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Vapor-Phase Thermal Conductivity Measurements of Refrigerants[1]

S. H. Jawad,[2] M. J. Dix,[2] and W. A. Wakeham[2, 3]

The paper reports further developments of the transient hot-wire technique. The particular development of interest is the extension of the technique to study polar, or electrically-conducting gases with a relatively low thermal conductivity but a high thermal diffusivity, circumstances which occur at low density and therefore low pressure, for gases of high molecular weight. The theory of the transient hot-wire instrument is examined again in order to guide a revised design of the thermal conductivity cell with this particular application in mind. Test measurements have then been conducted on helium, argon, and propane at low and moderate pressures to confirm that the instrument operates in accordance with the theory of it. The satisfactory completion of these tests demonstrates that the new equipment overcomes many of the defects observed in earlier variants of the instrument for application to the study of refrigerant gases.

KEY WORDS: argon; experimental method; helium; low density; propane; thermal conductivity.

1. INTRODUCTION

In an earlier paper [1] we considered the application of an existing transient hot-wire instrument for the measurement of the thermal conductivity of gases to the study of refrigerants. The motivation for that earlier study, as well as for the present one, was to seek a method for the measurement of the thermal conductivity of such gases, which are generally polar and frequently seem not to be complete electrical insulators [2]. The total

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[2] Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology, and Medicine, London SW7 2BY, United Kingdom.

[3] To whom correspondence should be addressed.

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range of pressures accessible to the usual instrument for such gases is very restricted, particularly at low temperatures [3].

Our initial study [1] concentrated on ways to decrease the lower pressure (density) limit for operation of a transient hot-wire cell for simple gases such as nitrogen and argon. It was concluded that a hot-wire cell with a bare platinum wire of 7 μm diameter should be employed and that measurements at short times only should be used.

In this work we have considered the same problem afresh, recognizing that if it is intended to study polar refrigerants with a similar experimental technique, then it is best to use an insulated hot wire [2]. Unfortunately, the smallest diameter of metallic wire that can be insulated with a noninterfering film, and is commercially available, is wire made of tantalum with a nominal diameter of 25 μm [3]. If this is employed in the same cell as described above, it follows that the heat capacity correction at short times will be a factor of 16 times larger than for the platinum wire. In consequence, unless there is careful design, there may be no time available during a transient run in which neither heat capacity nor outer boundary corrections are very small. The measurement of the thermal conductivity is then rendered impractical. Here we describe a means to escape from this difficulty and demonstrate the viability of a revised experimental installation.

2. CELL DESIGN

The fundamental theory of the transient hot-wire technique is described in detail in Ref. 3. For the current purpose it is sufficient to record that the measured transient response, ΔT_w, of the temperature of a finite segment of an insulated metallic wire (radius a) immersed in a fluid following initiation of a heat flux, q, within it conforms to the equation,

$$\Delta T_{\mathrm{id}} = \Delta T_{\mathrm{w}} + \sum_i \delta T_i = \frac{q}{4\pi\lambda} \ln \frac{4\kappa t}{a^2 C} \tag{1}$$

Here δT_i represents one of a series of corrections that describe the departure of the real cell from an ideal cell. We concentrate only upon the two corrections that are germane to the arguments presented in the paper. There is ample evidence that the remainder of the corrections, and their current method of application, such as those involving the presence of a thin insulating layer [4], are entirely adequate for accurate measurements [3].

The heat capacity correction, δT_1, is most often used in an approximate form derived by Healy et al. [5]. For the circumstances to be considered here

the approximation used by Healy et al. is inappropriate and we therefore use the full form of the correction [6],

$$\delta T_1 = \frac{q}{4\pi\lambda}\left[\ln\frac{4\kappa t}{a^2 c} - \frac{16q\lambda^2\kappa}{\pi^2 a^3}\int_0^\infty \frac{1-e^{-\kappa_w u^2 t}J_0(ur)\,J_1(ua)}{u^4[\varphi^2(u)+\psi^2(u)]}\,du\right] \tag{2}$$

Here

$$\varphi(u) = \lambda_w \kappa^{1/2} J_1(au)\,J_0(\sqrt{\kappa_w/\kappa}\,au) - \lambda\kappa^{1/2}J_0(au)\,J_1(\sqrt{\kappa_w/\kappa}\,au) \tag{3}$$

and

$$\psi(u) = \lambda_w \kappa^{1/2} J_1(au)\,J_0(\sqrt{\kappa_w/\kappa}\,au) - \lambda\kappa_w^{1/2}J_0(au)\,J_1(\sqrt{\kappa_w/\kappa}\,au). \tag{4}$$

In addition, λ signifies the thermal conductivity, κ the thermal diffusivity, and the subscript w refers to properties of the wire. Finally, J_0 and J_1 are Bessel functions.

The outer boundary correction, δT_2, is given by [5]

$$\delta T_2 = \frac{q}{4\pi\lambda}\left\{\ln\frac{4\kappa t}{b^2 C} + \sum_{\nu=1}^{\infty} e^{-g_\nu^2\kappa t/b^2}[\pi Y_0(g_\nu)]^2\right\} \tag{5}$$

where b is the radius o,f the cylindrical surface surrounding the fluid, which is assumed to remain at the constant equilibrium temperature of the cell during a transient run.

Both corrections δT_1 and δT_2 can be expressed as functions of three reduced variables for convenience of exposition; they are $t^* = \kappa t/a^2$, $h^* = (\rho C_p)_w/\rho C_p$ and $r^* = b/a$. Figures 1a and 1b illustrate the magnitudes of the two corrections for a variety of values of h^*, typical of a range of gases at 0.1 MPa and 300 K and for a typical series of ratios b/a. It can be seen that, for a particular fluid diffusivity, decreasing the reduced time t^* but increasing the radius of the wire dramatically increases the magnitude of the heat capacity correction. On the other hand, as Fig. 1b reveals, if we increase a **and** b so as to keep r^* constant, then the change in the outer boundary correction takes place along one of the lines of constant r^* in the figure and necessarily decreases as t^* is reduced. The implication of these results is that if we can tolerate and evaluate with sufficient accuracy a large heat capacity correction, we can reduce the outer boundary correction to negligible proportions by allowing r^* to increase by using a larger value of b. This means that a possible design of the thermal conductivity cell for the conditions of interest should make use of a larger wire diameter **and** a larger cell diameter than in our previous designs [3]. Such a design would allow operation at low gas densities and high gas

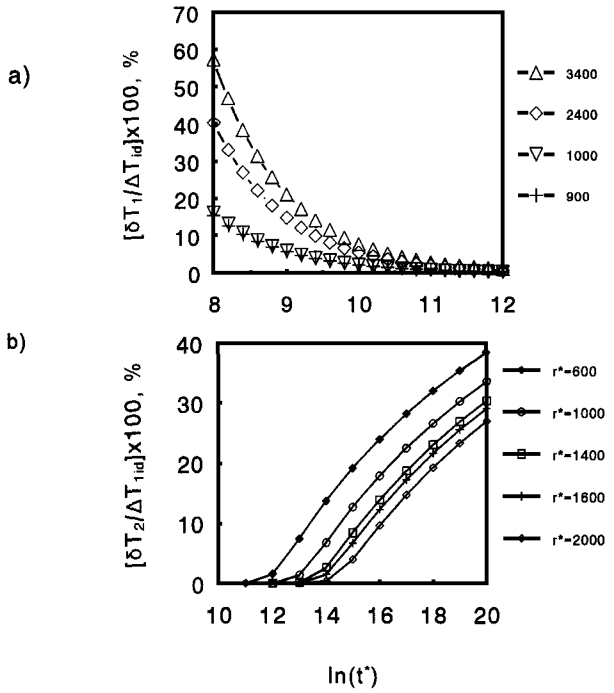

Fig. 1. (a) Fractional heat capacity correction for the transient hot wire as a function of reduced time with the heat capacity per unit volume of ratio $h^* = (\rho c_p)_w/\rho c_p$ as a parameter. (b) Outer boundary correction for the transient hot wire as a function of reduced time with the radius ratio $r^* = b/a$ as a parameter.

thermal diffusivities without the need to reduce the upper time limit of measurement to unacceptable limits.

3. EXPERIMENT

A transient hot-wire cell has been constructed guided by the principles set out in the previous section. A brief description of the essential features of the cell is given here although more details will be provided later [7]. The two hot wires themselves are made of 25 μm diameter tantalum wire. The long wire has a length of approximately 150 mm, and the short wire 50 mm. Each wire is mounted on the axis of a separate cylindrical, vertical tube of radius 7.9 mm. The wires are tensioned by an insulated cantilever spring arrangement at the top of each tube mounted on the top plate. The

top and bottom fixtures of the wire are spot-welded, and they are themselves connected to a tantalum support rod. These measures ensure that the transient thermal expansion of the hot wires during measurement is absorbed by the cantilever spring without introducing electrostrictive or thermal oscillations [8]. Furthermore, differential expansion of the wire supports and the wires at different equilibrium thermodynamic states that could introduce strains are avoided. The use of tantalum in the construction anticipates the eventual use of the cells for measurements on electrically conducting fluids since anodization of the entire assembly *in situ* is straightforward [9].

A new electronic measurement system has been developed to take advantage of the most modern methods for determining the change of the resistance difference between the long and short tantalum wires during transient heating by the same current. Details of the bridge are beyond the scope of this paper but it suffices to say that the bridge permits 1000 measurements of the resistance change to be carried out in the time interval from 1 ms to 1 s. The resolution of the temperature rise measurements is estimated to be $\pm 0.1\%$, and time is measured with a precision of $\pm 1\,\mu$s. The temperature coefficient of resistance for tantalum necessary for the analysis of the data was taken from the work of Assael et al. [10].

In order to confirm that the instrument described operates in accordance with the theory of it and, in particular, that the argument set out in favor of the use of larger wire diameters and large cell diameters is correct for work with low density gases, we have conducted a series of test measurements. To be specific, we have carried out measurements of the thermal conductivity of argon, helium, and propane at pressures within the range 0.1 to 8.0 MPa and temperatures in the range 305 to 363 K. In the following section we consider the results which confirm correct operation of the instrument and report some new thermal conductivity data.

4. RESULTS

4.1. Confirmation of the Operation of the Instrument

Figure 2 shows a plot of the deviations of experimental measurements of the temperature rise of the hot wires (in argon at 305 K at a pressure of 0.1 MPa) from a fit of ΔT_{exp} vs $\ln t$ to the data for times in the range 100 ms to 1 s. Inset in Fig. 2 we show the magnitude of the heat capacity correction as a fraction of the temperature rise as a function of time. It can be see that, over the time interval 50 ms to 1 s, the behavior of the corrected experimental data conforms to that predicted by Eq. (2). Given that at 50 ms the heat capacity correction in this case amounts to 63% of

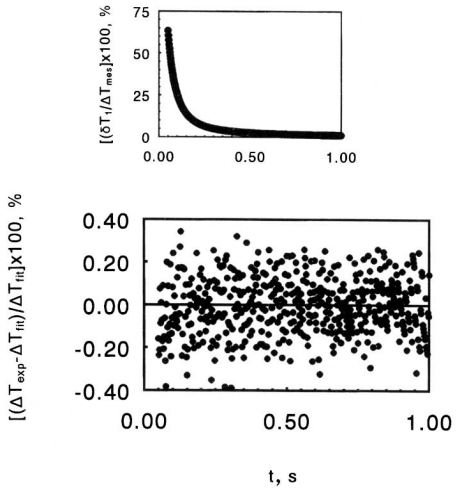

Fig. 2. Deviation of the experimental temperature rise from a linear fit over the time range 50 ms to 1 s for argon at 308.15 K and 0.15 MPa. Inset: the value of the heat capacity correction as a fraction of the measured temperature rise.

the temperature rise, this is an impressive demonstration of the degree of uniformity between the theoretical model of the experiment and actual measurements.

In routine measurements, of course, it is neither necessary nor good practice to include points for transient runs in which the heat capacity correction, or any other, is so large that its evaluation may introduce errors into the corrected temperature rise that are larger than the random error of measurement. Thus, we routinely impose the condition that the estimated error in the heat capacity correction should not exceed 0.1% of the temperature rise and exclude all points from the fit (at short times) for which this condition is not fulfilled. The results contained in Fig. 2 support the fact that we may be able to evaluate the heat capacity correction to within $\pm 2\%$ so that we routinely reject all points in transient runs for which the heat capacity correction exceeds 5% of the temperature rise.

Figures 3a–c show the deviations of the results of transient temperature rise measurements (a) in argon at 505 MPa and 333 K, (b) in helium at 1.0 MPa and 365 K, and (c) in propane at 0.1 MPa and 333 K for linear fits in $\ln t$ over the time range satisfying this condition.

In no case is there any evidence of systematic curvature in a time range that for helium encompasses 30 ms to 1 s, while for propane it is

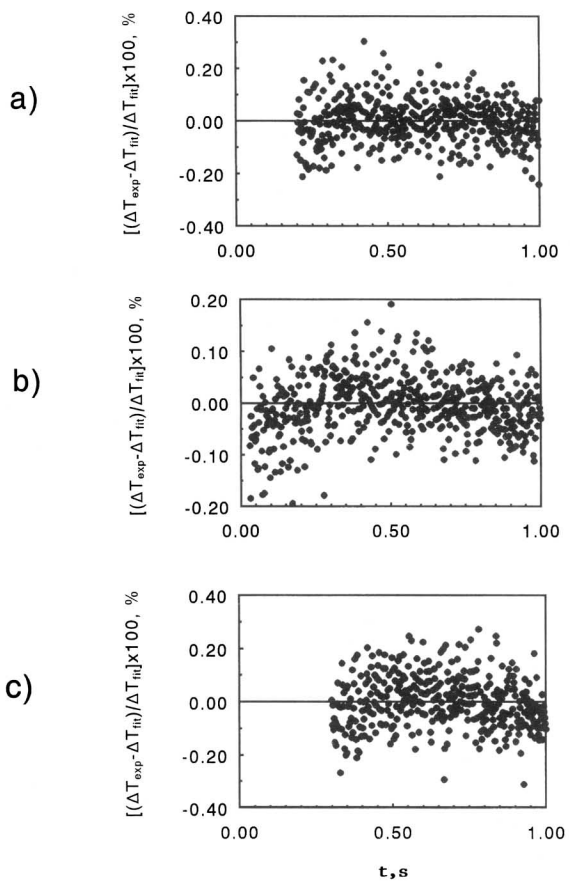

Fig. 3. Deviations of experimental temperature rise from a linear fit. (a) Argon at 335.15 K and 5.5 MPa. (b) Helium at 338.15 K and 1.0 MPa. (c) Propane at 355.15 K and 0.1 MPa.

restricted to 0.3 to 1 s. This range of times is entirely adequate to obtain the slope of the line relating ΔT_{id} vs ln t and to evaluate the thermal conductivity of the fluid from Eq. (1).

The results presented in Fig. 3 for low pressures are to be contrasted with those reported earlier [1] for a wire with a much smaller diameter in a smaller cell. The difficulties revealed in the earlier results, where at long times there was curvature of the plot of temperature rise against ln t have been completely removed. This is attributed to the fact that for no case in the present work, even at the lowest pressure, did the outer boundary correction, even estimated approximately, exceed 0.8%.

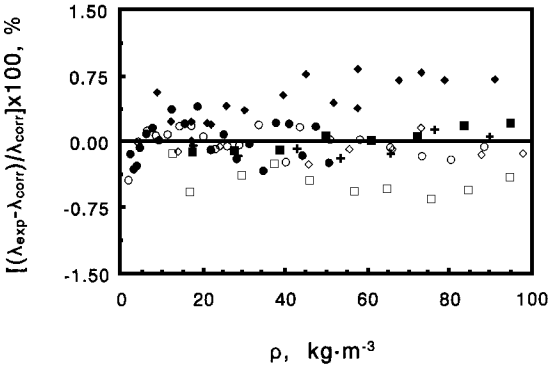

Fig. 4. Deviations of the thermal conductivity of argon from the correlation of the present results. (●) Present data, 308.15 K; (■) 308.15 K [11]; (+) 308.15 K [12]; (◆) 308.15 K [13]. (○) Present data, 335.15 K; (□) 333.15 K [11]; (△) 335.15 K [13].

4.2. Thermal Conductivity Data

Figure 4 presents a comparison of the present data for the thermal conductivity of argon at $T = 308.15$ K and $T = 335.15$ K with a fit to the data. The same figure includes comparisons with the results of earlier work [11–14]. Figure 5 contains a similar comparison for helium at $T = 338.15$ K. The deviations are at most $\pm 0.5\%$ except for the lowest density points for helium reported by Mustafa et al. [14]. The fact that the present data extend smoothly to lower densities than hitherto is apparent.

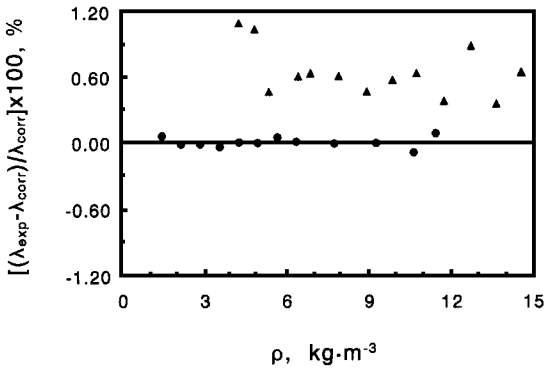

Fig. 5. Deviations of the thermal conductivity of helium from the correlation of the present results. (●) Present data, 338.15 K; (▲) 338.15 K [13].

Table I. Optimum Values of Thermal Conductivity in the Limit of Zero Density and Experimental Eucken Factors

T (K)	$\lambda_0 \pm \sigma_{\lambda 0}$ ($mW \cdot m^{-1}K^{-1}$)	η_0 [16] ($\mu Pa \cdot s$)	Eu*
	Argon		
308.15	18.10 ± 0.02	23.24	0.998
335.15	19.50 ± 0.02	24.81	1.007
	Helium		
338.15	168.92 ± 0.03	21.64	1.002
365.15	179.15 ± 0.06	22.82	1.008
	Propane		
355.15	26.23 ± 0.03		

A further test of the equipment for the monatomic gases is afforded by the Eucken relation which requires (according to rigorous theory) that for monatomic gases [15]

$$\frac{15}{4}\frac{\lambda_0 R\mathscr{F}}{\eta_0 M} = 1 \tag{6}$$

where λ_0 and η_0 are the zero-density limits of the thermal conductivity and viscosity, respectively, and $\mathscr{F}$ is a higher-order kinetic theory correction factor. Using the best available viscosity data for helium and argon under the conditions of interest [16], and values of λ_0 deduced by statistical analysis of our data [17], we have evaluated the ratio in Eq. (6). The results are contained in Table I and show that within $\pm 0.7\%$, the theoretical result is attained. Accounting for errors in the viscosity data employed, this indicates that the error in the absolute thermal conductivity reported in the present work is $\pm 0.5\%$.

For propane there are no reliable data available for comparison in an overlapping range of temperature and pressure. We thus confine our comparison here to a report of the single value of λ_0 so far obtained, which is contained in Table I.

5 CONCLUSIONS

It has been shown that it is possible to design a transient hot-wire thermal conductivity apparatus to work at low densities for gases of low

thermal conductivity and relatively high thermal diffusivity. This demonstration, conducted in an apparatus that employs electrically insulated hot wires, opens the route to accurate measurements on the thermal conductivity of the vapor phase of new refrigerants under subcritical conditions.

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