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Thermal Diffusivity Measurement by the Transient Hot-Wire Technique: A Reappraisal

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The theory of the transient hot-wire technique for thermal conductivity measurements is reassessed in the special context of thermal diffusivity measurements. A careful examination of the working equation and an error analysis are employed to identify the principal sources of error. Notwithstanding earlier claims to the contrary, the best precision that can be attained in thermal diffusivity measurements is of the order of ±3%, while the accuracy is inevitably poorer. Experimental evidence is adduced from two different instruments that supports the analysis given here. Although the technique cannot yield values of the thermal diffusivity, κ, as accurate as can be achieved by the use of the best possible individual values of λ, ρ, and C_p in the relation $\kappa = \lambda/\rho C_p$, the simplicity of the technique makes it attractive for many purposes. It is even possible to derive values of the isobaric heat capacity C_p for many fluids not available from other methods.

KEY WORDS: argon; thermal conductivity; thermal diffusivity; toluene; transient hot-wire technique; *m*-xylene.

1. INTRODUCTION

The transient hot-wire technique for thermal conductivity measurements has now become established as the primary method for accurate determinations over a wide variety of thermodynamic states [1–3]. Since the very first application of the technique [4] it has been recognized that it is possible, in principle, to obtain both the thermal conductivity and the ther-

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mal diffusivity from the same experiment. In the last few years there have been a number of independent rediscoveries of the fact represented in several publications [5–9]. The accuracy claimed for the corresponding thermal diffusivity measurements has varied between ±1% [7] and ±11% [9] and has not always been in direct proportion to the precision of the measurement of the primary experimental variables. In other cases only an estimate of the precision of the measurements, based upon reproducibility, has been made [5].

Only in a few cases [7, 8] has any attempt been made to modify existing thermal conductivity instruments to perform thermal diffusivity studies. Given that the instruments were therefore not optimized for the latter mode of operation, it is not surprising that the claimed precision has never approached that of the best thermal conductivity measurements (±0.3%).

It is the purpose of this paper to present a complete analysis of the application of the transient hot-wire technique to thermal diffusivity measurements. The treatment is intended to provide not only the full working equations but also a reliable means of assessing experimental errors and a guide to the optimum design for thermal diffusivity measurements.

2. THEORY OF THE METHOD

For a constant infinite line source of heat, with power input per unit length q, initiated at time $t=0$ and immersed in a fluid of constant fluid properties and infinite extent, the temperature of the fluid at a radial position r from the heat source conforms to the equation

$$\Delta T_{\mathrm{id}}(r, t) = T(r, t) - T_0 = \frac{q}{4\pi\lambda} E_1\left(\frac{r^2}{4\kappa t}\right) \tag{1}$$

where T_0 is the initial, uniform temperature of the fluid, λ the thermal conductivity of the fluid, and

$$\kappa = \left(\frac{\lambda}{\rho C_{\mathrm{p}}}\right) \tag{2}$$

its thermal diffusivity in which ρ is the density and C_{p} the isobaric heat capacity. E_1 is the exponential integral.

For large values of $\kappa t/r^2$, the exponential integral in Eq. (1) can be expanded to yield

$$\Delta T_{\mathrm{id}}(r, t) = \frac{q}{4\pi\lambda} \ln\frac{4\kappa t}{r^2 C} + \mathcal{O}\left(\frac{r^2}{4\kappa t}\right) \tag{3}$$

where $C = 1.781...$ is the exponential of Euler's constant.

If the wire radius is chosen such that the second term on the right-hand side of Eq. (3) is less than 0.01% of ΔT_{id}, it becomes clear that in this ideal arrangement the thermal conductivity can be deduced from the slope of the straight line ΔT_{id} vs $\ln t$, while the thermal diffusivity may be obtained from its intercept or, more correctly, the absolute value of ΔT_{id} at a fixed time.

In any practical instrument, the source of heating is provided by a finite length of metallic wire which also serves as a resistance thermometer. As a consequence, the measured temperature rise of the wire, ΔT_{w}, departs from the ideal of Eq. (3) even at the surface of the wire where $r = \mathrm{a}$. Most of the possible causes of departure of the measured temperature rise from the ideal value have been investigated by Healy et al. [10]. Their results were expressed in the form of small corrections, δT_i, to be applied to the measured temperature rise, ΔT_{w}, so that

$$\Delta T_{\mathrm{id}} = \Delta T_{\mathrm{w}} + \sum_i \delta T_i \tag{4}$$

The temperature, T_{r}, to which the measured thermal conductivity is referred, must also be corrected by a set of values, δT_i^*, so that

$$T_{\mathrm{r}} = T_0 + \sum_i \delta T_i^* \tag{5}$$

Healy et al. [10] were concerned solely with the deduction of approximate, additive corrections to be applied to the measurement of the thermal conductivity of the fluid determined from the slope of the line ΔT_{id} vs $\ln t$. Consequently, they presumed all corrections to be small and considered in detail only those effects that were time dependent. Because time-independent effects may also contribute systematically to the error in the determination of the thermal diffusivity, it is necessary to consider some of the corrections here afresh.

2.1. Corrections to the Temperature Rise

We illustrate the magnitude of the corrections with examples from gas and liquid phases using two instruments: the low-temperature, general-purpose instrument described by Roder [11] and the high-pressure, liquid-phase apparatus first described by Menashe and Wakeham [3]. In the former instrument, the diameter of the sensing wire is 12.5 μm, while in the latter it is 7 μm. For the gas phase, we select conditions for an experiment on argon with

$$T_0 = 200.63\ \mathrm{K}$$

$$P_0 = 3.548\ \mathrm{MPa}$$

$$\lambda = 0.01438\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$$

$$\rho = 92.86\ \mathrm{kg \cdot m^{-3}}$$

$$C_\mathrm{p} = 664.7\ \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$$

whereas for the liquid phase we select conditions appropriate to a measurement on *m*-xylene [12] with

$$T_0 = 305.6\ \mathrm{K}$$

$$P_0 = 3.4\ \mathrm{MPa}$$

$$\lambda = 0.129\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$$

$$\rho = 855\ \mathrm{kg \cdot m^{-3}}$$

$$C_\mathrm{p} = 1720\ \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$$

We next consider each of the corrections to the ideal model and subsequently examine the magnitude of the significant corrections for each of the two instruments. Wherever possible, we adhere to the notation introduced by Healy et al. [10].

As a result of the expansion of the exponential integral employed in the derivation of Eq. (1), there is a truncation error given by

$$\frac{\delta T_9}{\Delta T_\mathrm{id}} = a^2/[4\kappa t \ln(4\kappa t/a^2 C)] \tag{6}$$

which decreases with increasing time. Even in the worst case for the two instruments mentioned above, the correction δT_9 does not exceed 0.01% of ΔT_id and is therefore negligible. For the liquid phase, effects due to radial convection and viscous dissipation [11, 13] are also negligible.

However, in gas-phase measurements, we find minor contributions due to radial convection and viscous dissipation. The analysis by Healy et al. [10] has shown that convection and compression effects were always negligible in the evaluation of the thermal conductivity, compared with density-induced variations of the thermal diffusivity. Their analysis was extended to the dense gas and liquid states [13, 14] for the case when the variation in density, $\Delta\rho$, during a measurement was much smaller than the density, ρ_0. The result obtained was

$$\delta T_4 = -\left(\frac{q}{4\pi\lambda}\right)^2 \alpha_\mathrm{P} \left[\ln 4 + \frac{Prg^2 t^2 \alpha_\mathrm{P}}{2C_\mathrm{P}}\right] \tag{7}$$

where α_P is the thermal expansion coefficient of the fluid at constant pressure, g the acceleration of gravity, and $Pr = \eta C_P/\lambda$ the Prandtl number. The correction, δT_4, is approximately constant with time; it is about 0.4% of the ideal temperature rise at low densities. Therefore, this correction has to be considered in the thermal diffusivity determination. It is assumed in this paper that vertical convection in any fluid phase is avoided by a careful choice of the time scale of measurement [1, 11, 15.]

A number of other corrections are not negligible. First we consider the fact that the sensing wire has a nonzero radius a, a heat capacity $(C_p)_w$, and a finite thermal conductivity λ_w. As a result, a correction δT_1, which decreases with increasing time, must be applied to the measured wire temperature rise [10].

$$\delta T_1 = \frac{q}{4\pi\lambda}\left\{\frac{a^2[(\rho C_P)_w - \rho C_P]}{2\lambda t}\ln\frac{4\kappa t}{a^2 C} - \frac{a^2}{4\kappa t} + \frac{a^2}{4\kappa_w t} - \frac{\lambda}{2\lambda_w}\right\} \tag{8}$$

where κ_w is the thermal diffusivity of the wire material, and the subscript w means wire properties. Whereas for thermal conductivity measurements only the time-dependent corrections need be considered, for the thermal diffusivity all are important, although small, and the full correction in Eq. (8) must be employed.

Because the test fluid must be contained within a vessel with an isothermal, finite outer boundary (of radius b) in place of the infinite fluid considered in the ideal model, a further correction is necessary. The correction, which increases with increasing time, is

$$\delta T_2 = \frac{q}{4\pi\lambda}\left\{\ln\left(\frac{4\kappa t}{b^2 C}\right) + \sum_{\nu=1}^{\infty} e^{-g_\nu^2 \kappa t/b^2}[\pi Y_0(g_\nu)]^2\right\} \tag{9}$$

where the g_ν are the roots of $J_0(g_\nu) = 0$, and J_0 and Y_0 are Bessel functions.

In the special case of a dilute gas, it is necessary to consider that the mean free path of the gas molecules may approach the diameter of the sensing wire. In such cases, there may be a temperature discontinuity at the wire surface which leads to a further correction to the measured wire temperature. An approximate evaluation of this effect shows that the correction is [10]

$$\delta T_6 \simeq \frac{q\Lambda}{2\pi\lambda a}\frac{\Delta T_{id}}{T_0} \tag{10}$$

where Λ is the mean free path of the gas. The approximation used to evaluate δT_6 is not sufficiently reliable to allow application of the correction when it is significant. Consequently, it is preferable to avoid measurements within a density range where the effect is significant, as outlined by de Groot et al. [15].

A group of effects arises from the fact that the physical properties of the fluid are, in practice, functions of temperature and not constants as supposed in the ideal model.

First we consider the direct effect of their dependence on temperature. When it is accounted for, by means of a linear perturbation[4] to the properties about the equilibrium temperature, both a time-dependent correction and a time-independent contribution emerge. The time-dependent contribution is most easily accounted for by referring the thermal conductivity determined from the slope of the ΔT vs ln t line to a reference state (T_r, ρ_r). The appropriate correction to the bath temperature in Eq. (5) is usually

$$\delta T_1^* = \frac{1}{2}(\Delta T(t_i) + \Delta T(t_f)) \tag{11}$$

where t_i and t_f are the initial and final times of measurement. The corresponding reference density is $\rho_r(T_r, P_0)$, where P_0 is the equilibrium pressure. In cases where the distribution of measured points in ln t is not uniform, a rather more complicated formula is necessary [16].

The time-independent part of the correction is best applied to the measured temperature rise itself and can be written

$$\delta T_7 = -\left[\frac{q}{4\pi\lambda(T_0)}\right]^2 (\chi - \phi) \ln 4 \tag{12}$$

where χ and ϕ are the linear coefficients in the temperature expansions of λ and ρC_P for the fluid

$$\lambda(T, \rho) = \lambda_0(1 + \chi \, \Delta T) \tag{13}$$

and

$$\rho C_P(\rho, T) = (\rho C_P)_0 \, (1 + \phi \, \Delta T) \tag{14}$$

This method of application ensures that the thermal diffusivity determined refers to the initial, equilibrium state (T_0, ρ_0) and the initial pressure.

A further effect arising from the variation of the fluid physical properties is compression work. An approximate analysis of this effect has been

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[4] In regions of state where the properties are exceptionally strong functions of temperature, such as near the critical point, more complicated functional dependences may be necessary, leading to correction term δT_8 presented elsewhere [14].

given by Healy et al. [10]. It leads to the result that the correction to be applied to the measured temperature rise is[5]

$$\delta T_3 = -\left[\frac{qLRt}{\rho C_p C_v V}\left(1 - e^{-b^2/4\kappa t}\right) + \frac{qR}{4C_v \lambda} E_1\left(\frac{b^2}{4\kappa t}\right)\right] \tag{15}$$

where L is the length of the heated wire, V the volume of the vessel containing the test fluid, C_v the isocoric heat capacity, and R the gas constant.

The calculation of this correction is not sufficiently accurate to allow its application to measurements directly. Instead, it is preferable to avoid the range of conditions in which the correction, judged by Eq. (15), is significant. This can be achieved by operating above a prescribed density limit or by making the volume of the test vessel sufficiently large. As shown later for the gaseous phase, its effect at the beginning of the experiment is negligible and does not affect the evaluation of the thermal diffusivity.

In any event the magnitude of the correction can be tested by increasing the volume, V, experimentally and observing any consequent changes in the temperature rise. It is therefore assumed in what follows that the precautions to render δT_3 negligible have been taken. For typical experiments in gaseous argon we are limited to densities above 1 mol · liter^{-1} (40 kg · m^{-3}).

An entirely different type of correction arises from the fact that any conductive heat transfer must be accompanied by a simultaneous radiative transfer. In this case the correction depends upon whether or not the fluid absorbs radiation. If the fluid is transparent to radiation in the wavelength range of significance, then the treatment of the effect is straightforward and the correction is

$$\delta T_5 = 8\pi a \sigma T_0^3 \, \Delta T_{\mathrm{id}}^2 / q \tag{16}$$

in which σ is the Stefan–Boltzmann constant. This correction is invariably small.

If the fluid absorbs radiation, then a completely different analysis, carried out by Menashe and Wakeham [17] and, subsequently, by Nieto de Castro et al. [18], is necessary. The correction in this case is [18]

$$\delta T_5 = -\frac{qB}{4\pi\lambda}\left\{\frac{a^2}{4\kappa}\ln\left(\frac{4\kappa t}{a^2 C}\right) + \frac{a^2}{4\kappa} - t\right\} \tag{17}$$

in which

$$B \simeq \frac{16 K n^2 \sigma T_0^3}{\rho C_p} \tag{18}$$

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[5] The final algebraic result in Ref. 10 is in error, although the numerical difference from the present result is small.

where K is a mean extinction coefficient for the radiation and n is the refractive index of the fluid. The difficulty with this correction arises because it is experimentally impossible to alter its magnitude and no useful measurements of K exist. However, in the case of every fluid studied thus far, $Ba^2/4\kappa$ has been shown experimentally to be less than 10^{-5} [18], which implies that the radiation correction is again negligible. However, because B is proportional to T_0^3, it is quite possible that operation at high temperatures may require application of a significant correction in order to eliminate the effect from both the thermal conductivity and the thermal diffusivity [18].

Two final effects that should be considered arise because it is necessary to use a finite wire in an experiment in place of the infinite wire of the theory and because the heat dissipation in the wire must be a constant to within 0.05% during an experiment. These effects are generally compensated by experimental means. Consequently, we consider the former later, in the context of experimental errors, as distinct from corrections to the working equation.

2.2. The Magnitude of the Corrections

Among the various corrections listed in the preceding section there are a number that are sufficiently large that they must be applied in the determination of the thermal conductivity and thermal diffusivity. However, because many of them are time dependent, it is important to examine them quantitatively in order to optimize the experiment.

Apart from the corrections discussed below, it is assumed that sufficient precautions have been taken to render all of the remaining corrections negligible so far as the thermal diffusivity is concerned. In this context, we define negligible to be less than 0.01% of the temperature rise, for reasons discussed later.

Figure 1 contains the time dependence of each of the significant corrections of which account must be taken in the determination of the thermal diffusivity in the liquid-phase measurement on *m*-xylene discussed earlier. We note that the truncation error, δT_9, decreases with increasing time, while the outer boundary correction, δT_2, increases and the effect of variable fluid properties, δT_7, is constant. The finite-wire properties correction, δT_1, initially falls rapidly with increasing time to zero at 300 ms. It subsequently changes sign and, because of the term $(\lambda/2\lambda_w)$ in Eq. (8), asymptotically approaches a small, constant, negative value. At very short times, the correction δT_1 is so large that it contributes significantly to the absolute temperature rise. Consequently, in contrast to the suggestions of earlier workers [7, 8], it is not best to use the measured temperature rise at

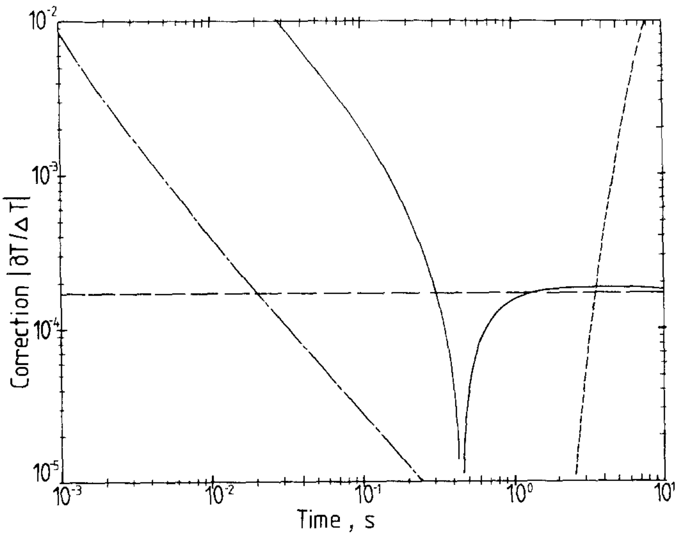

Fig. 1. Time dependence of some of the corrections for the transient hot-wire technique for typical liquid state measurements. (——) δT_1, finite-wire properties; (----) δT_2, outer boundary; (— —) δT_7, variable fluid properties; (–·–·–·–) δT_9, truncation error.

short times because the evaluation of the corrections can never be better than an estimate. Conversely, at very long times (~ 1 s), the outer boundary correction becomes the largest time-dependent correction, although it is still very small. The correction, δT_7, is always very small. On this basis, it must be concluded that for these systems the most accurate measurements of the thermal diffusivity measurement would be obtained by the use of the temperature rise measurements around $t = 1$ s.

Figure 2 contains similar information for the gas-phase measurement. The outer boundary correction, δT_2, the temperature jump correction, δT_6, and the truncation error correction, δT_9, are nearly zero to within 0.004% of ΔT. The finite-wire properties correction δT_1 is most important at short times, decreasing as time increases. For $t \leqslant 0.15$ s, $\delta T_1 \geqslant 2.3\%$ of ΔT, confirming the result already found for the liquid phase, namely, that the temperature rise at short times should not be used for the measurement of thermal diffusivity. The compression work correction, δT_3, varies with time and it is significant at the lower densities, accounting for about 0.4% of ΔT at $t = 1$ s. However, its effect on the determination of the intercept of the line is negligible. The radiation correction, δT_5, is slightly dependent on time, increasing to about 0.4% of ΔT at $\simeq 1$ s. The effect of both the viscous dissipation correction, δT_4, and the variable fluid properties, δT_7, is constant and small.

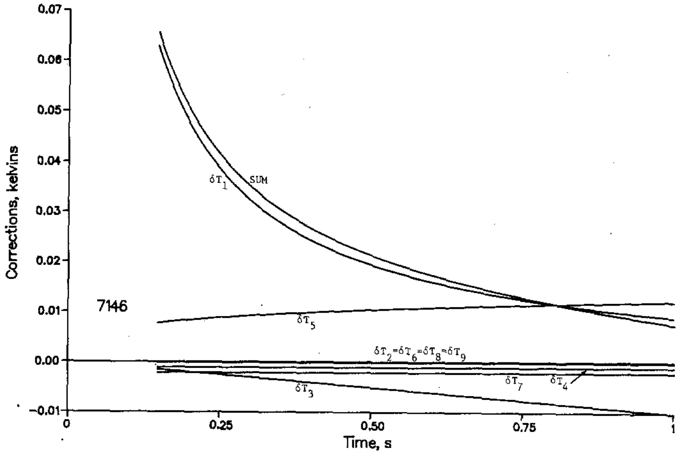

Fig. 2. Time dependence of the corrections for the transient hot-wire technique for typical moderately dense gas measurements. Corrections identified according to text. SUM is the summation of all corrections. δT_8 identifies an additional variable fluid properties correction when critical effects are observed [14].

Figure 2 also displays the sum of all corrections, that is, the overall temperature rise correction to the experimental data. It can be seen that the sum is almost identical to δT_1; the other corrections almost cancel each other. As in the case of liquid measurements, we conclude from Fig. 2 that measurements of the thermal diffusivity in the gas phase should be evaluated at times around 1 s, where the $\sum_i \delta T_i \simeq 0.3\%$ of ΔT for the best accuracy, rather than at short times as suggested by other authors [7, 8].

The corrections which must be applied to ΔT_w in order to obtain ΔT_{id} cannot be known exactly. Consequently, the error in the correction contributes an additional uncertainty to ΔT_{id}. We denote this added uncertainty by $\delta T_s / \Delta T$. It is, in principle, calculable from estimates of the uncertainty in calculating the various corrections. However, as we have seen by using the temperature rise at around 1 s, the sum of the corrections can be reduced to less than 0.3% of the temperature rise. In this case it is quite reasonable to assign a value of $\delta T_s / \Delta T = 0.01\%$ as an upper limit.

3. ERROR ANALYSIS

3.1. Primary Measured Variables

In the previous section we considered sources of systematic error in the measurement of the thermal diffusivity arising from the theory of the experimental method. In this section we consider sources of error arising from the measurements themselves that may be either random or systematic. The former contribute to the precision of the measurements, whereas the latter contribute to the accuracy.

Figure 3 shows a schematic diagram of the bridge circuit employed to determine the temperature rise of the sensing wire as a function of time. The bridge is employed to determine the resistance difference between two wires, R_L and R_S, one longer than the other, at various instants of time after the transient heating is initiated. By this mechanism, the effects of the ends of the wires are eliminated entirely in a carefully designed instrument [10, 19]. If we denote the resistance difference at time t by

$$R_W(t) = R_L(t) - R_S(t)$$

where L and S denote the long and short wire, then the measured value can be used to obtain a temperature rise by means of the equation [19]

$$\Delta T_W = \frac{R_W(t) - R_W(0)}{\alpha R_W(0)} \tag{19}$$

Here, α is a pseudolinear temperature coefficient of resistance of the sensing wire material. In addition, $R_W(0)$ is $\lim_{t \to 0} R_W(t)$. In practice, it is exceedingly difficult to measure $R_W(0)$ and it is usually replaced by R_{W_0}, the resistance of the wire at the equilibrium temperature of the experiment, T_0, determined in an independent measurement. In principle, the two values should be identical, but because R_{W_0} is determined in a separate

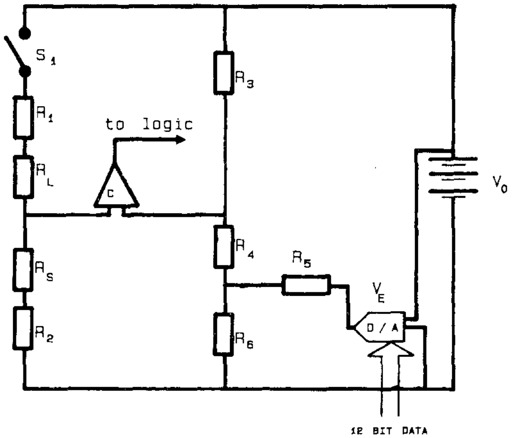

Fig. 3. A schematic measurement bridge for the transient hot-wire technique.

experiment [3, 11] using the same bridge, this is not necessarily true. Nilsson et al. [8] have made an attempt to determine $R_W(0)$ itself to avoid this difficulty.

An error analysis of Eq. (19) shows that

$$\left|\frac{\delta\,\Delta T_W}{\Delta T_W(t)}\right|_R = \left|\frac{\delta[R_W(t)-R_W(0)]}{[R_W(t)-R_W(0)]}\right| + \left|\frac{\delta R_W(0)}{R_W(0)}\right| + \left|\frac{\delta\alpha}{\alpha}\right| \tag{20}$$

or if we use R_{W_0} in place of $R_W(0)$, we find

$$\left|\frac{\delta\,\Delta T_W}{\Delta T_W(t)}\right|_R = \left|\frac{\delta[R_W(t)-R_{W_0}]}{R_W(t)-R_{W_0}}\right| + \left|\frac{\delta R_{W_0}}{[R_W(t)-R_{W_0}]}\right| + \left|\frac{\delta R_{W_0}}{R_{W_0}}\right| + \left|\frac{\delta\alpha}{\alpha}\right| \tag{21}$$

where δR_{W_0} represents the error in R_{W_0} and incorporates its difference from $R_W(0)$.

If we consider first just the time dependence of ΔT_W which is employed to determine the thermal conductivity, we see from Eq. (19) that the only contributions arise from the first, third, and fourth terms in Eq. (21). This is because an error in R_{W_0} is important only in the denominator of Eq. (19), and not in the numerator. Furthermore, as long as δR_{W_0} is small in comparison with R_{W_0}, the effect is small. On the other hand, for the thermal diffusivity it is not only the time dependence of ΔT_W that is of concern but also its *absolute value*. Thus the error in R_{W_0} makes a direct contribution in the numerator of Eq. (19), expressed in the second term in Eq. (21). Here the contribution is of the order $\delta R_{W_0}/[R_W(t)-R_{W_0}]$, which can be quite large because $R_W(t)-R_{W_0} \ll R_{W_0}$ in all experiments.

It should be emphasized that Eq. (21) refers to the random errors in the resistance measurements. Evidently any systematic error in the measurement of $R_W(t)$, $R_W(0)$, or R_{W_0}, owing to unaccounted contact resistances, will cancel in the numerator of Eq. (19) although they will remain in the denominator, where they have a small significance. For this reason, it is essential that no contacts in the bridge are altered between the measurement of R_{W_0} and that of $R_W(t)$.

The remaining prime variable determined in a transient hot-wire measurement is the time. It is a straightforward matter to eliminate imprecision in the time base and systematic delays by careful electronic design. Consequently, we need be concerned only with the imprecision related to assigning a specific time to a specific measurement of the temperature rise. Whereas the actual value of the error varies among different instruments, it is always handled in the same way. That is, the error in time is projected into an additional error in the temperature rise by means of a least-squares fitting procedure applied to sets of $\Delta T_{\mathrm{id}}(t_i)$ data in which the t_i are assumed exact. If we denote the additional error in the temperature rise measurements resulting from the timing by $(\delta\Delta T_{\mathrm{W}}/\Delta T_{\mathrm{W}})_t$, then we have, finally, for the total error in the temperature rise measurements, $\delta\Delta T_{\mathrm{W}}/\Delta T_{\mathrm{W}}$

$$\left|\frac{\delta\Delta T_{\mathrm{W}}}{\Delta T_{\mathrm{W}}}\right| \simeq \left|\frac{\delta\Delta T_{\mathrm{W}}}{\Delta T_{\mathrm{W}}}\right|_R + \left|\frac{\delta\Delta T_{\mathrm{W}}}{\Delta T_{\mathrm{W}}}\right|_t \tag{22}$$

3.2 The Thermal Diffusivity

In order to obtain the fundamental working equation for the thermal diffusivity, Eq. (3) is solved for

$$\kappa = \frac{a^2C}{4t'} \exp[4\pi\lambda(T_{\mathrm{r}}, \rho_{\mathrm{r}})\,\Delta T_{\mathrm{id}}(t')/q] \tag{23}$$

where t' is the specific time at which ΔT_{id} is evaluated. In order to obtain κ from the regression line of ΔT as a function of $\ln t$, it can be demonstrated that when $t' = 1$ s, κ_0 can be given by [14]

$$\kappa_0 = \frac{a^2C}{4 \times 1\ \mathrm{s}} \exp(I/S) \tag{24}$$

where I is the intercept of the regression line, $S = q/4\pi\lambda(T_{\mathrm{r}}, \rho_{\mathrm{r}})$ is its slope, and κ_0 refers to the thermal diffusivity at zero-time conditions (bath temperature), that is,

$$\kappa_0 = \kappa(T_0, \rho_0) = \lambda(T_0, \rho_0)/\rho_0(C_{\mathrm{p}})_0$$

with

$$\rho_0 = \rho(P_0, T_0) \tag{25}$$

It is straightforward to carry out the error analysis to yield $\delta\kappa_0/\kappa_0$ and the result is

$$\frac{\delta\kappa_0}{\kappa_0} \simeq 2\left|\frac{\delta a}{a}\right| + \ln\left(\frac{4\kappa_0}{a^2C}\right)\left|\frac{\delta[\Delta T_{\mathrm{W}}(t')]}{\Delta T(t')}\right| + \ln\left(\frac{4\kappa_0}{a^2C}\right)\left|\frac{\delta S}{S}\right| \tag{26}$$

The prescribed time, t', from the foregoing discussion, should be chosen to be around 1 s, to minimize errors.

Collecting together all of the preceding results we find

$$\frac{\delta\kappa_0}{\kappa_0} \cong 2\left|\frac{\delta a}{a}\right| + \ln\left(\frac{4\kappa_0}{a^2C}\right)\left\{\left|\frac{\delta T_s}{\Delta T_W}\right| + \left[\left|\frac{\delta[R_W(t)-R_{W_0}]}{R_W(t)-R_{W_0}}\right| + \left|\frac{\delta\Delta T_W}{\Delta T_W}\right|_t\right]\right.$$
$$\left. + \left|\frac{\delta\alpha}{\alpha}\right| + \left|\frac{\delta S}{S}\right| + \left|\frac{\delta R_{W_0}}{R_{W_0}}\right| + \left|\frac{\delta R_{W_0}}{[R_W(t)-R_{W_0}]}\right|\right\} \tag{27}$$

We may now apply this error estimate to the two measurements considered earlier in the liquid and gaseous phases.

In the liquid-phase instrument $a = 3.5$ μm and the determination of the radius of the wire by electron microscopy leads to $\delta a/a \simeq 0.02$. For the same instrument the statistical estimate of $\delta S/S$ from the linear regression of a set of $\Delta T(\ln t)$ points leads to $\delta S/S \simeq 2 \times 10^{-4}$. Furthermore, the instrument has been designed [20] so that

$$\frac{\delta[R_W(t)-R_{W_0}]}{R_W(t)-R_{W_0}} + \left(\frac{\delta\Delta T_W}{\Delta T_W}\right)_t = 5 \times 10^{-4} \tag{28}$$

a figure confirmed by experiment [20]. Thus, if we assign a value $\delta\alpha/\alpha = 1 \times 10^{-4}$ to the temperature coefficient of resistance of platinum and recall that $\delta T_s/\Delta T_W = 1 \times 10^{-4}$ because of the choice of operating conditions, then the only remaining errors arise from the uncertainties in the absolute value of R_{W_0}. For the liquid-phase instrument considered here $\delta R_{W_0} = 7 \times 10^{-3}\ \Omega$, while $R_{W_0} \cong 250\ \Omega$ and $R_W(t) - R_W(0) \cong 1.8\ \Omega$. We evaluate Eq. (27) retaining the order of terms and inserting appropriate values of κ_0, a, and C. The final estimate for the uncertainty in κ_0 for the absolute measurements is

$$\frac{\delta\kappa_0}{\kappa_0} = 0.04 + 9.5(1 \times 10^{-4} + 5 \times 10^{-4} + 1 \times 10^{-4}$$
$$+ 2 \times 10^{-4} + 3 \times 10^{-5} + 4 \times 10^{-3}) \tag{29}$$

or

$$\frac{\delta\kappa_0}{\kappa_0} = 8.7 \times 10^{-2} \tag{30}$$

That is, the error with which we should be able to obtain the thermal diffusivity is about 9%.

For the general-purpose instrument (gas and liquid phase) $a = 6.57$ μm determined with an error of $\delta a/a = 0.005$, four times smaller than for a

3.5 μm wire. Other differences from the liquid-phase instrument are an accuracy of 1×10^{-3} for the increase in the wire resistance [Eq. (28)]; a wire resistance calibration error, $\delta\alpha/\alpha$, of 2×10^{-4}; a determination of the zero-time resistance error, $\delta R_{\mathrm{W}_0}/R_{\mathrm{W}_0}$, of 1.2×10^{-4}; and an error for the term $\delta R_{\mathrm{W}_0}/[R_{\mathrm{W}}(t) - R_{\mathrm{W}_0}]$ of 4.3×10^{-3}.

A calculation similar to Eq. (29), valid for a moderately dense gas, gives

$$\frac{\delta\kappa_0}{\kappa_0} = 0.01 + 9.4(1 \times 10^{-4} + 1 \times 10^{-3} + 2 \times 10^{-4} + 2 \times 10^{-4} + 1.2 \times 10^{-4} + 4.3 \times 10^{-3}) \tag{31}$$

or

$$\frac{\delta\kappa_0}{\kappa_0} = 6.5 \times 10^{-2} \tag{32}$$

Therefore, the error with which we should be able to obtain the thermal diffusivity in the gaseous phase with this instrument is about 7%.

Because the liquid- and gas-phase instruments chosen as examples yield thermal conductivity data with an uncertainty of ±0.3 and 1%, respectively, it is worthwhile emphasizing the source of the very much larger estimated uncertainty in the thermal diffusivity. First, it is clear that unlike the case of the thermal conductivity, the radius of the wire enters into the evaluation of the diffusivity. The wire radius is difficult to evaluate with a high precision and may indeed vary along the wire length, when it is small. Second, we note that the factor $\ln(4\kappa/a^2C)$ that multiplies the remaining errors is large and amplifies individual errors. This is inevitable if the underlying conditions of the theory are to be met. Of the remaining errors, the dominant contribution arises from the uncertainty $\delta R_{\mathrm{W}_0}/[R_{\mathrm{W}}(t) - R_{\mathrm{W}_0}]$. While it is possible to reduce the uncertainty in the measurement of absolute resistance, it is difficult to do so with a bridge also capable of performing the transient measurements, which is essential to avoid systematic errors. Thus, this single source of error contributes ±4% to the uncertainty in the thermal diffusivity. The remaining contributions to the error in κ_0 are small but equally difficult to reduce.

3.3. Relative Measurements

Some improvement in the accuracy of thermal diffusivity measurements can be achieved by performing relative measurements. Thus, we see from the working equation [Eq. (23)] that for two fluids (or for two states of the same fluid) denoted by the subscripts 1 and 2, the ratio of the two thermal diffusivities is

$$\frac{[\kappa_0]_1}{[\kappa_0]_2} = \exp\left\{\left[\frac{\Delta T_{\mathrm{id}}(t')}{S}\right]_1 - \left[\frac{\Delta T_{\mathrm{id}}(t')}{S}\right]_2\right\} \tag{33}$$

If the thermal diffusivity of one fluid is known accurately under one set of conditions, then the same property may be determined for other fluids as a ratio. The advantages of this arrangement are that some of the errors set out in Eq. (27) are eliminated and only the random errors in the determination of ΔT_{id} and S remain. Thus, it is possible to determine thermal diffusivities with a precision of approximately $\pm 4\%$. The accuracy of the measurements is inevitably worse owing to the error in the reference value of the thermal diffusivity.

Because

$$\kappa = \frac{\lambda}{\rho C_{\mathrm{p}}} \tag{34}$$

the isobaric heat capacity can be obtained from measurements of thermal conductivity and thermal diffusivity with an error comparable to that of the diffusivity itself. While an error in C_{P} of the order of 5% is not the best that can be achieved in favorable circumstances, the current application of the transient hot-wire method permits this modest accuracy to be maintained over a wide range of conditions, including those where other methods have not been applied.

4. EXPERIMENTAL APPLICATION

In order to confirm the analysis presented here, we have carried out measurements with both the liquid [3] and the general-purpose instruments [11] described earlier.

For the liquid phase we have employed the instrument described in Ref. 3, unchanged except for the replacement of the sensing wires and the use of the new bridge measurement described elsewhere [20]. We have used as our reference datum the thermal diffusivity of toluene at a pressure of 0.1 MPa and a temperature of 328.5 K. To construct the reference value we have used the thermal conductivity given by Nieto de Castro et al. [21], the density reported by Kashiwagi et al. [22], and the heat capacity tabulated by Vargaftik [23]. The final value is

$$\kappa_{\mathrm{ref}} = \kappa(P = 0.1\ \mathrm{MPa},\ T = 328.5\ \mathrm{K}) = 8.01 \times 10^{-8}\ \mathrm{m}^2 \cdot \mathrm{s}^{-1}$$

We have carried out transient hot-wire measurements of κ for toluene and *m*-xylene over the temperature range 308 to 360 K and for pressures up to 380 MPa. In particular, for *m*-xylene we have carried out a series of measurements under nominally identical conditions ($T = 307.7$ K, $P = 95$ MPa) to determine the reproducibility of the measurements for comparison with our estimate of their precision. Table I contains the results of this series of measurements; the ratio $[\kappa/\kappa_{\text{ref}}]$ is given, together with an absolute value of κ. The standard deviation over the set of seven measurements is $\pm 2.7\%$, whereas the maximum deviation from the mean is $\pm 4.9\%$. These figures are entirely consistent with the estimate of the precision of the thermal diffusivity measurements for this instrument given earlier.

A similar test has been carried out for the general purpose instrument, using argon as a test material. The instrument is described in Ref. 11, unchanged except for the inclusion of an R-C filter and an operational amplifier across the arms of the bridge, described elsewhere [24]. We have employed as our reference datum the thermal diffusivity of argon at a pressure of 3.548 MPa and a temperature of 200.63 K, obtained from the measured thermal conductivity given by Roder and Nieto de Castro [25], the density and the heat capacity being taken from the equation of state developed by Stewart et al. [26]. The final value is

$$\kappa_{\text{ref}} = \kappa(P = 3.548\ \text{MPa},\ T = 200.63\ \text{K}) = 2.33 \times 10^{-7}\ \text{m}^2 \cdot \text{s}^{-1}$$

The repeated series of measurements of the diffusivity of argon have been carried out at a pressure of 3.548 MPa and a temperature of 200.63 K, and the results are contained in Table II. The standard deviation of the set of κ values from the mean is $\pm 3.3\%$, while the maximum deviation is one of

Table I. The Reproducibility of Thermal Diffusivity Measurements

m-xylene: $P_0 = 95$ MPa; $T_0 = 305.5$ K; $\kappa_{\text{ref}} = 80.1 \times 10^{-9}\ \text{m}^2 \cdot \text{s}^{-1}$

Run No.	$\kappa/\kappa_{\text{ref}}$	κ ($10^{-9}\ \text{m}^2 \cdot \text{s}^{-1}$)
1	1.110	88.9
2	1.088	87.2
3	1.147	91.9
4	1.055	84.5
5	1.080	86.5
6	1.081	86.6
7	1.095	87.7
$\bar{\kappa} \pm \sigma_{\bar{\kappa}}$	1.094 ± 0.029	87.6 ± 2.3

Table II. The Reproducibility of Thermal Diffusivity Measurements

Argon: $P_0 = 3.548$ MPa; $T_0 = 200.63$ K; $\kappa_{\mathrm{ref}} = 233 \times 10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$		
Run No.	$\kappa/\kappa_{\mathrm{ref}}$	$\kappa\ (10^{-9}\ \mathrm{m^2 \cdot s^{-1}})$
7145	0.910	212
7146	0.957	223
7147	0.936	218
7148	0.983	229
$\bar{\kappa} \pm \sigma_{\bar{\kappa}}$	0.947 ± 0.031	221 ± 7

4.1%. These figures are, once again, commensurate with our estimated precision for this instrument.

To complete the present investigation we have performed thermal diffusivity measurements on toluene over the temperature range 308 to 345 K at pressures up to 70 MPa and on argon over the temperature range 172 to 325 K at pressures up to 70 MPa. The results for a sample isotherm of toluene in the form of ratios to the appropriate reference values and the absolute values are contained in Table III. In the case of argon we calculated the thermal diffusivity in both the absolute and the relative method. Table IV presents only the absolute data obtained. No significant differences were found in the values of the thermal diffusivity obtained from the two methods. We expected the use of a relative measurement to improve the accuracy of the data. Since this did not occur, we interpret the result to mean (a) that any existing error in the measurement of the wire radius is very small and (b) that the errors shown in Table IV are random

Table III. The Thermal Diffusivity and Heat Capacity of Toluene

$T_0 = 345.0$ K; $\kappa_{\mathrm{ref}} = 80.1 \times 10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$				
Run No.	P (MPa)	$\kappa \vert \kappa_{\mathrm{ref}}$	κ $(10^{-9}\ \mathrm{m^2 \cdot s^{-1}})$	C_p $(\mathrm{J \cdot kg^{-1} \cdot K^{-1}})$
1	0.1	0.968	77.6	1850
2	4.1	0.955	76.5	1890
3	12.0	0.941	75.4	1960
4	22.9	0.987	79.0	1910
5	37.1	1.042	83.5	1850
6	51.2	0.982	78.7	2010
7	67.5	1.023	81.9	1970

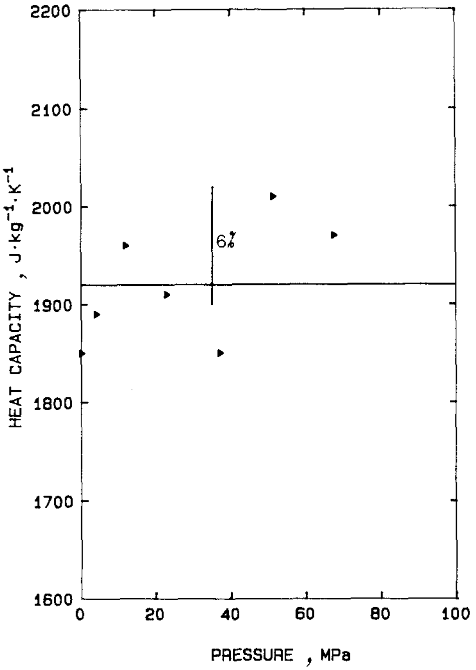

Fig. 4. The isobaric heat capacity of toluene as a function of pressure at a temperature of 345 K. (▶) Present experiment; (——) the value at $P = 0.1$ MPa taken from Vargaftik [23].

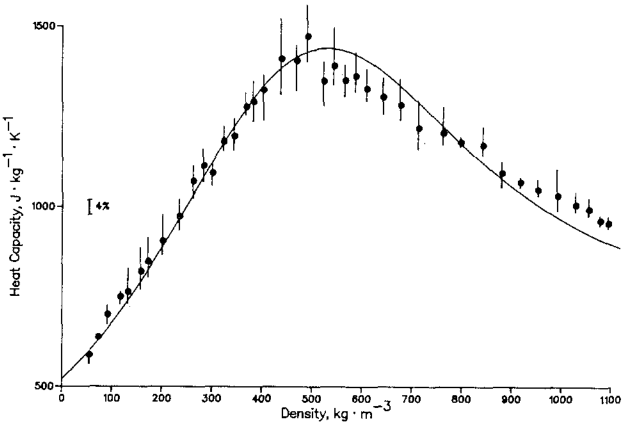

Fig. 5. The isobaric heat capacity of argon as a function of density at a temperature of 200.63 K. (●) Averaged experimental points, with error bars; (——) calculated from the equation of state [26].

Table IV. The Thermal Diffusivity and Heat Capacity of Argon[a]

				$T_0 = 200.63$ K			
Point No.	P (MPa)	ρ $(\mathrm{kg \cdot m^{-3}})$	κ $(10^{-9}\ \mathrm{m^2 \cdot s^{-1}})$	κ_{cal} $(10^{-9}\ \mathrm{m^2 \cdot s^{-1}})$	C_{p} $(\mathrm{J \cdot kg^{-1} \cdot K^{-1}})$	$C_{\mathrm{p_{cal}}}$ $(\mathrm{J \cdot kg^{-1} \cdot K^{-1}})$	$C_{\mathrm{p}}/C_{\mathrm{p_{cal}}}$
1	67.512	1095.12	77.42	82.15	955.2	899.9	1.0615
2	63.757	1078.76	75.60	79.97	962.5	909.3	1.0585
3	58.838	1055.66	71.67	77.07	993.5	923.8	1.0755
4	53.568	1029.23	69.10	73.70	1005.6	942.2	1.0673
5	47.446	992.77	65.40	69.35	1031.0	970.4	1.0625
6	41.871	953.96	62.50	65.28	1048.5	1004.1	1.0443
7	37.327	918.74	59.78	61.53	1069.3	1038.3	1.0298
8	33.467	881.57	57.25	58.10	1094.7	1078.1	1.0154
9	30.067	844.25	52.48	52.48	1173.0	1121.2	1.0462
10	26.797	799.94	51.30	51.50	1181.6	1176.8	1.0041
11	24.539	764.79	49.90	49.18	1206.7	1222.9	.9867
12	21.887	715.06	49.33	46.58	1220.3	1289.6	.9463
13	20.136	678.67	46.58	44.68	1283.7	1335.4	.9613
14	18.738	644.60	45.85	43.53	1305.8	1374.3	.9502
15	17.556	611.39	45.38	42.88	1328.8	1405.4	.9455
16	16.787	589.14	44.30	42.45	1363.0	1421.3	.9589
17	16.124	568.17	44.95	42.35	1351.6	1433.0	.9432

18	15.456	545.57	43.70	42.25	1391.7	1437.4	.9682
19	14.906	525.41	45.58	42.68	1349.3	1438.9	.9377
20	13.990	492.05	42.25	43.43	1473.2	1430.3	1.0300
21	13.447	470.87	44.65	44.23	1406.3	1417.3	.9922
22	12.686	439.79	45.35	45.98	1411.1	1386.9	1.0175
23	11.861	404.92	49.28	48.73	1325.0	1338.2	.9901
24	11.396	384.58	51.25	50.83	1293.7	1303.4	.9926
25	11.016	369.41	52.30	52.48	1297.2	1274.7	1.0035
26	10.484	346.17	57.10	55.73	1198.0	1227.0	.9763
27	10.000	325.34	59.15	59.30	1184.0	1181.2	1.0023
28	9.460	302.38	65.77	63.80	1095.4	1128.3	.9709
29	9.031	284.64	66.45	68.17	1115.5	1086.4	1.0268
30	8.527	264.12	71.40	73.72	1072.5	1037.2	1.0340
31	7.823	236.10	83.17	83.37	973.8	969.8	1.0040
32	6.929	203.17	96.87	98.22	905.3	892.7	1.0142
33	6.107	173.90	114.00	116.75	848.0	826.9	1.0256
34	5.659	158.91	125.25	129.00	821.3	794.5	1.0336
35	4.876	133.25	152.00	156.50	764.7	741.5	1.0314
36	4.392	118.15	169.67	179.00	751.1	711.8	1.0551
37	3.548	92.86	220.50	232.50	701.7	664.7	1.0555
38	2.870	73.60	295.75	299.50	639.5	631.2	1.0131
39	2.240	56.35	408.33	398.67	588.5	602.7	.9765

[a] The root mean square deviation of $C_{p_{\mathrm{exp}}}$ from $C_{p_{\mathrm{cal}}}$ is 4.0%.

and should be attributed to a random error in R_{W_0}. For both fluids the data have been used to derive the isobaric heat capacity of the fluid with the aid of the available density data for toluene [22] and argon [26] and the simultaneously measured values of the thermal conductivity. From Tables III and IV it is estimated that the error in the diffusivity and heat capacity data is ±6% for toluene and ±4% for argon.

Figure 4 contains a plot of the measured heat capacity of toluene as a function of pressure along an isotherm. The same figure includes the value from Vargaftik [23] at atmospheric pressure. It is just possible to discern an increase in the heat capacity with pressure within the uncertainty shown.

Figure 5 displays the heat capacity values given in Table IV in graphical form. Each experimental point shown is an average of four points measured with different powers. The reproducibility for a particular pressure level has already been shown in Table II. The error bars correspond to the variation with power. The line represents the values of the heat capacities calculated from the equation of state [26], with a possible uncertainty of 3% at low and high densities and 5% around the critical density. The root mean square deviation between experimental heat capacities and values derived from the equation of state is 4%, as shown in Table IV. The comparison shows that the variation of C_P with density can be obtained completely with the transient hot-wire technique and that the experimental results obtained agree with those obtained from the equation of state, within their mutual uncertainties. We note, however, that the agreement of ±4% is slightly better than the estimated uncertainty of 7% in Section 3.3.

The extrapolation of the heat capacity values, measured in the absolute way, to zero density yields a C_p^0 of $20.21 \pm 0.96\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$, an accuracy of 4.8%, confirming the accuracy already presented for other isotherms in Ref. 24.

5. CONCLUSIONS

A thorough analysis of the transient hot-wire instrument for the measurement of thermal diffusivity has been given. It has been shown that under favorable conditions an error of 7 to 9% in absolute measurements is almost inevitable, especially when very small wire diameters are used, notwithstanding earlier claims for greatly superior accuracy. If the wire diameter is known very accurately or if relative measurements are made, then the accuracy can be of the order of a few percent and this has been confirmed by direct measurements on two instruments.

Although the transient hot-wire technique at present cannot produce heat capacity values with accuracies achieved by the best available direct experimental techniques, it can be used very easily to advantage in regions of the phase diagram where direct measurements are difficult. Moreover, the accuracy presently achieved with this technique to obtain the heat capacity of fluids is satisfactory for many chemical engineering applications, when no other sources of experimental data are available.

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