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An Improved Hot Wire Cell for Accurate Measurements of Thermal Conductivities of Gases over a Wide Temperature Range

Results with Air between 87° and 375°K

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An improved hot wire cell of the potential lead type is described, and theoretical treatments given for radiation, end conduction, potential lead conduction, and the "temperature jump" effect. The latter is found to be satisfactorily eliminated by linear extrapolation of reciprocal plots of "apparent conductivities" as a function of pressure. Convection effects are absent at pressures below about 20 cm of mercury. The emissivity from bright platinum was measured. The results confirm the measurements by Milverton. The thermal conductivity of air was measured at seventeen temperatures between 87° and 375°K. Our results, which are believed accurate to within ±0.5 percent, are generally lower than other results which have been reported in recent years, for air. Tabulation of our results is given, together with a critical analysis of possible sources of error. The advantage of our method over either the "thick wire" or "compensating lead" type of cells is pointed out.

A RESEARCH program on the accurate measurement of the absolute thermal conductivities of gases, over a wide temperature range, is being undertaken in this laboratory to supplement investigations on measurements of heat capacity by the velocity of sound method. Investigation of the literature reveals that the only reliable thermal conductivity data on gases, at temperatures other than 0°C, heretofore reported, are those of Archer[2] and of Sherrat and Griffiths[3] on carbon dioxide; of Gregory and Dock[4] on hydrogen; and the older data of Eucken[5] for several gases. The latter measurements were relative to air, and were made at widely spaced intervals.

Data on the thermal conductivities of gases is also of interest in connection with further development of the theory of transport properties of gases. The classical theory is well developed for spherically symmetric molecules possessing translational energy only,[6] but very little progress has been made on the more difficult problem of molecules with internal degrees of freedom. The Chapman-Enskog relationship

$$K = \epsilon \eta C_v \qquad (1)$$

between thermal conductivity (K), viscosity (η), and heat capacity (C_v) is of particular interest.

[1] Fellow of the Charles A. Coffin Foundation 1939–40, E. I. du Pont Fellow 1940–41.
[2] C. T. Archer, Phil. Mag. **19**, 901 (1935).
[3] G. G. Sherrat and E. Griffiths, Phil. Mag. **27**, 68 (1939).
[4] H. Gregory and E. H. Dock, Phil. Mag. **25**, 129 (1938).
[5] (*a*) A. Eucken, Phys. Zeits. **12**, 1101 (1911); (*b*) **14**, 324
[6] S. Chapman and T. G. Cowling, *Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, New York, 1939).

Other work from this laboratory[7] has supplied data on viscosity and on heat capacity, covering a wide temperature range. It was felt desirable to supplement these results with extensive data on thermal conductivity.

Nearly all precise thermal conductivity measurements on gases have been made with some modification of the hot wire cell. The general method of operation of these cells is well known. In all of them a wire, fixed along the axis of a cylindrical tube, is heated by an electric current. The rise in temperature of the wire, as determined from its resistance increases, together with the power dissipated and the dimensions of the wire and tube, permit calculation of the thermal conductivity of the gas in the tube. The principal correction is for heat conducted longitudinally by the wire, since the thermal conductivity of the metal is much greater than that of the gas. Various modifications of the hot wire cell represent attempts to deal with this difficulty. The principal types that have been used may be referred to as: (1) compensating cells; (2) the "thick-wire" cell; and (3) the potential lead type of cell. Compensating cells[8] involve the use of two cells that differ only in length, so that differential measurements refer, effectively, to the central portion of the longer cell. In the "thick-wire" cell, developed by Kannuluik and Martin,[9] no attempt is made to minimize end conduction by the use of fine wires. Instead, the ends of the cell are so constructed as to lead to relatively simple boundary conditions, so that the problem of the complete heat flow (along the wire and through the gas) may be solved.

In the potential lead type of cell, which has been used by Weber,[10] very fine potential leads are attached to the cell wire so as to give the potential drop through a central segment. End conduction is thus reduced to a small correction.

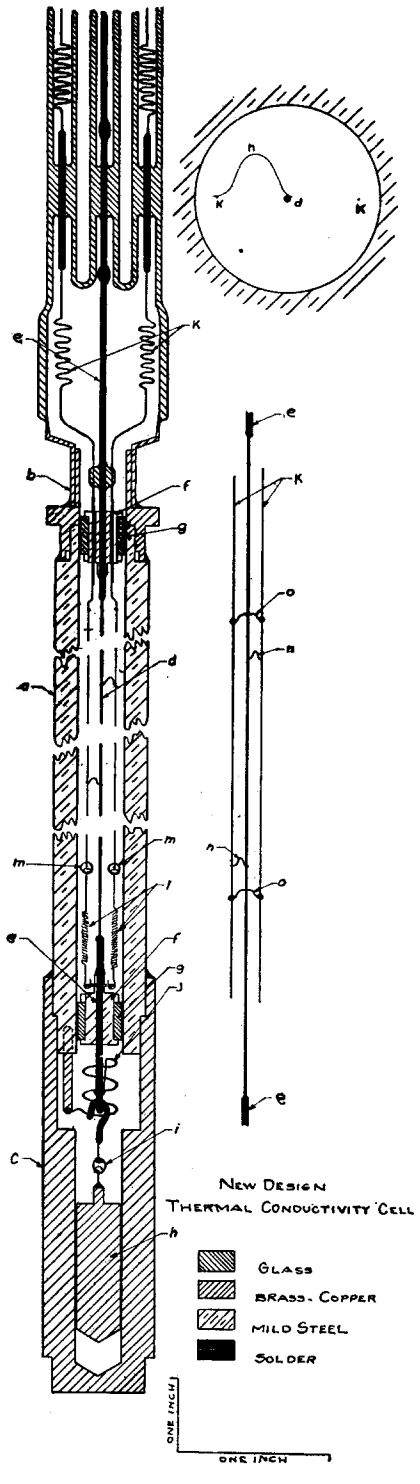

FIG. 1. Thermal conductivity cell.

[7] *Viscosities:* (*a*) H. L. Johnston and K. E. McCloskey, J. Phys. Chem. **44**, 1038 (1940); (*b*) H. L. Johnston and E. R. Grilly, *ibid.* **46**, 948 (1942).
Heat capacities: (*c*) H. L. Johnston and A. T. Chapman, J. Am. Chem. Soc. **55**, 153 (1933); (*d*) H. L. Johnston and M. K. Walker, *ibid.* **55**, 172 (1933); (*e*) H. L. Johnston and D. H. Dawson, *ibid.* **55**, 2744 (1933); (*f*) H. L. Johnston and C. O. Davis, *ibid.* **56**, 271 (1934); (*g*) C. O. Davis and H. L. Johnston, *ibid.* **56**, 1045 (1934); (*h*) H. L. Johnston and E. A. Long, J. Chem. Phys. **2**, 389 (1934); (*i*) H. L. Johnston and M. K. Walker, J. Am. Chem. Soc. **57**, 682 (1935).

[8] A recent investigation with compensating cells is that by B. G. Dickens, Proc. Roy. Soc. **A143**, 517 (1934).

[9] W. G. Kannuluik and L. H. Martin, Proc. Roy. Soc. **A141**, 144 (1933); **A144**, 496 (1934).

[10] S. Weber, Ann. d. Physik **54**, 325 (1917).

The characteristics of these three types of cell may be summarized by the statement that the end conduction is canceled out in the compensating type of cell; is large but subject to a relatively exact correction in the "thick-wire" type of cell; and is essentially absent in the potential lead type of cell.

The potential lead type of cell was chosen for the present series of investigations because of the simplicity of the calculations in the treatment of the data and because the near absence of end-conduction removes the possibility of serious systematic error. Important improvements were made in the design of the cell.

The present paper is limited to a description of the apparatus and method, and to results obtained with air. A subsequent paper by one of us will present data obtained with several other gases.

Air used in this investigation was taken from outside the laboratory and freed from carbon dioxide and water vapor by slowly bubbling it through a train consisting of: (*a*) concentrated sodium hydroxide; (*b*) concentrated sulfuric acid; (*c*) stick potassium hydroxide; and (*d*) phosphorus pentoxide. Finally, it was passed through a liquid nitrogen trap (at less than atmospheric pressure so that no air condensed).

DESCRIPTION OF APPARATUS

The apparatus consists of: (1) the cell; (2) the thermostated bath; and (3) the electrical circuits. Their description follows.

(1) The Cell

An accurately bored steel tube, with a diameter sufficiently small to insure the absence of convection, was used for the cell. Positive centering of the 0.01-inch platinum cell wire was obtained by the use of cylindrical pistons sliding in the tube. Constant tension on the cell wire was maintained by means of a weight, so chosen that there was negligible vibration of the wire. Platinum potential leads, 0.0005 inch in diameter, were used. A more detailed description follows.

The construction of the cell is illustrated in Fig. 1, where it should be noted that the vertical scale of the main drawing is compressed in the ratio 1:2 with respect to the horizontal scale. The full length inset of the wire system is on the same scale as the cell, while the inset showing the cross-sectional view of the tube interior and wires is on an enlarged scale.

The central portion of the cell consists of a mild steel tube, (*a*), 11 inches in length, $\frac{5}{8}$ inch in outside diameter, and approximately 0.800 cm in internal diameter, which was accurately bored by the Winchester Repeating Arms Company, New Haven, Connecticut. The exterior of the tube was chromium plated, to prevent corrosion. At the upper end this tube is soft soldered to a copper-Pyrex glass seal, (*b*), about 2.5 cm in diameter, and at the lower end to a long brass cap, (*c*), forming an extension of the tube.

The cell wire was selected for freedom from irregularities from Bishop C. P. 0.01-inch platinum wire. A 22-cm length, (*d*), was fused to 1-mm platinum leads (*e*, *e*), which, in turn, were silver soldered through holes drilled centrally in small steel cylinders, (*f*, *f*), 0.43 cm in diameter by 1.5 cm in length. The cell wire was brought to the axis of these cylinders by slightly bending the heavy platinum wires until observation with a micrometer comparator showed proper centering. Glass tubes (*g*, *g*), 1.5 cm long, fit closely over the steel cylinders (*f*, *f*), and fit closely within the steel tube. These tubes were specially moulded by the Fischer-Schurman Company, and were selected for concentricity. The glass served to insulate the cell wire, electrically, from the tube. In order to permit the free passage of gas, a 60° section was cut from each of the glass insulators. This use of glass insulated "pistons" insures accurate centering of the cell wire within the tube and at the same time permits vertical motion made necessary to compensate for thermal expansion or contraction of either the upper lead wire or of the cell wire. The possible departure of the cell wire from center is estimated as not more than 0.014 cm, which is about the radius of the wire.

A constant tension is maintained on the cell wire by means of an 18-gram weight, (*h*), suspended from the lower "piston" but insulated from it by a glass bead, (*i*). It is important to maintain constant tension on the cell wire since it is used as a sensitive resistance thermometer. It was determined that, with this amount of loading, vibration of the cell wire was negligible

under normal operating conditions (maximum amplitude 0.001 cm).

The current lead to the upper end of the cell wire enters by way of a tungsten through Pyrex seal. The external portion of this lead is insulated from the bath by a glass tube fused to the seal. The lower end of the cell wire is connected to the steel tube by means of a short spiral, (j), of 0.01-inch copper wire of small rigidity. The lower external current connection is made directly to the metal cell.

The system of potential leads (k, k) enters the cell by tungsten-through-Pyrex seals at the upper end of the copper-Pyrex seal. Like the upper current leads, the external portions of the potential leads are insulated from the bath by glass tubes. The external leads and the portions of these leads that extend between the tungsten to Pyrex seals and the upper piston are of 0.01-inch platinum. The 0.01-inch platinum leads pass downward through 0.02-inch holes in the upper piston, from which they are insulated by means of glass capillaries. Between the two pistons the leads continue as 0.003-inch platinum wires parallel to and 0.3-cm distant from the cell wire. These 0.003-inch wires are held under a 2-gram tension by means of springs (l, l) consisting of 0.15-cm helices of 0.003-inch piano wire, hooked to the lower piston but insulated from the platinum leads by glass beads (m, m).

From the 0.003-inch platinum lead wires connections are made to the central portion of the cell wire—6.3 cm in length—by 0.5-cm lengths of 0.0005-inch diameter platinum Wollaston wire (n, n), the junctions being gold soldered. The junctions with the cell wire each required only 0.015 mg of gold (a 1×5-mm strip of gold leaf) but inspection with a 20× microscope showed that the Wollaston wires emerged cleanly from the gold and normal to the cell wire.

In order to prevent injury to the Wollaston wires by an accidental movement of the parallel "side wires" it was found necessary to add the two semi-circular braces (o, o), of 0.003-inch platinum wire shown in the inset of Fig. 1. These braces are 1 cm distant from the Wollaston wires and are at no point nearer than about 0.25 cm to the cell wire. They are insulated from the "side wires" by 0.5-mm glass beads.

Tests with the completed cell showed that no anomalous effects were caused by the use of the fine Wollaston wires, even though the voltages were measured with a precision of 0.1 microvolt (or 1 part per million). It was determined, by reversing the current in the cell, that no perceptible thermoelectric force was produced in the potential leads by heating of the cell wire.

TABLE I. Dimensions (at 300°K) that enter directly into the calculations of thermal conductivity.

Internal radius of tube (r_2)	=0.40017 cm	(±0.02%)
Radius of cell wire (r_1)	=0.01277 cm	(±0.18%)
Effective length of cell wire (L)	=6.327 cm	(±0.03%)

Dimensions of the cell which enter directly into the accurate calculation of the conductivity of the gas are the internal radius of the cell tube, the radius of the cell wire, and the effective length of the cell wire (that is, the length between the potential leads). The radius of the tube was calculated from its length and volume; the length was measured on a Société Genevoise micrometer comparator and the volume was determined by weighing the mercury required to fill the tube (using plane end pieces). The radius of the platinum cell wire was determined by weighing the segment used in the cell. The length of the segment was measured with a Gaertner cathetometer, after annealing the wire for eight days at 600°C under a tension of 20 grams. The value selected for the density of platinum, which was required in the calculation, was 21.40±0.06 grams cm^{-3} at 20°C.[11]

The effective length of the cell wire was measured with a Gaertner micrometer comparator after the potential leads were attached. The final values obtained for the principal dimensions of the cell at 300°K, and the estimated uncertainties, are given in Table I.

Dimensions that are required only for calculating corrections to the conductivity were

[11] Kahlbaum and Sturm, Zeits. f. anorg. Chemie **46**, 217 (1905), report a density of 21.44 grams cm^{-3} for pure annealed platinum wire; Stas, Oeuvres Complètes, Bruxelles-Leipzig 2, 742 (1894) found platinum to approach an upper limiting density of 21.46 grams cm^{-3} on working and annealing. The widely quoted value of 21.37 g cm^{-3} is due to a misinterpretation of the work of Richards and Stull, Carnegie Inst. Pub. **76**, 55 (1907), who reported a density of 21.31 grams cm^{-3} but also tabulated the specific gravity referred to 20°C, namely 21.37. Since Richards and Stull worked with a platinum cylinder it might be expected that their result would be lower than the maximum densities quoted above.

determined with less accuracy. They are listed in Table II, together with the estimated uncertainties.

The lengths of the end segments of the cell wire differ by only 0.04 cm and it is permissible to consider them equal, and equal to $(l_0-l)/2$.

(2) Thermostat

In the completed experimental arrangement, the cell is mounted in a thermostat, containing a suitable bath liquid, which may be adjusted to maintain any temperature in the range 120° to 400°K. When the thermostat is carefully adjusted the oscillations of the temperature about its mean value may be reduced to ±0.003°. The mean temperature may vary on the order of 0.01° per hour, but these slow variations introduce no error into the measurements. The thermostat is similar to the cryostat described by Scott and Brickwedde,[12] but the smaller Dewar tube available made necessary a different placement of the cooling and heating surfaces. An improvement is the use of a continuously variable heater control circuit which decreases the tendency of the temperature to oscillate about its mean value.

A Dewar tube 4 inches in diameter and 36 inches deep holds the bath liquid. It stands beneath a circular hole cut in a heavy (400-pound) stone table top, to which the support for the thermal conductivity cell is bolted; the cell makes no direct contact with the other objects in the thermostat. Sections of red-fiber were introduced into all metal supports descending into the bath to minimize heat leak, and the cell is further insulated from its support by red-fiber washers.

The heavy (20-pound) brass stirring well, 2 inches in internal diameter, is placed at one side of the Dewar. A $\frac{3}{8}$-inch stainless steel shaft, turning in brass bearings mounted on the outside of the stirring well, drives a $2\frac{1}{2}$-inch propeller at the bottom of the Dewar tube. The shaft is coupled by means of a red-fiber rod to the drive shaft above, which is equipped with oversized ball bearings. With the cooling tube (to be described) in place, the bath liquid is circulated (up through the stirring well) two to four times per minute at 400 r.p.m.

TABLE II. Dimensions (at 300°K) that enter only into correction terms.

Total length of cell wire (l_0)	=22.09 cm	(±0.2%)
External radius of tube (r_3)	= 0.795 cm	(±1%)
Radius of potential leads (Wollaston) (r_L)	= 6.25×10^{-4} cm	(±10%)
Length of potential leads (l_L)	= 0.5 cm	(±10%)

The cooling tube, an unsilvered Pyrex Dewar tube $1\frac{1}{2}$ inches in external diameter and 30 inches deep, with a separation of 1 mm between the walls, is mounted so that the lower 24 inches descends into the stirring well. When cooling is required, liquid oxygen (or nitrogen) is maintained at a constant level in the cooling tube by a float and relay arrangement which controls the flow of liquid oxygen from a reservoir. Control of the cooling rate is effected by varying the gas pressure between the double walls of the cooling tube. A pressure of 0.5-mm Hg of hydrogen gives sufficient cooling at 125°K while it is possible to thermostat a few degrees below room temperature with liquid oxygen in the Dewar by reducing the pressure to 0.002-mm Hg. With 1-cm Hg of hydrogen in the tube, the bath is cooled at an initial rate of 50 degrees per hour; the rate drops to 20 degrees per hour at 160°K and to 5 degrees per hour at 120°K.

The heater consists of 30 ohms of bare Nichrome wire wound bifilarly directly on the part of the cooling tube in the bath. The bath liquid thus circulates through the annular space between the cooling tube and the stirring well, in intimate and simultaneous contact with the cooling and heating surfaces. It is convenient to adjust the pressure in the cooling tube to give somewhat greater than optimum rate of cooling at the desired temperature, and then to reduce the cooling rate to the small optimum value by supplying a constant heating current to the heater. Similarly, in thermostating above room temperature, the constant heating current is adjusted to give a small rate of cooling at the desired temperature.

The actual thermostating, in both cases, is then accomplished by automatic regulation of a few watts of variable heating. A six-junction copper-constantan thermocouple, with the junctions exposed directly to the bath, is balanced against a Leeds and Northrup Type K poten-

[12] R. B. Scott and F. G. Brickwedde, J. Research Nat. Bur. Stand. 6, 401 (1931).

tiometer. A beam of light is reflected by a Leeds and Northrup Type R galvanometer onto a gas-filled photoelectric cell, which in turn controls the variable component of the heating through a phase shift Thyratron circuit, as described by Strong.[13]

Several bath liquids were employed. Above room temperature a low viscosity mineral oil was used; water was not satisfactory as it was absorbed by the red-fiber. Difluorodichloromethane was used from a degree or two above its melting point, 120°K, to about 160°K. This bath gave excellent thermostating because of its low viscosity. A mixture of 32.7 percent ethyl bromide, 26.5 percent methylene chloride, 15.6 percent trichloroethylene, 13.6 percent chloroform, and 11.6 percent transdichlorethylene (by volume), as described by Scott and Brickwedde,[12] was satisfactory in the range 150° to 250°K. In the range 205° to 300°K, a mixture of equal parts by weight of chloroform and carbon tetrachloride was employed.

Temperatures near 80° and 90°K were obtained by filling the thermostat with liquid nitrogen or liquid oxygen, respectively. It was necessary to stir these baths vigorously to maintain a steady temperature.

(3) Electrical Circuits

The electrical circuit used to measure both the resistance of the "effective length" of the cell wire, and its energy dissipation, is quite simple. Its resistance—which ranged from about 0.029 ohm at 80°K to about 0.177 ohm at 380°K—was determined by dividing the potential difference between the potential leads by the current through the wire. The latter was determined by measuring the potential difference across a standardized manganin resistance of 0.128477 ± 0.000025 ohm, at 25°C, which was inserted in the external circuit of the current leads. Potential differences were measured with a White double potentiometer of 100,000 microvolt range, with a precision of 0.1 microvolt. The current through the cell, and standard resistance, was supplied by two 2-volt heavy duty lead storage cells, of 450-ampere hour capacity, in parallel, and amounted to about 0.1 ampere during (resistance thermometer) calibration of the cell wire and to about 0.5 ampere during thermal conductivity measurements. The current was varied in steps, as desired, by a set of manganin resistors, with mercury contacts, which were in series with the cell wire and were adjustable in steps of 0.01 ohm.

Since it is important that the standardized resistance in series with the cell wire be practically independent of the cell current special attention was given to its design and its construction. It consists of 15 parallel strands of bare manganin wire (0.25 ohm per cm) soldered between copper bars (5×10^{-6} ohm per cm). The entire unit is immersed in yellow ceresin wax. It was calibrated by comparison with National Bureau of Standards certified resistances of nominal 10 ohms, 100 ohms, and 10,000 ohms, respectively. A ratio method was employed, and potential differences were measured on the White potentiometer. The final value of this calibration is given above, its uncertainty being fixed by the small uncertainties assigned to the National Bureau of Standards certification of the standard resistances. The resistance of the standardized resistance proved constant, to within 0.01 percent for currents ranging from 0.06 to 0.6 ampere.

Intercomparisons of the decade coils of the White potentiometer were made in the manner recommended by the manufacturer (Leeds and Northrup) and the resistance ratios were found to lie within permissible tolerances. In the course of the measurements, small contact and thermal electromotive forces in the potentiometer circuit and in external circuits were determined and the proper corrections applied.

TEMPERATURE MEASUREMENTS

(1) Temperature Scale

The temperature scale for this research was established by means of a standard thermocouple, thermocouple *C*, which was mounted in the thermostat. The junction was about 1 cm from the central portion of the steel cell tube. Thermocouple *C* was calibrated against University of California thermocouple No. 101, which

[13] J. Strong, *Procedures in Experimental Physics* (Prentice-Hall, Inc., New York, 1938), p. 447. Note that the connection shown by Strong between the cathode of the photoelectric cell and the plate of the Thyratron should be eliminated.

had been calibrated by Greensfelder and Milner[14] in terms of the hydrogen scale of Giauque, Buffington, and Schulze.[14] The original calibration of couple *C* extended over the range 110° to 300°K. The correction curve was extrapolated to 80°K. The calibration was extended to higher temperatures by comparison, at 323°, 343°, and 373°K, with a mercury-in-glass thermometer certified by the National Bureau of Standards. The three new calibration points lie on a smooth extrapolation of the original table. It is believed that the temperature scale is reliable to about ±0.05 degree over the entire range. The electromotive force of the thermocouple is read on a Leeds and Northrup, White double potentiometer, with a range of 10,000 microvolts in steps of 1 microvolt, and a galvanometer sensitivity of 6 cm on the scale per microvolt. The sensitivity of the thermocouple varies from 20 to 50 microvolts per degree. The precision of measurement of the temperature was 0.003 degree, in a series of measurements at a given temperature.

(2) Calibration of Cell Wire

The calibration of the resistance of the cell wire was carried out concurrently with the thermal conductivity measurements on air. The wire had previously been annealed at 600°C by passing a current through the evacuated cell. The calibration involved a measurement of the resistance of the wire when heated by a current of about 0.1 amp. This value was a compromise between the requirement for minimum heating of the cell wire and the necessity for sensitivity in the measurement of the temperature of the wire. The resultant heating of the cell wire was about 0.50 degree (approximately independent of temperature), and the precision of measurement was 0.003 degree.

The initial correction for the heating of the cell wire was effected by a linear extrapolation of the wire resistance against the square of the current, to zero current. This was possible through the use of the conductivity measurement, made concurrently with about 0.5 ampere. A preliminary correction curve for the wire was then computed, and preliminary thermal conductivities of air calculated. The latter then permitted an accurate calculation of the heating of the wire in the 0.1 ampere runs, and thus the calculation of the final correction curve. The final curve differed from the preliminary curve by 0.07 degree at the lowest temperature and by 0.01 degree at the highest, in just the way it was anticipated the dependence of the resistance and the gas conductivity on the absolute temperature would affect the linearity of the aforementioned extrapolation.

The corrected resistance readings were compared with the temperature, read on the standard thermocouple by means of a deviation plot, on which deviations of the observed resistances from an equation in T were plotted against temperature. The average deviation of the 20 calibration points from a smooth curve on the deviation plot was ±0.015 degree. However, the average deviation of 17 of the 20 points was only ±0.008 degree.

CALCULATION OF THE CONDUCTIVITY

(1) General

The heat produced in the effective length of the cell wire is dissipated principally by conduction through the gas to the cell wall. Corrections are required for longitudinal conduction in the cell wire, for conduction of heat from the cell wire by the potential leads, and for radiation from the cell wire. Correction must also be made for the temperature drop through the cell wall, and for temperature discontinuities between the gas and the surfaces of the cell wire and cell wall —the well-known "temperature-jump" effect.[15]

The temperature-jump correction requires that measurements be carried out at two or more gas pressures.

The heat flow in the gas in the central region of the cell may be regarded as radial—that is, the effect of longitudinal heat flow in the gas is negligible.[16] The differential equation governing the heat flow is, therefore

$$-\partial T/\partial r=(Q-\sum q_i)/2\pi LKr, \qquad (2)$$

where T is the temperature at the radial distance

[14] (*a*) B. S. Greensfelder and R. T. Milner, J. Am. Chem. Soc. **50**, 2205 (1928); (*b*) W. F. Giauque, R. M. Buffington, and W. Schulze, *ibid.* **49**, 2343 (1927).

[15] E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1938), Chap. VIII.

[16] W. G. Kannuluik and L. H. Martin, Proc. Roy. Soc. (London), have given the necessary equations for calculating the latter effect (see reference 9).

r; Q is the total heat produced per unit time in the effective length, L, of the wire; q_i is the heat flowing per unit time from the effective length of the cell wire by any mechanism other than conduction through the gas; and K is the thermal conductivity of the gas at the temperature T.

(2) Temperature-Jump Correction

In order to account for an apparent small dependence of the conductivity, as measured in a hot wire cell, on the pressure of the gas, it is found necessary to allow for the temperature-jump effect at the surface of the wire and, to a lesser extent, at the cell wall. The existence of such a temperature discontinuity when heat flows across a gas-solid interface is well established, and the temperature jump, δT, is known to be proportional to the temperature gradient in the gas and inversely proportional to the pressure of the gas.[15]

$$\delta T = g\partial T/\partial r = (g'/p)\partial T/\partial r. \tag{3}$$

When account is taken of the temperature jump, Eq. (2) may be integrated to yield the relation

$$1/K_a = (1/K) + (A/p), \tag{4}$$

where K is the true average conductivity of the gas over the range T_1 to T_2, and K_a, the apparent conductivity at the pressure p, is calculated from the relation

$$K_a = K_u - \sum_i K_i. \tag{5}$$

K_u is the uncorrected conductivity of the gas calculated from the experimental data and the equation

$$K_u = Q \ln (r_2/r_1)/2\pi L(T_1 - T_2). \tag{6}$$

K_i is an effective conductivity for the ith subsidiary mechanism of heat conduction, as defined by

$$K_i = q_i \ln (r_2/r_1)/2\pi L(T_1 - T_2). \tag{7}$$

The constant A in the small correction term in Eq. (4) is given by the expression

$$A = [1/\ln (r_2/r_1)][(g_1'/K_1 r_1) + (g_2'/K_2 r_2)], \tag{8}$$

where K_1 and K_2 are the conductivities of the gas at T_1 and T_2, respectively.

It follows from Eq. (4) that a plot of $(1/K_a)$ against $(1/p)$, for constant T_1 and T_2, yields a straight line, and that extrapolation of the line to its intercept at $(1/p)=0$ yields $(1/K)$, where K is the true conductivity. It is clear from Eq. (3) that the temperature jump effect vanishes at $(1/p)=0$, but actual measurements at very high pressures are not practicable because of the great increase of convection at high pressures. The use of Eq. (4) is thus a method of correcting for the temperature-jump effect and at the same time avoiding convection in the gas. Careful experimental tests of Eq. (4), as applied to a hot wire cell, have been made by B. G. Dickens.[8] The results of the present investigation also confirm the correctness of the linear relation predicted by Eq. (4), as will be shown later.

(3) Correction for End Conduction

The correction for end conduction, or for the heat flowing from the effective length of the cell wire into the end-segments of the cell wire, may be calculated with considerable accuracy. The differential equation for the longitudinal temperature distribution in the cell wire may be written

$$\frac{d^2\Theta}{dx^2} - B_1^2\Theta + B_2 = 0, \tag{9}$$

$$B_1 = \left[\frac{2K}{\lambda r_1^2 \ln (r_2/r_1)} - (B_2 R_0'/R_0)\right]^{\frac{1}{2}}, \tag{10}$$

$$B_2 = (R_0 I^2/\pi r_1^2 L\lambda J), \tag{11}$$

where $\Theta = (T_1 - T_2)$, at constant T_2, and x is the longitudinal distance along the wire. The radii of the cell wire and of the cell are r_1 and r_2, respectively, and L is the length of the effective portion of the cell wire. K is the average thermal conductivity of the gas, and λ is the thermal conductivity of the (platinum) cell wire. R_0 is the resistance of the effective length of the cell wire at $\Theta=0$, $(T_1=T_2)$, and R_0' is the temperature coefficient, (dR_0/dT_2). I is the current flowing through the cell wire, and J is the mechanical equivalent of heat.

The boundary conditions on Eq. (9) are that $\Theta=0$ at the ends of the wire, $x=0$ and $x=L_0$, where L_0 is the total length of the cell wire. The nature of the solution depends upon whether the constant B_1 is real or imaginary; B_1 is real for the present cell, under the conditions of opera-

tion. Instead of calculating directly the heat flowing from the effective length of the cell wire, Θ may be integrated over the range $x=(L_0-L)/2$ to $x=(L_0+L)/2$ to give the average temperature, Θ av., of the effective length, which is related to the observed resistance R. The result is:

$$\Theta \text{ av.} = [(R-R_0)/R_0'] = (B_2/B_1^2)\left[1-(2/B_1L)\frac{\sinh (B_1L/2)}{\cosh (B_1L_0/2)}\right]. \quad (12)$$

As L_0 increases without limit, the correction for end conduction vanishes, and Θ av. approaches the constant value (B_2/B_1^2). The effective conductivity for end conduction, K_e, is therefore:

$$K_e=[(2/B_1L)\sinh (B_1L/2)/\cosh (B_1L_0/2)]K_u, \quad (13)$$

where K_u is given by Eq. (6).

For the present cell, and for $I=0.5$ ampere, K_e decreases from 0.0086×10^{-5} to 0.0006×10^{-5} cal. deg.$^{-1}$ cm^{-1} sec.$^{-1}$ as K_u increases from 2×10^{-5} to 5×10^{-5} cal. deg.$^{-1}$ cm^{-1} sec.$^{-1}$. The maximum value of the correction in the present investigation was 0.5 percent.

(4) Lead Wire Correction

The correction for the heat flowing from the cell wire to the platinum potential leads is not susceptible to as accurate a calculation as the other corrections. The following treatment is a modification of that of S. Weber.[10] The temperature distribution in the potential lead, as a function of the distance from the cell wire, x, should satisfy Eq. (9) approximately, with $B_2=0$ and

$$B_1=[2K/\lambda(r_1')^2 \ln (r_2'/r_1')]^{\frac{1}{2}}, \quad (14)$$

where r_1' is the radius of the potential lead, and r_2' is an effective radius, of the order of magnitude of the radius of the tube, r_2. The boundary conditions are $\Theta=(T_1-T_2)$ at $x=0$ and $\Theta=0$ at $x=L'$, where L' is the length of the potential leads. The heat flowing into the potential leads may be calculated from the value of $(d\Theta/dx)$ at $x=0$ (only half of this heat contributes to the correction). The result may be expressed as the effective conductivity of the potential leads, K_p, by means of Eq. (7),

$$K_p=\lambda(r_1')^2B_1 \ln (r_2/r_1)/2L \tanh (B_1L'). \quad (15)$$

It is clear that K_p is not sensitive to the value of (r_2'/r_1'). It seems safe to assume that

$$10^2<(r_2'/r_1')<10^4$$

since these limits correspond to

$$0.06 \text{ cm}<r_2'<6 \text{ cm}$$

and r_2' should be of the order of magnitude of $r_2=0.4$ cm. For (r_2'/r_1') in this range, and for the values of the gas conductivity that occur

$$0.99<\tanh (B_1L')<1,$$

so that the correction is essentially independent of L'. On setting $\tanh (B_1L')$ equal to unity, and introducing the above mentioned limits for (r_2'/r_1') and the numerical values of the other constants, Eq. (15) reduces to

$$K_p\times10^5=(0.012\pm0.002)(K\times10^5)^{\frac{1}{2}}. \quad (16)$$

The largest value of the correction in the measurements on air was 0.80 percent, and the average value was 0.50 percent.

(5) Radiation Correction

A correction is required for the transfer of heat by radiation from the cell wire. Milverton[17] has measured the radiation loss from a polished platinum wire in a hot-wire cell, over the range 0° to 100°C. His results are in essential agreement with the theoretical expression for radiation between two coaxial cylindrical surfaces.[18] A measurement of the radiation loss from the present cell was carried out at 317°K. Conduction of heat by the residual gas in the evacuated cell was negligible. Under the conditions of the measurement, Eqs. (10)–(12) applied, with an obvious change in the meaning of K, since radiation replaced thermal conduction. The result of the measurement, expressed as the emissivity of the platinum wire, was 5.3 percent higher than the value found by Milverton at the same temperature.

For the calculation of the radiation correction in the thermal conductivity measurements, the value of the emissivity of platinum measured at 317°K in the present cell was adopted, together

[17] S. W. Milverton, Phil. Mag. **17**, 414 (1934).
[18] M. Jakobs and G. A. Hawkins, *Elements of Heat Transfer* (John Wiley and Sons, Inc., New York, 1942), pp. 125–126.

TABLE III. Thermal conductivity of air at 273.263°K.

Time (A.M.)		2:08	2:50	3:26	4:06	4:39	7:46
Pressure, p	(cm Hg)	19.55	8.94	4.37	1.70	0.615	8.30
Reciprocal of pressure, $(1/p)$		0.051	0.112	0.229	0.588	1.63	0.120
E.m.f. of thermocouple C	(microvolts)	254.2	254.3	254.2	254.3	254.4	254.1
Wall temperature, T_2	(°K)	266.457	266.454	266.457	266.454	266.452	266.460
E.m.f. across 0.128477 ohm resistor	(microvolts)	69437.3	69433.6	69429.2	69422.9	69410.3	69435.8
Cell current, I	(ampere)	0.54046	0.54044	0.54040	0.54035	0.54025	0.54045
E.m.f. across cell	(microvolts)	70047.5	70049.4	70056.5	70084.4	70175.7	70053.8
Cell resistance, R	(ohm)	0.129606	0.129616	0.129638	0.129701	0.129894	0.129620
Wire temperature, T_1	(°K)	280.068	280.089	280.134	280.265	280.663	280.097
Average temperature, $T_{av}=\frac{1}{2}(T_1+T_2)$	(°K)	273.263	273.272	273.296	273.360	273.558	273.279
Temperature interval, $\Theta=(T_1-T_2)$	(°K)	13.611	13.635	13.677	13.811	14.211	13.637
Uncorrected conductivity, $K_u=0.020720(RI^2/\Theta)$	(cal./cm sec. deg.)	5.763	5.753	5.735	5.681	5.528	5.752×10^{-5}
Sum of effective conductivities of end conduction, potential leads and radiation	(cal./cm sec. deg)	0.105	0.105	0.105	0.105	0.105	0.105×10^{-5}
Apparent conductivity, K_a (at T_{av} and p)	(cal./cm sec. deg.)	5.658	5.648	5.630	5.576	5.423	5.647×10^{-5}
Apparent conductivity, K_a (at 273.263°K and p)	(cal./cm sec. deg.)	5.658	5.648	5.629	5.574	5.418	5.647×10^{-5}
$(1/K_a)$, at p cm Hg)		1.7674	1.7705	1.7765	1.7940	1.8457	1.7709×10^{4}
$[1.7650+0.0496(1/p)]\times10^4$		1.7675	1.7706	1.7764	1.7942	1.8458	1.7710×10^{4}

True conductivity, at 273.263°K, $K=(1/1.7650\times10^4)=5.666\times10^{-5}$ cal. cm^{-1} sec.$^{-1}$ deg.$^{-1}$.

with the temperature coefficient found by Milverton. The effective conductivity for radiation, K_r, was then calculated from Eq. (7). In the thermal conductivity measurements on air, the correction amounted to 0.20 percent at 100°K, 0.74 percent at 200°K, 1.65 percent at 300°K, and 2.59 percent at 375°K.

(6) Wall Correction

A small correction for the temperature drop through the wall of the steel cell tube is readily calculated from the internal and external radii of the tube, and the thermal conductivity of the steel, 0.11 cal. cm^{-1} sec.$^{-1}$ deg.$^{-1}$. The greatest value of the correction in the measurements on air was 0.01 percent.

SAMPLE CALCULATION

The complete calculation of the thermal conductivity of air at 273.263°K is given in Table III for purposes of illustration. In this particular experiment the conductivity of air was measured at six pressures, over a period of about six hours. The uncorrected conductivity, K_u, at each pressure, is first calculated from Eq. (6). The effective conductivities for end conduction, K_e, the potential leads, K_p, and radiation, K_r, were 0.0004, 0.0286, and 0.0764×10^{-5} cal. cm^{-1} sec.$^{-1}$ deg.$^{-1}$, respectively. Subtraction of the sum of these corrections from K_u, as in Eq. (5), yields the apparent conductivity, K_a, at the pressure p and the average temperature for the experiment. The values of K_a are then corrected to a constant temperature, which is taken here as the average temperature of the measurement at the highest pressure, 273.263°K. These minute corrections may be made with an approximate temperature coefficient. According to Eq. (4) a linear relation should exist between $(1/K_a)$ and $(1/p)$. As shown in the table, the six points show a maximum deviation from a linear relation in $(1/p)$ of about 0.02 percent. Extrapolation of this linear relation to $(1/p)=0$ yields the true thermal conductivity of air at 273.263°K, 5.666×10^{-5} cal. cm^{-1} sec.$^{-1}$ deg.$^{-1}$.

EXPERIMENTAL RESULTS

Results obtained with air, in the temperature range 87° to 376°K, are given in Table IV. All data were obtained in August 1941 and the dates, listed in the first column, indicate the order in which measurements were made. Temperatures, in the second column, are the mean of the wire and the cell wall, which usually differed by about 13° in temperature. Pressures, in the third column, are those at which apparent

conductivities were measured. The true conductivities, in the fourth column, were obtained by plotting $(1/K_a)$ against $(1/p)$ and extrapolating to $(1/p)$ equal zero as described in the Sample Calculation.

The average percentage deviations from a straight line, in the $(1/p)$ plots, are shown in the fifth column and the percentage deviations from a smooth curve of K *versus* temperature, in the sixth. These indicate the precision of the data.

Values of the slopes in the $(1/K_a)$ *versus* $(1/p)$ plots are given in the seventh column. These will be referred to in a subsequent paper dealing with accommodation coefficients. For immediate purposes, they serve as a sensitive check on the reliability of the K's determined by extrapolation. Thus, the abnormally high slope in the 149.12° runs—which is clear out of line with the values at adjacent temperatures—makes the accuracy of that K somewhat suspect. Indeed, this is confirmed by the relatively large deviation of this K from the smooth curve of K *versus* temperature, as shown in Fig. 2.

The runs at 268.72° and at 279.45°K were taken with a single pressure only—namely 8.30 cm of Hg—and were made for the purpose of investigating the possible effect of the magnitude of the temperature interval. Their K's were obtained by using the observed $d(1/K)/d(1/p)$ at 273.26° for extrapolation to $(1/p)$ equals zero. Neither these two runs nor the one at 149.12° were given any weight in obtaining the smoothed curve of K *versus* T.

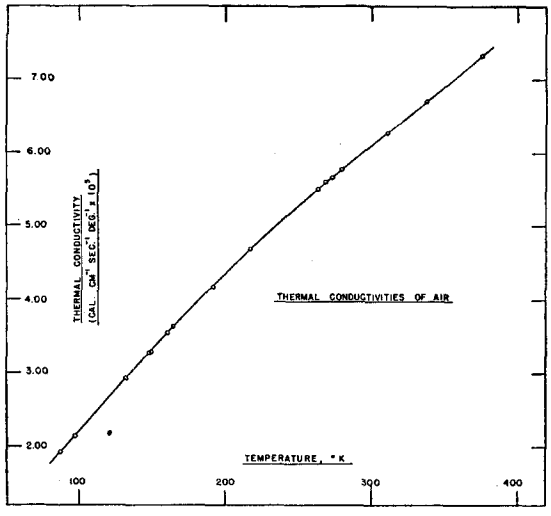

FIG. 2. Thermal conductivities of air.

Smoothed values of the thermal conductivities, at even temperatures, are given in Table V.

The table includes temperature coefficients, together with the smoothed conductivities, for use in making interpolations.

ACCURACY OF THE RESULTS

The average deviation of our 14 experimental values (the 149.12, 268.72, and 279.45° runs excepted for the reasons previously given) from the smooth curve on which Table V is based is

TABLE IV. Thermal conductivities of air.

Date (1941)	T, °K	Pressures (cm Hg, 0°C)	$K \times 10^5$	% dev. $(1/K_a)$	% dev. K	$\frac{d(1/K)}{d(1/P)}$
Aug. 31	87.50	1.58, 9.53	1.922		−0.05	378
Aug. 30	97.04	2.04, 4.96, 9.595	2.141	0.03	+0.19	145
Aug. 28	132.33	2.135, 5.18, 9.69	2.924	0.04	−0.17	254
Aug. 28	147.61	2.01, 9.305	3.268		+0.09	299
Aug. 23	149.12	2.43, 9.66	3.283		−0.45*	1444
Aug. 24	160.41	1.955, 9.92	3.542		−0.03	505
Aug. 29	164.13	2.25, 10.06	3.628		+0.17	383
Aug. 25	191.30	2.075, 4.95, 10.12	4.171	0.00	−0.31	313
Aug. 26	217.42	1.74, 4.76, 10.36	4.684	0.02	−0.11	405
Aug. 26	240.78	2.24, 9.79	5.114		+0.04	434
Aug. 26	262.99	1.975, 5.28, 10.50	5.503	0.02	+0.20	448
Aug. 7	268.72	8.30	5.607		+0.34*	
Aug. 7	273.263	19.55, 8.94, 4.37, 1.70, 0.615, 8.30	5.666	0.02	+0.04	496
Aug. 7	279.45	8.31	5.774		+0.17*	
Aug. 13	310.75	1.87, 11.39	6.268		−0.05	547
Aug. 14	337.56	1.745, 10.32	6.705		+0.00	576
Aug. 14	375.76	1.16, 2.66, 5.68, 12.30	7.319	0.01	−0.01	574
			Average deviation		±0.104	

* These points were given no weight in obtaining the smoothed values of K, and have been omitted from the average deviation.

TABLE V. Smoothed values of the thermal conductivities of air as a function of the temperature.

T, °K	$K \times 10^6$	(dK/dT)
80	1.755	0.0224
90	1.979	224
100	2.203	224
110	2.427	224
120	2.651	224
130	2.875	223
140	3.097	221
150	3.317	2185
160	3.534	215
170	3.747	2105
180	3.955	2055
190	4.158	2005
200	4.356	1955
210	4.549	1905
220	4.737	1855
230	4.920	1805
240	5.098	176
250	5.272	172
260	5.442	1685
270	5.609	1655
280	5.773	163
290	5.935	162
300	6.097	162
310	6.259	162
320	6.421	162
330	6.583	1615
340	6.744	161
350	6.905	161
360	7.066	161
370	7.227	161
380	7.388	161
273.1	5.660	1647

± 0.104 percent. This corresponds to approximately $\pm 0.014°$ in the temperature interval and is about the precision with which we were able to maintain, and to measure, the temperature of the thermostated bath. Our precision is therefore limited, principally, by the evaluation of bath temperature.

To evaluate the accuracy of the smoothed values given in Table V consideration must be given to the influence of possible systematic errors. These are as follows:

(1) Shape Factor

A small systematic error, which may amount to 0.12 percent as a maximum, may enter through slight uncertainties in the dimension of the cell or slight inaccuracy in the centering of the wire. This limit is arrived at by considerations of the figures presented in Table I, in conjunction with application of the formula given by Kannuluik and Martin[9] for the effect of the possible 0.014-cm inaccuracy in the centering of the wire (cf. infra).

(2) Energy Input

A maximum systematic error of ± 0.06 percent may enter through slight errors in (*a*) standard cell voltage, (*b*) standard resistance, and (*c*) potentiometer calibration—all of which contribute to the measured energy input.

(3) Temperature Head Between Cell Wire and Cell Wall

Systematic errors associated with evaluation of the radial temperature difference between the cell wire and the cell wall may contribute ± 0.20 percent at most to errors in thermal conductivities. This figure is regarded as a liberal estimate and takes into account: (*a*) inaccuracies in the potentiometer coils (0.01 percent) which may contribute both to thermocouple and wire resistance measurements; (*b*) drift in the standard cell used with the potentiometer (<0.005 percent); (*c*) drift in the standard 0.128477-ohm resistance during the month in which measurements were made; (*d*) error in calibration of the cell wire ($<0.01°$); (*e*) drift in calibration of the cell wire ($<0.01°$); (*f*) error in the temperature coefficient of e.m.f. of the thermocouple (<0.05 percent); (*g*) the very small temperature difference between the inner and outer surfaces of the cell wall (<0.01 percent); and (*h*) the possible existence of a small temperature difference between the outer surface of the cell wall and the thermocouple. The relatively large external surface of the metal cell and the rapid stirring of the bath liquid make it unlikely that any significant temperature difference of the type (*h*) existed.

TABLE VI. Limits in systematic errors introduced through determination of average gas temperature and through radiation and conduction corrections, as functions of the temperature (°K).

Source of error	Total magnitude of correction (percent of conductivity)	Limiting systematic errors (percent of conductivity) 80°	180°	280°	380°
Gas temperature		±0.08	±0.03	±0.02	±0.01
Radiation correction	0.1 to 2.5	0.02	0.05	0.07	0.18
End conduction correction	0.5	0.08	0.01	0.00	0.00
Potential leads cond. corr.	0.15 to 0.8	0.23	0.15	0.13	0.11

TABLE VII. Systematic error limits (total).

T, °K	Total systematic error (percent) Random	Additive
80	±0.35	±0.79
180	±0.29	±0.62
280	±0.28	±0.60
380	±0.32	±0.68

Drift in the standard 0.128477-ohm resistance amounted to only 8 parts in 13,000 over a period of eight months and could not have much exceeded 1 part in 13,000 during the month that measurements were under way.

The runs at 268.72°, 273.26°, and 279.45°K (previously mentioned) were made for the express purpose of finding if there might be any systematic trend in the results as a function of the magnitude of the temperature difference between cell wire and cell wall. To accomplish this, all three runs were made at a pressure of 8.30 cm of Hg and with a bath temperature of 266.45°K. All other conditions except the wire temperature were kept comparable. Temperature heads for the three runs were, respectively, 4.535°, 13.638°, and 25.985°. Corrected by the same $d(1/K)/d(1/p)$ to zero $(1/p)$ the K's of these three runs deviated from the smooth K *versus* T curve by the respective amounts +0.34 percent, +0.04 percent, and +0.17 percent. No systematic trend is evident and the 0.34 percent deviation corresponds to an error of only 0.015° in the temperature interval, which is within the recognized range of experimental error. We conclude that no systematic error has been introduced by our adoption of an approximate 13° temperature head for the majority of the runs.

(4) Average Gas Temperature

While temperature *differences* are measured much more accurately, we cannot claim much better than ±0.05°, in an absolute sense, for our temperature scale. With account taken of some further error in calibration of the cell wire, we regard ±0.06° as a liberal estimate of the uncertainty in the average temperature of the gas in the cell. This is equivalent to a systematic error of ±0.08 percent in the thermal conductivity of air at 80°K and to ±0.013 percent at 380°K. Equivalent errors at intermediate temperatures are shown in Table VI.

(5) Systematic Errors in Corrections for Radiation, End Conduction, and Conduction of Heat by the Potential Leads

The corrections referred to here have been discussed in a previous section, and magnitudes of the corrections indicated. Like the error in average gas temperature, systematic errors in making these corrections are dependent on the temperature at which runs are made. Table VI summarizes the magnitude of these corrections at several temperatures and of the errors in the thermal conductivity which may enter through their presence. In arriving at these estimates consideration has been given to the error limits in both the correction equations and in the data they employ.

(6) Temperature-Jump Correction

The short extrapolation in the $(1/K_a)$ *versus* $(1/p)$ plot, which corrects for the temperature discontinuities between gas and wire and between

TABLE VIII. Comparison of our own results on the thermal conductivity of air with those of other observers.

T, °K	This research $K\times10^5$	Published values $K\times10^5$	Method*	Worker	Year
81.6	1.791	1.80	*HW(C)*	Eucken[a]	1913
194.6	4.250	4.26	*HW(C)*	Eucken[a]	1913
273.1	5.660	5.62	*HW(PL)*	Schleiermacher[b]	1888
273.1	5.660	5.72	*HW(PL)*	Schwarze[c]	1901
273.1	5.660	5.69	*HW(PL)*	Schwarze[c]	1902
273.1	5.660	(5.66)	*HW(C)*	Eucken[a]	1913
273.1	5.660	5.68	*HW(PL)*	Weber[d]	1917
273.1	5.660	5.67		Putzki[e]	1918
273.1	5.660	5.92	*HW(PL)*	Schneider[f]	1926
273.1	5.660	5.74	*HW(C)*	Weber[g]	1927
273.1	5.660	5.85	*HW(C)*	Gregory and Archer[h]	1933
273.1	5.660	5.81	*HW(C)*	Milverton[i]	1934
273.1	5.660	5.84	*HW(C)*	Dickens[j]	1934
273.1	5.660	5.76	*HW(TW)*	Kannuluik and Martin[k]	1934
273.1	5.660	5.72	*P P*	Hercus and Sutherland[l]	1934
273.1	5.660	5.78	*HW(C)*	Northdurft[m]	1937
313.1	6.308	6.84	*HW(PL)*	Schneider[f]	1926
323.1	6.470	6.68	*HW(AH)*	Sherratt and Griffiths[n]	1939
353.1	6.953	7.18	*HW(C)*	Milverton[i]	1934
373.1	7.275	7.18	*HW(C)*	Eucken[a]	1913
373.1	7.275	7.59	*HW(AH)*	Sherratt and Griffiths[n]	1939

* *Key to symbols:*
HW(C), compensating type of hot wire cell.
HW(PL), potential lead type of hot wire cell.
HW(TW), thick wire type of not wire cell.
HW(AH), hot wire cell with auxiliary heaters.
PP, parallel plate method.

[a] See reference 5.
[b] Schleiermacher, Wied. Ann., **34**, 623 (1888).
[c] Schwarze, Phys. Zeits., **3**, 264 (1901, 1902); Diss. Halle, 1902; Ann. d. Physik **11**, 303 (1903).
[d] See reference 10.
[e] Putzki, Diss. Halle, 1918; cf. Trautz and Zündel, Zeits. f. tech. Physik **12**, 273 (1931), Table I.
[f] E. Schneider, Ann. d. Physik **79**, 177 (1926).
[g] S. Weber, Ann. d. Physik **54**, 437 (1917); **82**, 479 (1927).
[h] H. S. Gregory and C. T. Archer, Phil. Mag. **15**, 301 (1933).
[i] See reference 17.
[j] See reference 8.
[k] See reference 16.
[l] E. C. Hercus and Sutherland, Proc. Roy. Soc. **A145**, 599 (1934).
[m] W. Northdurft, Ann. d. Physik **28**, 137 (1937).
[n] See reference 3.

gas and cell wall, is made with great accuracy. In the 273.26° series of runs the linearity of the reciprocal plot was well established in runs at six pressures that varied between 0.615 and 19.55 cm of Hg (cf. Table III), and the precision was high (±0.02 percent) on individual runs. The average difference between the apparent conductivity measured at the highest pressure and the true conductivity obtained by extrapolation was 0.18 percent, and the maximum difference was 0.37 percent (except for the 149.12° run for which the slope was anomalously high and the difference 0.49 percent). We estimate that the error introduced by the extrapolations —where runs were made at two or more different pressures—cannot exceed about 0.03 percent.

(7) Convection

The linearity in the reciprocal plots referred to in the previous paragraph indicates freedom from effects of convection. This was further confirmed in a separate series of runs made with oxygen in the cell, at 322.06°K. Seven runs were made in this series. Five runs in the pressure range 0.75 to 11.29 cm of Hg gave an average deviation from a straight line of only 0.01 percent, while runs at 28.5 and 75 cm, respectively, deviated from the linear plot by amounts of 0.08 percent and 0.14 percent, respectively. The deviations at these higher pressures were the result of convection. Convection was suspected in these two runs, even before the results were calculated and plotted because a small but continuous fluctuation of the cell resistance was observed that disappeared upon reducing the pressure. In the measurements on air at 273.26°K no convection was observed at 19.55-cm pressure.

We are confident that there is no significant influence of convection in the conductivities obtained for air.

(8) Over-all Systematic Error

The combined effect of the several sources of systematic error referred to in the paragraphs above has been calculated, as a function of temperature, on the basis of two limiting assumptions: (*a*) that the several errors are random in sign and (*b*) that they are all additive. Results are shown in Table VII.

The true situation must be somewhere between these extremes (for the *maximum* error) and can probably be regarded as 0.5±0.1 percent. We thus believe that our smoothed values of the conductivities in Table V are correct to within about one-half of one percent in an absolute sense. *Probable errors* are, of course, even less than this.

COMPARISON WITH THE RESULTS OF OTHER INVESTIGATORS

Comparison of our own results (smoothed values of Table V) with those of other workers is shown in Table VIII.

As is apparent from the table, very few measurements have been made, by other workers, at temperatures other than 0°C. Below the ice point the only published data are the two values reported by Eucken, which are relative to air at 0°C. These agree well with our own measurements.

Our own value at 273.1, which we believe to be reliable to within 0.5 percent, lies 2.5 percent below the average of values obtained with compensating cells; about 1.5 percent below Kannuluik and Martin's result with the thick wire cell; 1 percent below Hercus and Sutherland's determination by the parallel plate method; and from 0.2 percent to 1 percent below most other values by the potential lead type cell.

The errors in our own measurements have been carefully considered (cf. infra) and it is difficult to see how our results can be low beyond the ±0.5 percent claimed for accuracy unless we have overcorrected for end conduction, radiation or conduction by potential leads. However, the *total* correction for end conduction, at 273.1°, is only 0.01 percent. The radiation correction is 1.34 percent but can be applied accurately. It

TABLE IX. Temperature coefficient of the thermal conductivity of air at 273.1°K.

Investigator	$(dK/dT) \times 10^3$
This research	2.91
Schneider	3.9
Gregory and Archer	2.97
Dickens	2.9
Milverton	2.81
Schwarze	2.53
Weber	3.65
Schleiermacher	2.81
Eucken	2.71

was determined experimentally by us and is in agreement with the careful work of Milverton.[17] Furthermore, it corresponds to a reflectivity of 96 percent, which is in reasonable agreement with optical measurements for the wave-lengths of maximum intensity at 273.1°K (~10 microns). While the potential lead correction is less certain its full magnitude at 273.1° is only 0.51 percent.

From the standpoint of absolute accuracy the advantage of our method is that the energy and temperature measurements are made directly on the effective length of the cell wire, with a correction of only 0.5 percent necessary for the cell leads. The use of compensating cells assumes cancellation of end effects in the two cells amounting to 5 or 10 percent of the heat produced in the effective length of the wire. In the thick wire cell as much as 50 percent of the heat flows from the ends of the cell, and is evaluated by means of an auxiliary determination of the thermal conductivity of the wire. It would seem that the possibility of serious systematic error is least with the potential lead method.

The temperature coefficient of the thermal conductivity of air at 273.1°K has been much in dispute.[17] The value obtained in this research is 0.00291. A tabulation of values obtained, by various workers, is shown in Table IX.

ACCOMMODATION COEFFICIENTS

Accommodation coefficients may be computed from the slope of the $(1/K_a)$ *versus* $(1/p)$ plots. A theoretical treatment of this will be reserved for a subsequent paper from this laboratory. The paper will include tabulations of accommodation coefficients on bright platinum for air, from the data of this research, and for nine other gases, from data obtained by Johnston and Grilly.

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The Thermal Conductivites of Eight Common Gases between 80° and 380°K

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Thermal conductivities of O_2, N_2, CO, NO, H_2, He, N_2O, CO_2, and CH_4 have been measured between 80°K and 380°K, with the potential lead type of hot wire cell developed by Taylor and Johnston. Results—which have a precision generally better than 0.1 of one percent and are believed to be accurate to ±0.5 of one percent—are tabulated for the eight gases. Comparisons with the results of other investigators are also shown in tabular form.

WE have measured thermal conductivities of oxygen, nitric oxide, hydrogen, carbon monoxide, carbon dioxide, nitrous oxide, methane, and helium over the temperature range 80°K (or temperatures at which the vapor pressures amounted to about 10 cm of Hg) to 380°K. Measurements were made at intervals of about 15°.

APPARATUS AND METHOD

Apparatus and method have been described in an earlier paper by Taylor and Johnston.[1] The following slight modifications were made for this work:

(1) Thermocouple *C*, used by Taylor and Johnston, was replaced by two new copper-constantan thermocouples, designated couples *V* and *W*. These were calibrated at 90°K (b.p. O_2), 195°K (s.p. CO_2), 234°K (f.p. Hg), 273°K (m.p. H_2O), 305°K (t.p. Na_2SO_4), and 373°K (b.p. H_2O) by the method suggested in the Symposium on Temperature.[2] The two thermocouples were used simultaneously to measure the bath temperature. They always agreed with each other to within 0.1 microvolt, which is within 0.005°, throughout the course of the measurements.

[1] W. J. Taylor and H. L. Johnston, J. Chem. Phys. **14**, 219 (1946).

[2] *Temperature, Its Measurement and Control in Science and Industry*, American Institute of Physics (Reinhold Publishing Corporation, New York, 1941).