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Radiative Heat Transfer in Transient Hot-Wire Measurements of Thermal Conductivity

C. A. Nieto de Castro,[1,2] R. A. Perkins,[3] and H. M. Roder[3]

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New measurements of the thermal conductivity of liquid toluene between 300 and 550 K have been used to study the importance of radiative heat transfer when using the transient hot-wire technique. The experimental data were used to obtain the radiation correction to the hot-wire temperature rises. Radiation-corrected values of thermal conductivity are reported. This study shows that the transient hot-wire method is much less affected by radiation than steady-state techniques.

KEY WORDS: radiative heat transfer; thermal conductivity; toluene; transient hot-wire technique.

1. INTRODUCTION

The contribution of radiative heat transfer to thermal conductivity measurements has been the subject of general controversy for a considerable time [1–6]. In different instruments, using different techniques and different liquids, the radiative heat flux was found to range in magnitude between 2 and 50% of the applied heat conduction flux. Several recent papers analyze the effect of the radiative heat transfer flux in transient hot-wire instruments [7, 8] and in steady-state concentric cyclinder instruments [9–11] for fluids which absorb in the infrared region of the electromagnetic spectrum. When the fluid does not contribute directly or indirectly to radiation through absorption, the radiative energy transport associated with the measurement of thermal conductivity is easily

[1] Departamento de Quimica, Faculdade de Ciencias, Universidade de Lisboa, 1700 Lisboa, Portugal.

[2] Centro de Quimica Estrutural, Complexo I, IST, 1096 Lisboa Codex, Portugal.

[3] Thermophysics Division, National Institute of Standards and Technology, Boulder, Colorado 80303, U.S.A.

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treated, for either transient or steady-state techniques, by considering the fluid as a transparent medium bounded by gray surfaces [12, 13].

However, if the fluid absorbs and emits radiation, the problem is very complex because the radiative and conductive fluxes are coupled. This situation can be described by an integropartial differential equation [7]. A number of solutions of the coupled radiation-conduction equation for steady-state instruments have been proposed [2, 5]. In most cases, optical properties of the fluid under the conditions of the measurement are required, yet they are rarely available. The careful work of Fisher and Obermeier [11], including both a theoretical [9] and an experimental [10] study of the contribution of radiative heat transfer to the measurement of thermal conductivity of liquids in a steady-state concentric cylinder apparatus, was published only recently. These papers have added some insight to the problem. The experiments were carried out with several annular layer thicknesses, over the temperature range 253 to 473 K, in several liquids. The results show that in some of the measurements, the contribution of radiation could be as much as 40%. Thus, the correction to obtain radiation-free values of the thermal conductivity can add a significant uncertainty to the experiment data.

In the case of transient methods, Wakeham and co-workers [7, 8] presented a detailed analysis of the problem. In their first paper [7], they performed a numerical solution of the conduction-radiation equations for a transient hot-wire instrument. Evaluation of the correction proved to be too time consuming and expensive to be used routinely. The correction also requires knowledge of certain optical properties of the fluid and of its bounding surfaces, the wire and the cell wall, that are not usually available. For these reasons, the complete solution [7] was used as a basis for the development of an approximate analytic solution [8].

This radiation analysis showed that the transient hot-wire thermal conductivity results for absorbing fluids have not been affected by significant contributions of radiative heat transfer, within their experimental uncertainty, for temperatures below 360 K. It was therefore possible to develop standard reference data for the thermal conductivity of toluene [14], water [14], and benzene [15] with an uncertainty less than 1% over this limited temperature range.

We decided to measure the thermal conductivity of toluene, between 300 and 550 K, to test a new high-temperature apparatus and to examine the importance of the radiative contribution in transient hot-wire instruments. This new instrument was developed at the Boulder laboratories of the National Institute of Standards and Technology (NIST) [16] and is designed for operation between 220 and 750 K at pressures to 70 MPa.

In this paper, we report a study of the effect of radiative heat transfer on thermal conductivity measurements of liquid toluene, an absorbing fluid, at high temperatures. The thermal conductivity and thermal diffusivity data, as well as the experimental details, are given in Ref. 16.

2. THE RADIATIVE HEAT TRANSFER PROBLEM

For fluids that absorb and emit radiation, the full form of the integrodifferential equation presented by Menashe and Wakeham [7] cannot be solved analytically. However, these authors derived a numerical solution using only the assumptions that the mean extinction coefficient of the fluid is temperature independent over the small temperature range involved in a transient hot-wire measurement, 2–5 K, and that the outer bounding cylinder wall is black. This numerical solution is time-consuming and expensive to evaluate, and it was not possible to apply it universally. Nieto de Castro et al. [8] showed that the dominant correction term in the heat flux gradient arises from the emission of radiation by the fluid, and not from absorption.

These considerations allowed the authors to obtain a simplified equation for the heat transfer problem, given by

$$\frac{\partial \Theta}{\partial t} = \frac{\lambda}{\rho C_p r_0^2}\left[\frac{\partial^2 \Theta}{\partial R^2} + \frac{1}{R}\frac{\partial \Theta}{\partial R}\right] - \frac{16 K n^2 \sigma T_0^3 \Theta}{\rho C_p} \tag{1}$$

where $\Theta(r, t) = (T - T_0)/T_0$ and $R = r/r_0$.

In this equation T_0 is the initial cell temperature, and $\Delta T(r_0, t) = T - T_0$ is the temperature rise at the hot wire of radius r_0 at elapsed time t. λ, C_p, ρ, K, and n are the thermal conductivity, isobaric heat capacity, density, mean absorption coefficient, and refractive index of the liquid. σ is the Stefan–Boltzmann constant.

The solution of Eq. (1) subject to the boundary conditions

$$\frac{q}{2\pi T_0} = -\lambda \lim_{R \to 1}\left[R \frac{\partial \Theta}{\partial R}\right] \qquad (t > 0) \tag{2}$$

$$\Theta = 0 \qquad (R \to \infty, t > 0), \tag{3}$$

and

$$\Theta = 0 \qquad (t \leqslant 0), \tag{4}$$

is given in Ref. 8 as

$$\Delta T = \frac{q}{4\pi\lambda}\left[1 + \frac{B r_0^2}{4a}\right] \ln\left(\frac{4at}{r_0^2 C}\right) - \frac{Bqt}{4\pi\lambda} + \frac{Bqr_0^2}{16\pi a\lambda} + \cdots \tag{5}$$

where

$$B = \frac{16Kn^2\sigma T_0^3}{\rho C_p} \tag{6}$$

and

$$a = \frac{\lambda}{\rho c_p} \tag{7}$$

If we use the ideal profile ΔT_{id}, given by

$$\Delta T_{id} = \Delta T_w + \sum \delta T_i = \frac{q}{4\pi\lambda} \ln\left(\frac{4at}{r_0^2 C}\right) \tag{8}$$

where ΔT_w is the measured temperature rise and δT_i are the nonradiative corrections to the ideal profile, fully described in Refs. 17–19, we obtain

$$\Delta T_{id} = \Delta T + \delta T_5 \tag{9}$$

where

$$\delta T_5 = -\frac{qB}{4\pi\lambda}\left[\frac{r_0^2}{4a} \ln\left(\frac{4at}{r_0^2 C}\right) - t + \frac{r_0^2}{4a}\right] \tag{10}$$

As stated in Ref. 8, if ΔT_{exp} is fitted to a function of the form suggested by Eq. (5),

$$\Delta T = C_1 \ln(t) + C_2 t + C_3 \tag{11}$$

an experimentally derived value of B can be obtained from the coefficient C_2 using

$$B = C_2\left(-\frac{4\pi\lambda}{q}\right) \tag{12}$$

This experimentally derived value of B can be used in Eq. (10) to evaluate δT_5 and thus obtain corrected thermal conductivity data, without any prior knowledge of the optical properties of the fluid. This is quite important since these optical properties are seldom known at elevated temperatures and pressures.

If Eq. (8) is valid, the effect of the radiative contribution to the heat transfer in a transient hot-wire experiment will be to introduce a curvature in the line of ΔT_{id} versus the logarithm of time, concave toward the time axis. Results presented until now and obtained with instruments accurate

to 0.5% have not shown a significant, systematic curvature. For example, the most recent data published on toluene were obtained by Ramires et al. [20]. These data agree with the standard reference correlation [14] within 0.6% up to 367 K. Moreover these data do not show appreciable curvature in the ΔT-versus-ln(t) lines to within 0.05%. However, our new measurements on toluene extend to temperatures much higher than 360 K, and they exhibit the curvature of Eq. (11), which in turn can be corrected by obtaining a value of B from the experimental data.

3. TOLUENE

The sample used for the measurements was spectroscopic-grade toluene, which was dried over calcium hydride and subsequently distilled. Chromatographic analysis of the purified sample revealed less than 50 parts per billion (ppb) of benzene and less than 100 ppb of water. The measurements were made near the saturation line, at a pressure slightly larger than the saturation vapor pressure to avoid boiling at the wire surface during the experiment, for temperatures between 300 and 550 K. The full set of results is reported elsewhere [16], and the new instrument is capable of measuring the thermal conductivity with an uncertainty of $\pm 1\%$ and the thermal diffusivity with an uncertainty of $\pm 5\%$.

Figure la shows a deviation plot for the temperature rise of the wire for a data point at $T = 552.306$ K and $P = 2.686$ MPa, before applying the radiation correction δT_5. A systematic curvature can be identified, although the deviations do not amount to more than 0.2%. Figure 1b shows the deviation plot for the same data point, after an empirical value for B is applied. No curvature is found and the maximum deviation decreased to 0.1%, that is, by a factor of 2. The corresponding change in the thermal conductivity value is 3.1%, while the heat capacity value obtained from the measured thermal diffusivity changes by 25%.

Figure 1 shows that the addition of a time-dependent correction, using an empirically determined value for B, can be used to straighten out the curvature which we observe at high temperatures. We have not yet demonstrated that this time-dependent correction is indeed due to thermal radiation as our model assumes. An examination of this correction with respect to the fluid density and temperature should add evidence in support of the model.

The radiation correction parameter B is defined by Eq. (6) in terms of the fluid properties. All of the properties are known over the temperature and pressure range of interest with the exception of the refractive index, n, and the fluid absorption coefficient, K. These two optical properties should be functions of the fluid density with minimal temperature dependence.

Figure 2 shows the behavior of the product Kn^2 as a function of the fluid density. The figure contains both saturated liquid and compressed liquid data. A simple linear fit is also shown on the figure and is given by

$$Kn^2(\rho) = 1.111 - 0.07348\rho \tag{13}$$

where Kn^2 is in m^{-1}, and ρ is in $mol \cdot L^{-1}$. The experimentally determined optical properties have an uncertainty of about 25% and the linear fit is an adequate representation of their behavior. Kn^2 decreases with increasing

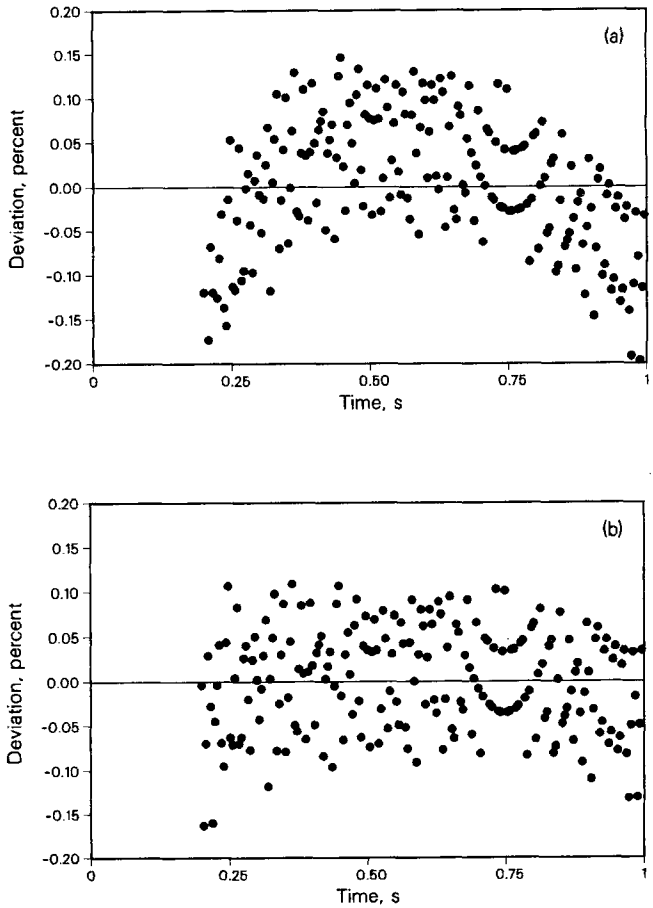

Fig. 1. Deviations between the experimental temperature rise ΔT_w and the heat transfer model as a function of time for liquid toluene data point 2105 at $T = 552.306$ K and $P = 2.686$ MPa. (a) Before application of the radiation correction, Eq. (10). (b) After application of the radiation correction, Eq. (10).

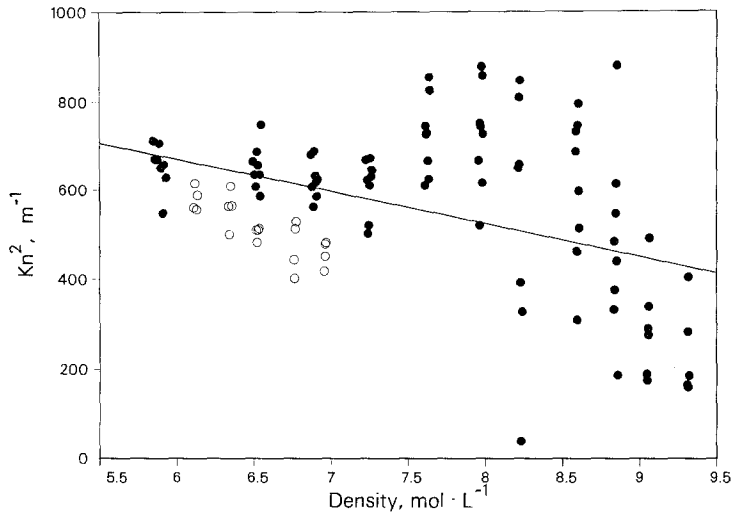

Fig. 2. Experimental optical parameters, Kn^2, as a function of density. Filled circles indicate points near the saturation curve. Open circles indicate compressed liquid points at $T_0 = 548$ K. The line is a linear fit through the data as a function of density.

density, both along an isotherm and along the saturation boundary with decreasing temperature.

The radiation correction model [8] explicitly assumes that the fluid properties are temperature independent during the course of an experiment. If this is true, then the empirical optical properties should not be a function of the experiment temperature rise or applied power. Figure 3 shows the experimentally determined values of Kn^2 as a function of the temperature rise at initial temperatures near 422 K. The empirical values of Kn^2 values are not a function of the temperature rise, and the assumption of temperature-independent fluid properties in the radiation correction model appears to be justified.

Figure 4 shows the values obtained for B as a function of T_0, the cell temperature prior to a measurement, for data near the saturation line. The dashed line is given by Eq. (6) using the linear fit of Kn^2 as a function of density in Eq. (13). The dashed line exhibits a T_0^3 temperature dependence as anticipated by examining Eq. (6). The experimental B values appear to have a linear temperature dependence, although the dashed line certainly represents the data within its experimental uncertainty of about 25%. A linear fit of B with respect to temperature is also shown in Fig. 4 as a solid line, given by the equation

$$B(T_0) = -6.858 \times 10^{-2} + 2.31 \times 10^{-4}\, T_0 \tag{14}$$

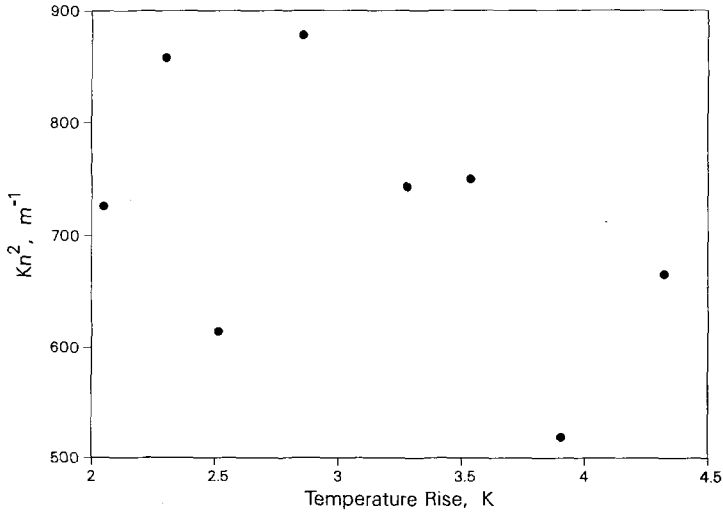

Fig. 3. Independence of experimental optical parameters, Kn^2, from the temperature rise incurred during the experiment at $T_0 = 422$ K.

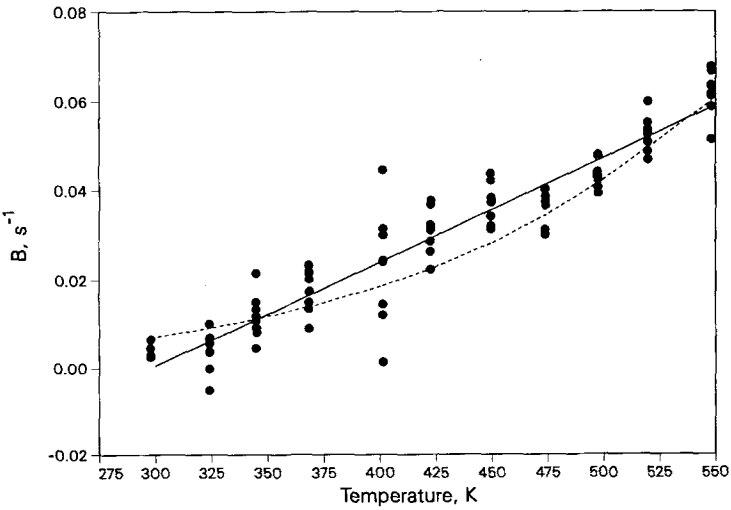

Fig. 4. The radiation parameter B as a function of temperature T_0. The solid line is given by the direct temperature fit to the saturated liquid data, Eq. (14). The dashed line is given by Eq. (6) using the fit to all the Kn^2 data as a function of density, Eq. (13).

where B is in s^{-1} and T_0 is in K. Either the combination of Eqs. (6) and (13), in conjunction with a good equation of state, or Eq. (14) could be used to correct the saturated liquid data for thermal radiative heat transfer using Eq. (10).

The value of $B(T_0)$ given by Eq. (14) was used in Eq. (10) to correct all the experimental values of the measured temperature rises in the hot-wire experiments and, consequently, the thermal conductivity and the thermal diffusivity. Figure 5 shows both uncorrected and corrected thermal conductivity values of liquid toluene near the saturation line, as a function of temperature. The standard reference correlation of Nieto de Castro et al. [14], which is based on data to 360 K, is shown as a solid line. Also displayed are the measurements of Fisher and Oermeier [11] obtained with the rotating-concentric cylinder apparatus (SSRC) operating in a steady-state mode, for different gaps between the cylinders. We have also shown their extrapolation to zero gap to obtain radiation-free thermal conductivities.

Figure 5 shows that the transient hot-wire data have a significant radiative contribution at elevated temperatures, that is, up to 3.1% at 550 K. However, this radiation contribution is much smaller than that for the steady-state apparatus, a conclusion reached several years ago by Mani and Venart [21] using an alternative radiative correction. For example,

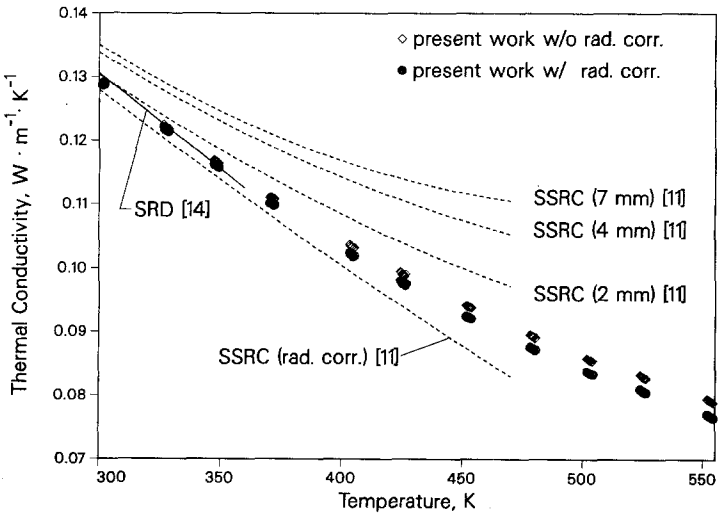

Fig. 5. The thermal conductivity of liquid toluene near the saturation line, with and without the radiation correction of Eq. (10). SSRC, steady-state rotating cylinder at various spacings from Ref. 11. SRD, standard reference data correlation from Ref. 14.

in the steady-state apparatus [11] the radiation correction to the measurements at a 2-mm plate spacing is 16% at 470 K. Any uncertainty in the radiative correction, such as optical properties, becomes more significant as the magnitude of the radiative correction becomes larger. Thus, uncertainties in the measured thermal conductivity for absorbing fluids will always be larger for steady-state instruments, at any given temperature, simply because the magnitude of the correction is larger.

4. DISCUSSION

The new data on saturated liquid toluene were fit to a polynomial in temperature given by

$$\lambda = 0.25179 - 5.159 \times 10^{-4}\, T + 3.61 \times 10^{-7}\, T^2 \qquad (15)$$

where λ is in $W \cdot m^{-1} \cdot K^{-1}$ and T is in K. The standard deviation of this fit is 0.00015 $W \cdot m^{-1} \cdot K^{-1}$. Using Eq. (15) as a base line, Fig. 6 shows the deviations between the present data and the data sets of Fisher and Obermeier [11], Ramires et al. [20], Mani and Venart [21], Perkins [22], and Shulga et al. [23]. The standard reference data correlation [14], which is valid up to 360 K, is also shown as a solid line. It can be seen that

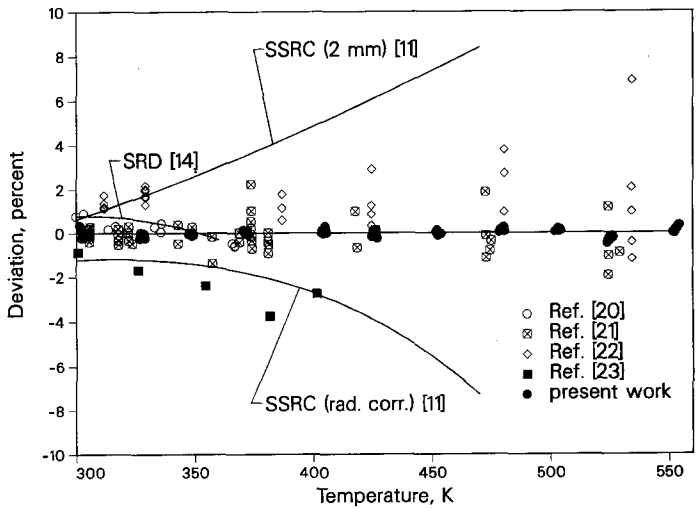

Fig. 6. Deviations between the thermal conductivity of toluene, near the saturation line, given by Eq. (15) and several sets of data. Also included are the deviations from SSRC measurements, at a 2-mm spacing and corrected for radiation [11], and the standard reference correlation [14].

the present data do not deviate by more than 0.8% from the standard reference data correlation or the data of Ramires et al. [20], up to 370 K. The data of Mani and Venart [21] agree to within 2%, while the data of Perkins [22] agree within 4%, except at 550 K, where the deviation increases to a maximum of 6%. In both these cases the agreement with the present results is within experimental uncertainty.

The comparison of the present data with the data of Fisher and Obermeier [11] shows that their values for a 2-mm spacing are higher by up to 8% at 473 K, and the values proposed as radiation-free (zero gap) are about 7% lower at this temperature. A new examination of the radiation analysis of Fisher and Obermeier [11] is warranted.

The data of Shulga et al. [23] were obtained with an AC-powered hot wire. The authors claimed that there was no radiative effect in their measurements and estimated that there was 1% uncertainty in the reported thermal conductivity. Their results agree with the present data at 300 K to within 1%, but the deviations increase to about 4% at the higher temperatures, following a pattern similar to the data of Fisher and Obermeier [11].

Based on spectroscopic data at 298 K, n is 1.4961 and K is estimated to be 4630 m^{-1} for liquid toluene [8]. The empirical value for K which we obtain is 200 m^{-1} at 300 K. This is 23 times smaller than the estimated value but is consistent with the observation [8, 20] that no curvature is found in the temperature rise versus logarithm of time for toluene near 300 K. If K actually were 4630 m^{-1} as estimated in Ref. 8, then the radiation correction at 300 K would generate a 5% correction to the thermal conductivity at 300 K and a 40% correction to the thermal diffusivity. This is not plausible since the transient hot-wire data for toluene are only 1% higher than the radiation corrected data of Fisher and Obermier [11], which were obtained by a steady-state technique at 300 K. In addition, heat capacities from our radiation-corrected transient hot-wire data [16] are in excellent agreement with calorimetric data near 300 K. This is ample evidence that the estimated value of K of 4630 m^{-1} from Ref. 8 is incorrect and that the present empirical value for K are correct.

5. CONCLUSIONS

Examination of the empirical values of the optical property Kn^2, as a function of temperature and density, provides evidence that the time-dependent nonlinearity which we observe for liquid toluene is due to radiative heat transfer. First, we find that the empitical Kn^2 is a function primarily of the fluid density. Second, these optical properties are not influenced by the magnitude of the wire temperature rise. Finally, using a

fit to Kn^2 as a function of density, in conjunction with an equation of state, we obtain good predictions of the correction parameter B as a function of temperature.

For infrared absorbing fluids we can obtain empirical estimates for the fluid optical property Kn^2 with an uncertainty of $\pm 25\%$. The magnitude of the radiation correction is a function of T_0^3. For the maximum temperature studied here of 548 K the radiation correction is 3.1% in thermal conductivity and 25% in thermal diffusivity. The uncertainty in the empirical optical properties for absorbing fluids translates to a $\pm 0.8\%$ uncertainty in thermal conductivity and a $\pm 6\%$ uncertainty in thermal diffusivity at 548 K. The values reported are radiation-corrected values, and the model previously reported by Wakeham and co-workers [7, 8] is a good description of the influence of radiative heat transfer in transient hot-wire measurements.

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