops and the increased field in the developing region. The three results are shown in Fig. (4).

Figure 3. Centerline Current Density and Temperature as a Function of Total Arc Current

Figure 4. Voltage Gradient as a Function of Total Arc Current

4. Flow Measurements

A pressure probe system was designed to measure the difference between stagnation and static pressures. This probe is shown in Fig. (5).

Figure 5. Stagnation Pressure Probe and Charge Amplifier

The probe system consists of two crystal pressure transducers which are mounted in identical water-cooled probes. One probe is wall mounted so that it measures fluctuations in static pressure. The other probe is mounted on the traversing mechanism in order to measure the radial stagnation pressure distribution. Each of the transducers is connected to a separate charge amplifier, and the two signals from the amplifiers are electronically combined so that their difference is measured and the common-mode noise is eliminated. This system gives a good representation of the difference between static and stagnation pressures even though small variations in static pressure may occur.

The probe is subject to small acceleration effects caused by the traversing mechanism, and the corresponding corrections must be applied before the data is reduced. This is accomplished by injecting the probe into the arc chamber with no gas flow. The output is then used as a base line for future measurements.

This pulse, as illustrated in Fig. (6) may be represented by a Fourier series expansion involving only sine terms provided that the half period, t_0 , is chosen so that the system is in a quiescent state before and after the measurement. In order for a Fourier expansion to accurately represent the physical situation, the quiescent state must exist for at least the amount of time required for a sound wave to propagate through the tube. It is desirable to maintain the quiescent state longer than that, but more terms will be required in the expansion. The expression for the measured pulse is

$$\Delta P_m = \sum_n A_n \sin(n\omega t) \quad (13)$$

where $\omega_0 = \pi/t_0$. From the measured pulse, a computer code is used to calculate the A_n 's where

$$A_n = (2/t_0) \int_0^{t_0} \Delta P_m \sin(n\omega_0 t) dt \quad (14)$$

If the system may be represented by a linear differential equation with constant coefficients, then the corresponding pressure at the orifice can be represented by

$$\Delta P_u = \sum_n R_n A_n \sin(n\omega_0 t + \alpha_n) \quad (15)$$

Figure 6. Measured Pressure Pulse as a Function of Time

Measurements of the probe response using sinusoidal pressure waves showed that the required conditions exist, and the corresponding response data are shown in Fig. (7). The amplitude response (R_n) extrapolated to zero frequency is not unity because the two transducers used for these measurements did not have the same sensitivity. A computer code uses these response data to calculate the pressure at the probe orifice. Approximately forty terms are required in the Fourier expansion. Measured and corrected pressure profiles are illustrated in Fig. (8) and Fig. (9).

Calibration may be accomplished in two ways:

1. An absolute calibration of the electronic instrumentation can be performed by applying a known pressure pulse to the probe and measuring it with both the transducer and a manometer. The probe response data can be extrapolated to zero frequency at which point $P_{\text{probe}} / P_{\text{static}} = 1$. The intercept will be the calibration constant by which the measured pressure must be multiplied to yield the pressure distribution.

2. The measured pressure can be calibrated by normalizing the velocity profile to the measured mass flow rate.

Figure 7. Amplitude and Phase Response For the Stagnation Pressure Probe

Figure 8. Measured Radial Pressure Distribution

Figure 9. Corrected Radial Pressure Distribution

The latter method performs an electronic calibration and tends to compensate for flow effects due to the finite probe size. For this case, the mass flow rate can be expressed as

$$\dot{m} = 2\pi \int_0^{R_w} \rho_m v_m r \, dr \quad (16)$$

where R_w is the wall radius and the mass density ρ_m is determined from the temperature distribution (15). It remains then to express the axial velocity as a function of the measured difference between stagnation and static pressure ΔP . This is accomplished by writing the equation of motion for a fluid mass element. If the viscous effects are negligible compared with the acceleration effects in the region near the probe due to its presence, the integrated equation of motion becomes

$$v_m^2/2 = \int_{(\rho_m, P_m, T_m)}^{(\rho_o, P_o, T_o)} [dP/\rho] \quad (17)$$

where the integration is performed along the flow path from free stream conditions to stagnation conditions. For the argon plasmas investigated, the electron density is essentially equal to the ion density and

$$\rho = (n_i + n_a)m_a \quad (18)$$

$$P = (2n_i + n_a)kT \quad (19)$$

In addition, the thermodynamic process may be represented by a Taylor expansion which yields

$$T - T_m = a_1(P - P_m) + a_2(P - P_m)^2 + \dots \quad (20)$$

Eq's. (18) and (19) may be combined to yield

$$\rho = P \frac{Am_a}{kT} \quad (21)$$

$$\text{where } A = (n_e + n_a)/(2n_e + n_a) \quad (22)$$

If Eq's. (20) and (21) are used to eliminate ρ and T in the integrand of Eq. (17), the integration can be performed to give

$$v_m^2/2 \approx (P_m/\rho_m)[(P_0 - P_m)/P_m - 1/2 (P_0 - P_m)^2/P_m^2 + a_1 k \rho_m / 2 A m_a (P_0 - P_m)^2/P_m^2] \quad (23)$$

where A , which is assumed to be constant during the process, only appears in a second order term. Pressure measurements based on the first calibration technique show ΔP to be less than 7 inches of water, while P_m is in the order of 400 inches of water. Thus, it should be a good approximation to express the free-stream velocity as

$$v_m = [2(P_0 - P_m)/\rho_m]^{1/2} \quad (24)$$

where no assumptions are made on the thermodynamic process involved in the pressure change. In order to complete the calibration, let

$$(P_0 - P_m) = B^2 \Delta P_u \quad (25)$$

where B^2 is the calibration constant. Substituting this result in Eq. (24) yields

$$v_m = B[2\Delta P_u/\rho_m]^{1/2} \quad (26)$$

The mass flow rate is determined by a calibrated system of sonic nozzles, and the details of this system may be found in Ref. (15). By combining Eq's. (26) and (16), the calibration constant becomes

$$B = \dot{m} / \{ 2\pi \int_0^R [2\rho_m \Delta P_u]^{1/2} r dr \} \quad (27)$$

In the development of an expression for the velocity distribution, it was assumed that the second-order terms of $(P_0 - P_m)/P_m$ were negligible. The correctness of this assumption depends on the value of the unknown constant a_1 . It can be demonstrated that a_1 is small and the second-order terms are unimportant. According to the momentum balance equation, the velocity distribution in the constant-temperature region of the arc will be parabolic. If the velocity distribution depends only on first-order terms in $(P_0 - P_m)/P_m$, then a plot on log-log paper of the radial distribution of $\sqrt{\Delta P_{\text{centerline}}} - \sqrt{\Delta P}$ should yield a straight line with a slope of 2. Such a plot is shown in Fig. (10). The plot indicates that a_1 is small because the distribution is approximately parabolic as expected. Outside of the constant-temperature region the viscosity is not constant and the velocity profile as indicated in Fig. (10) deviates from a parabolic profile. A velocity distribution calculated from pressure measurements calibrated by the mass flow rate is shown in Fig. (11).

Figure 10. Log-Log Plot to Check Parabolic Velocity Distribution

Figure 11. Radial Velocity Distribution

One additional comparison can be made to test the accuracy of the velocity distribution. The calibration constant determined by method (1) is 0.67 and the constant determined by method (2) is 0.65. Since the two methods of determining the constant are independent, the close correspondence of the two calibration constants indicates that the pressure distribution was measured accurately and that the velocity may be expressed as indicated.

5. Total Radiation

The total effective radiation, defined by Eq. (9), is determined by the total specific, electrical power input measured in the constant temperature region of the discharge. These data, which are integrated over the entire frequency range, should yield the most reliable total radiative source strength as a function of temperature.

In addition to the above data, external radiative measurements are made with calibrated radiometers (16). Included in these measurements, are total radiant power per unit arc length and lateral profiles of the total intensity $[J = \int I_v dv]$. The first measurement is achieved with a FT-19, Hilger-Watts thermopile having a time response of 0.01 sec, and representative data are shown in Fig. (12). This procedure and its limitations are discussed in Ref. (16). Lateral profiles are obtained by sweeping the arc image over the element

Figure 12. Axial Static Pressure Gradient and Total Power Radiated as Functions of Arc Current

of a thermistor detector having a time response of 0.001 sec (1). Because of large drift in the zero base line, an a-c amplifier is used with a low frequency response down to 1 hertz. In order to eliminate these problems and improve the spatial resolution, profiles are obtained by moving the arc image across the optical axis in small steps, and recording the data with a FT-19 thermopile. Because the thermopile is more sensitive than the thermistor, it can be placed behind a narrow slit which enhances spatial resolution. Also, the d-c output eliminates low frequency response problems. For these lateral profiles, a mirror is required to focus the arc image on the radiometer element or slit; therefore, these data are normalized to the total measured radiation per unit arc length in order to reduce errors caused by reflection losses.

If the absorbed power is significant, it is questionable whether the total specific radiation can be determined by external measurements. This can be seen by investigating the operations which must be performed on the radiation transport equation, Eq. (5), in order to yield the total specific radiation. For this case, the equation must be integrated over the frequency interval in which the radiometric system is sensitive. The term on the left-hand side of Eq. (5) can be integrated to yield dI , but it is impossible to integrate the second term on the right-hand side for the general case.

If it is assumed that the entire plasma is at a constant temperature and that the optical depth ($\tau_v = 2\alpha_v R_w$) is small, then it is possible to express the power absorbed at the discharge axis in terms of two radiometric measurements of the intensity made through the center of the arc. The first measurement is made as usual, and the second is made with a mirror placed behind the arc (16). For the first case, the integration of the transport equation through a diameter yields

$$I_{v1} = B_v(T)[1 - e^{-2\alpha_v R_w}] \quad (28)$$

where Kirchoff's law, Eq. (7), was used to substitute for ϵ_v . If a mirror is placed behind the plasma, the intensity becomes

$$I_{v2} = I_{v1} + R_v B_v(T)[1 - e^{-2\alpha_v R_w}]e^{-2\alpha_v R_w} \quad (29)$$

where R_v is the reflectivity of the mirror.

For small $2\alpha_v R_w$, Maclaurin expansions for Eq's. (28) and (29) yield

$$I_{v1} \approx 2B_v(T)\alpha_v R_w = 2R_w \epsilon_v \quad (30)$$

and

$$I_{v2} - I_{v1} \approx R_v I_{v1} [1 - 2\alpha_v R_w] + \dots \quad (31)$$

If R_v is assumed to be approximately constant and replaced by $\bar{R}$, then Eq. (30) can be integrated over a frequency interval Δv to yield

$$I_2 - (1 + \bar{R})I_1 = -(4R_w\bar{R}) \int_{\Delta v} B_v(T) \alpha_v^2 dv \quad (32)$$

where Eq. (30) was used to substitute for I_{v1} on the right-hand side. Eq. (32) may be solved for the unknown integral. This integral will allow the power absorbed per unit volume over the frequency interval Δv to be estimated. This estimation will serve as a correction to the corresponding measured total specific radiation.

The absorbed power per unit volume is expressed in Eq. (6). In the limit of an infinitely long arc column, Eq. (6) for the axial case becomes

$$P_A = \int_{\Delta v} \int_{4\pi} \alpha_v I_v d\omega dv$$

where the first approximation for I_v is given by

$$I_v \approx \alpha_v s \quad (33)$$

and $d\omega$ is given by

$$d\omega = 2\pi R_w d\theta/s \quad (34)$$

Integration over the solid angle yields

$$P_A = 2\pi^2 R_w \int_{\Delta v} B_v(T) \alpha_v^2 dv \quad (35)$$

This last equation can be combined with Eq. (32) to yield

$$P_A = (\pi^2 I_1 / 2R_w \bar{R}) [(1 + \bar{R}) - I_2/I_1] \quad (36)$$

For the constant temperature arc, the total power radiated per unit arc length in the interval Δv may be expressed as

$$P_{RL} = \int_{\Delta v} \pi R_w^2 (4\pi) \epsilon_v dv \quad (37)$$

By using Eq. (30) to substitute for ϵ_v and integrating, Eq. (37) becomes

$$P_{RL} = 2\pi^2 R_w I_1 \quad (38)$$

Substituting for I_1 from Eq. (38) into Eq. (36) gives for the absorbed power per unit volume at the arc centerline

$$P_A = (P_{RL}/4R_w^2 \bar{R})[(1 + \bar{R}) - I_2/I_1]$$

Because the thermopile has a linear response,

$$I_1/I_2 = V_1/V_2$$

where V_1 and V_2 are the measured voltages. Thus, absolute intensities are not required for the estimation of P_A . Measurements of $\bar{R}$ are made by using the arc as a source and results compare well with estimates made from the reflectivity curves for the mirrors in use (16).

IV. RESULTS AND CONCLUSIONS

1. Diagnostic Measurements

Centerline temperature measurements are reproducible within $\pm 100^\circ$ K. The accuracy of the absolute values is dependent upon the National Bureau of Standards spectral standard and the data relating continuum intensity to temperature (13). Measured centerline temperatures agree with values based on calculations using Emmons' data (5) at $10,700^\circ$ K and deviate to a maximum of 500° K higher at approximately $12,700^\circ$ K.

The measurements of current density are most reproducible at the centerline, and these measurements were used in the data analysis. A correction of approximately 10% was made for plasma disturbance due to the probe (14). The total error in these measurements is estimated to be $\pm 5\%$.

Probe measurements of the voltage gradient are subject to a $\pm 3\%$ instrumentation error; however, the effect of the plasma sheath around the probe has not been determined. Nevertheless, the data is consistent with the measured total voltage and is considered to be the most accurate. The instrumentation error for calorimetric determinations of the voltage gradient is estimated to be $\pm 4\%$. Errors associated with radiation loss due to finite arc length are estimated to be -8% at the higher current levels although no correction was applied in the data reduction.

2. Transport Properties

From the measurements of voltage gradient, current density, and temperature, it is estimated that the error in the magnitude of electrical conductivity is $\pm 6\%$ and the error in temperature is $\pm 100^\circ \text{K}$. Plots of σ vs. T in Fig. (13) agree very well with Emmons' data.

Figure 13. Electrical Conductivity as a Function of Temperature

The measurements of the effective radiated power, P_E , are correct within $\pm 6\%$. These results agree with Emmons' at $10,700^\circ \text{K}$ but are lower at higher temperatures. Data published by AVCO and Northwestern University were obtained with radiometers and quartz optics (17, 18). Our probe and radiometric data, which have not been corrected for absorption, are compared with the data of the other investigators in Fig. (14). A single measurement of the absorption correction at the centerline was made at $12,700^\circ \text{K}$ and was found to be approximately 50 watts/cm^3 . If our radiometer data were corrected for absorption, it appears that it would agree well with Northwestern's results. The probe measurements of P_E are higher than our radiometric data. This is consistent since they include the radiation over the entire spectrum.

The measured thermal conductivity has a much larger limit of error. A preliminary investigation shows that the error is large in the radiation dominated region but becomes less where the energy transport is dominated by thermal conduction. A computer program is being written to calculate the relative error in the thermal conductivity measurements. This is possible because of the direct methods used to reduce data to transport properties. Fig. (15) compares our thermal conductivity with the results obtained by other investigators. Because limits of error are not given, no reasonable correlations can be given on the reliability of measured data.

Figure 14. Effective Radiated Power Density as a Function of Temperature

Figure 15. Thermal Conductivity as a Function of Temperature

The errors in the viscosity measurement cannot be precisely determined because the analysis of the pressure probe is still in an elementary stage; however, a few comments on the measured data are appropriate. Static pressure gradient measurements are reproducible with $\pm 5\%$, and the extremes of the data are shown in Fig (12). Each curve represents data obtained for a measured mass flow rate of 0.0055 lb/sec. The difference between the curves represents data taken on different days and includes the maximum error associated with reproducing the flow rate. Measurements of the difference between stagnation and static pressure are reproducible within 10% for insertion and extraction of the pressure probe. The velocity distribution

appears to be parabolic, and the independent calibrations of the pressure probe yield essentially the same result. The measured data were substituted into Eq (12) to obtain viscosity. Table I compares our viscosity at 12,700°K with values determined by other investigators.

TABLE I
VISCOSITY OF ARGON AT 12,700° K
(Millipoise)

This Study	* Devcto	Stojanoff	* Carnevale	* Amdur and Mason	* Brokaw
1.6	1.8	1 to 3	2.5 - 4	3.7	2.8

* Estimated from reported data

V. NOMENCLATURE

A_n	Fourier coefficient
B^2	Pressure probe calibration constant
B_v	Planck's blackbody function
c	Speed of sound
V	Voltage gradient
I	Radiative intensity
I_t	Total arc current
j	Current density
k	Boltzmann's constant
$\dot{m}$	Mass flow rate
m_a	Atomic mass
n_i, n_a, n_e	Respective number densities of ions, atoms, and electrons
P	Pressure

ΔP	Difference between stagnation and static pressure
$\frac{dP}{dz}$	Static pressure gradient
P_A	Total radiation power absorbed per unit volume
P_E	Total power radiated per unit volume
P_R	Effective radiated power density
P_{trans}	Pressure measured by crystal transducer
$\dot{Q}$	Rate of heat transfer to the wall per unit length
R	Mirror reflectivity
r	Radius
R_n	Pressure response of pressure probe at angular frequency $n\omega_0$
R_w	Wall radius of arc discharge
s	Path length
T	Temperature
t	Time
v	Axial velocity
V	Voltage
α_n	Pressure probe phase angle response at angular frequency $n\omega_0$
α	Thermal diffusivity
α_v	Absorption coefficient
ϵ_v	Emission coefficient
θ	Angle
λ	Thermal conductivity
μ	Viscosity
ν	Frequency of radiant energy
ρ_0, ρ_m	Stagnation and free-stream mass density
σ	Electrical conductivity

τ	Optical depth
ϕ	Heat flux potential
ω	Solid angle
ω_0	Angular frequency

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HEAT CONDUCTION OF BINARY MONOATOMIC GAS MIXTURES

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Abstract - Heat conduction of binary mixtures of monoatomic gases is investigated. The experimental data available are analysed. These are compared with the theoretical results predicted by different formulas. Two effects are discussed which take place during heat transfer through a gaseous mixture.

Within many years the elementary theory of gaseous mixtures developed by Wassiljewa /1/ has been attracting attention of scientists because of its simple analytic form.

Assuming that heat in a gaseous mixture is transferred by molecules of all components and the total heat quantity is equal to the sum of the heat quantities transferred by each component of the mixture, Wassiljewa has obtained

$$\lambda = n_1 f \frac{1}{3} \bar{v}_1 \bar{\ell}'_1 \rho_1 c_{v1} + n_2 f \frac{1}{3} \bar{v}_2 \bar{\ell}'_2 \rho_2 c_{v2} , \quad (1)$$

where $\bar{\ell}'_1$ and $\bar{\ell}'_2$ are mean free paths of the components. For the first species the mean free path expression before collision with any molecule of the same or other species is of the form /2/

$$\bar{\ell}'_1 = \left(\sqrt{2} \pi d_1^2 n_1 + \pi \sigma^2 n_2 \sqrt{\frac{n_1 + n_2}{n_2}} \right)^{-1} . \quad (2)$$

A similar expression may be written for the second species

$$\bar{\ell}'_2 = \left(\sqrt{2} \pi d_2^2 n_2 + \pi \sigma^2 n_1 \sqrt{\frac{n_1 + n_2}{n_1}} \right)^{-1} . \quad (3)$$

Simple manipulations transform equations (1) - (3) into

$$\lambda = \frac{\lambda_1}{1 + \frac{x_2}{x_1} A_{12}} + \frac{\lambda_2}{1 + \frac{x_1}{x_2} A_{21}} , \quad (4)$$

which is referred to as Wassiljewa's equation. The constants A_{ij} entering into this relation are found from the formula

$$A_{ij} = \sqrt{\frac{m_i + m_j}{2m_j}} \left(\frac{\sigma}{d_i}\right)^2$$

Next we shall consider the case of monoatomic gases. Comparison of the predicted thermal conductivities and experimental data /3/ shows the greatest divergence of -40% ($m_1/m_2 = 0.0305$) for mixture He-Xe and the smallest one of -1.5% ($m_1/m_2 = 0.64$). The divergence of experimental data and the predicted values is a function of the component mass ratio and may be attributed to the difference in the mean paths for the appropriate mechanisms of diffusion and heat conduction.

Some investigators who have made attempts to obtain a better agreement between the experimental data and theoretical values have suggested other relations for constants A_{ij} . The methods for determination of A_{ij} are classified as approximate, semi-empirical and empirical.

The work of T. Cowling /4/ is worthwhile to be considered in more detail. In his work the author treats heat conduction in gaseous mixtures with the aid of two conventional effects.

1. The first effect is that molecules of one species impede transport of heat by other species.

2. The second effect is transfer of the transport of heat from molecules of one species to another.

Cowling has developed his theory and obtained the relation for heat conductivity of monoatomic gaseous mixtures. Simple manipulations reduce this relation to equation (4), the constants A_{ij} being of the form

$$A_{12} = \frac{B_{12} - \frac{B}{(x_2/x_1) + B_{21}}}{1 + \frac{B}{1 + B_{21} x_1/x_2}}, \quad (5)$$

$$A_{21} = \frac{B_{21} - \frac{B}{(x_1/x_2) + B_{12}}}{1 + \frac{B}{1 + B_{12} x_2/x_1}},$$

where

$$B_{12} = 0.5c + \sqrt{0.25c^2 - b}$$

$$B_{21} = b^{-1} B_{12}; B = B_{21} a (\lambda_1 + \lambda_2)^{-1}$$

$$c = (\alpha_{21} R_1)^{-1} (R_1 R_2 + \alpha_{12} \alpha_{21} - \beta_{12} \beta_{21}); b = \frac{\alpha_{12}}{\alpha_{21}} \frac{\lambda_1}{\lambda_2},$$

$$R_i = \frac{1}{\lambda_i}, \quad a = (\alpha_{21} R_1) (R_1 + R_2 + \beta_{12} + \beta_{21}),$$

$$\alpha_{ij} = T(5pD_{ij})^{-1} (M_i + M_j)^{-2} [6M_i^2 + (5 - 4B_{ij})M_j^2 + 8A_{ij}M_iM_j],$$

$$\beta_{ij} = T(5pD_{ij})^{-1} (M_i + M_j)^{-2} (11 - 4B_{ij} - 8A_{ij}).$$

T.Cowling considers that in determination of her formula, Wassiljewa included the first effect alone and neglected the transfer of transport. In fact, the physical meaning of equations (2) and (3) implies that each term of relation (1) includes both transfer of heat by one species to other species and transport of heat between molecules of the same species

Introduction of a number of terms into equation (4) has allowed Cowling to modify relations (2)-(3) for a mean free molecular paths and to demonstrate that it is a function of molecular concentration.

Fig.1 presents a comparison of experimental data with the values predicted by formula (1), constants A_{ij} being found by relation (5). The greatest divergence is found for mixtures with small molecular mass ratios.

E.A.Mason and S.C.Saxena/3/ have derived relation (4) with constants

$$A_{ij} = \frac{1065}{2\sqrt{2}} \left(1 + \frac{m_i}{m_j}\right)^{-1} \left[1 + \left(\frac{A_i}{A_j}\right)^{1/2} \left(\frac{m_i}{m_j}\right)^{1/4}\right]^2$$

proceeding from the main statements of the rigorous kinetic theory with the aid of some assumptions.

The comparison of experimental data and predicted values has shown the following divergence for monoatomic gaseous mixtures at 793°K :

He-Xe	-10.8%	Ne-Kr	- 1.4%
He-Kr	- 7.0%	Ne-Xe	- 1.2%
He-Ar	-4.9%	Ar-Kr	- 1.7%
He-Ne	- 4.2%	Ar-Xe	-1.8 %
Ne-Ar	-3.1 %	Kr-Xe	- 5.4%

Many works dealing with thermal conductivity of monoatomic gaseous mixtures are not mentioned here because they are generally known. It is necessary to state that in most cases thermal conductivity is found by semi-empirical and empirical methods.

There are some works /4,5,6/ on experimental determination of thermal conductivity of monoatomic gaseous mixtures. For comparison of experimental and predicted values the reliability of the experimental data should be known.

The analysis of experimental data obtained by different authors has shown that for mixtures, Ne-Ar, Ne-Kr, Ne-Xe, Ar-Kr, Ar-Xe, Kr-Xe, the divergence is within the experimental error, whereas for the mixtures He-Xe, He-Kr, He-Ne, He-Ar such agreement is not found. Divergence of experimental data for these four mixtures compared to S.C.Saxena's data is 5% (Ubish's experiments /7/) and 10 % (Thornton's experiments).

Unfortunately, the authors do not always report all conditions of the experiments and do not mention which errors are taken into account. The divergence between experimental data of different workers for mixtures with helium is not casual since they are mainly found in the range of low concentrations of heavy components and may be probably attributed to the fact that thermodiffusion is not accounted for.

To conclude the paper, it is necessary to note that both experimental and theoretical methods of determination of mixture thermal conductivities produce an essential error in case of a small molecular mass ratios. Therefore the main task at present is a comparison of available experimental heat conductivities of monoatomic gaseous mixtures, correlation of different workers' data by introduction of appropriate corrections into the experimental data and specification of the existing

Fig. 1

into the experimental data and specification of the existing concepts of heat conduction of gaseous mixtures.

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Low Temperature Measurements

II

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Thermal Conductivity of Dilute Copper-Manganese Alloys at Helium Temperatures and in Magnetic Fields

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The electrical (σ) and thermal (λ) conductivities of thin rods of copper, containing respectively 0.3, 0.21, 0.11 and 0.035 atoms per cent of manganese in solid solution, have been studied at liquid helium temperatures in a zero field and in transverse magnetic fields (H) upto 17 Kilo-Oersteds. Plots of λ (H) against σ (H)T, at the temperature T, give straight lines suggesting an electronic Lorenz number independent of the strength of the magnetic field. By this method, it has been possible to derive, firstly, estimates for the lattice thermal conductivity, which is found to have a T^3 -dependence, suggesting phonon scattering at the boundaries, presumably of the ferro/antiferromagnetic domains. Secondly, the electronic Lorenz number is found to be temperature-dependent, dipping considerably below the normal Sommerfeld value L_n and attaining that value at the lowest temperatures.

When correction is made for the normal, positive, electrical magneto-resistivity, the resulting magneto-resistivity comes out negative and (numerically) increases with the field strength, as does also the thermal magneto-resistivity. The Kohler rule is not obeyed.

Key words : Copper manganese alloys, dilute magnetic alloys, electrical resistivity, Kohler plot, Lorenz number, magneto-resistivity, thermal conductivity.

1. Introduction

Small amounts of certain transition metals, when introduced in solid solution, in certain simpler metals are known to form localised magnetic moments and to give rise to anomalies in their conduction and allied properties at low temperatures (1). The most common feature of such dilute magnetic alloys is a minimum in the electrical resistivity near about liquid hydrogen temperatures, which is sometimes accompanied, at somewhat higher solute concentrations, by a maximum at liquid helium temperatures or somewhat above. The former is considered to be a consequence of

the effects of the Pauli Exclusion Principle on the intermediate states of the higher order scattering for s-d exchange scattering (2). Magnetic studies of dilute magnetic alloys (3) at temperatures near about the resistivity maximum show a slow transition to anti-ferromagnetism, with indications of ferromagnetism as well. The resistivity maximum is therefore associated with the ordering of the impurity spins. The temperature of occurrence of the maximum (T_M) is found to be directly proportional to the solute concentration (c) whereas the temperature of the minimum (T_m) varies somewhat as $c^{1/5}$.

The specific heat C of such alloys is anomalous, the C/T versus T curve presenting a pronounced hump near about helium temperatures (4). The electrical as well as the thermal magnetoresistance is large and negative (1,5,6) near and below T_M .

The thermal conductivity behaviour of dilute Ag-Mn alloys was studied in detail by one of the present authors and de Nobel (6,7) and by Malm and Woods (8). In the present paper are reported the thermal and electrical conductivities of dilute Cu-Mn alloys at liquid helium temperatures, in magnetic fields ranging from zero to 17 kilo-Oersteds.

2. The alloy specimens used :

The polycrystalline rod specimens of Cu-Mn were kindly made available to us by Prof. C.J. Gorter, Director, Kamerlingh Onnes Laboratory, Leiden, Holland. They were prepared in vacuo from pure Johnson-Matthey copper and manganese, in appropriate proportions in quartz tubes. The concentrations of manganese in the samples were also estimated by measuring the electrical resistivity at the steam and the ice points. No further annealing was done by us. The specimens should therefore be considered as strained specimens.

3. Experimental details

3.1 Electrical Resistivity

The electrical resistance of the specimens was measured at liquid helium temperatures by keeping them immersed in the coolant and passing a suitable current through them. Potential leads are attached (by means of non-superconducting solder) at the same spots where thermometers are attached for thermal conductivity measurements. This potential difference is compared with that across a standard resistance of comparable value (supplied by Messrs Otto Wolff, Germany) connected in series with them, but placed outside the cryostat. The potential differences are measured by means of a thermo-force-free Diesselhorst type potentiometer (made by Messrs Otto Wolff, Germany). For measurements in magnetic fields, the specimens are kept in tailed dewars between the pole faces of an A.D. Little Electro-magnet.

3.2 Thermal conductivity

For the thermal conductivity measurements, the specimen is kept in a polished copper vessel evacuated to 10^{-6} torr, with one end protruding into the bath liquid, a small electric heater

having been attached to the other end. Two Allen-Bradley carbon composition resistors (we have also used carbon film resistors made according to the method described by De Vroomen (6,9)) are attached at suitable points on the specimen and their temperatures measured when equilibrium has been attained.

4. Discussion

4.1 Electrical and Thermal Resistivity

Figures 1 and 2 show the electrical resistivity (ρ) and thermal conductivity (λ) of the dilute Cu-Mn alloys plotted against the temperature T ($^{\circ}\text{K}$). These specimens have manganese contents of respectively 0.30, 0.21, 0.11 and 0.035 atoms per cent, as determined from the slope of the ρ - T curves in the temperature range 273-373 $^{\circ}\text{K}$.

The ρ - T curves show minima and maxima which are well-known features of dilute magnetic alloys in this concentration range. The thermal conductivities of these specimens in different transverse magnetic fields are also shown in fig. 2. The zero-field thermal conductivity presents a knee between 2 and 3 $^{\circ}\text{K}$, which persists in the largest fields employed. One is therefore apt to associate it with the lattice thermal conductivity.

4.2 Electronic Lorenz Number

Following Gruneisen (10), De Haas (11) and their respective co-workers, one can write $\lambda(H) = L_e \sigma(H) T + \lambda_g$, where (H) indicates the external magnetic field, and σ, λ the electrical and thermal conductivities at the temperature T . L_e is the electronic Lorenz number and is looked upon simply as the quotient $\lambda_e T^{-1} / \sigma$. We make no assumptions regarding the behaviour of L_e with respect to the temperature. λ_g is assumed to be unaffected by a magnetic field. Fig. 3 shows the plots of $\lambda(H)$ against $\sigma(H)T$ at various fixed temperatures. They come out more or less as straight lines and this suggests that L_e is not significantly affected by the magnetic fields, within the limits of the experimental accuracy.

The slope of the $\lambda(H) - \sigma(H)T$ curve gives the value of the electronic Lorenz number at the temperatures T . Fig. 4 shows how the L_e (as derived by the above analysis) at helium temperatures varies with T , for the three more concentrated specimens. The alloy containing 0.035 atoms per cent manganese has a negative (corrected) electrical magneto-resistivity but a positive thermal magneto-resistivity. The above analysis could therefore not be applied to it. The dip in the electronic Lorenz number is reminiscent of that observed for dilute Ag-Mn alloys of comparable dilutions (7) and could be explained as being due to inelastic scattering of the conduction electrons by the impurity centres, each of which could occupy one or the other of a number of closely spaced energy states.

Plots of $w_e T$ against T show shallow peaks, wherefrom one can estimate the maximum fractional inelastic scattering f' given by $f' = \left[\frac{(w_e T)_m}{(w_e T)_o} - 1 \right]$, where the subscripts m and o indicate the maximum and the residual values. f' comes out

for these alloys to be 0.65, 0.35 and 0.30, in the order of increasing manganese content. One therefore infers that as the impurity content (at low concentrations) increases, the elastic scattering component is enhanced at the expense of the inelastic component. It is this fraction f' which is responsible for the dip in L_e . The fact that L_e tends to the normal Sommerfeld value L_0 at $T=0$ is explained by the inelastic scattering getting frozen out. Fig. 5 shows the variation of the fraction f' with the manganese content in these and in Ag-Mn alloys. The parallelism in the concentration dependence of f' and the transverse (negative) electrical magnetoresistivity shows that both have the same origin in these alloys (12).

4.3 The Lattice Thermal Conductivity

The lattice thermal conductivity, derived at each temperature, as the intercept of the $\lambda(H) - \sigma(H)T$ curve on the $\lambda(H)$ axis, is found to have a T^3 dependence (fig. 6). This would mean that the phonons are now subjected to boundary scattering and λ_e is now limited by the dimensions, presumably of the (ferro-/anti-ferromagnetic domains in the alloys. Using the Casimir (13) formula and the specific heat data of De Nobel and Du Chatenier (4) on copper and on dilute Cu-Mn alloys, we derive these domain sizes to be 17, 6 and 5 microns, in the order of increasing manganese content.

The knees in the $\lambda - T$ curves (fig. 1) are not present in the lattice component of the thermal conductivity.

4.4 The Electronic Thermal Conductivity

The electronic thermal conductivity of these alloys, as derived from the relation $\lambda_e = L_e T / \rho$, is shown in fig. 7. One can now see that the knee in the $\lambda - T$ curves between 2 and 3 °K is a feature of the electronic component and arises from the behaviour of the electronic Lorenz number. The persistence of the knee even at the highest magnetic fields used here is a consequence of the electronic Lorenz number remaining significantly unaffected in these fields.

It has been pointed out (14) that, if the inelastic scattering contributes the predominant portion of the electronic thermal resistivity, there should be an anomalous hump at a temperature T_h given by $k T_h = \Delta E / 4$ (where k is the Boltzmann constant and ΔE the energy difference between the degenerate levels of the impurity ion, resolved by the internal field H_i). The $w_e - T$ plot of the alloy containing 0.11 per cent manganese shows a small hump at about 2.5 °K. This would give $\Delta E / k = 10$ °K, agreeing with that obtained (7) for dilute Ag-Mn alloys. The magnetic moment μ of the manganese ion in these alloys is 5 Bohr magnetons, so that, from the relation $\Delta E = \mu H_i$, we estimate H_i to be about 30 kilo Oersteds. This seems to agree with earlier estimates (15).

With this estimate for H_i and our earlier estimates for J and A (the exchange and Coulomb interaction parameters) (15), it can be shown, as was done for Ag-Mn alloys (15) that the theories of Kasuya (16) and Yosida (17) on the transport properties of such alloys lead to less than 5 per cent variation of L_e in magnetic

fields of 20 kilo-Oersteds.

4.5 The Magneto-resistivity

The transverse, negative, electrical magneto-resistivity of these alloys (after applying correction for the normal positive magneto-resistivity), expressed as reduced Kohler diagrams (log-log plots of $\Delta\rho/\rho(0)$ against $H \rho_{273}/\rho(0)$, where 273 is the ice-point) gives $\Delta\rho/\rho(0) \propto [H \rho_{273}/\rho(0)]^n$. The plots are approximately straight lines and give n about 1.7. The plots for the more concentrated alloys show no significant displacement with temperature between 4 and 2 °K. For the most dilute one, containing 0.035 atoms per cent manganese, the plots at different temperatures do not coincide, nor do the plots for the different manganese concentrations coincide. In short, the Kohler rule is not valid for these alloys.

Writing $\Delta\rho/\rho(0) = B (H/\rho(0))^2$, we find for the alloy containing 0.21 atoms % Mn, at 2.8 °K, in a field of 13.8 Kilo-Oersteds, $B \approx 1.4 \times 10^{-26}$ ohm² m² Oersted⁻². The theoretical calculation by Mikoshiba and Yoshihiro (18) taking the Kondo effect into account gives a value of the same order.

We have also plotted the thermal magneto-resistive reduced Kohler plots in the form $\Delta w/w_e(0) \propto [H/(L_e w_e(0) T)]^m$. Here also m comes out about 1.6 and the behaviour is similar to their electrical counterparts.

5. Acknowledgments

Our grateful thanks are due to Prof. C.J. Gorter, Director, Kamerlingh Onnes Laboratory, Leiden, Holland, for making the Cu-Mn alloy specimens available to us and also to the Director, National Physical Laboratory of India for interest in this work and for permission to publish it.

Some of the work reported here will form part of a thesis to be submitted shortly by one of us (N.S.N) to the University of Delhi, India, for a Doctorate Degree.

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Fig. 1. Electrical resistivity of dilute Cu - Mn alloys at liquid helium temperatures, in transverse magnetic fields:

Top five curves: Cu-0.30% Mn : $H = 0, 8.7, 12, 16.8$ and 20.4 kilo-Oersteds respectively marked $\bigcirc, \triangle, \square, \nabla$ and $\bullet$.

Middle six curves: Cu-0.21% Mn: $H = 0, 5.24, 8.3, 10.5, 13.85$ and 19.4 kilo - Oersteds respectively marked $\bigcirc, \triangle, \square, \nabla, \bullet$, and $\diamond$.

Bottom five curves: Cu-0.11% Mn: $H = 0, 8.7, 12, 16.8$ and 20.4 kilo-Oersteds, markings as for the Cu-0.30% Mn.

Fig. 2. Thermal conductivity of dilute Cu - Mn alloys at liquid helium temperatures, in transverse magnetic fields:

Top five curves: Cu-0.11% Mn: Middle four curves: Cu-0.21% Mn: Bottom four curves: Cu-0.30% Mn.

Note different ordinates for the three concentrations.

$H = 0, 10.4, 13.75$ and 17.4 kilo - Oersteds marked $\bigcirc, \triangle, \square$, and ∇ .

Fig. 3. Plots of $\lambda(H)$ against $\sigma(H)T$ for Cu-0.21% Mn alloy specimen at 2.8, 2.4, 2.0 and 1.8°K, respectively marked ∇ , $\bullet$, $\times$ and $\diamond$.

Fig. 4. Temperature-dependence of the electronic Lorenz number in the Cu-Mn alloys: Markings $\circ$, Δ and $\square$ in the order of increasing concentration.

Fig. 5. Concentration - dependence of the maximum fractional inelastic scattering $f'\lambda$ (ordinates at the right) and of the negative transverse electrical magneto-resistivity of the Cu-Mn alloys (Δ , $\circ$) and Ag-Mn alloys ($\blacktriangle$, $\bullet$).

Fig. 6. Temperature-dependence of the lattice thermal conductivity of Cu-Mn alloys: Markings as in fig. 4.

Fig. 7. Temperature-dependence of the electronic thermal conductivity of Cu-Mn alloys. Markings $\circ$, Δ and $\bullet$ in the order of increasing concentration.

Additional Contributions Due to Electron Scattering
In Antiferromagnetic Chromium

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On the basis of our thermal and electrical resistivity measurements on high purity polycrystalline Chromium we present clear evidence for

- (a) The existence of electron-electron scattering contributions to both the resistivities below 20°K
- (b) The effect of the change in polarization of the Spin-Density Waves on both the resistivities around the spin-flip temperature 122°K .
- (c) The existence of similar peaks in both the resistivities due to critical fluctuations in magnetization around the Neel temperature at about 311.5°K

The ratio of the coefficients to the additional quadratic terms of the resistivities which we believe accounts for the presence of s-d coulomb scattering, gives a value of 0.92×10^{-8} watt units, similar in magnitude to those observed in Ni, Pd. and other transition metals. At the spin-flip temperature the intrinsic electrical resistivity exhibits a change in temperature dependence from $T^{2.45}$ to $T^{2.25}$ above 122°K . Thermal resistivity data also shows a change compatible with this. High precision measurements around the Neel temperature provide evidence for a small peak in the thermal conductivity and the Wiedmann-Franz ratio. Both the thermal and electrical resistivities show similar changes that can be explained on the basis of the theory of critical fluctuations around antiferromagnetic transition temperatures. Above T_N , our data along with those by others fits well into the equation $\lambda = (2.89 \times 10^{-8} T / \rho) + 79.9/T$, indicating the possibility of some lattice contribution in addition to the electronic. The large departures from the Sommerfeld value for the calculated Wiedmann-Franz ratio above 90°K can be understood in terms of the Method of Moments proposed by Klemens¹ and the parabolic well model put forth by Goff².

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ELECTRON-ELECTRON SCATTERING EFFECTS IN THE LOW TEMPERATURE LORENZ
NUMBERS OF DILUTE Pd-Ni ALLOYS. THEORY AND EXPERIMENT

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The thermal and electrical resistivities of Pd-Ni alloys at concentrations ranging from 0 to 1.0 at.% Ni have been measured at temperatures between 2 and 20K. The Lorenz numbers, L_e , appropriate to electron-electron scattering have been extracted from the data and are found to be relatively insensitive to Ni concentration. A theoretical calculation of L_e has been carried out under the assumption that the entire current is carried by s-electrons which are scattered from spin density fluctuations of the electrons in the d band. A consistent interpretation of the data for the alloys is obtained by employing the "local enhancement" model, which assumes that the scattering is enhanced in the vicinity of the Ni atoms. On the other hand, the "uniform enhancement" model, which assumes that the addition of Ni increases the scattering uniformly throughout the matrix, is found to yield values of L_e which decrease too rapidly with increasing Ni concentration to reasonably represent the experimental results. The calculated value of L_e is significantly smaller than the experimental value for pure Pd; it is felt this may be due to the absence of detailed band structure effects in this work. Lorenz numbers for Baber scattering have also been calculated by using a Coulomb interaction screened by the d-electrons. It is found that the presence of Baber scattering cannot remove the discrepancy between theory and experiment for pure Pd. The Baber scattering model is also used to calculate the L_e for rhenium and gives very good agreement with experiment.

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THERMAL CONDUCTIVITY OF HIGH PURITY THORIUM^{*}

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The thermal conductivity and the electrical resistivity of three high-purity thorium samples with resistivity ratios 31, 140, and 480 have been measured as functions of temperature from 3 to 300 K. The samples were purified by the electrotransport method. Each of our higher-purity samples showed a large thermal conductivity maximum near 10 K and a constant thermal conductivity from 70 to 200 K. At low temperatures the Lorenz ratios of samples having intermediate purity show, in addition to the linear term arising from electronic thermal conductivity, a quadratic term arising from phonon thermal conductivity limited by phonon-electron scattering. At higher temperatures the phonon thermal conductivities of these samples vary inversely as the temperature owing to the dominance of umklapp phonon-phonon scattering. The ideal electronic thermal resistivity from 14 to 25 K was proportional to the square of the temperature as expected for electron-phonon scattering.

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LATTICE CONTRIBUTION TO THERMAL CONDUCTIVITY
OF SOME RARE EARTH FERROMAGNETS

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ABSTRACT.

A systematic analysis of most of the available thermal conductivity data on mono-crystalline rare earth ferromagnets, including our recent measurements on holmium and terbium is presented. Such an analysis strongly suggests that the additional contribution to thermal conductivity below 15°K is mostly due to phonons. At temperatures above 200°K the additional contribution is likely to be of electronic origin and a direct consequence of the multiband structure of these metals.

Transport properties of rare earth ferromagnets, thermal conductivity in particular, have shown quite complex features which render difficult any simple type of analysis. The observed Wiedmann-Franz ratio, for example, contains some unusual features and is universally larger than the Sommerfeld value 2.45×10^{-8} watt units throughout the temperature range from 1 to 300 K. This is because in addition to electrons and possible phonons as heat carriers in these magnetic materials one can expect magnons to play a significant role, at least at low temperatures. Any analysis is further complicated due to magneto-crystalline anisotropy clearly seen from recent studies on monocrystals with different orientations¹. In this paper, we present a systematic analysis of most of the monocrystal data available at present at low and high temperatures. This includes our recent measurements on holmium and terbium² along with most of the data published by the Ames group³. Such an analysis strongly suggests that in rare earth ferromagnets the additional contribution to thermal conductivity below 15°K is mostly due to phonons. At temperatures above 200°K the additional contribution to thermal conductivity is likely to be of electronic origin and a direct consequence of the multiband structure of these metals.

In a magnetic conductor the measured thermal

conductivity λ , consists of the sum of an electronic component λ_e , a lattice component λ_g and a magnetic component λ_m , that is

$$\lambda = \lambda_e + \lambda_g + \lambda_m \quad (1)$$

If the thermal analogue of Matthiessen's rule were obeyed, the individual components can be calculated as

$$\lambda_i = (\sum_j W_{ij})^{-1} \quad (2)$$

where $\sum_j W_{ij}$ is the sum of the resistances which the carrier 'i' suffers due to various scattering mechanisms.

Among the rare earth ferromagnets, in dysprosium⁴ and terbium⁵ there exists a spin-wave energy gap around 20°K.

One can therefore expect the major contributions to thermal conductivity in these metals, as due to only electrons and phonons, at least in the helium temperature range.

Figure 1, shows our recent measurements below 4°K on an annealed monocrystalline sample of terbium with its geometric axis in the basal plane. These measurements were made on a He³-He⁴ cryostat, using carbon thermometry to determine the temperature gradients. We have also extended the measurements from helium to room temperatures on another⁶ cryostat described elsewhere. For the purpose of this paper, only the relevant parts from our data on terbium and

holmium will be used. Clearly, in figure 1, in addition to the linear term, there is a quadratic temperature dependence in the total thermal conductivity. Below 4°K the data can be fitted into an equation of the type

$$\lambda = a T + b T^2 \quad (3)$$

From a least squares fit of the data the coefficients are obtained as $a = 4.37$ and $b = 0.21$ in milliwatt units. It must be mentioned that such a fit as in equation (3), has been observed in holmium and gadolinium also. Since, in terbium, at these temperatures one can safely neglect any possible magnon contribution, this quadratic term is very likely to be due to the phonons predominantly scattered by electrons. The conduction electrons on the other hand collide mainly with impurities giving the linear term.

Electrons scattered at impurities suffer large angle elastic collisions so that we can apply the 'classical' Wiedmann-Franz law to obtain a value for the coefficient 'a' as L_0/ρ_0 , where L_0 is the Sommerfeld value of the Lorenz number (2.45×10^{-8} watt units) and ρ_0 the residual electrical resistivity. Hence one can estimate λ_e , the electronic contribution to thermal conductivity. From the total conductivity then, the general pattern of the temperature dependence of the additional contribution ($\lambda - \lambda_e$) can be obtained as shown in figure 2. There is a clear

peak around 10°K in the $(\lambda - \lambda_e)$ curve. This peak around a temperature $\theta/15$, where θ is the Debye temperature of terbium, appears at a much lower temperature than the normal one observed around 24°K in the total thermal conductivity. In this $(\lambda - \lambda_e)$ curve, which has the typical characteristics of the curve for the phonon contribution to metals, between 3 and 10°K one expects a departure from the quadratic temperature dependence, that is very sensitive to the strains, dislocations and impurity contents in the sample. This probably explains (a) that above 5°K , no simple temperature dependence can be extracted for the additional $(\lambda - \lambda_e)$ contribution, and (b) that the obtained Wiedmann-Franz ratio's in these metals by various workers differs sensitively with the residual resistance around 4.2°K ⁷. If these effects of impurities are taken into consideration, one would also observe definite changes in the shape of the peak and the temperature dependence beyond the peak for a plot of $(\lambda - \lambda_e)$ against temperature of the same metal with different impurity contents.

Figure 3, shows such an analysis as discussed above from all the data available so far on monocrystalline terbium both from us and the Ames group. It is at once obvious from these curves that the additional contribution, phononic in nature, exhibits a much sharper peak in purer samples (as indicated by the residual resistivity) which also falls

off less sharply with less purer samples. If one considers the large mass difference between a typical impurity like say Cu and the host rare earth metal, this trend is not at all surprising. It is also interesting to note that from around the peak in each of these curves, where the electronic and phononic contributions become comparable, the total thermal resistivity $W = \lambda^{-1}$ can now be fitted into an equation of the type

$$WT = a + cT^3 \quad (4)$$

where the coefficient 'c' is the additional scattering of electrons due to electron-phonon interaction. Figure 4 illustrates, demonstrating a purely metallic behaviour in small temperature region. Such a nature has been observed in all the rare earth ferromagnets¹⁻³. The range for which one can fit the data into an equation for the type (4) is found to depend on the purity of the particular sample or indirectly on how the phonon contribution varies with the impurity content.

It is possible to show that below a temperature T given by

$$T \approx p^2 \theta_c \quad (5)$$

where p is the polarization at the Fermi-surface and θ_c the curie temperature, there should be no spin-wave scattering of electrons⁸. Due to the Rudermann-Kittel-Kasuya-

Yoshida type indirect exchange interaction between the localized moments,,at low temperatures one can expect a high polarization at the Fermi-surface. Let us then assume that possible magnon conduction in all the rare earth ferromagnets can be neglected below say 18°K and analyze the data in the same way as for terbium. Figures 5,6,7 ~~and 8~~ show such an analysis for dysprosium, erbium, gadolinium and holmium. All of them show similar behaviour as seen in terbium.

A similar analysis of the data on Lutetium¹ shown in figure 8, is most revealing. Since magnon contribution in non-magnetic Lutetium can be safely ruled out, the larger values for the Wiedmann-Franz ratio at low temperatures is most certainly due to a phonon contribution. From the sharp drop in the phonon contribution around 8°K , in this purest known sample of lutetium orientated along the c-axis, one would expect that at least in this set of data it should be possible to see a typical metallic behaviour even in the Wiedmann-Franz ratio plotted as a function of temperature. Figure 9, reproducing the data published by Boys and Legvold, does indeed show the dip in the Wiedmann-Franz ratio below the classical Sommerfeld value at least for a small temperature region between 15 and 60°K . This is a typical metallic behaviour where the conduction is mainly by electrons.

It must be recognized that so far no allowance has been made for 1) electron-phonon scattering, 2) complications due to spin-wave scattering and 3) deviations from Matthiessen's rule. It is impossible to obtain precise values for the total electronic contribution to thermal conductivity for the following reason: At any temperature there is considerable uncertainty as to whether the conduction electrons are predominantly scattered by phonons, magnons or other electrons. Since there is a different value for the Lorenz number appropriate to each of these scattering mechanisms, it is clear that the total electronic contribution cannot be obtained via the Wiedemann-Franz law. While at helium temperatures ($\lambda - \lambda_e$) calculated in our analysis could give realistic values for the phonon contribution, at higher temperatures it would not be so because: a) the λ_e obtained is overestimated since the resistivity arising from electron-phonon scattering is no longer negligible - in fact an allowance for this would shift the peak in figures 2,3,5-7 in the right direction and the change in slope beyond the peak would become more realistic with what one would expect from the debye temperature (around 175°K) and the impurity content, b) possible deviations from Matthiessen's rule has been neglected. Hence we again emphasize that the actual values of the phonon conductivity particularly at higher temperatures are very dependent on the estimates we have used

and should not be taken as true lattice conductivities. The important feature of our analysis here is to show that the set of curves we obtain makes it plausible to attribute the additional contributions to thermal conductivity as due to phonons.

The second part of this paper is to present our analysis of the available data around room temperatures where, except in gadolinium, all the heavy rare earths are in the paramagnetic state. In this state, the scattering processes will be mostly elastic and one would expect the standard Lorenz number to be valid. Also, since the Debye temperature for these metals is below 200°K, the Lorenz number would be almost independent of temperature above 200°K. Any higher value observed for the Wiedmann-Franz ratio is then customarily attributed as due to a phonon contribution. At these temperatures this additional contribution due to phonons, as predicted by Leibfried and Schlomann's formula⁹ should vary as A/T , where A is a constant characteristic of the metal in question. It should then be possible to fit the measured total thermal conductivity into an equation of the type

$$\lambda = \frac{L'T}{\rho} + \frac{A}{T} \quad (6)$$

where ρ is the electrical resistivity at temperature T and

L' the electronic Lorenz number for the metal as obtained from a fit to an equation of the type (6). Figure 10, shows a plot of λT against T^2/ρ , for terbium in its paramagnetic temperature region. A least squares fit of the data gives for the electronic Lorenz number a large value of 4.16×10^{-8} watt units and the coefficient 'A' for the "Lattice" contribution as 7.44 in watt units. Analysis of available data for holmium, dysprosium on the same basis as discussed above can be seen in figures 12 and 11. The values obtained for the parameters A and L' are tabulated in Table I. It is tempting to accept the large values for the electronic Lorenz ratio L' as typical for the metal and speculate its origin as due to the complicated band structure effects. One may note, first, that a scattering process that randomizes energies over a range of order KT about the Fermi-energies can give an L either greater or less than L_0 ¹⁰; this is the case for phonons scattering at low temperatures. If the energy-randomizing scattering is mainly backward, i.e., usually takes an electron to some state of nearly opposite velocity, then L will be greater than L_0 . The latter may well be the case for spin-fluctuation scattering near and above the phase transitions.

The magnitude of "Lattice" contribution given by the term A/T , accepting the values for 'A' from the least

squares fit of the data, is anomalously large when extrapolated to lower temperatures. This is incompatible with our low temperature findings unless additional scattering mechanisms in the intermediate temperature range are introduced. In which case, this will result in a double peak for the phonon contribution and that is highly unlikely. Hence, while phonons must play a role in the conduction processes even at high temperatures it appears to be only a minor one. This conclusion is further supported from an analysis of the data for mono-crystalline lutetium orientated along the c-axis shown in figure 13. The coefficient 'A' for the "Lattice" term is obtained as zero, which while being only an approximation resulting from this type of analysis, should be understood to indicate that the phonon contribution is indeed very small.

Both, transition metals and rare earth metals are characterized by overlapping bands of complicated structure. In view of the difficulties pointed out above, to understand the anomalous contribution to thermal conductivity and to be consistent with findings at all temperatures, it is obvious that one has to consider the details of the band structure and its consequences. The total electronic thermal conductivity need no longer be a simple summation of the individual components. The bipolar term suggested by Gallo¹¹ may play a role. Also, in cases such as these where the relaxation

time, density of states and other parameters may be very sensitive functions of the energy in the immediate vicinity of the Fermi-energy, to evaluate the proper coefficients, the "Method of Moments" proposed by Klemens¹² and recently extended by Goff¹³ would seem to be more appropriate.

In summary, our present analysis while it certainly does not arrive at any definite conclusions, strongly suggests that the additional contribution to thermal conductivity at low temperatures is mainly due to phonons. At higher temperatures it is likely to be of electronic origin and a direct consequence of the multiband structure of metals.

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Table I
A COMPARISON OF THE PARAMETERS FOR A
 $\lambda = L'T/\rho + A/T$
FOR THE RARE EARTH FERROMAGNETS AT LOW TEMPERATURES.

		A	L'
Tb	a -axis	1.63	3.63×10^{-8}
	c -axis	7.44	4.16×10^{-8}
Dy	a -axis	3.51	3.52×10^{-8}
	c -axis	6.26	2.49×10^{-8}
Ho	a -axis	3.92	4.30×10^{-8}
	c -axis	8.02	4.02×10^{-8}
Lu	c -axis	0	2.63×10^{-8}

- 1 Thermal conductivity of mono-crystalline terbium along the basal plane, as a function of temperature. The dashed line indicates electronic conductivity calculated from the residual resistance and using the standard Sommerfeld value for Lorenz number.

2 Total thermal conductivity λ (from ref. 3), electronic component calculated from the residual resistance, and the difference $(\lambda - \lambda_e)$ as a function of temperature for mono-crystalline terbium along a-axis.

3 Temperature dependence of the additional contribution ($\lambda - \lambda_e$) to thermal conductivity of terbium with different orientations and plurality (data from ref.2,3)

4 WT plotted as a function of T^3 , where W is the thermal resistivity at temperature T for terbium.

- 5 Temperature dependence of the additional contribution $(\lambda - \lambda_e)$ to the thermal conductivity of dysprosium and erbium. (data from ref.1)

6 Temperature dependence of the additional contribution
($\lambda - \lambda_e$) to the thermal conductivity of gadolinium (ref.3)

7 Temperature dependence of the additional contribution $(\lambda - \lambda_e)$ to the thermal conductivity of holmium (ref. 2, 3)

8 Temperature dependence of the additional contribution ($\lambda - \lambda_e$) to the thermal conductivity of lutetium (ref.1)

9 Observed Wiedemann-Franz ratio as a function of temperature for Lutetium. (data from ref. 1)

- 10 λT as a function of T^2/ρ for terbium with conductivity λ , and electrical resistivity ρ at temperature T (data from ref. 2,3) λ is in milliwatt units.

11 λT vs. T^2/ρ for dysprosium (data from ref. 1)

12 λT vs. T^2/ρ for holmium (data from ref. 2,3)

13 λT vs. T^2/ρ for lutetium (data from ref. 1)

Thermal Conductivity of Rhodium at Helium Temperatures and in Magnetic Fields

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The electrical (σ) and thermal (λ) conductivities of a 99.9995 per cent pure, thin, poly-crystalline rhodium rod are determined at liquid helium temperatures, in a zero field and in transverse magnetic fields (H) upto 17 kilo-Oersteds. Plots of λ (H) against σ (H)T, at the temperature T, give straight lines, justifying the assumption of an electronic Lorenz number independent of the strength of the magnetic field. It has been possible, in this manner to derive firstly, estimates for the lattice thermal conductivity, which is found to amount to about 10 per cent of the total thermal conductivity at 4 °K, and to have a roughly T^2 -dependence, suggesting that it is limited by conduction electron scattering.

Secondly, the electronic Lorenz number is found to drop from $2.44 \times 10^{-8} \text{ V}^2 \text{ }^\circ\text{K}^{-2}$ at 4 °K to about 1.9×10^{-8} at about 2 °K.

The electrical as well as the electronic thermal magneto-resistivity conforms to the Kohler rule, but varies in a direct proportion to the strength of the field, for the fields employed.

Key Words : Electrical resistivity, Kohler plot, Lorenz number, magneto-resistivity, rhodium, thermal conductivity.

1. Introduction

1.1 The Electronic Lorenz Number

The electrical resistivity ρ of a normal non-magnetic metal can be expressed by the Matthiessen rule $\rho = \rho_o + \rho_i$, where the sub-scripts o and i refer respectively to the residual and the

the ideal or intrinsic components. The heat conductivity (λ) in a metal can take place through the medium of the lattice waves (λ_g) as well as of the electrons (λ_e) so that $\lambda = \lambda_g + \lambda_e$. Analogous to the Matthiessen rule for the electrical resistivity we can write for the electronic thermal resistivity $ew_e = 1/\lambda_e = w_{e0} + w_{ei}$.

In the elastic impurity scattering region, where $\rho_0 \gg \rho_i$ and $w_{e0} \gg w_{ei}$, the relaxation times for the electrical and thermal conduction processes are identical (1) leading to the law of Wiedemann-Franz-Lorenz : $\rho T^{-1}/w_e = \rho_0 T^{-1}/w_{e0} = L_n$. In this case, the electron Lorenz number L_e has the universal value $L_n = 2.45 \times 10^{-8} \text{ V}^2 \text{ deg}^{-2}$, independent of the temperature, the relaxation time and the band structure of the metal. A similar situation obtains at high temperatures ($T \gg \theta$, the Debye temperature) but at intermediate temperatures, the electronic Lorenz number dips below the value L_n . Makinson (2) has evaluated this variation of L_e with temperature, in the case of a monovalent metal (of different degrees of purity) assuming the lattice waves to correspond to an isotropic continuum having an upper frequency limit.

In the case of a very pure specimen of a metal, the scattering of the conduction electrons by the elastic lattice waves could be significant even at liquid helium temperatures and the electronic Lorenz number should then drop below L_n , as has recently been reported for high-purity indium (3)

1.2 The Magneto-resistance of metals

The electrical resistivity of a (polycrystalline) metal normally increases on the application of magnetic fields. If $\rho_{(0)}$ is the resistivity in a zero field and $\rho(H)$ that in the field H at the same temperature, the relative magneto-resistivity $\Delta\rho/\rho_{(0)}$ is usually represented as a function $f(H/\rho_{(0)})$. Kohler (4) was the first to emphasise that if one assumes an isotropic relaxation time τ , $\Delta\rho/\rho_{(0)}$ will in general be a function of $H/\rho_{(0)}$ only. The introduction of isotropic scatterers (vacancies or impurity atoms) will cause an isotropic reduction in τ , leaving the functional dependence unaltered. Specimens of a given metal of different degrees of purity, should thus conform to a single Kohler curve. Even according to the two-band model, widely applied to transitional metals, the Kohler rule should be valid if the relative effects of the static impurities present is the same in both the bands (which condition also determines the validity of the Matthiessen rule).

In the more general 'reduced' Kohler diagram (5), one plots $\Delta\rho/\rho_{(0)}$ against H/r where the reduced resistivity $r = \rho_{(0),\pi}/\rho_{(0),0}$ where θ is the Debye temperature. In the case of metals where the number of electrons in one band (say n_s) equals the number of holes in the other (say n_d), the resistance increases quadratically with the field, whereas if $n_s \neq n_d$ the resistance should show saturation.

For the electronic thermal magneto-resistivity, a similar Kohler rule should hold (4,5), namely $\Delta w_e/w_{e(0)} = F(HL_e^{-1}T^{-1}/w_{e(0)})$

1.3 The Lattice Thermal Conductivity, λ_g .

It is of interest to know the lattice thermal conductivity of

a metal at low temperatures because this could give information as to the phonon scattering mechanism operating.

A number of methods have been used in the past to separate out the electron and lattice components of the thermal conductivity based on measurements in magnetic fields. All these assume λ_g to be unaffected by the fields.

In the method applied to bismuth by Reddemann(6) and also widely used by Gruneisen and co-workers (7) and by De Haas and co-workers (8), one writes $\lambda_H = L_e T \sigma_H + \lambda_g$, where λ_g and L_e are assumed unaffected by the magnetic fields. σ_H is the electrical conductivity. A plot of λ_H against $\sigma_H T$ at different field strengths, sometimes comes out reasonably rectilinear and one can therefrom derive simultaneously L_e and λ_g .

1.3 The Present Work

The electrical and thermal conductivities of a polycrystalline rod of pure rhodium are measured at liquid helium temperatures in transverse magnetic fields ranging from zero to 17 kilo-Oersteds. The data are analysed by the method described above, to extract the lattice thermal conductivity and also the electronic Lorenz number at various temperatures in the liquid helium region.

2. Experimental Details

2.1. The Specimen Used

The specimen used is a spectroscopically standardised material Lab No. 2357 obtained from Johnson-Matthey (London) and of a stated purity 99.995 per cent. It is used in our measurements without any further annealing treatment and should therefore be considered a strained specimen.

In the case of platinum, the temperature coefficient of resistance (α) between 0° and 100 °C namely $0.01(R_{100} - R_0)/R_0$ has been an accepted index of its purity. Very high purity platinum, as is recommended for use in resistance thermometry or in thermocouples, has $\alpha = 0.003928$ (9,10). Similarly, the highest value recorded for rhodium (11) is 0.00457, while Price and Taylor (12) report 0.00461 in a commercial purity sample and 0.00463 in a specially purified specimen. The latter value is also reported by Chaston (13). Our specimen has $R_0 = 42.74$ and $R_{100} = 62.46$ in units of 10^{-9} ohm-m giving $\alpha = 0.00463$ which is suggestive of its high purity.

The residual electrical resistivity ρ_0 of our specimen is 200×10^{-12} ohm-m compared to 155 of Kemp et al (14), 84 of White and Woods (15) and 240 of Powell et al (16). This is due to the physical defects in our specimen.

2.2 The Experimental Method

The basis of the electrical and thermal conductivity measurements is given in our paper on dilute copper-manganese alloys, also presented at this Conference.

3. Discussion

3.1 The Magneto-conductivities

Fig. 1 shows the electrical resistivity of our rhodium specimen at liquid helium temperatures in a zero field as well as in applied magnetic fields of 6.9, 10.2, 13.4, 16.5 and 19.4 kilo-Oersteds. The resistivity increases in a magnetic field more or less in a direct proportion to it. The reduced Kohler diagram wherein $\Delta\rho(H)/\rho(0)$ is plotted against $H\rho_0/\rho_0$ on a double log paper, is shown in fig. 2. The filled circles are the data of Schulze (17). The remaining points are the results of the present work. The agreement is satisfactory.

According to the two band theory, the magneto-resistance of a non-compensated metal (wherein the number of electrons and holes is not the same) should show saturation at sufficiently large magnetic fields. Since the capacity of the Brilluoin zone is 2 electrons per atom one can expect compensation for a metal having an even number of conduction electrons. However, a transition metal has a multiple valency, that is, the number of conduction electrons per atom is not definitely known. It has, therefore, been suggested that at any rate for transition metals having simple transitional lattices (rhodium is an f.c.c. metal, having an atomic number $z = 45$), an odd atomic number would correspond to non-compensation (18). The saturation of the magneto-resistivity observed by Schulze (17) and by Coles and Taylor (19) seem to conform to this.

Fig. 3 shows the thermal conductivity data (in watts/m-deg) at liquid helium temperatures, in a zero magnetic field and in external magnetic fields of 7.2, 10.7, 13.1 and 17.5 kilo-Oersteds. The total Lorenz number ($L = \rho T^{-1}/w$) of our specimen exhibits a temperature variation (falling below L_n at temperatures below about 3.2 °K) which can be considered roughly (to within 5 per cent) as being independent of the magnetic field strength.

3.2 The Lattice Thermal Conductivity

A number of methods are available for deriving the lattice thermal conductivity of a metal from a knowledge of its thermal and electrical resistivities in various fields. These assume that the lattice conductivity is unaffected by a magnetic field. In normal metals and alloys, λ_g in the low temperature region under consideration, becomes limited by scattering by the conduction electrons and the electron trajectories would be affected by the magnetic fields. Yet it was shown (2) that the electron-lattice interaction depends solely on the equilibrium constants of the lattice, provided no electric current is flowing (20). It is therefore justified to assume that the lattice conductivity is not significantly affected by a magnetic field. Under this assumption we have employed the method known after Gruneisen (7) and De Haas (8) for the separation of λ_g . Fig. 4 shows $\lambda(H)$ plotted against $\sigma(H) T$ at the temperatures 4.3, 3.2 and 2.4 °K. The approximate linearity of the plots lends some justification to the assumption that the electron Lorenz number is independent of the applied magnetic field. We should add that the total Lorenz number at a given temperature is found, from our experimental data, to be unaffected by the magnetic fields. From the slope and the

intercept on the Y axis, one at once gets respectively the electronic Lorenz number and the lattice thermal conductivity at the particular temperature.

The values for the lattice thermal conductivity of rhodium at liquid helium temperatures derived in this manner, are shown (fig.5) to conform to the quadratic temperature dependence predicted by theory and observed by many earlier investigations(21) on the supposition that the conduction electrons constitute the dominant scattering mechanism. One indicates the thermal conductivity in this case by λ_{gE} and expresses the corresponding resistivity by $w_{gE} = E T^{-2}$, E being the phonon-electron scattering. The magnitude of the lattice thermal conductivity derived above amounts to about 10 per cent at 4 °K dropping to about 4 per cent at 2 °K. We might mention that the scatter of points in the $\lambda(H)$ versus $\sigma(H)T$ plots is also 4-5 per cent. The fact that the total Lorenz number is some 10 per cent more than L_n above about 3.2 °K and becomes continuously smaller than L_n at low temperatures is in broad agreement with this.

3.3 The Number of Electrons per Atom (N_a)

In the liquid helium region, where the lattice thermal conductivity of rhodium is limited by scattering by the conduction electrons, one can, following Makinson (2) write

$$\lambda_{gE} = 4.93 T^2 L_n \theta^{-2} N_a^{-2} / (d\rho/dT)_\infty$$

$$\text{or } N_a^2 = 4.93 E \theta^{-2} L_n / (d\rho/dT)_\infty$$

where θ is the Debye temperature (taken as 370 °K). $(d\rho/dT)_\infty$ is the slope of the ρ - T curve at temperatures where the electronic thermal conductivity has attained a constant value.

For this, we have taken the slope between the ice-point and the steam point. Our measurements give $E = 0.65$ m-deg/watt and $(d\rho/dT)_\infty = 197 \times 10^{-12}$ ohm-m-deg $^{-1}$, from which we derive $N_a = 0.057$. Earlier estimates based on the ideal electronic thermal conductivity of metals (22, 23) have given a value near about 0.03 even for monovalent metals like copper and gold. We have, therefore, to conclude that the standard transport theory of metals of Makinson-Wilson overestimates the electron-phonon interaction by a factor of about 10.

3.4 The Electronic Lorenz Number

Fig. 6 gives the electronic Lorenz numbers derived by us for rhodium from the plots of $\lambda(H)$ versus $\sigma(H)T$ at liquid helium temperatures. They show a continuous, almost linear, drop with the fall of temperature amounting to somewhat more than 20 per cent between 4 and 2 °K. This does not seem to be in the category of the dipping Lorenz number, expected from inelastic phonon scattering of the conduction electrons. Makinson's curves of L_e / L_n versus T/θ are drawn for different values of the impurity parameter $\rho_0/4A$ where A/θ is the high-temperature slope of the ρ - T curve (we have taken the slope between the ice point and the steam point). ρ_0 for our specimen is 200×10^{-12} ohm-m and $A = 6.895 \times 10^{-8}$ ohm-m-deg $^{-1}$, giving an impurity parameter of

about 0.0007. The Makinson theory would give, at a temperature $T/\theta \approx 0.01$, $L_e/L_n = 0.95$, rising with the fall of temperature (see ref. 25, p. 291, fig. IX, 12 dotted curve for $\rho_0/(4A) = 0.0008$). Our L_e at 4 °K ≈ 2.35 , which agrees with the above estimate, but it falls with the fall of temperature.

Both in its magnitude and in its temperature dependence, this behaviour of L_e in rhodium is similar to that observed in dilute Ag-Mn (24) and Cu-Mn (25) alloys. The reason for this behaviour is not clear at the moment but we make the following tentative (and somewhat speculative) suggestion.

Johnson-Matthey rhodium (Lab No. 2357) was also used by Knook in preparing dilute Au-Rh alloys which were found to present a resistivity minimum and this was attributed to the possible traces of iron in the rhodium. The specially prepared sample of rhodium measured by Price and Taylor (12), having $\alpha = 0.00463$ (same as our rhodium specimen) was found on mass spectrographic analysis to contain about 100 ppm of iron. Could such an iron contamination be the cause for the anomalous temperature dependence of L_e in our specimen at helium temperatures ?

Preliminary electrical resistance measurements on this specimen above 4 °K show a minimum at about 10 °K and a maximum just above 4 °K. If this is confirmed the Lorenz number behaviour would have to be on the same lines as for dilute Ag-Mn (24) and Cu-Mn alloys (25). The positive magneto-resistivity in our rhodium specimen need not be considered inconsistent with the above discussion, considering that even the dilute Rh-Fe alloys containing 0.1 to 0.85 atom per cent iron (26), which have an anomalously dropping resistivity below about 20 °K have a positive magneto-resistivity.

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This paper will form part of a thesis to be submitted by one of us (N.S.N.) for the Doctorate Degree of the University of Delhi.

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Fig. 1. Temperature-dependence of the electrical resistivity of our rhodium specimen at liquid helium temperatures, in transverse magnetic fields of 0, 6.9, 10.2, 13.4, 16.5 and 19.4 kilo-Oersteds (respectively marked $\circ$, Δ , $\square$, ∇ , $\diamond$ and $\bullet$).

Fig. 2. Reduced Kohler diagram for rhodium: ($\bullet$ Schulze's data; $\circ$, Δ , $\square$: present data at 4, 3.2 and 2.4 $^{\circ}\text{K}$).

Fig. 3. Temperature-dependence of the thermal conductivity of our rhodium specimen in magnetic fields 0, 7.2, 10.7, 13.1 and 17.5 kilo-Oersteds (respectively marked $\circ$, Δ , ∇ , $\bullet$, $\square$).

Fig. 4. λ (H) versus σ (H) T for rhodium at 4, 3 and 2° K (respectively marked $\circ$, Δ and ∇).

Fig. 5. Temperature dependence of the lattice thermal conductivity of our rhodium specimen, as derived in the present analysis.

Fig. 6. Temperature dependence of the electronic Lorenz number of our rhodium specimen, as derived in the present analysis.

THERMAL CONDUCTIVITY STANDARD REFERENCE
MATERIALS FROM 4 to 300 K. I. ARMCO IRON

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ABSTRACT

Thermal conductivity, electrical resistivity, Lorenz ratio, and thermopower data are reported for several specimens of Armco iron for temperatures from 4 to 300 K. At low temperatures the electrical resistivity and thermal conductivity vary from specimen to specimen by more than 10%. However, the Lorenz ratios of these specimens differ by less than 2.5%, and the intrinsic resistivities calculated using Matthiessen's rule differ by less than 0.5% of the total resistivities. Thus, Armco iron specimens can be used as standards by measuring the residual resistivities and utilizing the Lorenz ratio reported here.

KEY WORDS

Cryogenics, electrical resistivity, iron, Lorenz ratio, Seebeck effect, thermal conductivity, transport properties.

1. Introduction

Design and development engineers in the aerospace industry continue to have urgent need for thermal and mechanical property data for new materials. For most materials, especially new or uncommon alloys, measured values of thermal conductivity are not available and predictions cannot be made with adequate confidence. To help satisfy these needs, we have constructed an apparatus for the simultaneous measurement of thermal conductivity, electrical resistivity and thermopower. Measurements have been conducted on several aerospace alloys, Hust, et al.^[1] Another phase of this program, to establish standard reference data on several reference materials (or specimens), has begun. We intend to measure several specimens of materials which appear to be useful as standards. For some materials, material variability may be so great that only standard specimens (not standard materials) will be useful. Standard reference specimens or materials are useful for intercomparison of existing apparatus, for debugging new apparatus, and for calibration of comparative apparatus. The apparent large

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differences between the results of various investigators for a given material (50% is not unheard of) is evidence of the need for intercomparisons, calibrations, and standardization. The availability of standard reference materials will result in more accurate and more permanent transport property data for technically important solids.

This paper contains the results of our measurements on the transport properties of Armco iron. Armco iron was investigated at low temperatures primarily because of its extensive use as a thermal conductivity standard at higher temperatures. [2]

2. Apparatus

The apparatus is based on the axial one-dimensional heat flow method. The specimen is a cylindrical rod 3.6 mm in diameter and 23 cm long with an electric heater at one end and a temperature controlled sink at the other. The specimen is surrounded by glass fiber and a temperature controlled shield. Eight thermocouples are mounted at equally spaced points along the length of the specimen to determine temperature gradients in the range 4 to 300 K. A detailed description of this apparatus will be presented by Hust, et al. [3].

3. Specimen Characterization

An Armco iron rod (2.54 cm diameter and 35.6 cm long) was obtained from Battelle Memorial Institute. This rod is from the same lot of stock as the specimens measured at several other laboratories. [4-9] We did not re-determine the composition of this rod in view of the repeated determinations by other investigators. [4, 7, 8, 9] Typical composition of Armco iron in weight percent is: 0.015 C, 0.028 Mn, 0.005 P, 0.025 S, 0.003 Si, 0.04 Cu, and 99.9 Fe. This rod was annealed by the supplier as follows: $\frac{1}{2}$ hour at 870°C in a gas-heated air muffle, and then in a quartz capsule at 1×10^{-6} torr for $1\frac{1}{2}$ hours at 875°C, furnace cooled to 150°C, held at 150°C for 24 hours, and furnace cooled to room temperature. We cut the rod into quarters along its axis and cut a 5 cm long piece from each end of each quadrant. These eight pieces were used for electrical residual resistivity ratio, hardness, and grain size measurements. Two of the center 25 cm sections were measured in the thermal conductivity apparatus. These specimens were chosen on the basis of the electrical resistivity measurements to maximize the difference between them. The division of the rod and the labeling of specimens is shown in figure 1.

The hardness of these specimens, after machining, was B-40.0. The specimens were subsequently reannealed using the same procedure indicated by the supplier. The hardness after anneal was B-37.1. The grain size approximated from ASTM Chart E112, plate 1 was 0.053 mm and 0.064 mm after machining and after reannealing respectively.

The use in this paper of trade names of specific products is essential to the proper understanding of the work presented. Their use in no way implies any approval, endorsement, or recommendations by NBS. Armco iron is a registered trade name of a commercially pure iron produced by Armco Steel Corporation.

The electrical residual resistivity ratios, $\rho_{273\text{ K}}/\rho_{4\text{ K}}$, of the eight specimens (1A.... 4A, 1B.... 4B) after machining and of two of these specimens after reannealing are recorded in table 1. These ratios, obtained from electrical resistance measurements at 273 K and 4 K in a specially fabricated dip probe, are estimated to be accurate to about 0.5%. Table 1 also contains the resistivity ratios of specimens 2C and 4C. The data marked with asterisks were obtained from the thermal conductivity apparatus.

C. F. Lucks of Battelle Memorial Institute performed similar measurements on another bar of Armco iron.^[10] The spread of his results on six specimens is $\pm 8.5\%$ of the mean while the spread of our ten specimens is $\pm 6.5\%$. The mean value of the residual resistivity ratio (13.65) determined from my data is 5.5% below the mean value measured by Lucks. It is noted from table 1 that the residual resistivity ratios are lower after annealing. This is probably caused by diffusion of impurities from the grain boundaries upon heat treatment. Impurities in solution are more effective electron scatterers than impurity precipitates at grain boundaries. Residual resistivity ratios reported by other investigators are also included in table 1.

4. Results

The transport properties of specimens 2C and 4C were measured in the thermal conductivity apparatus. Specimen 2C was subsequently annealed (same annealing procedure as described before) and remeasured

The experimental data were functionally represented with the following arbitrarily chosen equations:

$$\ln \lambda = \sum_{i=1}^n a_i [\ln T]^{i+1} \quad (1)$$

$$\rho = \sum_{i=1}^m b_i [\ln T]^{i+1} \quad (2)$$

$$S = \sum_{i=1}^l c_i [\ln T']^i / T'; T' = \frac{T}{10} + 1 \quad (3)$$

where λ = thermal conductivity, ρ = electrical resistivity, S = thermopower, and T = temperature. Temperatures are based on the IPTS-68 scale above 20 K and the NBS P2-20 (1965) scale below 20 K. The parameters, a_i , b_i , and c_i , determined by least squares, are presented in tables 2, 3, and 4. The number of terms used to represent each of the data sets is optimized, through the use of orthonormal functions, so that none of the precision of the data is lost by "underfitting" nor are any necessary oscillations introduced by "overfitting." Further details of this procedure will be described by Hust, et al.[3]. Calculated values of λ , ρ , S , and $L = \rho\lambda/T$ (Lorenz ratio) are presented in tables 5, 6, and 7.

A detailed error analysis for these measurements will be presented by Hust, et al. [3] Based on this analysis of systematic and random errors the uncertainty estimates (with 95% confidence) are as follows:

thermal conductivity:	2.5% at 300 K, decreasing as T^4 to 0.70% at 200 K, 0.70% from 200 K to 50 K, increasing inversely with temperature to 1.5% at 4 K.
electrical resistivity:	0.25%
thermopower:	0.5% + 0.2 $\mu\text{V/K}$ at 4 K, 0.2% + 0.05 $\mu\text{V/K}$ at 30 K, and 0.1% + 0.03 $\mu\text{V/K}$ above 76 K.

The thermopower values given here are absolute values although our measurements were carried out with respect to normal silver wire. The absolute thermopowers of normal silver reported by Borelius, et al. [11] were used to convert the experimental data to the absolute scale.

5. Discussion

The thermal conductivities of these specimens differ by as much as 10% at low temperatures; the differences observed in electrical resistivity are similar. The thermal conductivity deviations of the three sets of values are shown in figure 2. In figure 2, λ is the mean thermal conductivity for the three specimens at temperature, T . These data indicate that Armco iron is a poor thermal conductivity standard material at low temperatures. However, upon further examination it appears that one can determine the thermal conductivity of Armco iron specimens from residual resistivity measurements only. The Lorenz ratio, $\rho\lambda/T$, computed from these measurements is much less variable at low temperatures than either ρ or λ . This is expected for materials which are primarily electronic thermal conductors. Figure 3 illustrates the deviations of the Lorenz ratios for each specimen from the mean values. Since these deviations are not appreciably larger than the uncertainty in the computed Lorenz ratio, the Lorenz ratio is assumed to be essentially invariant from specimen to specimen. Thus, one can compute the thermal conductivity of a particular specimen of Armco iron from its electrical resistivity and the Lorenz ratios reported here.

In order for the above procedure to be practical one needs a relatively quick method of generating a ρ vs T curve for a particular specimen from relatively few measurements. Matthiessen's rule indicates that $\rho = \rho_0 + \rho_i$ where ρ_0 is the residual resistivity of the specimen and ρ_i is the intrinsic resistivity of the material. It is known that this rule is not satisfied exactly and that a correction term $\Delta(\rho_0, \rho_i)$ exists. However, if this correction term is sufficiently small one can construct a sufficiently accurate ρ vs T curve for a given specimen from ρ_i , assumed to be the same for all specimens, and the value of ρ_0 as measured for each specimen. To investigate this possibility, ρ_i was computed for each of the three specimens using Matthiessen's rule. The relative deviations of the computed values of ρ_i from the mean of three sets is shown in figure 4. This plot shows that ρ_i values for these three specimens, as computed from Matthiessen's rule, differ from the mean by less than 0.3% of the total resistivity. This deviation is only slightly larger than the estimated uncertainty of the measurements. It is not unreasonable to assume that ρ_i for other specimens is within a few tenths of a

percent of the mean values of these three specimens. Thus, Armco iron specimens are useful low temperature standards. This is especially significant, since Armco iron is already in extensive use as a high temperature standard reference material.[2] The thermal conductivity, λ , of a standard reference specimen of Armco iron according to these results may be computed from

$$\lambda = \frac{LT}{\rho} - \frac{LT}{\rho_1 + \rho_0} \quad (4)$$

where L and ρ_1 are given in table 8 and ρ_0 is determined by a relatively simple measurement.

Numerous thermal conductivity and electrical resistivity measurements on Armco iron have been reported, some of these measurements extend to temperatures as low as -200°C . Powell [2] reviewed the data published prior to 1962, this review indicates that the only low temperature data at that time were those of Lucks and Deem[12]. Since that time low temperature data have been reported by Fulkerson, et al.[4], Larsen, et al.[13], Shanks, et al.[8], and Watson, et al.[9]. These and other high temperature measurements have been done as a result of a proposal by C. F. Lucks (Battelle Memorial Institute) to carry out a round-robin experiment on Armco iron. This suggestion led to the distribution, by BMI, of several specimens of Armco iron. Reported data on these specimens can be interpreted to show (1) experimental differences between laboratories (assuming insignificant material variability), (2) material variability in a given lot of Armco iron (assuming insignificant experimental errors), or (3) a combination of (1) and (2) of comparable proportions. Not surprisingly, the latter seems to be the result of these measurements, as is indicated in the following discussion.

The electrical resistivity measurements are generally reported to be accurate to better than 1%. Thermal conductivity data are generally reported to be accurate to better than 3%. Thus, the uncertainty in Lorenz ratios caused by experimental measurement errors is expected to be less than 4%. The electrical resistivities measured by several investigators [4, 5, 7, 8, 9, 13] range from $0.09\mu\Omega\text{m}$, this 10% range is significantly larger than the expected uncertainty of the measurements. This is a larger material variation than I would expect on the following basis. Matthiessen's rule is expected to be reasonably correct, as confirmed by my measurements, and, thus, the same absolute variation observed in electrical resistivity at the ice point should also be observed in the residual resistivity. Since the residual resistivity ratios for the specimens measured range from 10 to 14, the extreme residual resistances should differ by about 100%. The available residual resistance measurements differ by, at most, 34%.

Some investigators [4, 8, 9] have measured the electrical resistivity of several specimens and also have investigated the effect of heat treatment, their results show possible differences of several percent but it seems unlikely that at room temperature the real material differences exceed about 5%.

Since the electronic component of thermal conductivity is the major conductivity component in Armco iron, the specimen-to-specimen variation

in electrical resistivity must be reflected in the thermal conductivity. However, since the experimental measurement uncertainty is not significantly smaller than the probable material variability, it is difficult to determine material differences. The variation in reported thermal conductivities from all sources near the ice point is about 6%, not unreasonable according to the previous comments.

As indicated previously, the Lorenz ratio should be more invariant from specimen-to-specimen than either electrical resistivity or thermal conductivity. Comparison of all the reported Lorenz ratios at 0°C shows a variation of about 2.5%. Considering the previously estimated uncertainty of 4% this is considered excellent agreement. However, it would appear that this agreement is fortuitous. Upon careful examination of the methods used by the various investigators, it is noted that the electrical resistivity and thermal conductivity measurements were performed either on different specimens or at different times. In the latter case the specimen was invariably either machined or heat treated between the two types of measurements. Since we know that specimen-to-specimen variations exist and, since we know that mechanical strain or heat treatment change the transport properties, it follows that the Lorenz ratio should be calculated from simultaneous measurements of electrical resistivity and thermal conductivity on the same specimen. This apparent operational discrepancy may explain the larger Lorenz ratio variation at low temperatures. For example at -150 and -200 °C the differences between the extreme values of Lorenz ratio are about 12%. As pointed out previously the specimen-to-specimen percentage variation in electrical resistivity and thermal conductivity is greater at low temperatures.

Although my purpose is primarily restricted to low temperatures, it seems that a comment regarding the use of Armco iron as a high temperature reference material is in order. It seems clear that variations from specimen-to-specimen and variations caused by heat treatment are several percent. Under these circumstances it seems prudent to make "in place" calibrations by electrical resistivity measurements whenever Armco iron is used at high temperatures. At low temperatures it is probably sufficient to make a residual resistivity measurement for calibration purposes as previously described.

In conclusion it appears that the available data neither confirm nor contradict my previous estimate of the invariance of the Lorenz ratio and the intrinsic electrical resistivity. However, since the specimens I used had a rather limited range of residual resistivity (0.0066 to 0.0076 $\mu\Omega/\text{m}$) compared to the high value observed by Fulkerson, et al, [4] (0.01 $\mu\Omega/\text{m}$) it would be desirable to make additional thermal and electrical measurements on a specimen having a higher residual resistivity.

The absolute thermopowers of these three specimens are compared in figure 5. The deviations between specimens are only slightly larger than the uncertainty in the tabulated values; thus no significant difference between specimens can be detected from this property.

6. Acknowledgments

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R. L. Durcholz of this laboratory did the hardness and grain size testing. This measurement program has been carried out under the helpful guidance of R. L. Powell.

7. References

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Table 1

Residual resistivity ratio (ρ_{273K}/ρ_{4K}) of Armco iron

Specimen	After machining	After annealing
1A	14.12	
2A	13.81	
3A	14.13	
4A	12.99	
1B	13.81	
2B	14.51	12.88
3B	14.09	
4B	12.77	11.52
2C	13.86, 13.93*	12.57*
4C	12.44, 12.53*	

* These values were determined from measurements using the thermal conductivity apparatus.

Source	ρ_{273K}/ρ_{4K}
Lucks ^[10]	$14.4 \pm 6.5\%$
Fulkerson, et al ^[4]	9.8, 10.0
Shanks, et al ^[8]	12.6

Table 2. Parameters in equations 1, 2, and 3 for Armco iron, specimen 2C.

Thermal Conductivity	Electrical Resistivity	Thermopower
4.51614994	$-4.95025810 \times 10^{-7}$	-3.44881675×10^2
-4.13926935	$1.65473929 \times 10^{-6}$	2.37913833×10^3
2.07599685	$-2.37099406 \times 10^{-6}$	-6.68364762×10^3
$-8.61606749 \times 10^{-1}$	$1.93668635 \times 10^{-6}$	9.99411766×10^3
$3.39315321 \times 10^{-1}$	$-9.93191337 \times 10^{-7}$	-8.67747098×10^3
$-9.99896812 \times 10^{-2}$	$3.31399468 \times 10^{-7}$	4.46376537×10^3
$1.79360964 \times 10^{-2}$	$-7.18946332 \times 10^{-8}$	-1.32173829×10^3
$-1.71155124 \times 10^{-3}$	$9.77121499 \times 10^{-9}$	2.08103179×10^2
$6.66070951 \times 10^{-5}$	$-7.54546890 \times 10^{-10}$	-1.35462989×10^1
	$2.52377946 \times 10^{-11}$	

Table 3. Parameters in equations 1, 2, and 3 for Armco iron, specimen 2C after annealing.

Thermal Conductivity	Electrical Resistivity	Thermopower
7.43890940	$-4.20510751 \times 10^{-7}$	-5.10933863×10^2
-1.14675555×10^1	$1.45081937 \times 10^{-6}$	3.36812410×10^3
9.73124560	$-2.12826875 \times 10^{-6}$	-9.06609424×10^3
-5.28250471	$1.77366602 \times 10^{-6}$	1.30552541×10^4
1.89245802	$-9.25249389 \times 10^{-7}$	-1.09917641×10^4
$-4.41102771 \times 10^{-1}$	$3.13228379 \times 10^{-7}$	5.52800895×10^3
$6.37973455 \times 10^{-2}$	$-6.87884712 \times 10^{-8}$	-1.61455399×10^3
$-5.17020759 \times 10^{-3}$	$9.44600166 \times 10^{-9}$	2.52389423×10^2
$1.78835874 \times 10^{-4}$	$-7.35822503 \times 10^{-10}$	-1.63749922×10^1
	$2.47951038 \times 10^{-11}$	

Table 4. Parameters in equations 1, 2, and 3 for Armco iron, specimen 4C.

Thermal Conductivity	Electrical Resistivity	Thermopower
8.21226100	$-5.03088441 \times 10^{-7}$	-6.42943844×10^2
-1.32577224×10^1	$1.69059561 \times 10^{-6}$	4.14540857×10^3
1.14738701×10^1	$-2.42733181 \times 10^{-6}$	-1.09289158×10^4
-6.21776147	$1.98402296 \times 10^{-6}$	1.54381788×10^4
2.19527810	$-1.01722378 \times 10^{-6}$	-1.27838650×10^4
$-5.01619108 \times 10^{-1}$	$3.39158569 \times 10^{-7}$	6.34295244×10^3
$7.10720281 \times 10^{-2}$	$-7.35034919 \times 10^{-8}$	-1.83456286×10^3
$-5.64940725 \times 10^{-3}$	$9.97927431 \times 10^{-9}$	2.84809534×10^2
$1.91995267 \times 10^{-4}$	$-7.69854134 \times 10^{-10}$	-1.83820643×10^1
	$2.57278514 \times 10^{-11}$	

Table 5. Transport properties of Armco iron (specimen 2c).

Temp (K)	Thermal Conductivity (Wm ⁻¹ K ⁻¹)	Electrical Resistivity (μohm m)	Lorenz ratio x 10 ⁸ (V ² /K ²)	Thermo- power (μV/K)
6	21.7	0.006905	2.49	2.02
7	25.6	0.006903	2.52	0.06
8	29.2	0.006911	2.53	0.07
9	32.8	0.006920	2.53	0.06
10	36.4	0.006926	2.52	0.07
12	43.5	0.006929	2.51	0.13
14	50.7	0.006932	2.51	0.22
16	57.9	0.006941	2.51	0.32
18	65.0	0.006957	2.51	0.43
20	71.8	0.006981	2.50	0.54
25	87.0	0.007067	2.46	0.82
30	98.9	0.007196	2.37	1.18
35	107	0.007386	2.26	1.67
40	113	0.007664	2.16	2.28
45	115	0.008051	2.06	3.00
50	116	0.008562	1.99	3.79
55	115	0.009202	1.93	4.63
60	114	0.009976	1.89	5.51
65	112	0.01088	1.87	6.38
70	110	0.01191	1.87	7.24
75	107	0.01306	1.87	8.07
80	105	0.01432	1.88	8.86
85	103	0.01568	1.89	9.60
90	100	0.01713	1.91	10.30
95	98.4	0.01867	1.93	10.95
100	96.6	0.02028	1.96	11.54
110	93.4	0.02371	2.01	12.58
120	90.8	0.02736	2.07	13.44
130	88.7	0.03119	2.13	14.13
140	87.1	0.03516	2.19	14.67
150	85.8	0.03923	2.24	15.07
160	84.7	0.04340	2.30	15.37
170	83.9	0.04765	2.35	15.57
180	83.1	0.05196	2.40	15.69
190	82.4	0.05633	2.44	15.74
200	81.8	0.06077	2.48	15.73
220	80.5	0.06983	2.55	15.56
240	79.1	0.07918	2.61	15.23
260	77.5	0.08888	2.65	14.77
280	75.9	0.09903	2.68	14.19
300	74.3	0.10970	2.72	13.51

Table 6. Transport properties of Armco iron (specimen 2c after annealing).

Temp (K)	Thermal Conductivity (Wm ⁻¹ K ⁻¹)	Electrical Resistivity (μ ohm m)	Lorenz ratio x 10 ⁸ (V ² /K ²)	Thermo- power (μV/K)
6	19.7	0.007645	2.52	-0.02
7	23.2	0.007645	2.53	0.08
8	26.6	0.007658	2.54	0.11
9	29.9	0.007669	2.55	0.11
10	33.2	0.007674	2.55	0.11
12	39.8	0.007676	2.54	0.15
14	46.4	0.007676	2.54	0.23
16	52.9	0.007685	2.54	0.33
18	59.4	0.007702	2.54	0.44
20	65.6	0.007726	2.53	0.56
25	79.8	0.007812	2.49	0.87
30	91.2	0.007936	2.41	1.25
35	99.6	0.008119	2.31	1.75
40	105	0.008388	2.21	2.37
45	108	0.008766	2.11	3.09
50	110	0.009268	2.04	3.87
55	110	0.009902	1.98	4.72
60	109	0.01067	1.94	5.58
65	108	0.01157	1.92	6.45
70	106	0.01259	1.91	7.30
75	104	0.01374	1.91	8.12
80	102	0.01500	1.91	8.91
85	100	0.01635	1.93	9.65
90	98.4	0.01781	1.95	10.34
95	96.7	0.01934	1.97	10.97
100	95.1	0.02096	1.99	11.56
110	92.3	0.02438	2.05	12.59
120	90.1	0.02803	2.10	13.43
130	88.3	0.03185	2.16	14.10
140	86.9	0.03581	2.22	14.63
150	85.7	0.03988	2.28	15.02
160	84.7	0.04404	2.33	15.31
170	83.8	0.04827	2.38	15.50
180	83.0	0.05258	2.42	15.62
190	82.2	0.05694	2.46	15.67
200	81.4	0.06137	2.50	15.66
220	79.8	0.07042	2.56	15.50
240	78.2	0.07978	2.60	15.18
260	76.6	0.08952	2.64	14.72
280	75.3	0.09971	2.68	14.14

Table 7. Transport properties of Armco iron (specimen 4c).

Temp (K)	Thermal Conductivity (Wm ⁻¹ K ⁻¹)	Electrical Resistivity (μohm m)	Lorenz ratio × 10 ⁸ (V ² /K ²)	Thermo- power (μV/K)
6	19.6	0.007675	2.51	-0.07
7	23.0	0.007664	2.52	0.07
8	26.3	0.007673	2.52	0.11
9	29.6	0.007685	2.53	0.11
10	32.9	0.007694	2.53	0.11
12	39.4	0.007702	2.53	0.13
14	46.0	0.007706	2.53	0.19
16	52.5	0.007715	2.53	0.28
18	58.9	0.007730	2.53	0.39
20	65.1	0.007752	2.52	0.50
25	79.1	0.007834	2.48	0.80
30	90.5	0.007960	2.40	1.18
35	98.9	0.008149	2.30	1.66
40	105	0.008427	2.20	2.27
45	108	0.008814	2.11	2.97
50	109	0.009324	2.04	3.74
55	110	0.009965	1.98	4.58
60	109	0.01074	1.95	5.44
65	107	0.01164	1.92	6.30
70	106	0.01267	1.91	7.15
75	104	0.01382	1.91	7.98
80	102	0.01507	1.92	8.77
85	99.8	0.01643	1.93	9.51
90	97.9	0.01789	1.95	10.20
95	96.2	0.01942	1.97	10.85
100	94.6	0.02104	1.99	11.44
110	91.8	0.02446	2.04	12.47
120	89.6	0.02811	2.10	13.31
130	87.9	0.03193	2.16	13.99
140	86.5	0.03589	2.22	14.51
150	85.4	0.03996	2.28	14.91
160	84.5	0.04412	2.33	15.20
170	83.8	0.04836	2.38	15.39
180	83.1	0.05267	2.43	15.51
190	82.4	0.05704	2.47	15.56
200	81.8	0.06146	2.51	15.55
220	80.4	0.07052	2.58	15.39
240	78.8	0.07986	2.62	15.07
260	77.0	0.08957	2.65	14.62
280	75.3	0.09973	2.68	14.05
300	73.8	0.11040	2.71	13.36

Table 8. The Lorenz ratio and intrinsic electrical resistivity
of Armco iron (average of the results from three specimens).

Temp (K)	Lorenz ratio $\times 10^8$ (V^2/K^2)	Intrinsic Electrical Resistivity (μ ohm m)
4	2.263	0.0000
5	2.455	0.0000
6	2.505	0.0000
7	2.523	0.0000
8	2.531	0.0000
9	2.533	0.0000
10	2.532	0.0000
12	2.529	0.0000
14	2.528	0.0000
16	2.528	0.0000
18	2.527	0.0001
20	2.521	0.0001
25	2.477	0.0002
30	2.395	0.0003
35	2.292	0.0005
40	2.188	0.0008
45	2.096	0.0011
50	2.021	0.0016
55	1.965	0.0023
60	1.927	0.0030
65	1.905	0.0040
70	1.895	0.0050
75	1.895	0.0061
80	1.903	0.0074
85	1.917	0.0087
90	1.935	0.0102
95	1.956	0.0117
100	1.980	0.0134
110	2.034	0.0168
120	2.091	0.0204
130	2.150	0.0242
140	2.209	0.0282
150	2.266	0.0323
160	2.320	0.0364
170	2.371	0.0407
180	2.418	0.0450
190	2.461	0.0494
200	2.499	0.0538
220	2.562	0.0628
240	2.610	0.0722
260	2.647	0.0819
280	2.682	0.0921
300	2.724	0.1028

Figure 1. Division of Armco iron rod. Each of the 12 pieces shown was machined into a circular cylinder for measurement.

Fig. 2. Deviations of the thermal conductivities of each specimen from the mean values.

Fig. 3. Deviations of the Lorenz ratios of each specimen from the mean values.

Fig. 4. Deviations of the computed intrinsic electrical resistivities of each specimen from the mean values.

Fig. 5. Deviations of the thermopowers of three specimens from the mean values.

THERMAL CONDUCTIVITY OF SOME CUBIC SODIUM TUNGSTEN BRONZES

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Abstract

The sodium tungsten bronzes are the nonstoichiometric compounds with the general formula, Na_xWO_3 . The thermal conductivity of a series of cubic sodium tungsten bronze crystals with $0.51 \leq x \leq 0.89$ have been measured at low temperatures. The temperature dependence of the thermal conductivity is similar to that of an impure metal. This result is consistent with the low resistivity ratios, 2 to 5, of these materials. The total thermal conductivity increases with the sodium concentration. We find apparent Lorenz ratios of 3.5 and $2.5 \times 10^{-8} \text{ V}^2/\text{K}^2$ at 200 K for samples with $x = 0.51$ and $x = 0.89$ respectively. If we assume that the electronic thermal conductivity is given by $L_0 \sigma T$, the Wiedemann-Franz-Lorenz rule, then we find that the lattice conductivity is a significant contribution to the total for the lower x -value bronzes. The lattice contribution shows a maximum as a function of x for our $x = 0.78$ sample. We attribute this result to the ordering of the sodium atoms that occurs near $x = 0.75$.

Introduction

The sodium tungsten bronzes are nonstoichiometric compounds with the general formula Na_xWO_3 . These bronzes exhibit metallic electrical properties for $1 \geq x \geq 0.25$ and a cubic crystal structure for $x > 0.48$. The electrical resistivity and Seebeck effect of metallic Na_xWO_3 have been discussed by Muhlestein and Danielson (1, 2). They reported an anomaly in the electrical resistivity versus x at $x = 0.75$. Atoji and Rundle (3) found evidence of a partial ordering of the sodium atoms in the WO_3 matrix at $x = 0.75$ in their neutron diffraction work. Muhlestein and Danielson interpreted their anomaly

in terms of this ordering. In addition their Hall effect results show that each sodium atom contributes one free electron to the conduction band. Measurements of the thermal conductivity should be interesting because it is possible to change the free electron concentration without changing the lattice symmetry and because of the $x = 0.75$ ordering of the sodium atoms. We are reporting here some preliminary measurements of the low temperature thermal conductivity. The only other known thermal conductivity results are those of Shanks and Redin (4) who measured several samples at temperatures above 300K.

Measurements

The thermal conductivities and electrical resistivities of four Na_xWO_3 single crystals have been measured at low temperatures by a conventional steady state longitudinal heat flow technique. The electrical resistivities of the samples are in good agreement with the results of Muhlestein and Danielson (1). Measurements on samples with $x = 0.78$ and 0.64 have been made from 4 to 300K and samples with $x = 0.89$ and $x = 0.51$ have been run from 50 to 300K. The room temperature electrical resistivities, thermal conductivities and Lorenz functions are given in Table I.

Table I Room Temperature Results

x	$\rho (\mu\text{-}\Omega\text{-m})$	$\lambda (\text{W/m-K})$	$L \times 10^8 \left(\frac{j^2}{K^2} \right)$
0.89	15.4	53	2.7
0.78	22.0	53	3.8
0.64	37.0	30	3.5
0.51	48.0	22	3.5

Figure 1 shows the thermal conductivity as a function of temperature for the four samples. The temperature dependence is similar to that of an impure metal or an alloy. Our $x = 0.51$ sample is in good agreement with Shanks and Redin's result on a similar sample (4).

Figure 2 shows the Lorenz function for the samples as a function of temperature. The $x = 0.89$ sample shows a Lorenz function very close to the theoretical value of $2.45 \times 10^{-8} \text{ V}^2/\text{K}^2$. The other samples show large deviations from the theoretical value. The upturn at low temperatures can probably be interpreted in terms of lattice conduction.

Conclusions

If we assume that the electronic thermal conductivity is given by $L_0 \propto T$ and subtract this function from the measured thermal conductivity we get the result shown in Figure 3. Whether these results should be interpreted as lattice conduction or as a deviation of L from L_0 is not clear at this time. The difference for the $x = 0.89$ sample certainly shows a T dependence that is reasonable for lattice conduction. Of the results for the other samples the $x = 0.78$ result is the most unusual and probably is caused by the partial ordering of the sodium atoms at $x = 0.75$. This result is perhaps an electronic effect since an ordering would introduce an additional symmetry requirement on the electronic structure which might cause large deviations from the Weidemann-Franz-Lorenz rule.

The measurements will be extended to other bronze samples particularly samples with x -values near 0.75 and to liquid helium temperatures. At low temperatures we should have $L = L_0$ and a calculation of the lattice conductivity should be possible.

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Figure 1. The thermal conductivities versus temperature for the four bronzes are shown.

Figure 2. The Lorenz ratio is shown as a function of temperature.

Figure 3. λ_L represents the difference between the measured thermal conductivity and that calculated from $L_0 \sigma T$.

Liquids

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The Thermal Conductivity of Fluids at High Pressures and Low Temperatures¹

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Abstract

Apparatus to make absolute measurements of the thermal conductivity of fluids in the temperature range -150 to $+100^{\circ}\text{C}$ and the pressure range 1 to 600 bar is described by reference to preliminary measurements now being undertaken on methane. The accuracy of the apparatus which employs a transient line source technique is demonstrated by reference to measurements performed on toluene in the temperature range 0 to 90°C at atmospheric pressure. The λ_{25} value of 129.3 watt/m $^{\circ}\text{K}$ agrees favourably with the recent very accurate "radiation component" free values obtained by Poltz (1)³ and Tree (2).

Key Words: conductivity, heat conductivity, liquids, toluene, methane, radiation, thermal conductivity.

INTRODUCTION - Previous attempts to obtain accurate liquid or dense fluid thermal conductivity data either for use in industrial design or in investigations of the effect of molecular structure on transport properties and have utilized, by large, steady state methods of measurement. The precise evaluation of the thermal conductivity of fluid mixtures requires for a rational and theoretical evaluation of the "interaction terms" (3) very accurate experimental values of the thermal conductivity.

In a recent review of available measurement techniques used in the determination of λ , Saxena (4) presented an extensive list of steady state methods. Some of these methods while now being able to yield values with an expected absolute accuracy of $\pm 0.5\%$ suffer from the fault of most steady state apparatus - lengthy apparatus time constant. Accurate measurements, therefore, require very constant temperature environments, precise temperature determination, exact geometrical measurement, and, as has now been shown by Poltz (5) and Tree and Leidenfrost (6), substantial correction for radiation in a fluid which participates in the radiative transfer, as, for example, does toluene.

Transient methods on the other hand replace the steady state difficulties of long term temperature stability, and exact geometry, with the problem of the exact measurement of a transient temperature. Methods such as those de-

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³ Figures in brackets indicate the literature references at the end of the paper.

veloped by Horrocks and McLaughlin (7) and Jobst (8), theoretically require only exact time and temperature measurement to yield about $\pm 0.5\%$ accurate values for most fluids. It would be expected, however, that even with this type of apparatus radiation effects such as described by Poltz would also be present, and, convection in addition could prove difficult.

In an attempt to provide accurate thermal conductivity data for methane which are to be used as a reference for future measurements on natural gas mixtures, the present apparatus has been constructed. During the course of construction several tests have been made using A.R. toluene in an attempt to (a) check the reproducibility of the measurement technique over a wide range of operating conditions, (b) examine the radiation component in the transient measurements and (c) check the experimental radiation component free work of Poltz (3) and Tree. On the strength of these results and comparisons, it is felt that the apparatus is accurate to about $\pm 0.5\%$.

Preliminary measurements have been made on C.P. methane as a check on the pressure system, although final modifications are still necessary to the system to allow convenient measurement at lower temperatures and higher pressures. Although some of this work has been reported (9) sufficient is repeated here to illustrate the range and capability of the instrument.

Theory of Measurement - The transient hot wire method (7,10) was adopted for the absolute determination of the thermal conductivity of fluids in this work. With this method heat is generated at a known rate in an electrically heated fine platinum wire immersed vertically in the fluid under consideration, which is contained in a cylindrical enclosure initially in thermal equilibrium. The apparatus to a first approximation simulates the behaviour of an infinite line source of constant heat generation in an extended medium. The solution of the Fourier equation of heat conduction using the initial boundary conditions of constant temperature is for this situation (11a).

$$T_{\infty}(r,t) = - \frac{q}{4\pi\lambda} \left\{ \text{Ei} \left(- \frac{r^2}{4\alpha t} \right) \right\} \quad (1)$$

At a fixed radial distance, say at the surface of the wire where $r = a$, the time dependence of temperature can be obtained from Equation (1) by expanding the exponential integral for small values (< 0.02) of $a^2/4\alpha t$. The result is

$$T_{\infty}(a,t) = \frac{q}{4\pi\lambda} \left\{ \ln(t) + \ln\left(-\frac{4\alpha}{a^2}\right) + \frac{a^2}{4\alpha t} + \dots \right\} \quad (2)$$

Provided that $\frac{a^2}{4\alpha t}$ is sufficiently small in the range t_1 to t_2 then

$$T_{\infty}(a,t_2) - T_{\infty}(a,t_1) \approx \frac{q}{4\pi\lambda} \cdot \ln\left(\frac{t_2}{t_1}\right) \quad (3)$$

A plot of temperature against $\log(\text{time})$, therefore, would enable the thermal conductivity to be obtained provided conduction was the only energy transfer mechanism operative.

In an actual experimental hot wire cell, the heating wire has a finite diameter, (finite heat capacity), a finite length, and, in addition, the medium is bounded. A critical examination of the limitations and necessary modifications of Equation (3) when applied to an experimental cell, has been done by Horrocks and McLaughlin (7). In the present apparatus modification need to be made only for the finite heat capacity of the wire, which changes the inner boundary condition for the solution of the Fourier equation of conduction and introduces into the solution, as given by Equation (2) a term dependent on the heat capacities of the wire and the medium. Thus the modified solution is (11b).

$$T_{\infty}(a,t) = \frac{q}{4\pi\lambda} \left[\ln(t) + \ln\left(-\frac{4\alpha}{a^2}\right) + \frac{a^2}{2\alpha t} + \left\{ \frac{(w-2)a^2}{2\omega\alpha t} \ln\left(\frac{4\alpha t}{a^2}\right) \right\} \right] \quad (4)$$

The wire is assumed to have no contact resistance with the medium and to be perfectly conducting with a constant temperature over its cross-section.

EXPERIMENTAL APPARATUS

The hot wire conductivity cell was located inside a pressure vessel of 3.3 cm inner diameter. A wire, made of 0.001 inch diameter thermo-pure platinum, with potential leads of 0.0005 inch diameter platinum was hung vertically by suspending, at its lower end, a 0.5 inch long platinum wire of 0.04 inch diameter. The length of the wire between potential leads was 7.5473×10^{-2} m. All electrical connections coming out of the pressure vessel were ensured pressure tight with a 'Conax' teflon sealing gland.

The pressure vessel was immersed inside a thermostat bath, filled with di-methyl-butane (F.P. = -168°C , B.P. = 28°C). This fluid was cooled by passing liquid nitrogen through the cooling coil. The temperature of the apparatus was measured accurately to hundredth of a degree with the help of a calibrated quartz thermometer. The rate of flow of liquid nitrogen through the thermostat could be maintained constant and the final temperature controlled by adjusting the power to a heating coil. When measurements were being made the control was carried out manually enabling the temperature of the bomb to be controlled within few hundredths of a degree.

In the present investigation on toluene, however, water was used as bath fluid and the liquid nitrogen coils were used for cooling water. The measurements were carried out in the range 0°C to 90°C , and there was no difficulty in maintaining the bath temperature to within a millidegree.

Figure 1 shows the details of high pressure system, consisting of two parts, one containing the experimental fluid and the other containing oil, both being separated by a differential pressure null detector. Pressure was applied to the test fluid by means of a "Ruska" positive displacement pump and the gas pressure balanced by applying pressure to the oil by means of a standard "Budenberg" dead weight tester. The balance point was indicated by a differential pressure null detector, which had an accuracy of 0.01 psi ΔP , and a sensitivity varying from 2×10^{-4} psi ΔP per meter division to 0.01 psi ΔP per meter division.

The above mentioned differential pressure null detector cannot be used for liquids directly. For this reason an additional mercury interface system is incorporated as shown in the figure.

MEASUREMENT TECHNIQUE

Measurement of the varying temperature of the hot wire, as a function of time, constitutes the major experimental problem in unsteady state thermal conductivity measurements. The most convenient parameter to measure is the wire resistance since from Equation (3),

$$\lambda = \frac{q}{4\pi} \cdot \frac{\Delta \ln(t)}{\Delta R} \cdot \left(\frac{\Delta R}{\Delta T}\right) \quad (5)$$

and, for small values of temperature rise, ΔT , $\frac{\Delta R}{\Delta T}$ can be approximated by

$\frac{dR}{dT}$ which can be considered effectively as a constant during each measurement since the temperature rise is small (approximately 2°C in two seconds). From Ohm's law,

Fig. 1. Schematic of Experimental Systems

$$\Delta R = \frac{\Delta V}{I} - \frac{V}{I^2} \cdot \Delta I$$

Thus the measurement of temperature rise requires the measurement of the current and voltage transients in and across the cell wire.

In the present investigation, the current transient in the wire was avoided by using a fast response constant current D.C. power supply (HP - 6112A) with the result, $\Delta R = \Delta V/I$, and

$$\lambda = \frac{q}{4\pi} \frac{\Delta \ln(t)}{(\Delta V/I)} \cdot \left(\frac{dR}{dT}\right) = \frac{V \cdot I^2}{4\pi \ell} \cdot \frac{\Delta \ln(t)}{\Delta V} \cdot \left(\frac{dR}{dT}\right) \quad (6)$$

where $q = VI/\ell$

Since this means that the heat flux was not a constant but a slowly varying function of time due to the change in resistance of the cell wire, a correction was necessary. The correction required never exceeded 0.5% of λ .

Figure 2 is a schematic layout of the electrical circuit used with the hot wire cell. The switching of the transistor switch (B.B) was preceded by a manual switch (SW). The circuits of the transistor switch were so arranged such that when the manual switch was kept in 'off' position, (1-6, 2-8, 3-10, 4-12) the transistor TR_2 would maintain a very high resistance, while TR_1 would allow current to flow from the constant current source through the ballast resistor circuit. When the manual switch was turned on (1-5, 2-7, 3-9, 4-11), TR_1 would become highly resistive and TR_2 would allow current to pass through the 'hot wire' circuit. This type of transistor circuit enabled the transfer of current flow from one branch to another within a micro-second. This avoided any possible open circuit condition on the current source for any significant length of time.

Prior to initiating an actual measurement, the ballast resistance was carefully matched to the cell resistance using a one-milliamp current. The steady state voltage across the cell, recorded by an integrating digital voltmeter (HP - 2402A) during a measurement, was, therefore, accurate to within one microvolt. The constant current in the circuit was also measured very precisely by recording the voltage across the standard resistance, as shown in Figure 2.

Once current was established in the hot wire circuit, by activating the transistor switch, the resistance of the hot wire continuously changed due to the temperature rise of the wire resulting from the dissipation of electrical energy through the wire

The out-of-balance transient potential across the cell resistance was measured as a function of time utilizing the Digital Voltmeter triggered externally to take measurements at the rate of 20 readings per second. The measured values were printed out at this rate by a (HP - 5050B) digital recorder. The time delay between the initiation of current in the hot wire and the DVM measuring the first voltage signal was recorded to within 0.1 micro-second using timer, T_1 (HP - 5325A). The 'period' of measurement also was indicated to within one micro-second by timer, T_2 .

Fig. 2. Electrical Circuit Details

DATA HANDLING AND REDUCTION TECHNIQUE

Measurements were normally carried out for about two seconds. A total of 40 readings were recorded by the DVM during this time. However, measurements below 0.2 seconds were ignored due to the fact that the logarithmic approximation of the exponential integral in Equation (1) was valid only beyond 0.2 seconds for toluene. The difference between the voltage readings in the time interval, $t_2 - t_1$, would give the transient voltage rise, ΔV . This value ΔV (the normal 'cut off' or ΔV minimum was 200 μV) and the corresponding ratio (t_2/t_1), along with V , I , ℓ , (dR/dT) were used in Equation (6) to determine λ .

Obviously, with about 35 readings, in the two second period, there are many possible ways of determining ΔV . The manner used here was to subdivide the readings so that each localized group gave about 25 individual determinations, each with standard deviations of about 0.3%. The mean values of all the groups were then extrapolated to time, $t = 0$ with $\partial\lambda/\partial t = 0$ at this point. This procedure was adopted since the extrapolated value, λ_0 , would be ideally free from all possible sources of heat loss errors, and not influenced by other modes of heat transfer (see Figure 3).

EXPERIMENTAL RESULTS

Methane - As mentioned previously only preliminary results are available for this fluid in the temperature range between 200 and 300K at pressures from 200 to 600 bar since modification is required to the cryostat to ensure its satisfactory performance. Table 1 details the results for 291 and 258 °K only. These preliminary data have been shown to agree reasonably well (+3%) with a recent review and correlation of existing data (9).

TABLE 1. PRELIMINARY EXPERIMENTAL RESULTS - METHANE

Pressure (bars)	Mean Temperature (°K)	Thermal Conductivity (w/m °C) × 10 ³		Percentage Deviation $\frac{(\lambda_{exp} - \lambda_{cor})}{\lambda_{exp}} \times 100$
		λ_{exp}	λ_{cor} (Ref. (9))	
518	291.31	101.21	96.85	+4.30
414	291.31	90.08	86.68	+3.74
313	291.31	79.18	76.21	+3.72
207	291.31	64.76	62.63	+3.29
553	258.52	115.27	109.43	+5.0
401	258.52	99.62	96.70	+2.91
311	258.52	89.24	87.23	+2.24
207	258.52	73.46	71.34	+2.86

Toluene - Reduced "radiation component" free data for this fluid are presented in Table 2. The fluid used was AR grade toluene and the data was obtained from two separate experimental programs over a period of one month. A total of sixty-nine runs were obtained in the temperature range 0 - 90° C. Twenty-three of these runs were made at 25° C and eight and eleven at 50 and 75° C respectively to check apparatus reproducibility. Each run, consisting of many individual measurements (up to several hundred in some instances) can be interpreted as shown in Figure 3 for a result obtained at approximately 10° C.

Fig. 3. Typical Measurement Result on Toluene at 10° C

Table 2. Comparison of Values of the Thermal Conductivity of Toluene ($\lambda = \lambda_0 + \bar{\alpha}T$)

Author	$\lambda_0 \times 10^3$	$\bar{\alpha} \times 10^3$	r	$\lambda_{25} \times 10^3$	$\lambda_{55} \times 10^3$
	(W/m °K)	(W/m °K ²)	(correlation coefficient)(Ref. (12))	(W/m °K)	(W/m °K)
Poltz (1)	136.5*	-0.290	-1.0000	129.2	120.5
Tree (2)	136.4*	-0.259	-0.9986	129.9	122.1
This work	136.4	-0.283	-0.9988	129.3	120.8

* extrapolated results from least square fit of data presented.

DISCUSSION OF RESULTS

Toluene - Perhaps the most interesting aspect of the present investigation for this fluid lies in the confirmation, by means of an entirely different apparatus, of the "radiation component free" measurements of the work of Poltz (1) and Tree (2). This was achieved mainly by measurements at short time, t , - that is from 0.5 seconds, and by extrapolation to $t = 0$. As is evident from Figure 3, any measurement at 10° C beyond a t of approximately two seconds would always have a fixed radiative component, prior to the onset of convection.

The analysis for radiative heat transfer in an absorbing medium, in an unsteady state apparatus, is rather complicated. However, the radiative flux in the optically thick regime does not depend on the geometric configuration of apparatus (13) and an approximate analysis, therefore, has been made utilizing the expression for radiative flux used by Poltz, for the optically thick limit. Though the analysis for poorly absorbing fluids is underway, a function, 'Y', (similar to that of Poltz's) which is a function of the thermal boundary layer (δ) expressed in optical thickness is anticipated. This, however, necessitates more precise determinations of the absorption coefficient of fluids at various temperatures.

CONCLUSIONS

1. An absolute transient apparatus capable of measuring the thermal conductivity of fluids in the temperature range -150 to 100°C and the pressure range 1 to 600 bars with an absolute accuracy of $\pm 0.5\%$ has been developed and described.
2. Preliminary measurements have been reported for methane for two temperatures, 258 and 291°K in the pressure range 100 to 300 bar.
3. The absolute measurements on toluene in the temperature range $0 - 90^{\circ}\text{C}$ at normal atmospheric pressure,
 - (i) show that the reproducibility of the method is better than $\pm 0.5\%$.
 - (ii) support the measurements of Poltz and Tree for this fluid by their excellent agreement over the reported temperature range.
 - (iii) show the existence of a radiative component even when utilizing the transient technique. It is speculated that this component will be connected with the pseudo-conduction boundary layer on the wire.

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NOMENCLATURE

a	=	radius of the wire (m)
C_p	=	specific heat at constant pressure (watt/kg sec $^{\circ}\text{C}$)
d	=	differential operator
Ei	=	exponential integral
I	=	constant current (amp)
ℓ	=	length of the wire (m)
p	=	pressure (bars)
q	=	heat generated per unit length of wire (watts/m)
R	=	resistance of the wire (ohm)
ΔR	=	change in resistance (ohm)
r	=	radius (m)
t	=	time (sec)
$\bar{t}$	=	mean time (sec)
T	=	temperature ($^{\circ}\text{K}$) or ($^{\circ}\text{C}$)
ΔT	=	change in temperature ($^{\circ}\text{K}$)

Greek Letters

λ	=	thermal conductivity coefficient (watts/m °C)
ρ	=	density (kg/m ³)
α	=	thermal diffusivity (m ² /sec) = $\lambda/\rho \cdot C_p$
ω	=	$2 \rho_m \cdot C_{pm} / \rho_w \cdot C_{pw}$
γ	=	Euler's constant
δ	=	conduction boundary layer thickness (m)

Subscripts

m	=	medium
w	=	wire

TRANSPORT PHENOMENA IN HIGHLY NONEQUILIBRIUM PLASMAS

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FINAL ABSTRACT

Transport phenomena in highly nonequilibrium plasmas are investigated both from exact solutions to first-, second-, and third-order kinetic equations and by using the Grad 13-moment velocity distribution function to close out the macroscopic equations of change. Significant differences appear in higher order contributions to the electrical and thermal conductivities, the electron traceless pressure tensor, and their phase lags behind an applied time-dependent electric field when the effective interparticle interaction potentials are much harder or softer than the Maxwellian variety. It is concluded that previous studies of large electron diffusion velocities perhaps should be reevaluated with distribution functions more accurate than the 13-moment approximation.

SPECIFIC HEAT OF NITRIC AND SULPHURIC ACID
AQUEOUS SOLUTIONS IN A TEMPERATURE RANGE
OF $-196 - +20^{\circ}\text{C}$

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Abstract- An installation is described for measuring specific heat capacity of acids in the range of low temperatures by the method of adiabatic heating with the help of a constant heat flux. The paper presents an analysis of the temperature field of a sample in the volume of a measuring chamber and equations for calculating an absolute measuring error. The results of investigation of nitric and sulphuric acids of different aqueous concentrations made it possible to elucidate interesting facts, i.e. that the majority of aqueous solutions of acids have complex dependence of specific heat capacity and that some of the solutions of both acids have effective specific heat capacity of negative value.

Experimental study of highly-aggressive media including acids involves great difficulties.

The adiabatic heating method used for determination of specific enthalpy and heat capacity is very useful in performance because it allows

(i) complete insulation of measuring instruments, heating elements, leads from the aggressive fluid to be tested,

(ii) investigation of liquid and solid phases as well as phase transitions,

(iii) obtaining continuous relations between heat capacity and temperature from a single run in a temperature range of $-195 - +20^{\circ}\text{C}$.

The present method provides for heating a vessel with a mixture to be investigated by a constant heat flux. A specific heat versus the temperature and specific enthalpy are found from a thermogram for any temperature range.

Comparison of various geometries of a vessel with the material tested has shown a cylindrical sealed chamber with a heater and a thermometer on its surface to be the best one (Fig.1). A cylindrical shape of a test chamber is convenient since it assures adiabatic conditions and allows simple analysis of the temperature distribution and mean volumetric temperature in heating.

Since heating is adiabatic the whole heat flux from a heater is supplied to the chamber surface. Then the heat supplied will be spent to change the initial energy or enthalpy of the chamber case and the material tested inside the chamber.

$$dQ = dI_1 + dI_2, \quad (1)$$

where Q is the heat quantity from the heater; I_1 , and I_2 are enthalpies of the chamber casing and the material tested.

Expression (1) is an energy balance equation for a test chamber with a test sample in it.

We may write expression (1) in a different form

$$Pd\tau = C_1 d\vartheta_1 + c_2 M_2 d\vartheta_v, \quad (2)$$

where P is the heater power; τ is the time; C_1 is the casing heat capacity; ϑ_1 is the excess temperature of the casing; C_2 is the specific heat of the test material; $\vartheta_v = \frac{1}{V} \int \vartheta_2 dV$ is the mean volume excess temperature of the test material.

The distribution of the excess temperature ϑ_2 in a test material over the radius r in a case of an infinite cylinder heated by constant heat flux q is of the form [1/

$$\vartheta_2(r, \tau) = \frac{q r_0}{\lambda} \left\{ 2Fo - \frac{1}{4} \left(1 - 2 \frac{r^2}{r_0^2} \right) - \sum_{n=1}^{\infty} \mu_n^2 I_0(\mu_n) \times \right. \\ \left. \times I_0\left(\mu_n \frac{r}{r_0}\right) \exp(-\mu_n^2 Fo) \right\}, \quad (3)$$

where r_0 is the external cylinder radius; λ is the thermal conductivity of the medium; $Fo = \frac{a\tau}{r_0^2}$ is the Fourier number a is the thermal diffusivity of the medium; $I_0(\mu_n)$, $I_0(\mu_n \frac{r}{r_0})$ are the Bessel functions of the first kind of the zero order; μ_n are the equation roots; $I_1(\mu) = 0$, $I_1(\mu)$ are the first order Bessel functions of the first kind.

Since the roots μ_n are large values then beginning from $Fo > 0,2$ the series (3) converges to zero and the distribution of temperature ϑ over radius r is a parabolic one (a quasi-steady regime)

$$\vartheta_2(r, \tau) = \frac{q r_0}{\lambda} \left[2Fo - \frac{1}{4} \left(1 - 2 \frac{r^2}{r_0^2} \right) \right]. \quad (4)$$

For an infinite cylinder the mean bulk temperature is equal to the mean one for the cross-section perpendicular to the cylinder axis

$$\vartheta_v = \frac{4}{\pi r_0^2} \int_0^{r_0} \int_0^{2\pi} \frac{q r_0}{\lambda} \left[2Fo - \frac{1}{4} \left(1 - 2 \frac{r^2}{r_0^2} \right) \right] r dr d\varphi, \quad (5)$$

where r , φ are the radius and angle in polar coordinates.
Double integration gives

$$\vartheta_v = -\frac{qr_0}{\lambda} - 2Fo. \quad (6)$$

The excess temperature of the cylinder surface may be found from expression (4) at $r = r_0$

$$\vartheta_1 = \vartheta_2(r_0, \tau) = \frac{qr_0}{\lambda} \left(2Fo - \frac{1}{4} \right). \quad (7)$$

In heating the surface cylinder temperature is higher than mean bulk one ϑ_v

$$\vartheta_1 - \vartheta_v = \frac{1}{4} \frac{qr_0}{\lambda}. \quad (8)$$

Expression (8) allows determination of the heat flux which gives rise to a certain difference between the surface temperature and the mean bulk one, the thermal conductivity of the medium being known.

The test sample in a chamber (Fig.1) is heated both from the cylindrical surface and from the bottom of the cylinder. In this case the derivation of the expression for the temperature difference $\vartheta_1 - \vartheta_v$ similar to expression (8) is much more complete. However, since the surface area of the chamber bottom is less than 10 per cent the cylindrical surface of the chamber and thus the heat supplied from the bottom is less than 10 per cent the heat quantity from the cylindrical surface and the difference $\vartheta_1 - \vartheta_v$ for the chamber is always less than that quantity for an infinite chamber equation (8) may be used for prediction of the heat flux in case when $\vartheta_1 - \vartheta_v$ is below a certain value.

Free convection which may appear in heating liquid involves less values of $\vartheta_1 - \vartheta_v$ compared to those predicted by (8) which includes heat transfer by conduction alone.

If we assume the temperature difference $\vartheta_1 - \vartheta_v$ of some degrees, then the rates of the change of the surface temperature and mean volumetric one are equal

$$\frac{d\vartheta_1}{d\tau} = \frac{d\vartheta_v}{d\tau} \quad (9)$$

Under the condition the predicted formula for thermal conductivity of a test material may be written from expression (2)

$$C_2 = \frac{P - C_1 b}{M_2 b}, \quad (10)$$

where $b = \frac{dT_1}{dt}$ is the rate of change of the chamber casing temperature at the absolute value of the temperature T .

The heat capacity C_1 is to be found from the time-temperature thermogram in case of an empty chamber heated adiabatically.

$$C_1 = \frac{P}{b} \quad (11)$$

Specific enthalpy for the temperature range $T_2 - T_1$ is obtained from expression (2) (12)

$$l_{(T_2 - T_1)} = \frac{P(\tau_2 - \tau_1) - I_1}{M_2},$$

where l is the specific enthalpy of the ; τ_1 and τ_2 are the times necessary for heating the test material up to the temperatures T_1 and T_2 ; I_1 is the enthalpy of the chamber casing in the temperature range $T_2 - T_1$.

The enthalpy of the chamber casing is found from the heat quantity supplied from the thermogram of heating an empty chamber

$$I_1 = \int_{T_1}^{T_2} C_1 dT = P(\tau'_2 - \tau'_1) \quad (13)$$

where $(\tau'_2 - \tau'_1)$ is the time interval necessary for heating the empty chamber in the temperature range $T_2 - T_1$.

A schematic drawing of a test chamber is presented in Fig.1.

Measuring cell 1, flange 4 and cover 6 are made of stainless steel. The chamber dimensions are as follows: diameter is 35mm, height is 140mm. The chamber weight is 336g. A flange having four studs is screwed at the upper portion of the measuring cell. The cylinder wall thickness is 1mm throughout except the edges which have the original thickness of the tube. The upper edge is provided with thread and the lower one is the place where the cylinder is welded to the chamber bottom. A recess made at the cylinder as well as those at the flange edge have allowed essential decrease of the chamber weight. The weight of the first chamber without recesses was 593g, that is 1.75 times the weight of the final chamber, internal dimensions being equal.

The cylindrical cell is covered by varnished cloth over the whole length of the recess. At the upper portion of the cylindrical cell a resistance thermometer coil 3 is wound over the varnished cloth. A resistance thermometer wound directly over the cylindrical cell undergoes considerable stress because of different heat expansion coefficients of the thermometer wire and the cylinder material over the temperature range -196 to $+20^\circ\text{C}$.

To avoid these stresses a coil resistance thermometer is used.

The heating wire is wound over the remaining portion of the recess. The heater wound height is 95mm.

The cylinder surface and varnish cloth are covered by vacuum lute. This is used to protect from water or acid. Besides

vacuum lute decreases heat resistance of the gaps and is a good electrical insulator.

Both windings of the heater and the thermometer are covered by varnish cloth. The upper layer is covered by vacuum lute and wound by aluminium foil, which completely protects varnish cloth from acid drops.

Each of two metal rings 7 over the foil is provided with three distance pieces. The distance pieces are made as small convexities 1-1,5mm in height and protect the foil from damage.

The resistance thermometer is made of copper wire ПЭВ-2, 0.15mm in diameter, the coil diameter being 2mm. The resistance of the thermometer is 30.506Ω at 0°C .

The heater is made of manganin wire ПЗММ, 0.18mm in diameter. Resistance of the heater is 650Ω . The measuring chamber is provided with 5 leads: two leads to the heater, two to the resistance thermometer and one to the chamber casing.

Temperature was measured and recorded by a bridge circuit one arm of which included a resistance thermometer R_T .

Bridge circuits for measuring resistance are almost as precise as potentiometric compensating ones which allow the most precise measurements. When a bridge circuit is used for measuring resistance, the resistance of the leads become of great significance. Although in general one pair of wires is quite sufficient, four leads are more convenient for performance.

The present bridge circuit M involving four wires allows considerable compensation of the leads since the resistance R_T is commensurable with their resistance at the boiling point of nitrogen ($R_T = 4,37 \Omega$, $t = -196^{\circ}\text{C}$).

The resistance R_T may be obtained from the arms ratio in balance of a bridge circuit from the formula

$$R_T = \frac{R_2 \cdot R_3}{R_1} \quad (14)$$

Each pair of wires connected to the ends of the thermometer conductor is soldered to a joint. $R_1 = 10000 \Omega$,

$R_3 = 2000 \Omega$. R_1 and R_3 should be much greater than R_2 and R_T . They may be evaluated from the condition that the measuring current of the bridge varies within $\pm 0.5\%$ when the resistance varies from the value at a room temperature to that at a nitrogen boiling temperature. In this case the error in the temperature introduced by changes of the measuring current is less than 0.5% . The current found from ampermeter R_4 was 9.23ma at -196°C and 9.14ma at $+15^{\circ}\text{C}$. Heating of the resistance by the said measuring current introduces negligible error which should be corrected only for very precise measurements.

The bridge is balanced according to the zero reading of galvanometer Γ .

Records of the temperature proportional to the disbalance voltage of the bridge circuit M are made by electronic potentiometer 2(ЭПН-09МЗ type) with a scale of 10mV. Measuring current was fitted so that 1mV of the scale would correspond to 1°C change of the temperature of the resistance thermometer

R_T . For records of voltage above 10mV a low-voltage potentiometer I was used as a voltage source, switched on with a polarity opposite to that of disbalance voltage. When records are necessary which exceed the value of the scale of potentio-

meter 2 a stage of 10mV of potentiometer 1 was switched on by hand which produced a zero input current and the records are made from the beginning of the scale. Thus, compensation by stages of 10mV allowed records over 60-70°C, then the bridge circuit was balanced and the temperature records continued in a similar way. Such records allow convenient treatment of the thermogram obtained. A systematic error accumulated in the temperature range 60-70°C was found by balance of the bridge circuit and may be easily eliminated by appropriate changes of the bridge measuring current.

Power of the test chamber heater was measured by wattmeter W. The heater and bridge circuit are fed from d.c. voltage stabilizer 3 (type П 136).

The adiabatic casing of the chamber (Fig.3), 180mm in height and 75mm in diameter is made of a copper sheet, 0.5mm in thickness. The upper section of the casing is removable. The winding of the adiabatic casing heater is made of manganin wire 0.5mm, 0.51mm in diameter and has a resistance of 195 Ω . A test chamber is placed into a thin-walled casing which is suspended inside the adiabatic casing and supported from below by nichrome wires, 0.1mm in diameter. Three differential thermocouples for measuring the temperature difference of the adiabatic casing and the test chamber are made of manganin-constantan and glued to the appropriate surfaces. The diameter of the lead to the thermocouples is 0.18mm.

Fig.4 is a block-diagram of maintaining the temperature of the adiabatic case to be the same as that of the test chamber due to small difference between these temperatures. This temperature difference is measured by three differential thermocouples. Thermoelectromotive force of the thermocouples is supplied to the outlet of a highly sensitive d.c. amplifier 1 (type Ф 116/2).

Amplified signal is supplied from the amplifier to voltage amplifier input 2 (type УИПД -2) and further to power amplifier input 3. The heater of the adiabatic case is switched on to power amplifier output 3. The maximum output power is 75wt at 200 Ω that corresponds to the presence of the adiabatic case heater resistance.

Heat from the adiabatic case heater constantly tends to reduction of the temperature difference of the adiabatic case and test chamber to a minimum value. This difference is not higher than 1°C.

The experimental procedure is described below. First, the heat capacity of the chamber itself was found from the thermogram of heating an empty chamber. The heat capacities of the chamber and the test material were found from the thermogram of heating the chamber containing a test sample. The specific heat from the material was found from the known weight of the sample, heat capacity of the empty chamber and the chamber with a test sample.

Heat capacity of the test chamber was found as follows.

The test chamber was placed into the adiabatic case. The latter was suspended by four thin wires to the flange of a low-temperature evacuated vessel (Fig.3) cooled by liquid nitrogen to a nitrogen boiling point. Then the test chamber cooled together with the adiabatic case were put under the low-temperature evacuated vessel which was sealed then by eight bolts. The low-temperature evacuated vessel was placed into a vacuum flask containing liquid nitrogen, rarefaction of 0.1 mm Hg being produced within the flask. Then a system of amplifiers was engaged

which maintained adiabatic case temperature to correspond to that of the chamber. Heating the chamber under adiabatic conditions is provided by a system of amplifiers.

Then the initial temperature of the test chamber cooled was found from a value of resistance R_T , the bridge circuit M being balanced (Fig.2). Next, the measuring diagonal of bridge M was engaged to potentiometer 2 for which aim switch was transported from the station "bridge balance" (station I) to the station "temperature record" (station 2). At last 2 is engaged and feed to the chamber heater is supplied.

During sealing the low-temperature vessel, the test chamber was heated by 3 -5°C. Therefore the test chamber was heated from -195°C to -190°C.

Power was measured in each 10°C. Since the heater resistance depends on the temperature, the heater power changed and was found to be highest at a low temperature. The largest change in power was found in the temperature range close to the nitrogen boiling point. Over the temperature range close to a room one, power variation was insignificant and its value was 3Wt. Maximum temperature variation was within 5 %.

Heat capacity of the test chamber C_t was found as a mean value for each step of 10°C.

The experiment with a chamber containing acids was similar to that with an empty chamber.

The weight of test samples found within 0.01 g was about 190 g.

The composition analysis was carried out before the experiment and after it and showed a constant composition within the experimental error (1.5 %).

An absolute error ε inspecific heat was not more than

$$\varepsilon = 0.03 c + 0.06$$

The experiments carried out have allowed the relation between the heat capacity and temperature (Fig.s 5-8) for aqueous solutions of nitric and sulphuric acids to be obtained.

Anomalous behaviour of $c(T)$ was found which consists in existence of a negative effective specific heat for aqueous solutions of 78%-HNO₃, 80%-H₂SO₄, 40%-H₂SO₄.

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Fig.1. Measuring chamber

1) cylinder; 2) resistance thermometer;
 3) heater; 4) removable flange of cylinder;
 5) lead washer; 6) cover; 7) metal rings
 with distance pieces

Fig.2. Electric scheme of measuring and recording temperature of measuring chamber

1)low-resistance potentiometer; 2)electronic potentiometer; 3)d.c. voltage stabilizer

Fig.3. Installation

- 1) low-temperature evacuated vessel;
- 2) adiabatic case; 3) resistance thermometer of test chamber; 4) adiabatic case heater;
- 5) three differential thermocouples;
- 6) test chamber heater; 7) test chamber case;
- 8) test chamber with test material

Fig.4. Block-diagram of maintaining adiabatic case temperature in accordance with that of test chamber

1)d.c.amplifier; 2)voltage amplifier; 3)power amplifier

Fig.5. Specific heat of nitric acid aqueous solutions against temperature in the range from -196 to +20 °C

Fig.6. Specific heat of sulphuric acid aqueous solutions (10,20,30%-H₂SO₄) against temperature in the range from -196 to +20°C

Fig.7. Specific heat of sulphuric acid aqueous solutions (40,50,60,70 % H_2SO_4) against temperature range from -196 to $+20^\circ\text{C}$

Fig.8. Specific heat of sulphuric acid aqueous solutions (80,90,95 % H_2SO_4) against temperature range from -196 to $+20^\circ\text{C}$

The Thermal Conductivity of Compressed Water

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ABSTRACT

New measurements are reported which were obtained by using a coaxial cylinder cell with automatically controlled guard heaters. The degree of precision required for the control system was determined in relation to the cell dimensions. The cell was immersed in a constant temperature bath capable of maintaining a steady state within ± 0.01 deg C.

A total of 92 measurement points was obtained between 80 and 390 °C, and 20 and 400 bar. Up to 250 °C the measurements show good agreement with the values of other researchers. They do not follow to the full extent the steep rise in VODAR's data which takes place above 250 °C, however, up to 340 °C they are still closer to his values than to those of AMIRKHANOV. Above this temperature the accuracy began to degrade due to an earlier than expected rise of convection triggered by weak vibrations of the cell.

The work was carried out at the Mechanical Engineering Research Annexe of The University of Glasgow, Scotland, and was supported by the South of Scotland Electricity Board and the Central Electricity Generating Board.

USE OF THERMAL METHODS IN COLUMN CHROMATOGRAPHY

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Recent increasing interest in high speed, high resolution liquid phase chromatography has led to an upsurge in the research dealing with suitable detectors. While the sensitivity of the spectrophotometric measurements has been markedly increased, the limitation imposed upon the system by the need for monochromatic light and the necessity for changing the source of light for various types of materials has led to interest in other modes of detecting liquid chromatographic effluents. One of the most recent developments has been the use of thermal methods for the detection of effluent material. This technique is generally based on a heat of absorption reaction which uses the heat as a detection signal. We have designed and built a simple, yet effective, heat of absorption detector for gas and liquid phase chromatography. The unit is useful as a gas phase detector due to built-in specificity and can often work as a selected detector without the benefit of a chromatographic column. The detector design is such that rapid change of the detector is possible (one minute), and comparable sensitivity to commercially available instrumentation is achieved. Variations in materials as to thermal conductivity and thermal flow for the optimization of the detector sensitivity have been investigated and used to design maximum sensitivity for the instrumentation.

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APPLICATION OF "PROBE" METHOD TO DETERMINATION OF
THERMAL CONDUCTIVITY OF CHEMICALLY ACTIVE MEDIA IN
THE TEMPERATURE RANGE $-196 - +20^{\circ}\text{C}$

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Abstract - A description is given of an experimental installation for measuring thermal conductivity of substances, aggressive fluids including, in liquid and solid states in the low temperature region. A detailed description is given of the installation design, the experimental procedure and manufacturing of the probe. An experimental error does not exceed 7 per cent. The results of measurements of thermal conductivity of acids are given.

For investigation of heat conduction in chemically active media over a wide temperature range when the material presents both liquid and solid states, a "probe" method is suggested. The name a "probe" method used at present for a transient method involving a cylindrical probe with constant power output per a unit length is well known. It was first used in 1969 by E.F.M. van der Held and F.G.van Drumen for determination of thermal conductivities of liquids (including chemically active ones) at room temperatures.

Most of workers /1-5/ dealing with the "probe" method use the solution of a continuous heat source in an infinite medium allowing the thermal conductivity to be determined.

The main disadvantages of the mathematical analysis and treatment of experimental data in these works are as follows:

1. In the solution of the heat-conduction equation a linear heat source is assumed that does not correspond to the probe design. The diameter of a probe is always finite and the probe has its own heat capacity.

2. Resistance to heat transfer between the medium and heater is neglected. In fact, such resistance exists in most cases, except that when a bare conductor in liquids and gases is used.

3. Estimation of the probe length is semi-intuitive.

4. Experimental data are often treated by points of the thermogram without analysis which may produce great errors because of random choice of the values.

In view of the abovesaid, Blackwell /6/ has formulated and solved a problem which includes thermal properties of a probe and heat resistance between the heater and medium.

A mathematical formulation of the problem for a temperature field created by a heated probe in the surrounding medium is as follows:

$$\frac{\partial \vartheta_2(r, \tau)}{\partial r} = a_2 \left[\frac{\partial^2 \vartheta_2(r, \tau)}{\partial r^2} + \frac{1}{r} \frac{\partial \vartheta_2(r, \tau)}{\partial r} \right], \quad (1)$$

$$(\tau > 0, \quad r_0 < r < \infty),$$

$$\vartheta_2(r, 0) = \vartheta_1(0) = 0, \quad (2)$$

$$-\lambda_2 \frac{\partial \vartheta_2(r, \tau)}{\partial r} \Big|_{r=r_0} = H [\vartheta_1(\tau) - \vartheta_2(r_0, \tau)], \quad (3)$$

$$(2\pi r_0) \left[-\lambda_2 \frac{\partial \vartheta_2(r, \tau)}{\partial r} \right]_{r=r_0} = q - m_1 c_1 \frac{\partial \vartheta_1(\tau)}{\partial \tau}, \quad (4)$$

$$\vartheta_2(\infty, \tau) \neq \infty. \quad (5)$$

The problem solution obtained by Laplace transformation for large times is of the form

$$\begin{aligned} \vartheta_1(\tau) = & \frac{q}{4\pi\lambda_2} \left\{ \ln 4Fo - \gamma - \frac{2\lambda_2}{H} + \frac{1}{2Fo} \left[\ln Fo - \right. \right. \\ & \left. \left. - \gamma + 1 - \frac{m_1 c_1 a_2}{\pi r_0^2 \lambda_2} \left(\ln Fo - \gamma + \frac{2\lambda_2}{r_0 H} \right) \right] + O \left[\frac{1}{(Fo)^2} \right] \right\}, \end{aligned} \quad (6)$$

where $\gamma = 0.5772$; $Fo = \frac{a_2 \tau}{r_0^2}$.

The problem (1)-(5) and, consequently, solution (6) is the best possible approximation to a real unsteady heating of a probe in the surrounding medium.

In Blackswell's work [7] the dependence of the error on a plane dimension of heat flux is presented and analysed. When $L/2r_0 = 20$, the maximum error $\Delta R = 5.3\%$, with $L/2r_0 = 25$, $\Delta R = 0.7\%$, and when $L/2r_0 = 30$, $\Delta R = 0.05\%$. In the last case a probe may be considered an infinite cylindrical heat flux source.

We shall write a more convenient form of expression (6)

$$\vartheta_1(\tau) \cong A \ln \tau + B + \frac{1}{\tau} (C \ln \tau + D), \quad (7)$$

where

$$A = \frac{q}{4\pi\lambda_2}, \quad (8)$$

$$B = \frac{q}{4\pi\lambda_2} \left(\ln a_2 - 2 \ln r_0 + \ln 4 + \frac{2\lambda_2}{r_0 H} \right), \quad (9)$$

$$C = \frac{2r_0^2}{a_2} - \frac{m_1 C_1}{\pi \lambda_2}, \quad (10)$$

$$D = \left(\frac{2r_0^2}{a_2} - \frac{m_1 C_1}{\pi \lambda_2} \right) (\ln 4 + \ln a_2 - 2 \ln r_0 - \gamma) + \frac{2r_0^2}{a_2} + \frac{2m_1 C_1}{\pi r_0 H}. \quad (11)$$

Expression (7) implies that in any case relation $\vartheta_1(\ln \tau)$ follows a linear asymptote with an angular factor equal to A. An analytic expression for the asymptote is

$$\vartheta_1(\tau) = A \ln \tau + B. \quad (12)$$

The analysis of expression (10) and (11) for coefficients C and D shows that they decrease in proportion to a squared radius of the probe r_0 , other things being equal.

Time necessary for heating to reach the asymptote is essential for investigation of liquids. In a low-viscous fluids natural convection occurs at the probe surface after a certain period of time. When power output on the probe heater decreases, the time after which natural convection becomes essential increases. However, some limitations to the power input exist.

Unsteady boundary conditions are of primary effect on formation of a temperature field at small heat fluxes. Readings of the excess probe temperature are not quite exact. However, for calculation of thermal properties of the fluid tested, a sufficient linear section of thermogram in semi-logarithmic coordinates $\vartheta, \ln \tau$ is necessary before beginning of natural convection at the probe. Therefore it is of importance to reach very quickly asymptotic heating that leads to decreasing the time of recording the excess temperature of the probe heating and optimum power to be supplied to the heater.

The predicted formula for determination of the medium thermal conductivity is obtained from expression (12). Subtracting the excess temperature $\vartheta_1(\tau_1)$ from the excess temperature $\vartheta_1(\tau_2)$ yields

$$\vartheta_1(\tau_2) - \vartheta_1(\tau_1) = A \ln \frac{\tau_2}{\tau_1} = \frac{K_1}{\lambda_2} \ln \frac{\tau_2}{\tau_1}, \quad (13)$$

hence we get for λ_2

$$\lambda_2 = \frac{K_1 \ln \frac{\tau_2}{\tau_1}}{\vartheta_1(\tau_2) - \vartheta_1(\tau_1)}, \quad (14)$$

where

$$K_1 = \frac{q}{4\pi} \quad (15)$$

It should be noted that a predicted formula for thermal diffusivity of the medium α_2 may be obtained from expression (12) /8/.

Now we shall describe the procedure of the method. First it is necessary to be sure that this method is applicable for measuring thermal conductivity of low viscous liquids. For this aim experiments were carried out using different designs of probes. The probe shown in Fig.1 was found to be the best one. A bunch of insulated wires of the heater and resistance thermometer 4 is placed into glass capillary 1 filled with liquid polysiloxane which provides fair thermal contact between wires inside the bunch and between the bunch and the capillary wall. The bunch consists of 20 wires. The heater is made of a manganin wire, 0.07 mm in dia. The resistance thermometer is made of a copper wire with the same diameter. The design of a probe described demands a relative variant of the method since if an absolute variant were used, it would not be clear which is the characteristic diameter of the probe and it would be difficult to find this diameter with sufficient accuracy. In a relative variant there is no such difficulty.

As is known from the aforesaid, coefficient K_1 (15) is constant for a certain probe and a constant power output in the heater. For determination of K_1 it is sufficient to write down an excess temperature of heating in a known medium (reference liquid) and to find from

$$K_1 = \frac{\lambda_{et} [\vartheta(\tau_2) - \vartheta(\tau_1)]}{\ln \frac{\tau_2}{\tau_1}}, \quad (16)$$

where λ_{et} is the thermal conductivity of a reference standard liquid.

It should be noted once again that the constant K_1 of a probe is a function of its power and the value of K_1 found from experiments is valid only for a certain power of the heater.

Fig.2 furnishes thermograms of the excess temperature for vaseline oil, toluene, glycerine and water at a heater power supply of 60 mWt. For the analysis, the thermograms obtained were plotted in semi-logarithmic coordinates $\vartheta, \ln \tau$ (Fig.3). As one can see, the time of asymptotic heating in toluene (curve 2) before the beginning of free convection is sufficient for the heat-conduction coefficient to be determined which proves applicability of the probe method to investigation of low-viscous liquids.

The thermal conductivities obtained by the "probe" method at 20°C are summarized in the table below.

The data on thermal conductivity in this table are taken from reference /9/. The heat conduction coefficient for each liquid is found as an arithmetic mean of different workers' data measured within 2 %. Glycerine was used as a reference standard.

Table

Liquid	$\lambda, \frac{\text{Wt}}{\text{m}^\circ \text{C}}$ at 20°C	$\lambda, \frac{\text{Wt}}{\text{m deg}}$ by "probe" method at 20°C	Deviation from reference data
Vaseline oil	0.126	0.122	-3.4
Toluene	0.135	0.141	+4.5
Glycerine	0.291	-	-
Water	0.600	0.591	- 1.5

For "probe" investigation of heat conduction in materials which are liquids at normal conditions (including chemically active ones) over a temperature range from a nitrogen boiling point to room ones, an experimental installation was made. A test chamber with a probe inside is shown in Fig.4. Test chamber 3 is stainless steel cylinder. Internal dimensions of the chamber are as follows: diameter is 40 mm, height is 140 mm. Weight, wall thickness, etc are not reported here as they are of no importance for the "probe" method. Probe 6 is inserted through a hole in the bottom of the chamber.

The whole surface of the chamber is covered by varnished cloth with resistance thermometer 5 wound over it. The distances between the turns of the thermometer ensure elimination of crossing the wires. The thermometer is covered by varnished cloth followed by a copper sheet. The latter is also covered by varnished cloth with a heater wound over it. The copper sheet between the thermometer and heater eliminates electric induction to the thermometer winding through the varnished cloth and provides more uniform heating. All possible heat flows from the heater which may be appreciable relative to the voltage at the resistance thermometer are closed to a metal screen connected with an earthed lead of the measuring circuit. The metal screen was a copper sheet, 0.3 mm in thickness.

The turns of the heater winding were close to each other. The heater was covered by varnished cloth. The surface of each component of the installation (cylinder, varnished cloth, thermometer, heater, copper sheet) were covered by a thin layer of vacuum lute which eliminates wetting of the gaps between windings. The external layer of varnished cloth is also covered with vacuum lute and wound with aluminium foil. The resistance thermometer of a chamber is made of a copper wire, 0.15 mm in dia. The thermometer resistance at 0°C is 9.23 Ohm.

The chamber heater is made of a manganin wire 0.18 mm in dia. The heater resistance is 240 Ohm.

In the first variant the probe used in a test chamber had a heater and resistance thermometer (Fig.1). Later it was decided to use a probe where one conductor served as a heater and resistance thermometer simultaneously. This is the essence of a new variant.

In heating the excess temperature is no more than 0.5°C for any liquids. The change in the power output of the heater-thermometer due to the change in its resistance from the initi-

al moment of heating to the end is

$$\Delta P = P_{t+\Delta t} - P_t, \quad (17)$$

where ΔP is the value of power increment at the end of heating; P_t and $P_{t+\Delta t}$ are the power outputs of the heater-thermometer at the beginning and the end of heating, respectively; t is the probe temperature at the beginning of heating; Δt is the temperature increment in heating a probe.

Expression (17) is rewritten as

$$\Delta P = I^2 \Delta R = I^2 R_0 \beta \Delta t, \quad (18)$$

where I is the current through a wire of the heater-thermometer of a probe; ΔR is the resistance increment of the heater-thermometer when it is heated by Δt ; R_0 is the resistance of the heater-thermometer at $t=0^\circ\text{C}$; β is the resistance temperature coefficient of the heater-thermometer.

The ratio of the power increment ΔP to the power P_t is

$$\frac{\Delta P}{P_t} = \frac{I^2 R_0 \beta \Delta t}{I^2 R_0 (1 + \beta t)} = \frac{\beta \Delta t}{1 + \beta t}. \quad (19)$$

For a copper wire at $t=0^\circ\text{C}$ $\Delta P/P_t=0.2\%$; at $t=-196^\circ\text{C}$ $\Delta P/P_t=1.0\%$.

The advantage of this variant of the probe design is that the value of the voltage $\Delta U = I \Delta R$ is high enough to be recorded at the automatic potentiometer without an intermediate d.c. amplifier. In this case it is necessary to determine and to fix the current of a probe for each new temperature when recording a thermogram from the condition $I^2 R = \text{const.}$

The value of the excess temperature is found from

$$\Delta t = \frac{\Delta U}{I \cdot R_0 \cdot \beta}. \quad (20)$$

Expression (20) implies that the excess temperature Δt is proportional to the voltage ΔU . The proportionality factor is

$\frac{1}{I \cdot R_0 \cdot \beta}$ whose value changes with I depending on the value of the probe resistance R_t .

The first runs were conducted with a probe inserted into a glass capillary. With some test materials at the end of the run the probe was broken under the weight of ice during its melting. Therefore, we did not use a glass probe any more.

A probe with a metallic shell was made. A syringe needle 1.3 mm in external diameter was taken as a shell.

The probe was made as follows. Preliminary the syringe needle was tested for interaction with a chemically active test material, in the present case with nitric acid. A section of a required length (110mm) was then cut out of the needle. The inner surface of the pipe was polished and covered with a thin layer of insulating varnish that allowed elimination of closing the wire bunch to the pipe. The bunch with its outlet ends was inserted into the pipe which was filled with a silica organic liquid by suction. The end of the pipe without the outlet ends of the bunch was flattened and folded in the middle. The folded end was slightly unriveted. The other end of the probe was open.

A ready probe was fixed in the hole of the bottom of the test chamber.

The temperature was measured and recorded by bridge circuit M (Fig.5) with a heater-thermometer of the probe engaged in one of the arms.

The resistance R is found from the arm ratio at bridge circuit balance from the formula

$$R = \frac{R_2 \cdot R_3}{R_1} \quad (21)$$

The bridge circuit balance is made by a galvanometer .At a circuit balance switch II is at station 1. The bridge current in this case is determined by the resistance R_4 and is 2-4 mA.

When the switch II is at station 2, the measuring diagonal is connected with recording potentiometer 2. The bridge is fed directly from a stabilized power supply 3. If the voltage of the disbalance when heating a probe exceeds the limit of the record of potentiometer 2 (10 mV), then the step of voltage compensation of disbalance of potentiometer I is switched by hand.

Power output in the probe was always constant and equal to 103.3 mWt.

When studying heat conduction of materials over the temperature range $-196 - +20^{\circ}\text{C}$ by the probe method, it is necessary to have a stationary state of a medium in the test chamber under certain temperature range. This is ensured by thermostating of a chamber.

The scheme of thermostating is shown in Fig.6. The resistance thermometer is located on the chamber case and is connected with a d.c. bridge I (type P333). Voltage of the measuring diagonal is supplied to the inlet of high-sensitive d.c.amplifier 2, then amplified by voltage amplifier 3 and power amplifier 4 in succession and supplied to a heater of the test chamber case. The power output (maximum 75 Wt) depends on a positive value of the disbalance and is zero at a balance bridge circuit. The thermostating temperature is prescribed by one of the arms of the d.c.bridge I.

When thermostating, it is possible that

(a) prescribed thermostating temperature is above the initial temperature of the test chamber. In this case a positive value of disbalance causes a maximum output power in the heater of the test chamber. As far as the chamber is heated, the value of the thermometer resistance will increase, and that of the disbalance will decrease. The power output of the heater will also decrease accordingly up to such a stationary heat state when heat losses into the surrounding medium are compensated by the power output of the heater,

(b) the prescribed thermostating temperature is less than the initial temperature of a medium. The value of the voltage disbalance is negative. The amplifier is closed, and the power is not supplied to the heater. The test chamber will be cooled due to heat transfer to a cold wall of the outer vessel. As far as the chamber is cooled, the value of the thermometer resistance will decrease, and this will lead to the fact that the negative value of the voltage disbalance will also decrease to zero and then will change its polarity, i.e. becomes positive. With an increase in the positive value of the disbalance voltage the power output of the heater will increase untill the stationary heat state of a chamber is established, i.e. there occurs ther-

mal equilibrium between heat transfer of the chamber into the surrounding medium and the supplied power of heater.

In both cases after the initial process, the thermostating scheme maintains the constant temperature of the case of the test chamber whose value is prescribed by the d.c. bridge. Stationary state of the medium is determined by ceasing a change of the temperature in the test chamber. The temperature of the medium under investigation is precisely measured by the thermometer located in the probe.

The thermograms are treated in the following way. The thermogram obtained at the self-recording potentiometer is plotted in new coordinates ($\Delta u, \ln \tau$). The asymptote is plotted to the thermogram.

The constant K_1 is written as

$$K_1 = \lambda \cdot \operatorname{tg} \alpha, \quad (22)$$

where $\tan \alpha = \frac{\vartheta(\tau_2) - \vartheta(\tau_1)}{\ln \tau_2 - \ln \tau_1}$ is the slope of the asymptote of the thermogram.

The constant of the probe K_1 is found from expression (22).

The formula for determining thermal conductivity of a test material is written thus

$$\lambda = K_1 \cdot \frac{1}{\operatorname{tg} \alpha}. \quad (23)$$

With the slope of the thermogram for the test material (using the same scale of the coordinates as in case of K_1) and the value of the constant K_1 known, we can find the thermal conductivity of the test material. The value of K_1 is valid for certain power of the heater.

Since the thermogram is plotted in the coordinates ($\Delta U, \ln \tau$), the aforesaid is valid only for one fixed temperature. For some other temperatures the proportionality factor between the voltage ΔU and the temperature of heating the probe varies and depends on the probe current I (expression (20)).

For any temperature T expression (22) with regard for expression (20) is rewritten in the following form

$$\lambda = \frac{I_T}{I_1} K_1 \cdot \frac{1}{\operatorname{tg} \alpha}, \quad (24)$$

where I_1 is the probe current at a temperature of 18°C; I_T is the probe current at temperature T .

For the temperature T the probe current is found from the condition $I_T \cdot R_{H-T} = 0.1033 \text{ Wt.}$

The relative error of $\delta \lambda$ in thermal conductivity found is equal to the sum of errors made by each term of the expression

$$\delta \lambda = \delta I_T + \delta I_1 + \delta K_1 + \delta \operatorname{tg} \alpha, \quad (25)$$

where $\delta I_T = \delta I_1 = 0.005$ is the error of the ammeter;

$$\delta K_1 = \delta \lambda_0 + \delta [\vartheta(\tau_2) - \vartheta(\tau_1)] + \delta \ln \frac{\tau_2}{\tau_1} = 0.04$$

is the error in constant K_1 ; $\delta \lambda_{\text{et}} = 0.02$ is the error in the thermal conductivity of a reference-standard liquid (glycerine);

$\delta [\vartheta(\tau_2) - \vartheta(\tau_1)] = 0.01$ is the error of a temperature record on electronic potentiometer;

$\delta \ln \frac{\tau_2}{\tau_1} = \frac{\delta \tau_2 - \delta \tau_1}{\ln \frac{\tau_2}{\tau_1}} \approx 0.01$ is the error of the term $\ln \frac{\tau_2}{\tau_1}$; $\delta \tau_2 = \delta \tau_1 = 0.05$ is the error of measuring time due to error of the band speed on the electronic potentiometer; $\delta \lg \alpha = \delta [\lg(\tau_2) - \lg(\tau_1)] + \delta \ln \frac{\tau_2}{\tau_1} = 0.02$ is the error of the asymptote slope of the thermogram plotted for the test material.

Upon substitution of the value of each term into expression (25) we obtain the value of the maximum relaxation error $\delta \lambda = 0.07$ or 7 %.

The deviation of the results in the repeated experiments is observed within 1 %.

Three substances were investigated: water (H_2O), nitric acid (HNO_3) and nitrogen tetroxide (N_2O_4). The thermal conductivity relations are plotted in Fig.7.

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Fig.1. Probe

1)probe shell; 2)resistance thermometer;
3)heater; 4)bunch wires of heater and
resistance thermometer

Fig. 4. Installation

- 1) vacuum flask; 2) liquid nitrogen;
 3) test chamber with test material;
 4) heater of test chamber;
 5) thermometer of test chamber;
 6) probe; 7) leads; 8) low-temperature vessel

Fig. 5. Electric circuit of measuring and recording temperature of probe

- 1) low-resistance potentiometer; 2) automatic electronic potentiometer; 3) d.c. voltage stabilizer

Fig.6. Block-diagram of thermostating of test chamber

1)d.c.bridge; 2)d.c.amplifier; 3)voltage amplifier; 4)power amplifier; 5)test chamber; 6)resistance thermometer; 7)heater

Fig.7. Thermal conductivity of water, nitric acid
 and nitrogen tetroxide over the range
 -196 + +20°C

THERMAL CONDUCTIVITY OF MOIST CAPILLARY-POROUS SYSTEMS

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Abstract - The results are considered of an experimental investigation of thermal properties of moist capillary-porous systems in the temperature range 80-400°K. To obtain experimental data, non-stationary methods are used based on the solution of a heat conduction equation for a hollow infinite cylinder with an internal constant power source.

Recently in connection with space developments an interest has considerably increased to heat and mass transfer in capillary-porous bodies since they possess great possibilities of transporting liquids in weak gravity fields due to capillary suction forces. In some cases not only hydrodynamics of liquid or gas motion over a porous body but also heat transfer in a body and, in particular, effective thermal properties of porous materials are of interest. For the study of interrelated heat and mass transfer processes in porous systems the knowledge of porous material permeability, diffusivity, thermal conductivity, thermal diffusivity and specific heat flux both of porous material and liquid in pores is necessary.

Usually for definition of thermal conductivity and thermal diffusivity of porous materials such a method is sought which would minimize the effect of mass transfer on heat transfer. This appears possible when non-stationary methods are used and when temperature gradient in porous material is small (3-4°).

The authors have developed a new method of simultaneous determination of thermophysical properties of moist porous materials in a wide temperature range.

The method is based on the Fourier equation for a hollow infinite cylinder with a constant heat flux from the internal surface and ideal heat insulation on the external one/1/.

$$\frac{\partial T}{\partial \tau} = \alpha \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) \quad (1)$$

Initial and boundary conditions

$$T(r,0)=f(r)=T_0 = \text{const} \quad \text{at } \tau = 0$$

$$q_1(r,\tau)=0; \quad q_2(r,\tau)=q_c = \text{const} \quad \text{at } \tau \neq 0$$

The solution to equation (1) is of the form /1/

$$\begin{aligned} T(r,\tau)-T_0 = & \frac{q}{\lambda} R_2 \left\{ \frac{R_2^2}{R_2^2 - R_1^2} \left[2Fo - \frac{1}{4} \left(1 - 2 \frac{r^2}{R_2^2} \right) - \right. \right. \\ & - \frac{R_1^2}{R_2^2} \left(\ln \frac{r}{R_1} - \frac{R_2^2}{R_2^2 - R_1^2} \ln \frac{R_1}{R_2} + \frac{3}{4} \right) \Big] + \\ & + \sum_{n=1}^{\infty} \frac{F}{\mu_n} \frac{I_1(\mu_n \frac{R_1}{R_2}) I_1(\mu_n)}{I_1^2(\mu_n \frac{R_1}{R_2}) - I_1^2(\mu_n)} \left[I_0(\mu_n \frac{r}{R_2}) Y_1 \right. \\ & \left. \left. (\mu_n \frac{R_1}{R_2}) - Y(\mu_n \frac{r}{R_2}) I_1(\mu_n \frac{R_1}{R_2}) \right] \exp(-\mu_n^2 Fo) \right\} \end{aligned} \quad (2)$$

However for a quasi-stationary solution of sample heating by an internal heat source of constant power, solutions (2) may be presented in the form

$$\begin{aligned} T(r,\tau)-T_0 = & \frac{q}{\lambda} R_2 \left\{ \frac{R_2^2}{R_2^2 - R_1^2} \left[2Fo - \frac{1}{4} \left(1 - 2 \frac{r^2}{R_2^2} \right) - \right. \right. \\ & - \frac{R_1^2}{R_2^2} \left(\ln \frac{r}{R_1} + \frac{R_2^2}{R_2^2 - R_1^2} \ln \frac{R_1}{R_2} + \frac{3}{4} \right) \Big] \Big\} \end{aligned} \quad (3)$$

By measuring the temperature at two points of the sample as well as the heat power of the heater, a calculation formula may be obtained by way of simple transformations for thermal conductivity, thermal diffusivity and specific heat flux

$$\lambda = \frac{q_w R_1}{2(R_2^2 - R_1^2) \Delta t} \left\{ R_1^2 - R_2^2 - 2R_2^2 \ln \frac{R_2}{R_1} \right\} \quad (4)$$

$$\alpha = \frac{1}{4 \Delta t} \frac{dt}{d\tau} \left\{ R_1^2 - R_2^2 - 2R_2^2 \ln \frac{R_2}{R_1} \right\} \quad (5)$$

$$C = \frac{q_w R_1}{dt/d\tau (R_2^2 - R_1^2) \gamma} \quad (6)$$

The experimental chamber (Fig.1) consisted of two coaxial cylinders of stainless steel 100 mm long, 40 and 30 mm in dia, and with a wall 0.07 mm thick and welded bottom. The tested material was placed into the gap (4-5 mm wide) between the cylinders. Temperature meters necessary for measuring the temperature drop and absolute temperature of the sample were stuck to the cylinder walls inside the gap. For measuring temperatures in the range of liquid nitrogen temperatures, copper-constantan thermocouples have been used and for measuring helium temperatures, platinum resistance thermometers. Thermometer readings were permanently recorded on a diagram tape of a six-point recording potentiometer ЭПН-09. To provide adiabatic heating conditions the experimental chamber has been surrounded by an adiabatic envelope. The electric energy supply was automatically controlled by a differential thermocouple which fixed temperature difference between the sample wall and envelope.

For compensation of a heat flux a guarding heater has been placed inside the cylinder of smaller diameter. Thus, the system of automatic guarding heaters ensured adiabatic conditions for heating the tested material from helium temperatures to room ones.

The heater stuck to the internal surface of the smaller diameter cylinder served for monotonic heating of the sample. The diagram tape of the automatic electronic recording potentiometer ЭПН-09 fixed the readings of the absolute thermocouple measuring temperature inside the sample, and those of the differential thermocouple registering the temperature drop at two points of the sample.

By determining Δt and $\frac{dt}{d\tau}$ from the thermocouple readings on the diagram tape, thermophysical characteristics (α, λ, c) of the tested material may be calculated by formulae (4,5,6).

Thermophysical characteristics (α, λ, c) have been determined by the authors experimentally within the temperature range from 80 to 300°K for the following multicomponent systems: powdery plexiglass AKP-15 - air $\Pi = 40$ per cent; AKP - silicoorganic liquid BKK-94; glass spheres ($d = 0.5$ mm, $\Pi = 35$ per cent) - air; glass spheres ($d = 1.5$ mm, $\Pi = 40$ per cent) - air; glass spheres ($d = 1.5$ mm, $\Pi = 40$ per cent) - silicoorganic liquid BKK-94; glass spheres ($d = 1.5$ mm, $\Pi = 40$ per cent) - silicoorganic liquid BKK-94 film - air; Al_2O_3 powder - air; Al_2O_3 powder ($\Pi = 75$ per cent) - silicoorganic liquid. The experimental data are presented in Figs 2 and 3, and Tables I and II.

In Table II the experimental results are compared with the calculation formula derived by the authors for determination of the effective thermal conductivity of moist porous materials (a two-phase system solid particles - liquid or gas) [3]:

$$\frac{\lambda_{ef}}{\lambda_{sk}} = \frac{1}{\frac{1}{(h/L)^2} + A} + \nu_g (1 - h/L)^2 + \frac{2}{1 + h/L + \frac{1}{\nu_g h/L}} \quad (7)$$

where

$$A = \frac{1}{\frac{\lambda_c}{\lambda_{sk}} + \frac{\nu_{gg}}{4K_c K_m} \left(\frac{h}{l}\right)^3 \cdot 10^3}$$

$$L = l/h; \quad h/L = \frac{h/l}{1 + h/l}; \quad \nu_g = \frac{\lambda_g}{\lambda_{sk}}; \quad \nu_{gg} = \frac{\lambda_{g-g}}{\lambda_{sk}}$$

This formula allows for different forms of heat energy transfer in porous materials. The main difficulty of calculation is to regard for the contact heat transfer between particles.

The comparison of the experimental data with those of other investigators proved the above method to be suitable for determination of thermal properties of powdery materials and fluids in a wide temperature range.

This method is also promising for determination of the effective thermal conductivity of the banks of screens (wicks) filled with liquid which are used in heat pipes.

It is seen from Figs 2 and 3 that this method allows the regions of material phase transitions to be registered. Thus, for example, phase transition of the first kind has been observed in silicoorganic liquid in the range from 100 to 140° K when the liquid converts to amorphous ice. Here two thermal conductivity peaks are observed at 110° and 140° K.

These phase transitions are more distinctly seen when the thermal conductivity of the mixture silicoorganic liquid - Al_2O_3 powder is studied since Al_2O_3 possesses high thermal conductivity of a monolith.

A fine agreement between the experimental data (Table II) and the values of λ_{eff} calculated by formula (6) indicates that in most cases thermal conductivity of composing systems may be determined without an experiment. Reference components being known the effective thermal conductivity of heterogeneous systems may be calculated.

Furthermore, the above systems may be composed with predicted thermophysical properties.

Great possibilities of changing thermal conductivity of heterogeneous systems are provided due to a complicated mechanism of heat transfer. Absolute values and relative relationships for the thermal conductivity of reference components, porosity, diameters of particles and pore sizes, optic properties of substances, surface properties, shape of particles, degree of their packing, mechanic loading on particles, their elastic properties and so on are the parameters affecting the effective thermal conductivity.

Thus, the authors think that two approaches exist to the study of thermophysical properties of substances and materials:

1. To experimentally determine thermophysical properties of pure substances in a wide range of temperatures and pressures;
2. To develop calculation models of heterogeneous systems and to predict composing materials by the corresponding analytic and semi-empiric formulae using the data of experiments with pure substances.

Such approaches will meet the requirements of industry producing and utilizing new and new materials.

NOMENCLATURE

q_w ,specific heat flux per unit surface;
 R_1 and R_2 ,external and internal radii of cylinder, respectively;
 Δt ,temperature drop;
 $\frac{dt}{dt}$,rate of sample heating;
 λ_{ef} ,effective thermal conductivity;
 α ,thermal diffusivity;
 q ,specific heat flux;
 γ ,specific weight of tested material;
 λ_{sk} ,thermal conductivity of particle (monolith);
 Π ,porosity;
 λ_c ,contact thermal conductivity;
 λ_g ,molecular and radiant heat conduction in pore;
 λ_{gg} ,molecular and radiant heat conduction in microgap
 between particles;
 L ,particle diameter;
 K_{ru}, K_c ,empiric coefficients.

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TABLE I
Experimental Data on Thermal Conductivity of Some Materials
 $P = 0.99 \cdot 10^5 \text{ N/m}^2$

Material	T°K	100°	140°	180°	220°	260°	300°	340°	Note
Powdery plexi- glass (d=0.5mm)	λ_{exp}	0.070	0.072	0.073	0.075	0.078	0.083	0.089	
- air	λ_{table}	0.660	0.070	0.072	0.075	0.080	0.088	0.095	/3/
Glass spheres (d = 1.5 mm)	λ_{exp}	0.070	0.098	0.128	0.150	0.165	0.175	0.182	
- air	λ_{table}	-	-	-	-	-	-	0.180	/2/
Glass spheres (d = 0.5 mm)	λ_{exp}	0.080	0.110	0.145	0.170	0.190	0.209	0.218	
- air	λ_{table}	-	-	-	-	-	-	0.220	/2,3/
Silicoorganic liquid BKЖ -94	λ_{exp}	0.200	0.165	0.180	0.162	0.158	0.150	0.145	
	λ_{table}	0.205	0.162	0.158	0.158	0.156	0.150	0.142	/4,5/

TABLE II

Effective Thermal Conductivity of Moist Porous Materials

$$T = 300^{\circ}\text{K} \quad P = 0.99 \cdot 10^5 \text{N/m}^2$$

Material	%	λ of liquid	λ_{sk}	λ_{ef}	λ_{calc}
Glass spheres (d = 0.5 mm) - air	35	0.028	1.2	0.22	0.25
Glass spheres (d = 0.5 mm) - water	35	0.62	1.2	0.945	0.95
Glass spheres (d = 0.5 mm) -ethyl alcohol	35	0.21	1.2	0.625	0.62
Glass spheres (d = 0.5 mm) - - benzol	35	0.14	1.2	0.5	0.52
Quartz sand (d = 0.6 mm) - water	32.4	0.62	5	2.33	2.2

Fig.1. Working chamber of low-temperature installation

- 1) experimental tank, 2) adiabatic envelope,
- 3) vacuum cylinder, 4) cap, 5) Dewar vessel,
- 6) liquid nitrogen, 7) tested substance,
- 8) pipe for wires

Fig.2. Experimental relationship $\lambda(T)$ for disperse materials

○ - Al_2O_3 powder - silicoorganic liquid (in pores);
 × - silicoorganic liquid; Δ - Al_2O_3 powder - air;
 ● - powdery plexiglass

Fig.3. Experimental relationship $\lambda(T)$ for disperse materials

○ - glass spheres $\varnothing$ 1.5 mm - air; ● - glass spheres $\varnothing$ 1.5 mm - air; × - glass spheres 1.5 mm - silicoorganic liquid film; Δ - glass spheres $\varnothing$ 1.5 mm - silicoorganic liquid (in pores)

Thermal Transpiration Measurements and the
Heat Conductivity of Polar Gases.¹

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Abstract

The thermal transpiration measurements of polyatomic polar gases have been made at mean temperatures of 366^o, 398^o, and 444^o K using the experimental procedure described previously². The dusty gas model of Mason, Evans and Watson³ successfully described the observed thermomolecular pressure difference as a function of pressure for each experimental temperature difference.

The thermal transpiration data for carbon monoxide, nitric oxide, sulfur dioxide and hydrogen sulfide were used to compute the translational part of the heat conductivity. The rotational collision numbers were then computed from these results and the total heat conductivity computed and compared to experimental values. The corrections to the rotational⁴ collision numbers due to resonant exchange proposed by Mason and Monchick⁴ were compared to the experimental results and it appears that both resonant and nonresonant rotational exchange are important for these dipolar gases.

The computed rotational collision numbers increase with temperature for all four polar gases studied. Loyalka⁵ recently developed an expression for the thermal transpiration effect in a cylindrical tube based upon the BKG model for thermal creep near the wall and Poiseuille back flow at the center of the tube. Using his procedure to compute the translational part of the gas heat conductivity the rotational collision numbers were obtained within the errors of these experiments.

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Thermophysical Properties of Biological Materials

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ABSTRACT

The increased significance of thermal properties in medicine has led to the need for a better understanding of heat transfer in biological systems. This paper reviews the results of recent thermal conductivity, thermal diffusivity, and heat flow measurements in living and non-living animal tissues. The methods of current interest to the medical and engineering professions are described and problems in their use are discussed. The variation in experimental results between different samples of experimental techniques are presented. The applicability of thermophysical property data to biomedical engineering and the requirements for future work are delineated.

Transport Properties of Rare Earth Metals

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THERMAL CONDUCTIVITY OF CERIUM DIOXIDE

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ABSTRACT. The thermal conductivity of cerium dioxide was measured in the 300-1200°C temperature range by means of the method of a cylinder with internal heating. The experiments were conducted in argon atmosphere. The bulk weight of the material to be studied and burnt at 1700°C temperature was 6.7 g/cm³. No experimental data on cerium dioxide thermal conductivity in the above temperature range has been available in literature.

There are but a very limited number of works devoted to the investigation of cerium dioxide (CeO₂) thermal conductivity [1]. These, in their turn, cover but a restricted temperature range, namely from 20 to 120 and from 1000 to 1700°C. In order to obtain thermal conductivity data between the ranges said the use of interpolation curve is recommended [1]. To close the gap in experimental data the authors have conducted experimental measurement of the thermal conductivity of cerium dioxide in the 300-1200°C temperature range.

To investigate thermal conductivity, the steady-state method of radial flux of heat was used, the heat emitting from an axial heater enclosed in a cylindrical specimen. The investigation method and measuring devices are described in detail by A.M. Banayev and V.Ya. Chekhovskoy [2]. The heater was a molybdenum rod of 6 mm in dia, to which a.c. is supplied from a step-down power transformer. The heater is vertical and coaxial with the cerium dioxide specimen. The specimen is a hollow cylinder with 320 mm height, 60 mm outer dia. and 11 mm inner dia. It consisted of a set of cylinders 20 mm high and one cylinder of 40 mm in the middle which has four blind bores parallel to the cylinder axis. The bores are of 20 mm length and of 3 mm dia. These bores are situated nearly every 90° of the circumference; their radial distances from the center of the cylinder are as follows: $r_1 = 8.30$; $r_2 = 11.41$; $r_3 = 14.56$ and $r_4 = 24.98$ mm.

Two-channel magnesia "straw" type packing (3 mm in dia) fitted with thermocouples was tightly packed into the bores, the thermocouple junctions pressing the bottoms of the bores. The thermocouple nearest to the heater was made of tungsten-rhenium alloys (the BP 5/20 type), while the other three thermocouples of class II were platinum-platinorhodium (10% Rh). The BP 5/20 thermocouple had 0.35 mm dia electrodes and was calib-

rated in All-Union Metrology Research Institute. named by D.I. Mendeleev. The thermoelectromotive force was measured by means of d.c. potentiometer of low omic value, type ПМС-48. The cold junctions of thermocouples were located in a Dewar vessel filled with melting ice.

The measurement of thermal conductivity was performed in argon atmosphere. The operating volume of the installation was filled with argon after the air had been evacuated from it with a vacuum pump down to pressure of 10^{-2} mm Hg. The calculation of thermal conductivity was made on the base of the following formula:

$$\lambda_{12} = \frac{Q \ln r_2/r_1}{2 \pi \ell (t_1 - t_2)}$$

and related to the average temperature $t_{I2} = \frac{1}{2}(t_1 + t_2)$. The indices I and 2 of the formula refer to t_I and t_2 temperatures which are measured with thermocouples located on the radii r_I and r_2 respectively. Having four thermocouples to measure temperatures t_1 , t_2 , t_3 and t_4 on the respective radii r_1 , r_2 , r_3 and r_4 , it is possible to calculate six values of the thermal conductivity coefficient: λ_{12} , λ_{13} , λ_{14} , λ_{23} , λ_{24} , λ_{34} .

Measuring radial temperature variation with four thermocouples instead of conventional two has the advantage of allowing one to check with the results thus obtained and increase their reliability.

The output power Q emitted on the active area of the heater was calculated on the basis of the voltage drop and the current density. These values were measured by means of a a.c. potentiometer, type P-56, class 0.3. The length of the heater active area, ℓ , is 46.0 mm which corresponds to the distance between the potentiometric leads.

The test specimens were made of cerium dioxide powder of the following chemical composition (mass per cent): matrix compound - 99.79 per cent, neodymium oxides - 0.2 per cent, ferric oxides - 0.01 per cent and annealing losses - 0.3 per cent. Over than 90 per cent of the powder grains are of nearly 4 micron the rest ones being of 5-12 micron. The powder and the binding compound (5 per cent aqueous solution of polyvinyl alcohol) was pressed at 500 atm and, after drying, burnt in air at 1700°C temperature for four hours. The bulk weight of the specimens was 6.7 g/cm³.

The cerium dioxide thermal conductivity was measured on the same specimen in two runs. During the first experiment the values of the thermal conductivity coefficient were obtained for gradual temperature increase from 300 to 920°C. Then, while temperature was going down thermal conductivity value was measured at about 720°C. (Fig. I, first run, light circles). During the second run, the highest temperature of 1200°C was obtained. Further temperature rise brought about the heater failure (Fig. I, second run, black circles).

Figure I. The results of study of temperature dependence of cerium dioxide thermal conductivity.

1 - λ_{I2} ; 2 - λ_{I3} ; 3 - λ_{I4} ; 4 - λ_{23} ; 5 - λ_{24} ;
6 - λ_{34} ;

solid line - averaged data of the present experimental results; dash line - the region of the measurement error ± 10 per cent.

One can see from Figure I that the points of the first and the second runs are in good agreement, which shows good reproducibility of the results obtained. There are but few points of the 60 ones which have a 10 per cent deviation from the mean curve. This deviation value corresponds to the highest calculated relative error of the experiment. On the basis of the data scatter the standard error of the thermal conductivity measurement was calculated and found to be ± 4.6 per cent, as well as doubled mean square deviation from the curve which was equal to

$$2 \sqrt{\frac{\sum (\Delta \lambda)^2}{n(n-1)}} = \pm 1.2 \%$$

Averaging the experimental data gives cerium dioxide thermal conductivity as a function of temperature:

t°C	300	400	500	600	700	800	900	1000	1100	1200
$\lambda \frac{W}{m \cdot ^\circ C}$	7.12	5.90	4.96	4.25	3.74	3.38	3.13	2.95	2.82	2.73

Figure 2 shows the comparison of the averaged experimental data with cerium dioxide thermal conductivity data known from literature. In the range of 300-700°C the present data lie (with in ± 1.5 per cent deviation) on interpolation curve offered in [1].

Figure 2. Comparison of the present data with those known from literature [1]. Solid line - averaged data of experimental results; dash line - interpolation curve given in [1].

However, as temperature increases, the deviation grows up reaching 50 per cent (as compared with the present data) at 1200°C.

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The Thermal and Electrical Conductivities of a Series of
Electrically Conducting Compounds

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ABSTRACT

Measurements have been undertaken between 300 and 1300K upon a series of zirconium and hafnium compounds containing carbon and silicon. At the highest temperature results are compared with those obtained elsewhere from thermal diffusivity measurements.

The electronic and lattice components of thermal conductivity are discussed with reference to results for other electrically conducting borides and carbides of titanium and zirconium.

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TUNGSTEN THERMAL CONDUCTIVITY AS MEASURED BY MODIFIED
METHOD OF EXPONENTIAL TEMPERATURE DISTRIBUTION

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ABSTRACT. Measurements have been performed on wire specimens heated by passing electrical current in vacuum. Use has been made of exponential temperature distribution gradually displaced along the specimen due to the rider temperature variation. The exponent has been determined from the comparison of the resistivity change of two specimen sections without using the temperature coefficient of electrical resistivity. Resistance bridge has also been used. Tungsten thermal conductivity has been determined for the temperature interval of 1300 to 2500°K on the specimens of 99.9% purity with 0.1% addition of Molybden. The calculated maximum random error of a single measurement does not exceed 6 per cent.

Much work has been done to measure thermal conductivity of tungsten at high temperatures [I-II]. The results of studies [6-II] are in good agreement in terms of the value and temperature dependence of the thermal conductivity coefficient. (Fig. I)

When compared to these, the values received in [4] seem to be too high, while in [1,2,3] thermal conductivity has an anomalous positive temperature coefficient. The data [5] are somewhat underestimated at temperatures up to 2000°K, which results in an anomalous positive temperature dependence of Lorentz number. However even values which are given as most reliable differ within 40 per cent. All this indicates the necessity for further investigation to arrive at more accurate data for tungsten thermal conductivity.

To study tungsten thermal conductivity at high temperatures a modification of the method [12] has been applied which uses exponential temperature distribution and determination of the exponent in terms of electrical parameters.

A long thin specimen was heated in vacuum by passing electrical current. Exponential distribution was obtained with the help of a rider with changeable temperature. Three sections l_0 , l_1 , l_2 (Fig.2) were isolated in the central part of the specimen by potential leads.

Fig. 1. Tungsten Thermal conductivity coefficient.

- 1 - Osborn [6]; 2 - Neymark, Voronin [II];
 3 - Simonova, Filippov [10];
 4 - Catler, Chaney [9];
 5 - Gumenyuk, Ivanov, Lebedev [7];
 6 - Timrot, Peletskiy [8];
 7 - Present data.

Sections l_1 and l_2 were partially overlapping their coinciding ends being situated in an isothermal zone, and the free ends spaced by the value l - in the zone of exponential temperature distribution. Section l adjacent to l_1 and l_2 , was completely within the isothermal zone.

The solution of a differential equation of thermal flow in the specimen at a low temperature gradient $\nabla = T_m - T$, where T_m is temperature of the central isothermal part of the specimen, leads to [13]

$$\vartheta = \vartheta_0 \exp(-Kx). \quad (I)$$

For the first section, it is possible to find resistivity difference that corresponds to two temperature regimes: 1) when the specimen is heated up to temperature T_m ; 2) in case of exponential temperature distribution. It is assumed that within the ϑ interval electrical resistivity is a linear function of temperature:

$$\rho = \rho_m - \frac{d\rho}{dT} \vartheta, \quad (2)$$

$$\Delta R = \int_{x_1}^{x \rightarrow \infty} \frac{\rho_m - \rho}{S} dx = \frac{\vartheta_0}{SK} \exp(-Kx), \quad (3)$$

where S is the specimen cross section.
By analogy, for the second section by the integration from $x_2 = x_I + \Delta l$ to $x \rightarrow \infty$:

$$\Delta R_2 = \frac{\sigma_0}{SK} \cdot \frac{d\rho}{dt} \cdot \exp(-Kx_2). \quad (4)$$

It follows from (3) and (4) that

$$\eta = \frac{\Delta R_1}{\Delta R_2} = \exp(K \cdot \Delta l). \quad (5)$$

Fig. 2. Measuring scheme

1' - specimen, 2 - rider,
a, b, c, d - points of lead contact

When varying the nonisothermity value at constant heating current ($T_m = \text{const}$) by changing the riders temperature, which

corresponds to equidistant temperature field displacement along the specimen, the values R_1 and R_2 would change so that the ratio of their increments remains constant:

$$\frac{\Delta R_1}{\Delta R_2} = \frac{dR_1}{dR_2} = \eta. \quad (6)$$

When switching the section l_0 , l_1 and l_2 together with highohmic resistances r_1 , r_2 and r_0 into two balanced bridge circuits (Fig. 2):

$$\eta = \frac{\Delta z_1}{\Delta z_2} = \frac{dz_1}{dz_2}. \quad (7)$$

The expression for the coefficient K in the formula exponent (I) can be presented as [14]:

$$K = \sqrt{\frac{4\gamma U_0}{\lambda \ell_0 S T_m} (1 + \delta)}, \quad (8)$$

where $\delta = \frac{1}{2} \frac{d \ln \gamma / T_m^2}{d \ln T_m}$ - a correction to the temperature dependence of electrical resistivity and emissivity.

I - current intensity;

U_0 - voltage drop along the section l_0 .

On the base of (6), (7), (8) the calculated formula for the thermal conductivity coefficient assumes the following shape:

$$\lambda = \frac{4\gamma U_0}{\ell_0 S T_m} \left(\frac{\Delta \ell}{\ell \eta \frac{dz_1}{dz_2}} \right)^2 (1 + \delta) \quad (9)$$

or

$$\lambda = \frac{4A\ell_0}{S} \frac{\gamma U_0}{T_m (\ln dz_1 / dz_2)^2} (1 + \delta) \quad (10)$$

where $A = \left(\frac{\Delta \ell}{\ell_0} \right)^2 = \left(\frac{\Delta U}{U_0} \right)^2$ - a value determined in

terms of the ratio of corresponding voltage drops at constant current intensity under isothermal conditions.

The wire specimens 0.2 mm in dia. and about 150 mm long were put horizontally in a water - cooled vacuum chamber (vacuum (1 + 5) 10 mm. Hg.) The leads to isolate specimen sections were made of thin tungsten wire with diameter of 0.02 or 0.012 mm. They were fixed to segments of a copper wire and hanging over the segments were pressed to the specimen by weights of about 0.25 g. When the specimen was being annealed, which was done just before the experiment, the leads became welded to the specimen in contact points.

The rider was 30 mm tungsten wire with diameter of 0.35 mm. heated by passing direct current from a stabilized power supply. One end of the rider was hinged and the current was supplied by flexible copper wires. This allowed one to make it contact the specimen after annealing without impairing the chamber vacu-

um. The rider was controlled with the help of a vacuum-tight movable joint which was also used for moving the shielding glass on the viewing window for the pyrometer.

Bridge resistances r , r_1 , r_2 were equal to $50 \pm 100 \cdot 10^3$ ohm; variable parts of r_1 and r_2 were resistance boxes of Class 0.05. The specimen was fed with d.c. storage batteries. The values of r_1 and r_2 were calculated as an arithmetic mean from the values, corresponding to two opposite current directions. Not less than four values of r_1 and r_2 corresponding to different degree of nonisothermity were recorded for each current value. A photocompensating microammeter was used as a zero-device of the bridge circuits.

The current intensity and voltage drop U were measured by potentiometer. The temperature T was measured by an optical micropyrometer OMN-054 using information available from literature on spectral emissivity [15,16]. The value l_0 was measured by an instrumental microscope. The specimen cross section after experiment was determined by weighing the central part of the specimen. In calculation use was made of the density value of annealed tungsten wire equal to 19.26 g/cm³ [17,18]. The control over the specimen thinking-out due to evaporation during the experiment was performed through electric parameters.

Special methodic experiments were performed to determine the lead resistance change with temperature. This change in a single experiment was found negligible in comparison with the change of r_1 and r_2 values. The effect of heat sink along the leads on the measured values of U and η was also estimated. It was established that the ratio U/l_0 dia. not vary within the accuracy of measurement when the value l_0 increased twice as much and the ratio of voltage drops along two unequal sections under isothermic conditions remained constant in a wide temperature range.

As far as η was concerned, in addition to what was said above it should be pointed out that this value could be noticeably affected only by temperature field distortion near the lead bounding l_2 section from the right (Fig. 2). On changing the nonisothermity value in one experiment, the heat sink along this lead did not change in the first approximation, because the absolute temperature change at the point of contact was about 1 per cent. Therefore, the sink effect on the value of η , which was determined from a differential relation (7), was negligible. This was confirmed experimentally by the fact that when changing values of l and lead diameter d from specimen to specimen. There was no dispersion of the value $\lg \eta / d^2 c$ (Fig. 3)

The tested material had 99.9% purity; the main impurity being of about 0.1% Mo.

The resistance of the present specimens in the studied temperature range, within 1 per cent coincided with the data cited in [19] as most reliable.

Results on the thermal conductivity coefficient and Lorentz number received from the experiments are shown in Table I (without regard to the change of geomentric dimensions with temperature).

Fig. 3. Temperature dependance of $\lg \eta / \Delta l$

1. $\Delta l = 4.74 \text{ mm}$; $d = 12$.

2. $\Delta l = 3.74 \text{ mm}$; $d = 20$.

3. $\Delta l = 3.25 \text{ mm}$; $d = 20$.

Table I.

T °K	1300	1500	1700	1900	2100	2300	2500
$\lambda [\text{w/m} \cdot \text{grad}]$	120	116	111	107	103	99	96
$\lambda \cdot 10^8 [\text{w} \cdot \text{cm} / \text{grad}]$	3,08	3,04	3,00	2,96	2,93	2,89	2,87

Calculated maximum random error of a single thermal conductivity coefficient measurement is 6 per cent. The comparison with the results of earlier studies is shown in Fig. I.

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The Lattice Thermal Conductivity of Nickel and
dilute Nickel-Rhenium Alloys above 400 °K

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The thermal conductivity data of Kirichenko and Mikryukov on high-purity nickel and on dilute nickel-rhenium alloys have been analysed by us. The deduced values of the electronic and lattice components are found to have a variation with the temperature and with the addition of the solute metal, compatible with the standard theory.

The method of Linde-Backlund is also found to be applicable to these data on high-purity nickel, apparently because the slope of the ρ -T curve (ρ being the electrical resistivity at the temperature T) above the Curie-temperature is large enough to give a correspondingly large $\bar{\rho}_0$ (on the negative side of the resistivity axis) which when added to ρ , can compensate for the use of the normal Sommerfeld value of the Lorenz number in lieu of the more appropriate temperature dependent value given by Makinson. This seems to us the reason why, in cases where $d\rho/dT$ is less steep above the Curie temperature (as in the case of the other 'pure' nickel specimens used by Schofield, Powell et al and Hogan and Sawyer) the Backlund method does not lead to understandable results.

Key Words : Electrical resistivity, electronic thermal resistivity, lattice thermal conductivity, Lorenz number, nickel, nickel-rhenium alloys, thermal conductivity.

1. Introduction

The electrical resistivity of ferromagnetic metals has been analysed by Weiss and Marotta (1) assuming the intrinsic electrical resistivity ρ_i to be given by the Bloch-Gruneisen expression and making use of the fact that the maximum value (ρ_M) of the

magnetic resistivity component (ρ_m) in the paramagnetic state (2) is proportional to $\sum p_i s_i (s_i + 1)$ where p_i is the fraction of the atoms in the spin state s_i (3). When the temperature T is high, compared to the Curie temperature T_c and the Debye temperature θ , the Bloch-Gruneisen term reduce to AT/θ (A being a constant for the metal). Since the experimental ρ - T curves at such high temperatures are linear, the slope gives A/θ whereby ρ_i at the temperature T can be obtained. Since the residual electrical resistivity ρ_0 is then negligibly small, ρ_m is given by $\rho - \rho_i$.

The electronic thermal resistivity component (w_{em}) corresponding to ρ_m (4,5), as also the residual component (w_{e0}) corresponding to ρ_0 is obtained by the Wiedemann-Franz relation employing the normal Sommerfeld value (L_n) of the Lorenz number. The intrinsic component (w_{ei}) of the thermal resistivity is obtained from ρ_i , employing the Makinson value (6) of L_e . From the experimental thermal conductivity data, one can thus separate out the electronic and the lattice thermal conductivity. The results obtained in this manner are in reasonable agreement in the case of iron (7,8), with those derived by Backlund (9). This latter method originates from the fact that the Bloch-Gruneisen expression for the intrinsic electrical resistivity leads to a reduced resistivity ($r = \rho T / \rho_\theta$) being a universal function of the reduced temperature $t = T/\theta$. Above $\theta/3$ this is a straight line given by (10) $r = -0.17 + 1.17t$, so that $d\rho/dT = 1.17 \rho_\theta/\theta$. From Linde's observation (11) for normal non-transition metals that w_{ei} is independent of T , as long as the electrical resistivity has a linear temperature-dependence, Backlund has evolved the modified Wiedemann-Franz relation $w_{ei} = (\rho_i + \rho_0)/L_n T$, applicable also to transition metals. ρ_0 is ρ_θ times the intercept on the negative side of the Y axis of the rectilinear ρ_i - T curve and is presumably associated with zero point energy (12). In a pure metal ρ_0 is numerically large enough for $(\rho_i + \rho_0)$ to compensate for using L_n in place of the more appropriate Makinson value L_e .

It would be of interest to apply these methods to data pertaining to nickel and its dilute alloys and to compare their results. We have accordingly analysed the electrical and thermal conductivity data on nickel, reported by Schofield (13), Hogan and Sawyer (14), Powell, Tye and Hickman (15) and by Kirichenko and Mikryukov (16), and on some dilute nickel-rhenium alloys (16) containing upto 8.33 per cent rhenium.

2. Analysis of data on pure nickel

2.1 The components of the electrical resistivity

Kirichenko and Mikryukov (16) have recently reported their electrical and thermal conductivity measurements on pure nickel (better than 99.999 per cent purity). The slope of their ρ - T curve above the Curie temperature is 35.2 whereas Weiss and Marotta (1) give 25 for Potter's data (17). Powell et al (15) give 27 for their sample 5 and 31 for their sample 1. Schofield's data (13) gives 32.5 that of Hogan and Sawyer (14) 30.3 and that of Kovensky and Samsonov (18) 36.9, all in $10^{-11} \Omega m / ^\circ K$. A tangent to the ρ - T curve of nickel is drawn with this slope and the separation of ρ into ρ_i , ρ_m and ρ_0 is then effected as was done by Weiss and Marotta (1,7).

2.2 The electronic thermal resistivity components - Method 1.

The corresponding components of the electronic thermal resistivity of nickel are evaluated using the normal value of the Lorenz number for the residual and magnetic components and the intrinsic value of L_e given by Makinson (6) for an ideal monovalent metal (his curve for $\Theta_0/4A = 0$) having Θ equal to that of nickel. The Debye temperatures listed by Gschneider (19) and Keesom and Pearlman (20) suggest $\Theta_{Ni} = 450$ °K. The recent discussion of the specific heat data of nickel by George and Thomson (21) indicates that the Θ of nickel above the room temperature is about 500 °K. We have used this value for nickel and for its dilute alloys, except where otherwise stated.

The electronic thermal resistivity of nickel resulting from the above analysis is shown in curve 1 of fig. 1. The dot-and-dash curve, adjacent to it, corresponds to $\Theta = 450$ °K and is drawn to show the effect of assuming a different value of Θ . Curve 6 (broken curve) gives the variation of w_{ei} with temperature.

In fig.2, the electronic thermal resistivity of nickel and its intrinsic and magnetic components are shown (as obtained in the present analysis) in comparison with the corresponding quantities for iron (taken from (7)). As in the case of iron, the electronic thermal resistivity values at the higher temperatures join smoothly to those given by White and Woods(22) for the temperatures below 150 °K. The value of w_e (at 600 °K for iron and at 400 °K for nickel) derived by us shows the upward trend attributed to the over-estimation of the electron-phonon interaction in the standard theory (which is also responsible for the predicted thermal conductivity minimum at somewhat lower temperatures in pure metals). w_e presents a peak at the Curie temperature, though in a less marked manner than in iron, the peak-value here being near about half of that of iron.

The magnetic component of the thermal resistivity also shows a broad maximum (less marked than in iron), its peak value being about a quarter of that for iron. Whereas in the case of iron, the intrinsic component of the thermal resistivity shows a little variation with temperature and forms less than a third of the electronic thermal resistivity at the Curie temperature, the w_{ei} in nickel has a comparatively larger rise with the fall of temperature, far exceeds the magnetic component and constitutes about 2/3 of the total electronic thermal resistivity at the Curie temperature.

The results of analysing Schofield's (13) data on 99.2 per cent pure nickel which give 32.5 for $d\rho/dT$ above T_c are also shown in fig. 2 (w_{eg} is not shown separately for Schofield's data; it almost coincides with those already plotted for nickel at 600°K and above, while it is slightly higher at lower temperatures). Hogan and Sawyers' (14) data on 99.48 per cent pure nickel extend to 1100 °K. The electronic thermal resistivity components derived by us from their data are shown as broken lines above 800 °K. At lower temperatures, they are little different from the results based on Schofield's data (13).

2.3 The analysis following Backlund : Method 2

The data of Kirichenko and Mikryukov (16) have also been analysed by us somewhat on the lines of Backlund (9). The electrical resistivity is expressed as $-a+bT+cT^3$ where $b=35.2$ (which is the value of $d\rho/dT$ above the Curie temperature). 'a' and 'c' are evaluated using the values of the electrical resistivity at 400 and 500 °K. At higher temperatures, ρ_m is obtained (not from cT^3 but) from $\rho_T + a - bT$. The maximum value (ρ_M) of ρ_m , thus obtained is $0.127 (\mu\Omega m)$ which is somewhat smaller than the value 0.150 derived by Weiss and Marotta (1). However, this fits in well with their rectilinear plot of ρ_M versus $\sum p_i s_i (s_i + 1)$. It gives $\sum p_i s_i (s_i + 1) = 0.42$ whereas it would be 0.45 on the basis of Van Vleck's proposal (3) that nickel consists of 60 per cent of the atoms in the $3d^9$ states (1 Bohr magneton) and 40 per cent in $3d^{10}$ states (0 Bohr magneton).

The intrinsic and magnetic components of the electronic thermal resistivity are now somewhat more (than derived above) and w_e is shown in fig. 2 as the dot-and-dash curve which does not join up satisfactorily with the low temperature data of White and Woods (22) on nickel.

2.4 The lattice conductivity of the nickel samples

The analysis (Method 1) of article 2.1 has been applied also to data on nickel reported by Powell, Tye and Hickman (samples 1 and 5) (15) and Hogan and Sawyer (14). Fig 3 shows the lattice thermal conductivity in each of these cases, based on the electronic thermal resistivity deduced above and the total thermal conductivity tabulated in their publications and in the case of Kirichenko and Mikryukov's data, roughly read off their published graphs. Curve 1 pertains to the data of Kirichenko and Mikryukov (16) (assuming $\theta = 500$ °K) and curve 2 to the same assuming $\theta = 450$ °K. An analysis following Backlund (described in article 2.2) gives higher values throughout (for instance $42.2 \text{ W m}^{-1} \text{ deg}^{-1}$ at 400 °K and 28.0 at 800 °K).

There is unfortunately no direct method of determining the lattice thermal conductivity in metallic conductors. The theoretical treatments (23,24) are based on models of simple cubic crystals and lead to $\lambda_g \simeq 3.6 A_0^3 \gamma^{-2} T^{-1} \text{ W cm}^{-1} \text{ deg}^{-1}$, where A_0 is the lattice constant, γ = the Gruneisen parameter = 2. At 400 °K this would give $16 \text{ W m}^{-1} \text{ deg}^{-1}$. The analysis of article 2.1 gives 26 for this and if one corrects for the rising trend of w_e at 400 °K (by reading w_e from the dashed curve joining to the lower temperature data), this would come out as 17 in good agreement with the theoretical value. In general, the thermal conductivity of dielectric solids and the lattice thermal conductivity in noble metal alloys are actually found somewhat smaller than predicted by this formula (25).

Curves 3 and 4 of fig 3 refer to the results from samples 5 and 1 respectively of Powell, Tye and Hickman (15), curve 5 refers to Schofield's (13) data and curve 6 to those of Hogan and Sawyer (14). In all these cases, the steep, almost quadratic rise of λ_g with the fall of temperature from 600 to 400 °K is also accounted for by the rising trend of w_{e1} (and consequently w_e), inherent in the standard theory (4).

The notable feature common to all these nickel specimens of different degrees of purity is that the lattice thermal conductivity in the paramagnetic state is higher than that in the ferromagnetic state. Numerically, this rise is more pronounced for the purest (and highest-conducting) specimen of Kirichenko and Mikryukov (16) but percentually it is the largest for the less pure (and lower conductivity) specimens. This rise contrasts with the behaviour observed in the case of iron (7, 9) namely the steplike drop in lattice conductivity at the Curie point. There is evidence from Mossbauer effect (26) that the Debye temperature is higher in the ferro-magnetic than in the paramagnetic state. λ_g is, roughly speaking, proportional to θ^3 and this should, if at all, give a decrease of λ_g at the Curie temperature. It is known that nickel undergoes an anomalous contraction in passing from the para - to the ferro-magnetic state while iron exhibits an expansion (27). This seems too small, however, to be able to account for the observed difference in the variation of λ_g at the Curie temperature.

3. Dilute Nickel-Rhenium alloys.

3.1 Analysis by Method 1.

The electrical and thermal conductivities of dilute Nickel-rhenium alloys have been measured by Kirichenko and Mikryukov (16) in view of their high acid and heat resistant properties. These contain respectively 0.55, 2.39, 4.94 and 8.83 weight per cent rhenium. Their ρ -T curves have inflections at their Curie temperatures which shift to lower temperatures (reported to range from 656 to 588 °K) as the rhenium content increases. Above the T_c their ρ -T curves have the same slope viz $35.2 \times 10^{-11} \text{ }^\circ\text{ohm-m-deg}^{-1}$ as their pure nickel specimen. In applying the method of article 2.1 to these alloys, we again assume $\theta = 500 \text{ }^\circ\text{K}$ so that ρ_i and w_{ei} come out to be the same as for pure nickel. Subtracting ρ_i at any given temperature from the electrical resistivity of the alloy at that temperature, would give $\rho_m + \rho_o$. The corresponding electronic thermal resistivity ($w_{em} + w_{eo}$) = $(\rho_m + \rho_o) T^{-1} / L_n$. The effects of alloying on the band structure are thus ignored.

The electronic thermal resistivity of the Ni-Re alloys of Kirichenko and Mikryukov (16) derived in this manner, are shown in fig.1 as curves 2,3,4 and 5 in the order of increasing rhenium content. If one identifies the peak in w_e with the T_c , the shift (at any rate for the more dilute alloys) broadly conforms to the inflections in the ρ -T curves. Figure 4 shows how, at any given temperature, in the region under discussion, the electronic thermal resistivity of nickel shows a sharp

rise on the addition of a small amount of rhenium, while beyond about 1/2 per cent rhenium, it shows a linear (less steep) rise.

Figure 5 shows the lattice thermal conductivity of these alloys as derived in this manner, the numbering being in the order of increasing rhenium concentration. The lattice conductivity of the most dilute alloy resembles curve 1 of fig 2 while in the alloys containing more than 4 per cent rhenium, the lattice conductivity shows a drop (as in the case of iron 7,8,9) at a temperature, which could presumably be identified as the Curie temperature without any rise thereafter, while their electrical resistivity does not show evidence of a Curie temperature.

3.2 Analysis by Method 2.

As has already been mentioned, Backlund's method also gives reasonable results when applied to iron and to the pure nickel specimen of Kirichenko and Mikryukov (16) which has a high $d\rho/dT$ above the Curie temperature. As has been pointed out by Powell, Tye and Hickman (15), their data on specimen No. 5 lead to (i) an electronic thermal conductivity larger than the experimental (total) thermal conductivity, if one used the value L_n for the Lorenz number and (ii) a lattice thermal conductivity rising with the rise of temperature, if Backlund's method is employed. We wish to mention that this specimen has a $d\rho/dT$ (above the Curie temperature) of 27 as compared with 35.2 for the pure nickel specimen of Kirichenko and Mikryukov (16). Their sample 1 on the other hand has $d\rho/dT$ of 31 and Schofield's specimen has 32.5 (in units of $10^{-11} \Omega \text{ m deg}^{-1}$) and we find Backlund's method perfectly valid in these cases giving w_e and λ_g agreeing closely with those plotted in figs. 1 and 3 for these. Finally, we wish to remark that the specimen of Hogan and Sawyer (14) has $d\rho/dT$ (above T_c) of 30.8 which is very close to that for sample 1 (of Powell, Tye and Hickman) and yet because the (total) thermal conductivity values are much smaller, the application of Backlund's method leads to $\lambda_e > \lambda$.

A smaller slope of the ρ - T curve (above T_c) gives (numerically) a smaller value for $\bar{\rho}$ leading to a reduced $w_e = (\rho + \bar{\rho}) T^{-1} L^{-1}$ and an enhanced λ_e . Further, the curves of Kirichenko and Mikryukov for the very dilute Ni-Re alloys show a large drop in the thermal conductivity at 400 °K (becoming less at higher temperatures) as compared to that for pure nickel. These two facts seem to be responsible for rendering the Backlund method invalid at these temperatures for nickel unless the metal is in a very pure state. It has been known (28) that the thermal conductivity and diffusivity of pure nickel

are much more sensitive than the electrical conductivity to the addition of impurities.

The rectilinear ρ -T curves of the Ni-Re alloys give intercepts on the positive side of the resistivity axis and if these are used in the Backlund method with the appropriate sign, lead again to difficulties. However, if one uses, for the alloys as well, the $\bar{\rho}_0$ value obtained for the pure nickel specimen, the Backlund method can also be applied, leading to values of w_e and λ_g closely conforming to those plotted in figures 1 and 5.

4. Summary :

In the past, whether one used an electronic Lorenz number equal to L_n or the modified Wiedemann-Franz-Lorenz relation of Linde-Backlund, the results obtained for the lattice thermal conductivity of nickel were found not to conform to the expectations of the standard theory. It has been shown here that, for sufficiently pure nickel specimens, whether one employs the modified W-F-L relation or the appropriate electronic Lorenz number derived by Makinson, in evaluating the intrinsic electronic thermal resistivity, one obtains meaningful results for the λ_g . Even for the 'pure' nickel specimens reported by earlier workers, reasonable results for λ_g are obtained by using the Makinson value for L_{ei} .

5. Acknowledgement

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Fig. 1 Temperature-dependence of the electronic thermal resistivity (in $\text{m-}^\circ\text{K/W}$) of nickel and dilute Ni-Re alloys (derived from the data of ref. 16). Curve 1: pure nickel, using $\theta = 500^\circ\text{K}$ (full line curve) and $\theta = 450^\circ\text{K}$ (dot-and-dash curve). Curves 2, 3, 4 and 5: Ni-Re alloys in the order of increasing rhenium content. Curve 6: Intrinsic component of the electronic thermal resistivity.

Fig. 2 Temperature dependence of the electronic thermal resistivity (w_e) and its components (w_{ei} and w_{em}) of nickel and iron as deduced in the present analysis and in ref. 7.

	Fe	Nickel Specimens		
		(ref. 16)	(ref. 13)	(ref. 14)
w_e	○	●	◐	As for ref. 13
w_{em}	△	▲	◀	up to 850°K
w_{ei}	▽	▼	◀	Broken lines at higher temperatures

—●— : w_e by Backlund method for data of ref. 16.

Fig. 3 Lattice thermal conductivity of nickel specimens derived by this analysis.

Curve 1: (data of ref. 16), $\theta = 500^\circ\text{K}$
 Curve 2: (-do-), $\theta = 450^\circ\text{K}$
 Curve 3: (data of ref. 15), Sample 5.
 Curve 4: (-do-), Sample 1.
 Curve 5: (data of ref. 13),
 Curve 6: (data of ref. 14).

Fig. 4 Electronic thermal resistivity of Nickel-Rhenium alloys (based on data read of ref. 16), plotted against the rhenium concentration.

Fig. 5 Lattice thermal conductivity of Nickel-Rhenium alloys (based on data read off ref. 16), plotted against the temperature. The curves 1, 2, 3 and 4 correspond to 0.55, 2.39, 4.94 and 8.83 weight per cent rhenium respectively.

EXPERIMENTAL STUDY OF THERMAL AND ELECTRICAL CONDUCTIVITIES OF SINGLE CRYSTALS OF TUNGSTEN AT HIGH TEMPERATURES

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I. INTRODUCTION

Two circumstances have prompted to conduct measurements of the thermal and electrical conductivities of single crystals of tungsten. One of them was due to the fact that notwithstanding a long history of measuring these parameters tungsten has been remained an example of material to demonstrate contradictory information concerning its thermal conductivity obtained through many an experiment. Suffice it to correlate the data gained by Allen et al[5] with the results of work[6] to make sure of carrying on further investigations.

Another circumstance is closely related to new policies in technology. In particular, recent development of electron beam melt, zonal purification and mastering the technology of single crystal growing would open a tempting prospect of approaching a perfect object of study, to verify, at last, theoretical deductions dealing with various structural factors.

2. EXPERIMENTAL TECHNIQUES AND FEATURES RELATED WITH MEASUREMENTS

a. Thermal Conductivity

The measurements of the coefficient of thermal conductivity were carried out by the method of longitudinal thermal flow with electron bombardment of the specimen.

The theory of the method and the principal design of the installation were shown in detail in a previous study [16].

Here it would be desirable to point out some of the features used as well as errors in the measurements done. A sample under study of cylindrical shape with diameter of 8 mm and length about 70 mm is fixed with one its butt-ends within a special calorimetric device which in conditions of steady-state regime permits the measurement of the total thermal flow travelling through one of the cross-section of the sample. The free end of the sample is heated by electron bombardment.

At the zone adjacent bilaterally to the working cross-section the sample has been provided with a number of radial cavities 6+7 mm deep and 0.6+0.8 mm in diameter.

The Effective radiant capacity of the bottom of the cavities mentioned along the axis closely approaches unity.

This permits the estimation with the aid of an optical micropyrometer a temperature distribution along the sample in the zone of its working cross-section as well as the calculation of the unknown quality of the longitudinal temperature gradient corresponding a quantity of heat estimated with the calorimetric device.

Subsequently, it is obvious that on having determined for the particular cross-section the local values for the temperature gradient and the thermal flow we shall have an information of local value for the thermal conductivity coefficient, a mean temperature interval of which is to be determined mainly by a temperature shift along the radius of the sample at a given cross-section (not more 27° at 2500°K).

The inaccuracy of the results obtained due to the fact that the calculation of thermal conductivity used its value corresponding to a certain radius rather than the longitudinal, temperature gradient averaged along the cross-section, as judged by a study I7, will not exceed in the present case 1% at 2500°K .

Results of the calculation of the thermal conductivity coefficient are to be corrected taking into account a number of factors. Consequently, a correction implying an increase of the thermal resistivity of the working zone as a result of pyrometric cavities ($\sim 2\%$). The influence of radiance heat exchange along the technological gaps between the calorimetric system and the elements of screening systems is considered, too. While considering all possible parasite overfalls of heat the correction factor does not exceed a magnitude of $0.8+1\%$.

The analysis of the error in measuring the thermal conductivity coefficient with the aid of an optical micropyrometer OM7-054 type (the instrumental error $\pm 0,2\%$, the principal error $\pm 0.5\%$) demonstrates that the maximal error of the results in the given case would not exceed 6.1% within the $1200-2500^\circ\text{K}$ range.

By characterizing the conditions of the measurements it is pointed out that the determination of the coefficient of thermal conductivity when using the given technique is carried on in the presence of considerable values of longitudinal gradients, at 2500°K the latter amounting as high as 500 grad/cm .

Each experiment was performed in vacuum not less than 10^{-5} tor. The walls of various construction elements, isolated from the sample by a vacuum gap, had a temperature not higher than $300-500^\circ\text{K}$. This practically eliminates any possible contamination of the sample through the whole temperature range under study.

b. Electrical Conductivity

The electrical conductivity of single crystal of tungsten was investigated within a 1200+2200°K range. The experimental sample appeared as a cylinder shape body with diameter 8 mm and length 60 mm. Its surface was heated by electron bombardment. The electrical resistivity of the working site of the sample was evaluated by the compensation technique. A low-ohmic dc potentiometer of p-330 type, class 0.015 was selected as a measuring unit, the source of measuring current being accumulation battery 4 v with capacity 720 a.-h.

The experimental arrangement and characteristic features of the given method of electrical conductivity estimation have been described previously [18]. While performing the present work the construction of potential electrodes underwent substantial modifications. Subsequently the potential electrodes were substituted for butt-end ones, passing through tubular current channels to the sample. The goal of these constructive modifications was to remove electrodes from the zone of intensive electron bombardment. Experience has learnt that the new electrode construction will essentially contribute to an increase of accuracy of voltage fall measurements of the sample. The study was performed in a vacuum chamber $\sim 10^{-5}$ tor created by diffusion pump.

Temperatures were measured at three points of the sample, the fact which permitted the calculation of a mean integral temperature of the working site, to which a specific electric resistivity was related. A disappearing filament optical pyrometer was used. The black body was modeled in the sample the same way as in measuring the thermal conductivity.

The utilization of a massive sample permitted the dependable and accurate measurement of its temperature and geometry of the working site. Combined with a most accurate (compensation) measuring method of the electrical resistivity this allowed a careful estimation of electrical conductivity temperature dependance. An inaccuracy of the experimental arrangement presents a magnitude $\pm 1.5\pm 2\%$.

3. CHARACTERISTIC OF SAMPLE UNDER STUDY

The research of the thermal conductivity was carried on a single crystal sample grown in crystallographic direction [111]. A deviation of the axis of the sample was $\sim 18^\circ$. A sample was obtained by the method of zone melting (two passages). A preexperimental analysis of the sample permitted the characterization of its purity 99.98% associated with contents of carbon 0.001 - 0.002 wt%, nitrogen $< 10^{-3}$ wt%, oxygen $< 10^{-3}$ wt%.

The sample to measure the specific electrical resistivity was prepared by the same technology using the same basic material

The specific electrical resistivity at the room temperature (20°C) equalled 5.28×10^{-4} ohm-meters.

4. THE RESULTS OF MEASUREMENTS

Estimated values of the thermal conductivity coefficient are shown in Fig. 1

Fig. 1 Determined values of the thermal conductivity coefficient of a single crystal of tungsten

The values obtained are in good linear agreement with the negative temperature coefficient. Sample dispersion is $\pm 2.2\%$.

"Smoothed" values for the conductivity coefficient are shown in Table I. Comparison of the data obtained with the results from other communications can be seen in Fig. 2.

Fig. 2. Comparison of the thermal conductivity coefficient of single crystal of tungsten with results of other investigators.

A shaded area seen here delineates a zone of possible inaccuracy in the present work. Within the latter there is a very close agreement of the present data with those of Osborn[4], Neumark et Voronin[12], Timrot et Peletskij [8].

Each experiment in question was carried on polycrystal tungsten samples with their purity approaching ours (99.9+99.8). In comparing all the data obtained the thermal conductivity of single crystal and polycrystal of tungsten at high temperatures may be practically assumed as equal. Dispersion at granulas boundaries does not exert an essential influence on conductivities.

In Fig. 2 are shown results of technical tungsten thermal conductivity investigations obtained by Filippov and Simonova [11], Gumenyuk and Lebedev [7], Platonov and Fedorov [10]. They markedly differ from each other seemingly due to unconsidered systemic errors which is characteristic for researches using fine wire specimens. Of interest are also data reported by Cutler and Cheney [9] as relevant to single crystal of tungsten. Unfortunately, the lack of information in their work pertinent to the sample composition impedes accurate evaluation of their results obtained on the basis of direct measurements of the thermal and electrical conductivity ratio.

Results of studying specific electrical resistivity are represented in Fig. 3.

Fig. 3. Results of study of specific electrical resistivity of single crystal of tungsten.

A deviation of most experimental points from the average curve does not exceed 1%. In the same figure the present results are being compared with those of other experimenters studying the electrical resistivity of tungsten. The closest agreement is noted for the data reported elsewhere [12], dealing with tungsten with purity 99.95%, maximum disagreement here being 0.6%. A good agreement was observed with the sample data published by Jones [13], Forsythe and Watson [15], where the disagreement noticed was not more than 3%). A marked deviation from the data reported by the majority of workers was noted in early investigations by Forsythe [8] and Tye [14].

The synchronous measurements of the coefficient for the thermal

conductivity and specific electrical resistivity permits the check-up of validity of the Law of Wiedemann-Franz for single crystal tungsten investigations. Table I contains Lorenz' values $L = \frac{\lambda}{\sigma T}$ computed in accordance with the Law.

One cannot escape drawing attention to a marked overweight of experimental values L over the theoretical ones $L_0 = 2.45 \times 10^{-8} \text{ v}^2 / \text{grad}^2$, which is indicative of a notable role of phonon mechanism of the thermal conductivity.

Fig. 4 gives a comparative determination of the values of Lorenz obtained in the present work with those published by others. This shows a good agreement between data concerning both single

Fig. 4. The magnitude of the values of Lorenz for single crystal of tungsten as compared with data of other authors. and polycrystal samples of tungsten, on our part [9], and on other author's part [4] and [11]. The results of the latter group of workers indicate a practical constancy of the values of Lorenz for tungsten within a fairly wide temperature range. The pattern of the curves $L(T)$ as obtained by some investigators [11], [7], [10], [6], in our opinion, will again confirm the deductions, derived from Fig. 2, of existence in the last works systemic uncertainties not considered while measuring the thermal conductivity coefficient.

A general conclusion which may be drawn from the present measurements is expressed as follows: within the limits of realistic uncertainty of the given experiments the transferring properties of single crystal and polycrystal tungsten of the same degree of purity are practically in perfect agreement within the range of high temperatures.

T A B L E I:
Kinetic properties of single crystal tungsten

$T^{\circ}\text{K}$	$\rho \times 10^4 \text{ ohm}\cdot\text{m}$	$\frac{T}{\rho} \cdot \frac{d\rho}{dT}$	$\frac{\rho}{T} \cdot 10^7$ $\text{ohm}\cdot\text{m} (\text{K})^{-1}$	λ $\text{watt}\cdot\text{m}^{-1}(\text{K})^{-1}$	$L \times 10^3$ $\text{V}^2 \cdot \text{grad}^{-2}$
293	5.28		18.03		
1200	30.2	1.35	25.15	115	2.90
1400	37.05	1.305	26.45	113	2.98
1600	43.95	1.257	27.50	110	3.03
1800	50.85	1.222	28.25	108	3.05
2000	57.75	1.196	28.90	105	3.03
2200	64.65	1.175	29.40	103	3.03

ABSTRACT

There has been studied single crystal tungsten having purity 99.98%. The thermal conductivity coefficient was measured by the method of the longitudinal thermal flow in cylindre-shaped specimen whose one butt-end was being heated by electron bombardment. The measurements have been carried out within the 1200-2500°K range. The uncertainty in the measurement of the thermal conductivity coefficient is assumed to be not higher than $\pm 6.1\%$. The specific electrical resistivity was determined within the 1200-2200°K range by the compensation method using direct current. Heating of the sample was realized through electron bombardment. The uncertainty in the measurements of the specific electrical resistivity equalled $\pm 1.5 \pm 2\%$. Every investigation was carried on in vacuum as low as 10^{-5} tor. The results of the studies has been compared with data from the special literature. An important conclusion of a perfect agreement as for the transferring properties of both poly crystal and single crystal tungsten was arrived at.

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Thermal Diffusivity of High Purity Thorium*

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Abstract

The thermal diffusivity and the electrical resistivity have been measured as functions of temperature, between 120 K and 1000 K, for high purity thorium metal. Thermal diffusivity measurements were made using a linear finite rod method. Results are compared with data of other investigators for lower purity samples. Thermal conductivity values calculated using the thermal diffusivity data of this investigation and published specific heat data are compared with low-temperature thermal conductivity data recently reported by other investigators.

Introduction

The first known measurements of the thermal diffusivity of thorium were reported by Sidles and Danielson¹ in 1952 for temperatures between 300 K and 775 K. They subsequently reported values of the thermal diffusivity and the electrical resistivity for temperatures up to 1273 K.² The thermal diffusivity measurements were accomplished using a modified angstrom method.³ The thorium samples were prepared in the Ames Laboratory and were reported to have a purity of 99.85%. Although no other thermal diffusivity data are known to have been published, Marsh and Keeler⁴ have published thermal conductivity results for the range 400-900 K and several other investigators have reported limited investigations of thermal conductivity near room temperature, mostly on early Ames thorium. Recently, Haen and Meaden⁵ and Schettler, Martin, Schmidt and Danielson⁶ reported the results of low temperature thermal conductivity investigations. Griffel and Skochdopole⁷ reported heat capacity data for thorium from room temperature down to 20 K. Wallace⁸ reported specific heat data for high purity thorium from room temperature to 1273 K. The availability of the composite specific heat data from the latter two investigations permits the calculation of thermal conductivity values from thermal diffusivity measurements and thus allows comparison with corresponding published thermal conductivity data.

* Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

All published thermal transport data for thorium reported prior to the work of Schettler, et al, and that of Haen and Meaden appear to be for samples of relatively low purity. This report indicates the results of an investigation of the thermal diffusivity and electrical resistivity of a sample of higher purity thorium with a resistivity ratio, $\rho_{273}/\rho_{4.2}$, of 55.2.

Sample Characterization and Experimental Procedure

The iodide thorium sample used was prepared by the metallurgy section at Ames Laboratory, using the deBoer-vanArkel process⁹ employed in the preparation of the crystal bar thorium samples investigated earlier by Wallace⁸ and by Griffel and Skochdopole⁷. Representative percentage impurities in Ames thorium prepared by this process were discussed by Wallace⁸. The major impurities present are carbon and oxygen at approximately 75 ppm and 58 ppm respectively.

The thermal diffusivity measurements were obtained by the finite-rod pulse-heating method developed and used extensively by Kennedy¹¹, Maycock¹², and others in this laboratory. Platinum and platinum-10% rhodium wires were spot welded to the thorium to provide the thermocouples above room temperature. Below room temperature, copper-constantan thermocouples were substituted.

The electrical resistivity data were determined utilizing a standard four-terminal configuration employing the platinum or the copper thermocouple leads as potential probes. Platinum wires were attached to the ends of the sample to serve as current leads for the resistivity measurements. Measurements of electrical resistivity were made immediately prior to each measurement of thermal diffusivity in order to optimize the reliability of the calculated Lorenz ratios.

Results of Measurements

A comparison of the electrical resistivity of our thorium sample with high purity samples of some other investigators is shown in Fig. 1, which shows the extrapolated residual resistivity at 0 K as a function of the resistivity ratio, $\rho_{273}/\rho_{4.2}$. An attempt to utilize this curve to calculate estimated resistivity ratios for the samples of Wallace and Sidles and Danielson, for which no experimentally determined ratios were reported, reveals that points characterizing their samples fall, in each instance, well above the indicated point for the sample of Haen and Meaden, indicating that resistivity ratios much less than twenty are necessitated for their samples. The linearity of this plot is implied by Matthiessen's rule, under the conditions that $\rho_{4.2} \ll \rho_{273}$ and $\rho_0 = \rho_{4.2}$. The data of Schettler, Martin, et al⁶ indicates that the latter condition is satisfied by thorium samples with resistivity

ratios ranging from 30 to 480.

Fig. 2 shows the electrical resistivity data. The results are consistent with the data of Wallace above room temperature and with the data of Schettler, Martin, et al below room temperature. The resistivity values are slightly higher than those for the Schettler sample with a resistivity ratio of 480, and are lower than those of the Wallace sample with an estimated resistivity ratio of less than twenty.

Fig. 3 shows the diffusivity data. A smooth curve of the results of Sidles and Danielson is shown for comparison. The values of the present investigation lie higher than those of Sidles and Danielson, as is to be expected for a sample of higher purity. The root mean square deviation of the experimental points from the curve shown is about 2.1%. Smoothed values read from this curve were combined with the specific heat data of Griffel and Skochdopole⁷ and of Wallace⁸, shown in Fig. 4, to calculate values of thermal conductivity (as the product of the thermal diffusivity, the specific heat and the density). The constant density value of $11.60 \times 10^3 \text{ kg/m}^3$ reported by Sidles² was used for this calculation. Thus a slight correction due to thermal expansion is ignored for the curves shown.

Fig. 5 shows the calculated thermal conductivities. A curve of the thermal conductivity data of Marsh and Keeler⁴ and a smooth curve of values calculated from the diffusivity data of Sidles and Danielson are shown for comparison. The thermal conductivities calculated from our data are seen to range from 16 to 30% higher than the values calculated from the data reported by Sidles and Danielson for their lower purity sample.

The calculated thermal conductivity is seen to decrease steadily with increasing temperature, contrary to the results of Marsh and Keeler which show an increase with increasing temperature. The considerably higher thermal conductivity which our data predicts below 200 K is reasonably consistent with the thermal conductivity values in the neighborhood of 65 W/m-K at 50 K reported by Schettler, Martin, et al.

Fig. 6 shows the apparent Lorenz ratio, $\frac{\lambda_0}{T}$, calculated from our measured electrical resistivities and the thermal conductivities from Fig. 5. The apparent Lorenz ratio falls from a value approximately 10% higher than the theoretical value of

$$L_o = \frac{\pi^2}{3} (k/e)^2 = 2.45 \times 10^{-8} \text{ V}^2/\text{K}^2$$

at 175 K to a value approximately 12% lower than the theoretical value at 1000 K.

Summary

The data of this investigation for thermal diffusivity and electrical

resistivity of high purity thorium are seen to vary from previously reported values for lower purity thorium in a manner consistent with the decreased impurity scattering expected for a higher purity sample. Further work is progressing on samples with higher resistivity ratios prepared by electro-transport methods¹². It is anticipated that the measurements will be extended to somewhat higher temperatures and that the decrease in apparent Lorenz ratio with temperature will be investigated. Preliminary results indicate slightly higher diffusivities than those reported for the present sample.

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Fig. 1. Comparison of electrical resistivity of the sample with data for samples of some previous investigators.

Fig. 2. Electrical resistivity as a function of temperature.

Fig. 3. Thermal diffusivity as a function of temperature.

Fig. 4. Composite specific heat curve used for calculation of thermal conductivities.

Fig. 5. Calculated thermal conductivity as a function of temperature.

Fig. 6. Apparent Lorenz ratio as a function of temperature.

~~THE RESEARCHING WORKS ON~~ TEMPERATURE DEPENDENCE OF
THERMAL CONDUCTIVITY AND TEMPERATURE CONDUCTIVITY OF
TANTALUM AND NIOBIUM.

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The article deals with the methods of fabrication and chemical composition of experimental specimens tantalum and niobium, obtained by the Method of Powder metallurgy. The illustration of a scheme of unit arrangement for measuring temperature conductivity is given. The quantitative values of temperature dependence of thermal conductivity and temperature conductivity of tantalum and niobium within temperature range of 273 up to 1273°K are also shown.

Tantalum and niobium are considered as the important metals in up-to-date technical progress. By the way no systematical researches of their thermal conductivity and temperature conductivities have been published in literature. O.A. Krajev and A.A. Stelmach were the first who had taken notice of this omission. They have made some researches on temperature conductivity of tantalum and niobium within the range from 1800 up to 3000°K(4). We were left to fill this omission from 20 and higher if possible up to the above-mentioned temperature limits. We showed the design of the unit for measuring the heat and thermal conductivities in the report at the 8th Conference on Thermal Conductivity in the USA(3). The unit for measuring temperature conductivity was described in details in the work.(6). The unit provides for the accuracy of experiment up to $\pm 5\%$. Experimental specimens were fabricated by method of powder metallurgy of electrolytic powders of tantalum and niobium with the following sizes: 100 mm long and $\varnothing 4$ mm for measuring thermal conductivity and 200 mm long and $\varnothing 5$ mm for measuring thermal conductivity. Mouldings of tantalum powder were compressed in dismountable molds under pressure equal to 245 mn/sq.m and 343 mn/sq.m - for niobium. The first sintering was done in the chamber-type vacuum kiln during 5 hours at temperatures equal to 1373°K (niobium) and 1723°K (tantalum) with residual pressure in the kiln equal to $1 \cdot 10^{-3}$ mm of mercury column. The cooling was performed with the help of the kiln. The secondary sintering (welding) of mouldings was done in the vacuum apparatus SKB-7013(8): tantalum was burnt at 2873°K and niobium - at 2623°K during 5 hours in the vacuum $1 \cdot 10^{-5}$ mm of mercury column. A description of welding apparatus design was made. The design slightly differs from well known structures (9).

After welding the mouldings were forged on the rotary engine before obtaining the given diameter. Then the templets were cut for the metal - logarithmic analysis and for samples for chemical analysis.

The chemical composition of experimental specimens is given in table 1.

THE RESEARCHING WORKS ON TEMPERATURE DEPENDENCE OF THERMAL CONDUCTIVITY AND TEMPERATURE CONDUCTIVITY OF TANTALUM AND NIOBIUM.

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Table 1

	Amount of admixtures, %							
	C	Fe	Ti	Si	W	Mo	Nb	Ta
Tantalum	0.002	0.06	0.008	0.003	0.005	0.001	0.5	the rest
Niobium	0.013	0.054	0.014	0.0014	0.017	0.04	the rest	5.0

Note: the content of oxygen, hydrogen, sulphur and phosphorus in specimens was not revealed by chemical analysis.

The measurements of temperature conductivity was carried out by methods of temperature waves with the use of the above-mentioned unit (6). This unit was modernized in its measuring part, consisting of self-recording potentiometer 9MM-09M-1, direct current amplifier, potentiometer MMTB-1 with galvanometer and plenty of position multiple switch of thermocouple (fig 1) (2).

After establishment of stationary state in the whole system, the self-recording device 9MM-09M-1 and d.c. amplifier were switched on. The temperature of the specimen which was examined and of electric furnace was measured with the help of 10 Chromel-Alumel thermocouples. Three of them are differential, soldered joints of which are located on the examined specimen and on the internal surface of unmovable half of the furnace. Differential thermocouples are designed for the registration of temperature variations in the specimen when it is heated with the help of "sinusoid" source of heat. The fourth thermocouple is fixed on the upper end of the examined specimen and controls the dying out of temperature variations in it. The fifth thermocouple measures the temperatures of the second soldered joints of differential thermocouples. The rest five thermocouples serve for registration of temperatures in different points of the furnace, for control of their stability and possible gradient of temperature along the furnace walls. Thermo-e.m.f. these thermocouples is measured by methods of compensation on the potentiometer MMTB-1 (fig. 1). Then selection is made of by-pass resistance for galvanometer of d.c. amplifier. The resistance box R_2 is used as a shunt. The selection of resistance value was done so that the light spot would not go out limits of photocells. Then by means of changing resistance of cathode load of one of lamps of double triode by approximately the medium of scale the carriage of printing device 9MM-09M1 is installed; thermo-e.m.f. is fed from the second differential ther-

Fig.1 Measuring part of the unit: $R_1=0-10\ 000$ ohm (resistance box); $R_2=0-10\ 000$ ohm (resistance box); $r_1=1.8$ kilohm (cathode resistance); $r_2=2.2$ kilohm (alternative cathode resistance); $r_3=3.6$ milliohm (lattice resistance); Φ -photocell CQB -51; YNT -intensification constants current; $\Pi 1, \Pi 2, \Pi 3, \Pi 4$ -- transfer current.

mocouple. The size of recording of amplitude of periodical curve on 3ПН-09М is regulated by the resistance R_1 and R_2 of d-c-amplifier. The use of three-spot self-recording device allows to record the data of all the three differential thermocouples on the specimen. The obtained periodical curves have been worked out by means of practical harmonic analysis by method of 12 ordinates. The results of researching works on temperature dependence of heat conductivity and temperature conductivity are given in table 2.

Table 2

Tantalum			Niobium		
Temperature of experiment OK	Thermal conductivity $\frac{w}{m \cdot degrees \cdot sec}$	Temperature conductivity $\frac{sq. m. 10^4}{sec}$	Temperature of exper. OK	Thermal conductivity $\frac{w}{m \cdot degrees \cdot sec}$	temperature conductivity $\frac{sq. m. 10^4}{sec}$
273	45.2	0.231	273	45.2	0.226
326	45.2	0.232	326	44.8	0.226
373	46.1	0.232	335	47.3	0.226
473	48.2	0.232	367	49.9	0.225
523	47.8	0.233	373	50.3	0.225

Fig.2 Temperature conductivity of tantalum and niobium acc.to the data of different authors: I-tantalum; II-niobium acc.to our experimental data; III-tantalum; IV-niobium acc.to works(4).

1	2	3	4	5	6
573	48.2	0.235	433	53.2	0.220
647	49.4	0.232	443	55.3	0.220
673	49.4	0.230	473	55.7	0.211
723	51.1	0.227	501	55.5	0.211
773	52.0	0.234	524	58.7	0.222
823	53.2	0.234	566	59.5	0.222
873	53.6	0.236	573	59.9	0.222
923	55.7	0.228	601	61.2	0.222
973	57.8	0.230	673	65.8	0.218
1023	58.7	0.23	733	66.2	0.225
1073	61.2	0.238	773	67.0	0.229
1178	63.8	0.240	796	67.9	0.229
1273	67.0	0.240	873	69.5	0.226
			973	72.9	0.228
			1073	75.4	0.230
			1173	79.2	0.23

On the basis of Table 2 conclusion can be made that heat conductivity of tantalum and niobium rises with the increased temperature; the process of heat transfer in tantalum and niobium is conducted both by current carriers and through conductivity of crystal lattice.

The temperature conductivity of tantalum within 300 to 1300°K temperature remains constant and that of niobium slightly grows. Fig.2 illustrates data of other authors in addition to ours. From data of paper(4) it is seen that temperature conductivity factor of niobium and tantalum comes down beginning approximately with 1500°K to melting temperature.

In these investigations took part late kandidat Phys. and Mach. Sc. K.G. Akhmetzyanov.

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N. Pozdnyak

THE THERMAL CONDUCTIVITY OF MINK-2000 THERMAL INSULATION
IN DIFFERENT ENVIRONMENTS TO HIGH TEMPERATURES

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ABSTRACT - A horizontal 200 mm diameter configuration guarded hot plate apparatus has been used for measurements according to ASTM C177-63, of the thermal conductivity of a MINK 2000 material between approximately 300 and 1000K in air, high vacuum and krypton environments. Due care was taken to carry out the tests under temperature conditions such that the possible edge losses from the stack were minimized in accordance with the authors' previous experience in running guarded plate measurements.

On the basis of the results obtained in air on three different samples it is suggested that this material be given possible consideration as a reference material of low thermal conductivity for temperatures well in excess of those for which present low conductivity reference materials can be used.

1. INTRODUCTION

The use of thermal insulations over wide temperature ranges and under varied and sometimes exotic test or environmental conditions has increased extensively in recent years. Most of the materials considered for such insulating purposes are either porous, cellular, fibrous, layered or a combination of these forms. Heat transmission through them, particularly at the higher temperatures, is by a combination of solid and gas conduction, radiation and possibly convection. Under such circumstances it is often a meaningless exercise to compare results of different investigations unless both measurement techniques and exact or similar test conditions have been imposed on the same material - it should really be the same sample.

These factors lead one immediately into the present basic problem concerning thermal conductivity measurements on insulating materials - the existence or otherwise of "reference materials".

The basic guarded hot plate method [1]² has been used successfully for a long time on these materials at or near room temperature. However it is now being used to much higher and lower temperatures and it is by no means certain that the techniques that were advocated and proved correct at 300K will be sufficiently stringent at very different temperature extremes. The present ASTM C177-63 standard is being upgraded on the state of present knowledge. The full facts of the matter will not be

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²Numbers in brackets designate references listed at the end of this paper.

known until a number of workers have measured a material or materials using the basic method coupled with their own varied experimental techniques. Only then will we know that the method is correct and that subsequent comparison of data on other materials by the same or a different method is meaningful.

At the present time it is fair to say that we have three possible low thermal conductivity reference materials with well known reproducible properties. These are a fibrous glass and a corkboard of a given density and a pure gum rubber of a given Federal Specification. The temperature limits of their useful applicability are very limited. Some "round-robin" studies have been made on the corkboard [2] and fibrous glass [3]. The results of these investigations have indicated that even at room temperature, differences in excess of ten percent are present. Since the materials are supposedly reproducible to much closer limits it would appear that results obtained by the basic guarded hot plate method can be subject to errors due to individual techniques. Since it is most likely that measurements at higher temperatures will involve many more problems than those encountered near 300K it becomes imperative that some attempt should be made to find some reproducible material or materials which could be used to check a method or technique.

The main requirements of a reference material are that it should be homogeneous, reproducible, isotropic, not affected by heat treatment and easily obtained. In the realm of high conductivity materials, extensive efforts have been made both historically [4-5] and concertedly [6] to provide such materials. As a result a few metals, alloys, and high density ceramics are available whose thermal properties are known to better than 5% up to 1300K or higher. Similar efforts are required in the more difficult lower conductivity regime. It may prove impossible to find a material whose properties are reproducible to 5%. This should not deter studies since a known reproducibility of say 10% would be a vast improvement on the present unknown value.

One of the reasons for presenting this paper concerns the fact that the author has had the opportunity to study three different samples of a well known commercial insulation over a period of two to three years and found that this material appears to have the attribute of a reference material for temperatures between 300 and 1000K. Data are also presented for the thermal conductivity of the material under different environmental conditions.

11. DETAILS OF MATERIAL STUDIED

The material studied was MINK 2000 in its nominal 320 Kg m^{-3} form. In each case the samples provided were stated to have been purchased through normal commercial means. In fact it so happened that the samples came from sources in the Eastern Seaboard, the West Coast, and the Mid-West regions, respectively, of the United States.

The first programme of work, undertaken on behalf of Westinghouse Electric Corporation under Contract 59-YJM-91488, measurements were required on this material up to approximately 1000K in air, vacuum, and different pressures of krypton gas. Since the material was of a fibrous nature with an apparent layered orientation a short study of possible anisotropy was to be made over a limited temperature range only. For the other two studies measurements were required up to 950 and 1100K respectively in air and vacuum and air only respectively.

In all, six different samples were studied over all or part of the approximate temperature range 200 to 1000K. Details of the respective samples are as follows:

(a) First investigation:- Four pieces of material each approximately 300 mm square and 25 mm thick were provided. All were dried to constant weight prior to any measurements being undertaken. Tests were undertaken on these pieces or from specially prepared samples cut from them.

#1 Two 200mm diameter discs 25 mm thick having a test density of 300 Kg m^{-3} . This pair were used for the main investigation by the guarded hot plate method according to ASTM C177-63 with heat flow in a direction perpendicular to the large surfaces. Prior to being cut a limited study was undertaken to approximately 500K by the heat meter method according to ASTM C518-67 on one of the required slabs.

#2 Twelve strips 300 mm long and 25 mm wide each turned through 90° in order to provide a composite slab 300 mm square and 25 mm thick. This had a test density of 307 Kg m^{-3} and was to be evaluated by the heat meter method with heat flow now in a direction perpendicular to that in #1.

#3 Sample #2 turned through 90° . This was to be used to check the results obtained so that any differences which occurred would be due to sample anisotropy alone and not also to sample configuration.

#4 A 300 mm square 25 mm thick slab having a test density of 309 Kg m^{-3} for measurement by the heat meter method.

(b) Second investigation:-

#5 Two pieces approximately 190 mm diameter and 25 mm thick having a test density of 318 Kg m^{-3} after drying to constant weight. These were to be evaluated by the guarded hot plate method to as high a temperature as could be attained or to breakdown of the material.

(c) Third investigation:-Two pieces of material 205 mm diameter and 12 mm thick. The samples were dried to constant weight and then evaluated by the heat meter method. Following this they were heated for sixteen hours at approximately 1200K, cooled measured by the heat meter method and then by the guarded hot plate method up to a mean temperature of 1100K.

#6 (a)-above pieces prior to heat treatment having a test density of 312 Kg m^{-3}

#6 (b)-above pieces after heat treatment having a test density of 280 Kg m^{-3}

111. EXPERIMENTAL DETAILS

(a) Heat meter method:-The apparatus used was a Dynatech Rapid k Instrument, a commercial type of heat meter apparatus with a special form of heat flow meter based upon a multi-junction thermocouple thermopile using copper/constantan strip material. [7]

In this method the 300 mm square slab, or the 200 mm disc surrounded by a dummy annulus of material of similar thermal conductivity and thickness to form a total sample 300 mm square, is placed under a slight load in series with the calibrated heat flow meter between hot and cold thick blackened aluminum plates. Each plate is controlled at a very steady fixed temperature some 20 to 25 degC apart by means of a combination of an automatically controlled electrical resistance heater and a controlled rate of flow of a fluid through coils in the plate. The heat flow meter consists of a central 150 mm square central metering section containing the thermo-elements wound onto and bonded into a high temperature plastic surrounded by a separate 75 mm annular section of the same thickness of the plastic.

At equilibrium conditions, normally attained within one hour, the temperatures of the hot and cold surfaces of the sample as measured with thermocouples embedded into the surfaces of the plates and heat meter together with the heat meter output are measured with a potentiometer. The thermal conductivity is then obtained using the derived heat flow, the temperature difference and the known dimensions of the sample, the thickness being measured in situ. Measurements were made at three mean temperatures the approximate range 300 to 500K.

The overall accuracy of the method is of the order of $\pm 5\%$ although the reproducibility is better than $\pm 1.5\%$. The heat flow meter is calibrated using a standard fiberglass material and it can be argued that this calibration may not hold for materials having a much different conductivity to that of the reference material. However, in a comparison of materials of similar dimensions and thermal conductivity under the same conditions a comparative accuracy of the same order as the reproducibility can be attained irrespective of the calibration material used.

(b) Guarded hot plate method:-The apparatus used was a horizontal plate laboratory version of the Dynatech TCFG N-20 commercial instrument with the test stack as shown schematically in Figure 1. Details of the modifications made to reduce radial heat losses from this type of configuration of hot plate and thus allow more accurate measurements to be made on low conductivity materials, materials at high temperatures have been described previously [8].

For the purposes of these measurements, very small grooves were cut into the surfaces of each sample with a sharp knife. Insulated fine wire chromel/alumel thermocouples were then fitted tightly into the grooves and cemented into position such that the thermocouple bead was flush with the surface. In this way thermocouples were attached at several places in the central 100 mm diameter section and at appropriate positions in the 50 mm wide guard ring section on each face of each pair of test sample pieces. Additional thermocouples were fixed at the mid-point of the outer edge of each sample.

A flat circular heater consisting of a spiralled pure alumina ceramic core containing coiled resistance wire uniformly wound and consisting of a 100 mm central heater surrounded by a separate 50 mm annular heater section each with separate metal surface plates of a nickel alloy with oxidised blackened surfaces was sandwiched between the two test pieces. Thermocouples were fitted tightly into small grooves cut into the surfaces of the metal plates. A multi-junction differential thermocouple was fitted into the heater unit such that alternate junctions were fixed into the central and annular sections on either side of the 3 mm gap between them. The gap was then packed with a loose filled insulation to reduce radiative heat transfer. The composite stack was then mounted between further layers consisting of an auxiliary heater (a wire wound ceramic core with metal surface plates and thermocouple instrumentation) some insulation and a fluid cooled heat sink. The stack was uniformly loaded and the central section was surrounded by a 420 mm diameter heated cylindrical guard tube with attached thermocouples. A further metal shroud surrounded the whole stack which was then filled with a low conductivity heat insulation powder carefully packed to avoid large air pockets. A glass bell jar covered the system so that it could be evacuated.

A steady temperature distribution was set up in the system by means of adjustment of the d c power to the central heater, the power to the auxiliary and outer cylindrical heaters and the rate of fluid flow through the heat sinks. The power to the guard heater was controlled automatically by the output of the differential thermocouple in the central plate in this way the temperature of the two sections were matched so that radial losses were kept to an absolute minimum. The temperature of the outer cylindrical heater was adjusted to be somewhat above the average temperature of the test sample to reduce the radial losses to ambient and keep the temperature of the edge of the test sample very close to that of the mean temperature of the sample. The temperature drops across each piece of the sample were kept closely similar and varied between 40 deg and 90 deg depending upon the overall mean temperature attained.

At equilibrium conditions the thermal conductivity was obtained in terms of the d c power to the central measuring section of the heater as measured using a precision resistor network and potentiometer, the temperature differences across each piece of the sample and their known dimensions allowance being made for the correct area factor since the samples were uncut.

In the first series of measurements the thermal conductivity was measured in air at regular intervals between 500 and 950K in air. At the highest temperature the pressure in the system was reduced to 2×10^{-4} torr and the thermal conductivity evaluated under these conditions at regular temperature intervals down to 500K. Pure dry krypton gas was bled slowly into the system until the pressure was approximately 0.33 atm. The thermal conductivity was measured at regular temperatures up to 950K. Additional values were obtained at pressures of 0.66 and 1 atm of krypton respectively at the highest temperature. The pressure was reduced once more and measurements taken at a static vacuum of 5×10^{-4} torr. Dry air was introduced slowly into the system and repeat measurements taken at regular intervals on cooling.

For the second investigation measurements were taken in air at regular intervals over the temperature range 400 to 1000K and repeat measurements taken at one temperature on cooling. The apparatus was evacuated to 5×10^{-4} torr and measurements undertaken up to 1100K before thermocouple failure stopped the investigation when trying to attain temperatures of approximately 1300K. On dismantling of the apparatus the material was found to have turned grey in colour and crumbled badly when handled.

In the third investigation measurements were carried out in air between 400 and 1000K and a repeat measurement taken in cooling.

In all measurements by this method it is believed that the accuracy of a sample measurement is $\pm 2\%$ below and $\pm 5\%$ above approximately 500K. The highest uncertainties are in the possible contamination of thermocouples at the higher temperatures and possible non-uniformities of heat flow due to working of the sample and surface plates the temperature increases. Every attempt was made to control the temperatures of the respective surfaces to be well within 0.5C over the whole surface even at the highest temperature attained.

IV. RESULTS

Figure 2 shows the results of the initial measurements undertaken on all the samples by the heat meter method. Because of the possibility of confusion, the experimental points for #5 are not included. However, at all three temperature levels the values obtained were extremely close to those for #1 and the resultant curves are identical in all respects.

The points for #2 and #3 indicate clearly that there is some 25 to 30% anisotropy in the thermal conductivity. It is interesting to note, however, that for the case of #3 where the sample was in the form of strips the values obtained for the $\perp$ direction are similar to those for the other three slab samples. There is some indication that the highest temperature value is higher than those for the slab material but this small difference could be attributed to the difference in sample configuration.

If a mean line is drawn through the collective results for the slab samples, 1, 4, 5, and 6, all experimental points are seen to be within $\pm 2\%$ of the line. If the points for #3 are included the value at the highest temperature measured is still only some 4% from this mean line.

These preliminary measurements would indicate, therefore, that this commercial material would seem to have one of the major attributes of a reference material in that it has a thermal conductivity reproducible to well within $\pm 4\%$ for the density range studied i.e. 280 to 318 Kg m⁻³.

The results for #6 (a) and 6 (b) indicated that the thermal conductivity increased by only 2% due to the influence of the heat treatment although the density changes in this particular case was some 11%. It is recommended, therefore, that in any future measurements on low thermal conductivity insulations the test samples should always be heated to the highest temperature of any study so that such changes be eliminated prior to the actual higher temperature measurements.

The results of the guarded hot plate investigations are shown in Figure 3 and 4 for sample #1 and samples #1, 5, and 6 (b) respectively. Also included in Figure 3 are the results obtained in vacuum on sample #5. They have been included here for comparison purposes although the vacuum levels in the two cases were not identical.

With regard to the results obtained on sample #1 the most significant factor is the really excellent agreement between the results obtained by the two methods used. These would indicate clearly below 500K the accuracy of measurement is within that claimed and would certainly give added confidence to those at the higher temperatures.

The expected large decrease in thermal conductivity is obtained when the gas is eliminated from the pores of the material either completely or by a gas of low thermal conductivity. However, as the temperature increases this difference is seen to diminish somewhat and at 1000K the values in the best vacuum are closely similar to those obtained with the krypton gas replacing the air. No ready explanation is available for the phenomenon which is apparent for both sample #1 and #5. The introduction of the krypton gas clearly has an effectiveness in increasing the thermal resistance of this material equivalent to maintaining it in a vacuum of the order of 10^{-4} torr. Repeat measurements were made at lower temperatures both in vacuum and again in air. The results were very similar to those obtained in the heating runs and thus there was little possibility of thermocouple contamination under these conditions.

Figure 4 contains the results for all three samples evaluated in air under very similar conditions. It can be seen that the results are in very good agreement. Table I contains values of thermal conductivity obtained at regular intervals from a smooth curve drawn through all of the experimental points for the three samples. The maximum deviation of any particular point from this line is 2%. Also included in Table 1 are values for the same material obtained from the manufacturer [9]. These were obtained also by a guarded hot plate method although the configuration and experimental conditions and techniques differed in some respects. The agreement is seen to be very good, only at the highest temperatures do the differences exceed 5%. It is not known how many different samples were evaluated to provide the latter data and therefore an exact comparison should not be made. They are included at this time only to indicate that for one commercial material there is good agreement between results up to the order of 1000K and clearly this material is worthy of further study as to its suitability as a thermal conductivity reference material.

The present material is suggested as a good reference material possibility. Other materials have been studied by the author but for only one sample and thus no reliable indications of applicability for reference material can be obtained. However, in my opinion there are certain candidates among them. These include a foamed glass having a density of the order of 130 to 140 Kg m^{-3} , MIN K 1300 and the so called glass beads having a very definite particle size and hence reproducible packing density. A final suggestion would be a reproducible foamed form of one of the present high density ceramics such as Pyroceram or Zirconia.

It is hoped, therefore, that this investigation will stimulate others interested in the vital area of thermal conductivity measurements into action relating to materials in the approximate thermal conductivity range 2 to $20 \times 10^2 \text{ W m}^{-1} \text{ C}^{-1}$ and that organisers of the future Thermal Conductivity Conferences will devote specific attention to the matter.

V ACKNOWLEDGEMENTS

The author wishes to thank Westinghouse Electric Company for permission to publish the results obtained on sample #1 and Mr. R. Ammon of Westinghouse for various helpful discussions during the course of the investigation. He would like particularly to thank his own colleague Mr. R. W. Hayden who carried out much of the careful experimental work described in the account.

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Table I

Thermal Conductivity of MIN K 2000 Thermal Insulation

Mean Temperature, C	Thermal Conductivity, $10^2 \text{ W m}^{-1} \text{ C}^{-1}$		
	Present Work	Manufacturers Data	Difference %
100	2.8	2.9	-3.5
200	3.02	3.05	-1
300	3.3	3.3	0
400	3.58	3.52	+1.5
500	4.0	3.85	+3.9
600	4.5	4.25	+5.9
650	4.85	4.5	+7.5
700	5.1 *	-	-

* Sample #5 only

Figure 1. Arrangement of the Measurement Section of the Dynatech Guarded Hot Plate Thermal Conductivity Instrument

FIGURE 2. λ OF MIN K 2000 SAMPLES BY HEAT METER

FIGURE 3. λ OF MIN K 2000 IN DIFFERENT ENVIRONMENTS

FIGURE 4. λ OF MIN K 2000: COLLECTED RESULTS IN AIR

THE ELECTRICAL RESISTIVITY AND THERMAL CONDUCTIVITY OF RUTHENIUM

by

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Abstract

In connection with work on the NSRDS-NBS program concerning the thermal conductivity of the elements, the need became apparent for further determinations to be made of the thermal conductivity and electrical resistivity of ruthenium. The thermal conductivity measurements at present available only extend to 592 K, whilst the one set of electrical resistivity determinations made to much higher temperatures (Jaeger and Rosenbohm, Proc. Ned. Akad. v Wetensch., Amsterdam, 44, 144-52, 1941) possess most unusual features which make the data of doubtful value for use in the estimation of thermal conductivity.

The samples used previously for measurements to 592 K (Powell, Tye and Woodman, Proceedings of the Sixth Conference on Thermal Conductivity, 853-64, 1966; J. Less-Common Metals, 12, 1-10, 1967) had included two single crystal rods and a polycrystalline rod each about 10 cm long and 0.65 cm diameter. Both thermal and electrical conductivities of these same samples are now being determined to high temperatures as part of a program supported by the National Science Foundation. The determinations are being made by the direct electrical heating method described at the 1968 Thermal Conductivity Conference.

The present paper deals with the first stage of this investigation and contains electrical resistivity values for these samples to nearly 2000 C. The anomalies which Jaeger and Rosenbohm reported are not confirmed. The thermal conductivity can be expected to decrease smoothly to a value of about $84 \text{ W m}^{-1} \text{ K}^{-1}$ at 2000 K.

I. Introduction

The investigation described in the present paper arose directly from a program of work in hand at the TPRC [1, 2]⁴ on behalf of the National Standard Reference Data System to evaluate most probable values over a wide range of temperature for the thermal conductivity of the elements. Figure 1 contains the experimental data [3, 4, 5] available for the thermal conductivity of ruthenium. These data show ruthenium to be another example of a high melting-point metal for which values have only been measured for about one-fourth of the solid-state temperature range. In a paper on the general progress of this work presented to the Seventh Thermal Conductivity Conference, Powell

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⁴Numbers in brackets designate references listed at the end of this paper.

and Ho [6] included the curve shown by the broken line in Figure 1 as the possible curve for polycrystalline ruthenium and continued this curve to 2000 K. This however was a very tentative prediction for which confirmation was required. It was not included in the subsequent report [7].

The purpose of this paper is to explain why the provisional curve then produced appeared to be much less certain and in greater need of confirmation than other extrapolations made at the same time, for instance, for iridium, osmium and rhodium. The basis of all such predictions to higher temperatures has been the Wiedemann-Franz-Lorenz law, $\lambda = LT\rho^{-1}$, relating thermal conductivity, λ , electrical resistivity, ρ , and absolute temperature, T , with a numerical coefficient, L , which for many metals approximates to the theoretical value of the Lorenz constant, $2.443 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$, but for some of the transition metals may be 20 percent or so greater. With ruthenium, in addition to the uncertainty regarding L , there appeared to be doubt as to the temperature variation of ρ , and the effect of the many reported phase transformations.

At the time of these deliberations, the only available values of ρ extending well above the measurements made by Powell et al. [4], were those of Jaeger and Rosenbohm [8]. These authors had previously made determinations of the specific heat [9] which indicated the occurrence in ruthenium of phase transformations at temperatures of 1035, 1200 and 1500 C, and their electrical measurements were undertaken to substantiate these results.

Jaeger and Rosenbohm [8] tabulate data at 25 C intervals over the range 0 to 1475 C for R_T , the resistance at T , R_T/R_0 , the resistance ratio at T and 0 C and for $(1/R_0) (dR/dT)$, the temperature coefficient of resistance. These values for R_T/R_0 and $(1/R_0) (dR/dT)$ are reproduced in Figure 2⁵. Even at temperatures well below the transformation temperatures indicated in [9], these results show marked departures from the relatively smooth curves that hold for most metals. Their curve for the temperature coefficient of resistance is seen to have a strong maximum at 300 C, a flat minimum from 550 to 700 C, a smaller but broader maximum with a peak at 1100 C and another flat minimum from 1325 to 1375 C.

Figure 3 contains values of the electrical resistivity of ruthenium, as derived from the R_T/R_0 data of Figure 2, on the assumption that $R_0 = \rho_0 = 7 \times 10^{-8} \text{ ohm m}$ in accordance with the approximate value reported for Jaeger and Rosenbohm's specimen [8]. This figure also contains the data of Powell, Tye and Woodman [4] for samples (a), (b) and (c) of Figure 1. Over the limited range of the measurements of [4] the resistivity of each sample had increased almost linearly with increase in temperature, and the very different results of Jaeger and Rosenbohm are considered in need of confirmation. The dotted curve of Figure 1, derived from the resistivity data of Jaeger and Rosenbohm, also appears questionable.

The lack of information on the high temperature electrical resistivity of ruthenium forced the TPRC, when preparing another collection of high-temperature data [10], to reproduce the curve of Jaeger and Rosenbohm despite its doubtful validity.

Following the decision to re-measure the resistivity of ruthenium, a paper by Panteleimonov and Nesterova [5] appeared, which contained the results of measurements made on sintered and cast rods of ruthenium, having densities of 11080 and 12260 kg m^{-3} , respectively. These data, which covered the range 25 to 700 C, are also plotted in Figure 3, and are seen to support the concern about the undulating curve of Jaeger and Rosenbohm.

The three rods originally used by Powell, Tye and Woodman were located and again acquired. The International Nickel Company, Inc., was contacted and kindly agreed that the rods could be used for the proposed further measurements to high temperatures. At first, only electrical resistivity measurements had been envisaged, but the good progress made with the direct electrical heating method [12,13] for high-temperature measurements of thermal conductivity and some other properties indicated that this method in which the determination of electrical resistivity is an essential part could also be applied to these samples.

⁵All the values tabulated by Jaeger and Rosenbohm for $(1/R_0) (dR/dT)$ were too small by a factor of 10 and these have been corrected in Figure 2.

The present paper deals with the electrical resistivity determinations made to 2235 K in the course of this continuing investigation, and contains revised estimates for the thermal conductivity of polycrystalline ruthenium.

II. Sample Details

The three sample rods, designated ruthenium (a), (b) and (c) were originally supplied by Dr. D.W. Rhys of Messrs. International Nickel (Mond) Co., Ltd. They were stated to have been prepared from powder containing the following impurities in parts per million, 300 osmium, 60 iron, 30 nickel and 10 palladium. Each bar was 10 cm in length and about 0.65 cm in diameter. Ruthenium (c) was a polycrystalline bar of uniform diameter prepared from the powder at a pressure of 20 ton per square inch and then sintered in vacuo at 1920 K and hot forged. Its residual resistance ratio ρ_{ice}/ρ_{He} was 388. The density as derived from weighings in air and water was 12240 kg m^{-3} .

Ruthenium (a) had been prepared as a single crystal by electron-bombardment zone melting using an orientated seed crystal to ensure that the axis of the rod was perpendicular to the hexagonal crystal axis. The stated resistance ratio, ρ_{ice}/ρ_{He} , was 94, and the measured density 12380 kg m^{-3} .

Ruthenium (b) was a single crystal similarly prepared but with the axis of the rod parallel to the hexagonal crystal axis. The stated resistance ratio, ρ_{ice}/ρ_{He} , was 76.5, and the measured density 12380 kg m^{-3} .

The above densities can be compared with a value of 12430 kg m^{-3} as calculated from the lattice parameters and atomic weight [11].

It was thought possible that traces of molybdenum and tungsten could have entered the samples during preparation. This may be a partial explanation of the lower residual resistance ratios of the single crystal rods since these have been melted during production. Also, the surfaces of both ruthenium (a) and (b) were slightly undulating and therefore of non-uniform diameter. All three samples had four small, No. 75 Morse, drill holes with depths of from 1 to 4 mm at positions some 1.2, 5.1, 7.0 and 8.9 cm from one end. These were the conditions in which the previous measurements of ρ and of λ had been made at the National Physical Laboratory⁶ over the approximate range 100 to 500 K. The decision was made to make electrical resistance measurements on each sample from room temperature to about 2000 C, and to attempt the thermal conductivity determinations on the polycrystalline rod before making any effort to grind the other rods to a more uniform diameter.

III. EXPERIMENTAL METHODS

Each of the ruthenium samples has been mounted in turn between the electrodes of the multiple-technique direct electrical heating apparatus previously described [12], [13], extension rods of tantalum being bolted to each end to ensure measurements for near isothermal conditions. Two tantalum wires to serve as potential leads were welded to the mid-section of each rod about 2.5 cm apart. The temperatures of this section were obtained from the readings of three Pt/Pt-10% Rh thermocouples also welded to the rod, one in the center and the others a little further from the center than each potential lead.

A tantalum foil composite heater and radiation shield, arranged around the specimen and its extension rods much as shown in Figures 1 and 3 of a recent report [14], served to heat the sample to an increasing series of steady temperatures. At each temperature the electrical resistance was measured by the normal potential drop

⁶Details of the NPL measurements of the effective cross-sectional areas were not given in the earlier publication [4]. These are now given in Appendix 1.

method, observations being made with a DC measuring current of about 4 amp. flowing in both positive and negative directions.

In order to extend the range to temperatures above the thermocouple range, the thermocouples were removed and the ruthenium sample fitted with a clamp-on black body and two clamp-on tantalum voltage probes, much as illustrated in Figure 3 of [14]. Temperatures were then measured by means of an optical pyrometer (Photomatic Model A-3 of the Pyrometer Instrument Co.) when sighted through small apertures in the heater and its shield and into the black-body hole.

The appropriate ratio of area, A, to length, L, to use with the clamp-on voltage probes was derived by intercomparison of the resistance values obtained in the 1200 to 1600 K region during the two stages of the experiment, L having been determined by means of a traveling microscope when the leads were spot welded to the sample. Room temperature values of A/L were therefore used, and no allowance is made at this time for any dimensional changes with temperature.

IV. RESULTS AND DISCUSSION

Figure 4 contains a plot of the electrical resistivity values obtained for the polycrystalline sample (ruthenium c) for the low temperature range by Powell et al. [4] and from room temperature to 2270 K in the present work. To assist in comparing these new values with those of Figure 3, the curves of Jaeger and Rosenbohm [8] and of Panteleimonov and Nesterova [5] for their cast sample are also included in Figure 4.

Good agreement is apparent over their short common temperature range between the present results and the earlier measurements on the same specimen. The new measurements increase almost linearly with temperature to about 950 K, above which the temperature coefficient tends to become slightly greater. No deviations of the kind reported by Jaeger and Rosenbohm are apparent, and from about 1100 to 1500 K the two sets of data lie on curves that are almost parallel, the new data being lower by about 7×10^{-8} ohm m, or 10 to 18 percent. The Russian data are in fair agreement near room temperature but become increasingly lower with increase in temperature, to be almost 25 percent below the present value at 950 K. Indeed this lower curve of Panteleimonov and Nesterova is in closer agreement with the curve which we have obtained for ruthenium (b), the single crystal sample for which measurements were made parallel to the axis.

The preliminary results obtained for the two single crystal samples are plotted in Figure 5. Here again the new measurements are seen to link on well with those of Powell, Tye and Woodman. Thus a problem, which emerged at the time of the earlier measurements, still persists. This relates to the similarity between the values obtained for samples (a) and (c). The insert of Figure 2 shows the curve for (c) to be slightly lower at low temperatures. At 1500 K the curve for (c) is higher than that for (a) but only by about 13 parts in 4500.

The close agreement between the curves for the perpendicular direction and for the polycrystal is not expected, and an explanation for this has yet to be found. The NPL determinations of effective areas of the non-uniform samples (see Appendix 1) led to values of 0.332 and 0.359 cm² being used for samples (a) and (b); the corresponding values used when evaluating the present data have been 0.332 and 0.363 cm². These values are subject to change when more careful determinations have been made. Also, it seems desirable for all three samples to be examined by X-rays to confirm the stated information about the single crystals and to ascertain the extent and nature of any preferred orientation that might be present in the polycrystalline sample.

The values obtained for the polycrystalline sample have much less uncertainty about the true cross-sectional area. All experimental observations lie within about ± 1 percent of a smooth curve. The equation for 120 points was found by least squares to be, with no allowance for dimensional changes with temperature,

$$\rho = -6.805 \times 10^{-9} + 2.6984 \times 10^{-10} T + 2.4727 \times 10^{-14} T^2$$

No deviations appear which confirm any of the phase transformations suggested by Jaeger and Robenbohm [8] as occurring at 1035, 1190 and about 1500 C (1308, 1463 and about 1773 K), nor the additional "anomaly" found by them in the range 301-312 C (574-585 K), and believed at that time, to be analogous to one found for iron between 150 and 200 C. This absence of phase transformations between the melting point and room temperature, is in accord with the deduction made by Rhys [11], based on the retention to room temperature of single crystals formed from the molten metal.

Reverting now to a further consideration of the thermal conductivity of polycrystalline ruthenium, the same uncertainty holds regarding the close agreement between the polycrystalline and the single crystal (perpendicular) data of Figure 1. The broken curve of that figure was derived on the assumption that the polycrystalline values were low by nearly 10 percent. At 400 K, a value of $110 \text{ W m}^{-1} \text{ K}^{-1}$ is within ± 5 percent of these two curves and, with the present electrical resistivity, yields a Lorenz function of $2.9 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$. Assuming that much the same decrease in L occurs for ruthenium or has been observed for tantalum [14] and for tungsten [13] suggests values of 2.76, 2.74 and $2.63 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$ at 1000, 1500 and 2000 K respectively. Using these values of L and the present electrical resistivity values for polycrystalline ruthenium confirms that the thermal conductivity can be expected to decrease smoothly from room temperature and to have values of 96, 91 and $84 \text{ W m}^{-1} \text{ K}^{-1}$ for temperatures of 1000, 1500 and 2000 K. This value at 2000 K is about 13 percent greater than the original prediction [6]. It is hoped that the present investigation will shortly be providing experimental data to temperatures of this order.

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APPENDIX 1

ORIGINAL MEASUREMENTS [4] OF EFFECTIVE AREA OF RUTHENIUM (a) and (b)⁷

The effective diameters of the single crystal samples (a) and (b) were obtained by three methods, (1) micrometers, both with normal and with pointed anvils, (2) by a displacement method where the rod was suspended vertically from a balance arm and the difference in mass measured when the lower end of the rod was immersed in water, first to the lower thermocouple hole and secondly to the upper hole; differences in height were determined with a cathetometer; (3) electrical resistance measurements with various knife-edge separations which included a length for which (1) indicated a relatively uniform diameter.

The results are given below, d being diameter (cm) and A the area (cm²).

Sample	Method 1		Method 2	Method 3
	d	A	A	A
(a)	0.65	0.332	0.334	0.330
(b)	0.68	0.363	0.354	0.359

The areas given are mean values between the extreme thermocouple holes. The actual areas used in the calculations of thermal and electrical conductivity [4] were 0.332 and 0.359 cm² for samples (a) and (b) respectively.

⁷The authors are indebted to Mr. M. J. Hickman (National Physical Laboratory) for this information, which was extracted from the original note book.

Fig. 1. Thermal Conductivity of Ruthenium

Fig. 2. Data of Jaeger and Rosenbohm (1941) for Ruthenium: Resistance Ratio, $\frac{R_{TC}}{R_{OC}}$, (continuous line) and Temperature Coefficient of Resistance, $\frac{1}{R_{OC}} \frac{dR}{dT}$ (broken line).

Fig. 3. Electrical Resistivity of Ruthenium

Fig. 4. Electrical Resistivity of Polycrystalline Ruthenium

Fig. 5. Electrical Resistivity of Single Crystal Ruthenium

Graphite

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THE THERMAL CONDUCTIVITY OF ATJ GRAPHITES 1,2

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ABSTRACT

Thermal conductivity measurements have been made by a variety of tandem and overlapping techniques on four formulations of ATJ graphite at General Electric Re-Entry and Environmental Systems during the past three years in support of increasingly closer scrutiny of high performance graphite nosetip thermostructural designs. The mechanical and thermal effects of variations in such process specifications as density, alkali and alkaline earth content has and is currently being examined on closely controlled billets of this well known premium grade graphite.

The four variations are the familiar commercial grade ATJ (1.72 gm/cc), "purified" ATJ-P (1.69, 1.72 and 1.79 gm/cc), ATJ-S (1.83 gm/cc) and ATJ-SP (1.82-1.84 gm/cc).

Measurements to 700°C were performed in both grain directions using a cut-bar comparator. With-grain measurements to 2200°C were made by radial out-flow. The thermal conductivity was found to be a straightforward, increasing function of density with no detectable effect due to the purification process.

Also included are a set of measurements made to determine the maximum in the ATJ thermal conductivity curve in the vicinity of 0°C, electrical resistivity measurements at room temperature, calibration results on CEP and RVD grade graphites and a discussion of the effects of carbonaceous samples on the tungsten heaters used for the radial flow measurements.

1. This work was partially sponsored by SAMSO, U. S. Air Force.
2. A portion of this paper was presented orally at the 8th Thermal Conductivity Conference and a preliminary abstract was published in the conference proceedings.

X THERMAL DIFFUSIVITY OF ATJ-S GRAPHITE

FROM 100° TO 3000°K

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ABSTRACT - The thermal diffusivity of a molded graphite, ATJ-S, was measured in the with-grain and across-grain directions from 100° to 3000°K by the laser flash technique. A neodymium glass laser system supplied the thermal energy pulse; thermocouples or a photomultiplier tube detected the transient time-temperature response of thin samples. The thermal diffusivity values, corrected for heat losses and finite pulse time, were fitted to an equation in reciprocal temperature by a least squares technique. Repeated measurements on duplicate samples demonstrated a precision of $\pm 4\%$. Accuracy was estimated at $\pm 7\%$ by comparison with published thermal diffusivity measurements on Armco iron.

KEY WORDS - Thermal diffusivity, thermal expansion, heat capacity, thermal conductivity, Armco iron, ATJ-S graphite, laser flash, equations for thermal diffusivity.

I. INTRODUCTION

The advanced nuclear rocket motors developed at Los Alamos Scientific Laboratory utilize graphite because of its excellent mechanical and thermal properties over a large range of temperature. Calculation of thermal stresses and heat transfer rates in graphitic fuel elements and reactor structures requires accurate values for the thermal conductivity, thermal diffusivity, thermal expansion and heat capacity. Since most graphite is anisotropic, variations in these parameters with respect to structural orientation must be measured.

This paper describes the measurement of the thermal diffusivity parallel and perpendicular to the pressing direction of a hot pressed, fine-grain graphite³, ATJ-S, from 100° to 3000°K. The laser flash technique, previously used to measure the thermal diffusivity of SX-5 graphite [1]⁴, was refined to include measurements from cryogenic temperatures, i.e., liquid nitrogen, to over 3000°K. The experimental precision is enhanced by smoothing the data from scores of measurements by a least squares technique. The laser flash technique is standardized by comparison of data produced from measurements on an Armco iron standard with those published by other investigators.

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³ Manufactured by Union Carbide Corporation

⁴ Numbers in brackets designate references listed at the end of this paper

Parker et al [2] proposed the pulse method for measurement of the thermal diffusivity of small samples rapidly and precisely. Essentially, the method consists of applying an instantaneous heat pulse to one side of a thin disc and recording the time-temperature response of the opposite side. The heat flow through the sample is described by the general Fourier equation for cylindrical coordinates with no internal heat generation:

$$\Delta^2 T(x, r, t) = \alpha^{-1} \frac{\partial T(x, r, t)}{\partial t} \quad (1)$$

The authors [2] made several simplifying assumptions in their analytical solution of the general equation. These include 1) heat flow is one dimensional, 2) the heat pulse is absorbed instantaneously in an infinitesimally thin layer on the sample face, and 3) there are no heat losses by conduction or radiation from the sample faces. These assumptions yield a simple solution of (1):

$$\alpha = \frac{0.139 \ell^2}{t_{\frac{1}{2}}} \quad (2)$$

where α is the thermal diffusivity (cm²/sec), ℓ is the sample thickness (cm), and $t_{\frac{1}{2}}$ is the time required for the back face temperature to reach one-half its maximum value (sec).

The above equation has been used to calculate the thermal diffusivity of Armco iron by G. L. Denman [3], R. E. Taylor [4], and R. A. diNovi [5], the thermal diffusivity of ZTA and SX-5 graphite by P. Wagner [6,7], the thermal diffusivity of BeO by R. J. Freeman [8], and the thermal diffusivity of UO₂ by C. Ferro et al [9].

Cape and Lehman [10] solved the general heat equation for heat loss from the sample and predicted temperature vs. time plots of these general shapes:

The thermal diffusivity is then defined by:

$$\alpha = \frac{\omega_{1/2} t^2}{t_{1/2}} \quad (3)$$

where the constant, 0.139, in eq. (2) has been replaced by the parameter, $\omega_{1/2}$, which is a function of the heat loss. Cowan [11] has published a graph which delineates this parameter:

Since the ordinate and abscissa are difficult to interpolate precisely from this graph, the original computer output data were obtained from Dr. Cowan and are listed in Table I.

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Figure 11. Thermal Expansion of ATJ-S Graphite

Figure 12. Specific Heat of Graphite

IV. DISCUSSION

Our techniques and equipment measured the thermal diffusivity of Armco iron with a precision of $\pm 3\%$ and an agreement of $\pm 2\%$ with other published values over a 350° to 900°K temperature interval. Agreement at values below 350°K is difficult to assess because of a lack of other experimental values. The thermal diffusivity of ATJ-S graphite as measured over the 350° to 900°K range was assumed to have a precision and accuracy equivalent to that demonstrated on Armco iron.

The thermal diffusivity of ATJ-S graphite must be converted to thermal conductivity via eq. 4 to permit comparisons with other published values. Tables III and IV were prepared using LASL diffusivity and density data and Spence's specific heat values. The thermal conductivities in the AG and WG directions are calculated in three of the more common units at intervals from 100° to 3000°K . Our calculated thermal conductivities as well as the UCC [13] values are plotted on Figure 13. The agreement is about $\pm 5\%$ over the 500° to 1300°K interval. At higher temperatures, the values agree poorly.

The UCC values of thermal conductivity of ATJ-S show apparent minima at $\sim 2500^\circ\text{K}$ in Figure 13. This anomaly does not appear in values for ATJ as shown as

Table III
Calculated Thermal Conductivity of ATJ-S Graphite
(AG) Heat Flow Perpendicular to Pressing Direction

Temperature $^\circ\text{K}$	Specific Heat, C_p $\frac{\text{J}}{\text{kg K}}$ (1)	Thermal Diffusivity α ($10^{-4} \frac{\text{m}^2}{\text{sec}}$)	Density ρ ($10^3 \frac{\text{kg}}{\text{m}^3}$)	Thermal Conductivity		
				λ_1	λ_2	λ_3
				W m K	Cal sec cm K	BTU hr ft F
100	140	2.32	1.822	59.2	0.141	34.2
150	269	1.91	1.821	93.5	.223	54.1
200	416	1.50	1.820	114	.271	65.7
250	568	1.18	1.820	122	.291	70.4
300	721	.944	1.820	124	.296	71.6
400	1025	.603	1.819	112	.269	65.0
500	1268	.439	1.817	101	.242	58.4
700	1548	.282	1.810	79.0	.189	45.7
1000	1760	.186	1.806	59.2	.141	34.2
1300	1890	.142	1.800	48.3	.115	27.9
1600	1980	.117	1.793	41.6	.0994	24.0
2000	2075	.0968	1.780	35.8	.0854	20.7
2400	2138	.0844	1.772	32.0	.0764	18.5
2600	2160	.0798	1.760	30.3	.0724	17.5
3000	2205	.0726	1.750	28.0	.0669	16.2

$$\lambda_1 = C_p \alpha \rho$$

$$\lambda_2 = 0.002389 \lambda_1$$

$$\lambda_3 = 0.5779 \lambda_1 = 241.9 \lambda_2$$

(1) Reference 14

Figure 13. Thermal Conductivities of ATJ-S Graphite

Figure 14. Thermal Conductivities of ATJ-S and ATJ Graphite

Table IV

Calculated Thermal Conductivity of ATJ-S Graphite
(WG) Heat Flow Perpendicular to Pressing Direction

Temperature °K	Specific Heat, Cp $\frac{\text{J}}{\text{kg K}}$ (1)	Thermal Diffusivity $\alpha (10^{-4} \frac{\text{m}^2}{\text{sec}})$	Density $\rho (10^3 \frac{\text{kg}}{\text{m}^3})$	Thermal Conductivity		
				λ_1	λ_2	λ_3
				$\frac{\text{W}}{\text{m K}}$	$\frac{\text{Cal}}{\text{sec cm K}}$	$\frac{\text{BTU}}{\text{hr ft F}}$
100	140	2.74	1.822	69.9	0.167	40.4
150	269	2.35	1.821	115.1	.275	66.5
200	416	1.85	1.820	140.1	.335	81.0
250	568	1.45	1.820	149.8	.358	86.6
300	721	1.14	1.820	149.6	.357	86.4
400	1025	.738	1.819	137.6	.329	79.5
500	1268	.538	1.817	124.0	.296	71.6
700	1548	.347	1.810	97.2	.232	56.2
1000	1760	.229	1.806	72.8	.174	42.1
1300	1890	.175	1.800	59.6	.142	34.4
1600	1980	.145	1.793	51.6	.123	29.8
2000	2075	.120	1.780	44.3	.106	25.6
2400	2138	.105	1.772	39.7	.0950	23.0
2600	2160	.0989	1.760	37.6	.0898	21.7
3000	2205	.0901	1.750	34.8	.0831	20.1

$$\lambda_1 = C_p \alpha \rho \quad \lambda_2 = 0.002389 \lambda_1 \quad \lambda_3 = 0.5779 \lambda_1 = 241.9 \lambda_2$$

(1) Reference 14

TPRC recommended thermal conductivity of graphites [19]. The TPRC conductivities have a continuous negative slope to the sublimation point of carbon. The thermal conductivity of ATJ-S graphite as calculated from our measured thermal diffusivities is consistently higher than that of ATJ graphite (Fig. 14).

In conclusion, the laser flash technique for measuring thermal diffusivity is capable of determining thermal anisotropy in ATJ-S graphite over the 100° to 3000°K temperature interval. The apparatus was standardized on the available standard, Armco iron, over a limited temperature range. The method is adaptable to small samples in various atmospheres, requires relatively simple equipment, is fairly rapid, and uses an uncomplicated mathematical formulation.

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X THE THERMAL CONDUCTIVITY OF
PYRO-CARB 406: A CARBON-
CARBON COMPOSITE*

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ABSTRACT

A series of measurements to determine the density and microstructure dependent anisotropic thermal conductivity of Pyro-Carb 406 carbon-carbon composite is described. Initial characterization by comparator measurements on flat plates established the thermal conductivity levels and the degree of anisotropy at temperatures from 300°K to 600°K. The GE transient thermal conductivity technique was then applied to determination of the across-lamina conductivity at temperatures up to 2200°K. The computer-coded data analysis of this technique also yielded the intrinsic density dependence of the conductivity for actual heatshield hardware--a critical aspect for the material's successful application.

The with-lamina (fill and warp direction) thermal conductivity was found to be an even more sensitive function of the varying microstructure through the Pyro-Carb wall thickness. To resolve this small scale variation of the with-lamina conductivity, a miniature cut-bar comparator was designed and constructed to take a 3/16-inch diameter sample. These measurements to 900°K were then complemented by the transient techniques which were used for measurements to 1900°K.

An anisotropy of 3:2:1 was shown for Pyro-Carb 406 Warp: Fill: Across-Lamina thermal conductivity, with a moderate positive slope in the temperature dependence.

The high density pyrolytic surface case material was found to have a processing-sensitive 1/T temperature dependence.

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I. INTRODUCTION: THE APOLLO/ SNAP-27 REACTOR GLFC HEAT SHIELD

According to current NASA plans, the second Apollo mission to land on the lunar surface will carry the Apollo Lunar Surface Experiment Package. The power supply, which will be left on the surface, is the SNAP-27 system, a radioisotope thermoelectric generator which utilizes plutonium 238 fuel as a heat source and is rated at 63.5 watts of electric power for one year of operation. The 15-pound fuel capsule is carried on the lunar module (LM) in the Graphite Lunar Module Fuel Cask (GLFC) (Figure 1). The graphite cask consists of an 8-inch OD Pyro-Carb 406 cylinder, 0.35-inch thick, which is attached to the plutonium fuel capsule by an internal titanium latch fitting (Figure 2). Two hemispherical Pyro-Carb end caps, having a minimum thickness of 0.70 inch, are attached to the cylinder by a breech lock. One of these is to be removed by an astronaut on the lunar surface in order to remove the fuel capsule from the GLFC and place it into the separately carried thermoelectric generator.

The GLFC is a self-contained reentry vehicle having omnidirectional reentry capability which must carry the radioactive fuel core intact to the earth's surface in the event of Apollo mission abort-whether during launch stage, earth orbit or failure to achieve the translunar stage. An internal, secondary beryllium thermal shield is required, primarily to prevent melting of the capsule from heat radiated by the primary graphite heat shield. The primary thermal shield requires a graphite material because of the relatively high ambient temperature (700°K - 800°K) resulting from continuous heating by the decaying radioactive fuel, and because of the high surface temperatures reached in the event of worst-case superorbital re-entry at a relatively steep angle. The re-entry of the GLFC under these conditions has been discussed by Kahn and Dohner of General Electric in an AIAA paper (Reference 1). As shown in Figure 3 (taken from their paper) temperatures above 3300°K (5900°R) were predicted in the outer portions of the cask, which would then be under compression, while inner wall temperature would be at relatively low temperatures (e.g., 1500°K). Consequently, fracture of the GLFC due to thermal stress was of concern to the Snap-27 program.

The overall comprehensive analytical and testing program conducted by the Isotope Power Systems Operation and the Aeromechanics and Materials Laboratory Operation of the General Electric Company, and by the Sandia Corporation, has been described at the recent Ninth Carbon Conference by Dr. E. Stover, et al., of GE (Reference 2). The purpose of this paper is to discuss in detail the thermal conductivity characterization of Pyro-Carb 406 as this material evolved in its application to the GLFC.

Figure 1. Attachment of the GLFC to LM

Figure 2. Graphite Lunar Fuel Cask
(Cutaway View Showing Primary Components)

II. THE MATERIAL CHARACTERISTICS OF PYRO-CARB 406

Initial consideration was given to manufacturing the cask from a variety of graphites and carbon composites; these included coke-based graphites and pyrolytic graphite (which were discarded because of the problems of fabricating the required shapes), and such considerations as thermal protection, and, especially, brittleness. In addition to mechanical handling, the cask is required to satisfactorily contain the radioactive plutonium fuel core throughout earth impact after re-entry.

The material considered most likely to provide the necessary properties, as well as manufacturing feasibility within the schedule requirements, was a pyrolyzed carbon phenolic laminate, infiltrated with pyrolytic carbon (termed "Pyro-Carb 406" by the manufacturer, HITCO, Gardena, California), and described as follows (Reference 3).

The material is composed of square-weave rayon cloth that is "graphitized" to 99.5 percent minimum carbon assay. It is impregnated with a phenyl aldehyde, carbonaceous filled resin (USP-39), which yields a 45-50 percent char. The impregnated system has a nominal 33 percent by weight of resin. This impregnated cloth is laid-up, molded and cured under pressure, and heated in stages to an ultimate temperature of 2500°K for 3 hours. The product is then machined to shape and exposed to an atmosphere containing methane at reduced pressure for 300 hours at 1400°K.

This last process of carbon vapor deposition (CVD) creates a graded density "case" of pyrolytic carbon, falling off in density from the deposition surface toward the central "core" of lower density material. A typical density gradient is shown in Figure 4. Both the increased density and the superimposed pyrolytic/amorphous character of this gradient region provide a higher thermal shock resistance in the surface layers of material by virtue of the higher thermal conductivity and mechanical strength. However, the small spatial scale of less than 1/10 of an inch over which this CVD gradient occurs makes effective measurement resolution of this thermal conductivity variation very difficult or impossible by conventional techniques. The internal core of lower density, more amorphous material provides thermal insulation and the considerable advantage of lower weight for the GLFC.

NOTE

1. EARTH ORBITAL DECAY REFERENCE CASE
2. STAGNATION LINE TEMPERATURES FOR ORIENTED, SIDE-ON HEATING

Figure 3. Temperature Response of GLFC

Figure 4. Typical Through-the-Thickness Density Gradient of Pyro-Carb GLFC

Pyro-Carb may be considered an orthotropic carbon-carbon composite material having three distinct orientations: the across-lamina direction between the cloth plies (c), the warp direction (a), which corresponds to the axial direction of the cask and the fill direction (b), corresponding to the circumferential direction of the cask. The warp and filled directions are found to be distinct even in the woven cloth. Photomicrographic inspection (Figure 5) reveals that the warp fibers are relatively straight, while the fill fibers travel in a sinusoidal pattern over and under the warps. The continuity of the fibers suggests a higher mechanical strength and thermal conductivity compared to the across-lamina properties, while the crimp and increased length of the thermal conduction path along the fill direction suggest a lower strength and thermal transport than along all warp direction. It will be seen that a nominal 3:2:1 thermal conductivity anisotropy was detected for the warp: fill: across-lamina directions.

In the development and characterization of the GLFC, the significance of these structural, density, and size effects was gradually determined; i. e. , the body of "characterization" information given above was most definitely not known. The Snap-27 program of thermal conductivity measurements and deduction of the nature of the thermal transport in the Pyro-Carb 406 GLFC heat shield are described in the following pages, in historical progression to show both the complete (or adequate) set of design data and its development from the simple early flat plate material to the final 3-D graded density composite shell. This development will be more easily understood, and perhaps anticipated by the reader, with foreknowledge of the structural characterization.

Figure 5. Photomicrographs of Pyro-Carb

III. THERMAL CONDUCTIVITY MEASUREMENTS

1. C-Directional, Across-Lamina Measurements

Three separate techniques, overlapping in temperature range and sampling, have been employed to make the thermal conductivity measurements reported here. The characteristics of the three are outlined below:

Technique	Temperature Range (°K)	Nominal Tolerance (%)	Comment
TC-1000 Comparator (Dyatech)	150 to 700	± 5 to ± 10 %	Axial heat flow through thickness of 2-1/2-inch square, 3/16-inch to 3/4-inch plate, isothermal metal guard.
Miniature Module Comparator (GE/RES construction)	300 to 1300	± 10 %	Axial heat flow through thickness of 1/2-inch diameter, 1/8-inch to 1/4-inch thick tablet, individually adjusted guard rings.
GE Transient Technique	700 to 2700	± 10 to 20 %	High, step heat flux down axis of 1/2-inch diameter model; transient temperature response reduced via computer code with input of low temperature conductivity, density, and specific heat values to give high temperature λ .

In the first two steady state techniques, a sample of material is placed between "heat meters," plates whose thermal conductivity is well known and stable. By continuity of the heat flow $\dot{Q}$ through this stack, the simple equation follows:

$$\dot{Q} \text{ (top heat meter)} = \dot{Q} \text{ (sample)} = \dot{Q} \text{ (bottom H.M.)}$$

$$= \left[\lambda_{HM} \frac{\Delta T_{HM}}{\Delta x_{HM}} \right]_{\text{Top}} \text{ Area} = \left[\lambda_s \frac{\Delta T_s}{\Delta x_s} \right]_{\text{Sample}} A = \left[\lambda_{HM} \frac{\Delta T_{HM}}{\Delta x_{HM}} \right]_{\text{Bottom}} A$$

$$\lambda_s = \bar{\lambda}_{HM} \frac{\bar{\Delta T}_{HM}}{\Delta T_s} \frac{\Delta x_s}{\Delta x_{HM}}$$

where:

λ_s = the thermal conductivity of the sample

$\bar{\lambda}_{HM}$ = the average thermal conductivity of the heat meters

$\overline{\Delta T}_{HM}$ = the average of temperature drops across the two heat meters

ΔT_s = the temperature drop across the sample

Δx = the relevant thickness

The results of these techniques have been applied with high confidence over the past five years to GE RESD heat shield material studies. With this experience, techniques have been developed which guarantee the ± 10 percent tolerance placed on most generated data. This tolerance designation encompasses both the concepts of precision (scatter) and accuracy (closeness to the true value). The precision of a series of measurements may be quantitatively indicated by such statistical measures as standard deviation, but this statistical concept really has little meaning for three data points on a sample material over a full range of test conditions. Similarly, the accuracy can be measured by running a standard material, certified to within about 2 percent by NBS, using optimum test conditions. Our tolerance is substantiated by measurement runs on such standards. The results of these runs show a grouping of our data points about the value, with a maximum deviation of 6 percent and no really significant systematic error (Reference 4). The departure of most samples from the more ideal conditions of this calibration cause us to enlarge the nominal tolerance band on our measurements to ± 10 percent, enveloping both considerations of precision and accuracy.

The thermal conductivities of six density variations of Pyro-Carb plates were measured early in this program, using the TC-1000 Comparator; the results are given in Figure 6 for temperatures up to about 600°K, with bulk density ($\bar{\rho}$) as a parameter. This bulk density can be defined as a function of the point-to-point density $\rho(x)$, through the thickness:

$$\bar{\rho} = \frac{1}{\Delta x} \int_0^{\Delta x} \rho(x) dx$$

The results are cross-plotted in Figure 7, which shows thermal conductivity as a function of the bulk densities for constant temperatures of 311°, 422°, and 588°K. The impact of

Figure 6. Comparator Measurements of Pyro-Carb Plate Thermal Conductivity

Figure 7. Thermal Conductivity of Pyro-Carb as a Function of Density, Low Temperature Steady-State Measurements

these measurements was to show the sharp dependence of Pyro-Carb thermal conductivity on the density, as influenced by the varying degree of diffusion of pyrolytic graphite formation during the pyrolyzing process used by Hitco. The inset schematic in Figure 7 shows the nature of the density gradient caused by this process for a typical 0.7-inch thick plate. Then the measurements shown in Figures 6 and 7 represent some average of the point-to-point thermal conductivity function in the depth of the material. The nature of this average can be seen by considering the "series" heat conduction through a composite slab (Reference 5).

$$\frac{\dot{Q}}{\text{unit area}} = - \frac{T_1 - T_2}{\frac{\Delta x_1}{\lambda_1} + \frac{\Delta x_2}{\lambda_2}} = - \bar{\lambda}_{\text{composite}} \frac{T_1 - T_2}{\Delta x_1 + \Delta x_2}$$

$$\therefore \bar{\lambda}_{\text{composite}} = \frac{\sum_i \Delta x_i}{\sum_i \frac{\Delta x_i}{\lambda_i}}$$

This may be generalized for our purposes to relate the point-to-point density dependent thermal conductivity function to that measured by the steady state techniques:

$$\bar{\lambda}_{\text{measured}} = \frac{\Delta x}{\int_0^{\Delta x} \frac{dx}{\lambda(x)}}$$

Study of this integral or of the previous discrete composite result shows that the measured result will be weighted toward the low conductivity values. Thus our measurements, conceptually, should form the lower bound of the probable values.

The obvious experimental refinement would be to slice off small thicknesses (Δx) of these slabs, approaching a homogeneous density. However, the high level of the Pyro-Carb conductivity function produces such a small ΔT that the steady flow measurement technique's accuracy begins to suffer for thicknesses smaller than 3/8 inch. Although the "skewness" of the measurement is believed by this laboratory to be well within the tolerance of the technique itself, some advantage of this insight is taken below in arriving at a final recommended across-lamina thermal conductivity function.

2. High Temperature, Transient Measurements

The GE Transient Thermal Conductivity Technique was used to extend these measurements to high temperature. This technique, described thoroughly in Reference 6, takes the rapid transient response of a suitably instrumented model of a material (Figure 8) and, through a computer-coded numerical solution, solves the one-dimensional heat conduction equation for thermal conductivity:

$$\rho C_p \frac{dT}{dt} = \lambda(T) \frac{d^2 T}{dx^2} + \frac{d\lambda(T)}{dT} \left(\frac{dT}{dx} \right)^2$$

The technique takes the in-depth material response at a specific time, at six suitably spaced thermocouple sensing positions, and converts this second order differential equation in T into a first order equation in $\lambda(T)$.

$$\frac{d\lambda(T)}{dT} + a_1 \lambda(T) = a_2 \quad \text{where:} \quad a_1 = \left[\frac{\frac{d^2 T}{dx^2}}{\left(\frac{dT}{dx} \right)^2} \right]$$

$$a_2 = \left[\rho C_p \frac{dT}{dt} \right] \left(\frac{dT}{dx} \right)^2$$

The terms needed for solution of this differential equation are the coefficients a_1 and a_2 , computed from the transient response, and density and specific heat data. One additional input is required. Because this is a first order differential equation, one boundary or "initial" value of λ , termed λ_0 , is needed. This λ_0 is necessarily provided by the lower temperature, steady-state measurements.

The reduced, end product of a successful transient thermal conductivity determination is a printed-out λ versus T function for a model of material at the specific time considered--the technique "back-computes" the $\lambda(T)$ required to "allow" that temperature distribution and response. Two outstanding aspects of these transient measurements on Pyro-Carb must be cited:

1. The computed conductivity is $\lambda(x)$, the conductivity at that point or depth in the sample, not the weighted average ($\bar{\lambda}$) as derived from steady state measurements through a (necessarily) appreciable thickness of material.
2. It is also $\lambda(t)$, a function of time. The conductivity is computed for a point in the solid, at a given temperature, and at the specified time chosen for the data analysis. As the temperature profile moves back through the model, this point with its specific density rises in temperature. By considering consecutive times the thermal conductivity at a point (x , $\rho(x)$) can be computed for several temperatures.

Figure 8. GE Transient Thermal Conductivity Technique (Instrumented Model)

Figure 9 illustrates the results of one such run and shows the effects of the density correction. The curve labelled $\lambda(\bar{\rho}, T)$ was computed assuming a uniform density ($\bar{\rho}$) equal to the bulk density. The curve labelled $\lambda(\rho, x, T, t)$ is the instantaneous thermal conductivity function for that macroscopic physical piece of Pyro-Carb with the temperature distribution then existent in the sample. The sample, therefore, contains a range of densities, as indicated, from 1.35 gms/cc to 1.41 gms/cc. By cross reference to the reported density profiles and the experimental temperature profile at this time, for this model, a specific density can be attributed to each temperature on this scale (see inset index of density). Having done this for two selected times for each of three transient model runs on a material, it is a matter of bookkeeping to once again cross-plot, picking off values of $\lambda(T)$, now for each specific density, and plot an average thermal conductivity as a function of temperature for each density.

Figure 10 presents this set of measured functions, for densities of 1.33, 1.35 and 1.38 gms/cc. Although it has been indicated by RESD shield-design personnel that still higher densities of 1.41 gm/cc and 1.44 gm/cc, corresponding to the Pyro-Carb skin, are of critical importance to their analysis, this range of densities could not be adequately represented in the instrumented zones of the Pyro-Carb transient models. Experience with other graphites suggested an examination of the relationship between the percentage increases in thermal conductivity and density. The form of the defining equation would then be:

$$\left[\frac{\lambda - \lambda_0}{\lambda_0} \right] = F \left[\frac{\rho - \rho_0}{\rho_0} \right]$$

where the zero subscripts in each case indicate a datum value and F will be some number on the order of a few percent, e. g. , commonly given as 3 percent for ATJ graphite, $\bar{\rho} = 1.73$ gm/cc. Values of F were computed from the three experimentally determined curves in Figure 10. The remarkably good correlation is presented in Figure 11. Using this function for F, values for 1.41 gm/cc and 1.44 gm/cc lb/ft³ density Pyro-Carb were computed and are indicated in Figure 10. Because of the declining value of F at high temperature, the higher density material begins to assume a declining dependence on temperature. This is to be expected, because denser monolithic graphites, such as

Figure 9. Computed Thermal Conductivity Function for Pyro-Carb Transient Model No. 1. Across-Lamina Direction

Figure 10. Thermal Conductivity Function of Pyro-Carb Normalized to Density, Across-Lamina Direction

ATJ (1.73 gm/cc) and pyrolytic graphite (2.19 gm/cc), display a $1/T$ dependence above room temperature. In the case of the 1.33 gm/cc material, a definite radiation contribution to thermal transport is obvious at high temperature, where the conductivity function begins to increase with the characteristic T^3 curvature. We therefore have the situation, well known from ceramics technology, that a porous solid with a low temperature conductivity well below that of a higher density version may well have the higher conductivity at the top of their service temperature range because of the onset of a large radiative transport through the porous structure.

To present a coherent one-source plot of Pyro-Carb C-directional thermal conductivity, the steady-state measurements presented in Figures 6 and 7 are also plotted in Figure 10. These functions are faired into the transient measurements, but are in all cases kept within the ± 10 percent tolerance placed on them in Figures 6 and 7.

A ± 10 percent band is also indicated in Figure 10 at the level of 11 W/M-K^0 . The initial program plan for these measurements gave ± 10 percent as the tolerance on steady-state, low temperature measurements, and ± 20 percent on transients. The 20-percent nominal tolerance is predominantly caused by the dynamic nature of the transient technique and all the attendant mishaps of high speed, very high accuracy temperature measurement, and data reduction requirements. In Reference 6, a "calibration" of the transient technique on ATJ graphite is given and indicates a maximum deviation of 8 percent from a band of possible ATJ values as determined by independent steady-state measurements. The thermal conductivity of ATJ, or any other high temperature material, is definitely not known to ± 10 percent at 1900°K . The conclusion that one hopes to draw from all this discussion of tolerance bands and fairing of data is that the measurements represented in Figure 10 and the density correlation of Figure 11 show a coherence far beyond the expectations of the personnel who performed the measurements or the ability of any existent or prospective techniques which might check the measurements.

A set of supplementary data has also been obtained by measurements made at Union Carbide Corporation on slightly lower density Pyro-Carb (Reference 7). These are also indicated in Figure 10 and confirm both the trend with temperature, to high temperature, and the density dependence detected in this work. The Union Carbide measurements were made by the phase-shift technique, a transient diffusivity method which uses 1/2-inch diameter discs of approximately 1/10-inch thickness.

Further C-directional measurements were made on Pyro-Carb material but were for purposes of checking specialized techniques for performing with-lamina, a-b measurements; these measurements are discussed in Section III-4.

3. Effect of Angle Layup/Flat Layup Seam Interface on C-Directional Thermal Conductivity

Figure 12 gives the results of miniature module measurements on a 1/2-inch diameter sample of angle layup/flat layup seamed material, with the seam interface running obliquely across the direction of heat flow as sketched in the figure. The experimental results are compared to a band of values computed for this lower density of 1.2 gm/cc by the "F" factor technique of the previous section. The seam result is well within 10 percent of this computed integral plate value, indicating that no significant resistance to heat flow is offered by this interface in the GLFC endcap fabrication.

4. With-Lamina Thermal Conductivity Measurements

The with-lamina thermal conductivity of the GLFC heat shield was at first not considered necessary for thermodynamic re-entry performance analyses, and only a few measurements were made in "Phase I" of the Snap-27 program on flat plate Pyro-Carb samples. A one-dimensional, through-the-thickness analysis was considered adequate. However, as the safety requirements of the GLFC were increased to include sharper re-entry angles, and even an oriented (non-spinning), side-on atmospheric entry heating of the cask, the enhanced heat accommodation provisions of a two-or three-dimensional analysis became apparent, and thermal conductivity data were requested for the fill direction, corresponding to the circumferential direction of the cask and necessary for a 2-D analysis, and the warp direction, corresponding to the axial direction of the cask and necessary for a 3-D analysis.

The with-lamina values obtained in the early portion of the program are plotted in Figure 13, along with the full range of measurements performed on a variety of sample sizes by several techniques. These techniques are outlined below and further discussed in relation to the results.

Figure 11. "F" Ratio for Percent Dependence of Thermal Conductivity on Percent Variation in Density, Plotted as Function of Temperature for Pyro-Carb, Across-Lamina

Figure 12. Effect of Angle Layup/Flat Layup Seam Interface on C-Direction Thermal Conductivity

Figure 13. Range of Observed Values: Pyro-Carb 406 With-Lamina Thermal Conductivity

Technique	Sample Configuration	Comment
TC-1000 Comparator (Dynatech)	Eight 5/16-inch square. 2-1/2 inches long strips. lapped and butted together to make 2-1/2-inch square	Strips could be rotated to measure across-lamina and fill or warp directions (see insert of Figure 13)
5/16-inch diameter cutbar (GE/RESO construction)	5/16-inch diameter cylinder, 3/4-inch to 1-inch long	Comparative rod technique using Armco iron or Inconel heat meters, tubular guard packed with asbestos: 5/16-inch diameter slightly larger than 0.30-inch thick GLFC cask and plate samples; pyrolytic "case" on samples complicated density, structure characterization with conductivity measurement.
GE transient technique	Triplicate determinations on 5/16-inch diameter cylinders from either of two preceding techniques	A thermal conductivity measurement at the low density, amorphous <u>core</u> of the sample, not compounded appreciably by the case material.
3/16-inch diameter cutbar (GE/RESO construction)	3/16-inch diameter <u>core</u> cylinders from Pyro-Carb cask	Comparative rod using Armco Iron heat meters. excellent guarding by Armco iron guard tube sized to match stack gradient. packed with asbestos

The "Phase I" measurements seemed straightforward. Strips were cut from some of the same CVD plate material used to determine C-directional properties (with a density gradient from face to center). These 5/16-inch square cross section. 2 1/2-inch long strips were assembled into a 2-1/2-inch square, 5/16-inch thick plaque sample for the TC-1000 Comparator, with heat passing through the C-direction. Both the early data for this orientation and the technique were confirmed. The strips were then rotated and determined in the warp or fill directions (see inset sample heat flow schematic in Figure 13). The basically contradictory apparent functional dependence of these two orientations was at first doubted, but similar differences in the warp versus fill mechanical properties were being discovered at this time, relatable to the nature of the fiber paths amid the more amorphous filler material in these two directions (Reference 2).

To determine the density dependence and further examine the orientation effect, a second lower density plate of material was determined in a 5/16-inch diameter cut bar apparatus which provided sample temperatures up to 900°K. Fortunately for our understanding of the effects of the two with-lamina orientations, a "flat-layup" sample had inadvertently been provided. This fabrication has layers of cloth laid down alternately rotated 22-1/2 degrees, so that no significant in-plane anisotropy effects should be expected. Accordingly, the 5/16-inch diameter cut bar measurements showed a 1/T temperature dependence with indistinguishable "a" and "b" direction thermal conductivity

At this point, the results seemed to indicate a strongly crystalline with-lamina thermal conductivity, i.e., a peak around room temperature and 1/T temperature dependence. This had only been seemingly contradicted by the fill direction comparator measurements on 5/16-inch (0.31-inch) square section strips. But it had been hypothesized that the two orientations were of basically different effective crystalline character--the warp being highly crystalline in effect (peaking, 1/T function, higher mechanical strength and modulus) and the fill being amorphous (a slightly increasing, linear conductivity dependence on temperature, lower strength and modulus).

This data package, meager as it seems in repeat samples and density ranges, was to be the substance of the overall recommended with-lamina thermal conductivity design data for the GLFC. The material itself was extremely expensive and the design personnel were concerned about their approaching deadline, with no idea of the circumferential or axial conductivity to within a factor of 2 or 3.

High temperature thermal conductivity measurements were then conducted using the GE transient thermal conductivity technique on 5/16-inch diameter rods turned down from the 5/16-inch square TC-1000 fill direction samples used to determine the low temperature conductivity (to be later input as λ_0 in the transient technique's data reduction). Because the heat flow and temperature gradient would then be down the axial direction of this cylinder, the resultant data would then be for the warp direction. These last measurements of "Phase I" resulted in the slightly linearly increasing or constant function shown in Figure 13. This is in direct conflict with the deductions made above about the nature of the two orientations--the warp direction was expected to show a 1/T temperature dependence.

After confirmation that the transient determinations had indeed been made in the warp direction, several additional 5/16-inch diameter cutbar measurements were made. As indicated in Figure 13, these were fill direction measurements on the same plate material done in "Phase I" (the TC-1000 warp sample, with heat now flowing along the turned-down strip length) and, for the first time, warp direction measurements on cask material. The positive dependence on bulk density was as expected, but the fill measurements showed a $1/T$ dependence. It should be noted here that this fill sample was made from a slightly undersize plate of 0.30-inch thickness instead of 5/16-inch, and that two flat opposite surfaces, small chords of a 5/16-inch diameter cylinder, were evident in the turned down lathe product. These surfaces were, of course, the high density CVD-infiltrated surfaces.

These results led to the above mentioned factor of 2-3 uncertainty in the in-plane conductivity. Closer examination of the data shows that only bulk density had thus far been considered. Each of the techniques, however miniaturized, only treated a resultant, apparent heat conductivity for several types of carbon material in each cross section, and a range of densities from the surface case to central core. In particular, the transient results must be realized to apply only to the central 1/8-inch diameter central core, along which the thermocouple instrumentation is placed. (See inset schematic in Figure 13 of transverse gradient and transient sample.) This transient curve was actually computed from the experimental temperature responses using the central core density of the relevant plate and a λ_0 at lower temperatures based on the Phase I and II steady-state results.

The steady-state measurements thus far are seen to be the resultant indications of the several conduction mechanisms in parallel, just as the C-directional measurements were a resultant series process. The analogous, but more complicated functional dependence with temperature, can be expressed as:

$$\bar{\lambda}_{||} = c_0 + c_1 T + c_2 / T$$

the combination of a constant, a linear, and an inverse temperature dependence.

In each of the steady-state measurements, a case of high density pyrolytic material was on the outside of the sample, conducting in parallel with the amorphous core. By accepting

the hypothesis that at low temperature this case material dominates the functional dependence of the conductivity, the steady-state measurements can be correlated.

A test of this hypothesis could only be made by a set of low temperature thermal conductivity determinations on virtually homogeneous samples down on the scale of the central lower density core, or by measurements on thin strips of high density case material only. Accordingly, a 3/16-inch diameter, 1-inch long cylindrical sample was specified, small enough to limit the density variation to 0.04 gm/cc and to ensure removal of the pyrolytic case material from a cylinder cut from either the axial or circumferential directions of the Pyro-Carb cask. A miniature comparator cut bar was designed and built; the plan of this instrument is shown in the inset of Figure 14. Combination Armco iron heaters (heat sinks/heat meters) are used, surrounded by a gradient heated guard of the same material, sized to provide the same cross section for heat conduction and thus match the gradient in the cutbar. The combination of matching the guard cutbar temperatures and filling the annular space between with asbestos powder results in a low radial heat loss, in practice less than 5 percent, as indicated by the temperature drops across the top and bottom Armco iron heat meters. The upper temperature limits of this class of instrument are usually considered to be in the range of 1100°K to 1300°K, where the radial losses become unmanageable, and the top heat meter runs too hot for reliable calibration. With this particular miniature instrument, it was found that about 900°K mean sample temperatures became the limit because of deterioration of the 3-mil chromel-alumel thermocouples inserted diametrically in the stack, as shown in the inset of Figure 14.

The "relative instrument accuracy" was tested by measuring a cylinder of the same Armco iron used for the heat meters; i. e. . an all-Armco iron stack was set up. The results of this calibration are shown in Figure 15, compared to the curve given by Powell, Ho, and Liley (Reference 8). An accuracy within 5 percent is demonstrated across the temperature range.

The three Pyro-Carb core measurements made by this technique are shown as the last entered curves in Figure 13, amid the plethora of earlier measurements by the various techniques. The temperature level of 800 to 900°K which was reached for these two warp and one fill measurements, together with the high accuracy demonstrated by the Armco iron calibration, confirm the linearly increasing temperature dependence of the

Figure 14. Recommended Design Data: Pyro-Carb With-Lamina Thermal Conductivity

Figure 15. Miniature Cut Bar Calibration on Armco Iron

lower density core material and accurately set the level and ratio of the warp and fill thermal conductivity.

If the density dependence of the warp thermal conductivity is computed from just these two curves following the analysis used for the C-direction:

$$\left[\frac{\lambda - \lambda_0}{\lambda_0} \right] = F \left[\frac{\rho - \rho_0}{\rho_0} \right] \quad \text{then at } 800^\circ\text{K:}$$

$$F = \frac{\frac{21.2 - 18.1}{18.1}}{\frac{1.35 - 1.27}{1.27}} = 2.7$$

A value of $F = 3$; a 3-percent variation of thermal conductivity with density is also the nominal value used for polycrystalline graphites, such as ATJ (Reference 9).

Although the fill direction was the more important for 2-D analysis of the cask, only one sample was determined, because of the extreme difficulty of obtaining core samples in even our miniaturized 3/16-inch diameter size. A high number of repeats was made on this run, and utmost care was taken to maximize the accuracy for the best basis for recommended high temperature, density-dependent design data.

5. Final Recommended With-Lamina Thermal Conductivity Data

The high temperature functional dependence of the final recommended data was taken from the indications of the "Phase I" transient curve shown in Figure 13. The transient measurement shows a continuing slight positive slope up to 1900°K . This was interpreted as a constant slope for the recommended data, which are shown Figure 14, with the solid lines indicating the range of actual measurements. Because of the lack of any provision for use in the actual 2-D analysis that was performed on the GLFC re-entry heating, and the apparent somewhat increased complexity of the warp-axial measurements, only fill direction data were used in the design, with some allowance in the node-spacing because of knowledge of the GLFC's axial conduction properties. The measurements do indicate a higher crystalline development in the warp direction--the conductivity is about 50 percent higher for a given density than the fill direction conductivity, which is, in turn, about twice as high as the C-direction. A warp: fill: C-direction anisotropy of about 3:2:1 can thus be given for the moderate to low range of Pyro-Carb 406 densities used in the GLFC heat shield.

IV. CONCLUSIONS

It is not apparent at this time whether future applications of Pyro-Carb 406--if the material continues to be produced and identified in the 406 series--will be able to make use of the specific data obtained during this program. The material, as it is now constituted for flight on the Apollo 12 mission, was in a continuous state of development throughout the program for enhanced thermostructural and ablative performance, in addition to the insulative considerations of the work described in this paper. However, the ramifications of the orientation, density gradient, and size effects uncovered during the Snap-27 Pyro-Carb thermal conductivity characterization program are equally applicable to the whole emerging generic class of graded density, carbon-carbon composites.

The thermal conductivity instrumentation utilized or developed specifically for this program is, with one exception, generally accessible throughout aerospace industry materials laboratories; they are conventional but miniaturized instruments, sometimes miniaturized in the extreme and quite difficult to operate, as was the 3/16-inch diameter cutbar described in the text.

The one exception to the conventionality of the instrumentation employed is the General Electric transient numerical thermal conductivity technique. This admittedly complex and quite expensive technique had been previously applied to determination of refractory char thermal conductivities under conditions simulating their application in atmospheric entry (Reference 6). The accent there was on short-time simulation of the actual experience of the material before time-at-temperature effects changed its crystalline nature. Other transient, small sample techniques have been developed, such as flash diffusivity and phase shift, which, when performed on an established large quantity basis, offer lower cost and more flexibility than the GE transient technique. But the unique advantage of the technique used to gather the data in Figure 9--the continuous generation of thermal conductivity data, $\lambda (\rho, x T)$, at a specific point, density, and changing temperature within the sample--has become apparent and immensely useful during the Snap-27 program.

V. ACKNOWLEDGEMENTS

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Thermal Conductivity, Electric Resistivity and
Heat Capacity of Dense Graphites

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ABSTRACT

The results of measurements of thermal conductivity, electric resistivity and heat capacity of graphites with density of 1.9 g/cm^3 and over in the temperature range 50 - 2500 K are presented. On the basis of modified Debye equation average crystal parameters and the thermal conductivity anisotropy of the graphites investigated have been calculated. It is concluded that irrespective of the perfection of the graphite crystalline lattice Umklapp processes markedly effect the thermal conductivity beginning from $T=130 - 140 \text{ K}$. It is shown that the curve of the thermal conductivity vs temperature at $T>140 \text{ K}$ is exponential, the exponent power increasing discretely at the excitation of the stiff modes of atom vibrations.

THE EFFECTIVE THERMAL CONDUCTIVITY OF PYROLYTIC GRAPHITE CYLINDERS IN VARIOUS GAS ENVIRONMENTS

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ABSTRACT

The effective thermal conductivity of thin wall pyrolytic graphite cylinders was determined experimentally in vacuum, nitrogen, and helium environments at temperatures from 800K to 2500K. Several techniques of measuring temperature gradients in the cylinders were explored and the errors associated with some of the classical methods using contact thermocouples were determined. The data were correlated with analytical expressions based on a mathematical model of the delaminated cylinder. These expressions were used to predict the effective conductivity at temperatures outside the range covered by the measurements and in other environments. It was shown that above 1370K the effective conductivity of cylinders in a helium or hydrogen environment is about 80 to 90% of the conductivity of undelaminated PG plates. In vacuum, the effective conductivity of cylinders is only about 10 to 20% of the conductivity of plates at 800K, but increases to about 70% of the plate value at 3000K as radiant transport across the delaminations becomes more significant.

INTRODUCTION

Because of their low c direction thermal conductivity and stability at elevated temperatures, pyrolytic graphite cylinders are used as thermal insulators in certain high temperature applications. A typical cylinder has a wall thickness of only about 1.25mm (0.050 inch), and contains several circumferential macrolaminations and numerous microdelaminations within the growth cones. These delaminations act to retard the radial flow of heat in a manner which is dependent on the conductivity of the interstitial gas, the heat flux density, and the geometrical pattern of the delaminations.

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This paper describes the results of an analytical program to establish the effective thermal conductivity of the cylinders in various gas environments at temperatures ranging from 800K to 3000K. Several experimental techniques for measuring the inside wall temperature of the cylinders are described and evaluated. Analytical values for the effective conductivity are presented and correlated with the experimental results

THE SPECIMEN MATERIAL

The specimens were thin walled cylinders nominally 1.17 cm O.D. x 0.91 cm I.D. x 5.08 cm long. The average bulk density of these cylinders was 2.15 gm/cm³. The macrostructure is illustrated by the photograph in Figure 1, which was constructed by splicing together photomicrographs taken at about 35X. Up to seven different delaminations can be seen, none of which extends completely around the circumference. However, due to the radial symmetry, the general appearance at any circumferential location is one of two or three partially continuous delaminations. The thicknesses of the delaminations ranged from less than 0.002 cm to about 0.013 cm. The structure is moderately regenerative, becoming more continuously regenerative (shorter growth cones) near the outer radius. Observe the large nucleation site at the right-hand side of the picture.

The propagation of the delaminations in the axial direction was determined from studies of radiographs. These showed that the delaminations generally extended over 60 to 100% of the length.

EXPERIMENTAL METHODS

Measurements of the effective thermal conductivity were made at steady-state conditions in a radial inflow apparatus. Over the range of mean temperatures (800 to 2500K) covered by the measurements, the outside surface temperature of the sleeves could be measured optically; however, at the lower mean temperatures it was necessary to use thermocouple techniques to measure the inside wall temperature. The inherent errors associated with measurements of surface temperatures by means of thermocouples led us to investigate several methods in an attempt to find a satisfactory solution. The following paragraphs describe the basic apparatus and the various techniques which were employed to measure inside surface temperatures.

Basic Radial Inflow Apparatus and High Temperature Furnace

The basic radial inflow apparatus has been described in detail in several prior publications;¹⁻³ therefore, only the essential elements are covered here. The method involves placing a cylindrical specimen on

¹Refer to the References.

a coaxial water flow calorimeter, heating the specimen radiantly on its outer surface, and measuring the heat flow and temperature gradient through it. Heat flow is determined by measuring water flow rate and temperature rise in the calorimeter, which is calibrated in a radiation furnace under near-blackbody conditions. In operation, the specimen assembly is placed in a graphite resistance furnace and heated radiantly from a concentric graphite heater tube. The annulus between the I.D. of the sleeve and the calorimeter is either filled with powdered aluminum oxide or left open, depending on the technique being used. Guarding against axial heat losses is provided by installing graphite cylinders filled with thermatomic carbon above and below the specimen.

The high temperature furnace used in the program is shown in Figure 2. This furnace utilized an electrically heated graphite element, 6.2 cm O.D. x 4.6 cm I.D., with the hot zone machined in a helical configuration. The length of the hot zone is 15.2 cm, providing a ratio of hot zone length to specimen length of 3:1. Insulation is provided by cylindrical graphite radiation shields and thermatomic carbon. The outer shell is water cooled. The furnace design permits operation from vacuum (minimum pressure of 10^{-4} torr) to 200 psig in inert atmospheres. Power is supplied from a 220V ac line to an autotransformer, which is, in turn, connected to a current transformer which feeds power to water-cooled copper electrodes. Maximum power input is about 25kVA at 2000 Amps. Electrodes and thermocouple leads are sealed in Conax glands.

The vacuum system for the furnace is a Welch 15 cfm mechanical pump and an NRC HS4 diffusion pump rated at 750 l/sec. Pressures are monitored by means of McLeod and thermocouple gages installed in gage ports in the furnace.

Specimen Configurations and Methods of Measuring Inside Wall Temperatures

The outside surface temperature was determined optically for all techniques using an L and N Type 8622 optical pyrometer. The inside surface temperature of the sleeve was determined by several experimental techniques, all but one of which involved the use of thermocouples. The various thermocouple methods used are shown schematically in Figure 3. A brief description of each experimental technique follows:

- (a) Standard Technique - Thermocouple leads (0.127 mm dia.) insulated with an 0.81 mm dia. double bore aluminum oxide insulator were welded to form a junction which was pressed against the inside wall of the sleeve. Care was taken to maintain contact between the bead and the wall during the buildup, and a final check was made with an ohmmeter prior to the run. The annulus was packed with aluminum oxide powder to provide a heat transfer medium between the sleeve and the calorimeter and to electrically insulate the short length of exposed thermocouple leads.
- (b) Boron Nitride Spring - This method utilized a slotted cylinder

of boron nitride which pressed flattened thermocouple leads against the inside wall of the PG sleeve. The BN spring was machined to an O.D. of 9.14mm and the PG sleeve was reamed to the same diameter. The thermocouple leads were flattened to a thickness of approximately 0.038mm over the length of contact, but were not joined, the junction being made through the PG sleeve. The annulus was packed with Al_2O_3 powder. This technique insured positive contact between the sleeve and the thermocouple and located a longer length of thermocouple wire adjacent to the wall.

- (c) Tantalum Foil - Individual thermocouple leads were welded to the tantalum foil and bent as shown in the figure to increase the length of isothermal lead wire.
- (d) Boron Nitride Spring with Tantalum Foil Backing - This method was a modification of Method (b). The tantalum foil backing was added to increase the effective contact area between the sleeve and the thermocouple junction. The wires were flattened and welded to the outer surface of the tantalum foil.
- (e) Boron Nitride Strips - The strips were pressed against the I.D. of the sleeve by the Al_2O_3 packing. An unbeaded thermocouple was installed in a slot in one of the strips. The wires were flattened but not joined, as in Method (b) above.
- (f) Boron Nitride Sleeve - This method was a variation of Methods (b) and (e). The slotted cylinder was used to provide more positive contact between the thermocouple and the PG sleeve. The BN sleeve was made the same length as the PG sleeve to eliminate any local temperature disturbances in the vicinity of the thermocouple junction. Flattened, unbeaded thermocouple wires were used as in (b) and (e) above.
- (g) "Getter" Technique - This method was similar to the standard technique except that the thermocouple was backed by a 6.3mm square of Grafoil or tungsten to increase the effective contact area. The wires were flattened but not joined, the junction being made through the foil.
- (h) Nickel Plating - The I.D. of the PG sleeve was electroplated with a layer of nickel less than 1mm thick and the thermocouple leads were individually welded to the plating.
- (i) Tin-Filled Annulus - This technique utilized the high thermal conductivity of liquid tin to reduce the temperature drop between the thermocouple and the wall. The buildup was made simply by placing the beaded thermocouple and sleeve on the calorimeter and filling the annulus with molten tin. The sleeve was maintained concentric with the calorimeter by packing the annulus to a level about 6.3mm from the bottom with graphite powder, and by inserting a centering

tool into the top of the sleeve. The tin was remelted during the run. Since for this method to be effective the tin had to be completely molten (melting point 503K), the method could be used only at specimen mean temperatures above about 800K. Tin was selected as the heat transfer medium because of its comparatively high boiling point (2560K) and low vapor pressure,⁴ the latter being essential for use in vacuum.

- (j) Graphite Insert - This method employed an ATJ graphite insert which was cemented to the I. D. of the sleeve and the O. D. of the calorimeter with a high temperature graphite glue (National No. 14 Cement, manufactured by Union Carbide Corporation). The thermal resistance of the glue was determined by calibrating an assembly made of two cylinders of ATJ graphite under gas and vacuum conditions.
- (k) Optical Measurement - The configuration for this technique is shown in Figure 4. The method involved measuring the inside and outside surface temperatures with an optical pyrometer. The PG sleeve was centered on the calorimeter by means of triangular graphite washers at the top and bottom. In order to provide an unobstructed view of the inner wall, no packing was used in the annulus, the heat transfer occurring by gas conduction and radiation. An ATJ graphite cylinder, 25.4mm in outside diameter, was glued to the outside of the PG sleeve and a hole 2.54mm in diameter was drilled through this cylinder to permit measurement of the outside surface temperature of the PG sleeve. The hole through the ATJ cylinder provided a blackbody cavity with a length-to-diameter ratio of about 2.5 to 1. A second hole, 2.54mm in diameter, was drilled through both cylinders after they were glued together. This hole was offset 3.30mm from the centerline so that the view of the inner wall would not be obstructed by the calorimeter. Since this method was limited to temperatures which could be measured optically, it was used only at mean temperatures above about 1200K. However, unlike the thermocouple methods, the optical technique could be employed to much higher temperatures.

Experimental Procedures for Sleeves

All measurements described in this report were made at steady-state conditions. At each temperature level, four to six readings of heat flow and temperature were made to determine normal data scatter and to minimize the error attendant to a single reading. Normally the furnaces were purged with helium at a rate of 80-160 std cc/sec. In those runs in which the effects of vacuum and different gas environments were to be evaluated, the following procedure was employed: For vacuum, the furnace was evacuated to the lowest pressure obtainable, usually in the range of 10^{-2} to 10^{-3} torr, and maintained at this pressure until steady-state conditions were achieved before taking data. When changing gases, the furnace was evacuated two to three times to the minimum pressure,

held at this pressure for 10 to 15 minutes, backfilled each time with the particular gas (nitrogen or helium) to a slight positive pressure (about 1.7 atm). After each backfill, the system was maintained under the slight positive pressure for 10 to 15 minutes, and after the final backfill, the pressure was relieved to one atmosphere and a constant purge was maintained at a rate of 80-160 std cc/sec. For some runs which were made at a positive pressure of 13.6 atm, the three evacuation-backfill cycles were employed prior to pressurization.

EXPERIMENTAL RESULTS

The data obtained by thermocouple measurements of the inside wall temperature are plotted in Figure 5 and the results of the optical measurements are shown in Figure 6. A comparison of the results obtained by all methods in vacuum, nitrogen, and helium is shown in Table I. Inspection of the data reveals the following: In vacuum the highest data were obtained by the tin technique (excluding the highest value measured by the graphite insert method), whereas the contact thermocouples generally yielded the lowest results. The lowest values in helium were measured by the standard method. In the helium atmosphere, the best precision was obtained by the tin method. For this technique, the coefficients of variation were 8.3 and 6.2% at 1370 and 1920K, respectively. The tin data were judged to be high in vacuum due to the tendency for tin to penetrate the delaminations, as observed in post-run dissection of several sleeves. In vacuum at 1370K, good agreement was obtained between the optical, BN spring, and BN sleeve techniques. At 1370 and 1920K, excellent agreement was obtained between the tin and optical methods.

The scatter in the optical data was rather high, particularly at 1920K, as evidenced by coefficients of variation which ranged from 10 to 20%. The highest scatter occurred in helium at 1920K. On some runs in both nitrogen and helium, the data at 1920K tended to fall below a smooth curve drawn through the data at lower and higher temperatures. This condition was judged to result from outgassing of the pyrolytic graphite at this temperature, which prevented the purge gas from filling the delaminations. It has been reported that graphite gives off CO at temperatures between 1600 and 2150K.⁵ CO, having a lower conductivity than helium, would contribute to a lower effective thermal conductivity unless it were displaced from the delaminations. In later runs, this problem was remedied by increasing the number of evacuation-backfill cycles before taking data in helium or nitrogen.

ANALYSIS OF EXPERIMENTAL ERRORS

The major cause of uncertainty in the temperature measurements on sleeves results from uncertainties in temperature measurements. The heat flow measurements were considered to be well within 5%, since the calorimeters are calibrated under blackbody conditions to within an uncertainty of about 3% and since experience on PG sleeves, tile, and standard

specimens has shown that axial losses are minor. Furthermore, it has been determined that errors in measurement of outside surface temperatures, measured optically, are small provided care is taken to guard against reflections from the hotter heater tube. Reflective errors may be significant at specimen hot face temperatures below about 1600K. Errors of this type can be eliminated by viewing the outside surface of the specimen through a blackbody cavity in the surrounding material. Thus, the problem is reduced to one of measuring the inside surface temperature. Both analytical and experimental methods were employed to evaluate the latter.

To verify the accuracy of the tin technique, a run was made on a cylinder of ATJ graphite, the conductivity of which had been determined in previous evaluations. The ATJ cylinder was 1.9 cm O.D. x 0.91 cm I.D. x 5.1 cm long, and was installed on the calorimeter in the same manner as the PG sleeves. The temperature drop through the ATJ cylinder was calculated from the measured heat flux and the known conductivity of ATJ graphite. The difference between the measured and calculated temperature gradients was assumed to be the error. When a correction, based on the excess temperature gradient, was calculated for the data on the PG sleeves, it was found to be less than 6%.

The tin method yielded good precision in both vacuum and helium, but as previously mentioned, the measurements in vacuum were systematically high due to penetration of liquid tin into the delaminations. This phenomenon was not observed in those runs made only at atmospheric pressure.

The validity of the optical technique was investigated by performing calculations of the effective emittances of the inside and outside holes and calculating the error in temperature caused by deviations from unity. The emittance calculations were based on analyses presented by Gouffe^{6,7} and Sparrow.⁸ These calculations gave effective emittances of 0.99⁺ and 0.98 for the outer and inner holes, respectively. For a heater tube temperature of 1480K and an outer surface temperature of 1360K, the error in the measured surface temperature would be about +2.2K.

To further verify the technique, experimental measurements were performed on PG sleeves to which coatings of copper and nickel were electroplated on the inside surface. These sleeves were installed on the calorimeter in the same manner employed for the conductivity measurements and the inner and outer surface temperatures and heat fluxes were measured. The temperature at which the copper and nickel platings melted was indicated by a sharp increase in heat flux as the graphite surface, with its higher emittance, became exposed. The observed melting points were compared with the theoretical melting temperatures of 1360K for copper and 1590K for a nickel-carbon eutectic.⁹ Agreement was within 45K for the copper coating and 9K for the nickel coating.

Errors associated with the contact thermocouple methods were determined by analysis and from observation of the data. Details of the analysis are not included, but are summarized in the following paragraphs.

Referring to Table I, one observes that the data obtained by contact thermocouple methods gave fair agreement with the optical data in vacuum but rather poor agreement in helium. The error in the contact thermocouple readings results from heat transfer from the leads to the surrounding medium and from conduction of heat down the leads.

These heat losses will cause temperature gradients in: (1) the material whose temperature is being measured (the PG cylinder), (2) the lead wires, and (3) a temperature drop across the interface between the thermocouple junction and the pyrolytic graphite cylinder. Various analyses are presented in the literature^{10, 11} for errors associated with thermocouple measurements of surface temperatures; however, such analyses usually are based on the assumption of intimate contact between the thermocouple and the surface. This is often a tenuous assumption at best. For the types of measurements reported here, approximate calculations of the aforementioned sources of error were made as follows: First, the effective thermal conductivity of the aluminum oxide packing in the annular space between the sleeve and the calorimeter was calculated from the measured data, using a corrected value for the temperature drop through the sleeve. Typical data and geometrical dimensions for a standard run in helium are presented in Figure 7. From these data, the conductivity of the packing was calculated to be 0.52 W/m K. From the data and the equation for the temperature distribution in a hollow cylinder, the temperature drop between the wall and the center of the insulator was found to be approximately 230K. An approximation of the error in the inside wall temperature was then made by calculating the temperature drop through the sleeve, assuming its true conductivity at 1700K to be 0.94 W/m K. The true temperature gradient was 178K and the error in the measured inside wall temperature was 260K. Observe that the apparent error is approximately equal to the temperature drop between the inside wall of the sleeve and the centerline of the insulator.

The heat loss from the thermocouple leads consists of conduction down the leads and convection and radiation to the surroundings. This heat loss can be equated to the heat flow across the interface between the thermocouple junction and the wall of the sleeve as follows:

$$q_1 = h_i A_i \Delta T = K A_c \frac{(T_j - T_s)}{l} + h_c A_s (T_l - T_s) \quad (1)$$

where

- h_i = interface conductance,
- A_i = cross-sectional area at interface,
- ΔT = temperature drop across interface,
- K = thermal conductivity of lead wires,
- A_c, A_s = cross-sectional and surface areas of exposed leads, respectively,
- T_j, T_l, T_s = temperatures of junction, leads, and surroundings, respectively,
- h_c = heat transfer coefficient between leads and surroundings, and
- l = length of exposed leads between junction and centerline of insulator.

The second term on the right side of Equation 1 may be replaced by the term $K_p A_s (dT/dx)$, where K_p and dT/dx are the thermal conductivity and temperature gradient in the packing, respectively. Calculations based on the foregoing equation show that heat loss from the thermocouple leads occurs predominantly by convection and radiation to the surroundings, the value being 0.47 Watts. For this heat flux the interface coefficient is 35,500 W/m² K. This value, while fairly high, still results in a temperature error of 260K.

The temperature gradient in the sleeve due to heat drain from the thermocouple junction can be calculated by treating the sleeve as a flat plate and assuming that heat flows radially (in the "a-b" direction) into the thermocouple junction. For this case, the following equation applies:

$$q = \frac{2 \pi t K_{pg} \Delta T}{\ln (r_2/r_1)} \quad (2)$$

where

t = the wall thickness of the sleeve and
 K_{pg} = thermal conductivity of the sleeve in the
a-b direction.

Equating q to the value previously calculated and assuming a large ratio for (r_2/r_1) , say 100, yields a ΔT of about 1K. This is not surprising, considering the high thermal conductivity of pyrolytic graphite in the a-b direction.

The foregoing analysis shows that the measurements in helium using contact thermocouples are subject to large errors. The apparent success of this method in vacuum can be attributed to the fact that the conductivity of the packing (and consequently the heat loss from the leads) is decreased by several orders of magnitude in vacuum. Thus, the methods used, namely, the boron nitride springs and sleeves, can be considered reasonably reliable for vacuum.

ANALYSIS OF HEAT FLOW THROUGH DELAMINATED SLEEVES

A two-dimensional thermal analysis of the temperature distribution within the PG sleeve was made in order to predict the effects of the delaminations and the gas in the delaminations on the effective thermal conductivity of the sleeves. The analysis was made independently of the experimental measurements, and hence the results were not influenced by the measured values. The only "tie-in" between the analysis and the measurements was that the boundary temperatures used in the analysis for the various temperature levels and gas conditions were chosen to correspond to the temperatures measured for the runs with the "optical" technique for measuring inside temperature.

The analytical model assumed for the analysis is shown in Figure 8. This model was developed from studies of the photomicrographs shown previously in Figures 1 and 2. The model was assumed to have three equally spaced delaminations, each of which was 0.0406mm thick. The two delaminations nearest the outside were assumed to occupy nine-tenths of the circumference, while the one nearest the inside was assumed to occupy only three-tenths of the circumference. The model just described was called Model 1. In order to investigate the effect of the lengths of the delaminations, another model, called Model 2, was investigated. For Model 2 the length of each delamination was reduced by 10% of the circumferential length as shown by the cross-hatched portions of the delaminations.

The major assumptions for the analysis were as follows:

1. The physical model shown in Figure 8.
2. Constant and known boundary temperatures at the inside and outside radii.
3. The PG between delaminations has the same value for thermal conductivity as undelaminated PG plate.
4. Two-dimensional heat flow.
5. No chemical reactions between the gas in the delamination and the pyrolytic graphite.

The temperature distribution was obtained by first writing a heat balance equation for each nodal point. The resulting 24 equations were then solved simultaneously on an IBM-1130 computer to obtain the temperature distribution. The total heat flow was obtained by calculating the individual heat flows from the outside surface to Nodes 1 through 6 and summing. This was also done by summing the heat flows between Nodes 19 through 24 and the inside surface. The two heat flows were in excellent agreement.

Finally, using the calculated heat flow, the effective thermal conductivity of the sleeve was calculated from the equation

$$K_{\text{eff}} = \frac{\ln(R_2/R_1)}{2 \pi L} \frac{Q}{\Delta T} \quad (3)$$

where

- R_2, R_1 = outside and inside radii, respectively,
- L = gage length = 1.27 cm,
- Q = total heat flow through 1.27 cm gage section, and
- ΔT = temperature difference between outside and inside radii.

The property data used in the analysis included data obtained at Southern for the conductivity of PG in the a-b and c directions, and data reported in the literature¹²⁻¹⁴ for the conductivities of nitrogen, helium, and hydrogen.

The solid and gas resistances were computed in the standard manner using the equation

$$R = \frac{\Delta X}{KA}$$

with the appropriate values substituted. The resistance to radiation across the delamination was calculated from the relation

$$R_r = \frac{1}{4AF_{1-2} \sigma T_m^3} \quad (4)$$

where

R_r = radiation resistance,

A = mean cross-sectional area of delamination normal to heat flow,

$F_{1-2} = \frac{\epsilon}{2\rho + \epsilon}$ = graybody shape factor (assuming shape factor $F_{1-2} = 1$),

ϵ = emittance,

ρ = reflectance,

σ = Stefan-Boltzman constant, and

T_m = average temperature of delamination.

It can be shown that Equation 4 applies if $\Delta T \leq 0.346T_m$. For the PG sleeves this condition would hold for heat flux densities (based on outside surface area) less than 630,000 W/m².

The results of the thermal analysis are presented in Figure 9. For Model 1 (see Figure 8), the calculations were performed over the entire temperature range under conditions of vacuum, nitrogen, helium, and hydrogen in the delaminations. These results are presented as the solid lines in the figure. For Model 2, the calculations were performed only for vacuum and nitrogen in the delaminations. The results for Model 2 are presented as the dashed lines. Also shown for comparison are the experimental results and some values reduced from diffusivity data reported by Morrison¹⁵ for sleeves having a wall thickness of 0.5mm. The diffusivity values were converted to conductivity using typical data obtained here on density and specific heat of pyrolytic graphite.

The results shown in Figure 9 point out that the effective thermal conductivity of the sleeves is sensitive to the gas in the delamination. With hydrogen and helium in the delaminations the character of the curve for the effective thermal conductivity was similar to that for the undelaminated PG and the absolute values of effective thermal conductivity were about 18% lower at 800K and only 6% lower at 3000K. With nitrogen in the delaminations, the character of the curve at low temperatures was altered from that for undelaminated PG and the absolute values were significantly lower. At 800K, the effective thermal conductivity with nitrogen in the delaminations was 41% of the thermal conductivity of the PG tile and at 3000K it was 76% of the value for tile. The curves for vacuum were similar to those for nitrogen, only the level of conductivity was even lower. The effective thermal conductivity values in vacuum

were 20% of the conductivity for tile at 800K and 60 to 70% of the value for tile at 3000K.

Note in Figure 9 that the effective thermal conductivity values for Model 2 were noticeably higher than those for Model 1. Also, the effect was more pronounced at the lower temperatures. The only difference between Model 1 and Model 2 was a slight variation in the lengths of the delaminations (see Figure 8). Thus, one can readily see that slight differences between the nature of the delaminations in sleeves can cause observable changes in thermal conductivity if the thermal conductivity of the gas in the delaminations is low.

Figure 9 shows the experimental data which were judged to be most reliable. Agreement between the experimental and theoretical values was generally good, the major discrepancy being that the experimental data were lower than the theoretical values in helium, while in vacuum, the optical data were higher than the calculated values at the lower temperatures. These discrepancies probably result from certain shortcomings in the theoretical calculations and the experimental techniques as well as certain physical phenomena.

The calculated values would be reduced if a greater number of delaminations were assumed. While the effect of this parameter was not studied in detail, approximate calculations showed that at 800K the effective conductivity would be reduced by about 10, 20, and 50% in helium, nitrogen, and vacuum, respectively, if the number of delaminations were increased from three to four.

The data obtained by the tin method may be lower than the calculated values due to the higher heat flux densities obtained in these runs. Pears¹⁶ has shown in a prior analysis that at heat flux densities above about 320,000 W/m² in a vacuum, the effective conductivity of the sleeves is substantially reduced over the value which would apply at the same mean temperature but lower heat flux densities. This effect results from the large temperature drops required to transport the heat across the delaminations, which, in turn, results in a lower effective conductivity. This effect would be less pronounced in helium.

RECOMMENDED VALUES FOR EFFECTIVE THERMAL CONDUCTIVITY IN SLEEVES

Based on the experimental and analytical results and their limitations as discussed in the prior section, the recommended curves for the effective conductivity of sleeves in various environments are plotted in Figure 10. The range of values for a given ambient environment is based on the most reliable experimental data obtained for that particular environment plus the results of the theoretical analysis. These curves are believed to be typical for 11.7mm O.D. x 9.1mm I.D. sleeves at heat flux densities up to 630,000 W/m² and having similar delaminations. Pending further analysis and experimental verification, particularly for vacuum, the curves are not recommended for higher heat flux densities.

CONCLUSIONS

The effective conductivity of pyrolytic graphite sleeves has been determined over most of the environmental spectrum. Experimental verification was obtained by two or more independent methods in vacuum, nitrogen, and helium at mean temperatures from 1370 to 1920K and by the optical technique to 2500K. Analytical results showed good agreement over this range and can be used to predict the conductivity at lower and higher temperatures in a specified gas environment at heat flux densities up to 630,000 W/m². The effective thermal conductivity of the sleeve is reasonably close (within 10%) to the conductivity of tile if the delaminations contain undiluted helium or hydrogen. For nitrogen (or gases having similar conductivities) in the delaminations, the effective conductivity is 50% to 80% of the conductivity of tile. In vacuum the effective conductivity of sleeves is only about 10 to 20% of the conductivity of tile at 800K, but increases to about 70% of the tile value at 3000K.

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Figure 1. Enlarged View of PG Sleeve in the As-Received Condition (~35X)

Figure 2. Picture of Furnace in Which Thermal Conductivity of Pyrolytic Graphite Sleeves Was Measured (Capable of Operation from 15 Microns to 200 psig).

Figure 3 Thermocouple Arrangements Employed for Measurement of Inside Surface Temperature.

Figure 3 (cont'd) Thermocouple Arrangements Employed for Measurement of Inside Surface Temperature.

Figure 4. Buildup for Optical Measurement of Inside Surface Temperature.

Figure 5. Experimental Values for Effective Thermal Conductivity Measured by Thermocouple Techniques

Figure 5 (cont'd) Experimental Values for Effective Thermal Conductivity Measured by Thermocouple Techniques

Figure 6 Effective Thermal Conductivity Measured by Optical Technique

- Notes:
 1. Dimensions in mm
 2. Temperatures in K

Typical Data (Helium Atmosphere)

T_o	T_{tc}	ΔT	T_m	q (watts)	K (W/mK)	$T_{H_2O \text{ mean}}$
1569	1189	380	1379	46	0.36	283.3
1928	1490	438	1709	56	0.38	288.9

Figure 7. Dimensions and Measured Values for a Typical Run in Helium Using Standard Thermocouple Technique

NOTES:

1. Model 1 consisted of all delaminations (including those shown cross-hatched).
2. Portions of delaminations shown by cross-hatching were removed for Model 2.
3. Numbers on sketch denote nodes used in calculations.

Figure 8. Analytical Model of Sleeve Used in Thermal Analysis (3 delaminations).

Figure 9 Comparison of Experimental and Theoretical Values for Delaminated Cylinders

Figure 10. Recommended Values of the Effective Thermal Conductivity of Delaminated PG Cylinders.

Table I
Summary of Experimental Data

Thermal Conductivity (W/mK) at 1370K

Method	Vacuum			Nitrogen			Helium		
	Avg ¹	Range	CV ²	Avg ¹	Range	CV	Avg ¹	Range	CV
Standard								0.22-0.36	
BN Spring		0.43 ³						0.36-0.95	
Getter								0.29-0.43	
BN Sleeve		0.29-0.40						0.43-0.57	
Electroplating								0.33-0.55	
Tin	0.79	0.71-0.86					0.92	0.74-0.98	8.3
ATJ Insert	0.33 ⁴	0.26-1.04		0.79	0.39-1.10		0.79	0.52-1.07	
Optical	0.50	0.40-0.62	16.0	0.69	0.53-0.82	14.3	0.88	0.73-1.00	11.0

1920K

Tin		0.69 ³					0.88	0.80-0.94	6.3
Optical	0.64	0.45-0.88	19.5	0.76	0.62-0.85	10.3	0.88	0.58-1.09	21.1

Notes:

1. Data normalized to temperatures shown.
2. CV = coefficient of variation in percent.
3. One measurement only.
4. Highest value of 1.04 omitted in computing average.

INVESTIGATION OF THE THERMAL CONDUCTIVITY OF PHENOLIC-NYLON CHAR¹

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Phenolic-nylon char was studied to determine the effects of degradation temperature and heating rate on thermal conductivity. The material was predegraded under controlled conditions and thermal conductivity was measured during subsequent exposures in a steady-state apparatus. A thermal model was used to reduce the intrinsic thermal conductivity of the char solid (matrix) from the measured values. Monitors such as x-ray defraction, matrix thermal conductivity and true density were used as indicators to establish carbon-like to graphite-like changes in the material. At low heating rates (less than about 20°K/min), some ordering of the structure with a resultant increase in the thermal conductivity of the matrix was observed as the degradation temperature was increased. However, at low heating rates, the char exhibited carbon-like behavior for both thermal conductivity and lattice spacing for charring temperatures to 3000°K. It is believed that the behavior is similar to that of hard (non-graphitizing) carbons and glassy (vitreous) carbon. Chars prepared to 3000°K at high heating rates (about 100°K/sec) and with a short-time exposure (6 minutes at temperatures above 2000°K) exhibited a more graphite-like behavior for thermal conductivity and had lattice spacings below those associated with non-graphitizing carbons. This behavior cannot be disassociated from the total heating environment but was very dramatic. The slope of the thermal conductivity curve at low temperatures was about zero for the chars prepared at low heating and was definitely negative for the chars prepared at high heating rates. At 500°K, the thermal conductivities of the matrix for the chars prepared at the high heating rate were from 3 to 6 times as high as those of the chars prepared at the low heating rates to 3000°K.

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NOMENCLATURE

Letter Symbols

C	-	heat capacity
d	-	bulk density
e	-	emittance
F_{iR_2}	-	total radiation factor for reradiating openings
l	-	thickness
L	-	Lorenz Number
$\dot{m}$	-	mass flux (mass flow rate per unit area)
M	-	interception cross section per unit volume
N	-	back scattering cross section per unit volume
P	-	porosity
T	-	temperature
T_m	-	mean temperature
$\dot{V}$	-	ablation velocity

Greek Symbols

ΔT	-	temperature difference
θ	-	time
λ	-	thermal conductivity
ρ	-	volume electrical resistivity
σ	-	Stefan-Boltzmann constant
ϕ	-	pore diameter

Subscripts

c	-	charred material
e	-	electronic
eff	-	effective
g	-	gas
L	-	lattice
m	-	matrix
r	-	radiation
v	-	virgin material
x	-	distance
∞	-	reference point at which $(\frac{dT}{dx}) = 0$

1. Introduction

The prediction of the thermal conductivity of charring ablators during active ablation is difficult because direct measurements cannot be made with certainty. In an effort to provide a rationale for such predictions, Pears¹ devised a 'boxing' technique. This approach essentially involved predegrading the materials to various temperature levels and measuring the thermal conductivity up to the degradation temperature during a second exposure. The assumption was that the value of thermal conductivity during an active process was boxed between the value measured at two different precharring temperatures. This approach appeared valid if (1) time-at-temperature effects were not of primary importance and (2) the material could be thermally modeled so that the results could be extrapolated to conditions other than those of the measurements.

The work presented in this paper (reported in detail in NASA CR-66731²) involved the utilization of the boxing technique to define the thermal conductivity of charred phenolic-nylon. The approach was extended to include limited studies of the effect of time-at-temperature and heating rate. Also, a first-order thermal model was used, along with the results of characterization measurements, to reduce the measured conductivities to intrinsic properties. The intrinsic properties were then compared with those of ATJ graphite and glassy carbon to provide some insight into the nature of the charred material. Further, the behavior of the thermal conductivity reduced for the char solid was speculatively rationalized in terms of an almost constant lattice component of thermal conductivity and an electronic component which increased with temperature. Lastly, predictions of the thermal conductivity during active ablation were compared with thermal conductivity values reduced from temperature-time measurements made during steady-state ablation in an arc-jet.

2. Specimen Material

The material studied was molded phenolic-nylon of the following composition:

Zytel 103 (-120 mesh)	40 PBW
Phenolic Microballoons (-50 to +230 mesh fraction)	23 PBW
Hughes HFN Novolac	37 PBW

¹Superscripts refer to references listed at end of paper.

The constituents in the material are similar to those described in Table 1. Formulation and molding of the material is described in Reference 2. The nominal bulk density of the virgin material was about 0.60 gm/cm³.

The phenolic-novolac resin in the material was a condensation polymer formed by the reaction of phenol and formaldehyde. The thermoplastic novolac polymer was converted to an infusible cross-linked polymer by the addition of additional sources of methylene linkages. The final product is a highly cross-linked infusible polymer. The phenolic microballoons were thought to be in about the same state as the resin.

3. Apparatus and Procedure

Thermal conductivity measurements were made primarily with the radial inflow apparatus described in the paper by Mann and Pears³. High temperature measurements were made in furnaces with graphite heater tubes. An inert gas purge was used to prevent oxidation. Argon was the primary gas used; however, some measurements were made in helium. Cylindrical specimens of char could not be prepared from this material without developing cracks; hence, a strip specimen technique was employed for the measurements. This technique is shown schematically in Figure 1. Thermatomic carbon was used as packing in the corners to limit heat flows other than those through the specimen. For a more detailed discussion of the technique see Reference 2. The basic uncertainty in measurements with the radial inflow apparatus is ± 7 percent for homogeneous, well-behaved materials. The random uncertainty is estimated to increase to ± 10 percent for measurements with the strip technique. In addition to the random uncertainty, there is a systematic uncertainty in the strip measurements of perhaps $+10$ percent at elevated temperatures. This uncertainty is based on estimates of the heat flow through the thermatomic carbon relative to that through the specimen.

Electrical resistivity was measured with the apparatus shown in Figure 2. Voltage was measured with split rings which had a radius on the inside to give point contact with the specimen. Thorndel fibers were used as voltage leads. During the measurements, the open circuit voltage was read prior to the readings made with current flowing through the specimen. The open circuit voltage was algebraically subtracted to obtain the voltage drop due to current flow. Volume electrical resistivity was calculated from the measurements. The intrinsic resistivity of the char matrix (solid) was obtained by correcting for porosity from the equation

$$\rho_m = (1 - P \frac{2}{3}) \rho_{eff} \quad (1)$$

In addition to the two measurements discussed, several other measurements were made. These included thermal conductivity with the comparative rod apparatus, sonic velocity, permeability, density (true and bulk), pore diameter by microscopy, x-ray diffraction and transmittance. For descriptions of the apparatuses and procedures used for these measurements the reader is referred to NASA CR-66731².

4. Preparation and Characterization of Samples

Chars were prepared by heating in a furnace which utilized a graphite heater tube. A helium purge was used during all char runs to provide an inert atmosphere. The chars were prepared from strips of virgin material about 1.27 cm square by about 7.5 cm long. The strips were cut from a billet of virgin material about 7.6 cm thick by 30.4 cm in diameter. The long dimension of the strips was oriented in the "a-b" direction or long dimension of the billet. Sonic velocity measurements on the virgin material showed a variation of about 3 percent between the average of the "a-b" and the "c" direction. After charring, the difference in sonic velocity between the long dimension and the two short dimensions was less than about 10 percent. Thus, neither the virgin or charred material was highly anisotropic.

The strip specimen was used because sound cylindrical chars could not be prepared. At low heating rates, the material underwent a linear shrinkage of about 25 percent upon heating above 1366°K. This severe shrinkage resulted in the development of gross cracks in the cylindrical specimens.

The basic charring cycles used to prepare the chars at low heating rates are shown in Figure 3. Variations to these cycles, such as using different hold times, were used. In addition to the low heating rates, some chars were prepared by heating rapidly to 3033°K. This was done by pre-heating the furnace to 3033°K and then immersing a cylinder of virgin material about 3.8 cm in diameter in the furnace. The cold wall heat flux density to the specimen was about 4.9 MW/m². In this manner, it took about 90 seconds for the char to degrade and reach 3033°K. This approach did not work below 1366°K as the sample fragmented.

Pictures of the chars prepared in the NASA Langley arc-jet and in the furnace at low and high heating rates are shown in Figure 4. Note that the arc-jet chars and furnace chars prepared at a high heating rate were similar in appearance. The char prepared at low heating rates appeared much more homogeneous. Pictures of a char prepared at the high heating rate are shown in Figure 5. Note that a void was created in the center of the specimen and that the crack pattern in the walls of the cylinder was similar to that in the thickness direction for the arc-jet chars. A strip cut from the cylinder charred at a high heating rate is also shown in Figure 5.

Photomicrographs of arc-jet chars and slow furnace chars are shown in Figure 6. The pore structures are similar.

A typical pore diameter histogram is shown in Figure 7. The distribution shown is similar to the ones obtained for the arc-jet chars. It should be mentioned that the distribution was obtained by sectioning in a plane and cannot be taken as a three-dimensional distribution. Note that Coulter counter measurements by NASA Langley on the virgin phenolic microballoons indicate that the microscopically measured values may be biased low. Measurements of the pore size of low density phenolic-nylon made with a mercury porosimeter are in reasonable agreement with the measurements made on a two-dimensional section⁴.

Pictures of thin sections of char are presented in Figure 8. These were the samples used for transmittance measurements. Note that the holes which communicate through the sections, which are 0.0127 and 0.0254 cm thick, occupy very little of the area.

The bulk densities of the chars as a function of charring temperature for arc-jet chars, slow furnace chars and rapid furnace chars are presented in Figure 9. Note that the bulk densities are less for higher heating rates (arc-jet and rapid chars). This can partially be attributed to the fact that the rapid furnace char did not exhibit the gross shrinkage that the slow furnace chars did.

The weight losses of the specimens resulting from charring are presented in Table 2. Note that chars 5000-R2 and R3, prepared at a high heating rate, exhibited significantly less weight loss than the slow furnace chars.

Characterization data on chars are presented in Table 3. Given in the table is bulk density, true density, lattice spacing and mean pore size (from two-dimensional microscopic analysis). It should be pointed out that the "true density" values reported were obtained by liquid pycnometry on samples pulverized to smaller than 44 microns. Reference in this paper to true density means the number obtained in this manner. Hence, these values may include the volume due to microporosity within the cell walls. However, it appears that the density measured is the one that one should correct results to for thermal modeling purposes. Thus, these values were used to calculate porosity for purposes of thermal modeling. Note that none of the lattice spacings shown in Table 2 reached the value normally associated with a very well-graphitized material (3.37Å) but that the chars prepared at a rapid heating to 3033°K approached it most closely (3.39Å).

5. Method of Data Analysis

A one-dimensional superposition model wherein it was assumed that

there were parallel heat flows by solid conduction, radiation and gas conduction was used for reduction of the intrinsic properties. The equation used was

$$\lambda_{\text{eff}} = (1 - P^{\frac{2}{3}}) \lambda_m + P^{\frac{2}{3}} \lambda_g + P^{\frac{2}{3}} \lambda_r \quad (2)$$

where

$$\lambda_r = 4 \left(\frac{e}{2-e} \right) \phi \sigma T_m^3 \quad (3)$$

Equation (2) essentially agrees with that of Ribaud (presented in paper by Francl and Kingery⁵) with regard to the treatment of porosity and also is within 9 percent of Russell's analysis⁶ for porosities above 70 percent. The treatment of radiation is in agreement with Russell's analysis also. For the analysis, it was assumed that all of the porosity was open so that two different gas phases would not have to be considered.

The expression used for radiant heat transfer across the pores (equation 3) has been criticized as not being an adequate model for a material as porous as the char because of the interconnectivity of the pores. Therefore, a calculation of the radiant heat transfer was made wherein it was assumed that the char consisted of a bundle of reradiating cylindrical tubes which were parallel to the direction of heat flow and occupied P percent of the area. The tubes were assumed to have a diameter of 0.0127 cm (about three times the average two-dimensional pore diameter of the chars measured microscopically) and a length of 0.475 cm (gage length for measurements). The radiant contribution to the effective conductivity was calculated from the equation

$$P \lambda_r = 4 P \sigma l F_{iR_2} T_m^3 \quad (4)$$

where

λ_r = radiant conductivity

σ = Stefan-Boltzmann constant

l = length of tubes of diameter ϕ and length over which measurements were made

F_{iR_2} = total radiation factor

T_m = mean temperature (absolute)

For the diameter to length ratio of the openings, the total radiation factor, F_{iR_2} , was found to be about 0.03 from solutions given by Jakob⁷.

Assuming a porosity of 85 percent, the radiant conductivity at 3000°K was calculated to be 0.74 W/m-K. This is about 1.35 times the value calculated from the model used in equation (2) for the same pore size. The absolute values in either case are not large relative to the measured values and since the pores may not be as large as was assumed and do not extend all the way through the char, it was tentatively concluded that the radiant conductivity given by equation (3) is reasonable for an opaque material which transfers heat by absorption and re-emission.

The expression $4 T_m^3 \Delta T$ was used in place of $(T_1^4 - T_2^4)$ in developing equation (3). It can be shown algebraically that this is a valid assumption (within less than 3 percent uncertainty) if ΔT is less than $0.346 T_m$.

The radiant component of thermal conductivity was also investigated with an analysis presented by Larkin and Churchill⁸. The radiant heat transfer equations in terms of interception, absorption and back scattering cross sections have been solved by these authors for restrictive boundary conditions. With a forward radiant flux of unity at one boundary ($x = 0$) and a backward radiant flux of zero at the other boundary ($x = 1$) the following equation gives the transmitted flux

$$I_1(1) = \frac{1}{\cosh l \sqrt{M^2 - N^2} + \frac{M}{\sqrt{M^2 - N^2}} \sinh l \sqrt{M^2 - N^2}} \quad (5)$$

This equation was used to attempt a correlation of the transmittance measurements. An important point to remember is that M is the interception cross section and must always be larger than N . For the case where absorption is dominant ($M \gg N$) the approximate solution given by Larkin and Churchill⁸ was

$$\lambda_r(0) = \frac{4 \sigma e_0 T^3}{M} \quad (6)$$

where

$\lambda_r(0)$ = radiant conductivity $x = 0$

e_0 = boundary emissivity at $x = 0$

The value of M in equation (5) was approximately determined at room temperature from transmittance measurements with the result that the values calculated from equations (3) and (6) were in reasonable agreement.

The treatment of radiation appears adequate if the material does not become somewhat transparent to thermal radiation at elevated temperatures. Transparency effects were not included in the model because we have no

direct evidence that these effects are significant.

A speculative attempt was made to rationalize the behavior of the reduced values for the thermal conductivity of the matrix. The lattice component of thermal conductivity was calculated at low temperatures from a fit of the data and extrapolated to high temperatures. The electronic component was calculated from the measured electrical resistivity and Lorenz numbers based on the Sommerfeld value at low temperatures and values reported by Kaspar⁹ above 2000°K. The equation assumed for these calculations was

$$\lambda_m = \lambda_L + \lambda_e$$

$$\lambda_m = \frac{1}{A T + B} + \frac{L T}{\rho} \quad (7)$$

The form $1/A T + B$ used for the lattice component is the same as that used by McElroy, et al. of ORNL¹⁰ to correlate thermal conductivity data for graphite to 1000°C.

Temperature-time measurements made during steady-state ablation in an arc-jet were reduced to obtain thermal conductivity values. The analysis used was based on a solution of the general heat conduction equation for the conditions of steady-state ablation (char surface receding at the same rate as the interface). The equations used for the virgin zone and char layers were

Virgin Zone

$$\lambda_{\text{eff}} = \frac{d_v C_v \dot{V}^2 (T_x - T_\infty)}{\left(\frac{dT}{d\theta}\right)_x} \quad (8)$$

Char Layer

$$\lambda_{\text{eff}} = \left[d_c C_c + (d_v - d_c) C_g \right] \frac{\dot{V}^2 (T_x - T_\infty)}{\left(\frac{dT}{dx}\right)_x} \quad (9)$$

Equations (8) and (9) were derived based on the assumption that the derivative $\left(\frac{dT}{d\theta}\right)$ is equivalent to $\dot{V} \left(\frac{dT}{dx}\right)_x$ during steady-state ablation. The mass flux of the gases was calculated as

$$\dot{m} = \dot{V} (d_v - d_c)$$

It was assumed that the gases and the char solid were in equilibrium. It was not necessary to assume constant thermal properties for the analysis.

6. Data and Results

Typical data for the effective thermal conductivity of the slow furnace char are presented in Figure 10. The data shown are for specimens which had been predegraded at 3033°K. Note that data were obtained in both the comparative rod and radial inflow apparatuses. Data are presented in Figure 11 for the char prepared at rapid heating rates. Note that data for arc-jet and slow furnace chars have also been presented in the figure for comparison.

A composite plot of the effective thermal conductivities of chars predegraded to various temperatures at low heating rates is shown in Figure 12. The thermal conductivity at low temperatures increased as the charring temperature was increased. Data on the arc-jet chars prepared at 1.13 MW/m² and 2.27 MW/m² are shown in the figure for comparison. The degradation temperature of the arc-jet chars is difficult to define because a gradient existed during the charring process.

As additional information, chars prepared by heating slowly to 1022°K, heating rapidly to 1366°K and shutting off power immediately upon reaching 1366°K had the same thermal conductivity at 800°K as chars which were held at 1366°K for 30 minutes. Also, it was established that once a sample had been exposed to 3033°K the thermal conductivity remained invariant for subsequent exposures.

Values of electrical resistivity measured as a function of temperature are presented in Figure 13 for a sample which was prepared by heating slowly to 3033°K. The values presented have been corrected to the true density with the use of equation (1). Electrical resistivity values for grades CFZ and CS graphite are presented in Figure 13 for comparison.

The results of transmittance measurements made with the sample at about 302°K are presented in Figure 14. An approximate interpretation of the data in terms of absorbing and back scattering cross sections was made from equation (5) which was taken from the work by Larkin and Churchill⁸. From the limited data, the parameters could not be determined exactly. However, the value of M (interception cross section) had to be 276 cm⁻¹ or greater to satisfy the data. As higher values of M were assumed the value of N had to be larger to satisfy the data and N could not be determined with certainty from the available data. It was concluded that the range of the parameter could be adequately covered by the following:

$M = 276 \text{ cm}^{-1}$ and $M \gg N$ (absorption predominates)

$M = 314 \text{ cm}^{-1}$, $N = 296 \text{ cm}^{-1}$; $M \approx N$

Since the char is opaque and absorbing at low temperatures one would believe that M would be much larger than N .

Characterization data are presented in Table 3. The observed true densities, lattice spacings, electrical resistivities and thermal conductivities for the slow furnace chars were in agreement with values reported in the literature ^{11,12} for non-graphitizing (glassy) carbons. In particular, Kobayashi, Sugawara, Toyoda and Honda¹¹ reported a lattice spacing of 3.44 Å for carbon from phenol formaldehyde which had been heat treated to 3273°K. This seems to be the smallest spacing that can be obtained for this class of materials. The value of 3.44 Å is considered to be significantly above the value of 3.37 Å normally associated with graphitic materials.

7. Discussion

Most changes which strongly influence the thermal conductivity of the char are related to the behavior of the solid. Hence, it is important to understand the solid behavior. The effective values of thermal conductivity were reduced to values for the matrix with equations (2) and (3). The values of porosity and pore size used in the calculations were those given in Table 3 except that the mean pore size was taken to be 130 microns (about 3 times as large as that measured in the two-dimensional sections and more in line with the values measured by NASA on the virgin phenolic microballoons). A typical data reduction (for the char prepared at low heating rates to 3033°K) is indicated in Figure 15 and in Table 4. This involved subtracting the radiant and gas contributions from the effective value and then correcting for porosity to obtain the thermal conductivity of the matrix.

The values of matrix conductivity which were reduced from the thermal conductivity data shown in Figures 11 and 12 are presented in Figure 16. The effect of heat treatment for the slow furnace chars was to drive the thermal conductivity of the matrix to higher values at low temperatures to a maximum of about 13 W/m - °K for the char prepared at 3033°K. The major observation to be drawn from these data is that heat treatment to 3033°K did not drive the thermal conductivity to a "graphitic" level. The boxing curve connecting the thermal conductivity values measured at each precharring temperature level represents the best estimate of the matrix thermal conductivity for charring conditions within the range of heating rates for which the data apply. One might suppose that during active ablation most subsurface locations would undergo rates within the range of the arc-jet chars which had thermal conductivity values within the range of the slow furnace chars (see Figure 16). However, the initial surface char layer might have different values because of heating rate effects.

The chars prepared at the high heating rate to 3033°K had significantly higher values for matrix thermal conductivity than the slow furnace chars and had an entirely different character (see Figure 16). Values for ATJ graphite are presented in Figure 16 for comparison. Note that specimen 5000-R2 had values approaching those of the ATJ graphite. The reasons for the behavior of the rapid furnace char are not understood. Phenolic-nylon is a cross-linked polymer and under normal conditions will not graphitize for heat treatments to 3000°K. Any conclusions without further study are purely speculative. However, two possibilities bear further consideration. One is that rapid heating through the degradation temperature range destroys the cross-links and allows the material to graphitize. The other is that the gases may have cracked and left pyrolytic-type deposits on the pore walls. Both of these could be related to the fact that the weight loss was less for the rapid heating rates. There is no doubt that the rapid char was different than the arc-jet and slow furnace chars since the lattice spacings and true density were significantly different (see Table 3) and more closely approached graphite-like values.

The thermal conductivity values reduced for the matrix of the slow char prepared at 3033°K are compared in Figure 17 with literature data¹³ for a similar non-graphitizing carbon of higher bulk density. Note in Figure 17 that the boxing values for the thermal conductivity of the matrix have also been presented under the assumption that the increase in thermal conductivity is explained by radiant transport. For this analysis, radiation was calculated by assuming that the thermal conductivity of the matrix for the 3033°K char remained constant at the value which it had at 1000°K. This analysis was performed on the boxing data shown in Figure 12. Electrical resistivity values for the char and carbon are presented in the upper portion of Figure 17. The disagreement in the thermal conductivity values for the reference data and the char prepared to 3033°K at a low heating rate is severe. One might conclude that the thermal model did not allow for enough radiant transport and hence the reduced values of λ_m are erroneously high at elevated temperatures. This problem cannot be completely resolved without further investigation. However, it would appear that if the increase were related to a severe problem with thermal modeling, the analysis of the data for the rapid furnace char would have been similarly affected. Nevertheless, other models and treatments of radiation (analytical and experimental) need investigation.

The lattice and electronic components of thermal conductivity were briefly investigated to see if the increase in matrix conductivity (for a property-stabilized char) could be rationalized. For the analysis, the data for the slow char prepared to 3033°K were used since this material was stable and did not change as a result of thermal exposure during the measurements. The electrical resistivity values used for the analysis were presented in Figure 13 and the thermal conductivity values were those shown in Figure 16. For the analysis, equation (7) was used with the Lorenz number assumed to

vary as shown in Figure 18. The constants in the expression for the lattice component were obtained by fitting the equation to the values of matrix conductivity reduced from the experimental measurements at 500 and 1000°K. The calculations are presented in Figure 19 and Table 4. Note in Figure 19 that the lattice component is rather constant with temperature whereas the electronic component increases significantly with temperature. There is some reason to believe that the lattice component might be relatively constant for a grossly disordered material such as this. The calculated value of λ_m has a different character than the value reduced from the experimental data but exhibits a comparable increase with temperature. Of course, these results are influenced by the choice of the functional relationship for the lattice conductivity. If a relation of the form C/T had been used the calculated value of λ_m at 3000°K would have been about 20 W/m - °K instead of 24 W/m - °K as shown in Figure 19. However, λ_m would still increase with temperature.

The properties of the char are compared with those of glassy carbon and ATJ graphite in Figure 20. These comparisons indicate that the properties of the arc-jet and slow furnace chars are more like those of glassy carbon (non-graphitizing) than graphite. The rapid furnace char had properties different than those of the glassy carbon and similar to those of graphite.

As a final point of interest, predictions of thermal conductivity were compared with values reduced from steady-state ablation data presented by Thompkins¹⁴ and Space General¹⁵. During those measurements, temperatures were measured with one thermocouple imbedded in the material. The temperature-time curves are shown in Figure 21. The ablation velocity was better defined in the work done by Thompkins. The data were analyzed by using equation (8) for the virgin material and equation (9) for the char layer. Note in Figure 21 that the data were extrapolated from 1500°K to the surface temperature. The surface temperature used for the analysis of Thompkins' data was estimated based on a familiarity with typical values reported in publications by NASA Langley for chars of the same material prepared in the arc-jet under similar conditions.

The values of thermal conductivity reduced for the virgin material from the steady-state ablation data are presented in Figure 22. Note the agreement between the values reduced from Thompkins' data and those measured at SRI in a steady-state apparatus. The values for the char are presented in Figure 23. For these calculations, values reported by Kratsch¹⁶ for the enthalpy of the gaseous products of pyrolysis for 50 phenolic - 50 nylon were used. The instantaneous density of the char was calculated by linear interpolation between values of 0.65 gm/cm³ at 800°K and 0.30 gm/cm³ at 1650°K and was assumed constant at 0.30 gm/cm³ above 1650°K. Calculations were also made by neglecting the heat absorption by the pyrolysis gases in order to show the effect of this parameter. Note that when absorption by the gases is considered there is good agree-

ment between the reduced values and the values predicted from the steady-state measurements. If the gases are not in equilibrium with the char, as is very likely, the effect might be to lower the reduced values of conductivity by an amount dependent upon the degree of non-equilibrium.

8. Conclusions

Chars of phenolic-nylon prepared at temperatures of 2000°K or below exhibit values for the thermal conductivity of the matrix which are mostly dependent upon the charring temperature and which are more carbon-like than graphite-like. The effect of time at temperature was not found to be significant for the times involved in preparing the chars and making the measurements. The same is true for temperatures to 3033°K if the heating rate is low. These conclusions were confirmed by measurements of thermal conductivity, true density, sonic velocity and electrical resistivity. High heating rates to 3033°K result in a char which has matrix thermal conductivity values which are more graphite-like.

The radiant heat transfer through the material was not separated experimentally. However, analysis led to the conclusion that the char must become transparent at temperatures above 2000°K for radiation to become significant. The small pores within the char appear to significantly retard radiant transport by absorption and re-emission. Equation (2), which was the thermal model used to analyze the data and provide the basis for extrapolation, is considered a reasonably acceptable model for the char except for the uncertainty in transparency to radiation. More work needs to be done in the area of thermal modeling and also in the area of direct experimental separation of the radiant component of heat transfer. This will involve a much more detailed characterization of the structure of the material than has yet been performed.

The boxing values presented for the thermal conductivity of the matrix seem to define the transient behavior of the solid to 2000°K with reasonable certainty. Between 2000°K and 3000°K the values are uncertain because of the uncertainty in radiant transport. For the particular thickness of chars investigated, the effective thermal conductivity in this temperature range would be about the same regardless of whether it was attributed to radiation or solid conduction, provided that the gases evolved during charring do not absorb radiant energy. However, for different thicknesses of char and higher temperature gradients, the radiant transmission would probably be different from that through the furnace chars, if the char is transparent. At 3033°K , the thermal conductivity of the matrix was reasonably well defined for conditions of rapid heating. This conclusion was drawn from the values of matrix thermal conductivity determined for the rapid furnace char prepared to 3033°K . The values were reduced under the assumption of an opaque material. The character of the curve followed that for a graphite and indicated that the assumption of opacity for a char prepared

under this particular condition was probably valid. Hence, the values of the matrix thermal conductivity of the char are defined within a reasonable certainty from 500°K to 2000°K and at 3000°K. These values when used in equation (2) along with the proper values of other variables (defined in Reference 2) allow a reasonable prediction of the transient behavior of the thermal conductivity of the char.

From an analysis of the data, it was found that the thermal conductivity of the matrix increased as a function of temperature. The thermal conductivity of the matrix increased from the effects of heat treatment but also was found to increase when the char was thermally stabilized. Part of the increase may be due to a bias in the experimental measurements but it appears that the increase is a real effect. An analysis of the thermal conductivity of the matrix in terms of the lattice and electronic components of thermal conductivity indicated that the behavior could be rationalized if the Lorenz number reaches a value of $9 \left(\frac{k}{e} \right)^2$ above 2000°K as reported by Kaspar⁹.

From all of the evidence it appears that one cannot analyze the behavior of non-graphitizing carbon in the same manner as one would a "soft" or graphitizing carbon. For the non-graphitizing carbon, the properties do not drive directly from carbonaceous to graphitic as a function of heat treatment.

The analysis of the transient temperature measurements during steady-state ablation reinforced the validity of extrapolating the steady-state boxing values of thermal conductivity to transient conditions. However, undertainties in the validity of the assumptions made in developing the equation for the analysis of the data and in the enthalpy of the pyrolysis gases disallow using that comparison as final proof.

9. Acknowledgements

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- Notes
1. Specimen is 5.08 cm long. Sight holes consist of 0.178 cm dia holes 2.54 cm deep counterbored 0.236 cm dia and 1.27 cm deep
 2. "A" dimension 0.0787 cm for some specimens and 0.127 cm for others

Figure 1. Strip specimen configuration for radial inflow apparatus

Figure 2. Schematic of apparatus used for high temperature electrical resistivity measurements

Figure 3 Temperature-time cycles used to prepare phenolic-nylon char at low heating rates

b. Arc-jet char prepared at 1.13 MW/m^2

c. Furnace chars

Figure 4. Pictures of arc-jet chars and furnace chars

a. Internal view of end section of cylinder charred at rapid heating rate

b. Heated surface of cylinder charred at rapid heating rate

a. Closeup view of heated surface

b. Full view

c. Strip from radial inflow thermal conductivity specimen 5000-R2

Figure 5. Pictures of phenolic-nylon charred in furnace at rapid heating rate

2.27 MW/m² arc-jet char
Heated Surface

1.13 MW/m² arc-jet char
Heated Surface

1366°K Furnace Char-Low
Heating Rate

3033°K Furnace Char-Low
Heating Rate

Figure 6. Photomicrographs at 100X Magnification of Phenolic-Nylon Charred in NASA Langley Arc-Jet and in Furnace at SRI

Figure 7. Two-Dimensional Pore diameter histogram for phenolic-nylon furnace charred at 3033°K (Low heating rate)

0.100 cm
0.039 in.

- a. 0.0254 cm (0.010 in.) thick
measured transmittance = 2.5%
measured area fraction of holes = 5.06%
using point count technique

0.100 cm
0.039 in.

- b. 0.0127 cm (0.005 in.) thick
measured transmittance = 11.4%
measured area fraction of holes = 12.5% to 16.8%
using point count technique

Figure 8. Pictures at about 10X Magnification of Thin Sections of Phenolic-Nylon Charred in a Furnace at a Low Heating Rate

Figure 9. Bulk density of phenolic-nylon char versus charring temperature

a. Internal view of end section of cylinder charred at rapid heating rate

b. Heated surface of cylinder charred at rapid heating rate

a. Closeup view of heated surface

b. Full view

c. Strip from radial inflow thermal conductivity specimen 5000-R2

Figure 5. Pictures of phenolic-nylon charred in furnace at rapid heating rate

2.27 MW/m² arc-jet char
Heated Surface

1.13 MW/m² arc-jet char
Heated Surface

1366°K Furnace Char-Low
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measured transmittance = 11.4%
measured area fraction of holes = 12.5% to 16.8%
using point count technique

Figure 8. Pictures at about 10X Magnification of Thin Sections of Phenolic-Nylon Charred in a Furnace at a Low Heating Rate

Figure 9. Bulk density of phenolic-nylon char versus charring temperature

Symbol	Spec.	Charring history	Density, gm/cm ³	Type references	Environment for measurements
Comparative Rod Apparatus					
●	1F5000-3	3033°K for 180 minutes	0.347	Pyroceram	Nitrogen
▲	4F5000-5	3033°K for 300 minutes	0.353	Pyroceram	Nitrogen
Radial Inflow Apparatus					
○	TC5	3033°K for 30 minutes	0.349		Argon purge, Run 3
△	2F5000-2	3033°K for 120 minutes	0.353		Argon purge, Run 2
⊗	TC13	3033°K for 30 minutes	0.351		Argon purge, 4 to 7 percent impregnation with thermatomic carbon

Figure 10 . The effective thermal conductivity of phenolic nylon furnace charred at low heating rate to 3033°K measured in argon

Figure 11. The effective thermal conductivity of chars prepared in the furnace at rapid heating rates (cold wall heat flux $\approx 4.9 \text{ MW/m}^2$)

Figure 12. Summary of effects of charring temperature level on thermal conductivity of char prepared in furnace at low heating rate

Figure 13. Electrical resistivity of phenolic-nylon charred at low heating rate to 3033°K (3 hours at temperature)

Figure 14. Transmittance at 294°K of phenolic-nylon charred at 3033°K for 30 minutes

Figure 15. Calculated Contributions of the Various Modes of Heat Transfer to the Effective Thermal Conductivity of the Char Prepared to 3033°K at a Low Heating Rate

Figure 16. Results of reductions of matrix (solid) thermal conductivity from effective thermal conductivity measurements using $4P^{2/3}/\sigma T_m^3$ as the radiant contribution

Figure 17 Comparison of values of λ_m (matrix) reduced from measurements with data on another carbon-like material

Figure 18. Values of Lorenz Number Used in Calculating Electronic Component of Thermal Conductivity of Matrix

Figure 19. Comparison of Calculated and Reduced Values of Thermal Conductivity of Matrix

Figure 20. Relation of properties measured to properties of glass-like carbon (nongraphitized) and ATJ graphite

Figure 20 continued

Figure 21. Temperature-time curves from ablation testing of low-density phenolic-nylon by other laboratories

Figure 22. Comparison of thermal conductivity of virgin phenolic-nylon with values obtained from data reductions of transient temperature measurements made during simulated ablation tests at other laboratories

Figure 23. Results of reduction of thermal conductivity values from temperature-time data on low-density phenolic-nylon during simulated ablation tests

Table 1

DESCRIPTION OF CONSTITUENTS (OR SIMILAR MATERIALS)
USED IN FORMULATING THE BILLETS OF LOW-DENSITY PHENOLIC-NYLON

The following detailed description of each constituent within the low-density phenolic-nylon was supplied by the NASA Langley Research Center.

Union Carbide BRP-5549
Phenolic Resin

The properties of the resin as published by the manufacturer are shown in the table below.

<u>Property</u>	<u>Property Value</u>
Density	16.8 to 19.4 lb/ft ³ (270 to 310 kg/m ³)
Sieve Analysis (U.S. Std. Mesh)	
on 40 mesh	0.0%
on 100 mesh	0.6%
on 200 mesh	2.0%
through 200 mesh	98.0%
Hexamethylene tetramine content	8.7 - 9.5%

Measurements with a Coulter Counter (Coulter Electronics Industrial Division) at the Langley Research Center indicate that the range of diameters of the phenolic resin powder particles is 0.0001 to 0.0048 in. (2 to 120 μ m) with about 80 percent by volume of powder having diameters ranging from 0.0003 to 0.0023 in. (6 to 58 μ m).

Table 1 - continued

Phenolic Microballoons

The properties of the Microballoons as published by the manufacturer are given in the following table:

Property	Property Value
Density (liquid displacement)	15.6 lb/ft ³ (250 kg/m ³)
Density (air displacement)	18.7 lb/ft ³ (300 kg/m ³)
Flotation in toluene dupanol solution	Not less than 90 % must float
Average particle size (dia)	0.0017 in. (43 μ m)
Size range (dia)	0.002 to 0.0005 in. (13 to 51 μ m)

Measurements with the Coulter Counter indicate that the range of diameters of the phenolic Microballoons is 0.0004 to 0.0100 in. (10 to 250 μ m), with approximately 85 percent by volume of the Microballoons having diameters ranging from 0.0024 to 0.0080 in. (60 to 200 μ m).

Nylon

Properties of the nylon powder as given by the manufacturer are listed in the table below:

Property	Property Value
Specific Gravity	1.3 - 1.15
Melting Point	482 - 500°F (523-533°K)
Tensile Strength	11,800 psi (81.4 MN/m ²)
Coefficient of Linear Thermal Expansion	45.0 x 10 ⁻⁶ in./in. - °F (81.1 x 10 ⁻⁶ m/m - °K)
Thermal Conductivity	1.31 x 10 ⁻⁴ Btu-in./ft ² sec °F 0.068 W/m °K
Specific Heat	0.3 - 0.5 Btu/lb °F 1.25 to 2.09 kJ/kg - °K

Preliminary studies using a Coulter Counter indicate that about 85 percent by volume of the nylon powder lies in the range from about 0.0012 to 0.0157 in. (30 to 400 μ m) in diameter, with about 5 percent below 30 μ m and 10 percent above 400 μ m.

Table 2

WEIGHT LOSS OF SPECIMENS DURING CHARRING

Specimen	Char history	Percent weight loss	Density of char (gm/cm ³)
TC19	Charred at slow rate to 812°K	67.6	0.289
TC16	" "	67.5	0.302
TC14	" "	67.1	0.323
TC1	" "	69.2	0.303
TC8S	" " 1366°K	74.9	0.365
TC17	" "	75.1	0.377
5R	Charred at slow rate to 922°K-rapid rate to 1366°K	73.4	0.342
TC10	Charred at slow rate to 1366°K	72.3	0.377
TC2	" "	74.4	0.363
TC6S	" " 1922°K	75.8	0.321
TC3	" "	75.6	0.335
TC11	" "	73.9	0.341
TC7S	" " 2400°K	78.1	0.330
TC4	" "	74.6	0.339
TC12	" "	74.2	0.344
1F5000-3	" " 3033°K	----	0.347
4F5000-5	" "	----	0.353
TC5	" "	74.9	0.349
2F-5000-2	" "	----	0.353
TC13	" "	73.2	0.351
5000R1	Charred at rapid rate to 3033°K	----	0.210
5000R2	" "	53.4	0.233
5000R3	" "	38.7	0.236
3F5000-3	Charred at slow rate to 3033°K	----	0.363
P1	" " 812°K	67.0	0.337
P2	" " 1366°K	71.8	0.387
P3	" " 1922°K	74.1	0.327
P4	" " 2480°K	76.5	0.320
P5	" " 3033°K	73.1	0.310

Table 3

SUMMARY OF RESULTS OF MEASUREMENTS MADE TO CHARACTERIZE PHENOLIC-NYLON CHARs

Material Description	Bulk Density (gm/cm ³)	"True Density" ¹⁶ (gm/cm ³)	Porosity (%)	"d" Lattice Spacing (Å)	Relative Intensity (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Mean Pore Size (microns)	
1.13 MW/m ² arc-jet char - 0 to 1.8 mm below surface	0.25	1.56	82/87	(002) 3.44	38/40 ⁴	90.1/ 98.6 ³	0.3/0.4 ²	0.4/1.2 ²	40	Spectrograph also indicated presence of Mg, Si and Ca in about equal concentrations
1.13 MW/m ² arc-jet char - 4.5 to 7.2 mm below surface	0.25	1.56	82/87	(002) 3.91/4.10	34/15 ⁴	90.2/ 91.2	0.4/0.8	0.9/1.1	28	
2.27 MW/m ² arc-jet char - 0 to 3.7 mm below surface	0.29	1.50	80/83	(002) 3.44/3.45	89/100 ⁴	93.4/ 98.4 ²	0 ² /0.4	0.2/0.3 ²	38	Spectrograph also indicated presence of Mn, Mg, Si, and Ca. Mn in highest concentration, Ca in lowest concentration.
2.27 MW/m ² arc-jet char - 5.0 to 7.9 mm below surface	0.29	1.50	80/83	(002) 3.44/3.45	89/100 ⁴	93.7/ 98.4	0.5/2.66	0.2/0.5	38	
812°K furnace char, low heating rate in helium held 30 minutes at temperature	0.304	1.44	79			81.2	2.89	1.87		
1366°K furnace char, low heating rate in helium, held 1 hr at temperature	0.374		74			84.4	1.37	1.46		
1922°K furnace char, low heating rate in helium, held 1 hr at temperature	0.331	1.43	77	(002) 3.83	26 ⁴					
3033°K furnace char, low heating rate in helium, held 1 hr at temperature	0.347	1.46	76	(002) 3.44	53 ⁴	83.65/ 99.69	0.3/0.5	<0.1 / <0.2	40	

Table 3 continued

Material Description	Bulk Density (gm/cm ³)	"True Density" ⁶ (gm/cm ³)	Porosity (%)	"d" Lattice Spacing (Å)	Relative Intensity (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Mean Pore Size (microns)	
(S) 216, 3033°K furnace char, low heating rate in helium, held one hour at temperature				(004) 3.43	83					
(RO) 218, Char prepared by immersing in furnace preheated to 3033°K - Sample from outer 2mm of char				(004) 3.41	77 ⁵					
(RI) 219, Char prepared by immersing in furnace preheated to 3033°K - Sample came from interior of charred material				(004) 3.40	90 ⁵					
(RK) 217, Char prepared by immersing in furnace preheated to 3033°K. Sample heated again to 3000°K during conductivity measurement	0.23	1.78	87	(004) 3.39	100 ⁵					
Very well - graphitized material				(004) 3.354						

- Notes: 1. Suspect incomplete oxidation of sample.
 2. Used better procedure to obtain more reliable measurement.
 3. Slashes give range of values where two or more measurements were made.
 4. Relative to intensity of the (002) line for the arc-jet char prepared at 2.27 MW/m²
 5. Relative to intensity of the (002) line for Sample (RK) 217
 6. "True density" is density measured by liquid pycnometer method.

Table 4

Data Reductions for Lorenz-Lattice Analysis of Data for Char
Prepared at Low Heating Rate to 3033 °K

Temperature °K	λ_{eff} W/m°K	$P^{\frac{2}{3}} \lambda_r$ W/m°K	$P^{\frac{2}{3}} \lambda_g$ W/m°K	λ_m Reduced From Measured Values W/m°K	L Lorenz Number $(\frac{k}{e})^2$	ρ Electrical Resistivity $\mu \text{ ohm-cm}$	λ_e W/m°K	λ_L W/m°K	λ_m Calculated W/m°K
500	2.20		0.03	13.6 ¹	3.3	3850	0.3 ¹	13.3 ¹	13.6 ¹
1000	2.27	0.02	0.06	13.7 ¹	6.3	2900	1.6 ¹	12.1 ¹	13.7 ¹
1500	2.45	0.07	0.07	14.4	8.2	2300	4.0	12.0	16.0
2000	2.90	0.16	0.10	16.5	9.0	2000	6.7	11.9	18.6
2500	3.65	0.31	0.12	20.1	9.0	1800 ²	9.3	11.8	21.1
3000	4.65	0.55	0.14	24.7	9.0	1650 ²	12.1	11.7	23.8

Notes:

1. Constants in equation for λ_L were established by fitting to these data taking $\lambda_L = \lambda_m - \lambda_e$
2. Obtained by extrapolating data above 2250 °K
3. Values of constants used in analysis were:
 P (porosity) = 0.77
 ϕ (pore size) = 130 microns ($\sim 5 \times 10^{-3}$ in.)
 e (emmittance) = 0.9
 r (reflectance) = 0.1

Experimental Methods I

Chairman: R. E. TAYLOR

Thermophysical Properties Research Center
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IMPROVEMENTS OF THE LINEAR HEAT-FLOW METHOD*

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ABSTRACT

Stable heat sink temperatures can be obtained anywhere within the ranges attainable by pumping over refrigerants. Outside these ranges this is more difficult so the resolution of thermal - conductivity measurements consequently is lower. We describe a system in which a large copper heat sink (1kg in weight) is adiabatically shielded to provide an infinitely variable heat-sink temperature stable to about 1 mK hr^{-1} . This is used in conjunction with differential thermocouple thermometry to determine the temperature gradient along the specimen. Even with samples with long equilibrium times (approaching 30 minutes), measurements can be made using different heat-flows through the sample whilst the temperature gradients along the thermocouple leads, and hence the spurious potentials, remain constant. We have found that it is essential to bring the leads up the vacuum line rather than through the refrigerant, otherwise the changing refrigerant levels cause variations.

The technique is being applied to ice (ferroelectric transition) and to Europium Oxide (ferromagnetic transition); in the latter sample a sharp anomaly is known to be present in the thermal conductivity. Data with a random scatter of less than 1% at temperatures defined to $\pm 50 \text{ mK}$ appears possible.

INTRODUCTION

Usually it is of little consequence if a measured value of thermal conductivity is a mean value over a range of a degree or two because this physical property rarely has fine detail. However Morris and Cason¹ have shown that the conductivity of Europium Oxide (EuO) decreases by a factor of ten near its Curie point; this singularity extends over a range of only a degree or so. In order to determine the critical exponents of this anomaly it is necessary to measure the conductivity with higher resolution than was possible with Morris's apparatus; we set out to obtain data whose temperature was defined to better than 50mK with a random error of less than 1%.

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Konantz² showed that the conductivity of PuO is strongly dependent upon magnetic field. A second instrument is being constructed which will accommodate a small superconducting magnet capable of producing very uniform fields of up to 3 Kilogauss.

Experimental System

Experimental problems fall into two categories, the first being the provision of a heat sink whose temperature can be adjusted to and maintained exactly at any desired temperature and the second is to measure temperature differences of 100mK to within 1mK over the entire temperature range 4 to 300°K. The system used is an improved version of the one described by Rechowicz, Ashworth and Steeples³ in which a large (1Kg.) thermally isolated copper block is surrounded by an adiabatic shield as shown in figure 1. In the original instrument heat sink temperatures stable to better than 1 mK hr⁻¹ were achieved near nitrogen temperatures. Improvements incorporated in the current instrument include the provision of a more efficient heat switch, servo-control of the adiabatic shield to better than 3 mK, and the addition of a temperature-controlled platform to which the leads are strapped before going to the adiabatic shield; this platform is part of the heat switch assembly and it also serves as a radiation baffle.

Differential thermocouples have many advantages over other systems for measuring small temperature differences at temperatures above 10°K. Recent developments in the field of solid state electronics have provided d.c. detectors capable of resolving to a few nV. so that sensitivity is no longer a problem. Also the recently developed Au-Fe series of alloys, particularly when referred to Chromel, provide a thermocouple with high sensitivity down to 1 K.^{4,5,6} Remaining are the problems of preventing noise in the signal and the elimination of the spurious e.m.f.'s. generated in the leads. Provision of both electrostatic and magnetic screening is the only precaution that can and need be taken to remove a.c. pickup, but the removal of parasitic d.c. signals is much more difficult.

Several authors^{5,7} have found that good quality copper wire (preferable with the lowest possible iron impurity) generates the lowest spurious signal when passing through regions of large temperature gradients; this is in agreement with the author's observations. Hence unjointed lengths of thermocouple grade copper wire⁸ were taken from the measuring potentiometer via an epoxy lead seal⁹ to the terminal block inside the heat sink. Where connection is made to the Chromel wires. With this arrangement temperature gradients are avoided along the Chromel wires and the stability of the temperature gradients along the copper wires has resulted in spurious signals which are stable to 10nV or better. Moreover, the stability achieved in the sink temperature allows measurements of the signal for two or more rates of supply to the gradient heater, all at the same temperature. Leads are thermally anchored to appropriate temperatures and then are brought up the vacuum tube; whilst this arrangement does not give an equilibrium temperature exactly equal to the boiling point of the refrigerant (with the heat switch closed and open we achieved temperatures of 4.2 and 4.9°K respectively) it has the great advantage over bringing the leads through the refrigerant that spurious signals are very much less dependent upon the refrigerant level.

An inner shield with heater was incorporated so that the sample temperature distribution could be matched on the surrounding surface.

Also the Chromel thermocouple wires are strapped to the temperature of the junction on this shield. The effect of radiative and other modes of heat loss from the sample could be investigated with this system.

The modifications to the system to facilitate measurements in a magnetic field are shown in figure 2; the magnet has a 1 1/2" core and produces a uniform field (to within 1%) over the entire region of the sample.

Performance

Mechanical heat-switches are desirable in instruments in which thermal measurements are carried out since they obviate the need for exchange gas and there is no chance of desorption effects. Figure 3 demonstrates the efficiency of the platform-type switch employed which facilitates the cooling of more than one component; this is much more difficult with jaw-type switches. About 1 hour is needed to cool to nitrogen temperatures, a temperature close to 50K is reached by pumping on the nitrogen but this requires a few hours. Helium temperatures are obtained within a few minutes of covering the can with liquid; the cooling charge required is less than 3 liters.

Test results have been taken on a nylon cell which is to be used for measurements on ice. This "sample" is ideal for this purpose since its low conductance and attendant long equilibrium time magnify any errors. Above room temperature the heat-sink temperature is stable to better than 1/2 mK hr⁻¹; at lower temperatures the stability improves even on this value.

It is easily shown that the errors caused by radiative heat losses is inversely proportional to the conductance of the sample. It was estimated that, with the inner shield at the temperature of the cold end of the sample, heat losses of greater than 1 mW could be sustained with a temperature difference of 1K between the thermocouple junctions; it was for this reason that the inner shield was incorporated and the results presented in figure 4 verify the need for this shield. Above room temperature some 50% of the heat supplied to the sample heater is lost by radiation and a small amount is lost by conduction along the heater leads. At 80 K radiation losses are negligible, the total heat losses here are about 10%.

Figure 4 also demonstrates the resolution that is being achieved. Measurements on this curve go down to a temperature difference of 50mK, which corresponds to a signal of only 1μV and even at this level the scatter of results is only ± 2% as shown in table 1. Figure 5 illustrates the consistency of the conductances obtained.

Table 1 Conductance of cell at 302K using inner shield heater

ΔT (K)	Conductance (mWK ⁻¹)
1.03	1.151
0.30	1.149
0.119	1.124
0.051	1.166

Conclusions

It is concluded that high resolution measurements are possible (approaching $\pm 1\%$ with $\Delta T \sim 1K$) on even the poorest conductors up to 300K. At lower temperatures where radiative losses are no longer a problem, measurements are possible to at least this accuracy thereby, allowing a determination of the shape of singularities to a greater accuracy than hitherto available.

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Figure 1 THERMAL CONDUCTIVITY CRYOSTAT

- a - Vacuum line; b - indium vacuum seal;
- c - heat switch assembly; d - heat sink (weight 1Kg);
- e - Adiabatic shield (controlled) to $\pm 3\text{mK}$;
- f - Lead anchoring bobbin; g - differential thermocouple;
- h - Sample cell; i - inner radiation shield;
- j - connection pins (not used for thermocouple leads);
- k - heat switch platform (controlled to $\pm 20 \text{ mK}$);
- l - platinum thermometer; m - germanium thermometer
- - heaters; x - points of thermal strapping

Figure 2 CRYOSTAT FOR WORK IN MAGNETIC FIELD

a through x - as figure 1

n - superconducting solenoid

Figure 3 COOLING CURVE

a - cooling with nitrogen; b - nitrogen pumped to below 50°K;
c - helium introduced

Figure 4 $\dot{Q} \text{ v } \Delta T$ FOR ICE SAMPLE CELL

Figure 5 CONDUCTANCE OF CELL

+ - inner shield heater off

⊙ - inner shield temperature matched to that of sample

THERMAL CONTACT RESISTANCE MEASUREMENTS BY OSCILLATING METHODS

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This apparatus was built in order to investigate the thermal performance of metal specimens in contact along a flat surface in oscillating thermal field.

The apparatus uses a flat slab symmetry and is therefore subjected to an unidirectional thermal field. The specimen has a cylindrical shape as a hot guard system maintains conditions equivalent to the symmetry of a flat slab.

The apparatus consists of a cylindrical specimen 40 mm long having diameter 20 mm; it is separated in three parts. On the surfaces between the central piece and the two outer we have the usual contact zone, matter of our experimentation.

The temperature oscillation is imposed on both the flat external surfaces by means of electrical heaters coupled with a water cooler on the outermost sides.

A cylindrical guard hinders radial thermal flux; it is built out of a cylindrical shell of the same material as the specimen and of an outer electrical resistance that compensates the radial thermal fluxes.

This latter electrical resistance is divided in zones in order to generate with automatic control the necessary dispersion flux for each zone.

¹ Assistant.

² Associate Professor.

A small hydraulic press holds at a constant pressure the coupled surfaces of the specimen which is held horizontal to eliminate the effects of its own weight.

The temperature oscillation (a small oscillation about a given temperature value) is generated by means of two coupled program controllers.

The controllers generate oscillations having the same amplitude and phase. The temperature waves propagate within the specimen and are attenuated on the way. With a suitable instrumentation of thermocouples we measure amplitude and phase lag of the temperature wave as distributed along the axis of the specimen.

Using a theory similar to the one already developed for temperature oscillations in composite walls, and numerical computer programs we evaluate the thermal contact resistance.

THE DIRECT DETERMINATION OF THERMAL CONDUCTIVITY
BY THE FLASH TECHNIQUE

by

I.D. Peggs and R.W. Mills

ABSTRACT

Due to its speed and small sample size requirement the flash technique is the ideal method for the determination of thermal conductivity (λ) values via thermal diffusivity (α) in a large materials assessment program. However, fast neutron irradiation of samples such as graphite and ceramics also cause changes in density and specific heat which makes post-irradiation determinations of λ unreliable unless these properties are determined too. The advantage of the method would thus be lost. If the heat input per unit surface area (Q) into the specimen and the maximum temperature (T_M) attained by the rear face can be measured the thermal conductivity can be determined directly from:

$$\lambda = \frac{\alpha Q}{l T_M}$$

where l is the specimen thickness. A method is described for making such measurements. A pulsed ruby laser is used as the heat source with the standard vacuum furnace/specimen holder assembly. Infra-red radiation from both specimen faces is collected by mirrors and photo-conductive cells. The response of the rear cell is calibrated against specimen temperature and the front cell calibrated against laser pulses of known energy incident upon a surface of known diffuse reflectance. The energy in the laser pulse is determined by a combination of a photo-conductive cell and a gas phototube to enable all measurements to be recorded at the moment of interest. Experimental details of the method are reported.

INFLUENCE OF HIGH CONDUCTIVITY THERMAL BRIDGES ON THE HEAT TRANSFER OF COMPOSITE INSULATING SLABS

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ABSTRACT - The author explains the results of a theoretical and experimental investigation on heat exange of composite insulating slabs presenting thermal bridges. The numerical calculating method used consist of integrating the fundamental conduction equation with the method of finite differences according to Liebmann (Gauss-Seidel), with constant thermal flux as a boundary condition. The calculation has results in good accordance with experimental ones also for thermal bridges presenting a high ratio (up to 10^4) of the thermal conductivities of bridge and insulating materials.

I. INTRODUCTION

Recent trends of light prefabrication, render more and more important and sensible the influence of joints on the thermal balance of buildings.

These joints in fact constitute an ensemble of thermal bridges that vary, much if metallic, the insulating properties of the walls. [1]

A considerable importance assumes therefore the careful and precise calculation of thermal bridges, since the extension of those same grows relating to the remaining structures.

The calculations usually made with the ponderal mean referred to the flow areas, give, as compared to experimental ones exaggerated values when the conductivities of insulating and thermal bridge-materials are much different, as in these opportunities we have no parallel thermal fluxes.

The problem was therefore reinvestigated from the beginning, with the intent to find a resolution acceptable for its precision and easy enough in order to be used without many difficulties in engineering calculations.

II. THE PROBLEM

The heat transfer phenomenon in insulating slabs was considered to be a problem of conduction only, as radiating and convection heat transfer phenomena, may be reduced by linearization to an equivalent thermal conductivity.

The fundamental equation of heat conduction in the case of steady thermal regime $\Delta_2 T = 0$, was resolved with the method of finite differences, imposing boundary conditions acceptable in the phisical reality of the phenomenon, and such as to give results confirmed by experiments.

Usually heat transfer to and from insulating slabs is by convection and irradiation, that is expressed by formulas such as:

$$\Psi = h_{i,c} \cdot S \cdot \Delta T ,$$

where ΔT is the difference of temperature between air and surface of walls.

The values of $h_{i,c}$ and of S are constant for a specified wall, the value of ΔT can vary right on the thermal bridge, but this variation can be held of small importance, in the first approximation and in the absence of phenomena of water vapor condensation.

A satisfying condition for resolving the analytical problem might thus be a constant thermal flux on the boundary of the wall with air. On the internal surfaces of contact among different materials, the equality of the normal outgoing thermal flux in a material and of the normal entering thermal flux in the neighboring is to be imposed:

$$\Psi_1 = \Psi_2 = \lambda_1 \cdot S \cdot \frac{\partial T_1}{\partial n} = \lambda_2 \cdot S \cdot \frac{\partial T_2}{\partial n} .$$

It carries to the condition:

$$\frac{\partial T_1}{\partial n} / \frac{\partial T_2}{\partial n} = \lambda_2 / \lambda_1$$

Here, using a computer, equation $\Delta_2 T = 0$ was integrated for the plane transversal section of a wall containing thermal bridges of various shapes, as the considered zone was limited to the minimum symmetry, being nil the thermal flux across the planes of symmetry.

Given on a plane Laplace equation:[2]

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} = 0$$

with suitable condition on boundary Γ of region D , it is resolved with the method of finite differences.

The method consists in dividing region D of boundary Γ on plane x, y with straight lines parallel to coordinated axes as to form a network. The value of the function in the region is then substituted by the succession of values in the discrete ensemble of the nodes of the network and derivatives with suitable incremental ratios we will analyze later.

This way we get a system of linear equations whose unknown quantities are the values of the function in the nodes of the network; the resolution of this system is an approximate resolution of the problem.

The considered Laplace equation has two independent variables, therefore the finite difference equation shall meet this condition.

Besides the equation is not unique as derivatives may be substituted with different incremental ratios according to whether forward or backward differences are used.

Let us develop the function $T(x, y_0)$ as a Taylor series around point (x_0, y_0) :

$$T(x, y_0) = T(x_0, y_0) + (x - x_0) T_x(x_0, y_0) + \frac{(x - x_0)^2}{2} T_{xx}(x_0, y_0); \quad x_0 < x < x$$

as

$$T_x = \frac{\partial T}{\partial x}, \quad \text{and} \quad T_{xx} = \frac{\partial^2 T}{\partial x^2}.$$

If we suppose : $x = x_0 + h$, we get:

$$T(x_0 + h, y_0) = T(x_0, y_0) + h T_x(x_0, y_0) + \frac{h^2}{2!} T_{xx}(\xi, y_0),$$

and approximating T_x with:

$$T_x(x_0, y_0) = \frac{T(x_0 + h, y_0) - T(x_0, y_0)}{h} \quad (1)$$

we have an error of truncation :

$$E_T = -\frac{h}{2} T_{xx}(\xi, y_0) \quad x_0 < \xi < x_0 + h$$

This incremental ratio was calculated through the forward difference.

By considering the backward difference (i.e.: $x = x_0 - h$) we get:

$$T_x = \frac{T(x_0, y_0) - T(x_0 - h, y_0)}{h}.$$

In approximating the second derivate $T_{xx}(x_0, y_0)$ we will use both forward and backward differences in order not to influence the final expression one way only.

If we calculate $T_{xx}(x_0, y_0)$ using the forward difference:

$$T_{xx}(x_0, y_0) = \frac{T_x(x_0 + h, y_0) - T_x(x_0, y_0)}{h}$$

and T_x using the backward difference, we have:

$$T_{xx}(x_0, y_0) = \frac{T(x_0 + h, y_0) - 2T(x_0, y_0) + T(x_0 - h, y_0)}{h^2}.$$

The truncation error can be shown equal to:

$$E_T = -\frac{h^2}{12} T_{xxx}(\xi, y_0) \quad x_0 - h \leq \xi \leq x_0 + h.$$

In analogy along y axis we get:

$$T_{yy}(x_0, y_0) = \frac{T(x_0, y_0 + k) - 2T(x_0, y_0) + T(x_0, y_0 - k)}{k^2}$$

$$E_T = -\frac{k^2}{12} T_{yyy}(x_0, \eta) \quad y_0 - k \leq \eta \leq y_0 + k$$

Laplace equation becomes thus:

$$\frac{T(x_0+h, y_0) - 2T(x_0, y_0) + T(x_0-h, y_0)}{h^2} + \frac{T(x_0, y_0+k) - 2T(x_0, y_0) + T(x_0, y_0-k)}{k^2} = 0.$$

Considering as region D a rectangle of sides a and b and as boundary condition:

$T(x, y) = F(s)$ or $\frac{\partial T}{\partial n} = F_1(s)$ (s = curvilinear abscissa on Γ), let us divide side a in n steps, each of amplitude $h = a/n$ and side b in m steps of amplitude $k = b/m$, and we get a network with $(n-1)(m-1)$ nodes within boundary Γ .

We indicate now the values of the function in each point within the network with:

$$T(ih, jk) = T_{i,j} \quad i = 1, 2, \dots, (n-1); \quad j = 1, 2, \dots, (m-1)$$

and on the points of the boundary with:

$$T(ih, jk) = f_{i,j}.$$

Imposing $\lambda' = k/h$ the Laplace differential equation is reduced to the following system of finite difference equations:

$$\lambda'^2 T_{i+1,j} + \lambda'^2 T_{i-1,j} + T_{i,j+1} + T_{i,j-1} - 2(1+\lambda'^2) T_{i,j} = 0$$

$$i = 1, 2, \dots, (n-1); \quad j = 1, 2, \dots, (m-1)$$

When $\lambda' = 1$, $T_{i,j}$ equals the average of the four contiguous points:

$$T_{i,j} = \frac{1}{4} (T_{i+1,j} + T_{i-1,j} + T_{i,j+1} + T_{i,j-1}).$$

We have now $(n-1)(m-1)$ equations and $(n+1)(m+1)$ unknown values $T_{i,j}$; the boundary conditions consent to eliminate $2(m+n)$ unknown values, and to make possible the resolution of the system.

For $h \rightarrow 0$ and $k \rightarrow 0$ the finite difference equation tends to equal the differential equation, but it is not always true that the solution of the finite difference equation tends to the solution of the differential equation, unless some conditions be satisfied.

In the opportunity of finite difference equations of elliptical type, just as we are considering, no condition is necessary.

Taking as an example a system of three equations with three unknown quantities:

$Ax = B$, we will resolve with the Gauss - Seidel method.

Supposing that $a_{ii} \neq 0$ for $i = 1, 2, 3$ the system is:

$$\begin{cases} x_1 = \frac{1}{a_{11}} (b_1 - a_{12} x_2 - a_{13} x_3) \\ x_2 = \frac{1}{a_{22}} (b_2 - a_{21} x_1 - a_{23} x_3) \\ x_3 = \frac{1}{a_{33}} (b_3 - a_{31} x_1 - a_{32} x_2) \end{cases} \quad (2)$$

Be $x_1^{(0)}, x_2^{(0)}, x_3^{(0)}$ a first approximate solution, by substitution in (2) we get:

$$\begin{cases} x_1^{(1)} = \frac{1}{a_{11}} (b_1 - a_{12} x_2^{(0)} - a_{13} x_3^{(0)}) \\ x_2^{(1)} = \frac{1}{a_{22}} (b_2 - a_{21} x_1^{(1)} - a_{23} x_3^{(0)}) \\ x_3^{(1)} = \frac{1}{a_{33}} (b_3 - a_{31} x_1^{(1)} - a_{32} x_2^{(1)}) \end{cases}$$

In particular in the 2nd and 3rd equation we used the values calculated previously.

Repeating this last cycle starting from values $x_1^{(1)}, x_2^{(1)}$ and $x_3^{(1)}$ we get the successive approximation.

In general k -th iteration gives values $x_1^{(k)}, x_2^{(k)}$ and $x_3^{(k)}$.

When $x_i^{(k)}$ is near $x_i^{(k-1)}$ enough the process is stopped.

In symbols:

$$M^{(k)} = \max_i |x_i^{(k)} - x_i^{(k-1)}| \quad i = 1, 2, \dots, n$$

if : $M^{(k)} < \epsilon$

where ϵ is positive, the iteration process is stopped.

The Gauss-Seidel method applied to finite difference equations coming from elliptic differential equations is called Liebmann method.

The iterative method can be accelerated introducing a convergence factor ω (valued between 1 and 2) which produces the following correction:

$$\begin{aligned} T_{i,j} &= T_{i,j} + \omega \frac{1}{4} (T_{i+1,j} + T_{i,j+1} + T_{i,j-1} + T_{i-1,j}) - T_{i,j} = \\ &= \frac{\omega}{4} (T_{i+1,j} + T_{i-1,j} + T_{i,j+1} + T_{i,j-1}) + (1-\omega) T_{i,j} \end{aligned}$$

with a good selection of ω value a lot of calculating time can be saved; for the considered problem $\omega \approx 1.8$ was found optimal.

III. RESULTS OF NUMERICAL CALCULATIONS

Numerical integrations allowed the drawing of isothermal lines on the considered section, having as a known term the constant thermal flux given and subtracted on the two opposed outer surfaces.

Wall samples presented in fig. 1 were studied.

From the computer, after a suitable number of iterations we get a diagram like the one in figure 2, related to specimen 1 in fig. 1.

It gives moreover the numerical values of temperatures in each point of the network.

The diagram is obtained, by ordering the printer to type in the position related to each node, a letter related to the temperature in the same node.

In figure 3 the isothermal lines for the four investigated specimens are reported.

The said diagrams are not suitable for an immediate comparison with other methods of calculation or with experimental measurements.

We calculated then, the equivalent thermal conductance [3]

$$q_e = \psi / (S \cdot \Delta T)$$

As the temperature of opposing surfaces is far from constant, the difference was calculated as the difference of weighted mean temperatures of the two surfaces.

Specimen 1	$q_e = 7.44 \text{ W/(m}^2 \text{ }^\circ\text{C)}$
" 2	$q_e = 6.54 \text{ "}$
" 3	$q_e = 2.19 \text{ "}$
" 4	$q_e = 2.48 \text{ "}$

From the diagrams we observe that the temperature of the metal surface of specimen 1 varies sensibly only up to a distance of 2.5 times the thickness from the thermal bridge, we can therefore hold that the influence of the bridge doesn't extend much beyond.

IV. EXPERIMENTAL MEASUREMENTS

Simultaneously with the calculations, experiments were performed in order to measure the equivalent thermal conductance [4] of specimens just like n. 2, 3 and 4; the following values resulted:

Specimen 2	$q_e = 6.35 \text{ W/(m}^2 \text{ }^\circ\text{C)}$
" 3	$q_e = 2.26 \text{ "}$
" 4	$q_e = 2.74 \text{ "}$

Thermocouples were placed on the external surface in order to measure the temperatures at various distances from the thermal bridge of specimen 2.

V. COMPARISONS

Figure 3 shows the isothermal lines in the considered specimens. It shows a marked influence of the metallic plate on the surface of the specimen. In the plate in fact we observe isothermal lines perpendicular to those we see within the insulating material.

The influence is evidenced by comparing specimens 1 and 3, in n. 3 the absence of plate on the external surface produces a minimal variation related to the case of insulating material only.

This observation can be verified by the values of equivalent thermal conductance, which varies a little only from that of the insulating slab alone:

insulating slab alone	$q_e = 1.96 \text{ W/(m}^2 \text{ }^\circ\text{C)}$
specimen 3	$q_e = 2.17 \text{ "}$

The comparison is interesting also observing fig. 4 which shows the form (qualitatively only because of the high conductivities ratio) of flow lines in a specimen like n. 1.

In fig. 5 a comparison is made between calculated and actual superficial temperature for specimen 2. In both diagrams the zone affected by the presence of metallic plate is 2.5 times the thickness of the specimen.

A calculation with the boundary condition $T = \text{constant}$ on the outer surfaces, would

produce no deformation of isothermal lines and therefore an excess thermal flux in the bridge, contrary to experiments.

In table I a comparison is made among values:

- 1)- calculated with the proposed method (finite differences $\psi = \text{constant}$),
- 2)- calculated with the traditional method ($T = \text{constant}$ boundary condition),
- 3)- measured experimentally.

TABLE I

Specimens	$q_e (\psi = \text{const.})$ $W/(m^2 \text{ } ^\circ C)$	$q_e (T = \text{const})$ $W/(m^2 \text{ } ^\circ C)$	$q_e (\text{exper.})$ $W/(m^2 \text{ } ^\circ C)$
1	7.44	104	--
2	6.54	53	6.35
3	2.19	44	2.26
4	2.48	49	2.74

In the opportunity of specimens like the considered ones, the calculation made with the parallel (i.e. boundary condition $T = \text{constant}$) of materials having so different thermal conductivities is certainly erroneous, as it doesn't even respect the order of magnitude of the experimental result.

VI. OBSERVATIONS

Either from experimental measurements, or from calculations that have an adequate response, the temperature on the outer surfaces is shown markedly variable in the presence of thermal bridges; it is therefore of utmost importance keeping in mind this fact both in the calculations and in the experiments, since equivalent conductance and conductivity are to be calculated using mean temperatures and the method for calculating mean values is to be specified.

The examined specimens represent beyond doubt extreme conditions, but if discrepancies become less evident as the ratio of conductivities diminishes, the possible error is very big.

Further calculations and experiments are envisioned to devise a reliable and swift method for calculating thermal bridges also in these extreme conditions.

The possibility of using a boundary condition nearer to expression $\psi = h_{i,c} \cdot S \cdot \Delta T$ are being considered as ΔT has been shown variable, but the good agreement of calculations and experiments, allows to be confident that no major variation in the ultimate values is to be expected.

SYMBOLS

h	amplitude of a step along x axis	m
$h_{i,c}$	heat transfer coefficient for irradiation and convection	$W/(m^2 \text{ } ^\circ C)$
k	amplitude of a step along y axis	m
n	perpendicular to S surface	m^2
S	heat transfer surface	m
T	temperature	$^\circ C$
q_e	equivalent thermal conductance	$W/(m^2 \text{ } ^\circ C)$
x,y	perpendicular axes in region D	m
Δ	difference operator	
Δ^2	Laplace operator	
∂	partial derivate	
λ	thermal conductivity	$W/(m \text{ } ^\circ C)$
ψ	thermal flux	W

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SPECIMEN N 1

SPECIMEN N 2

SPECIMEN N 3

SPECIMEN N 4

Fig. 1 - Specimens.

Fig. 2 - Graphical result of numerical integration for the minimum symmetry of specimen 1
 $(30^{\circ}\text{C} < L < 30.5^{\circ}\text{C} ; 31^{\circ}\text{C} < M < 31.5^{\circ}\text{C} ; \dots ; 39^{\circ}\text{C} < U < 39.5^{\circ}\text{C})$.

Fig. 3 - Isothermal lines calculated by numerical integration.
(Numbers are degrees Centigrade)

Fig. 4 - Flux lines in an insulating slab covered by metallic box. (The diagram has been exaggerated owing to the large conductivity ratio).

Fig. 5 - Plot of temperatures on the hot surface of specimen 2, perpendicular to the thermal bridge.

An Absolute Thermal Conductivity Cell for High Pressures
and Moderate Temperatures

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ABSTRACT

The paper describes the design, construction and calibration of a steady state concentric cylinders thermal conductivity cell. The cell was designed for operation at conditions up to 25,000 lbs. per square inch and temperature up to 700° F. The emitter and absorber are provided with several independently controlled heating and cooling circuits to provide temperature uniformity and the surface temperatures are carefully monitored at several points. Preliminary estimates indicate an overall uncertainty of $\pm 1\%$.

Technique for Measuring Thermal Conductivity in Cylindrical Geometry Using Small Temperature Gradients ‡

by
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Introduction

A dynamic technique is being developed to measure thermal conductivity. The technique will eventually be used to provide thermal conductivity data for radiation damage studies. It would be used in a low temperature irradiation facility such as that of the Argonne CP-5 and could provide a detailed conductivity vs. temperature profile in a reasonable experimental time.

This technique does not require a precise knowledge of either the density or specific heat of the material under study in order to obtain the conductivity. Moreover, cylindrical specimens used are not assumed infinite in the radial dimension.

An outline of the theoretical basis for the technique and preliminary data obtained using the technique are presented.

Theoretical Development

Consider a homogeneous cylindrical rod of diameter $2b$ containing a line heat source along its axis giving off Q watts/meter beginning at time $t = 0$. If the initial temperature of the sample ($t < 0$) is uniformly zero and there is no heat loss at the surfaces, it can be shown¹ that

$$T(r,t) = \frac{Q}{2\pi\lambda} \left\{ 2\alpha t/b^2 + r^2/2b^2 + \ln(b/r) - 3/4 \right. \\ \left. - 2 \sum_{m=1}^{\infty} \frac{\exp[-\alpha B_m^2 t]}{b^2 B_m^2 J_0^2(b B_m)} J_0(r B_m) \right\}$$

where λ = thermal conductivity (watt/meter Kelvin)
 α = thermal diffusivity (meters²/second)
 J_0 is the zero order Bessel function of the first kind
and the B_m are roots of

$$J'_0(b B_m) = 0 = J_1(b B_m)$$

If $\alpha t/b^2 \geq 0.3608$, the error involved in ignoring the summation is less than 1%. Thus

$$T(r,t \geq 0.3608 b^2/\alpha) \approx \frac{Q}{2\pi\lambda} \left\{ 2\alpha t/b^2 + r^2/2b^2 + \ln(b/r) - 3/4 \right\}.$$

‡ This Research has been funded under NSF Contract, USNSF GK 1595.

The temperature difference between two radial positions r_1 and r_2 where $0 < r_1 < r_2 < b$ then can be written as

$$T(r_1, t) - T(r_2, t) \bigg|_{t \geq .3608b^2/\alpha} \approx Q/2\pi\lambda \{1/2b^2 [r_1^2 - r_2^2] + \ln(r_2/r_1)\} \equiv \Delta T$$

The above expression indicates that the value of λ can be calculated from a knowledge of ΔT , Q , b , r_1 , and r_2 .

In experiments performed on silicon at room temperature and below, ΔT 's of less than 0.03°K have been measured to an accuracy of better than 5%. If the heating rate is reduced to zero at time $t = 0.5b^2/\alpha$, the temperature at the point r_1 at that time is given by

$$T(r_1, t = 0.5b^2/\alpha) \approx Q/2\pi\lambda \{1.0 + r_1^2/2b^2 + \ln(b/r_1) - 3/4\}$$

Taking typical values of $r_1/b = 0.20$ and $r_2/b = 0.90$, it is seen that

$$\Delta T \approx (1.11) Q/2\pi\lambda$$

and

$$T(r_1, t = 0.5b^2/\alpha) \approx (1.88) Q/2\pi\lambda$$

Thus the hotter thermocouple's temperature rise relative to measured temperature difference between the two thermocouples is quite compatible with the assumption that the conductivity of the specimen is not a function of temperature during a given measuring cycle. If a ΔT of 0.03°K is measured, the temperature rise of the hotter thermocouple at end of measurement could realistically be limited to $< 0.05^\circ\text{K}$. The time for one measuring cycle would be the order of $3.6 b^2/\alpha$.

The conditions of a line source and zero radial surface heat loss may be changed to more realistic conditions by considering a hollow cylinder with inner diameter $2a$ which exhibits linear heat transfer at the outer radial boundary, i.e.

$$-\lambda \partial T(r, t) / \partial r \bigg|_{r=b} = C T(b, t).$$

Axial heat flow is again ignored. From the general solution given in Carslaw and Jaeger² a second expression for the quantity ΔT calculated above can be obtained. This second solution for ΔT assumes the following conditions:

$$a < r_1 < r_2 < b$$

$$Cb/\lambda \leq 3.15 \times 10^{-4}$$

$$.005b\lambda/C\alpha > t > 6.9/\alpha(3.83)^2 = 0.47/\alpha$$

$$a/b \leq 0.034$$

$$Cb/2\lambda(a/b)^2 \leq 0.14$$

Under these conditions it is found that for the time interval defined above,

ΔT is given approximately by

$$\Delta T = Q/2\pi\lambda \{ \ln(r_2/r_1) + 1/2b^2 (r_1^2 - r_2^2) [1 - Cb/2\lambda(a/b)^2] \}.$$

The correction term involving λ is generally not very significant. For conditions in existence during the experiment reported in this paper, the correction term represented a maximum change of less than 4% in resulting values for λ . There are conditions, however, under which it could be much more significant.

The last criterion listed above for this corrected solution for ΔT is necessary to obtain the desired form for the solution. It is easily met for experimental work reported here. In cases where the term $(a/b)^2$ is significantly smaller relative to $Cb/2\lambda$, different approximations are necessary in order to obtain a meaningful expression for ΔT .

The constant C in the above analysis is given by

$$C = 4\sigma E T_o^3,$$

where σ is the Stefan-Boltzmann constant, E is the emissivity of the sample's surface, and T_o is the absolute temperature of the surroundings. This form for the constant C is justified experimentally by performing all measurements in a vacuum and employing a thermal shield which is maintained at a temperature close to that of the sample's surface.

Specimen for Preliminary Studies

Initial measurements have been made using a cylindrical specimen of single crystal silicon. The specimen is 1.90 cm long and 1.57 cm in diameter. Thermocouples of 6 mil copper and 6 mil constantan wires are located at $r_1 = 0.168$ cm and $r_2 = 0.655$ cm and are centered axially in the cylinder. The heat source is a constantan wire in a 21 mil hole along the axis of the cylinder.

The differential thermocouple output which provides the means of measuring the ΔT is monitored by an electronic chopping circuit feeding a lock-in amplifier. The combination of chopping circuit and amplifier provides a means of picking low level signals out of associated noise. The lowest level signals observed in work reported here was 0.083 microvolts, but further refinements in technique should make it possible to measure smaller signals with confidence.

Results

Initial conductivity measurements have been made over a temperature range of 20°C to -170°C. Results are shown in Fig. 1 and are there compared with results of Albany and Vandevyver.³

The comparison with Albany and Vandevyver was made with a view to future comparison of conductivity measurements on irradiated silicon with those made by Albany and Vandevyver on similarly irradiated material.

Fig. 1. Preliminary Thermal Conductivity Measurements on 500Ω-cm Silicon

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A RADIAL HEAT-FLOW METHOD FOR POOR CONDUCTORS

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ABSTRACT

This article describes a radial heat-flow method which has been developed for poorly conducting materials such as insulating foams. Several advantages have been found over the commonly utilized guarded hot-plate method. (described in ASTM method of test - C177-45) The sample is much smaller which allows easier measurement at cryogenic temperatures, the sample geometry eliminates most of the errors arising from stray heat transfers, and measurements can be taken using much smaller temperature gradients and then are therefore at a more closely defined temperature. Results have been taken on two types of expanded polystyrene, and these are compared with results by the guarded hot-plate method.

Introduction

The purpose of the experiments described in this paper were two-fold. Many expanded foams have a large coefficient of thermal expansion which can be a serious drawback. Two foams (Armalite¹ and Styrofoam²) were found to have a relatively low expansion of only $5 \times 10^{-5} \text{ K}^{-1}$ between 77 and 297 K. The first objective was to determine the thermal conductivity of these materials over the range 77 to 300 K in the environment of normal usage. Our second objective was to explore an alternative method to the guarded-plate system for measuring the thermal conductivity of insulating materials. Gilbo³ demonstrated that the latter method is critically dependent upon equality of the sample and the guard temperatures; he found that there was 50% effect on the value of conductivity obtained per K difference between the two components. It is apparent from Gilbo's article that the results also are sensitive to the ambient temperature, to the materials and techniques used in the construction of the apparatus and to small errors in the location of thermocouple junctions. These problems have been circumvented by strict definitions for procedures in the construction and operation of the system as laid down in the A.S.T.M. Method of Test C177-45⁴. Whenever it is necessary to define procedures to such close limits there is suspicion that the measured values may include a function of the apparatus and are not a property of the sample alone. Also, this method requires a large sample (6" x 6") which is inconvenient for measurement at low temperatures.

Alternative Methods

Trial measurements by an unguarded linear heat-flow technique

on a one inch cube sample indicated that the heat losses, mainly by convective transfer, were much too large to be measured and corrected for. This problem can be eliminated without incurring any of the drawbacks of the guarded-plate method by use of a sample shaped into a hollow sphere.⁵ This geometry insures that, apart from a small, calculable heat transfer along the heater leads, all the energy dissipated in the heater must flow through the sample. It is a trivial exercise to show that the rate of conduction $\dot{Q}$ across a spherical shell of radii r_1 and r_2 is given by

$$\dot{Q} = 4\pi\bar{\lambda} \Delta T \left(\frac{r_1 r_2}{r_2 - r_1} \right)$$

where $\bar{\lambda}$ is the mean conductivity and ΔT the temperature difference. Also in the general heat-flow equation the spatial and temperature variables are separable, hence, no matter what the functional dependence of λ on T , the definition of $\bar{\lambda}$ is always identical to that for linear heat flow. In addition, measurements can be made with temperature increments of 5 K and less so that the values obtained for thermal conductivity are close to the "instantaneous" value at the average temperature of the measurement rather than being an average value over 30° range as with the guarded hot-plate method.

Experimental

Figure 1 shows the experimental arrangement used. The 2" I.D. copper can forms an isothermal enclosure at the temperature of the refrigerant placed in the surrounding dewar. Two hemispheres of insulating material are used to form the sample, they are up to 1-3/4" O.D. and are hollowed out to accommodate the manganin heater (about 100Ω resistance) which is embedded uniformly in a thin layer of wax⁶ on the surface of a 3/4" ball bearing. Number 40 B&S gauge copper leads are taken to the heater, the two potential leads are attached in a configuration which compensates for heat produced in the current leads.⁷ Heat conduction along the thermocouple leads was minimized by use of a Chromel-Alumel rather than the usual copper-Constantan system. Also the wires leading to the junctions were anchored along isotherms in the specimen as shown in figure 1. The two halves of the sample were stuck together with a very small quantity of wax. Voltages developed by the thermoelectric power of Chromel-Alumel thermocouples were taken from N.B.S. Circular No. 561.

Convective heat transfer is the main mechanism for the removal of heat from the surface of the specimen. According to Zemanski⁸, convective coefficients are dependent upon the curvature and the inclination of a surface. Several thermocouple junctions were placed under the surface of this sample to determine whether any significant temperature differences were arising from variation of this coefficient, but, to within the accuracy of measurement (about 25 m°K), none were detected.

Figure 2 shows a typical set of data and the method used to eliminate the effect of spurious E.M.f.'s in the thermocouple leads. At each ambient temperature used (77, 180, 273 and 295 K) data were obtained for several values of $\dot{Q}$. Thus when $\dot{Q}$ is plotted as a function of the temperature difference ΔT between the differential thermocouple junctions, the parasitic signal causes only an effective displacement of the origin, so its influence upon the values of thermal conductivity is eliminated if the gradient of the $\dot{Q}$ v ΔT curve is used rather than the individual values of $\dot{Q}/\Delta T$. Each time the

heater power was changed a period of an hour or two was required for the re-establishment of equilibrium; the value of ΔT had to remain constant for a further period of 30 minutes before the reading was accepted.

Uncertainties in the determination of the radii r_1 and r_2 on which the thermocouple junctions are located account for the major portion of the uncertainties in the value of λ . This source of error was both estimated and checked experimentally. Radii were measured at the conclusion of the experiment by cutting away the sample to expose the junctions; a microscope mounted on a vernier scale was then used to determine their positions. Consideration of the individual uncertainties in r_1 and r_2 lead to an estimated error of less than 5% while independent values of λ taken on three samples fabricated from the same sheet of Armalite showed a variation of just under 3%. These results and those obtained for Styrofoam are shown in figure 3; numerical values are given in table 1. The figure also shows the manufacturers values for Armalite and data taken on Styrofoam by Haskins and Hertz⁹; both sets were taken by the guarded-plate method. Corrections for the heat conducted along leads were of the order of 1%.

Table 1. Thermal Conductivity of S.E. Armalite and Styrofoam 22.

Temperature (K)	$\lambda (\text{w cm}^{-1} \text{ K}^{-1})$	
	Armalite	Styrofoam
297	.0387	.0328
273	.0349	.0290
195	.0127	.0121
78	.0062	.0082

Discussion

It was observed that the radial method consistently gave lower values of conductivity than the guarded-plate method. This is significant because, with one exception, all the sources of spurious heat transfer would cause the results to be too high rather than too low. Conduction of heat away from the outer differential thermocouple junction via the Chromel lead is the exception. This possibility was checked out by varying the length of this wire which is strapped along the isotherm within the sample (figure 1). Only the normal, random scatter was found in the values of λ obtained, thus indicating that the leads were anchored to the temperature of the junction.

Agreement between results obtained by the two methods is good considering all the possible sources of discrepancy. The values for Armalite at 273 and 295 K are within 4% and the values for Styrofoam at 77°K are within 3%. Differences at intermediate temperatures are accentuated by the difference in the temperature gradients used. Also the nonlinear behaviour of $\dot{Q} \sqrt{\Delta T}$ for $\Delta T > 12\text{K}$ suggests that for small temperature gradients stratification of the intercellular gas occurs and as the temperature gradient increases there is an onset of convective flow; in the present work $\Delta T = 12\text{ K}$ corresponds to a gradient of 10 K cm^{-1} and the gradient used by Hoskins and Hertz was greater than 20 K cm^{-1} .

Acknowledgements

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Section AA

Figure 1 EXPERIMENTAL SYSTEM FOR RADIAL-FLOW MEASUREMENT

a - nylon suspension thread; b - metal sphere with heater;
c - heater leads; d - thermocouple leads; e - copper can

Figure 2 $\dot{Q} \propto \Delta T$ FOR ARMALITE AT 78°K

Figure 3 THERMAL CONDUCTIVITY OF SE ARMALITE AND STYROFOAM

Armalite: X - this research; — manufacturer's data

Styrofoam: O - this research; --- Haskins and Hertz

THERMAL CONDUCTIVITY APPARATUS FOR USE WITH SMALL TEST SAMPLES

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ABSTRACT - A simple apparatus of the absolute guarded longitudinal heat flow type is described, which is designed for thermal conductivity determinations at various temperatures near room temperature on small cylindrical samples. A novel feature is that the temperature gradient established in the test sample is determined from the readings of thermocouples held under slight tension so as to make contact with the curved surface of the sample. This procedure ensures that the thermocouple wires lie in an isothermal region; it also facilitates sample interchange.

The work which forms part of an investigation supported by the National Science Foundation, helps in the provision of samples of known thermal conductivity for use with the thermal comparator. It also provides a simple independent check method.

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Pressure Dependence of the Thermal
Conductivity of Non-Metals

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Abstract: The pressure dependence of the thermal conductivity is calculated in the extreme cases of a perfect crystal and a crystal with very high concentration of point defects.

The pressure dependence of the thermal conductivity of non-metallic solids is of interest in geophysics. In the case of amorphous solids we cannot make any theoretical predictions, as we lack a theory of thermal conductivity of non-crystalline solids except at very low temperatures.¹ We do have theoretical expressions for the thermal conductivity of crystals. There is some uncertainty about their numerical reliability, but they do tell us how the thermal conductivity depends on various parameters, and thus how it should change with volume, respectively pressure.

Mooney and Steg² have recently discussed the changes with pressure of thermal conductivity and of the related property of ultrasonic attenuation. In the case of thermal conductivity one must distinguish between the case of a pure crystal and one containing defects. In the former, the resistivity arises from anharmonic interactions, in the latter there is also a contribution from phonon scattering by defects.

The thermal conductivity at ordinary temperatures of a perfect crystal is of the form³

$$\lambda = A v^3 / \gamma^2 a^2 \quad (1)$$

where v is the phonon velocity, a^3 the atomic volume, γ the Grueneisen coefficient, which is a measure of the cubic anharmonicities, and A is a coefficient which incorporates all factors independent of dilatation.

The velocity v changes with dilatation Δ according to

$$v(\Delta) = v_0(1 - \gamma\Delta) \quad (2)$$

and γ itself also changes with dilatation. The derivative

$$\gamma' = d\gamma/d\Delta \quad (3)$$

is, of course, a measure of the quartic anharmonicities. It is in general not known. To first order in Δ we find

$$(1/\lambda)d\lambda/d\Delta = -3\gamma^{-2/3} - 2\gamma'/\gamma \quad (4)$$

In the case of a crystal of very high point defect concentration, the thermal conductivity is of the form⁴

$$\lambda = B v^2/\gamma a^2 \quad (5)$$

so that

$$(1/\lambda)d\lambda/d\Delta = -2\gamma^{-2/3} - \gamma'/\gamma \quad (6)$$

We see that the fractional change of a highly defect crystal is similar in magnitude, but not equal, to that of a perfect crystal.

One knows γ at least roughly from thermal expansion data, but γ' is generally not known. It can be determined from higher terms in the equation of state (as from the pressure dependence of the thermal expansion) or from the deviations of the high-temperature specific heat from the Dulong-Petit law. One may expect γ' to be negative to postpone the instability of the lattice for large positive Δ implied by (2).

Unless γ' is negative and of large magnitude, one would expect the thermal conductivity to increase with pressure (negative Δ). The magnitude of the fractional change should depend on point defect concentration, but from (4) and (6) it would appear that the variation is small.

Equation (4) implies that the fractional change in thermal conductivity is independent of temperature. A weak temperature dependence should appear in the presence of point defects, as there should be transition from (4) to (6) for a fixed point-defect concentration as the temperature is lowered.

Equation (6) assumes that the point defect concentration is independent of pressure, and that the fractional perturbation in the phonon velocity due to the defect is pressure independent. This would be the case for phonon scattering due to a mass difference, but need not be the case if the perturbation is due to distortion.

Obviously equation (4) applies only if the crystal structure is not changed with pressure. Another restriction is that very high temperatures have been assumed. If part of the thermal resistance is due to optical phonons, the high temperature limit is not yet reached at room temperatures. This may lead to an apparent temperature dependence of γ' in (4).

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CONTROLLABILITY IN HEAT CONDUCTION

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ABSTRACT

The work consists of two main parts. In the first the author begins with the investigation and discussion of the heat conduction equation which may be formally associated with the wave equation. Various forms of these equations are discussed and their solutions derived and elaborated. Besides the simple, standard solutions, for more complicated forms the author suggests the use of Bergman's integral operator technique, kernel function, Gilbert's function theoretic methods, etc. The second part begins with the presentation of the fundamental concepts of optimization theory, i.e., principles of the calculus of variations, Pontryagin's approach and the affiliated techniques. The mentioned methods were primarily developed for systems of ordinary differential equations. In partial differential systems the generalization is successful in particular cases only and various approximate techniques have to be developed. The field of optimization allows one to solve problems in which differential systems satisfy initial, boundary conditions and additional optimal one, i.e., the definite integral between two fixed limits from a function must be a minimum. This is achieved by applying dependence upon bounded "control" functions. By the proper choice of them one can "regulate" the heat flux and the temperature. Simple examples close the work.

1. Fundamental Equations and Forms

The fundamental heat equation is of the form:

$$\nabla^2 \phi = A \phi, t; \phi = \phi(x, y, z, t), \quad (1.1)$$

where ∇^2 represents the Laplace operator, or in the case when the coefficient of heat conductivity $\lambda = \lambda(x, y, z)$ is a point function:

$$\text{div} (\lambda \text{ grad } T) = c T, t; T = T(x, y, z, t), \quad (1.2)$$

where c denotes the specific heat of the material. In the case of a steady heat transfer the right hand side of (1.2) is equal to zero. The above equation can be remodelled into:

$$\nabla^2 T^* - a T^* - c \lambda^{-1} T^*, t = 0; \quad (1.3)$$

with: $\lambda^{1/2} T = T^*$; $a(x, y, z) = \lambda^{-1/2} \nabla^2 (\lambda^{1/2})$. Let us discuss a few techniques of solving these equations. Assuming the variation in time in the form of an exponential function, one can reduce the heat equation to an equation containing only functions of independent variables (x, y, z) . The wave equation containing the second derivative with respect to time can be also reduced to such a form, thus providing a formal link between these two kinds of equations: wave and heat. Some simple solutions are:

$$u_{,t} - k u_{,xx} = 0, k > 0 \text{ for } 0 < x < 1, t > 0; \quad (1.4)$$

$$u(x,0) = f(x) \text{ for } 0 \leq x \leq 1, u(0,t) = 0, u(1,t) = 0; \quad (1.5)$$

using the separation of variables yields with $u \sim XT$:

$$T'T^{-1} = kX''X^{-1}, kX'' + X = 0, X(0) = X(1) = 0; \quad (1.6)$$

$$T' + \varepsilon T = 0, \text{ eigenvalues } \varepsilon = n^2 \pi^2 k, \quad (1.7)$$

with eigenfunctions $\sin n\pi x$. The solution is:

$$u = \sum_1^\infty b_n \exp(-n^2 \pi^2 k t) \sin n\pi x; \quad (1.8)$$

$$f(x) = \sum_1^\infty b_n \sin n\pi x, b_n = 2\pi^{-1} \int_0^\pi f(x) \sin n x dx, \quad (1.9)$$

with $f(x)$ being a known function. The technique can be applied to $k = k(x)$ but the equation for X cannot be solved in a closed form. The above form of solution is valid as well for the equation (1.4) with the conditions:

$$0 < x < \pi, t > 0, u(0,t) = 0, u(\pi,t) = 0, u(x,0) = f(x). \quad (1.10)$$

Consider the forms:

$$(i) \quad u_{,t} - k u_{,xx} = 0, 0 < x < \pi, t > 0, u(0,t) = 0, u_{,x}(\pi,t) = 0; \quad (1.11)$$

$$u(x,0) = f(x), f(0) = 0, \quad (1.12)$$

with the solution:

$$u(x,t) = \sum_1^\infty c_n \exp \{-[n - (1/2)]^2 kt\} \sin(n - 1/2) x; \quad (1.13)$$

$$c_n = 2\pi^{-1} \int_0^\pi f(x) \sin(n - 1/2) x dx. \quad (1.14)$$

$$(ii) \quad u_{,t} - u_{,xx} = F(x,t) \text{ for } 0 < x < \pi, t > 0; \quad (1.15)$$

$$u(0,t) = u(\pi,t) = 0, u(x,0) = f(x), \quad (1.16)$$

$$u(x,t) = \sum_1^\infty \int \exp[n^2(t-\tau)] B_n(\tau) \sin nx d\tau + \sum_1^\infty b_n(0) \exp(-n^2 \tau) \sin nx; \quad (1.17)$$

$$B_n(\tau) = 2\pi^{-1} \int_0^\pi F(x,t) \sin nx dx; \quad (1.18)$$

$$b_n(0) = 2\pi^{-1} \int_0^\pi f(x) \sin nx dx. \quad (1.19)$$

$$(iii) \quad u_{,t} - u_{,xx} = 0, \text{ for } -\infty < x < +\infty, t > 0; \quad (1.20)$$

$$u(x,0) = f(x), u(x,t) = \text{bounded}; \quad (1.21)$$

$$\hat{f}_M(\omega) = \int_{-M}^{+M} f(x) \exp(i\omega x) dx; \quad (1.22)$$

$$\hat{u}(\omega,t) = \int_{-\infty}^\infty u(x,t) \exp(i\omega x) dx (\text{Fourier transform}); \quad (1.23)$$

$$w \equiv u; F[w, t] = \hat{u}, t; F[w, tt] = -\omega^2 \hat{u}; \hat{f}(\omega) = \hat{u}(\omega, 0); \quad (1.24)$$

$$u(x, t) = (2\pi)^{-1} \lim_{L \rightarrow \infty} \int_{-L}^L \exp(-i\omega x) \hat{f}(\omega) \exp(-\omega^2 t) d\omega. \quad (1.25)$$

$$(iv) \quad u, t - \nabla^2 u = 0, \text{ for } t > 0, u(x, y, z, 0) = f(x, y, z); \quad (1.26)$$

$$u(x, y, z, t) = \text{bounded} = (4\pi t)^{-3/2} \int_{-\infty}^{\infty} d\xi \int_{-\infty}^{\infty} d\eta \int_{-\infty}^{\infty} d\zeta \cdot f(\xi, \eta, \zeta) \exp \{ -[(x-\xi)^2 + (y-\eta)^2 + (z-\zeta)^2](4t)^{-1} \}, \quad (1.27)$$

called Laplace's solution. Other cases are:

$$(v) \quad u, t - u, xx = 0 \text{ for } -\infty < x < \infty, t > 0, u(x, 0) = f(x), \quad (1.28)$$

$$u(x, t) = [2(\pi t)^{1/2}]^{-1} \int_{-\infty}^{\infty} \exp[-(x-y)^2(4t)^{-1}] f(y) dy, \quad (1.29)$$

this being the classical initial value problem with u being bounded. In case of more complicated equations one can use Bergman's integral operator method [1], [3]. Consider an equation in (λ, θ) coordinates:

$$\psi, \lambda\lambda + \psi, \theta\theta = F(\lambda) \psi; \psi = f_0 + \sum_{n=1}^{\infty} f_n g_n; \quad (1.30)$$

$$f_n = f_n(z), g_n = g_n(\lambda), z = \lambda + i\theta. \quad (1.31)$$

Let us use the recursion formulas:

$$f_n = -\frac{1}{2} \int^z f_{n-1} dz; g_n = g'_{n-1} - \int^\lambda F g_{n-1} d\lambda, \quad (1.32)$$

then (1.30)₂ solves the equation with $g_0 = 1$ and f_0 arbitrary, depending possibly upon the boundary conditions. Another form of the function is:

$$f_n(z) = (-1)^n (n!2n)^{-1} \int_0^z (z-\xi)^n f'_0(\xi) d\xi, \quad (1.33)$$

$$\psi(\lambda, \theta) = \int_0^z f'_0(\xi) \sum_{n=0}^{\infty} [g_n(\lambda) (n!2n)^{-1} (\xi-z)^n] d\xi. \quad (1.34)$$

Depending upon coefficients in heat equation and their functional relation upon the independent variables, one may deal with the form:

$$U, xx + U, yy + aU, x + bU, y + cU = 0, \quad (1.35)$$

which ($z = x + iy, z^* = x - iy$) takes the form:

$$U, zz^* + AU, z + BU, z^* + CU = 0, \quad (1.36)$$

$$B = \bar{A}, F = -A, z - AB + C, \quad (1.37)$$

then a solution of (1.36) is provided by the form:

$$U(z, z^*) = \int_S E(z, z^*, t) f\left[\frac{1}{2} z(1-t^2)\right] (1-t^2)^{-1/2} dt, \quad (1.38)$$

$$E(z, z^*, t) = \exp\left[-\int_0^{z^*} A dz^* + n(z)\right] \tilde{E}(z, z^*, t), \quad (1.39)$$

with S denoting a path in the complex t -plane which connects -1 and 1 and omits the point $t = 0$. In the above, the coefficients A, B, C are continuously differentiable functions in a $n = 4$ dimensional neighborhood of the point

$(0, \dots, 0), U^4(0,0)$. The function $\tilde{E}$ depends upon the kind (first, second, etc.) of the integral operator. The integral operator of the first kind has the form:

$$\tilde{E}_1(z, z^*, t) = 1 + \sum_1^\infty t^{2n} z^n \int_0^{z^*} p^{(2n)}(z, z^*) dz^*, \quad (1.40)$$

$$p^{(2)} = 2F; (2n+1) p^{(2n+2)} = -2[p_z^{(2n)} + Dp^{(2n)} + F \int_0^{z^*} p^{(2n)} dz^*], \quad (1.41)$$

with $n = 1, 2, \dots$. Consider the equation:

$$\nabla^2 \psi + A(r^2) \vec{X} \cdot \nabla \psi + C(r^2) \psi = 0; \quad (1.42)$$

$$r^2 = x^2 + y^2 + z^2; \vec{X} = i_1 r + i_2 y + i_3 z. \quad (1.43)$$

Then the function $\psi(\vec{X})$ defined by (1.44) satisfies (1.42) in the neighborhood of $(0,0)$:

$$\psi(\vec{X}) = (2\pi i)^{-1} \int_{|\zeta|=1} d\zeta \int_{-1}^{+1} E(r, \tau) f(u(1-\tau^2), \zeta) \zeta^{-1} d\tau, \quad (1.44)$$

where $f(w, \zeta)$ is an analytic in the complex variables (w, ζ) for $w \in U^2(0)$ and $|\zeta| \leq 1$; moreover:

$$H(r, \tau) = 1 + \sum_{n=1}^\infty c_n(r) \tau^{2n}; \quad (1.45)$$

$$E(r, \tau) = \exp(-\frac{1}{2} \int_0^r A(r) dr) H(r, \tau); c_n(0) = 0; \quad (1.46)$$

$$(2n-1) \frac{dc_n}{dr} + r \frac{d^2 c_{n-1}}{dr^2} - (2n-3) \frac{dc_{n-1}}{dr} + r B c_{n-1} = 0, n > 1, \quad (1.47)$$

$$B = -\frac{3}{2} A - \frac{1}{2} r A_r - \frac{1}{4} r^2 A^2 + C, c_n(0) = 0 \quad (1.48)$$

for $n = 1, 2, 3, \dots$. The method of integral operators is used successfully for obtaining solutions of the following kinds of equations to which the heat equation may be reducible in some particular cases of the thermal conductivity dependence:

$$\nabla^2 \psi + F(y, z) \psi(x, y, z) = 0; \quad (1.49)$$

$$\psi_{,xx} + \psi_{,yy} + \psi_{,zz} + F(y, z) \psi = 0; \quad (1.50)$$

$$g^{\mu\nu} \nabla_\mu \nabla_\nu \phi + h^\mu \nabla_\mu \phi + k \phi = 0; \quad (1.51)$$

$$\nabla = i_1 \partial/\partial x + i_2 \partial/\partial y + i_3 \partial/\partial z; \quad (1.52)$$

in (1.51) we operate in the Riemannian space with the fundamental tensor $g^{\mu\nu}$. The symbol ∇_μ indicates the covariant differentiation, h^μ is an arbitrary contravariant vector, k is an arbitrary scalar. Also, $g^{\mu\nu}$, h^μ , k are real analytic functions of the coordinates. Using Bergman's operators, one can solve equation of the form:

$$\psi_{,xx} + \psi_{,yy} + \psi_{,zz} + F(y, z) \psi = 0, \quad (1.53)$$

and many others. The above technique does not allow one to solve the singular partial, differential equations like the axially symmetric equations. The

methods of solving these kinds of equations were proposed in recent years by Weinstein, Vekua, Gilbert, and others, and are collected in the recent book by Gilbert [4]. The following equations are attacked and solved: (a) general axially symmetric potential (GASP) equations; (b) general biaxially symmetric Helmholtz equation (GBSHE); (c) generalized biaxially symmetric Schroedinger equation (GBSSE); (d) generalized axially symmetric Helmholtz equation in (n+1) variables (GASHE), etc.

2. Optimization

Due to the impossibility of describing all of the existing optimization techniques, the author presents only one, so-called "generalized maximum principle."

Consider the behavior of a dynamic system or sub-system of a matter-full or matter-less continuous medium whose state at any instant of time is characterized by n real numbers, $w^1, w^2, \dots, w^n$ (these may be velocity components, coordinates, density, pressure, energy of any kind, etc.). The function space W of the variable $w = (w^1, w^2, \dots, w^n)$ is the function space of the system under consideration. The state (motion) of the system consists of the fact that variables $w^1, w^2, \dots, w^n$ change with the position. It is assumed that the state (motion) of the system can be controlled, i.e., that the system may be equipped with controllers on whose state (location, characteristic properties, etc.) the state (motion) of the dynamic system depends. The role of the controllers may take the form of the influx or outflux of the energy inward or outward of the dynamic sub-system under consideration, of the amount of work performed by the extraneous forces on the sub-system, etc. The state of the controllers is characterized by vector u , in a certain control region U , which may be any set in some function space E_r . Giving a vector $u = (u^1, u^2, \dots, u^r)$, is equivalent to giving a numerical system of parametric functions $u^1, u^2, \dots, u^r$. Often the region U may be closed region in E_r (a closed and bounded set in the r -dimensional function space E_r). We call U the control region. Thus, U is a certain set in the function space of the variables $u^1, u^2, \dots, u^r$, and $u = (u^1, \dots, u^r)$ is its vector located arbitrarily in U . We call every function $u = u(x^1, x^2, \dots, x^m)$, where $x = (x^1, x^2, \dots, x^m)$ are space coordinates, defined in a space-time region $x_0^1 \leq x^1 \leq x_1^1, x_0^2 \leq x^2 \leq x_1^2, \dots$, with $u \in U$, a control. Since U is a set in the function space of the control parametric functions $u^1, u^2, \dots, u^r$, each control $u(x) = (u^1(x), u^2(x), \dots, u^r(x))$ is a vector function (given for $x_0 \leq x \leq x_1$) whose region is in U . We assume some conditions superimposed upon $u(x)$ like piecewise continuity, differentiability (admissible controls). The admissible controls are arbitrary piecewise continuous functions; they are continuous for all (x) under consideration, with the exception of only a finite number of (x) , at which $u(x)$ may have discontinuities of the first kind, i.e., there is assumed the existence of finite limits:

$$u(\xi-0) = \lim_{\substack{x \rightarrow \xi, \\ x < \xi}} u(x); \quad (2.1)$$

$$u(\xi+0) = \lim_{\substack{x \rightarrow \xi, \\ x > \xi}} u(x), \quad (2.2)$$

at a discontinuity. Thus, every control is bounded. Concerning the magnitude of a control function at a discontinuity, it may be convenient to assume that at each discontinuity (ξ) the value of $u(x)$ is equal to its left-hand limit, i.e.:

$$u(\xi) = u(\xi-0), \quad (2.3)$$

or to any other pre-assigned value, and that each control function under consideration is continuous at the boundary of the region $x_0 \leq x \leq x_1$, in which it is given.

We assume that the laws of motion of the dynamic system can be given in the form of a system of partial differential equations:

$$L(w) = \frac{Dw^i}{Dt} = f^i(w^1, \dots, w^n, u^1, \dots, u^r) = f^i(w, u), \quad (2.4)$$

where the partial differential operator $L(w)$ is of the form (in coordinates of a three-dimensional space $X(x^1, x^2, x^3)$):

$$\frac{D}{Dt} = \frac{\partial}{\partial x} \frac{dx}{dt} + \frac{\partial}{\partial y} \frac{dy}{dt} + \frac{\partial}{\partial z} \frac{dz}{dt}, \quad (2.5)$$

with the symbols dx/dt , etc., denoting (from the physical standpoint) the velocity components in the corresponding directions x :

$$dx/dt = V_1; dy/dt = V_2; dz/dt = V_3. \quad (2.6)$$

Eq. (2.4) can be written in a vector form:

$$Dw/Dt = f(w, u), \quad (2.7)$$

where f is the vector with the components $f^1(w, u); f^2(w, u); \dots; f^n(w, u)$. The functions f^i are defined for $w \in W$ and for $u \in U$. They are assumed to be continuous in the variables $w^1, w^2, \dots, w^n, u^1, \dots, u^r$, and continuously differentiable with respect to $w^1, w^2, \dots, w^n$. Briefly, the functions

$$f^i(w, u); \frac{\partial f^i(w, u)}{\partial w^j}; i, j = 1, 2, \dots, n, \quad (2.8)$$

are defined and continuous on a direct product $W \times U$.

Suppose, a control function $u(x)$ is given for a certain region:

$$x_0 \leq x \leq x_1, \text{ and } (\xi_1, \xi_2, \dots, \xi_k)$$

are its discontinuities of the first kind with $x_0 < \xi_1 < \xi_2 < \dots < \xi_k < x_1$. Consider Eq. (2.7) in the region $x_0 \leq x < \xi_1$ in which the right-hand side of Eq. (2.7) is continuous. The solution of Eq. (2.7) with the initial conditions $w(x_0) = w_0$, is denoted by $w(x)$. If this solution is defined in the entire region $[x_0 \leq x < \xi_1]$ and has the value $w(\xi_1)$ at (ξ_1) , we can solve Eq. (2.7) in the region $\xi_1 \leq x < \xi_2$, using $w(\xi_1)$ as the initial value. In this way we can obtain the solution of Eq. (2.7) continuous and piecewise differentiable at all (x) , (except $(\xi_1), \dots, (\xi_k)$, where the function is defined) which is continuously differentiable, corresponding to the control function $u(x)$ for the initial conditions $w(x_0) = w_0$. The admissible control function $u(x)$, $x_0 \leq x \leq x_1$, transforms w from w_0 to w_1 if the corresponding solution $w(x)$ satisfying Eq. (2.7) and the initial condition $w(x_0) = w_0$, is defined for all (x) , $[x_0 \leq x \leq x_1]$ and passes through (x_1) which means that it also satisfies the boundary conditions $w(x_1) = w_1$. Suppose an additional function $F^0(w^1, w^2, \dots, w^n, u) = F^0(w, u)$ is given which is defined and is continuous together with $\partial F^0 / \partial w^i$, $i = 1, 2, \dots, n$, on $W \times U$. Then the problem of finding the optimum controls can be formulated as follows: "In the function space W there are given w_0 and w_1 . Among all the admissible control functions $u = u(x)$, which transfer $w(x)$ from w_0 to w_1 (provided that such control functions exist), find one for which the functional takes the least possible value."

$$J = \int_{x_0}^{x_1} F^0(w(x), u(x)) dx. \quad (2.8)$$

Obviously, here w is the solution of Eq. (2.7) with the initial conditions $w(x_0) = w_0$ corresponding to the control $u(x)$ and passing through $w(x_1)$. Let us note that for fixed w_0 and w_1 the upper and lower limits in (2.8) are not fixed numbers but depend upon the choice of the control function $u(x)$ which transfers $w(x)$ from w_0 to w_1 . The control $u(x)$ which furnishes the solution of the problem cited above is called an optimal control function corresponding to a transition from w_0 to w_1 .

We may reformulate the problem. Let us introduce a new coordinate into the system of coordinates $w^1, w^2, \dots, w^n$ in W , namely w^0 defined in the following way:

$$w^0 = \int_{x_0}^x F^0(w(x'), u(x')) dx' = K. \quad (2.9)$$

One can calculate the derivatives $\partial K / \partial x^i$ and construct the function

$$f^0(w, u) = V_1 \frac{\partial K}{\partial x} + V_2 \frac{\partial K}{\partial y} + V_3 \frac{\partial K}{\partial z} = \frac{DK}{Dt}. \quad (2.10)$$

Then we can write:

$$\frac{Dw^0}{Dt} = f^0(w^1, w^2, \dots, w^n, u). \quad (2.11)$$

Introducing the vector

$$\underline{w} = (w^0, w^1, w^2, \dots, w^n) = (w^0, w), \quad (2.12)$$

in the $(n+1)$ -dimensional function space $\underline{W}$, we consider the system of differential equations:

$$D\underline{w}/Dt = \underline{f}(w, u), \quad (2.13)$$

where $\underline{f}(w, u)$ is the vector in $\underline{W}$ with coordinates $f^0(w, u), f^1(w, u), \dots, f^n(w, u)$; Eq. (2.13) can be written in the form:

$$Dw^i/Dt = f^i(w^1, w^2, \dots, w^n, u^1, \dots, u^r), \quad i = 0, 1, \dots, n, \quad (2.14)$$

where the right-hand side does not depend upon the coordinate w^0 of the vector $\underline{w}$. Let $u(x)$ be an admissible control function transferring w_0 to w_1 , and let $w = w(x)$ be the corresponding solution of Eq. (2.7) with initial condition $w(x_0) = w_0$. We denote the point $(0, w_0) = (0, w_0^1, w_0^2, \dots, w_0^n)$ of $\underline{W}$ by $\underline{w}_0$ with $(w_0^1, w_0^2, \dots, w_0^n)$ being coordinates of w_0 in W . Then the solution of Eq. (2.13) with the initial condition $\underline{w}(x_0) = \underline{w}_0$, corresponding to the control $u(x)$, is defined in the entire region $x_0 \leq x \leq x_1$, and has the form:

$$w^0 = \int_{x_0}^x F^0(w(x'), u(x')) dx', \quad (2.15a)$$

$$w = w(x). \quad (2.15b)$$

For $x = x_1$, one has:

$$w^0 = \int_{x_0}^{x_1} F^0(w(x), u(x)) dx = J, \quad w = w_1, \quad (2.16)$$

which means that the solution $\underline{w}(x)$ of Eq. (2.13) with the initial condition

$w(x_0) = w_0$ passes through $w = (J, w_1)$. Assume in $\underline{W}$ a line "k" passing through the point $w = (0, w_1)$ and parallel to the w^0 axis; to construct it we find the locus of points in $\underline{W}$ passing through the point $w = (0, w_1)$ and having coordinates (ξ, w_1) where the number ξ is arbitrary. The solution $w(x)$ passes through a point on k having the coordinates $w^0 = J$ for $w = w_1(x = x_1)$. On the other hand, suppose that $u(x)$ is an admissible control of such a character that the corresponding solution $w(x)$ of Eq. (2.13) with initial condition $w(x_0) = w_0 = (0, w_0)$ for some (x_1) passes through $w_1 \in k$ which has the coordinate $w^0 = J$ (and $w = w_1(x = x_1)$). Then, the control function $u(x)$ transfers $w \in W$ from w_0 to w_1 and the functional (2.8) takes on the value J . We can express the above problem in the following form:

"In the $(n+1)$ - dimensional function space $\underline{W}$ the point $w_0 = (0, w_0)$ and the line "k" are given. The line "k" is assumed to be parallel to the w^0 axis, and to pass through the point $(0, w_1)$. Among all the admissible controls $u = u(x)$, having the property that the corresponding solution $w(x)$ of Eq. (2.13) with initial condition $w(x_0) = w_0$ intersects the line "k" find the one whose point of intersection with "k" has the smallest coordinate w^0 ."

The formulation of the optimal problem, cited above, presents a generalized formulation of the optimal problem in the sense of Pontryagin's maximum principle. There is a difference in the structure of the function spaces. In Pontryagin's maximum principle one deals with processes which can be described by a system of ordinary differential equations. We operate here in the vector space W of the vector variable $w = (w^1, \dots, w^n)$. The state of the object at any instant of time is characterized by "n" real numbers $w^1, \dots, w^n$. The space W is the phase space of the object under consideration, and $w = w(t)$ are functions of only one variable, t . The optimal trajectories $w(t)$ are curves. In the present problem the function spaces W (or $\underline{W}$) refer to the variable $w = (w^1, \dots, w^n)$, where $w^i = w^i(x^1, \dots, x^m)$, are functions of $(m+1)$ variables $x^m(t)$. The control functions are of the analogous forms, $u^r = u^r(x(t))$. Both w^i and u^r are hypersurfaces of the corresponding order. The control function $u(x)$ which yields the solution of the optimal problem, an optimal control corresponding to a transition from w_0 to w_1 , represents geometrically the optimal hypersurface. Thus, the generalized problem of controls consists of finding the optimum control function and of the corresponding optimal hypersurfaces.

Equations describing the system discussed above may possess partial derivatives of any order. By the proper substitutions we may always include the derivatives into the system of functions themselves. For example, $\partial^2 w^2 / \partial x \partial y$ may be treated in the following way:

$$\partial w^2 / \partial x = w^p; \quad \partial^2 w^2 / \partial x \partial y = \partial w^p / \partial y = w^{p+1}, \quad (2.17)$$

where the new functions $w^p, w^{p+1}, (p > n)$, have to be added to the set of functions $w, \dots, w$, in Eq. (2.4). In this case the differential operator D/Dt , Eq. (2.7), should refer to the representation in the form of Eq. (2.15) and to any other form like $\partial/\partial x$, etc. Hence, we may remodel Eq. (2.5) in the sense:

$$\begin{aligned} D/Dt &= \partial/\partial x(dx/dt) + \partial/\partial y(dy/dt) + \partial/\partial z(dz/dt), \\ \text{or } &= \partial/\partial x, = \partial^2/\partial x \partial y, \text{ etc.} \end{aligned} \quad (2.18)$$

The generalized problem of the optimal processes as formulated above (generalized optimum principle), has not been solved, as yet, and in some cases may have no solution at all. The reason is the following one: In the classical formulation of the mathematical theory of optimal processes by Pontryagin and his coworkers one deals with ordinary differential equations. In this

approach there appear convex cones as the essential element of the mathematical formalism. When dealing with the partial differential equations, having pre-scribed boundary conditions, the cones in question may be concave. This would result in an invalidation of the maximum principle. Also, we demonstrate below that for our purposes we need to reformulate the generalized optimum principle cited above.

3. Generalized Optimum Boundary Value Principle

As mentioned above, we assume that the control functions are functions of the boundary conditions, or, in nonsteady problems, of the boundary and initial conditions. Moreover, they have to be functions of the variable $w(x)$.

Briefly:

$$\begin{aligned} J &= \int_{x_0}^{x_1} F^0\{w(x) \mid u(w_0(x_0), w(x))\} dx \\ &= \int_{x_0}^{x_1} F^0(w(x), w_0(x_0)) dx. \end{aligned} \quad (3.1)$$

We assume that V_0 , called the boundary value region, is a certain set in the function space of the variables $w_0^1, w_0^2, \dots, w_0^n$, and $w_0 = (w_0^1, \dots, w_0^n)$ is its vector located in $V_0 \in W$. We call every function $w_0 = w(x_0^1, x_0^2, \dots, x_0^m)$, where $x_0 = (x_0^1, \dots, x_0^m)$ are space coordinates, with $w_0 \in V_0$, a boundary condition. Since V_0 is a set in the function space of the functions $w^1, w^2, \dots, w^n$, each boundary condition $w(x_0) = (w_0^1(x_0), \dots, w_0^n(x_0))$ is a vector function whose region is in $V_0 \in W$. Obviously, we deal with admissible boundary conditions. We specify that $w_0^{(1)} \leq w_0 \leq w_0^{(2)}$, with $w_0^{(1)} \in V_0, w_0^{(2)} \in V_0$, but that w_1 is not in V_0 . Briefly, the parametric boundary conditions are specified in a certain subdomain V_0 which does not contain w_1 , i.e., w_1 is located outside V_0 . The remaining part of the reasoning, presented in section 2 preserves its validity. Thus, we can formulate the generalized optimum boundary value principle: "In the $(n+1)$ -dimensional function space $\underline{W}$ the set $V_0 = (0, w_0^1, w_0^2, \dots, w_0^n) = (0, V_0)$ with $(w_0^1, w_0^2, \dots, w_0^n)$ being coordinates of w_0 in $V_0 \in W$, and the line "k" are given. The line "k" is assumed to be parallel to the w_0^0 axis, (this line "k" is made up of all the points (ξ, w_1) where the number ξ is arbitrary), and to pass through the point $(0, w_1)$. Among all the admissible boundary conditions w_0 , having the property that the corresponding solution $\underline{w}(x)$ of the system of equations in question with the boundary condition (to be found) $\underline{w}(x_0) = \underline{w}_0$ intersects the line "k", find the one whose point of intersection with "k" has the smallest coordinate w_0 ."

4. Controllability

The concept of a controllability of a certain variable is a new one and has its origin in the concept of optimization. Suppose that a certain variable, heat transfer, say, in the dynamic system of the flow of a medium around a re-entering body, say, should not be larger than some uniquely defined magnitude. The upper limit of the variable in question may be obtained from the experimental data. We denote this quantity by the symbol Q_u . The motion of the medium in question around the body is determined from the system of equations. By the known techniques one may calculate the value of the variable heat transfer at any required moment. We denote the variable so obtained by the symbol Q_c . We construct the functional of the form:

$$\int_{t_1}^{t_2} (Q_c - Q_u)^2 dt = \min., \quad (4.1)$$

where the integral is taken between two definite limits of the time, although without any loss of generality one can use any other interval like the length interval between two locations of the vehicle in space. Actually, we should require that in (4.1) there should be zero on the right hand side, but in the first approximation we accept the concept of a minimum. From the entire formalism of the optimization techniques it does not make too much difference whether there is zero or minimum on the right hand side of (4.1). By means of (4.1) we reduce the problem of controllability to the problem of optimization. We have to solve the entire system of equations determining the flow of the medium around the vehicle including the requirement (4.1). In the system there are included some admissible control functions like coefficient of heat conductivity, coefficients expressing the properties of the solid body, etc., which can be varied in certain known and given intervals or domains. By the appropriate variations of the control functions we may solve the system of equations, if, in general, a solution exists, and we may satisfy the optimum condition (4.1). As it is seen, the optimization theory superimposes upon the sought function additional requirements above the boundary and initial conditions in form of the integral to be minimized.

5. Reduction of Independent Variables

The optimization principle in its most general formulation, referring to partial differential equations, as presented above, at the present time may have no solution at all. In general, there are not yet known techniques, which may enable one to solve the optimization principle in such a general form in practical applications. Much better situation is prevailing in the field of ordinary differential equations. Actually, the most powerful tool in mathematics of attacking the optimization problems, the calculus of variations, was primarily proposed for solving the systems of the ordinary differential equations. In some cases it was possible to generalize the techniques of this kind to partial differential systems. The well-known Pontryagin maximum principle refers only to ordinary differential systems. Consequently, in the field of partial differential systems one has to refer to various kinds of approximate techniques. There are well-known difficulties associated with the numerical solutions on high speed computing machines of partial differential equations involving larger numbers of independent variables, i.e., in spaces of higher dimensions. Equations occurring in mathematical physics, in engineering, etc., are more than often nonlinear partial differential equations of higher order in more than two independent variables. When initial or boundary conditions are superimposed upon the system in question, the task of obtaining solutions becomes formidable. Even the application of high-speed computing devices appears inadequate for treating such problems in their more general aspects. One of the means of overcoming this difficulty is to reduce the number of independent variables. L. E. Dickson in an article published in 1924 showed how some differential equations could be integrated with the aid of group theory establishing an important link between the techniques of algebra and those of differential equations. G. Birkhoff in 1948 suggested that the reduction of independent variables in systems of partial differential equations could also be attacked by algebraic methods. The method of reducing the number of dimensions by a transformation from one space into another does not appear amenable to the standard methods of the theory of functions since the Jacobian determinant associated with such a transformation vanishes. However, algebraic methods do not break down under the above condition. The late Michal undertook the following difficult task: "Given a differential system in the space A of n dimensions, transform this system into the space B of $(n-r)$ dimensions ($1 \leq r$) such that a solution of the system in B determines a solution of it in A . The transformations involved are not to be one-to-one." The resulting theorems involve the application of the theory of Banach spaces and some elements of the theory of continuous transformation groups. In his dissertation Morgan applied the above method where the transformation was from n

to $(n-1)$ dimensions. He attacked two examples, one from two-dimensional boundary layer theory and the other from the theory of plates. However, the outline of a methodical approach was still missing. This task was undertaken by the present author. The section below deals with the transformation of systems of partial differential equations into systems of ordinary differential equations through the use of one-parameter groups. Each appropriate one-parameter group reduces the number of independent variables in the system by one by transforming the variables of the group into the invariants of the group. A method is developed for obtaining the proper groups for a given system of partial differential equations. Various classical differential equations (such as heat equation) are treated. It is found that such complex systems of equations as Navier-Stokes time dependent equations of motion of a three-dimensional, compressible, viscous, dissipative, real fluid can be treated by this method. The method is further generalized to integro-differential equations. The full success of the method in reducing the equations describing the nonsteady flow of a viscous, compressible fluid to a system of ordinary (nonlinear) differential equations (i.e., a reduction from four dimensions to one) appears to demonstrate the results and possibilities of this technique. Next paragraph deals with the boundary value problem in the group-theory method. Some concluding remarks on the relationship between all the methods given above, their mathematical fundamentals, and their possible future development close the section.

As the first one, we may mention the so-called similarity solutions. Consider a one-dimensional diffusion equations in (y, t) -plane. Introduction of a new independent variable, $\eta = \eta(y, t)$ analogous to the well-known Prandtl's variable, reduces the partial differential equation in (y, t) to an ordinary differential equation. A similar operation is applied to the equation describing the fluid motion over a suddenly accelerated plane. Some authors attempt to designate solutions so obtained as similarity solutions, since the non-dimensional velocity ratio uU_0^{-1} ($U_0 =$ constant reference velocity) is a function of the single variable η . For any $t = t_0$, the parameter η can be replaced by a multiple of y and the velocity profiles uU_0^{-1} are similar in form. The second method is the so-called free parameter method, where the new independent variable η is introduced pretty arbitrarily into the system of equations. In order to obtain its functional relation upon the previous independent variables, the coefficients of all the terms must be functions of η . In some cases it is possible to achieve that and to reduce the number of independent variables. The third technique is based upon the dimensional analysis. The classical dimensional analysis originates from the Buckingham Pi theorem: "Let n quantities be expressible in terms of certain dimensional quantities, m in number. Then the system can be described in terms of $(n-r)$ dimensionless quantities, r being the rank of the $m \times m$ matrix formed from the dimensions of n -quantities." A very extensive discussion and application of this technique was given by Sedov. The fourth method is that of the separation of variables, which is a well known and does not need any explanation. The mathematically most interesting method is the invariant group theory, discussed below in more detail.

Michal considers an r -parameter continuous transformation group:

$$G_r: \bar{x}^i = f(x^1, \dots, x^m; a^1, \dots, a^r) \equiv f(x; a),$$

$$\bar{y} = \phi(y; a^1, \dots, a^r) \equiv \phi(y; a), \quad (i = 1, \dots, m, m > 1, r \geq 1), \quad (5.1)$$

where the x 's and a 's are numerical and y is a variable of class $C^{(n)}$ with n sufficiently large, in Banach space B . The group $S_{G_r}(x^i \rightarrow \bar{x}^i)$ is assumed to possess $s \geq 1$ functionally independent Frechet differentiable, absolute invariants

$$\eta_1(x^1, \dots, x^m), \dots, \eta_s(x^1, \dots, x^m), \quad (5.2)$$

where $s < m$. It is further assumed that G_r possesses a B -valued, Frechet differentiable, absolute invariant $g(y, x^1, \dots, x^m)$ solvable in y for all admissible y and x 's. Definition 1.1-A B -valued function $y(x^1, \dots, x^m)$ of the numerical variables $(x^1, \dots, x^m)$ is called an invariant function under G_r if, under G_r , y is the same function of the x 's as $\bar{y}$ is of the $\bar{x}$'s, i.e., if $y = H(x)$ then $\bar{y} = H(\bar{x})$.

Theorem 1.1 — If B and B_1 are two reflexive Banach spaces (not necessarily distinct, i.e., they may be the same Banach space) and if,

$$\Omega(x, y(x), \frac{\partial y}{\partial x}, \dots, \frac{\partial^q y}{\partial x^q}), \quad (5.3)$$

is a B -valued q 'th order differential invariant of invariant B -valued functions $y(x^1, \dots, x^m)$ under the group G_r , then Ω is expressible in the form:

$$\omega(\eta, v(\eta), \frac{\partial v}{\partial \eta}, \dots, \frac{\partial^q v}{\partial \eta^q}), \quad (5.4)$$

where the corresponding B -valued functions $v(\eta_1, \dots, \eta_s)$ exist and are determined by the formula:

$$v(\eta_1(x^1, \dots, x^m), \dots, \eta_s(x^1, \dots, x^m)) = g(y(x^1, \dots, x^m), x^1, \dots, x^m). \quad (5.5)$$

Michal establishes the following partial converse to Theorem 1.1.

Theorem 1.2 — If B_1 and B are two Banach spaces (not necessarily distinct) and if $v(\eta_1, \dots, \eta_s)$ is an arbitrary B -valued function of the s invariants $\eta_1, \dots, \eta_s$ (Eq. (5.2)) then the corresponding B -valued function $y(x^1, \dots, x^m)$ determined by equation (5.5) is an invariant function under G_r . In addition, the B_1 -valued q 'th order differential expression $\omega(\eta, \dots)$ (Eq. (5.4)) may be expressed as a B_1 -valued q 'th order differential invariant Ω (Eq. (5.3)) of invariant B -valued functions $y(x^1, \dots, x^m)$ under G_r .

Definition 1.2 — If $y(x)$ is a solution to the partial differential equation:

$$\Omega(x, y(x), \frac{\partial y}{\partial x}, \dots, \frac{\partial^q y}{\partial x^q}) = 0. \quad (5.6)$$

where Ω is defined in the discussion following equation (5.3) and, in addition $y(x)$ is an invariant function (Def. 1.1) under G_r , the $y(x)$ is said to be an invariant solution of equation (5.6). Theorems 1.1 and 1.2 thus lead to the following theorem concerning partial differential equations.

Theorem 1.3 — An invariant solution $y(x^1, \dots, x^m)$ of equation (5.6) determines by means of equation (5.5), a solution $v(\eta_1, \dots, \eta_s)$ to the corresponding partial differential equation:

$$\omega(\eta, v(\eta), \frac{\partial v}{\partial \eta}, \dots, \frac{\partial^q v}{\partial \eta^q}) = 0, \quad (5.7)$$

where y , $v(\eta)$ and $\omega(\eta, v(\eta), \dots)$ are defined by Theorem 1.1.

Lemma I — To each solution $v(\eta)$ of equation (5.7) corresponds an invariant solution $y(x)$ of equation (5.6). The correspondence is given by equation (5.5). As was pointed out by Michal, Morgan deals with one-dimensional normed linear spaces and continuous groups in only one numerical parameter (a). Consider a system of partial differential equations:

$$\Omega_\lambda(x, y^1, \dots, y^n, \frac{\partial y^1}{\partial x^1}, \dots, \frac{\partial^k y^n}{\partial (x^m)^k}) = 0, (\lambda = 1, \dots, f), \quad (5.8)$$

with m independent variables $(x^1, \dots, x^m)$ where each of the functions Ω_λ is conformally invariant under Γ_1 . Morgan proves the following theorem relating to this system of equations.

Theorem 1.4 — The invariant solution of $\Omega = 0$ can be expressed in terms of the solutions of a system of the form:

$$\omega_\lambda(\eta, v_1, \dots, v_n, \frac{\partial v_1}{\partial \eta_1}, \dots, \frac{\partial^k v_n}{\partial \eta_{m-1}^k}) = 0, (\lambda = 1, \dots, f), \quad (5.9)$$

with ' $m - 1$ ' independent variables $\eta_1, \dots, \eta_{m-1}$. The correspondence is determined by n relations of the form:

$$v_j(\eta_1, \dots, \eta_{m-1}) = g_j(y^1, \dots, y^n, x^1, \dots, x^m), (j = 1, \dots, n), \quad (5.10)$$

where the v_j 's are of class $C^{(t)}$ ($t \geq 1$), the η 's are the invariants. Consider the equation:

$$\frac{\partial u}{\partial y} = 0, u = u(x, y). \quad (5.11)$$

The solution of equation (5.11) is, of course, given by: $u = u(x)$. We now inquire into the invariant solutions of equation under:

$$\Gamma_1: \bar{x} = f^1(x, y; a) = a^j x, \bar{y} = f^2(x, y; a) = a^k y, \bar{u} = f^3(u; a) = a^l u, \quad (5.12)$$

where j, k and l are any real numbers and a ($\neq 0$) is the parameter. From:

$$d\bar{x} = \frac{\partial \bar{x}}{\partial x} dx + \frac{\partial \bar{x}}{\partial y} dy, d\bar{y} = \frac{\partial \bar{y}}{\partial x} dx + \frac{\partial \bar{y}}{\partial y} dy, \quad (5.13)$$

$$\frac{\partial \bar{u}}{\partial \bar{y}} = \frac{\partial \bar{u}}{\partial x} \frac{\partial x}{\partial \bar{y}} + \frac{\partial \bar{u}}{\partial y} \frac{\partial y}{\partial \bar{y}} = a^{l-k} \frac{\partial u}{\partial y}, \quad (5.14)$$

which shows that equation (5.11) is constant conformally invariant under Γ_1 . Assume that the value of k in equation (5.12) is not equal to zero. The invariants of Γ_1 may be chosen as follows. Set

$$\eta = x f(y) = \bar{x} f(\bar{y}) = a^j x f(a^k y). \quad (5.15)$$

This equation is satisfied for $f(y) = y^{-j/k}$, $f(\bar{y}) = \bar{y}^{-j/k}$, since in this case:

$$\eta = \bar{x} f(\bar{y}) = \bar{x} \bar{y}^{-j/k} = a^j x (a^k y)^{-j/k} = x y^{-j/k} = x f(y). \quad (5.16)$$

Similarly, by analogy choose:

$$g = u h(y) = u y^{-1/k} = v(\eta). \quad (5.17)$$

This leads to the following equation:

$$\begin{aligned} \frac{\partial u}{\partial y} &= \frac{\partial}{\partial y} (v y^{1/k}) = y^{1/k} (1/k^{-1} v y^{-1} + \frac{\partial v}{\partial y}) = y^{1/k} (1/k^{-1} v y^{-1} + \frac{dv}{d\eta} \frac{\partial \eta}{\partial y}) = \\ &= y^{1/k-1} (1/k^{-1} v - j/k^{-1} \eta dv/d\eta) = 0. \end{aligned} \quad (5.18)$$

Since $y^{1/k-1} \neq 0$, it follows that:

$$1v - jndv/d\eta = 0. \quad (5.19)$$

is the sought equation. The above technique is generalized to n-tuple reduction method, i.e., one may reduce a partial differential equation in n-independent variables to an ordinary one. Various examples are solved like: wave equation, boundary layer flow, the sudden stopped flat plate, Stoke's First Problem, etc. It should be mentioned that there exists another approach to the algebraic technique of reducing the number of independent variables, e.g., the basic theory is the Lie groups theory. A considerable amount of work in this field was done by the Soviet and Polish schools of mathematics.

As the control functions in the heat conduction equation, one can assume the heat conduction coefficient, which leads to the necessity of having a possibility of using a "spectrum" of different materials with different heat conduction coefficients and specific properties. In the case of gases, there arises the necessity of adding some substances into the gaseous medium altering its heat conduction properties. One may also consider the initial or the boundary conditions as the control function (like the proper change of the initial temperature). A very crude technique of solving a controllability problem in the case of small number of independent variables (2 or 3 at most) is the following one. The control function is given, is bounded, and is contained in a certain domain. One can imagine that it is located on a certain hypersurface, on which we construct a grid of points. For each point (control function) we solve the system in question, i.e., in our case the heat conduction equation. Having obtained a solution for the point in question, we construct the integral to be minimized. The grid of points gives us a set of solutions and the minimum appears automatically. The computer program is the same for all the points. The requirements are that the functions included in the problem are decent, that they have no singularities in the domain in question, etc. But these requirements (no singularities, etc.) have to be known before the final numerical solution is attacked in the proposed way. The same technique may be used to attack the problem of the analysis of the controllability of the sensitivity (the rate of change of the optimum value). The considered cases include: heat flux in reentry including M.H.D., heat transfer in epihydrodynamics, effect of the intensity of the gravitational field upon the heat transfer, etc.

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THE KUBO APPROACH TO THERMAL CONDUCTIVITY IN A COUPLED SPIN-PHONON SYSTEM

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ABSTRACT

The elementary kinetic formula is often used to calculate the thermal conductivity of crystals containing paramagnetic ions but dispersion in sound velocity is usually ignored. To take account of this Elliot and Parkinson (1967) analyzed the system by means of coupled spin-phonon modes but assumed the kinetic formula applied to the coupled modes. We have attempted to justify this by using the Kubo formula which expresses the conductivity in terms of the correlation function for the energy current operator. For coupled spin-phonon modes one cannot use only the harmonic lattice energy flux but must include a term linear in the spin-lattice coupling. The correlation functions are evaluated by a Greens function method. The result is not identical to that obtained from the kinetic formula but the difference is small for modes close to the resonant frequency of the magnetic ions.

* * * * *

The simple kinetic formula $\lambda = (1/3) \sum_q C_q v_q^2 \tau_q$ is often used to calculate the thermal conductivity λ of crystals containing paramagnetic ions (Challis et al. 1968). Resonant scattering of phonons with frequencies ω_q close to the resonance frequency ω_0 is described by the relaxation time τ_q and v_q is taken to be the unperturbed sound velocity. The specific heat per mode C_q is given by the usual Bose-Einstein distribution. This procedure is inconsistent in that absorption of sound waves must be accompanied by corresponding dispersion in the velocity and modifications of the mode specific heat.

In practice experiments are directed at obtaining information on the energy level structure of complicated ions for which rigorous calculations of τ_q have not yet been carried out. For this purpose an elementary treatment may suffice but it is nevertheless an interesting problem to calculate the conductivity for a simple model taking into account dispersion and the effect of the spin-phonon coupling on the mode specific heat.

We use the model first introduced by Jacobsen and Stevens (1963). For a linear chain of atoms with one spin per atomic site, the total Hamiltonian is

$$\mathcal{H} = \mathcal{H}_L + \mathcal{H}_S + \mathcal{H}_{SL} ,$$

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where

$$\begin{aligned} \mathcal{H}_L &= \sum_n \left\{ \frac{p_n^2}{2m} + \frac{1}{2}K(u_{n+1} - u_n)^2 \right\} , \\ \mathcal{H}_S &= \sum_n \hbar \omega_0 S_{zn} , \\ \mathcal{H}_{SL} &= \sum_n \hbar \epsilon (u_{n+1} - u_{n-1}) S_{xn} , \end{aligned}$$

in which the atomic displacement at site n is u_n and the S_{xn} spin component is coupled to the local lattice strain $(u_{n+1} - u_{n-1})$ with coupling constant ϵ . Transitions between the spin eigenstates $|+\rangle$ and $|-\rangle$ with accompanying phonon absorption or emission are therefore induced by the spin-lattice interaction $\mathcal{H}_{SL}$. Because of the coupling a lattice wave will excite a disturbance in the spin system. The normal modes are mixed phonons and spin waves and the mixing is most severe when the phonon frequency $\omega_q = \omega_0$. This results in a coupled spin-phonon dispersion

Fig. 1. Dispersion curve for coupled spin-phonon modes (Elliot and Parkinson 1967)

curve first derived by Jacobsen and Stevens (1963) but later modified by Elliot and Parkinson (1967) who used a Greens function equation of motion method which also gives the damping (or relaxation time) of the excitations.

To calculate the thermal conductivity of such a coupled mode system Muller and Tucker (1966) treated these excitations as bosons and used the Bose-Einstein distribution for the specific heat per mode. Taking $v_q = \partial\omega/\partial q$, the group velocity, and τ_q from the Greens function method the conductivity was computed from the kinetic formula. However, paramagnetic spins cannot properly be treated as bosons (as can e.g. ferromagnetic spin waves at low temperatures) and the excitation spectrum is incorrect if calculated on this assumption (Sheard and Toombs 1969). Elliot and Parkinson (1967) calculated C_q rigorously from thermal averages computed from the appropriate Greens functions but again used the kinetic formula for the conductivity.

At this stage the calculation has become sufficiently complicated that the essential simplicity that is usually gained by using the kinetic formula is lost. We have avoided the assumptions inherent in the kinetic treatment by using the Kubo formula

$$\lambda = \frac{1}{kT^2} \lim_{s \rightarrow 0+} \int_0^\infty e^{-st} \langle Q(t)Q(0) \rangle dt ,$$

which expresses the conductivity λ in terms of the correlation function for the energy flux operator Q . Surprisingly little work has been carried out with the Kubo formula for thermal conductivity (Maradudin 1964) and it is of some interest to see how it works out for the unusual case of coupled modes.

Using the energy flow operator for a harmonic lattice $Q_L = \sum_q N_q \hbar \omega_q v_q$,

where N_q is the number density of phonons, Schieve and Peterson (1962) show that the Kubo formula reduces to the kinetic formula if the scattering is described by a relaxation time for each mode. This can be understood in a general way if we put $Q_q(t) = Q_q(0) \exp(-t/\tau_q)$, for the contribution from mode q . Then

$$\lambda \propto \sum_q \int_0^\infty \exp(-t/\tau_q) dt \langle Q_q^2(0) \rangle = \sum_q \tau_q \langle Q_q^2 \rangle.$$

But the fluctuations in heat current $\langle Q_q^2 \rangle$ are related to fluctuations in energy density which are proportional to the specific heat C_q and hence the kinetic formula is recovered.

For coupled spin-phonon modes however one cannot use only the harmonic lattice energy flux Q_L but must include a term Q_{SL} linear in the spin-lattice coupling. This is because in the crossover region of the dispersion curve the excitations are mixed spin waves and phonons. If the purely lattice energy flow Q_L is used the contribution of the spin waves is missed. The precise form of Q_{SL} is derived from conservation of energy (Swain 1967).

The calculation of the correlation functions follows standard Greens function procedures. There are 3 different types of correlation function $\langle Q_L Q_L \rangle$, $\langle Q_L Q_{SL} \rangle$ and $\langle Q_{SL} Q_{SL} \rangle$ but the latter may be neglected since it only contributes on the spin-like parts of the dispersion curve where the group velocity is small.

The results (Swain 1967) are very similar but not identical to that obtained by the kinetic formula. For modes with $\omega_q \sim \omega_0$ the difference however is very small. The differences may arise from the approximations made in evaluating the correlation functions and this is currently being investigated.

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The Description of a Method for Measuring the Transport
Coefficients of Metals and Alloys at Low Temperatures
After F. Kohlrausch and H. Diesselhorst

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In the stationary case of the Kohlrausch arrangement there is both thermal and electrical flow through the cylindrical sample. Solving the Fourier equation

$$c_p \cdot p \frac{\partial T}{\partial t} = W + \kappa \cdot \Delta T$$

(Where c_p is the total specific heat at constant pressure, p the density, T the absolute temperature, t the time, W the production of heat per unit volume and per second, κ the total thermal conductivity and Δ the Laplace differential operator) in cylindrical coordinates it is possible to measure the following physical quantities on the same sample at the same temperature:

1. The thermal conductivity κ
2. The electrical conductivity σ
3. The quotient κ/σ)
4. The Lorenz number $L = \kappa/\sigma \cdot T$) Without any influence of the geometry of
5. The thermopower S) the sample

There are two ways in evaluating these data:

A. The Onsager reciprocal relations

$$\vec{j} = L_{12} [e^2 \cdot \vec{E} + eT \cdot \nabla \left(\frac{\mu}{T} \right)] + L_{12} \frac{e}{T} \nabla T$$

$$\vec{q} = -L_{21} [e \cdot \vec{E} + T \cdot \nabla \left(\frac{\mu}{T} \right)] - L_{22} \frac{1}{T} \nabla T$$

(Where $\vec{j}$ is the density of heat flow, $\vec{q}$ the density of electric current, e the charge of the electron, $\vec{E}$ the electric field, μ the Fermi energy of the electrons. The L_{mn} are tensors of the 2nd degree)

B. The Kubo linear response theory

(Where $\beta = 1/kT$, k is the Boltzmann constant, $\vec{j}_v$ the electric current in v th direction, q_μ the heat flow density in the μ th direction, and so on)

Neglecting factors before the integrals one obtains the following integrals:

$$L_{11} = \int_{v\mu}^{\infty} \int_{\lambda=0}^{\beta} \langle \vec{j}_{v\mu} \vec{j}_{v\mu} (t + i\hbar\lambda) \rangle d\lambda dt$$

$$L_{12} = \int_{v\mu}^{\infty} \int_{\lambda=0}^{\beta} \langle \vec{j}_{v\mu} \vec{q}_{v\mu} (t + i\hbar\lambda) \rangle d\lambda dt$$

$$L_{21} = \int_{v\mu}^{\infty} \int_{\lambda=0}^{\beta} \langle \vec{q}_{v\mu} \vec{j}_{v\mu} (t + i\hbar\lambda) \rangle d\lambda dt$$

$$L_{22} = \int_{v\mu}^{\infty} \int_{\lambda=0}^{\beta} \langle \vec{q}_{v\mu} \vec{q}_{v\mu} (t + i\hbar\lambda) \rangle d\lambda dt$$

Though it is not as yet possible to solve the Kubo integrals we measure the kinetic coefficients L_{mn} as a function of the absolute temperature by the Kohlrausch method.

In the nonstationary case of the Kohlrausch method the Fourier equation goes to:

$$\frac{\partial T}{\partial t} = \frac{\kappa}{c_p \cdot p} \Delta T = a \cdot T \quad (a \text{ is the thermal diffusivity})$$

Solving this by the Green's function method one gets longly expressions for the experimental evaluation of the thermal diffusivity a . Both the thermal conductivity κ and the density p are known from the stationary case. Setting their values in the equation for the thermal diffusivity we obtain the specific heat.

By the Kohlrausch method we can measure at low temperatures the following physical quantities: The electronic and the lattice thermal conductivity; the electronic and the lattice specific heat; the residual electrical resistivity; the phonon drag of the thermoelectric power; the Lorenz number in the range of the validity of the Wiedemann-Franz-Lorenz law.

AN ANALYTICAL STUDY OF THERMAL CONTACT CONDUCTANCE FOR TWO
ROUGH AND WAVY SURFACES UNDER A PRESSURE CONTACT

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ABSTRACT

An attempt is made to predict the thermal contact conductance for two rough wavy surfaces in contact. A pressure contact between identical materials in a vacuum environment is considered. A model is proposed based on the assumption that the contacting surfaces have asperities distributed homogeneously and isotropically and the heights of the surface asperities are in a normal distribution. Probability theory is used to derive thermal contact conductance versus pressure relation with separation distance between two surfaces as a parameter. Also evaluated is the loading pressure when the contour area equals the apparent area.

Theoretical predictions are compared with the experimental data in the literature which satisfy the underlying assumptions for the model. A good agreement is found between theory and experiment for thermal contact conductance curves in the pressure range between 10^3 to 10^4 psi. Theoretical prediction gives a lower estimation of conductance for pressures below 10^3 psi. The disagreement increases with decreasing loading pressures. Theory shows that thermal contact conductance is a strong function of surface roughness. The pressure, when contour area equals the apparent area, is found to be of the order of 1 psi or less which substantiates the observation from calculated results that conductance is very weakly dependent on the surface waviness within the pressure range of interest (10^2 to 10^4 psi). Of particular importance is that it permits the omission of the consideration of the macroscopic constriction resistance at the interface.

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1. INTRODUCTION

It has long been realized that the calculation of heat transfer across two bodies in a pressure contact cannot be carried out in terms of the resistances of the bodies alone. Thermal contact conductance⁴ at interface is important. This is particularly true in the case of thermal design of modern systems and apparatus where a precise determination of heat transport is always required.

Omission of the consideration of contact conductance at interfaces could result in a gross error, thus defeating the attainment of the desired performance.

During the last decade, a large body of literature has been published on this subject which deals primarily with experimental measurements. A few attempts have been made on the analytical study on the subject with partial success. Indeed, accurate theoretical prediction of contact conductance over an extended pressure range is elusive to obtain, but is sorely needed in current engineering applications. This paper presents a method to predict thermal contact conductance for a pressure contact between two nominally wavy rough surfaces. It is intended that, through this study, a better insight is gained which will be helpful to future study of the subject.

2. REVIEW OF RELATED WORKS IN THE LITERATURE

Clausing and Chao [1]⁵ studied contacts of spherically wavy and smooth surfaces. Through a theoretical analysis, they showed that the contact conductance was predominantly determined by the macroscopic constriction resistance. Guided by this concept, their experimental study was limited to wavy smooth specimens. Their experimental results substantiated their theory which was essentially derived for a macroscopic constriction resistance.

Mikic and Rohsenow [2] and later Yovanovich and Rohsenow [3] made analytical studies on contacts of spherically wavy and rough surfaces. Their theories all based on the consideration that the thermal resistance at the interface consisted of two independent parts, namely, macroscopic resistance and microscopic resistance. Mikic and Rohsenow [2] showed that neglecting the effect of surface roughness as proposed in Clausing and Chao's theory resulted in predicted conductances approximately an order of magnitude larger than measured values. Neglecting the effect of surface waviness yielded predicted conductances lower than observed for low pressures (10^2 to 10^3 psi), while good agreement was found at high pressures ($>10^3$ psi). By simultaneously considering both waviness and roughness, Mikic and Rohsenow obtained a fair agreement between theory and test data over a wide pressure range (10^2 to 10^4 psi).

⁴Hereafter in this work thermal contact conductance will be abbreviated to read as "contact conductance" or "conductance" if no ambiguity is involved. The term "contact resistance" is understood to be the reciprocal of contact conductance.

⁵Numbers in brackets designate references at end of paper.

It is worth noting that Bloom [4] reported the effect of roughness on wavy surfaces in contact. He showed that a conductance theory based solely on the macroscopic resistance tended to overestimate conductance values. Fried [5] carried out a correlation further substantiating the importance of the consideration of roughness in the theory. While Mikic and Rohsenow's [2] theory agrees with their own test data, it is still inadequate from a physical stand point. That is to say, by including an additional resistance, namely, macroscopic resistance, in their theory would yield higher conductance values at lower loading pressures.

3. STATEMENT OF THE PROBLEM AND ASSUMPTIONS

This work deals with a theoretical analysis to predict the thermal contact conductance for two wavy rough surfaces in contact.⁶ The waviness is considered to be spherical in shape on which roughnesses are distributed homogeneously and isotropically. The heights of surface asperities are in a normal distribution. A pressure contact is considered to be formed of identical metals in a vacuum environment. Contacting surfaces are free from any contaminants. Thus, it follows that all metallic microcontacts are uniformly distributed and confined within a contour area which together with the microcontacts are circular. These microcontacts and contour area contribute respectively microscopic and macroscopic constriction resistances to heat flow.

4. MODEL FOR ANALYSIS

When two surfaces are arranged one on top of the other, the making or breaking of a contact of two asperities on these surfaces is governed by the distance between those surfaces and the heights of the asperities involved. For two wavy rough surfaces in contact, the above concept, although applicable, does not lend itself to manageable analysis. A simplified model is established as shown in Figure 1. The model for contacts consists of two surfaces; the roughnesses on the two original surfaces are incorporated into the lower model surface I, while their waviness deviations are lumped together to form the upper model surface II.

Probability theory is employed to construct the lower model surface I. This surface has a flat base plane on which conical asperities of equal apex angle are distributed homogeneously and isotropically. The heights of the asperities exhibit a normal distribution characterized by a standard deviation $\sigma = (\sigma_1^2 + \sigma_2^2)^{1/2}$, where σ_1 and σ_2 are the standard deviations for the heights of the asperities on the two original surfaces. The apex angle for the asperities on the model surface I is the smaller of the two apex angles for the original surfaces. Since the peak-to-valley height of the surfaces is eight times its standard deviation, it is permissible to assume that the model surface I is also characterized by a peak-to-valley height of 8σ [6, 7]. To further simplify analysis, it is assumed that the asperities on the lower model surface I are deformable whereas the smooth wavy surface II is

⁶This work will not concern with wavy smooth surfaces in contact. Such contacts have been successfully studied by Clausing and Chao [1].

nondeformable. The interference due to contact or deformation of neighboring asperities is considered negligible.

Now that the model has been clearly defined; the application of the model for analysis follows.

By choosing the base plane EE' of surface I in Figure 1 as a reference plane, the local separation distance between surfaces I and II is

$$u(r, d) = d + \frac{r^2}{2R_1} + \frac{r^2}{2R_2} = d + \frac{r^2}{2B}$$

where the last equality employs the relation $\frac{1}{B} = \frac{1}{R_1} + \frac{1}{R_2}$, R_1 and R_2 are radii of curvature for the original wavy surfaces, d is the minimum separation distance between surfaces EE' and FF' and r is the radius measured from the longitudinal axis of the cylindrical specimen. From the geometry of the contacting surfaces, the local separation distance u is, of course, a function of r and d .

By denoting the heights of the asperities on the model surface I by z , the contact is determined by the relative magnitude of z and the local separation distance $u(r, d)$. Contact is formed when $z \geq u(r, d)$. In mathematical terms, the probability of making a contact is given by the expression

$$P[z \geq u(r, d)] = \int_{d + \frac{r^2}{2B}}^{\infty} F(z) dz \quad (1)$$

where $F(z)$ is the normal distribution density function.

In conformity with the practical situation for a finite height of peak-to-valley roughness, a modified normal density function $F'(z)$ is used given by

$$F'(z) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{1}{2}\left(\frac{z-\mu}{\sigma}\right)^2} - \Omega \quad (2a)$$

and for z beyond the range (Figure 2)

$$F'(z) = 0. \quad (2b)$$

In Equation (2a), μ is the standard deviation, Ω the density evaluated at the limits of the range of heights, given as

$$\Omega = \frac{1.3383}{\sigma} \times 10^{-4}$$

In effect, the modified density function consists of a lowering of the original density function by a distance of Ω , hence it confines the asperities within the peak-to-valley height of asperities 8σ . Beyond this range, the density is zero.

From the characteristics of the normal density function it follows that the area under the original density curve for $z > 8\sigma$ and $z < 0$ is only 6.4×10^{-3} percent of the total area under the density curve. Thus, the expression

$$\int_0^{8\sigma} F'(z) dz = 1 \quad (3)$$

still holds with good approximation.

Substituting $F(z)$ in Equation (1) by $F'(z)$ one obtains

$$P[z \geq u(r, d)] = \int_{d + \frac{r^2}{2B}}^{8\sigma} \left[\frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{1}{2}\left(\frac{z-4\sigma}{\sigma}\right)^2} - \Omega \right] dz \quad (4)$$

where the upper integration limit and μ have been changed to 8σ and 4σ , respectively.

5. ANALYTICAL SOLUTION OF THERMAL CONTACT CONDUCTANCE

5.1 Derivation of Equation for the Number of Contact Points

It follows from probability theory that the mean value of a function $f(z)$ is expressed as

$$\bar{f}(z) = \int_{-\infty}^{\infty} f(z) F'(z) dz \quad (5)$$

Accordingly, the number of contact points per unit area at radius r , for a separation distance d is

$$\bar{N}(r, d) = \eta \int_{d + \frac{r^2}{2B}}^{8\sigma} F'(z) dz \quad (6)$$

where η is the density of asperities given by [8]

$$\eta = (8\sigma \tan \theta)^{-2} \quad (7)$$

In the above expression θ is the half apex angle of the asperities.

The number of contact spots in an elemental circular ring of area $da = 2\pi r dr$ is

$$dN(r, d) = \eta da \int_{d + \frac{r^2}{2B}}^{8\sigma} \left[\frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{1}{2}\left(\frac{z-4\sigma}{\sigma}\right)^2} - \Omega \right] dz \quad (8)$$

Integrating over the contour area, the number of contact spots contained in the contour area of radius R_c follows

$$N(d) = \eta 2\pi \int_0^{R_c} r \int_{d + \frac{r^2}{2B}}^{8\sigma} \left[\frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{1}{2}\left(\frac{z-4\sigma}{\sigma}\right)^2} - \Omega \right] dz dr \quad (9)$$

Thus, the number of contact spots in the apparent area⁷ becomes

$$n(d) = \frac{N(d)}{\pi R_a^2} = \frac{2\eta}{R_a^2} \int_0^{R_c} r \int_{d + \frac{r^2}{2B}}^{8\sigma} \left[\frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{1}{2}\left(\frac{z-4\sigma}{\sigma}\right)^2} - \Omega \right] dz dr \quad (10)$$

where, R_a is the radius of the apparent area.

5.2 Derivation of the Equation for Pressure at the Interface

By referring back to Figure 1, one readily sees that, if u is less than z , there will be a deformation at the tip of the asperity since the upper model surface II has been assumed to be rigid. For contacting surfaces of moderate waviness, one can write from geometrical considerations (Figure 3) the radius of contact spot as

$$a = (z - u) \tan \theta \quad (11)$$

In view of the extremely high local pressure prevailing at the tips of the asperities in contact, one can assume that the deformation of asperities is predominantly plastic in nature. The force acting on a contact spot is

$$F = cY\pi a^2 = cY\pi(z - u)^2 \tan^2 \theta \quad (12)$$

where $c \approx 3$, Y is the yield strength of the solid material.

The procedure in deriving the relation for the loading pressure at the interface is essentially identical to that employed in deriving $n(d)$ as

⁷Apparent area is defined as the total area at the interface. For cylindrical test specimens, the apparent area equals the cross-sectional area.

presented in the last section. Starting from the equation for the mean force acting on the contact spots at radius r

$$\bar{F}(r, d) = c \gamma \pi \tan^2 \theta \int_{d + \frac{r^2}{2B}}^{8\sigma} (z-u)^2 \left[\frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{1}{2} \left(\frac{z-4\sigma}{\sigma} \right)^2} - \Omega \right] dz \quad (13)$$

one derives the loading pressure at the interface as

$$p(d) = \frac{2}{R_a^2} \int_0^{R_c} r \left\{ \eta c \gamma \pi \tan^2 \theta \int_{d + \frac{r^2}{2B}}^{8\sigma} (z-u)^2 \left[\frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{1}{2} \left(\frac{z-4\sigma}{\sigma} \right)^2} - \Omega \right] dz \right\} dr \quad (14)$$

5.3 Derivation of Equation for Thermal Contact Conductance at the Interface

Thermal contact conductance for a single contact spot is

$$h_c = 2 a \lambda_s \quad (15)$$

where 'a' is the radius of the contact spot and λ_s the thermal conductivity of the contacting material. For the configuration of the model asperity as depicted in Figure 3, 'a' can be substituted by Equation (11). The thermal contact conductance for a single contact thus becomes

$$h_c = 2 \lambda_s (z-u) \tan \theta \quad (16)$$

Once again the procedures in deriving $n(d)$, Equation (10) can be used. However, consideration is given to the size effect of the contact spots. Roess (9) performed a pure analytical study which accounted for the fact that, when contacting surfaces are smooth, under a large loading pressure contact resistance tends to be diminishingly small. By including the size effect in analysis, thermal contact conductance for the elemental area da becomes

$$dh(r, d) = \left\{ 2 \eta da \lambda_s \tan \theta \int_{d + \frac{r^2}{2B}}^{8\sigma} (z-u) \left[\frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{1}{2} \left(\frac{z-4\sigma}{\sigma} \right)^2} - \Omega \right] dz \right\} \left[1 - 1.41 \left(\frac{\bar{a}}{R_e} \right) \right]^{-1} \quad (17)$$

where $\bar{a}$ is the mean radius of contact spots when the local separation distance is $u = d + \frac{r^2}{2B}$. Following probability theory, $\bar{a}$ is readily expressed as

$$\bar{a} = \tan \theta \int_{d + \frac{r^2}{2B}}^{8\sigma} (z-u) \left[\frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{1}{2} \left(\frac{z-4\sigma}{\sigma} \right)^2} - \Omega \right] dz \quad (18)$$

R_e can be derived from Equation (7) as

$$R_e = 4\sigma \tan \theta \quad (19)$$

Integrating Equation (17) over the contour area and subsequently dividing by the apparent area yields the thermal contact conductance at the interface as

$$h_s(d) = \frac{2}{R_a^2} \int_0^{R_c} r \left\{ \eta z \lambda_s \tan \theta \int_{d + \frac{r^2}{2B}}^{8\sigma} \left(\frac{1}{\sqrt{2\pi\sigma}} e^{-\frac{1}{2} \left(\frac{z-4\sigma}{\sigma} \right)^2} - \Omega \right) dz \right\} \left[1 - 1.41 \left(\frac{\bar{a}}{R_e} \right) \right]^{-1} dr \quad (20)$$

Examining Equations (14) and (20), one sees that both loading pressure and contact conductance are functions of the same parameter d , the minimum separation distance. Hence, by numerical evaluation of both contact conductance and pressure simultaneously parameterized by d , a relation between loading pressure and contact conductance is obtained.

6. COMPARISON OF PREDICTED AND EXPERIMENTAL DATA

The literature is searched for experimental data suitable for checking the above theory. It is found that the data by Mikic and Rohsenow [2] are good for this purpose in that their test specimens satisfy the underlying assumptions for this theory. In addition, the data for contacts of flat surfaces by Henry [10] and Yovanovich [11] are also employed to explore the feasibility of the theory to contacts of flat surfaces. In all numerical calculations, a 1130 computer is used.

Figures 4 through 8 show in log-log scale the variation of thermal contact conductance with pressure. In the legend to these figures σ is defined as $\sigma = (\sigma_1^2 + \sigma_2^2)^{1/2}$. The indicated waviness w is the total waviness deviation, $w = w_1 + w_2$.

It is readily seen that (Figures 4 and 6), in the pressure range between 10^3 and 10^4 psi, the agreement between theory and experiment is quite good. For Figure 5, there are no experimental data available within this pressure range. However, if the last data point (at 10^3 psi) in Figure 5 is ignored, the trend of the experimental data for increasing pressures still agrees with the theory. At lower loading pressures ($10^2 - 10^3$ psi), experimental values are generally higher than predicted, as is observed in all three figures. The deviation increases with decreasing loading pressures. This is discussed below.

It has been generally considered by investigators who have studied thermal contact conductance that the curvature for the trend of the experimental data at lower loading pressures is the result of the waviness of the contacting surfaces. No elaboration has been made in the past either from a theoretical or an experimental point of view.

An analytical study of this phenomenon can be carried out if consideration is given to the effect of waviness on thermal contact conductance. Such an effect has primarily two aspects; namely:

- (i) Waviness on surfaces gives rise to a macroscopic constriction resistance in addition to the microscopic constriction resistance; the latter being associated with contact spots only.
- (ii) Waviness may change the contact configuration of microscopic contact regions, thus greatly complicating the analysis and putting it beyond the capability of the simple model treated in this work. A detailed discussion follows.

It is expected that waviness on surfaces changes the contact configuration. For two spherically wavy surfaces in contact, contact spots are confined within a contour area which gives rise to the macroscopic constriction resistance to heat flow. This area grows with increasing load; a pressure thus exists when the contour area equals the apparent area, at which point the macroscopic resistance becomes zero. In effect, when such a pressure is reached, contact between wavy surfaces is much the same as that for flat surfaces. The problem now centers on the evaluation of the pressure with which we shall now concern ourselves. Consideration is given to the geometry of the original contacting surfaces, from which the model surfaces can be constructed. A separation distance d when the contour area equals the apparent area can thus be estimated from the model. This separation distance is subsequently substituted into Equation (14) to yield the desired pressure. In an alternative approach, use is made of Equation (13). It is expected that, for a separation distance d , $\bar{F}$ decreases with increasing r . Assigning $(z - u)$ in the equation a value zero for $z < u$, one finds the value of d when the zero-force radius $r|_{\bar{F}=0} = R_a$.

This d is subsequently substituted into Equation (14) to give the pressure of interest.

The theoretical calculations show clearly that the loading pressure, when the contour area equals the apparent area, is only of the order of 1 psi or less (Table 1). For the pressure ranges in Figures 4, 5 and 6, even the lowest pressure is far beyond this magnitude. Thus, for the pressure range of practical interest, waviness on surfaces does not give rise to a macroscopic resistance in addition to the microscopic resistance to heat flow.

TABLE 1

Loading Pressure When Contour Area Equals Apparent Area

<u>Material of the Specimen</u>	<u>Description of the Specimens⁸</u>		<u>Loading Pressures for Contour Area Equals Apparent Area (psi)</u>
	<u>Roughness (uin)</u>	<u>Waviness (uin)</u>	
Stainless Steel (303)	190	150	4.095
Stainless Steel (303)	152	80	0.55
Stainless Steel (303)	340	115	0.0227
Stainless Steel (416)	42	0	-----
Stainless Steel (416)	170	0	-----

⁸Thermal contact conductance versus pressure curves for these specimens are shown in Figures 4 through 8.

The second effect of waviness on contact conductance, however, is plausible in explaining the phenomenon. It is worth noting that, for wavy surfaces in contact, the contact configuration is quite complicated. The surface asperities on the protruding parts of two surfaces, being more free in establishing contacts, first wedge in each other. That is to say, the peak of the asperity on one surface slots into the valley of the other. As a result, the actual contact area is greater than calculated from Equation (18) that is derived on a model in which such effect is ignored. By inspecting Equation (20), one sees that a larger $\bar{a}$ leads to a higher conductance, which is consistent with the experimental observation. As pressure increases, more asperities are in contact. Nevertheless, for these asperities, the wedge-in phenomenon ceases to take place. This is due to the fact that prior established contact asperities have already locked the surfaces together securely from lateral movement. Furthermore, the actual contact configuration is also complicated by the expected cooling and contraction of the parts of surfaces which were already in contact during the early loading process.⁹ Finally, a state of equilibrium of contact is reached for which the simple analysis in this work is applicable (10^3 to 10^4 psi).

Figures 7 and 8 demonstrate the applicability of the theory to flat surfaces in contact. Stainless steel 416 specimens were used. Again, theoretical thermal contact conductance versus pressure curves show good agreement with experiment within the pressure range from 10^3 to 10^4 psi. Below this range, the specimen with $\sigma = 170 \mu$ in exhibits marked disagreement with experiment, while specimens with $\sigma = 42 \mu$ in still shows good agreement. The lack of experimental data for pressures below 10^3 psi precludes reaching a conclusion on the validity of the theory in this pressure range. However, the good agreement between theory and experiment within the pressure range from 10^3 to 10^4 psi is encouraging, as it is consistent with the observation for wavy surfaces in contact. Thus, one may use the theory to predict with good confidence the thermal contact conductance, at least, in the pressure range from 10^3 to 10^4 psi for contacts of combinations of both wavy, both flat, or even one wavy/one flat surfaces.

The theoretical analysis also permits a quantitative study of the effect of surface waviness on thermal contact conductance. Theoretical data for a specimen of stainless steel 303, surface roughness 190μ in and total waviness deviation w ranging from 150 to 600μ in are calculated and plotted in Figure 9. It is readily seen from the figure that, within the pressure range 10^2 to 10^4 psi theoretical values for contacts of different waviness fall quite closely within a narrow band with surfaces of lesser waviness exhibiting higher conductance. For pressures greater than 1.5×10^4 psi, such trend is reversed in that contacts for wavier surfaces take on higher conductance values. The difference, however, is still quite small. At 1.8×10^4 psi contact conductance for specimen of waviness 600μ in is about 25% higher than that for specimen of waviness 150μ in. The fact that thermal contact conductance is weakly dependent on the surface waviness is found to be quite a typical result seen from the computer predictions for contacts of many roughness and waviness combinations. Accordingly, an exhaustive presentation of data is not included here.

⁹Such contraction and/or expansion have been used to explain qualitatively the phenomenon that contact conductance depends on the direction of heat flow for different materials in contact [12 , 13].

A presentation of the effect of surface roughness on thermal contact conductance is given in Figure 10. Theoretically calculated values for stainless steel 303, surface waviness $150\text{ }\mu\text{ in}$ and roughness ranging from 190 to $760\text{ }\mu\text{ in}$ are plotted. As expected, these results show an increasing conductance with decreasing roughness. Furthermore, the strong dependence of conductance on surface roughness is also seen.

As a further remark to conclude this section, the prediction method presented in this work is compared with Hsieh's [8] earlier theoretical work on contacts of nominally flat surfaces. Dashed curves in Figures 5, 6 and 8 represent early theory. In all three figures, the present prediction gives lower conductance values which is not unexpected since waviness on surfaces are taken into consideration in this work. Figure 8 is, however, worth noting since, for nominally flat surfaces in contact, there is still a deviation in the results of two prediction methods. The present prediction shows better agreement with experiment in the pressure range $10^3 - 10^4$ psi.

7. CONCLUSIONS

An analytical study is presented of thermal contact conductance for wavy rough surfaces in contact. A comparison between the experimental data from the literature and the calculated results show that the capability of the theory in predicting contact conductance is not limited to wavy surfaces but is also good for wavy/flat or flat/flat surfaces in contact within the pressure range from 10^3 to 10^4 psi. For pressures below 10^3 psi, the theory gives low conductance values, which may be attributed to the oversimplification of the model used in the analysis. The effect of waviness and roughness on thermal contact conductance is also studied. It is found that thermal contact conductance is more strongly dependent on surface roughness than waviness. A check with more extensive experimental evidence is necessary to qualify the theory for general engineering use.

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Figure 1. Model for Analysis

Figure 2. Original Normal Distribution Density Function and its Modification

Figure 3. Schematic Diagram Showing the Deformation of a Surface Asperity

Figure 4. Comparison Between Experiment and Theory for Contact of Stainless Steel 303 (set 1)

Figure 5. Comparison Between Experiment and Theory for Contact of Stainless Steel 303 (set 2)

Figure 6 Comparison between Experiment and Theory for Contact of Stainless Steel 303 (set 3)

Figure 7 Comparison between experiment and Theory for Contact of Stainless Steel 416 (set 4)

Figure 8. Comparison Between Experiment and Theory for Contact of Stainless Steel 416 (set 5)

Figure 9. Trend of Theoretical Predictions for Varying Waviness Values for Contact of Stainless Steel 303

Figure 10. Trend of Theoretical Predictions for Varying Roughness Values for Contact of Stainless Steel 303

Prediction of the Gas Conductance at the Interface for a Pressure Contact
Between Two Rough and Wavy Surfaces

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Abstract

An analytical study is made to evaluate the effective gap thickness for two nominally wavy rough surfaces in a pressure contact. Waviness is considered to be spherical cap on which roughness are distributed isotropically and homogeneously. The heights of the surface asperities are in normal distribution. Probability theory is used in the analysis.

The effect of roughness and waviness on the effective gap thickness is also investigated. A good correlation is found by using dimensionless plot of effective gap thickness versus loading pressure. This theoretical analysis is valued in predicting the contribution of the gas conductance at the interface.

BOUNDARY LAYER STUDIES FOR THERMAL CONDUCTIVITY DETERMINATION

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ABSTRACT - Studies of temperature gradients in boundary layers as well as heat transfer through boundary layers are used at elevated temperatures $1000\text{ K} < T < 8000\text{ K}$ for transport property determinations. The attractive features of boundary layer flows, due to the simple equations of motion which describe a fluid in a boundary layer, are discussed. In addition, techniques are discussed to handle complications due to accommodation, relaxation, and diffusion. A differential interferometer is used to measure density gradients in the outer part of the boundary layer. The measurement of the density gradients together with a linearized energy equation valid in the outer edge of the boundary layer allows thermal conductivity values to be deduced. Thermal conductivity of nitrogen, air, and an argon-helium mixture at temperatures between 2000 to 5500 K are reported, and a comparison with independent theory and experiment is indicated.

Heat transfer studies were also discussed as a means of obtaining transport properties in high temperature gases. The type of information obtained and an error analysis are presented for the first time. The complementary nature of the heat transfer and interferometric methods of obtaining transport properties are indicated.

I. INTRODUCTION

The experimental determination of thermal conductivity of gases at temperatures beyond conventional techniques, $T < 2000\text{ K}$, has been under investigation at Panametrics for several years. We have made measurements with ultrasonic techniques in several simple gases and gas sources. Measurements using other techniques have been made in constricted areas in several other laboratories. However, both of these techniques (sound absorption (1), arc characteristics (2)) require supplemental information to reduce the measured quantities to thermal conductivity. In addition, arc techniques are limited to temperatures above the ionization temperature and the ultrasonic techniques are limited to temperatures where uniform hot gas flow conditions may be obtained.

Stagnation point (3), shock tube side wall (4), and shock tube end wall (5) boundary layers have been examined as potential high temperature gas sources for the determination of thermal conductivity. Optical measurements of temperature (6) or density (7, 8) gradients in the outer regions (free stream) of the boundary layer have been used to obtain thermal conductivity. The most successful measurements have been made with a Wollaston prism differential interferometer by Smeets (7) in air. The present work describes the technique and some new measurements in air, nitrogen and a helium-argon mixture with the differential interferometer. A linearized energy equation which is valid near the freestream was developed for reducing the measured density gradients to thermal conductivity.

Alternative techniques for the determination of thermal conductivity from the rate of heat transfer through the boundary layer to the end wall of the shock tube have been attempted by several investigators (5, 9, 10, 11). The simplicity of the heat transfer measurement with thin film gauges (or i. r. detectors) is attractive. However, the nonideal variation of density, pressure and temperature behind the reflected shock renders data reduction difficult. This in turn is a function of relaxation (12, 13, 14) and diffusive effects at the end wall and nonideal shock tube flow upstream (15, 16). Also, the heat transfer to the wall is a functional of the thermal conductivity as opposed to the usual single temperature measurement. Because of the complex relationship between the temperature dependence of the thermal conductivity and the heat transfer measurement no one has presented an error analysis for the heat transfer technique. The way errors enter into the information obtained about thermal conductivity determined from end wall heat transfer data is the subject of the second part of this paper.

II. THEORY OF END WALL BOUNDARY LAYERS

1. Nature of End Wall Boundary Layer

For an equilibrium or frozen end wall boundary layers the boundary layer equations follow from the Navier-Stokes equations under the assumptions that the flow is one dimensional, and viscous terms are negligible. While early work on the end wall neglected the convection of enthalpy due to the volume contraction of boundary layer gas as it cools, Thomson (17) pointed out the importance of convective heat transfer. Additional problems arise due to pressure and density variations caused by relaxation of internal modes (vibration, dissociation, etc.), and variations in the free stream conditions behind the reflected shock. Under the assumption that any perturbation of the boundary layer flow will decay leaving a boundary layer with its apparent starting time displaced, the simple constant pressure boundary layer theory may be used as the basis for heat transfer and interferometric data reduction. The governing equations are the mass equation

$$\frac{\partial \rho}{\partial t} + \frac{\partial (\rho v)}{\partial y} = 0 \quad (1)$$

and conservation of energy

$$\rho \frac{dh}{dt} - \frac{\partial p}{\partial t} = \frac{\partial}{\partial y} \left[k_t \frac{\partial T}{\partial y} \right] \quad (2)$$

where

$$k_t = k + k_r$$

and h is the enthalpy, k is the frozen thermal conductivity, and k_r is the reaction conductivity. The density is ρ , the pressure p , the velocity v , time t , and distance from the wall y .

There are terms in the energy equation which are due to thermal diffusion in mixtures. Thermal diffusive effects are neglected because little heat is transported this way. However, thermal diffusion does cause unmixing in the boundary layer particularly near the wall where $\partial T / \partial y$ is large. Therefore in binary mixtures, for instance, assume that enough time has passed for the rate of unmixing due to thermal diffusion to approach zero so that

$$\frac{\partial x}{\partial y} = \frac{x_1 x_2 a_T}{D_{12} T} \frac{\partial T}{\partial y} \quad (3)$$

where x_1 and x_2 are the mole fractions, a_T is the thermal diffusion ratio, and D_{12} the binary diffusion coefficient. The effect of thermal diffusion on Eq. (2) then is that the thermal conductivity must be evaluated at a variable mole fraction as a function of distance from the end wall determined by integrating Eq. (3). Because the effect of unmixing on the temperature gradient is not large, the temperature gradient with no unmixing may be used to integrate Eq. (3).

Under the above assumptions the simple equations of mass and energy conservation may be integrated to describe the end wall boundary layer in mixtures and relaxing gases. The pair of partial differential equations, reference (18), may be reduced to a single ordinary differential by replacing the distance from the end wall equation with the usual similarity variable

$$\eta = \frac{1}{\sqrt{2t}} \int \rho \, dy \quad (4)$$

giving

$$\frac{\partial}{\partial \eta} \left(\frac{\rho \lambda}{C_p} \frac{\partial h}{\partial \eta} \right) + \eta \frac{\partial h}{\partial \eta} = 0. \quad (5)$$

Physically this implies that the boundary layer thickens as $\sqrt{2t}$. However, it should be borne in mind the effective zero time will change abruptly during a relaxation.

2. Linearization Valid Near the End Wall

Near the free stream a linearized solution to Eq. (5) is most useful. Dividing each term by $\frac{\rho \lambda}{C_p} \frac{\partial h}{\partial \eta}$ and integrating between the wall $\eta = 0$, and some point at the outer edge of the boundary layer η_1 we get

$$\ln \left[\left(\frac{\rho \lambda}{C_p} \right)_w \left(\frac{\partial h}{\partial \eta} \right)_w \right] = \ln \left[\left(\frac{\rho \lambda}{C_p} \right)_1 \left(\frac{\partial h}{\partial \eta} \right)_1 \right] + \int_0^{\eta_1} \frac{C_p}{\rho \lambda} \eta \, d\eta. \quad (6)$$

Since $\frac{\partial \eta}{\partial \eta} \rightarrow 0$ as $\eta \rightarrow \infty$, the first term on the right is a large negative constant if we chose η_1 to be a point near the free stream. The second term on the right is positive and depends on all of the values of $\frac{\rho \lambda}{C_p}$ for all the temperatures in the boundary layer. $\left(\frac{\partial h}{\partial \eta} \right)$ varies almost linearly with η until the edge of the boundary layer is reached. At this point the $\frac{\partial h}{\partial \eta}$ goes to zero as e^{-x^2} . Once $\frac{\partial h}{\partial \eta}$ becomes very small the integral on the right hand of Eq. (6) does not add significant information about $\frac{\rho \lambda}{C_p}$. Therefore, the enthalpy gradient at the wall contains significant information concerning the thermal conductivity for temperature somewhat less than the free stream temperature.

Equation (6) may be used to obtain a formula for the thermal conductivity in the outer edge of the boundary layer in terms of the density gradients. This formula is useful for obtaining thermal conductivity from optical measurements on the end wall of the shock tube. A second equation such as (6) may be obtained by integrating to a second point near the outer edge of the boundary layer. Subtracting these equations, one obtains

$$\ln \left(\frac{\rho \lambda}{C_p} \right)_1 \left(\frac{\partial h}{\partial \eta} \right)_1 - \ln \left(\frac{\rho \lambda}{C_p} \right) \left(\frac{\partial h}{\partial \eta} \right) = \int_{\eta_1}^{\eta} \frac{C_p}{\rho \lambda} \eta \, d\eta. \quad (7)$$

Sufficiently near the outer edge of the boundary layer the density, specific heat and thermal conductivity are essentially the free stream values. In addition, if density is known as a function of enthalpy (the pressure in the boundary layer is constant) $h = h(\rho)$ then

$$\frac{\partial h}{\partial \eta} = \frac{\sqrt{2t}}{\rho_e} \frac{\partial h}{\partial y} = \frac{\sqrt{2t}}{\rho} \left(\frac{\partial h}{\partial \rho} \right)_p \frac{\partial \rho}{\partial y}. \quad (8)$$

The new thermodynamic variable $\left(\frac{\partial h}{\partial \rho} \right)_p$ may also be evaluated at the free stream density. Under these conditions the integral on the right hand side of Eq. (6) becomes

$$\frac{1}{2} - \frac{C_{pe}}{\rho \lambda} \left(\eta_2^2 - \eta_1^2 \right) \quad (9)$$

and η_2 may be expressed

$$\eta_2 = \eta_1 + \frac{\rho_e}{\sqrt{2t}} (y_2 - y_1) . \quad (10)$$

Finally, Eq. (7) becomes

$$- \ln \left(\frac{\partial \rho}{\partial y} \right) = A(y_2 - y_1)^2 + B(y_2 - y_1) + C \quad (11)$$

where

$$A = \frac{1}{2} - \frac{C_{pe}}{\lambda_e} \frac{\rho_e}{\sqrt{2t}} \quad (12)$$

and B and C are constants which follow by substitution of (9) and (10) in (7). Thus, fitting the logarithm of the measured density gradient (from a schlieren photograph) to a quadratic function of distance such as (11), the thermal conductivity may be obtained from

$$\lambda_e = \frac{1}{2} - \frac{\rho_e}{\sqrt{2t}} \frac{C_{pe}}{A} . \quad (13)$$

3. Series Expansion for Wall Conditions

A different approach to Eq. (6) leads to a formula which may be used to calculate thermal conductivity from heat transfer measurements. Variables normalized by the values at the wall will be used for numerical convenience. The normalized similarity variable, enthalpy and thermal conductivity ratio are respectively

$$\xi \left(\frac{C_{pw}}{\rho_w \lambda_w} \right)^{1/2} \eta , \quad g = \frac{h}{hw} , \quad r = \frac{\frac{C_p}{\rho \lambda}}{\frac{C_{pw}}{\rho_w \lambda_w}} \quad (14)$$

In addition, we introduce the heat flux potential

$$\phi = \int_1^g \frac{dg}{r} \quad (15)$$

The heat flux potential derivative at the wall may be calculated from the measured heat flux to the wall. In addition, the heat flux derivative at the wall may be expressed as a functional of the thermal conductivity ratio by integrating the energy equation.

$$\phi'_w = \int_1^{g_e} \xi dg . \quad (16)$$

The similarity variable ξ may be expanded in a power series in $\frac{\phi}{\phi'_w}$ by calculating the derivatives of ξ with respect to ϕ from the energy equation. The resulting series to the fifth order shown in Table I will serve as the basis for an error analysis of the end wall heat transfer experiments.

4. Error Analysis for an Argon Like Gas

Table I shows the dependence of ξ on the thermal conductivity through ϕ . This in turn is related to the measured quantity heat flux through Eq. (16). Using the linearization valid near the free stream we can show that if the series is used to integrate Eq. (16) out to some value of enthalpy g_1 the remainder is

$$\int_{g_1}^{g_e} \xi dg = \frac{1}{2} \phi'_w g_1. \quad (17)$$

For the case illustrated in Table I, the series gives the integral (Eq. 16) to about 5% at $g_1 = 17.1$. The remainder evaluated using Eq. (17) amounts to 2.82 which is 23% of ϕ'_w . The thermal conductivity ratio varies only 4% over this range. This is an indication of the fact that the heat flux is not sensitive to thermal conductivity in the outer 15% of the boundary layer.

Suppose the thermal conductivity is known up to 2000 K by other techniques and we wish to extend the range of measurement to 5000 K by the heat transfer technique. Numerical integration of $\eta \Delta g$ from Table I shows that for the measurement at 6000 K 12% of ϕ'_w comes from $T < 2000$ K. Since the outer part of the boundary layer contributes 23% to the magnitude of ϕ'_w with no increase in information, the significance of any information about thermal conductivity in the range $2000 < T < 5000$ K is reduced by a factor of 2/3. As measurements are made closer to 2000 K ϕ'_w is dominated by the temperature dependence of r below 2000 K.

The remaining errors may be evaluated by assuming, for simplicity, that Eq. (16) be written

$$\frac{C_{pw}}{\rho_w \lambda_w} \phi'^2_w = \alpha \int_1^{g_e} \int_1^g \frac{C_p}{\rho \lambda} dg \quad (18)$$

where g_e is the free stream temperature and α is a numerical factor determined by comparing (18) to exact numerical integrations for several reasonable $\lambda(T)$. Equation (18) is equivalent to assuming that only first term in the series in Table I is necessary and that $\frac{\phi}{\phi'_w}$ is corrected by α to cause minimum deviation for ξ . The $\frac{\phi}{\phi'_w}$ falls 25% below ξ on the average in Table I. This gives us $\alpha = 1.25$, which is essentially the same result obtained by Jepson(20) and Kemp(21) by numerical integration of many special cases.

The fact that ϕ'_w is the quantity which enters our analysis together with the factor of 3/2 mentioned above means that the uncertainty in ϕ'^2_w is multiplied by a factor of six before any data processing to obtain ϕ from ϕ'_w begins. (This is true even if more terms in the series of Table I are kept in an actual data reduction). Putting a functional form for λ

Table I. Series Expansion for ξ and Evaluation for Argon ($r = g^{-0.27}$)

$$T_e = 6000 \text{ K} \quad \phi'_w = 12.1 \quad \phi(g_e) = 12.4$$

g	$\frac{1}{\phi'_w} \left(\frac{d\phi}{d\xi} \right)$	ξ	$= \frac{\phi}{\phi'_w} + \frac{1}{3!} r_w \left(\frac{\phi}{\phi'_w} \right)^3 + \frac{2}{4!} \left(\frac{dr}{d\phi} \right)_w \phi'_w \left(\frac{\phi}{\phi'_w} \right)^4 + \frac{1}{5!} \left[3 \left(\frac{d^2 r}{d\phi^2} \right)_w \phi'^2_w + 7 r_w^2 \phi'_w \right] \left(\frac{\phi}{\phi'_w} \right)^5$			
2.37	0.994	0.1007	0.1	0.0007	10^{-5}	10^{-6}
4.00	0.9702	0.2057	0.2	0.0053	0.0004	10^{-5}
7.82	0.847	0.4523	0.4	0.0427	0.0070	0.0026
12.2	0.655*	0.7988	0.6	0.1440	0.0352	0.0196
17.1	0.446*	1.335	0.8	0.3414	0.1115	0.0824
19.4	0.260*	2.191>	1.0	0.6667	0.2722	0.2518

* Higher terms than $\left(\frac{\phi}{\phi'_w} \right)^5$ important.

$$\frac{C_p}{\rho \lambda} = \frac{\rho_w C_{pw}}{\lambda_w} g^{-s} \quad (19)$$

into Eq. (18) we get a polynomial in g^{-s} . Fitting the experimental quantity

$\frac{C_{pw}}{\rho_w \lambda_w} \phi_w'^2$ to such a polynomial allows a value for s to be deduced which best fits the data. Assuming heat transfer data with a standard deviation of $\sigma = 2\%$, the resulting standard deviation after considering the multiplication factor of 6 discussed above is 12%. The resulting uncertainty in $\frac{C_p}{\rho \lambda}$ at 5000 K is 22%.

The above analysis assumes that the free stream conditions are perfectly defined. In fact, incident boundary layer interaction with the reflected shock makes the density temperature and pressure change with time. This may be avoided by taking the heat transfer measurements as soon as possible after the reflection of the shock wave. The present understanding of nonideal shock tube flow is not good enough to specify free stream conditions to 1%, more than ~ 20 microseconds after shock reflection, except possibly in monatomic gases. For this reason measurement of thermal conductivity by the heat transfer technique of equilibrium boundary layers in dissociating or ionizing gases is generally not useful.

Even at short times after the reflection of the shock wave relaxation effects can introduce errors in thermal conductivities deduced from heat transfer measurements. The shock reflects initially as a frozen reflected shock traveling into a frozen incident shock (5). The boundary layer in the frozen region is very steep and the free stream temperature very high. As the gas begins to relax the heat flux to the end wall is very complex. Observing the early time dependence ($\sim 1 \mu\text{sec}$) of the heat transfer rate (14) gives an indication of when relaxation effects take place. Heat transfer measurements after relaxation effects have occurred are difficult to interpret. However, frozen heat transfer measurements may yield useful information about thermal conductivities which may be compared directly with molecular beam measurements. Heat transfer measurements with a precision of 0.1% are necessary to make such a comparison useful.

III. EXPERIMENTAL

1. Wollaston Prism Differential Interferometer

A differential interferometer measures the index of refraction gradient. This in turn is directly proportional to the density gradient for many systems of interest. The measurement of thermal conductivity by conventional techniques requires temperature derivatives to be calculated from temperature measurements. Since the differential interferometer measures gradients directly in the gas it has some interesting applications for thermal conductivity measurements. In the end wall boundary layer the temperature gradients in the conservation of energy equation may be eliminated in favor of the density gradient.

The "schlieren" or Wollaston prism differential interferometer is a very useful device in its own right. It is simple and not as sensitive to vibration as the usual interferometer. Wollaston prism differential interferometers have been described by Lamb and Schreiber (22) for arc applications and by Oertel (23) for shock tunnel applications. The primary interest in this instrument is based on Smeets (7) thermal conductivity determinations using the end wall boundary layer.

A schematic of the basic apparatus is shown in Fig. 1. The light from any point in the FX12 mercury light source is polarized so the electric vector is 45° to the optical axis of the Wollaston prism. The prism is constructed of two optically active quartz wedges (22) cemented together with crossed optical axis. The Wollaston prism breaks the polarized light into two rays of equal intensity diverging at an angle ϵ . The lens L_1 is focused through the Wollaston prism and the polarizer into the center of the light source. Therefore the diverging rays from the prism are converted into parallel rays by L_1 . In addition, the rays are separated by a distance d . A similar system recombines the two rays on the film plane of the camera. The lens L_2 is focused on an imaginary object in the center of the test region.

When the test region is uniform a fringe pattern develops due to phase shifts within the two Wollaston prisms. The location of the fringes (or equivalently the phase shifts in the system) depends on the wavelength of the light. Thus red fringes do not form at the same place on the photographic plane as the yellow or blue fringes. Visually the interference pattern from white light separates the colors. On a photograph the effect is to show fuzzy fringes since the camera does not discriminate among the colors. Very good fringes are obtained using a $100\text{\AA}$ wide filter centered on the $4671\text{\AA}$ xenon line.

2. Theory of Thermal Conductivity Measurements in the End Wall Boundary Layer

The detailed theory of the Wollaston prism differential interferometer is given in References 22 and 23. The basic theory for the thermal conductivity measurement in the end wall boundary layer may be understood by considering the two rays created by the Wollaston prism as they pass through the shock tube. The ray traveling through the cooler gas travels at a slightly slower speed because the density of the gas increases as it cools. The two rays

therefore develop a phase difference in the test gas given by

$$\frac{\Delta\phi}{2\pi} = \frac{\ell}{\lambda} (n_{+d} - n_{-d}) \quad (20)$$

where ℓ is the length of the test section, λ the wavelength of the light, n_{+d} and n_{-d} are the indexes of refraction a distance $y \pm \frac{d}{2}$ from the end wall. The theory of the optics gives the fringe shift Δs in terms of the phase shift and the undisturbed fringe separation s by the relation

$$\Delta s = \frac{\Delta}{2\pi} s = s \frac{\ell}{\lambda} (n_{+d} - n_{-d}) \quad (21)$$

or finally multiplying and dividing by the ray separation, d , we obtain a relation between the density (or index of refraction) gradient and the fringe shift

$$\frac{d\rho}{dy} = \frac{1}{a} \frac{dn}{dy} = \frac{1}{a} \frac{\Delta s}{s} \frac{\lambda}{\ell} \frac{1}{d} \quad (22)$$

where a is the Gladstone-Dale constant for the gas in question, ρ the density of the gas and y the distance from the end wall.

Equation (22) relates the measured fringe shift Δs to the density gradient. The relations needed to obtain thermal conductivity come from the boundary layer equations. The equation valid near the free stream of the boundary layer (equational) leads to such a relation

$$\ln \left(\frac{\frac{\partial \rho}{\partial y}}{\frac{\partial \rho}{\partial y}} \right)_1 = \frac{1}{4t} \frac{C_{pe} \rho_e}{\lambda_e} (y - y_1)^2 + \frac{\eta_1}{\sqrt{2t}} \frac{C_{pe}}{\lambda_e} (y - y_1) + C \quad (23)$$

where the subscript 1 refers to the reference point close to the end wall, C_{pe} is the specific heat, and λ_e the thermal conductivity.

3. Application of Differential Interferometer to the Wall Boundary Layer

The steps involved in applying Eqs. (22) and (23) to the measurement of thermal conductivity are (1) derive the density gradient from the measured fringe shift on the interferogram of the end wall boundary layer; (2) fit the density gradient to the quadratic function of distance from the reference point $(y_1 - y)^2$. The thermal conductivity is given by the coefficient of the quadratic term in Eq. (23). Additionally, the similarity parameter η_1 may be estimated to within a few percent and the linear term in (23) may then be used to determine thermal conductivity.

There are several important points about Eq. (23) which minimize experimental errors in the thermal conductivity measurements. First, since the ratio of the density gradients at two points is the important property in Eq. (23), the proportionality factors in Eq. (22) do not need to be known, that is,

$$\frac{\left(\frac{d\rho}{dy}\right)_1}{\left(\frac{d\rho}{dy}\right)} = \frac{\Delta s_1}{\Delta s} \quad (24)$$

In addition, the magnification in the direction parallel to the end wall drops out. The location of the end wall is also not necessary because only the differences in distance from the wall occur in the final expression for thermal conductivity (Eq. 23). The magnification in this direction is important and is easily determined by inserting an accurately known cylinder in the test section and photographing it. Finally, the accuracy of the linearization which leads to Eq. (23) is automatically determined by the size of the constant (C) which approaches zero as the deviation from free stream conditions decreases over the portion of the boundary layer in the schlieren field.

Some measurements of the fringe displacement on a typical end wall schlieren interferogram are shown in Fig. 2. The position of the end wall is indicated by the vertical arrow. The data are measured points on the fringe. Taking the factor of two magnification on the photograph into account the fringes are discernable to within 0.1 mm of the end wall. The separation of ordinary and extraordinary rays in the test section (the rays which interfere to give the fringes) is about 0.047 mm, much smaller than the boundary layer. The total boundary layer is 3 mm thick. The fringes are straight lines with ~20% slope in the uniform part of the reflected shock region. Closer to the end wall in the boundary layer the fringes bend upward. The total temperature change in the part of the boundary layer affecting the fringes is about 3000 K. This means that half of the temperature drop is in the outer 3 mm of boundary layer and half of the drop is in the remaining 0.1 mm. The temperature gradient near the end wall is very steep, while the outer regions show small temperature gradients. This is the basis of the linearization of the energy equation to give the useful relation Eq. (23).

4. Thermal Conductivity Measurements with Schlieren Interferometer

The thermal conductivity of nitrogen, 0.25 argon-0.75 helium mixture, and air, was measured at temperatures up to 5000 K and pressures up to 6 atm using the schlieren interferometer on the end wall of the shock tube. The free stream temperature and pressure of the test gas behind the reflected shock were determined from incident shock speed measurements(5). The transit time determined from heat transfer gauges 106.05 cm and 14.61 cm from the end wall was used to determine the wave speed. In addition, an end wall heat transfer gauge was used.

A heat transfer trace is shown in Fig. 3 along with a schlieren interferometer photograph of the end wall boundary layer. The upper heat transfer trace is the side wall gauge response, the lower trace is the end wall gauge response. The break in the end wall gauge response indicates the end of the uniform conditions in the gas close to the end wall. A burst of rf from the flash tube interrupting uniform end wall trace indicates when the schlieren photograph was taken. The time between the arrival of the shock wave at the

end wall (the step in the end wall trace) and the time of the schlieren photograph is given by the position of this rf pickup. This is the time which should be used in Eq. (23).

Some measurements of fringe displacements versus distance from the end wall for a measurement in air are shown in Fig. 2. The ratio of $\frac{\Delta s}{s}$ is averaged over a number of fringes. The resulting $\frac{\Delta s}{s}$ data are fit to a quadratic function of distance as described above in the discussion of Eq. (23). The resulting thermal conductivity values are tabulated in Table II. The measurements in nitrogen and air are compared to theoretical calculations of Yos (24) which have an estimated uncertainty of 20%. The present schlieren interferometric thermal conductivities are close at intermediate temperatures (2% at 4373 N₂, 16% at 2550 air), lower at the highest temperatures involved. Also shown are some independent experimental measurements by the differential interferometer technique (25). Except for the highest temperature, Smeets' results are lower than the present results. The maximum discrepancies of about 30% at the lower temperatures are difficult to explain. Discrepancies around the dissociation temperatures (~5200 K N₂, 2200 K O₂) may be due to difficulties in extrapolating the results of Yos and Smeets to the pressures of the author's data points. Discrepancies of up to 50% between theory and various controlled experiments are typical of the state-of-the-art.

IV. SUMMARY

The mathematical nature of the boundary layer was investigated in detail to assess the suitability of end wall boundary layers for thermal conductivity determinations. Simple solutions to the end wall boundary layer are presented which are valid for times soon after the shock reflection (frozen conditions) and for times hundreds of μ sec after the reflection (equilibrium conditions). A solution valid near the end wall is used to show how uncertainties in thermal conductivity determined from heat transfer measurements accumulate. In particular, for an argon like gas, the heat transfer data must have errors of about 0.1% to provide information with uncertainties of the order of 1%. The error analysis presented should be repeated for each gas studied. In addition, the importance of making heat transfer measurement early in time to avoid time dependence effects in the free stream is stressed. Finally, the importance of thermal diffusion on the thermal conductivity measurement by the heat transfer method is pointed out.

A second solution valid near the free stream was also developed. The free stream solution was applied to some data taken with a differential interferometer to extract thermal conductivities. The resulting thermal conductivity measurements compared well (2-30%) with independent experimental and theoretical work. The schlieren interferometric technique applied to the end wall boundary layer is the promising technique for accurate determination of thermal conductivity at temperatures between 2000 K and 8000 K.

Table II. Thermal Conductivity of Gases Measured by the Schlieren Technique mw/cm °K				
Temperature °K	Pressure atm	<u>Theoretical</u>	<u>Experimental</u>	
		Yos, 1967 <u>(Ref. 24)</u>	Smeets, 1965 <u>(Ref. 25)</u>	<u>Present Work</u>
<u>Nitrogen</u>				
2620	2.29	1.46		2.10
4373	4.86	3.13		3.20
4707	5.44	3.97		3.41
5141	6.34	6.12		4.10
<u>Air</u>				
2246	1.87	1.54	1.25	1.87
2258	2.04			2.26
2398	2.08			2.15
2550	1.15	1.93	1.50	2.30
2572	0.29			2.25
2999	0.30	4.01	2.50	3.00
3157	0.57			2.88
4539	5.53	4.74	4.90	3.10
<u>0.75 He-0.25 Ar</u>				
		<u>Amdur and Mason (Ref. 19)</u>	<u>Present Work</u>	<u>Deviation</u>
5571	1.24	4.88	5.43	10%

V. ACKNOWLEDGMENT

This work was sponsored under the direction of Arnold Engineering Development Center, Air Force Systems Command, with Captain Terry L. Hershey, Project Manager. The author would like to acknowledge David Winslow for performing the measurements, and Dr. Theodore Marshall (now at Suffolk University) for bringing the schlieren technique to our attention and directing the optical portions of the experiment.

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Fig. 1. Schlieren Interferometer

Fig. 2. Fringe Field of End Wall Boundary Layer

Fringe Field (x 2)

Heat Transfer Trace
200 μ sec/cm

Fig. 3. End wall boundary layer fringes and heat transfer gauge response

A PULSED THERMAL COMPARATOR FOR THE MEASUREMENT OF THERMAL CONDUCTIVITY

by

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Abstract

A small electrically pulsed thermal comparator probe which has been constructed at McDonnell Aircraft Company shows promise as a useful tool for making rapid thermal conductivity measurements of solids and liquids.

In use, a single current pulse is passed across the center of a small bar of single crystal germanium. The heat generated by this pulse travels toward the ends of the bar, which are connected electrically to an oscilloscope. If one of the ends of the bar is placed in contact with a second material, heat will be conducted away at a rate which is dependent upon the thermal conductivity of the specimen and there will be a difference in temperature between the two ends. The resultant temperature differential produces a voltage which is related to the thermal conductivity of the test material.

Experimental data at ambient temperatures give output voltages ranging from 2 millivolts for pyrex glass, which has a thermal conductivity of 1.1 W/m/K , to 14 millivolts for copper with a thermal conductivity of 400 W/m/K .

Key Words

comparator	pulsed thermal comparator
conductivity	surface finish
differential temperature	surface roughness
differential thermal comparator	thermal comparator
germanium	thermal conductivity
germanium thermocouple	thermal probe
probe	thermal pulse

Introduction

Most of the thermal comparators currently used utilize an isolated mass heated to $10\text{--}30^\circ\text{C}$ above the temperature of the test sample, and so instrumented that the temperature change of the mass, as it comes in contact with the specimen, gives an output which can be related to the thermal conductivity of the test sample. The output of most thermal comparators has been provided by a single thermocouple, thus the output has been less than one millivolt. Although good data has been obtained using these thermal comparators^{1,2,3} they are very sensitive to sample surface roughness and to probe loading.^{1,4}

This paper presents information on a small electrically pulsed thermal comparator utilizing germanium, which has a relatively large output voltage. Measurement errors caused by surface roughness and probe loading have been minimized by using water as a coupling agent between the probe and the test sample. This information shows the possibilities of such a device and some of its inherent limitations. Future development will undoubtedly improve both the sensitivity and accuracy of the device.

Principle of Operation

This thermal comparator consists of a small bar of thermoelectric material to which small leads have been attached (Figure 1). In operation, a single short pulse of electrical energy is applied between the leads B and B'. The heat generated in the bar by this current pulse travels toward the ends of the bar and causes the ends to change temperature with time. If the leads B and B' are located midway between the ends then both ends of the bar will have the same temperature history.

FIGURE 1 – THERMAL COMPARATOR PROBE
Basic Sensing Element Lead Attachment

The ends of the bar are connected as a differential thermocouple and the output voltage is taken from the two ends (Fig. 1, Leads A and A'). When one end of the bar is in thermal contact with a test sample, the two ends will be at different temperatures at a given instant, and the output voltage will change approximately as the temperature difference between the two ends. Thus the output signal for a sample of material with high thermal conductivity, such as copper, would be considerably larger than that resulting from contact with a sample having a low thermal conductivity.

A basic block diagram for a pulsed thermal comparator is shown in Figure 2.

FIGURE 2 – BASIC BLOCK DIAGRAM OF
PULSED THERMAL COMPARATOR

Thermal Comparator Probe Construction

A prototype thermal comparator probe based upon these principles was constructed. The thermoelectric material was a small bar of gallium-doped single-crystal germanium approximately .05 x .08 x .35 cm and having a resistivity of approximately $44 \Omega\text{-cm}$. Germanium was selected, in preference to metals, principally because of its high Seebeck coefficient of approximately one millivolt/ $^{\circ}\text{C}$.⁵ Gold wires, .0076 cm in diameter, were eutectically bonded to the germanium, thus providing good thermal and electrical contact to the germanium. The germanium bar with leads attached was potted in epoxy and the ends of the germanium and the flat faces of the epoxy were sanded flush. The exposed germanium ends were then electroplated with copper to protect the brittle germanium and to provide a durable high conductivity contact surface which extended slightly beyond the surface of the epoxy. The small copper contact surfaces were then lightly sanded with a fine grit emery paper. This sanding tended to round the contact surface so that it appeared spherical rather than planar. The prototype thermal comparator probe is shown in Figures 3 and 4

FIGURE 3 – THERMAL COMPARATOR PROBE

FIGURE 4 - THERMAL COMPARATOR PROBE
Principal Parts

Probe Evaluation

The instrumentation arrangement shown in Figure 5 was used for evaluation of the thermal comparator probe. The pulse generator was a HP Model 214A, and the driving pulse input to the center of the germanium bar is shown in Figure 6.

The output of the thermal comparator probe was placed in series with a millivolt potentiometer (L & N Model 8686) which acted as a bucking voltage and provided greater accuracy in measuring the peak voltages. The signal was then fed to an isolating amplifier (Astrodata TDA 875) so that the common ground of the pulse generator and oscilloscope (Techtronix 502) would not short out the output signal. Typical output signals on three randomly selected aluminum samples are shown in Figure 7. This is a multiple exposure with the sweep displaced horizontally before each exposure. The zero reference line is also shown. Only the peak amplitude of these waveforms is measured. Although the time of occurrence may yield further information concerning other thermophysical properties of the sample material, it has not been measured.

FIGURE 5 - THERMAL COMPARATOR INSTRUMENTATION

FIGURE 6 – DRIVING PULSE
10 Volts/cm Vertical
1 Millisecond/cm Horizontal

FIGURE 7 – TYPICAL OUTPUT SIGNALS
(3 Different Aluminum Samples)
Approximately 2 Millivolts/cm Vertical
50 Milliseconds/cm Horizontal

To determine the effects of surface roughness on the probe output, the following procedure was used: The probe with a 12- gram weight attached was placed on a 301 (1/4 hard) Stainless Steel test sample using a drop of water as the coupling agent. The test sample had been polished but the surface was not mirror smooth. The probe was then pulsed and the output was noted. The probe was moved to three other locations on the test sample and data were taken in a like manner. The surface of the 301 Stainless Steel test sample was then dry sanded using #600 grit emery paper. Data was then obtained at 4 different locations on the sanded surface again using water as the coupling agent. This procedure was then repeated several times using emery papers of increasing coarsenesses. A similar procedure was then followed without the use of water as the coupling agent. Data for both dry and wet coupling are shown in Figure 8. For all of the sanding with emery paper, except for the polished starting and finishing surfaces, the sample was not passed over any area of the emery paper more than once, in order to maintain surface finish uniformity from sample to sample.

FIGURE 8 – OUTPUT vs SURFACE ROUGHNESS – 12 GRAM LOADING
Sample 301 Stainless Steel (1/4 Hard)

To determine the effects of probe loading, the following procedure was used: The probe was placed on a smooth sample of 301 (1/4 hard) Stainless Steel, without a water coupling agent, a 12-gram weight was placed on top of the probe, the probe was pulsed at approximately 1-minute intervals and the output was recorded. Additional weights were then added and the pulsing was repeated. Care was taken not to move the probe from its original contact point. This entire procedure was then repeated with a drop of water serving as a coupling agent between the probe and the stainless steel test sample. Data are shown in Figure 9.

Fringe Field (x 2)

Heat Transfer Trace
200 μ sec/cm

Fig. 3. End wall boundary layer fringes and heat transfer gauge response

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To determine the effects of surface roughness on the probe output, the following procedure was used: The probe with a 12- gram weight attached was placed on a 301 (1/4 hard) Stainless Steel test sample using a drop of water as the coupling agent. The test sample had been polished but the surface was not mirror smooth. The probe was then pulsed and the output was noted. The probe was moved to three other locations on the test sample and data were taken in a like manner. The surface of the 301 Stainless Steel test sample was then dry sanded using #600 grit emery paper. Data was then obtained at 4 different locations on the sanded surface again using water as the coupling agent. This procedure was then repeated several times using emery papers of increasing coarsenesses. A similar procedure was then followed without the use of water as the coupling agent. Data for both dry and wet coupling are shown in Figure 8. For all of the sanding with emery paper, except for the polished starting and finishing surfaces, the sample was not passed over any area of the emery paper more than once, in order to maintain surface finish uniformity from sample to sample.

FIGURE 8 – OUTPUT vs SURFACE ROUGHNESS – 12 GRAM LOADING
Sample 301 Stainless Steel (1/4 Hard)

To determine the effects of probe loading, the following procedure was used: The probe was placed on a smooth sample of 301 (1/4 hard) Stainless Steel, without a water coupling agent, a 12-gram weight was placed on top of the probe, the probe was pulsed at approximately 1-minute intervals and the output was recorded. Additional weights were then added and the pulsing was repeated. Care was taken not to move the probe from its original contact point. This entire procedure was then repeated with a drop of water serving as a coupling agent between the probe and the stainless steel test sample. Data are shown in Figure 9.

FIGURE 9 – OUTPUT vs PROBE LOADING
Sample Material 301 Stainless Steel (1/4 Hard)

Several test samples were selected from materials readily available and the probe response vs thermal conductivity shown in Figure 10 was obtained. The test samples were not standards and the accuracy of the thermal conductivity of these test samples is estimated at about $\pm 20\%$. The value of thermal conductivities were taken from the references listed (Fig. 10).

The procedure for obtaining the output of the probe for each test sample was as follows:

- 1) A drop of water was placed on the sample. The probe with a 12-gram weight attached was placed on the sample, which had a surface roughness of 2μ inches RMS.
- 2) The probe was pulsed and the output was noted.
- 3) One minute was allowed for the probe to attain thermal equilibrium, then it was pulsed again.
- 4) The probe was then moved to a new location on the sample and two more readings were taken.

The reading precision by far exceeded the precision to which the thermal conductivities of the test samples were known. The reading precision was approximately ± 0.1 millivolt, which corresponds to $\pm 0.7\%$ of the peak amplitude for the high thermal conductivity materials such as copper. The repeatability of the probe on a highly polished sample was generally good. The length of the line for each test sample shown in Figure 10 indicates the maximum data scatter observed during these tests.

FIGURE 10 - PROBE RESPONSE IN RELATION TO THERMAL CONDUCTIVITY

Several liquid test samples such as water, alcohol, glycerol, ethylene glycol and carbon tetrachloride were used to check the probe response and some irregularities were noted in these data. These were due to attack of the epoxy and plastic in the probe by the liquids. Tests on liquids were discontinued; however, it was determined that the probe would be suitable for measuring the thermal conductivity of a liquid by placing it in direct contact with the liquid.

During all of the tests performed with the probe, one side of the probe was exposed to ambient air. With this air reference, the peak output occurs approximately 50 to 90 milliseconds after the driving pulse, the shorter times are observed with materials with higher thermal conductivity. If a reference other than air was to be used, the curve shown in Figure 10 would be shifted to the left or right.

Discussion

The principal goal of this program was to develop a quick, simple method of comparing the thermal properties of solid materials rather than to obtain absolute accuracy.

The data presented illustrates that the pulsed thermal comparator method is a relatively simple, straightforward method of measuring thermal conductivity; the probe and associated instrumentation are effectively calibrated at the same time using thermal conductivity standards. This method of calibration effectively eliminates the anomalies which may be inherent in the system and which seriously complicate mathematical analysis. For example, preliminary tests on the probe revealed that the output was somewhat dependent upon the driving pulse polarity and wave shape, possibly due to some slightly non-ohmic contacts to the germanium. The irregular driving pulse (Figure 6) was due to the overload on the pulse generator being activated after the first millisecond of the pulse. However, the pulse shape was repeatable and the resultant data was better with this waveshape than when a good square pulse was used.

Although it would appear that the peak output voltage should be dependent upon thermal diffusivity rather than thermal conductivity, this does not appear to be the case, as was also noted on earlier thermal comparators.^{1,4}

Because the data are taken in a relatively short time period (less than 0.1 sec.), the pulsed thermal comparator should be able to measure the thermal conductivity of very thin materials, although this has not been experimentally verified. Conversely, the probe might be used to determine the thickness of materials or platings on various substrates.

Probes of the type described in this paper should be useful over a wide range of temperatures when calibrated at the temperature of interest.

Conclusion

A small pulsed thermal comparator has been constructed and tested. It can be used to rapidly measure the thermal conductivity of solids and liquids having a range of conductivities from 0.4 to 400 W/m/K. This probe minimizes errors which are normally caused by surface roughness and probe loading.

Acknowledgment

I wish to express my appreciation to Dr. R.P. Bastian and Dr. G.H. Kesler, whose encouragement made this development possible. I also want to thank Mr. R.F. Kohl who so ably constructed the probe reported in this paper.

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Experimental Methods II

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ADVANCES IN DIRECT HEATING METHODS*

by

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Abstract

Recent progress in the evaluation of direct heating methods is presented. Numerical "solutions" of the second order non-linear differential equation describing heat transport in thin rods are discussed. These solutions yield values of the thermal conductivity and Thomson coefficient without restrictive mathematical approximations and include the temperature dependencies of these and other thermophysical properties. Typical data on the thermal conductivity, electrical resistivity, Lorenz function, total hemispherical emittance, spectral emittance (0.65 microns) and Thomson coefficient from about 1400 to 3000 K measured simultaneously or consecutively on the same sample in the multiple-property apparatus are given in order to illustrate the usefulness and practicality of multiple-property determinations. Future plans include extending the number of properties that are measured simultaneously or consecutively and computer evaluation of direct heating methods.

I. Introduction

At the last conference, a project to evaluate direct electrical heating methods was described [1].[†] Direct heating methods encompass all techniques in which the sample temperature is controlled by the passage of electrical current through the specimen. These methods are limited to electrical conductors and a number of variants have been reported in the literature.

These variants have resulted from the fact that the equation governing energy transport in thin current-carrying rods or wires is a second-order non-linear differential equation. It may be expressed as:

$$\lambda T'' + I^2 \rho / A^2 - P \epsilon_H \sigma (T^4 - T_0^4) / A - \mu (I/A) T' = c_p d(T/dt) \quad \text{Eq. (1)}$$

where λ is the thermal conductivity, T is the temperature at any position Z along the sample axis, I is the current, ρ is the electrical resistivity, A is the cross-sectional area, P is the circumference, ϵ_H is the total hemispherical emittance, σ is the Stefan-Boltzmann constant, T_0 is the ambient temperature, μ is the Thomson coefficient, c_p is the specific heat, d is the density, T' and T'' are the first and second

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temperature derivatives with respect to Z and t is time. The position Z may be expressed using an external reference point. Almost all direct heating methods are steady-state ($dT/dt = 0$) and ignore the Thomson effect ($\mu = 0$) and the temperature dependencies of λ , ρ , and ϵ_H . Even then very restrictive mathematical approximations are usually employed in order to linearize the equation. Because of the mathematical approximations, the temperature profiles $[T(Z)]$ must be a certain shape in order for reasonable values of λ to be calculated. The general steady-state method, which includes the Thomson coefficient, incorporates temperature dependent $\rho(T)$ and $\epsilon_H(T)$, and does not include restrictive mathematical assumptions, has been developed. As such, this method essentially supersedes and replaces earlier reported methods having drastically restrictive limitations.

It should be noted that Eq. (1) includes several physical properties (ρ , ϵ_H , λ , μ , c_p and d) and in practice, one cannot determine λ without a knowledge of at least some of these properties. It turns out that the direct heating method is admirably suited, particularly at high temperatures, for determining a number of physical properties simultaneously or consecutively on the same sample in the same apparatus. At present, six properties are being obtained more or less routinely. These properties are the spectral emittance at 0.65 microns, the total hemispherical emittance, electrical resistivity, thermal conductivity, Lorenz function, and Thomson coefficient. In the future it is planned to add other physical properties, such as specific heat, enthalpy, thermal diffusivity, Seebeck coefficient, Peltier coefficient, Richardson coefficient and thermal expansion to the list of properties already measured simultaneously or consecutively on the same sample. It may be practical to incorporate mechanical properties including elastic constants in this list.

II. Data Handling Procedures

The differential equation for the steady-state case involves four thermophysical properties (λ , ρ , ϵ_H , and μ) in addition to first and second temperature derivatives. Let us assume that we know $\rho(T)$ and $\epsilon_H(T)$ and that the term containing μ is negligible compared to the other terms in Eq. (1). Then three conditions are required in order to obtain a value for λ because the conductivity is unknown and a second order differential equation is involved. Procedures for obtaining numerical solutions for λ start at some point (Z_1) on the curve or use some other information at this point (initial conditions) and attempt to go through some other point (Z_2) on the curve (boundary condition). Two initial conditions could be the maximum temperature and $T' = 0$ at the maximum temperature. The numerical solution of the steady-state version of Eq. (1) using these two initial conditions and a boundary condition is designated here as the 2-point method. The development of the procedure to obtain conductivity values using the 2-point method was described at the last conference.

Almost all direct electrical heating methods developed heretofore use the central portion of the sample. These methods suffer from the disadvantage that most of the heat generated near the center of the sample is lost by radiation from the surface and only a small fraction is conducted towards the ends. The conductivity is determined from the difference between the rate of energy per unit volume generated by Joulean heating ($I^2\rho/A^2$) and rate of energy per unit volume lost by radiation ($P\epsilon_H\sigma)(T^4 - T_0^4)/A$. Thus, the errors in computing the conduction term are often greater than the errors associated with determining the heating or the radiation terms. For example, at a distance of one cm from the center of a 11.4 cm tungsten sample used in the present investigation (262 amp profile, Figure 1), the rate of heat conducted was only about 7% of the energy generated. If the total hemispherical emittance value were in error by 1%, this would lead to an error in the conduction term of 12%. At a distance of 2 cm from the center, 20% of the energy is conducted. At this location, a 1% error in emittance leads only to a 5% error in the conduction term.

This example demonstrates the advantage of using data away from the sample center. Methods developed in the past by other investigators could not utilize this

advantage because they did not solve the second order non-linear differential equation without making mathematical assumptions which are valid only near the center of the sample. However, the development of the analytical techniques detailed in a previous report[1] makes it possible to include some temperature data away from the sample center and significantly increases the accuracy and applicability of direct electrical heating methods.

A method which utilizes only data measured away from the sample center would not be subjected to large errors due to uncertainties in emittance values. Since it is possible to obtain conductivity values using Eq. (1) and three conditions, a computer program (the 3-point method) which utilizes one initial and two boundary conditions, i.e. the temperature at any three different positions, was developed. The 3-point method has the advantage that it is not necessary to locate the position of maximum temperature precisely, nor does it require the precise measurement of the center temperature which is required for the 2-point method. Thus, it is now possible to compute conductivity values using only data away from the center, only data near the center, or data from both the central and noncentral regions.

The 2- and 3-point methods can be used to obtain a large number of conductivity values from a small set of data. This is in marked contrast to the other methods which yield only one conductivity value and require very restrictive mathematical approximations. Consider the 262 amp. current "up" temperature profile shown in Figure 1 for a 11.4 cm long tungsten sample. Thermal conductivity values can be computed using the temperature measured at 19.24, 19.74 and 20.24 cm; or, at 19.74, 20.24 and 20.74 cm; or, at 19.74, 20.24 and 21.74 cm; or, at 20.24, 22.24 and 27.24 cm; etc. Thus, 576 separate conductivity values can be computed from this profile. By employing statistical techniques, it is possible to use these values to determine the best fit of conductivity as a function of temperature over the temperature range included in the profile.

The data in Figure 1 also clearly indicate the change in the temperature profile caused by reversing the current flow. It is seen that the temperatures on the left side of the sample are appreciably higher and the temperatures on the right side are appreciably lower when the current flow is in the reversed (down) direction. This is caused by the Thomson effect. Since the temperature gradient is positive on the left side of the sample and negative on the right side, the last term on the left hand side of Eq. (1) will have opposite signs on the two sides of the sample. Also, the quantity I/A comes from the vector $\vec{J}$ and has a positive and negative direction. Thus, reversing the current flow changes the sign of the last term on the left hand side of Eq. (1) and causes larger temperature changes at positions away from the center. For example, at 20.24 cm the temperature decreased from 2214.6 K to 2181.6 K upon current reversal. Both the 2-point and 3-point methods can be readily used with Eq. (1) providing the value of the Thomson coefficient is known.

A typical computer output is shown in Table I. In the upper part of the Table, the first line describes the sample, method of data reduction and nominal current employed. The second and third lines give the coefficients for a polynomial fit to electrical resistivity ρ , (RHO) and total hemispherical emittance ϵ (E). A is the cross-sectional area, T_A is the ambient temperature, I is the current, and PER the circumference. The temperatures $TZ1$, $TZ2$, $TZ3$ at three positions $Z1$, $Z2$ and $Z3$ are the inputs. The Thomson coefficient is represented by μ , (MU). The computed value of thermal conductivity is printed next and the effective temperature of the measurement is at the end of the lower part of the Table. The lower part of the Table reports from left to right, positions, computed temperatures, first temperature derivative with respect to position T' , ($T \neq Z$) and the magnitudes ($W\text{ cm}^{-3}$) of the terms concerned with heat conduction, Joulean heating, radiation and Thomson heating or cooling.

It should be noted that this computer procedure involves starting with an initial condition. In Table I, this condition is 2181.6 K at 20.2400 cm. Using Eq. (1), initial guesses for λ and T' , and the shooting technique discussed in a previous report[1] a temperature at $Z(2)$ is obtained. The value of the computed temperature at $Z(2)$ is

compared to the measured temperature at Z(2). Based upon the difference between computed and measured temperatures, new values of T' are tried. The procedure is repeated until the computed temperature at Z(2) closely matches the measured temperature. Then the procedure is continued over the range from Z(1) to Z(3) adjusting the value of λ until the computed temperatures at both Z(2) and Z(3) closely approach the observed values. In the case illustrated in Table I, the computed values at Z(2) and Z(3) are 2392.84 and 2429.49 K while the measured temperatures are 2392.8 and 2429.5 K, respectively.

Other computer output information of particular interest are the relative magnitudes of the Joulean, radiation, Thomson and conduction terms at various locations. We note that if the Thomson coefficient is $-20 \mu\text{V K}^{-1}$, the Thomson term is about 8% of the conduction term at 2.5 cm from the center, but is negligible at the center. Thus, a reasonable knowledge of the Thomson coefficient is required in order to obtain accurate conductivity values using data obtained away from the sample center and the mathematical techniques discussed so far. Since none of the previous direct heating conductivity methods has considered the Thomson term, the results using these methods may be in error for materials whose Thomson coefficient is greater than a few $\mu\text{V K}^{-1}$, providing DC current was employed in the measurements. DC current is preferred over AC current experimentally because the regulation is much better and phase shift problems do not exist. It should be emphasized that the Thomson effect is not eliminated in DC measurements by averaging the temperature profiles obtained with the current flow in both directions. Such a procedure will cause the computed conductivity value to be high (neglecting other errors). One should average the differential equations and not the temperature distributions, which are related to the differential equations in a complicated fashion.

Both the 2- and 3-point methods as presented so far have two drawbacks:

- (1) a value of the Thomson coefficient is required for accurate conductivity values and
- (2) each conductivity value depends on only two or three specific data points. Although these two methods can be used to obtain a large number of conductivity values from a small set of data, the two drawbacks cause these computed conductivity values to be scattered. Even when a reasonable value of the Thomson coefficient is used and computed values from adjacent data points are ignored, the scatter band may be $\pm 10\%$.

Several procedures for computing the Thomson coefficient from the data and for significantly reducing the scatter band have been worked out by the authors. One procedure involves the assumption that the values of T' obtained by the computer using the shooting method are independent of the Thomson coefficient used in the calculation. The validity of this assumption has been tested. Thus, it is possible to utilize the various computer outputs which use different data points to construct a graph of T' vs Z. The smooth line drawn through these data is derived from all the experimental data instead of being related to only two or three data points. Values of T'' may be obtained from the plot of T' using a straight edge or computer techniques. Once values of T' and T'' are known at a particular temperature for two profiles, it is possible to calculate λ and μ at that temperature using two simultaneous equations.

This procedure markedly reduces the scatter in λ values and simultaneously yields a value for the Thomson coefficient. Furthermore, these calculations are based on results obtained for the same temperature, i.e., the temperature assigned to the λ and μ values is uniquely defined without any averaging procedures.

Another procedure for using all the experimental data in determining the conductivity and Thomson coefficient involves using a spline fit [2] to obtain reasonable agreement with the entire experimental temperature profile. The spline fit is chosen so that the second temperature derivative is continuous. The function is then differentiated and a smoothed spline fit obtained for the first derivative. The procedure is repeated to obtain a smooth fit for the second derivative and the best values of conductivity and Thomson coefficient are obtained using a least squares routine. This approach is relatively rapid and involves no restrictive assumptions. Values of the Thomson coefficient can be ob-

tained using only one profile and the current need not be reversed. The optimum number of knots used in the spline fit can readily be determined and can be varied by one or two knots without significantly altering the results. In addition, the program permits both the thermal conductivity and Thomson coefficient to be either fixed or variable.

III. Typical Results

The results of measurements on tantalum, tungsten, and ATJS (1) graphite are detailed in a report [3]. Results for a tungsten sample are given here for the purpose of illustrating the usefulness of the direct heating technique as presently developed. Data on the spectral emittance, total hemispherical emittance, electrical resistivity, thermal conductivity, Lorenz function and Thomson coefficient over selected temperature ranges obtained on the same tungsten sample in the multiple purpose apparatus are shown. Future plans include adaptations necessary to obtain a number of additional physical properties on the same sample in this apparatus.

The spectral emittance (0.65 microns) from 1500 to 2450 K is shown in Figure 2. The reproducibility is generally within $\pm 1\%$ of the smooth curve representing the least squares line through these data. The total hemispherical emittance from 1600 to 1850 K is shown in Figure 3. This curve represents a portion of the data which were measured from 1500 to 2800 K for this sample. All the total hemispherical emittance data from 1600 to 1850 K were within $\pm 0.5\%$ of the least squares fit. Similarly, a portion of the electrical resistivity data (from 1600 to 1850 K) is shown in Figure 4. All the resistivity data from eight separate runs are within $\pm 0.5\%$ of the least squares fit for this temperature interval. Thermal conductivity values from 1700 to 2800 K calculated for the tungsten sample using the multiple point technique are shown in Figure 5. In general these data are within $\pm 4\%$ of the least squares curve. Using the least squares curves for electrical resistivity and thermal conductivity, values for the Lorenz function were calculated from 1700 to 2800 K. These results are shown in Figure 6. It is noted that the Lorenz function for tungsten at high temperature is significantly above the theoretical value ($2.443 \times 10^{-8} \text{ WK}^{-2} \text{ ohm}$). Computed Thomson coefficient values are shown in Figure 7 and compared to the smoothed values reported by Forsythe and Worthing [4] and by Lander [5]. The computed values of the Thomson coefficient exhibit a larger scatter and have a considerably greater uncertainty than the data shown in Figures 2 through 6. However, the Thomson coefficient results are believed to be as reliable as results previously reported in the literature. It is hoped that further improvements in data analysis will considerably reduce the uncertainty in the computed Thomson coefficient.

IV. Summary and Conclusions

The multiple purpose apparatus and associated mathematical techniques have been developed to the point where data for spectral emittance, electrical resistivity, thermal conductivity, Lorenz function and Thomson coefficient can be obtained above about 1200 K on the same long thin rod sample of an electrically-conducting material. The range of acceptable experimental conditions for direct heating methods has been greatly extended. Reproducibilities of the emittance and resistivity are usually within $\pm 1\%$ up to 2800 K. Thermal conductivity values computed using multiple point techniques are generally within $\pm 4\%$ of a smooth curve representing conductivity versus temperature. The accuracies are primarily limited by the accuracy of the temperature measurements and are believed to be less than $\pm 1\%$ for the resistivity, $\pm 2\%$ for the emittance and $\pm 5\%$ for the thermal conductivity. The values given in Figures 3 through 5 were not corrected for thermal expansion effects.

V. References

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Figure 1. Temperature Profiles for Tungsten(262 amps, 3.175 mm dia. by 11.4 cm long)

Figure 2. Spectral Emittance (0.65 microns) of Tungsten

Figure 3. Total Hemispherical Emittance of Tungsten

Figure 4. Electrical Resistivity of Tungsten

Figure 5. Thermal Conductivity of Tungsten

Figure 6. Lorenz Function of Tungsten

Figure 7. Thomson Coefficient of Tungsten

TABLE I. TYPICAL COMPUTER OUTPUT FOR 3-POINT METHOD

THREE POINT SECOND TUNGSTEN SAMPLE PART TWO 262 AMPS UP
 RHO = -3.0617000E-06 2.6300100E-08 1.7265000E-12
 F = -6.4049000E-03 1.5339600E-04 -1.6543000E-08
 A = 4.5107390E-02 TA = 2.9020000E+02
 I = -2.6295600E+02 PER = 1.0341620E+00
 T71 = 2.1816200E+03 Z1 = 2.0240000E+01
 T72 = 2.3927593E+03 Z2 = 2.1740000E+01
 T73 = 2.4295467E+03 Z3 = 2.3243000E+01
 MU = -2.0000000E-05
 THERMAL CONDUCTIVITY IS .91150

TEMPERATURE PROFILE

Z	T(7)	T*(Z)	CONDUCTION	HEATING	RADIATION	THOMSON
20.2400	2181.62	255.351	192.045	597.135	399.271	15.779
20.3901	2217.66	225.173	174.380	608.813	420.521	13.911
20.5403	2249.38	197.859	157.334	619.115	449.558	12.224
20.6904	2277.21	173.280	141.202	628.181	476.273	10.705
20.8406	2301.55	151.271	126.168	636.128	500.615	9.345
20.9907	2322.76	131.640	112.341	643.071	522.598	8.132
21.1409	2341.19	114.184	99.771	649.115	542.291	7.054
21.2910	2357.15	98.694	88.465	654.358	559.796	6.097
21.4412	2370.91	84.964	78.397	658.888	575.242	5.249
21.5913	2382.74	72.794	69.520	662.783	588.767	4.497
21.7415	2392.84	61.993	61.773	666.115	600.513	3.829
21.8916	2401.41	52.379	55.091	668.945	610.618	3.236
22.0418	2408.62	43.784	49.406	671.326	619.215	2.705
22.1919	2414.61	36.047	44.656	673.303	626.421	2.227
22.3421	2419.48	29.020	40.783	674.916	632.341	1.792
22.4922	2423.35	22.563	37.738	676.195	637.064	1.393
22.6424	2426.28	16.542	35.481	677.165	640.662	1.021
22.7925	2428.33	10.830	33.986	677.844	643.190	.669
22.9427	2429.54	5.303	33.234	678.244	644.683	.327
23.0929	2429.93	-.161	33.224	678.372	645.159	-.011
23.2430	2429.49	-5.684	33.962	678.226	644.616	-.352

FFF T= 2365.0

TRANSIENT TEMPERATURE PREDICTIONS ON A DISK

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ABSTRACT – The transient solution, in closed form, of the differential equation describing the heat transfer associated with the sensing disk of the asymptotic calorimeter has been derived. This solution was determined by purely mathematical methods using classical Fourier-Bessel expansions.

Two specific calorimeter disk geometries receiving a constant heat flux were studied, and the transient temperatures were computed using the exact solution. The disk sizes chosen are representative of a calorimeter for measuring heat flux values around 3400 kW/meter². Since most experimental measurements do not meet the boundary conditions of the exact solution, it is desirable to have the capability to solve this type of problem by means of a finite difference method. Thus, the same disk problems were solved by this method, and the results were compared to those of the exact solution.

The finite difference results were found to be in excellent agreement with the exact solutions. Thus, these results indicate that the method used for defining the thermal mass centers and area-to-length ratios for the finite difference solutions is satisfactory.

Limited experimental verification of the finite difference technique has been obtained. This was accomplished on a specially made calorimeter having temperature-measurement provisions on the disk.

I. INTRODUCTION

Several years ago Gardon (Ref. 1) reported on an instrument for measuring intense radiation to a surface. This instrument has come to be known as the asymptotic calorimeter, consisting of a small constantan circular foil mounted on a copper body as shown in the sketch presented in the next section. By attaching a copper wire at the center of the constantan disk, two thermocouple junctions are formed, one at the center of the disk and one at the edge. When a heat flux is applied to the gauge, the output from the two thermocouples indicates the temperature difference between the center and edge of the disk. This temperature difference is directly proportional to the heat flux applied, and this proportionality holds over an edge temperature range of -45°C to 230°C . Thus, by monitoring the EMF output of the gauge, an accurate measure of heat flux can be obtained.

The asymptotic calorimeter has been used extensively in measuring the heat transfer to the walls of combustion chambers of both solid- and liquid-fueled vehicles. In many cases it is desirable to obtain a measure of the heat transfer coefficient and the recovery or driving temperature. These values cannot be separated by just a measure of the heat flux. The idea is being investigated that, by measuring the center and edge disk temperatures independently, as well as the heat flux, one can separate the heat transfer coefficient from the driving temperature.

Thus far in this investigation, three accomplishments have been made: (1) An exact solution has been derived for the differential equation defining heat transfer in the disk; (2) a method has been determined for computing transient temperatures in the disk, using a finite difference method; (3) a calorimeter capable of measuring center and edge temperatures and their difference has been fabricated and tested. The results of these tests have been compared with theoretical values. The purpose of this paper is to present these accomplishments.

II. DISK HEAT TRANSFER - EXACT SOLUTION

Let us consider the circular foil gauge of thickness s and radius R . At R the foil is in contact with a heat sink that maintains the foil edge at a constant temperature $T(R, t) = 0$.

ASYMPTOTIC CALORIMETER

Since the foil is thin ($0.025 \text{ mm} < s < 0.100 \text{ mm}$) and maintained at relatively low temperatures, the assumptions can be made that (1) the thermal gradient in the s direction is zero, and (2) there is no heat lost from the faces of the foil. Also, the assumption is made that the heat flux q to the foil is uniform. With the above assumptions, and using the Fourier equation of heat conduction, the general differential equation describing the heat flow in the calorimeter disk can be determined to be

$$\frac{cd}{\lambda} \frac{\partial T}{\partial t} = \frac{q}{s\lambda} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2}, \quad (1)$$

with boundary conditions

$$T(r, 0) = 0, \quad 0 < r < R,$$

$$T(R, t) = 0, \quad 0 < t < \infty.$$

Here,

- T = temperature at any point and any time,
- q = heat flux,
- d = density of the material,
- c = specific heat of the material,
- s = thickness of foil,
- R = radius to outer edge of foil,
- r = radius,
- t = time,
- λ = thermal conductivity of the material.

The steady state solution is readily obtained by setting $\partial T / \partial t = 0$. Equation (1) then becomes an ordinary linear differential equation of first order. An integrating factor yields the steady state solution in the form

$$T^* = \frac{q}{4s\lambda} (R^2 - r^2), \quad (2)$$

where T^* denotes the steady state temperature at any radius r .

The determination of a transient solution to Eq. (1), which is the primary purpose of this section, is much more difficult to obtain, and it has been determined by pure mathematical methods. The methods applied are the classical Fourier-Bessel expansions. Equation (1) can first be simplified by the following substitutions:

$$a = \frac{cd}{\lambda}, \quad b = \frac{q}{s\lambda} \quad \text{and} \quad x = r.$$

Thus, Eq. (1) can be rewritten

$$\left. \begin{aligned} \frac{\partial^2 T}{\partial x^2} + \frac{1}{x} \frac{\partial T}{\partial x} + b &= a \frac{\partial T}{\partial t} \\ T(x, 0) &= 0, \quad 0 < x < R \\ T(R, t) &= 0, \quad 0 < t < \infty. \end{aligned} \right\} \quad (3)$$

We next perform a series of manipulations to obtain an equation equivalent to Eq. (3) but without the constant term b . First we solve the homogeneous equation

$$X'' + \frac{1}{x} X' + b = 0, \quad X(0) = 0,$$

thereby obtaining the particular solution of Eq. (3), which is given by

$$X = \frac{b}{4} (R^2 - x^2).$$

Let

$$T_1(x, t) = T(x, t) - \frac{b}{4}(R^2 - x^2), \quad (4)$$

then

$$\frac{\partial^2 T_1}{\partial x^2} + \frac{1}{x} \frac{\partial T_1}{\partial x} = \frac{\partial^2 T}{\partial x^2} + \frac{1}{x} \frac{\partial T}{\partial x} + b,$$

and

$$\frac{\partial T}{\partial t} = \frac{\partial T_1}{\partial t}.$$

Thus, solving Eq. (1) is equivalent to solving

$$\left. \begin{aligned} \frac{\partial^2 T_1}{\partial x^2} + \frac{1}{x} \frac{\partial T_1}{\partial x} &= a \frac{\partial T_1}{\partial t} \\ T_1(x, 0) &= -\frac{b}{4}(R^2 - x^2) \\ T_1(R, t) &= 0. \end{aligned} \right\} \quad (5)$$

Let

$$T_1(x, t) = u(x) v(t). \quad (6)$$

Substituting Eq. (6) into Eq. (5), we obtain

$$\frac{u''(x)}{u(x)} + \frac{1}{x} \frac{u'(x)}{u(x)} = a \frac{v'(t)}{v(t)}. \quad (7)$$

Since the variables separate and Eq. (7) holds for all x and t , it implies that each side must necessarily be equal to a constant, say $-\beta^2$. Hence the left-hand side of Eq. (7) becomes

$$u''(x) + \frac{1}{x} u'(x) + \beta^2 u(x) = 0, \quad (8)$$

which is the well known Bessel's equation of order zero. Its solution is given by McLachlan, (Ref. 2, p. 15) as

$$u(x) = A J_0(\beta x) + D Y_0(\beta x).$$

Since $Y_0(\beta x) \rightarrow \infty$ as $x \rightarrow 0$ the requirement that the solution be bounded means that $D = 0$, thus

$$u(x) = A J_0(\beta x). \quad (9)$$

Now, from Eqs. (5) and (6), $T_1(R, t) = 0 \Rightarrow u(R) v(t) = 0$, and thus $u(R) = 0$ since $v(t)$ is arbitrary.

Hence from Eq. (9),

$$u(R) = A J_0(\beta R) = 0 ;$$

thus

$$J_0(\beta R) = 0; \quad (10)$$

thus all values β which satisfy Eq. (10) are solutions of Eq. (8). Denoting the n^{th} positive root of $J_0(\beta R) = 0$ by β_n and the corresponding values of u by u_n , Eq. (9) can then be written as

$$u_n(x) = A_n J_0(\beta_n x), \quad n = 1, 2, \dots \quad (11)$$

For each $-\beta_n^2$ (n fixed) which satisfies the left-hand side of Eq. (7), the right-hand side of Eq. (7) becomes

$$a v'(t) + \beta_n^2 v(t) = 0,$$

whose solution is

$$v(t) = B e^{-\beta_n^2 t/a}, \quad n \text{ fixed.}$$

Denoting the solutions by

$$v_n(t) = B_n e^{-\beta_n^2 t/a}, \quad n = 1, 2, \dots,$$

we can then write the formal solution of the boundary value problem (Eq. (5)) by

$$T_1(x, t) = \sum_{n=1}^{\infty} u_n(x) v_n(t) = \sum_{n=1}^{\infty} c_n J_0(\beta_n x) e^{-\beta_n^2 t/a}, \quad (12)$$

where $c_n = A_n B_n$.

We next determine the c_n 's. From Eqs. (5) and (12) we have

$$T_1(x, 0) = \sum_{n=1}^{\infty} c_n J_0(\beta_n x) = \frac{b}{4} (x^2 - R^2). \quad (13)$$

Multiplying the terms on the right by $x J_0(\beta_m x)$ and integrating from 0 to R , we get

$$\sum_{n=1}^{\infty} c_n \int_0^R x J_0(\beta_m x) J_0(\beta_n x) dx = \frac{b}{4} \int_0^R x^3 J_0(\beta_m x) dx - \frac{bR^2}{4} \int_0^R x J_0(\beta_m x) dx. \quad (14)$$

The left-hand side of Eq. (14) becomes (see Churchill (Ref. 3, pp. 158-162))

$$\sum_{n=1}^{\infty} c_n \int_0^R x J_0(\beta_n x) J_0(\beta_n x) dx = \begin{cases} 0 & \text{if } m \neq n, \\ c_n \frac{R^2}{2} [J_1(\beta_n R)]^2 & \text{if } m = n. \end{cases} \quad (15)$$

Making the change of variable $y = \beta_m x$ the right-hand side of Eq. (14) becomes

$$\frac{b}{4\beta_m^4} \int_0^{\beta_m R} y^3 J_0(y) dy - \frac{bR^2}{4\beta_m^2} \int_0^{\beta_m R} y J_0(y) dy. \quad (16)$$

Integrating the first term in Eq. (16) by parts twice and applying several formulas in Wylie (Ref. 4, p. 270) the right-hand side of Eq. (14) reduces to

$$- \frac{bR}{\beta_m^3} J_1(\beta_m R). \quad (17)$$

Using Eqs. (15) and (17), the c_n 's in Eq. (13) are then given by

$$c_n = - \frac{2b}{R\beta_n^3} \frac{1}{J_1(\beta_n R)}. \quad (18)$$

From Eqs. (4), (12), and (18) the solution to the boundary value problem, Eq. (3), is determined to be

$$T(x, t) = - \frac{2b}{R} \sum_{n=1}^{\infty} \frac{1}{\beta_n^3} \frac{J_0(\beta_n x)}{J_1(\beta_n R)} e^{-\beta_n^2 t/a} + \frac{b}{4}(R^2 - x^2). \quad (19)$$

Note that as $t \rightarrow \infty$, $e^{-\beta_n^2 t/a} \rightarrow 0$ and the steady state solution T_{∞} becomes

$$T_{\infty} = \frac{b}{4}(R^2 - x^2).$$

Setting $b = \frac{q}{s\lambda}$ and $x = r$, we get

$$T_{\infty} = \frac{q}{4s\lambda} (R^2 - r^2), \quad (20)$$

which coincides with T^* of Eq. (2).

Churchill (Ref. 3, p. 167) gives the general solution in integral form of the boundary value problem of a type stated in Eq. (5). Using Churchill's integral solution it is not difficult to verify that the first term on the right of Eq. (19) is the solution of the problem stated by Eq. (5). Finally, let us mention for the interested reader the book by Carslaw & Jaeger (Ref. 5), which contains a wealth of material on heat conduction problems and presents the solution (without derivation) to the problem considered here.

III. DISK HEAT TRANSFER – FINITE DIFFERENCE SOLUTION

As is generally the case, the exact solution presented in the previous section is limited by the boundary conditions required to arrive at the solution. In some applications these boundary conditions (i. e. $T(R, t) = 0$ and uniform q) do not apply, and solutions are desired to problems in which $T(R, t) = f(t)$ and $q = f(t, r)$. For such problems it is necessary to make use of finite difference methods. By choosing problems containing the boundary conditions required by the exact solution, an evaluation can be made of the accuracy of the finite difference method. Once checked out, this method can then be applied to the more general problems.

In the past, transient heat transfer problems have been solved at the Applied Physics Laboratory by using the forward finite difference method described by Dusenberre (Ref. 6). This method has been incorporated into a general computer program (Ref. 7) capable of solving three-dimensional heat transfer problems. Two specific disk geometries were chosen for study, and temperature histories were computed for them using both the exact solution and the finite difference method.

A sketch showing the two thermal models that were analyzed is presented in Fig. 1. Also shown on this figure are the boundary conditions and thermal properties that were assumed for the study. The temperature at the edge of the constantan disk was assumed to be zero at all times. Also, the heat flux to the disk was assumed to be uniform and constant at 3400 kW/meter^2 . As may be noted, the only difference between the two models is the disk diameter which is 1.270 mm for Model 1 and 1.778 mm for Model 2.

Consideration was given to investigating the effect of changes in heat flux q and disk thickness s on the transient temperatures. However, study of the exact solution given in Eq. (19) discloses that the temperature is directly proportional to q and inversely proportional to s . Since there is a direct relationship between $T(x, t)$, q , and s , no variations in q and s were considered.

When defining the thermal model for the disk geometry, difficulty arose in specifying the location of the thermal mass centers and the effective conduction area-to-length ratios (A/ℓ). Initially the thermal mass centers were taken at the radial center of each element, and the A/ℓ 's were computed using the steady state cylindrical conduction equation; i. e. $A/\ell = 2\pi s/\ln(r_o/r_i)$ where r_o and r_i are the outer and inner element radii. This method gave poor correlation with the exact solution, so a different approach was taken. The thermal mass centers were placed at the centroids of each element, and the A/ℓ 's were computed using the steady state temperatures and the equation

$$(A/\ell)_r = \frac{Q_r}{\lambda(T_{r_i} - T_{r_o})} ,$$

where

- $(A/\ell)_r$ = area-to-length ratio for elements with interface at r , $r_i < r < r_o$ (meters),
- Q_r = heat transfer to the area encompassed by r (watts),
- T_{r_i} = steady state temperature of element whose outside radius is r ($^{\circ}\text{K}$),
- T_{r_o} = steady state temperature of element whose inside radius is r ($^{\circ}\text{K}$).

The steady state temperatures T_{r_i} and T_{r_o} were computed, using Eq. (2). Using the values of A/ℓ determined by the above method, calculations were performed using the computer program of Ref. 7 to obtain transient temperatures for both the models shown in Fig. 1.

Comparison of the computer results to the exact solutions for both disk models are shown in Figs. 2 and 3. Most of the comparisons were made for the center of each disk; however, on the 1.778-mm-diameter disk a comparison was also made at $r = 0.571$ mm. As may be noted, the finite difference results are in excellent agreement with the exact solutions. Thus, these results indicate that the method described above for defining thermal mass centers and A/ℓ 's for calorimeter disk problems is satisfactory. Accurate prediction of transient temperatures may also be expected from the finite difference method when it is applied to more complex models of the disk configuration (i. e., models where the peripheral temperature of the disk $T(R)$ varies with time, and the heat flux and thermal properties are temperature dependent).

Results were taken from the computer studies and plotted as a function of radius, with time as a parameter (Figs. 4 and 5). At early times the radial temperature distribution is relatively flat in the center portion of the disk, but as the steady state condition is approached, the distribution takes on a parabolic shape. Comparing Fig. 4 with 5, the increase in disk diameter from 1.27 mm (Fig. 4) to 1.778 mm (Fig. 5) has a significant effect on the magnitude of the temperatures, but the radial distribution is about the same. Also it is interesting to note that varying the disk diameter has only a small effect on the time to reach steady state.

IV. EXPERIMENTAL PROGRAM

After obtaining an analytical solution to a given problem, it is always desirable to conduct tests from which experimental verification of the analytical solutions' accuracy is determined. A brief test program was carried out, which may be divided into three phases: (1) calorimeter fabrication; (2) testing; and (3) correlation with theory. Each of these phases will be discussed in this section.

After careful examination of commercially available asymptotic calorimeters, we decided to fabricate the desired test gauge at APL. This decision was influenced by three factors: (a) It was necessary to have detailed definition of the gauge geometry so that it could be analytically duplicated. (b) The gauge desired was not available commercially. (c) We wished to gain experience in the fabrication techniques required to make this type of calorimeter. Needless to say, the third factor was the most significant even though there were many frustrations associated with manually working with small parts.

A sketch showing the calorimeter that was fabricated, and dimensions of the various parts, is shown in Fig. 6. The constantan disk was attached to the copper body by a minimum amount of 250°C solder. To minimize oxidation at the junction, the disk was soldered in an inert atmosphere. Attachment of the copper and constantan wires was accomplished by spot welding under a 30-X microscope. Prior to spot welding, the center of the disk was indicated under a traveling microscope; thus, the copper wire was accurately centered on the disk. A special probe was used to obtain spot welded joints. This probe, which had a relatively sharp point, was made of a tantalum 10% tungsten alloy that has high oxidation and melting temperatures. Using probes made of other materials, including pure tungsten, resulted in poor weldments. Finally, to provide safe operation of the calorimeter under high heat loads, a water cooling coil was soldered to the copper body.

Three independent electrical measurements were made from the calorimeter. By connecting a copper wire to the constantan wire and placing this junction in ice, temperatures of the center and edge of the disk could be measured accurately. Shown below is a sketch of the three electrical circuits that were used with the calorimeter. The voltage recorded by V_1 is used directly to obtain the heat flux to the disk. It can be shown that the voltage V_1 is a linear function of the heat flux applied to the disk. Voltages V_2 and V_3 can be used directly to obtain temperatures at the center and edge of the disk, respectively.

After fabricating the calorimeter-temperature gauge, several tests were performed to obtain experimental data for a correlation study. The calorimeter was first mounted in a 1.588-mm-thick copper angle so that the sensing face was flush with the surface of the copper angle. A thermocouple was attached to the copper near the calorimeter, and the thickness of the angle was carefully measured at the thermocouple location. This assembly, which was 50.8 mm square, was mounted in a close fitting opening in a 6.35-mm-thick copper plate so that it was flush with the surface of the plate. In the copper

plate alongside the angle was mounted a commercial calorimeter having a heat flux range of 0 to 681 kW/meter². A high-temperature coating of high absorptivity ($\alpha = 0.9$) was applied over the entire surface, which included the calorimeter, the 1.588-mm copper angle, and the 6.35-mm copper plate. This assembly was then mounted in front of a double bank of quartz heat lamps with a guillotine-type shutter, as shown in Fig. 7.

The test procedure and recording equipment used were developed over a period of time during which other commercial calorimeters were recalibrated. Outputs from the thermocouple on the copper angle V_5 (see Fig. 7), the commercial calorimeter V_6 and the calorimeter V_1 were recorded on Brown self-balancing potentiometers. The values of V_5 , when reduced to temperatures, could be used to obtain the heat flux from the lamps by assuming the copper angle to be a slug calorimeter. This procedure was found to give an accurate measure of the heat flux experienced by the test calorimeter. To provide further conformation of the heat flux, the data from the commercial calorimeter were recorded. Measurements of V_2 and V_3 were made on an oscillograph after being amplified by DC amplifiers. By running the paper speed at 50.8 cm/sec, a good high-resolution record was obtained of the calorimeter center and edge temperature histories. Voltage to the quartz heat lamps was controlled by a Research Inc. Controller that provided a wide range of power. When 440 volts were supplied, a total power of 72 kW was concentrated in the 465-cm² area of the heat lamps. To obtain as near a step input of heat flux to the calorimeter as practical, a shutter was placed between the heat lamps and the copper plate assembly. This shutter was made of Transite, which is a hard asbestos material having a high combustion temperature.

The test procedure can best be given as a series of steps:

1. Set shutter in front of lamps with solenoid stem supporting it.
2. Set voltage desired on heat lamps (this may be done without turning on lamps).
3. Turn on recorders.

4. Turn on heat lamps.
5. Excite solenoid, which drops shutter.
6. Monitor V_2 , and when approximately steady state conditions have been attained, terminate test.

Using this procedure tests were run at heat flux levels of 561 and 283 kW/meter². The temperature and heat flux records obtained during these tests are shown in Fig. 8. Since the test calorimeter had not previously been calibrated, only voltage output can be shown on Fig. 8. Noting the slopes of the temperature-versus-time curves of the slug calorimeter, however, an estimate of the calorimeter calibration can be made. It appears that a calibration constant of 121.7 kW/meter²/mV will apply. Further calibration will be necessary to verify this value. The curves for V_2 (converted to disk center temperature) in Fig. 9 indicate quite readily the fast response of the calorimeter. On this figure the reader should also note the parallel lines of V_2 (T_c) and V_3 (T_e). In the time period where these lines are parallel, one can note that V_1 is constant. This is the principle on which the asymptotic calorimeter is based.

Following the experimental measurements, a brief correlation study was conducted using the finite difference method discussed previously. The disk geometry was simulated by a thermal model also described previously. Instead of including the copper body of the calorimeter in the thermal model, the edge temperature history of the disk as recorded by V_3 was forced on the edge of the thermal model. This approach was taken in order to minimize computer time. If the copper body of the calorimeter had been included in the thermal model, computer time would have been approximately 300 seconds instead of 40 seconds. The heat flux q_t applied to the thermal model was varied from 0 to q during the first 0.04 second and held constant at q thereafter. This initial variation was based on the calculated time required for the shutter to completely expose the heat lamps. Based on the geometry of the test arrangement, q was determined to vary as

$$q_t = q \left[\frac{10.125 x - 11.25}{25.2 x^2 - 56.0 x + 56.3} + 0.402 \tan^{-1} (x - 1.11) + 0.535 \right] \quad (21)$$

where $x = 193.2 t^2 + 39.3 t$, and t is time in seconds measured from the instant the calorimeter began to be exposed to the heat lamps. Since it was computed that the lamps were fully exposed at $t = 0.04$ second, Eq. (21) applies only to that time, after which the heat flux was held constant.

Analytical results for both heat flux levels are compared to experimental data in Figs. 9 and 10. As mentioned, the analytical edge temperatures were forced to be equal to those measured. The correlation of center temperatures is quite good and indicates further that the finite difference method discussed in the previous section may be used to determine accurate transient temperatures on a thin disk. One observation made during this study was the small effect the magnitude of q has on the computed values of A/l . In

changing q from 3400 to 570 kW/meter², it was found that the A/ℓ 's only changed by about one percent. Thus it may be concluded that new A/ℓ 's need not be computed for a given disk if the only change is in the q applied.

V. CONCLUSIONS

An exact solution has been derived for the partial differential equation defining the transient heat transfer in a thin disk. Two problems were solved by this means, and the results were used to evaluate finite difference methods of solution. Based on the evaluation, it was shown that a dependable finite difference method could be obtained by using values of A/ℓ computed from the steady state solution for the particular disk under consideration.

To obtain a complete evaluation of the analytical solutions, an experimental program was conducted. It involved development and fabrication of a special heat flux-temperature gauge, test of this gauge, and correlation of the test results. The program demonstrated that the finite difference method described provides accurate temperature predictions during the transient heating of a thin disk.

Finally, we plan to continue work on the heat flux-temperature gauge. Our effort will be directed toward developing a method for determining, by measurement, the heat flux, heat transfer coefficient, and the recovery or driving temperature in a severe heating environment.

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Fig. 1 DISK THERMAL MODELS, BOUNDARY CONDITIONS AND ASSUMPTIONS

Fig. 2 TEMPERATURE VERSUS TIME—MODEL 1

Fig. 3 TEMPERATURE VERSUS TIME—MODEL 2

Fig. 4 TEMPERATURE VERSUS RADIUS—MODEL 1

Fig. 5 TEMPERATURE VERSUS RADIUS—MODEL 2

Fig. 6 HEAT FLUX CALORIMETER AND TEMPERATURE GAGE

Fig. 7 TEST ARRANGEMENT-HEAT FLUX TESTS

Fig. 8 EXPERIMENTAL RESULTS OF HEAT FLUX-TEMPERATURE GAGE TESTS

Fig. 10 DISK TEMPERATURES FOR LOW HEAT FLUX TEST; COMPARISON OF TEST AND THEORY

Fig. 9 DISK TEMPERATURES FOR HIGH HEAT FLUX TEST; COMPARISON OF TEST AND THEORY

OUTWARD AND INWARD RADIAL HEAT FLOW
APPARATUS FOR OPERATION TO 2800 K

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ABSTRACT

A radial heat flow apparatus is described for determining the thermal conductivity of carbonaceous materials to 2800 K. The apparatus has graphite heaters to generate either outward or inward heat flow through the wall of a specimen stack (6.35 cm.O.D by 1.27 cm.I.D by 15 cm long). Temperatures below 1200 K are measured with Chromel/Alumel thermocouples; above 1200 K the thermocouples are withdrawn and an automatic optical pyrometer is sighted through quartz windows. Retractable black body cavities are used inside the furnace for calibration and periodic check of possible build-up of deposits on the windows.

When outward heat flow tests are conducted, the power dissipated in the central 5 cm.length of the center heater of the apparatus is determined from voltage measured with retractable probes and current through a standard resistor. For inward heat flow studies, the center heater is removed and a water calorimeter is inserted up through the center of the specimen stack.

Results from measurements on RVD graphite with a variety of test conditions are presented to indicate the influence of system parameters on the precision of thermal conductivity data.

I. INTRODUCTION

The radial heat flow technique is one of the most commonly used methods for determining the thermal conductivity of solids at high temperatures. The apparatus which is designed to operate by this method generates radial heat flow through a thick-walled, right-circular cylinder. Heat flow along the wall of the cylinder is virtually eliminated by operating appropriate heaters at the ends of the cylinder and cutting the cylinder into discs to provide thermal resistance at the interfaces of the discs. In a practical sense, the apparatus

provides a set of conditions in the cylinder which allows Fourier's equation for steady-steady one-dimensional heat flow to be applied. Thus, by determining the heat flow and the temperatures at two particular radii, the thermal conductivity of the cylinder material can be calculated.

Two configurations of the radial flow apparatus are used; one type employs outward flow of heat and the other inward heat flow. The outward heat flow apparatus operates with a center heater which supplies the heat to the cylindrical specimen at its inner radius. The heat is conducted radially outward to the outer radius from which the heat is dissipated. In this apparatus, the outer heater merely provides heat to maintain the specimen at the desired temperature level. Thus, the apparatus can be operated with a 50 K or less temperature difference between the two radii of the specimen. The quantity of heat passing into the specimen can be calculated from the voltage across and the current through the middle section of the center heater. The principal limitation of this type of apparatus is the quantity of heat which can be transferred from the small radiating surface of the center heater to the specimen's inner radius. When determining the conductivity of high conductive materials such as metals at high temperatures, the center heater must operate near its deterioration temperature to establish a measurable temperature difference at the two radii. Thus, the useful life of the heater is short under these conditions.

The inward heat flow apparatus operates with a water calorimeter in the center of the thick-walled cylindrical specimen. The calorimeter must be operated below 350 K to maintain single phase water flow. The heat flow through the specimen is determined by measuring the temperature rise of the water being circulated at a constant flow rate (through the calorimeter). The heat, which is inwardly conducted by the specimen, is supplied only by the outer heater; hence, the temperature at the outer radius of the specimen may be 1000 K greater than that of the inner radius. This large temperature difference creates significant thermal stresses within the specimen and may cause the specimen to fracture; however, for certain types of materials, this large temperature difference is tolerable.

II. DESCRIPTION OF EQUIPMENT

The radial heat flow equipment includes the apparatus and the variety of instruments, controls, and power supplies which are necessary for the operation of the apparatus. A view of this equipment is given in Figure 1. This view indicates the relative size of apparatus with respect to the instrument console.

A. Apparatus

The apparatus consists of the heaters and water-cooled electrodes, the calorimeter, the specimen and insulating base, furnace insulation, the detectors for measuring the specimen and heater temperatures, furnace chamber,

Figure 1 - Overall View of Apparatus with Instrument and Control Console.

radiation ports, and retractable black body cavities. Side and top cross sections of the apparatus showing the orientation of the various components are given in Figures 2 and 3, respectively.

1. Graphite heaters: The heaters for the apparatus are graphite and include the external heaters and the center heater (see Figure 4).

a. External heaters: The external heaters consist of the outer heater in the form of a thin-wall, spiral-cut, right-circular cylinder, 7.6 cm. ID by 26 cm. length, and the upper and lower yoke heaters which are resistive arms threaded into the ends of the outer heater for its support and current connections. The arms of the upper and lower yoke heaters are readily screwed into or out of the ends of the outer heater to allow the outer heater to be quickly installed or removed. Graphite lock nuts are used to maintain tight threaded joints to minimize electrical resistance to the high currents which flow through the joints. The outer and yoke heaters are fabricated from Graph-I-Tite G* which has mechanical properties higher than most commercially available graphites.

* Trademark of Carborundum Company.

Figure 2 - Side View of Thermal Conductivity Apparatus.

Figure 3 - Top View of Thermal Conductivity Apparatus.

Figure 4 - Insulation Block (IB) of Foamed Carbon Enclose the Outer Heater and the Yoke Heaters of the Furnace; Visible are Water-Cooled Electrodes (E), the Top Electrode Posts (EP), the Specimen Stack (SS), the Retractable Insulated Black Body (BB), and the Window Mask (WM). The top end of the center heater can be seen as it protrudes above the specimen stack.

The electrodes for the two yoke heaters and the outer heater are water cooled and are mounted on the bottom plate of the furnace chamber. Sheet Teflon* insulates and seals the flanges on the electrodes at the bottom plate. The ends of the arms of both yoke heaters have vertical graphite plugs which are submerged in reservoirs of liquid metal (see Figure 4). This arrangement allows each yoke heater to maintain electrical contact while it freely expands during heating. An 83% gallium-17% indium eutectic alloy which melts at 17°C is used as the liquid metal; it has a vapor pressure sufficiently low to permit its use in an evacuated chamber. The reservoir for the liquid metal is formed by a graphite liner which is threaded into the upper end of the electrode. The liner is used to prevent contact of the corrosive liquid metal with the copper electrode.

b. Center heater: The center heater is a solid rod, 6 mm. dia. by 26 cm. long, and can operate to 3000 K to generate the outward heat flow through the specimen stack. The heater is suspended by a graphite electrode at the top of the apparatus. This electrode has holes which allow an operator to sight down into the specimen stack for temperature measurements. The electrode is supported by four posts from the base plate; they provide electrical connections through the base plate to the power cable below. The lower end of the heater is submerged in the 83% gallium-17% indium liquid metal to allow free thermal expansion of the heater and to provide the required electrical contact.

DC power dissipated from the center heater in the 5 cm. central length of the specimen stack is determined by measuring the voltage drop along this length of the center heater and the current through it. The voltage probes to the heater are retractable to permit specimen installation. The voltage probe is a spectrographic-grade graphite rod, 15 cm. long and 3 mm. dia. tapered to 1.5 mm. dia., and is mounted in a rhenium tube which is located on the centerline of a 19 mm. dia. stainless steel tube. This tube can be moved in or out of the furnace wall through a pressure sealing gland. A quartz window is mounted on the end of the 19 mm. tube to allow the operator to observe the position of the probe as he inserts it into the furnace interior. He can position the graphite rod in the X-Y directions when he pushes the probe through the insulation, the spiral slot of the outer heater, and the hole in the specimen to make contact with the center heater.

2. Calorimeter: A 9.5 mm.O.D. stainless steel calorimeter is provided to absorb the heat flow through the specimen stack when heat flow is conducted from the outer heater. A differential thermocouple senses the temperature rise of circulating water (at a known flow rate) through the 5 cm. central length of the calorimeter. The upper end of the calorimeter is slipped into the threaded hole of the graphite electrode from whence the top end of the center heater was unscrewed. Hence, the calorimeter is positioned on the same center line at which the heater was previously located. Graphite yarn is spiral-wrapped on the O.D. of the calorimeter to block convective heat losses between the I.D. of the specimen stack and the calorimeter.

* Trademark of E.I. duPont de Nemours.

3. Specimen and insulating base: The specimen is a stack of discs assembled to form a thick-walled, right-circular cylinder with an outer diameter of 6.35 cm., an inner diameter of 1.27 cm. and a length of 33.7 cm. The discs are 5 cm. thick except for the top one which is 3.7 cm. thick. Three graphite pins are used at each disc interface to align the assembly as indicated in Figure 2.

The insulating base provides mechanical support for the specimen stack and minimizes the heat flow from the stack to the base plate of the furnace chamber. The insulating base is shown in Figure 2 and consists of two 6 mm. thick discs of high density carbon foam in the high temperature zone next to the specimen, a 19 mm. thick, and a 25.4 mm. thick disc of medium density carbon foam beneath them; all the discs are separated by three layers of pyrolytic graphite paper. The stack is separated from the top carbon foam disc by six layers of the paper for additional insulation. All items of the base are aligned by graphite pins in the same manner as the specimen discs.

4. Furnace insulation: The furnace insulation is low and medium density carbon foam blocks and graphite paper discs. Figure 4 indicate the general shapes to which the foamed carbon blocks are machined to enclose the heating elements.

The upper yoke heater is covered with an annular block of low density foam which is machined to fit down over the arms of the yoke heater. The insulating cover for the specimen stack fills the center of the annular block directly below the top graphite electrode of the center heater, as shown in Figure 2. This cover is a composite which consists of five sheets of graphite paper supported by the top specimen disc, a 12.7 mm. thick disc of medium density carbon foam, another set of five sheets of graphite paper which fills the diameter of the center of the annulus and, on top, a 25.4 mm. thick disc of low density carbon foam. The composite layers are held in alignment with the specimen stack by graphite pins. The top insulating disc fits in the annular block with a clearance of less than 0.8 mm.; thus, the annular block locates the top insulating disc which, in turn, positions the top of the specimen stack with respect to the center heater. The annular block has a metal strap around it to hold four ceramic insulators, one adjacent to each of the electrode posts of the center heater. Wire loops from the ceramic insulators to the posts are adjusted to hold the entire insulating cover and the specimen stack concentric to the center heater.

5. Temperature detectors: The temperatures in the radial heat flow apparatus are measured with metal-sheathed Chromel/Alumel thermocouples below 1200 K and with radiation pyrometers above 1200 K.

Six temperature points are used for measuring the gradients through the specimen walls, one each near the inner and outer radii at three angular locations, 120 degrees apart. The six points are at the bottom of the 3 mm. dia. holes which are parallel to the specimen axis and extend to the mid-plane of the stack as indicated in Figure 2. Five additional temperature points are located at the surface along the front side of the stack; temperatures at three additional locations are measured for the controllers of the outer heater and the yoke

heaters. The five points are used for setting the controllers of the yoke heaters to establish uniform temperatures along the length of the specimen.

For operation below 1200 K, 14 thermocouples are placed at the required temperature measurement points by using sealing glands in the radiation ports of the wall and top of the furnace. At 1200 K the thermocouples can be withdrawn to a position behind the port valves, the valves closed, the sealing glands replaced by optical grade quartz windows, optical pyrometers installed, the air evacuated, and the valves reopened for higher temperature measurements. Hence, the apparatus does not have to be cooled to room temperature for this interchange of temperature sensors.

Two pyrometer types are provided with the equipment. The precision temperature measurements are obtained with a Photomatic* Model A3 automatic optical pyrometer; this pyrometer is the black box at the right side of the apparatus in Figures 1 and 5. It is mounted on a micrometer adjustable (two directions) stand which swivels to allow the pyrometer to be used either at the top of the apparatus for determining the temperatures at the bottom of the six holes in the specimen stack or at the side of the apparatus for determining the temperatures at the five locations along the side of the specimen stack. A prism, mounted on the end of the pyrometer, permits viewing of the specimen in the two planes perpendicular to each other.

Three radiation pyrometers, Honeywell Model 354546-9 Radiomatic detectors, provide the signals for the temperature controllers; they are the horizontal cylinders at the left of the furnace in Figure 1. One pyrometer sights on the outer graphite heater for its signal; the other two, on the upper and lower yoke heaters.

6. Furnace chamber: The furnace chamber is a 46 cm. dia. stainless steel shell with an integral water-cooling jacket; the front view of the chamber is shown in Figure 5.

7. Radiation ports: The radiation ports consist of nine quartz windows to permit measurement of the temperatures of the specimen stack and the heaters. Along the front of the furnace chamber are five 19 mm. dia. windows which are used for sighting the side of the specimen stack with the automatic optical pyrometer as indicated in Figure 5. Three 32 mm. dia. windows are located on the rear left side of the chamber for the Radiomatic pyrometers to sight on the yoke and outer heaters. An 82.7 mm. dia. window is installed on top of the chamber for all six of the top temperature measurements.

Any one of the nine windows can be removed and cleaned during a test run; each has a shut-off valve to isolate it from the chamber to permit its removal. Each window has a needle valve in its evacuation line to allow the air in the space between the window and its shut-off valve to be removed after the window has been cleaned.

* Trademark of Pyrometer Instrument Company.

Figure 5 - Front View of Furnace Chamber Showing Five Ports (P) for Sighting the Side of the Specimen Stack and the Automatic Optical Pyrometer (OP) Used for Temperature Measurements at the Top and Side of the Specimen Stack. The end of the pyrometer has a prism (P) for sighting into the furnace.

The top window has a water-cooled baffle below it to protect it from deposits and heat when observations are not being made. A window mask, Figure 4, is used to shield the five windows at the front of the chamber; it can be raised for shielding or lowered for temperature measurements as desired during a test.

8. Retractable black body cavities: Two retractable black body cavities are provided inside the furnace chamber; one swivels beneath the top window (Figure 2) and one slides up in line with the five side windows (Figure 5). These cavities are machined from nickel and oxidized for high emittance surfaces. Each cavity has its individual heating element and Pt10Rh/Pt thermocouple. The optical pyrometer can sight on the cavities through the windows to determine any change in the transmittance of the windows created by deposits from specimen deterioration.

B. Instruments and Controls

The instruments and controls for the radial heat flow apparatus are housed in the console as shown in Figure 1. The left panel contains the controllers for the outer, upper yoke, lower yoke, and center heaters. The right panel contains a vacuum gauge control, the Photomatic optical pyrometer electronics, a potentiometer, and the various switches for power and signal measurements. A socket is provided on the furnace frame for connecting all signal lines to a portable data acquisition system when desired.

A block diagram of the instruments and controls is given in Figure 6. The instruments for measuring the data needed for the thermal conductivity calculations are the automatic optical pyrometer and a Honeywell Rubicon Model 2745 potentiometer with a Joseph Kay Model 2110 automatic ice point thermocouple reference system.

The power to the outer heater and the two yoke heaters is a combination of AC and DC power.^{1/} Basically, each yoke heater is powered by a single phase 16-KVA transformer; both transformers are operated on the same power phase. Each transformer has a center tap in its secondary winding which is connected to DC rectifiers to power the outer heater. As indicated in Figure 6, saturable core reactors regulate the AC power to the transformers; the temperature controllers in the instrument console control the reactors. The yoke heaters are individually controlled by the use of the AC and DC power combination to create uniform temperatures along the specimen stack.

C. Specimen Environment

The specimen environment can be either vacuum (10^{-5} torr) or an overpressure of one atmosphere of any desired gas. High vacuum pumping is performed by a 1440 liter/sec. diffusion pump, a stainless steel cold trap with a 6 liter liquid nitrogen reservoir is also used. Roughing and backing are accomplished with a 17.7 cfm mechanical pump.

^{1/} Rasor, N.S., and J. D. McClelland, "Thermal Properties of Materials," WADC TR-56-400, Part I, 1957 (AD 118144).

Figure 6 - Diagram of Instruments, Controls, and Power Supplies.

IV. PARAMETRIC STUDIES

Parametric studies were made in the radial heat flow apparatus with outward heat flow and in argon atmosphere. These were conducted to determine the effect of the parameters on the accuracy of thermal conductivity data. The parameters were: (1) the radial temperature gradient through the specimen, (2) the longitudinal temperature gradient from the midplane to the top and the bottom of the specimen stack, and (3) various specimen temperatures.

The specimen material selected for the studies was RVD graphite from the Parmer Research Laboratory of Union Carbide Company. The material was similar to the RVD graphite used in the High Temperature Thermal Conductivity Standards Program sponsored by the Air Force Materials Laboratory, Wright-Patterson Air Force Base; it was supplied from the same billet as were specimens for the current cooperative program of AGARD. Densities of the four middle discs of the specimen stack were 1.899, 1.902, 1.903, and 1.908 gm. cm⁻³.

Typical results of the parametric studies are plotted in Figure 7. The basis for the comparison is the probable curve for RVD graphite with grain as recommended in the Final Report* of the Standards Program. Three test conditions are listed beside each data point. The first term, $\Delta\theta$, is the difference between the average temperatures at the inner and outer radii. The second and third terms, $\Delta(M-T)$ and $\Delta(M-B)$, are the differences of the specimen surface temperatures at the midplane (M) and at locations 10 cm. above (T) and 10 cm. below (B) the midplane.

The following observations can be made from the results with respect to the effects of specimen temperatures, radial gradients and longitudinal gradients.

A. Effects of Specimen Temperature

Data were collected at 1330 K and 1940 K for nearly identical radial and longitudinal gradients. The conductivity value at 1330 K was 39% above the curve, but at 1940 K it was 72% above. The data were high because of the excessive longitudinal heat flow out of the center section of the specimen stack, $\Delta(M-T)=49^\circ\text{K}$ and 25°K and $\Delta(M-B)=58^\circ\text{K}$ and 55°K for the respective temperatures. The greater error at the higher temperature indicates that other heat losses become significant when a very small radial gradient ($\Delta\theta \sim 12^\circ\text{K}$) occurs. These losses may be caused by nonsymmetric heating of the specimen by the outer heater or convective losses from the center heater. The conclusion from these data is that the errors for a given set of temperature gradients increase with increasing specimen temperature.

B. Effect of Radial Temperature Gradients

Three data points in the 1900 to 2000 K range are plotted in Figure 7 to show the effects of increasing the temperature gradient in the specimen wall. The gradients were 12.1°K , 23.2°K , and 37.6°K for the 15.9 mm. spacing between the inner and outer radii. The averages of $\Delta(M-T)$ and $\Delta(M-B)$ for these respective gradients were 40°K , 60°K , and 98°K ; nevertheless, the increase in the radii gradients from 12.1 to 37.6°K more than offset the increasing longitudinal gradients. Consequently, the overall effect was a reduction in the error in the data; i.e., 72, 42, and 24%.

* Arthur D. Little, Inc., "Development of High Temperature Thermal Conductivity Standards," AFML-TR-69-2, p. 112, June 1969.

Figure 7 - Typical Results of Parametric Studies in the Radial-Heat Flow Apparatus.

C. Effect of Longitudinal Temperature Gradients

All of the data plotted in Figure 7 can be used to show that the reduction of the longitudinal gradients (longitudinal heat flow) results in a reduction of the error in the thermal conductivity measurements. The reductions indicated in Figure 7 bring the data to within $\pm 10\%$ of the probable curve.

For the low radial gradients (12 to 16°K/15.9 mm.), a reduction of the average of $\Delta(M-T)$ and $\Delta(M-B)$ from approximately 50°K to less than 20°K caused the errors to drop to less than 10%. For higher radial gradients (23 to 38°K/15.9 mm.), a reduction of this average from 60°K to less than 30°K practically eliminated the error in the data.

The results of nonsymmetrical longitudinal gradients are also indicated in Figure 7. At 1675 and 1698 K, two conductivity values were obtained with one end of the specimen stack hotter than the middle which, in turn, was hotter than the other end. The data point at 1675 K had the bottom end 44°K hotter than the middle which was 81°K hotter than the top. This set of conditions caused heat to flow up through the stack so the net result was

a small error in the overall determination; in fact, the data point coincided with the probable curve.

As a result of these parametric studies, operating limits can be specified for the apparatus when highly conductive materials such as RVD graphite are being studied. For instance, the data in Figure 7 indicate that determinations accurate to within $\pm 10\%$ can be obtained with radial gradients as low as $15^\circ\text{K}/15.9\text{ mm.}$ when the average of $\Delta(M-T)$ and $\Delta(M-B)$ is less than 20°K. When higher gradients (25°K) are used, a larger average of $\Delta(M-T)$ and $\Delta(M-B)$ is permissible. The results of these studies can be extended somewhat to materials with lower conductivity, but exploratory studies should be made when insulating type materials are being studied.

V. CONCLUDING COMMENTS

The radial flow apparatus has demonstrated its capability of determining the thermal conductivity of carbonaceous materials at high temperatures. The apparatus has operated at 3150 K in argon for 15 min.; the power was reduced because the outer spiral heater started to sag. Therefore, the upper limit for the apparatus somewhat below this temperature.

The parametric studies indicate that acceptable data for high conductivity material can be obtained with radial temperature gradients as low as $12^\circ\text{K}/15.9\text{ mm.}$ in the specimen wall; however, longitudinal gradients must be maintained below $20^\circ\text{K}/10\text{ cm.}$ above and below the midplane of the specimen stack. Additional studies are under way to determine operational characteristics of the equipment for low conductivity materials.

A TECHNIQUE FOR PRECISE DETERMINATIONS OF HEAT
TRANSFER IN THE ABSENCE OF TEMPERATURE MEASUREMENTS
AND ITS EXTENDED APPLICATION TO THERMAL CONDUCTIVITY
AND OTHER PROPERTIES

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A multi-purpose instrument for the measurements of many properties of fluids has been designed and built and described in detail in (1, 2 and 3). In (4) the precise determination of fourteen properties with the new instrument operating under steady state conditions was demonstrated. There it also was indicated that seven more properties can be determined with the instrument when used under unsteady or transient conditions. The principle of one of these unsteady methods has been discussed and demonstrated only in (4). The present paper brings in addition the analysis and the derivation of the equations from which the transfer of heat and the thermal transport properties can be evaluated.

The test cell consists of two concentric cylinders with hemispherical ends. The fluid to be tested is placed inside the cavity between the cylinders. The instrument is so designed and built that very accurate measurements of the capacitance can be made. The study shows how the transient measurement of the capacitance can be related directly to the thermal conductivity and diffusivity. Certain constants associated with this mathematical derivation must be determined before the equation can be used. Due to the complex nature of the physical model, these constants must be determined experimentally for this instrument. Therefore, the instrument for this particular measurement must be calibrated. This method can be made as an absolute measurement for other instruments if the geometry of the instrument is carefully chosen.

INTRODUCTION

Heat transfer evaluation in most instances requires the knowledge of surface temperature of one or more solid bodies. The measurements of surface temperature cannot be done precisely for reasons that the sensory elements cannot be made a part of the surface. They are either attached to it or placed in holes drilled into the heat exchanging wall near the surface. These procedures have the disadvantage of disturbing the temperature field at the location of measurements. The surface becomes not only unisothermal but its true temperature outside the location of disturbance normally cannot be established precisely from the observed values. Therefore, heat transfer processes which are a function of surface temperature are indeterminable or at best inaccurate. The new

method observes dimensions by means of capacitance measurements thus eliminating determination of surface temperature but incorporating parameters which depend upon it and which can be observed very precisely. In addition, these measurements do not disturb in any way the conditions of the surfaces under investigation.

PRINCIPLE OF OPERATION

Consider two concentric spheres or cylinders or geometrically similar objects surrounding a fluid. The system originally is at thermal equilibrium. At a certain time one of the solid bodies is heated or cooled either suddenly or slowly to a new temperature level or heated or cooled continuously. If the material and wall thickness of the body are chosen properly, the temperature within it will be uniform at any instant of time and identical to the surface temperature. The dimensions of the body will change with temperature due to thermal expansion. The other originally unheated body receives heat from the first body as a result of the temperature difference established in time and in accordance to the heat transfer characteristics of the fluid separating the two solid bodies. The heat received will change the temperature and, therefore, the dimensions.

The geometry of the gap between the two bodies changes in accordance to the temperature history of the two solids. This change of geometry can easily be observed by capacitance measurements which will be a function of geometry only when the temperature changes are small enough for the assumption of constant dielectric constant.

Obviously, it is of advantage to change the temperature of the outside body first because the inner body then can receive heat only from the body surrounding it. In this arrangement heating will cause increase of gap width, therefore, decrease in capacitance, while cooling will have opposite effects. (In the latter case an additional advantage occurs. If the heat capacity of the inner body is accurately known as a function of temperature, its change in temperature enables a direct determination to be made of the amount of heat transferred.)

The observation of capacitance change with time, therefore, enables heat transfer to be determined without measuring surface temperatures or even the difference in temperatures of the two bodies. Capacitance measurements in addition bring the advantage that the readings can be used directly, no conversion is necessary as would be the case when temperatures are observed by means of thermocouples, resistance thermometers or optical devices. This is of importance for remote observations of heat transfer processes or for property determination in case the fluid between the two bodies is at rest.

EXPERIMENTAL PROOF OF THE FEASIBILITY OF THE NEW METHOD DETERMINATION OF THERMAL CONDUCTIVITY AND DIFFUSIVITY WITH THE MULTIPURPOSE INSTRUMENT

The multipurpose instrument described in detail elsewhere (1,2,3) is able to observe electrical, optical, thermodynamic and transport properties simultaneously over wide ranges of pressure and temperature and over wide ranges of frequency and electrical potential. The apparatus is wired using three lead techniques

and therefore able to observe capacitance very precisely. Fig. 1 shows schematically a cross-section through the apparatus and its connection to the capacitance bridge and temperature regulating devices. The so-called "hot" and "cold" bodies of the instrument are made out of Nimonic 80A. The high nickel chromium alloy material is of low thermal conductivity but the change of temperature of the system is established by means of a thermostatic fluid (transformer oil) which is of such poor heat transfer characteristics that the Biot number still can be assumed to be of very low value. Temperature, therefore, will be uniform within the cold body at any instant of time. The test fluid filling the gap between hot and cold body is supposed for demonstration reasons to be either a) a perfect insulator, b) a perfect conductor, or c) a finite conductor or a real substance.

Figures 2, 3 and 4 demonstrate schematically the temperature change which will occur for each case when the cold body originally at T_0 is heated by means of the thermostat continuously from $t = 0$ on or to a new steady value T . The figures demonstrate also schematically the change of capacitance resulting from the temperature changes.

In the case of a perfect insulator, Fig. 2 shows that the temperature of the cold body increases continuously or to a new steady value. Since the hot body is perfectly insulated from the cold body surrounding it, it will not receive any heat and its temperature will remain constant. The cold body diameter D and its length will continuously increase to a new higher value. As a result of this the gap width $D-d$ increased. The average heat transfer area A between hot and cold body also increases but by a smaller amount and therefore the capacitance of the arrangement will decrease in accordance with equation (1).

$$dC_T = k_0 \cdot \epsilon_g \frac{dA(T - T_0)}{D_T - dT_0} \quad (1)$$

where k_0 is the permittivity of free space ϵ_g the dielectric constant of the fluid filling the gap - assumed to remain constant. The change of capacitance is indicated schematically on the right hand side of Figure 2.

Figure 3 shows the temperatures as a function of time for a perfect conductor. Since the gap between the two bodies now contains a perfect conductor the two bodies change their temperatures simultaneously, and so will their dimensions. The change in geometry is given by:

$$\left(\frac{A}{L}\right)_T = 2\pi \left\{ \frac{h[1 + a(T-T_0)]}{\ln D/d} + \frac{D \cdot d[1 + a(T-T_0)]}{D-d} \right\} \quad (2)$$

which changes the capacitance in accordance with

$$C_T = C_{T_0} [1 + a(T-T_0)] \quad (3)$$

where a is the thermal expansion coefficient of the material of hot and cold bodies.

Continuous heating or heating to a new steady temperature value will cause the capacitance change with time as indicated on

the right hand side of Figure 3.

Figure 4 gives the conditions for a real conductor. Heating the system by means of the thermostat will change the temperature of the cold body first -- that of the hot body will follow with a certain time lag according to the heat transfer through the fluid separating the two bodies. The temperature difference $T_c - T_h$ will remain constant with time after a certain time when heating is continuous and for constant properties.

For limited heating the temperature difference will first increase to a maximum value and then decrease to zero as indicated in the figure. The capacitance will change as indicated for the two different heating cases. It is obvious that the temperature difference between cold and hot body will be smallest for highest heat transfer in the fluid and largest under low heat transfer conditions. For continuous heating the maximum decrease in capacitance will be small and established fast in case of good conducting fluids. The opposite holds true for poor conductors. For limited heating new steady state values of capacitance will be established fastest for best heat transfer conditions.

For four different fluids, where the heat transfer varied from very good to very poor, the method has been checked by using as test substances helium, nitrogen, argon and vacuum. In the latter case heat transfer occurs only along centering devices, by radiation and residual molecular conduction.

The temperature of the cold body in all cases was changed from 24°C to a new steady value of 38°C by means of the thermostat operating in all instances under identical heating rates.

The measured values of capacitance as functions of time are given in Figure 5. The maximum change in capacitance observed in helium is approximately one order of magnitude less than that of the vacuum and new steady state conditions are established approximately five times faster.

The capacitance values for each gas at the steady state conditions divided by the respective vacuum values yield the dielectric constants. The vacuum values at 24°C and 38°C differ from each other by the thermal expansion coefficient of the instrument material in accordance with equation (3).

The maximal capacitance change observed during the test with helium was approximately .05%. This accounts for a similar amount of change in gap width (nominally .5 mm) of 2.5×10^{-4} mm. If one assumes that the change occurred at a time when only the cold body had changed in temperature then its excess temperature was approximately 1°C. This is the maximum temperature difference between cold and hot bodies. In accordance with Figure 4, it will decrease in time and finally become zero.

The sensitivity of the instrumentation is so high that capacitance changes of the order of .001% can be detected. This refers to an increase in gap width by 5×10^{-6} mm which in turn is identical to the change in diameter the cold body will experience when heated by 2×10^{-2} degree. For other geometries the result of even much smaller changes in temperature and/or dimensions could easily be detected. This demonstrates again the very high

sensitive observations possible with capacitance measurements.

The measured points in each case scatter only in a few instances and only by a very small amount (not more than .001%) around a smooth curve. The curves are very similar in shape. The temperature differences within the test fluid during the measurements were small. Therefore, it can be assumed that free convection was not present. A further reason for assuming free convection to be absent is that the time provided might not be sufficiently long enough.

The measured data observed with our system of given geometry therefore are functions of the thermal conductivity and diffusivity of the test substance, but may be influenced by radiant heat transfer and heat flow along lead-ins and centering devices. Both transfer mechanisms are small. In case of opaque fluids radiant heat transfer would have no effect.

MATHEMATICAL EQUATIONS TO BE USED WITH EXPERIMENTAL DATA

Due to the geometry of the system as shown in Figure 1, a change in capacitance was obtained when a change in temperature of either body occurs. The complicated shape of the instrument makes it impossible to write a mathematical equation describing the temperature field within the gap. Since the gap width is very small compared to the diameter of either the hot or cold body, very little error in the calculated temperature field will be introduced by assuming a system of two infinitely large parallel plates separated by a small distance. Making the above assumption and letting

$$\theta = T - T_f \quad (1)$$

$$\theta_o = T_o - T_f \quad (2)$$

where T = temperature at any location and at any time
 T_f = final temperature of the system
 T_o = initial temperature of the system

the differential equation for the temperature field becomes:

$$\frac{\partial^2 \theta}{\partial x^2} = \frac{1}{a} \frac{\partial \theta}{\partial \tau} \quad (3)$$

where x = distance from cold plate
 τ = time
 a = thermal diffusivity of the fluid in the gap

The boundary conditions are:

$$\theta(0, \tau) = \theta_o e^{-R\tau} \quad (4)$$

and
$$\frac{\partial \theta(L, \tau)}{\partial x} = \frac{MC}{k_f A} \frac{\partial \theta(L, \tau)}{\partial \tau} \quad (5)$$

where R = heating rate of cold body
 M = mass of hot body
 C = specific heat of hot body
 k_f = thermal conductivity of fluid in gap

L = gap width ($D-d$)
 A = surface area of hot body

and the initial condition is

$$\theta(x,0) = \theta_0 \quad (6)$$

Theoretically, Equation 3 with boundary conditions 4 and 5 and initial condition 6 can be solved to give the temperature as a function of location and time, but the solution is very difficult to obtain. The main mathematical difficulty arises from the boundary condition at $X=L$. The problem could be greatly simplified in two ways:

- 1) if the hot body is made to have a very low heat capacity, then equation 5 would become:

$$\frac{\partial \theta(L,\tau)}{\partial x} = 0 \quad (6a)$$

This condition also holds true in the present instrument for a short time as shown in Figure 4.

- or 2) if the hot body is an infinite heat sink, equation 5 would be:

$$\theta(L,\tau) = 0 \quad (6b)$$

The temperature fields for both of these conditions have been solved and in general, the solution for both boundary conditions can be written:

$$\begin{aligned} \theta(x,\tau) = & C_1 \theta_0 e^{-R\tau} + C_2 \theta_0 x \\ & + \sum_{n=0}^{\infty} A_n (e^{-R\tau} - e^{-\lambda_n^2 a \tau}) \sin \lambda_n x \end{aligned} \quad (7)$$

Where C_1 , C_2 , A_n and λ_n are constants which depend on both the geometry of the system and the boundary conditions.

It is interesting to note that the two conditions solved give an upper and lower bound to the real problem. It is also interesting to note that they both have the same general form. It is then fair to assume that the solution to the real problem may be expressed in the same form as for the two limiting cases. One change must be made because of the boundary condition at $X=L$: A_n must be changed to

$$\frac{A_n}{R}$$

where R is the heating rate.

Another approach to the solution of this problem can be obtained by examining the change in internal energy of the hot body. Since in all data runs, the change in the temperature of the hot body was the same, then the change in the internal energy was also the same. The change in internal energy may be expressed as:

$$\Delta u = \int_0^{\tau_f} q_L d\tau \quad (8)$$

where q_L is the heat entering the hot body.

But

$$q_L = -k_f A \left. \frac{\partial \theta}{\partial x} \right|_{x=L} \quad (9)$$

Substituting equation 7 into equation 9 yields

$$q_L = \frac{-kAC_1 \theta_o}{R} e^{-R\tau} + \sum_{n=0}^{\infty} \frac{A A_n}{\lambda_n} (e^{-R\tau} - e^{-\lambda_n^2 a \tau}) \cos \lambda_n L \quad (10)$$

or

$$q_L = k_f C e^{-R\tau} + \sum_{n=0}^{\infty} B_n (e^{-R\tau} - e^{-\lambda_n^2 a \tau}) \cos \lambda_n L$$

where

$$C = \frac{-kAC_1 \theta_o}{R} \quad \text{and} \quad B_n = \frac{A A_n}{\lambda_n}$$

therefore,

$$\begin{aligned} \Delta U &= \int_0^{\tau_f} (k_f C e^{-R\tau}) d\tau + \sum_{n=0}^{\infty} B_n \cos \lambda_n L \int_0^{\tau_f} (e^{-R\tau} - e^{-\lambda_n^2 a \tau}) \\ &= \frac{-k_f C e^{-R\tau_f}}{R} + \sum_{n=1}^{\infty} B_n \cos \lambda_n L \left[\frac{1}{\lambda_n a} e^{-\lambda_n^2 a \tau_f} - \frac{1}{R} e^{-R\tau_f} \right] \end{aligned} \quad (11)$$

Equation 12 shows that the ΔU is a function of the geometry of the system (which is the same for all test runs), the thermal conductivity of the fluid (k_f), the thermal diffusivity of the fluid (a) and the time required to reach the final temperature (τ_f).

Since the constants in the system are the same for any test runs, the following is true.

$$\begin{aligned} &k_{fi} C e^{-R\tau_{fi}} + B_1 \cos \lambda_1 L \left[\frac{1}{\lambda_1 a_1} e^{-\lambda_1^2 a_1 \tau_{fi}} - \frac{1}{R} e^{-R\tau_{fi}} \right] \\ &+ B_1 \cos \lambda_1 L \left[\frac{1}{\lambda_1 a_1} e^{-\lambda_2^2 a_1 \tau_{fi}} + \frac{1}{R} e^{-R\tau_{fi}} \right] + \dots \end{aligned}$$

$$\begin{aligned}
&= \frac{k_{fj} C e^{-R\tau_{fj}}}{R} + B_1 \cos \lambda_1 L \left[\frac{1}{\lambda_1 a_j} e^{-\lambda_1 a_j \tau_{fj}} - \frac{1}{R} e^{-R\tau_{fj}} \right] \\
&+ B_2 \cos \lambda_1 L \left[\frac{1}{\lambda_1 a_j} e^{-\lambda_2 a_j \tau_{fj}} - \frac{1}{R} e^{-R\tau_{fj}} \right] + \dots \quad (12)
\end{aligned}$$

Where subscripts i and j on properties k and a indicate different substances and on τ time required for those substances to establish the final temperature.

Equation 12 can be true in two different ways: (1) The sum of all the terms is the same, but the individual terms are not identical, or (2) To have each individual term identical, if the second case is assumed, then

$$k_{fi} e^{-R\tau_{fi}} = k_{fj} e^{-R\tau_{fj}} \quad (13a)$$

$$\begin{aligned}
\text{and} \quad &\left[\frac{1}{\lambda_1 a_i} e^{-\lambda_1 a_i \tau_{fi}} - \frac{1}{R} e^{-R\tau_{fi}} \right] = \left[\frac{1}{\lambda_1 a_j} e^{-\lambda_1 a_j \tau_{fj}} - \frac{1}{R} e^{-R\tau_{fj}} \right] \\
&\text{etc.} \quad (13b)
\end{aligned}$$

Table 1 lists the time required to reach τ_f for three different fluids under the same heating rate.

TABLE 1. Time required for the system to reach new steady state values for three different fluids in the gap, and the thermal conductivity of these fluids.

FLUID	TIME IN MIN	THERMAL CONDUCTIVE $\times 10^3$ in Btu/(hr-ft-F)
Argon	125	10.2
Nitrogen	115	15.1
Helium	81	57.8

Using equation 13a

$$\frac{1}{R} = [\tau_{fj} - \tau_{fi}] = \ln \frac{k_{fj}}{k_{fi}}$$

If the values of τ_f and k_f for Argon and Nitrogen are used, $R = -0.0392/\text{sec}$. The thermal conductivity of helium using above R and the properties of Argon as given in Table 1 is calculated to be

$$k_{He} = 57.2 \times 10^{-3} \text{ Btu/(hr-ft-F)},$$

If the data for nitrogen is used

$$k_{He} = 57.5 \times 10^{-3} \text{ Btu/(hr-ft-F)}.$$

Other combinations can also be selected and yield similar results.

It is hoped that equation 13b could be used in the same way to find the thermal diffusivity, but this possibility has not yet been investigated.

It should be noted that the result of the above calculations are very sensitive to the final time measured. The change of the time by a few minutes can greatly change the results.

CONCLUSIONS

As was shown in Figure 1, the system consists of a thermostat filled with 20 l transformer oil and an instrument of more than 50 kg of mass representing a large heat capacity. Determination of capacitance change with time, therefore, required an appreciable time. In view of this, it is surprising that within one minute after heating was started, changes of conditions within the cell already can be observed.

A light-weight system could easily be made several orders of magnitude less in thermal inertia which would result in as many fold faster observations and only a very short time would be needed to establish new steady state conditions in the system when heating is limited. Heat transfer measurements under those conditions could be carried out by remote control and should be of advantage to use for:

- a) Quality control in continuous processing
- b) Studying of conditions and properties in oceanographic research
- c) Space research - measuring the properties of the atmosphere of planets or interstellar atmosphere or even systems containing charged particles.
- d) Any other kind of research observing heat transfer and properties of temperature sensitive material and materials of short life, such as (i) radioactive materials, (ii) metastable materials, (iii) diasosiating and ionizing materials, (iv) chemically reacting materials.

The multi-purpose instrument originally developed for measurements under steady state conditions can, as shown above and also demonstrated in Figure 5, produce thermal conductivity and diffusivity data under transient or unsteady state conditions. These observations are only relative ones because the system is too complex for analysis and calibration with a substance of known diffusivity is necessary. A light-weight device discussed above can be selected with a proper geometry for derivation of equations which yield the thermal diffusivity absolutely.

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Fig. 1 Multipurpose instrument used in transient conditions to determine thermal diffusivity of test fluids

Fig. 2 Schematics of $T=f(t)$ for hot and cold bodies and $C=f(T,t)$ for case a, test fluid is a perfect insulator

Fig. 3 Schematics of $T=f(t)$ for hot and cold bodies and $C=f(T,t)$ for case b, test fluid is a perfect conductor

Fig.4 Schematics of $T = f(t)$ for hot and cold bodies and $C = (T, t)$ for case c, test fluid is a finite conductor

Fig 5 Change of Capacitance with Time of MPI for the Measurement of Thermal Diffusivity of Fluids

Use of Hyperbolic Heat Equation in Analyzing
Thermal Diffusivity Data for High Polymers

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Experimental studies of the thermal diffusivity of various high polymers using a high precision apparatus [1] at our facility indicate that the usual two term one-dimensional parabolic heat equation is not adequate in at least two ways. First, because the phase shift of a sinusoidal heat wave between two measurement points rarely equals the natural logarithm of the ratio of the amplitudes, a term linear in the temperature must be added to account for radial and point losses. Second, the coefficient of this linear term is found to be negative under some conditions of specimen temperature or heat wave frequency. This is an apparent violation of the second law of thermodynamics. However, when the finiteness of the velocity of propagation of heat is accounted for thru the modified Fourier law [2], a hyperbolic heat equation is obtained and the apparent law violation is eliminated within experimental uncertainties. Because the final four term equation is hyperbolic, wave reflections are to be expected. To date measurements do not show any direct evidence of reflections, probably due to the high degree of attenuation of sinusoidal temperature waves by polymers. However, the coefficients of the hyperbolic equation have an expected temperature dependence, particularly in the vicinity of the glass-rubber transition. It is believed that the additional coefficient of the modified equations, not previously determined for polymers, will be useful in polymer characterization.

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GUARDED FLAT PLATE THERMAL CONDUCTIVITY APPARATUS
FOR TESTING MULTI-FOIL INSULATIONS IN THE
20°C - 1000°C RANGE*

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ABSTRACT - A guarded flat plate thermal conductivity apparatus for evaluating multiple foil thermal insulations is described. The steady state device measures one-dimensional heat flow through a 15 cm x 15 cm planar insulation sample, using a heat flow meter centrally located at the cold surface of the sample. Lateral heat flow in the highly anisotropic multi-foil insulations is minimized by matched multi-foil guard sections which fit closely around the edges of the 15 cm x 15 cm dual-sample configuration. The gap discontinuity between sample and guard sections is typically .05 cm or less in width. Mean effective thermal conductivities (λ_a) are computed from the one-dimensional Fourier equation.

Thermal conductivity data are presented for two multi-foil insulations -- aluminum-glass and nickel-quartz -- operating in vacuum and spanning a temperature range 20-1000°C. The λ_a data are presented as functions of hot-side temperature T_h and layer density N . Measured thermal conductivities range from $.05 \times 10^{-3}$ - 5.0×10^{-3} W M⁻¹°K⁻¹. For the nickel-quartz systems, flat plate data are compared with corresponding λ_a values obtained from a wrapped, cylindrical test configuration. Refined error analysis is currently in progress to more precisely estimate the percent deviation on the flat plate λ_a data. Initial studies, using somewhat idealized boundary conditions, indicated that inherent inaccuracy in the two-dimensional sample configuration, with .05 cm filled gap, is less than 5%. Measurement error is likewise estimated to be small (5-10%). Refined analysis, integrating both configurational and measurement errors and actual test boundary conditions, will serve to verify these estimates.

KEY WORDS - Guarded flat plate tester, heat flow meter, high temperature, mean thermal conductance, mean effective thermal conductivity, multi-foil or multi-layer insulations, steady state operation, two-dimensional Fourier analysis.

I. INTRODUCTION

The emergence of multilayer insulation systems as useful engineering materials [1,2]¹ at high temperatures has created new demands for thermal performance data on these systems. Data which relate thermal conductivity to temperature and compressive load (i.e., layer density) are particularly valuable in estimating thermal performance of installed multi-layer insulation

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systems. These demands for additional data have increased the need for efficient, accurate, and low cost methods of determining apparent thermal conductivities of these insulations.

The basic multi-foil insulation configuration is comprised of highly reflective, discrete metallic foils, oriented normal to the direction of heat flow and separated from each other by low conductance, thin fibrous spacers. These insulations are utilized in a vacuum environment ($p < 1 \times 10^{-3}$ mm Hg). Typical thermal conductivities and corresponding operating temperature ranges for several multi-foil insulations are described in Section II.

The primary problem in measuring thermal conductivity of these insulation systems, as discussed previously by Grunert et al [3], stems from the high thermal impedance of the insulation in the direction normal to the plane of the metallic foils in comparison to the very low impedance in the plane of the foils. Apparent thermal conductivities (λ_a) in the plane of the layers are typically 3 to 4 orders of magnitude higher than λ_a values normal to the layers. This high impedance in the normal direction combined with the high degree of anisotropy usually results in a substantial temperature difference across the small test sample thickness, which further complicates the edge guarding task.

In addition to the high impedance, high anisotropy characteristics of multi-layer insulations, an added degree of difficulty is introduced by the compressibility of the composites under mechanical load and the sensitivity of system conductance to the level of compression [4]. It would be desirable, therefore, that a device to be used for measuring thermal conductivity of these insulation composites incorporate the ability to accurately control the composite density.

Grunert [3], in introducing a transient method for measuring thermal conductivity of these materials, points to several methods of measurement which have been used by other investigators. It was noted that the somewhat idealized cylindrical tester described by DeWitt et al [5], although yielding useful conductivity data, is not entirely free from error. In addition, sample preparation and establishing steady state data points are both quite time consuming.

Recently, Hale, Reny, and Hyde [6] described a tester of cylindrical configuration which, although used only at lower temperature in testing to date, shows promise of minimizing errors associated with mechanical pressure (layer density) variations normally found in spirally wrapped cylindrical specimens.

The previously mentioned transient technique was itself an effort to reduce test complexity and cost, mitigate edge guarding requirements and, in addition, incorporate the ability to control specimen density.

The tester described in this paper brings together the fundamental characteristics of total enclosure design [5] and the compressible flat plate design [3] into a single steady-state tester where the sample is sufficiently guarded to make possible an accurate, one-dimensional heat flow measurement at the sample center. The tester concept and operation are described. Typical thermal conductivity values are presented and compared with data on similar materials obtained using the cylindrical tester.

II. GUARDED FLAT PLATE TEST CONCEPT

The passively guarded, flat plate test arrangement for measuring mean thermal conductance of high-temperature multi-layer insulations under steady-

1 Numbers in brackets designate references listed at the end of this paper.

FIGURE 1 Guarded Flat Plate Test Configuration

state conditions is shown schematically in Figure 1. Characteristic features of the test sample configuration are:

1. Flat, planar multi-layer insulation samples, typically 15 cm x 15 cm x 1 cm, are fabricated and installed to form a dual-sample, symmetrical test geometry.

2. The test configuration is such that the multi-layer insulation samples can be tested over a wide mechanical compression loading range (typically 0 - 1 atm.), and at several hot-side temperatures up to the service temperature limit for the insulation.

3. Multi-layer insulation guards, which are matched to the sample materials and layer density, minimize lateral losses in the highly anisotropic multi-layer sample so that one-dimensional heat flow is effectively maintained over the central 5.6 cm x 5.6 cm metering zone.

1. Thermal Performance Parameters

The parameter selected to describe performance of the multi-layer insulation systems is thermal conductance. It is defined as the time rate of heat flow per unit area, under steady-state conditions, in a direction normal to the multiple-foil insulation slab and across a temperature gradient, T_h to T_c . The conductance (C) is expressed as follows:

$$C = \frac{Q}{A (T_h - T_c)} \quad (1)$$

where A denotes unit area and T_h and T_c are temperatures of the hot-side and cold-side boundaries, respectively.

For multi-layer insulations of relatively high layer density, such as are encountered here, the parameter, mean apparent thermal conductivity (λ_a), is defined and used as a performance indicator. The λ_a parameter is expressed as:

$$\lambda_a = CX = \frac{QX}{A (T_h - T_c)} \quad (2)$$

where X is the multi-layer insulation slab thickness. The mean apparent thermal conductivity is a function of temperature T and layer density (N), where N denotes the number of reflective shields per unit thickness.

The λ_a parameter is essentially independent of thickness for multi-layer insulations containing a sufficient number of reflective shields such that the optical properties of the hot and cold-side boundary surfaces have a negligible effect on overall performance. For thermal boundaries whose surfaces are relatively black ($\epsilon \cong 1.0$), the product N.X greater than 20 effectively satisfies the above condition. The various high temperature multi-layer insulations tested are of sufficiently high layer density, and N.X greater than 20 is satisfied in all test cases. The λ_a parameter enables direct comparison of thermal performances for various multi-layer insulations, even though the systems are tested at somewhat different thicknesses.

2. Test Configuration

The principal functions of the guarded flat plate test assembly are to:

1. Achieve and maintain steady-state heat flow conditions for hot-side temperatures ranging from 200-1000°C. Corresponding cold side temperatures are 40-200°C.
2. Through the use of matched, multi-layer guards, lateral heat flow in the sample is minimized such that one-dimensional heat flow is closely approximated in the metering zone (32 cm² central zone out of a total sample area of 225 cm²).
3. Accurately measure (a) heat flux per unit area in the metered zone, (b) hot and cold boundary temperatures, T_h and T_c , and (c) sample thickness (X), to enable computation of corresponding mean apparent thermal conductivity.
4. Achieve and control the mechanical or compressive loading (i.e., layer or shield density) of the multi-layer sample. Typically, λ_a parameters are measured over a range of layer densities corresponding to 0 - 1 atm. loading range.

The multi-layer insulation test sample assembly of Figure 1 has been designed to achieve steady-state heat flow conditions from which λ_a values may be obtained. The dual-sample system, when assembled together with the prefabricated multi-layer insulation guard sections, provides a complete enclosure around the resistance heater. Power input to the heater controls heat flux to the insulation and, ultimately, the temperature gradient through the insulation sample. Hot-side temperature T_h is assumed to be essentially uniform over the hot surface of both sample and guard sections. Temperatures are measured by thermocouple sensors as shown.

Under the conditions of sample symmetry and uniform boundary temperatures, the temperature profiles through the guard and sample sections are approximately matched in the interior as well as in the vicinity of the perpendicular gap; i.e., butt joint between sample and guard. This gradient correspondence at the gap (.05 cm width or less) implies minimum radiation

transfer across the gap and low edge heat loss from the sample sections. In addition, maintaining the gap width at .05 cm or less and using a fibrous gap filler (extended spacer material or powdered filler) further attenuates radiant interchange between sample and guard, as well as the net radiation loss from the gap.

Direct thermal coupling between guard and sample sections (such as by interconnecting foil shields) is avoided. Should the two be strongly coupled, the relatively ill-defined installed guard configuration could significantly alter the correspondence between the measured thermal conductivity and the thermophysical properties of the accurately defined, planar multi-layer sample.² However, in its function of an uncoupled, but approximately matched guard section, it acts as an effective deterrent to radiative heat loss from the sample edges. Previous, two-dimensional heat flow analysis on the sample-guard configuration of Figure 1 indicates that gap widths of .05 cm (unfilled) and .125 cm (filled) could exist with deviations in λ_a still maintained at less than 15%. Results of this analysis are discussed further in Section IV.

3. Application of the Testing Concept

The steady-state, flat plate testing technique has been used successfully in the evaluation of several high temperature multi-foil insulation systems, operating in a vacuum environment, at hot-side temperatures to 1000°C. The excellent radiation attenuation capability of these systems is due to a multiplicity of highly reflective metallic foil shields, oriented normal to the direction of heat flow and thermally separated from one another by low conductance, thin fibrous spacers. Shields and spacers are alternated on a one to one basis.

Typical multi-foil insulations for application from cryogenic temperatures to 1000°C are indicated in Figure 2. Specific thermal and physical characteristics of the tested high temperature systems are summarized in Table I.

Table I. Multi-foil Insulation Systems

Materials

Shields ($\leq$.0012 cm thick)	Spacers ($\leq$.012 cm thick)
Aluminum	Glass fiber paper
Copper	Quartz fiber paper
Nickel	Quartz woven cloth

Thermal Characteristics

Hot-side Operating Temperature	--- 200°C-1000°C
Mean Thermal Conductivity* Range	--- $.05 \times 10^{-3}$ - 10×10^{-3} W-M ⁻¹ -°K ⁻¹
Typical $\frac{\lambda_l}{\lambda_n}$ Range**	--- 10^3 to 10^4

* Vacuum Environment ($p \leq 1 \times 10^{-3}$ mm Hg)

** Ratio of effective λ_a in lateral direction (parallel to metallic foils) to λ_a in the normal direction.

Physical Characteristics

Layer (Shield) Density Range --- 20 L/cm to 180 L/cm (0-1 atm. compressive load)

² A strongly coupled condition would result in a measured λ_a corresponding to the sample-guard system rather than the desired λ_a -value for the well-defined multi-foil sample alone.

FIGURE 2 Graded Multi-foil Insulation Systems and Corresponding Mean Thermal Conductivities

III. TEST APPARATUS AND PROCEDURE

The flat plate sample-guard assembly, with pertinent design features and dimensions, is shown in section view in Figure 3. During testing, the sample assembly is contained completely within a bell jar enclosure 45 cm diameter x 75 cm high. The enclosed volume is maintained at a vacuum pressure p of 1×10^{-3} mm Hg or less by means of dynamic pumping, using an oil diffusion pump system. The installed sample assembly and test enclosure apparatus are pictured in Figures 4 and 5.

1. Apparatus - Instrumentation

With reference to Figures 3, 4, and 5, the principal hardware components and instrumentation are described.

Hardware Components

Resistance Heater --- The resistance heating element is constructed of woven graphite tape, Type WCB, 2.5 cm wide by .06 cm thick, wound on a flat ceramic plate. Electrical isolation of the heating element is provided by ceramic (quartz or alumina) edge sections and surface plates. Electrical leads are of stranded molybdenum wire. Input power is variac controlled from the 220 volt, 110 amp source.

Cold Face Sink Plates --- Steel sink plates, 20 cm x 20 cm x 1.5 cm, act as the cold-side boundaries for the 15 cm x 15 cm multi-foil samples as well

FIGURE 3 Guarded, Dual-Sample Test Assembly

FIGURE 4 Installed Multi-Foil Insulation Test Assembly

FIGURE 5 Flat Plate Test Apparatus - Instrumentation

as the flat, planar portions of the guard sections. The 5.6 cm x 5.6 cm heat flow meter is mounted on the upper sink plate, as shown. Water cooling coils have recently been added to provide improved control of cold-side temperatures (see Figure 4).

Compression Loading Device --- Compression loading on the sample is regulated through variation of the total gap width between the upper (movable) and lower (stationary) sink plates. Load-deflection data for the tested multi-foil insulations relate compressive load to sample thickness (i.e., total gap width)³.

The upper sink plate is adjusted vertically by means of a threaded coupling, mounted external to the vacuum space, and connected to the upper sink plate by two load transmission rods. The entire sample and planar sections of the guard are compressed simultaneously. The load range specified in testing is 0 - 1 atm.

Base Plate Assembly --- The stainless steel, 50 cm diameter base plate, provides a machined bearing surface for the gasket-sealed bell jar enclosure. All vacuum feed-throughs for electrical power leads, instrumentation, and load transmission rods are located in the base plate assembly.

Instrumentation

Pertinent instrumentation for heat flux, temperature, sample thickness, and vacuum pressure measurement are described below. Various readout and control devices used in controlling and monitoring test conditions are also indicated.

Heat Flow Meter --- Model H 11 (Thermometrics Corporation). Thermopile metering device with dimensions 5.6 cm x 5.6 cm x .17 cm. Calibration constant is $31 \text{ W-M}^{-2} - \text{mv}^{-1}$ and manufacturers rated accuracy is 3%. Maximum use temperature is 230°C.

Thermocouple Sensors --- Chromel/Alumel,⁴ ISA Type K. Chromel/Alumel thermocouples, .025 cm wire diameter, insulated with quartz sleeving. Thermocouples are calibrated against a certified Pt/Pt-10 Rh thermocouple traceable to NBS standards. Typical deviation is $\pm 1\%$ or less.

Input Power Controller --- Controller has a range of 0-1200°C with a readability of $\pm 5^\circ\text{C}$. Its function is to attenuate and control input power to the sample heater to establish steady state test conditions at up to five hot-side temperatures ranging from $\sim 200^\circ\text{C}$ to maximum service temperature for the tested insulation. The power attenuation program (i.e., input power level and dwell time) is preselected for each sample.

Strip Chart Millivolt Recorders --- Millivolt recorders provide a continuous monitoring of thermocouple and flux meter outputs. In general, millivolt recorder sensitivity is $\pm .25\%$. Readability accuracy ranges from .2 - 1.0% of full scale. All recorders are calibrated against an NBS standard potentiometer.

Vacuum Gauge --- A Philips cold cathode ionization gauge is used to monitor vacuum pressure within the test volume. The gauge is calibrated against a

³ The load-deflection characteristics relate compressive load to multi-foil insulation layer density (i.e., thickness of sample where sample contains a defined number of reflective shields).

⁴ Trademark of Hoskins Company.

McLeod standard vacuum gauge.

Thickness Indicator --- A dial indicator, readable to .0025 cm, monitors the total gap width between compression loading (sink) plates.

2. Sample Fabrication and Assembly

In fabricating the 15 cm x 15 cm multi-foil insulation samples, the foil and fibrous spacer materials are cut individually to the precise final dimensions. In assemblies where the spacer material also acts as gap filler, the spacers are cut oversize by .10 cm on each dimension. Sample assemblies using a powder filled gap have shield and spacer layers cut to identical 15 cm x 15 cm dimensions. The alternate-layer samples are then stacked to form the final sample configuration, using a specially designed aligning fixture. Typical multi-foil samples are 1 cm thick, and contain from 25 to 40 reflective shields.

The guard sections are of the same materials and at the same layer density as the samples. The edge guard envelopes, as shown in Figure 3, are assembled, retained in their desired configuration, and finish cut to the final dimensions.

The sample-guard assembly is constructed as follows:

- (a) The two multi-foil insulation samples are positioned on either side of the resistance heater.
- (b) Edge guard sections or "envelopes" are installed around the perimeter of the 20 cm x 20 cm heater assembly, and are drawn up to meet the insulation samples at a butt joint with gap width $\leq .05$ cm.
- (c) Cold side sink plates, including the mounted heat flow meter, are positioned at upper and lower sample-guard surfaces.
- (d) The completed assembly is installed within the bell jar enclosure.

Thermocouple sensors are installed during sample assembly. Two Chromel/Alumel thermocouples are at the hot-side boundary, to monitor and control temperature T_h . Cold-side Chromel/Alumel thermocouples are located at: (1) the center of the upper cold surface, in the heat metering zone, (2) the upper cold surface of the edge guard section, and (3) the center of the lower cold surface. All thermocouples are monitored continuously and give a record of hot and cold-side temperatures as well as an indication of the thermal balance between sample and guard.

3. Testing Procedure

Prior to thermal testing, load-deflection characteristics of the multi-foil insulation system are determined using either dead weight or pneumatic apparatus. These P vs. δ data describe the compressibility characteristics of the insulation and give an accurate relationship between layer (shield) density and compressive loading. This relationship is used in subsequently establishing the desired compressive load conditions during thermal testing.

After the sample-guard assembly is installed and instrumented, the test enclosure is evacuated to the desired pressure level ($p \leq 1 \times 10^{-3}$ mm Hg). The initial mechanical loading (i.e., shield density) condition is set, and the hot-side temperature program is begun. The input power controller achieves and maintains temperature (T_h) values which are pre-selected and programmed for the particular multi-foil sample. Dwell time to achieve steady-

state conditions at any temperature level ranges from 6 to 8 hours. After this elapsed time, power is attenuated automatically to obtain the next hot-side temperature point.

Heat flow data are obtained at a minimum of four or five hot-side temperature points for each loading condition. Subsequent load conditions are set manually; the hot-side temperature program is repeated for each new setting.

From the measured heat flow, temperatures T_h and T_c , and thickness X , the mean apparent thermal conductivity (λ_a) values are computed from equation 2. Thermal conductivity data (as a function of T_h) for each of five shield densities (corresponding to the 0-1 atm. load range) are normally generated for each multi-foil system, and presented in graphical and tabular form.

IV. THERMAL CONDUCTIVITY RESULTS

1. Typical Thermal Conductivity Data

Several multi-foil insulations have been evaluated experimentally using the guarded flat plate test apparatus previously described. The full matrix of λ_a values for two multi-foil systems are presented in Figures 6 and 7.

FIGURE 6 Thermal Conductivity Data -- Aluminum-Glass Multi-foil

FIGURE 7 Thermal Conductivity Data -- Nickel-Quartz Multi-foil

Insulations were tested in a vacuum environment ($p < 1 \times 10^{-3}$ mm Hg). The indicated layer density ranges correspond to a 0-1 atm. compressive load range for the aluminum-glass system and a 0-.4 atm. range for the nickel quartz.

The comprehensive λ_a data for the multi-foil systems are extremely useful in examining thermal behavior of these insulations and the key thermophysical properties which control their behavior. From these data, empirical correlations have been developed which express λ_a as a function of temperature T_h and layer density N . These expressions are used to regenerate thermal conduc-

tivity values at other boundary temperatures and compressive loads within the service range. They are especially useful in estimating thermal performance of multi-layer systems in various high temperature insulation applications.

The comprehensive λ_a (T,N) data mapping also gives further insight into the heat transfer mechanisms which control thermal performance of the multi-foil insulations. For example, empirical studies [4,5] based on this type of performance data have substantiated: (a) the strong temperature dependence of λ_a , particularly at low (near-zero) compressive loads where heat transfer through multi-foil systems is radiation dominated, and (b) the high sensitivity of λ_a to compressive load, especially at the lower temperatures and lower loads where solid conductance and interface resistance effects are most significant.

Figures 8 and 9 compare flat plate λ_a data for nickel-quartz multi-layer insulations with values obtained with a steady-state calorimetric test device under similar test conditions. This apparatus, previously described by DeWitt [5], utilizes a spirally-wrapped multi-foil sample of cylindrical geometry. This sample configuration completely encloses the heat source, and attempts to eliminate any longitudinal heat flow by maintaining physical continuity of each foil shield around the entire enclosure.

The configuration is, in concept, close to an ideal specimen construction. However, physical discontinuities are introduced in applying the insulation, notably at the end closures and in non-uniform mechanical pressures (affecting layer density) resulting from the spiral-wrap technique. Accounting for these discontinuities, as well as measurement and computational errors associated with λ_a determination, results in an estimated deviation of up to -25%⁵ for these thermal conductivity data.

FIGURE 8 Thermal Conductivity Data Comparisons

FIGURE 9 Thermal Conductivity Data Comparisons

⁵ Error estimates indicate that the physical discontinuities in the test system result in a high measured λ_a .

Comparison of λ_a values obtained by the two test methods reveals that:

(a) The relationships of λ_a to hot-side temperature T_h , as established by the two types of test data, are in agreement.

(b) The λ_a values from flat plate tests are approximately 25% lower than cylindrical test data.

The difference in absolute λ_a values, as noted in (b), may be due in part to the uncertainties associated with the average layer density for the cylindrical samples. Because of the sensitivity of thermal conductivity to compressive load and the non-uniform loads (i.e., layer density) inherent in the cylindrical sample, it is difficult to establish accurate correspondence in installed layer density conditions between flat plate and cylindrical test samples.

Although the overall or average N_a corresponds with the N measured for the flat plate samples, the cylindrical wrap may actually be at a higher density near the core (hot surface) due to the pressure amplification effects inherent in the spiral wrapping process. This inner layer compaction and accompanying shield distortion would likely result in higher λ_a values for the cylindrical test samples. These non-idealities are more significant in multiple foil systems than in non-foil⁶ multi-layer systems such as the nickel opacified quartz. The resultant higher deviations in the multi-foil data are indicated in Figure 9.

2. Error Analysis

Precise error analysis of the flat plate test data is difficult. Reliable multi-foil insulation standard materials for use in calibrating the tester do not exist. An error-free test configuration which would achieve idealized, one-dimensional heat flow, for use in generating reference λ_a data, is not available as well.

However, some estimates as to accuracy and consistency of the flat plate thermal conductivity data can be made through: (a) comparison of corresponding λ_a values obtained by various testing methods, (b) comparison of analytical and experimental results, and (c) evaluation of errors associated with the experimental method. Some of this work has been done. Additional analysis is currently in progress to more precisely define the error band for λ_a data on multi-foil systems tested to date in the flat plate apparatus.

Errors in the measured λ_a values can develop from two sources --- the non-idealities (e.g., gap discontinuity) which exist in the sample-guard configuration and the errors associated with data measurement.

In conjunction with flat plate tester design, the effect of the gap discontinuity on resultant λ_a values has been evaluated through analysis of two-dimensional heat flow in the anisotropic, 15 cm x 15 cm multi-foil sample. The analysis was made for filled and unfilled gaps of .05 cm and .25 cm width, with temperatures T_h and T_c considered uniform across sample and guard sections. Results of this early analysis are presented in Table II.

The non-ideality of the test configuration is indicated by the (λ_a) calc. to (λ_a) ref. ratio. The (λ_a) calc. term is computed from two-dimensional heat transfer analysis of the sample-guard configuration, and corresponds to a λ_a value based on heat flow measurement within the metered zone (5.6 cm x 5.6 cm) of the sample. The (λ_a) ref. term denotes the ideal, one-dimensional thermal conductivity. The computed ratios indicate that:

⁶ Nickel opacified insulation (no foil shields) achieves improved radiation attenuation by fine-mesh nickel flakes dispersed in quartz fiber paper[8].

Table II. Thermal Analysis of the Multi-Foil Insulation Guard - Sample Configuration

Foil	Spacer	$T_h(^{\circ}\text{C})$	$T_c(^{\circ}\text{C})$	Gap Width (cm)	$\frac{(\lambda_a) \text{ calc } (2-d)^{**}}{(\lambda_a) \text{ ref } (1-d)}$	$\frac{(\lambda_a) \text{ calc } (2-d)^{**}}{(\lambda_a) \text{ ref } (1-d)}$
					(no gap filler)	(gap filler)*
Al	Al-Opacified	480	20	.05	1.086	1.001
Al	Al-Opacified	480	20	.25	1.548	1.008
Cu	Cu-Opacified	760	20	.05	1.137	1.031
Cu	Cu-Opacified	760	20	.25	1.888	1.145
Ni	Refrasil Quartz	1000	20	.05	1.034	1.002
Ni	Refrasil Quartz	1000	20	.25	1.223	1.007

* Metal flake - opacified fibrous paper

** Tabulated ratios are based on computed heat flow over the 5.6 cm x 5.6 cm metered zone, for two-dimensional and one-dimensional cases.

(a) Percent deviation from the true, one-dimensional value is highly sensitive to gap width. This is especially evident in the unfilled gap cases.

(b) A gap filler insulation (to attenuate radiation) reduces the two-dimensional (i.e., lateral heat flow) effects considerably.

Based on these indications, a filled gap with average width of .05 cm is acceptable, and would essentially maintain one-dimensional heat flow in the metered zone.

Table III presents estimated measurement errors, based on calibration and readability deviations for instrumentation used in measuring heat flow, boundary temperatures, and sample thickness. The resultant percent deviations in computed λ_a values, as noted in Table III, are relatively small.

Table III. Estimated Measurement Error

<u>Multi-foil System</u>	<u>$T_h(^{\circ}\text{C})$</u>	<u>$T_c(^{\circ}\text{C})$</u>	<u>Deviation in Measured λ_a (%)</u>
Al-Glass N = 56 L/cm	480	40	± 3.6
Cu-Refrasil Quartz N = 32 L/cm	760	100	± 1.6
Ni-Refrasil Quartz N = 33 L/cm	1000	200	± 1.4

The root-mean-square method of Kline and McClintock [7] was used in determining total deviation. In this method, uncertainty in measured thermal conductivity is expressed as:

$$\lambda_u = [(\frac{\partial \lambda}{\partial Q} Q_u)^2 + (\frac{\partial \lambda}{\partial T} T_u)^2 + (\frac{\partial \lambda}{\partial X} X_u)^2]^{1/2} \quad (3)$$

where λ is a function of Q, T, and X and the terms λ_u , Q_u , T_u , and X_u represent uncertainties in the measured or computed values.

Additional deviation could occur in the heat flow meter when operating

at very low heat flux levels (associated with the low temperature, low load measurements) due to added uncertainty in the manufacturer's calibration constant. The lack of suitable standard materials has prevented precise meter calibration checks at these low flux levels.

The two-dimensional analysis is currently being refined to reflect variations in boundary conditions (e.g., non-uniform surface temperatures between sample and guard) which have been detected in actual tests. Also, in the new approach the measurement error analysis will be integrated with the two-dimensional configurational analysis. This combined analysis should give a more comprehensive indication of probable total error band.

In conjunction with the refined error analysis, a general re-evaluation of the test apparatus, sample-guard configuration, and test procedures will be undertaken. Based on our flat plate testing experiences, it is felt that some significant refinements and modifications can be made, particularly with regard to sample preparation, installation and instrumentation. Along with these system improvements, the tester will be upgraded for operation in the 1400-1650°C range.

V. CONCLUSIONS

1. The guarded flat plate thermal conductivity tester is operational. The multi-foil insulation edge guard sections appear to adequately limit edge heat loss from the highly anisotropic, 15 cm x 15 cm multi-foil insulation samples, such that essentially one-dimensional heat flow is maintained in the metering zone.

2. Extensive mean apparent thermal conductivity (λ_a) data have been obtained for several multi-foil insulations, operating in vacuum at hot-side temperatures ranging up to 1000°C, and at layer (shield) densities corresponding to a 0-1 atm. mechanical loading range. These comprehensive λ_a data have been used widely to:

(a) Define empirical correlations of thermal conductivity to temperature and layer density.

(b) Estimate thermal performance of installed multi-foil insulation systems.

3. Data comparisons for wrapped nickel multi-foil samples show the flat plate λ_a values to be approximately 25% lower than corresponding cylindrical test values. The cylindrical data are judged to be high due to densification and end closure problems inherent in the wrapped configuration.

4. Initial estimates and analysis indicate that the flat plate tester has an accuracy potential in the order of ± 10 -15%. These estimates were made using somewhat idealized boundary conditions. A new, refined error analysis will compute total deviation in λ_a considering combined effects of basic configuration, thermal imbalance between sample and guard, and measurement error. The latter two effects will be defined from actual test data and boundary conditions.

5. With current test experience as a guide, the flat plate tester is being re-evaluated to define potential improvements which may be made in apparatus design and test procedures. Special efforts are being directed to further simplification of sample fabrication and installation techniques, and improved temperature sensing instrumentation. Concurrently, the tester is being upgraded for service in the 1400-1650°C range.

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VII. NOMENCLATURE

C	-	thermal conductance	$W.M^{-2}.^{\circ}K^{-1}$
λ	-	thermal conductivity	$W.M^{-1}.^{\circ}K^{-1}$
Q	-	heat flow rate	W
T	-	temperature	$^{\circ}C, ^{\circ}K$
L	-	number of layers (shields)	
N	-	layer (shield) density	cm^{-1}
X	-	sample thickness	cm
δ	-	deflection	cm
P	-	mechanical loading	atm.
p	-	gas pressure	mm Hg
A	-	area	cm^2

Subscripts

a	-	denotes mean effective, mean apparent, or average value
h	-	denotes hot side
c	-	denotes cold side
n	-	denotes normal direction
l	-	denotes lateral direction
u	-	denotes uncertainty

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THE MEASUREMENT OF 14 PROPERTIES
WITH THE MULTI-PURPOSE INSTRUMENT

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ABSTRACT

The multi-purpose instrument originally designed to determine seven properties was extended in its capabilities to measure additional properties. The paper describes briefly the instrument and the operational procedures and brings the results of measurements of some of the properties, namely: four properties of the instrument or its wall material, thermal conductivity of He, N₂ and C₄F₈ (in vapor and liquid state), p-v-T data of N₂, dielectric constant of N₂, He, A, and C₄F₈ - vapor and liquid, vapor pressure of methanol, electrical conductivity and dissipation factor of C₄F₈-liquid, thermal expansion coefficient of Benzene, index of refraction and polarizability of N₂ and heat transport observations in He, A, N₂ and vacuum for the unsteady determination of thermal conductivity and diffusivity.

Whenever possible comparison with reference data were made. The agreement is in practically all cases excellent.

1. INTRODUCTION

Much efforts are currently expended to measure and/or calculate the properties of materials over continuously widening ranges of pressure, temperature and, in the case of mixtures, composition. The user of such data has the task of reconciling different types of quality information and often estimating new values for a needed condition. This is true for a single property. Often more than on property is needed and the necessary information cannot be found. Even if it can be found the values usually are not physically concordant. In order to overcome these difficulties the concept of a instrument able to measure many properties of substance was introduced and followed up by the construction of the apparatus which, when properly functioning, should (a) eliminate variations in sample in different tests (b) secure identical conditions for all different properties and (c) greatly reduce the time and expenses otherwise needed for separately measuring all the properties. The instrument further should allow most of the data to be observed absolutely, with high precision and over as wide ranges of temperature and pressure as feasible for accurate

measurements. The data therefore should be usable for theoretical studies, to verify and check models for prediction of properties by statistical mechanics especially for those ranges of temperature where it is impossible to carry out measurements. The theory and design of the development of the instrument have been described in detail in reports (1)* seminars (2,3) and presentations at national and international meetings (4,5,6) and so were the facilities of the laboratory and the experimental setup necessary for operating the instrument (7). This paper discusses first the procedure to obtain the properties of the instrument and then the results of measurements of properties of various test fluids. It was not attempted to measure for each of the test fluids all the properties the instrument can determine but to demonstrate that the apparatus can be used to determine with high accuracy as many properties as was proposed.

For comparison reasons such test fluids in most instances were chosen of which the property or properties to be determined were well known. The ranges of pressure and temperature were selected accordingly. In some other cases samples were selected of which only one or two properties were known accurately but not the others - or given only for single conditions of pressure and temperature. For safety reasons the measurements were carried out at pressures and temperatures which are far from the extremes of the design capability of the instrument. Some of the measurements are used for theoretical studies but those are beyond the scope of this paper and therefore not included.

For the sake of easier reading a short description of the instrument and its operation is felt necessary despite the fact that detailed information are given in the above references.

2. SHORT DESCRIPTION OF THE INSTRUMENT AND THE PROCEDURE TO MEASURE THE VARIOUS PROPERTIES

The instrument shown schematically in Figure 1 consists of four major parts. A heating element (the so called "hot body") of cylindrical shape with hemispherical ends enclosed in a similarly formed but slightly larger upper cavity of the cold body, which is made out of three parts. The lower part encloses a pressure measuring device, valve arrangements and a standard Pt-resistance thermometer which is located in the lower spherical cavity formed between the lower and middle parts of the cold body. The upper part suspends and centers the hot body by means of a centering rod. It furthermore houses a feed-in device. The test fluid is filled into the system either from below or through the feed-in device. The instrument can be sealed off completely for constant volume measurements or possibly in connection with outside instrumentations for other types of measurements. The temperature of the instrument is regulated by means of thermostat fluids channeled bifilarly through passages provided as indicated in the figure. The temperature of the hot body is determined by a Pt-resistance thermometer placed in a coiled capillary hard soldered in the wall at a well known distance from the surface. The temperature of the cold body is also measured by a Pt-resistance thermometer similarly mounted in the wall at a location where it surrounds the hot body. The

* () refers to References

Multipurpose instrument

Fig. 1

range of temperature is from -190°C to $+650^{\circ}\text{C}$, the pressure range from vacuum to 500 atm.

The hot body contains a heater element and serves to generate a thermal potential between it and the cold body when thermal conductivity is to be determined. Likewise by establishing an electrical potential difference between the hot and cold bodies the fluid electrical conductivity can be measured. In the first case Fourier's Law is applied, in the latter case Ohm's Law. The geometric constant, i.e., the ratio of overall area and average width of the gap between hot and cold body for both cases, is determined by capacitance measurements under vacuum and the value of permittivity of free space. Measuring the capacitance of the arrangement as a function of temperature will yield the change of geometry with temperature which allows the thermal expansion coefficient of the instrument material to be computed. It will be shown below that repeating of these measurements under slightly eccentric positions of the hot body within the cold body cavity will yield the thermal expansion coefficient of the centering rod. Change of geometry of instrument with pressure can be determined by observing pressure changes of capacitance with a test fluid of which the dielectric constant is known as a function of pressure. Measuring the capacitance with a test fluid in the system allows to evaluate the dielectric constant of the sample when the capacitance value is divided by the vacuum value observed at identical temperature and corrected for possible change of geometry due to pressure. In many cases the index of refraction can simply be computed from the dielectric constant.

The measurements of capacitance are carried out by a three lead technique with the aid of a capacitance bridge (General Radio: Type 1615A) which for highest sensitivity must be balanced in respect to dissipation. This yields together with the frequency of operation the a.c. electrical conductivity.

The volume of the instrument accomodating the test fluid can be determined as shown below precisely at a given condition of temperature and pressure. From the properties of the instrument known the volume value for other conditions can be computed. Therefore p-v-T properties of vapors and gases can be determined by observing under various specific volume conditions the change of pressure with temperature.

Likewise vapor pressure can be measured when the instrument is filled only by a certain amount of liquid. If the instrument is filled completely with a liquid which is in contact with outside instrumentation then its volume change with pressure or temperature can be observed and its compressibility and thermal expansion coefficients can be computed.

There are other steady state measuring possibilities of other properties which are in part described in (1) - also some others under quasi-steady state. Those are not utilized in the present paper. In addition the instrument can be used under unsteady state conditions for the observation of six other properties. Only one of those, namely the determination of thermal diffusivity (and conductivity), will be demonstrated and discussed in detail below.

The measurements of most of the properties listed are carried

out and made possible by altering only outside connections as shown schematically in Figure 2 for the electrical observations. A more detailed wiring is given in Figure 3 showing the arrangements to measure power input to the hot body by voltage and current measurements with the aid of standard resistors and a potentiometer. The current and potential leads of heater coil are connected by means of a master and main switch to the potentiometer and the standard resistors. In another position of the master switch the four leads of the heater coil (and also those of hot body thermometer - not shown) are combined and connected to the ground wire of the hot body. The so formed single lead is connected in one position of the master switch to the low side of the capacitance bridge. In another similar position of the master switch* the single lead is connected to a conductance bridge. The cold body is connected to the high sides of

the bridges by means of an antenna switch activated accordingly by the masterswitch. (The antenna switch is shown in the upper right hand corner of Figure 3).

A considerable effort was spent to assure in the wiring least possible dissipation in respect to capacitance measurements and highest possible d.c. insulation in respect to conductance measurements. The conductance bridge (Honeywell Model 1700) is a Wheatstone type bridge utilizing in their arms two simultaneously changeable standard resistors which are of 33 Megohm value when extremely low conductivity values are to be observed. The wiring of the instrument represents many parallel resistors to

* The master switch is a rotary switch with 60 positions circumferentially and 50 positions axially. From the 3000 possible switch combinations only 300 are used for the wiring. Other positions of master switch refers to a different position circumferentially and activation of other contacts.

these bridges resistors. For the sake of high accuracy in the measurements it was therefore necessary to insulate the wiring from the shield as well as possible. This was achieved by selecting wires with high grade insulation and placing them into metallic and insulated tubes which are connected to a metallic box enclosing the masterswitch. This box is on shield or guard potential and the metallic tubes represent shield or guard continuation. The box is maintained continuously under a slight positive pressure of dry nitrogen which leaks out at the open ends of the tubes. Moist air therefore never can enter the system. Dissipation losses could be disregarded completely (at least in the most common range of frequency used) and a total d.c. resistance between wires and shield of better than 10^{12} Ohm could be established and maintained.

Figure 4 shows a photograph of the experimental setup of the laboratory and the arrangements of the operational facilities. Starting at the right hand side Figure 4 shows first the capacitance bridge, next to it the conductance bridge and the masterswitch. Further to the left can be seen the potentiometer and the main-switch. All these bridges are mounted in consoles which are insulated from ground and represent shield respectively guards which are connected to the mounting platform of the multi-purpose instrument shown in the center of the photograph. The console on the right hand side of the instrument houses devices for filling and emptying the test fluid, further pressure measuring equipment and devices to observe volume changes of test liquids. On the other side of the instrument are located vacuum pumps and thermostats. Further to the left is a automatic control unit needed to heat or cool the cold body to the temperature of the calorimeter container when specific heats are measured. (see Ref. 1 - specific heat measurements are not included in the present work.) Next to this unit is a Mueller bridge used to calibrate with the aid of a NBS standard the Pt-resistance thermometers built into the cell. The equipment is arranged in such a way that it can be run by a single observer.

3. EXPERIMENTAL RESULTS UNDER STEADY STATE CONDITIONS

3A Determination of the Properties of the Instrument

3A1 Measurements of the Geometric Constant B

The geometry of layer of test fluid bounded by the walls of hot and cold bodies is given by

$$\frac{A}{L} = B = 2\pi \left[\frac{h}{\ln D/d} + \frac{D \cdot d}{D-d} \right] \quad (1)$$

where h is the cylindrical length of hot body and of cold body's upper cavity, d and D are their respective diameters.

This relationship is correct only for perfect geometry, i.e., homogeneous field everywhere. Influences of surface roughness and interruption of the layer by the bore at the bottom and at the top and at the location where the upper and middle part of the cold body join together are neglected.

It is impossible to correct the relationship analytically but it is possible to measure its true value which includes all the effects of these disturbances by determining the capacitance of the arrangement according to the equation

Figure 4. Experimental setup of the laboratory and the arrangement of the operational facilities.

$$C = B \epsilon_0 \epsilon_f \quad (2)$$

where ϵ_0 is the permittivity of free space, a physical constant precisely known and ϵ_f the dielectric constant of the test fluid. Measuring under vacuum makes ϵ_f equal unity and therefore

$$B = \frac{C}{\epsilon_0} \quad (3)$$

This value of B is correct for the measurements of the transport properties only if in those cases identical conditions exist, i.e., isopotential surfaces and/or homogeneity of the field can be assumed or assured. For electrical measurements isopotential surface normally can be achieved more easily than in thermal cases. In order to aid the conditions for the latter measurements the cold body's sink represented by the channels for the thermostat fluid has been given the geometrical shape of the hot body. (The influence of non uniform heat flow due to disturbance in its path will be discussed below.)

The value of the capacitance measured and therefore of B will have a minimum at a position of hot body within cold body's cavity where the most homogeneous field is present. In case of perfect geometry this position will be at a perfectly centered one. Due to the disturbances mentioned above (especially caused by the bores) a minimum value will occur at a slightly eccentric position in axial direction as was proven in (8). It is of advantage to measure properties under homogeneous field conditions and therefore it was necessary to determine this position. This was achieved by measuring the capacitance of the arrangement under vacuum and constant temperature as a function of axial displacement of the hot body in the cold body's cavity. The results of the measurements are given in Figure 5. The almost parabolic curve was observed by moving the hot body by means of a screw arrangement from

Fig 5 Capacitance as a function of vertical displacement of hot body at 25 °C under vacuum

Fig 6 Capacitance of Geometrical Arrangement Under Vacuum As A Function Of Temperature

a lowest possible position to the upper most position. The latter one occurs at a less displacement off center because of the sealing arrangement between centering rod and upper part of the cold body. The measurements were carried out at 25°C. In order to establish the geometric constant for other temperatures of interest to the measurements of the transport properties and the dielectric constant it was necessary to determine the capacitance of the arrangement at minimum setting and under vacuum as a function of temperature. The results of these measurements are shown in Figure 6. The data observed under increasing and decreasing temperatures scatter only in a few cases and then only by thousandths of a percent around the smooth curve.

During the measurements of each point it was observed that the capacitance values given were not established at the instant thermodynamic equilibrium was reached but with a certain time lag of the order of 1/2 hour. In case of capacitance measurement under increasing temperatures the data increased by a few thousandths of a percent to the final value. The opposite was observed when measured under decreasing temperature. This observation indicates that the change of dimensions due to thermal expansion do not occur simultaneously with the change in temperature.

3A2 Determination of Thermal Expansion Coefficient of Instrument Material and Centering Rod

The capacitance curve of Figure 6 shows an increase in slope with temperature. Inspection of equation 1 demonstrates that the geometric constant will increase linearly with temperature for constant thermal expansion coefficient. The curvature therefore could be explained with an increase in thermal expansion coefficient with temperature. An analysis of the curve yields values of thermal expansion coefficient and its temperature dependence which are both considerably higher than literature data. Therefore an additional temperature dependent influence on the capacitance measurements must exist. Those changes are possible only when changing temperature will cause displacement of the hot body relative to the cold body. An axial displacement is likely to occur for reasons that the centering rod being a structure composed of three different metals and ceramic not necessarily has the same thermal expansion as the material of the cold body - despite the fact that during the design and construction a matching of thermal expansion coefficient of the two bodies was attempted.

Figure 5 demonstrates that an axial displacement in either direction from a minimum setting will increase the capacitance. The axial displacement due to temperature changing from 25°C (at this temperature hot body was placed such to achieve minimum capacitance of the arrangement) is

$$e = L_{R_T} - L_{N_T} \quad (4)$$

with length of centering rod at $T \neq 25^\circ\text{C}$

$$L_{R_T} = L_{R_{25}} (1 + \alpha_R \Delta T)$$

and length of cold body surrounding centering rod

$$L_{N_T} = L_{N_{25}} (1 + \alpha_N \Delta T)$$

for

$$L_{R25} = L_{N25} = L_{25}$$

$$e = L_{25} (\alpha_R - \alpha_N) \quad (5)$$

Increasing temperature will cause a motion of the hot body relative to the cold body in a downward direction when the thermal expansion coefficient of the rod α_R is larger than that of the cold body α_N . For $\alpha_R < \alpha_N$ motion in the opposite direction will occur.

Repeating the measurements of capacitance change with temperature will allow to determine if $\alpha_R > \alpha_N$ or visa versa when in the arrangement the hot body is placed eccentric at 25°C.

Fig 7 Capacitance as a function of temperature for hot body displaced off center

The capacitance curve of the arrangement obtained with hot body originally displaced downward is given in Figure 7. The curve deviates from linear but now by a slope decreasing with temperature. This indicates that axial displacement was in an upward direction and therefore $\alpha_R < \alpha_N$. The curves of Figures 6 and 7 allow the values of α_R and α_N to be evaluated as follows.

The axis of the centering rod is perfectly aligned with the axis of the cold body. Similarly well aligned is the bore accommodating the rod in the upper part of the cold body with the axis of the upper cavity. Therefore it can be assumed that eccentricity in a radial direction does not exist and will not be introduced by temperature changes. The curve of Figure 5 therefore gives only the change of capacitance with axial displacement - and the curves of Figures 6 and 7 are influenced by eccentricity in axial direction only. In the neighborhood of the minimum value the curve of Figure 5 can be represented by an equation which results from eccentricity in the spherical part of the arrangement only as was proved in Ref. (8)

$$(C_e)_{\text{total}} = (C_e)_{\text{sphere}} + (C_o)_{\text{cyl.}} \quad (6)$$

where the subscript e refers to axial eccentricity and the subscript o to zero eccentricity and

$$(C_e)_{\text{sphere}} = (C_o)_{\text{sphere}} \left[1 + 2 \left(\frac{d}{D(D-d)} \right)^2 e^2 \right] \quad (7)$$

is the capacitance of the spherical arrangement influenced by eccentricity, neglecting higher order terms. $(C_o)_{\text{sphere}}$ is the capacitance value of the spherical part of $(C_o)_{\text{total}}$ of Figure 5.

The C_e value observed at 25°C in Figure 7 yields from Figure 5 or eq. 6 and 7 the initial axial displacement. The capacitance

values observed in the temperature range of Figure 6 and 7 introduced into equations 1, 5, 6 and 7 allow the thermal expansion coefficients of the centering rod and of the Nimonic 80A wall material of the instrument to be determined - at any temperature. Since the computation is quite involved only averaged values (0 - 100°C) were calculated with the results.

$$\alpha_N = 12.56 \times 10^{-6} (\text{°K})^{-1}$$

$$\alpha_R = 12.02 \times 10^{-6} (\text{°K})^{-1}$$

Of these two values only α_N is of interest to the measurements with the multi-purpose instrument mainly for reasons to correct the volume of the test fluid enclosed within the cell when p-v-T, thermal expansion and compressibility are determined as function of temperature.

A literature value of thermal expansion coefficient of Nimonic 80A (9) is

$$\alpha_N = 11.9 \times 10^{-6} (\text{°K})^{-1}$$

and deviates from the value given above by approximately 5%. The walls of the multi-purpose instrument as shown in Figure 1 are lined at its wetted surfaces by a 1 mm thick gold layer. Taking the thermal expansion coefficient of gold $\alpha_g = 14 \times 10^{-6} (\text{°K})^{-1}$ into account will yield for the combined structure a higher coefficient which is in very good agreement with the value computed from the measurement.

The averaging procedure followed for the computation introduces a certain degree of uncertainty. But this error is small enough to be neglected.

3A3 Determination of the Volume of the Instrument Accomodating the Test Fluids

The multi-purpose instrument as discussed in section 2 is operated either with the test fluid connected to outside instrumentation or hermetically sealed. This is accomplished by using two different valve arrangements seated differently into the lower part of the cold body. The valve shown in Figure 1 is seated at a location close to the lower spherical cavity. In this condition the test fluid is connected with the outside. In case p-v-T data will be observed or other properties under constant volume conditions another valve is used which is then seated at a somewhat lower location and at a wider rim. The instrument can be evacuated by means of this valve and test fluid either can be charged into the cell through this valve or by means of the feed-in device. After charging both devices will be sealed off. The pressure of the sample is then measured by means of the pressure measuring device which is at the temperature of the test fluid and its readings therefore cannot be influenced by condensation and/or evaporation.

The volume occupied by the test fluid within the instrument under these different sealing conditions must be precisely known. They were determined by measuring the volume of mercury necessary to replace a gas which fills the instrument from vacuum to a pre-set pressure. The arrangement is shown in Figure 8. The two self-explanatory steps of measurements yield the unknown volume

FIG 8 ARRANGEMENT FOR MEASURING VOLUME OF MPI

- a., Valve seated at upper rim: $V_L = 83.8730 \text{ cm}^3 \pm 0.0018 \text{ cm}^3$
 b., Valve seated at lower rim: $V_V^L = 84.2284 \text{ cm}^3 \pm 0.0007 \text{ cm}^3$

These values can be corrected for other temperatures by means of α_N .

Together with the geometric constant the most important properties of the instrument itself are therefore known and properties of test samples can be determined absolutely and with a high accuracy. Obviously in addition it is necessary to determine changes of volume and of geometric constant with pressure. Due to the complexity of the geometry only an estimate can be made analytically.

For this it was assumed that the volume of the cell is enclosed in a cylinder of inside bore equal in diameter to the bore of the upper cavity and of identical wall thickness.

For an infinitely long cylinder (inside pressure $p_i = p$ outside pressure $p_o = 0$)

$$\frac{\Delta r}{r_i} = \frac{1}{E} (\sigma_t - \nu \sigma_r) = \frac{p}{E} \left[\frac{(r_o/r_i)^2 + 1}{(r_o/r_i)^2 - 1} + \nu \right] \quad (9)$$

where r_i = inside radius = 17.5 mm
 r_o = outside radius = 45 mm
 E = module of elasticity = $1.9 \times 10^6 \text{ kp/cm}^2$
 ν = Poisson's ratio = 0.3

For $p = 500 \text{ at}$

according to the equation

$$V = \frac{M_1 - M_2}{\rho} \quad (8)$$

where M_1 is the mass of mercury of density ρ observed in the reservoir at step 1 and M_2 the mass remaining in the reservoir after the mercury piston did compress the gas charging the instrument to the original pressure p_2 . M_1 and M_2 were determined with the aid of a precision balance which readings were corrected for buoyancy.

The dotted lines surrounding the experimental setup represent an isothermal envelope. In the present case the laboratory itself was maintained by controlled heating and cooling at a temperature of 28.15°C . The volumes observed at this temperature are:

$$\frac{\Delta r}{r} = 4.36 \times 10^{-4} \text{ and}$$

$$\frac{\Delta V}{V} = 8.72 \times 10^{-4}$$

The change of volume is less than .1% and will be approximately .1% when the change of volume of the hot body is included.

The real volume change with pressure will be smaller for reasons of the heavier walls of the spherical cavity which occupies approximately 75% of the total volume.

The remaining uncertainties in determining the volume as a function of internal pressure therefore might be of the order of a few hundredths of a percent at highest pressure and negligibly small at lower pressures.

The situation is much more critical in respect to the geometric constant because Δr is relatively large compared to the layer of test fluid. Together with the decrease of diameter of hot body the total increase in width will be 2.6% at 500 at. This large influence necessitates a more careful evaluation as follows.

Equation 1 can be rewritten

$$B_2 = 2\pi \left[\frac{\sqrt{h_{c2}} \cdot \sqrt{h_{h2}}}{\ln D_2/d_2} + \frac{D_2 \cdot d_2}{D_2 \cdot d_2} \right] \quad (10)$$

the subscript 2 refers to the dimensions of hot and cold body under a different pressure than when B was determined. B_2 cannot be analyzed properly but it can be determined by measurements of capacitance with a test fluid of known dielectric constant at two (or more) different pressures.

$$C_1 = B_1 \epsilon_0 \epsilon_1 \quad \text{observed at pressure } p_1 \text{ (preferably 1 at - since } \epsilon_1 \text{ is known)}$$

$$C_2 = B_2 \epsilon_0 \epsilon_2 \quad \text{observed at pressure } p_2$$

Introducing $B_2 = \beta B_1$ yields

$$\beta = \frac{C_2 \epsilon_1}{C_1 \epsilon_2} \quad (11)$$

Measurements with helium at 1 and 15 at and 20°C resulted in

$$\beta = \frac{156.878 \times 1.000065}{156.913 \times 1.000650} = .99919$$

where ϵ_2 was evaluated from ϵ_1 by assuming perfect gas behavior. β indicates a decrease in geometric constant by .08%. Linear extrapolation to 500 at. yields 2.69% a slightly higher value than estimated above which is understandable because the analysis regarded only changes in radial direction.

If the change of dimensions of each of the terms in equation (10) could be evaluated properly in terms of p and E the latter one could be evaluated. But only when the pressure does not introduce eccentricity in the arrangement.

The measurements of β will include possible eccentricities which are only a function of geometry and properties of the instrument and the pressure forces. β itself therefore is a property of the instrument and must be remeasurable under identical pressures independent of the test substance, as long as the respective fluid is ideal and ϵ_2 can be computed properly. If measurements with a gas do not reproduce β than the gas is not ideal and the deviation in β is a measure of the deviation from perfect gas conditions for this sample at the respective pressure.

Since E is practically temperature independent β will remain constant with temperature when corrected for thermal expansion. The change of geometry with pressure observed above can be used to determine a pressure coefficient of B by introducing

$$B_2 = B_1 (1 - \alpha_p \Delta P) \quad (12)$$

which yields with β

$$\alpha_p = 57.9 \times 10^{-6} / \text{at}$$

Changing pressures from 1 at to vacuum will result in an increase of B . Whenever a gas of susceptibility $= 57.9 \times 10^{-6}$ is in the system then changing the pressure from 1 at to vacuum will not change the capacitance despite the fact that the dielectric constant of the gas decreases to unity. For gases having a susceptibility smaller than 57.9×10^{-6} the capacitance of the evacuated system will be larger than at 1 at. This effect was observed with the multi-purpose instrument at elevated temperatures and helium as the test gas.

The temperatures as already stated above are measured by means of resistance thermometers made out of standard grade platinum. Those thermometers mounted and sealed securely into the instrument were calibrated in place. The properties observed were used to compute tables with one thousandths of a degree Kelvin interval.

The properties of the thermometers are:

Standard	R_0	$= 25.6168 \text{ Ohm}$
	α_0	$= 0.003924846$
	δ	$= 1.55367$
	β	$= 0.110$
Hot Body	R_0	$= 1.62968 \text{ Ohm}$
	α_0	$= 0.003919673$
	δ	$= 1.61647$
	β	$= 0.110$
Cold Body	R_0	$= 1.73489 \text{ Ohm}$
	α_0	$= 0.003912994$
	δ	$= 1.59571$
	β	$= 0.110$

The pressure is measured by means of mercury or water manometers, by calibrated Heise gauges and by a pressure balance. Unfortunately the pressure balance only covers the range 250 to 500 atm. The measurements of this report were restricted for small pressure ranges whenever precision in the readings were necessary. It is hoped that funds become available to cover the total range of pressure measurements with more sensitive and reliable instruments. The pressure measuring device mentioned above observes the pressure

indirectly by means of a diaphragm opening and closing an electrical contact. At contact position the diaphragm is very sensitive but due to the fact that it was not perfectly flat when mounted into the device a slight pressure differential must be overcome first. This value has been determined and is known to a fraction of .1 mm Hg for the temperature range of the measurements.

3B Determination of Various Properties of Selected Substances

3B1 Thermal Conductivity of Helium at 20 and 30°C in a Range of Pressure

The measurements of thermal conductivity were the most critical ones for reasons that they not only check a considerable part of the total system but most of all the quality of the gold bond. Values observed too low would indicate a faulty bond for reasons of apparently too high values of temperature difference. An unsufficient and/or non-uniform bond obviously would in addition influence or possibly even prevent the measurements of most of the other properties. It was therefore a great relief when the first value of thermal conductivity ever measured with the multi-purpose instrument was identical to the data given in Ref. (10). Further measurements under increasing and decreasing pressure agreed very satisfactorily with the well established pressure dependence of helium for the two isotherms. The hump in the curve observed first in (10) seems to be verified by the measurements. The data given in Figure 9 were computed from the measurements of ΔT between hot and cold body and the power input q and the geometric constant at the respective temperatures from Fourier's Law.

$$k = \frac{q}{B\Delta T} \quad (13)$$

B was correct for change with pressure and for the influence of $T_h > T_c$ other corrections were not applied for reasons that radiant heat transfer between the highly polished gold surfaces is very small in this temperature range. Free convection practically does not exist because of very low Rayleigh number, and lead-in losses also are very small in accordance with Ref. (11).

To the best knowledge of the author it is the first time that correction of temperature drop in the walls are also not necessary. Due to the proper mounting of the thermometers, the true surface temperature existing at the regions outside the ranges of homogeneous heat flow in the wall is measured. This was proved in (1 and 12). In (12) it was also shown that the disturbances of the heat flow by the sensing elements in the walls does influence the geometric constant by only a negligibly small amount.

FIG.9 THERMAL CONDUCTIVITY OF HELIUM GAS vs PRESSURE

The data in Figure 9 scatter by .2% around the smooth curve. This scatter possibly results from the fact that after each pressure change not enough time was allowed to reestablish thermodynamic equilibrium. This was proved by measuring the time needed by the gas to reach its original temperature after a pressure change. The instrument itself was kept at a constant temperature. The time observed was approximately equal the time normally allowed between the readings taken at different pressures. Providing more time resulted in a much less scatter as demonstrated for the 30°C isotherm of Figure 9.

3B2 Measurements of Dielectric Constant, Thermal Conductivity and p-v-T Data of Nitrogen at Three Constant Densities in a Temperature Range 0 - 100°C. And Evaluation of Susceptibility, Polarizability and Index of Refraction.

The instrument was evacuated and pressurized several times with high purity nitrogen gas and finally sealed hermetically after enough mass had entered to establish a certain pressure at ambient temperature. After equilibrium was established pressure and temperature were recorded and the capacitance measured. Power was then provided for the heater coil in order to establish a steady state temperature difference for the measurements of thermal conductivity. This procedure was repeated stepwise under increasing temperatures up to 100°C and then under decreasing temperatures until 0°C was reached. Finally the measurements taken at ambient

Fig 10 Pressure & Dielectric Constant Of Nitrogen Vs. Temperature At Constant Density

Fig 11 Pressure & Dielectric Constant Of Nitrogen Vs. Temperature At Constant Density

conditions were repeated. Identical results of the readings especially in respect to pressure gave assurance that the system had been sealed perfectly. All measurements therefore were taken at constant mass conditions. The valve was then opened and the instrument was charged with additional mass of nitrogen and a second set of data taken in a similar way as demonstrated above.

The pressures observed were corrected for the volume change of the instrument due to thermal expansion. Therefore the curves given in Figures 10, 11 and 12 refer to constant density conditions. The density values were calculated by means of thermodynamic relationships. Normally it is anticipated to determine the mass introduced into the system before and/or after the test.

The pressure curves appear to be linear in the

Fig 12 Pressure & Dielectric Constant Of Nitrogen Vs Temperature At Constant Density

Fig 13 Thermal Conductivity Of Nitrogen At Pressures Of 0.2 To 14 Atm VS Temperature

graphs but the data demonstrate for each plot a different curvature which will be used later and when more measurements have been completed to evaluate compressibility factors and virial coefficients. The same figures show also the measurements of the dielectric constant. Those values remain practically constant with temperature as was expected. The scatter of the values is very small and mainly caused by small deviation from thermodynamic equilibrium conditions i.e., the temperature of hot and cold bodies were not identical. Temperature differences of the order of one hundredths of a degree will influence the readings of ϵ by one thousandths of one percent. For hot body warmer than cold body ϵ apparently will be higher.

A similarly small temperature deviation of the temperature difference will cause errors in thermal conductivity of the order of 1 percent. Which demonstrates again that those measurements are much more difficult to achieve and much more

attention is necessary. The thermal conductivity data observed at the three different values of density are represented in Figure 13 by a single curve. Each point on the curve represents an averaged value of the data measured under the three density conditions and at the respective temperatures. The deviation between the readings were small and of the order of a few tenths of a percent. The thermal conductivity of nitrogen therefore can be reported as pressure independent in the small pressure range of the measurements and within the accuracy of the determination. The values agree very well with NBS data (13) but are approximately one percent higher than recommended by TPRC (14).

From the values of dielectric constant and density the specific susceptibility the polarizability and index of refraction can be computed.

The constant density measurements of p and ϵ taken close to atmospheric conditions as shown in Figure 11 resulted in a value of

susceptibility

$$\epsilon - 1 = 605 \times 10^{-6}$$

Applying the relationship

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = \frac{4\pi}{3} N_L \alpha \quad (14)$$

allows to evaluate the polarizability of nitrogen. With $M = 28$ the molecular weight of nitrogen $\rho = 1.2723 \text{ kg/m}^3$ the density and $N_L = 2.68719 \times 10^{25}/\text{m}^3$ Loschmidt's number one obtains

$$\alpha = 17.58 \times 10^{-25} \text{ cm}^3$$

which is practically identical to the value of $17.6 \times 10^{-25} \text{ cm}^3$ given in the literature.

The pressure observed under constant density conditions at 20°C was 829.4 mm Hg. Reducing the value for comparison reasons to 760 mm Hg yields

$$(\epsilon)_{20^\circ\text{C}, 760} = 1.000554$$

which deviates only by 6 ppm from the value given in NBS circular 537.

According to Maxwell

$$n^2 = \epsilon \quad (15)$$

and

$$(n)_{20, 760} = 1.000277$$

This value reduces for comparison reasons to 0°C yields

$$(n)_{0, 760} = 1.000297$$

which again is in agreement with data listed in Smithsonian tables.

3B3 Determination of Thermal Conductivity and Dielectric Constant of Octafluorocyclobutane C_4F_8 - Vapor at 1 atm in the Range of Temperature 0 - 100°C

The vapor thermal conductivity of this substance is known only for a single point which is in large disagreement with data estimated later. The test material used for the investigation is of "Food-grade" purity and was furnished by DuPont under the trade name Freon C-318. The measurements were carried out under increasing and decreasing temperatures by holding the pressure constant at 760 Torr.

The values of thermal conductivity and dielectric constant observed are

given in Figure 14. The thermal conductivity curve agrees in curvature and slope with the estimated temperature dependence shown in DuPont's Bulletin C-30A. The values of conductivity measured are lower by 2%. The single point given in Bulletin EL-1 is lower by 15 resp. 17%.

The measured values of dielectric constant decrease with temperature due to the decrease in density. The data practically have no scatter around the smooth curve but the one point observed close to saturation condition. A single literature value (15) observed at 283.16 °K agrees with the measured data within a few thousandths of a percent.

3B4 Vapor Pressure Measurements of Methanol* in the Temperature Range 0 - 100°C

The instrument was first filled with vapor and evacuated repeatedly. After high purity conditions of the vapor could be expected within the cell an additional small amount of sample in liquid form was charged into the instrument which then was sealed hermetically. The vapor pressure was determined by means of the diaphragm device and a mercury manometer.

The pressures observed under increasing and decreasing temperatures in a first run were higher than values cited in physical tables (16). This disagreement could have been a result of leakage of air into the system at low temperatures i.e., low pressure conditions. But this was ruled out by remeasuring exactly the value which had been taken at low pressure and before the temperature had been raised. Since the literature data were regarded as correct and because the measurements of pressure cannot be faulty by the amount observed only the test fluid itself must have provided the conditions for the different readings.

The correctness of this reasoning easily could be checked by measuring other properties of the vapor known at certain conditions. The measurements of thermal conductivity and dielectric constant at these respective conditions yielded results which did not agree with literature data. In case of thermal conductivity the value measured was too high; the dielectric constant was too low. Both results indicate that not pure vapor but a mixture possibly with moist air was present. (This demonstrates one of the features of the multi-purpose instrument; namely that the measurements of more than one property allow checking if anomalies or deviations observed in one of the properties really exist.)

The methanol was delivered in a bottle not sealed hermetically and it must be assumed that moist air and/or other gases were absorbed by the fluid in time. Boiling of the sample at low temperature yielded better results of the vapor pressure which are still slightly higher than the table values represented by the solid curve in Figure 15 but they are in a very good agreement with newer data (17).

The solid curve is represented in accordance with (16) by an equation based on four references.

* Purity 99.96% (Impurities: .039% H₂O
.001% acetone
.002% CH₃OH)

Fig. 15 Vapor Pressure Of Methanol

$$\log p = - \frac{0.05223a}{T[^\circ K]} + b \quad (16)$$

where the constants are

$$a = 38.324$$

$$b = 8.8017$$

The data of (17) are based on more information (thirty two references) which resulted in

$$\log p = - \frac{a}{c + t[^\circ C]} + b \quad (17)$$

when

$$a = 1474.08$$

$$b = 7.89750$$

$$c = 229.13$$

3B5 Determination of Thermal Conductivity, Dielectric Constant, Electrical Conductivity and Dissipation Factor of C_4F_8 Liquid at 15 at in the Temperature Range 0 - 80°C.

The instrument first was filled with pure vapor under vacuum and then connected by means of a valve to a reservoir containing the test substance under its vapor pressure - which forced the liquid to enter the system. The decrease of weight of the reservoir was observed and when the conditions of complete charging was assured the liquid in the reservoir was pressurized further to 15 at. with nitrogen. All the measurements were carried out under constant pressure at 15 at. assuring that boiling could not occur at the highest test temperature.

Fig 16 Thermal Conductivity & Dielectric Constant Of C_4F_8 Liquid At 15 Atm

The reservoir is connected with the cell by high pressure tubing of small inside bore and of such a length that the liquid within the instrument will not be contaminated by diffusion of N_2 even in a very long time.

The observations of the properties were carried out by measuring heat input ΔT and/or capacitance and computing the properties

with the respective equations and the geometric constant corrected for pressure and temperature. The results are given in Figure 16. It can be seen that ϵ and k decrease with temperature but the curves have opposite curvature.

The thermal conductivity data are in very good agreement with values observed at lower pressures and listed in (18, 19). The simple observation by (18) is identical to the data of the curve at the respective temperature. The values of (19) are a few tenths of a percent higher than the present data.

Measuring the capacitance necessitates balancing the bridge for dissipation. The dissipation factor is observed by direct read-out of the bridge.

The conductance bridge connected by means of the masterswitch to the system measures directly the conductance

$$G = \lambda \frac{A}{L} = \lambda B$$

From this the d.c. electrical conductivity λ is obtained.

Dissipation (observed at 1 kHz) and electrical conductivity are of very low value as can be seen in Figure 17. Dissipation and electrical conductivity remain practically constant in the low temperature range.

At temperatures above 40°C measurements were difficult to obtain for reasons of fluctuations in the readings. The values of the properties increase as indicated by the dotted lines. These lines represent readings averaged over the range of fluctuation and must be regarded as inaccurate to a certain degree.

The unstable measurements could be a result of impurities introduced into the liquid. The impurities might be minute residues of previous test samples which had remained on the walls. They became dissolved by the Freon in time and the particles started to move under the influence of the electrical field at higher temperature when the viscosity became low enough.

3B6 Determination of Thermal Expansion Coefficient of Liquid Benzene at 1 at. at Various Temperatures

The instrument was filled completely with the liquid in the same way as described above. The cell was then prepared for the

Fig 17 Electrical Conductivity And Dissipation Factor Of C_6H_6 At 15 Atm VS Temperature

Fig 18 Thermal Expansion Coefficient Of C_6H_6 VS. Temperature

Fig 19 Multipurpose instrument used in transient conditions to determine thermal diffusivity of test fluids

measurements simply by closing the valve at the reservoir. The liquid within the cell is now only connected with a pressure balance arrangement. The free piston properly loaded maintains the pressure in the test fluid. Measuring the motion of the piston when the temperature of the instrument is changed by a value of ΔT allows to evaluate the thermal expansion coefficient from the volume displaced and the volume of the instrument V_L at the respective pressure and temperature.

The measurements were carried out at several temperature levels.

Since the motion of the piston is limited to approximately 2 cm and because the volume displaced is rather small it is necessary to bleed some of the liquid back into the reservoir (at a slightly lower pressure) in order to bring and hold the piston in proper starting position. Obviously the smaller the amount of liquid released the smaller the temperature increments between the measurements.

Fig 20 Schematics of $T=f(t)$ for hot and cold bodies and $C=f(T,t)$ for case a, test fluid is a perfect insulator

Fig 21 Schematics of $T=f(t)$ for hot and cold bodies and $C=f(T,t)$ for case b, test fluid is a perfect conductor

Fig 22 Schematics of $T=f(t)$ for hot and cold bodies and $C=f(T,t)$ for case c, test fluid is a finite conductor

The values measured at different temperatures are given in Figure 18. The solid curve represents data of physical tables. The measured points scatter around this curve by a few tenths of a percent.

4. UNSTEADY STATE EXPERIMENTS

Under section 2 of this paper it was pointed out that the multi-purpose instrument can also be used under conditions other than steady state. In this paper only the procedure for the unsteady observation of one property is included.

The procedures followed to determine thermal diffusivity (and conductivity) represents a novelty in measuring thermal properties

and heat flow (i.e., heat transfer) insofar as the observations are carried out in the absence of temperature measurements. But by very sensitive observation of other quantities depending on true surface conditions which otherwise can be determined inaccurately or indirectly only.

A short description of the technique is included for the sake of demonstration. A detailed analysis will be given elsewhere (20).

The technique easily can be followed as demonstrated in Figures 19, 20, 21 and 22. Figure 19 shows schematically a cross-section through the multi-purpose instrument. Hot body and cold body are properly connected to the capacitance bridge. The cold body originally is kept at a constant temperature T_0 by means of the thermostat. At time $t = 0$ the thermostat begins to heat (or cool) the cold body continuously or to a new steady value T . The test fluid enclosed in the gap between hot and cold body is considered to be:

- a. a perfect insulator
- b. a perfect conductor
- c. a finite conductor.

The heat input to the cold body obviously never will be noticed by the hot body when the test fluid is a perfect insulator. For a perfect conductor it will change its temperature simultaneously with the cold body. In case of a real substance the hot body will follow after a certain time lag the temperature change of the cold body.

The temperature change experienced by the two bodies under constant or limited heating are given schematically in Figure 20, 21 and 22. (Under cooling the effects will be similar.)

The temperature change within each of the two bodies will be uniform (therefore identical the change of surface temperature) for sufficiently small Bi-numbers. The poor heat transfer of the thermostat fluid guarantees those conditions. The dimensions of the bodies change therefore with temperature only due to thermal expansion. (Changes due to stress can be neglected.) Eq. 1 demonstrates that the change of dimension will cause a change of capacitance. These capacitance changes are given schematically also in Figures 20, 21 and 22 for the respective test fluids.

4.1 Determination of Thermal Transport Properties of Helium, Nitrogen, and Argon at 1 at. and Vacuum in a Small Temperature Range

For four different cases where the heat transfer between the two bodies varied from good to poor the method has been checked by using as test substances helium, nitrogen, argon and vacuum. In the latter case heat transfer occurs only along the centering rod, by radiation and residual molecular conduction.

The results of the measurements are given in Figure 23. The change in capacitance observed verifies the change predicted in Figure 22. (The initial and final capacitance values of each curve divided by the C_0 -value of Figure 6 yield the dielectric constant of the test substance at the respective temperatures.) The maximum change in capacitance measured in helium is approximately one order of magnitude less than in the case of vacuum and

Fig 23 Change Of Capacitance With Time Of MPI For The Measurement Of Thermal Diffusivity Of Fluids

new steady state conditions were established five times faster.

The maximum capacitance change observed in helium is of the order of .05%. This accounts for a similar change in gap width (nominal .5 mm) of 2.5×10^{-4} mm. If one assumes that the maximum change occurred at a time when the cold body only had changed in temperature than its excess temperature was approximately 1°C . (Free convection can be assumed negligibly small.)

This is the maximum temperature difference between cold and hot bodies. In accordance with Figure 22 it will decrease in time and finally become zero.

The sensitivity of the instrumentation is so high that change of capacitance of the order of .001% can be detected. This refers to a change in gap width of the order of 5×10^{-6} mm which in turn is identical to the change in diameter the cold body will experience when heated by $2 \times 10^{-2}^{\circ}\text{C}$.

The capacitance time curves observed are perfectly similar and can be made to form a single curve by proper reduction. Due to the complexity of the geometry an analysis is impossible. Therefore calibration becomes necessary and the measurements will be relative ones only.

Another system of simple geometry easily could be built which could be made of lesser heat capacity. Absolute and much faster measurements would then be possible.

The measurements by this technique* utilize electrical observations directly. This demonstrates the advantage of using it for remote control measurements of heat transfer and properties in many instances. Since diffusivity, thermal conductivity and dielectric constant are observed simultaneously the measurements also could be used for quality control and/or to determine the test substance itself in cases the sample is not known before hand.

The analysis of the technique and more detailed information of its use are outside the scope of this report - and will be given in another paper as already stated above.

5. SUMMARY AND FUTURE PROGRAM

The measurements of the various properties carried out so far have indicated that the data observed compare favorably with literature values of separately measured properties. It is safe to assume that the determination of the properties of the instrument and instrument material in all cases did aid the research on test fluids. In some of the cases it was demonstrated that the capability to measure more than one property under perfectly identical conditions is of advantage to determine other properties more reliably. It is hoped that the statements hold true in respect to the other properties which also can be determined with the instrument. This will be investigated shortly. Neglecting initial costs for the more complex and more involved experimental total set-up it also seems to be reasonable to state the measurements with a multi-purpose instrument will produce properties more cheaply.

* patent disclosed by W. Leidenfrost

For the future it is planned to determine properties of gases of different molecular structure and over wider ranges of pressure and temperature for theoretical studies. Selected liquids will be tested in respect to their heat transfer and electrical qualities in order to establish their suitability as coolants of powerful compact electronic devices. It is furthermore anticipated to develop instruments applying the transient technique described under section 4.

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Low Conductivity Methods

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On the Mechanism of Thermal Conductance Between Metal
Surfaces in Contact

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A theoretical analysis of a thermal contact is first carried out on the assumption that the asperities are cones the angle of which depends on the surface roughness. To check the validity of the theory and also to determine the effects of surface films and the plastic deformations of asperities at the interfaces of contact, the electrical contact resistances for a conical indenter with various apical angles on a smooth flat surface are measured under light applied load. The deviation of the measured values with silver from theoretical ones suggests that the real contact area through which the electric current passes is smaller than that estimated from the flow pressure of the metal for a given applied load. The results as above mentioned are also observed for two flat silver surfaces in contact and for any combination of metals besides silver.

To further check the validity of the theory in estimation of the thermal contact resistance, the resistances between two flat surfaces of silver and other metals are measured in a vacuum vessel. A comparison of calculated values based on the theory with experimental data shows good agreement.

Effect of thermal radiation on thermal conductivity of insulation with respect to its thickness.

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Measurement of thermal conductivity of insulating materials was made by the author with respect to various thickness of samples of the same material by the method of comparison under the condition kept so as to eliminate convection of the air existing in the samples.

According to the result of the experiment, at the point of specific thickness the thermal conductivity of the material shows its maximum value among all throughout the range of measurement.

Above phenomena is due to the effect of radiation in the material. After the experiment on many actual insulating materials and model insulation which was made for the purpose to clear the effect of radiation, the author suggests the following new formula of thermal conductivity:

$$\lambda = \lambda_{sg} + \frac{4}{100} \left(\frac{T_m}{100} \right)^3 B t e^{-x f t}$$

Where: λ = Thermal conductivity of insulation in kcal/mh°C.
 λ_{sg} = Thermal conductivity of insulation, except radiation effect, it means thermal conductivity of the same material of large thickness of insulation in kcal/mh°C.
 T_m = Mean temperature of insulation in °K.
 t = Thickness of insulation in m.
 f = Volume fraction of insulation.
 B, x = Experimental factors.

X A Study of Some of the Factors
Affecting Thermal Properties in
Packed Bed Systems

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Abstract

Thermal property studies of vibratory compacted materials have shown a definite increase in conductivity with increase in density for a given material. This effect may, also, be described as a function of the decrease in porosity of the composite system, porosity being the percent void fraction. In order to examine the surface contact resistance and other effects an investigation has been conducted using similar particles of a material in various size ranges varying both the size and the mixture of sizes used. An effort is made to relate the observed changes in thermal properties on the basis of parameters of the packed bed system.

The experimental study was carried out in connection with the problem of selecting the most appropriate fuel material makeup for the proposed fast reactor fuel assemblies. Parameters are needed to determine the optimum design for these elements from both the thermal and mechanical property points of view. Studies of the effect of the number of contact points and condition of these contact points are examples of the parametric studies which are important in this area.

Measurements were made using a special apparatus described elsewhere (1). This system uses a plane heat source which allowed the materials of the various sizes and combinations of sizes to be packed into the test chamber and mechanically vibrated to assure complete and uniform loading. Glass beads were chosen as the material since accurately sized particles of uniform quality can be easily obtained. Particles ranging in size from -6 +9 to -40 + 50 mesh size were used in the tests. All results reported are from tests made at room temperature using air as the coupling gas.

I. Introduction

Nuclear fuel elements loaded with spherical or granular fuel material packed by vibratory techniques offer advantages both in fabrication and in nuclear performance. On the other hand lower effective thermal conductivities of these elements when compared to solid pellets are a distinct disadvantage. Higher center-line temperatures are required in the packed fuel for the same

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²This work was done under the auspices of the U.S.A.E.C.

heat transferred. With the emphasis on maximum heat transfer to reduce core size every advantage must be used in the design of high performance fuel elements. Parameters connected with the various mechanisms such as the solid to solid contact take on a new level of importance.

The major factors affecting thermal transport in an unconsolidated fuel particle bed can be examined by analysis of the results of experiments with other solid-gas systems. It is generally agreed that the transport of thermal energy in an unconsolidated bed occurs by four basic mechanisms:

1. Through the gas phase via interconnecting all gas channels.
2. Through a series path, solid-gas-solid.
3. Through the solid phase by conduction across the contact points.
4. By radiant exchange between the solid surfaces and to a lesser extent between the solid and the fluid.

Figure 1. Model for Spherical Contact Areas

Most experiments on packed bed systems neglect radiation. However, at high temperatures such as we find in some nuclear fuel applications, radiation could be a major contributor to heat flow. We will assume radiant heat transfer is negligible for this study of the solid to solid transport mechanism.

Of the other three mechanisms or paths the first two have been widely studied in connection with chemical processing and other chemical engineering applications. (2,3,4) Mechanism three will be the object of this report. Two basic variables will be investigated. First, the number of contact points will be studied using the same void fraction by changing particle sizes. Secondly, the number of contact points will be increased by infiltrating a fine material into a larger particle system. This process also increases the density of the packed bed. Glass beads of three sizes (44 microns, μ , 125 μ , 350 μ) were used as the solid phase and tests were run in an air at 10^{-2} Torr and at atmospheric pressure.

II. Theoretical Considerations of Thermal Transport in Unconsolidated Porous Media

A theoretical expression for the effective thermal conductivity in a porous bed is reported by Masamune and Smith (1). Contributions by each of the first three mechanisms are included.

$$\lambda_{\text{eff}} = \gamma \epsilon \lambda_g + \frac{(1-\gamma\epsilon)(1-\delta)}{\frac{\phi}{\lambda_g^*} + \frac{1-\phi}{\lambda_s}} + (1-\gamma\epsilon) \delta \lambda_s \quad (1)$$

Where γ , δ and ϕ are dimensionless parameters; ϵ is the void fraction; λ_s and λ_g are the respective conductivities of the solid and the gas; and λ_g^* is an appropriate conductivity in the gas phase near the contact areas of adjacent solid particles.

Masamune (1) reports expressions for γ and ϕ in terms of the void fraction, ϵ , and the number of contact points, n , on a hemispheric particle (4).

$$\phi = [n] (\sec \theta_2 - 1)^2 \left[1 - \left(\frac{\pi}{2} - \theta_2\right) \tan \theta_2\right] \quad (2)$$

$$n = 6.93 - 5.51 \frac{\epsilon - 0.260}{0.476 - 0.260} \quad (3)$$

$$\theta_2 = \cos^{-1} \left(1 - \frac{1}{n}\right) \quad (4)$$

$$\gamma = 1 - \frac{3}{2} \left(\frac{1-\epsilon}{\epsilon}\right) \phi \quad (5)$$

The void fraction, ϵ , can be determined from weighing the amount of material and knowing the measurements of the test container. δ is the parameter which gives the ratio of the contact area to the surface area of the half-bead. See Figure 1.

$$\begin{aligned} \delta &= \frac{n \pi R^2 \sin^2 \theta_1}{\pi R^2} \\ &= n \sin^2 \theta_1 \end{aligned} \quad (6)$$

where R is the radius of the bead, n , the number of contact points, and θ , the angle subtended by the center of the contact area and the perimeter of the contact area. δ can also be related to the conductivity under vacuum conditions (1) since then,

$$\delta = \frac{1}{1-\gamma\epsilon} \cdot \frac{\lambda_{\text{eff}}}{\lambda_s} \quad (7)$$

The above equations provide a method to calculate the effective conductivity based primarily on the void fraction. Table I shows the results of such

Table I

Theoretical Thermal Conductivities for Glass Spheres

ϵ	Mechanism I w/mK x 10	Mechanism II w/mK x 10	Mechanism III w/mK x 10	Total w/mK x 10
0.172	1.76×10^{-4}	2.37×10^{-2}	3.56×10^{-3}	2.75×10^{-2}
0.204	1.67×10^{-4}	2.33×10^{-2}	3.56×10^{-3}	2.71×10^{-2}
0.279	1.67×10^{-4}	2.02×10^{-2}	3.56×10^{-3}	2.39×10^{-2}
0.351	1.67×10^{-4}	1.68×10^{-2}	3.56×10^{-3}	2.07×10^{-2}
0.352	1.63×10^{-4}	1.71×10^{-2}	3.56×10^{-3}	2.09×10^{-2}
0.378	1.46×10^{-4}	1.71×10^{-2}	3.56×10^{-3}	2.08×10^{-2}
0.401	1.51×10^{-4}	1.52×10^{-2}	3.56×10^{-3}	2.02×10^{-2}

calculations for the glass bead and air system. Since it is possible to pack porous beds of different sized particles to the same void fraction (5), the contact surfaces cannot be accounted for in this model. The number of contact surfaces can be estimated by determining the number of particles per unit volume and multiplying by n , the number of contact points per half sphere. The question is does the introduction of many more parallel heat flow paths actually increase the total heat transferred? The smaller particle used to increase the parallel paths also introduce more surfaces per unit path length of heat flow. Surface contact resistance may overcome any additional advantage of more paths.

III. Experimental System

The test container was a ceramic rectangular box having interior dimensions of 5.08 x 5.08 x 10.16 cm. The heating foil was a rolled sheet of constantan 0.0025 cm thick. The foil was held at the ends in copper bus bars. Temperature recordings were made using a special thin foil iron-constantan thermocouple. This foil was rigidly supported by a ceramic holder which also supported the lead wires. See Figure 2.

The mathematical model used to analyze the data is taken from Carslaw and Jaeger (6) for the case of an infinite solid in transient heating. This model has been discussed elsewhere (7,8) and only the results are reproduced here.

$$\frac{\lambda_{\text{eff}} T(\ell, t)}{Q\ell} = \left[\frac{\alpha t}{\ell^2}\right]^{1/2} \text{ierfc} \left[\frac{\ell^2}{\alpha t}\right]^{1/2} \quad (8)$$

Figure 2. Experimental Test Assembly

$$\frac{T(\ell, 2t)}{T(\ell, t)} = \sqrt{2} \frac{\text{ierfc} \left[\frac{1}{2\sqrt{2}} \left(\frac{\ell^2}{\alpha t} \right)^{1/2} \right]}{\text{ierfc} \left[\frac{1}{2} \left(\frac{\ell^2}{\alpha t} \right)^{1/2} \right]} \quad (9)$$

$T(\ell, t)$ - temperature, Kelvins

ℓ - distance from foil heater to thermocouple, meters

α - diffusivity, meters²/second

t - time, seconds

Q - watts/m²

If the value of $T(\ell, 2t)/T(\ell, t)$ is known for a given time t the value of $\alpha t/\ell^2$ can be found. Since t and ℓ are known the diffusivity, α , can be calculated. The value of $\alpha t/\ell^2$ allows λ_{eff} to be calculated from equation (8) if the heat rate per unit area, Q , is known. Q can be measured by knowing the area of the foil and the current and voltage across the heating foil.

The test specimens were packed into the test assembly using a Syntron vibrator. The smaller spheres were infiltrated into the larger spheres using a special screen weight to prevent levitation of the larger sizes (5).

The vacuum runs were made by placing the test system in a bell jar and evacuating during the test.

IV. Results and Discussion

The experimental results from a series of tests have been compiled and recorded in Table II. These compared to those in Table I for the vacuum tests show that increasing the number of paths for heat flow by reducing particle size does increase the thermal conductivity. Thus, the point contact of the larger spheres does appear to impede thermal transport to a greater degree than the resistance found at the interfaces of the small spheres.

The value of 42×10^{-3} w/mK for the -325 vacuum tests is not as high as the previous tests might indicate. However, the density has been reduced probably indicating that the packing was not complete. We see this effect again in the atmospheric results as the conductivity drops to 186×10^{-3} w/mK from 235×10^{-3} w/mK for the -100 + 140 results.

The theoretical value for the solid heat transfer (mechanism 3) was found to be 35.6×10^{-3} w/mK. This is in excellent agreement with the experimental value of 33×10^{-3} w/mK. Since the model did not account for increase in the number of heat transfer paths due to smaller size, the variation observed in the experimental results requires a refinement in the model used.

The values of diffusivity vary approximately as the thermal conductivity although one must suspect a density effect on the diffusivity for the mixed size results. These density effects have been documented by other experiments results (7).

The important conclusion of this study is that fuel materials in spherical shape, such as the sol-gel fuel, should be fabricated in the smallest possible

Table II

Experiment Values for Thermal Conductivity and Thermal Diffusivity

Particle Size STD. Sieve Size	Void Fraction	10 ⁻² Torr	
		Thermal Conductivity (w/mK) x 10 ³	Thermal Diffusivity (m ² /sec) x 10 ⁴
1) -40 + 50	0.351	33	0.21
2) -100 + 140	0.352	37	0.28
3) -325	0.401	42	0.35
4) -40 + 50 -325	0.279	101	0.71
Atmospheric Pressure		Average Diameter	
Thermal Conductivity w/mK x 10 ³	Thermal Diffusivity (m ² /sec) x 10 ⁴	mm	
1) 170	1.33	0.35	
2) 234	2.40	0.125	
3) 186	1.88	0.044	
4) 302	2.25	—	

sizes which will conveniently pack into a fuel case. This means to obtain theoretical densities of 80 to 90% the largest particle size should probably be about -100 + 140 or slightly smaller. Ayer (5) has discussed the necessary requirements for such fabrication procedures. A design question for the fuel element fabrication process is to specify the two or three smallest compatible sizes of fuel required to get the desired density.

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Grease Thermal Bonds at Liquid Helium Temperatures.*

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The temperature dependence of the thermal conductivity of Apiezon N grease, silicon high vacuum grease, Eccotherm TC-4 (a specially formulated paste based on silicones and fillers), and Cry-Con (a copper loaded grease) has been measured in the liquid helium temperature range. The thermal conductivities were observed to correspond approximately to those of thermal insulators. These results are summarized and employed in a discussion of the use of grease bonds for heat transfer purposes at liquid helium temperatures.

INTRODUCTION

The use of electrically insulating grease to produce thermal bonds at liquid helium temperatures is widespread among researchers. Some have assumed the thermal conductivity of grease to be fairly good. Others have used grease because their experimental method would permit no other substitute. Studies of heat transfer properties of grease at low temperatures have for the most part involved thin films of the grease. Recent observations of the bulk thermal conductivity of several greases in the liquid helium temperature range have been reported to correspond approximately to those of thermal insulators.¹⁻³

SUMMARY OF RECENT RESULTS

A summary of bulk thermal conductivity measurements on four greases which have been used to establish thermal bonds is shown in Fig. 1. References 2 and 3 include details of measurements carried out on grease samples which were packed into thin wall nylon tubes equipped with carbon resistor thermometry. All results in Fig. 1 have been corrected for the thermal shorting effect of the nylon tubes and the thermal contraction of nylon.

Nylon was chosen as a reference for comparison because of the high reproducibility of its low temperature thermal conductivity data, and its wide use as a thermal insulator. Because nylon is frequently used in the construction of specimen holders and other parts of cryogenic apparatus, the low temperature thermal conductivity of nylon has been the subject of investigations over the past 16 years, and the results of these measurements have produced data which are in general quite similar. In fact it has already been noted by Anderson, Reese, and Wheatley⁴ that the agreement of measurements on nylon appears to be independent of the source of the nylon or the sample preparation. Our measurements on nylon support this conclusion. These facts argue in favor of the choice of nylon as a reference standard for low temperature thermal conductivity measurements on thermal insulators.

Fig. 1. A comparison of recent experimental results on the bulk thermal conductivity of various greases, with that of nylon. Nylon is represented by the solid line labeled N; Cry-Con grease by the dashed line C; Ecco-therm TC-4 by the dotted line, E; Vacuum grease by the dashed line, V; the first Apiezon N grease experiment by the open triangles; the second, by the open circles; and the third, by the darkened triangles.

The conductivity of grease, as illustrated in Fig. 1, is influenced by a number of factors and among these, the type of the grease is an important agent. Of the four greases measured, Dow Corning Vacuum Grease and Emerson and Cuming Eccotherm TC-4 grease, both of which are silicon based greases, produced nearly identical results. (See curves E and V of Fig. 1) However the conductivity of Air Products copper loaded Cry-Con grease was observed to yield values almost an order of magnitude higher than the silicone based greases. (Fig. 1 curve C).

In addition, recent measurements on 3 different Apiezon N grease samples have been observed to give quite different results. The experimental procedure was varied in the third Apiezon N grease experiment. (See darkened triangles in Fig. 1) The grease was allowed to cool to nitrogen temperature in an atmosphere of helium before evacuation for isolation. In all of the previous experiments the specimens were subjected to vacuum at room temperatures prior to cooling. The results given by the third Apiezon N experiment indicates that the conductivity of the grease is enhanced by cooling the grease before pumping is begun.³

The rate of cooling and the presence of cracks, or separations in the grease column produces a marked effect on the conductivity. Hence, the cross-sectional area of the grease column may also have some influence on the results. Grease samples for the second and third Apiezon N experiments (open circles and darkened triangles in Fig. 1) possessed an area of 0.495 cm^2 while the grease samples used in earlier experiments, i.e., the first Apiezon N experiment (open triangles) were performed on samples with a cross-sectional area of 0.178 cm^2 . Experiments on larger diameter samples therefore, appear to yield lower conductivities with greater temperature dependencies.

The cracks or separations first observed in Apiezon N grease samples when they are cooled to nitrogen temperatures are approximately isotropic. They grow larger with temperature cycling. A few cycles between room and nitrogen temperature can produce separations greater than half a centimeter in grease columns in which much of the absorbed gas was previously removed by gentle warming to the melting temperature.³ It is obvious that if the cracks grow with temperature cycling then the conductivity will depend on how many cycles have been made prior to the measurement. Therefore reasonable suspicion can be cast at the reproducibility of the Apiezon N results. Since the Cry-Con grease has been noted to be highly resistant to cracking under thermal shock its results are under less suspicion.⁵ The reproducibility of the Cry-Con results has been demonstrated.²

APPLICATIONS

For many applications the thermal conductivity of a grease does not need to be known with great precession. Therefore, an application of these results to some common experiment arrangements can be considered. Two popular usages of grease thermal bonds are shown in Fig. 2. Grease is often used in low temperature experimental arrangements in order to establish thermal contact between small resistance thermometers which have been placed within holes drilled into heat sinks. At other times grease has been used to hold specimens onto heat sinks. It is generally assumed that the thermometer or the specimen is at the same temperature as the heat sink. However, it must be obvious that the actual temperature of the thermometer will depend on the rate at which energy is generated within its volume by the measuring current and the rate at which it is able to effuse the heat to the cold finger. A similar situation exists for the specimen which receives its heat input from a light source. The rate of effusion from either depends on the thermal contact resistance between the thermometer, grease and cold finger, and the thickness, cross-sectional area and thermal conductivity of the grease. If the grease layer between the specimen is not especially thin then for even low light illumination, the specimen temperature can rise several degrees above that of the cold finger leading to a serious error in its temperature. The seriousness of the error in temperature can be

Fig. 2. Two popular low temperature uses for electrically insulating thermal grease.

TABLE I. TABLE OF MINIMUM TEMPERATURE DIFFERENCES BETWEEN HEAT SINK AND SPECIMEN FOR DIFFERENT INPUT POWERS^{a,b}

	Input Powers (mW)		
	0.1 mW	1.0 mW	10.0 mW
4.0 K	0.01 K	0.1 K	1.3 K
	—	—	—
3.5 K	0.02 K	0.2 K	1.6 K
	0.08 K	0.8 K	8.3 K
3.0 K	0.02 K	0.2 K	1.9 K
	0.2 K	1.5 K	15. K
2.5 K	0.03 K	0.3 K	2.5 K
	0.3 K	2.6 K	26. K
2.0 K	0.03 K	0.3 K	3.3 K
	—	—	—
1.5 K	0.05 K	0.5 K	5.3 K
	—	—	—

- a. For $A/L = 10$ cm corresponding to a grease thickness of 0.3 mm.
- b. The first entree in the table represents Cry-Con grease and the second entree represents Dow-Corning Vacuum grease or Emerson and Cuming Eccotherm TC-4 grease.

seen in Table I.

In the table, typical experimental data based only on the results of bulk thermal conductivity measurements of several greases (Dow Corning Vacuum Grease or Emerson and Cuming Eccotherm TC-4 and Air Products Cry-Con grease) was used to obtain minimum temperature differences (between heat sink and specimen) assuming the specimen to be mounted with a grease thickness of 0.3 mm on an area of approximately $1/3$ of a square centimeter of the heat sink. The powers assumed in the table represent medium to low values of typical light sources used in optical measurements. A maximum continuous source might have a value of about 100 milliwatts. However even 10 mW power levels can produce temperature errors of several degrees. For example, the power contained in blackbody radiation at room temperatures on an area of $1/3 \text{ cm}^2$ is about 14 mW. Although we must consider such things as the solid angle, and the spectral region, in many cases it is possible for this long wave length radiation to heat the specimen.

The temperature differences between the cold finger and specimen shown in the table increase as the temperature decreases, because the thermal conductivity of the grease decreases with temperature. It should be noted that entries in the table reflect only the results of the poor thermal conductivity of the grease. That is, they do not include a consideration of the resistance of the boundary, between the heat sink and the grease and between the specimen and the grease, each of which acts, of course, to impede the heat flow. Therefore, the actual temperature difference between the specimen and the heat sink is even greater than that given in the table. It should also be pointed out that the numbers in the table are more accurate for the smaller temperature differences because of the strong temperature dependent thermal conductivity of the grease.

One may conclude from this discussion that careful attention should be given to those occasions where bulk quantities of grease are used to set up low temperature thermal bonds between materials.

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THE THERMAL CONDUCTIVITY OF LiF FROM 80 TO 1100 K*

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ABSTRACT. The thermal conductivity λ of single and polycrystal lithium fluoride was measured between 80 K and the melting point (1118 K) using an absolute longitudinal (80–360 K) and a radial heat flow apparatus (330–1083 K). Our lower temperature results are in excellent agreement with the low temperature data of other investigators. Above 200 K the thermal resistivity λ^{-1} of both specimens shows a linear dependency with temperature. Between 450 and 550 K, however, λ^{-1} of both materials deviates from a straight line. The thermal resistances attain maximum values at about 900 K for the single crystal and 840 K for the polycrystal; and above the temperatures of the maxima, the λ^{-1} values decrease with increasing temperature. The thermal conductivity of the polycrystal sample was higher than that of the single crystal over the entire temperature measurement range, and this difference increased with increasing temperature. These results are analyzed in terms of different radiation conditions in the two samples to provide an estimation of the lattice thermal conductivity of LiF.

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The Thermal Conductivity of some Electrical Engineering Materials

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Transient methods have been used to measure thermal conductivities of laminated core steel and of oil-impregnated paper and press-board. Results obtained show some of the factors affecting these values and their use in the accurate thermal design of electrical machines is illustrated.

Key Words: Contact pressure, electric generators and alternators, electric transformers, electrical steels, electrical insulation, temperature dependence, thermal conductivity, thermal diffusivity, thermal measurements.

1. Introduction

Electrical machines comprise a pair of interlinked circuits, one electrical and one magnetic, separated by an insulation system. Both circuits are metallic, the electrical one of copper or aluminium, the magnetic one of laminated ferromagnetic alloy. Accurate methods are now available for the thermal design of large rotating machines (1)* and high voltage power transformers (2). They can only be fully utilised if accurate thermal conductivities are known for the materials actually used. The limited published data only reveals the extent of their disagreement and emphasises the need for measurement methods suitable for these materials. Two transient methods have been used. The paper describes these and gives data obtained.

2. Magnetic Core Materials

To reduce losses in the parts of the magnetic circuit carrying alternating flux, these are formed from steel laminations. These laminations are separated by a thin film of insulation and the whole structure is clamped and maintained under pressure. The magnetic core therefore forms, thermally as well as magnetically and electrically, an anisotropic medium.

*Figures in parentheses indicate the literature references at the end.

The core thermal conductivity λ_x in the lamination plane is influenced by the same factors as solid steel, e.g. silicon content (3). Normal to the lamination plane, thermal conductivity λ_y is controlled by:

- (1) Individual lamination thickness.
- (2) Type and thickness of interlaminar insulation.
- (3) Lamination surface finish. (4) Clamping pressure.

Although published values are available, they have little meaning since in most cases the above factors have not been evaluated. Typical ratios quoted for

$\frac{\lambda_x}{\lambda_y}$ are 60 (4) and between 13 and 34 (5). Thus there is need for a fairly simple and convenient method, readily applicable to measuring thermal conductivities of this laminar material.

3. High Voltage Insulation

The situation is similar with the commonly used high voltage insulants, oil-impregnated paper and pressboard. Both are grained and so anisotropic, both are sheets, manufactured by cementing together or winding in the dry state and then subjecting to a rigorous process of heat and vacuum cycles, culminating in oil-impregnation under vacuum. The scarce published values of their thermal conductivities show an apparently wide and random variation. However, Figure 1 shows available data for thermal conductivity through the laminations, at 60°C when oil impregnated, graphed against density in the dry state. Despite some scatter, probably due mainly to deviations from the nominally specified density, the trend is unmistakable. There is a very strong dependence on density but no appreciable lamination thickness effect. Accurate design analysis requires thermal conductivities in the lamination plane also (2). These vary widely and the need for convenient measurement methods applicable in the "as used" condition is evident.

4. Measurement methods

Transient methods are now well established and can readily be applied to electrical engineering materials "as used". The transient line source method gives thermal conductivity directly and has been used for liquids (6). Recently it has been applied over large ranges of temperature and pressure aided by sophisticated electronics (7) or digital data logging and processing (8). Its errors have been analysed in detail (8,9). It can also be applied using simple standard apparatus and, as described in Section 5, can be used with anisotropic, as well as uniform, materials. An alternative method, particularly suitable for high-voltage insulants, is given in Section 6. In this, one subjects the surfaces of a pair of specimens to a common temperature step (10). It has the disadvantage that it measures diffusivity rather than conductivity but the apparatus is very simple and results for repeated tests can readily be correlated.

Using transient methods, the equipment associated with the test specimen itself is reduced to embedded elements - thermojunctions and/or line sources - easily introduced between laminations during manufacture. These interfere minimally with manufacturing processes such as dry-out and oil-impregnation or with equipment to vary temperature, pressure, etc..

5. Transient Line Source Method for Anisotropic Solids

The line source method can be used with anisotropic materials by adding two sets of temperature detectors.

5.1 Theory of Method

At distances x_1 and y_1 in the x and y directions from a line source along the z axis emitting heat at constant rate q into an anisotropic medium the times t_x and t_y taken to reach a common temperature can be shown (1) to be related by:

$$\frac{\lambda_x}{\lambda_y} = \left(\frac{x_1}{y_1}\right)^2 \frac{t_y}{t_x} \quad (1)$$

where λ_x and λ_y are the thermal conductivities in the x and y directions. In addition, at large times or small distances from the source, differences between temperatures θ_p and θ_q at corresponding times t_p and t_q are given by:

$$\theta_p - \theta_q = \frac{q}{4\pi\sqrt{\lambda_x\lambda_y}} \log_n \left(\frac{t_p}{t_q}\right) \quad (2)$$

Thus values of λ_x and λ_y can be evaluated from equations(1) and (2).

5.2 Practical considerations

A 25 μ m diameter platinum wire line source was aligned along the z axis of a stack of rectangular laminations. Its length is fixed by power requirements and by the characteristics of the triode used in the constant power circuit (10). The clamping force was measured by the compression of stacks of precalibrated Belville washes on the bolts used on the clamping frame. The stack dimensions depend on the time taken before heat losses from its outer surfaces become significant. Typically, 610 mm by 152 mm laminations were used, stacked 152 mm high. Much smaller heights could be used and 50 mm is suggested as more than adequate.

Tests were performed using the constant power circuit described by Allen (10) incorporating a 13 E 1 valve. (A transistorized version is described in Appendix I). These gave $k_x k_y$ products using equation (2). A dummy resistor set slightly above the "cold" resistance of the line source gave steady conditions until, at $t = 0$, the platinum wire was switched into the valve cathode circuit. This was to avoid relatively large initial changes in the source resistance. These were probably due to a thin air film around the wire. Appendix II shows that the error due to this is insignificant.

The distance x_1 between the line source and thermocouples in the x, z plane can be measured accurately during sample construction. In the y, z plane, the temperature detectors are conveniently located at an integral number of laminations from the source. Accurate measurement of y_1 is therefore more difficult. Measurements can be made before assembling the stack and again during tests if the laminations involved protrude slightly. The thermocouple temperatures were logged on precalibrated 0 - 100 μ V pen recorders. Alternatively, a single recorder may be used with switching between the couples at fixed time intervals, e.g. 40 s. By appropriate adjustment of x_1 and y_1 , an overlap in the temperature ranges is obtained. Equation (1) gives the ratio

λ_x to λ_y .

5.3 Results

Figures 2 and 3 give results obtained for three different types of sheet steel lamination. In the plane of the laminations (Figure 2) the results show variable agreement with other workers (3,5,11). Variations with clamping pressure were quite random and the values shown are extreme ones of the ranges. Small differences in nominally identical samples are to be expected because of variations in silicon content. Normal to the lamination plane, results for thermal conductivity (Figure 3) show the same tendency as for magnetic space factor, i.e. a marked decrease in its rate of change with pressure above about 3×10^5 N/m.

The method is fairly simple to use and tests may readily be performed over a range of temperature by putting the stack into a constant temperature enclosure. For transformer laminations, this can take the form of an oil filled thermostat.

6. Surface Temperature Step Method for Anisotropic Solids

6.1 Theory of Method

Newmann (12) showed how easily transient thermal problems in anisotropic media can be handled using product solutions. If temperature $\theta_{1..n}$ at a point $(x_1...x_n)$ in a n-dimensional solid formed by the intersection of n semi-infinite solids and having surfaces subjected to a step temperature change θ_0 to θ_∞ at time $t = 0$ is expressed as:

$$\frac{\theta_\infty - \theta_{1..n}}{\theta_\infty - \theta_0}$$

then:

$$\frac{\theta_\infty - \theta_{1..n}}{\theta_\infty - \theta_0} = \left(\frac{\theta_\infty - \theta_1}{\theta_\infty - \theta_0} \right) \dots \left(\frac{\theta_\infty - \theta_n}{\theta_\infty - \theta_0} \right) \quad (3)$$

where the right hand side terms are solutions for corresponding coordinates in the component semi-infinite solids. Each is a series having terms decreasing with t . The "natural" configuration of manufactured electrical insulation is a hollow cylinder. Considering this as formed by the intersection of an infinite slab, thickness $2Z$ and a hollow cylinder, inner and outer radii R_1, R_2 , of infinite axial length, for t sufficiently large:

$$\frac{\theta_\infty - \theta_{rz}}{\theta_\infty - \theta_0} \approx \left(A(r, z, R_1, R_2, Z) \right) \left(\exp \left\{ -B(R_1, R_2, Z, \alpha_r, \alpha_z) t \right\} \right) \quad (4)$$

Details of this expression are available (10). For present purposes the complexity of $A(r, z, R_1, R_2, Z)$ is unimportant as, by measuring θ_{rz} at $z = 0$ (specimen mid-plane), it becomes independent of Z . The exponential term:

$$B(R_1, R_2, Z, \alpha_r, \alpha_z) = \alpha_z \left(\frac{\pi}{2Z} \right)^2 + \alpha_r b_1^2 \quad (5)$$

where b_1 is the first root of a Bessel function equation in R_2/R_1 . Thus graphs

of $\log \frac{\theta_{\infty} - \theta_{rz}}{\theta_{\infty} - \theta_0}$ against t have slopes $-\left(a_z \left(\frac{\pi}{2Z}\right)^2 + a_r b_1^2\right)$.

Two unknowns, a_r and a_z , are involved so that two experiments are necessary.

6.2 Practical considerations

The two experiments are most simply performed simultaneously by subjecting the surfaces of two specimens to the same $\theta_{\infty} - \theta_0$. For liquid impregnated insulants, kept immersed in their impregnant, this can be done by quickly transferring them from one thermostat filled with impregnant at θ_0 to another at θ_{∞} . $\theta_{\infty} - \theta_{rz}$ can be measured directly by locating the reference junction in the second thermostat, which should be kept effectively stirred. To keep $A(r, z, R_1, R_2, Z)$ the same for both specimens, Z rather than b_1 is different while the thermojunctions in both are located at the same radius.

Specimen design is governed, firstly, by available values (13) of b_1 which are:

Ratio R_2/R_1	b_1 (to 5 significant figures)	Ratio R_2/R_1	b_1 (to 5 significant figures)
$1\frac{1}{2}$	6.2702	3	1.5485
2	3.1230	$3\frac{1}{2}$	1.2339
$2\frac{1}{2}$	2.0732	4	1.0244

and by the following considerations:

- (1) Thermal capacity of specimens relative to the thermostat contents and to the heater capacity. A perfect "step" $\theta_{\infty} - \theta_0$ is hardly possible. Little error is however, due to the imperfection θ_0 (10).
- (2) Time taken for the approximation of equation (4) to apply. This increases with Z .

(1) and (2) limit maximum size. Minimum size is limited by:

- (3) Proportionate error in dimensions and thermojunction location.
- (4) Rate of change θ_{rz} for accurate and convenient measurement.

Other accuracy considerations arise from the fact that for a pair of specimens, lengths $2Z_1$ and $2Z_2$, giving graph negative slopes B_1 and B_2 ($B_1 > B_2$):

$$a_z = \frac{B_1 - B_2}{\pi^2 \left(\frac{1}{(2Z_2)^2} - \frac{1}{(2Z_1)^2} \right)} \quad (6)$$

$$a_r = \frac{(2Z_1)^2 B_2 - (2Z_2)^2 B_1}{\left((2Z_1)^2 - (2Z_2)^2 \right) b_1^2} \quad (7)$$

and there is a real danger of small differences between large quantities arising. One can only say that, for oil-impregnated paper and pressboard, the following dimensions have given satisfactory performance.

	R_1	R_2	$2Z_1$	$2Z_2$	
Paper	50	75	40	70	mm
Pressboard	50, 70	75, 105	40	70	mm

Paper specimens can be made by winding around an inner copper tube, pressboard ones by successive lining within an outer copper former. Thermo-junction leads are brought circumferentially through 180° before leaving the specimens axially. Specimens made "naturally" i.e. with the material grain circumferential, give α_z values across the material grain in the lamination plane. For diffusivity along the grain, "cross grain" specimens must be made. The same α_r is measured with both pairs.

6.3 Results.

As specimen pairs have a common value of $A(r, z, R_1, R_2, Z)$ they have a common apparent θ_{rz} value at $t = 0$. This helps to align their slopes along the linear portion of each $\log(\theta_\infty - \theta_{rz})$ versus t graph. Also, when tests are repeated, $\log(\frac{\theta_\infty - \theta_{rz}}{\theta_\infty - \theta_0})$ versus t curves coincide giving a convenient correlation as shown in Figure 4. Values of thermal diffusivity measured in this way are given in Figure 5. Their accuracy is estimated at about $\pm 5\%$. The main trends evident are:

- (1) Thermal diffusivities can be several times greater along and across the grain within the laminations than through them. (This can be used to advantage in design (14).
- (2) Dry density has a considerable, lamination thickness little, effect on thermal diffusivity.
- (3) Temperature has negligible effect on thermal diffusivity through laminations. In other directions, there is some increase with temperature.

7. Application of measurements

The results presented do not purport to be an exhaustive investigation of a particular class of material. Measurements were made as required on materials actually used. Using them, very good agreement has been obtained in predicting temperatures in the windings of rotating machines (Figure 6) and transformers (Figure 7).

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10. Appendixes

I. A constant power source using a transistor.

In the circuit of Figure 8, the voltage drop V_{BE} from base to emitter of the transistor is:

$$V_{BE} = V(1 - \frac{R_a}{R_a + R_b}) - I_E(R_c(1 - \bar{\alpha}) + R_L + R_X) \quad (8)$$

where $\bar{\alpha}$ = transistor large signal current gain in common base connection,

$R_c = \frac{R_a R_b}{R_a + R_b}$, R_L = line source resistance in which constant power is to be dissipated, and other terms are as defined in Figure 8. From equation (8):

$$\frac{\Delta V_{BE}}{\Delta R_L} \approx \frac{\partial V_{BE}}{\partial R_L} = - \frac{\partial I_E}{\partial R_L} (R_c (1 - \bar{\alpha}) + R_L + R_x) - I_E \quad (9)$$

The mutual conductance g_m is defined:

$$g_m = \frac{\Delta I_C}{\Delta V_{BE}} = \frac{\Delta I_C}{\Delta I_E} \frac{\Delta I_E}{\Delta R_L} \frac{\Delta R_L}{\Delta V_{BE}} = \bar{\alpha} \frac{\Delta I_E}{\Delta R_L} \frac{\Delta R_L}{\Delta V_{BE}} \quad (10)$$

Since $\bar{\alpha}$ is defined as $\frac{\Delta I_C}{\Delta I_E}$. The condition for constant power in R_L is (10):

$$\frac{\Delta I_E}{\Delta R_L} = - \frac{1}{2} \frac{I_E}{R_L} \quad (11)$$

and using this, first, equation (9) becomes:

$$\frac{\Delta V_{BE}}{\Delta R_L} \approx \frac{I_E}{2 R_L} (R_c (1 - \bar{\alpha}) + R_L + R_x) - I_E \quad (12)$$

while equation (10) becomes:

$$g_m = - \bar{\alpha} \frac{I_E}{2 R_L} \frac{\Delta R_L}{\Delta V_{BE}} \quad (13)$$

Then substituting (12) in (13):

$$g_m = \frac{\bar{\alpha}}{(R_L - R_x) - (1 - \bar{\alpha})R_c} \approx \frac{\bar{\alpha}}{R_L - R_x} \quad (14)$$

for $\bar{\alpha} \rightarrow 1$. R_x can thus be adjusted according to R_L and the g_m of the transistor used. An OC 72 maintained the power dissipation in a 5.5 ohm (mean) load (equivalent to about 25 mm of 2 μ m diameter platinum wire) within $\pm 0.7\%$ for a voltage change of $\pm 7\%$.

II. The effect of an air layer at the line source.

Two approaches are possible:

(1) Considering the temperature θ at any point between the parallel surfaces, $2d$ apart, of two semi-infinite masses of highly conducting material due to a line source located centrally between them. At r from a line source strength q in an infinite medium, thermal conductivity λ (15):

$$\theta = \frac{-q}{4\pi\lambda} \text{Ei} \left(\frac{-r^2}{4\alpha t} \right) \quad (15)$$

Assuming equal thermal diffusivity α for air and iron (actually 18.7×10^{-6} and $12 \times 10^{-6} \text{ m}^2/\text{s}$, respectively) and letting their thermal conductivities be λ_a and λ_i , the problem can be solved between the surfaces by the method of images. Thus q has first image q_1 behind one surface, which itself has image q'_1 behind the other, and so on to give a system of images $q, q_1 \dots q_n, q'_1 \dots q'_n, q''_1 \dots q''_n$. The boundary conditions are that both θ and normal thermal flux are continuous

at the surfaces. Applying these it can be shown that:

$$q_n = q'_n = q \left(\frac{1-m}{1+m} \right)^n \quad (16)$$

where $m = \frac{\lambda_i}{\lambda_a}$. As $m \approx 1.7 \times 10^3$ the series representing the effect of the source images will converge very slowly for small d .

(2) Alternatively, considering a cylinder radius R , thermal diffusivity α , initially at uniform (datum) temperature throughout, with surface temperature $\theta_s = kt$ for $t > 0$. At distance $r (< R)$ from the cylinder axis, temperature θ is given by (15):

$$\theta = k \left(t - \frac{R^2 - r^2}{4\alpha} + \frac{2}{R\alpha} \sum_{n=1}^{n=\infty} \left(\exp(-\alpha c_n^2 t) \frac{J_0(r c_n)}{c_n^2 J_1(R c_n)} \right) \right) \quad (17)$$

where $\pm c_n$ are the roots of the Bessel function equation: $J_0(Rc) = 0$. The temperature along the axis is given by putting $r = 0$ in equation (17) and considering t sufficiently large for the third (series) term to be neglected. Then:

$$\theta \approx k \left(t - \frac{R^2}{4\alpha} \right) \quad (18)$$

which indicates the time lag $\Delta t \approx \frac{R^2}{4\alpha}$ due to an air film $2R$ thick. For

$R = 25 \mu\text{m}$, $\Delta t = 8 \mu\text{s}$ and for $R = 51 \mu\text{m}$, $\Delta t = 70 \mu\text{s}$. Also, for $R = 51 \mu\text{m}$, the series term in equation (17) is less than 1% of the first after $40 \mu\text{s}$.

Thermal Conductivity, λ , W/mK.

Material	Point	Lamination thickness, mm	Source
Paper	1	0.13	Own work
	2	0.19	
	3	0.045	
	4	0.06	Gotter (3)
	5	0.10	
	6	0.13	Marshall (16)
Pressboard	7	0.64	Own work
	8	2.5	
	9	1.0	Gotter (3)
	10	3.2	

Figure 1. Effect of density before impregnation on the 60°C thermal conductivity through laminations of oil-impregnated paper and pressboard.

Curve from Gotter (3)

—

Present work

⊙

Banks and Redfearn (11)

●

Schumichen (5)

□

Figure 2. Effect of silicon content on thermal conductivity of steel

Thermal conductivity,
 λ , W/mK

<u>Type of steel</u>	<u>Lamination thickness</u>	<u>Silicon content</u>	<u>Symbol</u>
Cold rolled	0.51 mm	2.30 %	○
Hot rolled	0.41 mm	1.83 %	●
Cold rolled	0.35 mm	3.10 %	□

Figure 3. Effect of clamping pressure on the thermal conductivity through flash enamelled steel laminations

Temperature step $\theta_{\infty} - \theta_0$:

- 4.7 °C
- 6.8 °C
- 11.6 °C

Figure 4. Correlated results of three tests on a pair of paper specimens

Thermal Diffusivity, α , m/s^2

Material	Density kg/m^3	Lamination thickness, mm	Through laminations	Along grain	Across grain
Paper	800	0.19	$\circ^*$		$\ominus$
		0.13	$\odot$	$\oplus$	$\ominus$
	700	0.045	Δ		Δ
Pressboard	1150	0.64	$\square^*$		$\boxplus$
		2.5	$\blacksquare$	$\boxplus$	
	1000	1.0	$\diamond$		$\diamond$

*All measurements, whether "along" or "across grain", give a "through laminations" value.

Figure 5. Thermal diffusivities of oil-impregnated paper and pressboard measured by surface temperature step method versus mean measurement temperature.

Temperature of
winding copper
°C 150

<u>Test condition</u>	<u>Location</u>	<u>Calculated</u>	<u>Measured</u>
Zero power factor	Bottom coil side	——	○
	Top coil side	----	●
Unity power factor	Bottom coil side	— · —	□
	Top coil side	— x —	■

Figure 6. Measured and calculated temperatures in a 15 MW alternator armature winding

	<u>Duct length</u>	<u>Mean thermal flux</u>	<u>Mean oil velocity</u>
Test values { ●	260 mm	4.65 kW/m ²	.0.10 m/s
○	870 mm	3.10 kW/m ²	0.08 m/s

Figure 7. Measured and calculated temperatures in experimental transformer windings.

Figure 8. Transistorized constant power circuit

Thermal Conductivity of Rubber From 134 to 314°K
Including the Glass Transition

Malcolm N. Pilsworth, Jr.
U.S. Army Natick Laboratories

and

Henry E. Robinson
National Bureau of Standards

ABSTRACT

The thermal conductivity λ of a typical soft vulcanized natural rubber was measured from a little above room temperature to well below the glass transition temperature. The samples (ASTM Formula 2A) were prepared at the National Bureau of Standards and several values of thermal conductivity near room temperature were determined there. At the U.S. Army Natick Laboratories measurements were made from 134 to 314°K using a specially-constructed guarded hot-plate apparatus with automatic control of cold-plate and guard-ring temperatures. The NLABS results were about 2% lower than the NBS values in the region of overlap. The uncertainty in the results is estimated to lie between 3 and 6%, being larger below T_g , the glass transition. There is a well-developed peak in λ at T_g , at about 212°K. At the peak, $\lambda = 0.155$ w/m°K. In the region below T_g the data scattered more than elsewhere and slow cooling was necessary to get reproducible results. The greater scatter in this region could be caused by warping of the sample as it becomes glassy, but there is also a possibility that some hysteresis in λ is present.

IMPROVED CUT BAR APPARATUS FOR THERMAL CONDUCTIVITY MEASUREMENTS

Ralph K. Day¹

ABSTRACT

A new thermal conductivity cut bar apparatus recognizes and solves basic experimental difficulties: 1. Hydraulic pressure axially aligned with a space gimbal, replaces soldered joints. 2. Joints between sample and meter bar are made thermally uniform with shims crushed at the measuring temperature. 3. Thermocouple technology is improved. 4. New bubble insulating powders in vacuum replace auxiliary heaters and extend the range to high temperatures. The usual $\frac{1}{2}$ "x $\frac{1}{2}$ " right cylinder sample has been extensively varied, extending the versatility of the instrument and its capability to even low conductivity sheet materials.

INTRODUCTION

The basic experimental problems which have hampered the old standard experimental method of measuring thermal conductivity ^{2,3}, variously called "cut bar" or "axial flow" or "ASTM C408-58"⁴, may be listed as follows:

The joint discontinuity between meter bar and unknown sample must have uniform thermal resistance across its area, otherwise the basic tenet of equal temperature in every single plane perpendicular to the axis is violated.

The originally proposed and obvious method of soldering these joints for improved and uniform thermal conductivity across the area of joining, has been theoretically challenged because of the demonstrated possibility of diffusion of the soldering and metalizing materials into sample and bar, thereby changing their nature and properties.

Different temperature gradients (due to different thermal conductivities) and different expansion coefficients between the measurement standard and the unknown material, unavoidably change the relative contour of the interface surfaces during test.

Attaching thermocouples at the critical locations to measure the true temperature gradient in different sections of the bars and sample has been experimentally difficult.

The practice of using auxiliary heaters to try to neutralize radial heat losses is theoretically difficult and experimentally complicated and often inaccurate.

The changes which have been made in this instrument from the presently specified ASTM C408-58 instrument have proven to be experimentally convenient solutions to these problems. The range of capability has thus been extended not only to materials of lower thermal conductivity range but also to much higher temperatures. Experimental limits for each of these parameters exist only in the basic principles of the test which will be discussed. Accuracy is limited only by the precision of execution and attention to detail in each actual test.

BASIC PRINCIPLES AND THEORY

This axial flow method is very simple in theory and geometry and has the great advantage of requiring only a relatively small sample. A cylindrical column of uniform diameter, usually vertical, is built up from right cylinder sections of known standard materials and called "meter bars" and the unknown material called the "sample". One end of this cylindrical composite is heated and the other end cooled and when equilibrium is established and the only heat flow is uniformly parallel to the cylindrical axis of the system, the thermal conductivity of the different sections is by definition inversely proportional to the temperature gradient in those sections.

$$\lambda_1 \left(\frac{dT}{dy} \right)_2 = \lambda_2 \left(\frac{dT}{dy} \right)_1$$

The condition that all the heat flow be parallel to the axis is really another way of saying that there must be no radial flow, or again, there must be no heat losses from the cylindrical surface. In any practical experiment the surface losses must be reduced to a value commensurate with the expected experimental error. In a particular measurement this is achieved variously as a result of some rough calculations which often result in putting the instrument inside a vacuum to lower heat loss by air conduction and polishing the composite cylindrical surface to lower radiation emissivity.

A theoretically interesting method of insulating the surface of the cylindrical column against radiant heat loss is to surround it as closely as possible with a highly reflecting sheet of aluminum or platinum foil. Radiation perpendicular to the axis would be reflected directly back on itself and the longitudinal components would be minimized in accordance with how close the radiation shield could practically be placed near the cylinder without touching and causing conduction losses.

The diameter of the system can be increased to lower the ratio of surface/cross-sectional area. Newly developed hollow sphere insulating powders⁵ with or without vacuum are effective especially at higher temperatures. Heated guard sections are not believed to be as effective in practice as is the use of these modern refractory insulating powders.

Much advantage can be taken of possessing materials of known and similar thermal conductivity as that of the unknown sample to measure and compensate for experimental error. Identical runs can be made with a known similar sample substituted for the unknown. Interpolation of measured temperature gradients between identical upper and lower bars to the "in between" sample helps correct for surface heat losses. This problem of setting up the experimental arrangement is not usually as difficult as are the basic joint, pressure and thermocouple problems.

THE JOINT PROBLEM

Since soldering has been given up, we are confronted, in the problem of joints between dissimilar materials, with unavoidable warpage of these joining surfaces. This warpage is due to the fact that practically all materials have a real and unique coefficient of thermal expansion and the nature of the test puts both the test cylinder of unknown material and the known meter bar under the strain of a temperature gradient of sufficient magnitude to distort their original shape, including particularly the surface which must contact the adjoining sample or bar.

A practical solution to the expected warpage between connecting surfaces is achieved by crushing a shim at each joint after the approximate temperature gradient and the resulting distortions of the contacting surfaces have been established. The shim can, for example, be made of screen wire of a chemically compatible material like copper, aluminum or platinum and of such wire diameter that after crushing at the equilibrium temperature at which measurements will be made, the percentage of thermal contact throughout the area will be closely equal. The shim can also be a simple disc of a relatively ductile but compatible material which has preferably been prick-punched with a uniform distribution of dents or holes to facilitate later flow deformation during crushing. Shims can usually be crushed several times at different temperatures at a slightly higher pressure each time.

AXIAL PRESSURE

The obvious substitute for soldering is axial pressure and it has been found, for instance, that a soft copper to hard ceramic joint is thermally improved at 100°C by increasing the pressure up to around 2000 psi on a $\frac{1}{2}$ " diameter system and that it does not improve very much more at pressures greater than that.

Early experiments⁶ used spring pressure without a gimbal and it was soon discovered that any small mis-alignment ended up with excess pressure at one edge of each joint. Search for an automatic alignment device ended with incorporation of a space gimbal which proves very satisfactory for that purpose.

The requirement that final pressure be increased to crush or re-crush the shims at approximate temperature equilibrium resulted in introducing a hydraulically controlled pressure multiplying diaphragm into the gimbal pan. Since most measurements were being made inside a vacuum, the ability to change pressure remotely from outside has proven to be a very great convenience.

TEMPERATURE MEASUREMENTS

Thermocouple technology is critical in this test because to accurately measure temperature gradients, precise differences in e.m.f. between carefully located couples is necessary. This technology requires:

a. Thermocouple wires should be of small diameter, low thermal conductivity, high e.m.f. per degree sensitivity and good stability with time. When the temperature range is suitable, chromel and constantan wires of 0.005" diameter fits the requirement very well. At very high or very low temperatures, highly alloyed thermocouple wire compositions are generally found to be more stable and lower in thermal conductivity, and therefore more satisfactory. For instance, two different alloys of platinum or rhenium make a better thermocouple than if one leg is of a pure metal.

b. The bead or junction must be in intimate thermal contact with the bars and sample at each location. Resistance welding of the individual wires to diametrically opposite locations on metal bars is a good method when possible. Bars made from soft high conductivity metals like copper or aluminum or platinum can have wires cold peened into slots which have been opened. Use of the smallest diamond dental drills to make a "bead-sized" hole and then cementing the bead with ceramic air-setting and expanding dental cement has proven satisfactory as the last resort.

c. Heat losses by conduction from the bead along the wires is minimized by laying the wires along the equi-temperature contours of the cylindrical surface. Sometimes a simple rubber band helps hold them in place.

STANDARDS

To measure the thermal conductivity of an unknown sample with an accuracy of a certain percentage, the thermal conductivity of the meter bars must of course be known more accurately than that. Sparked by the annual Thermal Conductivity Conferences now in their ninth year, knowledge about suitable standards and their temperature stability is increasing. The U.S. Air Force has awarded a development contract⁷ to the Arthur D. Little Company entitled "Development of High Temperature Thermal Conductivity Standards" which is now in its third year. Our National Bureau of Standards⁸ is continuing to follow an active research and standards development program.

A likely group of winners⁹ as thermal conductivity standards are Armco iron, OFHC copper, Inconel 702 and arc-fused tungsten among the metals; Corning's Pyrex 7740, Pyroceram 9606, pure alumina and pure beryllia among the ceramics. Especially in preparation for a series of measurements on a particular type of material, meter bars made of that material and calibrated with one or more known standards is a good approach.

APPARATUS ADJUSTMENTS

A quick review of the experimental procedure referring to the diagram of the apparatus, follows:

Choose and install known conductivity meter bars of a suitable material. These will generally be the ones most similar in thermal properties to the sample to be measured. However, some consideration should be given to the possibility of objectional creep or cold flow.

The use of four equally spaced, usually $\frac{1}{2}$ " apart, thermocouples on both upper and lower meter bars is an excellent experimental check on the uniformity of heat flow down the system and is accordingly recommended. Two couples appropriately spaced on the unknown sample usually suffice.

Special curved forceps are useful while mounting the unknown sample cylinder and shims between the upper and lower bars as just enough axial pressure is applied by means of the triple sprocket chain connected thumb screws at the top, to hold the assembly in place.

Check and adjust everything for level: the main platform by adjusting the feet; the gimbal platform by adjusting the turnbuckles; the top of the heater by slipping one or more sprocket wheels after loosening a set screw; and finally, the verticalness of the cylindrical column by "bending" the support rods with the 12 set screws provided; and in that order.

Check all thermocouple circuits for continuity and approximate equal resistance at the potentiometer.

Put on about 25% of the final hydraulic pressure.

Add powder and/or evacuate, turning on cooling water and heating current.

Wait for approximate temperature equilibrium at which time final hydraulic pressure is applied.

When temperature drifting has essentially ceased, read the usual ten thermocouples in order, first down then up the column and record. Examine the data to be sure that temperatures are not cycling.

SAMPLE SET OF READINGS & CALCULATIONS

The sample set of millivoltage temperature readings and calculations reproduced below represent calibration of a set of OFHC copper meter bars by mounting a standard sample of AR^MCO iron between them. Couples #1,2,3,4 and 7,8,9,10 were spaced $\frac{1}{2}$ " apart on the upper and lower copper bars; couples #5,6 were welded to the ARMCO iron 1" long sample $\frac{1}{2}$ " apart.

The following millivolt readings above room temperature (20.8°C) were taken at approximately equal time intervals in the order 1,2,3,4,5,6,7,8,9,10,9,8,7,6,5,4,3,2,1.

couple #1	2	3	4	5	6	7	8	9	10
10.885	10.430	10.008	9.569	7.760	5.405	3.653	3.277	2.890	2.517
10.870	10.419	9.996	9.562	7.760	5.403	3.652	3.275	2.890	

Av. 10.878 10.425 10.002 9.566 7.760 5.404 3.653 3.276 2.890 2.517

Diff. .453 .423 .436 1.806 2.356 1.751 .377 .386 .373

Av. Temperatures: Upper bar 173°C, Lower bar 70°C, sample 122°C at which ARMCO iron has a thermal conductivity of 0.655 watts/cm.°C(Powell)

at 173°C, the avge $\frac{1}{2}$ " temp. drop is 0.437mv.@0.0712mv/°C = 6.15°C

at 70°C, the avge $\frac{1}{2}$ " temp. drop is 0.379mv.@0.0630mv/°C =6.01°C

at 122°C, the avge $\frac{1}{2}$ " temp. drop is 2.356mv.@0.0680mv/°C =34.7°C

$$\lambda_{173^{\circ}\text{C}}^{\text{Cu}} = \frac{0.655 \times 34.7^{\circ}\text{C}}{6.15^{\circ}\text{C}} = 3.69 \text{ watts/cm}^{\circ}\text{C} \quad \lambda_{70^{\circ}\text{C}}^{\text{Cu}} = \frac{0.655 \times 34.7^{\circ}\text{C}}{6.01^{\circ}\text{C}} = 3.78 \text{ watts/cm}^{\circ}\text{C}$$

-
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 6. R.K.Day, Proc. Sixth Thermal Conductivity Conference 1966. "Thermal Conductivity by Axial Flow, Cut Bar Method ASTM C408"
 7. AF 33(615) - 2874
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 9. Materials for reference standards should be more closely identified than just by manufacturer's catalog names & numbers which are used here. The National Bureau of Standards can sometimes advise about special melts or lots of a material which has been set aside as reference standards.

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