

## **Thermal Conductivity of Benzene and Cyclohexane in the Temperature Range 36–90°C at Pressures up to 0.33 GPa**

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The paper describes new, accurate measurements of the thermal conductivity of benzene and cyclohexane in the temperature range 36–88°C and at pressures up to 0.33 GPa. The experimental data have an estimated accuracy of  $\pm 0.3\%$ . The density dependence of the thermal conductivity for both liquids is well represented by a simple power law relationship which is almost independent of temperature. The connection of this correlation to one previously established for normal alkanes is examined.

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**KEY WORDS:** benzene; cyclic hydrocarbons; cyclohexane; high pressure; liquids; thermal conductivity.

### **1. INTRODUCTION**

A series of earlier studies of the thermal conductivity of normal and branched alkanes [1–6] has shown that the density dependence of the thermal conductivity along an isotherm can be satisfactorily represented by a simple power law relationship based on the results of an empirical extension of the Enskog theory of dense fluids. Moreover, the power law has been found to be universal among the normal alkanes [4], although the universality does not extend to their branched isomers [6]. So far as other hydrocarbons are concerned the first liquid studied was toluene [7] for which the lack of suitable density data prevented a comparable analysis. Consequently, in this paper we report measurements of the thermal conductivity of

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Table I. Experimental Results for the Thermal Conductivity of Benzene

$T = 37^{\circ}\text{C}$				$T = 47.5^{\circ}\text{C}$			
$P$ (MPa)	$\rho_r$ ( $\text{kg} \cdot \text{m}^{-3}$ )	$\lambda(T_{\text{nom}}, \rho_r)$ ( $\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ )	$\lambda(T_{\text{nom}}, P)$ ( $\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ )	$P$ (MPa)	$\rho_r$ ( $\text{kg} \cdot \text{m}^{-3}$ )	$\lambda(T_{\text{nom}}, \rho_r)$ ( $\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ )	$\lambda(T_{\text{nom}}, P)$ ( $\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ )
1.6	862.1	137.6	137.7	4.6	853.4	135.5	135.6
7.9	867.8	140.3	140.2	10.9	858.8	137.4	137.5
10.3	869.8	141.4	141.3	13.4	861.1	139.1	139.2
19.7	876.9	144.3	144.3	20.1	866.7	141.5	141.6
30.7	885.0	148.0	148.0	41.0	882.5	148.9	148.9
41.7	892.6	151.6	151.6	60.7	895.6	154.9	154.9
51.4	898.7	154.9	154.8	79.4	906.5	160.3	160.3
61.3	904.8	157.6	157.5	81.5	907.8	161.0	160.9
74.5	912.4	161.7	161.5	100.2	917.5	166.0	165.9
81.8	916.3	163.4	163.3	122.6	928.1	171.3	171.3
91.4	920.5	166.4	166.6	122.4	927.9	171.3	171.3
				138.9	935.4	175.3	175.3
				147.1	939.1	176.9	176.8
				161.2	945.4	179.8	179.7

	$T = 71^{\circ}\text{C}$		$T = 87.5^{\circ}\text{C}$	
11.1	834.6	130.2	130.4	9.5
20.1	842.6	133.9	134.1	26.1
34.5	855.5	139.7	139.8	39.2
43.2	862.5	142.9	143.0	59.5
62.1	876.7	149.4	149.4	81.3
81.8	889.9	154.8	154.8	101.8
102.4	901.8	161.1	161.2	122.6
120.3	911.3	165.6	165.6	142.8
137.9	919.8	170.3	170.3	162.4
158.3	928.7	174.7	174.6	183.9
179.0	937.0	179.5	179.5	205.2
185.0	939.3	181.0	180.9	222.9
200.9	945.0	184.1	184.1	233.0
225.4	953.8	189.4	189.4	254.7
242.9	960.0	192.3	192.3	274.8
261.2	966.7	195.9	195.9	290.5
				312.3
				332.1
				816.1
				833.2
				845.3
				862.0
				877.5
				890.0
				901.0
				910.6
				919.0
				927.4
				934.9
				940.9
				944.2
				951.2
				957.5
				962.5
				969.9
				977.0
				124.5
				132.2
				136.8
				144.5
				151.2
				157.4
				163.2
				168.1
				173.0
				177.3
				182.4
				185.4
				187.9
				192.1
				195.8
				198.8
				202.6
				206.0

an aromatic hydrocarbon, benzene, and a cyclic alkane, cyclohexane, for which sufficient high-pressure density data exist to permit an analogous investigation.

## 2. EXPERIMENTAL PROCEDURE

The measurements have been carried out with the transient hot-wire instrument described in detail elsewhere [1]. Apart from the replacement of the platinum wires of the thermal conductivity cells, the equipment and operating procedures remained unchanged in the present work. The samples of benzene and cyclohexane were provided by B. D. H. Chemicals Ltd. The benzene had a stated purity of better than 99.8%, and the cyclohexane a purity in excess of 99.5%. Both purities were confirmed by analysis and the samples merely degassed before use.

The measurements were carried out along four nominal isotherms for each liquid. For benzene the nominal temperatures were 37, 47.5, 71, and 87.5°C; whereas for cyclohexane the temperatures were 36, 51, 80, and 88°C. At each isotherm the maximum pressure employed was set by the need to avoid solidification of the sample and did not exceed 332 MPa in any case. The heat capacities of the liquids, necessary for the application of small corrections, were taken from the compilation of Vargaftik [8]. For benzene the density was taken from the data of Dymond et al. [9], whereas for cyclohexane the combined results of two investigations by Isdale and his collaborators were employed [10, 11].

Each experimental run has been carefully analyzed to confirm the absence of any significant contribution from radiative heat transfer in the manner described earlier [7]. In none of the measurements was there any sign of such a contribution, so that the thermal conductivity data reported are radiation-free values.

## 3. RESULTS

Tables I and II contain the experimental results for the thermal conductivity of benzene and cyclohexane along the four isotherms. The tables list the thermal conductivity at the nominal temperature and the reference density,  $\lambda(T_{\text{nom}}, \rho_r)$ , as well as the values at the experimental pressure  $\lambda(T_{\text{nom}}, P)$ . The correction of the data to the nominal temperature has been carried out as described earlier [1]. The correction never amounted to more than  $\pm 0.1\%$  so that the additional uncertainty introduced into the thermal conductivity is negligible. It is estimated that the thermal conductivity data have an uncertainty of  $\pm 0.3\%$ . Within the range of the direct measurements, the errors in the density are estimated to be between  $\pm 0.1$  and  $\pm 0.2\%$ .

Table II. Experimental Results for the Thermal Conductivity of Cyclohexane

$T = 36^{\circ}\text{C}$						$T = 51^{\circ}\text{C}$					
$P$ (MPa)	$\rho_r$ ( $\text{kg} \cdot \text{m}^{-3}$ )	$\lambda(T_{\text{nom}}, \rho_r)$ ( $\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ )	$\lambda(T_{\text{nom}}, P)$ ( $\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ )	$P$ (MPa)	$\rho_r$ ( $\text{kg} \cdot \text{m}^{-3}$ )	$\lambda(T_{\text{nom}}, \rho_r)$ ( $\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ )	$\lambda(T_{\text{nom}}, P)$ ( $\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ )	$P$ (MPa)	$\rho_r$ ( $\text{kg} \cdot \text{m}^{-3}$ )	$\lambda(T_{\text{nom}}, \rho_r)$ ( $\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ )	$\lambda(T_{\text{nom}}, P)$ ( $\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ )
5.3	767.8	117.3	117.4	13.0	761.2	116.3	116.4				
11.3	772.8	119.8	120.0	23.4	769.9	120.1	120.2				
14.8	775.7	120.8	120.9	29.0	774.5	122.2	122.2				
15.8	776.4	121.3	121.4	31.6	776.5	123.1	123.2				
21.4	780.8	123.3	123.3	33.7	778.1	123.7	123.7				
25.2	783.6	124.6	124.7	40.1	782.8	127.0	127.0				
30.4	787.3	126.2	126.3	47.5	788.0	128.7	128.7				
38.1	792.5	128.7	128.7	52.2	791.2	129.8	129.8				
40.3	794.0	129.2	129.3	57.5	794.6	131.5	131.5				
44.4	796.5	130.5	130.6	61.6	797.1	132.5	132.5				
45.5	797.1	130.9	130.9	70.5	801.7	134.7	134.7				
				73.6	803.5	135.7	135.7				
				76.8	805.2	136.3	136.4				
$T = 80^{\circ}\text{C}$						$T = 88^{\circ}\text{C}$					
18.6	741.1	111.4	111.4	24.4	740.6 <sup>a</sup>	112.1	112.2				
32.0	754.1	116.7	116.8	35.4	751.0	116.3	116.3				
38.9	760.1	119.1	119.1	44.8	758.8	119.7	119.7				
51.3	769.8	123.3	123.3	50.8	762.7	121.4	121.6				
62.5	777.7	127.0	127.0	63.3	772.4	125.7	125.7				
71.7	783.6	129.6	129.6	75.2	779.4	129.4	129.4				
81.1	789.1	132.2	132.2	81.4	782.4	131.2	131.4				
85.0	790.5	133.3	133.5	103.7	792.8	137.4	137.5				
93.4	794.9	135.6	135.8	120.3	799.4	141.7	141.8				
102.8	799.4	138.0	138.1	133.4	804.1	144.3	144.4				
103.2	799.6	138.0	138.2	144.7	808.0	147.3	147.3				
112.4	803.7	140.5	140.6								
120.3	806.9	142.4	142.5								

<sup>a</sup> Values in this column are extrapolated values.

However, some of the thermal conductivity data reported here extend beyond the range of the direct density measurements, and the uncertainty of the extrapolated density is obviously greater. The data for which extrapolation of the density has been necessary are indicated in the tables, and the points have not been included in the analysis of the density dependence of the thermal conductivity discussed below.

The pressure dependence of the thermal conductivity of the two liquids along an isotherm has been represented by means of the equation

$$\lambda = b_0 \left( 1 + \sum_{i=1}^3 b_i x^i \right) \quad (1)$$

where

$$x = (P/P')^{1/2}$$

The coefficients of this correlation which secure the best representation of the experimental data are listed in Table III. Figure 1 displays the deviations of the experimental data from this correlation for benzene and cyclohexane. For benzene the maximum deviation is  $\pm 0.4\%$ , whereas the standard deviation is one of  $\pm 0.1\%$ ; for cyclohexane the corresponding values are  $\pm 0.6\%$  and  $\pm 0.1\%$ . The only previous measurements of the thermal conductivity of benzene over a range of pressures were carried out by Rastorguev and Pugach [12]. These earlier results are included in the deviation plot in Fig. 1 and are seen to depart from the present correlation by as much as 7%. The present data are to be preferred owing to their higher accuracy. For

Table III. Coefficients of the Correlation of Eq. (1) for Benzene and Cyclohexane

$T$ (°C)	$P'$ (MPa)	$b_0$ (mW · m <sup>-1</sup> · K <sup>-1</sup> )	$b_1$	$b_2$	$b_3$
Benzene					
37.0	50.0	136.60	0.0237	0.1128	-0.0082
47.5	90.0	133.50	-0.0003	0.3090	-0.0860
71.0	140.0	122.64	0.1262	0.3662	-0.1016
87.5	180.0	116.06	0.2165	0.4370	-0.1307
Cyclohexane					
36.0	20.0	114.78	0.0158	0.0614	-0.0067
51.0	40.0	115.93	-0.1658	0.3659	-0.1117
80.0	60.0	100.60	0.0963	0.1990	-0.0418
88.0	70.0	103.49	-0.0590	0.4071	-0.1126

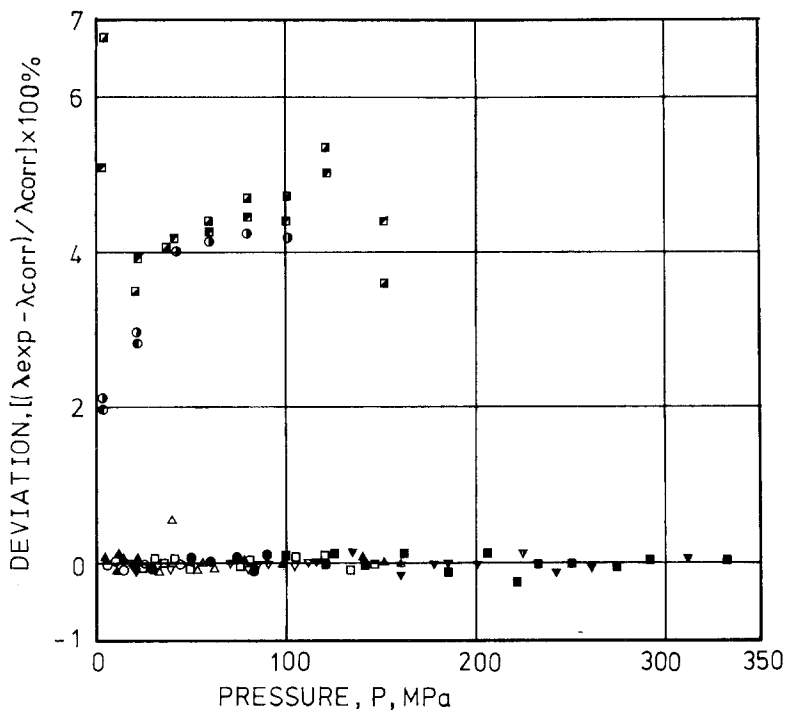


Fig. 1. Deviations of experimental data for the thermal conductivity of benzene and cyclohexane from the correlation of Eq. (1). Present work: Benzene, ● 37°C, ▲ 47.5°C, ▼ 71°C, ■ 87.5°C; cyclohexane, ○ 36°C, △ 51°C, ▽ 80°C, □ 88°C. Rastorguev and Pugach [12]: Benzene, ● 37°C, ○ 47.5°C, ■ 71°C, ▣ 87.5°C.

cyclohexane there have been no previous measurements at elevated pressures, and we postpone a comparison with the results at the saturation vapor pressure for both liquids until we have established a reliable method of extrapolation of the present data in the next section.

#### 4. THE DENSITY DEPENDENCE

The representation of the density dependence of the thermal conductivity of the normal alkanes studied previously has been based on the heuristic application of the Enskog theory to the van der Waals model of a liquid [4]. According to this analysis the experimental quantity

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

should be a function only of the ratio of  $V$ , the molar volume, to  $V_0$ , a characteristic rigid sphere volume of the fluid, so that

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

According to the model upon which Eq. (2) is based,  $V_0$  should exhibit only a weak temperature dependence, which reflects the finite steepness of the true repulsive intermolecular potential compared with that of a rigid sphere potential. In Eq. (2),  $C_{v,int}^0$  is the internal heat capacity of the fluid at zero density,  $R$  the universal gas constant, and  $M$  the molar mass. Equations (2) and (3) can form the basis of a correlation scheme for the density dependence of the thermal conductivity along an isotherm for both of the liquids studied here. Furthermore, small extensions to the analysis permit correlations to be developed which are of increasing generality and usefulness, but of marginally poorer accuracy. In the subsequent sections we examine three such correlations in turn.

#### 4.1. Individual Isotherms

In order to establish the most accurate representation of the present experimental data, we first treat each isotherm for each liquid independently. For benzene and cyclohexane we have adopted a value of the characteristic volume,  $V_0$ , at the lowest isotherm derived from the analysis of viscosity data by Dymond and his collaborators [9, 10]. Subsequently, values for  $V_0$  at the remaining temperatures have been deduced from the superposition of plots of  $\lambda^*$  against  $\ln V$  upon that for the lowest isotherm by shifts along the  $\ln V$  axis [4]. The values of  $V_0$  derived, together with the values of  $C_{v,int}^0$  employed in the calculations, are listed in Table IV. The same table includes the coefficients  $a_i$  in the equation

$$\ln \lambda^* = a_0 - a_1 \ln(V/V_0) \quad (4)$$

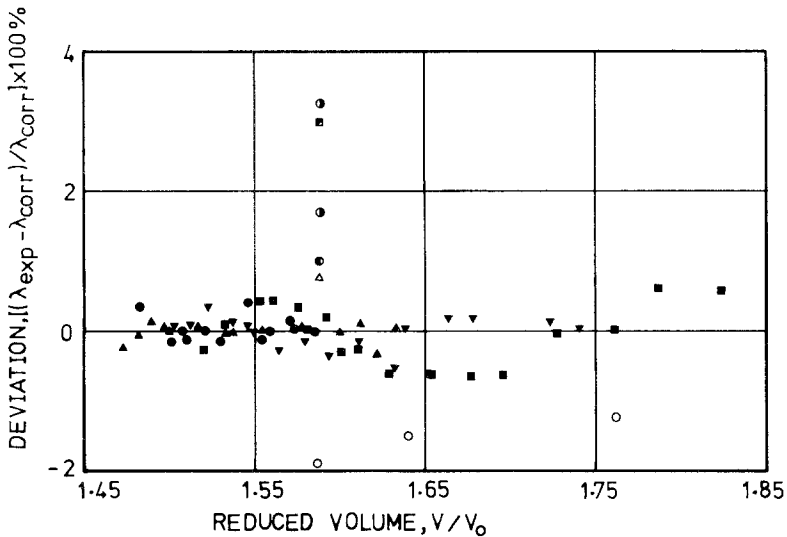
which provide the best representation of the experimental data for each fluid along individual isotherms. Figures 2 and 3 contain plots of the deviations from these correlations for benzene and cyclohexane, respectively. In no case do the deviations exceed  $\pm 0.7\%$ , whereas the standard deviation is  $\pm 0.18\%$  for benzene and  $\pm 0.17\%$  for cyclohexane. These figures are consistent with the estimated precision of the experimental data.

The correlation given by Eq. (4) and Table IV provides a secure means of extrapolation of the present thermal conductivity data to the conditions of saturation. Hence Figs. 2 and 3 include the departures of the most reliable of earlier results under these conditions [13–22] from this extrapolation. The



**Table IV.** Coefficients for the Correlation of Eq. (4), Internal Heat Capacities and Characteristic Volumes for Benzene and Cyclohexane

$T$ (°C)	$a_0$	$a_1$	$C_{v,int}^0/R$	$10^6 V_0$ ( $m^3 \cdot mol^{-1}$ )
Benzene				
37.0	3.071	2.175	7.772	57.17
47.5	3.050	2.127	8.165	56.06
71.0	3.041	2.111	9.026	53.78
87.5	3.071	2.176	9.616	52.49
Cyclohexane				
36.0	2.690	2.220	10.843	74.13
51.0	2.666	2.158	11.621	72.01
80.0	2.688	2.215	13.132	68.44



**Fig. 2.** Deviations of experimental data for the thermal conductivity of benzene from the correlation of Eq. (4). Present work: ● 47°C, ▲ 47.5°C, ▼ 71°C, ■ 85.5°C, ○, Kashiwagi et al. [13]; △, Horrocks et al. [14]; ○, Poltz and Jugel [15]; ○, Riedel [16]; ■, Schmidt and Leidenfrost [17].

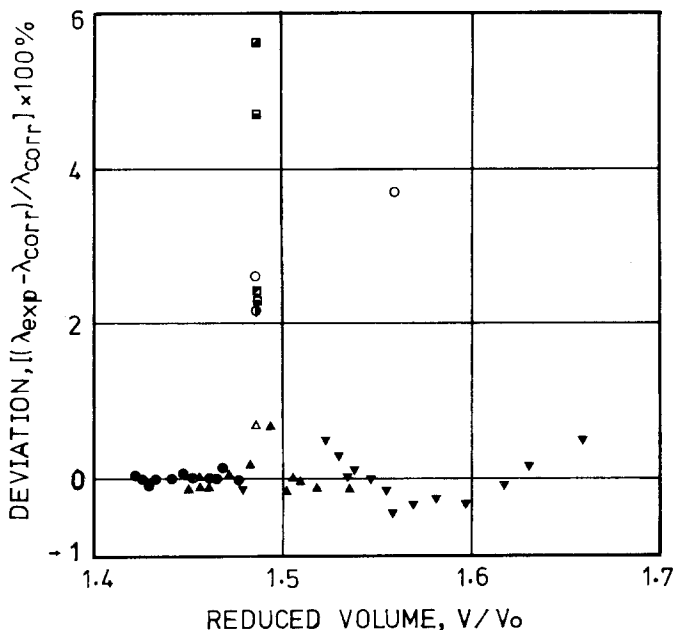


Fig. 3. Deviations of experimental data for the thermal conductivity of cyclohexane from the correlation of Eq. (4). Present work: ● 36°C, ▲ 51°C, ▼ 80°C. ○, Kashiwagi et al. [13]; △, Horrocks et al. [14]; ●, Barnette [18]; ■, Briggs [19]; ■, Mukhamedzyanov et al. [20]; ■, Sakiadis and Coates [21]; ■, Filippov [22].

deviations amount to as much as 5% in some cases although a few measurements are in much better agreement with those reported here.

#### 4.2. A Temperature-Independent Correlation

One of the results of the application of the Enskog theory to the van der Waals model of a fluid is the prediction that the function  $\lambda^* = F(V/V_0)$  is independent of temperature, although  $V_0$  is still a function of temperature. If this is the case, then it should be possible to describe the density dependence of the thermal conductivity along all isotherms by means of a single equation with temperature-independent values of  $a_0$  and  $a_1$ . To examine the extent to which the present experimental data conform to the result, we have fitted the entire body of data for each liquid studied here to a single equation of the form of Eq. (4), using the values of  $V_0$  listed in Table IV. For benzene the optimum correlation of this type is

$$\ln \lambda^* = 3.0612 - 2.1539 \ln(V/V_0) \quad (5)$$

whereas for cyclohexane the optimum correlation is

$$\ln \lambda^* = 2.6877 - 2.2136 \ln(V/V_0) \tag{6}$$

Figures 4 and 5 contain plots of the deviations from these temperature-independent correlations for benzene and cyclohexane, respectively. The maximum deviation now amounts to  $\pm 0.8\%$ , whereas the standard deviation is one of  $\pm 0.18\%$  for benzene and  $\pm 0.17\%$  for cyclohexane. These values are marginally worse than those which occur when the isotherms are represented by individual equations, so that the temperature independence of  $\lambda^*$  is not completely confirmed. However, this type of correlation permits us to predict the entire density dependence of the thermal conductivity for either liquid at a temperature for which the thermal conductivity is known at only one density. The comparison presented here indicates that the accuracy of the prediction is only slightly inferior to the precision of our measurements.

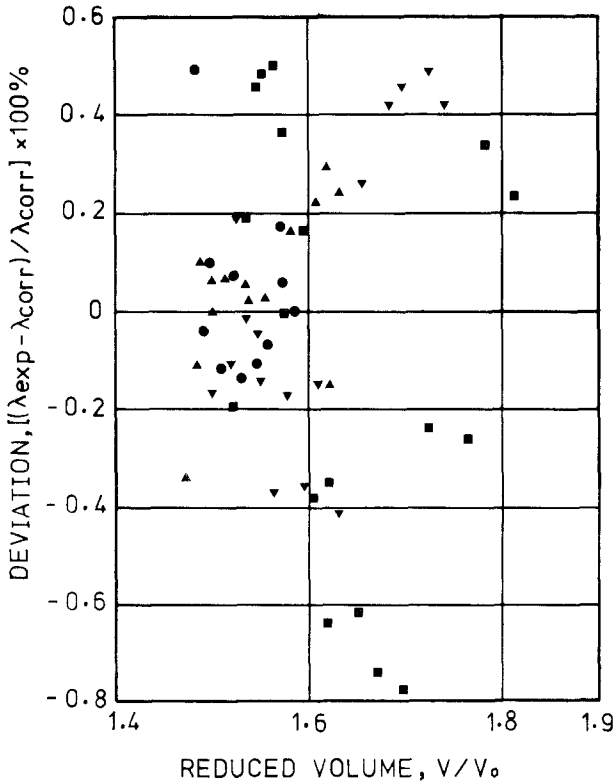


Fig. 4. Deviations of experimental data for the thermal conductivity of benzene from the correlation of Eq. (5): ●, 37°C; ▲, 47.5°C; ▼, 71°C; ■, 87.5°C.

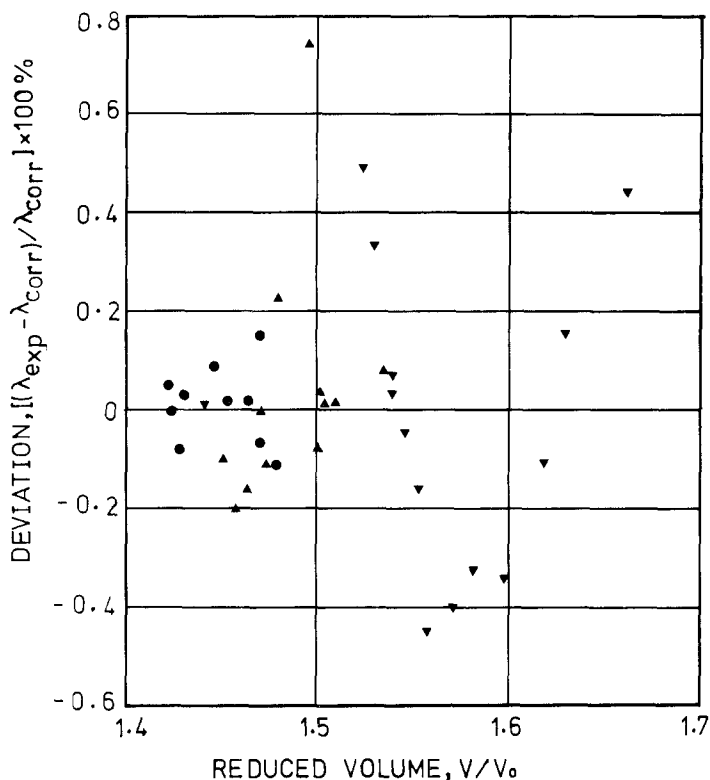


Fig. 5. Deviations of experimental data for the thermal conductivity of cyclohexane from the correlation of Eq. (6): ●, 36°C; ▲, 51°C; ▼, 80°C.

### 4.3. The Universal Correlation

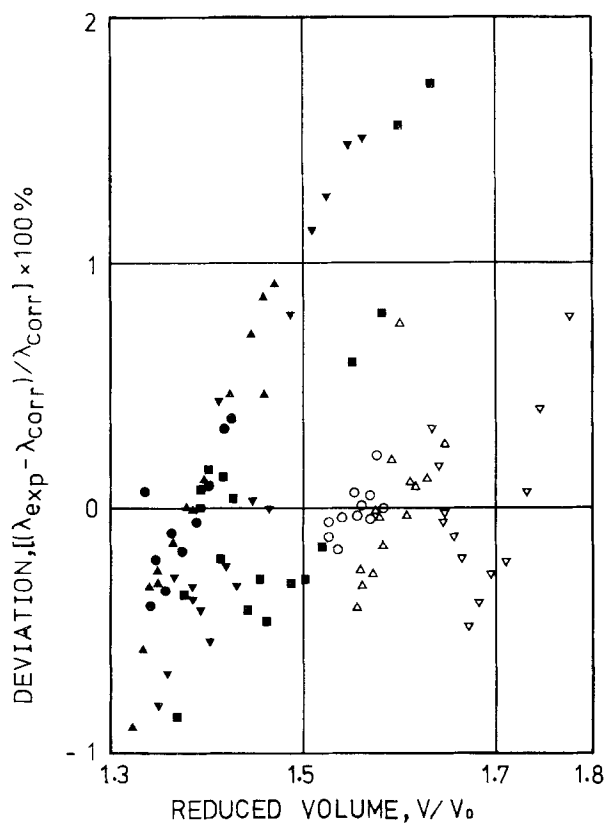
The density dependence of the thermal conductivity of most of the normal alkanes from propane to tridecane over a wide range of temperature has been represented by the single equation [4],

$$\ln \lambda^* = 2.8724 - 2.2735 \ln(V/V_0^u) \quad (7)$$

This equation is of the same form as those employed earlier, but the superscript  $u$  on  $V_0$  is employed to indicate that the basis for the selection of the characteristic volume [4] is different from that which we employed in the previous two sections. It is interesting to assess the extent to which a correlation developed for the normal alkanes is able to describe the experimental data for the cyclic hydrocarbons benzene and cyclohexane. Accordingly, we have fitted Eq. (7) to the present thermal conductivity data

**Table V.** Optimum Values of  $V_0^u$  Derived from the Universal Correlation of Eq. (7) for Benzene and Cyclohexane

Benzene		Cyclohexane	
$T$ (°C)	$10^6 V_0^u$ ( $\text{m}^3 \cdot \text{mol}^{-1}$ )	$T$ (°C)	$10^6 V_0^u$ ( $\text{m}^3 \cdot \text{mol}^{-1}$ )
37.0	63.54	36.0	69.02
47.5	62.32	51.0	67.09
71.0	59.87	80.0	63.85
87.5	58.48		

**Fig. 6.** Deviations of experimental data for the thermal conductivity of benzene and cyclohexane from the correlation of Eq. (7). Benzene: ●, 37°C; ▲, 47.5°C; ▼, 71°C; ■, 87.5°C. Cyclohexane: ○, 36°C; △, 51°C; □, 80°C.

along each isotherm for benzene and cyclohexane by the selection of the optimum values of  $V_0^u$ . The derived values of  $V_0^u$  are included in Table V, and Fig. 6 contains a plot of the deviations of the experimental data for benzene and cyclohexane from this universal correlation. The deviations now amount to as much as 1.7%, and the standard deviations are  $\pm 0.42\%$  for benzene and  $\pm 0.19\%$  for cyclohexane.

These values therefore exceed the estimated experimental error. On the one hand, this result indicates that the function  $\lambda^*$  is not exactly universal among all liquid hydrocarbons, and that therefore the rigid sphere model is not entirely adequate for a description of their thermal conductivity. On the other hand, the fact that a single equation is capable of describing the thermal conductivity of liquids as diverse as propane and benzene with an accuracy of  $\pm 3\%$  over a wide range of thermodynamic states is remarkable. Indeed, this last observation implies that Eq. (7) provides a quite reliable means of estimating the thermal conductivity of hydrocarbon liquids since all that is required for the equation is the effective rigid-sphere volume  $V_0^u$ . A number of methods for estimating the effective rigid-sphere volume have already been described [23].

## 5. CONCLUSIONS

Thermal conductivity data with an accuracy of  $\pm 0.3\%$  have been reported for benzene and cyclohexane over the temperature range 36–88°C at pressures up to 0.33 GPa. The density dependence of the thermal conductivity may be satisfactorily represented by a simple power law relationship along each isotherm. However, the experimental results do not exactly conform to all of the characteristics to be expected of a rigid-sphere fluid, even allowing for the temperature dependence of the rigid-sphere volume. Nevertheless, with only a small loss of accuracy, this model does allow the prediction of the thermal conductivity for thermodynamic states other than those studied experimentally. If a further loss of accuracy is tolerated, the model should also allow estimation of the thermal conductivity of a variety of hydrocarbons given a suitable value for the characteristic rigid-sphere volume.

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