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Thermal Conductivity of Liquid Mixtures of Benzene and 2,2,4-Trimethylpentane at Pressures up to 350 MPa

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This paper contains the results of new measurements of the thermal conductivity of mixtures of benzene and 2,2,4-trimethylpentane in the liquid phase within the temperature range 313 to 344 K at pressures up to 350 MPa. The measurements were carried out with a transient hot-wire instrument and have an estimated accuracy of ±0.3%. The study is the first conducted at high pressures on mixtures of components of greatly differing volatilities and therefore provides a further test of methods of representing the thermal conductivity of liquid mixtures based upon the hard-sphere theory of transport in liquids. It is shown that the procedure is capable of representing all of the present experimental data within ±5%. A more detailed examination of the results reveals small, but systematic, deviations from universality of the behavior of the thermal conductivity as a function of density implied by the hard-sphere theory, which merit further investigation.

KEY WORDS: benzene; high pressures; liquid mixtures; thermal conductivity; 2,2,4-trimethylpentane.

1. INTRODUCTION

In the last decade the combination of accurate measurements of the viscosity and thermal conductivity of liquids with developments in the application of the hard-sphere theory of transport properties to dense fluids has led to the establishment of a reliable procedure for the interpolation

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and prediction of liquid-phase transport properties [1–5]. The procedure has been successfully extended to the representation and prediction of the thermal conductivity of binary liquid mixtures [6–9]. However, in the latter case the comparisons with experiment have been confined either to studies at atmospheric pressure [6, 7] or to studies at high pressures on systems whose pure components have almost-equal volatilities [8, 9].

In the present paper we extend our experimental studies of the thermal conductivity at elevated pressures to a mixture whose components have quite different volatilities in order to provide a more general test of the proposed predictive procedure. The study is a precursor to a further examination of liquid mixtures under pressure whose thermodynamic behavior is far from ideal.

2. EXPERIMENTS

The basic transient hot-wire instrument employed for the present measurements has been described in detail elsewhere [10, 11]. Attention is therefore concentrated upon the differences in the experimental procedures adopted in this particular study. First, the hot-wire cell assembly employed is that described by Wakeham and Zalaf [12], which is constructed of materials resistant to chemical attack. This change was not necessary for the present study but will be important for future work on polar compounds. This cell was equipped, for the present work, with platinum wires of 7-μm nominal diameter in a fashion similar to that described in Ref. 10.

The other difference in experimental method arises from the need to fill the high-pressure enclosure with a liquid mixture of known composition when the components of the mixture have greatly different volatilities. In our earlier measurements, when the volatilities of the two components were essentially the same, it was possible to fill the evacuated cell with a prepared mixture using a gravity feed, since any vapor lost in the process was of the same composition as the liquid. However, when the components have different volatilities, such a procedure is not adequate. We therefore chose to fill the high-pressure enclosure with the mixture using a high-pressure pump, so that all of the material passing into the enclosure is condensed. This procedure ensures that the composition of the liquid sample under test is the same as that prepared gravimetrically from the pure components. The pure-component samples were provided by BDH Chemicals Ltd., with stated purities of 99.8% for 2,2,4-trimethylpentane and 99.7% for benzene. The samples were further purified by distillation and degassed before use. Three mixtures were manufactured with mole fractions of benzene of 0.2500, 0.5000, and 0.7500, with an uncertainty of ±0.0001 in each case.

The working equations for the analysis of the experimental data have been given elsewhere [13] and they are employed unchanged in this work. Values are required for the density and isobaric heat capacity of the pure fluids and mixtures in order to make a number of small corrections during the analysis of the experimental data. For 2,2,4-trimethylpentane and benzene, the values of the density were taken from the work of Dymond et al. [14, 15]. For the three mixtures, measurements of the density of mixtures of the same composition over the range of conditions of interest here were performed by Malhotra and Woolf [16] and their results have therefore been employed. The heat capacities of the pure liquids were taken from the compilation of Vargaftik [17], and the values for the mixtures estimated as the mole-fraction average of the pure component values. Since the magnitude of the corrections to be applied never exceeds ±0.1%, this procedure is sufficiently accurate.

3. RESULTS

3.1. The Pure Components

In order to verify the correct operation of the instrument we conducted new measurements of the thermal conductivity of 2,2,4-trimethylpentane and benzene, which have been studied previously [18, 19]. Tables I and II list the present results for these two liquids along three isotherms for 2,2,4-trimethylpentane and two isotherms for benzene. The data have been corrected to a nominal temperature by the application of small, linear temperature corrections. For purposes of comparison, the present experimental data were represented by an equation of the form

$$\lambda(x, T, P) = \lambda'(x, T)\left\{1 + \sum a_i P^{*i}\right\} \tag{1}$$

where

$$P^* = (P - P')/P' \tag{2}$$

and x is the mole fraction of benzene in the system. The values of the coefficients a_i and the normalizing pressure P' are collected in Table III. Figures 1 and 2 present comparisons of the present results with those correlating equations, as well as the results of our earlier work [18, 19]. These comparisons indicate that the differences between the two sets of

Table I. Thermal Conductivity of 2,2,4-Trimethylpentane

Temperature, T (K)	Pressure, P (MPa)	Density, ρ_r ($kg \cdot m^{-3}$)	Thermal conductivity ($mW \cdot m^{-1} \cdot K^{-1}$)	
			$\lambda(T_{nom}, \rho_r)$	$\lambda(T_{nom}, P)$
		$T_{nom} = 313.15$ K		
314.79	0.1	673.9	92.2	92.3
313.66	66.5	728.5	116.5	116.6
313.75	92.0	742.7	123.2	123.3
313.61	101.4	747.4	126.0	126.2
313.61	101.2	747.3	126.0	126.1
313.59	125.1	758.1	132.2	132.3
313.67	150.3	768.2	137.4	137.6
313.71	174.9	777.0	142.6	142.7
313.74	193.0	782.9	146.2	146.4
313.73	201.2	785.5	147.8	148.0
313.80	224.4	792.4	152.2	152.4
313.72	250.7	799.7	157.1	157.2
		$T_{nom} = 321.15$ K		
321.28	0.1	668.3	90.6	90.6
321.18	25.1	693.5	100.2	100.2
321.17	49.8	713.0	109.2	109.2
321.19	75.3	729.4	117.1	117.1
321.19	102.1	743.8	124.7	124.7
321.17	125.1	754.4	130.5	130.5
321.21	150.3	764.6	136.4	136.4
321.11	174.9	773.6	141.8	141.8
321.24	192.1	779.4	145.4	145.4
321.31	203.6	782.9	147.3	147.4
321.32	224.8	789.3	151.4	151.4
321.31	250.5	796.5	155.9	155.9
		$T_{nom} = 344.15$ K		
344.15	0.1	647.9	85.7	85.8
344.47	25.4	677.5	96.0	96.1
344.47	46.0	696.0	104.1	104.1
344.51	74.7	716.6	113.8	113.9
344.53	101.6	732.1	121.5	121.6
344.54	125.5	743.7	127.7	127.8
344.65	150.2	754.1	133.5	133.6
344.64	175.2	763.6	139.1	139.2
344.66	191.2	769.1	142.4	142.6
344.65	200.7	772.2	144.5	144.6
344.65	224.2	779.5	149.2	149.3
344.57	240.8	784.4	152.8	152.9
344.58	250.7	787.1	154.2	154.4

measurements are broadly consistent with the claimed uncertainty in the data of ±0.3%.

3.2. The Mixtures

The thermal conductivity data for the three mixtures studied along each of three isotherms are listed in Tables IV to VI. Once again, the data

Table II. Thermal Conductivity of Benzene

Temperature, T (K)	Pressure, P (MPa)	Density, ρ_r (kg·m^{-3})	Thermal conductivity (mW·m^{-1}·K^{-1})	
			$\lambda(T_{nom}, \rho_r)$	$\lambda(T_{nom}, P)$
		$T_{nom} = 321.15$ K		
320.35	0.1	850.0	134.3	134.3
320.26	7.5	856.8	136.1	135.8
320.37	14.2	862.5	139.3	139.0
320.36	25.0	871.3	143.4	143.0
320.44	43.5	884.5	149.6	149.4
320.42	50.6	889.3	152.4	152.2
320.54	75.6	904.1	159.8	159.6
320.58	99.0	916.6	165.6	165.4
320.68	120.9	927.1	171.2	171.0
320.66	125.6	929.3	172.8	172.7
320.68	140.3	936.0	176.4	176.2
320.66	150.4	940.4	178.5	178.3
320.64	160.9	945.0	180.8	180.6
		$T_{nom} = 344.15$ K		
344.31	0.1	823.7	125.9	126.0
344.88	11.3	835.1	129.3	129.6
345.37	20.1	843.3	133.7	134.1
344.65	23.8	847.3	135.3	135.5
344.66	50.9	869.3	145.4	145.6
344.76	125.2	912.5	167.2	167.4
344.89	140.6	919.6	170.7	170.8
344.96	150.3	923.8	172.9	173.1
344.83	176.4	935.3	179.5	179.4
345.08	200.6	943.9	184.3	184.6
345.09	225.2	952.9	189.1	189.4
345.09	241.3	958.5	191.8	192.1
345.09	250.9	961.8	194.1	194.4
345.13	261.2	965.3	195.7	195.7

Table III. Coefficients for the Representation of the Thermal Conductivity of Benzene, 2,2,4-Trimethylpentane, and Their Mixtures as a Function of Pressure According to Eq. (1)

Mole fraction benzene	T (K)	λ' ($mW \cdot m^{-1} \cdot K^{-1}$)	P' (MPa)	$10a_1$	10^2a_2	10^2a_3	10^3a_4
0.00	313.15	137.61	150	2.354	−5.347	3.209	−4.662
	321.15	136.37	150	2.474	−6.034	2.059	−8.047
	344.15	133.69	150	2.597	−5.886	2.991	−11.299
0.25	313.15	143.03	150	2.335	−5.744	2.168	4.128
	321.15	142.41	150	2.423	−6.453	2.106	−0.900
	344.15	138.55	150	2.802	−6.732	2.146	−1.569
0.50	313.15	148.87	150	2.232	−5.751	1.757	0.056
	321.15	147.91	150	2.290	−5.445	2.024	−5.860
	344.15	144.62	150	2.457	−5.787	2.379	−5.772
0.75	313.15	148.61	100	1.758	−2.932	2.391	18.627
	321.15	147.24	100	1.909	−3.728	−2.043	−13.549
	344.15	142.62	100	1.934	−4.169	1.247	−1.403
1.00	321.15	166.08	100	1.557	−3.139	1.685	7.699
	344.15	160.53	100	1.734	−3.289	0.961	−1.979

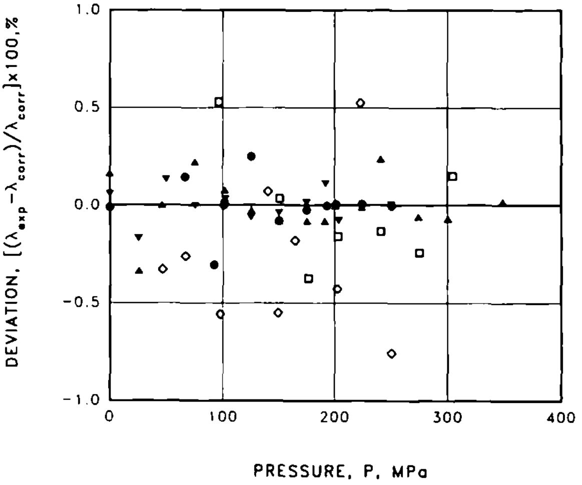

Fig. 1. Deviations of the experimental data for the thermal conductivity of 2,2,4-trimethylpentane from their representation by means of Eq. (1). Present work: (●) 313.15 K; (▼) 321.15 K; (▲) 344.15 K. Fareleira et al. [18]: (□) 321.15 K; (◇) 344.15 K.

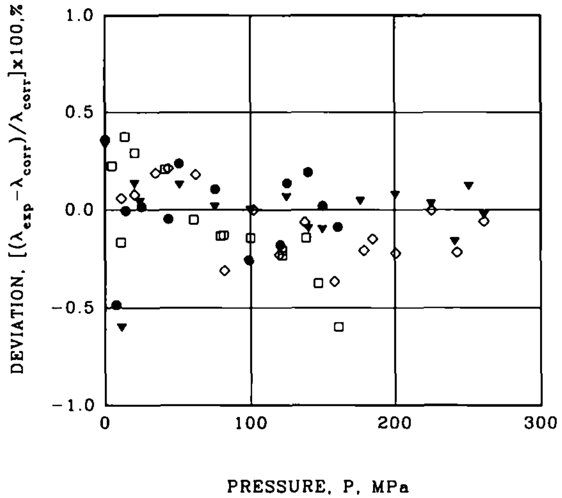

Fig. 2. Deviations of the experimental data of the thermal conductivity of benzene from the representation of it by means of Eq. (1). Present work: (●) 321.15 K; (▼) 344.15 K. Li et al. [19]: (□) 320.65 K; (◇) 344.15 K.

have been corrected to a nominal temperature by the application of small, linear teperature corrections and the results have an estimated accuracy of ±0.3%.

Equation (1) was again employed for the representation of the data as a function of pressure and the appropriate coefficients are listed in Table III. Figures 3, 4, and 5 display the deviations of the experimental data from the optimum representation for the three mixtures. The maximum deviation from the representation is ±0.5% and the standard deviation is ±0.2% which is consistent with the estimated uncertainty in the data.

Figures 6a–c show the isobaric, isothermal composition dependence of the thermal conductivity of the mixtures. Only for the lower pressures and high temperatures is it possible to cover the full range of compositions owing to the solidification of the benzene. However, it is clear that the composition dependence of the thermal conductivity is distinctly nonlinear. No attempt was made to represent the isobaric behavior of the thermal conductivity directly. Instead, it is preferable to consider the density dependence of the thermal conductivity of the mixture, from which the pressure dependence can be deduced indirectly.

Table IV. Thermal Conductivity of a Benzene-2,2,4-Trimethylpentane Mixture [$x(C_6H_6) = 0.25$]

Temperature, T (K)	Pressure, P (MPa)	Density, ρ_r ($kg \cdot m^{-3}$)	Thermal conductivity ($mW \cdot m^{-1} \cdot K^{-1}$)	
			$\lambda(T_{nom}, \rho_r)$	$\lambda(T_{nom}, P)$
		$T_{nom} = 313.15$ K		
313.27	0.1	701.7	97.7	97.8
313.42	26.0	727.1	107.6	107.7
313.48	50.4	745.6	116.0	116.1
313.35	74.5	760.7	123.9	124.0
313.37	98.7	773.6	130.8	130.8
313.63	126.9	786.6	137.2	137.3
313.60	150.1	796.3	142.3	142.4
313.44	174.6	805.6	148.7	148.8
313.49	202.2	815.1	153.5	153.6
313.55	225.3	822.5	158.4	158.5
313.62	252.8	830.6	162.9	163.1
313.67	274.3	836.6	166.1	166.2
313.77	300.8	843.5	170.6	170.7
313.65	323.8	849.3	174.4	174.5
313.74	343.7	854.0	177.4	177.5
		$T_{nom} = 321.15$ K		
320.78	0.1	695.0	95.7	95.7
320.79	26.4	722.3	105.9	106.0
320.83	50.4	741.1	114.7	114.6
320.70	73.0	755.8	122.4	122.3
320.74	100.5	770.8	129.9	129.8
320.75	125.1	782.5	136.4	136.3
320.80	175.7	803.0	147.4	147.4
320.64	197.7	810.8	152.9	152.9
320.77	251.0	827.5	162.7	162.6
321.02	298.3	840.4	170.3	170.3
321.03	324.3	847.0	174.1	174.1
321.17	346.3	852.3	178.5	178.5
		$T_{nom} = 344.15$ K		
344.85	0.1	673.3	90.2	90.3
344.80	25.5	704.2	100.1	100.2
344.83	50.1	725.8	109.4	109.6
344.87	73.3	742.1	117.6	117.8
345.08	100.3	757.8	125.4	125.6
345.15	125.6	770.6	131.8	132.1
345.08	149.9	781.6	138.1	138.4
345.05	176.0	792.2	144.0	144.4
345.09	202.1	801.8	150.1	150.4
345.01	227.3	810.3	154.8	155.0
345.10	253.2	818.4	159.0	159.3
344.94	278.2	825.8	164.0	164.2
344.63	302.5	832.6	168.1	168.3

Table V. Thermal Conductivity of a Benzene-2,2,4-Trimethylpentane Mixture [$x(C_6H_6) = 0.50$]

Temperature, T (K)	Pressure, P (MPa)	Density, ρ_r ($kg \cdot m^{-3}$)	Thermal conductivity ($mW \cdot m^{-1} \cdot K^{-1}$)	
			$\lambda(T_{nom}, \rho_r)$	$\lambda(T_{nom}, P)$
		$T_{nom} = 313.15$ K		
314.50	0.1	734.8	104.3	104.7
314.23	27.2	760.4	113.9	114.2
314.51	50.0	777.3	121.8	122.2
314.59	75.3	793.0	129.4	129.8
314.49	101.2	806.9	137.1	137.5
314.49	126.6	818.9	143.0	143.4
314.44	152.9	830.1	149.2	149.6
314.59	177.0	839.3	153.6	153.9
314.57	203.0	848.5	159.2	159.6
314.52	225.5	855.9	164.0	164.4
314.62	276.3	871.1	172.2	172.5
314.54	300.2	877.7	175.4	175.8
314.60	325.5	884.2	180.2	180.6
		$T_{nom} = 321.15$ K		
321.23	0.1	728.6	102.3	102.3
321.17	27.8	755.7	112.4	112.5
321.28	50.2	772.7	121.2	121.2
321.30	75.7	789.0	128.6	128.6
321.27	101.2	803.0	135.9	135.9
321.29	125.8	814.8	142.3	142.4
321.34	150.3	825.4	148.2	148.3
321.36	175.7	835.4	153.2	153.3
321.37	202.4	845.0	158.2	158.3
321.37	227.4	853.4	163.8	163.9
321.24	251.0	860.8	168.1	168.1
321.24	274.5	867.7	171.8	171.9
321.29	301.8	875.2	176.1	176.2
321.33	325.5	881.4	179.4	179.4
321.28	351.2	887.8	183.4	183.4
		$T_{nom} = 344.15$ K		
345.06	0.1	706.0	96.4	96.7
345.03	25.2	734.5	106.2	106.5
345.03	50.4	755.9	116.1	116.4
344.91	100.6	787.9	131.8	132.1
344.92	125.7	800.7	138.1	138.4
345.11	149.8	811.6	144.4	144.8
345.01	200.6	831.7	155.3	155.6
345.18	224.9	840.2	160.4	160.8
345.10	251.2	848.7	165.3	165.6
345.15	275.4	856.1	169.8	170.1
345.15	301.7	863.6	174.4	174.7
344.93	350.9	876.7	182.5	182.7

Table VI. Thermal Conductivity of a Benzene-2,2,4-Trimethylpentane Mixture [$x(C_6H_6) = 0.75$]

Temperature, T (K)	Pressure, P (MPa)	Density, ρ_r ($kg \cdot m^{-3}$)	Thermal conductivity ($mW \cdot m^{-1} \cdot K^{-1}$)	
			$\lambda(T_{nom}, \rho_r)$	$\lambda(T_{nom}, P)$
		$T_{nom} = 313.15$ K		
314.25	0.1	784.1	117.1	117.5
314.21	26.8	808.7	126.0	126.4
314.34	31.6	812.4	127.4	127.8
314.49	41.1	819.4	131.0	131.5
314.44	50.5	826.0	134.2	134.6
314.48	62.8	833.9	138.2	138.6
314.60	71.2	838.9	140.4	140.9
314.66	81.5	844.8	142.2	142.7
314.65	92.0	850.5	145.9	146.4
314.53	120.4	864.6	153.6	154.1
314.57	151.4	878.2	161.0	161.5
		$T_{nom} = 321.15$ K		
320.99	0.1	777.5	114.9	114.8
321.03	0.1	777.4	114.7	114.7
321.24	21.9	798.6	122.3	122.3
320.96	39.3	812.9	128.9	128.9
321.04	60.4	827.6	135.6	135.6
321.06	82.2	840.8	141.6	141.6
321.40	102.5	851.5	148.2	148.3
321.42	121.5	860.8	152.7	152.8
321.40	121.4	860.8	152.9	153.0
321.42	141.3	869.8	157.7	157.8
321.45	151.5	874.1	159.6	159.6
		$T_{nom} = 344.15$ K		
345.37	0.1	752.9	106.9	107.3
345.23	21.7	777.2	115.7	116.1
345.33	41.2	794.6	123.3	123.8
345.24	61.1	809.6	130.8	131.2
345.27	81.7	823.0	137.0	137.4
345.30	101.6	834.5	142.8	143.2
345.34	122.2	845.2	148.0	148.4
345.36	142.4	854.7	152.7	153.1
345.32	161.9	863.3	157.4	157.8
345.30	182.8	871.8	161.7	162.1
345.25	203.2	879.5	166.3	166.7
345.33	241.6	892.8	173.6	174.0
345.25	262.2	899.4	177.5	177.8

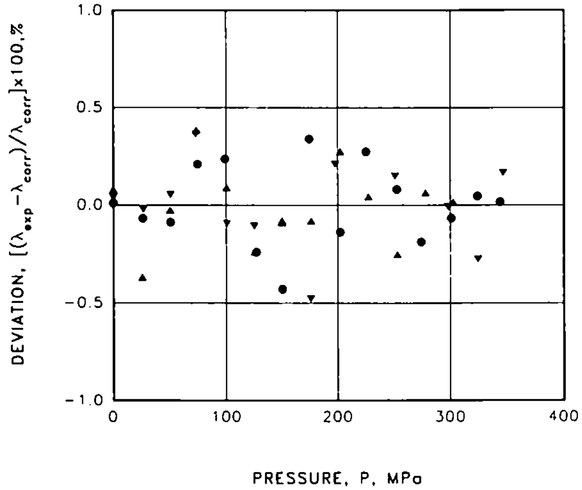

Fig. 3. Deviations of the present experimental data for the thermal conductivity of a mixture of 2,2,4-trimethylpentane and benzene with $x_{C_6H_6}=0.2500$. (●) 313.15 K; (▼) 321.15 K; (▲) 344.15 K.

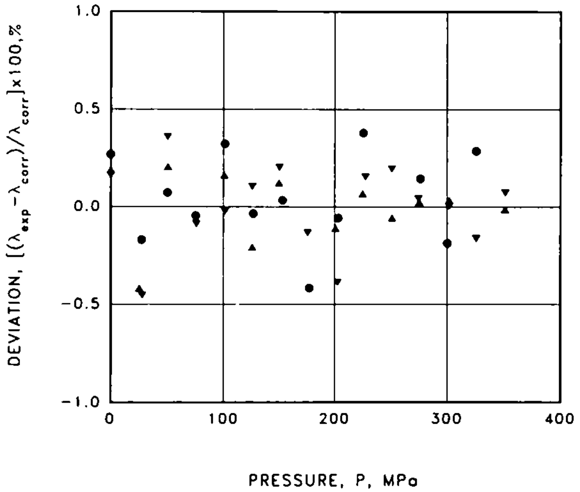

Fig. 4. Deviations of the present experimental data for the thermal conductivity of a mixture of 2,2,4-trimethylpentane and benzene with $x_{C_6H_6}=0.5000$. (●) 313.15 K; (▼) 321.15 K; (▲) 344.15 K.

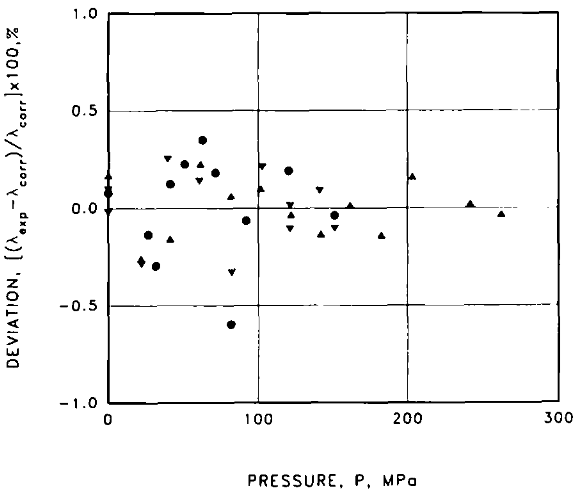

Fig. 5. Deviations of the present experimental data for the thermal conductivity of a mixture of 2,2,4-trimethylpentane and benzene with $x_{C_6H_6} = 0.7500$. (●) 313.15 K; (▼) 321.15 K; (▲) 344.15 K.

4. THE DENSITY DEPENDENCE OF THE THERMAL CONDUCTIVITY

4.1. The Hard-Sphere Theory

In a series of papers [5, 20–23], Dymond, Assael, and their collaborators have investigated the manner in which the model of a hard-sphere fluid can be used to represent the experimental data for the transport properties of polyatomic liquids and their mixtures. These analyses represent a synthesis of earlier developments. Among the systems studied in this development were normal alkanes, other organic and inorganic molecules, normal alkane mixtures, and, finally, pure aromatic hydrocarbons. The present system therefore has not been considered within these analyses since it is a mixture of an aromatic hydrocarbon with a branched alkane. However, given the success of the scheme proposed by Assael, Dymond et al. [5, 20–23], it is interesting to examine the extent to which the present mixture conforms to this established scheme. We concentrate our discussion here upon thermal conductivity, although it should be noted that the other transport properties can be incorporated within it.

From the rough hard-sphere model of a liquid, which is employed as a starting point of the analysis, one is led to the conclusions that the trans-

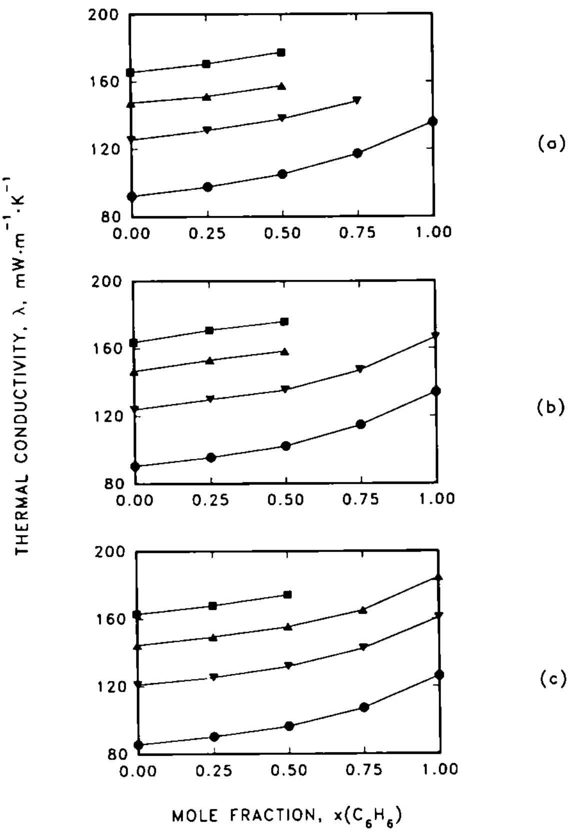

Fig. 6. The isobaric, isothermal composition dependence of the thermal conductivity of mixtures of 2,2,4-trimethylpentane and benzene. (a) $T = 313.15$ K; (b) $T = 321.15$ K; (c) $T = 344.15$ K. (●) 0.1 MPa; (▼) 100 MPa; (▲) 200 MPa; (■) 300 MPa.

port properties of the fluid are proportional to those of the smooth, hard-sphere fluid. In particular, for the thermal conductivity [23]

$$\lambda = R_{\lambda} \lambda^{*}_{\mathrm{SHS}} \tag{3}$$

where R_{λ} is a roughness factor for thermal conductivity, characteristic of the system but independent of temperature and density. Exact, smooth hard-sphere transport coefficients are given by the product of the values from Enskog theory [5] and the corrections computed from molecular dynamics simulations [23]. A reduced thermal conductivity, λ^*, is defined by

$$\lambda^* = R_\lambda \lambda^*_{\mathrm{SHS}} = R_\lambda \left[\frac{\lambda_{\mathrm{SHS}}}{\lambda_0}\right]\left[\frac{V}{V_0}\right]^{2/3} \tag{4}$$

where λ_0 is the zero-density thermal conductivity of the thermal conductivity, V the molar volume of the system, and V_0 the close-packed volume of the hard-sphere assembly. Experimental values of λ^* can be obtained by substituting the hard-sphere results for λ_0, which leads to

$$\lambda^*_{\mathrm{exp}} = 1.936 \times 10^7 \, R_\lambda \left[\frac{M}{RT}\right]^{1/2} \lambda_{\mathrm{exp}} V^{2/3} \tag{5}$$

in which λ_{exp} is the measured thermal conductivity of a pure fluid with a molar mass M at a temperature T and molar volume V.

The determination of V_0 and R_λ at any temperature is accomplished by a well-established curve-fitting procedure. A plot of $\log \lambda^*$ versus $\log V$ from experiment is superimposed on universal plots of $\log \lambda^*$ versus $\log(V/V_0)$ from hard-sphere theory by vertical and horizontal adjustments, from which the factors R_λ and V_0, respectively, are obtained. Dymond Assael, and their collaborators [21–23] have performed this analysis simultaneously for all three transport coefficients using a combination of data from hard-sphere theory and experiment on higher alkanes to define the universal curves.

4.2. Prediction

We therefore begin by examining the ability of the general scheme of Dymond, Assael, and their collaborators to predict the present experimental data. For this purpose we employed the universal representation of λ^* which they have proposed,

$$\log(\lambda^*_{\mathrm{exp}}/R_\lambda) = \sum_{i=0}^{4} a_{\lambda i}(1/V_r)^i \tag{6}$$

where

$$V_r = V/V_0^{\mathrm{u}} \tag{7}$$

and the superscript u indicates the use of the universal function of Eq. (6) in the definition of V_0. In addition, we employed the values of R_λ for benzene proposed by Assael et al. [23] as well as the value of V_0 given by their representation. For 2,2,4-trimethylpentane, Assael et al. have not reported values for either V_0 or R_λ. Thus, we determined them by means of the superposition of the experimental values of λ^* for this liquid at each temperature upon the universal function given by Eq. (6). Finally, the values of R_λ and V_0 for the three mixtures were evaluated according to the procedures proposed by Assael et al. [5], namely,

$$V_0(x, T) = V_{0_1} x + (1 - x)\, V_{0_2} \tag{8}$$

and

$$R_\lambda(x) = x R_{\lambda_1} + (1 - x)\, R_{\lambda_2} \tag{9}$$

and we employ in Eq. (5)

$$M = x M_1 + (1 - x)\, M_2 \tag{10}$$

in which x denotes the mole fraction of benzene, which is distinguished by the subscript 1. The values of R_λ and V_0 determined in this way are listed in Table VII.

Equations (5) to (10) then permit a prediction of the thermal conductivity of the mixtures using only experimental information on the behavior of the pure components. Figure 7 contains a plot of the deviations of the present experimental data from these predictions. It can be seen that the maximum deviation does not exceed 6%, a value which is entirely con-

Table VII. Values of Roughness Factor, R_λ, and Characteristic Volume, V_0

Mole fraction benzene	R_λ	T (K)	V_0 ($10^{-6} \cdot m^3 \cdot mol^{-1}$)
0.00	2.42	313.15	100.84
(2,2,4-trimethylpentane)		321.15	100.10
		344.15	99.91
0.25	2.197	313.15	90.60
		321.15	89.99
		344.15	89.75
0.50	1.974	313.15	80.35
		321.15	79.88
		344.15	79.58
0.75	1.751	313.15	70.10
		321.15	69.77
		344.15	69.42
1.00	1.528	313.15	59.86
(benzene)		321.15	59.66
		344.15	59.25

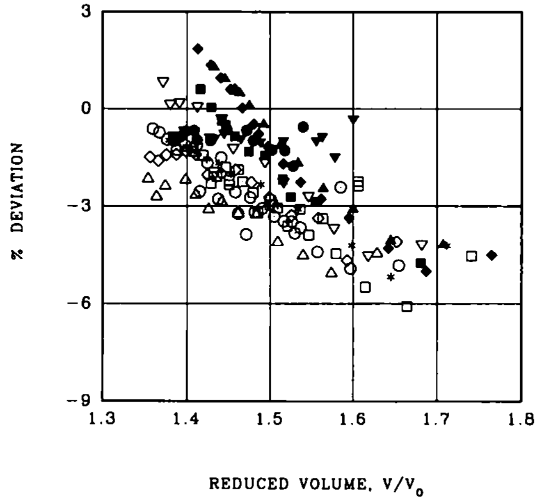

Fig. 7. Deviations of the present experimental data for the thermal conductivity for benzene, 2,2,4-trimethylpentane, and their mixtures from the predictions of the scheme of Dymond, Assael, and their collaborators based on Eqs. (5) to (9) and the parameters in Table VII. Benzene: (●) 321.15 K; (▼) 344.15 K. 2,2,4-Trimethylpentane: (■) 313.15 K; (▲) 321.15 K; (◆) 344.15 K. $x_{C_6H_6} = 0.2500$: (○) 313.15 K; (▽) 321.15 K; (□) 344.15 K. $x_{C_6H_6} = 0.5000$: (△) 313.15 K; (◇) 321.15 K; (★) 344.15 K. $x_{C_6H_6} = 0.7500$: (⊙) 313.15 K; (▣) 321.15 K; (◈) 344.15 K.

sistent with the uncertainty claimed for the predictive procedure of Dymond, Assael, and their collaborators. A corollary of this result is that the parameters listed in Table VII may be used to predict the thermal conductivity of mixtures of different composition over a wider range of thermodynamic states than covered here, as well as the viscosity of mixtures of benzene and 2,2,4-trimethylpentane, with the same level of confidence.

4.3. An Improved Representation

Despite the success of the predictive scheme described above and its usefulness for many practical purposes, it is possible to discern in Fig. 7 systematic deviations of the present experimental data from it. The deviations emerge as a function density, and not of temperature, and are different in magnitude and character for the two pure fluids and for each of the mixtures. In fact, there is a distinct trend in the pattern of the deviations as the mole fraction of benzene in the system diminishes. This result indicates that, at a level consistent with the precision of the present experimental data, the density dependence of the thermal conductivity of the system studied here is not universal. That the behavior of 2,2,4-trimethylpentane is different from that of its normal isomer was noted in our earlier report on this fluid [18]. It is therefore interesting to examine the behavior of the systems in more detail in order to seek an improved description of the present experimental data and, ultimately, to seek to improve the available theory upon which predictive procedures can be based.

We begin by retaining the most important element of the hard-sphere theory, which forms such a successful basis for the prediction of transport properties in the liquid phase, namely, that the temperature dependence of the reduced thermal conductivity, λ^*, is contained exclusively within the core volume V_0. However, we discard the idea that the density dependence of λ^* is universal among the different fluids. Thus, we seek to represent the density dependence of λ^* for the two pure fluids and their mixtures independently by means of an equation of the form

$$\left(\frac{\lambda^*}{R_\lambda}\right)(V/V_0)^{7/3} = \sum_{i=0}^{3} b_{\lambda_i}(V_0/V)^i \tag{11}$$

Here, the factor $(V/V_0)^{7/3}$ on the left-hand side is chosen to remove the dominant contribution to the density dependence of λ^*. In performing this analysis we retained the values of R_λ listed in Table VII for the pure com-

Table VIII. Values of Characteristic Volume, V_0, and Coefficients of Eq. (11)

Mole fraction benzene	T (K)	V_0 ($10^{-6}\,m^3 \cdot mol^{-1}$)	b_{λ_0}	b_{λ_1}	b_{λ_2}	b_{λ_3}
0.00	313.15	100.84	−7.467	75.0	−207.5	193.5
	321.15	100.10				
	344.15	99.91				
0.25	313.15	90.20	46.89	−184.1	204.5	−25.02
	321.15	89.65				
	344.15	89.10				
0.50	313.15	79.82	54.18	−219.05	261.6	−56.92
	321.15	79.77				
	344.15	79.45				
0.75	313.15	69.48	−24.94	148.23	−303.0	230.7
	321.15	69.30				
	344.15	68.85				
1.00	321.15	59.66	158.82	−683.8	951.9	−399.6
	344.15	59.25				

ponents and their mixtures. In addition, we retained, as reference values, the values of V_0^u for the lowest isotherm for the two pure components. For the mixtures the values of V_0 were determined by the condition that, for each system, they should be those yielding the optimum superposition according to Eq. (11), using the value of V_0 for benzene at the lowest temperature as a reference. The values of V_0 thus derived are listed in Table VIII together with the coefficients of b_{λ_i} of Eq. (11) that secure the optimum representation of the entire set of experimental data for each mixture.

Figures 8 to 12 contain plots of the deviations of the experimental data from these representations for individual fluids in the order of increasing benzene content. The maximum deviation does not now exceed ±0.8% for any individual fluid, while the standard deviation over the complete data set is ±0.4%. The latter value is broadly consistent with the combined experimental uncertainty in the thermal conductivity and density values.

It follows from this analysis that one of the essential features of the hard-sphere theory, that the temperature dependence of λ^* is contained entirely within V_0, is confirmed to a high degree of precision. It is also noteworthy that the optimum values of V_0 for the mixture, contained in Table VIII, depart only very slightly from those generated by the simple

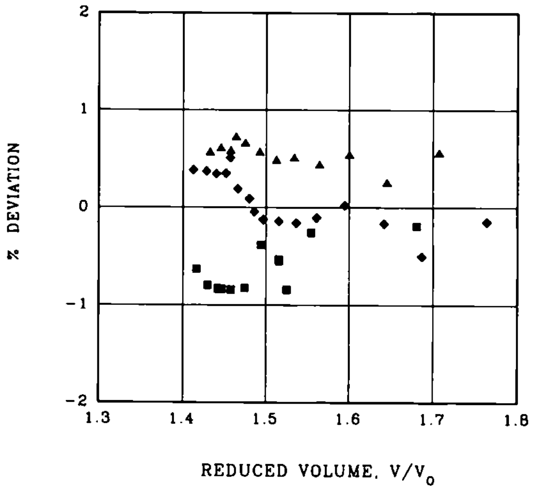

Fig. 8. Deviations of the present experimental data for the thermal conductivity of 2,2,4-trimethylpentane from their representation by means of Eq. (11) and the coefficients in Table VIII. (■) 313.15 K; (▲) 321.15 K; (◆) 344.15 K.

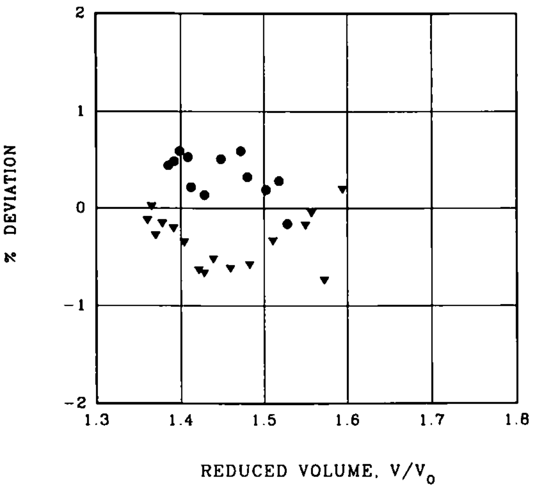

Fig. 9. Deviations of the present experimental data for the thermal conductivity of benzene from their representation by means of Eq. (11) and the coefficients in Table VIII. (●) 321.15 K; (▼) 344.15 K.

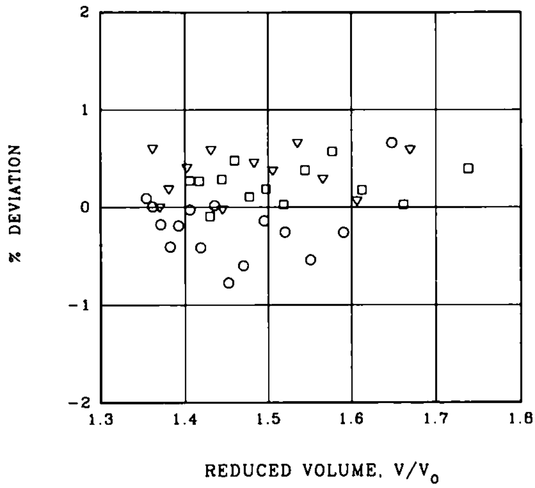

Fig. 10. Deviations of the experimental data for the thermal conductivity of a mixture of 2,2,4-trimethylpentane and benzene with $x_{C_6H_6} = 0.2500$ from their representation by means of Eq. (11) and the coefficients in Table VIII. (○) 313.15 K; (▽) 321.15 K; (□) 344.15 K.

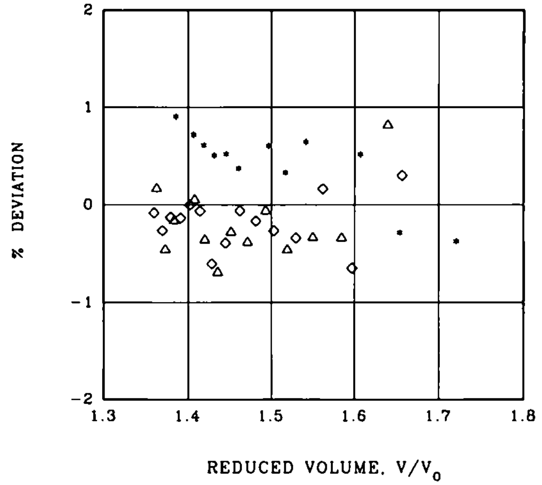

Fig. 11. Deviations of the experimental data for the thermal conductivity of a mixture of 2,2,4-trimethylpentane and benzene with $x_{C_6H_6} = 0.500$ from their representation by means of Eq. (11) and the coefficients in Table VIII. (△) 313.15 K; (◇) 321.15 K; (★) 344.15 K.

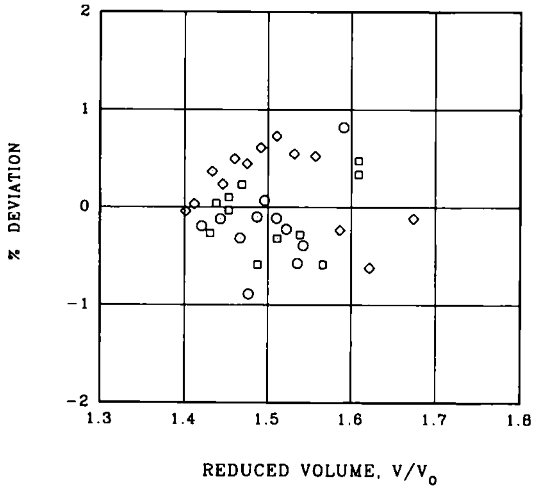

Fig. 12. Deviations of the experimental data for the thermal conductivity of a mixture of 2,2,4-trimethylpentane and benzene with $x_{C_6H_6} = 0.7500$ from their representation by means of Eq. (11) and the coefficients in Table VIII. (○) 313.15 K; (□) 321.15 K; (◇) 344.15 K.

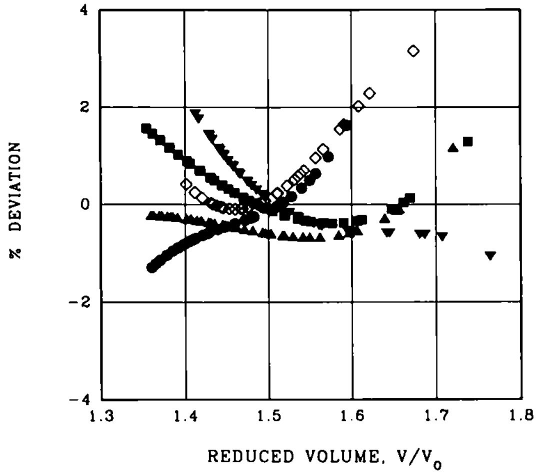

Fig. 13. Deviations of the present experimental data of the thermal conductivity 2,2,4-trimethylpentane, benzene, and their mixtures from a single function in the form of Eq. (11) which gives an optimum representation of the entire data. (▼) 2,2,4-Trimethylpentane; (●) benzene; (■) $x_{C_6H_6} = 0.2500$; (▲) $x_{C_6H_6} = 0.5000$; (◇) $x_{C_6H_6} = 0.7500$.

mixing rule of Eq. (8). However, the coefficients b_{λ_i} for the five systems studied here vary widely, confirming the observation concerning Fig. 7 that there are systematic departures from a universal density dependence for λ^*. This is illustrated in Fig. 13, which contains a plot of the deviations of the functions λ^* of Eq. (11) from a single function selected to secure an optimum representation of them all. It can be seen that, as the content of benzene in the mixture increases, the behavior of the density changes systematically and thus provides rather strong evidence that, at the highest level of precision, there are systematic departures from a universal density dependence of λ^* in this range of reduced volumes. It remains to be investigated whether such deviations are observed for other systems or are confined to those that involve branched alkanes which lie outside the general scheme of Dymond, Assael, and their collaborators. It would also be interesting to assess to what extent similar behavior is discernible among viscosity data for the same systems.

Equation (5), together with Eq. (11) and the parameters in Table VIII, evidently provides a concise means of representing the present experimental data within a standard deviation of $\pm 0.4\%$. If, in place of the values of V_0 listed in Table VIII, values deduced by the application of Eq. (8) are employed, the agreement is only slightly worsened, to $\pm 0.5\%$.

5. CONCLUSIONS

New experimental data for the thermal conductivity of a liquid mixture of benzene and 2,2,4-trimethylpentane have been obtained over a wide range of temperatures. The predictive procedure, available based upon rigid-sphere theory, is capable of reproducing the data within the claimed uncertainty of the former (±6%). At a higher level of precision, however, the present experimental data cast some doubt upon the universality of the density dependence of the reduced thermal conductivity of liquids, which is the basis of the proposed scheme. Clear evidence has been found for systematic departures from this universality which merit further investigation in an attempt to refine the theoretical desorption of transport in liquids.

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