

A Transient Hot-Wire Instrument for Thermal Conductivity Measurements in Electrically Conducting Liquids at Elevated Temperatures

A. Alloush,¹ W. B. Gosney,¹ and W. A. Wakeham²

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This paper describes a novel type of transient hot-wire cell for thermal conductivity measurements on electrically conducting liquids. A tantalum wire of 25 μm diameter is used as the sensing element in the cell, and it is insulated from the conducting liquids by an anodic film of tantalum pentoxide, 70 nm thick. The cell is suitable for measurements on conducting liquids at elevated temperatures. The results of test measurements on liquid water at its saturation vapor pressure are reported in order to confirm the correct operation of the thermal conductivity cell. The data, which have an estimated accuracy of $\pm 3\%$, depart by less than $\pm 1.8\%$ from the correlation proposed by the International Association for the Properties of Steam. Results are also presented for concentrated aqueous solutions of lithium bromide, which are frequently used in absorption refrigerator cycles.

KEY WORDS: hot-wire method; lithium bromide solution; thermal conductivity.

1. INTRODUCTION

The transient hot-wire technique [1] has now become established as an extremely accurate technique for the measurement of the thermal conductivity of gases and liquids [2–5]. The technique involves the measurement of the temporal evolution of the temperature of a thin, metallic wire immersed in the fluid following the stepwise application of a voltage across its ends [1]. The evolution of the temperature of the wire is determined either by

¹Department of Mechanical Engineering, King's College, London, England.

²Department of Chemical Engineering and Chemical Technology, Imperial College, London, England.

determining the times at which its resistance attains certain preset values [4, 6], or by recording the voltage change across a bridge containing the wire as a function of time [7]. In the case of liquids the application of the method has been mainly restricted to measurements on electrically insulating liquids [5]. This is because the contact between the bare metallic wire and the conducting liquid first provides a second path for the flow of current in the cell; secondly, it leads to polarization of the liquid on the surface of the wire; and finally, it can produce a distortion of the small signals to be observed [8]. Two methods have recently been developed to overcome these difficulties. The first, employed by Dietz *et al.* [9] for measurements on water, retains a bare metallic wire but makes use of an alternating current to obviate the effects of polarization. A second technique, described by Nagasaka and Nagashima [8], makes use of a metallic wire coated with a thin layer of an insulating polyester material or a liquid metal in a glass envelope [9]. The latter authors have also developed the working equations appropriate to measurements with coated wires [8]. However, owing to the degradation of the polyester coating on the wires, the first cells that they described [8] could not be used above 150°C.

The work described in the present paper had two motivations. Solutions of alkali metal halides in water have found increasing application in refrigeration cycles. For example, lithium bromide in water is widely used in large absorption refrigerators used in air conditioning [11].

However, there are very few measurements of the thermal conductivity of the most useful of these fluids despite the fact that such data are essential to the design of such refrigeration systems. Thus, the primary aim of the present work was to obtain thermal conductivity data for a variety of these fluids, with modest accuracy, over the temperature range 20–80°C at atmospheric pressure. Secondly, the increasing use of molten salts and liquid metals as heat transfer media implies that thermal conductivity data for such systems over a wide range of conditions, necessarily involving temperatures above 150°C, are required. Consequently, a further aim of the work was to obtain a practical prototype of transient hot-wire cells which could be employed under such conditions with electrically conducting liquids. With these aims in mind a cell was designed and constructed which could be employed with the electronic components of the existing experimental installation. Inevitably, since the two sections of the apparatus were not designed as a set, their application in this way represents something of a compromise. Nevertheless, the thermal conductivity of several conducting liquids has been determined with an estimated uncertainty of $\pm 3\%$, and the preliminary study confirms the viability of the cell design for operation at higher temperatures.

2. THE THERMAL CONDUCTIVITY CELL

The design of the present thermal conductivity cell is shown in Fig. 1. The outer wall of the cell is formed by a Pyrex glass tube (1), 160 mm long and 22 mm in internal diameter. At its upper end the tube is terminated by a pyropholite plug (2) sealed into the tube with adhesive and held secure by the clamping mechanism (3 and 4). The pyropholite plug forms the support for the hot-wire assembly and its adjustment mechanism. The hot wire itself (5) consists of a 25 μm diameter tantalum wire (purity 99.9%) insulated with a layer of tantalum pentoxide 70 nm thick, which is formed on the wire *in situ* in a manner to be described below. At its lower end the wire is soft-soldered to a 0.6 mm diameter copper lead (6), which passes

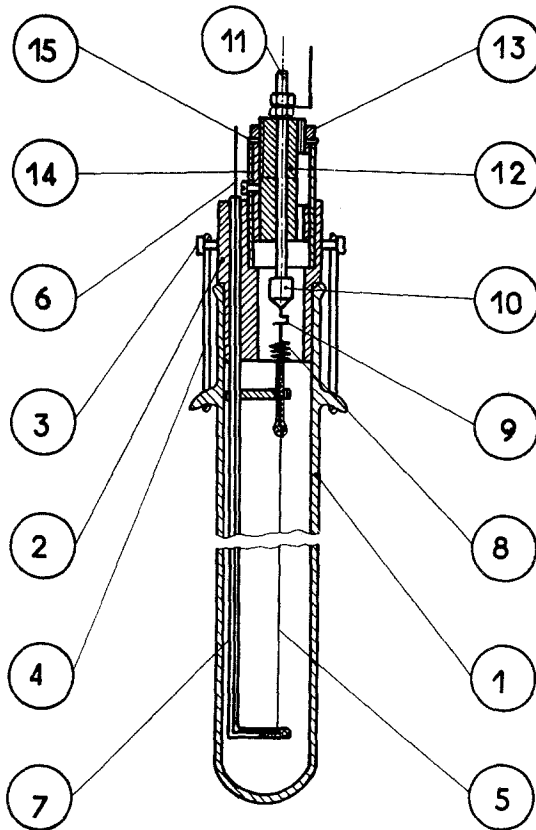


Fig. 1. The design of the thermal conductivity cell for electrically conducting fluids.

through an insulating glass tube (7) to the pyropholite plug, in which it is fixed. At its upper end the hot wire is soldered to a helical spring (8) of coil diameter 3 mm made from three turns of 0.3 mm diameter gold wire. The upper end of the spring is soldered in turn to a platinum hook (9) mounted in a brass cone (10) with a silver alloy solder. The brass terminal pin (11), which is screwed into the cone, is threaded into a pyropholite bush (12) so that rotation of the pin, accompanied by a vertical movement, is possible. Simple vertical movement of the pin is achieved by means of the nut (13) threaded on to the bush. The bush is a sliding fit inside the composite metal cylinder (14), which is fitted with a finger engaged in a slot in the bush and thereby prevents its rotation. The thread of the nut (13) is calibrated so that the vertical movement of the pin, which results from the rotation of the nut, is known. The P.T.F.E. washer (15) is included to reduce friction at the bearing surface of the nut and the bush, whereas the support pillar (16) serves to prevent violent motion of the wire during handling and filling the cell. All metal parts of the cell which are below the liquid surface during measurement are insulated with silicone rubber to prevent electrical contact with the test liquid.

The spring is included in the design in order to maintain the wire taut at different equilibrium temperatures of the cell as well as during the transient heating of the wire [12]. To achieve this function the spring has been designed in accordance with the general principles detailed elsewhere [12] and calibrated to determine its elastic characteristics. During assembly at ambient conditions, the spring is preloaded by means of the vertical adjustment mechanism so that under no circumstances does the stress in the wire exceed 10% of the yield stress of tantalum.

The novel feature of the present cell is the use of an oxide layer to form an insulating coating on the wire. The solution to the problem of insulation of the wires was the result of a series of trials with other coatings for platinum wires such as organic polymers and vacuum sputtered silica. Neither of these approaches proved successful because in the first case, the coating was generally nonuniform, and in the second, because the thin layer was too brittle. The tantalum oxide layer, which was formed on the tantalum wire by anodization *in situ*, proved robust and adhered to the wire throughout a series of temperature cycles. This encourages the view that similar wires could be used to much higher temperatures than those employed here.

Prior to coating of the wire, the completely assembled cell, filled with air, was mounted in a thermostat, and the resistance of the wire was measured at a fixed temperature. Subsequently the wire assembly was removed from the cell and the wire was chemically polished in a bath containing 98% H_2SO_4 , 70% HNO_3 , and 40% HF solutions in the ratio

10:4:3 by volume [13] for a period of a few seconds. Following this period the cell was immediately leached in boiling water for 15 min to remove the film formed during chemical polishing. Anodic films produced on surfaces prepared in this way have previously been found to be strongly adherent [14].

In order to form the oxide layer on the tantalum wire, the thermal conductivity cell was filled with a solution of 0.2 M H_2SO_4 solution in demineralized water. The tantalum wire was then connected as the anode of an electrolytic cell with a 0.6 mm diameter platinum wire introduced into the cell acting as a cathode. An anodizing current density of about $2 \text{ mA} \cdot \text{cm}^{-2}$ was established in the cell by increasing the applied voltage. When the voltage reached 50 V, it was held at this value for some time until the current density fell to about $30 \mu\text{A} \cdot \text{cm}^{-2}$. Under these conditions a layer of tantalum pentoxide (Ta_2O_5) with a thickness of about 75 nm is formed on the surface of the tantalum wire [15]. When the anodization was complete, the cell was cleaned, filled with distilled water, and replaced in the thermostatic bath, and its resistance was remeasured. The change of resistance of the wire from its value before anodization enables the change in its diameter to be calculated.

2.1. Experimental Procedure

The remainder of the instrumentation employed for the measurements is similar to that employed by Nieto de Castro *et al.* [4] and is described in detail elsewhere [16]. It consists of an automatic dc Wheatstone bridge, which determines the time at which the resistance of the hot wire attains preset values during the 1 s of the transient heating period. In order to reduce the level of electrical noise, the bridge is operated with its output near ground potential, and the end effects in the wires [11] are automatically eliminated by connecting two wires of different length in opposite arms of the bridge [4, 17]. In the present measurements, this scheme could not be carried through in its entirety because tantalum pentoxide is unstable when exposed to negative voltages and therefore can only act as an insulator for a wire above ground potential. Thus, with the existing installation, it was necessary to work with just one wire and to calculate the correction to be applied as a result of the end effects. It should be pointed out that this is not a general limitation of the method employed here since other arrangements could be developed to retain a low noise level with the entire bridge raised above ground potential.

A further consequence of the use of the existing electrical system follows from the decrease in wire resistance attendant upon the replacement of the usual $7 \mu\text{m}$ platinum wire, used for measurements in nonconducting liquids [5], by the $25 \mu\text{m}$ tantalum wire. This substitution, under

otherwise identical conditions, leads to a four-fold decrease in the resistance change to be measured during a run and thereby to a loss in the resolution of the time measurements [4]. Although, in principle, this loss may be offset by the use of larger temperature rises, the existing installation was not suitable for this purpose. Consequently, it has been necessary to accept the somewhat poorer resolution and the subsequent reduction in precision of the measurements. This approach is consistent with the accuracy within a few percent required in the present thermal conductivity measurements and the aim of establishing the principle of the new cells. Further refinement of the technique to recover the precision and accuracy associated with measurements in nonconducting liquids is clearly possible.

The water employed for the present measurements was distilled and deionized. The lithium bromide was supplied by BDH Chemical Ltd. with a purity of 99.2% and the solutions were manufactured gravimetrically. Density and heat capacity data for water were taken from standard tables [18]. For the salt solutions the density was determined directly and the heat capacity was taken from ref. [11]. Because only small corrections are necessary for these thermophysical properties in the evaluation of the thermal conductivity, the effect of uncertainties in their values is negligible.

3. WORKING EQUATIONS

The fundamental working equation of the transient hot-wire technique takes the form

$$\Delta T_{id} = \frac{q}{4\pi\lambda(T_r, P)} \ln \frac{4\kappa t}{a^2 C} \quad (1)$$

in which ΔT_{id} represents the temperature rise in an ideal instrument [1], $\lambda(T_r, P)$ the thermal conductivity of the fluid at a reference temperature T_r and the working pressure P , κ is the thermal diffusivity, a the hot-wire radius, q the rate of heat generation per unit length in the wire, t the time, and C a numerical constant. All practical instruments depart from this ideal to some extent, and it is therefore necessary to apply small corrections to the measured wire temperature rise, ΔT_w , to recover that for the ideal case. In the present measurements just four of these corrections are significant ($> 0.01\%$ of the wire temperature rise) so that [1]

$$\Delta T_{id} = \Delta T_w + \sum_{i=1}^4 \delta T_i \quad (2)$$

The first correction, δT_1 , accounts for the finite heat capacity of the wire and its coating as well as for their finite thermal conductivity. An analytic

expression for this correction has been given by Nagasaka and Nagashima [8] which involves the thermophysical properties of the fluid, the wire, and its coating. In the present measurements the total correction amounts to no more than 0.3% of the wire temperature rise, of which only 0.02% arises from the wire coating. Consequently, any errors in the application of this correction make a negligible contribution to the final thermal conductivity of the fluid.

The correction δT_2 of Eq. (2) arises from the effects of axial conduction in the wire and the fluid near the supports. For the reasons given earlier, the end effects could not be compensated experimentally in the present arrangement as in earlier measurements [5]. Consequently, it has been necessary to obtain the correction δT_2 from an analysis given by Haarman [19]. Because this correction never amounted to more than 0.4% of the temperature rise, the error in this estimation has an effect upon the measured thermal conductivity which is much less than that arising in other ways. The correction δT_3 , which arises from the presence of an outer boundary to the fluid, has been derived elsewhere [1]. In the present work the correction never amounted to more than 0.01% of the wire temperature rise.

Finally, the term δT_4 expresses the correction to be applied because of the absorption and emission of radiant energy by the fluid. It has not yet proved possible to develop an analytic description of the conduction-radiation process in the transient hot-wire cell so that we are not able to apply the correction δT_4 . Nevertheless, numerical studies of the process have shown [20] that the complete neglect of the correction leads to reported thermal conductivity data which may be systematically in error by no more than 1 or 2%. Consequently, in view of the computational effort required to apply the correction deduced by Menashe and Wakeham, we prefer to report here thermal conductivity data uncorrected for radiation, and to admit that they may be burdened with an uncertainty of 2% [5, 20].

A further equation is required to complete the description of the working equations, which defines the reference temperature, T_r , to which the measured thermal conductivity relates. For this purpose we have uniformly adopted the relation given by Nagasaka and Nagashima [8], although it departs by less than 0.05 K from the value appropriate to a bare wire [1].

4. PERFORMANCE OF THE EQUIPMENT

It is a requirement of the working equation (1) that the measured temperature rise of the wire, suitably corrected according to Eq. (2), should be a linear function of $\ln t$, within the resolution of the measurements.

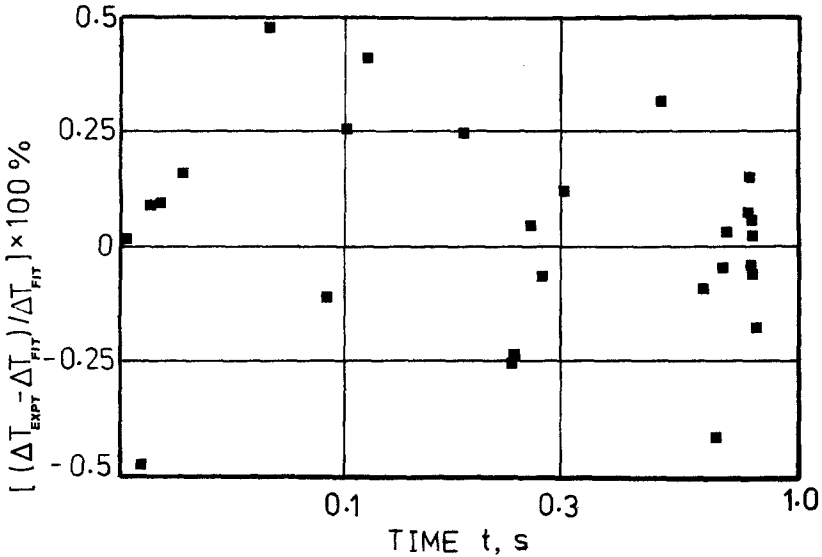


Fig. 2. The deviations of the measured temperature rise of the wire from a least squares fit to the data for an experiment with an aqueous solution of lithium bromide with a mass fraction of salt, $\xi = 0.55$, at a temperature of 23°C .

Figure 2 contains a plot of the deviations of the temperature rise measurements from a least squares fit of a straight line to the data for a measurement in an aqueous solution of lithium bromide, with a lithium bromide mass fraction of 0.55 at a temperature of 23°C . The deviations do not display any systematic pattern and do not exceed $\pm 0.5\%$, which is consistent with the estimated resolution of each measurement, and representative of all the runs reported here. The magnitude of the random scatter is of course somewhat worse than that found in nonconducting liquids for the reasons mentioned above. The linearity of the experimental data confirms that the operation of the instrument is consistent with the mathematical description of it. The precision of the thermal conductivity measurements has been based upon the reproducibility of the values obtained from a number of independent measurements on a single liquid and has been found to be $\pm 0.7\%$. Combining this with the errors arising from the temperature coefficient of resistance of the wire employed and the effects discussed earlier, it is estimated that the uncertainty in the thermal conductivity data is one of $\pm 3\%$.

5. RESULTS

The results of the present thermal conductivity measurements for pure water and some aqueous solutions of lithium bromide are listed in Table I.

Table I. The Thermal Conductivity of Aqueous Solutions of Lithium Bromide at a Pressure of 0.1 MPa

Lithium bromide mass fraction, ξ	Temperature, T (K)	Thermal conductivity, λ (mW · m ⁻¹ · K ⁻¹)
0	297.0	608
	305.0	614
	315.0	619
0.500	297.0	473
	305.0	478
	315.0	484
	335.0	500
	357.0	511
0.550	297.0	465
	305.0	467
	315.0	469
	335.0	483
	357.0	499
0.600	297.0	457
	305.0	463
	315.0	464
	335.0	478
	357.0	493
0.650	297.0	452
	305.0	457
	315.0	461
	335.0	474

In each case the data have been adjusted to nominal temperatures by the application of linear corrections amounting to no more than $\pm 0.16\%$. The measurements on pure water were carried out to establish confidence in the absolute values of the thermal conductivity, and the values reported here differ from the correlation of the International Association for the Properties of Steam [21] by less than 1.8%, which is consistent with their estimated uncertainty.

Figure 3 illustrates the composition dependence of the thermal conductivity of the aqueous solutions of lithium bromide. The entire body of experimental data may be represented by an equation of the form

$$\lambda = 434.14 - 367.69\xi + 191.64\xi^2 + 0.5875T \tag{3}$$

in which λ is the thermal conductivity measured in mW · m⁻¹ · K⁻¹, ξ is the salt mass fraction, and T is the absolute temperature in Kelvins. The

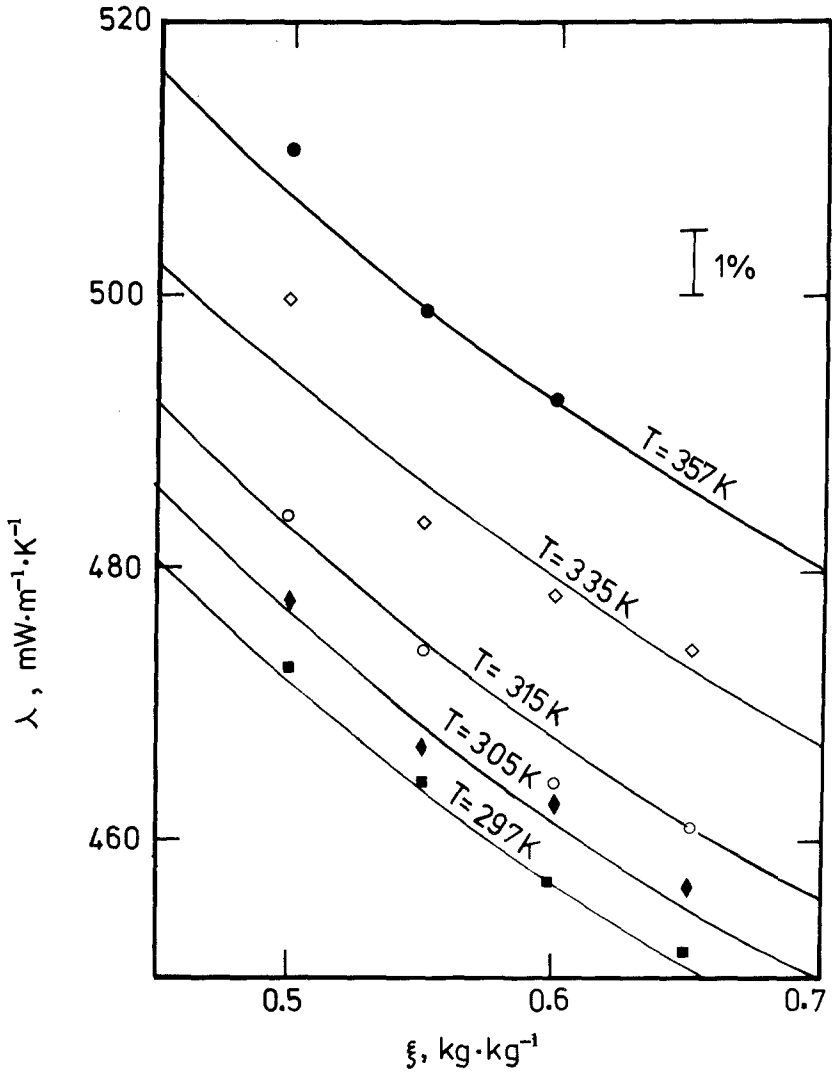


Fig. 3. The thermal conductivity of aqueous lithium bromide solutions along several isotherms. Curves represent values calculated according to the correlation of Eq. (3).

deviation from this correlation does not exceed $\pm 0.8\%$. The linear temperature dependence of the thermal conductivity implied by this correlation is characteristic of the behavior of liquids over a wider temperature range than that studied here [22], and it is expected that the correlation may be extrapolated to higher temperatures without significant additional error.

6. CONCLUSIONS

The set of experimental results presented for electrically conducting liquids confirms the usefulness of the anodized tantalum wire in thermal conductivity instruments of the transient hot-wire type. The available information [23] indicates that the oxide layer is impervious to attack by a wide range of materials and adheres strongly to the metal substrate at much higher temperatures than those employed here. The present cell design may therefore form a suitable prototype for the development of thermal conductivity cells for measurements on a number of technologically important fluids.

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