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Compression Work Using the Transient Hot-Wire Method

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A new treatment of the effect of the work of compression upon thermal conductivity measurements by the transient hot-wire technique is presented. The new analysis improves upon those given earlier and leads to quite a different result. The result makes it clear that the dilute gaseous state need not be excluded from the range of thermodynamic states in which accurate measurements are made owing to this effect, in contrast to the conclusions of earlier work.

KEY WORDS: dilute gas; thermal conductivity; thermal diffusivity; transient hot wire.

1. INTRODUCTION

The transient hot-wire technique has become established as the method of choice for accurate measurements of the thermal conductivity of fluids over a wide range of thermodynamic states [1]. In this technique the observed temporal history of the temperature rise of a wire, ΔT, subject to an imposed heat flux per unit length, q, is used to determine the thermal conductivity of a fluid, λ, from the equation

$$\Delta T = \frac{q}{4\pi\lambda} \ln \frac{4\kappa t}{a^2 C} \tag{1}$$

in which a is the radius of the wire and κ the thermal diffusivity

$$\kappa = \lambda/\rho\, C_p \tag{2}$$

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Despite the considerable advantages of the technique, two particular regions of state have not proved amenable to study. The first is the neighborhood of the critical region of a pure fluid. Here the large vertical extent of the transient hot-wire cell means that the critical point is sampled by only one location on the wire. Furthermore, the relatively large temperature difference applied ($\Delta T \sim 1$ K) means that the singular dependencies of some of the physical properties of the fluid on temperature render measurement impractical [2].

The second region of state excluded from study is that of the dilute gas. In this case, there are also two reasons for the exclusion. At extremely low densities the continuum hydrodynamics upon which the method is based become inapplicable since the dimensions of the hot wires involved become comparable with the mean-free path of the gas leading to temperature discontinuities at the gas/wire interface [3]. In practice, the densities at which this effect becomes significant are very low ($P \leqslant 0.01$ MPa) and are therefore not a severe limitation [3]. On the other hand, a second effect, that of compressible work, has been found to be of greater significance [3]. This effect arises because the transient heating of a compressible fluid by a central wire causes the expanding gas to do work on the surrounding, cooler gas contained within a finite volume within which the pressure increases [3].

The latter process has been analyzed by Healy *et al.* [3], who derived an approximate expression for the magnitude of the effect on the temperature rise of the wire. The derivation, and therefore the result, was not seen to be sufficiently accurate to permit the application of a correction during measurements. Rather, it was intended to be a guide as to the conditions to be imposed during design and measurement so as to render the effect negligible. Procedures for the verification that the practical instrument satisfied these conditions were proposed [3] and implemented [4]. These procedures replaced an earlier suggestion by Haarman [5] of experimental means to compensate for the effect. In essence, the practical procedures constrained measurements to be performed above a minimum density and in a sufficiently large volume of fluid. Typically, a lower pressure of about 0.6 MPa was found to be suitable [4].

For supercritical temperatures, this constraint proved unimportant because it has been possible to measure the thermal conductivity over a range of pressures (densities) along an isotherm and to determine the limiting dilute gas thermal conductivity by extrapolation [6]. For subcritical temperatures, however, the scope for the application of the same technique is more limited because, for many fluids, the critical pressure is sufficiently low that the total range of densities available for measurement is very restricted and a reliable extrapolation therefore precluded. This is particularly true of the new fluids proposed as replacement refrigerants, which have critical pressures in the range of 3–4 MPa.

Occasionally, measurements have been performed at densities sufficiently low that the effect of compressible work deduced by Healy *et al.* [3] should have been significant, although the results have not been reported in the literature. It was found that the magnitude of the correction given by the result of Healy *et al.* [3] was far greater than that observed in practice. For example, for a typical measurement in argon at 300 K and 0.1 MPa, with an imposed temperature rise of 3 K, the correction according to the result of Healy *et al.* is 0.06 K at a time of 0.1 s and 0.55 K at a time of 1 s. Although deviations from the ideal behavior of the system represented by Eq. (1) have been observed, they have been very much smaller than predicted by the analysis of Healy *et al.* [3].

The present paper is therefore concerned with a reexamination of the effect of compressible work in the transient hot-wire experiment in order to establish a correction which can be applied to measurements performed under appropriate conditions. The results should permit the extension of the range of thermodynamic states to which the experimental technique is applicable and are of current importance.

2. ANALYSIS

2.1. The Ideal Model

The theory of the transient hot-wire technique for the measurement of the thermal conductivity, λ, of a fluid is founded upon an ideal model of the experiment. In the ideal model an infinitely long line source of heat, $q\,(\mathrm{W \cdot m^{-1}})$, is initiated at time $t=0$ in a fluid of infinite extent and constant physical properties. The temperature rise of the fluid at a radial position r from the line source is then given by [1, 3]

$$\Delta T_{\mathrm{id}} = \frac{q}{4\pi\lambda} E_1(\xi) = \frac{q}{4\pi\lambda} \int_\xi^\infty \frac{e^{-x}}{x}\, dx \tag{3}$$

where

$$\xi = r^2/4\kappa t \tag{4}$$

For small values of ξ, such as are easily achieved in practice [3, 4], the expansion of the exponential integral $E_1(\xi)$ may be employed and

$$\Delta T_{\mathrm{id}} \simeq \frac{q}{4\pi} \ln\left(\frac{4\kappa t}{r^2 C}\right) + o\left(\frac{r^2}{\kappa t}\right) \tag{5}$$

where

$$C = \exp(\gamma)$$

and γ is Euler's constant, $\gamma = 0.5772157$.... Thus, measurement of ΔT_{id} as a function of time may be employed to determine λ from the slope of the line relating ΔT_{id} to $\ln t$.

In practice, the line source of heat is provided by a thin (3- to 5-μm radius) metallic wire, fixed at both ends to a support, within which electrical energy is dissipated [1]. The resistance of the wire is used as a monitor of the temperature of the fluid in contact with its surface. Evidently, this arrangement departs from the ideal arrangement in several respects, so that it is necessary to develop corrections to the working equation to account for them. This was performed systematically by Healy *et al.* [3], and subsequently, a number of other effects have been considered [1]. The basis of these analyses has always been that all of the corrections are rendered small enough by design that they can be treated independently. A summary of all known corrections is given elsewhere [1].

One of the deviations from the ideal model that has to be considered arises from the fact that density of the real fluid depends on temperature. In the real instrument this has several consequences, including the development of a vertical velocity component (natural convection). The present analysis is concerned with two other resulting effects: the radial velocity component of the gas and the consequent work of compression. The two effects are treated together because, as will emerge, there is a considerable cancellation of their effects that is not observed if they are treated separately.

2.2. The Effect of Compressibility

2.2.1. A Perfect Gas of Infinite Extent

To derive the correction we consider the situation in which an infinitely long line source of heat is placed at the center of a radial coordinate system (r, θ, z) within an infinite fluid for which all thermophysical properties are constants except the density, which obeys the perfect gas equation of state,

$$P = \rho R T \tag{6}$$

In these circumstances, owing to the symmetry of the problem, the hydrodynamic conservation equations may be written as follows:

for mass,

$$\frac{1}{P}\frac{\partial P}{\partial t}-\frac{\beta}{T}\frac{\partial T}{\partial t}+v\left[\frac{1}{P}\frac{\partial P}{\partial r}-\frac{\beta}{T}\frac{\partial T}{\partial r}\right]+\frac{1}{r}\frac{\partial}{\partial r}(rv)=0 \tag{7}$$

for momentum,

$$\frac{\partial v}{\partial t}+v\frac{\partial v}{\partial r}=-\frac{RT}{P}\frac{\partial P}{\partial r}+\frac{\nu}{r}\frac{\partial}{\partial r}\left(r\frac{\partial v}{\partial r}\right) \tag{8}$$

and for energy,

$$\frac{\partial T}{\partial t}+v\frac{\partial T}{\partial r}=\frac{\lambda}{\rho C_{\mathrm{p}}}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right)+\frac{\beta}{\rho C_{\mathrm{p}}}\left[\frac{\partial P}{\partial t}+v\frac{\partial P}{\partial r}\right] \tag{9}$$

Here

$$\beta=\left[\frac{\partial \ln(1/\rho)}{\partial \ln T}\right]_P \tag{10}$$

so that

$$\beta=1$$

for a perfect gas, and

$$\nu=\mu/(\rho M) \tag{11}$$

is the kinematic viscosity, where M is the molecular weight of the gas.

In order to derive the required correction, it is necessary to find the difference between the temperature rise of the fluid in the ideal case and that given by the solution of Eqs. (7) to (9) subject to the initial conditions

$$\left.\begin{aligned} &T=T_0\\ &P=P_0\\ &v=0\\ &\rho=\rho_0=P_0/RT_0\end{aligned}\qquad t<0 \text{ for all } r\right\} \tag{12}$$

the boundary conditions

$$T=T_0, \qquad r\to\infty \text{ for all } t \tag{13}$$

and

$$v=0, \qquad r=0 \text{ for all } t$$

$$\lim_{r\to 0} r\frac{\partial T}{\partial r}=-\frac{q}{2\pi\lambda}, \qquad t\geqslant 0 \tag{14}$$

To proceed we make all variables dimensionless and of order unity and seek a perturbation solution for the temperature rise about that of the ideal model.

At first sight, it might seem that the natural perturbation parameter would be β because, when $\beta = 0$, the problem reduces to that for an incompressible fluid. However, this is not appropriate since $\beta \not\ll 1$. Accordingly, the only possible perturbation parameter is a dimensionless heat flux $\delta = q/\lambda T_0$.

The next problem concerns the estimation of the order of magnitude of the temperature change, the pressure change, and the velocity, v. With the exception of the temperature change the magnitudes cannot be known *a priori*, and it is necessary to try a number of possibilities to establish that combination which is internally consistent, that is, where the final perturbation sought is small compared with the unperturbed under all circumstances. The only combination that secures this result is to use a dimensionless temperature rise,

$$\theta = \frac{T - T_0}{q/\lambda}$$

and to assume that the perturbation to the temperature rise in the case of the compressible fluid is of order δ, so that

$$\theta(r, t) = \theta_0(r, t) + \theta_1(r, t)\,\delta \tag{15}$$

where $\theta_0(r, t)$ is the solution of the incompressible fluid problem of Eq. (3),

$$\theta_0 = \Delta T_{\mathrm{id}}/(q/\lambda) = \frac{1}{4\pi} E_1(r^2/4\kappa t) \tag{16}$$

For the dimensionless velocity we employ

$$v^* = v r_1/\nu \tag{17}$$

where r_1 is a characteristic length in the problem (the wire radius in practice). We then assume that v^* is also of order δ so that

$$v^* = \phi\delta \tag{18}$$

For the pressure we use the dimensionless form

$$\pi = \left(\frac{P - P_0}{P_0}\right) \Big/ \delta^2 \tag{19}$$

which is of second order in δ. Finally, for the dimensionless radial coordinate we use $\sigma = r/r_1$, and for time $t^* = \alpha t/r_1^2$. We now further assume, following Healy *et al.* [3], that radial variations in the pressure on the time scale of the measurements (0.1 − 1 s) are very small, having been eliminated by the transmission of sound waves. In fact, it is only necessary to assume that $\partial P/\partial r \sim \delta^3$ for the following analysis to be valid. In addition, because the principal effects of the dependence of the density or temperature have now been incorporated, we use $\rho = \rho_0$ (a constant) wherever it still occurs in the energy equation.

We now substitute Eqs. (15), (18), and (19) into the conservation Eqs. (7)–(9), expand to order δ^3, and equate the terms of order δ and δ^2 independently.

To order δ we find for the mass conservation equation

$$-\beta \frac{\partial \theta_0}{\partial t^*} = -\frac{\Pr}{\sigma} \frac{\partial(\sigma\phi)}{\partial \sigma} \tag{20}$$

where Pr is the Prandtl number $\Pr = (\mu C_p/\lambda M)$, and to order δ^2 we find

$$\frac{\partial \pi}{\partial t^*} + \beta\theta_0 \frac{\partial \theta_0}{\partial t^*} - \beta \frac{\partial \theta_1}{\partial t^*} - \beta \Pr \phi \frac{\partial \theta_0}{\partial \sigma} = 0 \tag{21}$$

To neither of these orders is the momentum equation significant so that for the energy equation we find to order 1

$$\frac{\partial \theta_0}{\partial t^*} = \frac{1}{\sigma} \frac{\partial}{\partial \sigma}\left(\sigma \frac{\partial \theta_0}{\partial \sigma}\right) \tag{22}$$

and to order δ

$$\frac{\partial \theta_1}{\partial t^*} + \Pr \phi \frac{\partial \theta_0}{\partial \sigma} = \frac{1}{\sigma} \frac{\partial}{\partial \sigma}\left(\sigma \frac{\partial \theta_1}{\partial \sigma}\right) + \frac{\beta R}{C_p} \frac{\partial \pi}{\partial t^*} \tag{23}$$

The solution of Eq. (22) subject to the initial condition

$$\theta_0 = 0, \qquad t^* < 0 \text{ for all } \sigma$$

and the boundary conditions

$$\theta_0 = 0, \qquad r \to \infty \text{ for all } t$$

and

$$\lim_{\sigma \to 0} \sigma \frac{\partial \theta_0}{\partial \sigma} = -\frac{1}{2\pi}$$

is of course Eq. (16) so that this enables Eq. (20) to be integrated to find ϕ, the dimensionless velocity, which is

$$\phi=\frac{\beta}{2\pi \mathrm{Pr}}\left[1-e^{-\sigma^2/4t^*}\right]\frac{1}{\sigma} \tag{24}$$

after application of the boundary condition $\phi=0$ at $\sigma=0$. We note here that, although no boundary condition on ϕ as $\sigma \to \infty$ has been imposed, $\phi \to 0$ in this limit.

This result for ϕ can be employed to eliminate ϕ from Eqs. (21) and (23) and, from the pair, $\partial\pi/\partial t^*$ can be eliminated by subtraction. This leads to a partial differential equation for θ_1,

$$\begin{aligned}\frac{\partial\theta_1}{\partial t^*}\{1-\varepsilon\}-\frac{1}{\sigma}\frac{\partial}{\partial\sigma}\left(\sigma\frac{\partial\theta_1}{\partial\sigma}\right)\\ = -\frac{\varepsilon}{4\pi}E_1\left(\frac{\sigma^2}{4t^*}\right)\frac{1}{4\pi t^*}e^{-\sigma^2/4t^*}+\frac{\beta}{2\pi\sigma}\\ \times(1-e^{-\sigma^2/4t^*})\frac{1}{2\pi\sigma}e^{-\sigma^2/4t^*}(1-\varepsilon)\end{aligned} \tag{25}$$

in which we have written

$$\varepsilon=\frac{\beta^2 R}{C_{\mathrm{p}}} \tag{26}$$

for convenience and used the known result for θ_0.

This equation can readily be solved by the use of the similarity variable $\xi=\sigma^2/4t^*$ and we find the correction, θ_1, as

$$\begin{aligned}\theta_1(\xi)= -\frac{1}{16\pi^2}\left\{\int_\xi^\infty \frac{E_1[(1+\varepsilon)z]\,e^{-(1-\varepsilon)z}[1-(1-\varepsilon)\beta]}{z}dz\right.\\ -\int_\xi^\infty\frac{e^{-z}E_1(z)}{z}dz+\int_\xi^\infty\frac{(1-\varepsilon)\beta E_1(\varepsilon z)\,e^{-(1-\varepsilon)z}}{z}dz\\ \left.+\left[\ln(1+\varepsilon)+(1-\varepsilon)\beta\ln\left(\frac{\varepsilon}{1+\varepsilon}\right)\right]\int_\xi^\infty\frac{e^{-(1-\varepsilon)z}}{z}dz\right\}\end{aligned} \tag{27}$$

by application of the boundary conditions $\theta_1(\infty)=0$ and $\mathrm{Lim}_{\sigma\to 0}\,\sigma\,\partial\theta_1/\partial\sigma=0$. The second and fourth of these integrals may be evaluated analytically in terms of defined functions, but the other two may not. However, we merely require an expansion of the result for small values of ξ. Such an expansion can be derived provided that the four integrals on the RHS of Eq. (27) are combined into one. It can be shown [7] that the expansion leads to

$$\theta_1(\xi) = \frac{-1}{16\pi^2}\{A + \varepsilon\xi \ln \xi + (\beta - \varepsilon\beta - 2\varepsilon + \varepsilon\gamma)\,\xi + o(\xi^2 \ln \xi)\} \tag{28}$$

where γ is Euler's constant, and

$$A = \beta(1-\varepsilon)\left\{G\left(\frac{1+\varepsilon}{1-\varepsilon}\right) - G\left(\frac{\varepsilon}{1-\varepsilon}\right)\right\} - G\left(\frac{1+\varepsilon}{1-\varepsilon}\right) - \frac{1}{2}[\ln(1-\varepsilon)]^2 \tag{29}$$

with

$$\left.\begin{aligned} G(\tau) &= \int_\tau^1 \frac{\ln(1+x)}{x}\,dx \\ G(0) &= \frac{\pi^2}{12} \\ G(\tau) &= -G(1/\tau) - \frac{1}{2}(\ln \tau)^2 \end{aligned}\right\} \tag{30}$$

The function $G(\tau)$ is readily evaluated by numerical quadrature.

Thus, the difference between the temperature rise of the fluid and that for an incompressible fluid, which arises from the combined effects of radial convection and compression work, is

$$\delta T_c = \Delta T_{id}(r, t) - \Delta T(r, t) \tag{31}$$

so that for this infinite perfect gas,

$$\delta T_c(r, t) = +\left(\frac{q}{4\pi\lambda}\right)^2 \frac{1}{T_0}\left[A + \varepsilon\frac{r^2}{4\kappa t}\ln\frac{r^2}{4\kappa t}\right] \tag{32}$$

to leading order. Thus, in a practical thermal conductivity cell with a heat source of finite radius a, the correction to be applied to the measured temperature rise of the wire to recover the temperature rise of the ideal model is

$$\delta T_c(a, t) = \left(\frac{q}{4\pi\lambda}\right)^2 \frac{1}{T_0}\left[A + \frac{\varepsilon a^2}{4\kappa t}\ln\frac{a^2}{4\kappa t}\right] \tag{33}$$

2.2.2. A Perfect Gas of Finite Extent

If the perfect gas is of finite extent, bounded internally by a solid wall of radius a, acting as the heat source, and externally by a solid wall of radius b, both of length L, with $b/a \gg 1$, the preceding analysis cannot be carried through in its entirety. This is because it is not possible to use the similarity variable $\xi = \sigma^2/4t^*$ to solve the equivalent of Eq. (25). Thus, to examine this case we have solved Eqs. (7)–(9) numerically subject to the initial conditions

$$P = P_0, \qquad T = T_0, \qquad v = 0, \qquad t \leqslant 0 \text{ for all } r \tag{34}$$

and the boundary conditions

$$v = 0 \text{ at } r = a, \qquad r = b \text{ for all } t \tag{35}$$

and

$$2\pi a \left| \frac{\partial T}{\partial r} \right|_{r=a} = \frac{-q}{\lambda} \tag{36}$$

The numerical solution has been obtained by casting the equations and boundary and initial conditions in finite-difference form. Radial derivatives are replaced by central differences, with 18 nonuniform mesh steps: the mesh is smaller near the inner radius (the wire), where gradients are largest. Time derivatives are replaced by backward differences with a time step of 5×10^{-8} s, leading to an implicit set of equations which are solved by successive overrelaxation [8], with an overrelaxation parameter of 1.2. This yields the correction δT_c defined by Eq. (31) and evaluated at $r = a$. It should, however, be noted that the correction δT_c is extremely small compared with the temperature difference ΔT_{id}, as shown in Section 3. Thus, the numerical solution is likely not to be very accurate. Since the purpose of obtaining the numerical solution is, however, only to show that δT_c is no larger (to within an order of magnitude) in the finite case than in the infinite case, this inaccuracy is of no real consequence.

3. RESULTS

In order to examine the magnitude of the correction δT_c for both finite and infinite perfect gases, we consider just the example of measurements in argon at $P_0 = 0.1$ MPa, $T_0 = 300$ K. For a transient hot-wire cell equipped with a heat source of radius $a \simeq 3.8$ μm, the heat input required is of the order of $q \simeq 0.05$ W $\cdot$ m^{-1}. The properties of argon under the conditions of interest are $\lambda \simeq 20$ mW $\cdot$ m^{-1} $\cdot$ K^{-1}, $\rho \simeq 40$ mol $\cdot$ m^{-3}, $C_p = 5/2\, R$, so that $\kappa \simeq 2.5 \times 10^{-5}$ m^2 $\cdot$ s^{-1}, and $\varepsilon = 2/5$.

Inserting these values into Eqs. (6) and (32) we find the results listed in Table I for ΔT_{id} and δT_c at a selection of times during the course of a measurement for a gas of infinite extent. The same table includes the results obtained from the numerical solution of the case of the finite perfect gas

Table I. The Magnitude of the Correction δT_c for a Typical Measurement in Argon at a Pressure of 0.1 MPa and a Temperature of 300 K

		Present result		
		Perfect gas of infinite extent	Perfect gas of finite extent	Result of Healy *et al.* [3]
Time, t(s)	ΔT_{id} (K)	δT_c (K)	δT_c (K)	δT_c (K)
0.1	2.56	5.3520×10^{-6}	6.450×10^{-6}	0.06
0.5	2.88	5.3525×10^{-6}	1.487×10^{-7}	0.27
1.0	3.02	5.3529×10^{-6}	7.628×10^{-8}	0.55

with outer radius $b = 5 \times 10^{-3}$ m. It is clear that in both cases δT_c is extremely small ($\leqslant 2 \times 10^{-5}$ K) and therefore negligible by comparison with ΔT_{id}. As mentioned earlier, the differences between the analytic solution of the infinite fluid and the numerical solution for the finite fluid are not significant in the context of the present analysis beyond the demonstration that the effect in the latter case is clearly *not* much larger than in the former case. Furthermore, the time dependence of the correction is very small; for the case of an infinite fluid the correction changes by less than 1×10^{-9} K, from 0.1 to 1 s. This last observation follows from the fact that within Eq. (33), $A \gg (\varepsilon a^2/4\kappa t) \ln a^2/4\kappa t$. It is also worthy of note that the results for the finite case are essentially the same, within the limits of error of the numerical solution, as those for the infinite case. The analysis in Section 2.2.1 shows that this is because the principal effect arises not from the pressure increase in the gas but from the expansion of the gas at essentially constant pressure and that, because the velocity of the gas is small for large r, there is essentially no difference between the radial velocity profile in the finite and that in the infinite case.

The consequences of these results for measurements with the transient hot-wire technique are significant because it is clearly possible to neglect the compression-work effect completely for both thermal-conductivity and thermal-diffusivity determinations [1].

3.1. A Comparison with an Earlier Result

The analysis of nominally the same effect by Healy *et al.* [3] leads to quite a different result, namely,

$$\delta T_c = \frac{qLR_t}{\rho C_p C_v V} \tag{37}$$

where $V = \pi(b^2 - a^2) L$ is the (finite) volume of the container. Table I includes the values of this correction for the same example of a measurement in argon. The result given by Eq. (37) is five orders of magnitude larger than that which is obtained from the present analysis. Since the present result is more consistent with experimental observation, it is necessary to establish the cause of the discrepancy. Indeed, the discrepancy is severe because, whereas the present result decays with time and increases with fluid density, the result of Healy *et al.* has completely opposing behavior.

Healy *et al.* solved an energy equation containing only the compression work term, i.e.,

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho C_p} \frac{1}{r} \left(r \frac{\partial T}{\partial r} \right) + \frac{\beta}{\rho C_p} \frac{\partial P}{\partial t} \tag{38}$$

Thus, they neglected the radial convection of heat contained in the term $v\, \partial T/\partial r$ of Eq. (9), which they treated in a separate analysis. The present result indicates that it is inconsistent to ignore the term $v\, \partial T/\partial r$ in the energy equation since it is of the same order as the compression work term but of the opposite sign. The magnitude of the term can be attributed to the fact that whereas v, the radial velocity, is very small, the temperature gradients is very large ($\sim 10^6\ \mathrm{K \cdot m^{-1}}$). It seems therefore that the analysis of Healy *et al.* [3] neglects a significant cancellation which occurs among the terms of the complete energy equation and therefore greatly overestimates the effect.

4. CONCLUSION

The effects of compression work in the transient hot-wire technique have been shown to be negligible. Thus, measurements under a range of thermodynamic states precluded from study by the technique hitherto may now be carried out.

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