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A TECHNIQUE FOR DETERMINING THERMAL AND ELECTRICAL CONDUCTIVITY AND ABSOLUTE SEEBECK COEFFICIENT BETWEEN 300 AND 1000 K

J. P. Moore, D. L. McElroy, and R. S. Graves

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SEPTEMBER 1974

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ABSTRACT

A guarded-longitudinal-heat-flow technique for measuring thermal conductivity (λ), electrical resistivity (ρ), and Seebeck coefficient (S) on small rods (1 cm diam by 7 cm long) between 300 and 1000 K is described in detail. The thermal conductivity of the powder insulation in the system annuli was low enough to permit use of the thin-rod approximation for calculating λ of metals. Determinate errors were ±0.4% for ρ, ±0.14 μV/K for S respect to platinum, and ±1.3% and ±2.2% for λ at 300 and 1000 K, respectively. The apparatus was tested with an Armco iron reference specimen, which had a λ known to within ±1.9%. One test was performed with the specimen brazed onto heater and heat sink, and results from this test were within the determinate error. Measurements on the reference when it was threaded onto heater and heat sink produced ρ and S results that agreed with those from the brazed specimen to within determinate error but produced λ results that were 2 to 6% above the reference values. The cause of this discrepancy with a threaded specimen is not completely understood but may be indirectly related to the large temperature drop that occurs at the threaded interfaces.

LIST OF SYMBOLS

λ = Thermal conductivity of specimen (W cm^{-1} K^{-1}).

ρ = Electrical resistivity of specimen ($\mu\Omega$-cm).

$S_{Spec-Pt}$ = Specimen Seebeck coefficient with respect to thermocouple-grade platinum (μV/K).

S = Absolute Seebeck coefficient of specimen (μV/K).

z = Axial distance as measured upward from top of nickel base (cm).

$T_s(z)$ = Temperature along surface of specimen between $z = 0$ and $z = l_0$ (K).

r = Radius of specimen (cm).

r_g = Inside radius of guard (cm).

Q_e = Joule heat dissipated in specimen heater (W).

λ_{ins} = Thermal conductivity of powder in annuli (W cm^{-1} K^{-1}).

l_0 = Value of z where specimen attaches to specimen heater (cm).

$Q_r(z)$ = Radial heat flow between specimen and guard (W).

$Q(z)$ = Total heat flow in specimen (W).

A^{Δ} = Temperature of guard at $z = 0$ during $Q_e = 0$ test (K).

A^{δ} = Temperature of guard at $z = 0$ during $Q_e \neq 0$ test (K).

$B^{\Delta} = \dfrac{dT_g(z)}{dz}$ during $Q_e = 0$ test (K/cm).

$B^{\delta} = \dfrac{dT_g(z)}{dz}$ during $Q_e \neq 0$ test (K/cm).

E^{Δ} = EMF between adjacent platinum thermoelements when $Q_e = 0$(μV).

E^{δ} = EMF between adjacent platinum thermoelements when $Q_e \neq 0$(μV).

α = Mean coefficient of thermal expansion of specimen (K^{-1}).

I = Direct current flow through specimen during ρ measurement (A).

V = Voltage drop between adjacent Pt–10% Rh thermoelements due to I flow through specimen (μV).

r' = Radius of H1 (cm).

r' = Inside radius of H2 (cm).

l' = Distance between top of H1 and lid of H2 (cm).

A_{top} = Area of the top of H1 (cm^2).

P_{ext} = Heat flow between H1 and H2 (W).

P_w = Heat flow along wires between H1 and H2 (W).

P_{ins} = Heat flow through insulation between H1 and H2 (W).

V' = Voltage drop between two central heater probes (μV).

I' = Current flow through central heater (A).

b = Inside radius of cannister for λ_{ins} measurement (cm).

a = Outside radius of core heater for λ_{ins} measurement (cm).

l = Distance between core heater probes (cm).

t_i = Temperature of core heater surface (K).

t_o = Temperature of cannister surface (K).

C = Correction for temperature drop across metal walls of core heater and cannister during λ_{ins} measurement (K).

ΔT = Temperature difference between H1 and H2 during $Q_e \neq 0$ test (K).

E_m = EMF output of a thermocouple (μV).

INTRODUCTION

The primary objective of this work was the development of a thermal conductivity (λ) technique for measurements on small cylindrical rods approximately 1 cm in diameter × 7 cm long over the range from 300 to 1000 K. Many research projects require λ measurements on small samples because of material scarcity or external factors that limit specimen size. For instance, the immediate use of this apparatus was to measure the λ of neutron-irradiated graphites,[1] which were limited in diameter to 1.3 cm because of the restricted size of the irradiation capsule. This particular use required that the specimen be easily detached from any heaters or holders to prevent specimen damage. A secondary objective was to determine the electrical resistivity (ρ) and absolute Seebeck coefficient (S) since λ is often related to ρ and a knowledge of S can assist in interpreting λ results.

Numerous systems have been developed for measuring λ with longitudinal heat flow through the specimen.[2] Some of these yielded good results[3] but appeared to be difficult to assemble or require large specimens when examined in terms of immediate system use. Therefore, we developed a steady-state guarded longitudinal heat flow system that could be employed on small-diameter specimens and could be assembled with only a 0.5-hr exposure of an individual's hands to a radioactive specimen.

Following sections include a description of the apparatus, calculation procedure, an error analysis, and results on a material of known thermal conductivity. The guarded high-temperature longitudinal system (henceforth called the HTL) was tested with a reference specimen installed in two different ways during three assemblies. During the two initial tests, the specimen heater and heat sink were attached to the specimen with threaded connections. This attachment technique led to operational difficulties, which were reduced in later measurements by brazing the specimen to heat source and sink.

DESCRIPTION OF APPARATUS

The HTL is shown in Fig. 1 with the specimen heater (H1) threaded onto the specimen and with a machine screw holding the lower part of the specimen to a nickel plate. This plate, which serves as a base for specimen, guard, and outer furnace, rested on a base heater assembly (H4), which was thermally coupled to a water-cooled heat sink through three nickel tubes. A nickel guard cylinder surrounded the specimen. This

---

[1] J. P. Moore, R. S. Graves, and D. L. McElroy, "Thermal and Electrical Conductivities and Seebeck Coefficients of Unirradiated and Irradiated Graphites from 300 to 1000 K," *Nucl. Tech Vol* 22(1): 88–93 (April 1974).

[2] M. J. Laubitz, Chap. 3 in *Thermal Conductivity*, Vol. 1, R. P. Tye, ed., Academic Press, London, 1969.

[3] L. D. Armstrong and T. M. Dauphinee, "Thermal Conductivity of Metals at High Temperatures — 1 Description of the Apparatus and Measurements on Iron," *Can. J. Phys.* A25: 357–374, 1947.

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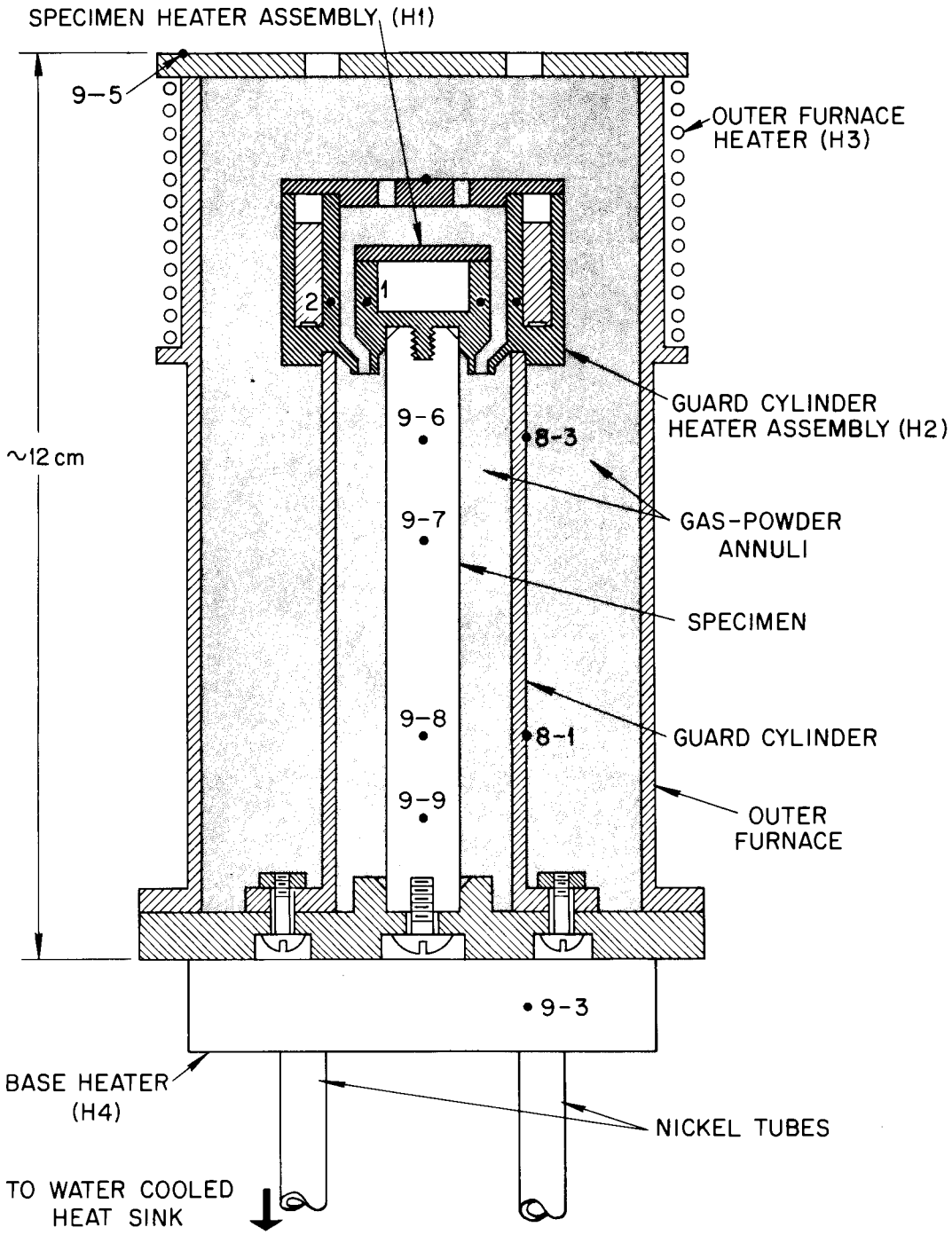

Fig. 1. High-Temperature Longitudinal Heat Flow Apparatus with the Specimen Heater and Heat Sink Threaded onto the Specimen and with Four Thermocouples Attached to the Specimen.

cylinder contained a heater assembly (H2) on the free end and was attached to the nickel base with machine screws. The metal parts of H1 and H2 were fabricated from a copper-chromium alloy,[4] which had high machinability and high thermal conductivity.

The outer furnace was made of nickel and had radially wound heaters at the top, H3, and lower section of the cylinder. This unit served as a secondary guard to reduce heat losses from the primary guard and thus reduce local temperature variations on the guard.

The annuli between specimen and guard cylinder and between guard cylinder and outer furnace were filled with Al_2O_3 powder[5] and argon. The entire assembly of Fig. 1 was enclosed in a water-cooled chamber, which could be evacuated, flushed with argon, and maintained at pressures below 1×10^5 N/m^2.

Specimen

The specimen was a right circular cylinder approximately 1 cm in diameter × 7.8 cm long with machine threads tapped into each end for attaching to the base and heater. Platinum and Pt—10% Rh thermocouple (0.025 cm diam) wires were welded to the specimen, with each hot junction being made through the specimen. The thermocouples at each end of the specimen were mounted at least 1 cm away from H1 and the heat sink, and this should be sufficient distance from any end effect, as discussed by Jury et al.[6] The wires were insulated with flexible woven fiber glass sleeving and passed around the specimen at nearly the same height as the hot junction, as shown in Fig. 2(a), entered two-hole Al_2O_3 tubes, and exited under the bottom of the guard cylinder. This configuration placed the first few centimeters of the wires in an isothermal region and minimized temperature measurement error due to heat flow into or out of the hot junctions. The distances between adjacent thermoelements were determined electrically by passing a direct current through the sample and comparing the voltage drops between similar legs of the thermocouples with that between two points of known spacing (knife edges). Ideally, the two wires of a thermocouple should be welded to the specimen so that the axes of the wires are colinear and their contact points with the specimen are on an isothermal plane. This was difficult to achieve in practice, and the distances between contact points were measured electrically by determining the difference in a thermocouple emf when a known current flowed in both directions through the specimen. This voltage difference was then compared with the voltage drop between knife edges of known spacing.

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[4]W. R. Hibbard, Jr. et al., "The Consititution and Properties of Copper-Rich Copper-Chromium and Copper-Nickel-Chromium Alloys," *Metals Technol.* 15(2): 1—12 (February 1948). Cu—8 wt. % Cr purchased from Philadelphia Bronze and Brass Corp.

[5]Aluminum Company of America, Calcined alumina particles. Particle size between 100 and 300 μm.

[6]S. H. Jury, D. Arnurius, T. G. Godfrey, D. L. McElroy, and J. P. Moore, "End Effects on the Flow of Heat, Mass, or Electrical Energy Through a Cylindrical Rod," *Journal of the Franklin Institute* 298(4) (October 1974).

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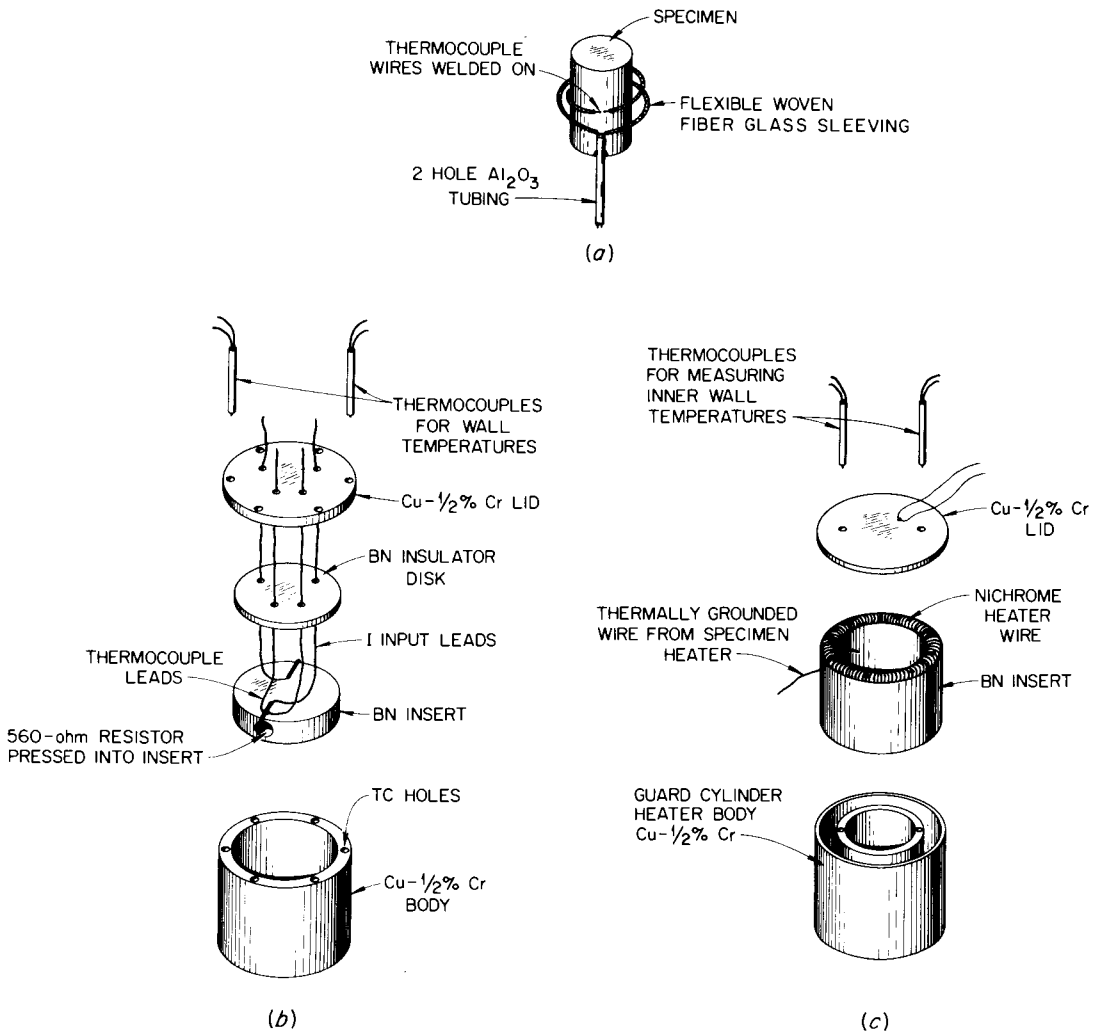

Fig. 2. (a) Detail of Thermocouple Attachment to Specimen. (b) Exploded view of specimen heater assembly (H1) showing BN insert and thermocouple arrangement. (c) Exploded view of guard cylinder heater (H2).

Specimen Heater Assembly

The specimen heater assembly is shown in an expanded view in Fig. 2(b). The heater was a commercial ceramic-coated 560-Ω, wire-wound resistor[7] pressed into a hole in the boron nitride (BN) insert, which was then lowered into the large heater-body cavity. The high thermal conductivity of BN ensured good heat transfer between the resistor and the heater body, and its low electrical conductivity minimized electrical breakdown at the higher temperatures.

During the gradient test, when well regulated direct current[8] was passed through this heater, the heater leads could have been at a higher temperature than the surrounding heater components. A thermocouple was attached to one current lead of the resistor to monitor its temperature during operation and provide enough information for calculation of lead heat loss. Holes were drilled through the lid to permit passage of the current input leads and the thermocouple. The lid was bolted on with six machine screws and was tight enough to exert pressure on the BN insert. Thermocouples for checking the wall temperatures of the heater body were inserted into blind holes with ceramic beads in the bottom to prevent electrical shorting of the thermocouples. One of the wall thermocouples was used to control differentially to a thermocouple mounted on the guard-cylinder heater assembly. Potential taps for determining the voltage drop across the specimen heater were attached to the current leads after they left the guard cylinder heater. The small error due to Joule heating in the sections of heater lead wire that were not physically located in H1 was easily correctable since the lead wire resistance was known.

Guard Cylinder

The guard cylinder was fabricated from a 2.87-cm-OD by 2.38-cm-ID nickel tube. The cylinder had a flange on one end for bolting to the base; and a heater assembly (H2), which is illustrated in Fig. 2(c), was brazed to the free end. The annulus between the inner and outer walls of the heater body contained a BN tube with numerous 0.05-cm-diam vertical holes. Nichrome heater wire passed through these holes, and eight holes uniformly spaced around the ring were left open to serve as thermal ground positions for wires coming from the specimen heater assembly. These thermal grounds were made by inserting 0.050-cm-diam wires, approximately 1 cm long, part way into the vacant holes in the BN ring to serve as binding posts. A wire coming from the specimen heater assembly was welded near the top of the post, and the post was then pressed firmly into the hole. Since thermocouple wire can be easily contaminated when in contact with a dissimilar metal, the posts were formed with the same material as the wire (i.e., platinum posts were used for platinum wires and Pt—10% Rh posts for the Pt—10% Rh wires).

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[7]Ohmite Manufacturing Co., Skokie, Illinois; 560 ohms, 1 1/2 watts, Stock #4113; Nominal Wire Composition 75 Ni 20 Cr 2 1/2 Al 2 1/2 Cu.

[8]Power supply by Kepco, Inc., ±0.01% stability and RMS ripple less than 0.01%, Model KS60-5M.

Thermocouples, insulated with 0.159-cm-diam two-hole Al_2O_3 tubing, were pushed into the holes in the inner wall of the heater assembly with ceramic beads at the hole bottoms to prevent electrical contact. Since the heater lid was not firmly attached to the guard heater, there was concern that it might not be at the same temperature as the alloy body of H2. Therefore, the lid temperature was monitored with a thermocouple.

The instrumented specimen (with five thermocouples attached) and the uninstrumented guard are shown in Fig. 3. This figure shows the specimen as brazed to the nickel base and H1. Radial exit slots for the two-hole high-purity Al_2O_3 tube insulation can be seen recessed on the nickel base. A BN disk and small resistor similar to the ones used in H1 are also shown.

Thermometry and Instrumentation

All thermocouples were made from 0.025-cm-diam platinum and Pt—10% Rh wire. These thermocouples left the system through epoxy feedthroughs and were connected to pure copper wire in an ice-water-filled Dewar. These reference junctions to copper wires were made inside mineral-oil-filled tubes, which were positioned inside a copper block in the Dewar. All thermocouple emf's as well as other low-voltage measurements were made with a Leeds and Northrup K-5 potentiometer[9] with a photocell galvanometer[10] for null detection. All emfs could also be determined with a more accurate potentiometer,[11] and this was done occasionally to insure accuracy of the K-5 system.

The dc power supplies[8] for the specimen heater and for measuring electrical resistivity had stabilities of ±0.01% and RMS ripples less than 0.01%. Currents through the specimen heater and through the sample during ρ measurements were determined by measuring the voltage drops across 0.1-Ω standard resistors. The current from each supply passed through a reversing switch. The voltage drop across the specimen heater during the data tests was reduced to levels that could be measured on the potentiometer using a voltage divider.[12] Circuits used to control the temperatures of the base heater, the guard cylinder, and the outer furnace have been described elsewhere.[13] Two thermocouples were welded to the outside wall of the guard cylinder to determine the profile along the guard.

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[9]Leeds and Northrup Co., potentiometer type K-5 (7555), uncertainty ±0.005% of reading plus 0.1 μV.

[10]Guildline Instruments Ltd., models 9461A and 9460.

[11]Guildline Instruments Ltd., direct-current comparator potentiometer, type 9930, uncertainty on ×0.1 range = ±0.0001% + 0.01 μV.

[12]Leeds and Northrup Co., volt box, catalog No. 7593, uncertainty was ±0.02%.

[13]T. G. Kollie, *Contributions to the Specific Heat Capacity of Nickel, Iron, and the Alloy Ni_3Fe*, ORNL-TM-2649 (December 1969).

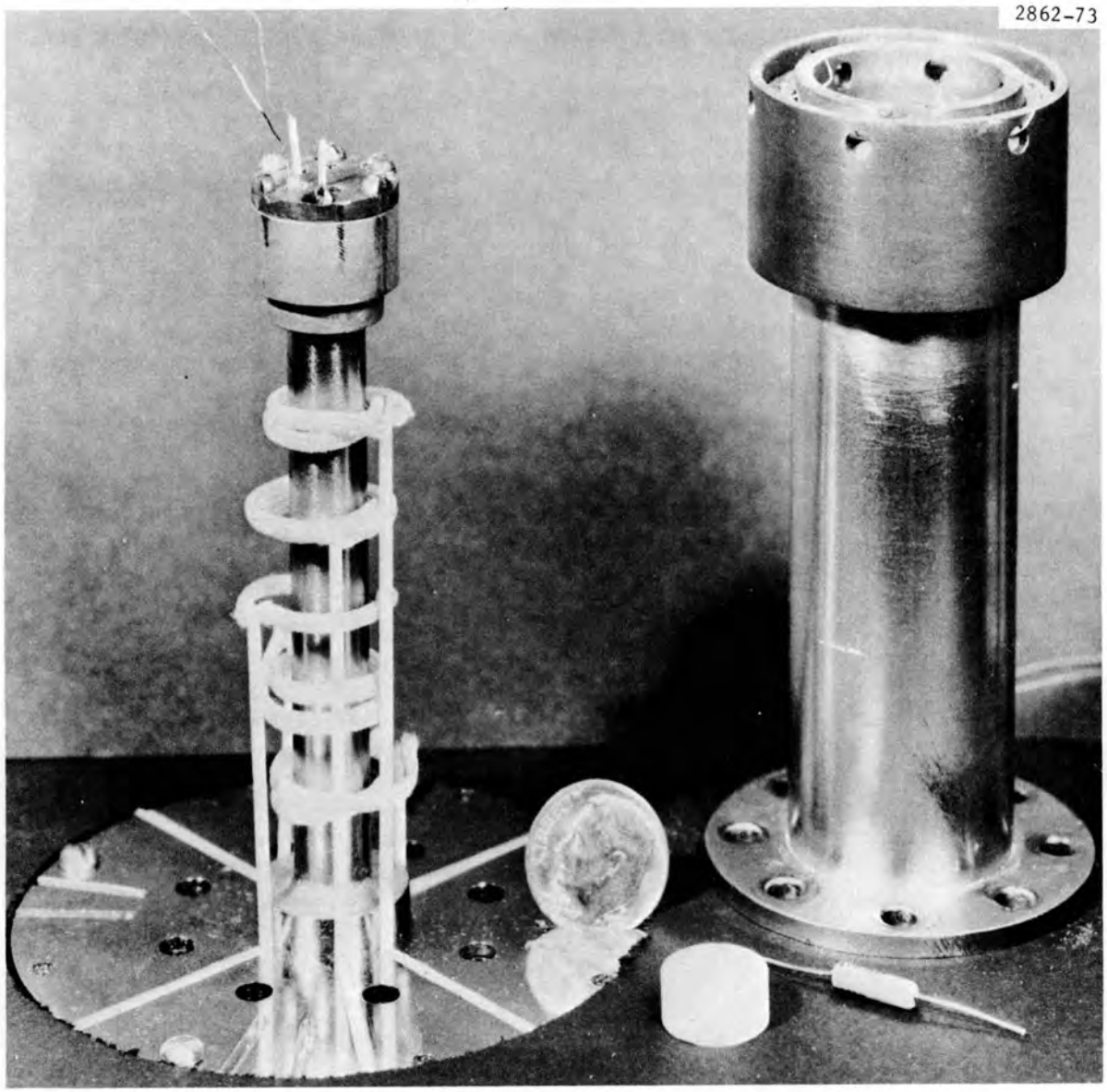

Fig. 3. Armco Iron Specimen Brazed to H1 and Nickel Base. The five thermocouples are visible as well as their exit slots on the nickel base. The guard cylinder is uninstrumented in this view.

Miscellaneous

Although it is not shown in Fig. 1, a getter of zirconium turnings compressed between molybdenum foils was positioned under the outer furnace lid to protect the sample from contamination.

All machine screws were spray coated with a fine colloidal synthetic graphite to prevent screw binding and thus ease disassembly. The flange mating surfaces of the guard cylinder and outer furnace were also spray coated to improve heat transfer.

OPERATION PROCEDURE

After each assembly, the chamber was evacuated and backfilled with argon several times to remove oxygen and moisture traces. Caution was exercised during this cycling because rapid pressure changes would cause drastic rearrangement of the Al_2O_3 powder. The argon pressure was adjusted to about 1.3×10^3 N/m^2 and H4 was used to raise the entire assembly to any desired operating temperature. The measurement temperature was maintained by controlling H4 to within ±0.02 K, and this led to a steady-state condition in which the specimen drift rate was less than 2×10^{-5} K/sec. At each temperature all the thermocouple emf's, the emf's between similar wires of adjacent thermocouples on the specimen, the current flow through H1, and the voltage across H1 were measured at steady state for at least two values of Joule heat dissipated in H1. One of these was with the electrical power in H1 (Q_e) large enough to establish an accurately measurable temperature gradient of 1 to 3 K/cm along the specimen. The other was with $Q_e = 0$. Heater H4 was used to maintain the specimen at the same average temperature during the two tests. The temperature difference between the surfaces of H1 and H2 was maintained at zero (to within ±0.05 K) by controlling the power to H2. The guard furnace temperature was normally maintained at 1 to 10 K below the surface of H2. Although various differences between outer guard and H2 surface were employed, for any two given steady-state conditions the differences were the same. All thermocouple emf's were converted to temperature on the IPTS 68 scale by use of functions of Adams and Simpson.[14]

The temperature distribution with $Q_e = 0$ was commonly referred to as the "isothermal" in other techniques and provided *in situ* intercomparisons of specimen thermocouples.[15,16] In the present system, however, the specimen was not isothermal during the $Q_e = 0$ test because of radial heat

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[14]R. K. Adams and R. L. Simpson, "Review of Techniques for Determining Thermocouple EMF-Temperature Characteristics," pp. 1603–15 in *Fifth Temperature Symposium* (Washington, D. C., June 1971), Instrument Society of America, Pittsburgh, Pa.

[15]W. Fulkerson, J. P. Moore, and D. L. McElroy, "Comparison of the Thermal Conductivity, Electrical Resistivity, and Seebeck Coefficient of a High-Purity Iron and an Armco Iron to 1000°C," *J. Appl. Phys.* 37(7): 2639–53 (1966).

[16]M. J. Laubitz and D. L. McElroy, "Precise Measurement of Thermal Conductivity at High Temperatures (100–1200 K)," *Metrologia* 7(1): 1–15 (January 1971).

flow between specimen and guard cylinder. This does not prevent the $Q_e = 0$ test from providing intercomparison corrections for the specimen thermocouples, but the corrections must be obtained in a different fashion.

The ρ of the specimens were determined by passing a regulated reversible direct current[17] through the samples and measuring the attendant voltage drops between adjacent thermoelements.

CALCULATION PROCEDURES

When $\lambda/\lambda_{ins} > 100$, where λ_{ins} is the thermal conductivity of the powder in the specimen-guard annulus, an approximate equation can be used to describe the temperature profile along the surface of a longitudinal specimen.[18] This is the thin-rod approximation, which assumes that the radial temperature gradient within the specimen is zero. In this case,

$$\frac{d^2T_s(z)}{dz^2} = \frac{\beta^2}{r^2}\,[T_s(z) - T_g(z)] \quad , \tag{1}$$

where

$$\beta^2 = \frac{2\lambda_{ins}}{\lambda\ \ln(r_g/r)} \quad , \tag{2}$$

and $T_s(z)$ and $T_g(z)$ are the temperatures along the specimen surface and inside surface of the guard cylinder, respectively. The radii of the specimen and inside wall of the guard cylinder are given by r and r_g respectively.

A high-thermal-conductivity metal was used to fabricate H1 and H2 so that the opposing surfaces would be isothermal over their lengths. With this situation the heater assemblies behave as transverse heaters located at $z = l_0$ where z is measured from the base of the specimen and l_0 is the distance between the nickel base and the bottom of H1 and H2. Experiments have indicated that

$$T_g(z) = A + Bz \quad , \tag{3}$$

so that Eq. (1) becomes

$$\frac{d^2T_s(z)}{dz^2} - \frac{\beta^2}{r^2}\,T_s(z) = -\frac{\beta^2}{r^2}\,[A + Bz] \quad . \tag{4}$$

---

[17]Power supply by Kepco, Inc., ±0.01% stability and RMS ripple less than 0.01%, Model KS60-5M.

[18]M. J. Laubitz, Chap. 3 in *Thermal Conductivity*, Vol. 1, R. P. Tye, ed., Academic Press, London, 1969, p. 128.

This equation has the solution

$$T_s(z) = C_1 \exp(\beta z/r) + C_2 \exp(-\beta z/r) + A + Bz \quad . \tag{5}$$

As mentioned previously, all thermocouple and other emf's were determined at 2 conditions for each datum point, and we have used the superscript Δ to apply for the values during the $Q_e = 0$ test and superscript δ to apply when direct current was passed through H1.

At each measurement temperature, the value of β was calculated by use of λ_{ins} from Eq. (A2) in Appendix A and an approximate value of λ. The temperature indicated by the thermocouples on the specimen and the guard cylinder during the $Q_e = 0$ test were used to calculate A^Δ and B^Δ and to calculate the quantity $T_s{}^\Delta - A^\Delta - B^\Delta z$ for each specimen thermocouple. These quantities were then fitted to $C_1^\Delta \exp(\beta z/r) + C_2^\Delta \exp(-\beta z/r)$ by the method of linear least squares. The deviation of each specimen thermocouple from this function was assumed to represent small thermal emf's due to any or all of several possible sources. These deviations were then applied as corrections to the appropriate thermocouple during the $Q_e \neq 0$ test.

An additional adjustment was made to each specimen thermocouple during the $Q_e \neq 0$ test. This adjustment was necessitated by small thermocouple errors due to a combination of gradient presence, differences in S between specimen and thermoelements, and the impossibility of thermocouple attachment with the wire axes perfectly aligned. This correction and its magnitude are discussed in Appendix B.

All the system thermocouples and emf's were read for the $Q_e \neq 0$ test; and after the two corrections were applied to each specimen thermocouple, the quantity $T_s^\delta(z) - A^\delta - B^\delta z$ was fitted to $C_1^\delta \exp(\beta z/r) + C_2^\delta \exp(-\beta z/r)$ for determination of $C_1{}^\delta$ and $C_2{}^\delta$. The small radial heat flow between specimen and guard indicates that the heat flow $Q(z)$ down the rod does not remain constant. The radial flow, Q_r, can be approximated[19] so that

$$Q(z) = Q_e + \frac{2\pi\lambda_{ins}}{\ln(r_g/r)} \int_{l_0}^{z} (T_s^\delta - T_g^\delta)dz \tag{6}$$

This equation can then be used with the temperature profile along the specimen,

$$T_s^\delta(z) = C_1{}^\delta \exp(\beta z/r) + C_2{}^\delta \exp(-\beta z/r) + A^\delta + B^\delta z \ , \tag{7}$$

---

[19]T. W. Watson and H. E. Robinson, *Trans. Amer. Soc. Mech. Engrs.* 83C: 403 (1961).

and Fourier's law (for this sign convention),

$$\frac{Q(z)}{\pi r^2} = +\lambda \frac{dT(z)}{dz} \quad , \tag{8}$$

to obtain

$$\lambda = \frac{Q_e - \frac{2\pi\lambda_{ins}}{\ln(r_g/r)} \frac{r}{\beta} \left\{ C_1{}^{\delta} \left[\exp\left(\frac{\beta l_0}{r}\right) - \exp\left(\frac{\beta z}{r}\right) \right] - C_2{}^{\delta} \left[\exp\left(\frac{-\beta l_0}{r}\right) - \exp\left(\frac{-\beta z}{r}\right) \right] \right\}}{\pi r^2 \left[C_1{}^{\delta} \frac{\beta}{r} \exp\left(\frac{\beta z}{r}\right) - C_2{}^{\delta} \frac{\beta}{r} \exp\left(\frac{-\beta z}{r}\right) + B^{\delta} \right]} \quad . \tag{9}$$

this equation was used to calculate thermal conductivity at any specimen thermocouple position, and the results were corrected for thermal expansion by use of

$$\lambda = \lambda_m / [1 + \alpha(T - 300)] \quad , \tag{10}$$

where λ_m is the measured value and α the mean coefficient of thermal expansion. The same value of λ was obtained when all the system dimensions were corrected for thermal expansion before Eq. (8).

The Seebeck coefficient of the specimen with respect to platinum ($S_{\text{spec-Pt}}$) was calculated from each adjacent pair of specimen thermocouples by use of

$$S_{\text{spec-Pt}} = \frac{E^{\delta} - E^{\Delta}}{\Delta T^{\delta} - \Delta T^{\Delta}} \tag{11}$$

where E^{δ} and E^{Δ} are the emf's between platinum thermoelements of adjacent thermocouples during the $Q_e \neq 0$ and $Q_e = 0$ tests, respectively, and ΔT^{δ} and ΔT^{Δ} are the temperature differences between the same thermocouples. The temperatures used in calculating ΔT^{δ} were corrected to the platinum wire positions as described in Appendix B. When the λ measurements were made on the brazed specimen, five thermocouples on the specimen permitted calculation of four values of $S_{\text{spec-Pt}}$. These four values were averaged. The absolute Seebeck coefficient of the specimen was then calculated with

$$S = S_{\text{spec-Pt}} + S_{\text{Pt}} \quad , \tag{12}$$

where S_{Pt} is the absolute Seebeck coefficient of platinum.[20]

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[20] J. P. Moore and R. S. Graves, "The Absolute Seebeck Coefficient of Platinum from 80 to 340 K and Thermal and Electrical Conductivities of Lead from 80 to 400 K," *J. Appl. Phys.* 44: 1174–78 (1973).

ERROR ANALYSIS

Errors involved in measuring λ, S, and ρ can be grouped into two categories — determinate and indeterminate. The determinate errors are associated with errors in measuring the quantities used for calculating a particular property. These errors are readily discernable from inaccuracies of instruments employed in measuring the quantities. No absolute calculation can be made of indeterminate errors since these are based on deviation of the system from assumed boundary conditions. The latter can, however, be estimated.

The percentage determinate errors for ρ and λ are shown in Table 1. The determinate uncertainty in λ is given at two temperatures since the error from one source varies with T. The determinate error in $S_{\text{Spec-Pt}}$ is given in μV/K since this term can pass through zero, and percentage uncertainty would have little meaning. Area uncertainty is based on micrometer uncertainty, and errors in z, $E^{\delta} - E^{\Delta}$, $\Delta T^{\delta} - \Delta T^{\Delta}$, and V are based on those of the K-5 potentiometer. Errors in I and Q_e include contributions from standard resistors, voltage divider, and potentiometer. The large uncertainty in Q_R was due to the λ_{ins} uncertainty which increases with T.

An annealed thermocouple from the supply used for this experiment was calibrated at five temperatures from 300 to 1300 K and found to be within ±1 K of functions by Adams and Simpson.[21] This maximum deviation of 1 K would cause small errors in each property measurement due to property variation with T, and these errors are shown in Table 1. The total determinate errors were ±0.14 μV K^{-1}, ±0.4%, and ±1.3% for $S_{\text{Spec-Pt}}$, ρ, and λ at 300 K, respectively.

Indeterminate errors are those due to system variation from assumed boundary conditions and those from sources that are often difficult to eliminate. The latter include small errors in temperature measurement from wire inhomogeneity and error in $Q(z)$ from mismatch of H1 and H2.

Two assumptions made in the calculation of λ can lead to indeterminate error. The first is the thin rod approximation. Laubitz[22] discusses this error, and his Fig. 2 relates the error magnitude to the ratio $\lambda/\lambda_{\text{ins}}$. The minimum value of this ratio during the HTL (guarded high-temperature longitudinal system) tests was 300 at 1000 K, which would indicate a maximum error of 0.2%. The second assumption was that $T_g(z)$ was linear, although only two thermocouples were normally attached to the guard surface. This was a valid approximation according to $T_g(z)$ determinations with additional thermocouples on the guard.

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[21] R. K. Adams and R. L. Simpson, "Review of Techniques for Determining Thermocouple EMF-Temperature Characteristics," pp. 1603–15 in *Fifth Temperature Symposium* (Washington, D. C., June 1971), Instrument Society of America, Pittsburgh, Pa.

[22] M. J. Laubitz, "Transport Properties of Pure Metals at High Temperatures — 1. Copper," *Can. J. Phys.* 45: 3677 (1967).

Table 1. Percentage Determinate Errors in λ and ρ Measurements from Various Sources and Absolute Error in $S_{Spec-Pt}$ in μV/K

Error Component	Determinate Errors			
	$S_{Spec-Pt}$ (μV/K)	ρ (%)	λ (%)	
			300 K	1000 K
A		±0.05	±0.05	±0.05
z		±0.02	a	a
$E^{\delta} - E^{\Delta}$	±0.09[b]			
$\Delta T^{\delta} - \Delta T^{\Delta}$	±0.02[b]		a	a
V		±0.2		
I		±0.02		
Q_e			±0.03	±0.03
Q_r			±0.1	±1.0
T_s	±0.03	±0.1	±0.1	±0.1
$dT(z)/dz$			±1.0	±1.0
Total Determinate Error	±0.14	±0.4	±1.3	±2.2

[a]Effect of this on λ appears in $dt(z)/dz$ term at bottom.

[b]Since 3 or 4 values were obtained and averaged, this number was calculated assuming that the errors were random and dividing the total error by either 3 or 4.

One possible error was due to mismatch in T of H1 and H2 during the $Q_e \neq 0$ test, and experimental checks of this are discussed in a later section. Although the use of two temperature distributions (or values of Q_e) for each test reduces some indeterminate errors, the best way to assure that these are small is to test the system on a reference material, and such a test is described below.

MEASUREMENT RESULTS ON THE REFERENCE USING THE HTL

Description of Armco Iron Reference Specimen

Since Armco iron has long been recognized as an ad hoc thermal conductivity reference,[23] a specimen was fabricated from this material for testing the HTL. The procedure used for determining reference values for the specimen is described completely in Appendix C. Basically, the values were determined from measurements of λ in a low-temperature technique[24] and calculations of λ from measured ρ values and work of others.[25,26]

Electrical Resistivity

Figure C1 of Appendix C shows the electrical resistivity results obtained on the Armco iron reference during the three assemblies (threaded assemblies 1 and 2 and the brazed assembly). Previous results by Fulkerson et al.[25] are also shown for comparison. From 295 to 1004 K, the ρ of the Armco iron used to test the HTL is between the values reported by Fulkerson et al. on another Armco iron and on a high-purity iron. The good agreement of results from the three assemblies and the data precision can be seen in Fig. 4, where results are plotted as percentage deviations from

$$\rho(\mu\Omega\text{-cm}) = -3.88668 + 0.0449084T + 5.2226 \times 10^{-8}\ T^3 \quad . \qquad (13)$$

Although the data indicate that small ρ differences were caused by the brazing operation, all data are within a band of ±0.8% about the smooth line. Thermal cycling, which occurred during measurements on the brazed specimen, had only a small effect on ρ, as shown by the agreement (±0.37%) of values obtained near 300 K.

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[23] R. W. Powell, "Armco Iron as a Thermal Conductivity Standard, Part I, Review of Published Data," p. 454 in *Progress in International Research on Thermodynamic and Transport Properties*, J. F. Masi and D. H. Tsai (eds.), ASME and Academic Press, New York, 1962.

[24] M. J. Laubitz and D. L. McElroy, "Precise Measurement of Thermal Conductivity at High Temperatures (100–1200 K)," *Metrologia* 7(1): 1–15 (January 1971).

[25] W. Fulkerson, J. P. Moore, and D. L. McElroy, "Comparison of the Thermal Conductivity, Electrical Resistivity, and Seebeck Coefficient of a High-Purity Iron and an Armco Iron to 1000°C," *J. Appl. Phys.* 37(7): 2639–53 (1966).

[26] C. F. Lucks, "Armco Iron: New Concept and Broad-Data Base Justify Its Use as a Thermal Conductivity Reference Material," *J. Test. Eval.* 1(5): 422 (1973).

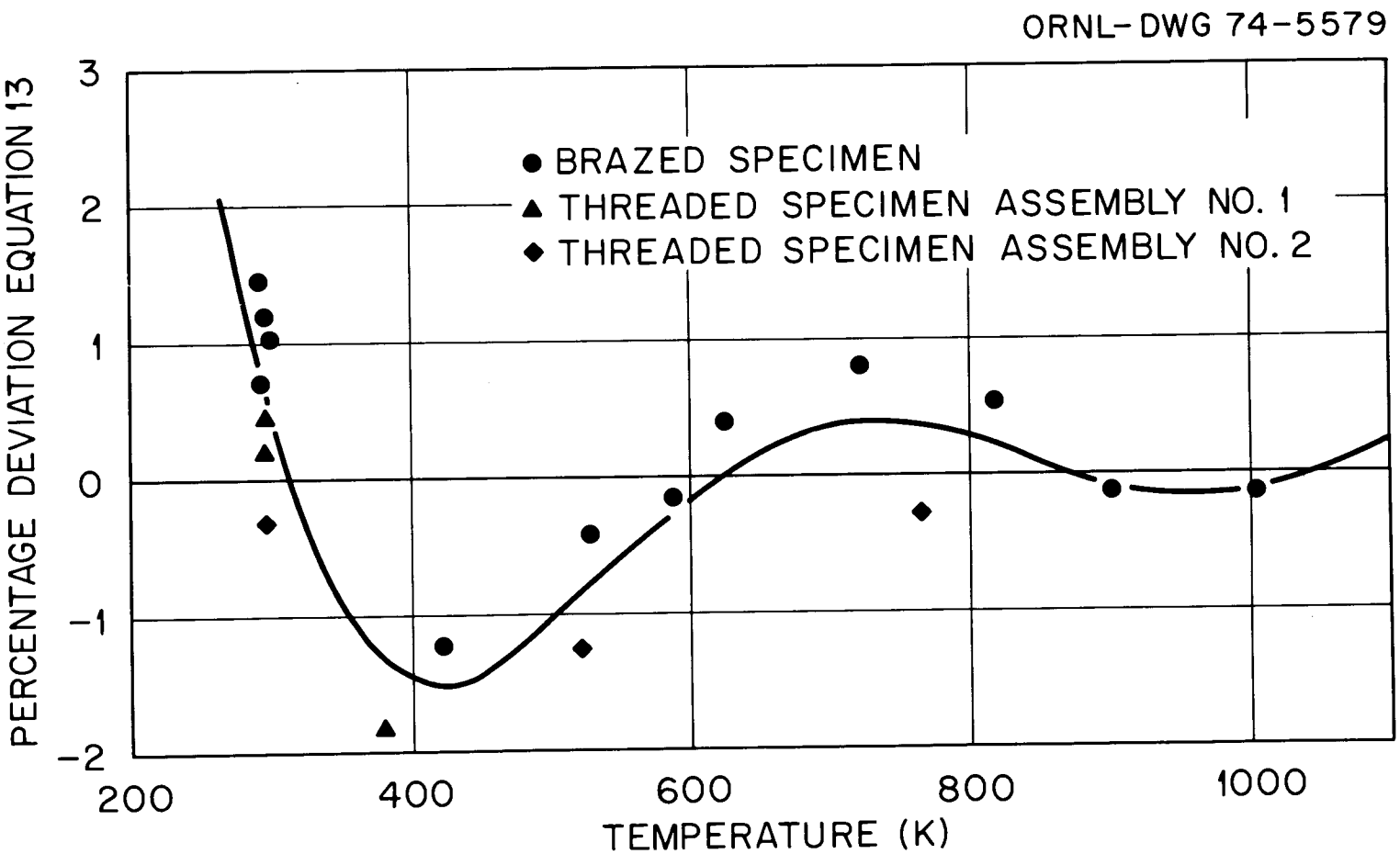

Fig. 4. Percentage Deviations of ρ Data from the Equation $\rho = -3.8868 + 0.0449084T + 5.2226 \times 10^{-8}T^3$, where T is in K and ρ in μΩ-cm.

Absolute Seebeck Coefficient

Absolute Seebeck coefficient results from all three specimen assemblies are compared to previous ones[25] in Fig. 5, and a smooth curve has been drawn through the present data. All values from the three assemblies and results from the low-temperature longitudinal are within ±0.1 μV/K of the smooth curve, and this is within the determinate error of the measurements. The shape of the S curve is of interest since two aspects of system operation are sensitive to S.

The correction to each thermocouple due to gradient presence (see Appendix B) was proportional to the Seebeck coefficient of iron with respect to that of Pt–10% Rh (S_{Rh}), which is also shown in Fig. 5. Near the middle of the temperature measurement range, where S is a minimum, the difference between S of iron and that of Pt–10% Rh is small, and the thermocouple corrections were correspondingly small. The reverse of this is true at the lower and upper ends of the temperature measurement range, where the difference between S of iron and that of Pt–10% Rh became large.

Measurements of ρ are also affected by S_{Rh}. Peltier heating and cooling occur at the sample ends from passage of direct current through the specimen. When the polarity of the current is reversed, a heat wave is propagated down the specimen and interferes with measurement of the voltage drop between adjacent Pt–10% Rh thermoelements that are used to determine voltage drops along the specimen. This problem is most severe at the lower and upper temperatures, where S of iron differs markedly from S_{Rh}.

Thermal Conductivity Results

The initial use of this apparatus was to measure λ of specimens that had heaters, temperature sensors, and heat sinks readily detachable. For this reason, initial tests were made with heater (H1) and heat sink attached with mechanical threaded connections. Initial results from the first two assemblies were not the best because of several suboptimum aspects. These include the following.

1. The small corrections to temperature measurements discussed in Appendix B were not made in either threaded assembly because the importance of these corrections was not realized until the specimen had been disassembled.
2. The first assembly of the threaded specimen included a poorer design for H1 than the one shown in Fig. 2.
3. Differential control of the temperature difference between H2 and H1 was not as good as achieved in later tests on the brazed specimen.
4. Only four thermocouples were attached to the specimen for the measurements with the threaded connections, whereas five were used on the brazed iron tests.
5. Last, and probably more important than all the others, were the temperature drops that occurred at both ends of the specimen during $Q_e \neq 0$ tests.

Although these difficulties existed, tests of system behavior with the specimen threaded into place revealed the effect of apparatus variables on

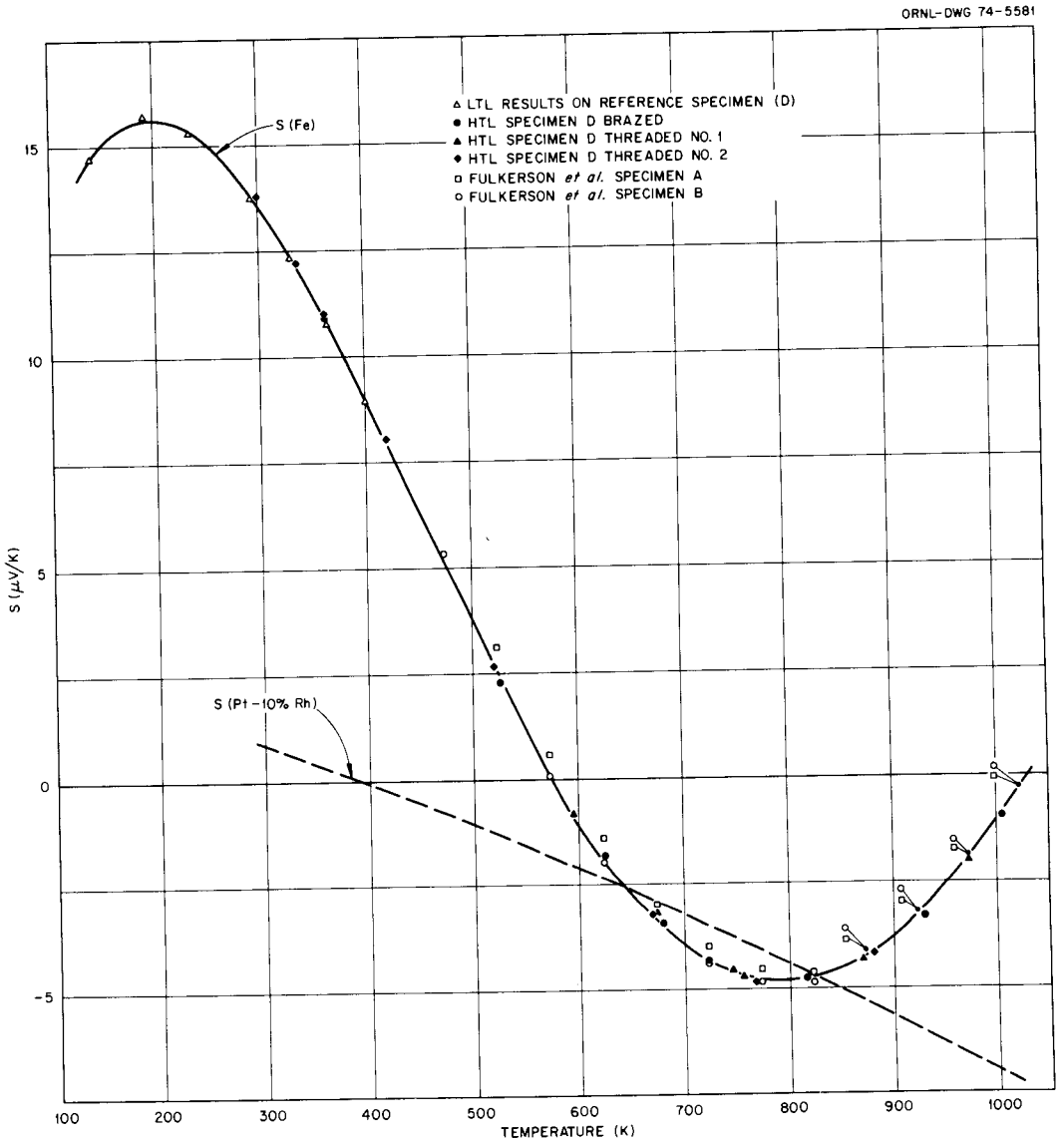

Fig. 5. Absolute Seebeck Coefficient (μV/K) of Armco Iron Reference as Determined During Three Assemblies of the HTL, and the Absolute Seebeck Coefficient of Pt–10% Rh.

measured λ. Results from these two assemblies are shown in Fig. C2 of Appendix C and are shown in Fig. 6 as deviations from the assumed λ values of the reference. The results are about 2 or 3% higher at 300 to 400 K, but this difference increases with increasing T to a maximum of 5.5% at 973 K. Reproducibility and precision are indicated by the ±1% band, which encompasses both sets of data. The data error is within the combined uncertainties of measurement and reference value at the lower end of the T range but definitely exceeds them above 600 K. Several system parameters were tested in an attempt to define the error source.

Measurements were made at gas pressures from 600 to 2500 N/m^2 and with the outer furnace at various differential temperatures with respect to the guard cylinder temperature. During these tests, H1 and H2 were matched in temperature, while the temperature of H3 was maintained at various levels below and above that of H2. Results from this study are shown in Fig. 7 and indicate that the variation of gas pressure and the temperature of H3 affect λ by less than 0.5% over the ranges tested.

The effect of temperature mismatch between H1 and H2 on the λ measurements was also examined. In this instance there was heat flow, P_w, along the wires between H1 and the wire thermal ground positions on H2 and heat flow, P_{ins}, through the insulation between H1 and H2. This was important because the λ calculation method did not account for heat exchange between H1 and H2, and this exchange could have occurred because of any one or a combination of things, which include small differences in the emf output of the thermocouples on H1 and H2 and small spurious emf's in the control circuitry. The total heat flow, P_{ext}, between H1 and H2 was

$$P_{ext} = P_w + P_{ins} \quad ; \tag{14}$$

and since P_{ins} was an order of magnitude greater than P_w,

$$P_{ext} \sim P_{ins} \sim \lambda_{ins} A_{top} \frac{\Delta T}{l'} + \lambda_{ins} \frac{2\pi l'' \Delta T}{\ln(r''/r')} \tag{15}$$

$$P_{ext} \sim \lambda_{ins} \Delta T \frac{A_{top}}{l'} + \left[\frac{2\pi l''}{\ln(r''/r')}\right] \tag{16}$$

where A_{top} was the area of the top of H1, l' the distance between this top and the lid of H2, l'' the length of H1, and r'' and r' were the radii of the inside surfaces of H2 and H1 respectively. The measured temperature difference between the two surfaces was ΔT. Calculated values from this equation at 520 K are plotted in Fig. 8 against temperature mismatch. When the temperature of H1 exceeds that of H2 by 1.1 K, a heat flow away from H1 results in a P_{ext} of .036 W or a positive error of about 5.5%.

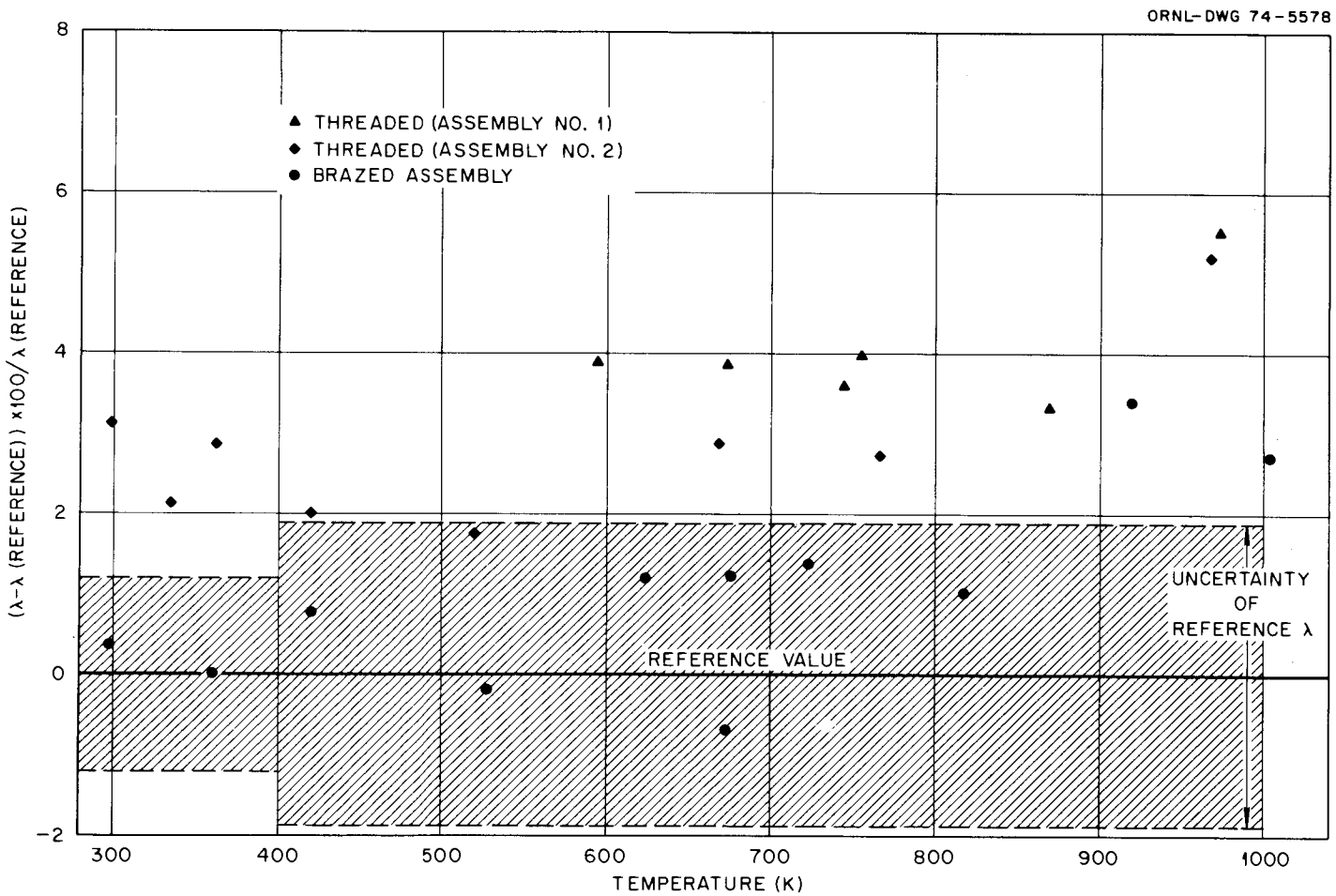

Fig. 6. Percentage Deviation of Measured λ from the Reference Value: $100(\lambda - \lambda_{reference})/\lambda_{reference}$. The dashed lines indicate the uncertainty of the reference λ.

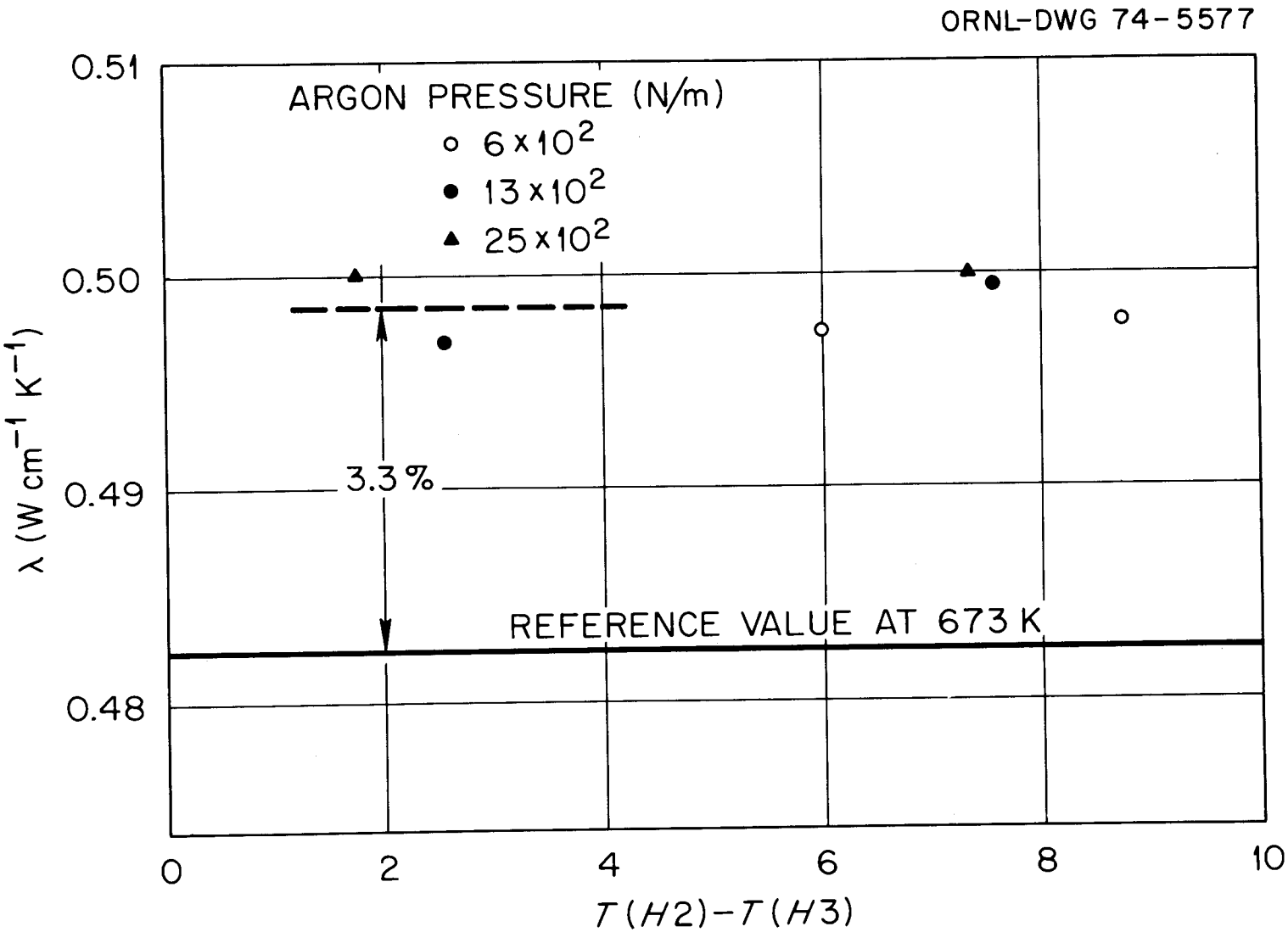

Fig. 7. Thermal Conductivity Results from One of the Threaded Assemblies as a Function of Gas Pressure and Temperature Difference Between H3 and H2. Temperature of H1 = T(H2).

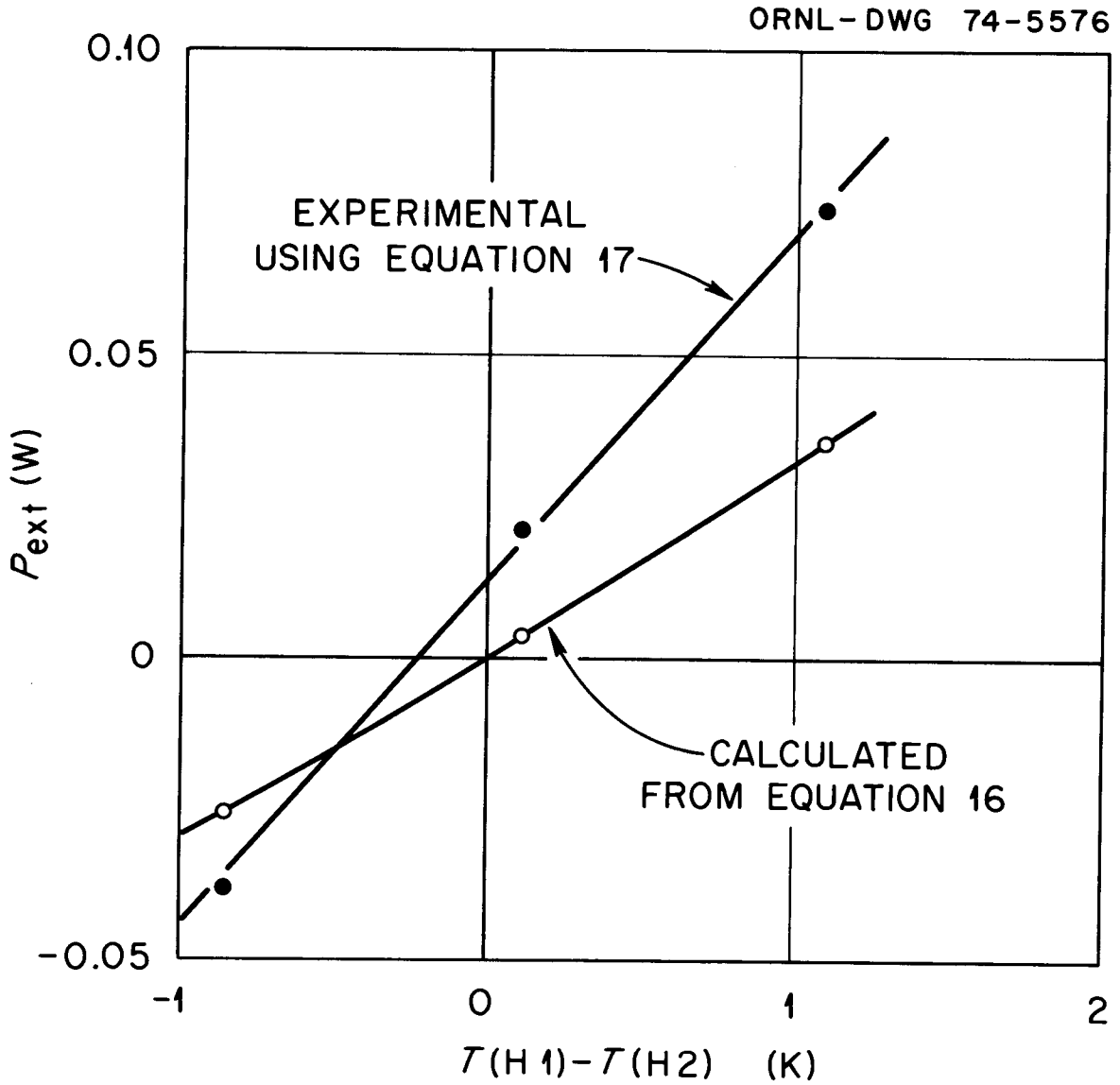

Fig. 8. Heat Exchange Between H1 and H2 as Calculated from Eq. (16) and as Determined Experimentally While the Specimen was Threaded to H1 and the Nickel Base.

Heat exchange between H1 and H2 was determined experimentally by measurements with H2 above and below H1. At three mismatch values, P_{ext} was obtained from

$$P_{ext} = Q_e - \lambda \pi r^2 \frac{dT}{dz} , \qquad (17)$$

where λ is the value assumed for the reference and dT/dz was calculated at the position of the top specimen thermocouple. These experimental values are also shown in Fig. 8 and are higher than calculated values based on

λ_{ins}. This difference represents a dilemma since the experimental results indicate a stronger dependence on temperature mismatch between H1 and H2 than anticipated. This effect may also be the source of the high λ values at all temperatures for the two threaded assemblies. Although the calculated corrections for P_{ext} were too low based on this test, the corrections based on Eq. (16) were applied to each datum point obtained with ΔT greater than 0.02 K.

Part of the error in the threaded specimen assemblies may have been due to the large drops in temperature at the interfaces of the specimen with H1 and with the heat sink. This is shown in Fig. 9, where $T_s(z)$ and $T_g(z)$ are plotted for the $Q_e = 0$ and $Q_e \neq 0$ tests at a nominal T of 675 K. Although $T_s(z)$ and $T_g(z)$ were not the same during the $Q_e = 0$ test, they both merge smoothly with the temperatures of H1 and H2, respectively. When $Q_e \neq 0$, the heat flow from H1 caused a temperature drop of about 3 K at the H1-specimen interface. This also created a condition $T_s(z) < T_g(z)$ at higher values of z.

The large temperature drops at the interfaces were eliminated by brazing the specimen to H1 and to the nickel base. The result of the improved thermal contacts by brazing is shown by $T_s(z)$ and $T_g(z)$ in Fig. 10 for measurements near 725 K. In this case, $T_s(z)$ extrapolates to within 0.5 K of the temperature measured on H1, and the mismatch between $T_s(z)$ and $T_g(z)$ was similar for $Q_e = 0$ and $Q_e \neq 0$. As shown in Figs. 6 and C2, the λ results from the brazed Armco iron reference were within ±1.5% of the standard value from 300 to 820 K and had a maximum deviation of +3.2% at 920 K. The ±1.5% is within the uncertainty of the reference, and the 3.2% is well within the combined uncertainties of the reference λ (±1.9%) and determinate measurement error (±2.2%). Data were obtained on the brazed specimen at 675 K using two gradients or two values of $Q_e \neq 0$. One had a temperature difference of 14 K between top and bottom specimen thermocouple and the other had a difference of 9 K. The two λ values differed by only 0.2%, which indicates insensitivity of measured λ to gradient magnitude.

A calculation of λ at 624 K for the brazed iron is given in Appendix D. This calculation shows that Eq. (5) describes $T_s(z)$ to within ±0.005 K, which is within the uncertainty of the K-5 potentiometer. This was true for all data on the brazed iron except the datum at 1005 K, where the middle specimen thermocouple deviated from the least squares fit by −0.07 K.

The temperature profile along the brazed specimen was better defined than that of the threaded assemblies because of the larger number of thermocouples, and this permits a calculation of the heat flow between H1 and H2 during the $Q_e = 0$ test. If this heat flow was the same for both $Q_e = 0$ and $Q_e \neq 0$ tests, it could be applied as a correction to the λ data. This heat flow would be given by Eq. (17) as

$$P_{ext} = \lambda A \frac{dT_s^{\Delta}(z)}{dz}\bigg|_{z = l_0} \tag{18}$$

or

$$P_{ext} = \lambda A \frac{\beta}{r}\left[C_1^{\Delta} \exp\left(\frac{\beta l_0}{r}\right) - C_2^{\Delta} \exp\left(-\frac{\beta l_0}{r}\right) + \frac{B^{\Delta} r}{\beta}\right] ,$$

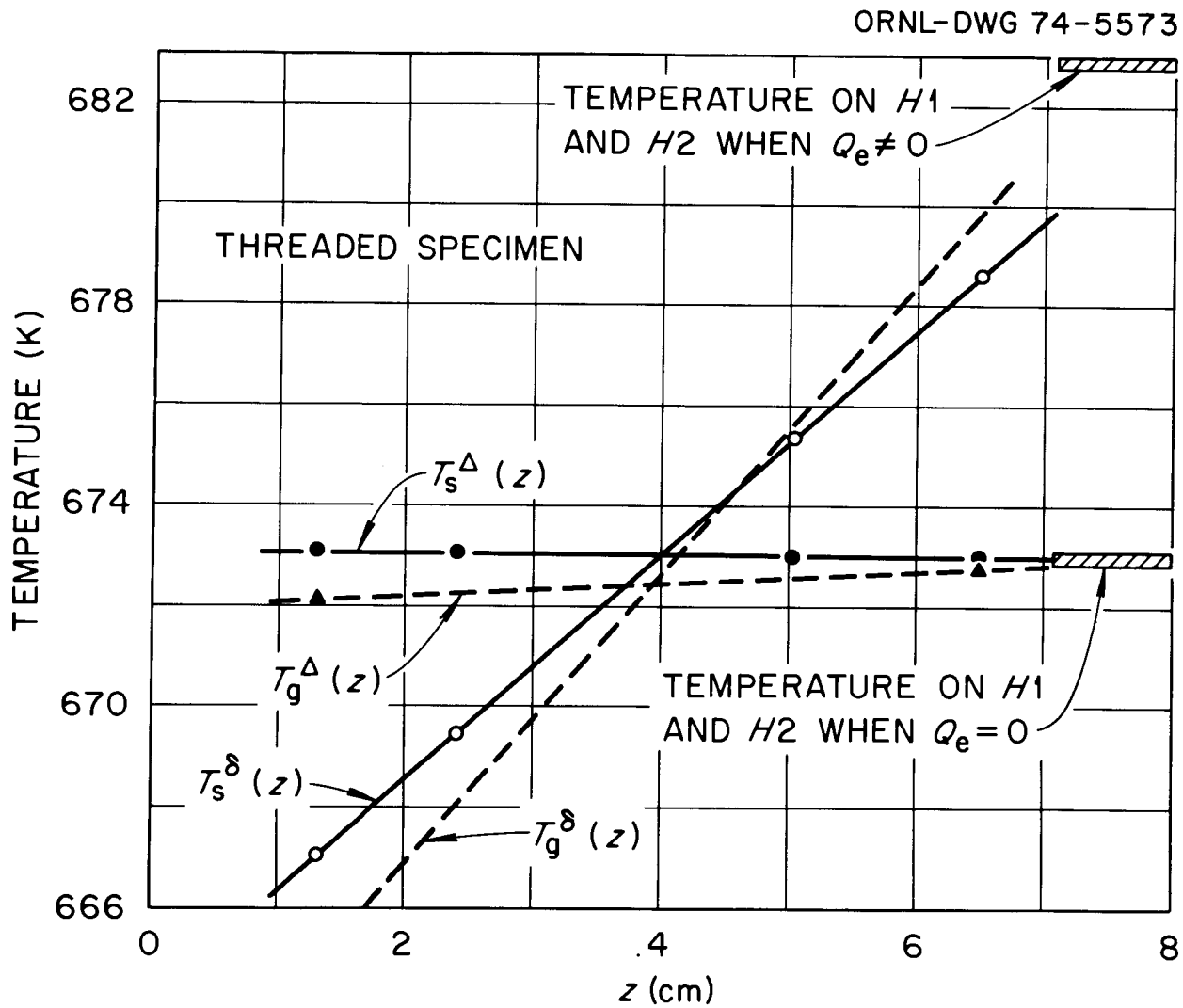

Fig. 9. Plots of $T_s(z)$ and $T_g(z)$ for the $Q_e = 0$ and $Q_e \neq 0$ measurements on One of the Threaded Specimen Assemblies near 675 K, showing the Difference in Temperature Profiles and the Large T Drop at the Specimen-H1 Interface.

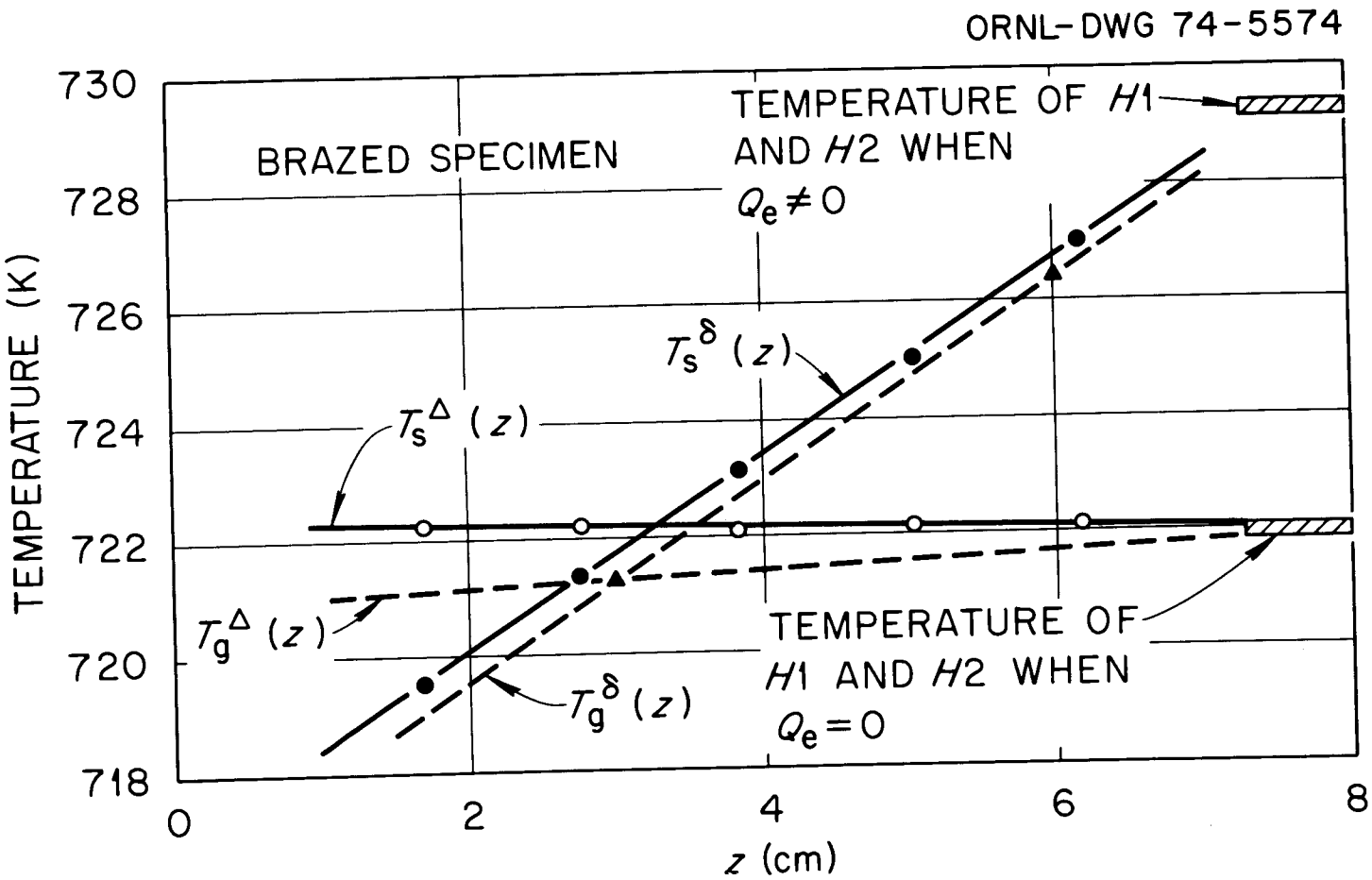

Fig. 10. Plots of $T_s(z)$ and $T_g(z)$ for the $Q_e = 0$ and $Q_e \neq 0$ Measurements on the Brazed Iron Near 725 K.

where λ is an initial estimate of the specimen conductivity. If this calculation is done for the example of Appendix D, it can be seen that P_{ext} would be less than 0.1% of Q_e and relatively insignificant. This might not always be the case, however, since small errors in the thermocouples attached to H1 and H2 as well as errors in the differential control circuit might vary with assembly.

During the λ measurements with the three assemblies the resistance of H1 behaved the same. From 300 to 530 K, the resistance increased slightly with increasing temperature but decreased rapidly at high temperature. We feared that this was caused by partial shunting of the current to H1 either through the two-hole Al_2O_3 tubes that contained the wires or through the BN of the thermal ground on H2. If this occurred, it would have caused an error in λ measurements. The resistance of the wire-wound ceramic heater was tested in another system where possibilities of current shunting were eliminated. The resistance of the heater with increasing temperature behaved exactly as observed during the three HTL assemblies, which indicates that the resistor was becoming more conductive at high temperature because of a decrease in the heater wire resistivity and/or higher electrical conductivity of the oxide potting material at high temperature. The former was more probable since the ρ of most nickel-chromium alloys behaves in this fashion, but in either case there would not be an effect on λ measurements.

One assumption in all λ measurements was that the surfaces of H1 and H2 were isothermal, although H1 and H2 were not necessarily at the same temperature. Calculations of the temperature profile on the surfaces of H1 and H2 using a finite difference technique indicated that the opposing surfaces of the two heater assemblies should have been isothermal to within ±0.1 K. Temperature measurements on H2 and H1 at three and two positions, respectively, agreed within this range, substantiating the assumption involved in calculation of λ.

Smoothed values of ρ, λ, and S for the reference specimen are presented in Table 2. The ρ and S were from measurements made in the HTL and the smoothed λ values are those calculated for the reference in Appendix C.

CONCLUSIONS

Based on results obtained on the Armco iron reference during several tests, several conclusions were reached.

1. The guarded longitudinal heat flow apparatus will measure λ, ρ, and S of small specimens (1 cm diam × 7 cm long) to within the determinate uncertainties of ±1.3% (300 K) and ±2.2% (1000 K), ±0.4%, and ±0.14 μV/K, respectively, when the specimen is brazed to both heater and heat sink.

2. When the specimen heater and heat sink were attached to the Armco iron reference specimen with threaded connections, ρ and S agreed with the results from the brazed specimen, whereas λ was higher by several percent. The greater error of the threaded specimen results may be associated with the large temperature drop at the specimen-heater interface; this drop cannot be matched by the guard cylinder.

Table 2. Smoothed λ, ρ, and S Values for the Reference Armco Iron Specimen

T(K)	ρ^a ($\mu\Omega$-cm)	S^b (μV/K)	λ^c (W cm^{-1} K^{-1})
250		15.05	0.7588
300	11.04	13.55	0.7258
400	17.17	8.98	0.6590
500	24.84	3.80	0.5925
600	34.29	−1.12	0.5265
700	45.63	−3.94	0.4660
800	58.95	−4.80	0.4148
900	74.53	−3.76	0.3685
1000	93.14	−1.06	0.3218

[a]Corrected for thermal expansion with a mean α of 14×10^{-6}/K.

[b]From smooth curve of Fig. 5.

[c]These are reference values for λ as determined in Appendix C. They form the base line for Figs. 6 and 7.

Nominal 1300

3. Measured values of λ with argon pressure from 600 to 2500 N/m^2 and the temperature of H3 from zero to 10 K below T(H2) are all within a 0.5% band, which indicates system insensitivity to these parameters.

4. Experimental determinations of the effect of temperature difference between H1 and H2, which were made on one of the threaded iron assemblies, were nearly double calculated values based on λ_{ins}. This aspect of the results is not understood but may be associated with the temperature discontinuity at the interfaces.

Several improvements could be made in this apparatus. No experimental technique gives as complete a picture of the temperature profiles as desired. Increasing the number of thermocouples could improve the knowledge, but this would increase assembly problems. A second improvement would involve better control of H1 and H2 since mismatch had a greater effect on λ than anticipated. Uncertainty in λ_{ins} contributes to the uncertainty in λ calculations at the upper end of the temperature range. This contribution could be reduced significantly by measurement of λ_{ins} at high temperature. Lastly, measurement uncertainty in λ would decrease with a larger specimen, which should always be used unless there is a valid reason for size restriction.

ACKNOWLEDGMENTS

We gratefully acknowledge the technical comments and encouragement of R. K. Williams and S. H. Jury. This technique development was supported by the Molten-Salt Reactor Program, and we appreciate the interest of H. E. McCoy and W. P. Eatherly. We also acknowledge A. J. Moorhead for his brazing effort, which improved thermal contacts with the specimen, and Claudette McKamey and Jo Anne Zody for their rapid and careful typing.

APPENDIX A

Thermal Conductivity of Powder Insulation

Since the thermal conducitivty, λ_{ins}, of the powder in system annuli was an important parameter in the calculation of λ, a special attempt was made to measure λ_{ins} versus argon pressure.

The technique employed, which is shown in Fig. A1, was similar to a radial heat flow device developed by Flynn.[1] We simplified Flynn's device by using a tubular stainless steel central heater and a copper cylinder for the outer container. One thermocouple was located in the center of the tubular core and three thermocouples were soldered onto the outer wall of the copper container. A direct current (I') was passed through the core heater to establish a radial temperature gradient in the powder. After the system had equilibrated, the voltage drop (V) across a known length l, of the core heater, and the current flow through the heater were determined and all thermocouples read. The λ_{ins} was then calculated from

$$\lambda_{ins} = \frac{V' I' \ln(b/a)}{2\pi(t_i - t_o - C)l} , \tag{A1}$$

where b is the inside radius of the copper cannister, a is the outside radius of the core heater, t_i and t_o are the temperatures of the core heater and copper, respectively, and C is a small correction for temperature drop in the walls of the tube and outer can. The tests were performed at various argon pressures as determined with a mercury manometer and a thermocouple vacuum gage, and the results at room temperature are shown in Fig. A2. In drawing a smooth curve through the data points, the value at 340 N/m^2 was ignored because this pressure was in a range where neither of the pressure measuring devices was accurate.

Pressure in the longitudinal system was between 600 and 1300 N/m^2 during actual measurements on a specimen. At these pressures λ_{ins} would be about 4×10^{-4} W cm^{-1} K^{-1}. We measured λ_{ins} at room temperature only, but λ_{ins} increases with increasing T. Values for λ_{ins} at higher T were approximated from our measured value and the results of Laubitz[2] on similar powder in air and in vacuum at higher T. We believe that the equation

$$\lambda_{ins} = \left[\frac{142.86}{T} + 2.28 + 0.003057T + 0.3619 \times 10^{-5}\, T^2\right] \times 10^{-4} \text{ W cm}^{-1} \text{ K}^{-1} \tag{A2}$$

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[1] D. R. Flynn, "A Radial Heat Flow Apparatus for Determining the Thermal Conductivity of Loose-Fill Insulations to High Temperatures," *J. Res. NBS* 67C(2): 129–37 (1963).

[2] M. J. Laubitz, "A Note on the Thermal Conductivity of Powders in Vacuum," p. 628 in *The 3rd Conference on Thermal Conductivity held at Mountain View Hotel, Gatlinburg, Tennessee, Oct. 16–18, 1963*, Oak Ridge National Laboratory, 1964.

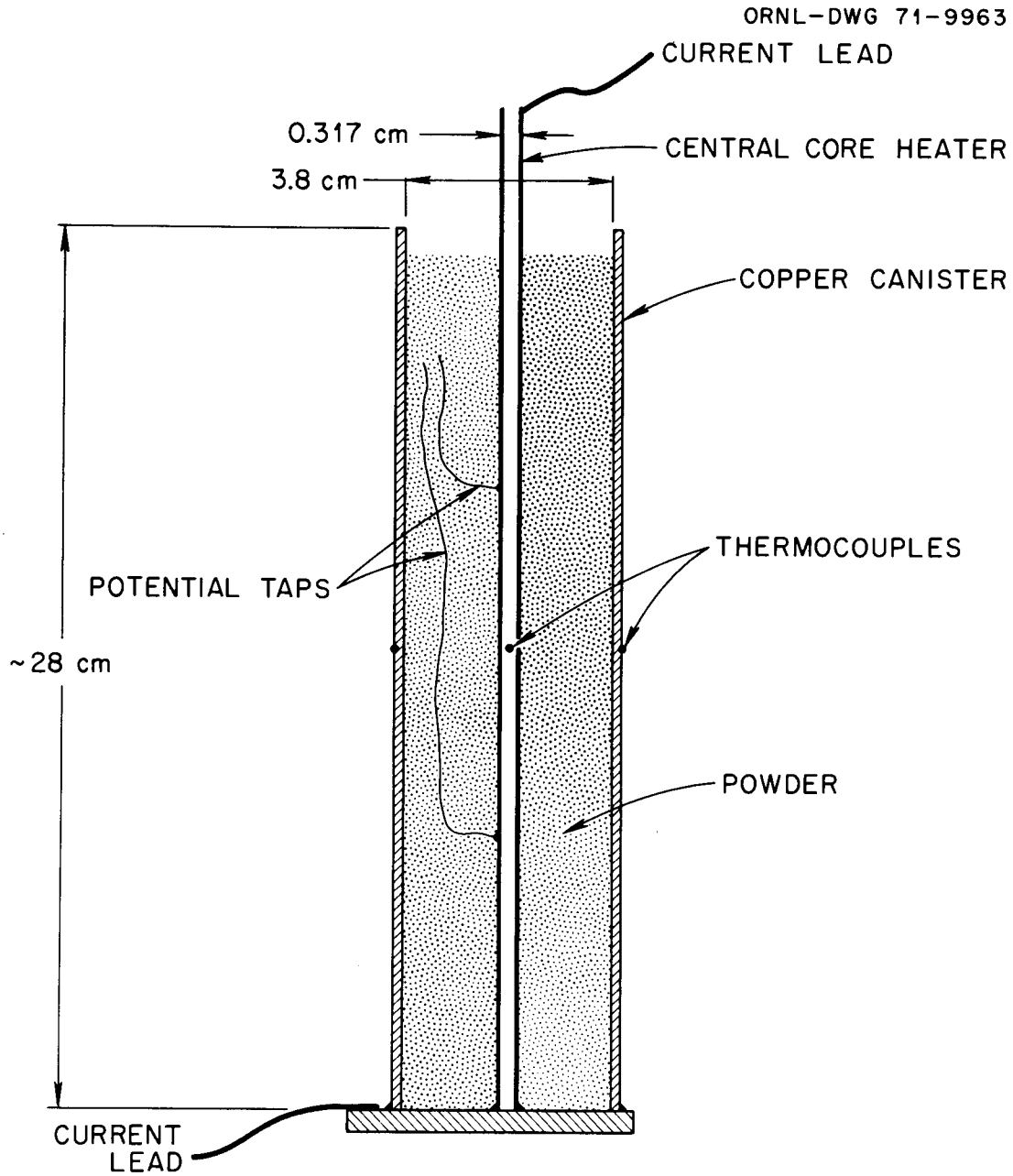

Fig. A1. Schematic of System Used to Measure λ_{ins} as a Function of Argon Pressure at 300 K.

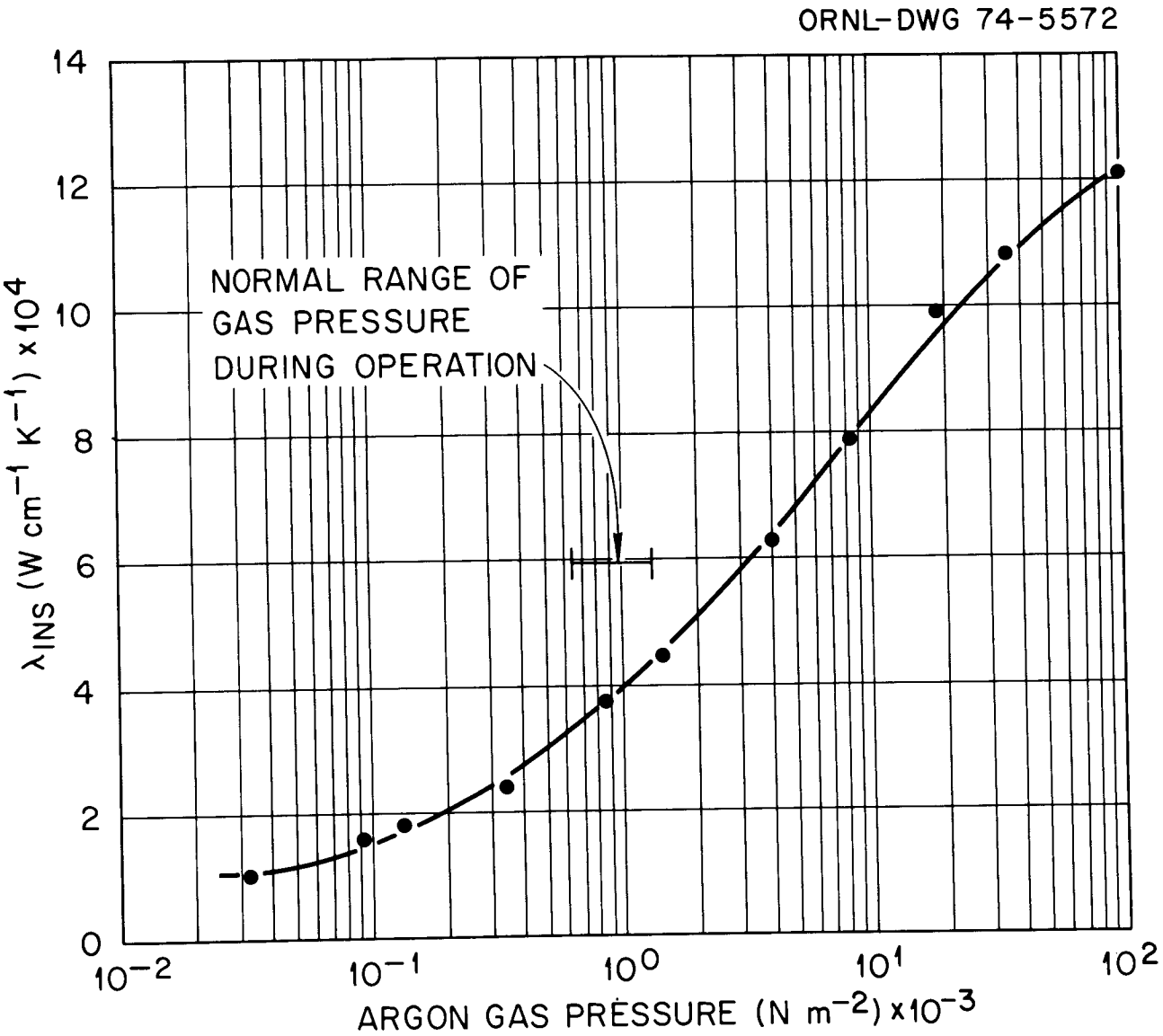

Fig. A2. Thermal Conductivity of Al_2O_3 Powder as a Function of Argon Pressure at 300 K.

describes λ_{ins} at the operating pressures to within ±20%, and this equation was used in all calculations of specimen λ.

APPENDIX B

Calculation of Surface Temperature When a Temperature Difference Exists Between Contact Positions of the Two Thermoelements

Ideally, the specimen thermocouple wires are attached so that they are at the same value of z. If the isotherms are horizontal planes down the longitudinal specimen, the contact points of these two thermoelements are the same T, and T can be determined properly. This is true if other error sources, such as heat flow down the thermoelement, wire inhomogeneity, and emf determination, have been eliminated. If, however, the ideal situation has not been achieved, a significant error can occur in the temperature measurement. This error depends on the lack of colinearity of the thermoelement wire axes and the Seebeck coefficient of the specimen with respect to the thermoelements. Fortunately, a correction can be applied for this effect, as shown in the following.

Assume we have a specimen with platinum and Pt—10% Rh wires attached as shown in Fig. B1. The platinum and Pt—10% Rh wires are attached to copper wire at T_0, which normally is the ice bath temperature of 273.15 K.

We will correct the measured emf of the hot junction to the position of the platinum wire along the thermal gradient since Seebeck measurements are made with respect to platinum and the temperature differences between platinum thermoelements must be known. The absolute Seebeck coefficient of Pt—10% Rh wire, S_{Rh}, is positive, and the total emf, E_m, of a thermocouple is given by

$$E_m = \int_{T_0}^{T_2} S_{Rh}\, dT + \int_{T_2}^{T_1} S\, dT + \int_{T_1}^{T_0} S_{Pt}\, dT \quad , \tag{B1}$$

leading to

$$E_m = \int_{T_0}^{T_2} S_{Rh}\, dT - \int_{T_0}^{T_1} S_{Pt}\, dT + \int_{T_2}^{T_1} S\, dT \quad , \tag{B2}$$

or

$$E_m = \int_{T_0}^{T_1} S_{Rh}\, dT + \int_{T_1}^{T_2} S_{Rh}\, dT - \int_{T_0}^{T_1} S_{Pt}\, dT - \int_{T_1}^{T_2} S\, dT \quad , \tag{B3}$$

where

S_{Pt} = Absolute Seebeck Coefficient of Pt,

S = Absolute Seebeck Coefficient of the specimen.

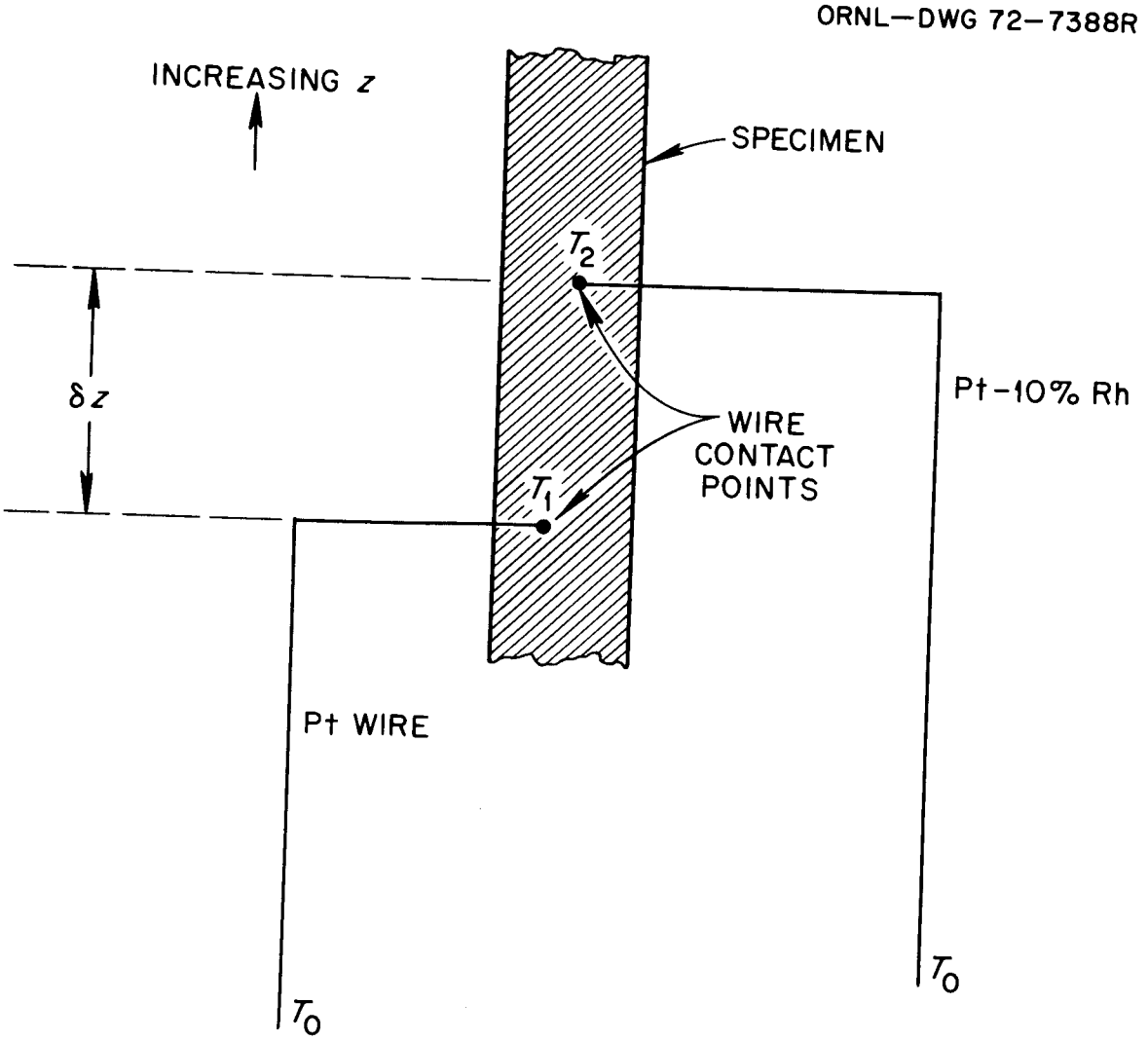

Fig. B1. Noncolinear Thermocouple Wires Attached to a Specimen.

Therefore,

$$E_m = \int_{T_0}^{T_1} S_{\text{Rh-Pt}}\, dT + \int_{T_1}^{T_2} S_{\text{Rh-spec}}\, dT \quad , \tag{B4}$$

where $S_{\text{Rh-Pt}}$ = Seebeck coefficient of Pt–10% Rh with respect to platinum and $S_{\text{Rh-spec}}$ = Seebeck coefficient of Pt–10% Rh with respect to the specimen.

The emf at temperature T_1, E_{T_1}, is $\int_{T_0}^{T_1} S_{\text{Rh-Pt}}\, dT$, and E_{T_1} becomes

$$E_{T_1} = E_m + \int_{T_1}^{T_2} S_{\text{spec-Rh}}\, dT \quad . \tag{B5}$$

This can be approximated with

$$E_{T_1} = E_m + \frac{dT}{dz}\,(\delta z)\, S_{\text{spec-Rh}} \quad , \tag{B6}$$

where dT/dz is an approximate gradient and δz is the distance between the contact points of the two wires. The distance δz for each thermocouple was determined electrically during knife edge measurements of the distances between adjacent thermocouples. This was done by measuring the emf of each thermocouple for a known direct current passing in both directions through the specimen. Since dT/dz and $S_{\text{spec-Rh}}$ appear in the correction determinations, approximate values of these must be determined initially by ignoring the correction.

It should be noted that this correction term is directly proportional to the gradient and is not eliminated by measurements with different values of Q_e. For materials such as irradiated graphites[1] and chromium[2] where $S_{\text{spec-Rh}}$ are large, this correction may amount to a few percent. For the measurements presented in this paper the corrections were small, with a maximum effect of 0.2% below 400 K.

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[1]J. P. Moore, R. S. Graves, and D. L. McElroy, "Thermal and Electrical Conductivities,and Seebeck Coefficients of Unirradiated and Irradiated Graphites from 300 to 1000 K," *Nucl. Technol.* 22(1): 88–93 (April 1974).

[2]J. P. Moore, R. K. Williams, and D. L. McElroy, "Physical Properties of Chromium from 77 to 400°K," pp. 297–310 in *Thermal Conductivity, Proc. 7th Conf. Gaithersburg, Maryland, Nov. 13–16, 1967, Nat. Bur. Std. Spec. Publ.* 302, ed. by D. R. Flynn and B. A. Peavy, Jr., National Bureau of Standards, Washington, D. C., September 1968.

APPENDIX C

Thermal Conductivity of Armco Iron Standard

Armco iron has been used extensively as a thermal conductivity reference material since Powell's measurements[1] on the material in a radial heat flow apparatus in 1934, and especially since the round-robin program on Armco iron, which has been summarized by Lucks.[2] The major disadvantage of this material as a reference is its variation in chemical composition which causes large λ differences between different samples. Additionally, the presence of oxygen in the iron causes the λ to vary somewhat with cooling rate. These problems can be mitigated by measuring the ρ of a specimen and calculating λ based on numerous previous experimental results. The λ of the Armco iron used to test the HTL was determined using data from the four materials listed in Table C1. It should

[1]R. W. Powell, "Armco Iron as a Thermal Conductivity Standard, Part I, Review of Published Data," p. 454 in *Progress in International Research on Thermodynamic and Transport Properties*, J. F. Masi and D. H. Tsai (eds.), ASME and Academic Press, New York, 1962.

[2]C. F. Lucks, "Armco Iron: New Concept and Broad-Data Base Justify Its Use as a Thermal Conductivity Reference Material," *J. Test. Eval.* 1(5): 422 (1973).

Table C1. Materials Used to Determine λ of the Standard

Material	$\rho_{273.15K}$	Specimen Designation	Data Source
High-Purity Iron	9.04	A	Fulkerson et al.[a]
An Armco Iron	9.97	B	Fulkerson et al.[a]
High-Purity Iron	8.66	C	Unpublished results by the authors using a low-temperature apparatus[b]
Armco Iron used to test the HTL	9.68	D	Unpublished results by the authors using a low-temperature apparatus[b]

[a]W. Fulkerson, J. P. Moore, and D. L. McElroy, "Comparison of the Thermal Conductivity, Electrical Resistivity, and Seebeck Coefficient of a High-Purity Iron and an Armco Iron to 1000°C," *J. Appl. Phys.* 37(7): 2639–53 (1966).

[b]Apparatus described by M. J. Laubitz and D. L. McElroy, "Precise Measurement of Thermal Conductivity at High Temperatures (100–1200 K)," *Metrologia* 7(1): 1–15 (January 1971).

be remembered that the term "high purity" is relative only and in this case is with respect to Armco iron. Even the purest specimen (C) had an impurity-induced ρ of 0.043 μΩ-cm. Specimen D was the specimen used to test the HTL, and auxiliary measurements of the λ were made in a low-temperature longitudinal device discussed by Laubitz and McElroy.[3] This technique has a most probable accuracy of ±1.2% on λ determinations but has a maximum temperature limit of 400 K.

The electrical resistivities of these materials from 290 to 1004 K are shown in Fig. C1. The ρ of specimen D is about 0.3 μΩ-cm below the Armco iron studied by Fulkerson et al.[4] This difference is a small percentage at high temperatures but is 3% at 300 K, where ρ is only about 10 μΩ-cm. The inset of Fig. C1 shows these ρ values from 273 to 323 K on expanded scales. The multiple ρ values for specimen D were obtained after various temperature cycles had been imposed on the specimen during the λ determinations. All ρ values from the HTL specimen were within a ±0.4% band, and we have concluded that changes in λ during temperature cycling were small and have, therefore, established one curve to use for the assumed λ of the reference.

Thermal conductivity values for the materials listed in Table C1 are shown in Fig. C2 as functions of T. The solid line represents the λ of specimen D, which was determined by using the measured values from the low temperature longitudinal below 400 K and calculating the high-temperature values from the measured electrical resistivity of specimen D by the procedure described by Fulkerson et al.[4] Specifically, above 370 K, λ of our reference (specimen D) was calculated with

$$\lambda = \frac{(0.02443 - S^2)T}{\rho} + \lambda_l \quad , \tag{C1}$$

where S is the absolute Seebeck coefficient and λ_l is the lattice component of λ from Table III of Fulkerson et al.[4]

The ρ of specimen D can also be used in the equations by Lucks[2] (using ρ data uncorrected for expansion) to calculate λ of the specimen. As shown in Fig. C2, these equations predict λ values that are within 0.8% of the line from 300 to 823 K, and the maximum difference is +2.7% at 925 K.

We believe that the λ values of the Armco iron reference are known to within ±1.2% from 100 to 400 K since they are based on the low-temperature longitudinal results. Above 400 K the reference values are based on

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[3]M. J. Laubitz and D. L. McElroy, "Precise Measurement of Thermal Conductivity at High Temperatures (100–1200 K)," *Metrologia* 7(1): 1–15 (January 1971).

[4]W. Fulkerson, J. P. Moore, and D. L. McElroy, "Comparison of the Thermal Conductivity, Electrical Resistivity, and Seebeck Coefficient of a High-Purity Iron and an Armco Iron to 1000°C," *J. Appl. Phys.* 37(7): 2639–53 (1966).

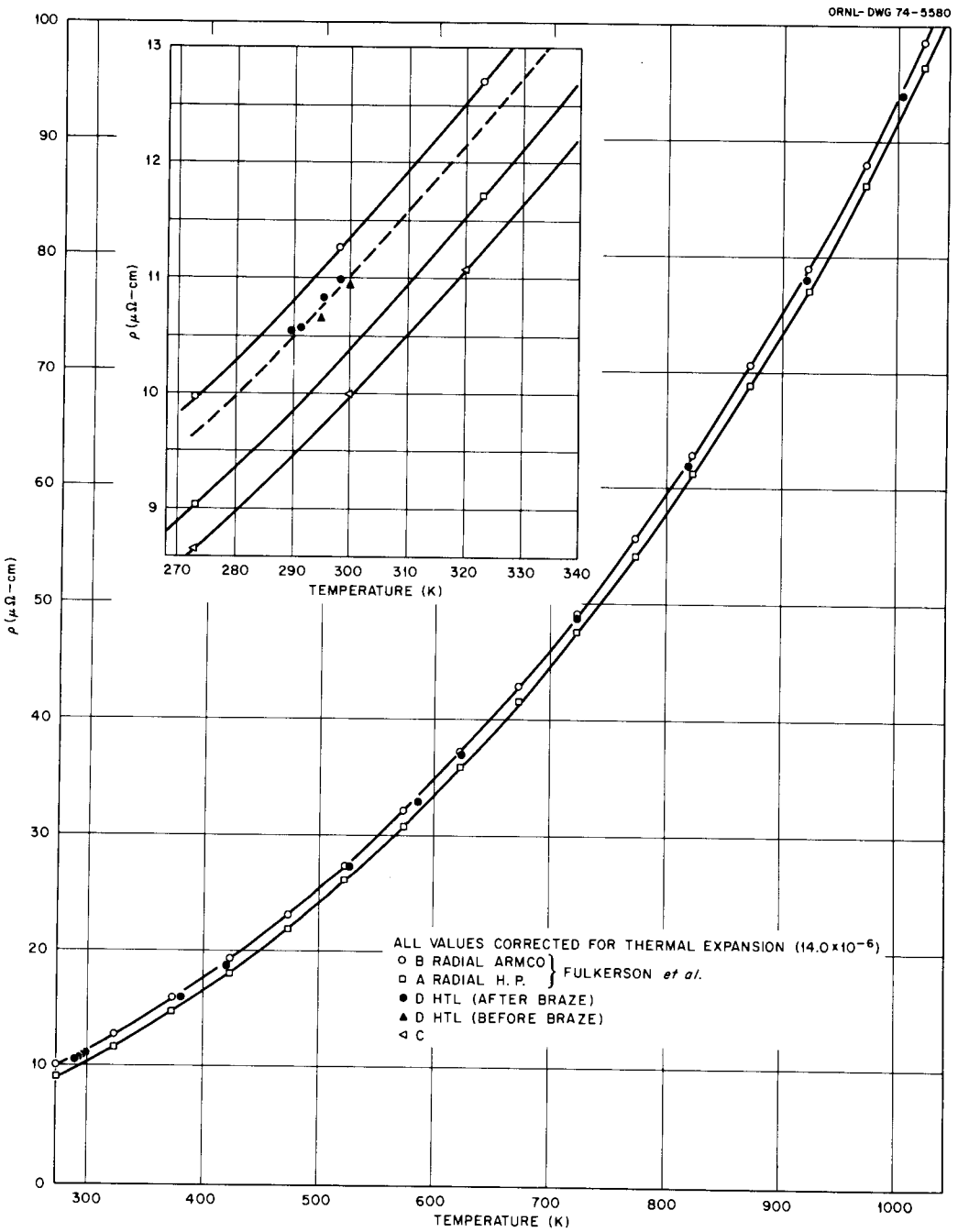

Fig. C1. Electrical Resistivity of Several Grades of Iron as a Function of T. The inset presents the values from 273 to 323 K on a more sensitive plot.

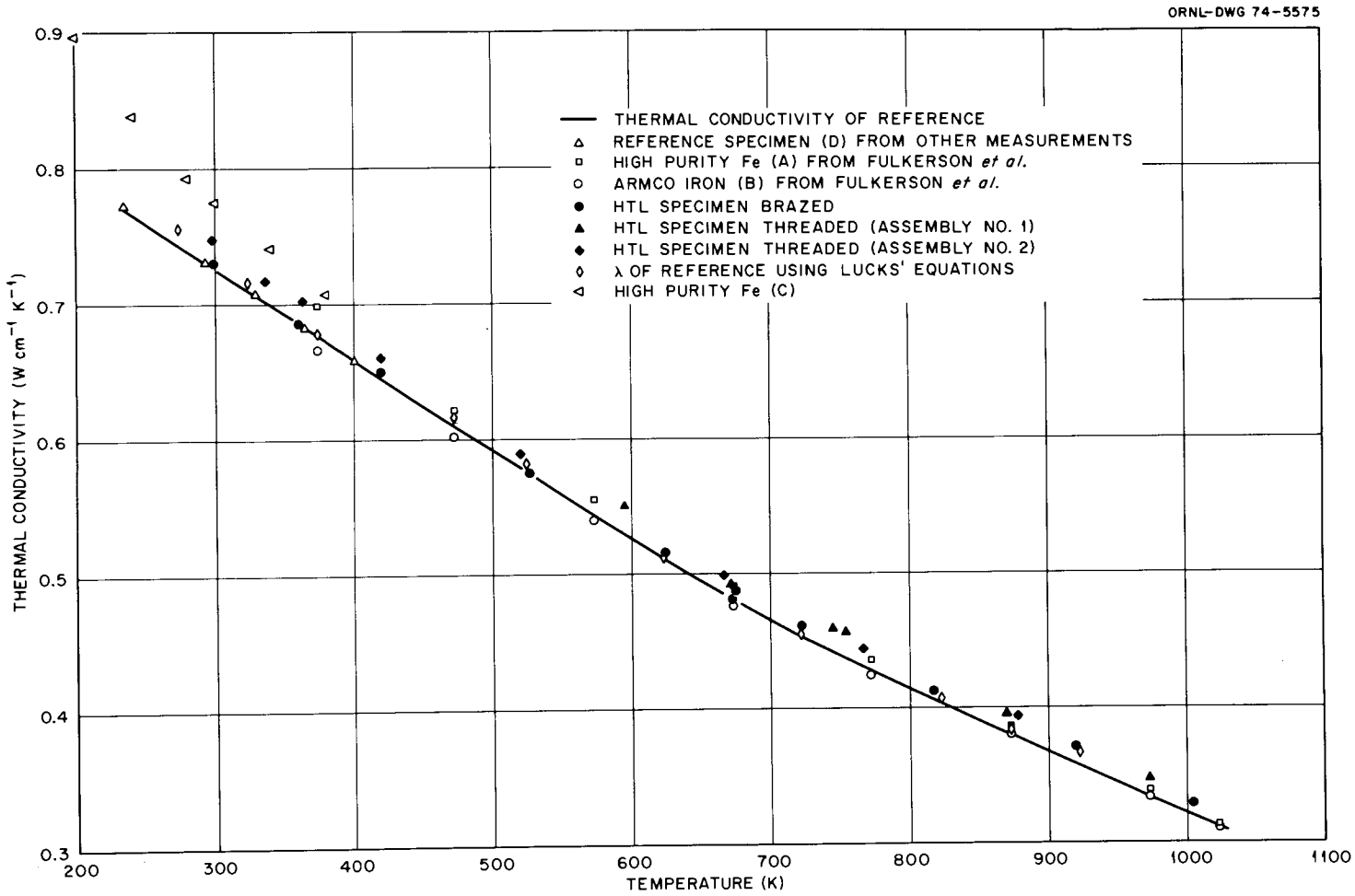

Fig. C2. Thermal Conductivity of Iron from Several Results. The solid line gives values that represent our reference specimen with an uncertainty of ±1.9%.

electrical resistivity measurements, which have a maximum uncertainty of ±0.4%, and λ results from Fulkerson et al.,[4] which have a probable uncertainty of ±1.5%. The uncertainty in assigned λ values for the Armco iron reference would thus be about ±1.9% above 400 K.

APPENDIX D

Calculation of λ for the Brazed Iron Specimen at 624 K

Calculation details from a datum on the brazed specimen are interesting since they show how well $T_s(z)$ is described by Eq. (5) and show the magnitude of Q_r. Some of the details are given in Table D1 for the $Q_e = 0$ test at 624 K. In this table, values of z and corresponding values of measured thermocouple emf and temperatures calculated from these emfs are given. Values of $T_s^{\Delta}(z)$, A^{Δ}, and B^{Δ} were used to calculate values of $T_s^{\Delta}(z) - A^{\Delta} - B^{\Delta}z$ for each of the five specimen thermocouples. These values were then fitted to $C_2^{\Delta} \exp(\beta z/r) + C_2 \exp(-\beta z/r)$ by use of the method of linear least squares. Results from this are shown in Table D2.

Table D1. Dimensions and Thermocouple EMF's for the $Q_e = 0$ Test at 624 K

Component	z (cm)	EMF (μV)	$T_s^{\Delta}(z)$ (K)
Specimen	1.700	2790.65	624.1627
	2.775	2790.92	624.1915
	3.850	2789.76	624.0677
	5.022	2790.30	624.1253
	6.172	2790.26	624.1211
Guard	3.05	2785.04	623.5641
	6.10	2786.93	623.7658
H1	7.28	2789.60	624.0507

A^{Δ} = 623.3624 K;
B^{Δ} = 0.066123 K/cm.

Table D2. Least Squares Fit of $T_s^{\Delta}(z) - A^{\Delta} - B^{\Delta}z$ to $C_1^{\Delta} \exp(\beta z/r) + C_2^{\Delta} \exp(-\beta z/r)$ for Obtaining Deviations of Thermocouples from Smooth Curve

z (cm)	$T_s^{\Delta}(z) - A^{\Delta} - B^{\Delta}z$		Deviation (K)
	Experimental	Least Squares Fit	
1.700	0.6878	0.6947	−0.0069
2.775	0.6456	0.5990	+0.0466
3.850	0.4507	0.5106	−0.0599
5.022	0.4308	0.4215	+0.0093
6.172	0.3506	0.3402	+0.0104

C_1^{Δ} = −0.084711 K;
C_2^{Δ} = +0.94898 K.

The thermocouple emf's obtained at steady state during the $Q_e \neq 0$ test are shown in Table D3. The δz were values used to correct the specimen thermocouples as described in Appendix B; at this temperature $S_{\text{Spec-Rh}}$ is so small that these gradient corrections are negligibly small. Values of $T_s^{\delta}(z) - A^{\delta} - B^{\delta}z$ were then fitted to $C_1^{\delta} \exp(\beta z/r) + C_2^{\delta} \exp(-\beta z/r)$, with the result shown in Table D4. Deviations of the specimen temperatures from the best curve are well within the measurement uncertainties of the emf's since only the K-5 potentiometer error would indicate a relative reading error (one thermocouple with respect to another) of ±0.02K.[1] The heat exchange between specimen and guard was about 0.5% of Q_e, as shown by the values of $Q(z)$ along the specimen. Use of information in Table D3 and Eq. (9) yields a λ of 0.5192 W cm^{-1} K^{-1} (uncorrected for thermal expansion) at each thermocouple position. Calculation of $dT_s^{\delta}(z)/dz$ using Eq. (7) forces the calculated values of λ at each thermocouple position to be identical because this has the effect of determining an average λ. If $Q(z)$ is used with $\Delta T/\Delta z$ values to calculate a λ at each interval between thermocouples, the effect of thermocouple error and error in $Q(z)$ becomes more apparent. From the bottom section of the specimen (from z = 1.700 to 2.775 cm) on to the top section, this gives four λ values of 0.5220, 0.5170, 0.5210, and 0.5170 W cm^{-1} K^{-1}, and these differ by less than 1%.

[1]All deviations for all data on the brazed specimen were within measurement uncertainty except for the z = 3.850 cm position for the datum at 1005 K.

Table D3. Dimensions, Thermocouple EMF's and Temperatures for the $Q_e \neq 0$ Test at 624 K

Component	z (cm)	δz (cm)	EMF (μV)	Temperatures, K: Uncorrected T	Correction from Q_e = 0 Test	Gradient Correction	T_s
Specimen[a]	1.700	0.0202	2756.79	620.5474	+0.0069	0.0014	620.5557
	2.775	0.0192	2773.34	622.3152	−0.0466	0.0014	622.2700
	3.850	0.0118	2788.58	623.9418	+0.0599	0.0008	624.0025
	5.022	0.0327	2806.84	625.8892	−0.0093	0.0023	625.8822
	6.172	0.0069	2824.29	627.7487	−0.0104	0.0005	627.7387
Guard[b]	3.05		2775.31	622.5256			
	6.10		2821.58	627.4600			
H1	7.28		2844.90	629.9432			

A^{δ} = 617.5911 K;
B^{δ} = 1.617853 K/cm;
β = 0.04963;
Q_e = 0.603717 W.

[a]Specimen radius = 0.47907 cm.

[b]Guard radius = 1.19 cm.

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