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DETERMINATION OF THE THERMAL CONDUCTIVITY OF TOLUENE—A PROPOSED DATA STANDARD—FROM 180 TO 400K UNDER SATURATION PRESSURE BY THE TRANSIENT HOT-WIRE METHOD

I. THE THEORY OF THE TECHNIQUE

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CONTENTS

The theory of the hot wire method of fluid thermal conductivity measurement is reviewed in detail and extended where necessary for application to an experimental system. Particular attention is given to assessing the size of approximations introduced in setting up the mathematical model of the cell which relates the observed quantities to the fluid thermal conductivity.

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1. Introduction

Data on the thermal conductivity of fluids are rather scarce in comparison with the data available on many other of their important physical properties, and in addition agreement between reported results has often been poor. The scatter in the data on a number of common fluids extends over 10 or 20 % (Powell, Ho & Liley 1966) and agreement within a few per cent must be regarded as indicative of careful work. A need is apparent for more high-precision data, over the widest possible ranges of temperature and pressure to help in establishing standards for thermal conductivity measurements. The same need is apparent in the heat transfer problems which occur under the increasingly extreme temperatures and pressures encountered in modern technology.

In a previous paper (Horrocks & McLaughlin 1963) it appeared that the transient line source technique for thermal conductivity measurement was intrinsically capable of accuracies comparable to those of the best steady-state methods. The technique consists in recording the temperature rise of a fine, steadily heated vertical wire immersed in the test fluid. The hot wire acts both as an electrical heating element and a resistance thermometer, and end effects are avoided by monitoring the central part of the wire via potential leads. The limiting factor in the precision of the measurement has formerly been the difficulty of recording the transient voltages sufficiently accurately. This can now be overcome by using high-speed digital data logging equipment, and the way is open for the exploitation of a number of features of the technique which make it particularly useful in helping to meet the need for data outlined above.

The hot-wire method has the important feature in use on dense fluids, of a small-volume, low-diameter cell making it particularly suitable for work at low temperatures or high pressures with the additional advantage that only four electrical connexions have to be brought out of the cell. The geometrical requirements of the cell are simple, leading to ease of construction and immunity from distortion under extremes of pressure or temperature. Furthermore, the geometrical factor of the cell consists simply of a single length, which is more easily obtained to a high accuracy than the geometrical factors of steady state cells.

The most serious sources of error in fluid thermal conductivity measurements are generally heat transfer by radiation and convection. In the steady-state technique these effects can be eliminated or shown to be negligible by repeated determinations in which the temperature drop across the fluid layer, or the layer thickness is varied. The present technique provides direct information about the presence, or absence, of these effects from a single measurement lasting a few seconds, and evidence is presented in part II which suggests that errors arising from radiation and convection can be successfully eliminated from individual determinations.

In the most carefully designed and operated cell it is inevitable that some of the measured power input will be lost along stray conduction paths such as metal components, ceramic spacers and others, rather than pass through the test layer. Ziebland (1969) compared typical guarded flat-plate, concentric cylinder and steady state hot-wire cells with regard to their susceptibility to error from this source. He concluded that the errors were by far the smallest in the hot-wire cell. It should be expected therefore that the transient version would be even less affected because of the fine wires and larger cell:wire diameter ratios used.

Measurements by the present technique are shown below to be unaffected by a constant thermal resistance at the surface between the hot wire and the fluid. Thus the temperature jump which would occur in measurements on dilute gases has no effect, and the influence of surface films or small gas bubbles on the hot wire is minimised. This contrasts with the steady-state methods

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where corrections must be applied for interfacial temperature jump in gases and where, because of the very small surface area of the wire, films of adherring gas bubbles can have a serious effect in measurement on liquids. The advantage of the transient hot-wire method for measurements on mixtures should also be mentioned, as the short duration of the measurement minimises the development of concentration gradients by thermal diffusion. A final decisive argument for further development of the transient hot-wire method is that it provides data obtained under conditions fundamentally different from those of the steady state methods. Agreement between data obtained by different methods provides valuable confirmation of the reliability of the techniques.

Part I of this work reviews and extends the theory of the transient hot-wire cell, establishes design criteria to minimise experimental error and provides means of correcting for the residual errors.

2. Notation

A	rate of absorption of radiant energy per unit volume
a	wire radius
b	radius of the cell walls
b^*	b/a
C_p, $C_{p\mathrm{w}}$	fluid, wire specific heats at constant pressure
C_v	fluid specific heat at constant volume
d	fluid layer thickness in a steady state thermal conductivity measurement
E	rate of emission of radiant energy per unit volume
Ei	exponential integral, $-\mathrm{Ei}(-x) = \int_x^\infty (\mathrm{e}^{-u}/u)\,\mathrm{d}u$
f	accommodation coefficient
g	acceleration of gravity
h	heat transfer coefficient; wire to fluid
h_s	surface heat transfer coefficient in the case of interfacial thermal resistance
H	truncation error after the first term of the series, equation (3.36)
I	current
J_0, J_1	Bessel functions of the first kind of order zero and one
L	length of active section of the hot wire
L'	total length of the hot wire
M	$(2h/\lambda_\mathrm{W} a)^{\frac{1}{2}}$
Pr	Prandtl number
P	thermodynamic pressure
P^*	$4\pi\eta\kappa z\lambda/\rho a^4 g\alpha q$ a reduced form of the penetration distance
P_V	vapour pressure
q	resistive energy dissipation rate per unit length in the hot wire, or power of a line source of heat
q_i	energy per unit length of an instantaneous line source
q_R	radiant energy flux per unit time and length from the hot wire
Q	conduction heat flux per unit area and time
r	radius
r^*	r/a

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R	active cell resistance
R'	total cell resistance
R_L	load resistance
S	increase of rate of radiant energy emission per unit volume by the fluid above the value at the start of a run
s	$r^2/\kappa t$
t	time
t^*	$\kappa t/a^2$
T	temperature rise of the hot wire
T_A	absolute temperature
T_h	wire temperature rise with allowance for interfacial thermal resistance
T_i	temperature rise due to an instantaneous line source of heat
T_q	wire temperature rise with allowance for time dependent power dissipation
T_R	temperature in the conduction equation containing a heat sink term approximating the effect of radiant emission
T_T	temperature in the conduction equation allowing for temperature dependent fluid properties
T_w	temperature within the hot wire
T_0	temperature predicted by the line source solution
U	internal energy
u	dummy variable
V	voltage
v^*	$4\pi\eta\lambda v_z/\rho a^2 g\alpha q$, a reduced velocity
$\boldsymbol{v}$	fluid velocity
v_z	fluid velocity in the z (axial direction)
Y_0, Y_1	Bessel function of the second kind of order 0 and 1
x	distance normal to a plane surface
α	$-\rho^{-1}(\partial\rho/\partial T)_p$
β	$\rho^{-1}(\partial\rho/\partial P)_T$
γ	Euler's constant, 0.577…
γ'	$\exp\gamma$
δT	a temperature increment
δT_s	interfacial temperature jump
ϵ	emissivity
η	absolute viscosity
θ	absorption coefficient
κ	thermal diffusivity
λ	fluid thermal conductivity
λ_w	thermal conductivity of the wire
Λ	mean free path
ρ	fluid density
ρ_w	density of the wire
σ	Stefan–Boltzmann constant
σ_T	Thompson coefficient
τ	stress tensor

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ϕ $\mathrm{d}(\rho C_p)/\mathrm{d}T$
χ $\mathrm{d}\lambda/\mathrm{d}T$
ω $2\rho C_p/\rho_{\mathrm{w}} C_{p\mathrm{w}}$

3. Mathematical modelling of the cell

3.1. *The line source solution*

The simplest mathematical description of the non-steady-state hot-wire cell is provided by the line-source solution of the conduction equation

$$\rho C_p \frac{\partial T}{\partial t} = \lambda\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right). \tag{3.1}$$

In this solution the medium is considered to be unbounded, isotropic, and have temperature independent properties and be initially at a uniform temperature. At zero time a line source of heat, of infinite length and with uniform power q per unit length originates at $r = 0$. The temperature at time t referred to the initial value, is (Carslaw & Jaeger 1959*a*)

$$T_0(r, t) = -\frac{q}{4\pi\lambda}\left[\mathrm{Ei}\left(\frac{-r^2}{4\kappa t}\right)\right]. \tag{3.2}$$

Now since (Abramowitz & Stegun 1956)

$$\begin{aligned} -\mathrm{Ei}(-x) &= \int_x^\infty \frac{\mathrm{e}^{-u}}{u}\,\mathrm{d}u \\ &= -\gamma - \ln x - \sum_{n=1}^{\infty} \frac{(-1)^n x^n}{n\,n!} \quad (|\arg x| < \pi), \end{aligned} \tag{3.3}$$

then taking the expansion to the second term of the summation, equation (3.2) becomes

$$\begin{aligned} T_0(r, t) &= \frac{q}{4\pi\lambda}\left[\ln\frac{4\kappa t}{r^2} - \gamma + \frac{r^2}{4\kappa t} - \ldots\right] \\ &= \frac{q}{4\pi\lambda}\left[\ln t + \ln\frac{4\kappa}{r^2\gamma'} + \frac{r^2}{4\kappa t} + \ldots\right], \end{aligned} \tag{3.4}$$

where $\gamma' = \exp\gamma$. The hot-wire temperature is obtained by substituting $r = a$, and, provided that $a^2/4\kappa t$ is sufficiently small in the range t_1 to t_2, we may write

$$T_0(a, t_2) - T_0(a, t_1) \simeq \frac{q}{4\pi\lambda}\ln\frac{t_2}{t_1}. \tag{3.5}$$

A first estimate of the conductivity can therefore be obtained from the slope of the hot-wire temperature plotted against ln (time), provided that q is known. In practice, the truncation errors are negligible only if terms to $\frac{1}{4}x^2$ are included in (3.4). In the present work the hot wire has a nominal diameter of one-thousandth of an inch, so that for a liquid such as toluene $a^2/4\kappa t$ is of order 10^{-2} when t equals 1 s and a typical measurement lasts about 10 s. In measurements on gases under normal conditions $a^2/4\kappa t$ would be of order 10^{-5} at 1 s. The use of equation (3.5), however, involves a large number of approximations in addition to truncation errors, and these are conveniently examined under two headings. Those involved in reducing the full energy conservation equation to equation (3.1) will be called set I, and the idealizations leading to the line-source solution set II. The experimental conditions can be chosen so that none of these

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approximations is important and the errors resulting from them can be examined one by one. This is done in the following sections with particular reference to the present measurements on liquids, but discussion of measurements on gases is also included.

3.2. *Set I approximations*

(*a*) *The conservation equations*

The fluid in the cell is, in reality, viscous, isotropic and compressible with temperature dependent specific heat, density and thermal conductivity. In addition it absorbs and emits thermal radiation and is also subject to free convection. The conservation equations are therefore:

$$\mathrm{D}\rho/\mathrm{D}t = \rho(\nabla\,.\,\boldsymbol{v}), \tag{3.6}$$

$$\rho\,\mathrm{D}\boldsymbol{v}/\mathrm{D}t = \nabla P - (\nabla\,.\,\tau) + \rho\boldsymbol{g}, \tag{3.7}$$

$$\rho\,\mathrm{D}U/\mathrm{D}t = \nabla\,.\,\boldsymbol{Q} - P\nabla\,.\,\boldsymbol{v} - \tau\!:\!\nabla\boldsymbol{v} + A - E. \tag{3.8}$$

To obtain an expression relating temperature to time, DU/Dt is written as

$$\frac{\mathrm{D}U}{\mathrm{D}t} = -\frac{1}{\rho^2}\left[-P + T\left(\frac{\partial P}{\partial T}\right)_\rho\right]\frac{\mathrm{D}\rho}{\mathrm{D}t} + C_v\frac{\mathrm{D}T}{\mathrm{D}t} \tag{3.9}$$

by virture of the thermodynamic equation

$$\mathrm{d}U = \left[-P + T\left(\frac{\partial P}{\partial T}\right)_\rho\right]\frac{\mathrm{d}\rho}{\rho^2} + C_v\,\mathrm{d}T. \tag{3.10}$$

By substituting (3.9) in (3.8) and cancelling terms by means of (3.6) we obtain

$$\rho C_v\frac{\mathrm{D}T}{\mathrm{D}t} - T\left(\frac{\alpha}{\beta}\right)\left[-\alpha + \beta\frac{\mathrm{D}P}{\mathrm{D}T}\right]\frac{\mathrm{D}T}{\mathrm{D}t} = -\nabla\,.\,\boldsymbol{Q} + \Phi + A - E, \tag{3.11}$$

where use has also been made of the thermodynamic relations

$$(\partial P/\partial T)_\rho = \alpha/\beta \quad \text{and} \quad \mathrm{d}\rho/\rho = -\alpha\,\mathrm{d}T + \beta\,\mathrm{d}P.$$

$\Phi = -\tau\!:\!\nabla\boldsymbol{v}$ is the irreversible rate of internal energy increase per unit volume resulting from viscous dissipation.

(*b*) *Effective specific heats*

In the present measurements on liquids at saturation vapour pressure, two factors give rise to changes in the total pressure on a fluid element during an experiment. First, the vapour pressure will increase as the fluid is heated and, secondly, the hydrostatic pressure on the element will fall as it moves upwards in convection. The substantive derivative of pressure with respect to temperature may therefore be written as

$$\frac{\mathrm{D}P}{\mathrm{D}T} = \frac{\mathrm{d}P_\mathrm{V}}{\mathrm{d}T} + \frac{\mathrm{d}}{\mathrm{d}T}(\rho g h). \tag{3.12}$$

The value of the first term on the right-hand side can be estimated using the Clausius–Clapeyron equation and Trouton's rule. For the second, we refer to the results on convection described below, where it can be seen that in a typical experiment a liquid element rises a distance of the order of 10 cm as it is heated through one degree Kelvin. With the use of data for toluene, it can

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be shown that DP/DT is $(O)\ 10^3\,\mathrm{N\,m^{-2}\,K^{-1}}$ and hence $\beta DP/DT$ is $(O)\ 10^{-6}\,\mathrm{K^{-1}}$, whereas α is $(O)\ 10^{-3}\,\mathrm{K^{-1}}$. In the present work therefore

$$\beta DP/DT \ll \alpha$$

and (3.11) may be reduced to

$$\rho C_p\,DT/Dt = -\nabla\,.\,\boldsymbol{Q} + \Phi + A - E, \tag{3.13}$$

with an error equivalent to less than 0.1 % in the specific heat.

In measurements on gases (3.13) does not hold; and although the cell forms a constant volume enclosure, it is not permissible merely to replace C_p by C_v in (3.13), since the system is not at equilibrium. This case is discussed more fully elsewhere (Pittman 1968).

(*c*) *Free convection and viscous dissipation*

In previous applications of the non-steady-state hot-wire technique it has been recognized that convection sets a limit to the duration of a measurement by eventually causing major departures from equation (3.5). Horrocks & McLaughlin (1963) and Van der Held & Van Drunen (1949) estimated the time at which this occurred by generalizing correlations of steady-state convection heat transfer. More recently Goldstein & Briggs (1964) obtained analytic expressions by solving the equation of motion during the early stages of the convection transient. Their approach relies on the fact that at points remote from the lower end of the heated wire the velocity field is virtually one-dimensional. This means that fluid rises without mixing, in shells concentric with the heat source, so that the temperature field corresponds closely to its one-dimensional, pure-conduction form. As convection develops, cool fluid rises from the lower, thick current lead, and it is clear that the conductivity measurement must end before this fluid begins to affect the temperature near the lower potential lead. Goldstein & Briggs estimated the maximum duration of a measurement by first substituting a solution to (3.1) into the buoyancy term of the equation of motion, and solving for the transient, one-dimensional velocity field. They then supposed that the front of cool liquid rose with the velocity of the fluid in the one-dimensional field above it, and that the conduction régime ended when the front had risen to the height under consideration, irrespective of radial distance of the leading edge of the front from the wire. Expressions for these so-called vertical penetration distances were obtained in the form of integrals requiring numerical integration, and in the case of the expression for a fluid of arbitrary Prandtl number the results are quite complex. For the present purposes it seemed preferable to integrate the equation of motion directly by a numerical method.

Following the approach described above, the equation of motion becomes

$$\frac{\partial^2 v_z}{\partial r^2} + \frac{1}{r}\frac{\partial v_z}{\partial r} + \frac{\alpha\rho g T}{\eta} = \frac{\rho}{\eta}\frac{\partial v_z}{\partial t}. \tag{3.14}$$

In reducing (3.7) to (3.14) the usual Boussinesq assumption has been made, namely that variable density is important only in the buoyancy term, and that the fluid may otherwise be treated as incompressible. The boundary conditions are

$$v_z = 0 \quad r = a \quad t > 0,$$

$$v_z = 0 \quad r = b \quad t > 0,$$

and T is taken as

$$T_0(r,t) = -\frac{q}{4\pi\lambda}\,\mathrm{Ei}\left(-\frac{r^2}{4\kappa t}\right), \tag{3.15}$$

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that is, the line source solution has been used to approximate the temperature field round the wire. Introducing the dimensionless variables

$$r^* = r/a, \quad t^* = \kappa t/a^2, \quad v^* = 4\pi\eta\lambda v_z/\rho a^2 g\alpha q,$$

equation (3.14) can be written

$$\frac{\partial^2 v^*}{\partial r^{*2}} + \frac{1}{r^*}\frac{\partial v^*}{\partial r^*} = \frac{1}{Pr}\frac{\partial v^*}{\partial t^*}\,\mathrm{Ei}\left(-\frac{r^{*2}}{4t^*}\right). \tag{3.16}$$

Computer solutions of this equation were obtained, by using the Crank–Nicholson method, for a wide range of parameters appropriate to measurements on liquids and gases. Reduced velocities v^* and reduced penetration distances P^* were generated as functions of r^*, t^* and Pr. The reduced penetration distance is defined as

$$P^* = \int_0^{t^*} v^*\,\mathrm{d}t^* = \frac{4\pi\eta\lambda\kappa z}{\rho a^4 g\alpha q},$$

where

$$z = \int_0^t v_z\,\mathrm{d}t.$$

Maximum values of P^* were also tabulated for a series of t^* values. Full results, together with details of the calculations and a discussion of their accuracy, are given elsewhere (Pittman 1968), but figures 1 and 2 show typical sets of values.

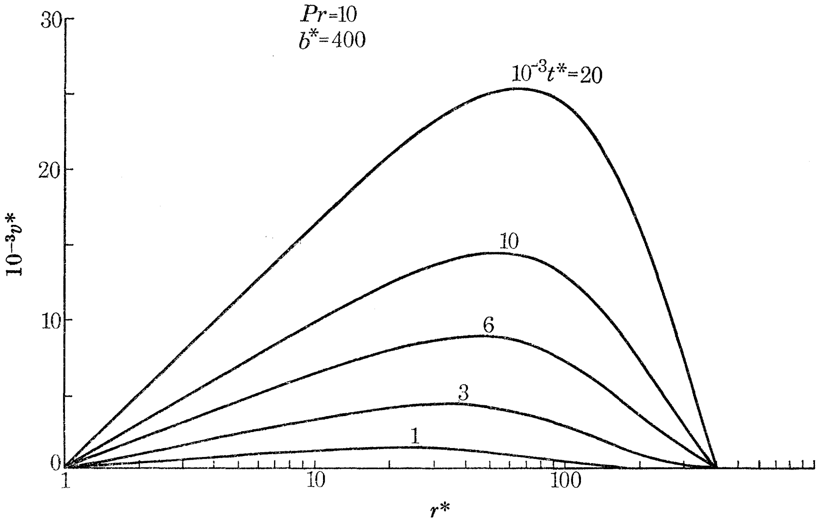

FIGURE 1. Computed velocity profiles during the initial free convection transient for a fluid in an annulus around a heated vertical cylinder.

The computed results serve two purposes. By using the appropriate heating rate and physical properties of the fluid, the maximum duration of a measurement can be estimated for any given position of the lower potential lead. The reasonableness of such estimates has been demonstrated experimentally by Dring & Gebhart (1966), and was confirmed in the present work. In addition, the data allow the importance of viscous dissipation to be examined.

For a velocity field in which the radial component is zero, we may write

$$\Phi = -(\boldsymbol{\tau}:\nabla\boldsymbol{v}) = -\tau_{rz}\left(\frac{\partial v_z}{\partial r}\right) = \eta\left(\frac{\partial v_z}{\partial r}\right)^2. \tag{3.17}$$

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Since convection is most fully developed at the end of an experiment we calculate Φ at $t = 10$ s. For toluene at 300 K, when $\eta \cong 0.27 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}$ and $Pr \cong 5$, it can be shown from the computed velocity data that $\partial v_z/\partial r$ close to a wire of radius 1.3×10^{-5} m, is about $50\,\mathrm{s^{-1}}$, and hence $\Phi \cong 0.6\,\mathrm{J\,m^{-3}\,s^{-1}}$. In the case of a dilute monatomic gas, such as argon at room temperature and pressure, when $\eta = 2 \times 10^{-5}\,\mathrm{kg\,m^{-1}\,s^{-1}}$ and $Pr \cong 2/3$, the value of $\partial v_z/\partial r$ near the wire at the end of a measurement (approximately 5 s) would be about $150\,\mathrm{s^{-1}}$, so that $\Phi \cong 0.4\,\mathrm{J\,m^{-3}\,s^{-1}}$.

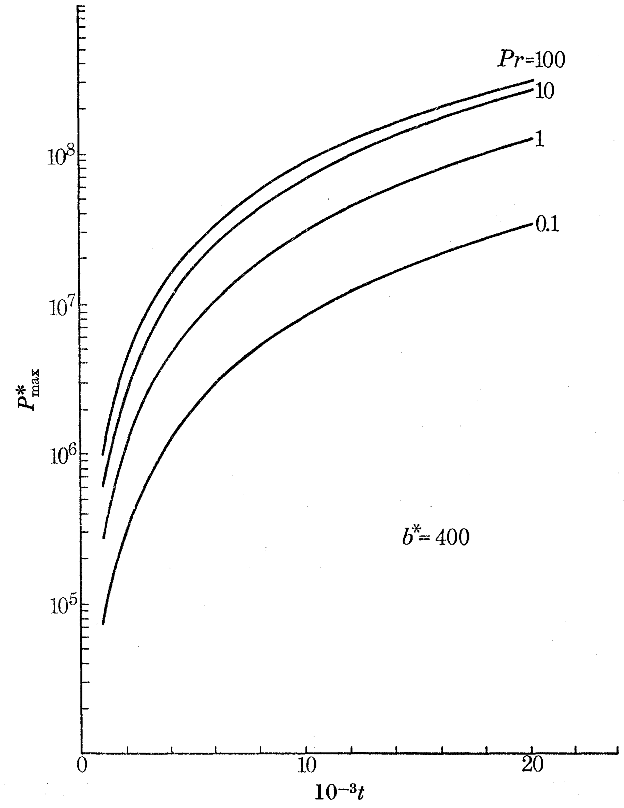

FIGURE 2. Computed maximum vertical penetration distance of fluid initially in the plane of the lower end of a heated vertical cylinder during the initial free convection transient.

These figures must be compared with the rate of heat input by conduction per unit volume of fluid, $\rho C_p(\partial T/\partial r)_{r=a}$. Differentiating (3.4) and using the physical properties of toluene at 300 K, with a typical q of $0.1\,\mathrm{J\,m^{-1}\,s^{-1}}$, we obtain a figure of about $8 \times 10^3\,\mathrm{J\,m^{-3}\,s^{-1}}$ when t is 10 s. In the argon example the heating rate q would be about $0.01\,\mathrm{J\,m^{-1}\,s^{-1}}$ and the heat input by conduction near the end of a measurement would be roughly $25\,\mathrm{J\,m^{-3}\,s^{-1}}$. It follows that in the present measurements on liquids viscous heating will not amount to more than 0.01 % of the conduction heating, and Φ may be dropped from (3.13) without significant error. However, in measurements on dilute gases, viscous heating could be as large as 2 % of the conduction heating near the wire, which might be significant in the most precise work. The effect could be largely avoided by using data from the earlier part of a run, when convection is less pronounced.

(*d*) *Radiation*

The remaining terms to be eliminated from the right-hand side of (3.13) are those allowing for the absorption and emission of thermal radiation by the fluid. Discussion of radiation in the

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non-steady-state hot-wire cell has previously neglected the effect and used the expression for radiant heat transfer through vacuum to a black enclosure (Horrocks & McLaughlin 1963)

$$q_{\mathrm{R}} = 2\pi a\sigma\epsilon[(T+T_{\mathrm{A}})^4 - T_{\mathrm{A}}^4]. \tag{3.18}$$

This is permissible where the ratio of the cell to wire diameter is large and the optical thickness of fluid in the annulus is small. These conditions are satisfied in measurements on dilute gases, but for liquids the optical thickness is not generally small. On the assumption of a value of 3.5 mm^{-1} for the absorption coefficient of toluene (Poltz 1965) averaged over the most important wavelengths at 25 °C, the optical thickness along the radius of the present cell (0.5 cm) is 17.5. The use of (3.18) is therefore not valid nor can it be taken to give a high estimate of the effect, since the radiant flux can be many times larger in an absorbing medium than in a transparent one within an identical enclosure.

Leidenfrost (1964) and Poltz (1965) have derived expressions estimating the radiative contribution to the apparent conductivity obtained in steady-state measurements. Poltz & Jugel (1967) substantially confirmed predictions by experiment, and showed that the contribution for toluene could be as large as 5 %, depending on the fluid layer thickness. He suggested that effects of similar size could be present in conductivity measurements by other techniques.

An expression for the effect of radiant heat transfer in the present technique is not available, and indeed the derivation of one seems intractable, but the following simplified treatment indicates the qualitative effects. The central difficulty in this problem of linked conduction and radiation is removed if we neglect reabsorption of all radiation emitted in excess of that emitted at the initial uniform temperature of the experiment. This, of course, results in a gross overestimate of the radiation effect, but the assumption will hold best in the early moments of a run, when the optical thickness of the layer of warmer fluid is small. Radiation can now be regarded as introducing a heat sink term into the conduction equation (3.1). Thus

$$\frac{1}{\kappa}\frac{\partial T_{\mathrm{R}}}{\partial t} = \frac{\partial^2 T_{\mathrm{R}}}{\partial r^2} + \frac{1}{r}\frac{\partial T_{\mathrm{R}}}{\partial r} - \frac{S}{\lambda}, \tag{3.19}$$

where S is the increase in radiant emission per unit volume above the initial value in the experiment. Equation (3.19) is to be compared with (3.1) and $(T - T_{\mathrm{R}})$ is the temperature reduction caused by radiation from the idealized pure-conduction value. We expect this quantity to be only a few parts per hundred, so equation (3.19) may be rewritten:

$$\frac{1}{\kappa}\frac{\partial T_{\mathrm{R}}}{\partial t} \cong \frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} - \frac{S}{\lambda}. \tag{3.20}$$

The effect of radiant heat transfer on the apparent conductivity is therefore measured by

$$\left(\frac{\partial T}{\partial t} - \frac{\partial T_{\mathrm{R}}}{\partial t}\right)\Big/\frac{\partial T}{\partial t} \cong \left(\frac{S}{\lambda\kappa}\right)\Big/\frac{\partial T}{\partial t}, \tag{3.21}$$

from (3.1) and (3.20). Now, for small temperature increases, S will be approximately proportional to T, and so will increase from zero with time. $\partial T/\partial t$, on the other hand, is large in the early part of an experiment and falls with time. The radiative contribution to the apparent conductivity is therefore least in the early part of the measurement. The use of very short experiments is not satisfactory however because of the low precision of the results, and the following procedure is therefore used in the present work. The apparent conductivity at a time t is defined as the value calculated from the first t seconds of a measurement on the assumption of pure

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conduction. These apparent conductivities are plotted against t and extrapolated back to $t = 0$ to give a 'radiation-free' value. In strongly absorbing fluids the radiative contribution will rise very early in a run to a constant value, which may be expressed by the radiation diffusion approximation (Rosseland 1937), and the procedure described above would not be expected to eliminate it. This is analogous to the presence of a radiative component in the conductivities of such substances determined by steady-state methods, using even the thinnest practicable fluid layers.

(*e*) *Reduction to the simple conduction equation*

Equation (3.13) may now be reduced to

$$\rho C_p \, \mathrm{D}T/\mathrm{D}t = -\nabla \cdot \boldsymbol{Q}. \tag{3.22}$$

It has been seen that an experiment is restricted to the period in which the fluid next to the active section of the hot wire convects in concentric shells, without mixing and without longitudinal temperature gradients. It has been shown above that the movement of a fluid element has no appreciable effect on its heating rate, and the substantive derivative may therefore be replaced by a partial derivative referring to conditions at a fixed point:

$$\rho C_p \, \partial T/\partial t = -\nabla \cdot \boldsymbol{Q}. \tag{3.23}$$

Introducing the definition of the coefficient of thermal conductivity by Fourier's law

$$\boldsymbol{Q} = -\lambda \nabla T, \tag{3.24}$$

we have therefore

$$\rho C_p \, \partial T/\partial t = \nabla \cdot (\lambda \nabla T). \tag{3.25}$$

If λ is assumed to be temperature independent and if no axial temperature gradients exist, then (3.1) is finally obtained.

3.3. *Set II approximations*

(*a*) *Temperature dependent fluid properties*

The line-source solution, (3.12), takes both λ and ρC_p to be temperature independent, and the approximation involved in this is now examined.

If we assume, over the temperature range of an experiment, a linear dependence on temperature

$$C(T) = (1+\phi T)\, C(0), \quad \lambda(T) = (1+\chi T)\, \lambda(0), \tag{3.26}$$

where $C = \rho C_p$ and ϕ and χ are constants, the conduction equation becomes†

$$C(0)\,(1+\phi T_{\mathrm{T}}) \frac{\partial T_{\mathrm{T}}}{\partial t} = \lambda(0)\,(1+\chi T_{\mathrm{T}}) \nabla^2 T_{\mathrm{T}} + \chi \left(\frac{\partial T_{\mathrm{T}}}{\partial r}\right)^2. \tag{3.27}$$

T_{T} is to be compared with T obtained from a solution of equation (3.1). Now T can be expressed as a function of $\kappa t/r^2$ and so of $s = r^2/\kappa t$, thus (3.1) may be written:

$$T'' + \frac{1}{S} T' + T' = 0. \tag{3.28}$$

Primes in the present subsection denote differentiation with respect to s. If further we let

$$T_{\mathrm{T}} = T + \delta T,$$

and T_{T} is also a function of s, then (3.27) can be written

$$\delta T'' + \frac{1}{S} \delta T' + \delta T' = \chi \left[T_{\mathrm{T}}'^2 + T T_{\mathrm{T}}'' + \frac{T_{\mathrm{T}} T'}{S} \right] - \phi T_{\mathrm{T}} T', \tag{3.29}$$

---

† The authors are indebted to Dr A. Fonda, Department of Mathematics, Imperial College, for the solution to this equation.

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which can be rearranged to

$$\delta T''+\frac{1}{S}\delta T'+\delta T' \simeq -\chi\left(T'^2+TT''+\frac{TT'}{S}\right)-\phi TT', \tag{3.30}$$

provided $\delta T \ll T$. If (3.28) is multiplied through by $\delta T'$ and the result subtracted from (3.30) multiplied through by T', the result can be rewritten

$$\frac{\partial}{\partial S}\left(\frac{\delta T'}{T'}\right) = T(\chi-\phi)-\chi T', \tag{3.31}$$

after substituting for T'' in the right-hand side from (3.28). Equation (3.31) is satisfied by

$$\delta T = \frac{\chi}{2}T^2+(\chi-\phi)\left(\frac{q}{4\pi\lambda}\right)^2\left(\mathrm{e}^{-s}\int_s^\infty \frac{\mathrm{e}^{-u}}{u}\,\mathrm{d}u-2\int_s^\infty\frac{\mathrm{e}^{-2u}}{u}\,\mathrm{d}u\right), \tag{3.32}$$

where, in the second term of the solution, T has been assumed to have the line-source value given by (3.2). The constants of integration in (3.32) are zero since $\delta T = 0$, when $\kappa t/a^2 = 0$, corresponding to $S = \infty$.

For gases at normal pressures the thermal diffusivity is of (O) $10^{-5}\,\mathrm{m^2\,s^{-1}}$, so that s is (O) 10^{-6} when $t = 5\,\mathrm{s}$ and $a \simeq 10^{-3}\,\mathrm{cm}$. In this case it is therefore sufficiently accurate to rewrite (3.32) as

$$\delta T = -\tfrac{1}{2}\chi T^2-(\chi-\phi)\,T^2/\ln 4t^*, \tag{3.33}$$

For the case of liquids, where the thermal diffusivity is (O) $10^{-7}\,\mathrm{m^2\,s^{-1}}$ the intermediate expression

$$\delta T = -\tfrac{1}{2}\chi T^2-(\chi-\phi)\,T^2\frac{(-\gamma-\ln s-\ln 4)}{(-\gamma-\ln s)^2} \tag{3.34}$$

should be used. Equation (3.34) is obtained by changing the variable in the second integral to $2u$ and using the expansion of the exponential integral given by (3.3). Calculations show that δT in a typical experiment is never greater than a fraction of a percent of T.

(*b*) *Finite wire diameter*

The error involved in assuming a heat-source of zero diameter can be estimated using a result obtained by Jaeger (1956). In the solution of (3.1) the heat-source is considered to be of diameter $2a$, and have infinite thermal conductivity. Heat is generated at a rate q per unit length in the source. The other conditions are the same as those leading to the line-source solution. The temperature rise of the heat-source is given by

$$T(a,t) = qG/\lambda \tag{3.35}$$

with
$$G = \frac{2\omega^2}{\pi^3}\int_0^\infty \frac{[1-\exp(-x^2t^*)]}{x^3\Delta(x)}\,\mathrm{d}x$$

where
$$\Delta(x) = [xJ_0(x)-\omega J_1(x)]^2+[xY_0(x)-\omega Y_1(x)]^2$$

and
$$\omega = 2\rho C_p/\rho_{\mathrm{w}}C_{p\mathrm{w}}.$$

For large t^*, (3.35) is well represented by

$$T(a,t) = \frac{q}{4\pi\lambda}\left[\ln\frac{4t^*}{\gamma'}+\frac{1}{2t^*}+\left\{\frac{\omega-2}{2\omega t^*}\ln\frac{4t^*}{\gamma'}\right\}+\dots\right], \tag{3.36}$$

which is seen to converge at large t^*, to (3.4) with r set equal to a. The error involved in truncating the series in (3.36) after three terms was determined by evaluating the quantity G to an accuracy

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of better than 0.01 % by numerical integration. The results agree with those given by Jaeger (1956) to the limit of accuracy claimed by him (three significant figures). Jaeger's values, however, do not cover the range of interest in the present work.

TABLE 1. VARIATION OF G AS A FUNCTION OF t^* AND ω

t^*	ω	G	H%
100	0.5	0.42474	−1.44
	1.0	0.42921	−0.38
	1.5	0.43066	−0.04
	2.0	0.43138	+0.12
200	0.5	0.48264	−0.70
	1.0	0.48513	−0.18
	1.5	0.48594	−0.01
	2.0	0.48635	+0.07
300	0.5	0.51593	−0.45
	1.0	0.51769	−0.11
	1.5	0.51827	−0.01
	2.0	0.51856	+0.05
400	0.5	0.53937	−0.33
	1.0	0.54075	−0.08
	1.5	0.54120	+0.01
	2.0	0.54142	+0.05
500	0.5	0.55747	−0.26
	1.0	0.55861	−0.06
	1.5	0.55898	+0.01
	2.0	0.55917	+0.02

Table 1 gives the values of G for a range of t^* and ω applicable to measurements on liquids. H is the percentage error involved in truncating (3.36) after the first term. The truncation error after the third term was found to be below 0.05 % in all the cases shown.

The quantity H may be thought of as a correction to be applied to the measured temperatures before they are fitted as a straight line against the logarithm of time to obtain the thermal conductivity. Its value at a given moment is seen to depend on t^* and ω, which in general are known only approximately, and this means that data taken at the earliest moment of an experiment, when H is largest, may have to be discarded because of unacceptable uncertainties in its value. This question is dealt with more fully in the experimental section (part II).

(*c*) *Finite conductivity wire*

Equation (3.36) shows that at large t^* the flux at the surface of the infinite conductivity heat source tends to the constant value q, as it must also do in the case of a wire of finite conductivity. Under these conditions the temperature profile in the wire is most fully developed, and is given by

$$T_{\mathrm{w}}(r) = \frac{q}{4\pi\lambda_{\mathrm{w}}}\left(\frac{a^2-r^2}{a^2}\right), \tag{3.37}$$

where $T_{\mathrm{w}}(r)$ is the temperature in the wire at a radius r, relative to the surface value. This parabolic profile contrasts with the idealized flat profile in the infinite-conductivity source. If we assume that the specific heats of the fluid and wire are the same in the real ($\lambda_{\mathrm{w}} \neq \infty$) and idealized ($\lambda_{\mathrm{w}} = \infty$) cases, then the areas below plots of the temperature profiles in the wire and fluid can, by suitable scaling of the axes, be interpreted as representing heat contents. If the heat generation is the same in both cases, then so also must be the areas at corresponding times. But, since

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the surface temperature of the wire will always be lower in the real case, we see that the idealized flat profile must intersect the real parabolic one. The maximum wire temperature error resulting from the assumption of infinite conductivity cannot, therefore, be greater than the greatest temperature difference existing in the real wire, $q/4\pi\lambda_w$. In a typical experiment on a liquid using a platinum wire, $q \cong 0.1\,\mathrm{J\,m^{-1}\,s^{-1}}$ and $\lambda_w \cong 68\,\mathrm{J\,m^{-1}\,s^{-1}}$, so $q/4\pi\lambda_w$ is $(O)\,10^{-4}\,\mathrm{K}$. The temperature rise of the hot wire in an experiment is about 0.5 K, so this upper estimate of the error comes to 0.2 %. In practice, since we make use of the rate of change of the temperature, it is only changes in the error which are of importance. The effect on the determined conductivity will therefore be well below 0.1 %.

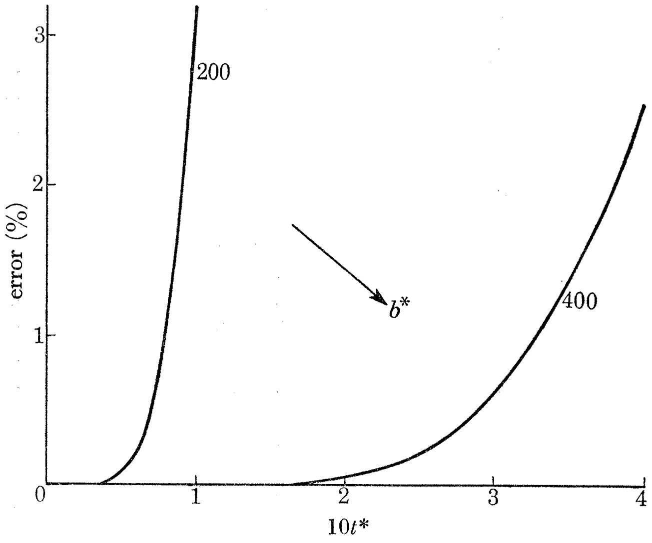

FIGURE 3. Percentage error (departure from the line source value) of the hot-wire temperature due to wall effects. (Range of b^* and t^* applicable to liquids).

(*d*) *Wall effects*

The effect of the cell wall at a finite radius b can be investigated by using a solution to (3.1) with the following boundary conditions:

$$\left.\begin{aligned} T(r,t) &= 0 \quad (a \leqslant r \leqslant b, t = 0) \\ -\partial T(a,t)/\partial t &= -q/2\pi a\lambda \quad (t \geqslant 0) \\ T(b,t) &= 0 \quad (t \geqslant 0). \end{aligned}\right\} \tag{3.38}$$

The third boundary condition is reasonable, in view of the high mass and conductivity of the metal cell walls, and the difference between the second boundary condition and the corresponding one assumed in (3.35) is unimportant at the large times which are of interest in considering wall effects. The solution obtained by Fischer (1939) is

$$T(a,t) = \frac{q}{4\pi\lambda}\left[2\ln b^* - 4\sum_{\nu=1}^{\infty}\frac{\exp(-\kappa k_\nu^2 t)}{k_\nu^2 a^2\left\{\left(\frac{J_1(k_\nu a)}{J_0(k_\nu b)}\right)^2 - 1\right\}}\right], \tag{3.39}$$

where k_ν are the roots of $J_0(k_\nu b)\,Y_1(k_\nu a) - Y_0(k_\nu b)\,J_1(k_\nu a) = 0,$ (3.40)

with $\nu = 1, 2, \ldots, \infty$. When $b/a = b^* \gg 1$, (3.39) is closely approximated by

$$T(a,t) = \frac{q}{4\pi\lambda}\left[2\ln b^* - 4\sum_{\nu=1}^{\infty}\frac{\exp(-t^* g_\nu^2/b^{*2})}{\frac{g_\nu^2}{b^{*2}}\left\{\left(\frac{Y_1(g_\nu/b^*)}{Y_0(g_\nu)}\right)^2 - 1\right\}}\right], \tag{3.41}$$

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where g_ν are the roots of $$J_0(g_\nu) = 0. \tag{3.42}$$

Calculations show that for values of b^* of practical interest (3.41) is sufficiently accurate, and may be used to predict the effect of the walls on the hot-wire temperature. In a computer evaluation of the solution, Bessel functions were generated from a polynomial approximation (Abramowitz & Stegun 1956) and the roots of (3.42) were taken from tables (Royal Society Mathematical Tables 1960). Truncation of the series at various values of ν showed that inclusion of the first 50 terms gave more than adequate accuracy. The results were compared with those predicted for an infinite extent of fluid by the line-source solution. Figures 3 and 4 show the difference expressed as a percentage of the wire temperature in the idealized case. The ranges of b^* and t^* covered are those of interest in measurements on liquids and gases, and it will be seen that experimental conditions can be chosen so that the errors remain negligible.

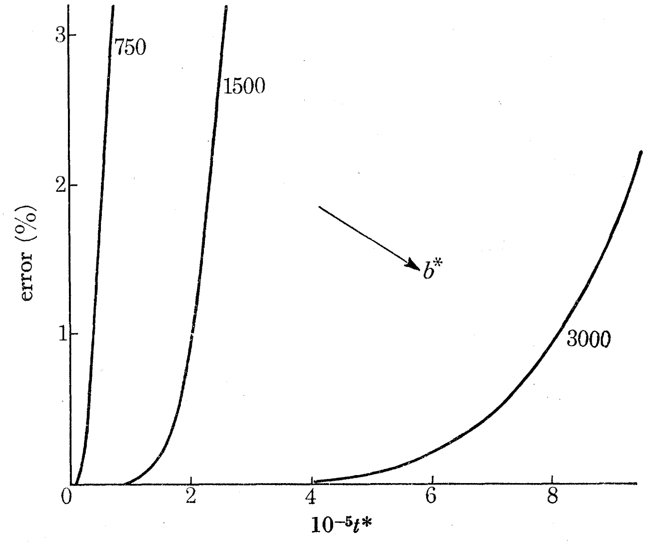

FIGURE 4. Percentage error (departure from the line source value) of the hot-wire temperature due to wall effects. (Range of b^* and t^* applicable to gases).

(e) *Interfacial thermal resistance*

Jaeger (1956) has solved the conduction equation with boundary conditions as for (3.35) but including a constant surface resistance to heat transfer, $1/h_\mathrm{s}$, defined by

$$q = 2\pi a h_\mathrm{s}\,\delta T_\mathrm{s},$$

where δT_s is the temperature jump at the interface between the heat source and the fluid.

The heat-source temperature under these conditions is given at large t^* by

$$T_\mathrm{h}(a,t) = \frac{q}{4\pi\lambda}\left\{\frac{2\lambda}{ah_\mathrm{s}} + \ln\frac{4t^*}{\gamma'} + \frac{1}{2t^*} - \frac{2\lambda}{ah_\mathrm{s}\,\omega t^*} + \left(\frac{\omega-2}{2\omega t^*}\ln\frac{4t^*}{\gamma'}\right) + \dots\right\}. \tag{3.43}$$

By comparison with (3.36) it can be seen that the effect on the slope of the temperature–time relation is given by

$$\left(\frac{\mathrm{d}T_\mathrm{h}}{\mathrm{d}t^*} - \frac{\mathrm{d}T}{\mathrm{d}t^*}\right)\Big/\frac{\mathrm{d}T}{\mathrm{d}t^*} \simeq \frac{2\lambda}{ah_\mathrm{s}\,\omega t^*}, \tag{3.44}$$

since $$\frac{\mathrm{d}T}{\mathrm{d}t^*} \simeq \frac{q}{4\pi\lambda}\left(\frac{1}{t^*}\right) \quad \text{at large } t.$$

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The condition for interfacial resistance to be negligible is therefore that $2\lambda/ah_s\omega t^*$ should be small. For dilute gases the temperature discontinuity at a solid surface is well known experimentally, and is predicted by kinetic theory for a flat surface as

$$\delta T_s = \frac{2-f}{f}\Lambda\frac{\mathrm{d}T}{\mathrm{d}x}. \tag{3.45}$$

The mean free path, except at very low pressures, will be orders of magnitude smaller than the wire diameter, so that (3.45) can be used to obtain h_s. Hence

$$h_s = \frac{f}{2-f}\frac{\lambda}{\Lambda}. \tag{3.46}$$

The mean free path for nitrogen gas at standard conditions is approximately 6×10^{-6} cm. In a typical conductivity determination the platinum wire diameter is 2.5×10^{-3} cm and the accommodation coefficient may be taken (Taylor & Glasstone 1951) as 0.8 with $\lambda = 0.03\,\mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}}$ and $\omega = 2\times10^{-3}$ then $2\lambda/ah_s\omega t^* \simeq 1.5\times10^{-4}$ when t^* is 0.5×10^5, which corresponds to an early time in a gas measurement. At pressures not very much below atmospheric, constant interfacial resistance thus has a negligible effect on the determination of gas conductivites. The existence of a temperature discontinuity at a solid/liquid interface has not been established experimentally, and would seem unlikely in view of the efficient accommodation which would be expected and the short distance between molecular collisions.

(*f*) *Time-dependent heat-source power*

In the present work, current is supplied to the hot wire from a regulated high-voltage source via a large, stable load resistor. Thus the current in the circuit at time t is

$$I(t) = \frac{V}{R_L + R' + \delta R'(t)}, \tag{3.47}$$

where V is the supply voltage, R_L the load resistance, and R' and $\delta R'(t)$ are respectively the initial value of total resistance of the hot wire and its increase during an experiment. Writing an expression for power dissipation in the cell as a function of time we therefore have

$$q(t) = \frac{1}{L'}\left(\frac{V}{R_L + R' + \delta R'(t)}\right)^2 (R' + \delta R'(t)), \tag{3.48}$$

where L' is the total hot-wire length. Resistance values are chosen so that current variations make a negligible contribution to the dependence of q on t (see part II of this paper), so we may write

$$q(t) = \frac{1}{L'}I^2(R' + \delta R'(t))$$

or

$$q(t) = q + \frac{I^2}{L'}T_q(a,t)\frac{\mathrm{d}R'}{\mathrm{d}T}. \tag{3.49}$$

where $q = I^2R'/L'$ is the initial heating rate per unit length, $T_q(a,t)$ is the temperature rise of the hot wire and $\mathrm{d}R'/\mathrm{d}T$ its temperature coefficient of resistance, which is taken as constant over the range. An expression for the effect of a small variation of the heating rate is derived by first considering the temperature rise produced by an instantaneous, infinite line-source of heat, of energy q_i per unit length occurring at $t = 0$. Say,

$$T_i(r,t) = q_i f(r,t). \tag{3.50}$$

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The temperature rise at a fixed radius a resulting from a continuous source originating at $t = 0$, and having time-dependent power, is obtained (Carslaw & Jaeger 1959 *a*) by integrating (3.50)

$$T_q(a,t) = \int_0^t q(u) f(u)\, \mathrm{d}u, \tag{3.51}$$

whereas for a constant power source

$$T(a,t) = q\int_0^t f(u)\, \mathrm{d}u. \tag{3.52}$$

The effect of the variable power source is therefore given as

$$T_q(a,t) - T(a,t) = \frac{I^2}{L'}\frac{\mathrm{d}R'}{\mathrm{d}T}\int_0^t f(u)\, T(a,u)\, \mathrm{d}u \tag{3.53}$$

from (3.49), (3.51) and (3.52); or provided that the effect is small by

$$T_q(a,t) - T(a,t) \simeq \frac{I^2}{L'}\frac{\mathrm{d}R'}{\mathrm{d}T}\int_0^t f(u)\, T(a,u)\, \mathrm{d}u. \tag{3.54}$$

But from (3.52)

$$f(t) = \frac{1}{q}\frac{\mathrm{d}T(a,t)}{\mathrm{d}t}. \tag{3.55}$$

Substituting (3.55) in (3.54) and integrating,

$$T_q(a,t) - T(a,t) \simeq \frac{I^2}{2qL'}\frac{\mathrm{d}R'}{\mathrm{d}T}(T(a,t))^2. \tag{3.56}$$

Gillam, Romben, Nissen & Lamm (1955) obtained the same result in an analysis based on Duhamel's theorem. In a typical experiment the effect on the hot-wire temperature amounts to no more than a fraction of one per cent, as can be seen from the specimen calculation of results. The approximation in (3.54) is therefore permissible.

(*g*) *End effects*

Equation (3.1) allows for no axial temperature variations and would be expected to hold only at points remote from the ends of a uniformly heated wire. In practice the temperature of the hot wire falls towards its ends, and the distance over which this disturbance extends can be estimated using a steady-state result of Carslaw & Jaeger (1959 *b*). The temperature distribution along a heated wire of total length L' and radius a with its ends held at a constant reference temperature is

$$T(z) = \frac{q}{2\pi a h}\left(1 - \frac{\cosh M(\frac{1}{2}L' - z)}{\cosh M\frac{1}{2}L'}\right). \tag{3.57}$$

The radial heat loss from the wire is taken to be $2\pi a h T(z)$, where h is a constant heat transfer coefficient. The quantity M is defined by

$$M = (2h/\lambda_{\mathrm{W}}\, a)^{\frac{1}{2}},$$

and the value of h may be taken from (3.4) as

$$h \simeq 2\lambda/a(\ln 4t^* - \gamma), \tag{3.58}$$

t^* should be chosen to correspond to the end of a measurement, since the end effects are most important then.

On the basis of such estimates, and allowing a large safety margin because of their approximate nature, the potential leads are positioned to avoid major end effects. However, the potential

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leads themselves provide a high conductivity heat path away from the hot wire and inevitably produce a temperature distortion near their point of attachment. Briggs (1965) estimated the heat loss from the central wire into the potential leads by treating them as cooling fins. An alternative treatment, estimating the temperature reduction in the hot wire at the point of attachment of the potential lead, is as follows.

A steady-state situation is visualized with h a constant heat transfer coefficient. $T(z)$ is the temperature in the active section of the hot wire between the potential leads, $T_{\mathrm{E}}(y)$ is the temperature in the end section of the hot wire outside the potential lead and $T_{\mathrm{P}}(x)$ the temperature in the potential lead. The radial heat loss per unit length from the active section of the wire is then $2\pi ahT(z)$ with similar expressions for the other wires. Equations governing the temperature distribution along the wires can be obtained by writing heat balances. For example, over an element of the active section, where there is heat generation at a rate q per unit length

$$q\delta z-\lambda\frac{\mathrm{d}T}{\mathrm{d}z}\pi a^2=-\lambda\left(\frac{\mathrm{d}T}{\mathrm{d}z}+\frac{\mathrm{d}^2T}{\mathrm{d}z^2}\delta z\right)\pi a^2+2\pi ahT\delta z,$$

giving
$$\mathrm{d}^2T/\mathrm{d}z^2-B^2T+A^2=0 \tag{3.59}$$
and, similarly,
$$\mathrm{d}^2T_{\mathrm{E}}/\mathrm{d}y^2-B^2T_{\mathrm{E}}+A^2=0 \tag{3.60}$$
and
$$\mathrm{d}^2T_{\mathrm{P}}/\mathrm{d}x^2-B^2T_{\mathrm{P}}=0, \tag{3.61}$$

where $B^2=2h/a\lambda_{\mathrm{W}}$ and $A^2=q/\pi a^2\lambda_{\mathrm{W}}$. The boundary conditions are taken as

$$T_{\mathrm{E}}(0)=T_{\mathrm{P}}(0)=0,$$
$$T_{\mathrm{E}}(l)=T_{\mathrm{P}}(l)=T(0),$$
and
$$\left(\frac{\mathrm{d}T}{\mathrm{d}z}\right)_{z=0}=\left(\frac{\mathrm{d}T_{\mathrm{E}}}{\mathrm{d}y}\right)_{y=l}+\left(\frac{\mathrm{d}T_{\mathrm{P}}}{\mathrm{d}x}\right)_{x=l}, \tag{3.62}$$

which equates the heat flux into the potential lead to the sum of the fluxes towards the junction in the hot wire. The position coordinate for the active section is measured from the junction, and for the other sections from their ends. These two latter sections are assumed to be of length l. Solution of the simultaneous differential equations gives

$$T(z)=C\exp\left(-Bz\right)+A^2/B^2, \tag{3.63}$$

where
$$C=-(A^2/B^2)\left(1+2\tanh Bl\right)^{-1}\left\{1+2\tanh Bl\exp\left(-Bl\right)+\frac{1-\exp\left(-Bl\right)}{\tanh Bl}\right\},$$
which for large Bl
$$\simeq-(A^2/3B^2)\left\{1+2\exp\left(-Bl\right)\right\},$$
so that
$$T(z)\simeq(A^2/B^2)\left\{1-\tfrac{1}{3}\exp\left(-Bz\right)\right\}. \tag{3.64}$$

To justify this simplification an estimate of h is required. The heat transfer coefficient in an experiment will always be greater than the value for steady-state conduction between concentric cylinders

$$h=\lambda/a\ln\left(b/a\right). \tag{3.65}$$

Using this expression one can therefore say

$$B>\frac{1}{a}\left(\frac{\lambda}{\lambda_{\mathrm{W}}}\frac{1}{\ln\left(b/a\right)}\right)^{\frac{1}{2}}. \tag{3.66}$$

Taking data for platinum and typical liquids, it can be shown that B is large when $a=1.3\times10^{-3}$ cm and $b=0.5$ cm. For example, $B\simeq25$ for toluene at 25 °C. In practice l is not less than 1 cm, so the simplification of (3.64) is permissible.

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The fractional reduction in the hot-wire temperature at the point of attachment of the potential lead is therefore found to be independent of h, and is given by

$$(T(\infty)-T(0))/T(\infty) \simeq \tfrac{1}{3}. \tag{3.67}$$

In reality the potential-lead errors would be expected to become larger in the later stages of an experiment for two reasons: first the heat transfer coefficient from the potential leads will rise as convection develops and the fluid velocity across them increases. Secondly, the leads will inevitably disturb the cylindrical symmetry of the convection flow pattern and produce some radial convective heat transfer. These effects, which may be called secondary convection heat effects to distinguish them from the primary effect which limits the duration of a run, will cause the apparent thermal conductivity, as defined above, to increase with the duration of an experiment. The extrapolation back to zero time, which was suggested in § 3.2 (*d*), will also minimize these errors, and leave only those due to conduction losses along the potential leads into a virtually stationary fluid.

In view of the large size of the temperature distortion estimated by (3.67) it seemed advisable to determine the resulting error experimentally. This is described in an appendix. It was found, however, that the average temperature distortion in a 10 cm cell was only a fraction of a percent.

A final point which should be mentioned in connexion with temperature variations along the active section of the hot wire is their effect on the power dissipation rate per unit length. This comes about in two ways. First, the resistance per unit length is no longer constant, but since the resistance change in an experiment is only about 0.1 %, the change in power dissipation resulting from this non-uniformity is completely negligible. Secondly, since direct current is used, the Thompson effect causes a small negative or positive power to be superimposed on the resistive heating where temperature gradients exist. The size of the effect is given by

$$\delta q = \sigma_{\mathrm{T}} I \,\mathrm{d}T/\mathrm{d}z. \tag{3.68}$$

The Thompson coefficient for platinum is (National Research Council 1926)

$$\sigma_{\mathrm{T}} \simeq 9\times 10^{-6}\,\mathrm{V\,K^{-1}},$$

and the experimental measurements of the temperature profile in the hot wire near the potential leads (see appendix) show that

$$\mathrm{d}T/\mathrm{d}z \simeq 0.3\,\mathrm{K\,cm^{-1}} \quad \text{with the result} \quad \delta q \simeq 6\times 10^{-8}\,\mathrm{W\,cm^{-1}}.$$

This is to be compared with $q \simeq 10^{-3}\,\mathrm{W\,cm^{-1}}$ and is therefore negligible.

(*h*) *Initial fluid temperature distribution*

An expression for the rate of re-equilibration of the cell after a measurement is required in order to estimate the minimum permissible interval between runs. The temperature at time t and radius r produced by a line source originating at $t=0$ and $r=0$ with time dependent power $q(t)$ is in general (Carslaw & Jaeger 1959)

$$T(r,t) = \int_0^t \frac{q(u)}{\rho C_{\mathrm{P}}} \exp\left(-r^2/4\kappa(t-u)\right)\frac{\mathrm{d}u}{t-u}. \tag{3.69}$$

If we say that

$$q(t) = q \quad (0 < t \leqslant t_1),$$
$$q(t) = 0 \quad (t_1 < t \leqslant t_2),$$

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then $T(r, t_2)$ can be taken to represent the temperature at a time (t_2-t_1) after the end of a run of duration t_1. Changing the variable to $r^2/4\kappa t$ and noting that the integrand is zero in $t_1 < t \leqslant t_2$ we have

$$T(r, t_2) = \frac{q}{\rho C_p}\left\{\int_{r^2/4\kappa t_2}^{\infty} \frac{\mathrm{e}^{-u}}{u}\,\mathrm{d}u - \int_{r^2/4\kappa(t_2-t_1)}^{\infty} \frac{\mathrm{e}^{-u}}{u}\,\mathrm{d}u\right\}. \tag{3.70}$$

From (3.3) and (3.4), for large t_2 and (t_2-t_1) the wire temperature is therefore given by

$$T(a, t_2) = \frac{q}{4\pi\lambda}\left\{\ln\frac{t_2}{t_2-t_1} - \frac{a^2}{4\kappa}\frac{t_1}{t_2(t_2-t_1)} + \ldots\right\} \tag{3.71}$$

or, expressed as a fraction of the final temperature in the previous run, by

$$\frac{T(a, t_2)}{T(a, t_1)} \simeq \frac{\ln\{t_2/(t_2-t_1)\}}{\ln\{4\kappa t_1/a^2\gamma'\}}. \tag{3.72}$$

The neglect of the second term in (3.71) is permissible if t_2 is chosen sufficiently large for $T(a, t_2)/T(a, t_1)$ to be of the order of 0.1 %. The interval between runs, calculated on this basis, will be a safe estimate, since the presence of the cell walls and convection will both speed up re-equilibration.

APPENDIX. MEASUREMENT OF THE EFFECT OF THE POTENTIAL LEADS ON THE HOT-WIRE TEMPERATURE

We are concerned here with the effect of the potential leads on the average temperature over the active section of the hot wire in the early moments of an experiment, when convection is only slightly developed and the fluid is virtually stationary. Under these conditions suppose that the fractional lowering of the hot-wire temperature at a distance z from the potential-lead junction is given, for a particular geometry, by

$$T(\infty) - T(z) = F(t, a, z, \rho, C_p, \rho_{\mathrm{w}}, C_{p\mathrm{w}}, \lambda, \lambda_{\mathrm{w}})$$

or

$$[T(\infty) - T(z/a)]/T(\infty) = F'(t^*, z/a, \lambda/\lambda_{\mathrm{w}}, \omega). \tag{A 1}$$

In using a resistance measurement to obtain the hot-wire temperature we are concerned with the averaged value of the temperature reduction:

$$\delta T = \frac{2a}{L}\int_0^{2L/a} \frac{T(\infty) - T(z/a)}{T(\infty)}\,\mathrm{d}(z/a). \tag{A 2}$$

This quantity was evaluated by means of measurements on a large-scale model immersed in a tank of glycerol sufficiently large for end and wall effects to be negligible. Nickel wire of 0.018 in. diameter was used, and heating was by a constant alternating current chosen to produce a temperature rise of about 1.50 K over 5 min. The temperatures at points along the nickel wire were measured by 0.05 mm diameter chromelalumel thermocouples spotwelded to the wire. The thermocouples were connected to the floating input of the integrating digital voltmeter, which recorded the d.c. voltages with a resolution of 0.1 μV at intervals of 5 s.

Before the model was completed by attaching the analogue of the potential lead, a series of runs was made in which the output of each thermocouple was recorded as the nickel wire heated. Ideally, of course, the voltages should have agreed at corresponding times, but reproducible scatter of a few microvolts was observed. The output from each couple was plotted against the logarithm of time and good straight lines were obtained. Smoothed values from these plots were

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used to calculate mean outputs at given times, and the corrections required to bring each thermocouple reading onto the mean were noted.

The model was then completed by attaching the potential-lead analogue and a further series of runs made. Corrected thermocouple readings were again smoothed by plotting against the logarithm of time, and then crossplots were made for a series of times, showing the output as a function of the distance of the thermocouple from the junction. A sample set of results is shown in figure A 1. It is interesting to note that the prediction of a 30 % temperature reduction at the junction by (3.67) of the text is approximately confirmed.

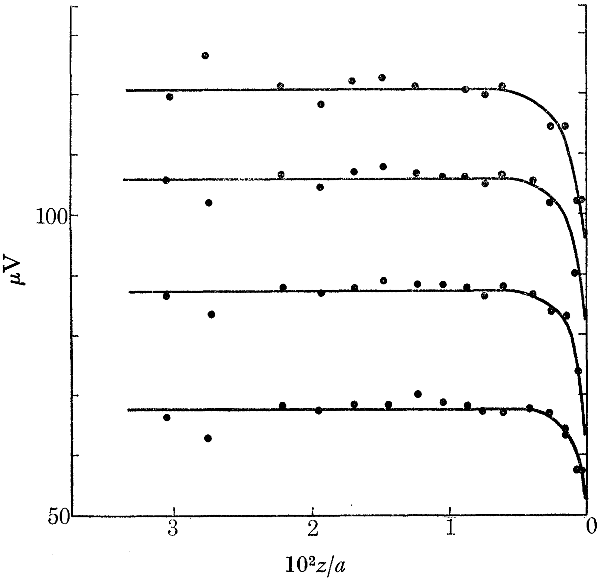

FIGURE A 1. Temperature profiles (in terms of thermocouple outputs) in the model of the hot-wire junction. The analogue of the potential-lead junction is at $z/a = 0$. The results are for the nickel wire/glycerol system.

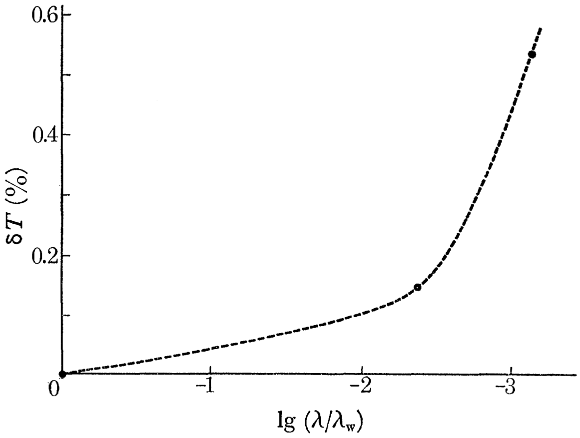

FIGURE A 2. Percentage error in the average temperature of the active section of the hot wire as a function of the ratio of the thermal conductivities of the wire and fluid.

The error in the average hot-wire temperature (equation (A 2)) was obtained from plots such as those in figure A 1 by integration using a planimeter and was found to be independent of time. For $L/2a = 2 \times 10^3$ (corresponding to the experimental cell) the value was equal to 0.15 %.

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The values of λ/λ_w and ω in the nickel-glycerol experiment are of the same order as those which apply when using the cell in measurements on organic liquids, so this result shows that errors in the determined conductivities will be small. Equation (3.4) of part I suggests that the dependence of the error on ω will be slight for t^* $O(100)$—corresponding to a few tenths of a second in a conductivity measurement—and the dependence on λ/λ_w is likely to be much more important. To obtain some indication of this dependence the experiment was repeated using copper wires immersed in glycerol. Again the error was found to be independent of time, but was now equal to 0.53 % for $L/2a = 2\times 10^3$. These two values are plotted against lg (λ/λ_w) in figure A 2 together with a further point at the origin (since no error occurs when $\lambda/\lambda_w = 1$). In view of the smallness of the error these three points were considered to give sufficient indication of the dependence on λ/λ_w, and corrections were read from the tentative curve shown in figure A 2 (in the present work the values of lg (λ/λ_w) lie within the range -2.6 to -2.8). The corrections are considered to be accurate within about 25 %, so the residual errors in the conductivities, from this source, should be below 0.1 %.

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