THERMAL CONDUCTIVITY OF CHLOROBENZENE AT PRESSURES UP TO 430 MPa

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New, absolute measurements of the thermal conductivity of the moderately polar liquid, chlorobenzene, are reported for four isotherms in the temperature range 308–360 K for pressures up to 430 MPa. The results have an estimated accuracy of ±0.3%.

The density dependence of the thermal conductivity is found to be represented by a single equation for all isotherms, each isotherm being distinguished only by the value of the characteristic molar volume for chlorobenzene. This method of representation of the experimental data is similar to that employed for non-polar fluids such as hydrocarbons and, in particular, benzene. However, the details of the density dependence for the thermal conductivity for benzene and chlorobenzene are significantly different.

1. Introduction

In a series of papers, exemplified by the most recent [1], an experimental investigation of the behaviour of the thermal conductivity of organic, predominantly hydrocarbon, liquids has been reported. All of the measurements have been carried out in a transient hot-wire instrument described in detail earlier [2]. In a parallel development [3], a specially-designed version of the instrument has been used to study electrically-conducting and polar liquids such as water and methanol.

In the present paper we report measurements of the thermal conductivity of chlorobenzene, which has a dipole moment of 1.6 D. The measurements have been carried out in the instrument not specifically designed for such fluids, and the purpose of the investigation is twofold. On the one hand, it is important for the overall programme of measurements of the thermal conductivity of liquids to establish the degree of polarity in the fluid which necessitates the use of the specially-built instrument. To this end, a modified experimental arrangement

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has been developed which extends the range of polar liquids that can be studied. On the other hand, it is interesting to ascertain whether a relatively strongly polar liquid such as chlorobenzene conforms to the nearly universal behaviour of the density dependence of the thermal conductivity observed among a broad class of hydrocarbons [1, 4].

2. Experimental

The majority of the features of the transient hot-wire instrument employed for the measurements have been described elsewhere [2]. Consequently, it is only necessary here to recall that the essential elements consist of two platinum wires of nominal diameter 7 μm, each suspended along the axis of a cylindrical metal cell with a diameter of about 10 mm. The test fluid surrounds the wires and during a measurement the increase of the resistance difference of the wires is measured as a function of time following initiation of a known current in the wires at time $t = 0$. This measured resistance change can be converted into a temperature rise of the wire by means of a prior resistance-temperature calibration. The measured temperature rise as a function of time, after application of a few, small corrections, ΔT_{id}, then yields the thermal conductivity, λ, by application of the equation [2]:

$$\Delta T_{id} = \frac{q}{4\pi\lambda} \ln \frac{4\kappa t}{a^2 C} , \tag{1}$$

in which q is the heat generated in the wire per unit length, κ is the thermal diffusivity of the fluid, a is the wire radius, and C is a numerical constant.

The transient resistance measurements in the present installation are carried out with the aid of an automatic bridge shown schematically in fig. 1 [3]. The long and short wires of the hot-wire cells are denoted by R_L and R_S, respectively. The two wires are connected in opposite arms of the bridge, together with appropriate fixed resistors, R_1 and R_2, so that $R_1 + R_L \approx R_2 + R_S$. Furthermore, in the right-hand arm of the bridge, R_3 is a fixed resistance, while R_4 is effectively a variable resistance that can be adjusted to a number of preset values under computer control [3] in order to provide a sequence of balance points for the bridge as the resistances of the wires in the left-hand arm change. Again, circumstances are arranged so that $R_3 \approx R_4$ throughout the measurement cycle. The d.c. constant voltage source, V, used as the bridge supply, is centre-tapped and effectively shunted to ground through the capacitors, C, and the resistors, R. Thus, points A and B of the bridge are both very close to ground potential, the difference between them
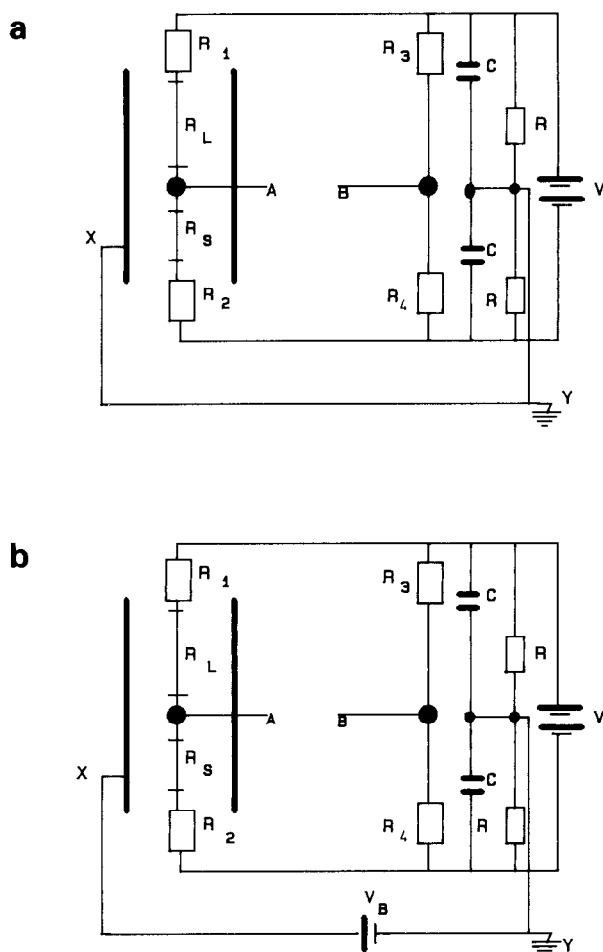
Fig. 1. (a) The automatic bridge configuration for use with non-polar, electrically insulating liquids. (b) The automatic bridge configuration employed for chlorobenzene.

representing just the transient out-of-balance of the bridge amounting to a few millivolts at most.

In normal operation [fig. 1(a)] the walls of the metallic cell are connected directly to the single ground by means of the path XY. Thus, if the fluid separating the wires from the cell walls is a non-electrolyte and hence not electrically conducting, the performance of transient resistance measurements contributes to the charging of the small capacitor (100 pF) formed by the wires and the cell walls. The associated timescale is such as not to interfere with the resistance measurements of the bridge (typically 20 ps).

With a polar liquid such as chlorobenzene, it has been observed that two related new phenomena occur in the transient hot-wire cell. First, a small potential difference (of the order of 25 mV) is observed to develop between the walls of the cell and the wires. Secondly, the impedance between the wires and the cell walls is reduced to about 20 MΩ. Following a systematic investigation, the origin of both effects has been traced to the formation of an electrolytic cell between the wire supports and the cell wall owing to the presence of just a few ions in the polar fluid, probably enhanced by the presence of slightly porous insulators. In such circumstances the performance of a transient hot-wire measurement causes a small, but fluctuating current to flow from the wires to the cell walls and thence to ground, as the potential of the wires changes. Because the equivalent impedance is in parallel with the wires, its effect is to induce a small (~0.1%) curvature into the measured line relating ΔT_{id} to $\ln t$.

Provided that the effect is small (as it is for chlorobenzene) a simple remedy is afforded by the scheme shown in fig. 1(b), where the cell walls are biased with respect to ground by a d.c., V_B, potential supplied by a battery of 9 V. In this arrangement the fluctuations in the potential of the wires have a very small influence on the leakage current flowing and hence a negligible effect on the measured impedance of the wires.

Fig. 2 illustrates the success of the procedure for one of the present measurements on chlorobenzene. The diagram contains a plot of the deviations
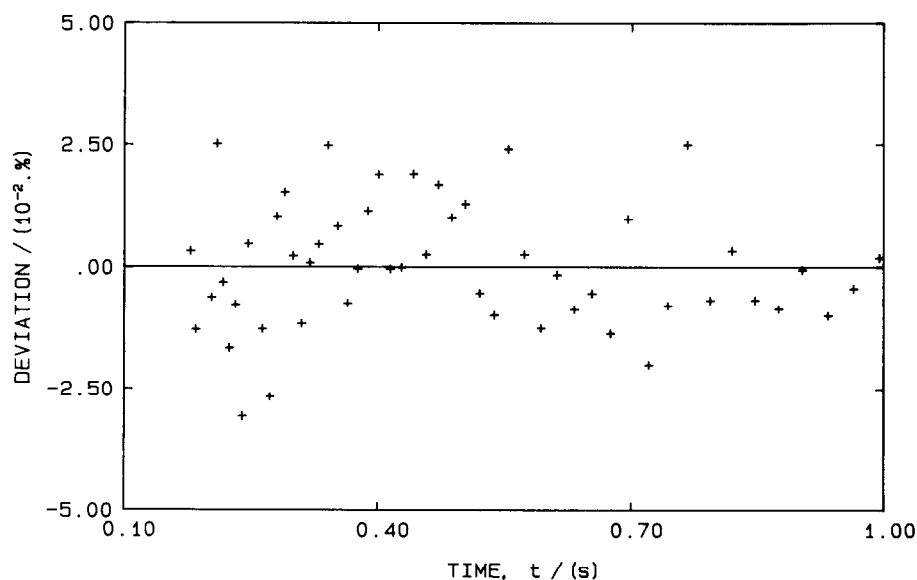

Fig. 2. The deviations of the corrected temperature rise measurements from a linear fit to them as a function of $\ln t$ for a run in chlorobenzene at a pressure of 300 MPa and a temperature of 318 K.

of the measured values of ΔT_{id} from a linear fit to them as a function of $\ln t$. It can be seen that the deviations are entirely random and that they do not exceed $\pm 0.05\%$. Since the temperature rise employed in the measurements is typically 2 K, the maximum deviation corresponds to ± 1 mK. This is taken as ample evidence of the correct operation of the instrument.

In the reduction of the experimental data it is necessary to apply small corrections to the measured temperature rise which require values for the heat capacity and density of the fluid. The former have been estimated using the methods described by Reid et al. [5], whereas for the latter we have employed the results of Gibson and Loeffler [6]. The influence of these two properties on the evaluation of the thermal conductivity is very small ($<0.1\%$) so that the contribution of uncertainties in these quantities in the final results is negligible.

3. Results

Tables I–IV list the thermal conductivity for chlorobenzene along four isotherms at 308.15 K, 319.15 K, 337.65 K and 359.55 K in the pressure range up to 430 MPa. The tables list the thermal conductivity at the reference temperature and the experimental pressure, together with the thermal conductivity along a nominal isotherm. The correction of the data to a common isotherm has been accomplished with the procedure detailed earlier [2].

There are four determinations of the density of chlorobenzene at high pressures [6–9]. The earliest, due to Bridgman [7], extend over both the temperature and density range of interest here, but the results are inconsistent with later measurements, possibly owing to the impurity of the sample so that they are not used. Of the other three sets of results, two [8, 9] extend to pressures as high as 500 MPa, but do not cover the temperature range required. On the other hand, the data of Gibson and Loeffler [6] cover the necessary temperature range, but extend only to 100 MPa. It has been verified that the Tait equation recommended by Gibson and Loeffler [6] represents the density measurements of Skinner et al. [8] at 303.15 K within $\pm 0.2\%$, even at 500 MPa. Consequently, we have employed the Tait equation recommended by Gibson and Loeffler [6] to evaluate the density of chlorobenzene at all pressures and temperatures and these are the data quoted in tables I–IV.

It is estimated that the uncertainty in the thermal conductivity data listed in tables I–IV may be $\pm 0.3\%$, while the uncertainty in the density up to 100 MPa is $\pm 0.2\%$, whereas at high pressures it may amount to $\pm 0.5\%$.

For the purposes of interpolation the thermal conductivity along the nominal isotherms have been represented by a polynomial of the form:

Table I

The thermal conductivity of chlorobenzene at $T_{nom} = 308.15$ K.

Pressure, P (MPa)	Reference density, ρ_r (kg m^{-3})	Thermal conductivity	
		$\lambda(T_{nom}, \rho_r)$ (mW m^{-1} K^{-1})	$\lambda(T_{nom}, P)$ (mW m^{-1} K^{-1})
6.4	1096	123.9	123.8
6.4	1096	123.8	123.7
14.3	1102	125.9	125.8
24.9	1110	128.8	128.7
24.9	1111	128.8	128.8
40.9	1122	132.5	132.5
40.8	1122	132.6	132.6
40.6	1122	132.6	132.6
40.8	1122	132.5	132.5
73.2	1142	139.7	139.7
73.2	1142	139.8	139.7
97.2	1156	144.4	144.4
97.2	1156	144.4	144.4
124.4	1170	149.3	149.3
124.3	1170	149.3	149.3
152.6	1183	154.1	154.1
152.4	1183	154.2	154.3
152.4	1183	154.1	154.2
177.9	1194	157.9	157.9
177.9	1194	157.9	158.0
177.9	1194	157.8	157.8
203.1	1204	161.8	161.8
203.1	1204	162.0	162.0
234.8	1216	166.1	166.1
234.9	1216	166.3	166.3
267.2	1227	170.3	170.4
267.3	1227	170.4	170.4
295.8	1236	173.7	173.7
326.0	1246	176.0	176.0
352.8	1253	179.9	179.9
384.3	1262	183.4	183.4
384.0	1262	183.3	183.3
416.8	1271	186.4	186.4
416.9	1271	186.4	186.4
426.8	1273	187.4	187.4

$$\lambda = \lambda' \left[1 + \sum_{i=1} a_i \left(\frac{p - p'}{p'} \right)^i \right]. \tag{2}$$

The coefficients λ', p' and a_i, which secure the optimum representation of the data, are collected in table V. Fig. 3 contains a plot of the deviations of the data from these representations which do not exceed $\pm 0.5\%$, the standard

Table II
The thermal conductivity of chlorobenzene at $T_{nom} = 319.15$ K.

Pressure, P (MPa)	Reference density, ρ_r (kg m^{-3})	Thermal conductivity	
		$\lambda(T_{nom}, \rho_r)$ (mW m^{-1} K^{-1})	$\lambda(T_{nom}, P)$ (mW m^{-1} K^{-1})
1.9	1081	119.8	120.0
1.9	1081	119.9	120.1
1.5	1080	119.8	120.0
1.5	1080	119.8	120.0
4.3	1083	120.7	120.9
4.7	1083	120.7	120.9
14.1	1092	123.2	123.4
14.1	1092	123.2	123.4
14.1	1092	123.1	123.4
25.2	1101	126.1	126.4
25.2	1101	126.1	126.3
40.8	1110	130.0	129.6
55.6	1121	133.4	133.0
76.3	1134	138.0	137.6
76.1	1134	137.5	137.2
102.6	1149	143.5	143.1
102.6	1149	143.4	143.1
116.7	1157	146.1	145.8
151.1	1174	152.2	152.0
172.6	1183	155.8	155.6
203.9	1196	160.4	160.2
236.0	1209	165.3	165.2
276.0	1223	170.4	170.2
317.2	1236	175.5	175.3
377.2	1254	182.2	182.0
413.9	1264	185.4	185.3
453.4	1275	189.1	188.9
348.6	1246	178.8	178.7
348.6	1246	178.8	178.7

deviation of the entire body of data being ±0.1% and hence consistent with the estimated precision.

4. The density dependence of the thermal conductivity

A number of earlier investigations have demonstrated that among a wide class of non-polar liquids, the dependence of a reduced thermal conductivity upon density is universal [4]. The appropriate reduction of the thermal conductivity suggested by the rigid-sphere theory for dense fluids [4, 10] is:

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

Table III
The thermal conductivity of chlorobenzene at T_{nom} = 337.65 K.

Pressure, P (MPa)	Reference density, ρ_r (kg m^{-3})	Thermal conductivity	
		$\lambda(T_{nom}, \rho_r)$ (mW m^{-1} K^{-1})	$\lambda(T_{nom}, P)$ (mW m^{-1} K^{-1})
1.5	1059	115.0	114.9
3.8	1062	115.8	115.7
11.0	1069	117.9	117.8
11.0	1069	117.9	117.8
22.7	1080	121.3	121.3
45.1	1098	127.2	127.1
72.0	1117	133.8	133.8
102.1	1136	140.5	140.5
138.6	1156	147.4	147.4
184.8	1178	155.5	155.5
184.8	1178	155.5	155.5
236.9	1200	163.5	163.5
291.1	1219	171.1	171.1
337.4	1234	176.7	176.7
392.9	1251	183.4	183.4
393.0	1251	183.3	183.3
456.5	1268	189.8	189.8

Table IV
The thermal conductivity of chlorobenzene at T_{nom} = 359.55 K.

Pressure, P (MPa)	Reference density, ρ_r (kg m^{-3})	Thermal conductivity	
		$\lambda(T_{nom}, \rho_r)$ (mW m^{-1} K^{-1})	$\lambda(T_{nom}, P)$ (mW m^{-1} K^{-1})
1.6	1035	109.7	109.5
1.6	1035	110.0	109.9
5.7	1040	111.2	111.2
27.9	1064	117.9	117.9
58.2	1091	126.2	126.2
58.2	1091	126.1	126.1
90.1	1114	134.0	134.0
90.0	1114	133.9	133.9
131.8	1140	140.7	140.7
167.7	1159	149.6	149.5
208.6	1178	156.7	156.7
260.8	1200	164.9	164.9
311.2	1218	171.9	171.9
374.6	1239	179.9	179.9
428.4	1255	186.0	186.0

Table V
Coefficients of the correlation of the thermal conductivity of chlorobenzene as a function of pressure according to eq. (2).

T (K)	λ' (mW m^{-1} K^{-1})	p' (MPa)	$10a_1$	10^2a_2	10^2a_3	10^3a_4
308.15	161.30	200	1.7546	−4.3239	1.8476	−5.2266
319.15	160.02	200	1.8695	−4.6705	1.5568	−4.7561
337.65	157.94	200	1.9841	−4.5542	2.1753	−8.8235
359.55	154.89	200	2.1878	−4.3155	1.8898	−12.6431

and it is a result of the same theory that

$$\lambda^* = F(V/V_0) \quad \text{only} . \tag{4}$$

Here, V is the molar volume of the fluid, M the molar mass of the species, R the universal gas constant and V_0 a characteristic molar volume for the fluid, weakly dependent on temperature.

The result embodied in eq. (4) is readily examined for chlorobenzene alone with the aid of the present data, since it implies that it should be possible to superimpose curves of λ^* vs. $\ln V$ along various isotherms upon each other simply by an appropriate choice of V_0 for each temperature.
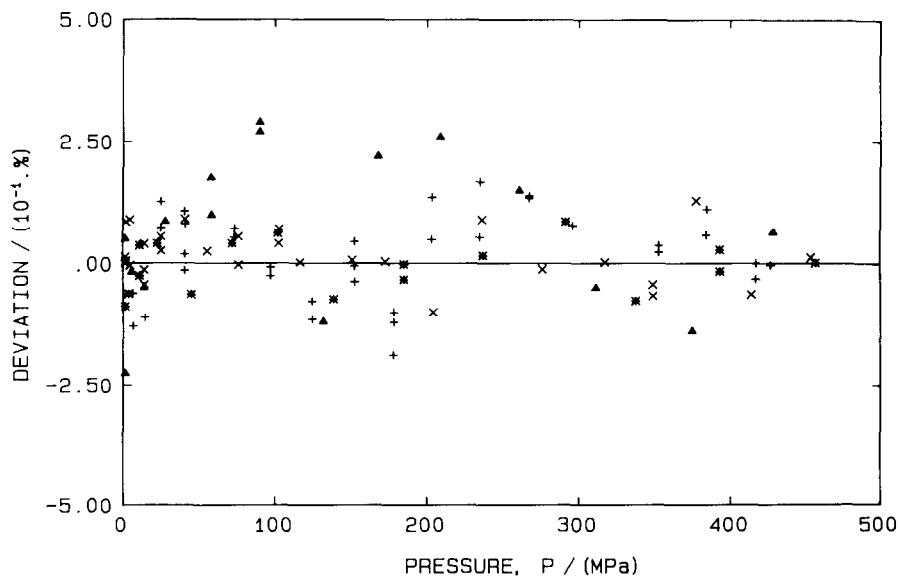

Fig. 3. Deviations of the thermal conductivity data for chlorobenzene from its correlation as a function of pressure with eq. (2). + 308.15 K; × 319.15 K; * 337.65 K; △ 359.55 K.

Fig. 4 contains the results of this superimposition which demonstrates that the procedure works remarkably well for this polar material as it has for non-polar fluids [11]. The volume dependence of the thermal conductivity of non-polar fluids has always been well represented by an equation of the form [11]:

$$\ln \lambda^* = A - B \ln(V/V_0) . \tag{5}$$

This same form of equation has been applied to the thermal conductivity data for chlorobenzene and the optimum values of the coefficients are
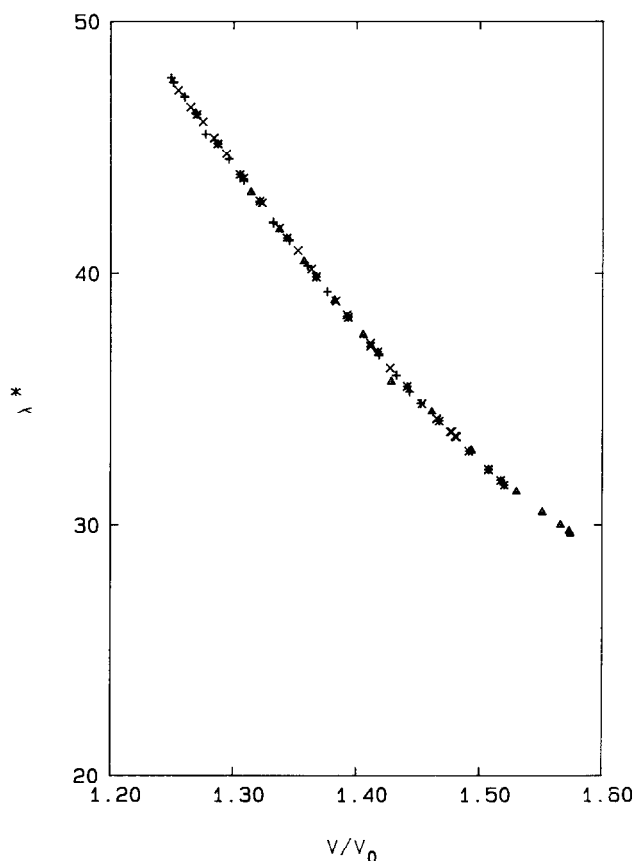
$$A = 4.3419 ; \qquad B = 2.110 . \tag{6}$$

Fig. 4. The reduced thermal conductivity of chlorobenzene as a function of volume. + 308.15 K; × 319.15 K; * 337.65 K; △ 359.55 K.

Fig. 5 shows the deviations of the experimental data from this representation while table VI lists the values of V_0 for each isotherm determined with respect to a reference value for benzene, $V_0(310.5 \text{ K}) = 57.62 \text{ m}^3 \text{ mole}^{-1}$ [12]. Although there is evidently a systematic pattern to the deviations, it does not exceed $\pm 0.8\%$ in the thermal conductivity itself and this is within the combined uncertainty of the thermal conductivity and density data so that it cannot be regarded as significant. At the same time, the figure serves to reinforce the close correspondence of the reduced thermal conductivity of chlorobenzene for various isotherms.

4.1. A comparison with the behaviour of non-polar fluids

It is interesting now to compare the behaviour of the function λ^* for the polar fluid chlorobenzene with that of a non-polar material. The most suitable
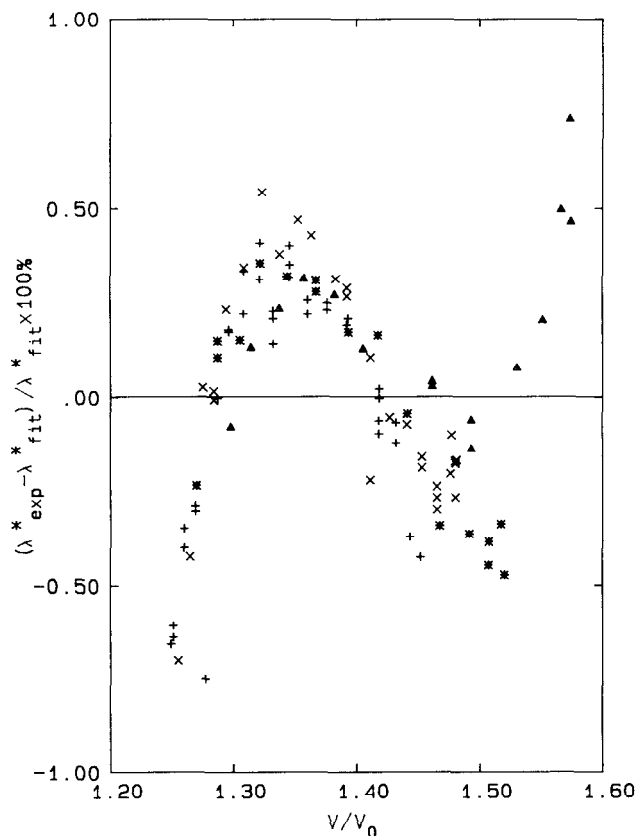

Fig. 5. Deviations of the thermal conductivity data for chlorobenzene from its correlation as a function of volume by means of eqs. (3) and (5). + 308.15 K; × 319.15 K; * 337.65 K; △ 359.55 K.

Table VI
Characteristic molar volumes for benzene and chlorobenzene.

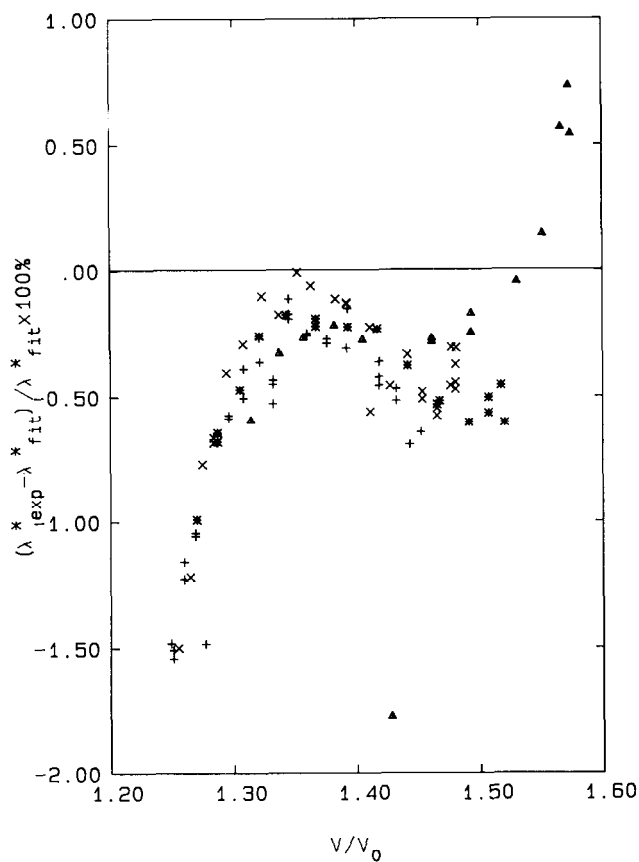| T (K)	Benzene	Chlorobenzene
308.15	–	70.77
310.0	57.67	–
319.15	–	70.40
320.5	57.50	–
337.65	–	69.92
344.00	57.11	–
359.55	–	69.14
360.50	57.00	–

Fig. 6. Deviations of the thermal conductivity data for chlorobenzene from its optimum representation by the correlation developed for benzene [12]. + 308.15 K; × 319.15 K; * 337.65 K; △ 359.55 K.

material for such a comparison is benzene for which thermal conductivity data and a representation of λ^* vs. V/V_0 were reported earlier [12]. Such a comparison allows us to examine the effect of the addition of a single chlorine atom to the molecule. Fig. 6 shows deviations of the values of λ^* for chlorobenzene from the optimum representation of it by the equation describing the thermal conductivity of benzene. Table VI includes the values of V_0 for benzene deduced using the same reference value as employed for chlorobenzene.

From fig. 6 is is clear that the density dependence of the thermal conductivity of chlorobenzene is significantly and systematically different from that of benzene. Furthermore, the values of the characteristic molar volume for chlorobenzene are significantly larger than those characteristic of benzene itself. The latter feature is consistent with the recent findings of Assael et al. [13] concerning a group contribution concept for the characteristic volume V_0. Further work on chlorinated hydrocarbons will, however, be necessary before it is possible to establish definitely a contribution to V_0 arising from the addition of a chlorine atom to a hydrocarbon.

Acknowledgements

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