Research and technical notes

Heat capacity, C_p, of fluids from transient hot wire measurements*

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We report here the first thermal diffusivity measurements that cover a wide range of thermodynamic states including the dilute gas, the dense gas, the compressed liquid, and conditions close to the critical point. The heat capacity is obtained from simultaneous measurements of thermal conductivity and thermal diffusivity in a transient hot wire instrument, while the density is obtained from an equation of state. Values for the heat capacity, C_p, of argon were obtained at two temperatures, 172 and 275 K, with pressures up to 70 MPa. For these temperatures the densities range from that of the dilute gas to 2.2 times critical density while the heat capacity varies by a factor of seven from the dilute gas value.

The transient hot wire apparatus developed during the past 15 years[1–6] has become the method of choice for thermal conductivity measurements on fluids. In fact, the improvement in accuracy obtained with instruments of this type has led to several recent proposals of standard reference data for the thermal conductivity of fluids[7,8]. In addition, it has been known for some time that, with appropriate apparatus design, it should be possible to obtain the thermal diffusivity as well as the thermal conductivity[9–11]. Early attempts to measure the thermal diffusivity have been restricted to liquids, such as toluene and n-heptane, where the corrections that have to be applied are of minor importance. We report here the first thermal diffusivity measurements that cover a wide range of thermodynamic states including the dilute gas, the dense gas, the compressed liquid, and conditions near the critical point. We report the results in terms of the heat capacity, C_p, because this variable, in a practical sense, is far more important than the thermal diffusivity. Finally, we use the rare gas argon as the sample fluid, because then a direct check on the accuracy of the C_p measurements is available by extrapolating the C_ps measured at low density to zero density and comparing the result to the theoretical value, $C_p^o = 5/2\, R$.

The transient hot wire system has been defined as an absolute primary instrument[12]. Its working equation is a linear relation between the temperature rise, ΔT, at the wire and the logarithm of the time, t, after application of a step voltage to the wire. Thus

$$\Delta T = A + B \ln(t) = (Q/4\pi\lambda)\ln(K/4a^2 C) + (Q/4\pi\lambda)\ln(t) \quad (1)$$

where: Q is the applied power; λ the thermal conductivity; K the thermal diffusivity; a the wire radius; and C a constant equal to the exponential of Euler's constant. The actual experimental set-up approximates as closely as possible the relation given in Equation (1) and accounts for the deviations from ideal circumstances through a number of corrections[6]. In the present apparatus[13], we measure the temperature rise in the hot wire at 250 fixed time increments of 4 ms with a modified Wheatstone bridge and use linear regression to arrive at the two coefficients of the straight line. The slope of the line is inversely proportional to the thermal conductivity, while the thermal diffusivity can be evaluated by using both coefficients.

To obtain accurate results for the heat capacity through the thermal diffusivity, changes had to be made in the apparatus as well as in the data reduction scheme. Changes in the apparatus were made to improve the measurement of resistance for both bridge and wires, to improve the nulling of the bridge prior to applying the power, to improve the timing of the experiment, to provide some redundancy in the measurement capability, and, finally, to reduce the noise level in the voltage measurements across the bridge. The changes in data reduction involved a complete review of all corrections to Equation (1) to include effects on the thermal diffusivity, since in the initial development[6] only the effects on the thermal conductivity were considered. In several cases we included second order terms into the corrections. A complete survey of the theory will be presented in a future paper.

The heat capacity is obtained from simultaneous measurements of thermal conductivity and thermal diffusivity. The equation used is

$$C_p = \lambda/\rho K \quad (2)$$

where the density is obtained from an equation of state[14]. The heat capacity, C_p, was measured at two temperatures, 172 and 275 K, with pressures up to 70 MPa; the values are shown in *Figure 1*. For these temperatures, the densities range from that of the dilute gas to 2.2 times the critical density, i.e. up to 30 mol dm^{-3}. At each pressure, replicate measurements made at the same cell temperature, but with different applied power, verify the absence of convection, as the onset of convection can be determined experimentally in the transient hot wire
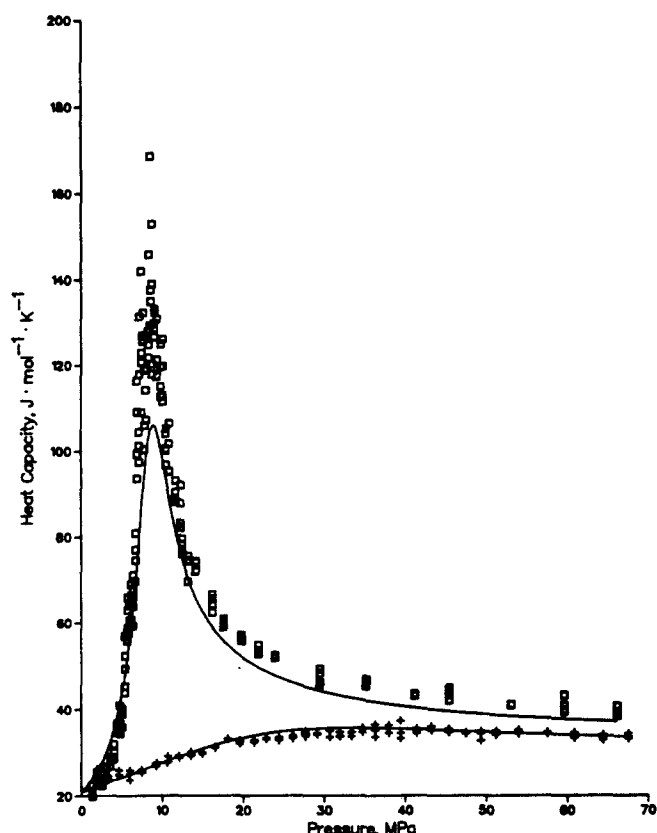
Figure 1 Heat capacity, C_p, of argon along two isotherms. □, 172.5 K; +, 275.0 K; ——, BWR equation of state[14]

technique[13,15,16]. The results along the 275 K isotherm fall into a band of $\approx$ 5%; however, these measurements were taken before we had introduced a filter for the voltage measurements across the bridge. For this isotherm with 122 points the average absolute deviation between measured values and values calculated from the equation of state is 2.8%. The extrapolation of the measured C_ps yields a C_p^o of 20.828 ± 0.82 J mol^{-1} K^{-1}, a precision of 4% and an absolute error in C_p^o of 0.2%. For the 172 K isotherm the precision is $\approx$ ± 3% at either high or low densities. The precision deteriorates to ± 10% as the density approaches critical density from either direction. Extrapolation of this isotherm to zero density is complicated by its sharp curvature at the low densities, yielding a value of 20.63 ± 1.0 J mol^{-1} K^{-1}, a precision of 5% and an absolute error in C_p^o of 0.7%.

We picked argon as a sample because we felt that the heat capacity would be well-known; however, it turns out that the modified Benedict–Webb–Rubin (BWR) equation of state[14] is based primarily on PVT measurements and includes only a very limited amount of experimental data for either C_p or C_v. We note that the heat capacities obtained from the BWR equation of state

are virtually identical to those derived numerically from the compressibility isotherms[17]. The measured heat capacities show good agreement with the values calculated from the equation of state for the higher temperature and at both low and high densities for the lower temperature. Large differences in C_p between measured values and the equation of state are found in the middle of the density range. It is well-known that near the critical point the heat capacity is distinctly greater than can be predicted by an analytical equation of state[18]. The failure of a modified BWR equation of state to represent heat capacity data in the region close to the critical point has been noted previously, particularly for ethane[19]. However, the present measurements were taken at a temperature 22 K larger than T_c, i.e. $\Delta T^* = (T - T_c)/T_c = 0.143$. Therefore, the deficiency of the analytical equation of state should not affect the comparison in a major way. The experimental values of C_p show a slight dependence on power, especially at densities near critical where the density is changing considerably during the course of a single measurement. Work is presently underway to re-examine all of the corrections to see if we can identify the cause of this slight dependence on power, and we hope to report on the complete set of experimental data in the near future.

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