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Thermal Conductivity of Isopentane in the Temperature Range 307–355 K at Pressures up to 0.4 GPa

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This paper reports the results of new, absolute measurements of thermal conductivity of isopentane in the temperature range 307–335 K at pressures up to 0.4 GPa. The experimental data have an estimated uncertainty of ±0.3%. The density dependence of the thermal conductivity along the various isotherms has been represented with the aid of a single universal equation derived for a series of alkanes and based upon the hard-sphere model of dense fluids. An even more general prediction scheme for the thermal conductivity of liquids developed initially for normal alkanes is found to predict the present data within ±5%.

KEY WORDS: hard-sphere theory; isopentane; thermal conductivity.

1. INTRODUCTION

In a series of earlier papers [1–4], the thermal conductivity of a series of liquid hydrocarbons had been determined with a high accuracy over a range of pressures up to 700 MPa. Among these fluids have been included normal alkanes, branched alkanes, and cyclic compounds. It has been shown [5] that the thermal conductivity can be represented over this wide range of temperatures by means of a single consistent equation based upon a hard-sphere model of the fluid. One feature revealed in two of these studies [6, 7] was the substantial difference between the thermal

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conductivity of isomers under the same conditions of temperature and pressure. The analysis of the results for such systems indicated that this was the result of a substantial difference of the density of the two isomers, under similar conditions of temperature and pressure, combined with a small difference in the characteristic molar volume of the molecules.

In an attempt to confirm this observation, the present paper reports the results of measurements of the thermal conductivity of isopentane as a complement to the earlier measurements of *n*-pentane [4].

2. EXPERIMENTAL

The thermal conductivity measurements have been performed in the high-pressure transient hot-wire instrument described elsewhere [1]. The measurements have been carried out along four isotherms in the temperature range 307 to 355 K at pressures up to 0.4 GPa. The isopentane sample has been supplied by BDH Chemicals with a stated purity better than 99%. Following distillation and degassing, a purity in excess of 99.9% was achieved.

The density of isopentane has been measured by Bridgman [8] under the conditions of interest. For the purpose of interpolation in the tabulated densities, we have employed an equation proposed by Hudleston [9], which provided a satisfactory description of the data. The heat capacity of isopentane required for the application of small corrections to the experimental data has been taken from the compilation of Vargaftik [10] and has been assumed to be pressure independent. Since the corrections required are very small, the effect of this assumption on the final thermal conductivity data reported is negligible.

3. RESULTS

Table I lists the experimental data for the thermal conductivity of isopentane along the four isotherms at 307.65, 321.15, 336.15, and 355.15K. In this table we provide the thermal conductivity adjusted to a nominal temperature by means of a linear correction, which never exceeded ±0.2% at both the experimental pressure, P, and the reference density, ρ_r [11].

It is estimated that the accuracy of the thermal conductivity data is ±0.3%. The accuracy of the density data reported by Bridgman [8] included in the tables is more difficult to estimate but an uncertainty of ±0.5% seems reasonable.

The thermal conductivity of isopentane has been correlated with pressure along each isotherm, for the purpose of interpolation only, by an equation of the form

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

The optimum coefficients are listed in Table II, while Fig. 1 is an illustration of the deviations of the experimental data from the correlating equation. In no case do the deviations exceed ±0.8 %, while the standard deviation is ±0.3 % and is consistent with the estimated accuracy of the data.

The thermal conductivity of isopentane is typically 10 % lower than that of the normal isomer [4] under similar conditions of temperature and pressure.

Table I. Thermal Conductivity of Isopentane

Pressure P (MPa)	Density $\rho_r(P, T_r)$ $(\mathrm{kg \cdot m^{-3}})$	Thermal conductivity $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$	
		$\lambda(T_{nom}, \rho_r)$	$\lambda(T_{nom}, P)$
	$T_{nom} = 307.65$ K		
31.7	640.7	117.5	117.4
68.3	669.8	131.7	131.6
149.2	709.8	158.2	157.8
164.8	715.7	163.0	162.8
205.0	729.8	172.6	172.2
252.8	744.9	184.3	183.9
307.0	760.2	195.3	195.1
406.1	783.1	212.5	212.6
	$T_{nom} = 321.15$ K		
46.4	643.8	119.6	120.0
47.4	644.7	119.7	120.0
77.4	667.0	133.5	133.4
105.8	683.2	142.1	142.3
107.7	684.2	141.6	141.9
143.4	700.4	151.8	152.8
163.2	708.4	158.0	158.1
195.9	720.4	167.3	167.0
221.9	729.3	173.5	173.3
265.8	743.1	181.6	182.9
269.5	744.2	183.6	183.8
301.0	753.1	190.4	190.4
360.6	767.9	201.8	202.2
395.1	755.5	207.5	207.7

Table I. *(Continued)*

Pressure P (MPa)	Density $\rho_r(P, T_r)$ ($kg \cdot m^{-3}$)	Thermal conductivity ($mW \cdot m^{-1} \cdot K^{-1}$) $\lambda(T_{nom}, \rho_r)$	Thermal conductivity ($mW \cdot m^{-1} \cdot K^{-1}$) $\lambda(T_{nom}, P)$
	$T_{nom} = 336.15$ K		
53.2	637.8	119.3	119.6
74.3	654.6	129.1	129.1
105.6	674.0	139.2	139.5
133.3	688.0	148.4	148.3
152.9	696.7	153.7	153.7
192.3	712.1	163.9	163.8
218.6	721.3	170.3	170.6
259.6	734.6	179.5	179.6
303.0	747.1	188.0	188.8
354.5	760.3	198.6	198.7
391.3	768.8	205.6	205.4
	$T_{nom} = 355.15$ K		
52.9	621.2	118.5	118.7
80.8	645.1	129.4	129.5
108.4	663.8	139.1	139.1
158.0	689.3	153.6	153.5
195.6	704.4	164.1	163.6
200.9	706.3	164.7	164.6
253.7	723.9	176.9	177.0
307.9	739.8	188.4	188.2
351.1	751.5	196.2	194.5
389.8	761.2	202.4	202.2

Table II. Optimum Values for the Coefficients of the Correlation of the Thermal Conductivity of Isopentane as a Function of Pressure

T (K)	λ' ($mW \cdot m^{-1} \cdot K^{-1}$)	P' (MPa)	$10a_1$	10^2a_2	10^2a_3	10^2a_4
307.65	171.39	200	3.0352	−9.4113	0.3495	2.1314
321.15	167.69	200	2.8952	−4.8005	4.2870	−4.1893
336.15	165.93	200	2.9054	−6.4730	5.1148	−3.0886
355.15	164.60	200	3.0917	−10.2126	0.4623	2.6598

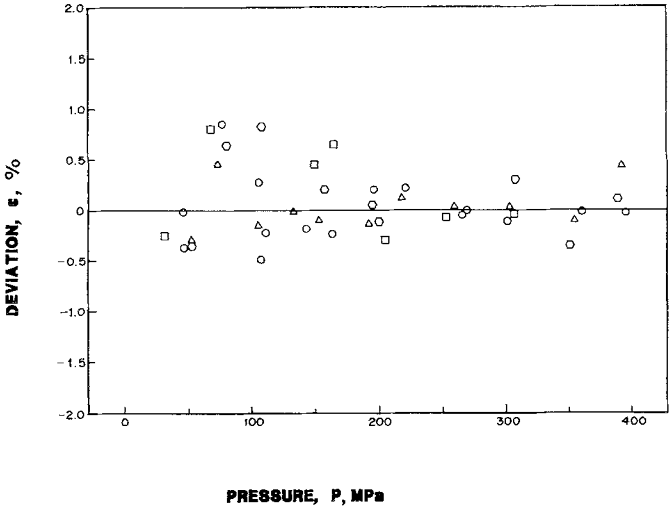

Fig. 1. Deviations of the thermal conductivity data from their representation as a function of pressure according to Eq. (1). Deviation, $\varepsilon = [(\lambda_{\text{exp}} - \lambda_{\text{calc}})/\lambda_{\text{calc}}] \times 100$.

4. THE DENSITY DEPENDENCE

Whereas the correlation of the pressure dependence of the thermal conductivity by means of Eq. (1) is suitable for interpolation, it has little or no value for extrapolation and prediction. For such purposes it has been shown [5] that a correlation in terms of the molar volume or density is much more suitable. The hard-sphere model of the dense fluid state [12] suggests the form of such a correlation since it leads to the result that for a monatomic fluid the quantity, λ^*, defined by the equation

$$\lambda^* = 1.963 \times 10^7 \, \lambda V^{2/3} (RT/M)^{-1/2} = F_\lambda(V/V_0) \qquad (2)$$

is a function of the reduced molar volume (V/V_0) only, where V_0 is a characteristic molar volume of the fluid which is but weakly temperature dependent.

Earlier studies have shown that if the result of Eq. (2) is carried over to polyatomic fluids, the function F_λ is nearly universal among a large group of normal alkanes, although the function is not that predicted from the hard-sphere theory [5]. It has also been shown that the same function, F_λ, is universal among a larger group of liquids including other hydrocarbons, alcohols, and diols, and this has been made the basis of a powerful prediction scheme for the thermal conductivity of such fluids [13].

For the normal alkanes the most recent and refined form for the function F_λ is that given by Assael et al. [14] as a result of a successful attempt to obtain a simultaneous representation of the thermal conductivity, viscosity, and self-diffusion coefficients of liquid normal alkanes over the temperature range 100–400 K and pressures up to 600 MPa. In this more sophisticated study, it emerges that it is not the function λ^* which is universal, but a slightly modified version of it, namely,

$$\log \frac{\lambda^*}{R_\lambda} = 1.0655 - 3.538\, V_r^{-1} + 12.121\, V_r^{-2} - 12.469\, V_r^{-3} + 4.562\, V_r^{-4} \tag{3}$$

in which

$$V_r = V/V_0 \tag{4}$$

and where R_λ is a factor introduced to account for deviations from the behaviour of smooth hard-spheres. The factor R_λ has been correlated as a function of carbon number, C, by the expression

$$R_\lambda = 0.1989\, C + 1.199 - 2.547\, C^{-1} + 6.404\, C^{-2} - 4.094\, C^{-3} \tag{5}$$

Evidently, the universal representation of the thermal conductivity of liquid alkanes contained in Eqs. (2) to (5) permits the evaluation of V_0 for isopentane for the four isotherms studied here. The results are contained in Table III, where they are compared with the results derived [14] from earlier measurements on *n*-pentane [4]. Both sets of V_0 values have been derived using the common reference value employed by Assael et al. for methane at 140 K, V_M, where

$$V_M = 20.825 \times 10^{-6}\ \text{m}^3 \cdot \text{mol}^{-1} \tag{6}$$

Figure 2 shows the deviations of the present data from this representation which is universal among all alkanes and shows that the departures do

Table III. Characteristic Molar Volume of *n*-Pentane and Isopentane

T (K)	$10^6\, V_0\ (\text{m}^3 \cdot \text{mol}^{-1})$ *n*-Pentane	Isopentane
307.65	66.3	65.1
321.15	66.0	65.0
336.15	65.7	64.9
355.15	65.5	64.8

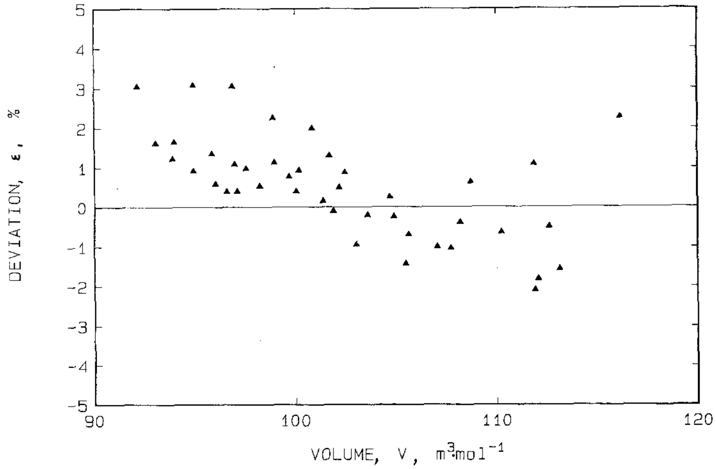

Fig. 2. Deviations of the thermal conductivity data from their representation by the universal correlation for alkanes of Eqs. (2) to (6).

not exceed ±3%. The fact that the deviations are systematic reflects the fact that there are small differences between the universal correlation and the behavior of isopentane which are of little practical significance. It is also noteworthy in Table III that the characteristic molar volume for isopentane is significantly smaller than that for the normal isomer as has been found for other branched isomers of alkanes [6, 7].

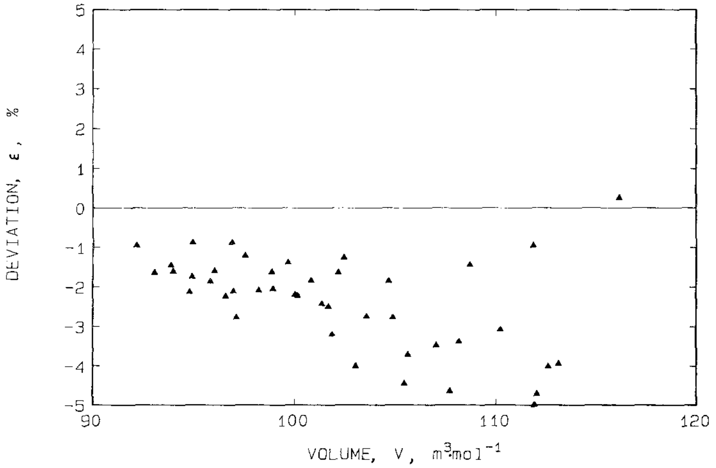

Fig. 3. Deviations of the thermal conductivity data for isopentane from the predictions of Eqs. (2) to (6) using Eqs. (7) and (8) to evaluate V_0.

Assael et al. [13, 14] have gone one step further in the representation of the thermal conductivity of normal alkanes by representing the characteristic molar volume, V_0, of the series in terms of temperature and the carbon number. For alkanes with carbon numbers in the range C_5–C_{16} their representation is

$$10^6 V_0 = 106.677 - 13.655\,\theta + 1.6266\,\theta^2 + (C-6)(18.028 - 1.2\,\theta) \times (0.944 + 0.0035\,C) \tag{7}$$

where

$$\theta = T/100 \tag{8}$$

and V_0 is in $\mathrm{m^3 \cdot mol^{-1}}$. They have suggested that the same representation can be employed in conjunction with Eqs. (2) to (5) for the prediction of the thermal conductivity of branched isomers of alkanes with a relatively small error. Their argument suggests that it is the effect of the relative density of the isomers at the same temperature and pressure that leads to the greatly different thermal conductivity rather than the change in V_0. In order to test this suggestion we have evaluated V_0 for isopentane ($C=5$) using Eqs. (7) and (8) and then evaluated the thermal conductivity for the fluid according to Eqs. (2) to (6). Figure 3 compares the results of these predictions with the present experimental data. It can be seen that the deviations are no more than ±5% and that they are again systematic. Given that the prediction makes no use of experimental information on the thermal conductivity of isopentane, it may be regarded as satisfactory for many practical purposes. Evidently, though, a comparison of Figs. 2 and 3 demonstrates that the differences in the values of V_0 for the two isomers do have a physical significance.

5. CONCLUSIONS

New, absolute measurements of the thermal conductivity of liquid isopentane have been reported. An analysis using representations based on the hard-sphere theory of dense fluids shows that the principal source of difference between the thermal conductivity of two alkane isomers arises from the different densities of the fluids. The universal procedure for the evaluation of the thermal conductivity of liquid alkanes is shown to be able to predict the present data with an accuracy acceptable for many purposes.

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