International Journal of Thermophysics, Vol. 15, No. 1, 1994

Application of the Transient Hot-Wire Method to Gases at Low Pressures

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Received June 10, 1993

The need to determine the thermal conductivity of non-ozone-depleting refrigerants implies measurements at pressures below 10 bar in the gaseous phase. In order to apply the transient hot-wire method with proven accuracy to this state, possible sources of systematic errors in the measurements have been carefully assessed theoretically and experimentally. The influence of the finite heat capacity of the hot wire and of the isothermal outer wall of the cell have been identified to affect the measurements substantially. An improved correction method to account for the wire heat capacity is presented, as well as criteria to choose the parameters in the experiments in order to avoid errors due to the outer boundary and due to the finite wire length. The results are presented in dimensionless quantities, and as an example, they are discussed for argon.

KEY WORDS: argon; low pressure; refrigerants; thermal conductivity; transient hot-wire method.

1. INTRODUCTION

The thermal conductivity in the limit of zero density contains most of the temperature dependence of the fluid region, as experience with the residual concept shows [1–4]. Therefore, accurate measurements in the gas phase are crucial for the entire thermal-conductivity surface. The importance of such experiments justifies another assessment of errors when the transient hot-wire method at low pressures is used.

The transient hot-wire method is widely used to determine thermal conductivities of gases and liquids with an accuracy down to $\pm 0.3\%$ [5]. Yet investigations in the gas phase in the range below 10 bar have been avoided so far because experiments indicated a loss of accuracy. More-

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0195-928X/94/0100-0141$07.00/0

over, in supercritical gases such as argon, nitrogen, and oxygen, the measurements at low pressures contained information which could be substituted by a linear extrapolation of the thermal conductivity measured at the same temperature but at higher pressures [2, 3, 6]. This procedure fails for refrigerants, because the technically interesting range is at subcritical temperatures, where the saturation line imposes an upper limit to the pressure, which is partly below 10 bar. The need to investigate refrigerants motivates this paper. Argon was chosen as the sample fluid because its behavior is well-known from kinetic theory.

Former investigations suspected the compression work to cause an error at low pressures [7]. According to a recent extensive analytical and numerical study [8], the magnitude of the compression work is negligibly small. In this paper detailed measurements of the transient temperature rise at low and high pressures over an extended time interval are presented in order to describe the experimental phenomena. Three error sources are employed to explain the behavior: the influence of the isothermal outer boundary, of the axial end effects, and of the heat capacity of the hot wire.

2. EFFECTS AT THE OUTER BOUNDARY

The working equation for the transient hot-wire method was derived assuming a line source in an incompressible fluid of infinite extent and constant physical properties [9]. The temperature rise ΔT_{id} at any time t at the wire surface $r = r_w$,

$$\Delta T_{id}(r_w, t) = \frac{\dot{q}}{4\pi\lambda} \ln\left(\frac{4at}{Cr_w^2}\right) \tag{1}$$

depends linearly on $\ln(t)$ with the slope $\dot{q}/4\pi\lambda$, where $\dot{q}$ stands for the heat generated per unit length, λ for the thermal conductivity; and a for the thermal diffusivity, and $C = 1.7811$ is derived from the Euler constant. Any deviation from the linear relationship indicates error sources in the experiments. In practice, the line source is approximated by a very thin metallic wire, which is suspended in a hollow cylinder, the cell. The characteristic data for our experimental set up are as follows.

Wire radius:	$r_w = 4.0\ \mu m$
Cell radius:	$r_c = 6.0$ mm
Time interval:	$t = 0.002\ s \cdots 1\ s$
Sampling rate:	$f = 303$ Hz
Temperature rise:	$\Delta T(t = 1\ s) = 2$ K

The temperature gradient at the surface of the wire is very steep, therefore, the temperature rise affects, in most cases, only the fluid close to the wire.

The higher the thermal diffusivity of the fluid, however, the more the temperature field extends in the radial direction. In fact, the thermal diffusivity of a gas is inversely proportional to the pressure and rises strongly at low pressures as Fig. 1 shows for argon at the temperatures 275, 320, and 380 K. The thermal diffusivity was calculated as $a = \lambda/(\rho c_p)$ using the thermal conductivity λ from measurements [10], and the density ρ and the isobaric specific heat capacity c_p from an equation of state [11]. The higher the temperature of the gas, the greater is the thermal diffusivity at a given pressure, and the influence of the outer boundary grows.

When the transient temperature field expands radially toward the isothermal wall of the measurement cell, a steady state can be reached for sufficient long times. In fact, this is the principle of the steady-state hot-wire method. The temperature in the steady-state ΔT_∞ depends on the heat generation and the thermal conductivity as well as on the radius of the wire and the cell [9],

$$\Delta T_\infty = \frac{\dot{q}}{4\pi\lambda} \ln\left(\frac{r_c}{r_w}\right)^2 \tag{2}$$

In order to investigate the behavior at low pressures we measured the temperature rise over an extended time interval of 10 s for three pressures in argon at 320 K, which are plotted in Fig. 2. At first there is a linear increase in the temperature-versus-logarithmic time relationship for all three runs, followed by a transition region, and then a steady state is observed. The measured temperature rises (symbols) are compared with a fit of the linear region (lines). For argon at 5 bar (circles) and at 50 bar (crosses) the transition starts outside the usually evaluated time interval of 1 s. In argon at

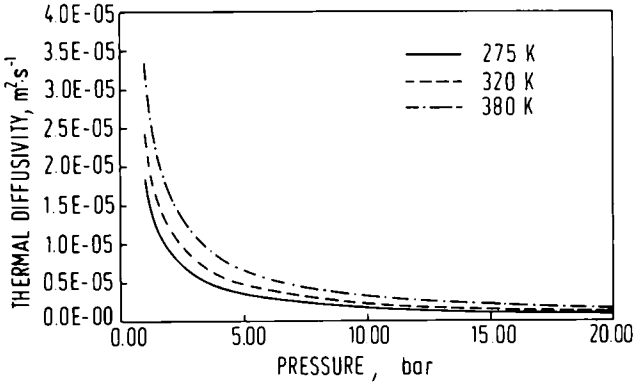

Fig. 1. Thermal diffusivity of argon versus pressure at different temperatures.

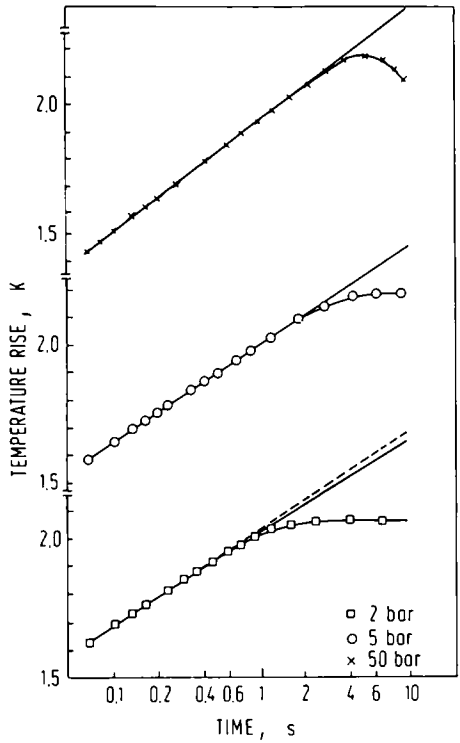

Fig. 2. Measured temperature rises (symbols) at three pressures in argon at 320 K compared with the linear fit of the region up to 1 s (solid lines) and with the fit of the truly linear region at 2 bar (dashed line).

2 bar (squares) the beginning of the transition to constant temperature falls into the time interval of a transient measurement. The slope of the usually evaluated region up to 1 s (solid line) is lower than in the truly linear region, which is denoted by the dashed line in Fig. 2. Thus, the thermal conductivity, which is inversely proportional to the slope, would appear greater. Indeed, a higher thermal conductivity at low pressures was observed in our experiments with refrigerants, nitrogen and argon. The upper curve in Fig. 2 denotes the experiment at 50 bar (crosses). The linear region is followed by a maximum in temperature and then there is a decline. At high pressures we obviously have a different behavior at long times, which is discussed later. The three runs can be compared better when only the deviations from the linear fit are plotted lineary versus time as shown in Fig. 3. The zero line denotes the linear region. For the 2-bar measure-

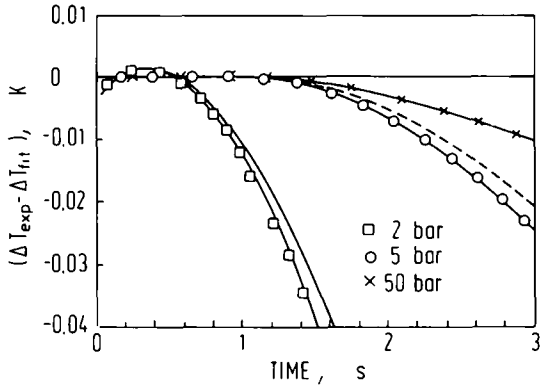

Fig. 3. Deviation from the straight-line fit in argon at different pressures versus time to illustrate the influence of the outer boundary: experiments (symbols) compared with the theory (solid line, 2 bar; dashed line, 5 bar).

ment (squares) a small curvature can be identified even before the transition. The transition is said to start where deviations are greater than 2 mK or 0.1 % of the temperature rise, which is at 0.64 s. For 5 bar (circles) the linear region is perfect and at 1.55 s the measured temperature rises deviate markedly from the fit, whereas for 50 bar (crosses) a systematic departure occurs at 1.8 s. The lines are discussed in the next section. The lower the pressure, the earlier a deviation from the linear region is detected. The trend is consistent with the influence of the outer boundary due to growing thermal diffusivity.

The tools to calculate the temperature rise considering an isothermal outer boundary are listed in a comprehensive study by Healy et al. [9], and we use their results. The exact solution has to be evaluated numerically [12], but for the chosen wire and cell diameter and the time scale employed in the experiments, a series expansion [13] is recommended. We checked it with regard to the low-pressure properties, and indeed, it approximates the exact solution very well and is easier to handle. The temperature rise at the wire surface in the transition region is [9]

$$\Delta T(r_w, t) = \frac{\dot{q}}{4\pi\lambda}\left\{2\ln\left(\frac{r_c}{r_w}\right) - \sum_{n=1}^{\infty} \exp(-g_n^2\,\mathrm{Fo})[\pi Y_0(g_n)]^2\right\} \qquad (3)$$

The first term in parentheses denotes the steady-state temperature; the summation term describes the time-dependent transition using the Fourier number Fo

$$\mathrm{Fo} = at/r_c^2, \qquad (4)$$

the Bessel series Y_0, and the roots g_n of the Bessel series $J_0(g_n) = 0$ [9, 13]. Equation (3) holds under the assumption that $r_w g_n/r_c \ll 1$, which is fulfilled for small eigenvalues g_n. One can show [13] that for small eigenvalues the term $r_w g_n/r_c$ is of the order 10^{-4} to 10^{-3}. The results generated with Eq. (3) for two argon runs are included in Fig. 3 as lines. For 2 bar (solid) and 5 bar (dashed) the calculated deviation from the straight-line fit is slightly smaller than the measured one. It is, however, noteworthy that the outer boundary influence predicts the changeover within the uncertainty of the experiments. For 50 bar the calculated changeover due to the outer boundary is after 20 s and therefore not visible in Fig. 3. The transition to steady state at such high pressures is due to natural convection rather than to the outer boundary.

From the comparison it can be concluded that the behavior at low pressures can be explained with the isothermal boundary in the radial direction. The outer boundary correction derived from Eq. (3) by Healy et al. [9] is applicable to allow a modest extension of the linear range, and we support their recommendation that it should not amount to more than 0.02 K or 1% of the temperature rise. However, we feel that measurements become less reliable at low pressures when a large part of the measured temperature rise has to be corrected, at short times due to the heat capacity of the hot wire as discussed in the next section and at longer times due to the outer boundary influence. Therefore, we propose a more rigorous design criterion compared with that of Healy et al. to avoid any correction at all. For existing instruments which are not designed for experiments at low pressures, we derive the limit in pressure, where the outer boundary influence can be neglected altogether.

From Eq. (3) the dimensionless difference δT_s of the wire temperature and the steady-state temperature can be derived, which depends only on the Fourier number

$$\delta T_s(\mathrm{Fo}) = 4\pi\lambda\, \Delta T(r_w, t)/\dot{q} - 2\ln(r_c/r_w) = -\sum_{n=1}^{\infty} \exp(-g_n^2 \mathrm{Fo})[\pi Y_0(g_n)]^2 \tag{5}$$

The deviation from steady-state δT_s is plotted in Fig. 4 versus the Fourier number on a logarithmic scale. At small Fourier numbers it shows a linear increase, then there is a change in slope and the transition to zero deviation from steady state. The linear dependence is denoted by the dimensionless difference of ideal temperature rise and steady-state temperature derived from Eqs. (1) and (2),

$$\delta T_{id} = 4\pi\lambda\, \Delta T_{id}/\dot{q} - 2\ln(r_c/r_w) = \ln(4\,\mathrm{Fo}/C) \tag{6}$$

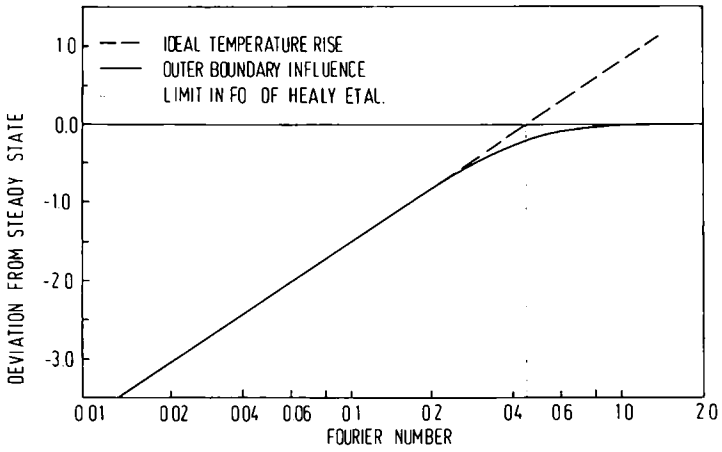

Fig. 4. The transition to steady state due to the outer boundary in dimensionless parameters versus Fourier number and comparison with ideal temperature rise and limit in Fo according to Healy et al. [9].

illustrated as a dashed line in Fig. 4. The design criterion of Healy et al. [9] is the Fourier number $Fo_{hea} = C/4 = 0.445$, where the linear increasing ideal temperature is as high as the steady-state temperature. It is shown by the vertical dotted line in Fig. 4 and already falls into the changeover and makes a small correction necessary. There is no difference between the solid and the dashed line below the limiting Fourier number

$$Fo_{lim} \leqslant 0.20 \tag{7}$$

which means that the influence of the outer boundary is less than 0.1 % of the temperature rise and can be safely neglected. For an existing instrument with a given cell radius, this criterion leads to an upper limit in thermal diffusivity $a \leqslant Fo_{lim}\, r_c^2/t$ and therefore to a lower pressure limit. For our instrument we obtain $a \leqslant 7.2 \times 10^{-6}\ m^2 \cdot s^{-1}$, corresponding to a pressure $p \geqslant 2.6$ bar at 275 K, $p \geqslant 3.4$ bar at 320 K, and $p \geqslant 4.7$ bar at 380 K in argon.

If a new instrument is to be designed, the cell radius can be determined with the aid of Eq. (7), so that there is a negligible influence of the outer boundary even at low pressures; for example, a good measurement at 1 bar and 380 K in argon with $a = 3.3 \times 10^{-5}\ m^2 \cdot s^{-1}$ would require a cell radius of 13 mm.

The low-pressure results in refrigerants of several transient hot-wire instruments with different cell sizes have been compared. The instrument at NIST, Boulder, Colorado, with $r_c = 4$ mm shows a pronounced apparent

increase in λ at higher temperatures [14], our instrument with $r_c = 6$ mm showed an apparent increase to a lesser extent, and the apparatus of Gross et al. [15] with $r_c = 13.5$ mm did not show any increase at all. This observation supports the findings in this paper.

3. HEAT-CAPACITY CORRECTION

The energy supplied to the hot wire is initially used to heat up the wire itself, and is not transfered to the fluid. Therefore, the measured temperature rise at the beginning of the transient heating is lower than predicted from the model. The finite heat capacity of the wire has always caused the largest correction in the transient hot-wire method. In turn, very thin wires must be used. The finest wires available and suitable for the technique are made of platinum. The magnitude of the correction increases the lower the density of the fluid, which may be expressed by the ratio α,

$$\alpha = 2\rho c_p/(\rho c)_w \tag{8}$$

of the heat capacity per unit volume of the fluid to that of the wire [12]. The ratio α for a gas is lower than for a liquid. In gases at low pressures the approximate heat capacity correction given by Healy et al. [9] exceeds the maximal recommended magnitude of about 1% in temperature rise, and an error of more than 0.1% in ΔT would be introduced. To maintain a small uncertainty even when the correction amounts to about 3% of the temperature rise, the correction given by the above-mentioned authors was modified.

The exact solution for the coupled system of wire and fluid is given by Carslaw and Jaeger [12] and reads, for $r = r_w$,

$$\Delta T(r_w, t) = \frac{\dot{q}\alpha}{2\pi\lambda}\frac{1}{2\pi i}\int_{-\infty}^{0^+} \frac{\exp(ut)}{u}\frac{K_0(r_w\mu)}{r_w^2\mu^2 K_0(r_w\mu) + \alpha r_w \mu K_1(r_w\mu)}\,du \tag{9}$$

where $\mu^2 = u/a$. It contains the Bessel series K_0 and K_1 as an integrand and can be evaluated only numerically. For the parameters of a hot-wire instrument, a series expansion [12] is possible which leads to an approximate analytical expression. We employed one more term of the both Bessel series than before,

$$K_0(r_w\mu) = -\ln\left(\frac{r_w\mu C}{2}\right) + \left(\frac{r_w\mu}{2}\right)^2\left\{1 - \ln\left(\frac{r_w\mu C}{2}\right)\right\} + \frac{1}{4}\left(\frac{r_w\mu}{2}\right)^4\left\{\frac{3}{2} - \ln\left(\frac{r_w\mu C}{2}\right)\right\} \tag{10}$$

$$r_w \mu K_1(r_w \mu) = 1 + \ln\left(\frac{r_w \mu C}{2}\right)\left\{\frac{(r_w \mu)^2}{2} + \frac{(r_w \mu)^4}{16}\right\} - \frac{(r_w \mu)^2}{4}\left\{1 + \frac{5}{16}(r_w \mu)^2\right\} \tag{11}$$

In the integrand we kept terms up to r_w^4 and α^2 for the series expansion and conducted a termwise inverse Laplace transformation. The following modified formula for the heat-capacity correction was derived:

$$\delta T_1 = \frac{\dot{q}}{4\pi\lambda}\frac{r_w^2}{2at}\left[\left(\frac{2}{\alpha} - 1\right)\ln\frac{4at}{r_w^2 C} - 1 - \frac{r_w^2}{8at}\left(\frac{\pi^2 - 1}{2} + \frac{2\pi^2}{\alpha^2}(1-\alpha)\right) - \frac{r_w^2}{8at}\ln\frac{4at}{r_w^2 C}\left(1 + \frac{8}{\alpha^2}(3 - 2\alpha)\right) + \frac{3r_w^2}{8at}\left(1 - \frac{2}{\alpha}\right)^2\left(\ln\frac{4at}{r_w^2 C}\right)^2\right] \tag{12}$$

The first line is identical to the correction of Healy et al. [9] for a uniform temperature in a wire cross section.

The modified formula was compared with the numerically evaluated exact solution of Eq. (9) and the correction given by Healy as plotted in Fig. 5 for argon at 5 bar and 320 K. As expected the influence of the heat capacity of the wire is large at small times and decreases quickly. The modified formula (short-dashed line) is much closer to the exact solution (solid line) than the correction of Healy (long-dashed line) The error in the temperature rise is smaller than 0.1% at times above 50 ms. The new equation allows evaluation of the temperature rise starting at 50 ms instead of the previous 200 ms, which assures a sufficiently long time interval for evaluation.

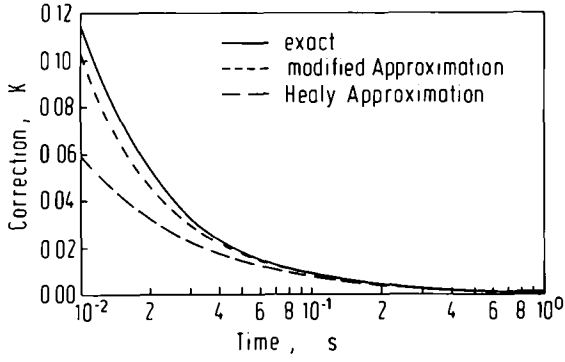

Fig. 5. Comparison of approximations and exact calculation for the heat-capacity correction versus time for argon at 320 K and 5 bar.

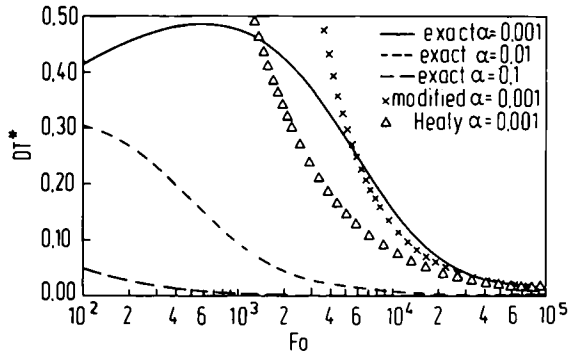

Fig. 6. Influence of the ratio α of the volumetric heat capacities on the heat-capacity correction in dimensionless parameters.

The influence of the heat-capacity ratio α on the magnitude and time scale of the correction can be deduced from Fig. 6. There a dimensionless temperature correction $\delta T^* = (4\pi\lambda\,\delta T_1)/\dot{q}$ is plotted versus a Fourier number with the wire radius $\mathrm{Fo} = at/r_w^2$. The lines denote the numerically evaluated exact solution for $\alpha = 0.001$ (solid line), for $\alpha = 0.01$ (short-dashed line), and for $\alpha = 0.1$ (long-dashed line). The smallest α is close to the conditions at low pressures in gases and shows the largest correction. The triangles stand for the Healy correction, and the crosses for the modified formula at $\alpha = 0.001$. Again, the modified formula approximates the exact solution down to smaller times.

4. AXIAL END EFFECTS

The thermal diffusivity of a gas increases at low pressures as discussed in Section 1. The temperature field expands further out around the hot wire in the radial and in the axial direction as well. Therefore, the heat flux in the axial direction through the fluid at the ends of the hot wire is growing. It is well-known, however, that it can be compensated for by using two wires of different length. Only when the temperature in the middle of the short wire deviates from the ideal temperature rise will the compensation fail. In order to demonstrate that the compensation works properly for the conditions of our long time measurements in argon, we determined the time of axial compensation failure t_f according to a simple criterion of Blackwell [16]. Blackwell gives an estimate of the error of the slope s of the temperature rise in the middle of a heated wire which was quoted without simplifications by Healy et al. [9]. If the thermal diffusivity of a gas at low pressures becomes comparable to that of the wire, the axial heat

Table I. Failure Times t_f for the Comparison of Axial End Effects in Argon at 320 K

Pressure (bar)	Thermal diffusivity ($m^2 \cdot s^{-1}$)	t_f (s) Blackwell [16]	t_f (s) Kierkus et al. [17]
2	11.56×10^{-6}	1.24	2.0
5	4.67×10^{-6}	3.07	6.0

losses are dominated by the flux through the fluid and the relative error of the slope $\delta s/s$ can be written

$$\frac{\delta s}{s} = \operatorname{erfc}(z); \qquad z = \frac{l}{4\sqrt{at}} \tag{13}$$

where l stands for the length of the short wire. The error should be smaller than 0.1%; the argument z of the error function complement is then $\leqslant 2.333$. For a given length of the short wire the axial end effects will be felt earlier the greater the thermal diffusivity of the fluid. The failure times t_f for our instrument with $l = 0.03536$ m and the argon measurements at 320 K are given in Table I.

At the lowest pressure the breakdown of the axial compensation is predicted to occur within the transition to steady state. This is not consistent with the results of our measurements. Therefore, we used the more detailed work of Kierkus et al. [17] to calculate the temperature in the middle of the short wire:[2]

$$\begin{aligned}
\Delta T(r = r_w, z = l/2, t) &= \frac{\dot{q}}{\lambda}\frac{8}{\pi^3}\sum_{k=1}^{\infty}\frac{1}{(2k-1)}\sin(2k-1)\frac{\pi}{2} \\
&\quad \times \int_0^{\infty}\frac{(1-\exp[-(f_1+u^2)\mathrm{Fo}}{f_1+u^2}\,du \\
f_1 &= \left(\frac{(2k-1)\pi r_w}{l}\right)^2; \qquad \mathrm{Fo} = \frac{at}{r_w^2}; \qquad f_2 = \left(\frac{\lambda_w}{\lambda} - \frac{2}{\alpha}\right) \\
f_3(u) &= \frac{[Y_0(u)\,\phi(u) - J_0(u)\,\psi(u)]}{\phi^2(u) + \psi^2(u)}; \qquad (14) \\
\phi(u) &= 2uJ_1(u) + \left(f_2 f_1 - \frac{2u^2}{\alpha}\right)J_0(u) \\
\psi(u) &= 2uY_1(u) + \left(f_2 f_1 - \frac{2u^2}{\alpha}\right)Y_0(u)
\end{aligned}$$

[2] In Eq. (12) of Ref. 17 a factor 2 was missing. Now we get the proper form for the simplified case $\alpha = 2$, which leads to the working equation of the transient hot-wire method.

The temperature deviates more than 0.1 % from the ideal temperature rise at the times t_f also included in Table I. According to the work of Kierkus et al. [17], the axial compensation breakdown occurs later than estimated by Blackwell and does not fail within the transition to steady state. It is noteworthy that we are not far away from a significant influence of the axial end effects. The simple criterion Eq. (13) of Blackwell includes a safety factor of approximately 1.6 and may be used to determine the length of the short wire when designing a transient hot-wire cell.

5. CONCLUSIONS

The experiments revealed a significant influence of the isothermal outer boundary at long times in gases at low pressures, whereas natural convection dominates the behavior at high pressures. The evaluation of the thermal conductivity from the steady-state temperature at low pressures in gases seems to be possible. Further work is required to estimate the error of such a steady-state measurement.

Most of the existing transient hot-wire instruments show a significant influence of the isothermal outer boundary at pressures between 2 and 5 bar. The well-known correction could be applied, but in new instruments it is recommended to avoid it altogether with a more rigorous design criterion. Even with the finest wires the heat-capacity correction is rather large. To account for the heat capacity of the wire, a new and more accurate formula is given. The axial end effects are growing at low pressures but still can be compensated for by using two wires of suitable length. A well-known simplified design criterion for the short wire length was verified by a numerical study of the wire temperature. For accurate thermal-conductivity measurements at low pressures in gases, very fine wires in large cells should be used. The measures presented allow extension of the range where the transient hot-wire method is applicable toward the dilute gas state.

ACKNOWLEDGMENTS

The authors are grateful to Professor W. A. Wakeham for valuable discussions in the early stage of the investigations and to B. Heines and K. Sekot for their support with the experiments.

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