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A Computer-Controlled Instrument for the Measurement of the Thermal Conductivity of Liquids

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A new instrument for the measurement of the thermal conductivity of liquids by the transient hot-wire method is described. The instrument has features in common with earlier versions but employs a novel technique for the determination of the transient temperature rise of the hot wire during the course of a measurement. New determinations of the thermal conductivity of toluene confirm the accuracy of the instrument to be better than 0.5%.

KEY WORDS: liquids; measurement technique; thermal conductivity; toluene; transient hot-wire method.

1. INTRODUCTION

In recent years the transient hot-wire method has become established as the preferred technique for the measurement of the thermal conductivity of liquids [1]. The essential feature of an instrument of this type must always be the precise determination of the transient temperature rise of a thin metallic wire from measurements of its resistance over a period of about 1 s following the initiation of a heating cycle [2, 3]. There are three distinct ways in which this resistance measurement has been performed. In the first methods, a four-terminal measurement of resistance is employed directly with a suitable digital multimeter [4]. In this case, a single wire is used for

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the measurements and effects at the ends are largely eliminated by the positioning of the two potential leads. In the second method, two wires of different lengths are incorporated in the arms of a bridge and the out-of-balance voltage of the bridge during a transient run is recorded with a digital voltmeter [4, 5]. The resistance difference of the wires can be described directly from the measurements in terms of the fixed resistors in the bridge. It is a characteristic of both of these two techniques that if the number of measurements to be made in a given time is to be increased, it is necessarily at the expense of their precision. The fact that the thermal conductivity is derived from the slope of a linear regression of a set of such data mitigates the loss of precision somewhat. Nevertheless, the overall effect on the thermal conductivity is a loss of precision approximately proportional to the number of transient data points.

In the third technique, a bridge is again employed for the resistance measurements but one arm is arranged to provide a preset sequence of balance points as the resistance difference of the two hot wires in the bridge increases. The time at which those preset balances occurs yields a series of temperature rise-time data for the regression analysis [6]. In this case, increasing the number of data points leaves the precision of each point unaltered so that the overall precision of the thermal conductivity is improved. In earlier versions of the instrumentation the preset balances have been generated by a set of suitable resistances in a parallel arm of the bridge. The dual constraints of cost and practicality have set limits to the number of data points attainable in one run in this scheme of between 6 and 12. Although repeated runs under nominally identical conditions can increase the total number of data points, the difficulties of cell temperature control over the significantly longer period of time required lead to a loss of precision.

In this paper, we describe a new version of this third technique that overcomes all of the deficiencies of earlier versions while retaining the advantages over other methods.

2. THE THERMAL CONDUCTIVITY INSTRUMENT

The thermal conductivity instrument described here is intended for studies of liquids and liquid mixtures including electrically conducting systems at moderate pressures over a wide range of temperature. To assess the performance of the instrument, bare platinum wires were used in the first stage to measure the thermal conductivity of toluene. Most of the elements of the instrument are similar to those described in earlier versions, so that we restrict the discussion of them here, preferring to concentrate on the novel electronic systems used for the measurements.

2.1. The Computer-Controlled Wheatstone Bridge

Figure 1 shows a schematic diagram of the bridge. In this circuit R_L and R_S represent two thin platinum wires (10-μm nominal diameter) that form the sensors and heat sources for the transient heating. They differ only in their lengths [7]. Resistances R_1, R_2, R_6, and R_7 are decade resistance boxes, while R_3, R_4, and R_5 are fixed resistors, all in a temperature-controlled environment. The numerical values of all resistors and their tolerances are shown in Table I. Relay S_1 is a high-speed mercury-wetted reed relay. V_0 is a stable, high-precision source of a dc voltage (HP 1116) and V_E is a digital-to-analogue converter whose reference voltage is derived from V_0. The diagram shows the bridge in its position prior to measurements. In this configuration, the resistance of the upper right-hand arm of the bridge is arranged so it slightly exceeds that of the upper left-hand arm. In addition, R_7 is adjusted so that $R_7 = R_1 + R_L(0) + R_S(0)$ to ensure that, upon switching S_1 to X, there is no significant change in the load on the power supply. $R_L(0)$ and $R_S(0)$ are the equilibrium resistances of the two platinum wires.

Figure 2 shows a schematic diagram of a measurement cycle. Prior to the initiation of a measurement a sequence of values V_E is established and stored in the memory of the computer that controls the bridge. The operation of switching S_1 to X, via the relay device with the computer, initiates a measurement cycle in the following way. A pulse generated by the current flowing in the two hot wires is used to initiate the counter and the timing sequence begins. The current flowing in R_L and R_S leads to heat

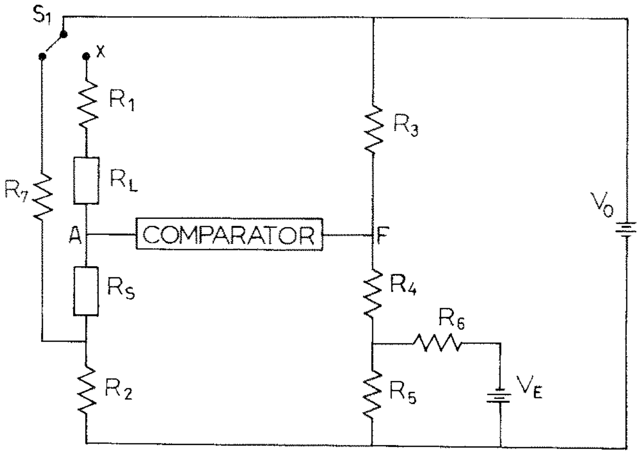

Fig. 1. Schematic diagram of the automatic Wheatstone bridge.

Table I. Values of the Resistors Used in the Automatic Wheatstone Bridge

Resistor	Resistance (Ω)	Tolerance (%)
R_1	0–1000	±0.05
R_2	0–1000	±0.05
R_3	2000	±0.001
R_4	1000	±0.001
R_5	1003	±0.001
R_6	10^5–10^6	±0.05
R_7	0–1000	±0.5

dissipation in these wires and their temperature rise, and thus their resistances increase. Because of the initial configuration of the bridge at some time equilibrium is reached between point A and point F (Fig. 1). This is detected by a sensitive high-impedance comparator, similar to the one described elsewhere [6], and the first time is registered in the computer memory via the 24-bit counter interface (Fig. 2). At the same time, the first value of V_E stored in the computer memory is recalled and applied to the bridge by means of a 12-bit D/A converter. This causes the bridge to

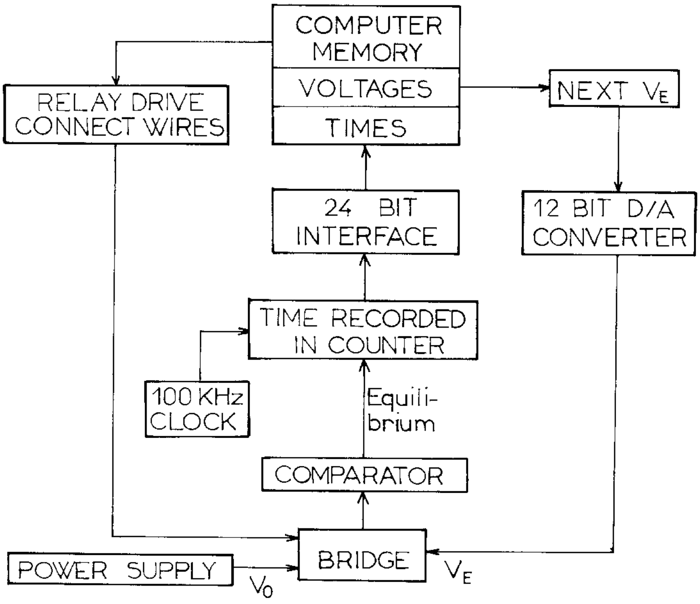

Fig. 2. Schematic diagram of a measurement cycle.

shift off equilibrium, and as the resistance of the platinum wires continues to increase a second equilibrium point is reached. From the balance conditions, the resistance difference $(R_L - R_S)$ at every equillibrium time may be determined, and thus the temperature rise ΔT of the wires. By repetition of this process, up to 1024 $(\Delta T, t)$ points may be acquired in a single run in 1 s. It is clear that increasing the number of points in this technique has no effect upon the precision of individual points in either the temperature rise or the time. Consequently, the precision of the thermal conductivity can be improved considerably. The noise level in the comparator is less than $\pm 10 \mu V$, which corresponds to less than 0.05% of the temperature rise in the wire.

The state of equilibrium in the bridge, between point A and point F, can be written as

$$R_L - R_S = \left(\frac{R_L}{R_S} - 1\right) \frac{CR_2 - (1-C)R_1}{(R_L/R_S)(1-C) - C} \tag{1}$$

$$C = \frac{(R_3/R_5) + (R_3/R_6) + V_E/V_0(R_3/R_6)}{\{[(R_6+R_5)(R_3+R_4)]/R_5R_6\} + 1} \tag{2}$$

Because the two platinum wires were chosen to be identical except for length, the equations above constitute the determination of the resistance of a single wire with no ends [7]. Hence, the temperature rise of this hypothetical wire as a function of time can be calculated. Thus after making due allowance for small corrections [8, 9] and calculating the heat dissipation in the wire per unit length, q, the thermal conductivity, λ, can be obtained from the data with the aid of the equation

$$\Delta T(a, t) = -(q/4\pi\lambda) \ln(4Kt/a^2C) \tag{3}$$

where a is the wire diameter, K the thermal diffusivity of the medium, and C Euler's constant.

2.2. The Thermal Conductivity Cells

The platinum wires used differ only in their lengths. Figure 3 shows the assembly of one of the two wires. The whole assembly is fixed inside a cell containing a fluid similar to that described by Assael et al. [3]. On the top a platinum hook is used to support the fold spring from which the platinum wire hangs. The wire is kept vertical by means of a platinum weight. The platinum weight keeps the wire under tension when the temperature is increased. The gold spring has the purpose of absorbing oscillations of the weight that would arise from the initiation of the heating

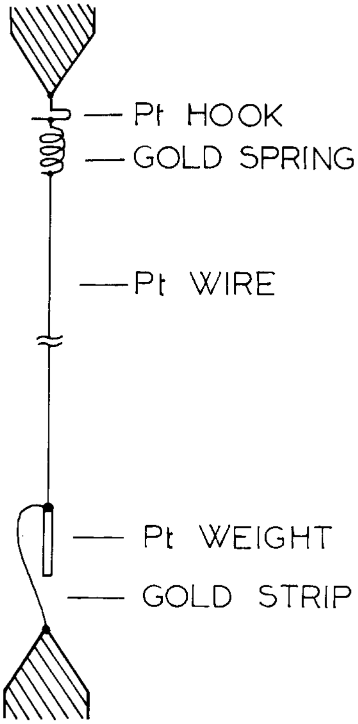

Fig. 3. The platinum wire assembly.

of the wire. The bottom electrical contact is achieved by means of a flattened, annealed, soft gold strip.

Two wires of this type were made and placed in the cells. The wires were subsequently annealed and placed in the vessel. The vessel is equipped with two platinum resistance thermometers for measuring the temperature of the measuring liquid. Heating is supplied to the vessel electrically and the stability of the temperature was found to be ±0.01 K.

3. CONFIRMATION OF OPERATION AND ACCURACY

In order to demonstrate that the new instrument described here operates in accordance with the theoretical model of it, we have carried out a number of measurements of the thermal conductivity of toluene just above its saturation vapor pressure. Toluene has recently been recommended by IUPAC as a liquid thermal conductivity standard [10] and therefore represents the best fluid for such a study.

Figure 4 shows a plot of the deviations of a set of corrected experimen-

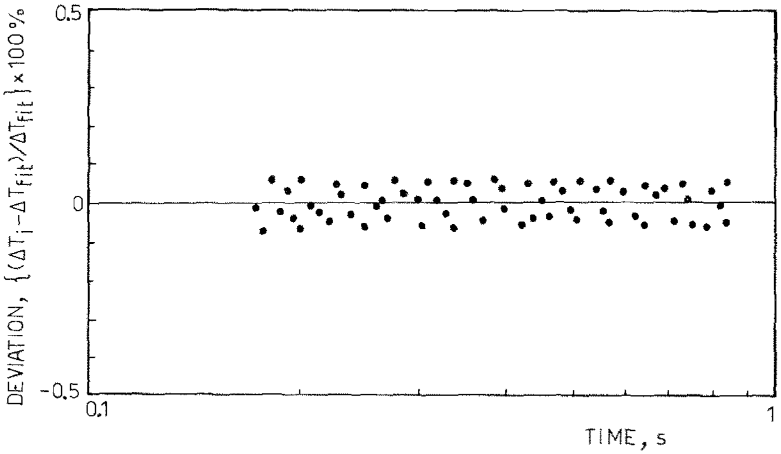

Fig. 4. Deviations of the experimental points from the least-squares straight line for a measurement of toluene at 319.8 K.

tal data (ΔT_i, ln t_i) from a linear fit to them. The experiment was carried out in toluene at a temperature of 319.8 K using a temperature rise of about 2.5 K.

It is clear that no datum departs from the straight line by more than 0.08% and that there is no evidence of any systematic departure. On the

Table II. The Experimental Values of the Thermal Conductivity of Toluene at Various Temperatures

Reference temperature (K)	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)
307.45	0.1287
307.86	0.1286
312.38	0.1273
313.13	0.1271
318.84	0.1255
322.30	0.1247
325.26	0.1237
329.82	0.1222
332.81	0.1212
338.29	0.1194
342.58	0.1179
346.27	0.1174

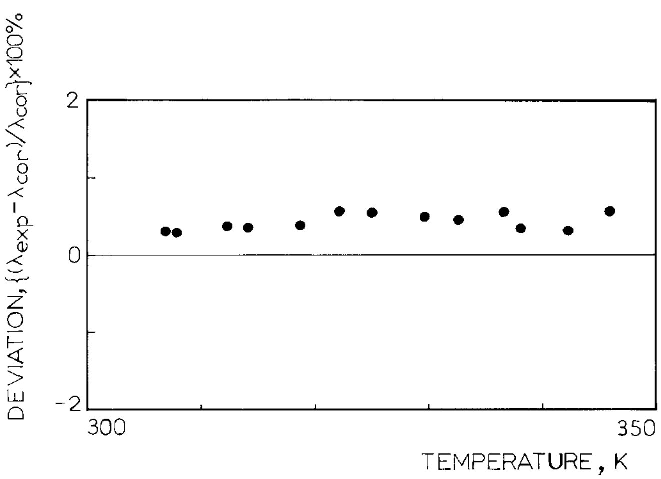

Fig. 5. Deviations of the experimental thermal conductivity values of toluene from the recommended correlation [1, 10].

basis of this and other similar plots we conclude that the instrument operates in accordance with the model of it. On the basis of the same information, we estimated that the precision of the thermal conductivity measurements is one of 0.2%. Accounting for a number of other small errors, such as the measurements of the wire lengths and the temperature coefficient of platinum, it is estimated that the thermal conductivity data have an accuracy better than 0.5%.

Table II lists the thermal conductivity of toluene as determined in the present study and Fig. 5 shows the departures of the results from the recommended correlation [1, 10].

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