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The Thermal Conductivity of the Mixtures of Liquid Hydrocarbons at Pressures up to 400 MPa

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The paper presents the results of measurements of the thermal conductivity of three binary mixtures of normal heptane and 2,2,4-trimethyl pentane. The measurements were carried out within the temperature range 308–359 K and over the pressure range 0.1–410 MPa with a transient hot-wire instrument. The experimental data have an estimated uncertainty of ±0.3%. The experimental data have been represented by simple polynomials along isotherms as a function of pressure for each composition for the purpose of interpolation. However, an alternative scheme of representation, based upon an heuristic extention of the hard-sphere theory, is shown to give a much more concise representation capable of extrapolation. Indeed, a procedure for the prediction of the thermal conductivity of the mixtures, based on the same theory, which uses no information derived from the present measurements, is shown to yield results of an accuracy sufficient for many purposes.

KEY WORDS: mixtures; normal heptane; thermal conductivity; 2,2,4-trimethyl pentane.

1. INTRODUCTION

In the last decade, a considerable body of accurate data on the thermal conductivity of pure liquids has been obtained with the transient hot-wire instrument over a range of conditions both along the saturation line [1, 2] and at elevated pressures [3]. In conjunction with these experiments, it has proved possible to adapt the rigid-sphere theory of dense fluids to provide

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an accurate representation of the data and to allow calculation of the property over a wider range of conditions than were covered by the measurements themselves [3].

More recently a similar calculation procedure, again based upon the results of the rigid-sphere theory, has been applied to mixtures of liquids with considerable success [4]. However, this new application has been confined to comparisons at atmospheric pressure owing to the lack of extensive and accurate experimental data on the thermal conductivity of liquid mixtures at high pressure.

In the present work, we have set out to provide just the experimental thermal conductivity data required for such a test of the proposed procedure. To this end, measurements of the thermal conductivity of three binary mixtures of *n*-heptane and 2,2,4-trimethyl pentane over the temperature range 308–359 K at pressures up to 400 MPa have been performed. This particular system has been chosen for study because the thermal conductivities of the two pure components differ by almost 40% under conditions of identical temperature and pressure, the mixtures behave almost ideally in the thermodynamic sense, and the volatilities of the two species are nearly equal. Furthermore, the system is one of the few for which accurate density measurements are available over a wide range of pressures and a moderate range of temperatures [5]. The results are represented with the aid of elements of the rigid-sphere theory of dense fluids and subsequently used as a test of a scheme for the prediction of the thermal conductivity of liquid mixtures.

2. EXPERIMENTAL

The measurements were carried out with the transient hot-wire thermal conductivity instrument described in detail elsewhere [6,7]. The samples of *n*-heptane and 2,2,4-trimethyl pentane employed for measurements were supplied by BDH Chemicals Ltd., U.K., with a stated purity of 99.5 and 99.9%, respectively. The pure component samples were distilled and degassed before use. The mixtures were manufactured gravimetrically to yield samples with mole fractions of *n*-heptane of 0.7513, 0.4858, and 0.2507. The uncertainty in the mole fraction of the mixture is estimated to be ±0.0001. The mixtures were introduced into the evacuated thermal conductivity cells as described elsewhere [6] and the near-equality of the volatilities of the two components ensured no significant change in composition in the process.

The thermal conductivity measurements were made along four isotherms for the mixtures with mole fractions of *n*-heptane of 0.4858 and 0.2507 and three isotherms for the mixture with a mole fraction of 0.7513.

The measurements extended over the pressure range 0.1–400 MPa for all compositions and temperatures.

The procedures for the analysis of the experimental data remain as described in our earlier work [1–7]. Thus, it is necessary to record that there was no sign of effects from convection or radiation in any of the runs for which results are reported here. For the reduction of the experimental data, it is necessary to have values for the density and isobaric heat capacity of the fluid [6]. For this purpose, estimates are more than adequate and a molar average of the properties of the pure components [8, 9] has been employed.

3. RESULTS

Tables I–III contain the experimental thermal conductivity data for the mixtures of *n*-heptane and 2,2,4-trimethyl pentane. The measured thermal conductivities have been corrected to the nominal temperature at the experimental pressure and at the reference density by means of simple linear corrections as described earlier [6].

In these tables, the quoted density of the mixtures for temperatures in the range 308–388 K have been taken from the direct measurements of Malhotra and Woolf [5] specially performed for the purpose. The data for the density as a function of pressure were represented by a Tait equation and interpolated for temperature and composition by conventional procedures [6]. The volume of mixing for the *n*-heptane–2,2,4-trimethyl pentane system is very small so that the density at temperatures far outside the temperature range of the direct measurements has been evaluated on the assumption of ideal mixing using the experimental data of Dymond *et al.* [10] for 2,2,4-trimethyl pentane and those of Doolittle [11] for *n*-heptane. As a consequence, the density for these temperatures must be viewed as slightly more uncertain. Thus, in the temperature range below 338 K, the uncertainty in the quoted density is estimated to be ±0.2% whereas at the higher temperatures it may be as much as ±0.4%.

The experimental data for the thermal conductivity along each isotherm were correlated as a function of pressure, P, by means of the representation

$$\lambda(x_1, T, P) = \sum_{i=0}^{4} a_i(x_1, T)\left(\frac{P - P'}{P'}\right)^i \tag{1}$$

in which x_1 is the mole fraction of *n*-heptane. The coefficients $a_i(x_1, T)$ are listed in Table IV. In each case, $P' = 200$ MPa.

Table I. The Thermal Conductivity of the Mixture with a Mole Fraction of n-Heptane, $x_1 = 0.7513$

P (MPa)	T_r (K)	ρ_r (kg·m^{-3})	$\lambda(T_r, \rho_r)$ (mW·m^{-1}·K^{-1})	$\lambda(T_n, P)$ (mW·m^{-1}·K^{-1})	$\lambda(T_n, \rho_r)$ (mW·m^{-1}·K^{-1})
$T_n = 308.15$ K					
2.1	308.17	675.8	111.6	111.6	111.6
8.86	308.13	682.3	114.9	114.9	115.0
24.2	308.14	695.4	121.4	121.4	121.4
44.0	308.06	710.1	128.9	128.9	129.0
104.3	307.79	742.6	147.8	147.8	147.9
152.4	307.72	762.5	160.1	160.1	160.2
205.3	307.74	780.6	172.1	172.1	172.2
256.8	307.72	795.7	182.3	182.3	182.4
307.1	307.63	808.7	191.0	191.1	191.2
353.6	307.64	819.5	198.7	198.7	198.9
409.7	307.65	831.3	207.2	207.2	207.3
$T_n = 337.15$ K					
2.2	337.39	650.8	106.0	106.1	106.0
14.9	337.43	665.1	112.1	112.1	112.0
52.6	336.94	696.7	126.3	126.3	126.3
101.4	336.75	725.4	142.0	142.0	142.1
151.0	336.83	747.6	155.4	155.4	155.5
200.1	336.86	765.6	166.5	166.5	166.6
205.4	336.54	767.3	167.6	167.6	167.8
254.5	336.76	782.4	177.6	177.6	177.7
305.2	336.95	796.2	186.8	186.8	186.9
305.6	336.91	796.3	187.0	187.0	187.1
353.1	337.00	808.7	195.0	195.0	195.0
412.3	336.96	820.7	204.1	204.2	204.2
$T_n = 359.65$ K					
18.6	360.68	652.8	109.0	109.1	108.8
44.8	359.77	675.0	120.1	120.1	120.1
82.3	359.75	701.0	133.3	133.3	133.2
128.5	359.53	725.6	143.7	143.1	143.7
201.1	359.42	754.5	164.2	164.2	164.2
263.3	359.45	773.7	176.3	176.3	176.4
331.0	359.61	791.3	187.7	187.1	187.7
341.4	359.59	793.7	189.8	189.8	189.8
364.3	359.71	799.0	193.4	193.4	193.4
380.9	359.49	805.2	196.4	196.4	196.5

Figure 1 contains the deviations of the data for the mixtures from this correlation, and it shows that the deviations only exceptionally exceed $\pm 0.5\%$, while the standard deviation is $\pm 0.2\%$ and is commensurate with the uncertainty in the experimental data. There are no previous measurements of the thermal conductivity of this system for comparison purposes.

4. DISCUSSION

There is now a considerable body of evidence which suggests that the dominant variable that determines the transport properties of fluids is the

Table II. The Thermal Conductivity of the Mixture with a Mole Fraction of *n*-Heptane, $x_1 = 0.4858$

P (MPa)	T_r (K)	ρ_r ($\mathrm{kg \cdot m^{-3}}$)	$\lambda(T_r, \rho_r)$ ($\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$)	$\lambda(T_n, P)$ ($\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$)	$\lambda(T_n, \rho_r)$ ($\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$)
			$T_n = 307.65$ K		
1.5	308.06	677.8	103.7	103.8	103.7
5.8	308.06	682.1	105.7	105.7	105.6
14.3	308.02	689.3	109.3	109.4	109.2
26.3	308.12	699.6	113.9	114.0	113.8
52.7	307.91	718.9	123.5	123.4	123.5
108.3	307.80	747.0	139.9	139.9	139.9
144.5	307.66	762.1	148.8	148.8	148.8
202.7	307.50	782.3	161.6	161.6	161.7
253.6	307.62	797.3	171.2	171.2	171.2
310.1	307.55	811.9	180.7	180.7	180.8
356.7	307.52	822.6	187.7	187.7	187.7
401.6	307.54	832.1	194.3	194.2	194.3
443.9	307.56	840.5	200.0	200.0	200.0
			$T_n = 318.5$ K		
0.74	318.02	668.0	102.0	102.0	102.0
1.0	318.39	668.4	102.1	102.1	102.0
9.7	318.53	677.4	106.1	106.2	106.0
25.9	318.36	691.8	112.4	112.5	112.4
52.2	318.21	710.8	122.9	122.9	122.9
151.3	317.91	759.5	150.8	150.8	150.9
205.8	318.02	778.5	162.5	162.5	162.5
255.7	317.87	793.3	171.7	171.7	171.8
306.1	317.91	806.6	180.6	180.6	180.7
355.6	317.98	818.2	188.6	188.6	188.6
403.3	317.99	828.4	195.7	195.7	195.7

Table II. (*Continued*)

P (MPa)	T_r (K)	ρ_r (kg · m^{-3})	$\lambda(T_r, \rho_r)$ (mW · m^{-1} · K^{-1})	$\lambda(T_n, P)$ (mW · m^{-1} · K^{-1})	$\lambda(T_n, \rho_r)$ (mW · m^{-1} · K^{-1})
			$T_n = 337.65$ K		
1.9	337.93	652.1	97.84	97.91	97.80
13.5	337.67	665.4	103.8	103.7	103.7
29.2	337.58	680.3	110.8	110.7	110.8
53.4	337.41	698.9	120.7	120.6	120.7
102.5	337.35	727.7	136.3	136.2	136.3
253.5	337.30	750.4	149.6	149.6	149.7
206.1	337.27	769.4	161.7	161.7	161.8
256.5	337.22	784.9	171.9	171.8	172.0
306.2	337.20	798.3	181.3	181.3	181.4
353.3	337.18	809.7	188.8	188.8	188.9
403.2	337.26	820.7	196.4	196.4	196.5
			$T_n = 359.65$ K		
3.54	359.95	634.8	93.03	93.11	92.99
16.9	359.77	648.3	101.2	101.2	101.1
102.1	359.67	712.1	132.9	132.9	132.9
155.6	359.57	736.9	147.4	147.4	147.4
155.6	359.49	737.0	147.6	147.6	147.6
206.4	359.77	756.2	160.9	160.9	160.9
257.3	359.75	772.7	167.6	167.6	167.5
405.3	359.82	811.2	193.2	193.2	193.2

density rather than the pressure or the temperature [12, 13]. Thus, the fact that most methods of predicting the thermal conductivity of liquid mixtures attempt to combine the properties of the pure fluids at the same pressure according to an empirical scheme [14] is contrary to the available theory, as noted in our earlier and preliminary work [15].

The most successful description of the transport properties of pure fluids is based upon the rigid-sphere model of the fluid supported by the appropriate kinetic theory due to Enskog and the appropriate results of computer simulation studies to apply corrections for the limitations of the theory [13]. For the thermal conductivity, this theory suggests that for a pure monatomic fluid, the dimensionless group

$$\lambda^* = 1.936 \times 10^7 \lambda V^{2/3} (MRT)^{1/2} \tag{2}$$

should be a function only of the ratio of the molar volume V to a characteristic molar volume V_0. Here, M is the molar mass of the species and R

Table III. The Thermal Conductivity of the Mixture with a Mole Fraction of *n*-Heptane, $x_1 = 0.2507$

P (MPa)	T_r (K)	ρ_r (kg·m^{-3})	$\lambda(T_r, \rho_r)$ (mW·m^{-1}·K^{-1})	$\lambda(T_n, P)$ (mW·m^{-1}·K^{-1})	$\lambda(T_n, \rho_r)$ (mW·m^{-1}·K^{-1})
$T_n = 307.15$ K					
6.5	307.50	685.1	104.4	104.4	104.3
17.1	307.50	694.6	108.1	108.2	108.1
27.4	307.40	703.0	111.5	111.5	111.4
39.1	307.29	711.4	115.5	115.5	115.4
49.6	307.33	718.4	118.8	118.8	118.8
63.5	307.19	726.8	122.7	122.8	122.7
77.5	307.19	734.5	126.4	126.4	126.3
97.8	307.24	744.7	131.0	131.0	131.0
123.7	307.16	756.2	137.1	137.1	137.1
142.2	307.11	763.7	141.5	141.4	141.5
173.8	307.01	775.3	148.1	148.1	148.1
202.6	306.99	784.8	153.5	153.5	153.6
228.3	306.96	792.6	158.1	158.1	158.1
248.6	307.38	798.4	161.3	161.3	161.2
269.8	306.81	804.2	165.0	165.0	165.1
297.4	307.05	811.2	170.2	170.2	170.2
322.7	307.13	817.3	173.6	173.6	173.6
351.3	307.02	823.9	177.8	177.8	177.8
377.1	307.20	829.5	181.1	181.1	181.1
401.8	307.15	834.6	184.5	184.5	184.4
$T_n = 317.15$ K					
5.2	317.63	675.2	102.1	102.2	102.1
15.5	317.46	685.6	105.8	105.8	105.7
25.9	317.38	694.7	109.4	109.5	109.4
37.0	317.32	703.2	114.1	114.2	114.1
56.3	317.35	716.3	119.8	119.8	119.7
76.5	317.01	728.2	125.4	125.4	125.5
96.3	317.16	738.5	130.7	130.6	130.7
110.6	316.99	745.3	134.4	134.4	134.5
128.1	317.20	752.9	138.0	138.0	138.0
147.4	317.19	760.8	141.6	141.6	141.6
172.8	317.13	770.2	146.9	146.9	146.9
202.8	317.04	780.3	152.8	152.8	152.8
232.2	316.92	789.3	158.0	158.0	158.8
263.1	316.97	798.1	163.3	163.2	163.3
294.8	317.35	806.4	168.0	168.0	168.0
325.2	317.13	813.9	173.0	173.0	173.0
352.9	316.92	820.3	171.8	176.8	176.9
381.8	316.96	826.6	180.9	180.9	180.9
412.5	316.82	832.9	184.5	184.5	184.5

Table III. (*Continued*)

P (MPa)	T_r (K)	ρ_r (kg · m^{-3})	$\lambda(T_r, \rho_r)$ (mW · m^{-1} · K^{-1})	$\lambda(T_n, P)$ (mW · m^{-1} · K^{-1})	$\lambda(T_n, \rho_r)$ (mW · m^{-1} · K^{-1})
$T_n = 337.15$ K					
0.1	337.80	652.2	96.67	96.83	96.6
4.1	337.91	657.3	98.05	98.23	97.9
14.0	337.83	668.5	103.0	103.2	102.9
24.7	337.78	678.9	106.9	107.1	106.9
41.2	337.52	692.8	113.0	113.1	113.0
54.1	337.42	702.2	117.5	117.5	117.4
61.2	337.26	707.0	120.3	120.3	120.3
77.8	337.44	717.2	124.6	124.7	124.6
98.1	337.11	728.3	129.3	129.9	129.9
124.1	337.07	740.7	135.6	135.5	135.6
146.8	337.02	750.4	140.5	140.5	140.6
175.7	337.03	761.6	146.3	146.3	146.3
203.5	336.97	771.2	151.3	151.3	151.4
236.8	336.89	781.8	157.6	157.6	157.6
271.8	336.94	791.8	163.1	163.1	163.2
299.4	337.03	799.2	169.1	169.1	169.1
343.4	336.89	809.0	175.5	175.5	175.6
419.4	337.09	826.5	185.2	185.2	185.2
$T_n = 357.15$ K					
6.69	357.61	634.9	96.33	96.42	96.28
13.80	357.51	642.6	99.49	99.55	99.45
22.90	357.48	653.6	102.9	102.9	102.9
36.59	357.33	667.4	108.1	108.1	108.1
52.84	357.25	681.1	113.7	113.7	113.7
68.64	357.16	692.4	118.7	118.7	118.7
86.22	357.16	703.5	124.0	124.0	124.0
108.93	357.20	716.2	129.8	129.9	129.8
133.05	357.28	728.0	135.7	135.7	135.6
159.36	357.15	739.5	141.5	141.5	141.5
174.87	357.06	745.7	144.8	144.8	144.8
204.36	357.69	756.7	150.3	150.3	150.2
235.28	357.25	767.1	156.0	156.0	156.0
266.75	356.93	776.6	161.8	161.8	161.8
298.83	357.12	785.6	167.0	167.0	167.0
325.46	356.91	792.6	171.3	171.3	171.3
354.35	357.12	799.6	175.8	175.8	175.8
381.45	357.10	805.9	179.9	179.9	179.9
411.07	356.98	812.4	185.6	185.6	185.6

Table IV. Coefficients of the Representation of the Thermal Conductivity of Mixtures of *n*-Heptane and 2,2,4-Trimethyl Pentane as a Function of Pressure According to Eq. (1)

x_1	T(K)	a_0 ($mW \cdot m^{-1} \cdot K^{-1}$)	a_1 ($mW \cdot m^{-1} \cdot K^{-1}$)	a_2 ($mW \cdot m^{-1} \cdot K^{-1}$)	a_3 ($mW \cdot m^{-1} \cdot K^{-1}$)	a_4 ($mW \cdot m^{-1} \cdot K^{-1}$)
0.7513	308.15	170.90	41.6756	−9.5578	5.72167	−2.92107
	337.15	166.58	42.9662	−10.3632	5.55472	−2.31821
	359.65	163.05	44.1264	−11.0658	4.34221	−1.52852
0.4858	307.65	161.04	39.9232	−10.4109	5.47144	−1.88970
	318.15	161.28	40.0834	−9.7569	6.70295	−3.08953
	337.65	160.29	42.5241	−8.4758	6.85270	−5.30834
	359.65	158.00	40.1695	−18.4023	9.74431	2.54289
0.2507	307.15	152.88	37.2355	−6.5628	3.76671	−3.19999
	317.15	152.19	36.1166	−6.5479	5.43942	−4.10343
	337.15	150.07	36.4693	−3.1764	6.90881	−7.52249
	357.15	149.68	37.5639	−8.9980	7.28096	−2.07045

the gas constant, and all quantities are expressed in SI units. Despite the fact that this result is rigorously true only for a rigid-sphere molecule, it has been found to be remarkably well obeyed by a wide range of fluids including a large group of normal alkanes and some of their isomers [12, 16]. However, the function λ^* observed empirically differs from that

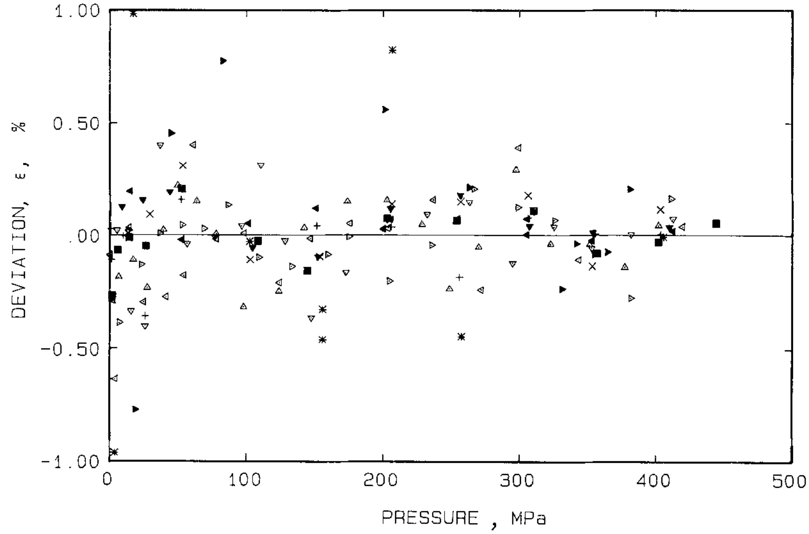

Fig. 1. Deviation of the thermal conductivity data from its representation as a function of pressure by Eq. (1) and the coefficients of Table IV. $\varepsilon = [(\lambda_{\text{expt}} - \lambda_{\text{corr}})/\lambda_{\text{corr}}] \times 100$. $x_1 = 0.7513$: (▼) 308.15 K; (◀) 337.15 K; (▶) 359.65 K. $x_1 = 0.4858$: (■) 307.65 K; (+) 318.15 K; (×) 337.65 K; (*) 359.65 K. $x_1 = 0.2507$: (△) 307.15 K; (▽) 317.15 K; (◁) 337.15 K; (▷) 357.15 K.

appropriate to rigid spheres. In principle, it is possible to use the Enskog theory for rigid-sphere mixtures to extend these ideas to dense fluid mixtures but this has never been carried through because the results of the computer simulation studies required are not available. Consequently, the application of these same ideas to mixtures have proceeded in a more empirical manner [4] in which Eq. (2) is written for the binary mixtures as

$$\lambda^* = 1.936 \times 10^7 \, \lambda(T, x_1, V) \, V^{2/3}(T, x_1) \left(\frac{x_1 M_1 + x_2 M_2}{RT} \right)^{1/2} \qquad (3)$$

where x_i is the mole fraction of species i with a molar mass M_i. It has been observed that the λ^* defined in this manner for binary mixtures can be represented by the same function of (V/V_0^{mix}) as is appropriate for pure fluids [4]. However, the test has been based on experimental information at atmospheric pressure over a range of temperatures [4] so that it is not as stringent as can be performed with the present data over a wide range of pressures.

4.1. Representation of the Density Dependence

Using the definition of λ^* in Eq. (3), it is possible to represent the density dependence of the thermal conductivity along isotherms and isopleths by the equation [12]

$$\ln \lambda^* = A(x_1, T) - B(x_1, T) \ln[V/V_0(x_1, T)] \qquad (4)$$

Accordingly, the optimum values of $A(x_1, T)$, $B(x_1, T)$ are listed in Table V, together with selected values of $V_0(x_1, T)$. The values of $V_0(x_1, T)$

Table V. Coefficients of the Optimum Representation of the Thermal Conductivity of the Mixtures as a Function of Density with Eq. (4)

x_1	T (K)	$A(x_1, T)$	$B(x_1, T)$	$10^6 \, V_0(x_1, T)$	$10^6 \, V_0^{\mathrm{I}}(x_1, T)$
0.7513	308.15	4.9160	2.3347	89.18	89.82
	337.15	4.8530	2.1863	88.63	89.25
	359.65	4.8553	2.1731	88.54	—
0.4858	307.65	4.9458	2.4096	91.06	91.88
	318.15	4.9418	2.3817	91.33	91.78
	337.65	4.9527	2.3856	91.24	91.56
	359.65	4.9207	2.3019	91.42	—
0.2507	307.15	4.8873	2.2539	93.27	93.72
	317.15	4.8561	2.1861	93.35	93.68
	337.15	4.8183	2.0922	93.65	93.49
	357.15	4.7799	1.9799	93.72	—

have been chosen in the manner described in Sect. 4.2. Figure 2 shows the deviations of the experimental data from this representation for each isotherm and each mixture. The standard deviation of the fit over all the data is ±0.2% although exceptional points depart from the representation by as much as ±1.5%. It can be seen from Table V that the coefficients $A(x_1, T)$, $B(x_1, T)$ reveal only a weak dependence on x_1 and T and that the largest changes take place at the highest temperatures where the uncertainty in the molar volume is greatest owing to the absence of direct experimental information.

4.2. A Universal Representation of the Density Dependence

One of the features of the behavior noted earlier was the fact that among many pure fluids, including the normal alkanes and some of their isomers, the function λ^* is universal [4, 12, 16]. The universal function has been represented by the equation [12]

$$\ln \lambda^* = 4.8991 - 2.2595 \ln(V/V_0) \tag{5}$$

for a series of hydrocarbons and has been shown by Assael and his co-workers [2, 4] to apply to a wider class of fluids and some mixtures at

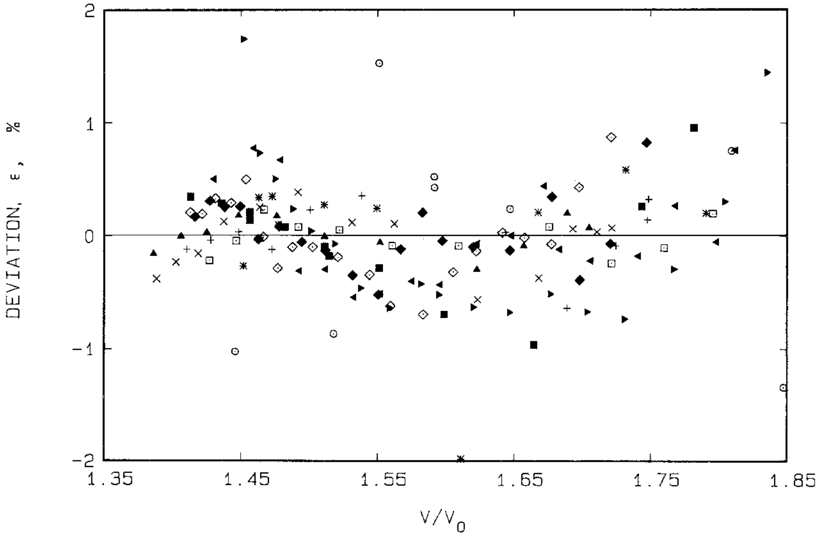

Fig. 2. Deviations of the thermal conductivity data from its representation as a function of density by Eq. (4) with the coefficients of Table V. $\varepsilon = [(\lambda_{\text{expr}} - \lambda_{\text{corr}})/\lambda_{\text{corr}}] \times 100$. $x_1 = 0.7513$: (▲) 308.15 K; (■) 337.15 K; (*) 359.65 K. $x_1 = 0.4858$: (×) 307.65 K; (+) 318.15 K; (□) 337.65 K; (○) 359.65 K. $x_1 = 0.2507$: (◇) 307.15 K; (◆) 317.15 K; (◀) 337.15 K; (▶) 357.15 K.

atmospheric pressure. We have therefore attempted to represent the present thermal conductivity data for the mixtures of *n*-heptane and 2,2,4-trimethyl pentane by this same universal equation. Thus, we have determined the values of $V_0(x_1, T)$ securing the optimum representation of the present data by means of Eq. (5). These optimum values are, in fact, those listed in Table V. However, because the coefficients of the representation are now fixed, the deviations of the data are inevitably greater than those resulting from Eq. (4) as is shown in Fig. 3. Nevertheless, they do not amount to more than ±2%, which is remarkably good for a representation univsersal among so many systems and extending to mixtures.

The representation secured by Eq. (5) is obviously one that allows the evaluation of the thermal conductivity of the three mixtures studied under conditions outside of those encompassed in the direct measurements. However, it does not allow the evaluation of the thermal conductivity of mixtures of arbitrary composition, which is considered in Sect. 4.3.

4.3. The Prediction of the Thermal Conductivity Data for the Mixtures

The thermal conductivity of both of the pure components involved in the mixtures studied here has been determined earlier over a similar range of conditions [6, 16]. These data have in fact been represented by Eq. (5)

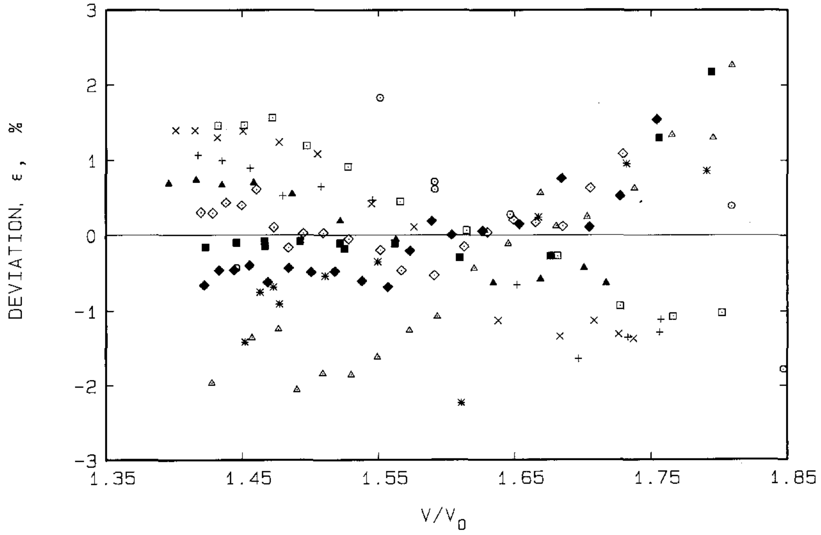

Fig. 3. Deviations of the thermal conductivity data from its representation as a function of density by the universal Eq. (5). $\varepsilon = [(\lambda_{\text{expt}} - \lambda_{\text{corr}})/\lambda_{\text{corr}}] \times 100$. $x_1 = 0.7513$: (▲) 308.15 K; (■) 337.15 K; (*) 359.65 K. $x_1 = 0.4858$: (×) 307.65 K; (+) 318.15 K; (□) 337.65 K; (⊙) 359.65 K. $x_1 = 0.2507$: (◇) 307.15 K; (◆) 317.15 K; (▶) 337.15 K; (◀) 357.15 K.

[12] and the corresponding values of V_{0_1} for *n*-heptane and V_{0_2} for 2,2,4-trimethyl pentane determined at temperatures from 308–340 K. In this limited temperature range, it is therefore possible to explore the possibility that the value of the characteristic volumes of the pure components can be used to predict $V_0(x_1, T)$ for the mixtures. For this purpose, we adopt the idea of Assael and his collaborators [4] for a suitable mixing rule except that for two components that form such a nearly ideal mixture, it can be simplified to

$$V_0^{\mathrm{I}}(x_1, T) = x_1 V_{0_1} + (1 - x_1) V_{0_2} \tag{6}$$

that is, a mole fraction average, in which the superscript I serves to identify the method of evaluating the characteristic volume of the mixture. Using the values of V_{0_1} and V_{0_2} derived earlier [12], V_0^{I} has been evaluated for each of the mixtures studied here and the results are included in Table V, from which it can be seen that they are remarkable close to those derived from the present data. If these estimated values of V_0 are used in Eq. (5), the results are essentially predictions of the thermal conductivity of the mixtures which have used no experimental information on the mixtures themselves. Figure 4 contains a comparison of these predictions with the experimental data which reveals that the differences amount to no more than ±3% over the entire range of conditions studied. For many purposes, this level of accuracy is more than adequate so that this simple scheme

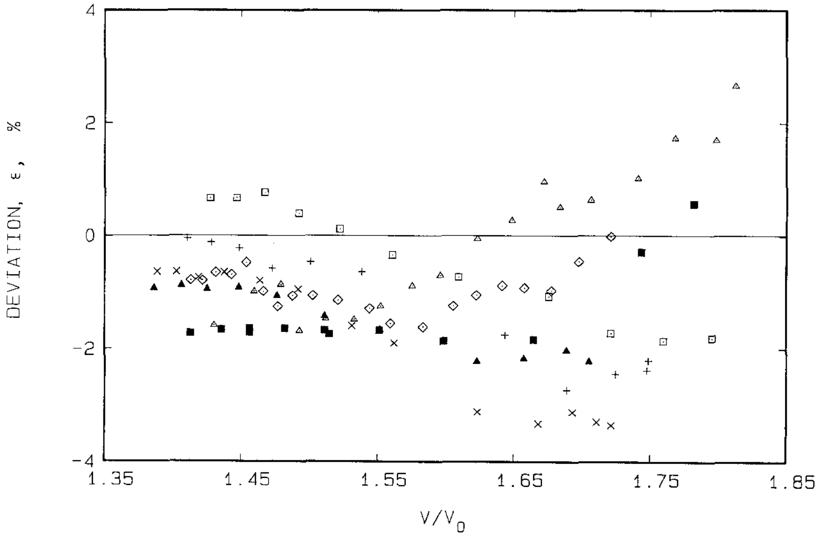

Fig. 4. Deviations of the thermal conductivity data from its prediction by means of Eqs. (5) and (6). $\varepsilon = [(\lambda_{\mathrm{expt}} - \lambda_{\mathrm{corr}})/\lambda_{\mathrm{corr}}] \times 100$. $x_1 = 0.7513$: (▲) 308.15 K; (■) 337.15 K; (*) 359.65 K. $x_1 = 0.4858$: (×) 307.65 K; (+) 318.15 K; (□) 337.65 K; (⊙) 359.65 K. $x_1 = 0.2507$: (◇) 307.15 K; (◆) 317.15 K; (◀) 337.15 K; (▶) 357.15 K.

provides a valuable means of predicting the thermal conductivity of nearly ideal liquid mixtures of arbitrary composition over a wide range of conditions.

5. CONCLUSIONS

The experimental data reported for the thermal conductivity of binary mixtures of *n*-heptane and 2,2,4-trimethyl pentane can be well represented by a formulation based on the results of the rigid-sphere theory of fluids. The data have allowed a scheme for the prediction of the thermal conductivity of nearly ideal mixtures to be tested which is simple and accurate and confirms, for elevated pressures, results hitherto based on data at atmospheric pressure alone.

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