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Thermal Conductivity of Carbon Tetrachloride in the Temperature Range 310 to 364 K at Pressures Up to 0.22 GPa

A. M. F. Palavra,[1] W. A. Wakeham,[2] and M. Zalaf[2]

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The paper reports new measurements of the thermal conductivity of carbon tetrachloride in the temperature range 310 to 364 K at pressures up to 0.22 GPa. The experimental data have an estimated uncertainty to ±0.3%. The hard-sphere theory of transport in dense fluids is employed to formulate a correlation scheme for the thermal conductivity as a function of density. A single equation represents the dependence of the thermal conductivity on density for all isotherms, the isotherms being distinguished by a characteristic value of the molar volume. It is shown that earlier measurements of the viscosity and self-diffusion coefficient of carbon tetrachloride may be represented in a similar fashion using consistent values of the characteristic volume.

KEY WORDS: carbon tetrachloride; hard-sphere theory; liquid; self-diffusion coefficient; thermal conductivity; viscosity.

1. INTRODUCTION

There are no materials consisting of monatomic species which are liquid at ambient temperatures where the experimental determination of their properties can be carried out with the greatest accuracy. Conversely, such theories of the transport properties of liquids as exist are most directly applicable to simple monatomic systems [1]. Consequently, particularly in the case of thermal conductivity, there are few data of high quality that may be used to provide a rigorous test of the available theories. The sim-

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[1] Instituto Superior Tecnico, Complexo Interdisciplinar, Avenida Rovisco Pais, Lisbon, Portugal.

[2] Department of Chemical Engineering and Chemical Technology, Imperial College, Prince Consort Road, London SW7 2BY, England.

plest group of systems which satisfy the requirement that they be liquid at normal conditions consists of small linear molecules or those with a high degree of spherical symmetry. In a previous paper [2] we reported accurate measurements of the thermal conductivity of the linear molecule carbon disulfide. In this paper we report the results of similar measurements for carbon tetrachloride. McCool and Woolf [3] have performed measurements of the self-diffusion coefficient of carbon tetrachloride over part of the range of thermodynamic states studied here, while Collings and McLaughlin [4] have determined the viscosity over a similar range of states. The present study therefore completes the set of the principal transport properties for this liquid.

2. EXPERIMENTAL

The thermal conductivity measurements have been performed in the high-pressure transient hot-wire instrument described earlier [5]. Apart from the installation of a new set of platinum wires for these measurements, the instrument and operating procedure remain unchanged. The measurements have been carried out along five isotherms in the temperature range 310–364 K at pressures up to 0.22 GPa. The carbon tetrachloride sample employed for the measurements was supplied by BDH Chemicals Ltd. and the purity was stated to be better than 99.5%. Nevertheless, samples were distilled and degassed before use, and chromatographic analysis then confirmed a purity in excess of 99.9%.

The density of carbon tetrachloride was measured over a part of the range of states appropriate to our work by Easteal and Woolf and the results are to be published separately [6]. The measurements of Easteal and Woolf were performed along three isotherms at 308.5, 318.15, and 338.15 K. Their data were represented by a modified form of the Tait equation,

$$1-\frac{V_P}{V_{0.1}}=C\log\left(\frac{B+P}{B+0.1}\right) \tag{1}$$

in which V_P represents the molar volume at a pressure P (MPa) and B and C are disposable parameters. The same equation has been used to represent the data of Gibson and Loeffler [7] for a temperature of 328.15 K. From the volume data at a given pressure for each of these four isotherms, it is possible to interpolate reliably to determine the density for the two lowest temperatures included in the present study. Furthermore, the small extrapolation required to obtain the density at our third isotherm, which lies only 4.5 K above that of the highest direct density measurement, introduces a very small extra error. However, the larger extrapolation necessary to reach the highest two isotherms of the present study seems likely to introduce errors that are unacceptably high. Consequently, we use such an extrapolation only to estimate the density of the liquid at these higher temperatures for the purposes of applying small corrections in the reduction of the thermal conductivity data [5]. The heat capacity of the liquid required for the same corrections has been taken from the tables of Vargaftik [8].

It is necessary to record here that none of the experimental measurements revealed any evidence of the effects of radiation absorption [9], so that the results reported in the next section are "radiation-free."

3. RESULTS

Tables I to IV list the experimental data for the thermal conductivity of carbon tetrachloride along the five isotherms at 310.15, 322.65, 342.65, 359.65, and 364.15 K. Owing to the relative unreliability of the density data at the higher temperatures, we prefer to list the thermal conductivity as a function of density, $\lambda(T_{\mathrm{nom}}, \rho_{\mathrm{r}})$, only for the three lowest isotherms. At the higher temperatures we merely provide a tabulation of the thermal conduc-

Table I. The Thermal Conductivity of Carbon Tetrachloride at $T_{\mathrm{nom}} = 310.15$ K

Pressure P (MPa)	Density ρ $(\mathrm{kg \cdot m^{-3}})$	Thermal conductivity $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$	
		$\lambda(T_{\mathrm{nom}}, \rho)$	$\lambda(T_{\mathrm{nom}}, P)$
5.376	1573.3	97.49	97.49
8.329	1578.2	98.52	98.47
14.44	1587.7	100.4	100.3
17.28	1591.7	101.0	101.0
22.85	1600.5	102.5	102.4
29.25	1609.6	104.1	104.1
36.26	1619.5	105.9	105.9
42.09	1627.4	107.3	107.3
47.59	1634.6	108.6	108.5
53.28	1641.6	110.0	110.0
58.94	1648.5	111.3	111.3
63.75	1652.5	111.6	111.8
68.23	1658.8	113.3	113.3
72.71	1663.6	114.2	114.2

Table II. The Thermal Conductivity of Carbon Tetrachloride at $T_{\text{nom}} = 322.65$ K

Pressure P (MPa)	Density ρ (kg · m^{-3})	Thermal conductivity (mW · m^{-1} · K^{-1})	
		$\lambda(T_{\text{nom}}, \rho)$	$\lambda(T_{\text{nom}}, P)$
1.367	1548.1	93.42	93.40
5.271	1555.1	94.42	94.41
9.805	1563.2	95.76	95.75
15.07	1571.9	97.51	97.50
20.33	1580.5	99.33	99.30
24.74	1587.2	100.8	100.8
26.42	1589.6	100.8	100.8
27.05	1590.4	100.8	100.8
32.39	1598.6	102.4	102.3
37.72	1606.1	104.1	104.0
44.38	1614.9	105.5	105.5
52.87	1625.9	107.6	107.6
61.40	1636.2	109.8	109.8
68.84	1644.7	111.4	111.5
77.38	1654.3	113.2	113.2
81.45	1658.7	114.3	114.3
84.49	1661.8	114.9	115.0
91.39	1668.8	116.1	116.2
95.15	1672.8	116.3	116.3
101.1	1678.9	118.2	118.1
105.9	1683.5	119.1	119.1
112.9	1690.2	120.3	120.3

tivity as a function of pressure, $\lambda(T_{\text{nom}}, P)$. In every case the data have been corrected to the nominal temperature by the application of a linear correction which never amounts to more than ±0.1 %, so that the process makes a negligible contribution to the error in the thermal conductivity. The uncertainty in the reported thermal conductivity data is estimated to be one of ±0.3 % and the uncertainty in the tabulated density is estimated to be no more than ±0.2 %.

For the purposes of interpolation we have represented the pressure dependence of the thermal conductivity along each isotherm by an equation of the form

$$\lambda = \lambda' \left\{ 1 + \sum_{i=1}^{4} a_i [(P - P')/P']^i \right\} \tag{2}$$

Table III. The Thermal Conductivity of Carbon Tetrachloride at $T_{\mathrm{nom}} = 342.65$ K

Pressure P (MPa)	Density ρ ($\mathrm{kg \cdot m^{-3}}$)	Thermal conductivity ($\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$)	
		$\lambda(T_{\mathrm{nom}}, \rho)$	$\lambda(T_{\mathrm{nom}}, P)$
6.220	1519.4	90.80	90.71
10.96	1529.3	92.46	92.32
14.86	1536.8	93.44	93.29
21.49	1548.7	95.67	95.53
30.09	1563.7	98.21	97.99
38.55	1576.5	100.3	100.1
44.90	1585.6	102.0	101.9
49.77	1592.4	102.4	102.3
55.75	1600.6	104.8	104.7
62.11	1609.0	106.5	106.3
68.84	1617.1	108.1	108.0
74.64	1624.4	109.5	109.3
80.43	1631.0	110.6	110.5
86.02	1636.9	111.7	111.6
89.36	1640.6	112.9	112.7
89.87	1641.3	112.7	112.5
94.74	1646.6	114.1	113.9
101.4	1653.4	115.2	115.1
108.6	1660.0	117.0	117.1
113.9	1665.3	118.2	118.1
121.6	1672.7	119.5	119.5
126.1	1676.7	120.5	120.5
132.6	1683.0	121.6	121.5
138.8	1687.9	122.9	122.9
146.8	1695.0	123.9	123.9
152.9	1700.0	124.9	124.9
156.1	1702.9	125.6	125.7

The coefficients which secure the optimum representation of this kind are listed in Table V. Figure 1 shows the deviations of the experimental data from this correlation, and it can be seen that they do not exceed ±0.5%, the standard deviation over the entire data set being one of ±0.15%. There appear to have been no previous measurements of the thermal conductivity of carbon tetrachloride under pressure against which to compare the present results.

Table IV. The Thermal Conductivity of Carbon Tetrachloride at $T_{\text{nom}} = 359.65$ K and $T_{\text{nom}} = 364.15$ K

$T_{\text{nom}} = 359.65$ K		$T_{\text{nom}} = 364.15$ K	
Pressure P (MPa)	Thermal conductivity λ $(\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1})$	Pressure P (MPa)	Thermal conductivity λ $(\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1})$
6.115	86.18	3.478	84.26
13.18	88.57	9.277	86.60
25.06	92.73	19.81	90.10
37.30	96.27	34.90	94.64
49.46	99.79	47.70	98.67
59.25	102.3	63.75	102.9
70.06	105.1	76.37	105.8
77.59	106.8	87.84	108.5
86.42	108.6	100.9	111.6
93.22	110.5	118.0	115.1
103.4	112.3	128.8	117.2
112.2	114.3		
121.0	116.2		
130.9	118.3		
141.6	120.0		
153.4	122.4		
164.0	124.4		
174.0	125.9		
184.3	127.8		
194.2	129.4		
204.4	131.0		
214.6	132.6		
224.6	134.2		

Table V. Coefficients of the Correlation of the Thermal Conductivity Data According to Eq. (2)

Temperature (K)	λ' $(\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1})$	P' (MPa)	$10a_1$	$10^2 a_2$	$10^3 a_3$	$10^3 a_4$
310.15	109.09	50	1.041	−0.79	9.00	−0.26
322.65	107.05	50	1.146	−1.71	2.09	1.081
342.65	103.09	50	1.236	−1.03	3.79	−1.722
359.65	99.87	50	1.355	−1.95	4.19	−0.472
364.15	99.16	50	1.381	−1.88	4.72	−1.183

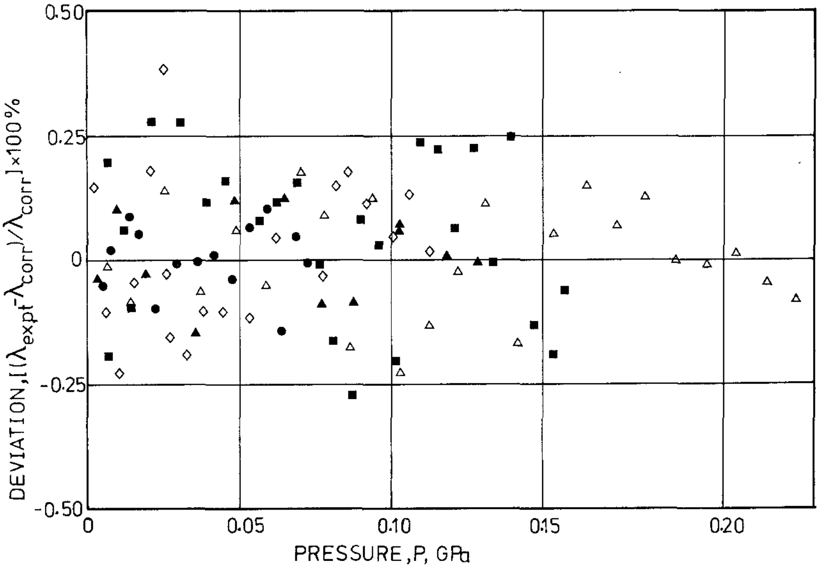

Fig. 1. The deviations of the thermal conductivity data from their correlation as a function of pressure by Eq. (2). ●, 310.15 K; ◇, 322.65 K; ■, 342.65 K; △, 359.65 K; ▲, 364.15 K.

4. DISCUSSION

The hard-sphere model of the dense fluid state [1] leads to the result that the quantity λ^*, defined by the equation

$$\begin{aligned}\lambda^* &= (\lambda/\lambda_0)(V/V_0)^{2/3} \\ &= 1.936\times 10^7 \lambda V^{2/3}(RT/M)^{-1/2} \qquad (3) \\ &= F_\lambda(V/V_0)\end{aligned}$$

is a function of a reduced molar volume (V/V_0) only. Here, λ is the thermal conductivity of the dense fluid, λ_0 the zero-density thermal conductivity, V the molar volume, R the universal gas constant, T the temperature, and M the molar mass. The quantity V_0 is the close-packed volume of the hard-sphere system.

The hard-sphere theory predicts the functional form of $F(V/V_0)$, but for polyatomic fluids, the result is not useful directly owing to the internal degrees of freedom of the molecules. However, the notion that λ^* depends only on a reduced volume for which V_0, the characteristic volume, varies weakly with temperature for real molecules has proved remarkably successful as a means of correlation and prediction for a number of complex liquids [10, 11]. Indeed, it has recently been shown [12] that a consistent description of both the viscosity and the thermal conductivity of polyatomic fluids (specifically normal alkanes) can be obtained with the aid of ideas based upon the hard-sphere theory.

In order to perform an analysis of the same kind for carbon tetrachloride, we first assign a value of V_0 to the isotherm at 322.65 K. We have selected a value reported by Dymond [1] from an analysis of self-diffusion coefficient data so that

$$V_0(322.65\ \mathrm{K}) = 6.080 \times 10^{-5}\ \mathrm{m^3 \cdot mol^{-1}}$$

Subsequently, we have determined the values of V_0 for the other two isotherms which secure an optimum representation of the thermal conductivity by means of a single, temperature-independent function $F_\lambda(V/V_0)$. The resulting values of V_0 are

$$V_0(310.15\ \mathrm{K}) = 6.115 \times 10^{-5}\ \mathrm{m^3 \cdot mol^{-1}}$$

and

$$V_0(342.65\ \mathrm{K}) = 6.056 \times 10^{-5}\ \mathrm{m^3 \cdot mol^{-1}}$$

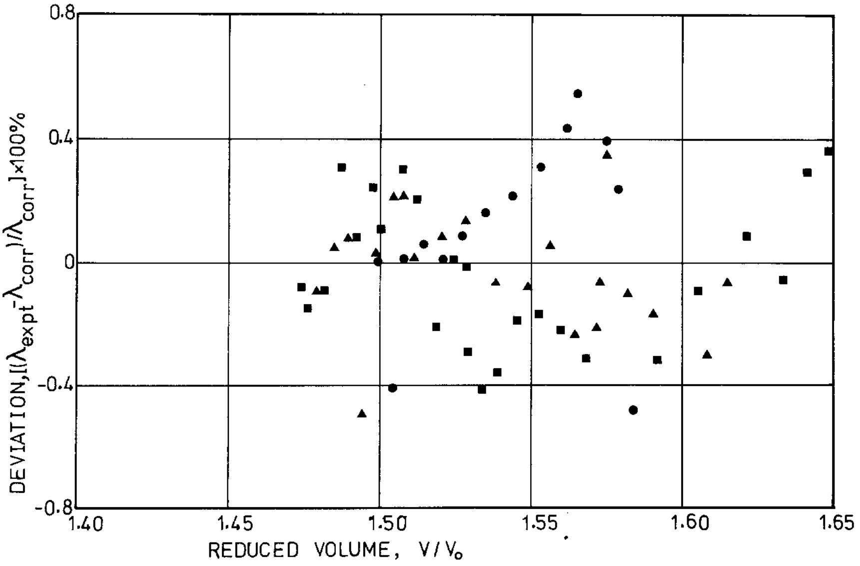

Fig. 2. The deviations of the thermal conductivity data from their correlation as a function of volume by Eq. (4). ●, 310.15 K; ▲, 322.65 K; ■, 342.65 K.

The corresponding single curve for λ^* as a function of (V/V_0) has been represented by the simple equation

$$\ln \lambda^* = 4.4294 - 2.2162 \ln(V/V_0) \tag{4}$$

Figure 2 contains a plot of the deviations of the experimental data from this correlation, and it can be seen that they do not exceed $\pm 0.4\%$, while the standard deviation amounts to $\pm 0.1\%$. These values are commensurate with the combined uncertainty in the density and the thermal conductivity and Fig. 2 provides considerable support for the hypothesis contained in Eq. (3).

It now remains to examine whether the same values of V_0 provide a similar descritpion of the other transport coefficients of carbon tetrachloride. For the viscosity the analogue of λ^* is a quantity η^* defined by the equation

$$\eta^* = 6.035 \times 10^8 \eta V^{2/3}/(MRT)^{1/2} \tag{5}$$

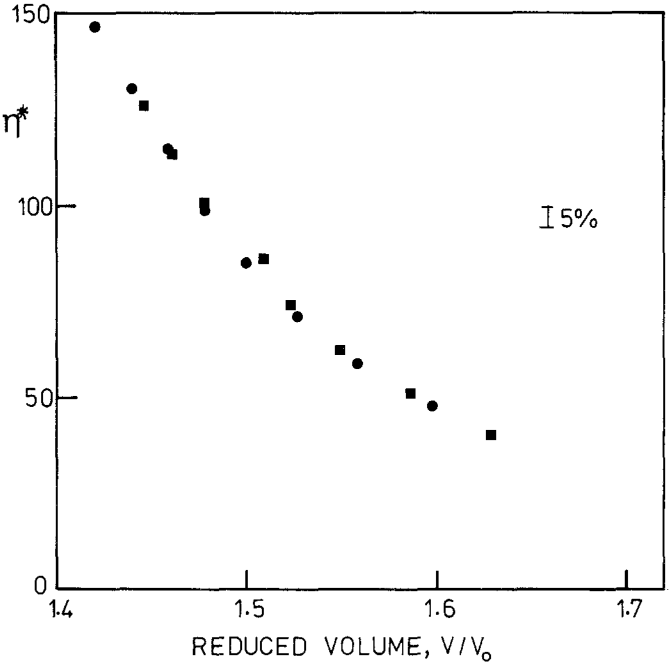

Fig. 3. The function η^* for carbon tetrachloride. Experimental data [4]: ●, 311.55 K; ■, 323.15 K.

Again, the hard-sphere theory leads to the result that

$$\eta^* = F_\eta(V/V_0) \tag{6}$$

where F_η is independent of temperature.

In order to test whether the values of V_0 derived from the thermal conductivity data are consistent with this result, we have employed the viscosity data of Collings and McLaughlin [4] to evaluate η^* along isotherms at 311.55 and 323.15 K. Values of V_0 for these temperatures have been interpolated from the values quoted earlier. Figure 3 contains a plot of η^* against V/V_0 for these two isotherms, and it can be seen that the data conform to a single curve within the uncertainty of the viscosity, which is estimated to be $\pm 2\%$.

An analogous treatment may be applied to the self-diffusion coefficient data of McCool and Woolf [3] for the two isotherms at 313.2 and 328.2 K. In this case we employ the quantity

$$D^* = 5.030 \times 10^8 (M/RT)^{1/2} D/V^{1/3} \tag{7}$$

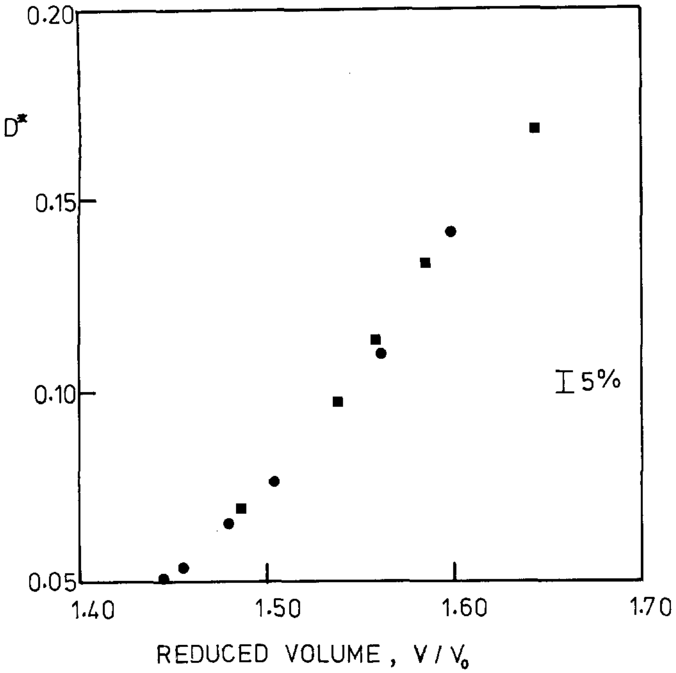

Fig. 4. The function D^* for carbon tetrachloride. Experimental data [3]: ●, 313.2 K; ■, 328.2 K.

for a test of the hypothesis that

$$D^* = F_D(V/V_0) \tag{8}$$

Again, the values of V_0 have been interpolated from the analysis of the thermal conductivity data. Figure 4 contains a plot of D^* against V/V_0 for the two isotherms and shows that the data fall on a single curve within their estimated uncertainty of $\pm 4\%$.

5. CONCLUSIONS

It has been shown that for carbon tetrachloride any of the three transport properties viscosity, thermal conductivity, and self-diffusion may be represented in the form

$$X^* = F_X(V/V_0)$$

in which X represents the particular property. The function F_X is temperature independent and the values of V_0, which are weakly temperature dependent, are consistent among the three properties. The form of this correlation is suggested by the hard-sphere theories of the fluid state but the various functions F_X have been derived empirically and not with the aid of that theory.

Although the temperature range of the data available for carbon tetrachloride is rather limited, these findings are similar to those revealed by an analogous study of liquid hydrocarbons over a much wider temperature range [12]. A correlation of this type has the advantage that measurements of one property over a range of thermodynamic states may be used to evaluate either the same property or another property over a different range of states. Further measurements of all three transport coefficients for a number of fluids over an extensive range of states are evidently necessary to confirm the usefulness of the scheme for predictive purposes.

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