

Thermal Conductivity of *n*-Tridecane at Pressures up to 500 MPa in the Temperature Range 35–75°C

M. Mustafa,¹ M. Sage,¹ and W. A. Wakeham¹

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Thermal conductivity coefficients are reported for liquid *n*-tridecane along three isotherms, 35, 48, and 73°C, and for pressures from 20 to 500 MPa. The measurements have been made with a transient hot-wire instrument, and the results, when corrected for the effects of radiation absorption, have an estimated uncertainty of $\pm 0.7\%$. The thermal conductivity as a function of density along isotherms can be represented by means of the same form of equation as that found suitable for other normal alkanes, and this is based upon a heuristic modification of the van der Waals theory of liquids.

KEY WORDS: high pressure; *n*-alkanes; *n*-tridecane; thermal conductivity.

1. INTRODUCTION

In a series of earlier publications [1–3], the transient hot-wire technique has been employed for the absolute measurement of the thermal conductivity of normal alkanes containing an odd number of carbon atoms. The results of the measurements have allowed the development of a correlation scheme for the thermal conductivity of these liquids [3] based upon a heuristic extension of the van der Waals model of a liquid [3–5]. The correlation scheme also permits the prediction of the density dependence of a normal alkane along an isotherm from a measurement at a single pressure with an accuracy commensurate with that of direct measurement [3]. In this paper, we report the results of new measurements of the thermal conductivity of *n*-tridecane along three isotherms, 35, 48, and 73°C. Tridecane is the heaviest alkane studied in our work and represents the final alkane with an

¹Department of Chemical Engineering and Chemical Technology, Imperial College, London SW7 2BY, England.

odd number of carbon atoms which it is our intention to examine at this stage.

2. EXPERIMENTAL

The transient hot-wire instrument employed for the measurements has been described in detail earlier [1]. The operating procedures and the methods of data analysis also remained unchanged [1,6]. The measurements have been carried out along three isotherms, 35, 48, and 73°C. The highest pressure at which measurements were performed was 500 MPa, but at the lower temperatures the upper pressure attained was limited by the need to avoid solidification of the material. The samples of *n*-tridecane were supplied by Koch–Light Laboratories and had a stated purity of better than 99.5%. Chromatographic analysis and refractive index measurements demonstrated that the purity was in excess of 99.9% so that the samples were merely degassed before use.

The density of the liquid has been taken from the data of Doolittle [7], whereas the heat capacity, required for the analysis of the experimental data, has been obtained from the results of Finke et al. [8]. The optical properties of the fluid, necessary to apply a correction for the effects of radiation absorption in the liquids [1,2,9], have been measured by standard techniques. In particular, the mean extinction coefficient, κ , has been determined under ambient conditions, and for *n*-tridecane it has been found that $\kappa = 1235 \text{ m}^{-1}$. Because it has not been possible to determine κ under any other conditions, this value has been employed uniformly in making the correction for radiation.

3. RESULTS

Tables I–III contain a summary of the experimental results for the thermal conductivity of *n*-tridecane at the three nominal temperatures, 35, 48, and 73°C, respectively. The tables include the apparent thermal conductivity at the nominal temperature and reference density, $\lambda_{\text{app}}(T_{\text{nom}}, \rho_r)$ and the radiation-free values $\lambda(T_{\text{nom}}, \rho_r)$. The thermal conductivity at the nominal temperature and the experimental pressure is also included.

The correction of the experimental thermal conductivities to a common nominal temperature has been performed by application of linear corrections [1] which did not exceed $\pm 0.1\%$. The additional uncertainty introduced into the data by this process is therefore insignificant.

The correction for radiation absorption has been applied in the manner detailed by Menashe and Wakeham [9]. In the worst case, for measurements at the lowest density and highest temperature, this correction

Table I. The Thermal Conductivity of *n*-Tridecane at $T_{\text{nom}} = 35^{\circ}\text{C}$

Pressure, P (MPa)	Density, ρ_r ($\text{kg} \cdot \text{m}^{-3}$)	Thermal conductivity		
		$\lambda_{\text{app}}(T_{\text{nom}}, \rho_r)$ ($\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	$\lambda(T_{\text{nom}}, \rho_r)$ ($\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	$\lambda(T_{\text{nom}}, P)$ ($\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)
24.3	762.3	143.1	140.3	140.4
35.0	768.9	147.3	144.4	144.4
46.2	775.0	150.9	148.0	148.0
56.5	780.4	153.7	150.8	150.7
66.0	784.8	155.9	152.9	152.9
76.9	789.8	158.1	155.1	155.1
86.4	794.3	162.7	159.7	159.5
94.0	797.3	163.6	160.6	160.6
107.0	802.5	167.0	163.9	163.8
117.2	806.3	169.1	166.0	165.9
126.5	809.7	171.6	168.4	168.3
142.1	815.0	175.5	172.3	172.2
151.5	818.3	176.9	173.7	173.6
163.0	821.9	179.7	176.5	176.4
178.3	826.8	182.4	179.1	178.9

Table II. The Thermal Conductivity of *n*-Tridecane at $T_{\text{nom}} = 48^{\circ}\text{C}$

Pressure, P (MPa)	Density, ρ_r ($\text{kg} \cdot \text{m}^{-3}$)	Thermal conductivity		
		$\lambda_{\text{app}}(T_{\text{nom}}, \rho_r)$ ($\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	$\lambda(T_{\text{nom}}, \rho_r)$ ($\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	$\lambda(T_{\text{nom}}, P)$ ($\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)
33.3	759.5	142.9	139.9	140.2
41.7	764.5	145.9	142.9	143.1
54.2	771.4	149.5	146.4	146.6
64.5	776.6	152.5	149.3	149.5
74.0	781.3	155.2	152.0	152.2
82.7	785.4	157.5	154.2	154.4
93.5	790.1	160.0	156.7	156.8
111.1	797.2	164.0	160.6	160.8
116.3	799.3	165.6	162.2	162.2
125.7	802.9	167.9	164.5	164.5
151.4	811.9	173.5	170.0	170.1
160.3	816.4	175.4	171.9	171.9
175.6	819.7	178.4	174.8	174.9
201.4	827.5	184.0	180.3	180.4
215.6	831.5	187.5	183.8	183.8
227.5	834.7	188.5	184.8	184.9
239.0	837.7	191.3	187.6	187.6
254.3	841.6	193.7	189.9	190.0

Table III. The Thermal Conductivity of *n*-Tridecane at $T_{\text{nom}} = 73^{\circ}\text{C}$

Pressure, P (MPa)	Density, ρ_r ($\text{kg} \cdot \text{m}^{-3}$)	Thermal conductivity		
		$\lambda_{\text{app}}(T_{\text{nom}}, \rho_r)$ ($\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	$\lambda(T_{\text{nom}}, \rho_r)$ ($\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	$\lambda(T_{\text{nom}}, P)$ ($\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)
51.6	756.1	144.4	140.5	140.7
64.8	763.6	148.5	144.5	144.7
76.1	769.5	152.0	147.9	148.1
90.1	777.1	156.2	152.1	152.3
118.5	788.6	162.7	158.4	158.6
120.4	789.4	163.3	159.1	159.3
134.5	795.0	166.8	162.5	162.6
141.0	797.4	167.9	163.6	163.7
152.8	801.7	170.8	166.5	166.6
167.2	806.7	173.6	169.2	169.3
181.3	811.5	177.0	172.6	172.7
202.0	818.0	181.5	177.0	177.0
216.3	822.2	183.1	178.5	178.6
241.7	829.4	187.7	183.1	183.2
259.1	834.1	191.0	186.3	186.4
274.7	838.2	193.2	188.6	188.6
292.6	842.6	196.4	191.7	191.7
318.1	848.7	200.4	195.6	195.6
341.1	853.9	204.1	199.3	199.2
362.3	858.6	207.8	202.9	202.9
388.6	864.2	211.1	206.2	206.2
413.7	869.3	215.0	210.0	209.9
436.1	873.8	218.2	213.2	213.1
468.4	879.9	222.6	217.6	217.5

amounts to as much as 2.6% in the thermal conductivity. It is estimated [1, 9] that the error in the evaluation of this correction may be as much as 20% [9]. The application of this correction therefore constitutes the major contribution to the uncertainty in the final thermal conductivity data. Accounting for the remaining random errors of measurement, it is estimated that the tabulated thermal conductivity has an uncertainty of $\pm 0.7\%$.

In order to permit a comparison with the results of earlier measurements, the pressure dependence of the thermal conductivity along each isotherm has been represented by the empirical equation

$$\lambda = b_0 \left[1 + b_1(P - P') + b_2(P - P')^2 + b_3(P - P')^3 \right] \quad (1)$$

The coefficients of this equation for each temperature are listed in Table IV, and Fig. 1 contains a plot of the deviations of the present experimental

Table IV. Coefficients of the Correlating Equation (1) for the Thermal Conductivity of *n*-Tridecane as a Function of Pressure

<i>T</i> (°C)	<i>P'</i> (MPa)	<i>b</i> ₀ (mW · m ⁻¹ · K ⁻¹)	10 ³ <i>b</i> ₁ (MPa) ⁻¹	10 ⁶ <i>b</i> ₂ (MPa) ⁻²	10 ⁹ <i>b</i> ₃ (MPa) ⁻³
35	100	162.10	1.527	- 2.595	2.35
48	100	158.45	1.538	- 2.168	4.01
73	200	176.01	1.078	- 1.371	2.44

data from the correlation. The maximum deviation amounts to ±0.6%, whereas the standard deviation of the entire body of data is one of ±0.2%. Figure 1 includes the results of Mustafaev [10] at a temperature of 35°C. The deviation of these earlier values from the present correlation is no more than 2%, which is consistent with the mutual uncertainty of the two sets of results. However, the pressure dependence indicated by the two sets of

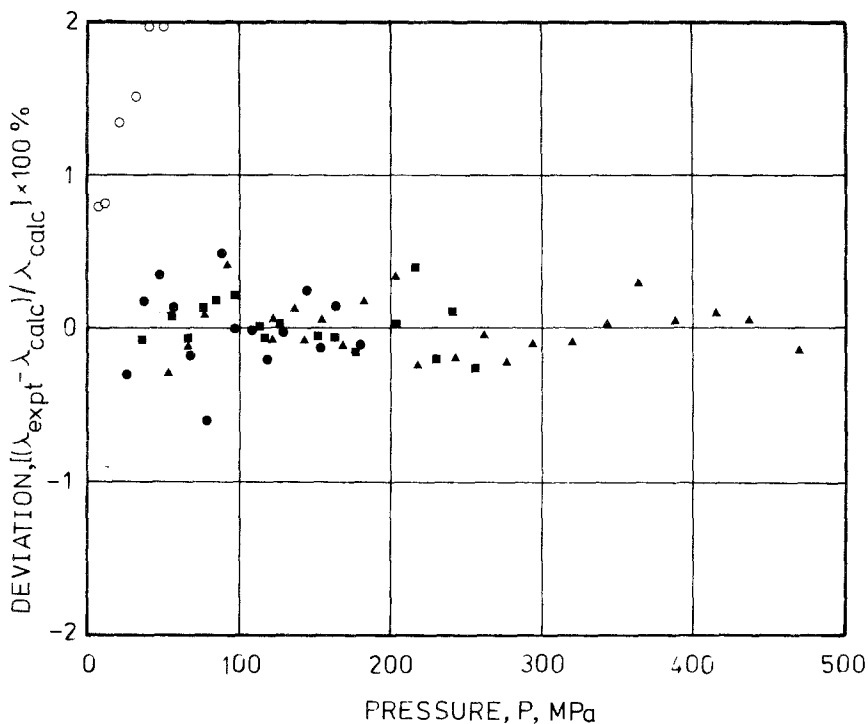


Fig. 1. Deviations of experimental thermal conductivity data from the correlation of Eq. (1). Present work: ●, 35°C; ■, 48°C; ▲, 73°C. Mustafaev [10]: ○, 35°C.

measurements shows a systematic discrepancy. The present results are to be preferred owing to their higher precision.

4. THE DENSITY DEPENDENCE

The van der Waals model of a liquid has often been employed for the development of effective methods for the description of the density dependence of the transport properties of monatomic and polyatomic liquids [5]. In the case of the thermal conductivity of polyatomic fluids, the use of this model and the application of the Enskog theory to it are less securely based than for other properties. Nevertheless, the model has proved remarkably successful for the purposes of correlation [2, 3]. The development of the correlation [3] makes use of a quantity λ^* defined by the equation

$$\lambda^* = \frac{1.936 \times 10^7 \lambda V^{2/3} (M/RT)^{1/2}}{[1 + 0.352 C_{v,int}^0/R]} \quad (2)$$

in terms of experimental quantities measured in S.I. units. Here, λ is the thermal conductivity of the fluid at a molar volume V and a temperature T , M is the molecular weight of the substance, and $C_{v,int}^0$ is the contribution of internal modes to its ideal gas heat capacity.

The essential feature of the development leading to Eq. (2) is that it suggests [3] that the quantity λ^* , for a particular fluid, should be a function only of a reduced molar volume

$$\lambda^* = f(V/V_0) \quad (3)$$

Consequently, it should be possible to superimpose plots of λ^* versus $\ln V$ for one fluid at different temperatures by means of translations along the $\ln V$ axis. Figure 2 shows the results of this process for the present measurements of the thermal conductivity of *n*-tridecane. The values of the characteristic volume, V_0 , at 35°C, taken from our earlier work [3], and the values derived at the other temperatures are given in Table V, together with the values adopted for $C_{v,int}^0$. Figure 2 confirms that the quantity λ^* is only a function of (V/V_0) as has already been found for *n*-heptane, *n*-nonane, and *n*-undecane [2]. The entire body of experimental data for *n*-tridecane may therefore be represented by the simple correlation

$$\ln \lambda^* = 2.8630 - 2.2374 \ln(V/V_0) \quad (4)$$

which has also proved appropriate for the lower members of the homologous series [2]. Figure 3 contains a plot of the deviations from this

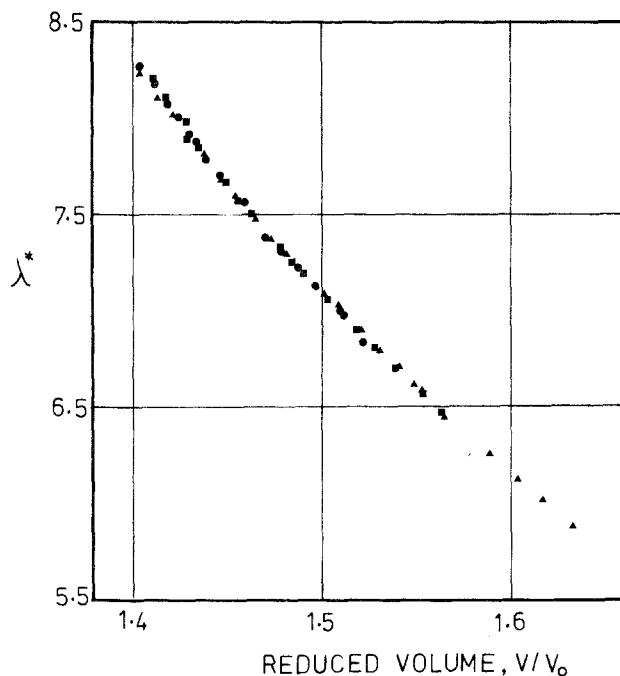


Fig. 2. The quantity λ^* , defined by Eq. (2) as a function of reduced molar volume for *n*-tridecane along three isotherms: ●, 35°C; ■, 48°C; ▲, 73°C.

correlation, and reveals that the maximum deviation is one of $\pm 0.8\%$, the standard deviation being one of $\pm 0.3\%$. These values are commensurate with the uncertainty of the experimental data.

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Table V. Characteristic Volumes and Internal Heat Capacities for the Correlation of the Thermal Conductivity of *n*-Tridecane as a Function of Density According to Equation (4)

T (°C)	Characteristic volume, $10^6 V_0$ ($\text{m}^3 \cdot \text{mol}^{-1}$)	$C_{v,int}^0 / R$
35	159.1	34.50
48	155.5	35.80
73	149.5	38.30

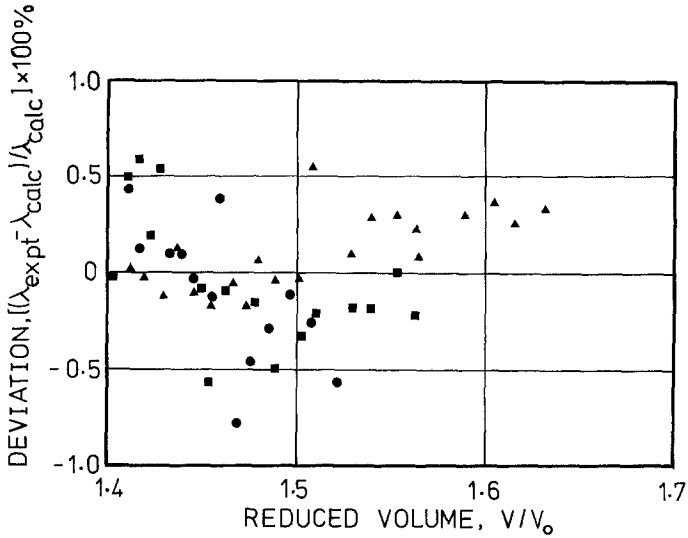


Fig. 3. Deviations of the thermal conductivity data from the correlation of Eq. (4). ●, 35°C; ■, 48°C; ▲, 73°C.

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