International Journal of Thermophysics, Vol. 4, No. 4, 1983

Thermal Conductivity of Toluene in the Temperature Range 35–90°C at Pressures up to 600 MPa

C. A. Nieto de Castro,[1] S. F. Y. Li,[2] G. C. Maitland,[2] and W. A. Wakeham[2]

Received December 14, 1983

New, absolute measurements of the thermal conductivity of liquid toluene are reported. The measurements extend over the temperature range 35–90°C and the pressure range 0.8–600 MPa. A new analytic evaluation of the contribution of radiation in an absorbing emitting fluid to the measurement process is presented. This analysis indicates that the thermal conductivity determined in a transient hot-wire instrument is the radiation-free value. As a consequence it is possible to assert that the overall uncertainty in the experimental data is one of ±0.3%. A comparison of the data with the results of independent measurements by the same technique shows that the various sets of data are consistent within their mutual uncertainty.

KEY WORDS: high pressure; thermal conductivity; toluene; radiation contribution.

1. INTRODUCTION

In a number of earlier publications [1–4] we have reported the results of measurements of the thermal conductivity of liquids over a moderate temperature range and at pressures up to 600 MPa. The measurements have been carried out by the transient hot-wire technique, which is capable of high precision [1]. However, the accuracy which it has been possible to claim for the final results has been inferior to their precision owing to the contribution of radiative heat transfer in an absorbing fluid to the measurement process [5]. The contribution of radiative heat transfer to thermal conductivity measurements on absorbing liquids has been the subject of

[1]Centro de Quimica Estrutural, Complexo I, Instituto Superior Tecnico, Lisbon, Portugal.
[2]Department of Chemical Engineering and Chemical Technology, Imperial College, London S.W. 7 2BY, England.

0195-928X/83/1200-0311$03.00/0

doubt for a considerable time [6–9]. In different instruments and different liquids the radiative heat flux has variously been estimated to be of a magnitude between 2 and 40% of the thermal conduction flux and exceptionally of differing sign [10, 11].

In our work we have performed a complete, numerical solution of the conduction-radiation equations for a transient hot-wire instrument in order to deduce a correction to be applied to our experimental data to yield radiation-free thermal conductivities [5]. Unfortunately, the evaluation of this correction has proved so time-consuming and expensive that it is not practicable to apply it on a routine basis. Furthermore, many of the optical properties of the fluid and its bounding surfaces, which are necessary for the evaluation of the correction, cannot be measured under the conditions of interest so that the reliability of the correction is considerably reduced.

Toluene, which is the subject of the present investigation, has often been proposed as a standard reference material for thermal conductivity [12–14]. These proposals have usually been founded upon estimates of the magnitude of the radiative heat flux contribution to the measurement, which has been found to be small [12–14]. In view of the uncertainty surrounding these estimates, it seems essential that the problem of radiation be considered afresh in reporting further experimental results, especially if the data are to be regarded as input to a set of standard tables for the thermal conductivity. Accordingly, in the present work we have employed our numerical solution of the conduction-radiation problem for a transient hot-wire instrument as the basis for the development of an analytic solution. This new analysis shows that when the effects of radiation are significant to the measurement of thermal conductivity, their influence is readily observed and a simple, rapid method of correction is possible. For toluene the effects of radiation are in fact negligibly small so that no correction is necessary. We are therefore able to report thermal conductivity data for toluene with an accuracy of $\pm 0.3\%$, which is comparable with the precision of our measurements.

2. RADIATION AND CONDUCTION IN AN ABSORBING MEDIUM

The contribution of radiative heat transport to the total heat flux in thermal conductivity measurements can only be analyzed simply in the case of fluids transparent to radiation when the radiative and conductive heat fluxes are additive. In these circumstances it may readily be shown that for a transient hot-wire instrument, the radiant heat flux is negligible [15]. Thus, the basic equation describing the operation of such an instrument is simply

$$\rho C_p \frac{\partial T}{\partial t} = \lambda \nabla^2 T \tag{1}$$

whose solution, subject to the usual boundary conditions [5]

$$t < 0 \qquad T(r,t) = T_0 \tag{2}$$

$$t > 0, \quad r = 0 \qquad -q/2\pi\lambda = \lim_{r\to 0}\left(r\frac{\partial T}{\partial r}\right) \tag{3}$$

and

$$t > 0, \quad r = \infty \qquad T(r,t) = T_0 \tag{4}$$

yields the temperature rise of the fluid as a function of time, t, following the initiation of a line source of heat, q, per unit length at $r = 0$. Here, ρ is the density of the fluid, C_p is its constant pressure heat capacity, λ is its thermal conductivity, T is the temperature, and T_0 is the initial, equilibrium temperature. The solution for the temperature rise, which forms the basic working equation for the method, is then [16]

$$T(r_1,t) - T_0 = \Delta T_{id}(r_1,t) = \left(\frac{q}{4\pi\lambda}\right)E_1(r_1^2/4\kappa t) \tag{5}$$

where [17]

$$E_1(\xi) = \int_1^\infty (e^{-\xi u}/u)\,du \tag{6}$$

and

$$E_1(\xi) = -\gamma - \ln\xi + \xi + 0(\xi^2)$$

Here, the subscript *id* denotes the ideal model of the apparatus and γ is Euler's constant. In practice, we are interested in the solution for small values of $(r_1^2/4\kappa t)$ so that we may employ just the leading terms of the expansion of the exponential integral. Furthermore, a practical instrument departs from the ideal in a number of respects so that it is necessary to apply a number of small corrections to the measured temperature rise of the wire, $\triangle T_w$, to recover the "ideal" value. Hence, the working equation takes the form [16]

$$\Delta T_{id} = \Delta T_w + \sum_i \delta T_i = (q/4\pi\lambda)\ln(4\kappa t/r_1^2 C) \tag{7}$$

where

$$C = \exp(\gamma) \tag{8}$$

All of the corrections, δT_i, necessary for operation in nonabsorbing fluids, have been given elsewhere [16, 18–20].

In the case of fluids which absorb and emit radiation, the situation is considerably more complicated, and for a transient hot-wire instrument in which an isotropic grey fluid is bounded internally by a wire radius r_1, area A_1, and externally by a surface radius r_2, area A_2, the equation governing the temperature rise of the wire is [5]:

$$\rho C_p \frac{\partial T}{\partial t} = \lambda \nabla^2 T + Q'_{V \to dV_i} + Q'_{A_1 \to dV_i} + Q'_{A_2 \to dV_i} - 4K_i E_i \tag{9}$$

Here, the second, third, and fourth terms on the right represent gradients of one-way radiant heat fluxes from, respectively, the entire volume of the fluid to a volume element dV_i, from the wire surface to the volume element, and from the outer boundary to the volume element. The final term represents the gradient of the radiative heat flux emitted by the volume element dV_i, in which K_i is the appropriate mean extinction coefficient of the fluid and

$$E_i = n^2 \sigma T^4 \tag{10}$$

where n is the refractive index of the fluid and σ the Stefan-Boltzmann constant.

The appropriate boundary conditions for the solution of Eq. (9) are

$$\frac{q}{2\pi r_1} = -\lambda \left(\frac{\partial T}{\partial r} \right)_{r=r_1} - \alpha_1 Q_{A_2 \to dA_1}$$

$$- \alpha_1 Q_{V \to dA_1} + \epsilon_1 n^2 \sigma T^4(r_1) \qquad r = r_1, \quad t \geqslant 0 \tag{11}$$

$$T(r_2, t) = T_0 \qquad 0 \leqslant t \leqslant \infty \tag{12}$$

together with the initial condition (2). Here, dA_1 is an elemental area in A_1, and the second and third terms represent one-way radiant heat fluxes to this element from the outer boundary surface and the bulk of the fluid. In addition, α_1 represents the absorptivity of the wire surface and ϵ_1 its emissivity.

The full form of the integro-partial differential equation (9) cannot be solved analytically. However, Menashe and Wakeham [5] have developed a technique for its numerical solution subject only to the additional assumptions that the extinction coefficient is temperature independent over the small temperature range involved, that the outer bounding cylinder is black, and that $\alpha_1 = \epsilon_1 \neq f(T)$. Because the evaluation of each of the

radiant heat fluxes and their gradients requires the computation of a two or three dimensional integral at each time step, the numerical solution is both time consuming and expensive. Thus, although it has been possible to implement the numerical procedure in a number of specific cases and to compare its results with those in which there is no radiation effect, it has not been possible to apply it universally [5]. Furthermore, in order to apply the technique to measurements in fluids over a wide range of conditions, both the emissivity of the wire, ϵ_1, and the extinction coefficient of the fluid must be known over the same range of conditions. In practice, this knowledge has never been available, and values characteristic of just one set of conditions have had to be employed [5].

An alternative use of the numerical solution, which we investigate here, is as a guide to the relative magnitudes of the various terms within the governing equation (9). The aim of such a study is the simplification of Eq. (9) to a level where it may be solved analytically. To this end we have employed the numerical procedures of Menashe and Wakeham [5] to simulate a transient hot-wire measurement on toluene using apparatus parameters characteristic of our equipment and representative properties of the pure liquid. All of the quantities employed in the simulation are set out in Table I, including the extinction coefficient, K, which was determined experimentally in the manner described elsewhere [5].

Figure 1 contains plots of the relative magnitudes of the terms on the right-hand side of Eq. (9) as a function of time at two different radial locations in the fluid, omitting the term $Q'_{A_2 \to dV_i}$, which is rendered zero by condition (11) [5]. Figure 1(a) refers to a radius $r = 1.02r_1$ and Fig. 1(b) to a radius $r = 115r_1$. In each case it is apparent that the dominant additional contribution to the conduction heat-flux gradient arises from the emission of radiation by the fluid and that both of these terms exceed those arising from absorption by several orders of magnitude. The only exception to this situation arises in Fig. 1(b) at short times, when each of the terms is so small as to be insignificant and the numerical solution is inaccurate. The

Table I. Parameters Employed for the Simulation of a Measurement on Toluene

Temperature, T	360 K
Hot-wire radius, r_1	3.89 μm
Cell radius, r_2	4.95 mm
Heat flux, q	0.538 $W \cdot m^{-1}$
Thermal conductivity, λ	113.7 $mW \cdot m^{-1} \cdot K^{-1}$
Density, ρ	802.9 $kg \cdot m^{-3}$
Heat capacity, C_p	1904.0 $J \cdot kg^{-1} \cdot K^{-1}$
Mean extinction coefficient, K	4630 m^{-1}
Refractive index, n	1.4961

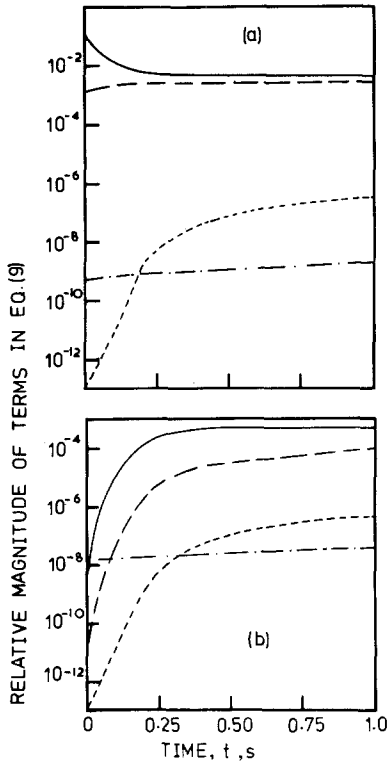

Fig. 1. Relative magnitude of the terms on the right-hand side of Eq. (9) as a function of time at two different radial coordinates: (a) $r = 1.02r_1$, and (b) $r = 115r_1$. Curves are as follows: conduction (solid); emission (long dash); $Q_{V\to dV_i}$ (short dash); $Q_{A_1\to dV_i}$ (dot-dash).

implication of these results, which are typical of other simulations we have carried out, is that we may neglect the terms $Q'_{V\to dV_i}$ and $Q'_{A_1\to dV_i}$ in Eq. (9). Physically, this means that, in the transient hot-wire experiment, the principal radiative contribution of the fluid to the heat transfer process arises from emission and not absorption as has frequently been assumed. This result may be understood by noting that the gradient of the radiant heat flux in an emitting volume element is determined by the local temperature gradient, and that in the transient hot-wire instrument the wire is so thin ($r_1 \simeq 3$ μm) that although the temperature rise of the fluid is only a few degrees Kelvin, its radial gradient is very large near the edge of the expanding temperature front arising from conduction. On the other hand, because the absorption terms are determined by the value of the extinction coefficient, which is temperature independent, their gradients are considerably smaller.

These observations enable Eq. (9) to be considerably simplified, so that

writing

$$\Theta = (T - T_0)/T_0 = \Delta T/T_0$$

and

$$R = r/r_1$$

we obtain

$$\frac{\partial \Theta}{\partial t} = \frac{\lambda}{\rho C_p r_1^2}\left[\frac{\partial^2 \Theta}{\partial R^2} + \frac{1}{R}\frac{\partial \Theta}{\partial R}\right] - \frac{16 Kn^2 \sigma T_0^3 \Theta}{\rho C_p} \tag{13}$$

in which we have made use of the definition of E_i from Eq. (10) and employed the linearization

$$T^4 - T_0^4 = 4T_0^4\Theta$$

which is justified for the small temperature rises employed in practice.

An analytic solution of Eq. (13) may now be attempted, but this is most easily accomplished by returning to the simplest model of the apparatus in which the heat source is vanishingly small and the outer boundary is situated at infinity. This is consistent with the approach adopted for other corrections to the ideal model in which all the departures of the real system from the ideal are treated as small, additive effects [16]. Using the fact that the radiation heat flux from the wire is negligibly small [16], the boundary conditions for Eq. (13) then become, following the same substitutions as before,

$$\frac{q}{2\pi T_0} = -\lambda \lim_{R \to 0} R\left(\frac{\partial \Theta}{\partial R}\right) \qquad \text{at} \quad R = 0, \quad t > 0 \tag{14}$$

$$\Theta = 0, \qquad R = \infty, \qquad t \geqslant 0 \tag{15}$$

and

$$\Theta = 0, \qquad t \leqslant 0 \tag{16}$$

Equation (13) is most easily solved by the use of the Laplace transform, denoted by a tilde, whose application leads to the equation

$$Z^2 \frac{d^2\tilde{\Theta}}{dZ^2} + Z\frac{d\tilde{\Theta}}{dZ} - Z^2\tilde{\Theta} = 0 \tag{17}$$

with the boundary conditions

$$\lim_{Z\to 0} Z\left(\frac{d\tilde{\Theta}}{dZ}\right) = \frac{-q}{2\pi\lambda s T_0} \tag{18}$$

and

$$Z = \infty, \qquad \tilde{\Theta} = 0 \tag{19}$$

Here,

$$Z = \left(\frac{s+B}{A}\right)^{1/2} R \tag{20}$$

where s is the Laplace transform variable

$$A = \lambda/\rho C_p r_1^2 \tag{21}$$

and

$$B = \frac{16 Kn^2 \sigma T_0^3}{\rho C_p} \tag{22}$$

The solution of Eq. (17) is [17]

$$\tilde{\Theta} = C_1 I_0(Z) + C_2 K_0(Z) \tag{23}$$

where I_0 and K_0 are modified Bessel functions. By virtue of the boundary condition (19) and the properties of I_0 [17], this becomes

$$\tilde{\Theta} = C_2 K_0(Z) \tag{24}$$

and from conditions (18) we obtain

$$\tilde{\Theta} = \frac{q}{2\pi\lambda s T_0} K_0(Z) \tag{25}$$

The inverse of the Laplace transform may be found by application of the convolution theorem and standard transforms [17] so that

$$\tilde{\Theta} = -\frac{q}{4\pi\lambda T_0} \int_{\infty}^{R^2/4At} e^{-BR^2/4Au} (e^{-u}/u)\, du \tag{26}$$

We now recognize that B is a measure of the contribution of radiant

emission by the fluid to the heat transfer process, and that $BR^2/4Au \leqslant 0.1$, even in the simulated case of toluene. Consequently, to obtain a first order estimate of the effect of radiation we may expand the first exponential in the integrand of Eq. (26) and carry out the integrations to yield the temperature rise in the form

$$\Delta T = \frac{q}{4\pi\lambda} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{(n-1)!} (Bt)^{n-1} E_n(r^2/4\kappa t) \tag{27}$$

where [17]

$$E_n(\xi) = \int_1^{\infty} (e^{-\xi u}/u^n)\, du \tag{28}$$

By means of expansion of the exponential integrals E_n [17] we finally obtain for the temperature rise at $r = r_1$,

$$\Delta T = \frac{q}{4\pi\lambda} \left[1 + \frac{Br_1^2}{4\kappa} \right] \ln\left(\frac{4\kappa t}{r_1^2 C} \right) + \frac{Bqr_1^2}{16\pi\kappa\lambda} - \frac{Bqt}{4\pi\lambda} + 0\left((Bt)^2, r_1^2/4\kappa t\right) \tag{29}$$

By comparison of this result with that of Eq. (7) it is possible to discern a radiation correction, δT_{rad}, which, if added to the temperature rise which is observed in the presence of radiation, recovers $\Delta T_{id}(r_1, t)$ of the ideal model. Therefore,

$$\Delta T_{id} = \Delta T + \delta T_{\text{rad}} \tag{30}$$

where

$$\delta T_{\text{rad}} = \frac{-qB}{4\pi\lambda} \left\{ \frac{r_1^2}{4\kappa} \ln\left(\frac{4\kappa t}{r_1^2 C} \right) + \frac{r_1^2}{4\kappa} - t \right\} \tag{31}$$

In the absence of any radiation effect the thermal conductivity is derived from the slope of the experimentally observed linear relationship between the temperature ΔT and $\ln t$. Equation (29) makes it clear that radiant emission from the fluid yields a relationship which is no longer linear, but is curved, concave to the $\ln t$ axis. Furthermore, the slope of the linear portion of the relationship is altered and a shift of the ΔT versus $\ln t$ line along the ΔT axis is produced. So far as the derivation of the thermal conductivity is concerned, the shift is of no significance; however, the remaining two effects are potentially important.

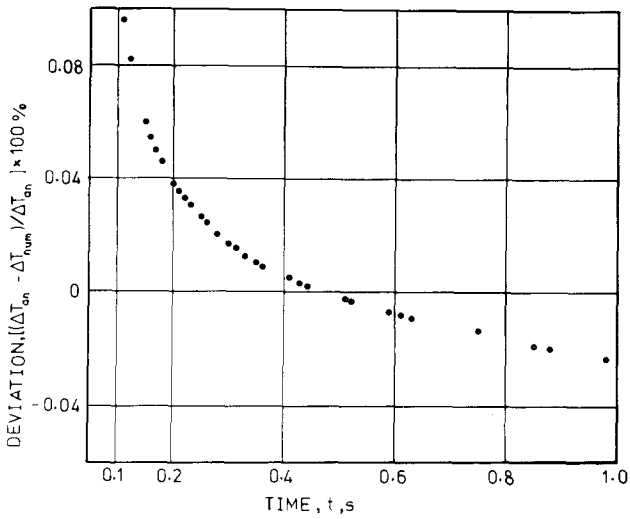

Fig. 2. The deviations between the numerical and analytic solutions of the radiation-conduction problem.

In order to confirm that the analytic solution of the conduction-radiation problem is consistent with the numerical solution, we have compared the temperature rises calculated in the two ways using the data given in Table I. For this purpose we have added the small correction owing to the finite outer boundary [16] to the analytic solution in order that the two solutions refer to the same model of the instrument. The comparison is presented in the form of a plot of the deviations between the two solutions in Fig. 2. It can be seen that the deviation does not exceed $\pm 0.1\%$, its systematic nature being merely a combined result of the small terms neglected in the analytic solution and the limited accuracy of the numerical solution.

The advantages to be gained from an analytic solution of the conduction-radiation problem are twofold. First, the experimental measurements of the temperature rise of the wire may themselves be used to ascertain whether radiation contributes significantly to the measurement process. Thus, if the measured temperature rise of the wire, ΔT_w, corrected for all other effects according to Eq. (7), does not conform to a linear equation in $\ln t$, it is likely that there is a significant radiation contribution. In such cases, if it can be established that there is no convective contribution to the measurement process, a value for the radiation parameter, B, may be estimated by fitting ΔT to the full form of Eq. (29). The derived value of B may then be employed to evaluate the correction δT_{rad} for each data point and the radiation-free thermal conductivity may be evaluated

from the slope of the linear relationship between ΔT_{id} and $\ln t$. The radiation parameter, B, evaluated in this manner is, of course, considerably more reliable than one deduced from independent, spectrophotometric measurements because it is the directly relevant parameter rather than one deduced from a series of assumptions about the optical characteristics of the fluid [5]. Moreover, the parameter may be determined for each set of experimental conditions.

The second advantage of the analytic solution of the problem is that it is also possible to discern when the radiation contributions to the measurement are negligible. If the experimentally observed temperature rise, ΔT, defined by Eq. (7), is a linear function of $\ln t$, it is possible to assert that the term $Bqt/4\pi\lambda$ in Eq. (29) is negligibly small by comparison with the term proportional to $\ln t$. In turn, this means that in our instrument,

$$\left(Br_1^2/4\kappa\right) \leqslant 10^{-5} \tag{32}$$

so that the thermal conductivity deduced from the slope of the line ΔT versus $\ln t$ is the radiation-free value. As we show in the next section for toluene, and as we have already found for liquids we have previously studied [1–4], there is no evidence of any curvature in the lines ΔT versus $\ln t$. We therefore conclude that the contribution of radiation to the measurement of thermal conductivity in a transient hot-wire apparatus of the type we employ is entirely negligible for these liquids. Furthermore, the corrections we have previously applied to our data to account for radiation [1–4] were not necessary because the relevant values of the radiation parameter B, or equivalently, the extinction coefficient K are very much smaller than those deduced from standard spectrophotometric studies. This conclusion means that in our earlier publications [1–4] the values quoted as radiation-free values should be disregarded and those quoted as apparent values may be taken to represent the true thermal conductivity of the liquid.

Finally, it should be emphasized that the arguments presented here are restricted to the transient hot-wire apparatus. In other experimental methods, usually of a steady state type, the temperature gradients involved are much smaller, so that it is not clear that a similar simplification of the problem of the influences of radiation in the fluid is possible.

3. EXPERIMENTAL PROCEDURE

The transient hot-wire instrument employed for the thermal conductivity measurements has been described in detail elsewhere [1]. For the present work, the only changes involved the installation of a new set of platinum

wires and a modest extension of the pressure range to lower pressure in order to allow a more reliable comparison with other measurements along the saturation line. The measurements have been carried out along five isotherms: 35, 47, 57, 72, and 87°C and pressures from 0.88 to 585 MPa. The toluene employed for the measurements was supplied by B. D. H. Chemicals Ltd. and had a stated purity in excess of 99.95%. The purity was confirmed by chromatographic analysis, and the liquid was degassed before use.

The heat capacity of the liquid, required for the application of small corrections, was obtained from the compilation of Vargaftik [21]. Direct measurements of the density over the complete range of thermodynamic states covered in this work are not available. The density has therefore been estimated from the variation along the saturation line given by Vargaftik [21], and the pressure dependence has been taken from the work of Toohey at 60°C [22]. These estimates are entirely adequate for the application of small corrections to the experimental data.

It was established in the previous section that the effects of radiation contribute negligibly to the measurement of the thermal conductivity of a liquid if the transient temperature rise ΔT, defined by Eq. (7), is a linear function of $\ln t$. In order to demonstrate that this is the case for toluene, Fig. 3 contains a plot of the deviations of one set of experimental values of ΔT from a linear fit to them in $\ln t$. It can be seen that the deviations have no systematic character. This is confirmed by the fact that when an equation of the form of (29) was fitted to the same data, the parameter B was found to be zero within its statistical uncertainty. On the basis of this and other, similar tests, we conclude that radiation contributes insignificantly to the measurements reported here.

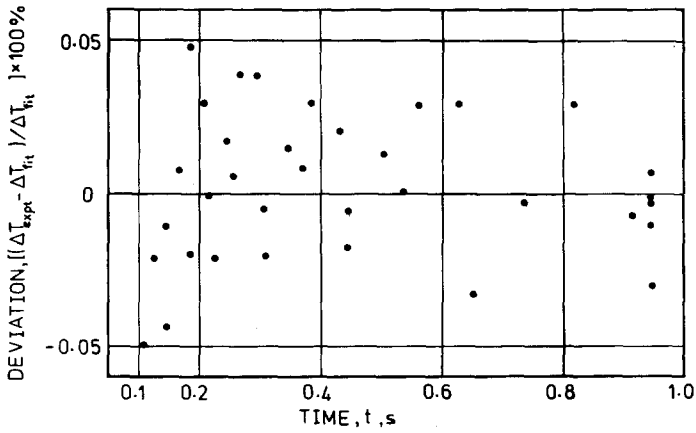

Fig. 3. Deviations of experimental values of ΔT from a linear fit to them.

Table II. Thermal Conductivity of Toluene

$T_{nom} = 35°C$		$T_{nom} = 47°C$		$T_{nom} = 57°C$		$T_{nom} = 72°C$		$T_{nom} = 87°C$	
P (MPa)	$\lambda(T_{nom}, P)$ (mW · m^{-1} · K^{-1})	P (MPa)	$\lambda(T_{nom}, P)$ (mW · m^{-1} · K^{-1})	P (MPa)	$\lambda(T_{nom}, P)$ (mW · m^{-1} · K^{-1})	P (MPa)	$\lambda(T_{nom}, P)$ (mW · m^{-1} · K^{-1})	P (MPa)	$\lambda(T_{nom}, P)$ (mW · m^{-1} · K^{-1})
0.9	128.9	1.4	125.3	7.3	124.5	2.3	118.2	3.2	113.7
1.5	129.1	2.4	126.6	11.5	125.3	2.4	118.5	26.5	123.4
3.7	129.6	24.1	133.6	19.9	128.3	13.3	122.0	49.2	131.2
11.4	132.4	32.2	135.6	33.2	132.8	23.4	126.5	50.6	130.2
16.8	134.6	59.1	143.5	37.3	135.0	51.3	136.1	74.5	139.5
33.4	139.6	85.0	150.4	51.0	138.0	101.1	150.4	104.2	146.6
51.7	145.5	109.5	156.2	77.7	146.0	127.6	156.0	126.8	152.0
55.9	146.3	132.5	161.7	101.7	152.0	153.2	161.7	152.3	157.7
64.3	148.7	164.0	168.0	126.1	158.6	175.7	166.3	203.7	167.8
66.3	149.1	202.0	175.2	153.3	163.9	203.2	171.6	255.7	177.5
129.8	163.9	252.8	183.4	177.6	168.7	253.1	180.5	304.3	185.1
153.6	168.1	303.7	191.7	201.9	172.9	306.0	189.4	338.6	190.7
202.5	177.7	353.5	198.5	252.3	182.0	355.4	197.3	353.2	192.7
253.7	186.1	358.1	199.3	302.4	189.7	402.8	203.3	405.8	199.9
303.9	193.4	402.3	205.0	352.8	197.3	452.0	209.4	453.1	205.8
354.0	200.3	439.0	209.2	375.4	200.1	455.3	209.4	497.9	212.0
401.3	206.5	460.3	212.0	400.6	204.0	497.6	214.6	508.3	212.0
450.2	212.0	501.6	216.7	451.7	209.7	543.0	220.1	543.8	216.9
463.5	213.2	542.1	221.4	546.0	220.1	584.8	224.1	577.6	220.2
463.5	213.3	556.0	223.0	583.8	223.4	585.3	224.3		
463.6	213.8	571.7	224.3						
495.3	217.1								
502.4	217.3								
531.4	221.0								
531.6	221.0								

4. RESULTS

Table II contains results of the present measurements of the thermal conductivity of toluene at five isotherms; 35, 47, 57, 72, and 87°C. The results have been corrected to nominal temperatures by the application of small, linear corrections, which in no case amounted to more than ±0.1% in the thermal conductivity. The correction therefore contributes a negligible amount to the uncertainty in the quoted results, which are estimated to have an accuracy ±0.3%.

The available density data for toluene at elevated pressures are not sufficiently reliable to allow us to report the data as a function of density in the usual fashion. Consequently, we confine our analysis here to a representation of the thermal conductivity as a function of pressure by means of an equation of the form

$$\lambda = b_0(1 + b_1 x + b_2 x^2 + b_3 x^3 + b_4 x^4) \tag{33}$$

where $x = (P - P')/P'$. Table III lists the values of the coefficients in this equation for each of the isotherms, whereas Fig. 4 contains a plot of the deviations of the present experimental data from the correlation. In no case does the deviation exceed ±0.7%, the standard deviation of the entire set of data being one of ±0.17%. The same figure includes the deviations of earlier results at elevated pressures from the present correlation. Here, the deviations rise to as much as 5%. The present results are to be preferred owing to their higher accuracy.

A large number of measurements of the thermal conductivity of toluene along the saturation line have been reported and they have recently been reviewed by Nagasaka and Nagashima [24]. These authors have proposed a correlation for the thermal conductivity of toluene along the saturation line, in the form

$$\lambda = 0.1377_2 - 2.91_3 \times 10^{-4}(T - 273.15) \tag{34}$$

Table III. Coefficients of the Correlation of the Thermal Conductivity as a Function of Pressure, from Equation (33)

T (°C)	P' (MPa)	b_0 (mW · m^{-1} · K^{-1})	b_1	b_2	b_3	b_4
35	250	185.39	0.2061	-4.898×10^{-2}	3.386×10^{-2}	-1.691×10^{-2}
47	250	183.31	0.2187	-5.703×10^{-2}	3.027×10^{-2}	-9.949×10^{-3}
57	250	181.67	0.2266	-5.772×10^{-2}	3.057×10^{-2}	-1.343×10^{-2}
72	250	180.29	0.2320	-6.019×10^{-2}	3.912×10^{-2}	-1.678×10^{-2}
87	250	176.53	0.2366	-6.031×10^{-2}	4.371×10^{-2}	-1.990×10^{-2}

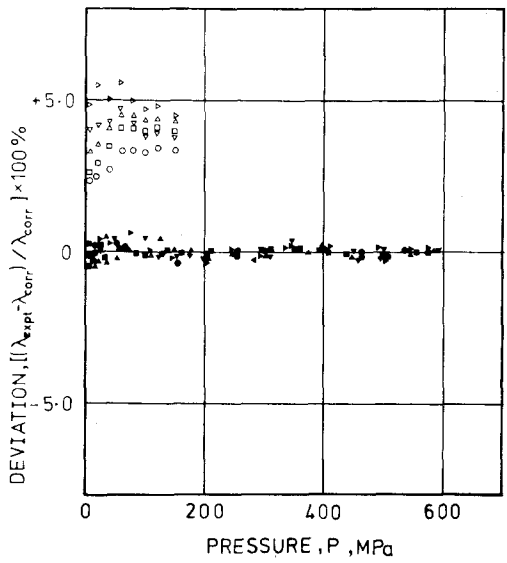

Fig. 4. The deviations of experimental thermal conductivity data for toluene from the correlation of Eq. (33). Present work: ● 35°C; ■ 47°C; ▲ 57°C; ▼ 72°C; ▶ 87°C. From ref. [23]: ○ 35°C; □ 47°C; △ 57°C; ▽ 72°C; ▷ 87°C.

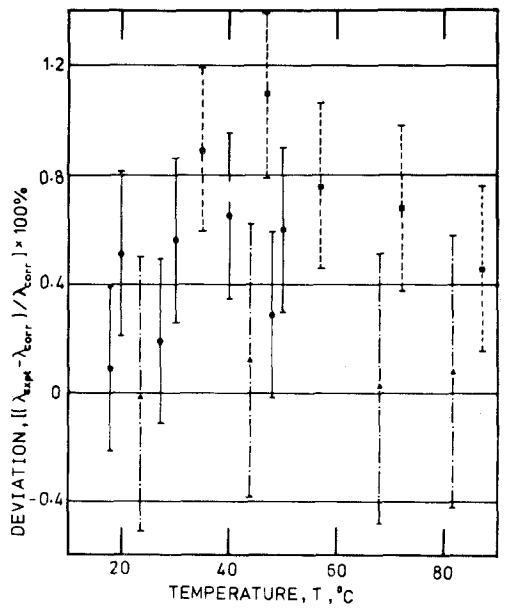

Fig. 5. The deviations of measurements of the thermal conductivity of toluene at its saturation vapor pressure from the recommended correlation of Nagasaka and Nagashima [24]: ■ extrapolation of present results; ● [25]; ▲ [26].

for $248 < T < 413$ K. We have extrapolated the correlation of our experimental data to the saturation vapor pressure in order to provide a comparison with this correlation. The comparison is included in Fig. 5, which also includes the deviations of the experimental results of Nagasaka and Nagashima [25] and Castro et al. [26] from the same correlation. These two sets of measurements were also performed with modern versions of the transient hot-wire instrument. The extrapolation of the present experimental results obviously degrades their accuracy somewhat; nevertheless, the three sets of measurements are seen to be consistent within their mutual uncertainty.

5. CONCLUSIONS

An analytic solution of the combined conduction-radiation equation for a transient hot-wire instrument for the measurement of the thermal conductivity of liquids has been presented. It has been used to demonstrate that the effects of radiant heat transfer in toluene have a negligible effect upon the measurements. The thermal conductivity of toluene has been measured over a wide range of pressure, and the results have been shown to be consistent with other accurate measurements along the saturation line. It seems therefore that it will now be possible to establish toluene as a standard reference material for liquid thermal conductivity and to formulate a series of accurate, standard reference values.

ACKNOWLEDGMENTS

The authors are grateful to Dr. S. M. Richardson for several stimulating discussions. The work described in this paper was supported by grants from the United Kingdom Science and Engineering Research Council and the North Atlantic Treaty Organization.

REFERENCES

1. J. Menashe and W. A. Wakeham, *Ber. Bunsenges. Phys. Chem.* **85**:340 (1981).
2. J. Menashe and W. A. Wakeham, *Ber. Bunsenges. Phys. Chem.* **86**:541 (1982).
3. M. Mustafa, M. Sage, and W. A. Wakeham, *Int. J. Thermophys.* **3**:217 (1982).
4. U. V. Mardolcar and W. A. Wakeham, *Int. J. Thermophys.* **4**:1 (1983).
5. J. Menashe and W. A. Wakeham, *Int. J. Heat Mass Transfer* **25**:661 (1982).
6. D. T. Jamieson, J. B. Irving, and J. S. Tudhope, *Liquid Thermal Conductivity: A Data Survey to 1973* (H.M.S.O., Edinburgh, 1973).
7. R. Viskanta and R. J. Grosh, *Trans. ASME, J. Heat Transfer* **84C**:63 (1963).
8. A. Saito, N. Mani, and J. E. S. Venart, Proc. 16th Nat. Heat Transfer Conf. 76-CSME/CSChE-6 (Canadian Society for Chemical Engineering, Ottawa, 1976).
9. A. Saito, and J. E. S. Venart, *Proc. 6th Int. Heat Transfer Conf.* (1978), Vol. 3, p. 79.
10. W. Leidenfrost, *Int. J. Heat Mass Transfer* 7:447-478 (1964).

11. W. Fritz and H. Poltz, *Int. J. Heat Mass Transfer* **3**:307 (1962).
12. L. Reidel, *Chem. Ing. Tech.* **23**:321 (1951).
13. R. W. Powell, C. Y. Ho, and P. E. Liley, Thermal conductivity of selected materials, NSRDS–NBS–8 (N.B.S., Washington, D.C., 1966).
14. H. Poltz, in *Proc. Seventh Conf. Thermal Conductivity*, N.B.S. Special Publ. 302 (1968), p. 47.
15. A. Michels, J. V. Sengers, and P. S. Van der Gulik, *Physica* **28**:1201 (1962).
16. J. J. Healy, J. J. Groot, and J. Kestin, *Physica* **82C**:392 (1976).
17. M. Abramowitz and I. A. Stegun, eds., *Handbook of Mathematical Functions* (N.B.S., Washington, D.C., 1964).
18. J. Kestin and W. A. Wakeham, *Physica* **92A**:102 (1978).
19. H. E. Khalifa, J. Kestin, and W. A. Wakeham, *Physica* **97A**:273 (1979).
20. A. A. Clifford, J. Kestin, and W. A. Wakeham, *Physica* **100A**:370 (1980).
21. N. B. Vargaftik, *Tables of the Thermophysical Properties of Liquids and Gases*, 2nd ed. (Wiley, New York, 1975).
22. A. C. Toohey, PhD thesis, Imperial College, London (1961).
23. Y. L. Rastorguev and V. V. Pugach, *Izv. vyssh. ucheb. Zaved., Neft' i Gaz* **13**(8):69 (1970).
24. Y. Nagasaka and A. Nagashima, in *Proc. First Jpn. Symp. on Thermophysical Properties* (1980), p. 67.
25. Y. Nagasaka and A. Nagashima, *I & EC Fundamentals* **20**:216 (1981).
26. C. A. Nieto de Castro, J. C. G. Calado, and W. A. Wakeham, *Proc. 7th Symp. Thermophys. Prop.*, A. Cezairliyan, ed. (ASME, New York, 1977), p. 730.