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# Thermal Conductivity of Nitrogen from 50° to 500°C and 1 to 100 Atmospheres*

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A new apparatus has been constructed for measurements of the thermal conductivity of gases up to 500°C and 100-atmosphere pressure. The parallel-plate method was used with a spacing of about 0.5 millimeter between the hotplate and coldplate. A capacitance method was used to measure the effective spacing and area of the plates under the conditions of the experiment. No solid material was used between the plates. The effect of radiation was minimized by use of polished silver parts and was accounted for by experiments with the conductivity cell evacuated. Measurements on nitrogen were made at 1, 50, and 100 atmospheres, and from 50° to 500°C. It is believed that the accuracy of the results is about 0.5 percent, except at the highest gas densities.

## 1. Introduction

Accurate data on the thermal conductivity of gases are needed for two reasons. First, they are needed to check present theories of heat conduction in gases. Experimental measurements at very high temperatures and pressures are extremely difficult, so that theoretical means of predicting thermal conductivities in this range are needed. Second, accurate data are needed on at least one gas so that engineering data on other gases can be obtained with relatively simple apparatus by a comparison method. The present apparatus was constructed primarily to furnish very accurate data for use as standards by others making thermal-conductivity measurements on gases. Nitrogen was chosen as the first gas to be measured for several reasons. More measurements have been made on nitrogen than on any other pure gas. It is readily available in a state of high purity and is entirely suitable as a standard reference gas for use in calibrating apparatus for relative measurements.

## 2. Method

Measurements of thermal conductivity of gases in a steady state have been made by two general methods, radial heat flow and linear heat flow. Most measurements have been made with radial heat flow, either from a hot wire or between coaxial cylinders. In principle, these measurements are susceptible to convection errors. Elimination of these errors at the high pressures requires extremely small dimensions, which may be difficult to determine. The linear heat flow method is free from convection if the heat flow is downward. For this reason, the parallel-plate method was chosen for these measurements up to 100 atm. The spacing between the plates was made small to minimize the error caused by radial heat transfer. In addition, the small spacing reduces the possibility of convection in case the plates are not quite horizontal.

The correction for heat transfer by radiation between the hotplate and the coldplate was evaluated by an experiment with the conductivity cell evacuated. Of course, this assumes that no appreciable part of the radiation is absorbed by the gas in the conductivity experiment. In all the experiments, it was necessary to know the effective spacing between the plates. Frequently, solid spacers (of known dimensions) are used between the hotplate and coldplate. No such spacers were used in this apparatus because it was believed that the heat transfer through the contact area of the spacers and plates might be different with gas present than with the cell evacuated. The radiation correction experiment would thus be partially invalidated. The effective spacing was measured by a capacitance method under the actual conditions of the experiment. This method has several advantages over the usual method with measured spacers. First, the above-mentioned uncertainty in the effect of contact is eliminated. Second, the capacitance method automatically accounts for any change in dimensions. Third, because the direct capacitance between the hotplate and coldplate is measured, nonlinear heat flow at the circumference of the hotplate is accounted for.

The thermal conductivity, $k$ (w cm$^{-1}$ deg C$^{-1}$), for heat flow between parallel plates is given by the equation

$$k=\frac{\dot{Q}\Delta X}{\Delta t A}, \tag{1}$$

where $Q$ is the rate of heat (watts) flowing only by conduction from the hotplate through the gas to the coldplate, $\Delta t$ is the temperature difference (deg C) between the hotplate and coldplate, $\Delta X$ is the effective distance (cm) between the two plates, and $A$ is the effective area (cm$^2$) of the hotplate. The factor $\Delta X/A$ may be considered as the constant of the "conductivity cell" determined by the capacitance method, so that

$$k=\frac{0.0885516\dot{Q}}{C\Delta t}, \tag{2}$$

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where $C$ is the direct capacitance (micromicrofarads) between the hotplate and the coldplate, assuming the material between the plates to have a dielectric constant of unity corresponding to a vacuum. With the gas between the plates, a small correction must be made for its dielectric constant. The conduction equation (2) would apply, of course, to any two surfaces, as well as to parallel plates, provided only that the temperature and electric fields are geometrically similar.

## 3. Experimental Procedure

### 3.1. Apparatus

The general assembly of the thermal-conductivity cell, the pressure vessel, and the surrounding furnace is shown in figure 1. The hotplate (H), coldplate (J), guard (F), and auxiliary guard (E) are shown schematically. The pressure vessel (G) is made of stainless steel and is sealed with a Monel gasket (D). This vessel is surrounded by a furnace (K) and furnace "neck" (C), which are made of aluminum and are equipped with electric heaters in numerous porcelain tubes in the aluminum. The furnace temperature was automatically controlled by means of a platinum resistance thermometer and bridge circuit. The furnace neck was controlled relative to the furnace by means of a thermocouple. The pressure vessel extends upward out of the furnace region so that the electric leads can be brought out of the pressure vessel in a cold region. The cooling coil (B) dissipates the heat from the furnace, so that the top is cool. The electric leads (all No. 32 gold wire) are brought up from the auxiliary guard through three Inconel tubes, which serve as electrostatic shields, as described later. There are 29 of these leads, which are brought out of the pressure vessel through a pressure seal, A. These leads go out radially between two "Kel-F" (polychlorotrifluoroethylene) disks, which are pressed together for the seal.

A number of difficulties were encountered before obtaining a successful seal at A. At first, the material Teflon (polytetrafluoroethylene) was used, but it was found to flow excessively at the high pressures necessary for the seal. The method finally used for this seal was to mold Kel-F around the gold wires at about 200° C.

The vital parts of the thermal-conductivity cell are shown in figure 2. The hotplate (M), coldplate (O), guard (E), and auxiliary guard (B) are all made of silver to minimize temperature gradients and heat transfer by radiation. The hotplate is made of three parts, silver-soldered together. The hotplate heater (L) is located between the lower parts and consists of about 55 ohms (at 25° C) of (0.05-mm diameter) platinum wire insulated with mica. Gold leads from this heater are brought out through the tempering region located at H between the upper two silver pieces of the hotplate and then to the thermal tie-down, F. The purpose of this thermal tie-down

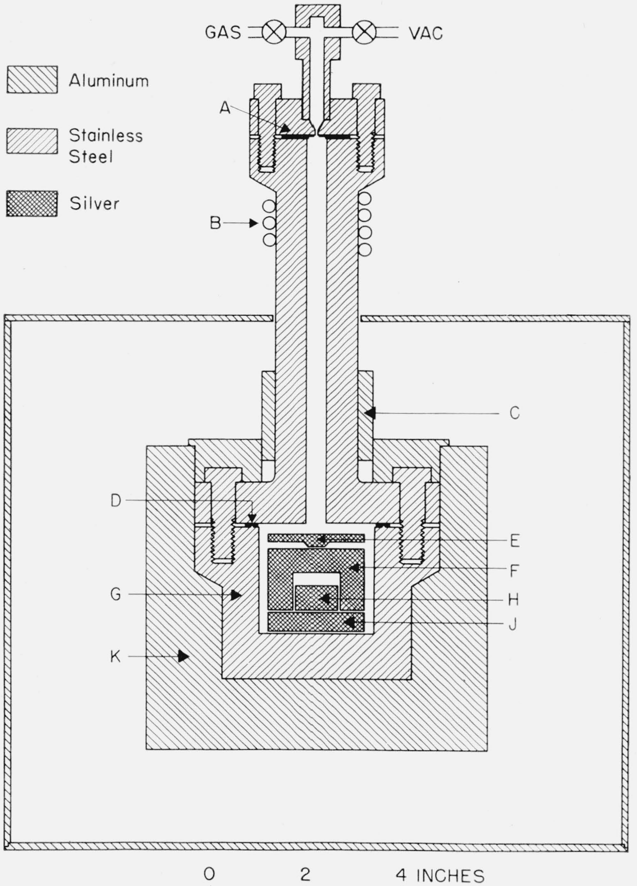

FIGURE 1. *Thermal-conductivity apparatus.*

A, Pressure seal for electric leads; B, cooling coil; C, furnace neck; D, Monel gasket; E, auxiliary guard; F, guard; G, pressure vessel; H, hotplate; J, coldplate; K, furnace.

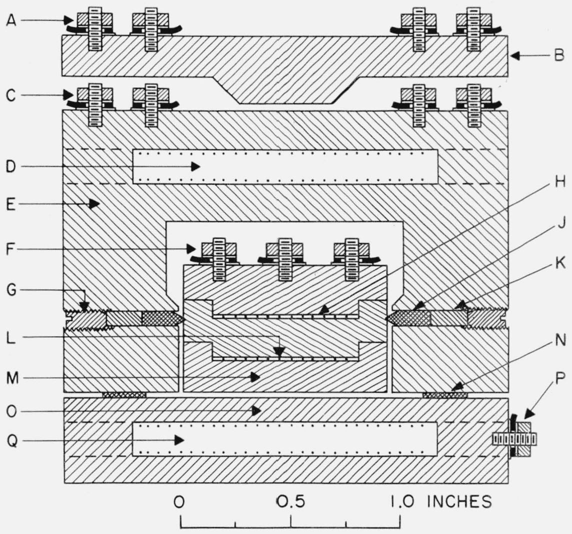

FIGURE 2. *Thermal-conductivity cell.*

A, C, F, H, P, Thermal tie-downs for electric leads; B, auxiliary guard; D. Q, platinum resistance thermometers; E, guard; G, silver screw; J, quartz supports for hotplate; K, aluminum insert; L, hotplate heater; M, hotplate; N, quartz spacers; O, coldplate.

is to bring the leads as close as possible to the temperature of the silver. This type of tie-down is used extensively throughout the apparatus and consists of a gold terminal insulated between thin mica disks and held down to the silver by a nut threaded on a machine screw. The gold terminal is spaced around the screw so that it is insulated from it.

The hotplate is supported by the guard ring at three points, using quartz supports (J), so that the bottom plane of the hotplate is in the same plane as the bottom of the guard ring. Because the coefficient of thermal expension of quartz is lower than that of silver, an aluminum insert (K) having a higher coefficient than quartz was used with the quartz for compensation. The quartz is held tightly against the hotplate by the silver screw (G) pressing against the aluminum insert. The guard (E) surrounds the hotplate, except where it is exposed to the coldplate. In the vital region near the coldplate, the guard is spaced about 0.5 mm from the hotplate. The assembly of the guard and hotplate is held about 0.5 mm from the coldplate by three quartz spacers (N) between the guard and coldplate. In this region, the silver was highly polished to reduce heat transfer by radiation. Heaters (not shown) are installed in both the guard and coldplate.

The temperatures of the guard and coldplate are measured by using the platinum resistance thermometers (D) and (Q), respectively, in conjunction with a Mueller bridge. These strain-free thermometers are not sealed. All leads (gold) from these two thermometers are thermally tied down at C and P, respectively, so that the temperatures of the platinum resistance thermometers are not affected by heat conduction along the leads. The temperature difference between the guard and hotplate is determined by means of a multiple-junction thermopile, using four No. 36 Chromel P-Alumel thermocouples in series. This thermopile has one set of electrically insulated junctions at F on the hotplate and the other set at C on the guard.

Experiments indicated the desirability of providing another thermal tie-down zone for all electric leads before they go out from C to the cold region. For this purpose, the silver auxiliary guard (B) was used with a heater built in to provide the bulk of the heat flow up along the electric leads. All three silver pieces, (B), (E), and (O), are held together by long machine screws fastened in the bottom of the surrounding pressure vessel. These four pieces are all electrically insulated from one another.

The effective operation of the thermal-conductivity apparatus depended upon the proper temperature control of the various components. For this purpose, five automatic thermoregulators were used to control the temperatures of the coldplate, guard, auxiliary guard, furnace, and the furnace neck. These thermoregulators were actuated by thermocouples or resistance thermometers (not the measuring resistance thermometers), and they consisted essentially of "chopper-amplifiers" operating saturable reactors in the heater circuits. The guard was maintained at the same temperature as that of the hotplate by means of the differential thermopile previously mentioned. This temperature control was the most important; it maintained constancy of temperature to about 0.001 deg C. The auxiliary guard was maintained at the same temperature as the guard by a single differential thermocouple. As a result of the effectiveness of the thermoregulation in the thermal-conductivity apparatus, all the observations on the thermal conductivity of nitrogen were made by one person. Both the electric power in the hotplate heater and the thermocouple readings were observed with a precision potentiometer.

A capacitance bridge was used to measure the capacitance between the hotplate and the coldplate. This bridge permitted the accurate measurement of small direct capacitances, even though relatively large capacitances exist between the "ground" and the plates. To eliminate, as far as possible, errors of measurement in capacitance, a calibrated capacitor having about the capacitance of the thermal-conductivity cell (about 10 $\mu\mu$f) was used as a reference and the measurements made by a substitution method. In this measurement, the same internal capacitance to ground was kept in the bridge circuit, so that the capacitance measurement approached very closely to the ideal comparative measurement, giving an accuracy comparable with the accuracy of the calibrated capacitor. Much care was taken to avoid significant capacitance between the leads from the hotplate and coldplate. They were effectively shielded from each other by bringing leads out through separate grounded Inconel tubes and by proper location of the leads that pass through the pressure seal.

For the measurement of the pressure of the gas in the conductivity cell, calibrated Bourdon gages were used. The requirement for accuracy on these gages was not great because the variation of thermal conductivity with pressure was much smaller than the change with temperature.

### 3.2. Purity of Nitrogen

The nitrogen used was extra-dry high-purity, obtained from the Linde Air Products Co., who stated that impurities did not exceed 100 ppm. Cryoscopic measurements made by G. F. Furukawa at the National Bureau of Standards with an adiabatic calorimeter showed liquid-soluble solid-insoluble impurities to be about 10 ppm. The conductivity cell was filled with this nitrogen, which had been passed through a silica-gel dryer and a filter made of glass wool.

### 3.3. Procedure

The general procedure was to set the furnace controls to the desired temperature, fill the conductivity cell with gas at the desired pressure, and put in a chosen electric power in the hotplate. With the coldplate automatically regulated to a constant temperature and the guard temperature automatically controlled to the temperature of the hotplate, the hotplate temperature became constant. After the capacitance between the two plates was measured, alternate measurements of electric power ($W$) and temperature difference ($\Delta t$) between the plates were made until the constancy of their values indicated that a steady state had been reached. The power in the hotplate was then changed so that similar measurements were made at three or more powers. The gas pressure was then changed and measurements were repeated for each of the pressures 0.7, 50, and 100 atm. All of these measurements were made at 50°, 100°, 200°, 300°, 400°, and 500°.

According to eq (2), the three quantities needed to determine the thermal-conductivity coefficient, $k$, are the rate of heat flow, $\dot{Q}$, the temperature difference, $\Delta t$, and the direct capacitance, $C$, between the hotplate and coldplate. Each of these quantities is discussed in detail below.

In order to obtain $\dot{Q}$ from $W$, the measured electric power in the hotplate, it is necessary to account for all heat flow from the hotplate other than by conduction through the gas. The possible paths of this heat flow are (1) to the surrounding guard by conduction and convection through gas, conduction through lead wires, and radiation, (2) to the coldplate by convection, and (3) to the coldplate by radiation.

Preliminary experiments were made to determine the heat-transfer coefficient between the guard and hotplate. Results of these experiments showed that an uncertainty in conductivity of less than 0.1 percent would be caused by a temperature difference between the guard and the hotplate of 0.001° C. It was found possible to control the temperature difference automatically to about this value.

The conductivity cell was designed to eliminate any convection currents. If convection does exist, it will cause an apparent change in the value of $k$ with change in power input. At the lower gas densities, no such change was observed, and convection effects seemed absent. However, at the higher gas densities, $k$ appeared to vary with power. The apparent $k$ values were corrected by extrapolating to zero power input. This apparent change in $k$ with power is believed to be due to a "chimney"-type convection resulting from gas flowing into the space between the guard and coldplate and out of the holes (not shown in fig. 2) provided for electric leads in the top of the guard. It is expected that blocking of these spaces would have eliminated this effect.

The heat transfer by radiation was accounted for by measurements with the cell evacuated. This power ($W_r$) transferred between two parallel plates can be expressed as

$$W_r = eA\sigma(T_2^4 - T_1^4), \tag{4}$$

where $e$ is an effective emissivity of the surfaces, $A$ is an effective area, $\sigma$ is the Stefan-Boltzmann constant, and $T_1$ and $T_2$ are the absolute temperatures. If the temperature difference, $\Delta t$, is small compared to the average temperature, $T=0.5\ (T_2+T_1)$, then the transfer equation can be simplified to

$$W_r = 4\ eA\sigma T^3 \Delta t = BT^3 \Delta t. \tag{5}$$

The constant $B$ was evaluated in preliminary experiments over the entire temperature range with the conductivity cell evacuated. The gas pressure in the cell in these experiments was estimated to be less than $10^{-5}$ mm of mercury. During the progress of the experiments with gas, the constant $B$ was checked periodically at temperatures of 350° C and below to test for possible changes in emissivity with time. Higher temperatures were not rechecked for reasons to be discussed later with temperature measurement.

The direct capacitance ($C$) between the hotplate and coldplate was measured by a substitution method using a calibrated standard and a Sylvania type 125 capacitance bridge. The precision of the bridge reading was better than the certified accuracy of the standard capacitor.

The capacitance, $C$, in eq (2) is that measured in vacuum. For measurements with gas in the cell, correction must be made for the dielectric constant, $\epsilon$, of the gas. $\epsilon$ was determined by using the Clausius-Mosotti equation

$$\frac{\epsilon-1}{\epsilon+2} = D\rho, \tag{6}$$

where $D$ is a constant independent of temperature for nonpolar gases, and $\rho$ is the gas density. The value used for $D$ was $1953\times10^{-7}$ [1] [2] when $\rho$ is in Amagat units [2]. Although the correction for the dielectric constant of the nitrogen may amount to 1 or 2 percent at the highest densities, it is believed that the uncertainties in $k$ due to this correction are less than 0.01 percent.

Temperature measurements were made with the resistance thermometers in the coldplate and the guard, together with the four-junction thermopile between the guard and the hotplate. These resistance thermometers were calibrated by the NBS Temperature Measurements Section before assembly of the cell. It was found, however, that when the system was kept under high vacuum at temperatures above 400° C, the thermometer characteristics changed slightly. This was probably due to contamination of the platinum by other metals in the system. Such a change took place during the determination of radiation corrections at 500° C. Rather than dismantle the apparatus to recalibrate the thermometers, it was thought that sufficient accuracy could be retained if the two thermometers were compared in place. In this way, the temperature difference would be known more accurately than the absolute temperature. This procedure is valid only because the evaluation of the temperature *difference*, $\Delta t$, is the important factor, whereas the change in thermal conductivity with temperature is small. It is estimated that after this procedure, the accuracy of the measurement of $\Delta t$ was 0.002 deg C and of average temperature $T$ was 0.01 deg C.

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[2] Figures in brackets indicate the literature references at the end of this paper.

## 4. Results

The results of the measurements are given in table 1. The first column gives the temperature of the experiment, which is the mean of the hotplate and coldplate temperatures. The second column gives the power ($W$) put into the hotplate (as measured electrically) with nitrogen in the conductivity cell. Values of power $W_r$, given in the third column, are based on experiments with the conductivity cell evacuated and are calculated from eq (5). These values are subtracted from the corresponding values of $W$ to give $\dot{Q}$, as used in eq (2). Over 40 experiments were made to determine the value of $B$ in this equation. A value of $B=4.90\times 10^{-12}$ w/deg$^4$ in this equation was found to fit the results best. The values of $B$ calculated from the individual vacuum experiments deviated on the average about 4 percent from the above value, and seemed to be independent of temperature. Because the *maximum* values of $W_r$ are only 3 percent of the corresponding values of $W$, an error of 4 percent in $B$ would cause a maximum error of only about 0.1 percent in conductivity $k$.

The values of temperature difference $\Delta t$ given in column 4 are based on measurements with the two resistance thermometers and the thermopile, which was used only as a "null" indicator. Column 5 gives the values of capacitance $C$ (as used in eq (2)) between the hotplate and coldplate as determined at the same time and under the same conditions of the conductivity experiment. These values have been corrected for the dielectric constant of the nitrogen.

The values of "apparent" thermal conductivity, $k^*$, given in column 6, were calculated from eq (2). These values, when corrected to even temperatures, seem to be free from error due to convection in that they are usually independent of power, except at some of the highest pressures, as mentioned earlier. Because this effect is believed to be due to a chimney-type convection, it should diminish at lower power inputs. Therefore, the values of $k^*$ were extrapolated to zero power to give "true" conductivities, $k$. In the worst case, at 100-atm pressure and 50° C, the extrapolation is over a large range of values of $k^*$. However, it is believed that this extrapolation should introduce only a relatively small error. The results from the three experiments at different powers were fitted by the method of least squares to a linear equation in power. The maximum deviation of the observed values of $k^*$ in this linear equation was only 0.28 percent, so that it is believed that the linear extrapolation was adequate.

At low pressures the effect of temperature discontinuity near the walls may become significant. This has been taken into account for the 0.7-atm data by use of the equation

$$k=k^*\left(1+\frac{2g}{\Delta X}\right). \tag{7}$$

Table 1. *Experimental results on nitrogen*

| Temperature, $t$ | Power— With nitrogen, $W$ | Power— With vacuum, $W_r$ | Temperature difference, $\Delta t$ | Capacitance, $C$ | Apparent conductivity, $k^*$ |
|---|---|---|---|---|---|
| Pressure, 0.7 atm | | | | | |
| °*C* | *w* | *w* | °*C* | *μμf* | *10⁻⁴ w/cm deg* |
| 51. 03 | 0. 05107 | 0. 00027 | 1. 647 | 9. 786 | 2. 790 |
| 52. 75 | . 1039 | . 00056 | 3. 332 | 9. 789 | 2. 804 |
| 57. 85 | . 2630 | . 0015 | 8. 306 | 9. 797 | 2. 846 |
| 100. 13 | . 05895 | . 00042 | 1. 664 | 9. 975 | 3. 122 |
| 101. 87 | . 1202 | . 0009 | 3. 371 | 10. 049 | 3. 120 |
| 106. 68 | . 2927 | . 0022 | 8. 117 | 10. 017 | 3. 165 |
| 200. 09 | . 07569 | . 00088 | 1. 696 | 10. 450 | 3. 737 |
| 201. 50 | . 1387 | . 0016 | 3. 101 | 10. 455 | 3. 744 |
| 205. 02 | . 2981 | . 0035 | 6. 614 | 10. 463 | 3. 769 |
| 204. 86 | . 2971 | . 0035 | 6. 615 | 10. 435 | 3. 767 |
| 300. 48 | . 09072 | . 0148 | 1. 704 | 10. 80 | 4. 293 |
| 302. 17 | . 1818 | . 0030 | 3. 404 | 10. 82 | 4. 299 |
| 304. 25 | . 2972 | . 0049 | 5. 534 | 10. 85 | 4. 312 |
| 306. 64 | . 4308 | . 0072 | 7. 991 | 10. 83 | 4. 336 |
| 306. 56 | . 3719 | . 0066 | 6. 891 | 10. 85 | 4. 326 |
| 401. 02 | . 1064 | . 0026 | 1. 706 | 11. 17 | 4. 822 |
| 402. 65 | . 2177 | . 0053 | 3. 484 | 11. 18 | 4. 829 |
| 406. 43 | . 4732 | . 0116 | 7. 539 | 11. 20 | 4. 841 |
| 501. 60 | . 1311 | . 0040 | 1. 776 | 11. 71 | 5. 408 |
| 502. 93 | . 2369 | . 0073 | 3. 205 | 11. 71 | 5. 416 |
| 506. 46 | . 5248 | . 0164 | 7. 045 | 11. 77 | 5. 430 |
| Pressure, 50 atm | | | | | |
| 50. 59 | 0. 04416 | 0. 00021 | 1. 290 | 9. 761 | 3. 090 |
| 51. 02 | . 05938 | . 00029 | 1. 718 | 9. 762 | 3. 120 |
| 52. 46 | . 1138 | . 0005 | 3. 179 | 9. 772 | 3. 228 |
| 55. 76 | . 2511 | . 0011 | 6. 519 | 9. 788 | 3. 470 |
| 99. 69 | . 04457 | . 00030 | 1. 172 | 9. 987 | 3. 348 |
| 100. 31 | . 06805 | . 00045 | 1. 781 | 9. 980 | 3. 368 |
| 101. 94 | . 1345 | . 0009 | 3. 434 | 9. 996 | 3. 446 |
| 105. 15 | . 2748 | . 0018 | 6. 716 | 10. 021 | 3. 592 |
| 200. 26 | . 09102 | . 00101 | 1. 937 | 10. 456 | 3. 937 |
| 201. 61 | . 1569 | . 0017 | 3. 322 | 10. 456 | 3. 956 |
| 206. 33 | . 3966 | . 0044 | 8. 165 | 10. 481 | 4. 058 |
| 301. 54 | . 1589 | . 0025 | 2. 835 | 10. 84 | 4. 505 |
| 305. 68 | . 4077 | . 0064 | 7. 158 | 10. 87 | 4. 567 |
| 302. 85 | . 2365 | . 0037 | 4. 194 | 10. 84 | 4. 535 |
| 400. 81 | . 1060 | . 0025 | 1. 616 | 11. 16 | 5. 085 |
| 402. 30 | . 2105 | . 0048 | 3. 197 | 11. 16 | 5. 104 |
| 405. 86 | . 4699 | . 0108 | 7. 067 | 11. 18 | 5. 145 |
| 501. 57 | . 1331 | . 0039 | 1. 720 | 11. 72 | 5. 674 |
| 502. 98 | . 2575 | . 0076 | 3. 316 | 11. 74 | 5. 685 |
| 507. 42 | . 6426 | . 0191 | 8. 195 | 11. 77 | 5. 724 |
| Pressure, 100 atm | | | | | |
| 50. 12 | 0. 03336 | 0. 00014 | 0. 835 | 9. 809 | 3. 591 |
| 50. 83 | . 06738 | . 00026 | 1. 576 | 9. 813 | 3. 843 |
| 51. 82 | . 1210 | . 0005 | 2. 615 | 9. 821 | 4. 158 |
| 99. 86 | . 0597 | . 0004 | 1. 423 | 10. 007 | 3. 689 |
| 101. 10 | . 1195 | . 0007 | 2. 675 | 10. 014 | 3. 926 |
| 104. 96 | . 3421 | . 0018 | 6. 689 | 10. 036 | 4. 490 |
| 199. 70 | . 07664 | . 00083 | 1. 603 | 10. 41 | 4. 023 |
| 201. 08 | . 1502 | . 0016 | 3. 021 | 10. 43 | 4. 177 |
| 204. 51 | . 3473 | . 0035 | 6. 556 | 10. 46 | 4. 440 |
| 299. 62 | . 04732 | . 00082 | 0. 889 | 10. 83 | 4. 276 |
| 300. 79 | . 1150 | . 0019 | 2. 048 | 10. 83 | 4. 516 |
| 302. 76 | . 2366 | . 0038 | 4. 079 | 10. 84 | 4. 662 |
| 305. 30 | . 4068 | . 0065 | 6. 811 | 10. 84 | 4. 802 |
| 400. 79 | . 1059 | . 0024 | 1. 570 | 11. 17 | 5. 231 |
| 402. 68 | . 2468 | . 0055 | 3. 641 | 11. 19 | 5. 244 |
| 405. 56 | . 4650 | . 0104 | 6. 778 | 11. 20 | 5. 303 |
| 501. 21 | . 1342 | . 0039 | 1. 698 | 11. 69 | 5. 816 |
| 502. 66 | . 2612 | . 0075 | 3. 290 | 11. 70 | 5. 836 |
| 506. 68 | . 6218 | . 0180 | 7. 727 | 11. 75 | 5. 890 |

The "temperature-jump distance", $g$, is related to the "accommodation coefficient", $a$, by the relation [16]:

$$g=\frac{2-a}{a}(2\pi RT)^{0.5}\frac{k}{(\gamma+1)C_vP}, \tag{8}$$

in which $R$ is the gas constant, $T$ the absolute temperature, $k$ the thermal conductivity, $C_v$ the constant-volume specific heat, $\gamma$ the specific-heat ratio, and $P$ the pressure of the gas. Values of $a$ for nitrogen on silver vary from about 0.8 at room temperature to 0.4 at 800° C [6]. The value of 0.5 was chosen as the most probable for the temperature range of these experiments.

Values of observed conductivity $k$, corrected to even temperatures, are listed in column 2 of table 2. In order to facilitate interpolation of the results between the observed points, empirical equations were derived to give conductivity as a function of temperature at each of the three pressures. These equations are as follows:

$$k=1.059\eta\left(C_v+\frac{9}{4}R\right) \qquad \text{(pressure, 0.7 atm)}, \tag{9}$$

$$10^4k=2.714+0.005897t \qquad \text{(pressure, 50 atm)}, \tag{10}$$

$$10^4k=3.161+2.9317\times10^{-3}t+9.0761\times10^{-6}t^2-8.8318\times10^{-9}t^3 \qquad \text{(pressure, 100 atm)} \tag{11}$$

In these equations, $k$ is in watts cm$^{-1}$ deg$^{-1}$, $t$ is in deg $C$, $\eta$ is viscosity (poise), $C_v$ is heat capacity (j g$^{-1}$ deg$^{-1}$), at constant volume, and $R$ is the gas constant (8.317/28.016 j g$^{-1}$ deg$^{-1}$). The values of viscosity and heat capacity used in eq (9) were obtained from NBS Circular 564 (Nov. 1955), which tabulates heat-transport properties for a number of gases. The constants of these equations were obtained by the method of least squares. Values of $k$ given in column 3 of table 2 are calculated from these equations. Column 4 gives the deviations of the observed results from these calculated values. The results are also given in figure 3, where the circles represent observed values and the solid lines the values from the above equations.

TABLE 2. *Thermal conductivity of nitrogen*

| Temperature | Conductivity, $k$ | | Observed minus calculated |
|---|---|---|---|
| | Observed | Calculated | |
| Pressure, 0.7 atm | | | |
| ° $C$ | $10^{-4}$ $w/cm$ $deg$ | $10^{-4}$ $w/cm$ $deg$ | % |
| 50 | 2. 794 | 2. 818 | −0. 9 |
| 100 | 3. 129 | 3. 131 | −. 1 |
| 200 | 3. 750 | 3. 727 | +. 6 |
| 300 | 4. 308 | 4. 308 | . 0 |
| 400 | 4. 836 | 4. 857 | −. 4 |
| 500 | 5. 430 | 5. 381 | +. 9 |
| Pressure, 50 atm | | | |
| 50 | 3. 003 | 3. 009 | −0. 2 |
| 100 | 3. 303 | 3. 304 | . 0 |
| 200 | 3. 905 | 3. 893 | +. 3 |
| 300 | 4. 477 | 4. 483 | −. 1 |
| 400 | 5. 075 | 5. 073 | . 0 |
| 500 | 5. 660 | 5. 662 | . 0 |
| Pressure, 100 atm | | | |
| 50 | 3. 340 | 3. 329 | +0. 3 |
| 100 | 3. 513 | 3. 536 | −. 6 |
| 200 | 4. 060 | 4. 040 | +. 5 |
| 300 | 4. 612 | 4. 619 | −. 1 |
| 400 | 5. 218 | 5. 221 | . 0 |
| 500 | 5. 794 | 5. 792 | . 0 |

The empirical eq (10) and (11) fit the observed values at 50- and 100-atm pressure, respectively, almost as well as would be expected from the precision of the data. The average deviation of eq (10) (which is linear in $t$) from the observed conductivities is only 0.1 percent, with a maximum deviation of 0.3 percent. The deviations from eq (11) are also quite small except below 200°C, where there was increased difficulty, both experimentally and in fitting the observed points with an equation. The deviations of eq (9) from the observed values seem to be larger than can be attributed to experimental errors. Equation (9) is the same semi-empirical equation proposed by Eucken [3], except for the constant factor. A factor of 1.059 was found to fit the present data, as compared to a factor of 1 originally proposed by Eucken. More recent modifications of Eucken's equation by other investigators generally have predicted a value slightly greater than 1. An alternative equation for 0.7 atm, which fits well up to 400°C, and which may be easier for use in numerical interpolation in this region, is

$$k=2.495\times10^{-4}+6.366\times10^{-7}t-1.065\times10^{-10}t^2, \tag{12}$$

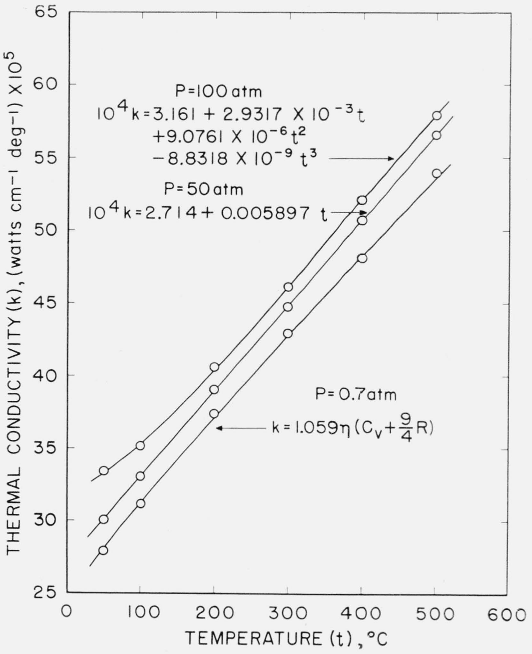

FIGURE 3. *Thermal conductivity of nitrogen.*

where $k$ is in w cm$^{-1}$ deg$^{-1}$, and $t$ is in deg C. Although all of these equations are suitable for interpolation at their respective pressures, they may not be valid for extrapolation beyond the experimental range. Equation (9) is probably the most suitable for extrapolation to higher temperatures.

## 5. Discussion of Results

### 5.1. Accuracy

In order to estimate the accuracy of the final results, it is necessary to consider the effect of each of the terms in the conductivity equation

$$k=\frac{0.0885516\dot{Q}}{C\Delta t}.$$

The constant 0.0885516 is a conversion factor to allow for the system of units. It has negligible uncertainty in its use here. Some possible sources of error in the measured capacitance, $C$, are the capacitance between electric leads and the relatively large capacitance to ground (the guard is grounded) of the hotplate and coldplates. The electric leads were carefully shielded to avoid significant error from this source. The effect of the ground capacitance is largely eliminated by the design of the bridge used in its measurement. Use of a substitution method that compares the conductivity-cell capacitance with that of a standard capacitor minimizes a number of possible errors. By using this method, it is believed that this comparison is accurate to better than 0.1 percent. The absolute value of the standard capacitor is certified by the NBS (with a high probability) to only 0.3 percent.

In the experiments with nitrogen, the effect of the dielectric constant of the gas must be considered. It is estimated that uncertainty in the value of the dielectric constant of nitrogen is less than 0.01 percent, giving the same uncertainty in $C$ and $k$. The total uncertainty in the capacitance measurement is believed to be about 0.3 percent. This is the largest uncertainty in most of the measurements, and it is based on 1 chance in 10 that the error will be larger than 0.3 percent.

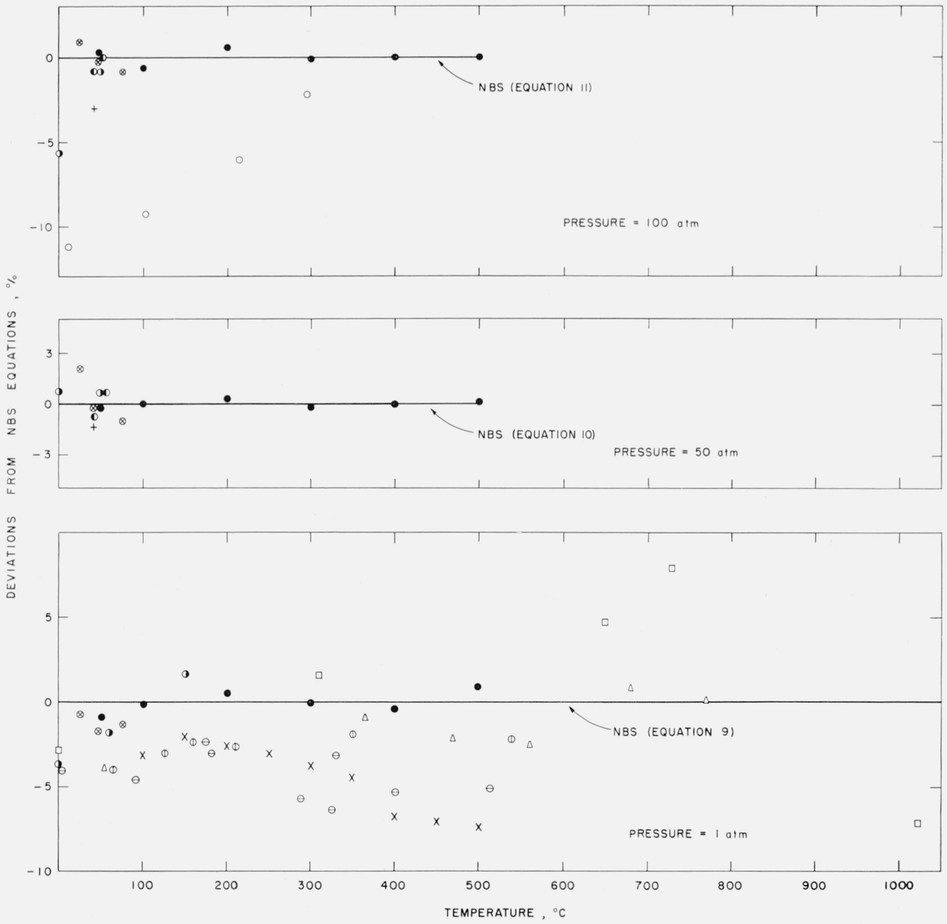

FIGURE 4. *Comparisons with others.*

●, NBS; ○, Stolyarov, Ipat'ev, and Teodorovich; ◑, Keyes; ◐, Vargaftik; ⊖, Frank; ⦶, Vargaftik and Oleschuk; ×, Schottky; △, Rothman and Bromley; ⊗, Michels and Botzen; □, Stops; +, Lenoir and Comings.

The factor $\dot{Q}$ in eq (2) is evaluated from the two powers $W$ and $W_r$. The electrical measurement of $W$ is believed to have negligible error. The uncertainty in the value of $W_r$ determined from vacuum experiments is estimated to be less than 0.1 percent, except at the highest temperatures, where it may be as large as 0.1 to 0.2 percent. It is possible that the vacuum experiments do not account completely for all heat flow (other than $\dot{Q}$) from the hotplate during the gas experiments. This may be due to imperfect matching of the guard temperature to the hotplate temperature. It is estimated that the error from this source is less than 0.1 percent.

The measurement of $\Delta t$, which has been discussed earlier, has an estimated uncertainty of 0.002 deg C. This introduces uncertainties in the values of $k$ of from 0.02 to 0.2 percent, depending on the magnitude of $\Delta t$. The uncertainty in the temperature scale, estimated to be about 0.01 deg C, is believed to introduce negligible error in $k$.

In estimating the over-all accuracy of the results, the authors believe that with most of the results, there is only 1 chance in 10 that the true conductivity values will deviate more than 0.5 percent from the observed values given in table 2. In the case of a few values at the highest pressures, it is believed that this tolerance might be increased by as much as 1 percent.

### 5.2. Comparison With Others

A comparison of the results of this investigation with the observed conductivity values from some other recent researches is given in figure 4. No attempt was made to include in the figure all the available data at low temperatures and low pressures, although all known high-pressure data are given. The data are plotted as deviations from eq (9), (10), and (11), which represent the NBS data for the three pressure ranges. At low pressures (approximately 1 atm), Frank [4] and Schottky [5] made measurements up to 500° C, Rothman and Bromley [6] up to 800° C, Stops [7] up to 1,020° C, Michels and Botzen [8] up to 75° C, and Vargaftik and Oleschuk [9] up to 541° C. Keyes and Sandell [10] have also made measurements up to 400° C at various pressures. Their results are not shown here because they believe their conductivity values to be too low over most of the temperature range. Later observed values of Keyes [11] up to 150° C are shown. Further measurements by Keyes [12] have been made up to about 350° C, but no observed values of conductivity have been published. At higher pressures, Michels and Botzen [8] made measurements up to 2,500 atm and 75° C, Stolyarov, Ipat'ev, and Teodorovich [13] up to 300 atm and 300° C, Vargaftik [4] up to 90 atm and 62° C, and Lenoir and Comings [15] up to 200 atm at 41° C. As in the low-pressure measurements, the results of Keyes and Sandell are not shown, although later results of Keyes are given up to 100 atm and 50° C.

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