Physica 92A (1978) 117–144 © *North-Holland Publishing Co.*

THE THERMAL CONDUCTIVITY OF FOUR MONATOMIC GASES AS A FUNCTION OF DENSITY NEAR ROOM TEMPERATURE

J.J. DE GROOT*, J. KESTIN, H. SOOKIAZIAN†

Division of Engineering, Brown University, Providence, R.I., U.S.A.

and

W.A. WAKEHAM

Department of Chemical Engineering and Chemical Technology, Imperial College, London, England

Received 17 November 1977

The paper describes absolute measurements of the thermal conductivity of four pure monatomic gases, He, Ne, Ar and Kr. The measurements were performed at room temperature (≈300 K) in a high-precision instrument based on the transient hot-wire principle. In the cases of He, Ne and Ar the measurements were performed in the pressure range 0.8 MPa to 35 MPa, whereas for Kr the pressure range covered was 1.1 to 16 MPa. The precision and reproducibility of the experimental data are estimated to be 0.2%, whereas their accuracy is judged to be one of ±1.5%.

In addition to the absolute values of the thermal conductivity, we have evaluated our results on a relative basis to take full advantage of their high precision. This has been made possible through the known Eucken factors for the monatomic gases at low density in combination with accurate viscosity data. The uncertainty in the reported thermal conductivity evaluated on the relative basis is one of ±0.4%.

The thermal conductivity as a function of density for Ne, Ar and Kr has been subjected to a statistical analysis in order to ascertain whether a logarithmic term exists in its density expansion. It is concluded in all cases that a polynomial density expansion represents the data as well as a polynomial of second order plus a logarithmic term. This supports the view that a logarithmic term, if it exists, must be multiplied by a very small coefficient.

1. Introduction

The establishment of accurate values for the viscosity of all the monatomic gases[1]) has allowed us to perform a critical assessment of the available thermal conductivity data for the same gases. This assessment has been carried out with the aid of the theoretical relationship[2,3]),

$$\lambda_0/\mu_0 c_v \mathcal{F}(T) = 2.500 \tag{1}$$

* Present address: Akzo Chemie Nederland bv, Deventer, Holland.

† Present address; Fairchild Space and Electronics Co., Germantown, Maryland.

which is valid in the limit of zero density. Here, $\mathcal{F}(T)$ is a function of order unity for which a correlation is given in ref. 2. Comparisons of this nature have shown that almost all measured values of the thermal conductivity depart from the values generated from eq. (1) and the best viscosity data[1]) by more than their claimed uncertainty.

The preceding observations have prompted us to search for a method of determining the thermal conductivity of gases which does not suffer from the difficulties normally associated with such measurements. In particular, the method chosen must eliminate the debilitating effect of natural convection. In two papers[4,5]) the development of an instrument conforming to these requirements has been described. The instrument operates on the transient hot-wire principle, and its theory has now been refined[4,6–8]) to an extent which allows us to use the technique for absolute measurement. The instrument is a later version of one constructed by J.W. Haarman[6,7]).

In the present paper we describe the results of our first measurements of the thermal conductivity of the four monatomic gases, helium, neon, argon and krypton. The measurements were performed as a function of density at room temperature within the pressure range 0.8 to 35 MPa. Measurements have also been carried out to ascertain the reproducibility of our instrument to support our preliminary findings[5]).

In our earlier work[5]) the precision of the measurements of thermal conductivity was estimated as one of $\pm 0.2\%$, and this figure represents the present claim as well. Owing to the experimental difficulties associated with the calibration of the resistance–temperature characteristics employed in the hot-wire cells we estimate the accuracy of our experimental data, evaluated on an absolute basis, to be one of $\pm 1.5\%$. However, we have also been able to evaluate our data on a relative basis by means of eq. (1) and our own accurate viscosity data[1]). When the data are evaluated on this basis we estimate that the reported thermal conductivites have an uncertainty of $\pm 0.4\%$.

The present experimental data make it possible to perform an investigation of the form of the density expansion for the thermal conductivity of gases similar to the one performed earlier for viscosity[9]). The Enskog theory for a gas of rigid spheres[10]) represents the first attempt to extend the kinetic theory to dense gases. The simplifying assumption of molecular chaos for the molecular velocity distribution in the theory leads to a power series expansion for each of the transport coefficients. In particular, the thermal conductivity of the dense gas may be written

$$\lambda = \lambda_0 + c_1\rho + c_2\rho^2 + c_3\rho^3 + \cdots, \tag{2}$$

where the coefficients of the series represent the effect of successively higher-order correlations in configuration space. Necessarily, these spatial correlations extend over a range closely related to that of the intermolecular potential.

If a systematic generalization of the Boltzmann equation is made to include the effect of sequences of correlated collisions in the gas, then the expansion

for the thermal conductivity of a dense gas must be written[11])

$$\lambda = \lambda_0 + c_1\rho + c_2'\rho^2 \ln \rho + c_2\rho^2 + \cdots, \tag{3}$$

as a replacement for eq. (2). Eq. (3) shows that the coefficient of the quadratic term in density contains a contribution which is proportional to the logarithm of the density. This term arises because the more complex treatment embodied in the generalization of the Boltzmann equation takes into account, in velocity space, correlations between collisions. These correlations extend over the distance of the mean free path in the gas; they have been specifically excluded from the theory leading to the power series expansion[2]).

An investigation of experimental data by Hanley, McCarty and Sengers in 1969[12]) indicated that the viscosity data available at that time were not sufficiently precise to allow discrimination between the representations afforded by eqs. (2) or (3). This prompted a very careful set of measurements of the viscosity of some simple gases as a function of density near room temperature[9]). The latter investigation was unable to establish any firm evidence in favor of eq. (3).

With regard to thermal conductivity, Hanley, McCarty and Sengers[12]) concluded that the more extensive data for this property supported the inclusion of the logarithmic term, a view later expressed by LeNeindre and co-workers[13]). However, their conclusions were, in the first case, based on experimental data with a precision of only 1.0%, and in both cases, the density intervals of the measurements used for the analysis were quite large. The latter point required that data be included from a density range beyond that included in eqs. (2) and (3) in order that statistically significant information could be obtained. The neglect of the higher-order terms in such analyses cannot be justified *a priori*. In the present work the measurements have been carried out at density intervals sufficiently small that useful information can be gained without recourse to higher densities. In addition, it should be emphasized that for the purposes of this analysis it is the precision of the measurements which is significant and not their absolute accuracy, since it is the functional form of the dependence on density which is under investigation.

2. Experimental

The apparatus employed for the present measurements has been described in detail elsewhere[5]). Consequently, we may confine ourselves here to a listing of the particular characteristics of the transient hot-wire cells employed for these measurements, the specific experimental procedures followed and the necessary working equations.

The characteristics of both cells employed in the present work are given in table I. The platinum wire employed as the sensing element in the cells was of the Wollaston type and was supplied by Sigmund Cohn, Inc. Its diameter was

TABLE I
Characteristics of the hot-wire cells

The long cell
Cell length 250 mm
Cell radius, b 9.5 ± 0.1 mm
Wire length 164.98 ± 0.01 mm
Wire radius, a 2.50 ± 0.01 μm
Resistance of the wire in helium (1.0 MPa, 23°C) $894.26 \pm 0.08\ \Omega$
$\alpha_0 = 0.003530\ K^{-1}$ at 23°C

The short cell
Cell length 150 mm
Cell radius, b 9.5 ± 0.1 mm
Wire length 87.75 ± 0.01 mm
Wire radius, a 2.50 ± 0.01 μm
Resistance of the wire in helium (1.0 MPa, 23°C) $479.07 \pm 0.05\ \Omega$
$\alpha_0 = 0.003530\ K^{-1}$ at 23°C

measured with the aid of an electron microscope, and the lengths of the etched segments of the wire measured with a cathetometer.

At the time of the measurements reported here it proved impossible to calibrate the resistance of the two etched platinum wires used for the measurements as a function of temperature *in situ*, owing to their extreme fragility. Consequently it was necessary to establish the resistance–temperature characteristics of a further wire taken from the same roll and mounted in a dummy cell. A calibration was carried out in the temperature range 0 to 100°C and yielded the result

$$R(T) = R(273.15)\{1 + A(T - 273.15) + B(T - 273.15)^2\}, \tag{4}$$

where

$$A = 3.875 \times 10^{-3}\ K^{-1} \quad \text{and} \quad B = -6.16 \times 10^{-7}\ K^{-2}. \tag{5}$$

Owing to inevitable small differences in the mechanical, chemical and annealing treatments given to the wires, each of which can influence its temperature coefficient of resistance, it is unrealistic to expect this surrogate calibration to apply exactly to the measurements. For this reason the accuracy of our present measurements is more limited than we would wish or than will be possible in the future. It should be noted that these observations in no way affect the precision of our experimental data.

For similar reasons it has been impractical to measure the resistance of the measuring wires at the triple point temperature of water, so that eq. (4) cannot be immediately employed to reduce the resistance changes of the wires in our experiments to their temperature rises[5,8]). However, it is possible to measure the resistance of each wire at the equilibrium temperature of the bath, T_0, by operating the automatic Wheatstone bridge in its manual mode[5,14]). Using these conditions as the reference state for the resistance of the wires we may

define a linear temperature coefficient of resistance for the wires over the small temperature changes involved in our measurements ($\Delta R \leqslant 5°$ C) by the equation

$$R(T) = R(T_0)\{1 + \alpha_0(T - T_0)\}. \tag{5}$$

The factor $\alpha_0(T)$ may be easily related to the coefficients A and B as

$$\alpha_0(T_0) = \frac{A + B[2(T_0 - 273.15) + \Delta T]}{1 + A(T_0 - 273.15) + B(T_0 - 273.15)^2}. \tag{6}$$

Owing to the smallness of ΔT and B, α_0 may safely be regarded as a constant for a particular equilibrium temperature T_0. The value of α_0 at 23°C is quoted in table I for the δ calibration of the dummy wire. It is this value which has been used for our absolute evaluation of the thermal conductivity.

The resistance of the wires under the equilibrium conditions has been measured with the Wheatstone bridge by means of a linear extrapolation to zero power of measurements made for a series of low powers. Our preliminary measurements[5]) have shown that the accuracy of the present bridge network for absolute resistance measurements is one of ±0.01%, which is entirely adequate for our purposes. As well as the resistance of the individual wires, the resistance difference between the two wires under the same conditions was measured. It is noteworthy that the difference of resistance resulting from the measurements on individual wires was entirely consistent with the directly measured difference.

The pressure measurements were made by means of four Bourdon-tube pressure gauges manufactured by the Heise Company. The four gauges covered the ranges 0–1.0 MPa, 0–6.0 MPa, 0–16.0 MPa and 0–50.0 MPa. The appropriate gauge was selected to provide optimum accuracy over the entire pressure range covered. The uncertainty in the pressure measurement does not exceed 0.1% of the maximum pressure for a particular gauge.

The temperature of the pressure vessel containing the hot-wire cells[5]) was controlled at 23°C to within ±0.1°C over a period of several hours by thermostating the entire room containing the experimental installation. The temperature of the sample gas was measured by means of chromel-alumel thermocouples with an uncertainty of ±0.1 K[5]).

The purity of the gases employed together with their suppliers and the

TABLE II
The gases employed for the measurements

Gas	Supplier	Purity	Pressure range (MPa)	Density range (kg/m³)
Helium	Matheson Co., Inc.	> 99.9999%	1–34	2–50
Neon	Matheson Co., Inc.	> 99.995%	1–34	9–240
Argon	Matheson Co., Inc.	> 99.9995%	0.5–32	9–520
Krypton	Matheson Co., Inc.	> 99.995%	0.9–13	38–600

ranges of pressure and density covered for each gas are listed in table II. Pressures in excess of those available in commercial cylinders were generated with the aid of an Aminco diaphragm compressor. Although the density of the gas enters the evaluation of its thermal conductivity from the raw data only in a small correction, the investigation of the density dependence of the thermal conductivity requires the best possible values. The densities have been calculated from the $P-V-T$ data obtained in the Van der Waals laboratory[15-18]), using the measured pressure and temperatures.

3. The working equations

All the necessary working equations for the analysis of our raw experimental data have already been given[4,5,8]). Consequently, we confine ourselves here to a statement of those needed to an understanding of the procedure.

The essential measurements of our apparatus are the times t_i at which the resistance difference between the two hot wire cells attain certain preset values as the temperature of the wire and gas adjacent to it rises[5,8,14]). Each resistance difference may be translated into a temperature rise of the long wire acting as a finite segment of an infinitely long wire by means of the equation

$$\Delta T_w = \Delta T'/(1+\epsilon_5), \tag{7}$$

where

$$\epsilon_5 = \frac{R_2(0)}{\Delta R(0)} \frac{[1+\ln(4\kappa_0 t/a^2 C)}{\ln[4\kappa_0 t/a^2 C]^{\epsilon}}, \tag{8}$$

with

$$\epsilon = 1-\sigma_2/\sigma_1,$$

and

$$\Delta T' = \frac{\Delta R(t)-\Delta R(0)}{\alpha_0 \Delta R(0)}. \tag{9}$$

Here, α_0 is defined by eqs. (6) and $R_2(0)$ is the resistance of the shorter wire under the equilibrium conditions and $\Delta R(T)$ is the resistance difference between the two wires at time t. In addition, σ_1 represents the resistance per unit length of the longer wire and σ_2 the corresponding quantity for the shorter wire, whereas κ_0 represents the thermal diffusivity of the fluid at the equilibrium conditions, a the wire radius, and $C = 1.781\ldots$ is the exponential of Euler's constant. It should be noted that the quantity ϵ has the value -0.006 for the present cells so that the first order the analysis of ref. 8 is adequate for the interpretation of our experimental data.

The theory of the transient hot-wire technique given by Healy et al.[4]) shows that the thermal conductivity of the fluid in the hot-wire cells, λ, at a

temperature T_r may be obtained from the set of experimental data $\{\Delta T_w(t_\delta), t_\delta\}$ with the aid of the equations

$$\Delta T = \frac{q_1}{4\pi\lambda(T_r, \rho_r)} \ln\left\{\frac{4\kappa_0 t}{a^2 C}\right\}, \tag{10}$$

$$\Delta T = \Delta T_w + \sum_i \delta T_i \tag{11}$$

and

$$T_r = T_0 + \sum_i \delta T_i^*. \tag{12}$$

Here q_1 represents the heat flux per unit length in the longer wire and ρ_r represents the density of the fluid at the temperature T_r and the pressure of the measurement. The quantity q_1 is evaluated from the parameters of the automatic Wheatstone bridge[8]).

The correction terms δT_i and δT_i^* have been detailed in ref. 4. The present experimental arrangement has been designed so that only three such corrections are significant (>0.01%). These are given below.

(1) The finite heat capacity of the wire:

$$\delta T_1 = \frac{q_1}{4\pi\lambda}\left[\frac{(\rho c_p)_w - (\rho c_p)}{2\lambda t}\right] a^2 \ln\left(\frac{4\kappa_0 t}{a^2 C}\right). \tag{13}$$

Here, $(\rho c_p)_w$ represents the heat capacity of the wire per unit volume and ρc_p the same quantity for the gas.

(2) The finite dimensions of the hot-wire cell:

$$\delta T_2 = \frac{q}{4\pi\lambda}\left[\ln\left(\frac{4\kappa t}{b^2 C}\right) + \sum_{\nu=1}^{\infty} \exp(-g_\nu \kappa t/b^2)[\pi Y_0(g_\nu)]^2\right]. \tag{14}$$

Here, g_ν are the consecutive roots of $J_0(g_\nu) = 0$, and J_0 and Y_0 represent zero-order Bessel functions of the first and second kind, respectively.

(3) The temperature dependence of the fluid properties:

$$\delta T_2^* = \tfrac{1}{2}[\Delta T(t_1) + \delta T(t_2)]. \tag{15}$$

Here t_1 and t_2 are the initial and final instants of a measurement.

The two corrections δT_1 and δT_2 were not allowed to exceed 0.5% of the wire temperature rise. The former is significant only at short times whereas the latter is significant at long times[4]). Consequently a first-iterate value for the thermal conductivity, which is necessary to evaluate the corrections δT_1 and δT_2, may be obtained from eqs. (10) and (11) in the intermediate time range with $\delta T_1 = \delta T_2 = 0$. In practice, this value is obtained from the slope of the ΔT_w vs $\ln t$ line in this region and the known heat generation in the long wire. The first iterate value for λ together with density and heat capacity data is then used to evaluate ΔT at each experimental point from eqs. (11), (13) and (14). For this purpose we have evaluated the densities and heat capacities from the empirical equations of state given in refs. 15 to 18.

The set of data points $\{\Delta T(t_\delta), \ln t_\delta\}$ is then subjected to a further linear regression analysis to yield a better estimate of the thermal conductivity from the slope of the line as before. In this analysis, any point for which δT_1 or δT_2 exceeded 0.5% of the temperature rise of the wire is excluded before the fitting. If this second iterate value of the thermal conductivity differed by more than a few tenths of a percent from the first-iterate then the procedure was repeated. In general further iteration was unnecessary. The details of the deviations from the final linear regression line were always examined carefully to ensure that there was no evidence of systematic curvature in the corrected experimental line of ΔT vs $\ln t$, which would indicate the probable onset of natural convection during the run.

As a final step in the analysis, the temperature T_r was evaluated from eqs. (12) and (14), and the density ρ_r at the temperature calculated from the empirical equations of state[15–18]).

Eqs. (10) and (12) show that even if the equilibrium temperature remained constant throughout a series of measurements as a function of pressure, the reference temperature, T_r, would change owing to the change in the thermal diffusivity. Consequently, small temperature corrections were necessary to refer all the thermal conductivities to a single, nominal temperature T_{nom}. These corrections have been applied by means of the linear relation

$$\lambda(T_{nom}, \rho_r) = \lambda(T_r, \rho_r) + (\partial\lambda/\partial T)_{\rho,T_{nom}}(T_{nom} - T_r). \tag{16}$$

The derivative $(\partial\lambda/\partial T)_{\rho,T_{nom}}$ has been evaluated from the extended law of corresponding states[2]) together with the assumption that the excess thermal conductivity, $[\lambda(\rho) - \lambda_0]$ is a function of temperature only so that $(\partial\lambda/\partial T)_{\rho,T_{nom}} = (\partial\lambda_0/\partial T)_{T_{nom}}$. In no case did this correction amount to more than $\pm 0.6\%$ so that the error introduced is negligible.

4. Precision, reproducibility and accuracy

The working equations (10) to (12) provide a stringent test for the correct operation of our instrument since if, and only if, the instrument conforms to the mathematical description of it will the final ΔT vs. $\ln t$ line be linear. Fig. 1 contains a representative plot of the deviations of the corrected temperature rises, ΔT, from the least-squares linear regression line that best fits the data; it refers to argon at 22.88°C and 20.6 MPa. It is evident that the deviations do not exceed 0.1%, which represents the precision of our measurement of the temperature rise.

The final thermal conductivity for a gas under particular experimental conditions is obtained from a least-squares analysis of a set of 42 individual points. Thus, the repeatability of independent measurements of the thermal conductivity of a particular gas sample, under nominally identical conditions, is not necessarily identical with that of the individual temperature rise measurements. In the particular case of argon we have examined the repea-

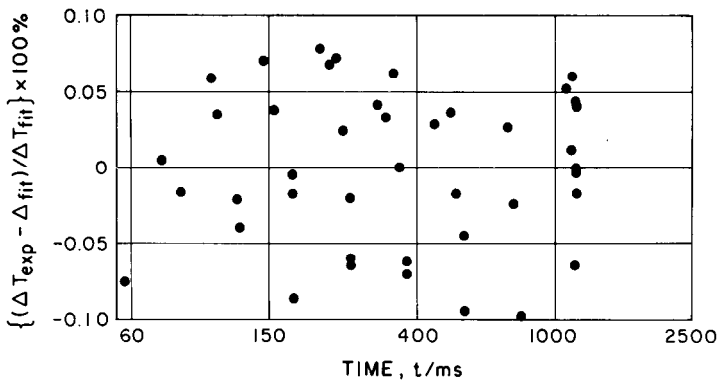

Fig. 1. The deviations of the experimentally measured temperature rises from the optimum straight line.

tability of the final thermal conductivity values by carrying out a series of tests on the same gas sample. The values obtained differed from each other by less than $\pm 0.05\%$.

Measurements have also been carried out to determine the long-term reproducibility of the apparatus. Thus over a period of a year we have remeasured the thermal conductivity of helium, argon and krypton. Fig. 2 contains a plot of the deviations of the repeated measurements from the correlation of our original results. The reproducibility is seen to be of the order of $\pm 0.2\%$. The foregoing observations serve to confirm our earlier claim[5]) that the precision of our measurements is one of $\pm 0.2\%$.

Unlike the precision of our experimental data, their accuracy is determined by both the accuracy of our absolute resistance measurements to determine $\Delta R(0)$ and the accuracy of the resistance temperature calibration to determine α_0. It has been mentioned already that the accuracy of our absolute resistance

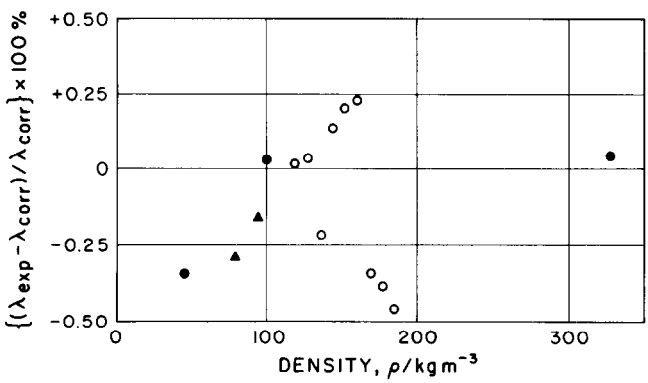

Fig. 2. The deviations of repeated thermal conductivity measurements from the correlation of the original results. ▲ Neon; ● Argon; ○ Krypton.

measurements is of the order of $\pm 0.01\%$. On the other hand, although the accuracy of the resistance-temperature calibration carried out on a dummy wire was of a similar order, there is no guarantee that the calibration is identical for the samples of wire used in the measurements. Thus, in order to establish the accuracy of our experimental data, we prefer to utilize the result of eq. (1) together with viscosity data at zero density[1]) and our present thermal conductivity data. It will be shown in the next section the accuracy of our absolute thermal conductivity data is $\pm 1.5\%$.

5. Experimental results

Because the precision of our measurements of the thermal conductivity is superior to their accuracy, the data have been evaluated on both the absolute basis discussed earlier and a relative basis. We first present the data evaluated on the absolute basis, then use them to construct the relative method of evaluation and finally present the data obtained in this way.

5.1. *The absolute evaluation*

Tables III to VI list the entire body of our experimental data for He, Ne, Ar and Kr evaluated on an absolute basis. Each table includes the pressure of the measurement, the reference temperature, T_r, the density of this temperature, the thermal conductivity at this temperature and the thermal conductivity at the nominal temperature. In addition, the value of the temperature derivative $(\partial\lambda_0/\partial T)_{T_{nom}}$ employed to carry out the correction to the nominal temperature is also given.

For the purpose of establishing the accuracy of our experimental data, the absolute results for each gas have been subjected to a polynomial regression analysis. Since this analysis will be described in detail in section 7, it is sufficient at this stage to state that the analysis yields a reliable value for the thermal conductivity at zero density, λ_0. These values have been combined with our own viscosity data at zero density for the four monatomic gases[1]) and the correlated function $\mathcal{F}^2$ to yield Eucken factors. The results are contained in table VII. It is evident that the Eucken factors of all four gases are systematically lower than the theoretical value of 2.500 by about 1.5%. On this basis we may conclude that the accuracy of the data contained in tables III to VI have an associated uncertainty of $\pm 1.5\%$. We attribute the inaccuracies in the data to the calibration of the temperature coefficient of resistance for the platinum wires.

TABLE III
The thermal conductivity of helium evaluated on the absolute basis at $T_{nom} = 25.00°C$

Pressure P(MPa)	Reference temperature T_r(°C)	Thermal conductivity $\lambda(T_r)$(mWm^{-1}K^{-1})	Density $\rho(T_r, P)$(kgm^{-3})	Thermal conductivity $\lambda(T_{nom})$(mWm^{-1}K^{-1})
1.04	25.13	153.2	1.713	153.2
1.99	25.14	153.8	3.270	153.7
2.79	25.10	154.2	4.571	154.1
3.79	25.05	154.7	6.175	154.7
4.81	25.01	155.3	7.790	155.3
5.83	24.98	155.5	9.410	155.6
6.76	24.95	155.8	10.86	155.8
7.84	24.89	156.3	12.54	156.4
9.02	24.87	156.9	14.35	156.9
10.02	24.84	157.3	15.86	157.4
11.03	24.83	157.4	17.38	157.4
12.09	24.83	157.6	18.96	157.7
13.06	24.83	157.9	20.40	157.9
14.09	24.84	158.2	21.92	158.2
15.07	24.85	158.7	23.34	158.8
16.06	24.83	159.0	24.77	159.1
17.56	24.83	159.4	26.90	159.5
18.84	24.77	159.6	28.71	159.7
20.25	24.76	160.3	30.68	160.4
21.59	24.75	161.1	32.53	161.2
22.93	24.81	161.5	34.35	161.5
24.27	24.76	162.1	36.17	162.2
25.58	2 .74	162.5	37.91	162.6
26.96	24.67	163.0	39.75	163.1
28.30	24.70	163.3	41.50	163.4
29.65	24.75	163.8	43.22	163.9
31.00	24.67	164.6	44.97	164.8
32.37	24.64	164.8	46.70	164.9
33.96	24.64	165.6	48.69	165.7

$(\partial\lambda_0/\partial T)_{25°C} = 0.35$ mW · m^{-1}K^{-2}.

TABLE IV
The thermal conductivity of neon evaluated on the absolute basis at $T_{nom} = 26.83°C$

Pressure P(MPa)	Relative temperature T_r(°C)	Thermal conductivity $\lambda(T_r)$(mWm^{-1}K^{-1})	Density $\rho(T_r, P)$(kgm^{-3})	Thermal conductivity $\lambda(T_{nom})$(mWm^{-1}K^{-1})
0.57	28.01	48.96	4.707	48.83
1.07	27.87	49.19	8.829	49.08
1.62	27.70	49.38	13.35	49.28
2.15	27.58	49.51	17.67	49.43
2.66	27.50	49.65	21.75	49.58
3.16	27.42	49.75	25.82	49.68
3.66	27.34	49.87	29.87	49.82
4.17	27.36	49.94	33.89	49.88
4.67	27.30	50.06	37.85	50.01
5.14	27.20	50.18	41.59	50.13
5.68	27.14	50.30	45.88	50.26
6.16	27.15	50.39	49.62	50.35
6.64	27.05	50.52	53.41	50.50
7.16	27.06	50.64	57.43	50.62
7.66	27.01	50.86	61.34	50.84
8.17	27.04	50.93	65.21	50.91
8.66	27.02	51.04	69.02	51.02
9.18	26.97	51.18	72.97	51.17
9.67	26.92	51.33	76.70	51.32
10.20	26.91	51.32	80.71	51.31
10.88	26.85	51.50	85.82	51.50
11.55	26.79	51.75	90.84	51.76
12.24	26.77	51.85	95.96	51.86
12.91	26.69	52.05	100.9	52.07
13.56	26.68	52.24	105.7	52.26
14.56	26.66	52.47	113.0	52.49
15.81	26.58	52.76	122.0	52.79
16.95	26.56	53.01	130.1	53.04
18.10	26.53	53.30	138.1	53.34
19.24	26.51	53.56	146.0	53.60
20.38	26.50	53.94	153.9	53.98
21.45	26.46	54.17	161.2	54.21
22.73	26.48	54.61	169.8	54.65
23.84	26.34	54.88	177.2	54.93
24.88	26.31	55.16	184.0	55.22
25.99	26.29	55.47	191.3	55.53
27.14	26.28	55.77	198.7	55.84
28.24	26.26	56.06	205.7	56.12
29.31	26.28	56.35	212.4	56.42
30.25	26.27	56.62	218.3	56.68
31.33	26.21	56.95	225.0	57.02
32.33	26.19	57.19	231.2	57.27
33.28	26.17	57.50	236.9	57.57
34.28	26.18	57.79	242.9	57.87

$(\partial\lambda_0/\partial T)_{26.83°C} = 0.111$ mWm^{-1}K^{-2}.

TABLE V
The thermal conductivity of argon evaluated on the absolute basis at 27.5°C

Pressure P(MPa)	Reference temperature T_r(°C)	Thermal conductivity $\lambda(T_r)$(mWm^{-1}K^{-1})	Density $\rho(T_r, P)$(kgm^{-3})	Thermal conductivity $\lambda(T_{nom})$(mWm^{-1}K^{-1})
0.59	28.80	17.81	9.608	17.74
0.73	28.59	17.86	12.06	17.81
0.88	28.50	17.89	14.44	17.84
1.02	28.43	17.94	16.81	17.89
1.15	28.36	17.98	18.95	17.93
1.30	28.33	18.04	21.40	18.00
1.44	28.39	18.09	23.78	18.05
1.57	28.29	18.12	25.85	18.08
1.71	28.20	18.19	28.27	18.15
1.84	28.13	18.24	30.52	18.20
1.98	28.10	18.27	32.77	18.24
2.11	28.02	18.32	34.92	18.30
2.24	27.99	18.36	37.18	18.34
2.38	27.87	18.42	39.58	18.40
2.52	27.77	18.47	41.86	18.45
2.65	27.77	18.52	44.12	18.51
2.80	27.70	18.57	46.63	18.56
3.05	27.67	18.65	50.96	18.64
3.26	27.89	18.66	54.54	18.64
3.46	28.31	18.76	57.66	18.72
3.66	28.28	18.86	61.10	18.82
3.86	28.24	18.93	64.54	18.89
4.06	28.19	19.01	67.99	18.97
4.26	28.23	19.08	71.42	19.04
4.46	28.17	19.14	74.88	19.11
4.67	28.15	19.22	78.37	19.18
4.87	28.10	19.32	81.94	19.29
5.07	28.02	19.40	85.34	19.38
5.28	28.01	19.47	89.04	19.45
5.48	27.95	19.56	92.41	19.53
5.69	27.90	19.63	96.02	19.61
5.89	27.76	19.73	99.56	19.72
6.10	27.64	19.80	103.1	19.80
6.28	27.59	19.87	106.4	19.87
6.48	27.54	19.97	109.9	19.97
7.00	27.44	20.20	119.1	20.20
7.86	27.31	20.57	134.0	20.58
8.73	27.17	20.96	149.6	20.97
9.59	27.03	21.40	164.8	21.42
10.47	26.87	21.84	180.4	21.87
11.34	26.71	22.32	196.2	22.35
12.21	26.50	22.75	211.5	22.80
13.06	26.36	23.22	226.3	23.38
13.92	26.14	23.81	242.1	23.88
14.75	26.03	24.29	256.7	24.36
15.58	25.89	24.85	271.4	24.93

TABLE V (cont.)

Pressure P(MPa)	Reference temperature T_r(°C)	Thermal conductivity $\lambda(T_r)$(mWm^{-1}K^{-1})	Density $\rho(T_r, P)$(kgm^{-3})	Thermal conductivity $\lambda(T_{nom})$(mWm^{-1}K^{-1})
16.43	25.83	25.32	286.1	25.40
17.37	25.70	25.84	302.5	25.93
18.20	25.67	26.33	316.5	26.42
18.94	25.63	26.83	328.9	26.92
20.24	25.69	27.65	350.4	27.74
21.64	25.63	28.51	373.1	28.61
22.93	25.58	29.29	393.4	29.39
24.28	25.53	30.14	414.2	30.24
25.53	25.43	30.99	433.3	31.09
26.83	25.43	31.80	452.3	31.91
28.17	25.38	32.68	471.4	32.79
29.41	25.36	33.50	488.5	33.61
30.71	25.33	34.32	505.9	34.43
32.10	25.30	35.21	523.9	35.32

$(\partial\lambda_0/\partial T)_{27.5} = 0.0501$ mWm^{-1}K^{-2}.

TABLE VI

The thermal conductivity of krypton evaluated on the absolute basis at 27.5°C

Pressure P(MPa)	Reference temperature T_r(°C)	Thermal conductivity $\lambda(T_r)$(mWm^{-1}K^{-1})	Density $\rho(T_r, P)$(kgm^{-3})	Thermal conductivity $\lambda(T_{nom})$(mWm^{-1}K^{-1})
1.11	29.64	9.756	38.72	9.694
1.38	29.47	9.816	49.69	9.759
1.65	29.31	9.896	58.32	9.843
1.98	29.18	10.01	70.52	9.959
2.32	28.97	10.12	83.47	10.08
2.66	29.01	10.22	96.09	10.18
2.99	28.73	10.34	109.1	10.31
3.19	28.69	10.41	116.8	10.38
3.46	28.58	10.52	127.7	10.49
3.81	28.46	10.65	141.4	10.62
4.14	28.35	10.78	155.1	10.76
4.50	28.25	10.94	170.1	10.92
4.94	28.10	11.13	188.7	11.11
5.35	28.98	11.32	206.2	11.31
5.81	28.00	11.38	226.3	11.37
6.17	27.77	11.73	242.3	11.72
6.65	2.67	11.95	264.3	11.95
7.08	26.98	12.16	285.2	12.17
7.56	26.84	12.43	307.8	12.45
8.00	26.75	12.69	328.9	12.71
8.49	26.63	13.01	353.4	13.04

TABLE VI (cont.)

Pressure P(MPa)	Reference temperature T_r(°C)	Thermal conductivity $\lambda(T_r)$(mWm^{-1}K^{-1})	Density $\rho(T_r P)$(kgm^{-3})	Thermal conductivity $\lambda(T_{nom})$(mWm^{-1}K^{-1})
9.06	26.49	13.38	381.7	13.41
9.61	26.05	13.79	410.7	13.84
10.11	25.96	14.16	436.5	14.21
10.58	25.83	14.55	461.4	14.60
10.88	25.75	14.79	477.8	14.85
11.17	25.61	15.01	493.6	15.06
11.17	25.61	14.99	493.6	15.05
11.48	25.54	15.26	510.2	15.32
11.82	25.56	15.60	528.4	15.66
12.20	25.39	15.95	549.3	16.01
12.58	25.29	16.30	570.0	16.37
12.91	25.21	16.59	588.1	16.65
13.27	25.91	16.91	604.2	16.95

$(\partial\lambda_0/\partial T)_{27.5°C} = 0.029\ \mathrm{mWm^{-1}K^{-2}}$.

TABLE VII
Eucken factors evaluated on the absolute basis

Gas	Temperature T(K)	Zero density viscosity $\mu_0(\mu\mathrm{Pas})$ [1]	Zero density thermal conductivity λ_0(mWm^{-1}K^{-1})	$\mathcal{F}(T)$ [2]	Eucken factor (Eu)	Dev. from eq. (1) (%)
He	298.15	19.86_1	153.0	1.0042	2.462	−1.52
Ne	299.98	31.88_4	48.63	1.0035	2.459	−1.64
Ar	300.65	22.76_1	17.56	1.0011	2.469	−1.25
Kr	300.65	25.55_7	9.339	1.0006	2.454	−1.84

5.2. *The relative evaluation*

The relative method is based upon the exactness of eq. (1) and the availability of accurate data for the viscosity of the monatomic gases[1]). Since the inability of our absolute evaluation to yield the correct values of λ_0 is attributed mostly to the uncertainty in temperature coefficient α_0 employed, we may use the zero-density viscosity to generate λ_0 from eq. (1) and employ these to correct the temperature coefficient resistance, α_0, by means of eqs. (7) and (10).

Evidently this program could be carried out for each monatomic gas and an average taken. Alternatively, the corrected value of α_0 could be deduced for one gas and used to re-evaluate the thermal conductivity data for the other gases. We have chosen to adopt the latter course and have employed our data

for argon for this purpose. In this way we have obtained

$$\alpha_0 = 0.00357_5 \pm 0.00001.$$

The uncertainty in this value arises from the uncertainty in the zero density viscosity of argon (±0.1%) and from the precision of our thermal conductivity data.

We have recalculated all of our experimental data employing this new value of the temperature coefficient of resistance. The results are listed in tables VIII to XI. We have used a statistical regression analysis to determine the zero-density thermal conductivity of each gas and constructed the new Eucken factors; they are listed in table XII. The present departure from the theoretical value of 2.500 does not exceed ±0.6% for any gas. This result demonstrates the internal consistency of our experimental measurements and supports the contention that the inaccuracies in our absolute evaluation are attributable to an error in α_0.

TABLE VIII

The thermal conductivity of helium evaluated on the relative basis at $T_{nom} = 25.00°C$

Pressure P(MPa)	Reference temperature T_r(°C)	Thermal conductivity $\lambda(T_r)$(mWm^{-1}K^{-1})	Density $\rho(T_r, P)$(kgm^{-3})	Thermal conductivity $\lambda(T_{nom})$(mWm^{-1}K^{-1})
1.04	25.10	155.3	1.713	155.3
1.99	25.11	155.6	3.270	155.6
2.79	25.08	156.0	4.572	156.0
3.79	25.03	156.7	6.175	156.6
4.81	24.99	157.2	7.790	157.2
5.83	24.95	157.5	9.411	157.6
6.76	24.93	157.9	10.86	157.9
7.84	24.87	158.3	12.54	158.3
9.02	24.85	158.9	14.35	158.9
10.02	24.82	159.3	15.86	159.4
11.03	24.81	159.4	17.38	159.4
12.09	24.81	159.7	18.96	159.7
13.06	24.81	159.9	20.41	159.9
14.09	24.82	160.2	21.92	160.3
15.07	24.83	160.8	23.34	160.8
16.06	24.81	161.1	24.77	161.1
17.56	24.81	161.5	26.91	161.5
18.84	24.75	161.6	28.71	161.7
20.25	24.74	162.4	30.68	162.5
21.59	24.73	163.2	32.53	163.3
22.93	24.80	163.5	34.35	163.6
24.27	24.74	164.1	36.17	164.2
25.58	24.72	164.6	37.91	164.7
26.96	24.65	165.1	39.75	165.2
28.30	24.68	165.4	41.50	165.5
29.65	24.73	165.9	43.23	166.0
31.00	24.65	166.7	44.97	166.8
32.37	24.62	166.9	46.70	167.0
33.96	24.62	167.7	48.69	167.8

TABLE IX
Thermal conductivity of neon evaluated on the relative basis at $T_{nom} = 26.83°C$

Pressure P(MPa)	Reference temperature T_r(°C)	Thermal conductivity $\lambda(T_r)$(mWm^{-1}K^{-1})	Density $\rho(T_r, P)$(kgm^{-3})	Thermal conductivity $\lambda(T_{nom})$(mWm^{-1}K^{-1})
0.57	27.95	49.52	4.708	49.39
1.07	27.81	49.78	8.831	49.67
1.62	27.64	50.00	13.35	49.91
2.15	27.52	50.14	17.67	50.07
2.66	27.44	50.28	21.75	50.22
3.16	27.36	50.38	25.83	50.32
3.66	27.28	50.50	29.87	50.45
4.17	27.30	50.57	33.90	50.52
4.67	27.25	50.70	37.86	50.65
5.14	27.15	50.81	41.59	50.78
5.68	27.09	50.94	45.89	50.91
6.16	27.10	51.03	49.63	51.00
6.64	27.00	51.16	53.42	51.14
7.16	27.01	51.28	57.44	51.26
7.66	26.96	51.50	61.35	51.49
8.17	26.99	51.58	65.22	51.56
8.66	26.97	51.69	69.03	51.67
9.18	26.92	51.83	72.98	51.82
9.67	26.87	51.90	76.71	51.98
10.20	26.87	51.97	80.72	51.97
10.88	26.80	52.16	85.83	52.16
11.55	26.74	52.41	90.85	52.42
12.24	26.72	52.51	95.98	52.53
12.91	26.64	52.72	100.9	52.74
13.56	26.64	52.90	105.7	52.92
14.56	26.61	53.14	113.0	53.16
15.81	26.54	53.43	122.0	53.46
16.95	26.52	53.69	130.1	53.72
18.10	26.49	53.98	138.1	54.02
19.24	26.47	54.24	146.1	54.28
20.38	26.46	54.63	153.9	54.67
21.45	26.42	54.86	161.2	54.91
22.73	26.44	55.30	169.8	55.35
23.84	26.30	55.57	177.2	55.63
24.88	26.27	55.85	184.1	55.92
25.99	26.25	56.17	191.3	56.24
27.14	26.24	56.48	198.7	56.55
28.24	26.22	56.77	205.7	56.84
29.31	26.24	57.07	212.5	57.14
30.25	26.23	57.34	218.3	57.41
31.33	26.18	57.68	225.1	57.75
32.33	26.15	57.92	231.2	58.00
33.28	26.13	58.23	237.0	58.31
34.28	26.14	58.53	243.0	58.61

TABLE X
Thermal conductivity of argon evaluated on the relative basis at $T_{nom} = 27.5°C$

Pressure P(MPa)	Reference temperature T_r(°C)	Thermal conductivity $\lambda(T_r)$(mWm^{-1}K^{-1})	Density $\rho(T_r, P)$(kgm^{-3})	Thermal conductivity $\lambda(T_{nom})$(mWm^{-1}K^{-1})
0.59	28.73	18.03	9.610	17.97
0.73	28.51	18.08	12.06	18.03
0.88	28.42	18.11	14.44	18.06
1.02	28.36	18.16	16.82	18.12
1.15	28.29	18.20	18.95	18.16
1.30	28.27	18.26	21.41	18.23
1.44	28.32	18.32	23.78	18.28
1.57	28.22	18.35	25.86	18.32
1.71	28.13	18.41	28.28	18.38
1.84	28.06	18.46	30.53	18.44
1.98	28.03	18.50	32.78	18.47
2.11	27.96	18.55	34.93	18.53
2.24	27.93	18.59	37.19	18.57
2.38	27.75	18.65	39.60	18.64
2.52	27.71	18.70	41.86	18.69
2.65	27.71	18.76	44.13	18.75
2.80	27.64	18.80	46.64	18.80
3.05	27.62	18.88	50.97	18.88
3.26	27.82	18.90	54.44	18.88
3.46	28.24	19.00	57.68	18.96
3.66	28.21	19.10	61.11	19.07
3.86	28.18	19.17	64.55	19.13
4.06	28.12	19.25	68.00	19.22
4.26	28.17	19.31	71.43	19.28
4.46	28.11	19.39	74.90	19.36
4.67	28.08	19.46	78.38	19.43
4.87	28.04	19.56	81.96	19.53
5.07	27.96	19.65	85.36	19.63
5.28	27.95	19.70	89.06	19.70
5.48	27.89	19.80	92.43	19.79
5.69	27.85	19.88	96.05	19.86
5.89	27.70	19.97	99.58	19.97
6.10	27.58	20.05	103.1	20.05
6.28	27.53	20.13	106.4	20.12
6.48	27.48	20.23	110.0	20.23
7.00	27.38	20.46	119.2	20.46
7.86	27.25	20.83	134.0	20.85
8.73	27.11	21.22	149.6	21.24
9.59	26.98	21.67	164.8	21.70
10.47	26.82	22.11	180.4	22.14
11.34	26.67	22.60	196.2	22.64
12.21	26.45	23.04	211.6	23.09
13.06	26.32	23.52	226.4	23.58
13.92	26.10	24.12	242.2	24.19
14.75	25.99	24.60	256.8	24.67
15.58	25.86	25.17	271.5	25.25

TABLE X (cont.)

Pressure P(MPa)	Reference temperature T_r(°C)	Thermal conductivity $\lambda(T_r)$(mWm^{-1}K^{-1})	Density $\rho(T_r, P)$(kgm^{-3})	Thermal conductivity $\lambda(T_{nom})$(mWm^{-1}K^{-1})
16.43	25.79	25.64	286.2	25.72
17.37	25.67	26.16	302.6	26.26
18.20	25.63	26.66	316.5	26.76
18.94	25.59	27.17	328.9	27.26
20.24	25.66	28.00	350.4	28.09
21.64	25.60	28.88	373.2	28.97
22.93	25.55	29.67	393.5	29.76
24.28	25.50	30.53	414.3	30.63
25.53	25.40	31.38	433.4	31.49
26.83	25.40	32.21	452.3	32.31
28.17	25.36	33.10	471.4	33.20
29.41	25.33	33.93	488.6	34.03
30.71	25.31	34.76	505.9	34.87
32.10	25.28	35.66	524.0	35.77

TABLE XI

The thermal conductivity of krypton evaluated on the relative basis at 27.5°C

Pressure P(MPa)	Reference temperature T_r(°C)	Thermal conductivity $\lambda(T_r)$(mWm^{-1}K^{-1})	Density $\rho(T_r, P)$(kgm^{-3})	Thermal conductivity $\lambda(T_{nom})$(mWm^{-1}K^{-1})
1.11	29.56	9.878	38.73	9.819
1.38	29.39	9.940	49.71	9.885
1.65	29.23	10.02	58.34	9.970
1.98	29.11	10.13	70.54	10.09
2.32	28.90	10.25	83.49	10.21
2.66	28.94	10.35	96.11	10.31
2.99	28.66	10.47	109.1	10.44
3.19	28.62	10.54	116.8	10.51
3.46	28.44	10.65	127.7	10.63
3.81	28.40	10.79	141.4	10.76
4.14	28.29	10.92	155.1	10.90
4.50	28.19	11.08	170.2	11.06
4.94	28.04	11.27	188.7	11.26
5.35	27.92	11.47	206.2	11.45
5.81	27.94	11.53	226.4	11.51
6.17	27.71	11.87	242.4	11.87
6.65	27.61	12.10	264.4	12.10
7.08	26.92	12.31	285.2	12.33
7.56	26.79	12.59	307.9	12.61
8.00	26.71	12.85	329.0	12.87
8.49	26.58	13.18	353.5	13.20
9.06	26.45	13.55	381.8	13.58

TABLE XI (cont.)

Pressure P(MPa)	Relative temperature T_r(°C)	Thermal conductivity $\lambda(T_r)$(mWm^{-1}K^{-1})	Density $\rho(T_r, P)$(kgm^{-3})	Thermal conductivity $\lambda(T_{nom})$(mWm^{-1}K^{-1})
9.61	26.01	13.97	410.8	14.01
10.11	25.92	14.34	436.6	14.39
10.58	25.79	14.73	461.5	14.78
10.88	25.71	14.98	478.0	15.03
11.17	25.57	15.20	493.7	15.25
11.17	25.57	15.18	493.7	15.24
11.48	25.50	15.51	510.3	15.51
11.82	25.52	15.80	528.5	15.85
12.20	25.36	16.15	549.5	16.21
12.58	25.26	16.51	570.2	16.58
12.91	25.18	16.80	588.3	16.87
13.27	24.88	17.12	604.4	17.17

TABLE XII
Eucken factors evaluated on the relative basis

Gas	Temperature T(K)	Zero density viscosity $\mu_0(\mu$Pas)[1])	Zero density thermal conductivity λ_0(mWm^{-1}K^{-1})	$\mathcal{F}(T)$[2])	Eucken factor (Eu)	Dev. from eq. (1) (%)
He	298.15	19.86_1	154.9	1.0042	2.4926	−0.29
Ne	299.98	31.88_4	49.41	1.0035	2.4987	−0.05
Ar	300.65	22.76_1	17.78	1.0011	2.5000	0.0
Kr	300.65	25.55_7	9.461	1.0006	2.4859	−0.56

5.3. *Correlation*

In order to provide a convenient method of representing our experimental data, we have fitted the results for each gas, evaluated on the relative basis with a truncated polynomial expression of the form

$$\lambda(\rho) = b_0 + b_1\rho + b_2\rho^2 + b_3\rho^3 \tag{17}$$

with the aid of a least squares procedure. It has been found that a cubic expression is sufficient to represent the entire body of our experimental data with their uncertainty (±0.2%). The optimum values of the coefficients b_i are listed in table XIII. It should be emphasized that eq. (17) merely serves to correlate our data and to facilitate a comparison with earlier work. The coefficients themselves are to be distinguished from those obtained by the statistical procedure described in section 7, since the latter are deduced from

TABLE XIII
The coefficients of the correlating polynomial, eq. (17)

Gas	b_0 ($mWm^{-1}K^{-1}$)	b_1 ($\mu Wm^2K^{-1}kg^{-1}$)	b_2 ($nWm^5K^{-1}kg^{-2}$)	b_3 ($pWm^8K^{-1}kg^{-3}$)	Standard deviation (%)
He	154.93	256	0.0	0.0	±0.14
Ne	49.418	33.01	−16.3	150.3	±0.1
Ar	17.817	18.433	32.692	−5.162	±0.15
Kr	9.491	7.982	6.157	2.77	±0.25

a subset of the data up to some maximum density and are endowed with a physical significance.

6. Comparison with other work

Figs. 3 to 6 illustrate the density dependence of the thermal conductivity of the four gases graphically. The small scatter of the experimental data is immediately apparent. In addition, figs. 3, 4, and 6 contain the results of our earlier work for the gases helium, neon and krypton[19-23]). For the purposes of this comparison we have not attempted to include all previous measurements but only those judged to be of the greatest reliability. With the exception of helium, the results of earlier work are in reasonable agreement with the present data; in most cases the discrepancy is within the mutual uncertainty.

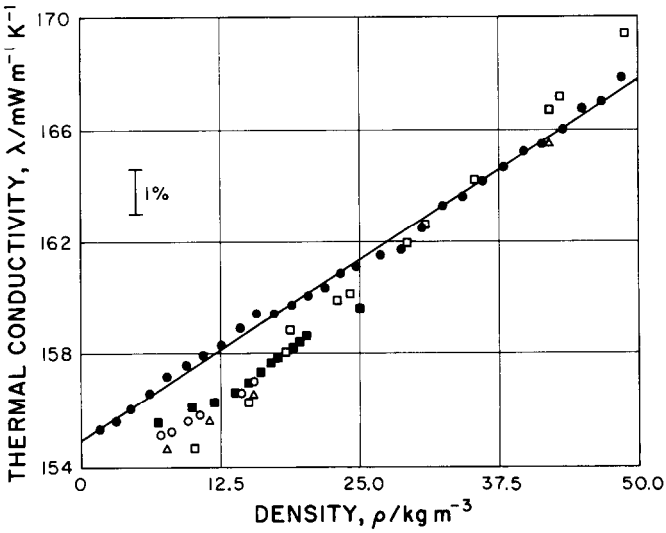

Fig. 3. The thermal conductivity of helium as a function of density at 25°C, evaluated on the relative basis. ● Present work; □ ref. 13; △ ref. 19; ○ ref. 20; ■ ref. 21.

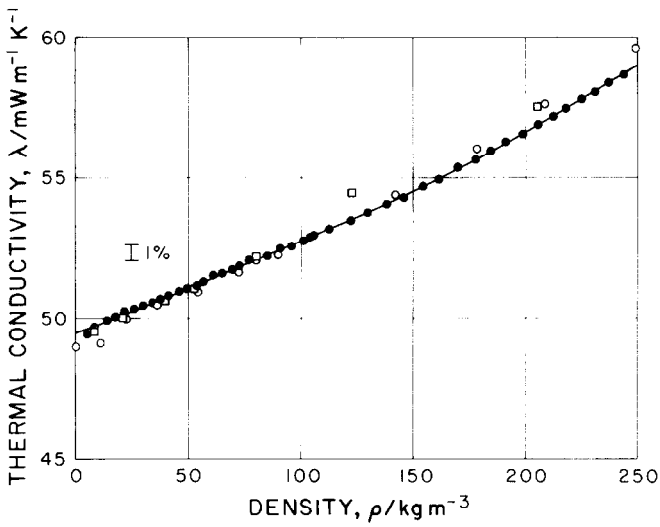

Fig. 4. The thermal conductivity of neon as function of density at 26.83°C evaluated on the relative basis. ● Present work; □ ref. 19; ○ ref. 21.

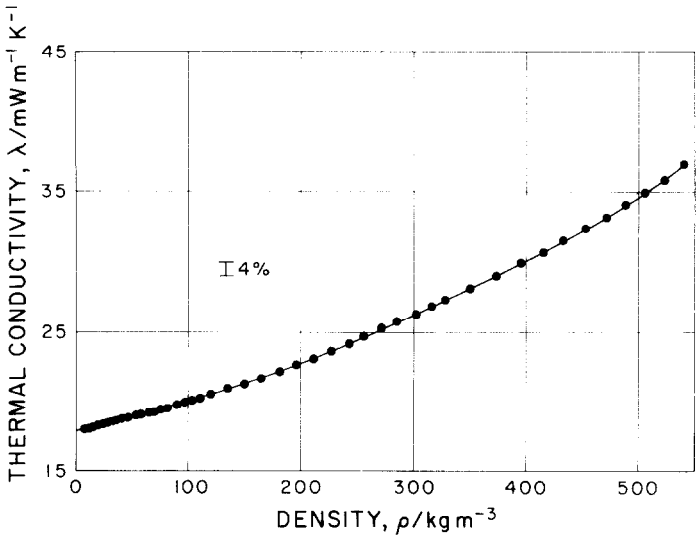

Fig. 5. The thermal conductivity of argon as a function of density at 27.5°C evaluated on the relative basis. ● Present work.

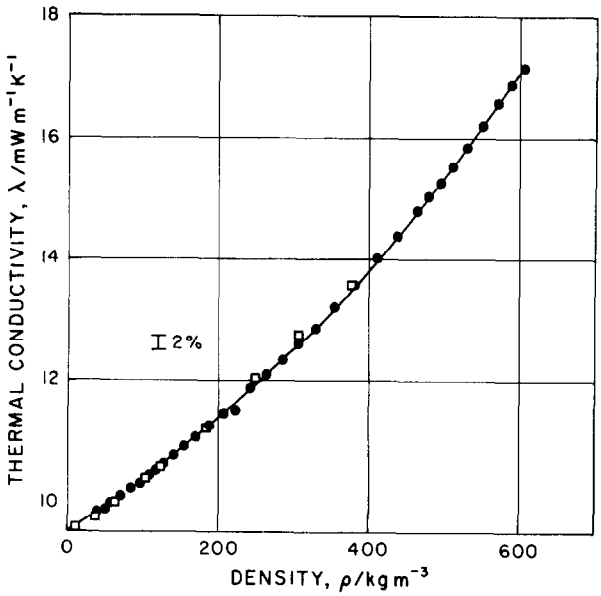

Fig. 6. The thermal conductivity of krypton as a function of density at 27.5°C evaluated on the relative basis. ● Present work; □ ref. 23.

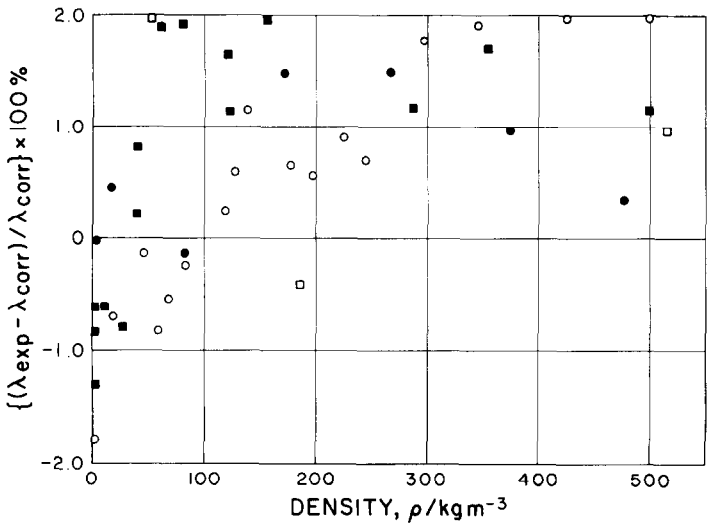

Fig. 7. A comparison between the present data for the thermal conductivity of argon at 27.5°C. ● ref. 19; ○ ref. 13; ■ ref. 24; □ ref. 25.

For helium the low-density results of all other workers are systematically lower than the present ones, although by not much more than the mutual uncertainty.

In order to preserve clarity, the differences between the correlation of the present data for argon and the results of earlier work[13,19,24,25]) are given as a deviation plot in fig. 7. There is general good agreement again although most of the earlier results are higher than the present data. The present data are characterized by a higher precision.

7. The density expansion for thermal conductivity

In this section we undertake a systematic study of the density dependence of the thermal conductivity with the aid of the present experimental data. The present investigation is analogous to that performed earlier for the viscosity[9]), so that we refer the reader to this earlier paper for a full description of the statistical procedure and confine ourselves here to a brief statement of the algorithm. For the sake of completeness we also include a recapitulation of the criteria used to discriminate between the two mathematical forms for the density dependence of the thermal conductivity.

7.1. *The algorithm*

The analytical procedure is commenced by obtaining a fit to the first five ($n = 5$) data points at the lowest densities in the table of results for a particular gas to the equation

$$\lambda = \lambda_0 + c_1\rho. \tag{18}$$

The values of λ_0, c_1, their standard deviations and the variance of the fit to the data set, σ_λ, are recorded. The procedure is repeated with n increased by unity until σ_λ passes through a stationary value ($n = n'$, or equivalently $\rho = \rho'$). From this point a similar analysis is performed for the equation

$$\lambda = \lambda_0 + c_1\rho + c_2\rho^2, \tag{19}$$

until σ_λ for this equation too passes through a stationary value, when the fitting procedure is continued for the equation

$$\lambda = \lambda_0 + c_1\rho + c_2\rho^2 + c_3\rho^3. \tag{20}$$

This procedure allows us to determine an interval $0 < \rho < \rho'$ within which a particular equation provides a best fit to the data. Exactly the same analysis is also performed with respect to the alternative form

$$\lambda = \lambda_0 + c_1\rho + c_2'\rho^2 \ln\rho + c_2\rho^2. \tag{21}$$

7.2. *The criteria for discrimination*

On the basis of the foregoing algorithm a particular equation is said to be consistent with the experimental data if the following conditions are satisfied:

(a) The deviations of the experimental data from these calculated with a fitted equation should be random, so that the standard deviation can be interpreted as a true measure of the experimental precision.

(b) When the values returned for the coefficients of the equation are studied as functions of n (or ρ), they should be independent of n within the limits prescribed by their standard deviations.

(c) Within their standard deviations the coefficients should not change when the next term is added to the equation and the density interval is increased correspondingly.

In practice, criterion (c) is the one ultimately used for the discrimination between the mathematical forms for the density expansion.

7.3. *Selection of the data*

In order to provide the optimum degree of self-consistency for the data used in the statistical analysis, we have used only those data acquired during a single experimental run. In this way any small, systematic differences between completely independent measurements are removed. In addition, we have consistently employed the data evaluated on the relative basis for the analysis although the functional form of the density dependence is essentially independent of this choice. This has been done in order to ensure that the values of the coefficients c_1, c_2, c_3 are not burdened with a systematic error arising from the use of the incorrect temperature coefficient of resistance. In the case of helium for which the density dependence is linear over the entire range of density, the analysis has been carried out solely to determine the zero density thermal conductivity and the first density coefficient.

7.4. *Results of the analysis*

The most probable values of the coefficients of eqs. (18)–(21) are listed in table XIV for each gas in addition to the standard deviation of the fit. As an example of the application of criterion (a), fig. 8 contains the deviations of the data for argon from the statistical fit to eq. (20) whereas fig. 9 contains a similar plot with respect to eq. (21). This figure illustrates that both equations satisfy criterion (a) equally well for argon in the range of their validity. A similar conclusion can be reached for the other gases examined.

If we now apply criterion (c) to the data contained in table XIV, we see that the power series, eq. (20), is consistent with the experimental data for all gases to a high degree. That is, the linear, quadratic and cubic equations all require the same values for the lower-order coefficients within their mutual uncertainty limits. On the other hand, the same table indicates that the degree

TABLE XIV
Statistical analysis of the thermal conductivity data

Gas	n'	ρ' (kgm^{-3})	$\lambda_0 \pm \sigma\lambda_0$ ($mWm^{-1}K^{-1}$)	$c_1 \pm \sigma_{c_1}$ ($\mu Wm^2K^{-1}kg^{-1}$)	$c_2 \pm \sigma_{c_2}$ ($nWm^5K^{-1}kg^{-2}$)	$c_3 \pm \sigma_{c_3}$ ($pWm^8K^{-1}kg^{-2}$)	$c_2' \pm \sigma_{c_2'}$ ($nWm^5K^{-1}kg^{-2}$)	σ_λ ($mWm^{-1}K^{-1}$)	σ_λ (%)
He	29	49	154.93 ± 0.08	256 ± 3	—	—	—	± 0.23	± 0.14
Ne	19	77	49.41 ± 0.02	33.2 ± 0.6	—	—	—	± 0.06	± 0.15
	27	122	49.41 ± 0.03	32.7 ± 1.3	2 ± 10	—	—	± 0.05	± 0.1
	42	218	49.41 ± 0.03	33.4 ± 1.2	-20 ± 11	166 ± 34	—	± 0.05	± 0.1
	37	199	49.33 ± 0.04	41.5 ± 2	-442 ± 82	—	79 ± 13	± 0.05	± 0.1
Ar	26	78	17.778 ± 0.008	21.2 ± 0.2	—	—	—	± 0.019	± 0.1
	34	106	17.794 ± 0.014	19.9 ± 0.6	18.0 ± 5.0	—	—	± 0.021	± 0.1
	43	196	17.803 ± 0.013	19.4 ± 0.5	19.3 ± 6.0	34 ± 18	—	± 0.020	± 0.1
	41	226	17.771 ± 0.017	22.1 ± 1.0	-108 ± 40	—	23 ± 7	± 0.019	± 0.1
	6		9.461 ± 0.013	8.8 ± 0.2	—	—	—	± 0.009	± 0.1
Kr	12		9.497 ± 0.013	7.6 ± 0.3	9 ± 1	—	—	± 0.006	± 0.07
	26		9.473 ± 0.03	8.4 ± 0.6	4 ± 3	5.8 ± 3	—	± 0.03	± 0.3
	28		9.474 ± 0.04	8.5 ± 0.9	-8 ± 14	—	2 ± 2	± 0.03	± 0.3

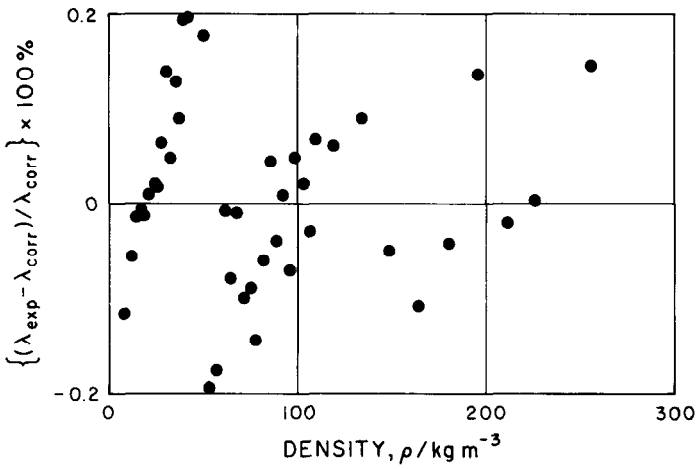

Fig. 8. Deviations of the experimental thermal conductivity data from eq. (20).

of consistency for the fit involving the logarithmic term is certainly no better, if as good. We are therefore forced to conclude that our data do not support the inclusion of a logarithmic term in the density expansion for the thermal conductivity. If such a term exists, it must be multiplied by a very small coefficient.

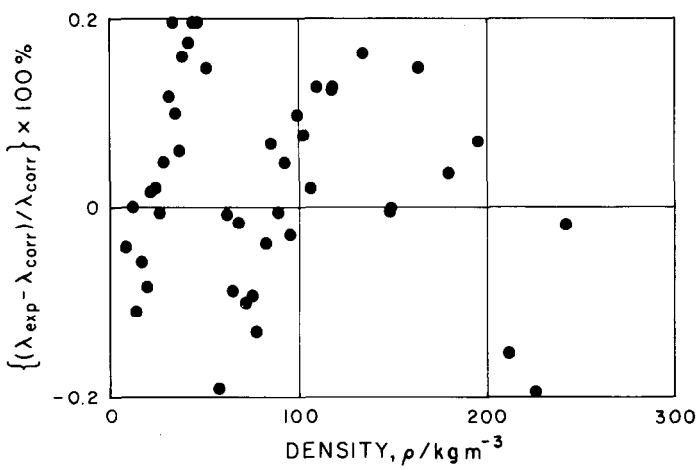

Fig. 9. Deviations of the experimental thermal conductivity data from eq. (21).

Acknowledments

The authors wish to express their gratitude to Mr. M.E. Schreiner for his assistance with the electron microscopy and to Mr. R. Paul for maintaining our experimental installation in good working order. Finally, we would like to thank Professor E.A. Mason for several stimulating discussions.

The work was performed under Grant ENG 73-08308 A02 awarded to Brown University by the National Science Foundation.

References

1) J. Kestin, S.T. Ro and W.A. Wakeham, J. Chem. Phys. **56** (1972) 4119.
2) J. Kestin, S.T. Ro and W.A. Wakeham, J. Chem. Phys. **56** (1972) 4036.
3) J. Kestin, Proceedings of the 14th International Thermal Conductivity Conference, P.G. Klemens and T.K. Chu, eds. (Plenum Press, New York, 1976), p. 315.
4) J.J. de Groot, J. Healy and J. Kestin, Physica **82C** (1976) 392.
5) J.J. de Groot, J. Kestin and H. Sookiazian, Physica **75** (1974) 454.
6) J.W. Haarman, Thesis, Technische Hogeschool, Delft, 1969.
7) J.W. Haarman, Physica **52** (1971) 605.
8) J. Kestin and W.A. Wakeham, Physica (in press).
9) J. Kestin, E. Paykoc and J.V. Sengers, Physica **54** (1971) 1.
10) S. Chapman and T.G. Cowling, The Mathematical Theory of Non-Uniform Gases (Cambridge Univ. Press, London, 3rd ed. 1970), Chap. 16.
11) J.R. Dorfman and E.G.D. Cohen, J. Math. Phys. **8** (1967) 282.
12) H.J.M. Hanley, R.D. McCarty and J.V. Sengers, J. Chem. Phys. **50** (1969) 857.
13) B. LeNeindre, R. Tufeu, P. Bury, P. Johannin and B. Vodar, Proceedings of the 8th International Thermal Conductivity Conference, C.Y. Ho and R.E. Taylor, eds. (Plenum Press, New York, 1968), p. 75.
14) G.P. Anderson, J.J. de Groot, J. Kestin and W.A. Wakeham, J. Phys. E: Sci. Instr. 7 (1974) 948.
15) A. Michels and H. Wouters, Physica **8** (1961) 923.
16) A. Michels, T. Wassenaar and P. Louwerse, Physica **26** (1960) 539.
17) A. Michels, Hub. Wijker and H.K. Wijker, Physica **15** (1949) 627.
18) N.J. Trappeniers, T. Wassenaar and G.J. Wolkers, Physica **32** (1966) 1503.
19) R. Tufeu, Ph.D. Thesis, University of Paris IV, 1971.
20) C.W. Ho and W. Leidenfrost, Progress in Heat and Mass Transfer, U. Grigull and E. Hahne, eds. (Pergamon Press, New York, 1969), vol. 1, p. 55.
21) P. Johannin, J.M. Wilson and B. Vodar, in International Research on Thermodynamic and Transport Properties, 2nd Symposium on Thermophysical Properties, J.F. Masi and D.H. Tsai, eds. (Academic Press, New York, 1962), pp. 418–433.
22) J.V. Sengers, W.T. Bolk and C.J. Stigter, Physica **30** (1964) 1018.
23) J.A.A. Snel, Ph.D. Thesis, Rotterdam, 1973.
24) A. Michels, J.V. Sengers and L.J.M. van de Klumdent, Physica **29** (1973) 149.
25) B.M. Rosenbaum, S. Oshen and G. Thodos, J. Chem. Phys. **44** (1966) 2831.