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The Thermal Conductivity of Benzene and Toluene[1]

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The thermal conductivity of liquid toluene and benzene was measured in the temperature range 298 to 370 K, near the saturation line, using an absolute transient hot-wire technique. The measurements were made in a modified version of an existing instrument, equipped with a new automatic Wheatstone bridge, computer controlled. The bridge measures the time that the resistance of a 7-μm-diameter platinum wire takes to reach predetermined values, programmed by the computer. The computer can generate up to 1024 analog voltages, via a 12-bit D/A converter. The accuracy of the measurements with this new arrangement was assessed by measuring the thermal conductivity of a primary standard, toluene, at several temperatures and was found to be of the order of 0.3%. Benzene was chosen because it is under study as a possible secondary standard for liquid thermal conductivity by the Subcommittee on Transport Properties of IUPAC.

KEY WORDS: benzene; thermal conductivity; toluene; transient hot-wire method.

1. INTRODUCTION

This paper describes measurements of the thermal conductivity of benzene and toluene, made with the transient hot-wire technique. This technique is an absolute method, proven in recent years to be the most accurate method for the measurement of the thermal conductivity of fluids, outside the critical zone. This situation was made possible by the correct development of the theory of the method, which permits the separation of pure conduction

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from the other forms of heat transfer, convection and radiation, unavoidably present in any experimental measurement.

There has been a considerable effort in the last decade on the definition and characterization of standard reference fluids for the measurement of the thermal conductivity [1]. It is now accepted [1] that a standard fluid must satisfy the following conditions: have an extended liquid range, be nontoxic and noncorrosive, have a low cost, be amenable to being obtained with a high purity, and have accurate density data available.

The transient hot-wire technique is at present the best technique for obtaining standard reference data. The liquids proposed by IUPAC (toluene and water as primary standards) were measured with this technique with an accuracy of 1% or better.

New measurements were made for toluene in order to test the accuracy of a new automatic Wheatstone bridge and for benzene to substantiate a future proposal as a secondary standard by the Subcommittee on Transport Properties of IUPAC.

The high purity of benzene (99.999%) and the availability of excellent values of the density, normally used to calibrate densimeters [2], make this liquid a strong candidate as a standard, possibly a secondary one due to the fact that it is a carcinogenic fluid.

2. EXPERIMENTAL

The thermal conductivity measurements have been performed in the transient hot-wire instrument described elsewhere [3]. The working equation of this method is based on the temporal solution of the Fourier heat conduction equation, which describes the time evolution of the temperature increase in a thin platinum wire, when a heat pulse is generated in it.

After correcting the measured temperature rises for all the deviations to the ideal line source, the temperature rise at the surface of the wire is given by

$$\Delta T = \frac{q}{4\pi\lambda} \ln \frac{4at}{r_0^2 C} \tag{1}$$

where q is the heat dissipation in the wire per unit length, r_0 is the wire radius, t is the time elapsed from the beginning of the experiment, λ is the thermal conductivity of the liquid, and $a = \lambda/\rho C_p$ is the thermal diffusivity of the liquid. C_p is the heat capacity of the liquid, ρ is the density, and $C = 1.781\ldots$.

The automatic Wheatstone bridge used in the present work is similar to the one described by Charitidou et al. [4], and details of its geometry can be found in that paper. The former equipment [3] has been proved to be able to measure the thermal conductivity of fluids with an accuracy better than 0.5% [5–7].

Some modifications were introduced in the filling line in order to have a permanent overpressure of gaseous helium, to avoid boiling of the liquid.

The liquids studied were obtained as pure as possible, by using standard purification techniques. Toluene (Merck p.a.) and benzene (Merck p.a.) were dried under reflux with calcium hydride in a nitrogen atmosphere and further distilled and degasified. This purity was checked with gas chromatographic (GC) analysis and found to be better than 99.99%.

3. RESULTS

In order to demonstrate the accuracy of the new bridge a number of measurements of the thermal conductivity of toluene near its saturation vapor pressure were carried out. The values of C_p and density used in the corrections of the ideal temperature rise were obtained from the compilation of Vargaftik [8].

Figure 1 shows a plot of the deviations of a set of corrected experimental data (ΔT, $\ln t$) from a linear fit to them. The experiment was performed at a reference temperature of 335.5 K, near the saturation line, and it can be seen that no datum departs from the straight line by more than 0.05%.

Table I contains the experimental results for the thermal conductivity of toluene at the reference temperature as well as the density at the saturation line in the same temperature. The deviations of the present experimental data from the recommended correlation [1] are plotted in Fig. 2. In no case does the deviation exceed ±0.6%. The same figure includes the devia-

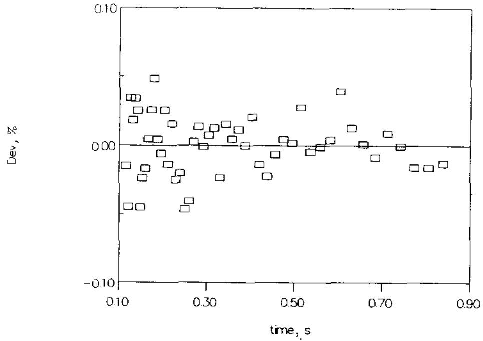

Fig. 1. The deviations of experimental data (ΔT, $\ln t$) from the straight-line fit for toluene at the reference temperature $T_{\mathrm{ref}} = 335.5$ K near the saturation line.

Table I. Experimental Data of the Thermal Conductivity of Toluene Near the Saturation Line at the Reference Temperature and Reference Density [8]

T_{ref} (K)	λ_{ref} $(W \cdot m^{-1} \cdot K^{-1})$	ρ_{ref} $(kg \cdot m^{-3})$
299.73	0.1306	860.47
302.94	0.1298	857.43
313.35	0.1258	847.55
316.42	0.1251	844.64
316.44	0.1251	844.62
332.89	0.1204	828.96
335.53	0.1194	826.45
335.79	0.1198	826.20
365.66	0.1109	797.63
366.67	0.1105	796.66
366.82	0.1105	796.51

tion of the experimental results, of Charitidou et al. [4] near the saturation line and Nieto de Castro et al. [9] extrapolated from high density to the saturation line. It can be seen that the agreement is excellent within the mutual uncertainties of different sets of data and the accuracy of the correlation. Therefore, we can conclude that our instrument operates in accordance with its model and we estimate that the precision of the thermal conductivity measurements is one of 0.2%.

Table II shows our experimental data for the thermal conductivity of

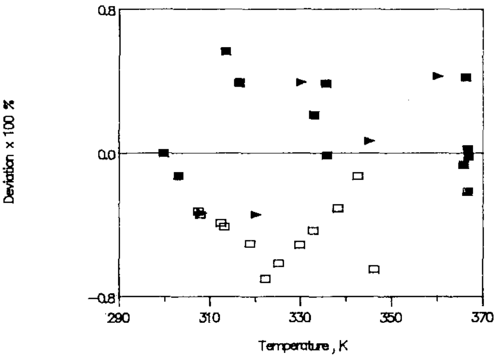

Fig. 2. The deviations of measurements of the thermal conductivity for toluene near its saturation vapor pressure, from the recommended correlation [1]. (■) Present work; (□) Charitidou et al. [4]; (▶) Nieto de Castro et al. [9] extrapolation from high pressures.

Table II. Experimental Data of the Thermal Conductivity of Benzene Near the Saturation Line at the Reference Temperature and Reference Density [10]

T_{ref} (K)	λ_{ref} ($\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	ρ_{ref} ($\text{kg} \cdot \text{m}^{-3}$)
298.59	140.18	873.23
298.76	140.07	873.05
305.49	138.20	865.90
305.66	138.07	865.90
305.88	138.08	865.49
309.55	137.06	861.56
312.89	135.99	857.98
318.51	134.36	851.91
323.10	133.18	846.93
323.66	133.01	846.32
331.37	130.68	837.89

benzene near its saturation vapor pressure as a function of the reference temperature and reference density at the saturation line. The values for C_p and density were obtained from the compilation of Goodwin [10].

The temperature dependence of the thermal conductivity has been represented by a linear function as

$$\lambda = 225.98 - 0.28744\,T \tag{2}$$

with λ expressed in $\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ and T in K, and Fig. 3 shows a plot of this representation. The maximum deviation of the measurements from the above equation, as can be seen in Fig. 4, is 0.09%, whereas the standard deviation is 0.06%.

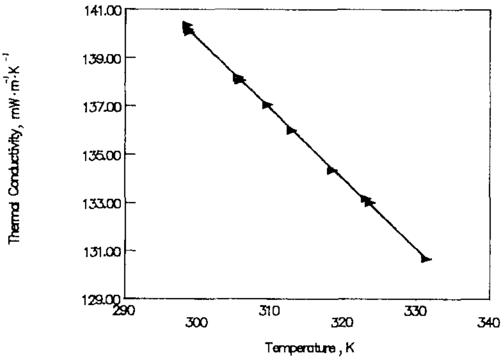

Fig. 3. The thermal conductivity of benzene as a function of temperature.

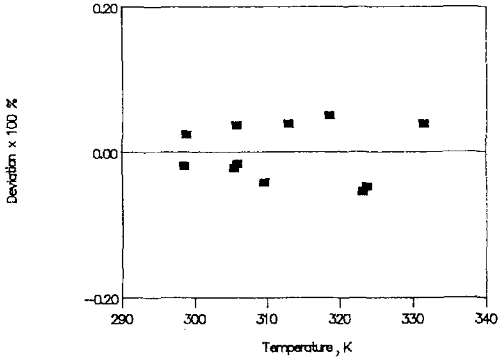

Fig. 4. The deviation of present experimental measurements for benzene, from Eq. (2).

To examine the extent to which the present experimental data conform to the result of the correlation proposed by Li et al. [11], we plotted in Fig. 5 the deviations of our results from the correlation, together with the results of other workers [11–15]; our deviations do not exceed 0.6%, while the other data have a maximum deviation of less than ±2%.

4. CONCLUSIONS

Thermal conductivity data have been reported for toluene and benzene, near the saturation line. The experimental results for toluene have been shown to be consistent with other accurate measurements along the

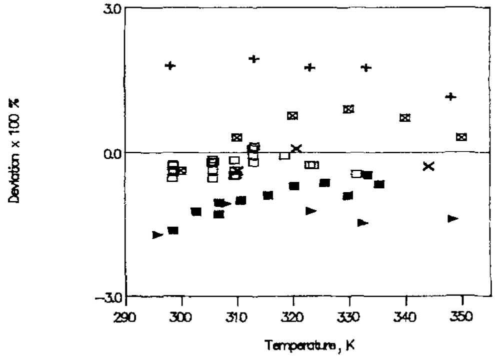

Fig. 5. The deviations of measurements of the thermal conductivity of benzene at its saturation vapor pressure from the correlation recommended by Li et al. [11]. (□) Present work; (×) Li et al. [11]; (■) Charitidou et al. [12]; (▶) Horrocks et al. [13]; (+) Kashiwagi et al. [14]; (⊠) Fisher et al. [15]

saturation line, as well as with the standard reference data, thus confirming the accuracy of 0.3% claimed for our present instrument. The experimental results for benzene are, for the moment, the most reliable results near the saturation line. The quality of available experimental data is such that liquid benzene could be proposed in the near-future as a primary standard for thermal conductivity in the saturation line.

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NOTE ADDED IN PROOF

The proposition of benzene as a primary standard has been made recently. Please see M. J. Assael, M. L. V. Ramires, C. A. Nieto de Castro and W. A. Wakeham, *J. Phys. Chem. Ref. Data*, submitted (1989).

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