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Thermal Conductivity of Air in the Range 312 to 373 K and 0.1 to 24 MPa

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We have used the transient hot-wire technique to make absolute measurements of the thermal conductivity of dry, CO_2-free air in the temperature range from 312 to 373 K and at pressures of up to 24 MPa. The precision of the data is typically ±0.1%, and the overall absolute uncertainty is thought to be less than 0.5%. The data may be expressed, within their uncertainty, by polynomials of second degree in the density. The values at zero-density agree with other reported data to within their combined uncertainties. The excess thermal conductivity as a function of density is found to be independent of the temperature in the experimental range. The excess values at the higher densities are lower than those reported in earlier work.

KEY WORDS: Air; hot-wire technique; thermal conductivity; transient technique.

1. INTRODUCTION

Air is a commonly used fluid in many industrial processes, and accurate values of the thermodynamic and transport properties are required for design purposes. In particular the thermal conductivity coefficient of gaseous air is required over a wide range of temperatures and pressures for heat transfer design calculations. Many measurements of the thermal conductivity have been made at atmospheric pressure or below (nominally "zero density"), and most of these have been analyzed in a recent compilation [1], hereafter referred to as the TPRC report. Although the value at 0°C appears to be well established, the data show two distinct trends with increasing temperatures, the divergence reaching 5% at 100°C. The TPRC recommended values are

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intermediate between the two sets. Measurements reported since the TPRC report have failed to distinguish between the trends. Irving et al. [2] have obtained data which lie 1–2% below the TPRC values; Tsederberg and Ivanova [3] report results in good agreement in the range 0–100°C; and Tarzimanov and Sal'manov [19] obtained values 1–2% higher in this temperature range.

At higher pressures, where the thermal conductivity exhibits a density dependence, the data have been analyzed by Vargaftik et al. [5]. These authors show that the excess thermal conductivity[3]

$$\Delta\lambda = \lambda(\rho,T) - \lambda(0,T), \tag{1}$$

where $\lambda(\rho, T)$, the thermal conductivity at density ρ and temperature T, is a unique function of density independent of temperature within the quoted experimental error.

The transient hot-wire method has recently been reintroduced as an accurate means for measurement of the thermal conductivity of gases and liquids because of the recent advances in electronic techniques. In 1969 Haarman [6] developed an automatic Wheatstone bridge system with electronic timers, and this method was extended by Kestin and co-workers [7–9]. We have constructed an improved version of the apparatus, which is fully described elsewhere [10], and have measured the thermal conductivity of dry, CO_2-free air at temperatures of from 312 to 373 K and at pressures of up to 25 MPa.

2. THEORY OF THE METHOD

The theory of the transient hot-wire method has been fully described in previous publications [10–12], and only brief details are given below. When a step voltage is applied to a thin wire immersed in a test fluid, the temperature rise as a function of time is given by

$$\Delta T_{\text{id}} = \left(\frac{q}{4\pi\lambda_{\text{f}}}\right) \ln \left(\frac{4K_{\text{f}}t}{a^2C}\right) \tag{2}$$

where q is the heat input per unit length, λ_f and K_f are the thermal conductivity and thermal diffusivity of the fluid, a is the wire radius, and C is exp γ, where γ is Euler's constant. The thermal conductivity may thus in principle be derived from the slope of a (ΔT, ln$t$) plot. In practice measure-

[3]Definitions of symbols and associated units are given under Nomenclature at the end of the paper.

ments are made of the times taken to reach certain temperature rises ΔT which are fixed by inserting standard resistances sequentially into a Wheatstone bridge circuit. These are related to the ΔT values via the resistance–temperature characteristic of the platinum wire.

Several corrections need to be applied to the basic Eq. (2) [10–12], but the apparatus is designed such that only three are significant. First, as two wires of different lengths are used to eliminate major end effects, there is a need for a correction due to the possible nonuniformity of the two wires. This correction has been detailed by Kestin and Wakeham [12] and is given by

$$\Delta T' = \Delta T_W(1 + \epsilon), \tag{3}$$

where ϵ is a correction factor which is mainly determined by the resistance per unit length of each of the wires, and ΔT_W is the calculated temperature rise from the resistance network. Two further corrections are needed as the ideal situation considers a wire of zero heat capacity immersed in an infinite fluid medium. The temperature rises have thus to be corrected for the effects due to the finite heat capacity of the wire and the finite outer boundary of the hot-wire cell. These corrections are expressed as

$$\Delta T_{corr} = \Delta T' + \delta T_1 + \delta T_2, \tag{4}$$

where δT_1 and δT_2 are detailed elsewhere [11]. ΔT_{corr} now varies from ΔT_{id} only due to some minor corrections which are much less than 0.1% for the present apparatus.

3. EXPERIMENTAL

The characteristics of the two hot-wire cells, which are identical except in length, are given in Table I. The pure platinum wires were supplied by

Table I. Details of the Thermal Conductivity Cells

Long cell	
Overall length	0.20 m
Cell diameter	12.7 mm
Wire radius	3.705 ± 0.005 μm
Wire length (273.15 K)	162.75 ± 0.04 mm
Short cell	
Overall length	0.12 m
Cell diameter	12.7 mm
Wire diameter	3.705 ± 0.005 μm
Wire length (273.15 K)	86.68 ± 0.02 mm

Sigmund Cohn Ltd. and have a nominal diameter of 0.0003 in. The lengths were measured with a precision cathetometer and the average radius was determined from resistance measurements at known equilibrium temperatures, using the resistivity of pure platinum. The wires were held under tension at approximately 25% of their tensile strength using a gold spring system. In a series of earlier experiments the resistance–temperature characteristic of the wire had been determined and found to agree with the values quoted for pure platinum to within experimental error. These values were therefore used in the working equation, and this procedure appears to be justified by the results obtained with these cells for the thermal conductivity of helium and argon [10], which agree with values predicted by kinetic theory to within 0.2%.

The cells were placed in an air thermostat which gave a long-term temperature stability of ±0.01°C, although during a run the control was typically ±0.001°C. The temperature was measured with a platinum resistance element (Rosemount Engineering Type E712C), which was calibrated against a Tinsley primary transfer standard.

The pressure of the test gas was measured indirectly, using a gas–oil separator developed in this laboratory. The oil pressure was generated by the capstan of a deadweight tester and at balance the pressure was read on one of three 10-in. test gauges (Budenburg Type 215F) which covered the ranges 0–6, 0–16, and 0–40 MPa. The quoted accuracy of the gauges was 0.1% of full-scale reading. The maximum errors in this work were 2, 0.8, and 0.3%, respectively.

A set of 12 (ΔT_i, t_i) values is obtained in one experimental run, and usually four or five runs are carried out at one pressure, using different bridge configurations. Thus up to 60 points are obtained for the analysis. The basic set of points is used to obtain an estimate of the thermal conductivity, which is required for the calculation of the finite heat capacity and finite outer boundary corrections. The values δT_1 and δT_2 are determined and any points for which the corrections are greater than 0.5% of the total temperature rise are ignored in the subsequent analysis. In practice this limits the earliest usable times to $\geq$100 ms and also limits the minimum working pressure to ~0.5 MPa. Runs were carried out with the final time varying from 1 to 2 s to determine the experimental onset of convection, which is shown by curvature in the plot of ΔT versus $\ln t$. For this system convection was apparent above 1.5 s, and all runs were therefore carried out with a final time of about 1 s. As the wire temperature changes during the run, the thermal conductivity value obtained does not refer to the equilibrium temperature T_0 but to some reference temperature T_r. Analysis has shown that [11]

$$T_r = T_0 + \delta T_r \tag{5}$$

with

$$\delta T_r = [\Delta T(t_i) + \Delta T(t_f)/2, \tag{6}$$

where $\Delta T(t_i)$ and $\Delta T(t_f)$ are the initial and final temperature rises used in the final analysis after the raw data have been corrected.

The dry CO_2-free air was supplied by B.O.C. Ltd., with impurities CO_2 < 1 vpm and H_2O and hydrocarbons < 3 vpm. The density and constant pressure specific heat capacity values which are required in the analysis were taken from the recent PVT data of Vukalovich et al. [13], which are in substantial agreement with the earlier recommended values produced by Vasserman et al. [14].

4. RESULTS

Although the equilibrium temperature is essentially constant during the course of the measurements, the reference temperature varies because of the change in thermal diffusivity. Thus small corrections were required to convert all data to a single nominal temperature T_n,

$$\begin{aligned}\lambda(T_n, \rho_r) &= \lambda(T_r, \rho_r) + \left(\frac{\partial\lambda}{\partial T}\right)_{\rho, T_n}(T_n - T_r)\\ &\simeq \lambda(T_r, \rho_r) + \left(\frac{\partial\lambda}{\partial T}\right)_{\rho=0}(T_n - T_r).\end{aligned} \tag{7}$$

The derivative $(\partial\lambda/\partial T)_{\rho=0}$ has been taken from the thermal conductivity data presented in the TPRC report. The correction was never greater than $\pm 0.5\%$ and the error introduced from a slightly incorrect temperature dependence is negligible.

The experimental thermal conductivity values at 312 and 373 K are presented in Tables II and III and shown in Fig. 1. The data have been submitted to a polynomial regression analysis using the method of least squares and the data are well represented by an equation of the form

$$\lambda = a_0 + a_1\rho + a_2\rho^2. \tag{8}$$

Two points arise from the analysis. First, the range of densities is insufficiently high to warrant the inclusion of extra terms in the power series. Second, the data have been analyzed according to the method suggested by Hanley et al. [15] in which a fit at a particular degree of polynomial is made with the five lowest density points and the coefficients and overall standard deviation recorded. The procedure is then repeated each time adding the next

Table II. Experimental Results for the Thermal Conductivity of Dry, CO_2-Free Air at 312 K

p (MPA)	T_r (K)	$\rho(T_r p)$ ($kg \cdot m^{-3}$)	$\lambda(T_r)$ ($mW \cdot m^{-1} \cdot K^{-1}$)	$\lambda(T_n)$ ($mW \cdot m^{-1} \cdot K^{-1}$)
0.95	313.91	10.56	27.62	27.48
0.95	312.61	10.60	27.58	27.54
0.95	311.63	10.64	27.49	27.52
2.17	312.08	24.31	27.97	27.97
3.16	311.71	35.48	28.34	28.36
4.02	311.40	45.21	28.73	28.78
5.06	312.10	56.78	29.28	29.27
6.88	311.62	77.26	30.21	30.24
8.88	311.28	99.59	31.18	31.24
10.75	310.95	120.24	32.24	32.31
12.79	310.50	142.46	33.39	33.50
15.60	310.14	172.15	35.03	35.16
18.23	309.81	198.92	36.69	36.85
20.80	310.17	223.42	38.36	38.49
23.80	309.04	251.96	40.30	40.51

Table III. Experimental Results for the Thermal Conductivity of Dry, CO_2-Free Air at 373 K

p (MPA)	T_r (K)	$\rho(T_r, p)$ ($kg \cdot m^{-3}$)	$\lambda(T_r)$ ($mW \cdot m^{-1} \cdot K^{-1}$)	$\lambda(T_n)$ ($mW \cdot m^{-1} \cdot K^{-1}$)
0.87	375.11	8.07	31.89	31.75
0.87	375.11	8.07	31.83	31.69
1.38	374.83	12.80	32.07	31.95
2.02	374.64	18.73	32.22	32.11
2.95	374.03	27.35	32.49	32.42
4.02	373.74	37.22	32.86	32.81
5.21	373.65	48.11	33.27	33.23
7.13	373.40	65.56	33.94	33.91
9.05	372.94	82.83	34.74	34.74
11.18	372.96	101.55	35.63	35.66
14.12	372.49	126.92	36.75	36.79
14.12	372.49	126.92	36.92	36.95
16.75	372.07	148.96	38.05	38.11
19.60	371.83	171.96	39.33	39.40
19.60	371.81	171.98	39.27	39.35
20.68	372.44	180.08	39.86	39.90
22.90	372.31	197.06	40.90	40.95

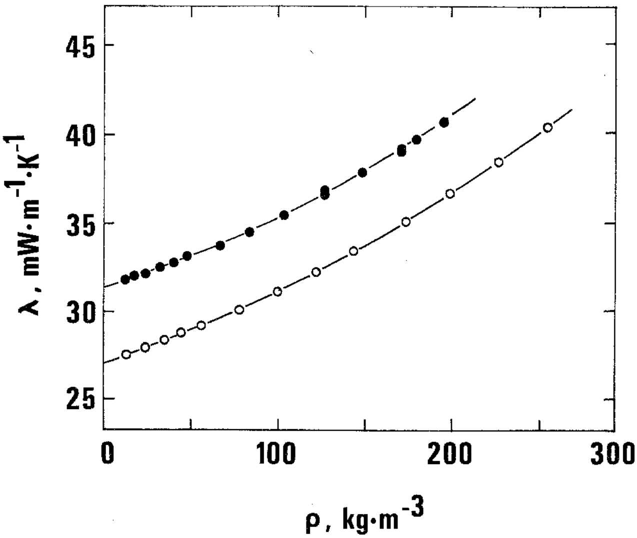

Fig. 1. Thermal conductivity of dry, CO_2-free air as a function of density. (○) 312 K; (●) 373 K.

higher density point. With our data at both temperatures the overall standard deviation for a second-order fit decreases as each point is added. Thus we may say the data are well represented by Eq. (8) and that the coefficient a_0 may be equated with the thermal conductivity at zero density, λ_0. The coefficients of Eq. (8) are given in Table IV.

At temperatures removed from the critical, the "excess" thermal conductivity is often found to be independent of the temperature and a function of the density only,

$$\Delta\lambda = a_1\rho + a_2\rho^2 + \dots \quad (9)$$

We have used the λ_0 values obtained above to calculate $\Delta\lambda$ values at both temperatures. Figure 2 shows that within the experimental error the $\Delta\lambda$

Table IV. Best Estimates[a] of the Coefficients in the Correlating Equation $y = a_0 + a_{1\rho} + a_{2\rho}{}^2$ (312 and 373 K, $y = \lambda$; Combined Data, $y = \Delta\lambda$)

	$a_0 \pm \epsilon(a_0)$	$a_1 \pm \epsilon(a_1)$	$a_2 \pm \epsilon(a_2)$
λ(312 K)	27.12 ± 0.04	33.72 ± 0.78	76.8 ± 3.2
λ(373 K)	31.46 ± 0.06	32.97 ± 1.42	76.9 ± 6.7
Δλ(all points)		33.30 ± 0.54	78.1 ± 2.9

[a]Uncertainty limits are the 95% confidence levels.

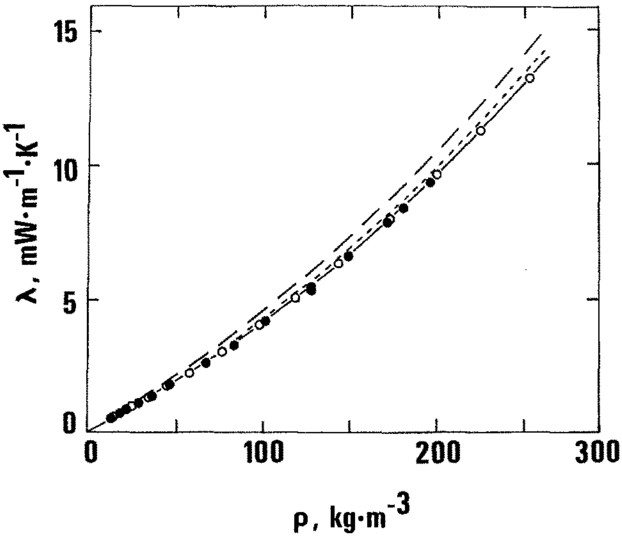

Fig. 2. Excess thermal conductivity of air as a function of density. (○) This work, 312 K; (●) this work, 373K; (----) Vargaftik et al. [5]; (———) Carroll et al. [16].

values may be represented as a second-degree polynomial using the coefficients given in Table IV.

We have also measured the thermal conductivity of air at selected densities at temperatures between 312 and 373 K. As the $(\Delta\lambda, \rho)$ curve is temperature independent, we may derive $\Delta\lambda$ values using the experimental densities and obtain λ_0 values at each temperature. These results are summarized in Table V, and it is gratifying to observe the agreement in λ_0 values of results at different densities.

5. DISCUSSION

An estimate of the precision of the data may be obtained from the standard deviation of the thermal conductivity derived from a set of results at one pressure. This is typically $\pm 0.1\%$, and the reproducibility of the measurements is also of this order. The overall accuracy is more difficult to determine, but as stated earlier the same apparatus has been used to determine the thermal conductivity of argon and helium over a range of temperatures [10], and the experimental values agree with rigorous kinetic theory results to within $\pm 0.25\%$. Thus we believe the absolute uncertainty in the measured values to be less than $\pm 0.5\%$.

Table V. Experimental Results for the Thermal Conductivity of Dry, CO_2-Free Air Between 316 and 363 K

p (MPa)	T_r (K)	$\rho(T_r, p)$ ($kg \cdot m^{-3}$)	$\lambda(T_r)$ ($mW \cdot m^{-1} \cdot K^{-1}$)	T_n (K)	$\lambda(T_n)$ ($mW \cdot m^{-1} \cdot K^{-1}$)	$\Delta\lambda$ ($mW \cdot m^{-1} \cdot K^{-1}$)	$\lambda_0(T_n)$ ($mW \cdot m^{-1} \cdot K^{-1}$)
3.99	315.91	44.18	29.15	316.0	29.16	1.63	27.53
6.13	324.71	65.80	30.64	325.0	30.66	2.53	28.13
8.03	324.42	86.01	31.53	325.0	31.57	3.44	28.13
4.91	334.80	51.05	30.71	335.0	30.72	1.91	28.81
6.32	334.53	65.61	31.38	335.0	31.41	2.52	28.79
6.33	343.67	63.80	31.84	344.0	31.86	2.44	29.42
9.18	343.36	91.99	33.09	344.0	33.13	3.72	29.41
6.30	353.89	61.51	32.51	354.0	32.51	2.35	30.16
8.88	353.59	86.20	33.59	354.0	33.62	3.45	30.17
6.93	363.29	65.67	33.28	363.0	33.26	2.53	30.73
9.75	362.96	91.71	34.47	363.0	34.47	3.71	30.76

In order to compare our data for the thermal conductivity at zero density with published values, we have fitted the data to an equation of the form

$$\lambda_0 = b_1 + b_2 T + b_3 T^2, \quad (10)$$

where T is the absolute temperature. In addition to our own values, we have used the TPRC values at 0 and 200°C to give the correlation equation the essentially correct temperature dependence outside our experimental temperature range. The values of the coefficients are $b_1 = -1.2847$, $b_2 = 0.10729$, and $b_3 = -5.2146 \times 10^{-5}$.

A comparison of the published data with our own values is shown in Fig. 3. It may be observed that both the TPRC correlation and the values obtained by Tsederberg and Ivanova [3] lie between 0.4 and 0.8% below our data. The correlation by Carroll et al. [16] is consistently 2% above this work, but this used mainly older data, in particular that of Vines [17], which is now known to be in error [18]. The data of Irving et al. [2] lie 2% below our results, whereas the results of Tarzimanov and Lozovoi [4] are approximately 1% higher. However, in all cases the accuracy of the published data is ±2% or higher, and the deviations lie within the combined uncertainties in the data.

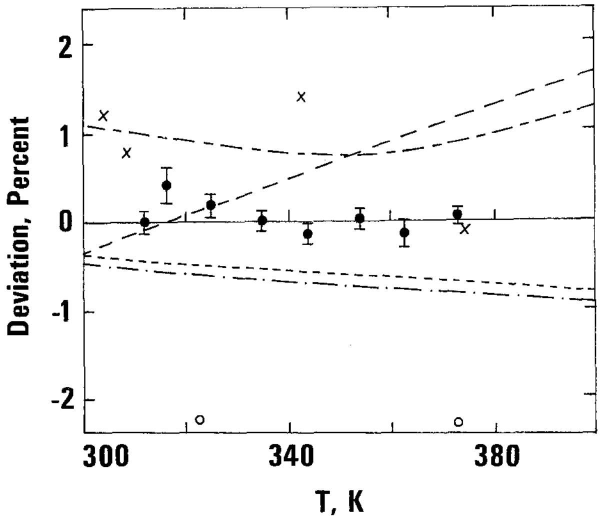

Fig. 3. Comparison of experimental data for the thermal conductivity of dry, CO_2-free air at zero density with the correlating equation λ_0 ($mW \cdot m^{-1} \cdot K^{-1}$) $= -1.2847 + 0.10729\ T - 5.2146 \times 10^{-5}\ T^2$. (ɪ) This work; (—·—·—) TPRC [11]; (----) Tsederberg and Ivanova [3]; (———) Vargaftik et al [5]; (——-——) Carroll et al. [16]; (O) Irving et al. [2]; (x) Tarzimanov and Lozovoi [4].

At higher densities we have compared our results in the form of excess thermal conductivity since the latter appear to be independent of temperature in the experimental range. The comparison is shown in Fig. 2. Vargaftik et al. [5] have collected the data published up to 1971 and produced an equation which correlated the data to within 2–3%. This line lies approximately 1% higher than our experimental values. The only published data since 1971 are those of Tarzimanov and Sal'manov [19], who measured thermal conductivities in the range 400–1200 K and 0.1–100 MPa. They found some statification in the excess thermal conductivity curves at the highest temperatures. At lower temperatures where the densities were in our experimental range, their values are 2–3% higher than our data, which is the uncertainty in their measurements. It is interesting to note that most of the earlier measurements, at both low and high densities, lie above the current values, which may be due to the effects of convection in the earlier work. Carroll et al. [16] attempted to use the method of corresponding states to predict the thermal conductivity of air at high density, using an equation which reproduced the excess thermal conductivity of nitrogen. We have calculated the excess thermal conductivity using this equation and the currently accepted pseudocritical constants for air ($p_c = 3.769$ MPa, $T_c = 132.55$ K, $\rho_c = 313\ \mathrm{kg \cdot m^{-3}}$). Carroll et al. assumed that $Z_c(N_2) = Z_c(\mathrm{air})$, but did not state the critical constants which they used for air. Using recommended values, we find that $Z_c(N_2) = 0.289$ and $Z_c(\mathrm{air}) = 0.316$. The results are presented in Fig. 2 and show that the predicted values are several percent higher than our current data.

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NOMENCLATURE

λ	Thermal conductivity, $\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$
ρ	Density, $\mathrm{kg \cdot m^{-3}}$
C_p	Specific heat capacity at constant pressure, $\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$
T	Absolute temperature, K
q	Heat input per unit wire length, $\mathrm{W \cdot m^{-1}}$
t	Time, s
$K(= \lambda/\rho C_p)$	Thermal diffusivity, $\mathrm{m^2 \cdot s^{-1}}$
a	Wire radius, m
γ	Euler's constant ($= 0.5772\ldots$)

p_c	Critical pressure, MPa
T_c	Critical temperature, K
ρ_c	Critical density, $kg \cdot m^{-3}$
R	Gas constant ($= 8.314\ J \cdot mol^{-1} \cdot K^{-1}$)
V_c	Critical volume, $m^3 \cdot mol^{-1}$
$Z_c(= p_c V_c / RT_c)$	Critical compressibility factor

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