agree with the experimental values calculated from $D' - D_0$ within the limits of error. The experimental results, therefore, are self-consistent and confirm the steady state theory in every detail regarding the influence of the extent of reaction, light intensity and temperature upon the steady state concentration of the intermediate species and the build-up and decay of the concentration of this species.

It seems worthwhile to distinguish between the duration, t, and extent, A', of photolysis required to attain a given value of x and consequently a given fraction of the steady state value. Consider the equations $t = x/(''k\phi I)^{1/2}$ and $A' = x(\phi I/''k)^{1/2}$. The first of these equations shows that the duration of the photochemical reaction required to reach a stated value of x or fraction of the steady state is decreased by increasing either the temperature (*i.e.*, $''k$) or the light intensity, I, or the quantum yield, ϕ, or all of them. The decrease in this time is seen to be inversely proportional to the square root of the per cent. increase in these variables. The second of these equations shows that the extent of photolysis required to reach a stated value of x or fraction of the steady state is decreased by increasing the temp. (*i.e.*, $''k$) but that the opposite effect is obtained by an increase in light intensity or quantum yield or both. It follows that both the time and extent of photolysis required to reach within 1 or 10% of the steady state becomes smaller the larger the rate of decay of the intermediate species, *i.e.*, the shorter the after-effect and *vice versa*.

In the case of reactions in which the intermediate species is thermally produced as well as destroyed, $2\phi I$ is replaced by the thermal rate of formation of the intermediate species so that again both the time and extent of reaction required to establish the steady state will be small when the rate of decay is large and the steady state concentration of the intermediate species is small.

Finally the results of this research show that one can deal satisfactorily in a simple way with the kinetics of photochemical reactions involving intermediate species even when the actinic light is strongly absorbed by a thin layer of the solution next to the wall of the reaction vessel provided the solution is adequately stirred and provided the actinic light is monochromatic and one knows or holds constant the fraction of this light absorbed by the photosensitive species.

CAMBRIDGE 39, MASS.

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Thermal Conductivities of Condensed Gases. I. The Thermal Conductivity of Liquid Nitrogen between 65 and 90°K.

BY ROBERT W. POWERS, ROBERT W. MATTOX AND HERRICK L. JOHNSTON

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A cell for measuring the thermal conductivity of liquids at low temperatures is described in this paper. Data on the conductivity of liquid nitrogen from 65 to 90°K are presented. These data are considerably lower than those of Hammann[1] (1938) and compare closely with those given by Borovik, Matveev and Panin[2] (1940). Our research, as well as that of Hammann, employed the parallel plate arrangement; whereas measurements made by Borovik, Matveev and Panin were made by using a radial flow type of cell.

Introduction

Previously published data on the thermal conductivity of liquid nitrogen display great inconsistency. For example, Hammann,[1] whose measurements cover the range 64.7–73.5°, reported a thermal conductivity coefficient, K, of 4.96×10^{-4} cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$ at 73°K.; whereas the data of Borovik, Matveev and Panin[2] for the range 77.9–111.8°K. lead to an extrapolated value of 3.9×10^{-4} at 73°K. Moreover, Hammann found K to be practically independent of temperature; whereas Borovik, Matveev and Panin report that the conductivity decreases at a constant rate with temperature. Consequently, we were led to reinvestigate the conductivity of liquid nitrogen at low temperatures, as part of a program, in this Laboratory, for measuring the thermal conductivities of condensed gases.

Apparatus.—The conductivity cell used in this work is of the parallel plate type. A line drawing of our cell is shown in Fig. 1. Essentially, it consists of a thin-walled cylindrical container for the liquid under study, which is heated at a measured rate at its upper end and is in thermal contact with a constant-temperature cryostating bath at its lower end. A multiple-junction-difference thermocouple is used to determine the thermal gradient through the liquid.

The Measuring Cell.—The cell wall, A in Fig. 1, is made of No. 26 gage stainless steel, type 302, and has an internal diameter of 3 in. and a length of 1 in. Its top is soft-soldered onto a nickel disk, B, whose lower surface is grooved to fit it. The disk serves as a heating plate and its upper surface is grooved to hold a pancake heater of 40 ohms of No. 30 B and S insulated manganin wire. The lower end of the cell wall is soft-soldered into a circular groove in the nickel-plated upper surface of a thick copper plate, C.

The tube D, which leads the liquid into the chamber through a small hole in the center of the heater plate, is usually filled with liquid during an experiment. To prevent convection, a cylindrical copper block, E, wrapped with a heating coil, is placed in the tube line, $1^5/_8$ in. above the heater plate. During an experiment it is maintained, when possible, at the temperature of the pancake heater. Besides preventing convection in the entrant tube, the block traps out any heat that tends to flow to the heater, B, through thermocouples and heater leads from outside the apparatus, and also prevents the measuring chamber from "seeing" parts of the apparatus at room temperature. Heat is leaked away from this block through five short lengths of No. 12 braided copper wire, soldered at one end to the top of the block and at the other end to the $^3/_4$-in. monel tube, F, which is immersed in the cryostating bath.

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[1] G. Hammann, *Ann. Physik*, **32**, 593 (1938).

[2] E. Borovik, A. Matveev and E. Panin, *J. Tech. Phys.* (*USSR*), **10**, 988 (1940).

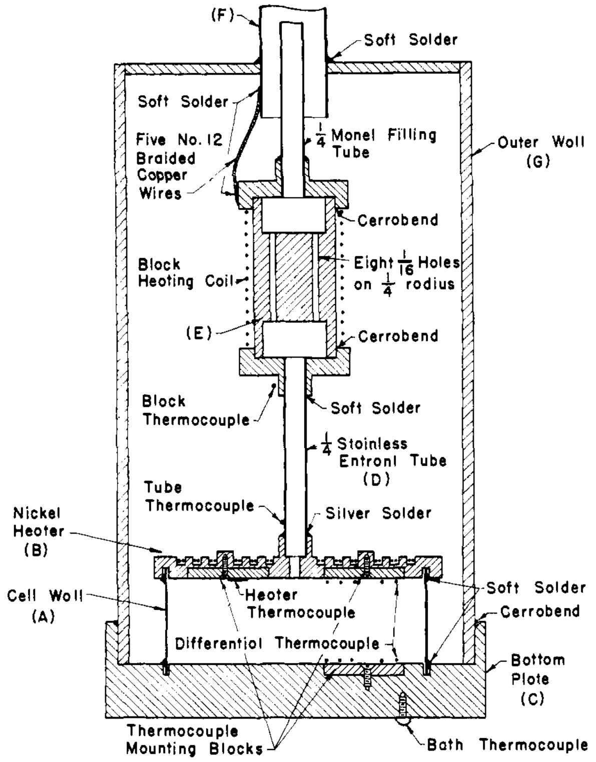

Fig. 1.—Thermal conductivity cell for liquids. All parts made of copper unless otherwise specified.

The measuring chamber is surrounded by a 4-in. copper tube, G, with top plate, which serves as the outer wall of the vacuum space surrounding the liquid chamber. A high vacuum (10^{-5} mm. or better) is drawn through the tube F. The entire measuring chamber is immersed in a suitable cryostat bath whose temperature must be lower than that of the liquid in A.

The thermal gradient in the liquid is measured with a five-junction copper–constantan difference thermocouple (36 gage copper wire and 30 gage constantan). The junctions, mounted on two rectangular nickel blocks, $^{15}/_{16}$ in. $\times$ $^{1}/_{4}$ in. $\times$ $^{1}/_{8}$ in., are fastened with small machine screws into recesses machined into blocks B and C. Each individual junction is held in place with very fine insulated manganin wire and is electrically insulated from the mounting blocks and other junctions by small strips of 0.007-in. Fiberglas tape. A copper–constantan thermocouple, intercompared with Laboratory Standard Thermocouple No. 80, is soldered to another nickel mounting block recessed into heating block B.

Figure 2 shows the way in which thermocouple and heater leads are brought to the outside from within the vacuum space and the liquid chamber. This is accomplished by sectional brass joints, held together by Allen screws. The wires are brought out in grooves cut lengthwise along the tapered portions of the various sections, the space between wire and groove wall being filled with crumpled lens paper. The assembly is made pressure- and vacuum-tight by complete immersion in Dicks–Pontius red sealing wax.

Auxiliary Apparatus.—The source of energy for the pancake heater is a battery of 15 nickel–cadmium cells of 120-amp. hr. capacity. Current is regulated by means of decade power resistors in series with the heater. The copper block or heat trap is heated with alternating current stabilized by means of a Sola-type transformer and regulated by a combination of Variac and decade power resistors.

The rate of heat developed is measured by the potential drop across a standard 0.1-ohm resistor in series with the heater and the drop across a portion of a voltage divider in parallel with it. Both thermoelectric e.m.f.'s and those needed for power measurement are read on a White 10,000-μv. potentiometer.

The liquid chamber is joined to a manifold having valved connections to a gas cylinder, a pressure gage, a high vacuum pump, a safety blow-off and a vent. All connections are made with copper tubing.

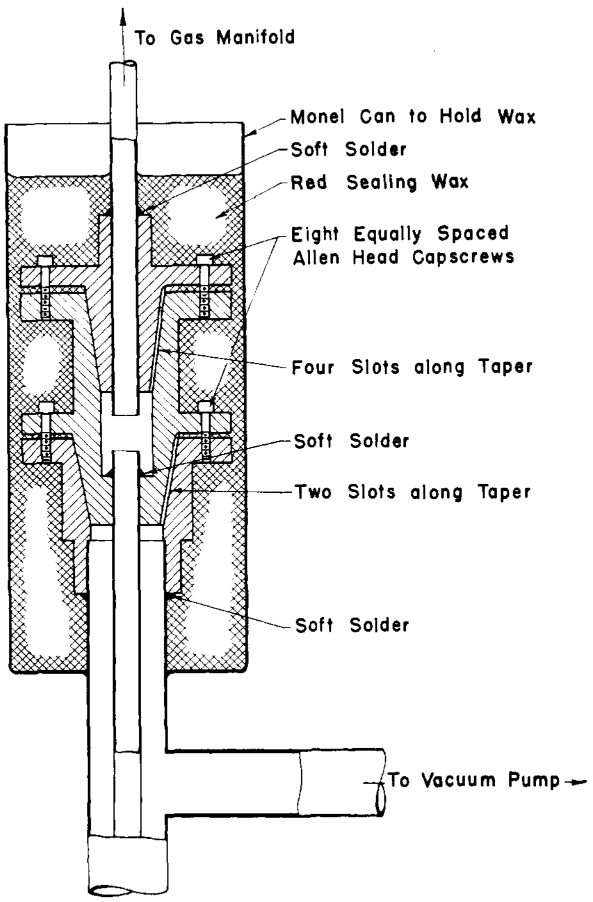

Fig. 2.—Fixture for leading wires from within vacuum and liquid chambers to outside.

The cell assembly is placed inside a silvered glass Dewar, 6 in. i.d. × 54 in. long, on which two lengthwise strips are left unsilvered so that the level of cryostating fluid inside is visible. The Dewar, in turn, is placed inside a brass case fitted with Lucite windows.[3] The whole assembly is aligned with a level so that the heater at the top of the liquid chamber rests in the horizontal plane.

For temperatures from 65 to 78.3°K., the cryostating bath was liquid nitrogen. The temperature was regulated by throttling the intake of a vacuum pump. During the hour, or so, when observations were being taken, the bath temperature seldom drifted more than 0.03°. For temperatures from 77.3 to 86°K., baths of liquid nitrogen and oxygen of various compositions were allowed to boil at atmospheric pressure. Because of the large capacity of the Dewar, the bath composition changed so slightly that the temperature drift did not exceed 0.1° per hr. under the worst conditions. To prevent superheating of the bath, we found it necessary to maintain nuclear boiling from the bottom of the cell. This was accomplished by means of a small electric heater placed near the bottom of the bath, which liberated a steady stream of bubbles that stirred the bath.

Cell Dimensions.—The inner diameter of the liquid chamber measures 2.999 in. The distance from the center of the upper junctions of the difference couple to the center of the lower junctions is 0.963 in.

Calibration of the Difference Couple.—Before inserting it in the cell, we calibrated our difference couple by determining the parameter f

$$\left(\frac{dE}{dT}\right)\Bigg|_{\substack{\text{difference}\\\text{couple}}} = f\left(\frac{dE}{dT}\right)_{\substack{\text{Standard}\\\text{No. 80}}}$$

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[3] H. L. Johnston, *Rev. Sci. Instruments*, **23**, No. 10, 569 (1952).

where E is the thermoelectric e.m.f. and T is the absolute temperature. The e.m.f. of Laboratory Standard Thermocouple No. 80 was determined as a function of the absolute temperature in a helium gas thermometer by another group in this Laboratory.[4] We might term f the effective number of junctions of the difference couple. We obtained a value of 4.97 for f at 80°K. on two calibrations of our five-junction couple.

Correction for Wall Conductivity.—In an apparatus of the type described here, correction must be made for heat flow through the walls of the liquid chamber. Our first attempt to determine the necessary correction, made with the liquid chamber held under high vacuum, gave results that appeared too high. We later concluded that conduction along the couple wires prevented the junctions of the difference couple from coming to temperature equilibrium with the top and bottom plates of the chamber.

We found that a more satisfactory approach is to measure the conductivity of the wall when the cell is filled with helium at 40–200 mm. of pressure. The conductivity of helium gas is known accurately from the work of Johnston and Grilly[5] and the procedure has the added advantage that it reduces the effect of an error in the dimensional constant of the apparatus. In general

$$K_{\text{liq. N}_2} = \left[\frac{l}{A}\right]\frac{\dot{q}}{\Delta T}$$

where $\dot{q}$ is the rate of heat flow through the liquid nitrogen, ΔT is the temperature difference indicated by the difference thermocouple, l is the distance between centers of junctions of the difference couple, and A is the cross-sectional area of the liquid chamber. More specifically, for our apparatus

$$K_{\text{liq. N}_2} = \left[\frac{l}{A}\right]\left(\frac{\dot{q}}{\Delta T}\bigg|_{\substack{\text{walls +}\\ \text{liq. N}_2}} - \frac{\dot{q}}{\Delta T}\bigg|_{\substack{\text{walls +}\\ \text{He}}}\right) + K_{\text{He}} = (K_{\text{wall + liq. N}_2} - K_{\text{wall + He}}) + K_{\text{He}}$$

A plot of K_{wall} at various temperatures is shown in Fig. 3.

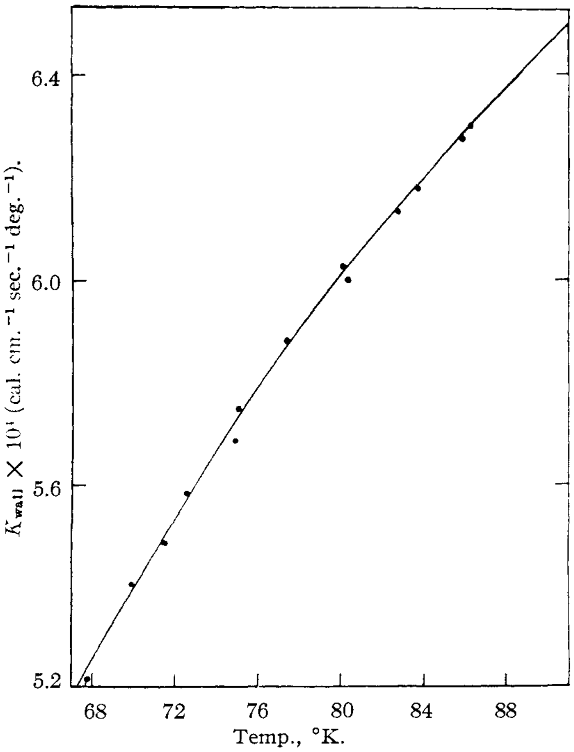

Fig. 3.—K_{wall} as a function of temperature.

Technique.—After filling the cell and bringing the cryostating bath to constant temperature, the copper block E, and then the liquid chamber heater, are warmed about 5° above the bath temperature. When ΔT exceeded 8 to 10°, low and usually erratic results were noted; perhaps bubble formation under the chamber heater was responsible. Current through the heater is then adjusted until the difference couple remains constant; the current through the block heater being adjusted meanwhile to maintain E at the same temperature as B. When steady-state conditions appear to have been established, thermocouple temperatures and the heating current and voltage drop are measured at 20-min. intervals for a period of one hour.

ΔT and $T_{\text{av.}}$ for the cell are then computed from the steady-state readings of the difference couple and of the heater couple. The calculation of ΔT is based on the laboratory temperature scale and the standard values of (dE/dT) for couple No. 80, as a function of temperature, with the factor f applied.

Experimental Data

Our data on the heat conductivity of liquid nitrogen are summarized in Table I and are shown graphically in Fig. 4. The conductivity at any given mean temperature is obtained by subtracting from individually determined values of $K_{\text{liq. N}_2}$ + wall smoothed values of K_{wall} read off a large graph similar to Fig. 3. These data have been fitted to the equation of a straight line by the method of least squares. The equation

$$K = (5.838 \times 10^{-4} - 3.236 \times 10^{-6}\ T)\ \text{cal. cm.}^{-1}\ \text{sec.}^{-1}\ \text{deg.}^{-1}$$

fits our data within a r.m.s. deviation of 0.9%.

TABLE I

THERMAL CONDUCTIVITY OF LIQUID NITROGEN AT VARIOUS TEMPERATURES

Mean temp., °K.	ΔT	$K_{\text{liq. N}_2\text{+ wall}}$, cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$ × 10^4	K_{wall}, cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$ × 10^4	$K_{\text{liq. N}_2}$, cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$ × 10^4
68.68	4.978	8.947	5.312	3.64
69.92	4.980	8.928	5.398	3.53
70.94	4.982	9.058	5.470	3.59
73.66	4.982	9.092	5.653	3.44
76.26	4.958	9.200	5.814	3.39
77.66	5.007	9.225	5.893	3.33
78.73	4.984	9.258	5.951	3.31
81.11	5.022	9.249	6.070	3.18
81.77	4.989	9.250	6.099	3.15
83.77	4.974	9.306	6.190	3.12
86.44	4.962	9.357	6.305	3.07
88.12	4.867	9.379	6.376	3.00

Experimental Errors

Systematic errors, arising from the dimensional constant l/A or the f factor, may affect our results. The uncertainty in l/A is predominantly that in l, since the cross-sectional area, A, is known to within 0.02%. It is our belief that the error in l does not exceed the diameter of a junction of our difference couple—0.020 in., or 2%. It is unlikely that f is in error by more than 0.5%.

Some indication of the internal consistency of our values for l/A and f is given by determination of *f in situ*. The ratio, r, of the e.m.f. of the difference couple to the difference in e.m.f. of the bath and heater couples can be determined fairly accurately for sufficiently large values of ΔT. In determining the wall correction, a few points were obtained with ΔT's of 15–25°. Now f should equal $r(L/l)$, where L is the distance from the bottom of the heater plate to the top of the bottom plate. L measured 0.998 in., with an

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[4] T. Rubin, H. Altman and H. L. Johnston, THIS JOURNAL, **76**, 5289 (1954).

[5] H. L. Johnston and E. R. Grilly, *J. Chem. Phys.*, **14**, 233 (1946).

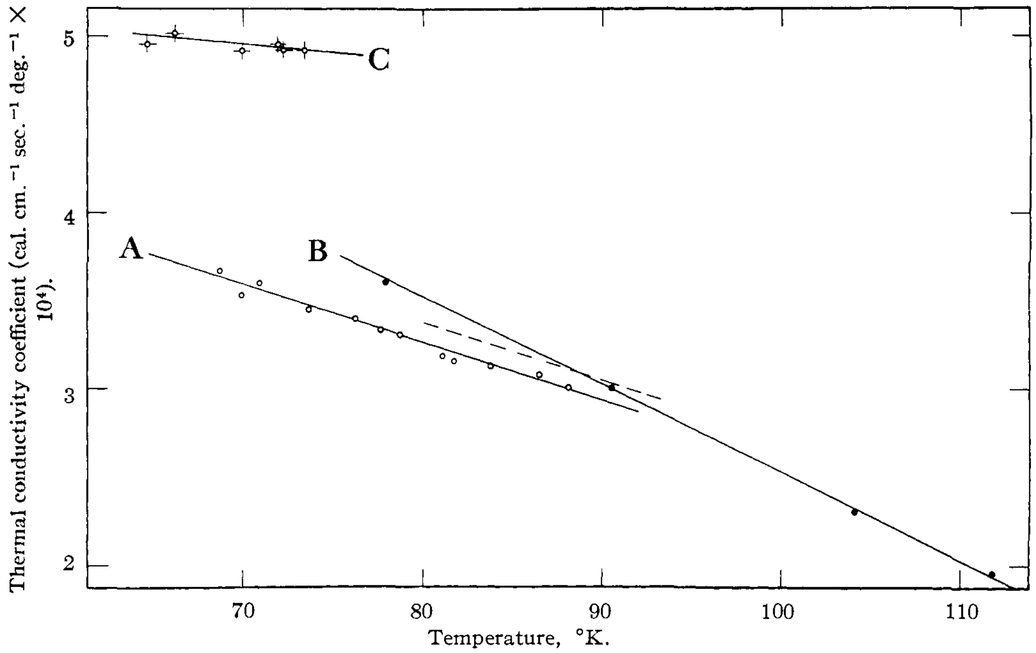

Fig. 4.—Thermal conductivity of nitrogen *vs.* temperature: A (○), this research (O.S.U.) 1951; B (●), data of Borovik, Matveev and Panin (Karkov)[2]; C (⌖), data of Hammann (Munich).[1]

error of less than 0.0005 in., leading to a value of 5.02 for *f*, as compared to 4.97, the value obtained in calibrating the difference couple. Thus, our aggregate error in *l*/*A* and *f* is apparently 1%, but our final results should not be affected by more than 0.5%, owing to our method of determining the wall correction.

Systematic errors might also arise from calibration errors in our voltage divider, standard resistance or potentiometer standard cell, but these would be well under the limits imposed by *l* or by *f*. Other possible sources of error are the values used for the heat conductivity of helium and values of dE/dT for thermocouple No. 80. We do not believe that the sum of these errors can exceed 0.3% in our final results. As for the random errors that might arise in our work, principally owing to deviation from true steady-state conditions, an index of accuracy is the 0.9% deviation of our points from the straight line plotted in Fig. 4. The r.m.s. deviation of the wall calibration data from a smoothed curve drawn through the points is 0.3%.

In summation, we believe that our data are reliable to within 1.5%.

Comparison with Other Work

The first measurement of the heat conductivity of liquid nitrogen was made by Hammann,[1] using a parallel plate arrangement. His results, as shown in Fig. 4, appear extraordinarily high. Borovik, Matveev and Panin[2] suggested that considerable convection occurred in his filling tube.

A later set of measurements were made by Borovik, Matveev and Panin, using a radial flow type of cell. Their results fall in the same general range as those from this Laboratory but are somewhat higher and their temperature coefficient of conductivity is somewhat larger in absolute value. We believe that the discrepancy arises in part from calibration errors by the Russian workers. These investigators checked their cell by measuring the heat conductivity of gaseous hydrogen and nitrogen; their results are compared in Table II with those of Eucken, whose data compare favorably with data from this Laboratory.

TABLE II

Substance	Temp., °K.	*k*, cal. cm.⁻¹ sec.⁻¹ deg.⁻¹ Eucken's data	Borovik, Matveev and Panin's data	Dev., %
Gaseous H_2	90.7	14.88	14.6	1.9, low
Gaseous N_2	79.8	1.786	1.87	4.5, high
Gaseous N_2	91.7	2.050	2.02	1.5, low

Now if we adjust the data of Borovik, *et al.*, according to the deviations indicated in Table II, the dashed line shown in Fig. 4 is obtained. Our curves now parallel each other with a difference of about 3.5% in the conductivity. This difference suggests another source of systematic error. We think that it may be due to inadequate correction in the type of hot wire cell used by Borovik, Matveev and Panin. On the other hand, if the heat flow pattern for liquid nitrogen within our cell differed appreciably from that for gaseous helium, this might give rise to a systematic error in our own measurements. The symmetry of our cell is disturbed by the presence of the difference and heater thermocouples, and the flow pattern about these obstructions may vary slightly for difference substances, although we doubt that this effect is serious.

Acknowledgments.—The authors wish to acknowledge their indebtedness to Mr. L. E. Cox, Cryogenic Laboratory Shop Foreman, and to Mr. Paul Danford, machinist, for valuable advice and assistance in the shop design of the cell.

COLUMBUS, OHIO