The Thermal Conductivity of *n*-Hexane, *n*-Heptane, and *n*-Decane by the Transient Hot-Wire Method

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New absolute measurements of the thermal conductivity of liquid *n*-hexane, *n*-heptane, and *n*-decane are reported. The measurements have been carried out in the temperature range 300–370 K at atmospheric pressure in a transient hot-wire instrument. The accuracy of the measurements is estimated to be $\pm 0.5\%$. The density dependence of the thermal conductivity of *n*-hexane and *n*-heptane is found to be well described by a universal equation for the hydrocarbons based on a rough hard-sphere model. The measurements of the three hydrocarbons studied are also employed to generate more accurate effective core volumes, which are the only parameters characteristic of the fluid required for the application of the proposed universal scheme.

KEY WORDS: *n*-hexane; *n*-heptane; *n*-decane; thermal conductivity; transient hot-wire method.

1. INTRODUCTION

In a previous paper [1], an instrument for the measurement of the thermal conductivity of liquids was described and experimental data for the thermal conductivity of toluene in the temperature range 300–350 K and atmospheric pressure were reported. The accuracy of the experimental results was estimated to be $\pm 0.5\%$ and the advantages of the present instrument over other similar devices were discussed. In this paper we

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present measurements of three normal alkanes, n-hexane, n-heptane, and n-decane in the temperature range 300–370 K at atmospheric pressure.

At present, there is no rigorous exact kinetic theory of transport processes in liquids. There are, however, a number of simplified statistical mechanical theories which can form the basis of a reliable correlation and prediction scheme. Such a scheme, based on the application of the Enskog theory [2] to the van der Waals model of a fluid [3], has been proposed by Li et al. [4]. The proposed correlation procedure allows the thermal conductivity of 11 hydrocarbon liquids, over the temperature range 112–370 K and for pressures up to 700 MPa, to be represented by a single universal equation containing just one parameter characteristic of the fluid at each temperature. The measurements presented in this paper are compared with thermal conductivity values calculated by this scheme.

2. EXPERIMENTAL

The transient hot-wire instrument, described in detail elsewhere [1], has been employed unchanged for the present thermal conductivity measurements. The measurements were all carried out at 390 Pa above atmospheric pressure. The temperature range examined was 295–325 K for n-hexane, 300–345 K for n-heptane, and 300–365 K for n-decane. The sample of n-hexane was supplied by Merck and the purity was better then 99.5%. The samples of n-heptane and n-decane were supplied by B.D.H. Chemicals Ltd. and the purity was found to be better than 99.5%.

The method of treating the effect of radiative heat transport adopted is the same as that proposed by Li et al. [5] and Castro et al. [6], according to which if no curvature appears in a plot of the temperature rise against the logarithm of the time, no correction to the thermal conductivity values is necessary. In this work, we have thus examined each experimental run for signs of curvature by a statistical method [6], and in no case was such an effect noticed.

As a check of the continuing good operation of the instrument, toluene was measured before and after each liquid. The values obtained were in full agreement with those reported earlier [1].

3. RESULTS

Table I lists the experimental data for the thermal conductivity of n-hexane, n-heptane, and n-decane at atmospheric pressure[4] as a function of

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[4] As $(\partial\lambda/\partial P)_T \sim 0$ near the saturation boundary, we can assume that the results were obtained at 0.1 MPa.

Table I. The Thermal Conductivity of n-Hexane, n-Heptane, and n-Decane at $P = 0.1$ MPa

n-Hexane		n-Heptane		n-Decane	
T (K)	λ (mW·m^{-1}·K^{-1})	T (K)	λ (mW·m^{-1}·K^{-1})	T (K)	λ (mW·m^{-1}·K^{-1})
297.35	120.9	305.80	120.9	300.08	132.4
300.52	119.8	307.00	120.4	305.60	131.1
301.65	119.6	309.09	119.7	310.82	129.7
305.09	118.5	311.91	119.0	315.05	128.4
307.26	117.6	315.02	118.1	320.31	127.2
309.31	116.9	317.31	117.3	325.00	125.9
310.63	116.3	320.81	116.3	332.12	124.4
313.51	115.5	324.18	115.3	339.59	122.2
316.92	114.6	327.00	114.6	344.07	121.5
318.90	113.8	328.52	114.1	349.00	120.1
321.80	113.3	329.86	113.6	354.23	118.7
324.77	112.3	331.93	113.2	357.92	117.9
		335.76	112.0	360.98	116.8
		342.63	109.6		

temperature. Accounting for all of the random errors of measurement, it is estimated that the tabulated thermal conductivity data have an uncertainty of better than $\pm 0.5\%$.

For the purposes of comparison of the present experimental data with the results of other investigators, the thermal conductivity values for each liquid have been represented by a linear function of the absolute temperature T as

$$\lambda = \alpha_0 + \alpha_1 T \tag{1}$$

Second-order fits showed no improvement. The coefficients α_i for each liquid, together with the standard deviation of the fit, are presented in Table II.

Table II. Coefficients of the Least-Squares Straight-Line Fit of the Thermal Conductivity as a Function of Temperature

	α_0 (mW·m^{-1}·K^{-1})	α_1 (μW·m^{-1}·K^{-2})	σ (%)
n-Hexane	215.5 ± 0.8	-318 ± 6	± 0.15
n-Heptane	211.9 ± 0.8	-298 ± 2	± 0.10
n-Decane	208.4 ± 0.7	-253 ± 2	± 0.13

Figure 1 contains a plot of the deviations of the present results from Eq. (1) for *n*-hexane. The maximum deviation of the measurements from the correlation is one of $\pm 0.2\%$, whereas the standard deviation is one of $\pm 0.15\%$. Figure 1 also includes the results of other investigators. We have been unable to compare our measurements with the high-accuracy measurements of Li et al. [5] because the latter were conducted at elevated pressures, so that the extrapolation to atmospheric pressure could be done only at the expense of their accuracy. The results of Mukhamedzyanov et al. [7] were found to be in good agreement with the present correlation. The measurements of other investigators were found to depart as much as 8% from the present correlation.

Figure 2 contains a plot of the deviations of the new results from Eq. (1) for *n*-heptane. The maximum deviation of our measurements from the correlation is one of $\pm 0.2\%$, whereas the standard deviation is one of $\pm 0.1\%$. In Fig. 2, a comparison with the measurements of other investigators is also presented. In addition to the comments for *n*-hexane, we note the good agreement (within 0.2%) with a correlation based on accurate transient measurements for *n*-heptane proposed as a secondary standard by Castro et al. [14], based partially on the transient measurements of Castro et al. [17] and Nagasaka and Nagashima [15].

Finally, in Fig. 3, a plot of the deviations of the new results from Eq. (1) for *n*-decane is presented. The maximum deviation of our measurements from the correlation is one of $\pm 0.2\%$, whereas the standard
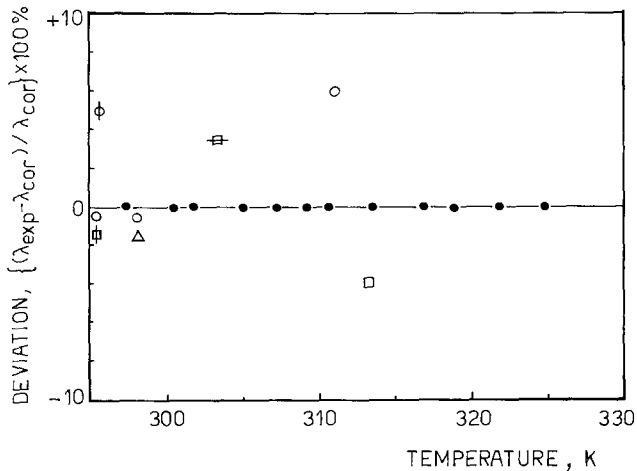

Fig. 1. Deviations of the experimental thermal conductivity values for *n*-hexane from Eq. (1). (●) Present work; (○) Ref. 7; (□) Ref. 8; (△) Ref. 9; (⊕) Ref. 10; (—⊖—) Ref. 11; (—⊟—) Ref. 12; (⊡) Ref. 13.
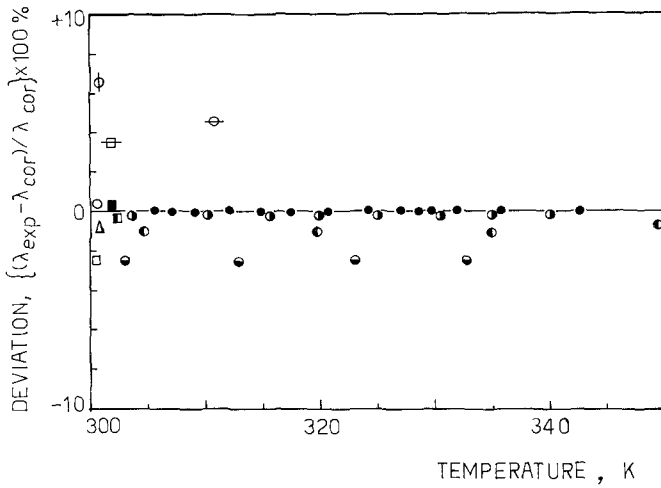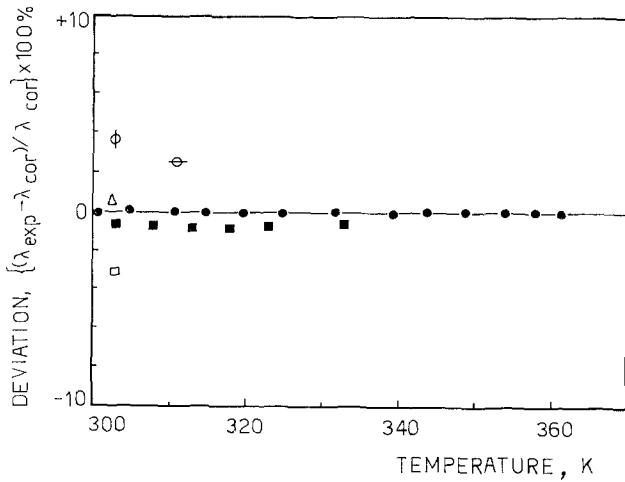
Fig. 2. Deviations of the experimental thermal conductivity values for n-heptane from Eq. (1). ($\bullet$) Present work; ($\circledcirc$) Ref. 15; ($\ominus$) Ref. 16; ($\blacksquare$) Ref. 17; ($\blacksquare$) Ref. 18; ($\bigcirc$) Ref. 7; ($\square$) Ref. 8; ($\triangle$) Ref. 9; ($\oplus$) Ref. 10; ($-\ominus-$) Ref. 11; ($-\boxminus-$) Ref. 12. Also presented are the deviations from the standard reference data proposed by Nieto de Castro et al. [14] ($\circledcirc$).

Fig. 3. Deviations of the experimental thermal conductivity values for n-decane from Eq. (1). ($\bullet$) Present work; ($\blacksquare$) Ref. 19; ($\square$) Ref. 8; ($\triangle$) Ref. 9; ($-\ominus-$) Ref. 11; ($\oplus$) Ref. 20.

deviation is one of $\pm 0.13\%$. Comparisons with other investigators, in this case, are limited. However, there is good agreement (within 0.8%) with the transient measurements of Castro et al. [19], if these measurements are properly corrected for radiation effects.

4. DISCUSSION

A heuristic modification of the application of the Enskog theory [2] to the van der Waals model of a dense fluid [3] suggests that the experimental quantity [4, 21]

$$\lambda^* = \frac{64}{75} \left\{ \frac{m\pi}{k^3 T} \right\}^{1/2} \frac{2^{1/3}}{N^{2/3}} \lambda V^{2/3} \tag{2}$$

for a particular liquid is a function only of ratio of the molar volume, V, to an effective core volume, V_0, so that

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

Here m is the molecular mass, k the Boltzmann constant, N the Avogadro number, T the absolute temperature, and λ the experimentally measured thermal conductivity. This implies that it should be possible to superimpose plots of λ^* against $\ln V$ for one fluid along several isotherms upon one another merely by shifts along the $\ln V$ axis. The amount of the relative shift for two isotherms, then, determines the ratio of the effective core volume V_0 at the two temperatures. Assigning an arbitrary, but realistic, value to the core volume V_0 at the lowest temperature for which accurate measurements of the thermal conductivity exist, the values of $V_0(T)$ can be determined for each isotherm. Li et al. [4] used the accurate measurements of 11 hydrocarbon liquids over the temperature range 112–370 K and for pressures up to 700 MPa to determine the function $F(V/V_0)$ of Eq. (3). The simple curve of λ^* as a function of reduced molar volume can be represented by the equation

$$\lambda^* = 4.8991 - 2.2595 \ln(V/V_0) \tag{4}$$

where the effective core volume values for every liquid hydrocarbon studied were also calculated and tabulated [4]. The maximum deviation from the correlation ammounted to $\pm 4\%$. Although this deviation exceeds that which was achieved for individual liquids and the experimental errors, it is remarkable that such a wide body of data may be correlated by a single equation containing just one parameter characteristic of the fluid.

For our measurements of n-hexane and n-heptane we have used the density [22] and the effective core volumes calculated by Li et al. [4] to

Table III. Smoothed Effective Core Volume Values Calculated from Eqs. (2) and (4) and Our Experimental Data of the Thermal Conductivity

T (K)	$10^6 V_0$ ($m^3 \cdot mol^{-1}$)		
	n-Hexane	n-Heptane	n-Decane
300	73.15	88.40	142.66
305	73.12	88.35	142.55
310	73.09	88.30	142.44
315	73.07	88.25	142.34
320	73.06	88.21	142.24
325	73.05	88.17	142.14
330		88.14	142.04
335		88.11	141.95
340		88.08	141.86
345		88.05	141.77
350			141.68
355			141.60
360			141.52
365			141.45

calculate the thermal conductivity from the Eqs. (2) and (4). The predicted values for both n-hexane and n-heptane differ by less then 2.5% from our experimental values. Since data at atmospheric pressure were not included in the deviation of Eq. (4), the deviations, which are well within the accuracy of the proposed scheme, confirm the predictive power.

In the case of n-decane no values of effective core volumes were given or exist in the literature. We have therefore used the same Eqs. (2) and (4) to compute the effective core volume values as a function of temperature for n-decane using just our atmospheric pressure data. In Table III, the smoothed effective core volume values that reproduce the experimental values of the thermal conductivity of n-hexane, n-heptane, and n-decane within ± 0.1% are given.

ACKNOWLEDGMENTS

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