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EFFECT OF ABSORPTION OF RADIATION ON THERMAL CONDUCTIVITY MEASUREMENTS BY THE TRANSIENT HOT-WIRE TECHNIQUE

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Abstract—The paper presents an analysis of the effects of the absorption of radiation by fluids during measurements of their thermal conductivity by the transient hot-wire technique. The full integro-partial differential equation governing the simultaneous conduction and radiation in a transient hot-wire cell is simplified by means of a small number of physically reasonable assumptions and solved numerically. The numerical solution has been employed to deduce the effect of radiation absorption on the wire temperature rise in measurements of three normal alkanes. Absorption of radiation is shown to produce changes in the wire temperature rise which are comparable with the best available resolution in its measurement and are therefore not directly discernible. Nevertheless, the contribution of radiative transport to the transient heating process means that the thermal conductivity derived from such measurements is systematically in error by as much as 2.5% at 75°C. A procedure whereby thermal conductivity data may be corrected for the effects of radiation is described and the correction factor given for *n*-heptane, *n*-nonane and *n*-undecane in the temperature range 35–75°C and the pressures in the range 0.1–500 MPa.

NOMENCLATURE

a, radius of inner cylinder [m];
A, area of cylinder [m^2];
b, radius of outer cylinder [m];
B, dimensionless radius of outer cylinder;
C, exp γ where γ is Euler's constant;
C_p, heat capacity of fluid at constant pressure [$J\,kg^{-1}\,K^{-1}$];
dA, surface area element;
dV, volume element;
E, emissive power [$W\,m^{-2}$];
E_1, exponential integral;
K, absorption coefficient [m^{-1}];
L_i, Lagrange polynomial;
m, order of Lagrange polynomial;
n, refractive index;
N, number of grid points in annulus;
p_ν, successive roots of zeroth-order Bessel function of first kind;
P, pressure [MPa];
q, heat flux per unit length [$W\,m^{-1}$];
Q, radiant heat flux [$W\,m^{-2}$];
Q', radiant heat flux gradient [$W\,m^{-3}$];
$\tilde{Q}$, linearized heat fluxes [$W\,m^{-2}$];
$\tilde{Q}'$, linearized heat flux gradients [$W\,m^{-3}$];
r, radial coordinate [m];
R, dimensionless radial coordinate;
R_i, radial coordinate of grid point for method of lines;
t, time [s];
T, absolute temperature [K];
V, volume of fluid [m^3];
Y_0, zeroth-order Bessel function of the second kind;
z, axial position [m];
Z, difference of axial positions [m].

Greek symbols

α, absorptivity;
β, ratio of apparent to true thermal conductivity;
$\delta(R)$, decay function;
δT, temperature correction [K];
δT_2, outer boundary correction [K];
δT_5, radiation correction [K];
$\Delta\lambda$, difference between apparent and true thermal conductivity;
$\Delta T'$, corrected temperature rise of wire [K];
ΔT_{id}, temperature rise of the fluid in the ideal model [K];
ΔT_W, temperature rise of the wire [K];
ε, emissivity;
ε_Λ, Planck's distribution function [$W\,m^{-3}$];
η, angular integration limit [rad];
θ, angle of incidence [rad];
Θ, dimensionless temperature;
$\tilde{\Theta}$, dimensionless temperature rise;
κ, thermal diffusivity [$m^2\,s^{-1}$];
λ, thermal conductivity [$W\,m^{-1}\,K^{-1}$];
λ_{app}, apparent thermal conductivity [$W\,m^{-1}\,K^{-1}$];
Λ, wavelength of radiation [m];
ρ, fluid density [$kg\,m^{-3}$];
σ, Stefan–Boltzmann constant [$W\,m^{-2}\,K^{-4}$];
τ, decay function;
ϕ, azimuthal angle of spherical coordinate system [rad];
Φ, polar angle between two points [rad];

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ψ, polar angle in cylindrical coordinates [rad].

Subscripts

0, equilibrium conditions;
1, inner cylinder;
2, outer cylinder;
$A_1 \rightarrow dV_i$, from inner cylinder to volume element;
$A_2 \rightarrow dV_i$, from outer cylinder to volume element;
$A_2 \rightarrow dA_1$, from outer surface to element of inner surface;
$V \rightarrow dV_i$, from bulk of fluid to volume element;
$V \rightarrow dA_1$, from fluid to surface element of inner cylinder.

1. INTRODUCTION

RECENT developments in both the theory [1–4] and practice [5–8] of the transient hot-wire technique have brought it to the stage when it offers the most precise method for the measurement of the thermal conductivity of fluids. Using the most refined instruments it has been possible to attain a precision of $\pm 0.2\%$ in the measurements in both gas and liquid phases [6–13]. However, only in the cases of dilute and moderately dense gases has it been possible to identify this precision with the accuracy of the reported thermal conductivity data [6, 13]. For other fluids, specifically those which absorb electromagnetic radiation, the theoretical description of the measurement process has been less than complete, and for such systems it has been necessary to accept that the thermal conductivity data may be burdened with a systematic error of the order of 1% [11, 14].

Because the thermal conductivity of a material can only be practically determined by the imposition of a temperature gradient within it, there is, in principle, always a radiative contribution to the measured total heat flux. In the case when the material is transparent to the radiation and is confined between two surfaces the radiative contribution to the heat flux may be evaluated independently of the conductive contribution, either in a separate experiment in the absence of a medium between the two surfaces, or by a relatively simple calculation [15]. However, in the case when the fluid absorbs some of the radiation, the radiative contribution to the heat flux is coupled to the conductive heat flux through the medium itself and hence cannot be determined in an experiment in which the medium is absent. Furthermore, direct calculation of the radiative heat flux, which depends upon the instrument employed for the measurement, becomes a very much more complicated problem. It is likely that at least some part of the large discrepancies between thermal conductivity data for absorbing fluids obtained in different types of instrument [16] may be attributed to the effects of radiative heat transfer.

The majority of studies of the contribution of radiation to heat transport in absorbing media have been confined to steady state conditions for parallel plate arrangements [17–23]. Even in this relatively simple case the exact solution of the energy equation given by [17] is too complicated for routine analysis of experimental data, although it does confirm the existence of a significant effect upon thermal conductivity measurements. On the other hand, approximate treatments such as that of [18] based on the Rosseland diffusion approximation [20] are not generally quantitatively correct. In the transient hot-wire method the essential measurement is that of the temperature rise of a thin wire immersed in the fluid as a function of time following the stepwise initiation of a heat flux within it [1]. By means of a suitable design and a careful choice of operating conditions [5–7] it is possible to arrange that the instrument operates in very close accord with the simplest mathematical treatment of it. Among the idealizations of this mathematical treatment is the assumption that the heat transfer from the wire takes place solely by conduction. In order to account for this, as well as the other departures of the experimental arrangement from the ideal, small, additive corrections must be applied to the observed temperature rises of the wire so that the data can be interpreted with a simple working equation [1]. Explicit expressions for many of these corrections have already been given [1–4] including that for the radiation heat loss, δT_5, when the fluid is transparent to radiation [1]. In most instruments used with transparent fluids, this correction is negligible, amounting to less than $5 \times 10^{-3}\%$ of the total temperature rise [5]. However, in the case of absorbing liquids an equivalent expression for the correction is not available and it cannot be assumed that the effect is similarly negligible judged on the evidence for the steady state, parallel plate case.

There have been a number of attempts to carry out an analysis of the process of simultaneous conduction and radiation in an absorbing fluid for the transient hot-wire instrument [21–23]. All of the approaches have been founded on simplifications of the energy equation, usually related to somewhat artificial assumptions about the optical thickness of the medium at different radial positions [23]. The predictions of these approximate analyses have not been confirmed by subsequent measurements in transient hot-wire measurements of thermal conductivity [7, 8, 11, 14]. The present paper provides a more rigorous analysis of simultaneous radiation and conduction in a transient hot-wire instrument than has been given before. The analysis is based on a numerical solution of the full energy equation describing the process. It is intended to provide a means whereby measurements of thermal conductivity performed in such an instrument may be corrected for the effects of radiation, so that the high precision of the experimental technique may be translated into a comparable accuracy.

2. THE MODEL

The ideal model of the transient hot-wire instrument consists of an infinitely long line source of a radial heat flux, q, initiated at time $t = 0$, immersed in a fluid of infinite extent with temperature independent physical properties, initially at a temperature T_0. It is presumed that all the heat loss from the wire occurs by conduction, and it can then be shown that the temperature rise of the fluid at a radial position r conforms to the equation [1]:

$$\Delta T_{id}(r, t) = \frac{q}{4\pi\lambda} E_1(r^2/4\kappa t). \quad (1)$$

For the small values of $r^2/\kappa t$ relevant in most instruments, this reduces to

$$\Delta T_{id}(r, t) = \frac{q}{4\pi\lambda} \ln(4\kappa t/r^2 C). \quad (2)$$

In practice, the heat source is a thin metallic wire of radius, a, and finite length, immersed in a fluid with temperature dependent physical properties, which is confined in a cylinder of radius b. The wire is also employed as a thermometer in the measurements and its temperature rise, ΔT_W, is identified with that of the fluid in contact with it at the radial location $r = a$. Owing to the differences between the real system and the ideal model of it, the temperature rise ΔT_W differs from ΔT_{id} by a small amount. However, because each of the departures from the ideal model may be rendered small by an appropriate design, the corresponding corrections may be treated independently in the formulation of the theory of the method and viewed as small additive corrections [1].

Thus we write

$$\Delta T_{id} = \Delta T_W + \sum_i \delta T_i \quad (3)$$

where the δT_i represent the various additive corrections. Among these, adopting a notation consistent with reference [1], δT_5 denotes the correction to be applied to the measured temperature rise to eliminate the effects of radiation. One purpose of the present analysis is to evaluate the correction δT_5 for absorbing liquids. Because the remaining corrections, $\delta T_i (i \neq 5)$, have already been evaluated [1–4], it is convenient to define a temperature rise $\Delta T'$, which is the experimental temperature rise corrected for all effects except radiation, by the equation

$$\Delta T' = \Delta T_W + \sum_{\substack{i \\ i \neq 5}} \delta T_i. \quad (4)$$

The model adopted for the determination of the radiation correction is shown in Fig. 1, which also defines the cylindrical polar coordinate system employed. The heat source consists of an infinitely long cylinder of radius a with negligible heat capacity and infinite thermal conductivity. The fluid, which has temperature-independent physical properties, is confined in the annulus between this cylinder and an infinitely long outer cylinder of radius b. The bounding surfaces of the fluid are assumed to be grey and the fluid itself is assumed to be isotropic, grey and non-scattering. The conductive and radiative heat fluxes are assumed to be additive and Kirchhoff's Law for emission and absorption of radiant energy by the fluid and the bounding surfaces is assumed to be valid. In addition to the effects of radiation, the present model departs from the ideal by virtue of the finite outer boundary and the presence of a non-zero diameter heat source. The inclusion of the latter two features simplifies the numerical procedures required for a solution of the problem, and because account may readily be taken of their effects, it is still possible to determine the consequences of radiation absorption alone.

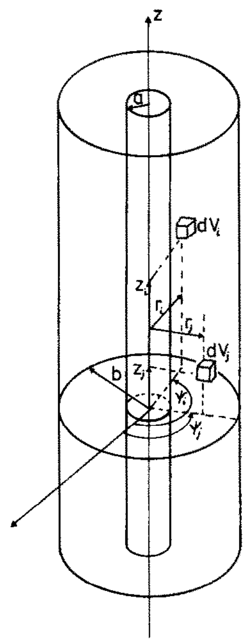

FIG. 1. The model of the transient hot-wire cell adopted for the determination of the radiation correction.

2.1. *The energy equation*

Applying an energy balance to the elemental volume of fluid dV_i in Fig. 1, we obtain the equation

$$\rho C_p \frac{\partial T}{\partial t} = \lambda \nabla^2 T + Q'_{V \to dV_i} + Q'_{A_1 \to dV_i} + Q'_{A_2 \to dV_i} - 4K_i E_i. \quad (5)$$

The first term on the right of this equation represents the conductive heat flux gradient whereas the second, third and fourth terms represent the gradients of the one-way heat fluxes from the remainder of the fluid volume, and the inner and outer surfaces of the annulus respectively, to the volume element. The final term represents the total outgoing radiative heat flux from the volume element dV_i.

At the surface of the inner cylinder ($r = a$) the boundary condition for the solution of equation (5) appropriate to the present model takes the form

$$\frac{q}{2\pi a} = -\lambda\left(\frac{\partial T}{\partial r}\right)_{r=a} - \alpha_1 Q_{A_2\to dA_1} - \alpha_1 Q_{V\to dA_1} + \varepsilon_1 n^2\ \sigma T^4(a), \quad (6)$$

$$r = a,\ t \geqslant 0,$$

where dA_1 is an element of area on the surface of the inner cylinder and the second and third terms represent the one-way radiant transfer to this element from the outer surface and the fluid volume respectively.

At the surface of the outer cylinder we impose the condition that the temperature remains constant at its initial equilibrium value

$$T(b, t) = T_0, \qquad 0 \leqslant t \leqslant \infty. \quad (7)$$

This is just the same condition that has been employed to deduce a correction to the ideal model of the apparatus arising from the presence of a finite outer boundary in the pure conductive case [1].

The initial condition for the solution of the equation is provided by the requirement of thermal equilibrium so that

$$T = T_0, \qquad 0 \leqslant r \leqslant b, \qquad t \leqslant 0. \quad (8)$$

Each of the radiative terms in equations (5) and (6) may be written explicitly using standard procedures [24] so that equation (5) becomes

$$\rho C_P \frac{\partial T}{\partial t} = \lambda \nabla^2 T + \int_V \frac{K_i K_j \tau(r) E_j dV_j}{\pi r^2} + \int_{A_1} \frac{K_i (E_1 + \tilde{R}_1)\cos\theta_1 \tau(r) dA_1}{\pi r^2} + \int_{A_2} \frac{K_i (E_2 + \tilde{R}_2)\cos\theta_2 \tau(r) dA_2}{\pi r^2} - 4K_i E_i. \quad (9)$$

Applying similar methods the boundary condition (6) may be written

$$\frac{q}{2\pi a} = -\lambda\left(\frac{\partial T}{\partial r}\right)_{r=a} - \alpha_1 \int_{A_2} \frac{(E_2 + \tilde{R}_2)\cos\theta_1 \cos\theta_2 \tau(r) dA_2}{\pi r^2} - \alpha_1 \int_V \frac{E_j \tau(r) K_j \cos\theta_1 dV_j}{\pi r^2} + \varepsilon_1 n^2 \sigma T^4. \quad (10)$$

In these equations

$$\tau(r) = \exp\left(-\int_0^r K dr\right). \quad (11)$$

In addition, θ_1 represents the angle between the normal to an element, dA_1, of the surface of the inner cylinder and the vector r, whereas θ_2 is a similar angle at the element dA_2 of the outer cylinder. The symbol $\tilde{R}$ represents the fraction of energy falling on a surface element which is not absorbed.

In order to proceed it is desirable to introduce a small number of further simplifications into the model. In each case the additional approximation is consistent with the desire to obtain a small, 1st-order correction to the ideal model of the transient hot-wire instrument. Thus, it is assumed that the absorption coefficient of the fluid is independent of temperature so that

$$K_i = K_j = K \text{ and } \tau(r) = \exp - Kr. \quad (12)$$

First this is consistent with the assumption that the remainder of the physical properties of the fluid are temperature independent, and secondly, the temperature changes involved in measurements are only of the order of 5 K so that the error introduced should, in any event, be very small. It is further assumed that the surface of the outer cylinder of the instrument is black so that $\varepsilon_2 = \alpha_2 = 1$, $\tilde{R}_2 = 0$ and

$$\tilde{R}_1 = (1 - \alpha_1)\{Q_{V\to dA_1} + Q_{A_2\to dA_1}\}.$$

Because in practice the thermal conduction wave from the heat source does not penetrate to the outer cylinder of the cell, and because most of the radiant energy is absorbed in the fluid before it reaches the outer cylinder, this approximation is thought to introduce a negligible error. Finally, the absorbtivity and emissivity of the inner cylinder are assumed to be equal and temperature independent so that

$$\varepsilon_1 = \alpha_1 = \varepsilon. \quad (13)$$

Introducing these assumptions into the energy equation we obtain

$$\rho C_P \frac{\partial T}{\partial t} = \lambda \nabla^2 T + \frac{K^2}{\pi}\int_V \frac{E_j \tau(r) dV_j}{r^2} + \frac{K}{\pi}\int_{A_1} \times \frac{[E_1 + (1-\varepsilon)\{Q_{V\to dA_1} + Q_{A_2\to dA_1}\}]\cos\theta_1 \tau(r) dA_1}{r^2} + \frac{K}{\pi}\int_{A_2} \frac{E_2 \cos\theta_2 \tau(r) dA_2}{r^2} - 4KE_i \quad (14)$$

where

$$Q_{V\to dA_1} = \frac{K}{\pi}\int_V \frac{E_j \tau(r)\cos\theta_1 dV_j}{r^2} \quad (15)$$

and

$$Q_{A_2\to dA_1} = \frac{1}{\pi}\int_{A_2} \frac{E_2 \cos\theta_1 \cos\theta_2 \tau(r) dA_2}{r^2}. \quad (16)$$

At the same time the boundary condition (6) becomes

$$\frac{q}{2\pi a} = -\lambda\left(\frac{\partial T}{\partial r}\right)_{r=a} - \varepsilon(Q_{A_2\to dA_1} + Q_{V\to dA_1} - n^2\sigma T^4). \quad (17)$$

2.2. *The radiative contributions to the heat flux*

The evaluation of the surface and volume integrals

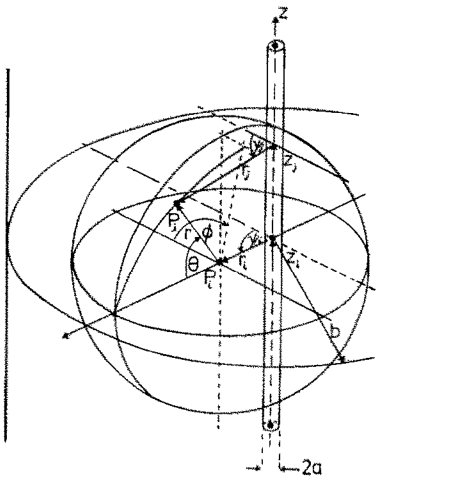

FIG. 2. Coordinate systems for the evaluation of the radiant heat fluxes and their gradients.

which occur in the radiative contributions to the heat flux is most conveniently performed with the coordinate system defined by Fig. 2. Here (r_i, z_i, ψ_i) are the coordinates of point P_i in a cylindrical system centered on the axis of the inner cylinder. On the other hand (r, θ, ϕ) are the coordinates of a spherical polar system centered on the point P_i. With the aid of the definitions,

$$\Phi = \psi_j - \psi_i \tag{18}$$

and

$$Z = z_j - z_i, \tag{19}$$

which relate the cylindrical coordinates of two points P_i and P_j, each of the integrals in equations (14)–(17) may be expressed in terms of the coordinates (r_i, Z, Φ). The equations for the transformation including the Jacobian $\partial(r, \theta, \phi)/\partial(r_i, Z, \Phi)$ are given in the Appendix.

From equation (15) we obtain

$$Q_{V\to dA_1} = \frac{4K}{\pi}\int_0^\infty\int_a^b\int_0^{\eta_{1j}} \times \frac{E_j(r_j\cos\Phi - a)\tau(r_a)\mathrm{d}\Phi r_j \mathrm{d}r_j\mathrm{d}Z}{r_a^3} \tag{20}$$

where

$$r_a = [r_j^2 + a^2 - 2ar_j\cos\Phi + Z^2]^{1/2}, \tag{21}$$

$$\eta_{1j} = \cos^{-1}\left(\frac{a}{r_j}\right), \tag{22}$$

and Fig. 3(a) illustrates a section of the region of the fluid contributing to the integrals.

The transformation of equation (16) leads to the result that

$$Q_{A_2\to dA_1} = \frac{4E_2 b}{\pi}\int_0^\infty\int_0^{\eta_{12}} \times \frac{(b\cos\Phi - a)(b - a\cos\Phi)\tau(r_b)\mathrm{d}\Phi\mathrm{d}Z}{r_b^4} \tag{23}$$

where

$$r_b = [b^2 + a^2 - 2ab\cos\Phi + Z^2]^{1/2}, \tag{24}$$

$$\eta_{12} = \cos^{-1}(a/b), \tag{25}$$

and Fig. 3(b) illustrates a section of the contributing region of the outer surface. The flux gradients of equation (14) may also be written in the same coordinates. Thus the contribution owing to radiation from the bulk of the fluid at a volume element situated at P_i becomes

$$Q'_{V\to dV_i} = \frac{4K^2}{\pi}\int_0^\infty\int_a^b\int_0^{\eta_{1i}+\eta_{1j}} \frac{E_j\tau(r_c)\mathrm{d}\Phi r_j\mathrm{d}r_j\mathrm{d}Z}{r_c^2}, \tag{26}$$

where

$$r_c = [r_j^2 + r_i^2 - 2r_ir_j\cos\Phi + Z^2]^{1/2} \tag{27}$$

$$\eta_{1i} = \cos^{-1}\left(\frac{a}{r_i}\right), \tag{28}$$

and Fig. 3(c) illustrates a section of the contributing portion of the fluid.

For transport from the surface of the inner cylinder to a volume element at P_i we find

$$Q'_{A_1\to dV_i} = \frac{4Ka}{\pi}[E_1 + (1-\varepsilon)\{Q_{V\to dA_1} + Q_{A_2\to dA_1}\}] \times \int_0^\infty\int_0^{\eta_{1i}} \frac{(r_i\cos\Phi - a)\tau(r_d)\mathrm{d}\Phi\mathrm{d}Z}{r_d^3}, \tag{29}$$

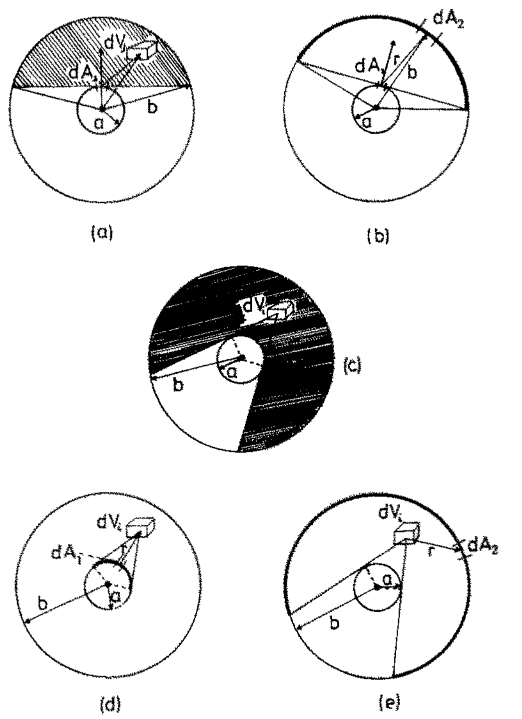

FIG. 3. The regions of fluid and bounding surfaces contributing to radiant heat fluxes and heat flux gradients. Volumes of the fluid contributing are shown hatched, surfaces contributing are indicated by thick lines. (a) $Q_{V\to dA_1}$; (b) $Q_{A_2\to dA_1}$; (c) $Q'_{V\to dV_i}$; (d) $Q'_{A_1\to dV}$; (e) $Q'_{A_2\to dV_i}$.

where

$$r_d = [r_i^2 + a^2 - 2ar_i\cos\Phi + Z^2]^{1/2} \quad (30)$$

and Fig. 3(d) shows the section of the inner cylinder contributing to the integrals.

Finally, the contribution from radiative transport to the volume element at P_i from the outer surface A_2, may be similarly transformed,

$$Q'_{A_2\to dV_i} = \frac{KE_2 b}{\pi}\int_0^{\infty}\int_0^{\eta_{1i}+\eta_{12}} \frac{(b-r_i\cos\Phi)\tau(r_e)d\Phi dZ}{r_e^3} \quad (31)$$

where

$$r_e = (r_i^2 + b^2 - 2r_i b\cos\Phi + Z^2) \quad (32)$$

and Fig. 3(e) defines the limits of integration for the contributing surface of the outer cylinder.

Equation (14), together with the definition

$$E_j(r_j, t) = n^2\sigma T^4(r_j, t) \quad (33)$$

and the preceding results for the radiative flux gradients is an integropartial differential equation for the temperature rise of the fluid as a function of time and position in a transient hot-wire instrument in which the fluid is absorbing. The solution of this equation, when compared with the solution for a non-absorbing fluid, yields directly the effect of radiation on the system. An analytic solution to equation (14) subject to the boundary and initial conditions (7), (8) and (17) is not feasible without further assumptions so that it has been necessary to obtain a numerical solution.

3. METHOD OF SOLUTION

3.1. *Linearization*

In order to carry out the numerical solution of the energy equation we first transform to the dimensionless variables

$$\Theta = T/T_0,\ R = r/a \text{ and } B = b/a. \quad (34)$$

Secondly, because the energy equation (14) is non-linear we have found it advantageous to linearize it. This second procedure is not essential to the process of obtaining a numerical solution because methods for solving such non-linear equations are available. However, the computational effort required for the present problem is extremely large. Furthermore, the linearization is consistent with our aim of attaining a 1st-order correction arising from the effects of radiation absorption, and is justified by the fact that the temperature rise in the fluid is typically only a few degrees Kelvin. Hence, if we define a dimensionless temperature rise by the equation

$$\tilde{\Theta} = \frac{\Delta T}{T_0} = \Theta - 1. \quad (35)$$

then

$$\tilde{\Theta} \ll 1$$

and we can write

$$\Theta^4 = 1 + 4\tilde{\Theta} \quad (36)$$

so that the dimensionless, linearized energy equation becomes

$$\frac{\partial\tilde{\Theta}}{\partial t} = \frac{\lambda}{\rho C_p a^2}\left[\frac{\partial^2\tilde{\Theta}}{\partial R^2} + \frac{1}{R}\frac{\partial\tilde{\Theta}}{\partial R}\right] + \frac{1}{\rho C_p T_0}[\tilde{Q}'_{V\to dV_i} + \tilde{Q}'_{A_1\to dV_i} + \tilde{Q}'_{A_2\to dV_i} - 16Kn^2\sigma T_0^4\tilde{\Theta}(R_i)] \quad (37)$$

whereas the boundary conditions are

$$\frac{q}{2\pi T_0} = -\lambda\left(\frac{\partial\tilde{\Theta}}{\partial R}\right)_{R=1} - \frac{\varepsilon a}{T_0}[\tilde{Q}_{A2\to dA_1} + \tilde{Q}_{V\to dA_1}] + 4\varepsilon n^2\sigma a T_0^3\tilde{\Theta}(1), \quad (38)$$

and

$$\tilde{\Theta}(B) = 0, \quad 0 \leqslant t \leqslant \infty, \quad (39)$$

and the initial condition is

$$\tilde{\Theta}(R) = 0, \quad t \leqslant 0, \quad 1 \leqslant R \leqslant B. \quad (40)$$

The same procedures may be applied to the one-way radiation heat fluxes and gradients to yield

$$\tilde{Q}_{V\to dA_1} = \frac{16n^2\sigma K T_0^4}{\pi}\int_0^{\infty}\int_1^{B}\int_0^{\eta_{1j}} \times \frac{R_j\tilde{\Theta}(R_j)[R_j\cos\Phi - 1]\delta(R_a)d\Phi dR_j dZ}{R_a^3}, \quad (41)$$

$$\tilde{Q}_{A_2\to dA_1} = 0, \quad (42)$$

by virtue of boundary condition (39),

$$\tilde{Q}'_{V\to dV_i} = \frac{16n^2K^2\sigma T_0^4}{\pi}\int_0^{\infty}\int_1^{B}\int_0^{\eta_{1j}+\eta_{1j}} \times \frac{R_j\tilde{\Theta}(R_j)\delta(R_c)d\Phi dR_j dZ}{R_c^3}, \quad (43)$$

$$\tilde{Q}'_{A_1\to dV_i} = D\int_0^{\infty}\int_0^{\eta_{1i}} \frac{(R_i\cos\Phi - 1)\delta(R_d)d\Phi dZ}{R_d^3} \quad (44)$$

and finally

$$\tilde{Q}'_{A_2\to dV_i} = 0 \quad (45)$$

again because of the boundary condition (39).

In these equations we have employed the definitions

$$\delta(R) = \exp - KaR, \quad (46)$$

and

$$D = \frac{4K}{a\pi}[4\varepsilon n^2\sigma T_0^4\tilde{\Theta}(1) + (1-\varepsilon)(Q_{V\to dA_1} + Q_{A_2-dA_1})], \quad (47)$$

together with obvious definitions of R_i, R_j, R_a, R_e and R_d. The tilde denotes that the radiation heat fluxes and gradients have been linearized.

3.2. *Numerical methods*

The first step in the numerical solution of equation (37) involves the conversion of the multidimensional integrals in the expressions for the radiation heat fluxes and gradients into algebraic series by means of a suitable quadrature procedure. For each integral we have employed Gauss–Legendre quadrature for a finite interval [25], even for the integration over the axial coordinate Z which, in principle, extends to infinity. The latter procedure is necessary to avoid underflow in the machine calculations at the pivot points of quadrature formulae for an infinite interval caused by the rapid decay of the integrand. The finite upper limit of the integration over the axial coordinate, $Z_{\lim}$, was selected by numerical experimentation; it has been found that a value of

$$Z_{\lim} = 50/K,$$

is generally satisfactory. For the liquids considered in this study this limit corresponds to a vertical distance of about 5 cm.

The application of the quadrature formulae reduces the energy equation (37) to a linear, partial differential equation which has been solved by the Method of Lines [26]. This method involves the conversion of the partial differential equation to a set of coupled ordinary differential equations. To implement the method in this case, the annular space between the two cylinders is discretized into a number, N, of points R_i at each of which the temperature rise of the fluid at a time t is denoted by $\tilde{\Theta}_i(t)$. The function $\tilde{\Theta}(R, t)$ is then represented by a series of approximating Lagrange polynomials in the spatial coordinate, $L_i(R)$, so that

$$\tilde{\Theta}_a(R, t) = \sum_{i=1}^{m} L_i(R)\tilde{\Theta}_i(t)$$

where

$$L_i(R) = \prod_{j=1}^{m} (R-R_j) \Big/ \prod_{j=1}^{m} (R_i-R_j), \quad j \neq i$$

and $(m-1)$ is the degree of the polynomial, and $m < N$. The subscript, a, on the function $\tilde{\Theta}$ denotes it is an approximation to the solution $\tilde{\Theta}(R, t)$. Because $L_i(R_i) = 1$ and $L_i(R_j) = 0, j \neq i, R_j \neq 0$ then

$$\tilde{\Theta}_a(R_i, t) = \tilde{\Theta}_i(t)$$

and the polynomial passes through the given data points. The partial derivatives of $\tilde{\Theta}(R, t)$ may also be approximated by the derivatives of the polynomial at the spatial location R_i

$$\left(\frac{\partial\tilde{\Theta}}{\partial R}\right)_{R_i} \simeq \left(\frac{\partial\tilde{\Theta}_a}{\partial R}\right)_{R_i} = \sum_{i=1}^{m} L_i'(R)\tilde{\Theta}_i(t)$$

and

$$\left(\frac{\partial^2\tilde{\Theta}}{\partial R^2}\right)_{R_i} \left(\frac{\partial^2\tilde{\Theta}_a}{\partial R^2}\right)_{R_i} = \sum_{i=1}^{m} L_i''(R)\tilde{\Theta}_i(t)$$

where the prime denotes differentiation of the polynomial with respect to R. Introduction of these results into the energy equation (37) at each spatial location leads to a coupled set of N ordinary differential equations in the time domain. In the present work, the fundamental form of the temperature profile in space is known to be that corresponding to the ideal model for pure conduction [equation (1)] because the radiative perturbations are small. Consequently, the grid points R_i for the method of lines have been chosen according to the scheme

$$R_i = B^{[(i-1)/(N-1)]}$$

in order to obtain a finer grid spacing near to the inner cylinder which represents the most important region of the fluid for the effects considered. The coupled ordinary differential equations obtained by the foregoing method are stiff and they have therefore been integrated using an algorithm developed by Gear [27] and Hindmarsh [28], which allows both variable order of integration and variable step size.

During the integration of the ordinary differential equations in the time domain it is necessary to evaluate the linearized radiant heat fluxes and heat flux gradients according to the quadrature formulae approximating the integrals. Because the pivot points of the Gauss–Legendre scheme employed do not coincide with the grid adopted for the method of lines it is necessary at each step to interpolate in the grid to determine the temperature rise of the fluid at the pivot points. For this purpose a 5-point interpolation scheme proposed by Akima [29] has been used. Some of the integrals contained in the radiant heat fluxes and their gradients are time independent and for these, which need only be computed once, a 16 point Gauss–Legendre scheme was used. For the remainder of the integrals, which must be continually recalculated at each step, a 3- or 5-point quadrature was employed and was found to be sufficiently rapid and accurate.

3.3. *Precision of the numerical solution*

For each iterative step in the numerical procedure outlined above it has been found that a convergence limit corresponding to a relative error of 10^{-6} represents a satisfactory compromise between accuracy and the need to avoid machine round-off errors. The remaining parameters of the numerical method also represent a compromise between the need to limit the computation time and the need to maintain sufficiently high accuracy. Appropriate values of the order of coupling in the ordinary differential equations, m, and the number of grid points in the annular space, N, have been determined by numerical trials. For this purpose it is desirable to use an analytic solution to the problem as a reference, because this also allows the accuracy of the numerical solution to be assessed. The only analytic solution which is available is that in which the effects of radiation are negligible, that is, for a model of the instrument which contains an outer boundary but in which the fluid is not absorbing. This solution for the temperature rise of the fluid at the surface of the inner cylinder takes the form [1]

$$\tilde{\Theta}(1, t) = \frac{\Delta T_{\rm id}}{T_0} - \frac{\delta T_2}{T_0} \tag{48}$$

where for sufficiently large values of $\kappa t/a^2$, $\Delta T_{\rm id}$ is given by equation (2). The correction δT_2, which accounts for the departures of the apparatus from the ideal model because of the presence of the outer cylinder is given by [1]

$$\delta T_2 = \frac{q}{4\pi\lambda}\left[\ln\left(\frac{4\kappa t}{b^2 C}\right) + \sum_{\nu=0}^{\infty} e^{-p_\nu^2 \kappa t/b^2}(\pi Y_0(p_\nu))^2\right] \tag{49}$$

for the large values of b/a characteristic of all instruments.

In order to compare the numerical solution with that of equation (48), we have carried out calculations for a fluid possessing physical properties close to those of n-heptane. The conditions chosen for the calculation, 300 K and a pressure of 0.1 MPa, are similar to those employed in recent measurements of the thermal conductivity of n-heptane, and they and the appropriate physical properties of the fluid are collected in Table 1. In order to simulate conditions in which radiation plays an insignificant role, both the emissivity of the inner cylinder and the absorption coefficient of the liquid were set to very small values in these calculations, but the algorithm employed for the calculations was in every respect identical to that described earlier.

Following a number of trial calculations of this type [30] with different parameters for the numerical solution it was determined that third order coupling of the differential equations combined with 301 grid points in the annular space led to adequate precision.

Figure 4 displays the deviations between the analytic solution of equation (48) and the numerical solution for these parameters, in the range of times 0.1–1.0 s of interest experimentally. The deviation is typically only ±0.02%. This agreement is taken as evidence of the precision of the calculation and because the algorithm employed is identical when radiation effects are significant, it is expected that the accuracy of the results will be similar. Unfortunately, no more direct confirmation of this contention is possible.

4. RESULTS

In order to relate the present calculations of the effect of radiation absorption as closely as possible to a real experiment, we have applied the algorithm described earlier to a transient hot-wire apparatus employed for thermal conductivity measurements on three alkanes, n-heptane, n-nonane and n-undecane [7, 12]. This particular apparatus consists of a platinum wire of radius a = 3.9 μm on the axis of a cylinder of radius b = 4.95 mm, and was used at the three

Table 1. Physical properties of the alkanes and values of the experimental parameters employed for the evaluation of the effect of radiation absorption

T_0/K	n	λ/mW m^{-1} K^{-1}	ρ/kg m^{-3}	C_p/J kg^{-1} K^{-1}	K/m^{-1}	q/W m^{-1}
			n-heptane, 50 MPa			
300	1.385	128.2	697	2252	1070	1.0
308	1.385	144.0	716	2826	1070	0.66
323	1.385	138.3	704	2826	1070	0.64
348	1.385	137.1	698	2826	1070	0.63
			n-heptane, 500 MPa			
308	1.385	233.5	846	2826	1070	0.66
323	1.385	233.3	841	2826	1070	0.64
348	1.385	232.5	834	2826	1070	0.63
			n-nonane, 50 MPa			
308	1.405	146.1	743	2200	1120	0.66
323	1.405	143.6	724	2200	1120	0.64
348	1.405	141.3	727	2200	1120	0.77
			n-nonane, 500 MPa			
308	1.405	231.3	870	2200	1120	0.66
323	1.405	231.4	866	2200	1120	0.64
348	1.405	231.5	859	2200	1120	0.77
			n-undecane, 50 MPa			
308	1.418	147.8	760	2250	1150	0.89
323	1.418	146.0	753	2250	1150	0.86
348	1.418	140.8	739	2250	1150	0.84
			n-undecane, 500 MPa			
308	1.418	215.3	864	2250	1150	0.90
323	1.418	217.5	863	2250	1150	0.87
348	1.418	214.6	855	2250	1150	0.84

For all calculations: inner cylinder radius, a = 3.9 μm; outer cylinder radius, b = 4.95 mm; wire emissivity, ε = 0.037.

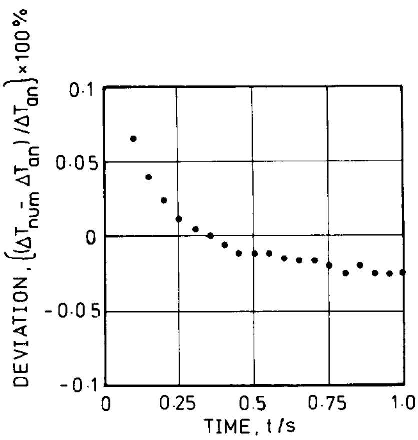

FIG. 4. Deviations of the numerical solution from the analytic solution for 3rd-order coupling with 301 points.

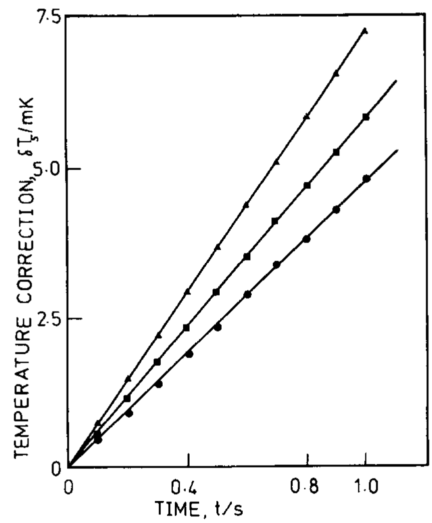

FIG. 5. The temperature correction, δT_5, owing to radiation absorption in *n*-heptane. ● T_0 = 308 K; P = 500 MPa; ■ T_0 = 323 K, P = 500 MPa; ▲ T_0 = 348 K, P = 500 MPa.

temperatures 35, 50 and 75°C, over a range of pressures from 50–500 MPa.

In order to estimate the effects of radiation absorption on these measurements, we have used the foregoing algorithm to compute $\tilde{\Theta}(1, t)$ for several sets of conditions representative of those encountered in the measurements. For this purpose, we have employed heat fluxes, q, in the calculations similar to those used in the measurements, as well as the physical properties of the alkanes appropriate to the thermodynamic state involved. The properties of the fluids and the characteristics of the instrument are all collected in Table 1. Among the physical properties of the fluids required for the calculation are the refractive index and an absorption coefficient, K. For the former we have employed values measured at 25°C in all cases. For the latter, we have employed a mean absorption coefficient, defined by the relation

$$K = -\frac{1}{L}\ln\left[\frac{\int_0^\infty (I_\Lambda/I_\Lambda^\circ)\varepsilon_\Lambda \mathrm{d}\Lambda}{\int_0^\infty \varepsilon_\Lambda \mathrm{d}\Lambda}\right] \tag{50}$$

and determined directly at room temperature in an i.r. spectrophotometer [30]. This mean absorption coefficient is not the same as the more usual Planck mean extinction coefficient [24] but is appropriate for the present purpose if the fluids are treated as grey. Values for K and n under other conditions are not available, so that those appropriate to ambient conditions have had to be used in other thermodynamic states.

The effect of radiation absorption on the wire temperature rise is quantified by the definition

$$\delta T_5 = \Delta T_{id} - \delta T_2 - \Delta T. \tag{51}$$

Here, ΔT_{id} is the temperature rise of the inner cylinder according to the ideal model of the instrument [equation (2)], δT_2 is the correction owing to the outer boundary of the fluid [equation (49)] and $\Delta T = T_0\tilde{\Theta}(1, t)$ is the computed temperature rise when radiation absorption occurs. According to this definition δT_5 can also be identified as the correction to be added to the temperature rise observed experimentally in an absorbing fluid to account for the effects of the absorption and thereby recover the ideal temperature rise ΔT_{id}.

Figure 5 contains a plot of $\delta T_5(t)$ for the simulation of measurements in *n*-heptane at three temperatures. In each case the total temperature rise of the wire was of the order of 5 K. The effect of radiation is to produce a positive value of δT_5, increasing with time in an approximately linear fashion to about 0.007 K or 0.15% at a time of 1 s. Similar, but slightly greater effects are found in the cases of *n*-nonane and *n*-undecane. The effects of radiation absorption on the fluid temperature are therefore small and there is no sign of the rather large effects suggested by the work of Saito and Venart for toluene [23]. In general, the effect increases with absolute temperature and with the absorption coefficient of the liquid in the range studied. Despite the small magnitude of the effect of radiation on the temperature rise of the wire, its systematic nature has significant consequences for the measurmenent of thermal conductivity which are discussed in the next section.

5. APPLICATION TO TRANSIENT HOT-WIRE MEASUREMENTS OF THERMAL CONDUCTIVITY

The thermal conductivity of a fluid is determined from a set of data points $(\Delta T_W(t_i), t_i)$ obtained in a transient hot-wire measurement by application of linear regression to the corrected data set $(\Delta T_{id}(t_i), \ln t_i)$ where [1, 6]

$$\Delta T_{id} = \Delta T_W + \sum_j \delta T_j \tag{52}$$

and, according to equation (2),

$$\lambda = \frac{q}{4\pi}[1/(\mathrm{d}\Delta T_{id}/\mathrm{d}\ln t)]. \quad (53)$$

If the complete set of corrections δT_i is available this procedure should yield the true thermal conductivity of the fluid at an appropriate reference temperature [1]. Thus, in principle, the correct application of the preceding results would be to compute the correction δT_5 for each experimental point for each run and to combine the results with the measurements of ΔT_W according to equation (52). However, the enormous computational effort required (about 10^5 words of storage and 750 s of C.P.U. time on a CDC 7600 computer for a single run) this is evidently an impractical approach. Thus, whereas the present calculations of δT_5 may serve as a test of later and simpler analytic solutions to the problem, they cannot be applied directly to the correction of experimental observations.

In order to discuss alternative methods of applying the radiation correction, we first consider the magnitude of the effect in a different manner. According to equation (4) $\Delta T'$ represents the temperature rise of the wire corrected for all departures from the ideal model except that arising from radiation. If the set of data points $(\Delta T'(t_i), \ln t_i)$ obtained in an experiment are subjected to linear regression, then the time dependence of $\delta T_5(t)$ leads to a small curvature in the line $\Delta T'$ vs $\ln t_i$. Figure 6 contains a plot of the deviations of the points $(\Delta T'(t_i), \ln t_i)$ from a straight line fitted to data generated by the simulation of a measurmeent in n-heptane at 348 K. The fit has been carried out over the range of times 0.1–1.0 s usually employed in measurements. The systematic curvature of the deviation plot corresponding to the curvature of the line ($\Delta T'$ vs $\ln t$) can be seen to amount to only 0.05% of the temperature rise even in this worst case. Because, in even the most precise thermal conductivity instruments, the resolution of the temperature rise measurements is not better than $\pm 0.05\%$, such a curvature could not be discerned experimentally. This finding is consistent with the experimental observations of Menashe and Wakeham [7]. On the other hand, if the average slope of the plot of $\Delta T'$ vs $\ln t$ is obtained from a least-squares fitted straight line the apparent thermal conductivity, defined by the equation,

$$\lambda_{app} = \frac{q}{4\pi}[1/(\mathrm{d}\Delta T'/\mathrm{d}\ln t)], \quad (54)$$

is found to be

$$\lambda_{app} = 139.8\ \mathrm{mW\,m^{-1}\,K^{-1}}$$

which is greater by 1.9% than the true value listed in Table 1. It must therefore be concluded that although the systematic effect of radiation on the wire temperature rise cannot be distinguished from the random error of measurements it introduces a systematic error into the thermal conductivity derived.

These observations suggest that the correction to the data to account for radiation absorption should be applied to the slope of the fitted straight line, or equivalently, the thermal conductivity, rather than to the individual temperature rises. We therefore define a ratio of the apparent and real thermal conductivities as

$$\beta = \frac{\lambda_{app}}{\lambda} = 1 + \frac{\Delta\lambda}{\lambda}. \quad (55)$$

Here, λ_{app} is the apparent thermal conductivity of the fluid determined according to equation (54) and λ the true thermal conductivity. In general the ratio β depends upon the characteristics of the instrument employed for the measurements, such as its dimensions, the emissivity of the material of the inner cylinder, the heat flux employed for the measurements, and the time range over which measurements are made. In addition, the ratio depends upon all the physical properties of the fluid, for example, the thermal conductivity, density, heat capacity, refractive index and the absorption coefficient as well as upon the absolute temperature of the measurement.

For one particular experimental installation, the number of instrumental variables which need to be considered is reduced to just the heat flux and the time range employed. In practice, for any particular liquid, measurements along an isotherm as a function of density are generally carried out at a constant heat flux and in the same range of times so that calculations of β need only be performed to account for the varying physical properties of the fluid along each isotherm. Furthermore, because there is very little information available concerning the refractive indices and absorption coefficients of liquids except under ambient conditions the only recourse is to maintain these values constant. Thus the best that can be done at present is to compute the ratio β for each liquid to be studied at each isotherm as a function of thermal conductivity or equivalently density. If the calculations are restricted to the minimum set of those at the extremes of the density range along each isotherm for each liquid this procedure reduces the computational effort required considerably and brings it within practical bounds.

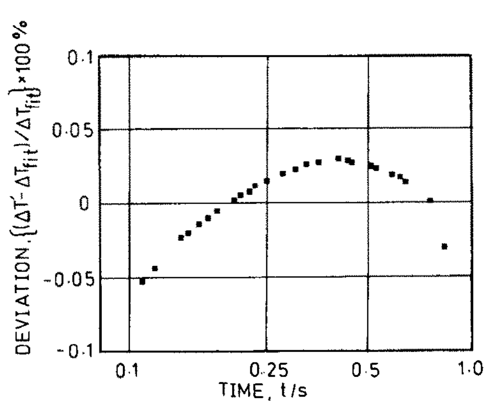

Fig. 6. Deviations of the temperature rise $\Delta T'$ obtained by simulation of a measurement in n-heptane at 348 K from the best fit straight line.

Figure 7 displays the fraction $\Delta\lambda/\lambda$ of the ratio β for n-heptane, n-nonane and n-undecane corresponding to the measurements carried out by Menashe and Wakeham [7, 12] along isotherms as a function of thermal conductivity, over a range corresponding to the pressure range 50–500 MPa. The effect of radiation is therefore to make the apparent thermal conductivity of the fluid as much as 2.5% greater than the true value for n-undecane at 348 K, whereas for n-heptane at the lowest temperatures and highest densities (highest thermal conductivity) the effect is only about 1%. The change of the effect with density is a result, primarily of the change in thermal conductivity, which is the reason for this choice of independent variable in the presentation of the data. The plots presented in Fig. 7 allow thermal conductivity data for the liquids considered to be corrected for the effects of radiation over the entire density range covered in the measurements of Menashe and Wakeham [7, 12].

Under otherwise identical conditions, it has been found that the fractional correction, $\Delta\lambda/\lambda$ is approximately proportional to the cube of the equilibrium temperature,

$$\Delta\lambda/\lambda \propto T_0^3$$

and is approximately linear in the absorption coefficient K,

$$\Delta\lambda/\lambda \propto K.$$

These observations may allow modest extrapolations of the results presented here to other temperatures and other liquids. Nevertheless, it is preferable to treat each new liquid and each new temperature afresh.

The uncertainty in the ratio $\Delta\lambda/\lambda$ is thought to arise mainly from the lack of accurate thermophysical and optical properties of the liquids under all conditions. Although the mathematical model of the radiation process and its numerical solution introduce further uncertainties, these are thought to be small. The overall error in $\Delta\lambda/\lambda$ is estimated to be no more than $\pm 20\%$ for the liquids studied here. Because the correction applied to deduce radiation-free thermal conductivities amounts to 2.5% at most, the residual error in the reported thermal conductivity data after correction which can be attributed to this cause, is one of $\pm 0.5\%$.

6. CONCLUSIONS

It has been shown that the effects of the absorption of radiation in the fluid are significant for the accurate measurement of the thermal conductivity of liquids by the transient hot-wire technique. On the one hand, the calculations presented in the paper show that a systematic error of as much as 2.5% can be incurred in the measurements if radiation effects are neglected entirely. On the other hand, the same calculations make it possible to apply a correction so that radiation-free thermal conductivities may be derived. Although the corrections derived here are specific to the liquids considered, the method for their calculation is general. If more accurate data on the optical properties of fluids became available over a range of thermodynamic states, it would be possible to perform more accurate estimates of the correction and hence improve the accuracy of thermal conductivity data for liquids. The effects of radiation become more pronounced for stronger absorbing liquids at least in the range studied. Therefore, it would seem, on the basis of the present calculations, that any liquid adopted as a standard for thermal conductivity should be as weakly absorbing as possible, and that the standard temperature of reference should be low.

REFERENCES

1. J. J. Healy, J. J. de Groot and J. Kestin, The theory of the transient hot-wire method for measuring thermal conductivity, *Physica* **82C**, 392–408 (1976).
2. J. Kestin and W. A. Wakeham. A contribution to the theory of the transient hot-wire technique for thermal conductivity measurements, *Physica* **92A**, 102–116 (1978).
3. H. E. Khalifa, J. Kestin and W. A. Wakeham. The theory of the transient hot-wire cell for measuring the thermal conductivity of gaseous mixtures, *Physica* **97A**, 273–286 (1979).
4. A. A. Clifford, J. Kestin and W. A. Wakeham. A further contribution to the theory of the transient hot-wire technique for thermal conductivity measurements, *Physica* **100A**, 370–374 (1980).
5. J. J. de Groot, J. Kestin and H. Sookiazian. Instrument to measure the thermal conductivity of gases, *Physica* **75**, 454–482 (1974).
6. M. J. Assael, M. Dix, A Lucas and W. A. Wakeham. An absolute determination of the thermal conductivity of the noble gases and two of their binary mixtures, *J. Chem. Soc., Faraday Trans. I* **77**, 439–464 (1981).
7. J. Menashe and W. A. Wakeham, Absolute measurements of the thermal conductivity of liquids at pressure up to 500 MPa, *Ber. Bunsenges. Phys. Chem.* **85**, 340–347 (1981).

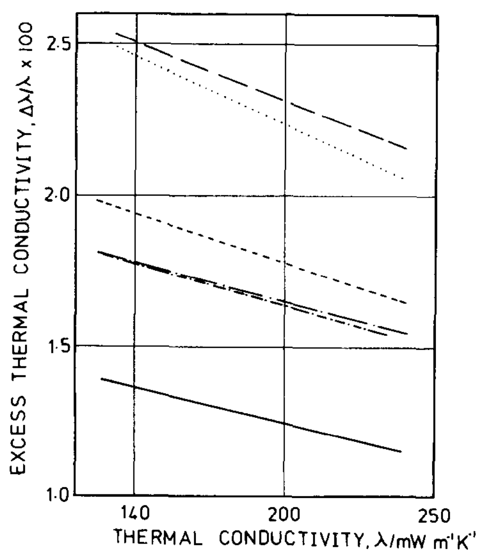

FIG. 7. The fraction $\Delta\lambda/\lambda$ for thermal conductivity measurements in n-heptane, n-nonane and n-undecane. n-heptane —— 308 K, - - - 348 K; n-nonane – · – · – 308 K, · · · · 348 K; n-undecane — · — · 308 K, — — 348 K.

8. C. A. Nieto de Castro, J. C. G. Calado, M. Dix and W. A. Wakeham. An apparatus to measure the thermal conductivity of liquids, *J. Phys. E: Sci. Instrum.* **9,** 1073–1080 (1976).
9. A. A. Clifford, J. Kestin and W. A. Wakeham. Thermal conductivity of N_2, CH_4 and CO_2 at room temperature and at pressures up to 35 MPa, *Physica* **97A,** 287–295 (1979).
10. M. J. Assael and W. A. Wakeham. The thermal conductivity of mixtures of hydrogen in the monatomic gases, *Ber. Bunsenges. Phys. Chem.* **84,** 840–848 (1980).
11. C. A. Nieto de Castro, J. C. G. Calado and W. A. Wakeham. Absolute measurements of the thermal conductivity of liquids using a transient hot-wire technique, *Proc. 7th Symposium on Thermophysical Properties,* pp. 730–738. A.S.M.E. (New York) (1978).
12. J. Menashe and W. A. Wakeham. The thermal conducitivity of *n*-nonane and *n*-undecane at pressures up to 500 MPa (to be published).
13. J. Kestin, R. Paul, A. A. Clifford and W. A. Wakeham. Absolute determination of the thermal conductivity of the noble gases at room temperature and up to 35 MPa, *Physica* **100A,** 349–362 (1980).
14. C. A. Nieto de Castro, J. C. G. Calado and W. A. Wakeham. Thermal conductivity of organic liquids using a transient hot-wire technique, *High Temp., High Press.* **11,** 551–559 (1979).
15. A. Michels, J. V. Sengers and P. S. Van der Gulik. The thermal conductivity of carbon dioxide in the critical region. I. The thermal conductivity apparatus, *Physica* **28,** 1201–1215 (1962).
16. D. T. Jamieson, J. B. Irving and J. S. Tudhope. Liquid thermal conductivity: A data survey to 1973, H.M.S.O., (Edinburgh) (1973).
17. R. Viskanta and R. J. Grosh. Heat transfer by simultaneous conduction and radiation in an absorbing medium, *Trans. ASME, J. Heat Transfer* **84C,** 63–72 (1963).
18. W. Leidenfrost. An attempt to measure the thermal conductivity of liquids, gases and vapors with a high degree of accuracy over wide ranges of temperature (– 180 to 500°C) and pressures (vacuum to 500 atm), *Int. J. Heat Mass Transfer* **7,** 447–478 (1964).
19. W. Fritz and H. Poltz. Absolutbestimmung der Wärmeleitfähigkeit von Flüssigkeiten—I, Kritische Versuche an einer neuen Plattenapparatus, *Int. J. Heat Mass Transfer* **3,** 307–316 (1962).
20. S. Rosseland. *Astrophysik und Atomtheoretische Grundlage,* pp. 41–44. Springer, Berlin (1931).
21. E. F. M. Van der Held. The contribution of radiation to the conduction of heat, *Appl. Sci. Res.* **3A,** 237–249 (1952).
22. A. Saito, N. Mani and J. E. S. Venart. Combined transient conduction/radiation effects with the line source technique of measuring thermal conductivity, *Proc. 16th National Heat Transfer Conf.,* 76-CSME/CSChE-6 (1976).
23. A. Saito and J. E. S. Venart. Radiation effects with the transient line source measurement of thermal conductivity, *Proc. 6th Int. Heat Transfer Conf.,* **3,** 79–84, (1978).
24. H. C. Hottel and A. F. Sarofim. *Radiative Transfer.* McGraw-Hill, New York (1967).
25. M. Abramowitz and I. A. Stegun (eds.). *Handbook of Mathematical Functions.* N.B.S. (1964).
26. O. A. Liskovets. The Method of Lines (English translation), *J. Diff. Eqs.* **1,** 1308–24 (1965).
27. C. W. Gear. The automatic integration of ordinary differential equations, *Comm. A.C.M.,* **14,** 176–180, 185–190 (1971).
28. A. C. Hindmarsh. Gear: Ordinary differential equation system solver, Lawrence Livermore Laboratory Report, UCID-30001, Rev. 2, (1972).
29. H. Akima. A new method of interpolation and smooth curve fitting based on local procedures, *J. Assoc. Comput. Mach.* **17,** 589–602 (1970).
30. J. Menashe. Accurate measurements of the thermal conductivity liquids. Ph.D. thesis, Imperial College, London (1981).

APPENDIX

The transformation of coordinates

Integrals of the form

$$I = \iint_V \int f(r, \theta, \phi)\,\mathrm{d}V \qquad \text{(A1)}$$

must be evaluated to determine the radiative contribution to the heat flux in the energy equation. Here (r, θ, ϕ) are the spherical polar coordinates of a point P_j with reference to point P_i of Fig. 2. In terms of the cylindrical polar coordinates (r_j, ψ_j, z_j) of the same figure, the integral may be written

$$I = \iint_V \int r^2 \bar{f}(r_j, \Phi, Z) \sin\theta \frac{\partial(r, \theta, \phi)}{\partial(r_j, \Phi, z)} \mathrm{d}r_j \mathrm{d}\Phi \mathrm{d}Z \qquad \text{(A2)}$$

where

$$\Phi = \psi_j - \psi_i \quad \text{and} \quad Z = z_j - z_i. \qquad \text{(A3)}$$

Straightforward trigonometry applied to Fig. 2 leads to the results that

$$\begin{aligned} r &= [r_j^2 + r_i^2 - 2r_i r_j \cos\Phi + Z^2]^{1/2} \\ \cos\theta &= [r_j \cos\Phi - r_i]/r \\ \sin\phi &= Z/[r_j^2 \sin^2\Phi + Z^2]^{1/2} \end{aligned} \qquad \text{(A4)}$$

Evaluation of the Jacobian in equation (A2) then yields

$$\frac{\partial(r, \theta, \phi)}{\partial(r_j, \Phi, Z)} = r_j/[(r_j^2 + r_i^2 - 2r_i r_j \cos\Phi + Z^2) \times (r_j^2 \sin^2\Phi + Z^2)]^{1/2} \qquad \text{(A5)}$$

so that

$$I = \iiint \bar{f}(r_j, \Phi, Z)\, r_j \mathrm{d}r_j \mathrm{d}\Phi \mathrm{d}Z. \qquad \text{(A6)}$$

EFFET DE L'ABSORPTION DU RAYONNEMENT SUR LA CONDUCTIVITE THERMIQUE MESURES PAR LA METHODE TRANSITOIRE DU FIL CHAUD

Résumé—On analyse les effets de l'absorption du rayonnement par les fluides pendant la mesure de leur conductivité thermique par la méthode du fil chaud en transitoire. L'équation intégro-différentielle qui gouverne la conduction associée au rayonnement dans une cellule à fil chaud est simplifiée au moyen d'un petit nombre d'hypothèses raisonnables physiquement et elle est résolue numériquement. La solution numérique est employée pour déduire l'effet de l'absorption du rayonnement sur l'élévation de température du fil pour trois alkanes normaux. L'absorption produit des modifications dans l'élévation de température qui sont comparables à la limite de précision de sa mesure et n'est donc pas discernable directement. Néanmoins la contribution du transport radiatif au chauffage transitoire montre que la conductivité thermique déterminée par de telles méthodes est systématiquement frappée d'une erreur de l'ordre de 2,5% à 75°C. Une procédure de correction de la conductivité est décrite et la facteur est donné pour *n*-heptane, *n*-nonen et *n*-undécane, dans le domaine de température 35–75°C et pour des pressions allant de 0,1 à 500 MPa.

EINFLUSS DER WÄRMESTRAHLUNG AUF DIE MESSUNG DER WÄRMELEITFÄHIGKEIT MIT DER INSTATIONÄREN HITZDRAHTMETHODE

Zusammenfassung—Es wurde der Einfluß der Strahlungsabsorption in Flüssigkeiten bei der Bestimmung ihrer Wärmeleitfähigkeit mit Hilfe der instationären Hitzdrahtmethode berechnet. Die vollständige partielle Integral-Differential-Gleichung, welche den gleichzeitigen Wärmetransport durch Leitung und Strahlung für das instationäre Verhalten einer Hitzdrahtzelle beschreibt, wurde unter physikalisch vernünftigen Annahmen numerisch gelöst. Aus der numerischen Lösung wurde der Einfluß der absorbierten Strahlung auf das Ansteigen der Drahttemperatur bei Messungen an drei Normal-Alkanen abgeleitet. Die durch die Strahlungsabsorption hervorgerufene Änderung des Anstiegs der Drahttemperatur ist vergleichbar mit der bestmöglichen Auflösegenauigkeit der Messung und deshalb nicht direkt feststellbar. Nichtsdestoweniger bedeutet das Vorhandensein des Strahlungsaustausches für die nach dieser Meßmethode bestimmten Wärmeleitfähigkeiten einen systematischen Fehler von z.B. 2,5% bei 75°C. Es wird ein Verfahren zur Korrektur der Wärmeleitfähigkeiten, welches die Strahlung berücksichtigt, beschrieben. Die Korrekturfaktoren für *n*-Heptan, *n*-Nonan und *n*-Undecan, gültig für einen Temperaturbereich von 35–75°C und Drücke von 0,1–500 MPa, werden angegeben.

ВЛИЯНИЕ ПОГЛОЩЕНИЯ ИЗЛУЧЕНИЯ НА РЕЗУЛЬТАТЫ ИЗМЕРЕНИЙ ТЕПЛОПРОВОДНОСТИ НЕСТАЦИОНАРНЫМ МЕТОДОМ НАГРЕТОЙ НИТИ

Аннотация — Представлен анализ влияния поглощения излучения в жидкостях на результаты измерений их теплопроводности нестационарным методом нагретой нити. Полное интегро-дифференциальное уравнение в частных производных, описывающее одновременно протекающие процессы теплопроводности и излучения в выделенном объеме жидкости с нестационарно нагретой нитью, приведено к более простому виду с помощью нескольких физически обоснованных допущений и решено численно. Численное решение использовалось для того, чтобы определить влияние поглощения излучения на рост температуры нити при измерениях теплопроводности трех нормальных алканов. Показано, что изменение в росте температуры за счет влияния поглощения сравнимы с наилучшей разрешающей способностью измерений, а поэтому трудноразличимы. Тем не менее, из-за влияния лучистого переноса на нестационарный процесс нагрева систематически получаются неточные значения теплопроводности. Так, при 75°C погрешность составляет 2,5%. Предложен метод, с помощью которого можно уточнить данные по теплопроводности за счет учета влияния излучения, и дан поправочный коэффициент для н-гептана, н-нонана и н-индекана для диапазона температур от 35 до 75°C и давлений от 0,1 до 500 МПа.