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# An apparatus to measure the thermal conductivity of liquids

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**Abstract** The paper describes an apparatus for the measurement of the thermal conductivity of non-conducting liquids under their saturation vapour pressure. The instrument, which is based upon the transient hot wire principle, has been designed so that the measuring element conforms as closely as possible to an infinite line source of heat in an infinite fluid. Under these conditions the thermal conductivity of the liquid can be determined from the slope of a plot of the temperature rise of the heating element against the logarithm of time. The measurement system has been arranged so as to provide as many as 60 points on this plot for any particular thermodynamic state of the fluid under investigation. The reproducibility of the instrument is of the order of 0.03% and the precision of the measurements is estimated as  $\pm 0.1\%$ . Owing to a lack of a suitable theory for the effects of radiative heat transfer, the accuracy of the thermal conductivity values cannot be defined unequivocally, but a reasoned upper bound is  $\pm 0.3\%$ . Preliminary results are presented for n-heptane at three temperatures in the range 20 to 30°C.

## 1 Introduction

The thermal conductivity of fluids has, historically, proved to be an extremely difficult transport property to measure accurately. In the case of gases Kestin *et al* (1972) and de Groot *et al* (1974) have demonstrated conclusively that almost all early measurements of the thermal conductivity at low densities have been subject to large errors. This conclusion has been based upon the results of the Chapman-Enskog theory of dilute gas mixtures, which in the case of monatomic gases yields a well defined, exact relation between the viscosity of a gas and its thermal conductivity (Kestin *et al* 1972). For liquids no such thermodynamically consistent relation exists, so that statements with regard to the accuracy of thermal conductivity data must be based on inference. Thus, the disparity between independent workers' results for specific systems, which in general is greater than the claimed mutual uncertainty of the data, strongly suggests that for liquids too many of the earlier measurements must be in error. For

instance, the available data for n-C<sub>5</sub>H<sub>10</sub> show a spread of  $\pm 6\%$  about a mean value, whereas for n-C<sub>18</sub>H<sub>38</sub> the spread is  $\pm 2\%$ .

In this paper we describe the design and operation of an instrument which eliminates the major faults associated with earlier measurements of liquid thermal conductivities, and allows their accurate measurement near room temperature under their saturation vapour pressure. The underlying difficulty associated with the measurement of the thermal conductivity of fluids is the onset of free convection in the fluid when subject to temperature gradients in the earth's gravitational field. This problem is most acute in steady state methods and has only occasionally been overcome (Michels and Botzen 1952, Michels *et al* 1962). Even in some transient measurement techniques the eventual onset of convection has been observed (Pittman 1968) and may have vitiated the results. Thus, although it is clear that a transient measurement technique provides the best possible scheme for obviating the convection problem, proper consideration must be given to the apparatus design with regard to this point. Furthermore, the experimental and theoretical consequences of this choice of technique must be carefully analysed, and the analysis used to optimize the instrument design.

The most recent theory of the transient hot wire measurement scheme was originated by Haarman (1969, 1971, 1973) and has subsequently been refined and extended by Healy *et al* (1976). Application of this theory to instrument design and experimental measurement has so far been restricted to gas phase measurements (Haarman 1969, de Groot *et al* 1974) but most of the analysis can be carried over intact to the case of non-conducting liquids. The only additional complication introduced into the theory of the instrument arises because of the absorptive properties of the liquid medium for radiation (Pittman 1968, McLaughlin and Pittman 1971). However, this effect leads to only a small correction to the observed thermal conductivities and therefore can be ignored for the present purpose of instrument design and reconsidered when definitive results are presented.

The availability of a considerable literature upon the general topic of the transient hot wire method allows us here to omit a detailed exposition of the theory and to concentrate instead on its application to measurements in the liquid phase.

## 2 Principle of measurement

In the transient hot wire technique a thin, straight platinum wire immersed in an isotropic fluid and initially at equilibrium with it, is subjected at time  $t=0$  to a step change in the voltage applied to it. Following this change the wire appears as a line source of heat with a constant magnitude,  $q$ , per unit length, and the time evolution of the temperature of the wire is determined by the thermal conductivity of the fluid.

In the ideal situation of an infinitely thin and long wire immersed in, and initially at equilibrium with, a fluid of infinite extent at a temperature  $\theta_0$ , the temperature field around the wire following the initiation of a constant heat dissipation in it at time zero is given by (Carslaw and Jaeger 1959)

$$\Delta T(r, t) = \theta(r, t) - \theta_0 = (-q/4\pi\lambda)\text{Ei}(-r^2/4\kappa t). \quad (1)$$

Here,  $\lambda$  is the thermal conductivity of the fluid, assumed to be temperature independent, and  $r$  is the radial coordinate measured from the wire centre. In addition the thermal diffusivity,  $\kappa$ , of the medium is given as

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

where  $\rho$ , the fluid density and  $C_p$ , the constant pressure specific heat, are also assumed to be temperature independent.

For a wire of radius  $a$  the wire temperature can be obtained by setting  $r=a$  and expanding equation (1) as

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

for sufficiently small values of  $a^2/4\kappa t$ . Here,  $C$  is Euler's constant. Thus equation (3) provides the simplest possible relation between the temperature rise of the wire and time, and allows evaluation of the thermal conductivity provided that this relation can be measured experimentally.

Although any experimental realization of this principle must inevitably depart from the ideal situation described above, de Groot *et al* (1974) and Healy *et al* (1976) have shown that a suitable choice of experimental conditions can reduce some of these departures to the level of small calculable corrections of the order of 1%, and render others insignificant <0.01%. Thus, in arriving at the instrument design described in the next section we have performed a detailed study of each correction independently, following the work of Healy *et al* (1976), modifying their expressions only to make them appropriate for the liquid phase. It is therefore unnecessary for us to provide a detailed description of the search for an optimum design for the present apparatus. We prefer instead to present the final forms and magnitudes of the corrections to be applied when equation (3) is used to interpret measurements with the present apparatus, with the understanding that their magnitudes are a deliberate result of the design study undertaken.

3 Instrument design

The essential measurement to be performed by the instrument is the determination of the temperature rise of the heat source as a function of time following initiation of a current in it. In the present work this is achieved by making the heating element a thin platinum wire and connecting it in one arm of an automatic DC Wheatstone bridge, which is a variant of that described by Anderson *et al* (1974). The times at which the resistance of this wire attains several predetermined values are then found by using sequential balances of the bridge to stop a series of electronic timers started at the initiation of the heat dissipation.

Figure 1 shows a schematic diagram of the automatic Wheatstone bridge designed to perform this measurement. In this circuit  $R_L$  represents the resistance of a long, thin platinum wire and  $R_S$  the resistance of a wire differing only from the former in its length. Both of these wires are enclosed in fluid-filled cells which will be described later (§3.2). Resistances

$R_1, R_2$  and  $R_{17}$  are decade resistance boxes (Cropico type RBB5) whereas the remainder of the resistances of the bridge are ultrastable metal film resistors (Welwyn Electric Company, Vishay type) mounted in a temperature-controlled environment. Resistors  $R_4, R_3, R_9, R_{10}$  are all equal and their value will be subsequently designated by  $R$ . The numerical values of all resistors are collected in table 1 for ease of reference. The

Table 1 Resistances of the elements in figure 1

Resistor	Resistance ( $\Omega$ )	Tolerance (%)
$R_L$ at 20°C	195.64	$\pm 0.05$
$R_S$ at 20°C	58.81	$\pm 0.05$
$R_1$	0-1000	$\pm 0.05$
$R_2$	0-1000	$\pm 0.05$
$R_3, R_4, R_9, R_{10}$	4200	$\pm 0.05$
$R_5$	2000	$\pm 0.05$
$R_6$	4000	$\pm 0.05$
$R_7$	8000	$\pm 0.05$
$R_8$	16 000	$\pm 0.05$
$R_{11}$	$10^6$	$\pm 0.05$
$R_{12}$	$5 \times 10^5$	$\pm 0.05$
$R_{13}$	$3.3 \times 10^5$	$\pm 0.05$
$R_{14}$	$2.5 \times 10^5$	$\pm 0.05$
$R_{15}$	$2.0 \times 10^5$	$\pm 0.001$
$R_{17}$	0-1000	$\pm 0.01$

switching relays  $S_2$ - $S_7$  are high-speed reed relays (Kemreed M301C),  $S_1$  is a mercury-wetted reed relay (Hamlin MRC-DT),  $S_{10}$  is a low-contact-resistance manual selection switch and  $S_{11}$  a single-pole manual switch. Voltage polarity changes between points A and F are detected by a high-input-impedance electronic comparator to be described later (§3.1.1). Finally, the bridge DC power is provided by a constant voltage unit (Hewlett-Packard type 6112A) and is arranged so that point A of the bridge is always close to earth potential.

Figure 1 shows the bridge in its reset position prior to measurement. In this configuration it is arranged that the resistance of the upper right-hand arm of the bridge slightly exceeds that of the upper left-hand arm. In addition,  $R_{17}$  is adjusted so that  $R_{17} = R_L(0) + R_S(0)$  to ensure that upon switching  $S_1$  from its rest position to X there is no significant change in the load on the power supply.  $R_L(0), R_S(0)$  are the equilibrium resistances of the two platinum wires. The operation of switching  $S_1$  to X initiates a measurement cycle in the following way. The pulse generated through  $S_2$  and C by the current flowing in the two platinum wires is used to open gates between six electronic counters and a crystal-controlled clock, so that the timing sequence is begun. The current flowing in  $R_L$  and  $R_S$  leads to heat dissipation in these wires and their temperature and (consequently) resistance increase. Because of the initial configuration of the bridge, the polarity of the signal between points A and F will change at some time later indicating passage through a balance point. This event is detected by the comparator which causes the first electronic counter to be stopped, thereby recording the time of the balance condition. Subsequently, the associated logic circuitry (§3.1.2) causes switch  $S_7$  to be opened and  $S_6$  to be closed replacing  $R_{15}$  by  $R_{14}$  in the circuit and thereby increasing the effective resistance of the upper right-hand arm of the bridge. The continuing temperature rise of the wires  $R_L$  and  $R_S$  then causes a further polarity reversal between A and F which stops the second counter, recording the time of the second balance point. The next resistor in the parallel arm then replaces  $R_{14}$  and the

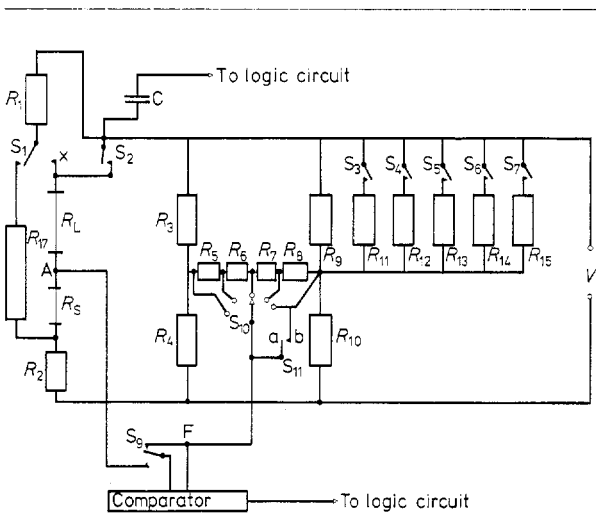


Figure 1 The automatic measurement bridge. C: 0.1  $\mu$ F

sequence is repeated until all six counters have been stopped, the last time measurement being made with all switches  $S_3$ – $S_7$  open. The logic circuitry then returns the system to its initial reset state automatically. As a result of this single experimental run therefore, six times of bridge balance are stored in counters and they can be independently recalled to a visual display for recording purposes.

With switch  $S_{11}$  in position (a), the condition for polarity reversal between A and F can be written as

$$R_L - R_S = \frac{C_1 R_2 - R_1}{(R_L/R_S) - C_1} \left( \frac{R_L}{R_S} - 1 \right). \quad (4)$$

Here

$$C_1 = \{1 - [(B+1)/D]\}/(1 + B/D) \quad (4a)$$

with

$$B = \beta R'/R \quad (4b)$$

$$D = (2R_{1i}/R + 1)(1 + R'/R) \quad (i = 1 \text{ to } 6) \quad (4c)$$

and

$$R' = R_5 + R_6 + R_7 + R_8. \quad (4d)$$

In addition,  $\beta$  is the fraction of  $R'$  included in the comparator circuit, and therefore can take five discrete values (figure 1).

With switch  $S_{11}$  in position (b) a corresponding condition for polarity reversal between A and F can be written as

$$R_L - R_S = \frac{C_2 R_2 - R_1}{(R_L/R_S) - C_2} \left( \frac{R_L}{R_S} - 1 \right). \quad (5)$$

Here

$$C_2 = \{1 - [(B+1)/E]\}/(1 + B/E) \quad (5a)$$

and

$$E = (2R_{1i}/R + 1)(1 + \beta R'/R). \quad (5b)$$

The experimental arrangement has been chosen so that the ratio  $R_L/R_S$  departs insignificantly from the known ratio of the lengths of the two wires  $l_L/l_S$  during the course of the measurement (§4.1.2). Thus equations (4) and (5) both demonstrate that the bridge shown in figure 1 allows, in one cycle, measurement of the difference in resistance between the long and short wires in terms of the known resistances of the remainder of the elements of the bridge at six recorded times from the beginning of the heating process. The measurement cycle described above can of course be repeated with switch  $S_{11}$  in position (a) for all values of  $\beta$ , and then again for all  $\beta$  with switch  $S_{11}$  in position (b). In this way, provided that the thermodynamic state of the fluid in the cells remains unaltered, 60 measurements of the value of  $R_L - R_S$  at various times can be obtained.

Because the two platinum wires were chosen to be identical except for length and they are mounted in identical cells, the above measurement constitutes the determination of the resistance of a wire of length  $l_L - l_S$  but with effectively no ends (de Groot *et al* 1974). Hence, provided that the resistance-temperature characteristics of the wires have been determined, the temperature rise of this hypothetical wire as a function of time can be calculated. Thus after making due allowance for small corrections (§4) and calculating the heat dissipation in the wire per unit length,  $q$ , the thermal conductivity can be obtained from the data with the aid of equation (3).

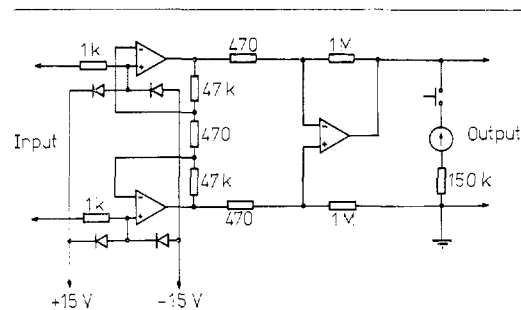
In order to assess the performance of the bridge network with regard to the measurement of an absolute resistance, it was used in a manual mode to determine the resistance of a 100  $\Omega$  standard resistor (Tinsley type S). The value obtained differed by less than 0.05% from the calibrated value.

### 3.1 Electronic components of the instrument

In this section the various individual electronic modules of the instrument are briefly described. They were designed to provide a time resolution of bridge polarity reversal of  $\pm 10 \mu s$ , to store

the six times resulting from a single run, to allow their subsequent recovery for recording purposes and to perform all the switching operations described in the previous sections in times commensurate with the desired operating characteristics of the instrument.

**3.1.1 The comparator** A diagram of the comparator circuit is given in figure 2. It consists of two input buffer amplifiers

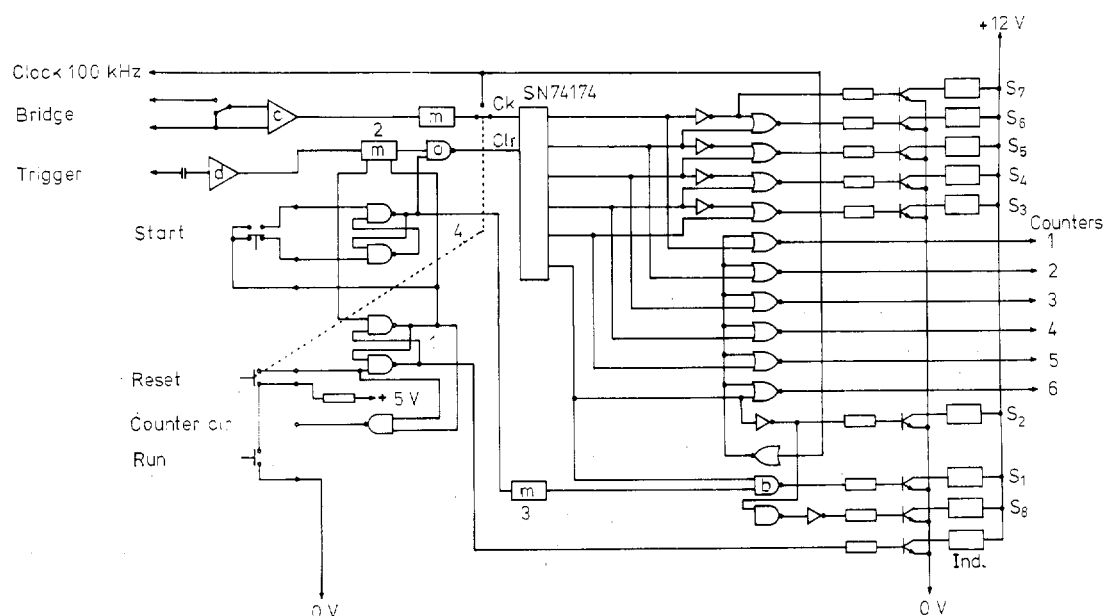


**Figure 2** The comparator. Diodes, SSD 708; meter, 50-0-50  $\mu A$

(Analog Devices type 43K) which are connected in a balanced, cross coupled mode to achieve a very high input impedance ( $> 10^{11} \Omega$ ) and common mode rejection ratio ( $> 80$  dB). The cross coupling has the advantage that common mode signals are passed at unity gain whereas differential signals are amplified. The outputs of the two buffers are connected to a conventional differential circuit (Ancom type 15A-2a), which is equipped with a zero set control and a meter to allow offset adjustment. The complete unit, which is mounted in a temperature-controlled environment to minimize offset drift, has a band width of 100 kHz, a gain of  $4 \times 10^6$  and a peak-to-peak noise level of approximately 20  $\mu V$ .

**3.1.2 Control logic** This unit controls the automatic sequencing of the bridge operation and the gating of the counters; a circuit diagram is shown in figure 3. Sequencing is accomplished by the six-stage shift register (SN74174) which is clocked by the comparator through a 2 ms monostable. The monostable ensures that only one pulse is passed to the register for each bridge balance and effectively masks the comparator output during the bridge resistor switching operation. Two sets of gates are connected to the shift register outputs. The first set selects for activation the appropriate buffer transistor from a group which drives the high-speed reed relays of the bridge. The second set feeds the corresponding counters from a master clock (Meon type MC105-TM). The system is provided with an interlock to the counter unit in order to minimize the risk of accidental triggering or resetting, so the 'run' button must be depressed before 'reset' and 'start' are operative.

To commence a run, the 'run' and 'reset' buttons are depressed. The 'reset' button connects the 100 kHz clock to the shift register clock input and thereby loads all stages to logic state '1'. In this state all counters are gated off and all relays de-energized. The 'reset' command also sets the bistable 1 (which provides a ready signal), enables the trigger monostable 2 and the 'start' button and resets all the counters. Depression of the 'start' button enables gate (a) and fires the 30 ms monostable 3 via the antibounce circuit 4. Monostable 3 then energizes the start relay  $S_1$  via gate (b). The current in the bridge produces a pulse through the capacitor C (figure 1) which is fed to the trigger monostable 2. A 2 ms pulse is then passed through gate (a) to the clear input of the shift register



**Figure 3** The control logic. Components: all resistors 4.7 k $\Omega$ ; Ind. is a 12 V indicator bulb; NAND gates,  $\frac{1}{4}$  of SN7400; Inverters,  $\frac{1}{8}$  of SN7404; NOR gates,  $\frac{1}{4}$  of SN7402; monostables, SN74121; shift register, SN74174

setting the output of all elements to logic '0', thereby energizing relay  $S_7$  and starting all counters, but leaving relays  $S_6$ – $S_3$  de-energized. The 2 ms pulse holds the shift register clear while the relay and comparator settle.

Following the first polarity reversal, detected by the comparator, a logic '1' is shifted into the first element of the shift register. The first counter is thereby stopped, relay  $S_7$  is de-energized and relay  $S_6$  is energized. A similar process is initiated by each successive polarity reversal of the bridge until all the counters are stopped. The present logic circuitry therefore differs from that of Anderson *et al* (1974) by virtue of the sequencing of the switching of  $S_3$ – $S_7$ . The logic elements used throughout are '74' series TTL.

The counting unit consists of six separate counters each of six decades (SN7490) with separate clock inputs and a common reset line. These counters are multiplexed to a six-decade, seven-segment display via push buttons enabling readout of any counter at will. This arrangement allows a great saving in cost compared with an earlier version (Anderson *et al* 1974) with no loss of flexibility or precision.

### 3.2 Fluid cell design

Figure 4 shows the final design of the hot wire cells. Two cells of this type have been constructed differing only in their lengths. The outer wall of the cell is formed by a stainless steel cylinder of internal diameter 10 mm fitted with detachable sides allowing access to the interior. When in position, these pieces fit flush with the inner wall of the tube and provide a cylindrical outer boundary to the cell. The platinum wire of 10  $\mu$ m diameter is supported between two threaded stainless steel pins, being mechanically and electrically connected to them with Wood's metal. The pins are mounted in pyrophyllite bushes at either end of the cell.

Following assembly of the wire in the cell it was annealed at red heat for a short time and then tightened by means of the threaded pins until, with a small current flowing through it, there was no observable deflection when a small bar magnet was brought close to it. Subsequently the length of the wire between the Wood's metal connections was measured with a cathetometer to  $\pm 0.01$  mm. Both cell assemblies were then washed in Decon 90 solution and acetone, the cylinder sides attached and the two cells mounted in a cylindrical stainless steel vessel sealed with a rubber O-ring, with their axes parallel

to the vessel axis. The vessel is equipped with thermocouples for temperature measurement, pipework for evacuation and admission of the test fluid, and ceramic/metal seals for electrical connections. The entire vessel was immersed in a liquid thermostat bath providing stability of  $\pm 0.005$  K at 288 K. The fluid temperature was measured with a platinum resistance thermometer immersed in the vessel. Details of this part of the assembly are omitted here because of its standard nature. During assembly extreme care was taken to ensure that the axis of the enclosing vessel was vertical. The verticality of the vessel could be adjusted by means of levelling screws on its supports, and could be checked with the aid of a spirit level to within an angle of  $\pm 1'$ . The machining of the cell supports within the vessel was such that the error in the verticality of the hot wires was insignificantly worse than this. An experimental check of the correct alignment of the hot wires was also possible (§4.1.1).

The resistance-temperature relation for the platinum wires was determined by *in situ* calibration. For this purpose the cells were filled with helium and their temperature measured with the platinum resistance thermometer with an accuracy of  $\pm 0.001$  K. Resistance measurements were performed by a four-terminal technique with the connections made externally to the enclosing vessel. The resulting uncertainty in the resistance of the wires (including possible lead resistances to the wires) was  $\pm 0.006\%$ . The calibration was carried out in the temperature range 8–41°C and the resulting data were correlated with a maximum deviation of 0.04% by the relation

$$R(T)/R(273.16) = 1 + 3.9985 \times 10^{-3}(T - 273.16) - 1.700 \times 10^{-6}(T - 273.16)^2 \quad (6)$$

where  $T$  is the absolute temperature.

It is noteworthy that a calibration repeated with the cells full of n-heptane showed no significant deviation from this correlation.

### 4 Measurement analysis

As indicated above, the design of the present instrument has been performed so as to minimize deviations of its operation from the simple mathematical description of it embodied in equation (3). In this section we demonstrate how the present experimental design has eliminated some of these deviations,

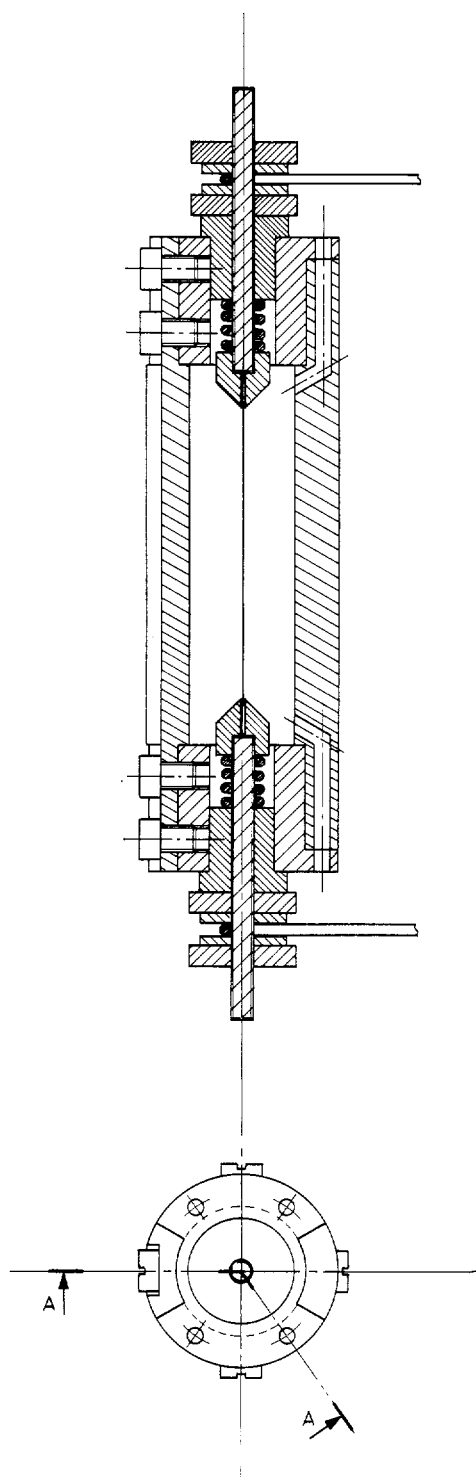


Figure 4 The hot wire cells

reduced others to negligible proportions and made the remainder amenable to evaluation. The corrections are arranged in every case so that their application brings the raw experimental data on to the straight line characterized by equation (3).

#### 4.1 Effects eliminated entirely

**4.1.1 Convection** The problem of convection in a vertical transient hot wire cell of the type described here has been discussed by a number of authors (e.g. Goldstein and Eckert 1960, Goldstein and Briggs 1964). The essential result of all such analyses is that there exists an estimable time limit  $t_c$ ,

measured from the initiation of the heating process, prior to which the one-dimensional regime of heat transfer implicit in equation (3) persists. For the present cells this time limit is approximately 10 s so that, provided that the measurement cycle is completed in a time less than this, convection is nominally eliminated. In the present measurements the time for one experiment cycle does not exceed 2 s and this criterion is easily fulfilled.

On the other hand, de Groot *et al* (1974) have shown that, in the gas phase, convective heat transfer can occur at times shorter than the limit  $t_c$ . However, the same authors have also demonstrated that in the transient hot wire cell the effects of convective heat transfer can be observed experimentally by virtue of the departures they cause from the behaviour predicted by equation (3). Therefore, while adopting 2 s as a suitable experiment time for the present measurements, the need to examine the experimental data for evidence of convective currents is to be borne in mind.

In particular, it should be emphasized that all the discussion of the convection problem has referred to a vertical wire. It is clear that the onset of convection will occur at shorter times if the wire is not truly vertical. Because the effect of convection is to increase the heat transfer from the wire, such an effect is clearly discernible as a curvature in the plot of  $\Delta T$  against  $\ln t$  at times following the beginning of convection. In this work no such curvature was detected for times as long as 10 s, so it may be concluded that the wires were sufficiently well aligned. However, it is noteworthy that when the cells were displaced by about  $1^\circ$  from vertical, curvature of the  $\Delta T$  against  $\ln t$  plot occurred after 0.5 s.

**4.1.2 Wire end effects** The mechanical and electrical connection of each platinum wire to a support in the fluid cell necessarily implies the presence of longitudinal temperature gradients in the wire and the fluid. Haarman (1971) and Healy *et al* (1976) have provided differing analyses of this problem. Both discussions show that the 'end effects' can be arranged to cause only small ( $\sim 0.01\%$ ) departures from the behaviour predicted by equation (3), by making the platinum wires sufficiently long. In formulating the present design we have employed Haarman's analysis (Haarman 1971) and have chosen to use a long wire of length 0.15 m and a short wire of length 0.04 m. Under these conditions, calculations (Castro *et al* 1974) show that the ratio of the resistances of the long and short wires does not differ by more than 0.01% from the ratio of their lengths during an experimental run. Thus equations (4) and (5) yield a measure of the difference of the resistance of the long and short wires directly. The small remaining end effects are therefore experimentally compensated and need not be considered further.

#### 4.2 Corrections rendered negligible

The corrections detailed by Healy *et al* (1976) which fall into the present category include Knudsen effects and effects due to viscous heating of the fluid (McLaughlin and Pittman 1971). In the present system these effects never amount to more than 0.01% of the measured temperature rise of the wire, and are therefore negligible.

#### 4.3 Remaining corrections

**4.3.1 Heat dissipation per unit wire length** A basic presumption of the derivation of equation (1) was that the heat dissipation per unit length of the platinum wires is constant. Evidently, the use of a constant voltage source for the bridge power and the changing resistances of the platinum wires combine to vitiate this assumption. However, if the fixed

resistances of the bridge  $R_1$  and  $R_2$  are chosen such that

$$R_1 + R_2 = R_L(0) + R_S(0) = R_0$$

it can be shown (de Groot *et al* 1974) that the heat dissipation in the wires as a function of time is, to a sufficient degree of accuracy,

$$q(t) \simeq \left( \frac{V}{2R_0} \right)^2 \left( \frac{R_0}{l_1 + l_2} \right) \left[ 1 - \left( \frac{\Delta R(t)}{2R_0} \right)^2 \right]. \quad (7)$$

Here,

$$\Delta R(t) = \Delta R_L(t) + \Delta R_S(t) \quad (8)$$

where  $\Delta R_L(t)$  and  $\Delta R_S(t)$  are the resistance increases of the long and short wires respectively during the heating process. Calculation for the bridge of figure 1 shows that  $q(t)$  departs from the value for  $t=0$  by at most 0.06% during the measurement cycle. This departure may be expected to lead to barely discernible deviations of the plot of  $\Delta T$  against  $\ln t$  from linearity.

However, because the deviation from constant  $q$  is so small, equation (7) also provides a means of correcting the observed temperature rises to those appropriate to  $q(0)$ . This may be performed most easily by an iterative technique, using  $q(0)$  to generate estimates of  $\Delta R_L(t)$  and  $\Delta R_S(t)$  and then equation (7) to find  $q(t)$ . Finally, the proportionality between  $\Delta T$  and  $q(t)$  may be used to obtain corrected values of  $\Delta T$ . In all cases the correction is so small that the first iteration is sufficient. Indeed, for the sample measurements reported here  $q$  did not deviate by more than  $\pm 0.01\%$  from a constant value, so that this iteration was unnecessary.

**4.3.2 Finite physical properties of the wire** Equation (1) was derived on the assumption of an infinitely thin line source of heat. In practice the platinum wire has a finite diameter, a finite heat capacity  $(\rho C_p)_w$  and a finite thermal conductivity  $\lambda_w$ . The consequences of all of these considerations have been investigated by Healy *et al* (1976); and according to their analysis the average temperature of the wire, which determines its resistance, is given by

$$\Delta T_w(t) = \frac{q}{4\pi\lambda} \left\{ \left[ 1 - a^2 \left( \frac{(\rho C_p)_w - (\rho C_p)}{2\lambda t} \right) \right] \ln \left( \frac{4\kappa t e}{a^2 C} \right) + \frac{a^2}{2\kappa t} - \frac{a^2}{4\kappa_w t} + \frac{\lambda}{2\lambda_w} \right\} \quad (9)$$

where  $\kappa_w = \lambda_w/(\rho C_p)_w$ .

The corrections to equation (3) incorporated in equation (9) are of two types. The term  $\lambda/2\lambda_w$  constitutes a small ( $\sim 0.1\%$ ) time-independent contribution. It therefore plays no part in the evaluation of the thermal conductivity of the fluid from the slope of the plot of  $\Delta T$  against  $\ln t$ . The smallest of the remaining time-dependent contributions, the term  $-a^2/4\kappa_w t$ , never amounts to more than  $1 \times 10^{-3}\%$  of the temperature rise and is therefore negligible. The other two, time-dependent corrections are more significant and can amount to about 1% of the temperature rise at the shortest times employed in the present measurements. However, the correction to be added to the observed temperature rise,

$$\delta T_1 = \frac{q}{4\pi\lambda} \left[ \left( \frac{(\rho C_p)_w - (\rho C_p)}{2\lambda t} \right) a^2 \ln \left( \frac{4\kappa t}{a^2 C} \right) - \frac{a^2}{2\kappa t} \right] \quad (10)$$

may be estimated to within a few per cent. Thus, provided that measurements for which the correction exceeds 1.0% of the temperature rise are ignored, the resulting uncertainty in the corrected temperature rise is only a few parts in ten thousand.

For the purposes of this correction the wire radius was measured with an electron microscope ( $a = 5.49 \pm 0.08 \mu\text{m}$ ).

**4.3.3 Finite dimensions of the fluid cell** The derivation of equation (1) presumes that the test fluid is of infinite extent in the radial direction. In practice the fluid is contained in a cylindrical vessel of radius  $b$  (1 cm for this work). A correction to the observed temperature rise, which is of greatest significance at long times, is given by de Groot *et al* (1974) as

$$\delta T_2 = \frac{q}{4\pi\lambda} \left[ \ln \left( \frac{4\kappa t}{b^2 C} \right) + \sum_{\nu=1}^{\infty} [\exp(-g_\nu^2 \kappa t/b^2)] [\pi Y_0(g_\nu)]^2 \right] \quad (11)$$

where  $g_\nu$  are the consecutive roots of  $J_0(g_\nu) = 0$ .  $J_0$  is the zero-order Bessel function of the first kind and  $Y_0$  the zero-order Bessel function of the second kind.

The present experimental arrangement was chosen to ensure that  $\delta T_2$  never exceeded 0.02% of the wire temperature rise. The remaining small correction is easily made if necessary by adding the value of  $\delta T_2$  to the observed wire temperature rise.

**4.3.4 Variable fluid properties** The fact that the density and thermal conductivity of the liquid vary with temperature introduces a further correction (Healy *et al* 1975). This is most conveniently viewed as a correction to the temperature with which the thermal conductivity, obtained from the plot of  $\Delta T$  against  $\ln t$ , is identified (de Groot *et al* 1974).

In the present work the slope of  $\Delta T$  against  $\ln t$  is usually obtained for the range  $\Delta T(t_1) = 5^\circ\text{C}$  to  $\Delta T(t_2) = 10^\circ\text{C}$ . The change in the liquid thermal conductivity over this range is only  $\sim 1\%$  and so it can be adequately described by a linear function of temperature. Thus it is possible to carry over the analysis of Healy *et al* (1976) for the variation of the fluid properties of a gas to the case of a liquid with only small changes (Castro *et al* 1974). This analysis indicates that if the temperature of the fluid before initiation of a run is  $\theta_0$ , the temperature to which the observed thermal conductivity refers,  $T_r$ , is given as

$$T_r = \theta_0 + \frac{1}{2}[\Delta T(t_1) + \Delta T(t_2)] \quad (12)$$

with negligible error. In §6 the correctness of this temperature assignment is confirmed experimentally.

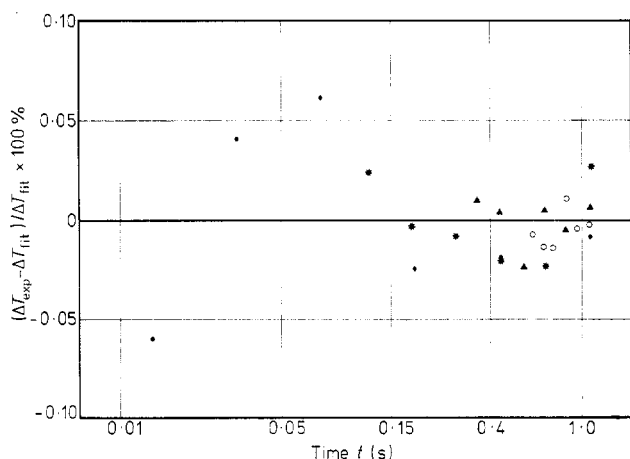
In principle, the variation of the fluid properties with temperature introduces a very small curvature to the plot of  $\Delta T$  against  $\ln t$  (de Groot *et al* 1974). However, in practice this curvature cannot be discerned. Nevertheless, for the sake of consistency, we have applied a correction for this effect as detailed by de Groot *et al* (1974).

**4.3.5 Radiation correction** The final correction to be considered involves the radiative heat transport from the heated wire to the fluid simultaneously with the conductive process. Mani (1971) has recently considered this problem for the transient hot wire apparatus. However, because his detailed results are not generally available, it is preferable to postpone a discussion of this last refinement of the measurement until definitive thermal conductivities are reported. At present it is sufficient to conclude that, in view of the small temperature rises involved in the present measurements, this final correction is not expected to amount to more than 1% in the thermal conductivity (Mani 1971). Thus even if only a crude estimate of the effect can be made the overall accuracy of the final thermal conductivity derived should be maintained.

## 5 Precision and accuracy

The precision of the time measurement for the present apparatus, with due regard to the noise level of the comparator

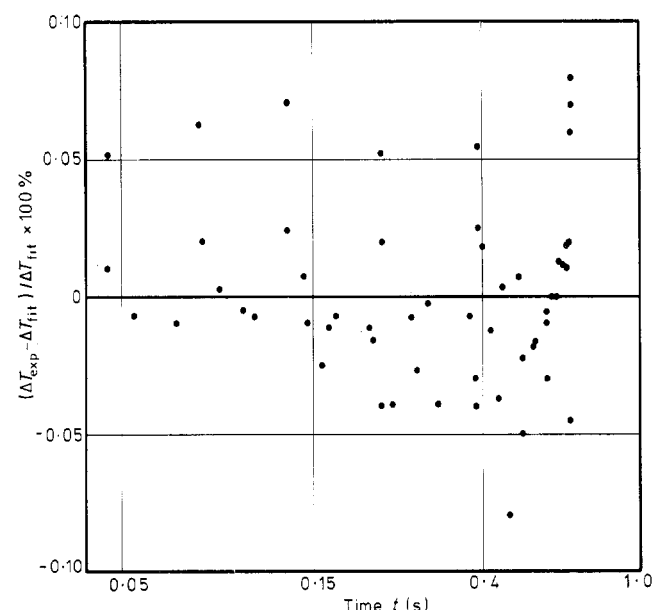
and the bridge network, is  $\pm 10 \mu\text{s}$ . On the other hand, the resistance change of the wire is determined with a precision of  $\pm 0.01\%$ , estimated from the tolerances of the fixed resistors in the bridge. Accounting for the uncertainties introduced by applying the small corrections to the measured temperature rise detailed earlier, we should expect that the maximum deviation of any experimental point from the linearity predicted by equation (3) for a single run, consisting of six time measurements, should be  $\sim \pm 0.05\%$ . In order to demonstrate that this expectation is fulfilled by the present apparatus we display in figure 5 the deviations from linearity obtained for



**Figure 5** Deviations of experimental data from the linearity predicted by equation (3) for individual runs.  
○ run 1; ▲ run 2; \* run 3; ● run 4

four discrete runs with the fluid cells filled with n-heptane. The maximum deviation is  $\pm 0.06\%$ , in accord with the foregoing description. It is also noteworthy that the average deviation from linearity for each of the four runs is  $\pm 0.02\%$ .

Because of unavoidable variations in the fluid temperature of the order of  $\pm 0.01^\circ\text{C}$  between successive runs, the deviations



**Figure 6** Deviations of experimental data from the linearity predicted by equation (3) for a complete set of measurements

from linearity are slightly degraded when a number of runs are combined to cover the entire accessible time regime. Nevertheless, the maximum deviation remains less than  $0.1\%$  as can be seen from figure 6. This graph contains the deviations of the results of ten successive runs from the straight line providing the best fit to the 60 points. The ten runs were performed under nominally identical equilibrium conditions with n-heptane as the test fluid. As a consequence of these considerations it is contended that the precision of the present measurements is  $\pm 0.1\%$ .

The accuracy of the thermal conductivity value deduced from the slope of  $\Delta T$  against  $\ln t$  plots is determined by the uncertainty in the resistance-temperature characteristics of the wires, by the uncertainty involved in merely obtaining the slope, and by any unaccounted corrections. Although the former two points contribute only an estimated  $\pm 0.1\%$  to the overall uncertainty, it is prudent to reserve a final estimate of the accuracy of the thermal conductivity until a later publication because no radiation correction can yet be applied. However, the discussion in §4.3.5 indicates that allowing for this correction the overall accuracy of the measurements will be in the range  $\pm 0.2$ – $0.3\%$ .

## 6 Sample measurement

The apparatus described here has been used to perform preliminary measurements of the thermal conductivity of n-heptane at four temperatures near room temperature. These measurements are in no way final results but are used here to illustrate the correct operation of the instrument described and the underlying theory for liquids. For these measurements the n-heptane used was commercial BDH n-heptane treated with 4A molecular sieves to remove water, degassed under vacuum and then distilled under its own vapour pressure.

For these measurements bath temperatures of 293.04 and 287.99 K were employed. At each temperature several different heat inputs to the wire were employed. The different temperature rises generated in consequence allow measurement of the thermal conductivity at different reference temperatures (§4.3.4). Conditions were chosen such that reference temperatures for some runs for both bath temperatures were almost the same. These tests then not only provide data for the thermal conductivity of n-heptane, but also enable the conclusions of §4.3.4 to be examined. In addition, they provide support for our contentions with regard to precision. Table 2 contains the thermal conductivities obtained as a result of these measurements; they have been corrected to nominal temperatures by

**Table 2** The thermal conductivity of n-heptane at various reference temperatures

Bath temperature, $T$ (K)	$q$ ( $\text{W m}^{-1}$ )	Reference temperature, $T_r$ (K)	$\lambda$ ( $\text{W m}^{-1} \text{K}^{-1}$ )
287.99	1.1874	293.60	0.1253
	1.8425	295.65	0.1242
	2.6303	298.15	0.1233
	2.6307	300.15	0.1227
	1.1762	298.15	0.1235
293.04	1.1493	298.15	0.1236
	1.8254	300.15	0.1229
	1.7842	300.15	0.1227
	2.6073	303.65	0.1217
	2.5471	303.65	0.1219
	2.5476	303.65	0.1220



application of small (0.1%) temperature corrections with the aid of  $d\lambda/dT$  given by Kandiyoti *et al* (1972). The table shows that the repeated measurements do not differ by more than 0.15% even for different bath temperatures. Thus the use of the reference temperature given by equation (12) is vindicated as are our claims for precision.

Finally table 3 compares the present data with those obtained in earlier studies (Kandiyoti *et al* 1972, Vilim 1960,

Michels A and Botzen A 1952 *Physica* **18** 605–12

Michels A, Sengers J V and van der Gulik P S 1962 *Physica* **28** 1201–15

Missenard F A 1965 *Rev. Gen. Termique* **4** 409–28

Pittman J F T 1968 *PhD Thesis* University of London

Tsederberg N V 1965 *Thermal Conductivity of Gases and Liquids* (Cambridge, Massachusetts: MIT Press)

Vilim O 1960 *Colln. Czech. Chem. Commun.* **25** 993–9

**Table 3** Thermal conductivity of n-heptane,  $\lambda$  ( $\text{W m}^{-1} \text{K}^{-1}$ )

$T=293.25 \text{ K}$	$T=303.15 \text{ K}$	Source
0.1244	0.1214	Kandiyoti <i>et al</i> (1972)
0.135	—	Vilim (1960)
—	0.126	Tsederberg (1965)
0.124	0.121	Jobst (1964)
0.127	0.124	Missenard (1965)
0.1254	0.1219	Present work

Tsederberg 1965, Jobst 1964, Missenard 1965). The agreement with the most reliable data (Kandiyoti *et al* 1972) is gratifying, being well within the claimed uncertainty for the earlier work (1%). However, because the present results are not corrected for any radiation effects, any further comment would be unwarranted at this stage.

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