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APPENDIX A

MEASUREMENT OF THE THERMAL PROPERTIES OF ELECTRICALLY CONDUCTING
FLUIDS USING COATED TRANSIENT HOT WIRES

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ABSTRACT

Measurements of fluid thermal properties using the transient hot-wire technique are described. When bare hot wires are used in electrically conducting fluids there are additional measurement uncertainties due to the formation of electric double layers on the surfaces of the wires and the cell wall. If the electrical conductivity of the fluid is large enough there is also significant power generation in the fluid. These measurement uncertainties can be eliminated by electrically insulating the hot wires with a thin film. The use of tantalum hot wires with an anodized layer of tantalum pentoxide is demonstrated with measurements on nonpolar argon and polar 1,1,1,2 tetrafluoroethane (R134a). Although coated tantalum hot wires have been used previously in a transient mode to measure the thermal conductivity of liquids, this work is the first demonstration of the use of coated wires to measure thermal conductivity in the liquid, vapor, and supercritical gas phases.

INTRODUCTION

MASTER

Absolute measurements of the thermal conductivity of gases and liquids can be made accurately using the transient hot-wire technique. In the transient hot-wire technique small diameter wires are immersed in the fluid of interest and are used simultaneously as electrical resistance heaters and as resistance thermometers. Using this technique, both the thermal conductivity and the thermal diffusivity can be obtained independently from a single measurement [1]. Polar liquids introduce additional measurement uncertainty due to the transient polarization of the fluid around the bare hot wires which are commonly used in transient hot-wire instruments. Bare hot wires exhibit an apparent power dependence on the measured thermal conductivity [2]. If the electrical conduction through the fluid is low enough, this power dependence can be suppressed by introducing a fixed dc polarization voltage between the hot wires and the cell wall [2,3]. An alternative to the application of a polarization voltage is the addition of an electrically insulating layer to the hot wires to eliminate both fluid polarization and electrical conduction problems.

This paper examines the use of an anodized tantalum pentoxide film as an electrical insulation layer on tantalum hot wires. Even though anodized-tantalum hot-wire cells have been widely used for transient studies in the liquid phase of polar fluids such as water [4-6], alcohols [7], and liquid phase refrigerants [8-10] there is no previous investigation of their use in the gas phase. Comparisons are made between the best available correlations and thermal conductivity measurements obtained with anodized 25.4 μm diameter

tantalum hot wires for argon gas, R134a vapor, and R134a liquid. Extension of the anodized hot-wire technique to include the vapor and supercritical gas phases allows us to use insulated hot-wires to measure the entire thermal conductivity surface of electrically conducting fluids.

THEORY

The theory for transient hot wire measurements is well developed [11,12], although proper application of the theory requires significant care and judgement. The hot wire cells are designed to approximate a transient line source as closely as possible, and deviations from this model are treated as corrections to the experimental temperature rise. The ideal temperature rise ΔT_{id} is given by

$$\Delta T_{id} = \frac{Q}{4\pi\lambda} \left[\ln(t) + \ln\left(\frac{4\kappa}{a^2 C}\right) \right] = \Delta T_w + \sum_{i=1}^{10} \delta T_i, \quad (1)$$

where Q is the power applied per unit length, λ is the thermal conductivity of the fluid, $\kappa = \lambda/\rho C_p$ is the thermal diffusivity of the fluid, t is the elapsed time, a is the radius of the hot wire, $C = 1.781...$ is the exponential of Euler's constant, ρ is the density of the fluid, C_p is the isobaric heat capacity of the fluid, ΔT_w is the measured wire temperature rise, and δT_i are corrections to account for nonideal heat transfer. Equation (1) shows that the thermal conductivity can be found from the slope of the ideal temperature rise as a function of the logarithm of elapsed time. The thermal diffusivity can be found from the intercept of this linear function. The principal corrections to the ideal model account for the finite dimensions of the wire δT_1 , penetration of the expanding thermal wave to the outer boundary δT_2 , and thermal radiation δT_3 . The standard corrections [12] are applied in this work, including the outer boundary correction and the thermal radiation correction for a transparent gas. The correction for the finite wire dimensions requires a careful examination.

The smallest available tantalum wire has a diameter of 25.4 μm which is 2 to 4 times the diameter of the platinum hot wires commonly used for thermal conductivity measurements in the gas phase. The dimensionless time ($\tau = \kappa t/a^2$) which is relevant in these experiments is inversely proportional to the square of the wire radius. Therefore, an experiment with tantalum wires occurs at dimensionless times of about 1/4 to 1/16 of those encountered during experiments with smaller wires. The standard corrections for the finite wire radius for bare wires [12] and coated wires [11] are first-order series expansions which are valid at long dimensionless times. Thus, these series expansion are not necessarily valid for our case of relatively large hot wires. However, examination of the differences between the two expansion solutions allows an assessment of the effect that the presence of the coating has on a measurement. This is shown in Fig. 1 for the case of a 25.4 μm tantalum hot wire with a 70 nm coating of tantalum pentoxide during a measurement on argon gas. Figure 1 shows that the contribution from the 70 nm thick oxide layer is significant only at extremely short times (<0.05 s) and can be neglected. A full solution is available which accounts for the effect of the finite wire radius of a bare hot wire [12]. This solution is an infinite integral of a complicated expression of Bessel functions but can be evaluated readily, even as a correction to the measured temperature rise data. Differences between the full correction [12] and the series correction [12] for a bare hot wire are also shown in Fig. 1. Figure 1 shows that the first order series correction does not converge in this case and that effects due to the wire coating are insignificant relative to this truncation error. Thus, the full correction [12] for the finite wire radius is used in the measurements described below.

Figure 1. Corrections associated with the finite dimensions of a 25.4 μm tantalum hot wire with a 70 nm coating of tantalum pentoxide in argon gas at 300 K and 0.1 MPa.

EXPERIMENTAL

The transient hot-wire instrumentation used in this work has a temperature range from 220 to 750 K with pressures up to 70 MPa and has been described elsewhere [1] for measurements on nonpolar fluids. The hot wires are placed in the fluid of interest and a current is passed through them for electrical heating. The instrument has two hot wires which are located in a Wheatstone bridge circuit such that the heating of the short wire is subtracted from the heating of the long wire. Measurement of the resistance change of the wires allows one to obtain the temperature rise through a calibration of the wire resistance as a function of temperature. The resistance characteristics of the hot wires are calibrated in-situ relative to the temperature obtained from a reference grade platinum resistance thermometer. Monitoring of the wire calibration allows detection of mechanical changes such as annealing and stress damage in the hot wires. In our previous cell [1] bare 12.7 μm diameter platinum hot wires have always been used. The new cell contains 25.4 μm diameter tantalum wires which have been anodized to form an electrically insulating layer of tantalum pentoxide with a thickness of 70 nm.

Since the tantalum hot-wire cell is designed for use in corrosive solutions which may contain halide salts it is constructed of a nickel alloy UNS-N10276. The tantalum hot-wire cell dimensions and geometry are the same as our previous cell [1] which was designed for less corrosive, nonpolar fluids. The cell is contained in a pressure vessel which is also made from this same corrosion resistant nickel alloy and has an upper working pressure of 70 MPa at 750 K. The cell has long and short cavities with diameters of 9.5 mm in which the hot wires are located. The total volume of the cell and supporting pressure system is relatively small, about 50 cm^3 , to facilitate measurements on scarce or hazardous materials. The wires are positioned near the centers of the cavities and are tensioned with weights. There are two leads to each end of each hot wire to eliminate lead resistance effects during the calibration process. All electrical connections in the cell are spot welded. In this assembly of the tantalum hot wires (25.4 μm diameter),

polytetrafluoroethane-insulated nickel/chromium alloy wire (254 μm diameter) and polyimide-insulated platinum (76 μm diameter) wire are used to make electrical connections inside the pressure system. The connections were welded, then all the bare leads were coated three times with a polyimide/polytetrafluoroethane resin and the assembly was baked at 550 K for several hours. The baking both cured the polymer resin and annealed the tantalum hot wires from their initial hard-drawn condition. The tantalum hot wires were then anodized in aqueous citric acid with up to 50 V to produce a tantalum pentoxide film with an estimated thickness of 70 nm. Although the temperature control and pressure systems are rated to 750 K, the upper operating temperature of the present tantalum hot-wire cell assembly is limited to about 550 K because of the melting point of the polytetrafluoroethane used as electrical insulation for the lead wires.

Argon

Argon gas was selected as the first test fluid, since it is a nonpolar monatomic gas. Kinetic theory is well developed for argon and agrees well with precise measurements of thermal conductivity and viscosity. The basis for our comparisons is the dilute gas thermal conductivity λ_0 of Aziz [13], combined with the first density coefficient λ_1 of Bich and Vogel [14]. Thus, the theoretical thermal conductivity of argon gas which is used as the basis of comparison is given by

$$\lambda_{Ar}(T) = \lambda_0(T) + \lambda_1(T)\rho . \quad (2)$$

Measurements were made along two isotherms using the anodized 25.4 μm diameter tantalum hot wires at 300 and 340 K. The argon sample used in these measurements was 99.998% pure. There were nominally 8 measurements at different applied powers for each initial cell temperature and pressure. Consistency between 8 applied powers verifies that the measurements do not have significant heat transport due to natural convection. The results of these measurements are summarized as deviations from the theoretical model of Eq. (2) in Fig. 2. The uncertainty of this theoretical model is estimated to be $\pm 2\%$.

The scatter for the anodized tantalum hot-wire measurements is within $\pm 1.2\%$. At densities below about $1 \text{ mol}\cdot\text{L}^{-1}$ systematic departures are apparent in the anodized tantalum hot-wire measurements. These deviations occur because the magnitude of both the finite wire radius correction and the outer boundary correction become much larger as the thermal diffusivity of the fluid increases. At low pressures the thermal diffusivity of the fluid increases almost linearly with the inverse of pressure. At these low pressures very small transient hot-wires ($a < 4 \mu\text{m}$) represent the most significant improvement in accuracy since small wires have a much smaller correction for finite wire radius. Figure 2 clearly shows that relatively large anodized tantalum hot wires can be used effectively for accurate measurements of gas phase thermal conductivity. The uncertainty of such gas phase measurements using the tantalum hot-wire cell is estimated to be $\pm 1.5\%$ at 95% confidence for pressures above 1 MPa ($1 \text{ mol}\cdot\text{L}^{-1}$).

R134a Vapor

No measurable electrical conductivity has been observed for R134a in the vapor phase [3], so polarization errors are assumed, therefore to be negligible for bare hot wires. These measurements were made on a standardized round robin sample in collaboration with the IUPAC Subcommittee on Transport Processes. This round robin sample has a purity of 99.91%. Measurements were made along 3 isotherms using the anodized 25.4 μm diameter tantalum hot wires at 300, 320, and 340 K. There were nominally 8 measurements at different applied powers for each initial cell temperature and pressure. These thermal conductivity measurements will ultimately be compared to other instruments and techniques at several laboratories around the world.

The basis for our comparisons in the vapor phase of R134a is the correlation of Krauss et al. [15].

Figure 2. Deviations of measurements from theoretical predictions [13,14] for argon gas. Open symbols for 12.5 μm platinum wires and filled symbols for 25.4 μm tantalum wires.

This correlation is based on experimental data derived from transient hot-wire measurements of thermal conductivity and from light-scattering measurements of thermal diffusivity. The thermal conductivity correlation is valid from 240 to 410 K and is claimed to have an uncertainty of $\pm 5\%$ [15]. This correlation includes a theoretically based term for the thermal conductivity critical enhancement. This is important in this work since the critical temperature is 374.274 K and our measurements are made from 300 to 340 K; at our upper temperature of 340 K, the saturated vapor thermal conductivity contains a critical enhancement contribution of about 10%.

Figure 3 shows the deviations between the 3 measured isotherms and the correlation [15]. At densities below $0.5 \text{ mol}\cdot\text{L}^{-1}$ the measurements with the anodized tantalum hot wires agree with the correlation to within $\pm 3\%$. Above this density the differences increase to $\pm 4\%$ but are still within the claimed uncertainty of the correlation.

R134a Liquid

Significant electrical conduction is observed when liquid phase R134a is present in a hot-wire cell using bare platinum hot wires [10]. Hence, this case represents the first test of the effectiveness of the oxide electrical insulation layer. The leakage current between the wires and the cell wall was monitored and found to be negligible during the measurements. The basis for our comparisons in the liquid phase is once again the correlation of Krauss et al. [15]. Measurements were made along 3 isotherms using the anodized 25.4 μm diameter tantalum hot wires at 300, 320, and 340 K on the IUPAC round robin sample described above.

Figure 3. Deviations of measurements using coated 25.4 μm tantalum hot wires from correlation of Krauss et al. [15] for R134a vapor.

There were nominally 8 measurements at different applied powers for each initial cell temperature and pressure.

Figure 4 shows the deviations between the 3 measured isotherms and the correlation [15]. All of the measurements agree with the correlation [15] within its claimed uncertainty of $\pm 5\%$. The power dependence of the measured thermal conductivity is within $\pm 1\%$ using the anodized tantalum hot wires. Based on the agreement between all 3 isotherms which were measured with the tantalum hot-wire cell, the uncertainty in the thermal conductivity data is estimated to be less than $\pm 1\%$. Thermal diffusivity values were also obtained from the data as discussed above which agree with equation of state predictions [15] to within $\pm 10\%$. The anodized tantalum hot wires are demonstrated to work well in electrically conducting liquids.

CONCLUSIONS

Good agreement is demonstrated between the best available correlations and measurements for nonpolar argon gas and polar R134a vapor and liquid using 25.4 μm tantalum hot wires which have been anodized to form a 70 nm thick layer of tantalum pentoxide. Further, when the full correction for the finite wire radius is used, the 25.4 μm tantalum hot wires can also be used for measurements of vapor phase thermal conductivity. Smaller platinum wires produce more accurate measurements of vapor thermal conductivity because their smaller diameter requires less correction for finite wire dimensions. The present 25.4 μm tantalum wires have significant advantages for polar liquid measurements since they are not

Figure 4. Deviations of measurements using coated 25.4 μm tantalum hot wires from correlation of Krauss et al. [15] for R134a liquid.

susceptible to transient polarization or electrical conduction effects. The correction for a 70 nm oxide coating is shown to be negligible relative to the correction for the finite wire dimensions for the present 25.4 μm diameter wires. In the vapor and supercritical gas phases, the uncertainty of the coated hot-wire thermal conductivity data is less than $\pm 1.5\%$. In the liquid phase, the uncertainty of the thermal conductivity data is less than $\pm 1\%$. Thermal diffusivity data in the liquid phase have an uncertainty of less than $\pm 10\%$. It should be possible to reduce these uncertainties if suitable wires with a smaller diameter can be found.

FUTURE WORK

The IUPAC round robin measurements on R134a are continuing and will include the supercritical region at temperatures to 450 K. Measurements will start soon using the tantalum hot-wire cell to study the thermal conductivity and thermal diffusivity of pure ammonia, water, and their mixtures. Other wires systems, such as 25.4 μm platinum with a polyimide coating, will be explored for use in reducing environments where anodized oxide coatings are not stable. Anodized tungsten wires will also be explored since measurements with extremely small wires ($4 < \mu\text{m}$) should have increased accuracy due to smaller corrections for the finite wire radius. Steady-state measurements using the present tantalum hot wires will also be assessed as a technique for measurements on dilute gases.

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