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Thermal Conductivity of Carbon Disulphide at Pressures up to 500 MPa

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The paper presents new, absolute measurements of the thermal conductivity of carbon disulphide in the temperature range 36–74°C and the pressure range 40–500 MPa. The measurements have been carried out in a transient hot-wire instrument, and the radiation-free thermal conductivity reported has an estimated uncertainty of ±0.5%. The correction for the contribution to heat transfer arising from absorption of radiation is particularly small for carbon disulphide, and it is proposed as a suitable standard reference material for liquid thermal conductivity.

KEY WORDS: carbon disulphide; high pressure; thermal conductivity; transport properties.

1. INTRODUCTION

Many measurements of the thermal conductivity of liquids are carried out in instruments which require calibration with respect to standard reference data. Unlike the situation for the gas phase [1], such reference data cannot be generated from independent measurements of other properties by means of exact theoretical results. The standard reference values must therefore be determined by direct, absolute measurements. At present, there is no consensus among workers in the field with respect to either the standard reference data or, indeed, the reference fluids. The origin of this difficulty may be traced to the large discrepancies between the results of thermal

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conductivity measurements for a single liquid in different instruments [2]. The discrepancies themselves may be attributed to undetected systematic errors in the measurements arising principally from the effects of convective and radiative heat transfer. The development of the transient hot-wire technique over the last decade [3–5] has provided the opportunity to eliminate convective heat transfer from the measurement process and, at the same time, to reduce the effects of radiative heat transfer. The remaining, small contribution from the latter may itself be estimated with the aid of a suitable mathematical model [6]. The transient hot-wire instrument, which yields absolute measurements of the thermal conductivity, is therefore eminently suitable for the determination of standard reference data.

The most popular fluids for thermal conductivity standards have been water, toluene, and dimethyl phthalate [6, 7]. All of these liquids absorb quite strongly in the infrared, which is the region of the spectrum that contributes most to radiative heat transfer in thermal conductivity measurements. Furthermore, the thermal conductivity of water exceeds that of most liquids by a factor of four under ambient conditions, so that it is not a particularly suitable reference fluid for many purposes. A more appropriate reference fluid should be nearly transparent in the infrared, have a thermal conductivity comparable with that of the majority of liquids, a liquid phase extending over a wide range of thermodynamic states and, finally, be readily available with a high purity. A survey of the infrared absorption spectra of liquids reveals that one of the most weakly absorbing is carbon disulphide. For this reason it is often employed as a solvent in spectrophotometric studies, and high purity samples are commercially available. Carbon disulphide also satisfies the remaining criteria for a thermal conductivity standard. In this paper we report the results of absolute measurements of the thermal conductivity of carbon disulphide in the temperature range 36–74°C and over the pressure range 40–500 MPa. The experimental data have an estimated uncertainty of ±0.5%. Ideally, the establishment of standard reference data requires measurements to be carried out in a number of laboratories, by means of different experimental methods. Furthermore, it is desirable that, for a liquid, the calibration data should extend to the saturation line in order to render the calibration procedure straightforward. Consequently, the present data alone cannot serve as reference standards. However, the analysis of the results presented here does confirm that carbon disulphide is a suitable reference material.

Carbon disulphide is also one of the simplest molecules which exists in the liquid state under ambient conditions and, recently, there have been a number of theoretical and experimental studies of its equilibrium and transport properties [8–11]. Although the theoretical studies have not yet been extended to the thermal conductivity, the present results provide the first reliable data against which future theoretical developments may be tested.

2. EXPERIMENTAL PROCEDURE

The thermal conductivity measurements have been performed in the transient hot-wire instrument described elsewhere [5], along three isotherms, 36°C, 48°C, and 74°C for pressures in the range 40–500 MPa. The samples of spectrophotometric-grade carbon disulphide were supplied by B.D.H. Chemicals Ltd. and had a stated purity in excess of 99.9%. The purity was confirmed by analysis of samples, and the liquid was therefore merely degassed before use.

The density of the liquid has been obtained from the data of Bridgman [12], whereas for the heat capacity of the liquid, required to apply small corrections in the analysis of the results, the data of Sutherland [13] have been employed. In order to apply a correction to the thermal conductivity data to account for the effects of radiative heat transfer in an absorbing medium [5, 14], it is necessary to determine the optical properties of the liquid. The refractive index and the mean extinction coefficient for radiation, κ, have been determined by standard techniques under ambient conditions. In particular, the mean extinction coefficient was found to be $\kappa = 500\ \mathrm{m}^{-1}$, which is approximately 2.5 times smaller than the value found for the normal alkanes studied earlier [5, 15, 16]. This value was employed uniformly over the entire range of thermodynamic states covered in the measurements, and the contribution to the uncertainty in the thermal conductivity that results from this assignment was included in the overall error analysis.

3. RESULTS

Tables I–III contain the experimental results for the thermal conductivity of carbon disulphide at the three nominal temperatures 36, 50, and 74°C, respectively. The tables provide the apparent thermal conductivity at the nominal temperature and reference density, $\lambda_{\mathrm{app}}(T_{\mathrm{nom}}, \rho_r)$, the radiation-free values $\lambda(T_{\mathrm{nom}}, \rho_r)$, and the radiation-free values corrected to the nominal temperature at the pressure of the measurement [5].

The reduction of the data to a common nominal temperature has been performed by means of linear corrections [5] which did not exceed $\pm 0.1\%$. The uncertainty introduced by the application of this correction is therefore negligible. The correction of the thermal conductivity data to account for the contribution of radiative heat transfer has been carried out in the manner described by Menashe and Wakeham [5, 14]. In the worst case, at

Table I. The Thermal Conductivity of Carbon Disulphide at $T_{\text{nom}} = 36°\text{C}$

		Thermal conductivity		
Pressure, P (MPa)	Density, ρ_r $(\text{kg}\cdot\text{m}^{-3})$	$\lambda_{\text{app}}(T_{\text{nom}}, \rho_r)$ $(\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$	$\lambda(T_{\text{nom}}, \rho_r)$ $(\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$	$\lambda(T_{\text{nom}}, P)$ $(\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$
42.0	1280.9	154.8	153.3	153.4
53.4	1291.2	157.0	155.5	155.6
64.4	1299.4	160.5	158.9	159.5
74.6	1308.3	164.2	162.7	163.2
74.6	1308.5	164.2	162.6	163.1
99.3	1328.9	171.4	169.8	170.1
117.9	1344.1	176.2	174.5	174.6
147.7	1363.3	184.2	182.5	183.0
165.0	1375.7	188.1	186.3	186.4
219.4	1406.9	200.3	198.5	198.6
260.8	1427.9	208.8	207.0	206.9
308.3	1449.5	217.0	215.0	214.9
344.2	1463.7	221.7	219.8	219.8
383.4	1478.4	228.7	226.7	226.9
421.6	1493.5	234.9	232.8	232.7
461.2	1507.5	240.4	238.3	238.3
503.7	1522.6	246.1	244.0	244.0

Table II. The Thermal Conductivity of Carbon Disulphide at $T_{\text{nom}} = 50°\text{C}$

		Thermal conductivity		
Pressure, P (MPa)	Density, ρ_r $(\text{kg}\cdot\text{m}^{-3})$	$\lambda_{\text{app}}(T_{\text{nom}}, \rho_r)$ $(\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$	$\lambda(T_{\text{nom}}, \rho_r)$ $(\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$	$\lambda(T_{\text{nom}}, P)$ $(\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$
50.1	1269.6	152.6	150.9	151.3
68.4	1285.9	157.6	155.8	156.6
97.0	1312.7	167.0	165.2	165.4
115.9	1328.0	172.0	170.2	170.3
135.8	1342.9	176.5	174.7	174.8
146.6	1350.8	179.6	177.8	177.8
170.2	1366.5	184.9	183.0	183.1
190.3	1378.9	189.7	187.8	187.8
212.2	1391.6	194.6	192.7	192.7
269.3	1420.7	205.4	203.4	203.3
305.0	1436.9	212.1	210.1	210.0
345.0	1453.6	219.2	217.1	216.9
398.5	1474.5	228.0	225.8	225.6
448.2	1493.0	235.3	233.1	232.9
503.0	1512.8	243.1	240.9	240.7

Table III. The Thermal Conductivity of Carbon Disulphide at $T_{\text{nom}} = 74°\text{C}$

		Thermal conductivity		
Pressure, P (MPa)	Density, ρ_r ($\text{kg} \cdot \text{m}^{-3}$)	$\lambda_{\text{app}}(T_{\text{nom}}, \rho_r)$ ($\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	$\lambda(T_{\text{nom}}, \rho_r)$ ($\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	$\lambda(T_{\text{nom}}, P)$ ($\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)
48.7	1238.0	144.1	142.1	142.3
71.1	1261.6	151.7	149.6	149.7
92.9	1283.0	158.1	156.0	156.0
126.2	1312.3	167.4	165.2	165.0
149.5	1330.2	173.3	171.1	170.9
188.6	1357.1	182.9	180.5	180.4
228.1	1380.6	191.8	189.4	189.2
267.9	1401.1	199.9	197.4	197.2
307.6	1419.5	207.5	204.9	204.7
352.5	1438.6	215.4	212.7	212.5
402.5	1458.6	223.3	220.6	220.4
452.2	1478.2	231.8	229.0	228.7
488.8	1492.3	237.4	234.6	234.4

the highest temperatures and lowest densities, the correction amounts to a reduction of the apparent thermal conductivity by 1.4%, which is a significantly smaller correction than was necessary for the normal alkanes [5, 15, 16]. Accounting for the random errors of measurement as well as the uncertainty in the application of the correction for radiation [15], it is estimated that the overall accuracy of the tabulated thermal conductivity data is one of ±0.5%.

There have been very few previous measurements of the thermal conductivity of carbon disulphide and only one set of determinations at elevated pressures performed by Bridgman [17]. In order to facilitate a comparison with these earlier results, the present data have been represented by means of a polynomial in pressure along each isotherm:

$$\lambda = b_0\left(1 + b_1 x + b_2 x^2 + b_3 x^3\right) \tag{1}$$

Table IV. Coefficients of the Correlating Eq. (1) for the Thermal Conductivity of Carbon Disulphide as a Function of Pressure

T (°C)	P' (MPa)	b_0 ($\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	b_1	b_2	b_3
36	200	194.52	0.2193	-5.540×10^{-2}	1.438×10^{-2}
50	200	189.88	0.2264	-5.006×10^{-2}	1.159×10^{-2}
74	200	183.06	0.2437	-5.476×10^{-2}	1.418×10^{-2}

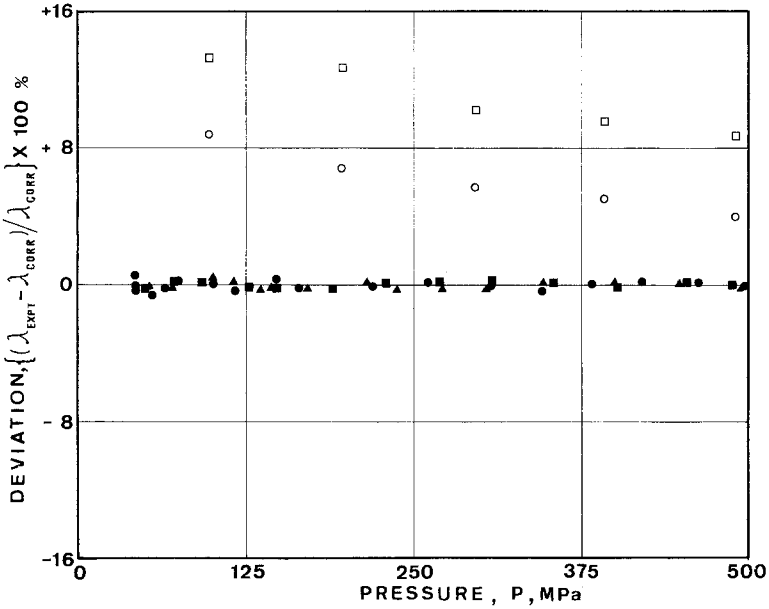

Fig. 1. The deviations of the thermal conductivity data from the correlation of Eq. (1). Present work: ● 36°C; ▲ 50°C; ■ 74°C. Bridgman [17]: ○ 36°C; □ 74°C.

where

$$x = (P - P')/P'$$

The optimum values of the coefficients of this empirical correlation are listed in Table IV. Figure 1 illustrates the deviations of the present experimental data as well as those of Bridgman from the correlation. The present results deviate by no more than ±0.4% from the correlation, the standard deviation of the entire set of data being one of ±0.2%. The earlier results lie some 5–12% above the present values, although the pressure dependence of the two sets of results is similar. The present data are to be preferred owing to their higher precision. It should be emphasized that the correlation represented by Eq. (1) is not suitable for extrapolation outside of the range of the present data.

4. THE DENSITY DEPENDENCE

The van der Waal's model of a liquid provides the basis for a satisfactory description of many of the transport properties of dense monatomic and polyatomic fluids [18]; in particular, for the self-diffusion coefficient for carbon disulphide [11]. However, the theoretical analysis of the model cannot formally be extended to include the thermal conductivity of polyatomic fluids owing to the importance of the transport of internal energy. Nevertheless, an empirical extension of the theory, which retains some of its principal results, has proved quite successful for the correlation of the thermal conductivity of liquid normal alkanes [19]. According to this extension, the dimensionless group

$$\lambda^* = \frac{1.936 \times 10^7 \lambda V^{2/3} (M/RT)^{1/2}}{\left[1 + 0.352 C^0_{v,\mathrm{int}}/R)\right]} \tag{2}$$

should be a function only of the reduced molar volume (V/V_0), for a particular fluid, so that

$$\lambda^* = f(V/V_0) \tag{3}$$

In these equations, V_0 is a characteristic molar volume for the fluid which is but weakly temperature-dependent, M is the molecular weight of the fluid, and $C^0_{v,\mathrm{int}}$ is the internal contribution to the ideal gas specific heat of the fluid; all quantities are measured in S.I. units.

Figure 2 contains an examination of the statement contained in Eqs. (2) and (3) with respect to the present thermal conductivity data for carbon disulphide. In this plot, the curves of λ^* against $\ln V$ for each isotherm have been superimposed on the isotherm at 36°C by translation along the $\ln V$ axis only. The amount of the translation yields the ratio of the V_0 values for each isotherm to that at 36°C. The value of V_0 at 36°C has been taken from the analysis of self-diffusion data for carbon disulphide carried out by Woolf [11]. This value, together with those derived at other temperatures, as well as the internal heat capacities employed in the calculation, are listed in Table V.

The curves λ^* against (V/V_0) for the three isotherms are in very close

Table V. Characteristic Volumes and Internal Heat Capacities for the Correlation of the Thermal Conductivity of Carbon Disulphide as a Function of Density According to Eq. (4)

T (°C)	Characteristic volume, V_0 ($\mathrm{m^3 \cdot mol^{-1}}$)	$C^0_{v,\mathrm{int}}/R$
36	3.290×10^{-5}	3.035
50	3.244×10^{-5}	3.104
74	3.167×10^{-5}	3.216

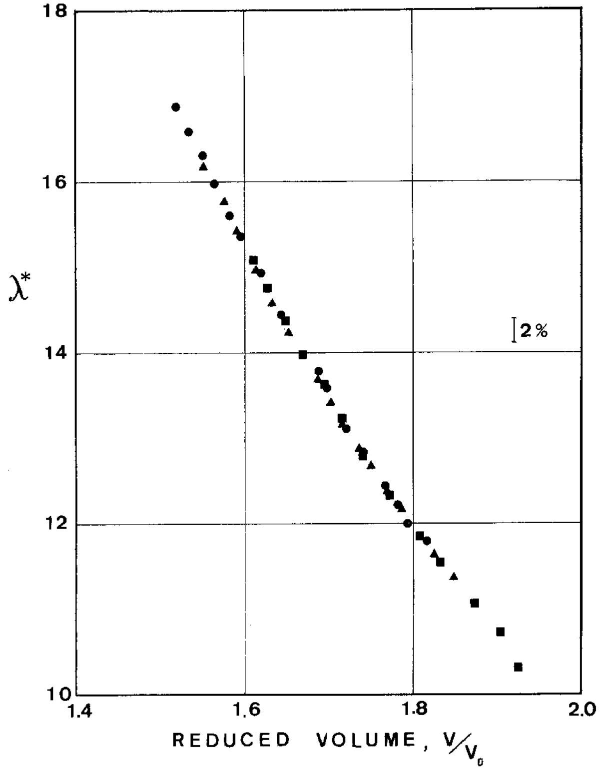

Fig. 2. The dimensionless quantity λ^* as a function of reduced molar volume for carbon disulphide. ● 36°C; ▲ 50°C; ■ 74°C.

agreement. The entire set of data may be represented by the equation

$$\ln \lambda^* = 3.6830 - 2.0405 \ln(V/V_0) \tag{4}$$

which is of the same form as that found appropriate for all of the normal alkanes [19]. However, the values of the coefficients for carbon disulphide differ considerably from those of the hydrocarbons.

Figure 3 shows that the deviations of the present data from the correlation of Eq. (4) do not exceed ±0.7%. The standard deviation is one of ±0.2%, which is commensurate with the combined uncertainty in the thermal conductivity and the density data. Figure 3 confirms that Eqs. (2) and (3) can form the basis of a reliable correlation scheme for the thermal conductivity of polyatomic liquids even though its physical basis is less secure than that of the corresponding expression for monatomic fluids [18]. Futhermore, judged on the evidence of the results for normal alkanes, the

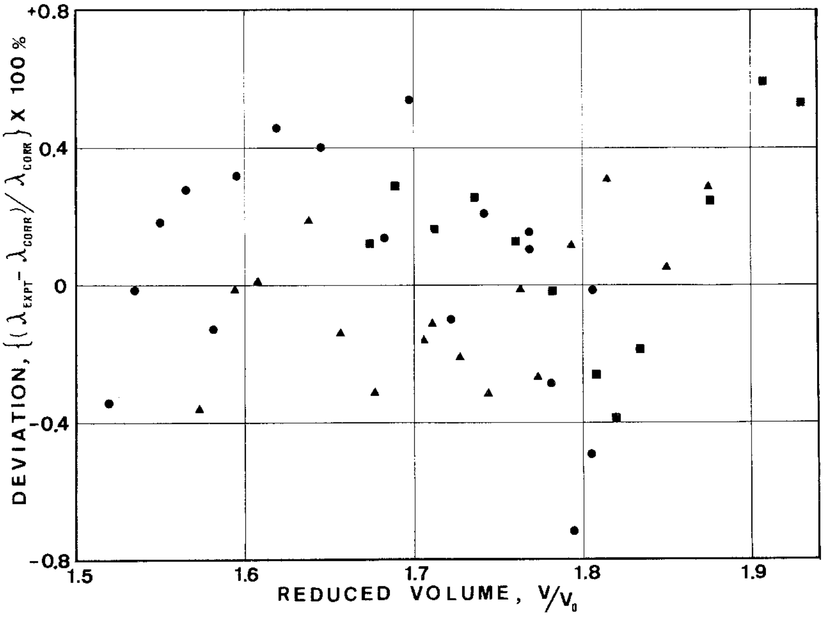

Fig. 3. The deviations of the experimental thermal conductivity from the corelation of Eq. (4). ● 36°C; ▲ 50°C; ■ 74°C.

same correlation scheme allows a modest extrapolation of the original set of data to other temperatures and pressures [19].

5. DISCUSSION

The experimental results presented in the paper confirm that the effect of the absorption of radiation upon thermal conductivity measurements in carbon disulphide is significantly smaller than for other liquids studied. In view of the other attributes of the liquid mentioned in the Introduction, it seems that carbon disulphide merits serious consideration as a standard reference material for liquid thermal conductivity. The availability of a reliable interpolation procedure for the data adds further weight to this argument.

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