PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

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Phil. Trans. R. Soc. Lond. A 1971 **270**, 579-602
doi: 10.1098/rsta.1971.0090

Phil. Trans. R. Soc. Lond. A. **270**, 579–602 (1971)
Printed in Great Britain

DETERMINATION OF THE THERMAL CONDUCTIVITY OF TOLUENE—A PROPOSED DATA STANDARD—FROM 180 TO 400K UNDER SATURATION PRESSURE BY THE TRANSIENT HOT-WIRE METHOD

II. NEW MEASUREMENTS AND A DISCUSSION OF EXISTING DATA

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(*Communicated by A. R. Ubbelohde, F.R.S.—Received* 19 *June* 1970—*Revised* 12 *May* 1971)

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The design of a transient hot-wire cell for measurements on liquids is described. The cell is incorporated in a high stability circuit and the temperature time function which yields the thermal conductivity logged by means of high-speed digital equipment. Ancillary equipment is developed to enable measurements to be made on liquids from 100 to 450 K and pressures to 100 bar (10 MPa).

Results are reported on liquid toluene at saturation pressure over the whole of its normal liquid range. Comparison is made with selected data taking into account the effect of heat transfer by radiation. It is suggested that most of the data reviewed are accurate, regarded as apparatus conductivity, uncorrected for radiation, to rather better than 1 %, and that the present data, over most of the temperature range, are true conductivities of similar accuracy. However, several anomalous relations with existing data are noted.

1. Introduction

The theory given in part I is now applied to the design of a cell for measurements on liquids. A description is given of the ancillary equipment for thermostatting the cell at temperatures from about 100 to 450 K at pressures from vacuum to 100 bar (10 MPa), and of the cell circuit and data logging system. These are designed as a module which can be connected to any one of a number of cells, so that, because of the short duration of the measurements, virtually simultaneous determinations are possible on a number of fluids under different conditions. Further reports will describe the measurements on liquefied normal paraffins under s.v.p. and on hydrocarbons at several thousand bar. This paper reports new data on toluene under s.v.p. at temperatures from the freezing-point to just above the normal boiling-point, and existing data are reviewed in the light of recent work on the effects of radiant heat transfer. Toluene was chosen for the first measurements because it has been recommended as a thermal conductivity standard. The recommendation was first made by Riedel (1951) and reinforced by Ziebland (1961) who noted that toluene meets the following requirements of a standard fluid: (*a*) the normal liquid range is long and includes thermometric fixed points; (*b*) the material is relatively non-toxic and non-corrosive in conventional engineering materials; and (*c*) it is easily obtained highly pure at reasonable cost.

Ziebland also suggested that more work on toluene be carried out with a view to arriving at internationally accepted values, which could be used (*a*) in establishing the accuracy of new equipment making absolute measurements; (*b*) in periodically checking existing instruments; and (*c*) as a reference fluid in relative measurements. These uses imply that measurements on a standard should have at least the same susceptibility to error as measurements on the test fluid, and the susceptibility is, of course, governed, in a given measurement, by the physical properties of the fluid under the conditions of the measurements. The most important sources of this type of error are: (*a*) heat transfer by convection, which is governed by the values of the Prandtl number and the coefficient of thermal expansion; (*b*) conduction of some of the measured heat input to the cell, not through the test layer, but through metal components or ceramic spacing pieces which fix the thickness of the fluid layer; (*c*) heat transfer by radiation in moderately absorbing fluids.

In non-absorbing fluids the radiant transfer is determined by the cell wall emissivities and is given by the Stefan–Boltzmann formula. In fluids which absorb strongly in the infra-red the apparent conductivity invariably contains a radiative component which is given by the radiation diffusion expression. But in moderately absorbing fluids (of which toluene is one) radiation can make a detectable contribution and the size of this depends on the thickness of the fluid layer, the cell-wall emissivities and the absorption coefficient of the fluid.

These last considerations reinforce the case for toluene as a standard fluid. If a technique gives the true conduction of toluene then it has been shown not to be susceptible to radiation errors and will give reliable conductivities of other fluids of similar absorption as well as accurate apparatus conductivities of strongly absorbing fluids. Toluene is therefore suitable as a standard in equipment for measurements on a wide range of liquids.

It is apparent, however, that one or more other standards are also required, having lower conductivities and greater susceptibility to convection than toluene, for example gases near to the critical region. It should, perhaps, finally be noted that successful measurements on toluene do not guarantee accurate results on any liquid (of similar susceptibility to convection) in any type of cell. For example when an unshielded electric heating element is used, as in the hot-wire methods, care must be taken with electrical conduction through the test fluids, and in non-steady state versions of this method false voltage transients can lead to error in measurements on polar liquids.

2. Apparatus

From the theoretical analysis of part I it follows that in order to make precise measurements of thermal conductivity using a hot-wire cell certain criteria on cell design and duration of measurements have to be fulfilled. In addition it is also preferable to be able to carry out measurements over a wide range of temperature. The apparatus and technique used to meet these requirements are discussed below.

2.1. *The cell*

The obvious choice of material for the hot wire and potential leads is platinum. In part I it has been shown that the diameter of the wire should be as low as practicable, and in fact a satisfactory design can be developed using platinum of nominal diameter 0.001 in.

On this basis, the importance of the term H (see part I § 3.3 (*b*)) is first examined. As a safe estimate assume 20 % errors in the values of ω and κ/a^2 used to evaluate H. It can be shown from the data in table 1, p. 593, that the resulting errors in T are less than 0.1 % for values of t^* as follows:

$$\begin{aligned} \omega &\geqslant 1.5 & t^* &\geqslant 100, \\ \omega &\geqslant 1 & t^* &\geqslant 200, \\ \omega &\leqslant 1 & t^* &\geqslant 500. \end{aligned}$$

Errors in κ in the logarithmic term of (3.36) of part I need not be considered because they do not affect the gradient of the temperature–time relation. The criteria above mean that in measurements on typical liquids data from about the first $\frac{1}{2}$ s of a run must be discarded.

In order to minimize end effects the overall length of the hot wire should clearly be as great as can conveniently be contained in the pressure vessel and thermostat. A value of 15 cm was chosen in the present case. The extent of the temperature distortion at the ends of the hot wire is estimated by using (3.57) of part I and is greatest in the later stages of a measurement. It will be seen that a measurement lasting 20 s provides more than enough data, so we may use a value of h ((3.58), part I) applying at this time. Substituting a wire radius of 0.00127 cm and the physical properties of platinum and a typical organic liquid we find the following values

δz	δT (%)	δz	δT (%)
0.2	0.6	0.4	0.006
0.3	0.1	0.6	0.003
0.35	0.04	0.8	0.000006

δT is the reduction in the wire temperature expressed in terms of the temperature infinitely far from the end, and z is the distance from the end. Attaching the potential leads not less than 1 cm from the ends of the hot wire will therefore provide a margin of safety in the design, and ensure that the temperature distortion at the end of the wire does not interact with that produced by the potential leads themselves. This is necessary so that the conditions under which the potential-lead corrections were determined (see part I, appendix) are reproduced.

The discussion of the way in which convection limits the duration of a measurement has shown, however, that the lower potential lead should be positioned further from the end of the hot wire than is necessary solely for the elimination of end effects. For a given heating current, increasing the proportion of the hot wire beneath the lower potential lead increases the possible duration of the measurement and the amount of data which may be collected, but it reduces the length and, therefore, the resistance of the active central section—so decreasing the size of the voltage changes to be recorded. Thus it seems that an optimum position may exist. Similarly, for a given position of the lower potential lead one might expect an optimum value for the hot-wire power. A low current allows a longer experiment but gives small voltage changes, while a high current gives the reverse. To investigate these possibilities calculations were made of the standard deviation which would be expected in thermal conductivity values determined under various conditions. The calculations used the simplifying assumption that the standard deviation of the voltage measurements was independent of the absolute value of the voltages, which is a good approximation to the performance of the measuring system described below. The results showed shallow minima in the standard deviation of the conductivity at positions which were only weakly dependent on the hot-wire power. For cases as different as liquid toluene and liquid argon the minima occurred with the potential lead between 3 and 4 cm from the end, and it was therefore concluded that a cell with this geometry would be close to the optimum design in a wide range of applications. No optimum value was found for the hot-wire power within the range considered. On the basis of the calculations, higher powers would result in more precise measurements, but it will be seen that the performance of the electrical circuit and secondary convection effects set an upper limit to the power which may be used with advantage.

In deciding on the diameter of the cell, the requirement is that throughout the measurement the hot wire is surrounded by an extent of fluid which is effectively infinite in the radial direction. For a wire of about 1.3×10^{-3} cm radius and a cell radius of 0.5 cm, b^* in (3.41), part I, is close to 400. Figure 3 in part I shows that the presence of the wall at this radius does not reduce the hot-wire temperature by more than 0.1 % until t^* is greater than 22×10^3. For typical liquids this corresponds to a time of between 40 and 50 s. The analysis on which this figure is based takes no account of the temperature disturbance near the wall caused by the outer half of the convection cell set up by the hot wire but, in practice, conductivities are calculated from data obtained at much shorter times, so this effect can safely be neglected.

The cell was mounted on a stainless steel frame consisting of two disks joined by side struts (see figure 1). Thermopure 26 s.w.g. platinum wire passes through glass-metal seals mounted centrally in the end disks, and forms the current leads to the hot wire. Further 26 s.w.g. wires run to intermediate points along the cell to connect with the potential tappings. The leads are insulated by Pyrex glass sleeves held against the side struts by platinum-iridium clips. 'High alpha'-grade drawn platinum wire (Johnson, Mathey & Co, Ltd) of nominal diameter 0.001 in (0.025 mm) was used both for the hot wire and the potential tappings. Assembly was by spot welding. To ensure that the hot wire remained vertical a small weight was hung at its lower end. The weight consisted of a piece of drilled gold rod threaded on to a short length of 26 s.w.g.

platinum, and the connexion between this and the lower current lead was made by a loose coil of the 0.001 in diameter wire.

Particular care was taken in attaching the potential tappings to the hot wire, so that the configuration should closely match that of the model used to investigate temperature distortion near the junction. A neat T-shaped junction was obtained by welding the wires in a right-angled cross and then bending the superfluous arm up and down until it broke off. Examination of photomicrographs showed that flattening of the wires near the weld had not caused them to spread by more than 50 % of their diameter, and this distortion did not extend beyond about 0.03 cm from the junction. The potential tappings were looped before connexion to the 26-gauge leads near the cell wall, to provide flexibility and allow the hot wire to take up its vertical alinement.

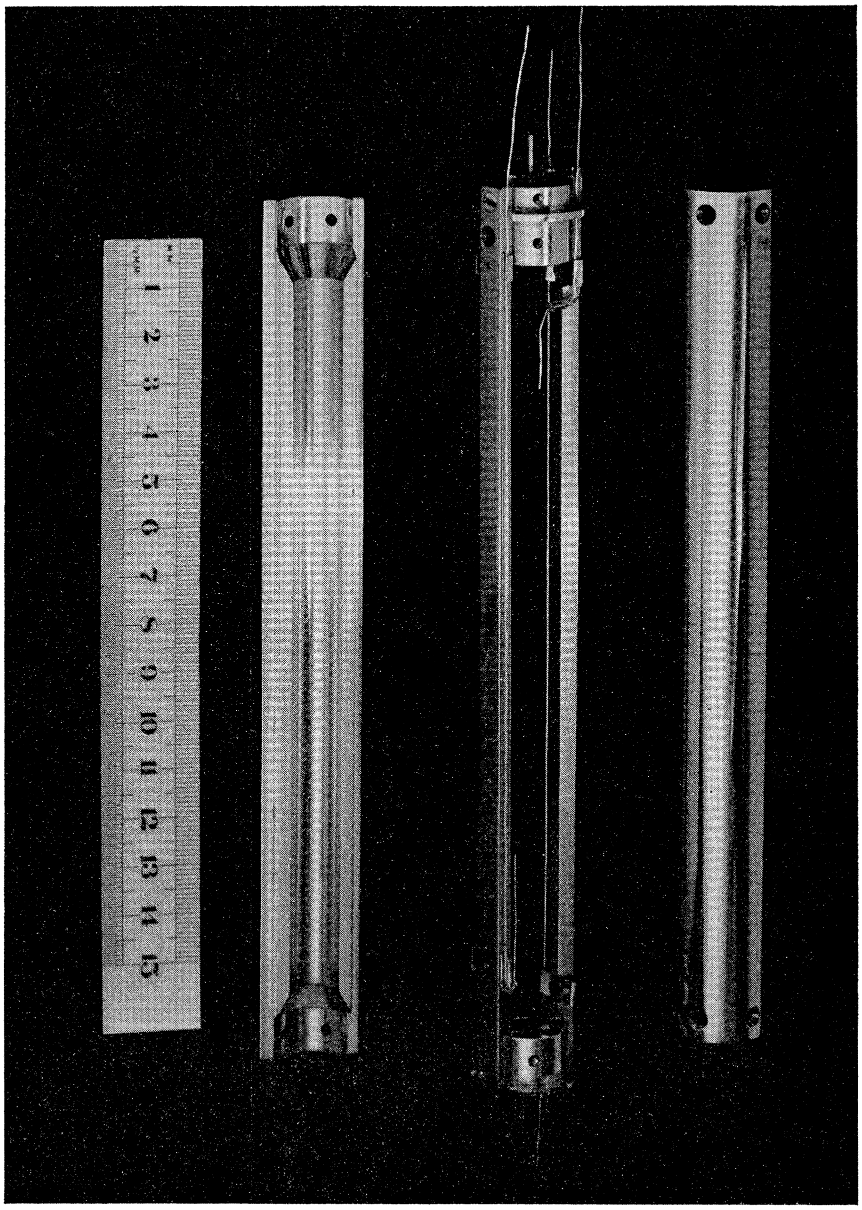

FIGURE 1. Thermal conductivity cell frame with side pieces.

The cell was degreased by Soxlet extraction, and then annealed by raising the temperature of the fine wires to red heat with direct current for 15 min. The hanging weight was supported during annealing so that the wire should not be under tension.

The length of the active section of the cell between the potential tappings was next measured by cathetometer with a resolution of 0.001 cm. The distances of the potential tappings from the wire ends were also noted. Careful examination of the hot wire with a Vickers Projection microscope showed it to be free from kinks and of uniform diameter.

The cell was completed by attaching two stainless steel side pieces to the frame, which reduce the free space round the hot wire to a cylinder 1.0 cm in diameter.

2.2. *Pressure vessel*

The assembly which has been described was mounted on the cap of a pressure vessel machined from stainless steel and designed for service at 100 atm (10 MPa) and temperatures from about 100 to 450 K. The 1 in. diameter bore of the vessel makes a sliding fit round the cell. Pressure seals are made on confined gold washers and the electrical connexions are brought out through Nilo-k Covar seals. The temperature of the vessel is measured by means of a resistance thermometer set in the base, and steel-sheathed, mineral-insulated thermocouples in the cap and base are used to detect temperature gradients.

2.3. *The thermostat*

Since the walls of the cell necessarily remain at their initial temperature throughout an experiment, no provision need be made for the rapid removal of heat from the pressure vessel. A steady temperature is therefore best obtained by containing the large thermal mass of the pressure vessel within a temperature-controlled vessel from which it is well insulated. The temperature-controlled vessel consists of a heavy-walled cylindrical vessel, or hollow block, machined from high conductivity copper castings. The upper and lower halves were faced with stainless steel and are bolted together on a gold washer to form a vacuum-tight enclosure round the pressure vessel, which hangs from within the upper half by thin stainless steel supports (see figure 2). To the outer surface of the block were brazed mineral-insulated, steel-sheathed heating cables and tubes for coolant circulation. Thermal insulation is provided by suspending the unit in a continuously pumped vacuum chamber. Connexions were arranged so that the space within the block, around the pressure vessel, could be filled with a heat transfer gas while maintaining the outer insulating vacuum. This facility is used only during equilibration, the inner space being evacuated during normal operation.

Materials are introduced into the cell via a stainless steel tube passing through the upper part of the block and coupled to the top of the pressure vessel. The electrical leads from the pressure vessel are of fibre-glass insulated copper, and are thermally anchored to the block by passing several bifilar turns round a spigot machined within its upper half. Sensing elements for the electronic temperature control system are provided by platinum resistance thermometers (Degussa, Germany), set in the top of the block, while gradients along the block are detected by means of thermocouples.

All electrical leads from the block and pressure vessel are brought through the top of the vacuum chamber via glass to metal seals enclosed in brass boxes to minimize temperature gradients near the connexions. All connexions were made with low-thermal solder (Enthoven Ltd, U.K.). The materials handling line and coolant connexions are vacuum jacketed for some distance after they emerge from the vacuum vessel, to prevent heating or cooling of the end plate. The possibility of heating arises because of the need to prevent convection in the line leading down into the cell when operating the thermostat above room temperature. This is achieved by providing an isolating valve in the line at the point where it emerges from the vacuum jacket and enclosing the valve and the end of the jacket in a small heater. In this way the section of the line connected to the cell may be maintained above the cell temperature.

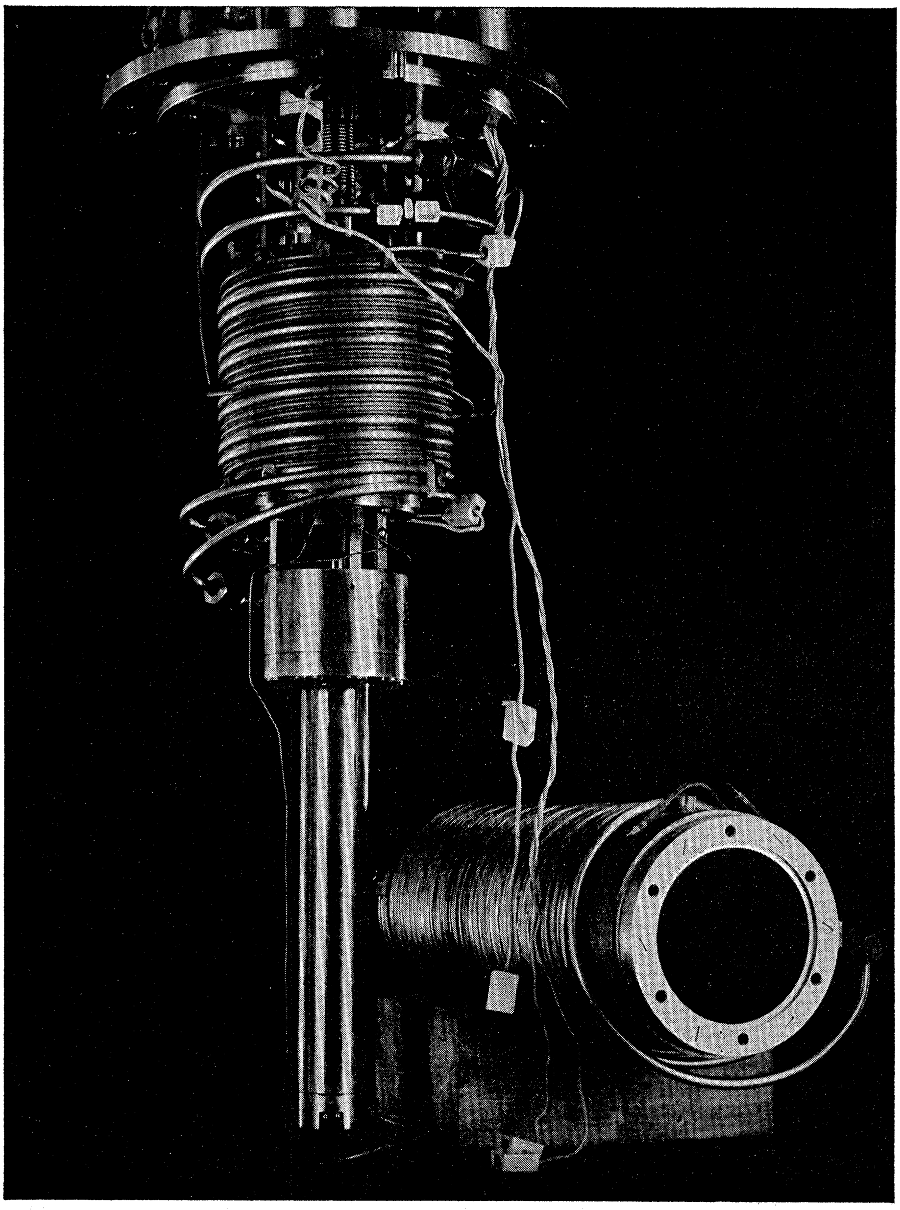

Figure 2. The thermostat block suspended from the top plate of the vacuum vessel. The lower half of the block is removed to show the pressure vessel.

For operation below or slightly above room temperature liquid nitrogen or cold nitrogen gas is circulated round the block at a steady rate. The electronically controlled heaters on the block offset the excess refrigeration, and balance the heat loss to ambient at higher temperatures.

The performance of the equipment is such that the temperature stability of the pressure vessel at temperatures from slightly above the normal boiling point of nitrogen to above 400 K apparently depends only on the completeness of equilibration with the thermostat. Drifts of about 0.02 K/h are usual, but after longer periods of equilibration values of 0.001 K/h are obtained.

2.4. *The cell circuit and measuring system*

The starting-point for the design of the cell circuit has been fixed by choosing the cell dimensions. The cell described above has a resistance between the potential tappings of about 15 Ω at room temperature and a total resistance of about 25 Ω. For heating rates of the order of 10^{-3} W cm^{-1} typical experiments can last for 10 to 20 s. These heating rates correspond to currents of 20 to 30 mA and produce temperature rises of between 0.25 and 0.5 K. The active cell resistance in a typical run therefore changes by about 10 mΩ and the cell output by two or three hundred mV, or approximately 0.1 %. The problem is to record this small change and relate it to the resistance of the cell. For microvolt measurements of this sort a d.c. system is clearly necessary, and since no voltmeter is available to give the required resolution on the total cell output either a bridge circuit (Gillam 1955) or backing-off voltage (Horrocks & McLaughlin 1963) must be used. If the cell current varies appreciably then it should ideally be monitored simultaneously with the voltages. In addition, large variations of cell power complicate the analysis of the measurements. These considerations favour the use of a constant current circuit, and this in turn indicates the use of a backing-off voltage rather than a bridge circuit, in which it is more difficult to secure a constant current as the cell resistance changes.

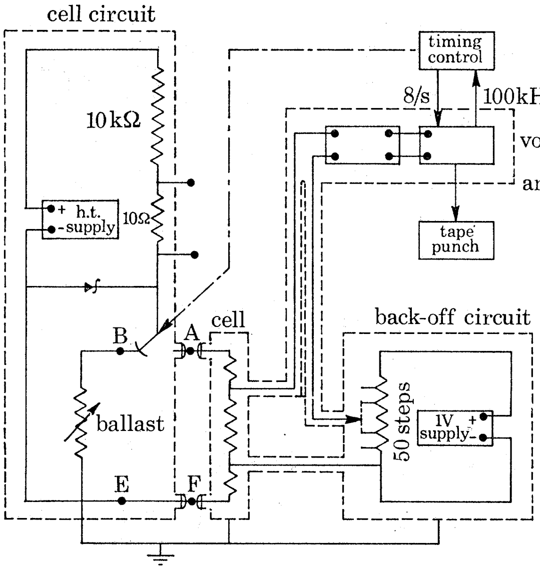

Figure 3. Diagram of the cell and back-off circuit coupled to the data logging system.

To avoid the need for simultaneous current and voltage measurements we may specify that cell resistance changes are to be directly related to output voltage changes to within a few parts per thousand. The current is then required to be constant within a few parts per million. The circuit in which this is achieved is shown in figure 3. A 10 kΩ load resistor ensures that the cell resistance changes amount to no more than a few millionths of the total circuit resistance, and power is drawn from a regulated high voltage source. The specially made load resistor is used in a thermostatically controlled oil bath, and power is supplied from a d.c. voltage standard (model 304, Kintel Division, COHU Electronics, U.S.A.). This high performance instrument provides stable, low-noise reference voltages up to 1000 V and delivers up to 50 mA.

At the start of a run a mercury-wetted relay switches current to the cell from a matched ballast, which is continuously variable up to 100 Ω and is required to be stable to within 10 mΩ over the period between setting up and starting a run. This is easily achieved by using switched decades and helipots, and ensures that the load on the power supply does not alter by more than one part in a million on switching.

A Zener diode is included in parallel with the ballast resistor and relay to prevent large voltages appearing at the contacts during crossover. The final element of the cell circuit is a 10 Ω N.P.L. calibrated standard resistor, which is mounted in the oil bath with the load resistor.

The backing-off circuit is supplied by a d.c. transfer standard (model 735 A, Hewlett Packard Co, U.S.A.) which provides a stable, low-noise, floating output of approximately 0.8 V when connected across a voltage divider of 2500 Ω. The take-off point may be switched in steps of one-fiftieth through the whole output. Untinned copper wire and low-thermal solder were used throughout the circuits for all permanent connexions, and heavy copper terminals were provided for voltage measurements and temporary connexions. The instruments and leads were carefully screened.

In previous applications of the hot wire technique voltages have been recorded by photographing galvanometer spots or using chart recorders. These methods often involve the complications of lag in the response of the instrument and require the conversion of analogue information to digital form. Both these factors represent potential sources of error and are avoided here by using a digital voltmeter (Model DY 2401 C with amplifier DY 2411 A, Hewlett Packard Co, U.S.A.). The integrating type of voltmeter was chosen for its ability to follow transient signals and yet provide a large measure of superimposed noise rejection. Allowance can be made for the fact that the measurements are time averages (see § 3.2).

In setting up the runs a one second sampling period was used, giving a resolution of one part in 3×10^5, or 0.1 μV on the most sensitive range. In monitoring the transient voltages a repetition rate of eight per second is possible with a 0.1 s sampling period and externally generated reset pulses. The resolution is then 1 μV in 30 mV on the most sensitive range. The input impedence of the amplifier is 10^{10} Ω. Both the amplifier and voltmeter are guarded and have high common mode rejection. The digital output is recorded using a high-speed tape punch.

After a run is set up the sequence of operations is controlled by specially built circuits. Initiation of a run is by a contact closure operating a Schmidt trigger, which in turn activates the relay. The falling edge of the pulse developed across the relay during cross-over triggers the opening of the gate to a counter circuit for a 100 kHz signal available from within the voltmeter. In this way zero-time in a measurement is set within 10 μs of the instant at which current begins to flow in the cell (see figure 4). Suitably shaped pulses are generated every 12500 counts and fed back to reset the voltmeter for readings. The delay between the reception of a reset pulse and the start of the sampling period is 9.67 ms. This period is a constant feature of the instrument, and is timed by the 100 kHz crystal oscillator. When low voltages are used in the cell circuit the relay may be switched without triggering the reset pulses. This facility is necessary when setting up the circuit. The duration of a run may be preset, or the run may be ended by a second contact closure. In both cases the reset pulses are discontinued and current is switched back to the ballast. To ensure the best possible performance, the instruments comprising the cell and backing-off circuits and measuring system are run from filtered, stabilized mains.

The stability and noise level of the circuits were tested by replacing the cell with three fixed resistors immersed in a stirred oil bath and chosen to match the resistance of the centre and end sections of the cell. The leads and screening arrangements were similar to those used with the cell. In a simulated run the backed-off voltages across the central resistor showed a small transient after switching, which died away completely during the first half second. In a typical run using a cell current of 20 mA the standard deviation of the measurements was estimated from forty readings, after the first half second, as 0.69 μV, or two parts per million on the signal before backing-off. The mean of eight readings over the period from 0.5 to 1.5 s did not differ from the mean over the next 5 s at the 99 % confidence level. It has been seen that readings from approximately the first half second must be discarded for other reasons (§ 1.1), so the switching transient does not limit the use of the circuit. The effect on the cell power at the start of a run is negligible, since the apparent variation in the cell output voltage was never larger than 20 parts per million.

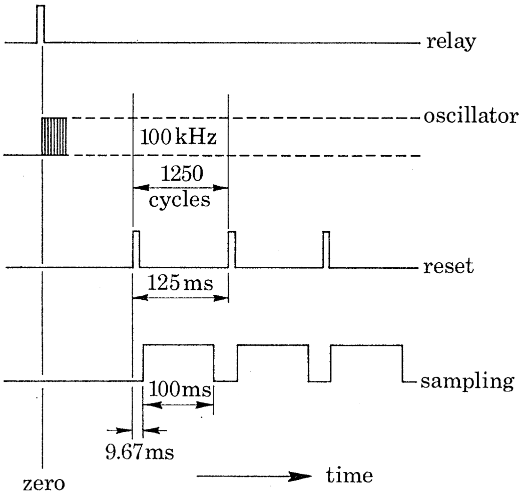

FIGURE 4. Timing sequence of the voltmeter sampling periods.

To check the constancy of the cell current during conductivity determinations representative runs were made in which the backed-off output from the 10 Ω standard was monitored, rather than the cell output. The results were smoothed by fitting a quadratic and showed that for currents up to about 30 mA the changes were between one and two parts per million. The possibility of false transients caused by capacitance or other phenomena in the cell itself was investigated by monitoring the cell output immediately after the current supply had been cut off. With the cell empty or filled with hydrocarbons the voltage fell immediately to zero. However, as was already known for water and other conductors a decaying voltage was observed with glycerol in the cell. This effect is probably due to polarization and at the start of a run the cell output voltage would show a corresponding rising transient. In the case of glycerol this would have resulted in a conductivity too low by a few parts per cent. It seems possible that corrections could be determined by measuring the polarization transient in the way mentioned above, but this was not attempted here, nor to the authors' knowledge has any correction been applied in previous applications of the technique to polar liquids.

3. Experimental procedure

3.1. *Cell temperature, drift rate and gradients*

Cell temperatures are measured using the N.P.L. calibrated resistance thermometer (Tinsley Ltd) set in the base of the pressure vessel. The calibration of this instrument was given as accurate within 0.01 K and used a measuring current of 1 mA. The same current was used in the present measurements, which were made with a Smith's Bridge (Cambridge Instrument Co, Ltd) giving a resolution of 10 $\mu\Omega$, corresponding to about 0.001 K. Measurements were made over a period of time before a series of runs to ensure that the drift rate was acceptably low.

3.2. *Setting up a run*

Before the start of a series of runs the electronic equipment was allowed to stablize, the voltmeter calibration was checked against its internal standard and the amplifier zero set. The temperature stability of the oil bath containing the load and standard resistors was also checked (typically ± 3 K/h). The h.t. supply was set and the current to be used in the runs allowed to flow through the load resistor and ballast for half an hour. Immediately before each run the active resistance of the cell was determined. Calculation and observation showed that a current of 1 mA produces changes in the voltage across the cell over a period of several minutes which are below the resolution of the measurements (0.1 μV). The sequence of operations in setting up and starting a run is therefore as follows:

(i) The h.t. supply is reset to provide a 1 mA measuring current, which is switched from the ballast to the cell. The total potential drop across the cell and its current leads is measured at terminals AE.

(ii) Current is switched back to the ballast resistor, which is manually adjusted until the potential across the terminals BE matches the value observed on AE to within 10 μV. Cell and ballast are therefore now matched within 10 mΩ.

(iii) The measuring current is again switched to the cell and the voltage across the active section measured via the potential leads. To reduce the effects of noise and any thermal voltages several readings are taken and repeated with reversed terminals. Resolution is 0.1 μV.

(iv) After switching current back to the ballast, to avoid any unnecessary heating in the cell, the voltage across the potential terminals of the standard resistor is measured. Several readings and reversed terminals are again used and the oil bath temperature is noted.

The adjustment of the ballast resistor has ensured that the current in the circuit will not change by more than 1 part in a million on switching from the ballast to the cell, so that the ratio of the voltages measured in (iii) and (iv) may be taken as the ratio of the resistances and using the N.P.L. calibration of the standard resistor, the active resistance of the cell may be calculated.

(v) After a timed period (usually 5 min) at the low output, the h.t. supply is reset to supply the current which will be used in the run (typically 250 V, giving about 25 mA). Current is at this time flowing through the ballast.

(vi) The voltage across the standard resistor is measured as before, to provide the precise value of the run current.

(vii) Using the known active cell resistance and run current, the expected cell output is calculated, and the potential divider adjusted to provide a backing-off voltage not more than 30 mV below this value. The backed-off cell output will then be within the full scale reading of the voltmeter in the mode used to record the transient voltages.

(viii) Connexions are set up, as shown in figure 3, so that the backed-off cell output will appear as a positive quantity on the voltmeter, which is now switched to the externally triggered mode using a sampling period of 0.1 s. The required duration of the run is set on the control panel.

(ix) The run is started after a timed interval (usually 5 min) from resetting the h.t. supply to its higher output

3.3. *Checking the current variation during a run*

Runs were carried out in groups of two to four using the same current and same timing sequence in each case. The purpose of this was to ensure complete reproducibility of any current variations due to factors other than the resistance change of the cell. Experience showed that no such variations, in fact, occurred, but this procedure was nevertheless adhered to. The current variation was measured in a final replicate run by monitoring the voltage across the standard resistor. The voltage was backed-off and the measurements were made at the same rate and with the same resolution as in the other runs.

3.4. *Overall programme of measurements*

At each temperature, determinations were made using two currents, such that the heating rates differed by a factor of about two. The currents chosen were the lowest consistent with adequate precision, because of the need to minimize the secondary convection effects described in § 3.3 (*g*) of part I.

A period of about 40 min was allowed between runs, which, according to (3.72), part I, is ample to ensure that temperature differences in the cell have fallen below 0.1 % of their final value in the previous run.

Determinations were carried out over a rising sequence of temperatures. The absolute accuracies of the measurements made with the voltmeter and amplifier were checked periodically against a standard cell. Errors were always below 0.01 %.

3.5. *Material purification and handling*

Analar grade toluene (Hopkin and Williams Ltd) was refluxed for several hours over sodium wire which had previously been washed in toluene. The dried toluene was fractionated and a middle cut retained. The mean of four refractive index measurements using a newly calibrated Abbe's Refractometer (Hilger and Watts Ltd) was $n_D = 1.494$ (25 ± 0.1 °C). The purified material was next distilled under vacuum into a break-seal ampoule which was connected by a glass-metal seal to the materials handling line. After evacuating the line and cell to better than 10^{-5} mmHg (1.3 mPa), the ampule was opened, allowing the toluene to flow into the cell under gravity.

4. CALCULATION OF RESULTS

4.1. *Temperature coefficient of the cell resistance*

During the course of the work approximately 100 measurements of the active cell resistance were made, and the temperature coefficient of resistance of the cell was obtained by differentiating polynomials fitted to these data. The resistance was represented by a cubic below and a quadratic above 0 °C.

A least squares fit to 63 points from 108 to 283 K gave with R in ohms

$$R = 15.3955 + 0.611673 \times 10^{-1} T_A - 0.933560 \times 10^{-5} T_A^2 + 0.190162 \times 10^{-7} T_A^3.$$

The r.m.s. deviation of the experimental points from this line was 0.012 Ω. The quadratic was fitted to 45 points from 269 to 395 K:

$$R = 15.3983 + 0.1611361 \times 10^{-1} T_A - 0.833329 \times 10^{-5}\, T_A^2.$$

The r.m.s. deviation was 0.012 Ω. The absolute resistance values given by these polynomials at 0 °C are within 0.02 %, and the slopes are within 0.002 %.

4.2. *Relation of the experimental data to the fluid thermal conductivity*

Over an infinitesimal period of time δt, the voltage change observed at the potential leads of the cell is

$$\delta V = R\delta I + I\delta T\, \mathrm{d}R/\mathrm{d}T, \tag{4.1}$$

where $\mathrm{d}R/\mathrm{d}T$ is the temperature coefficient of the active cell resistance. The resistance–temperature relationships mentioned above show that this varies by less than 0.02 % over the temperature change in an experiment. It has also been seen that the current variation during a measurement is no greater than a few parts in a million, so (4.1) can be integrated to give the instantaneous value of the increase in the cell output voltage during a run:

$$V_i(t) = R\Delta I(t) + I(\mathrm{d}R/\mathrm{d}T)\, T(a,t). \tag{4.2}$$

The voltmeter, however, records not instantaneous values, but averages over the sampling period δt

$$V(t) = \frac{1}{\delta t}\int_t^{t+\delta t} V_i(u)\,\mathrm{d}u, \tag{4.3}$$

where t is the instant at which the sampling period begins, and is given by

$$t = \text{constant} + n\Delta t \quad (n = 1, 2, 3, \ldots), \tag{4.4}$$

with Δt the period between measurements. Rewriting (4.2) in terms of the recorded voltages $V(t)$ we have

$$V(t) = R\Delta I(t) + I\frac{\mathrm{d}R}{\mathrm{d}T}\int_t^{t+\delta t} T(a,u)\,\mathrm{d}u. \tag{4.5}$$

Subject to the limitations set in part I it has been seen that (3.36) takes account of the finite wire diameter, and allowance for temperature-dependent fluid properties and variable power dissipation can be made using the results of §§ 3.3 (*a*) and (*f*). Thus, substituting (3.36) from part I into (4.5) and including correction terms for these two latter effects, gives

$$V(t) = R\Delta I(t) + I\frac{\mathrm{d}R}{\mathrm{d}T}\left\{\frac{q}{4\pi\lambda}f(t) + C_1(t) + C_2(t)\right\}, \tag{4.6}$$

where
$$f(t) = \frac{1}{\delta t}\left[t\ln\left(\frac{t+\delta t}{t}\right) + \delta t\ln(t+\delta t) - \delta t + \frac{a^2}{4\kappa}\ln\left(\frac{t+\delta t}{t}\right) + \frac{\omega-2}{2\omega}\frac{a^2}{2\kappa}\left\{\left(\frac{\ln 4\kappa(t+\delta t)}{a^2\gamma'}\right)^2 - \left(\frac{\ln 4\kappa t}{a^2\gamma'}\right)^2\right\} + \delta t\ln\frac{4\kappa}{a^2\gamma'} + \ldots\right],$$

and from (3.34), part I $$C_1(t) = -\tfrac{1}{2}\chi T - (\chi-\phi)\, T^2\frac{(-\gamma-\ln s-\ln 4)}{(-\gamma-\ln s)^2}$$

and from (3.56), part I $$C_2(t) = \frac{I^2}{2q}\frac{\mathrm{d}R}{\mathrm{d}T}T^2.$$

The group $I(\mathrm{d}R/\mathrm{d}T)\,(q/4\pi\lambda)$ may therefore be obtained as the slope of the linear relationship between

$$\{V(t) - R\Delta I(t) - I(\mathrm{d}R/\mathrm{d}T)\,(c_1(t) + c_2(t))\}$$

and $f(t)$.

4.3. *Computation of results*

A computer program was written to calculate the various corrections and fit the data by least squares. It processes at a single pass all the runs made at a particular temperature using the same cell current. The data tape is therefore made up of the records of the transient cell and standard resistor voltages, together with the measurements made in setting up the runs. Additional data, such as approximate fluid properties, cell dimensions, coefficients of the resistance–temperature polynomials of the cell and the run temperatures are also included. In outline the sequence of calculations is as follows.

Intially correction terms are neglected and a first estimate of the conductivity is calculated. This is then used, together with input data, to calculate the correction terms C_1 and C_2, assuming that T is given by (3.36) of part I. Corrections for current variations are calculated using the smoothed standard resistor voltages from the current check runs. These corrections are applied to each one of the transient cell voltages, which are then refitted against $f(t)$ in accumulating batches, starting from the earliest permissible moment in a run. Thus the first batch might include readings recorded between 0.5 and 1.5 s, the second, readings from 0.5 to 2.5 s, then 0.5 to 3.5 s, and so on. The apparent conductivities are calculated in each case, plotted against the time of the last reading used, and extrapolated back to $t = 0$. Finally, the zero-time values are corrected for the potential-lead errors (appendix part I).

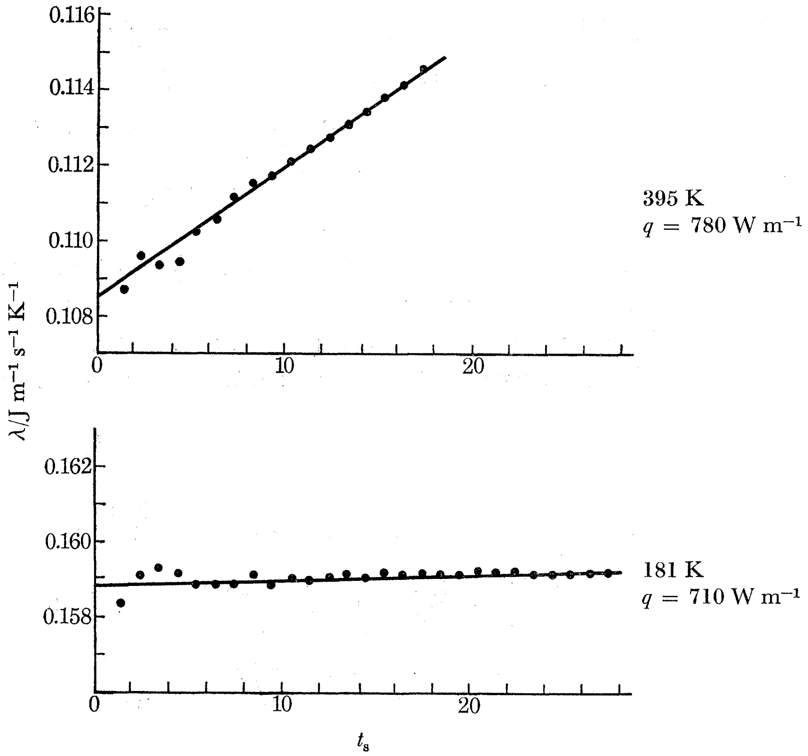

FIGURE 5. Extrapolation of apparent thermal conductivities of toluene to zero time for temperatures at the extremes of the range covered.

5. Results and discussion

5.1. *Specimen run records and calculations*

Table 1 shows a specimen run record and extracts from the computer calculation at one temperature. It should be noted that the determined conductivity is affected only by the changes in the corrections to the cell output voltage, and not by their absolute values. These changes are never greater than 0.25 % of the total voltage change during a run. Figure 5 shows the extrapolation of apparent conductivities to zero time for two runs at the extremes of the temperature range covered. The increased dependence of apparent conductivity on time at the higher temperature indicates the increased importance of convection and radiation effects. The plots also indicate the size of the corrections introduced by the extrapolation.

TABLE 1. SPECIMEN RUN RECORD: LIQUID TOLUENE UNDER S.V.P. AT 181.28 K

Cell temperature drift and gradient

cell temperature drift rate	$0.020\ \mathrm{K\ h^{-1}}$
temperature difference between top and bottom of the pressure vessel	0.035 K

Readings recorded in setting up the run

h.t. supply output	10 V
timing	12.37–46 p.m.
total cell plus current leads	17.2280 mV
ballast resistor set at	17.2280 mV
active cell	9.5217 mV
reversed terminals	9.5214 mV
standard resistor	9.8364 mV
reversed terminals	9.8360 mV
back-off voltage set at	228.4 mV
h.t. supply output	250 V
timing	12.46–52 p.m.
standard resistor	245.907 mV
reverse terminals	245.922 mV
run initiated at	12.52 p.m.
standard resistor temperature	30 °C
cell thermometer resistance	15.6980 Ω

Extracts from the computer calculations

active cell resistance	9.6815 Ω
operating current	24.588 mA
cell power	$7.1391\ \mathrm{W\ m^{-1}}$
preliminary data fitting from points 17 to 80 gives conductivity	$0.16\ \mathrm{J\ m^{-1}\ s^{-1}\ K^{-1}}$
first acceptable reading	5th

Examples of corrections applied to ln (time)

data point number	correction for voltmeter integration effect	correction for finite wire diameter
20	6.75×10^{-5}	-1.58×10^{-3}
36	2.01×10^{-5}	-9.36×10^{-4}
84	3.79×10^{-6}	-4.45×10^{-4}
180	8.27×10^{-7}	-2.27×10^{-4}

Corrections to cell voltages (V)

data point no.	correction for cell current variation	correction for cell power variation	correction for fluid property variation
20	8.20×10^{-8}	1.02×10^{-6}	-1.33×10^{-7}
84	8.66×10^{-8}	1.31×10^{-6}	-1.69×10^{-7}
184	3.49×10^{-9}	1.57×10^{-6}	-2.01×10^{-7}

TABLE 2. EXPERIMENTALLY DETERMINED THERMAL CONDUCTIVITY OF TOLUENE

temperature K	cell current mA	cell power 10^2 W m^{-1}	convection limit s	potential lead correction J m^{-1} s^{-1} K^{-1}	corrected conductivity J m^{-1} s^{-1} K^{-1}
181.37	20	4.6	30	−0.0005	0.1571
181.32	25	7.1	,,	,,	0.1595
181.28	25	7.1	,,	,,	0.1585
181.26	25	10.3	,,	,,	0.1595
181.26	30	10.3	,,	,,	0.1586
181.49	20	4.9	,,	,,	0.1579
189.43	20	4.9	,,	,,	0.1584
189.39	20	4.9	,,	,,	0.1580
200.92	20	5.1	,,	,,	0.1557
201.80	20	5.2	,,	,,	0.1557
201.89	20	5.2	,,	,,	0.1555
202.00	25	8.1	,,	,,	0.1556
202.02	25	8.1	,,	,,	0.1556
202.27	20	5.2	,,	,,	0.1554
221.83	20	5.8	,,	,,	0.1522
221.85	20	5.8	,,	,,	0.1521
221.91	25	9.0	,,	,,	0.1522
221.92	25	9.0	,,	,,	0.1522
230.94	20	6.0	,,	,,	0.1509
230.87	20	6.0	,,	,,	0.1509
230.87	20	6.0	,,	,,	0.1514
230.87	23	8.0	,,	,,	0.1508
235.40	20	6.0	,,	,,	0.1498
235.42	20	6.0	,,	,,	0.1500
235.43	20	6.0	,,	,,	0.1506
235.46	23	8.0	,,	,,	0.1501
239.87	20	6.3	,,	,,	0.1474
239.89	20	6.3	,,	,,	0.1468
239.91	17	4.6	,,	,,	0.1472
253.34	20	6.7	,,	,,	0.1443
253.34	20	6.7	,,	,,	0.1444
253.35	20	6.7	,,	,,	0.1445
253.38	17	5.1	,,	,,	0.1448
253.40	17	5.1	,,	,,	0.1447
268.59	20	7.1	,,	,,	0.1401
268.60	20	7.1	,,	,,	0.1402
268.61	20	7.1	,,	,,	0.1406
268.62	17	5.5	,,	,,	0.1399
283.90	20	7.6	,,	−0.0004	0.1342
283.90	20	7.6	,,	,,	0.1339
298.02	20	8.0	,,	,,	0.1311
298.05	20	8.0	,,	,,	0.1316
298.09	17	6.1	,,	,,	0.1326
309.97	20	8.3	,,	,,	0.1285
309.98	20	8.3	,,	,,	0.1285
309.99	20	8.3	,,	,,	0.1289
310.17	20	8.3	,,	,,	0.1290
310.17	20	6.4	,,	,,	0.1288
326.14	20	8.7	,,	,,	0.1237
326.16	20	8.7	,,	,,	0.1230
340.31	20	9.1	29	,,	0.1185
340.31	20	9.1	,,	,,	0.1197
358.97	17	7.4	29	,,	0.1155
358.97	17	7.4	,,	,,	0.1164
357.79	20	9.6	28	,,	0.1155
379.30	20	10.2	25	,,	0.1116
379.26	20	10.2	,,	,,	0.1120
379.22	17	7.8	28	,,	0.1105
379.20	17	7.8	,,	,,	0.1104
379.19	17	7.8	,,	,,	0.1115
395.56	17	8.2	27	,,	0.1085
395.55	17	8.2	,,	,,	0.1087
395.70	20	10.7	24	,,	0.1078
395.71	20	10.7	,,	,,	0.1078

5.2. *Experimental thermal conductivities of liquid toluene*

Table 2 shows the final corrected values which have been obtained for the thermal conductivity of liquid toluene under saturation pressure, over a range of temperatures from the freezing-point to a little above the normal boiling-point. The table also shows the more important experimental conditions, namely: rounded values of the cell current and power, and the calculated time for onset of major convection effects (§ 3.2 (*c*) of part I). The corrections which were applied for potential-lead errors are also recorded.

5.3. *Smoothed conductivities*

The results in table 2 show a linear relationship between conductivity and temperature in the range 230 to 340 K, while outside this range the temperature coefficient appears to become less negative. The data have been smoothed by fitting three straight lines, since, although gradual changes of slope would seem more reasonable on physical grounds, there is not sufficient data to justify fitting polynomials. Least squares fitting gave the correlations shown in table 4, and smoothed values at 10 K intervals are given in table 3.

TABLE 3. SMOOTHED THERMAL CONDUCTIVITIES OF LIQUID-TOLUENE AT S.V.P.

temperature / K	thermal conductivities / $J\ m^{-1}\ s^{-1}\ K^{-1}$	temperature / K	thermal conductivities / $J\ m^{-1}\ s^{-1}\ K^{-1}$
180	0.1591	300	0.1310
190	0.1575	310	0.1282
200	0.1559	320	0.1253
210	0.1543	330	0.1225
220	0.1527	340	0.1195
230	0.1510	350	0.1174
240	0.1482	360	0.1153
250	0.1454	370	0.1133
260	0.1425	380	0.1112
270	0.1396	390	0.1092
280	0.1368	400	0.1071
290	0.1339		

5.4. *Estimation of accuracy*

The accuracy of the electrical measurements depends largely on the accuracy of the voltmeter readings and the standard resistor calibration. Checks against a standard cell showed that errors in the voltage measurements were always below 0.01 %, and the N.P.L. standard resistor calibration was given as accurate within 0.005 %. By using the simple error propagation theory in which all possible errors are summed it can be shown (Pittman 1968) that the maximum error in the conductivity from these sources is below 0.1 %, and the probable error is, of course, much less. Thermal e.m.fs in the potential leads are not believed to be a significant source of error. The precautions which were taken in the circuit have been described above, and connexions within the cell are between wires of high purity platinum. The measurements which were repeated with reversed terminals during the setting-up procedure showed differences below 0.01 %. It should be noted that in the transient voltage measurements errors would occur only through changes in thermal e.m.fs.

Some indication of the confidence to be placed in the values of the resistance–temperature coefficient of the cell can be gained by examining the effects of fitting the data in different ways.

For example, if the data over the whole temperature range are represented by a cubic, the slope agrees with the values given by the procedure described in § 3.1 within 0.2 % between 180 and 360 K. Between 360 and 395 K the difference rises to 0.5 %. This is a reflexion of the fact that the resistance data do not extend above temperature range of the toluene measurements, although points below the range are available from the later work on cryogenic liquids. The procedure of § 3.1 was suggested by the form of the Callender equation, although since the hot wire is under stress, one would not expect the resistance to follow this relationship precisely. The $\mathrm{d}R/\mathrm{d}T$ values which have been used are estimated as accurate within 0.2 % at temperatures up to about 360 K, but towards 390 K the accuracy becomes rather lower, though probably remaining within 1 %.

The thermometer in the base of the cell, which was used to measure run temperatures, was calibrated by the N.P.L. to 0.01 K. Temperature differences between the top and bottom of the cell were never greater than 0.05 K, so a maximum uncertainty in the mean cell temperature can be estimated at about 0.035 K. Since the temperature coefficient of the thermal conductivity is about 1 %/K, this results in a maximum error in the conductivity from this source of 0.035 %.

A vertical temperature gradient in the cell can give rise to a second source of error. Although the gradient may be too small to produce convection by itself, errors can occur through interaction with the convection induced by the hot wire. Thus as a run proceeds, warmer or cooler fluid may be moved up the active section of the wire, affecting its mean temperature. This can give rise to an irregular dependence of apparent conductivity on time, which was observable in measurements on strongly convecting liquids when the cell temperature gradient was unduly large. An upper limit of 0.005 K/cm may be set for the gradient. If the fluid next to the hot wire is carried upwards a distance of 1 cm by convection, then the mean temperature of the hot wire will be affected to the extent of 0.005° K. The total hot-wire temperature change in a run might be about 0.5 K, so in this example, the error would be approximately 1 %. Fortunately, extrapolation of apparent conductivities to zero time largely eliminates this error, since values are then obtained which are virtually free from the effects of convection. However, a large part of the scatter in the present results is believed to derive from this effect.

The possible effects of vibration on the measurements were carefully investigated. The influence of building vibration was tested by repeating measurements outside normal working hours when the background vibration of the building was much reduced, and with all machinery in the vicinity switched off. No sytematic difference in the results was observed. The effect of the force exerted by the earth's magnetic field on the wire as current is switched into it, was also considered. Calculations (Pittman 1968) showed that it results in a negligible movement of the wire.

The length of the active section of the hot wire was measured to within 0.01 %. It was not convenient to remeasure the length after the toluene determinations, but the stability of the cell was tested by resistance measurements. Over a period of 30 weeks these agreed to 0.07 %.

Some evidence for the success of the extrapolation procedure in minimizing radiation and convection errors can be deduced from the results in table 2. At most temperatures, determinations were made at two heating rates, differing by factors of about 1.5. But, although the radiation and convection effects therefore differ, no systematic relationship between corrected conductivity and heating rate can be observed. Figure 5 shows that there is very little doubt about the result of a linear extrapolation of apparent conductivities to zero time. However, an element of uncertainty remains because there is not *a priori* justification for a *linear* extrapolation. The success of the procedure must therefore be judged partly on the basis of the internal evidence mentioned above, but also by comparing the present results with previous work.

Part I has shown that none of the approximations involved in the mathematical model of the cell results in errors above 0.1 %. Therefore, assuming that radiation and convection errors have been eliminated, the errors in the smoothed values are believed to be within 0.7 % below about 340 K but may rise to 1.5 % at the higher temperatures.

5.5. *Comparison with previous measurements*

There have been a large number of experimental investigations of the thermal conductivity of toluene. Powell, Ho & Liley (1966) have published a survey of the data which shows that the trend over the years has been towards lower values, largely owing to the more successful elimination of errors due to convection and stray heat losses, but the true importance of radiant heat transfer in measurements on dense fluids has been recognized only quite recently. With the exception of Leidenfrost (1964) and Poltz & Jugel (1967) experimentalists have followed Bridgman's (1923) suggestion that the thin layers of liquid which are generally used in thermal conductivity measurements may be assumed completely transparent to thermal radiation. Radiation errors estimated on this basis were invariably found to be negligible. However, as has already been pointed out in part I, this is now known not to be the case.

On the basis of a number of simplifying assumptions Poltz (1965) has derived a convenient expression for the effective conductivity of a plane layer of fluid of thickness d under steady state conditions

$$\lambda_{\text{eff}} = \lambda + \frac{16}{3}\frac{\bar{n}^2}{\bar{\theta}}\sigma T^3 Y. \tag{5.1}$$

Here λ is the true conductivity and the second term is the radiative contribution to the effective conductivity. Y is a function of the optical thickness of the fluid layer, $\bar{\theta}d$, and varies from 0 to 1 as $\bar{\theta}d$ varies from 0 to ∞. It is also a function of the emissivity of the walls bounding the fluid layer, and values are available (Poltz 1965) for regularly and diffusely reflecting surfaces. The quantities $\bar{n}$ and $\bar{\theta}$ are the refractive index and absorption coefficient averaged over the important wavelengths.

At large optical thicknesses (5.1) reduces to the radiation diffusion expression and predicts an asymptotic approach of the effective conductivity to an upper limiting value. As the optical thickness tends to zero it shows that the effective conductivity tends to the true conductivity. The dependence of effective conductivity on layer thickness was observed by Poltz & Jugel (1967) in measurements on a number of liquids using a guarded flat-plate cell. By fitting (5.1) to their experimental results they obtained values for the true conductivity and for the absorption coefficient corresponding to the observed dependence of λ_{eff} on d, the fluid-layer thickness. The radiative contribution in thick layers was found to be about 5 % in measurements on toluene, and an examination of previously published data showed that much of the scatter could be explained in terms of differing radiative contributions in the various determinations.

Comparison of previous data with the present results will not therefore be meaningful unless account is taken of these radiation effects. In many cases this is not possible because the relevant data are not available. However, there remain a small number of results to which (5.1) may be applied. These must be steady-state determinations which are free from all other significant sources of error, and in which the fluid-layer thickness has been recorded. The layers must also be plane or approximately so, and this restricts consideration to work with flat-plate, concentric cylinder or sphere cells. Strictly, the emisivity of the cell walls should also be recorded. However, in cells with polished metal walls the emissivities will certainly be below 0.1. The dependence of Y on emissivity is largest as a percentage at low optical thicknesses, and in the thinnest layers used ($\bar{\theta}d \cong 1$), Y varies by 12% as the emissivity varies from 0 to 0.1. It is therefore possible to assume an emissivity of, say, 0.04 in all cases without introducing errors of more than a few per cent into Y.

The data chosen for comparison are shown in table 4. Ziebland's (1961) data were originally represented by a single equation. For the present purposes separate least-squares lines have been fitted to the determinations using the two fluid-layer thicknesses. The data of Ziebland & Burton (1961) and that of Riedel (1951) have also been fitted to straight lines to permit interpolation.

Table 4. Summary of various thermal conductivity measurements on toluene

authors	cell type, no. of measurements and temp. range/K (to nearest degree)	fluid thickness mm	coefficients of $\lambda = A - BT$(K)		10 × correlation coefficient
			$10A$	10^4B	
Riedel (1951)	f.p. c.c. c.s. 3 3 1 193 293 353	1	2.194	2.871	9.98
Challoner & Powell (1956)	f.p. 9 273 — 353	2 and 3	2.294	3.125	—
Ziebland & Burton (1961)	c.c. 3 307 323 364	2	2.176	2.762	9.99
Ziebland (1961)	c.c. 13 258 — 311	0.258	2.220	2.987	9.84
	58 288 — 385	0.755	2.155	2.772	9.84
Venart (1964)	c.c. 34 288 — 353	0.51	2.166	2.84	—
Poltz & Jugel (1967)	f.p. 5 (at each T) 293 303 328	0 (extrapolated)	2.135	2.833	—
present work	transient method 26 181 — 230	—	1.883	1.62	9.90
	34 231 — 340	—	2.169	2.863	9.98
	14 340 — 396	—	1.892	2.052	9.81

Where only a few temperatures have been used these have been given to the nearest degree. In other cases the range is given. f.p., flat plates; c.c., coaxial cylinders; c.s., concentric spheres.

The smoothing lines for the data of Challoner & Powell (1956) and Venart (1964) are the ones used by those authors. In the first case the equation has been calculated from tabulated smoothed values. Comparisons between these results and the present ones will be made at 298.2 K, since an absorption coefficient value is available at this temperature, and at 338 K which is at the upper end of the central straight line representing the present results. Previous data above this temperature are relatively sparse (see figure 6) and have been lumped with data at lower temperatures in the linear correlations. Values calculated from these correlations at higher temperatures will therefore be either linear extrapolations from the lower temperature values, or will be heavily weighted towards such extrapolations, and it would not be reasonable to compare them with the present smoothed values in which allowance has been made for a change of slope.

Values of the reported conductivities from table 4 for the two temperatures are plotted against layer thickness in figures 7 and 8 and are summarized in table 5. The data of Challoner & Powell are plotted at 2.5 mm since no information is available on the weights to be given to their determinations at 2 and 3 mm. This is not a gross approximation since at these thicknesses the radiation diffusion approximations applied quite closely and the variation of effective conductivity between 2 and 3 mm is small. Despite some scatter a systematic relationship between the reported conductivities and the layer thickness is clearly quite discernible, and if the present results are plotted at zero layer thickness they lie close to a line extrapolated from the steady-state values

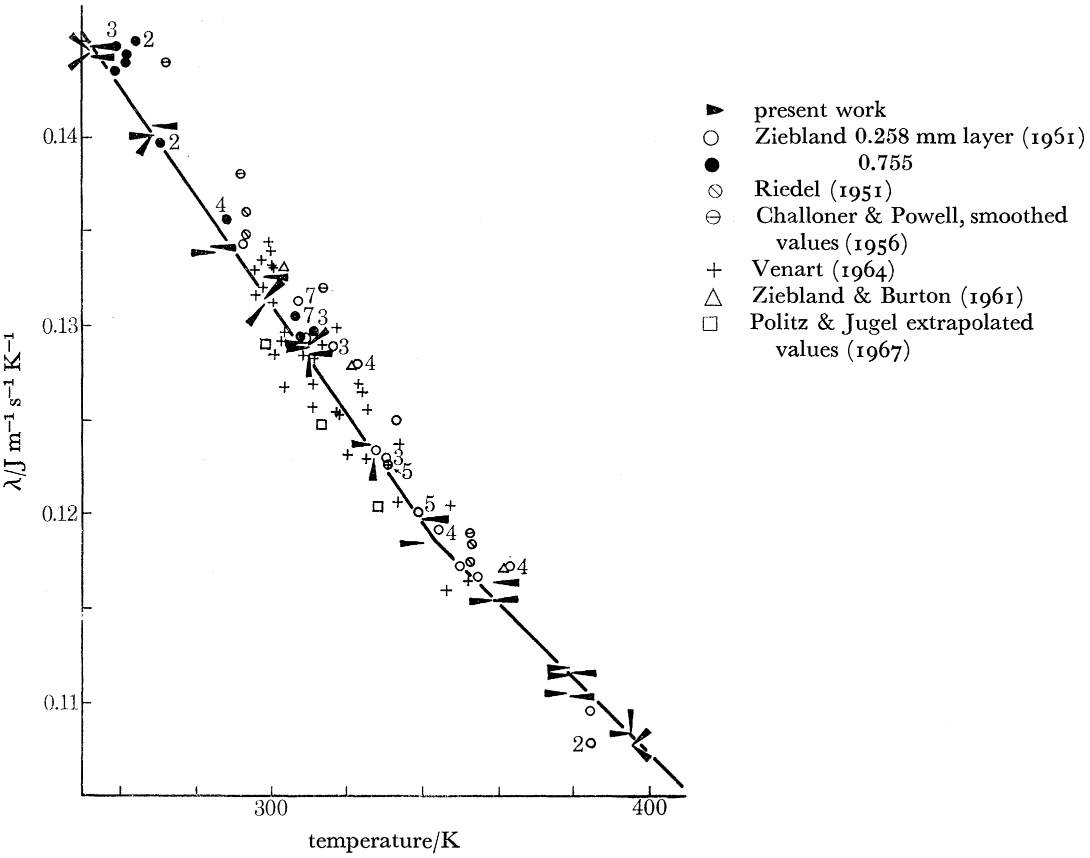

FIGURE 6. Comparison of the measurements, above room temperature, of the thermal conductivity of toluene by different investigators. (The point of the arrowhead indicates the location of the data point in the present work.) The solid lines are fitted only to the present values.

TABLE 5. COMPARISON OF STEADY STATE THERMAL CONDUCTIVITIES OF TOLUENE WITH VARYING THICKNESS OF EXPERIMENTAL LAYER

authors	test layer thickness mm	apparent conductivity J m^{-1} s^{-1} K^{-1} 298.2 K	338.0 K
Ziebland (1961)	0.258	0.1329	0.1210
Venart (1964)	0.51	0.1319	0.1206
Ziebland (1961)	0.755	0.1328	0.1218
Riedel (1951)	1	0.1338	0.1223
Ziebland & Burton (1961)	2	0.1352	0.1242
Challoner & Powell (1956)	2.5	0.1362	0.1238
present work	—	0.1316	0.1198

at various thicknesses. The measurements by Poltz & Jugel (1967) at 298.2 K are differentiated by open circles in figure 7 and it is seen that their extrapolated, radiation free value of 0.1290 J m^{-1} s^{-1} K^{-1} at zero fluid thickness is 2 % lower than the present work and their results at finite layer thicknesses are correspondingly lower than the other data considered.

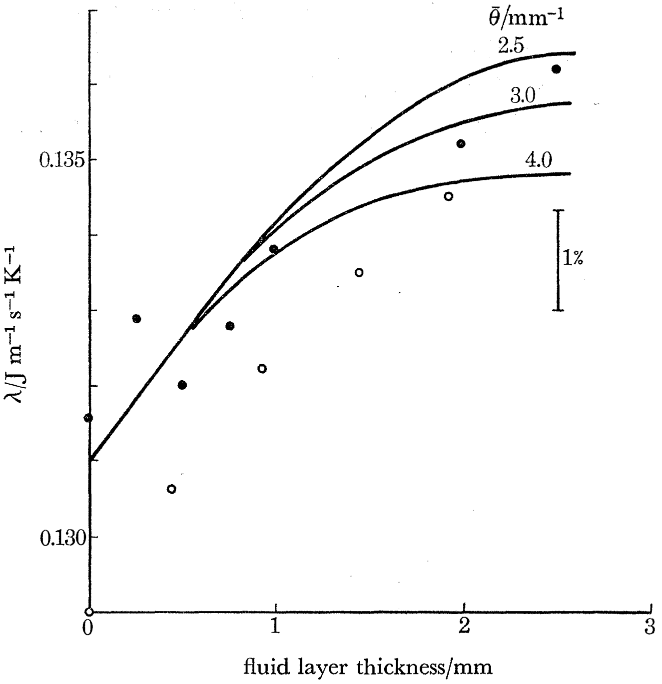

FIGURE 7. Reported thermal conductivities of toluene at 298.2 K plotted against thickness of the liquid layer as used by different investigators. The solid curves show calculated effective conductivities as a function of absorption coefficient $\bar{\theta}$ for a true conductivity of 0.1310 J m^{-1} s^{-1} K^{-1}. ●, Various workers (see table 7); ○, Poltz & Jugel (1967).

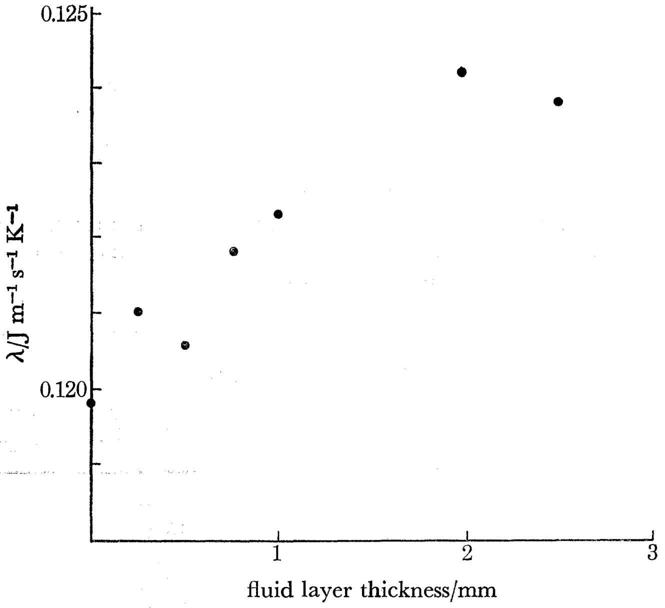

FIGURE 8. Reported thermal conductivities of toluene at 338 K plotted against the thickness of the liquid layer as used by different investigators. (Note no absorption data are available to enable calculated effective conductivities to be compared with the experimental results.)

Poltz & Jugel obtained a best fit of (5.1) to their data at 298.2 K with $\overline{\theta} = 2.3\,\mathrm{mm^{-1}}$ compared with their value of $3.5\,\mathrm{mm^{-1}}$ measured from an infrared spectrogram of toluene at this temperature. It is interesting to calculate the value of $\overline{\theta}$ corresponding to the other data in figure 7. To do this a value of $\bar{n}$ must be assumed, and following the procedure of Poltz (1965), $\bar{n}$ is taken equal to $n_D = 1.50$, which is permissible since the refractive index is only weakly dependent on wavelength in this region of the spectrum. If the present result is plotted at zero layer thickness then a best fit is given with $\overline{\theta} = 3.1\ (\pm 0.2)\,\mathrm{mm^{-1}}$ and a true conductivity of $0.1310\,\mathrm{J\,m^{-1}\,s^{-}\,K^{-1}}$, i.e. 0.45 % below the present result. Curves through a true conductivity of $0.1310\,\mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}}$ for various values of $\overline{\theta}$ are shown on figure 7. It can be seen from these that the value obtained for the true conductivity is very largely determined by the points at and below 1 mm, and that the effective conductivity is not very sensitive to $\overline{\theta}$ below this thickness. The result obtained for $\overline{\theta}$ is governed almost completely by the points at the two largest layer thicknesses, and it has been pointed out that some approximation may be involved in plotting the upper one at 2.5 mm. The figure of $3.1\,\mathrm{mm^{-1}}$ must not therefore be interpreted too precisely, but it is closer to the value obtained by Poltz & Jugel from a spectrogram than to the value calculated from their measurements of effective conductivity as a function of layer thickness.

The λd relation shown by the data from various investigations and represented by filled circles in figures 7 and 8 is striking when it is borne in mind that each of the previous results was obtained in a different cell, and that three different cell geometries and four independent experimentalists were involved. The conclusion which suggests itself is that these previous results—regarded as effective conductivities, uncorrected for radiation—are all accurate to rather better than 1 %, and that the present result is a true, radiation-free conductivity of similar accuracy. There remains, however, the discrepancy with the results of Poltz & Jugel, and further work will clearly be needed to resolve this point.

The present results are consistently the lowest of any which have been reported, save for those of Poltz & Jugel. The data summarized in table 4 are plotted, together with the present results at the upper temperatures, in figure 6. Above about 340 K, where the present results show a change of slope, the data of Abas-Zade (1947) which are about 20 % higher than the present values, and those of Osminim (1957) which are 4 to 5 % higher, are omitted. The only measurements for comparison at the upper temperatures are therefore three values by Ziebland at 385 K.

The fact that these fall below the present values, whereas all his other values are higher, leaves the results above 340 K open to further investigation. It has been seen that the errors to be expected in the present results at the high temperatures may be rather larger than elsewhere, largely due to increased uncertainty in $\mathrm{d}R/\mathrm{d}T$, but they seem unlikely to be large enough to account completely for the rise of the high temperature results above a linear extrapolation from data between 230 and 340 K. With regard to values below 230 K Ziebland (1961) noted that an extrapolation of his data lay about 2 % above Riedel's single value $0.1592\,\mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}}$ at 193.2 K, while the results of Challoner & Powell extrapolated to a value 6 % higher. The only other result at this temperature is due to Goldschmidt (1911) and it is about 2 % higher than Riedel's. However, in view of the excellent consistency of Riedel's results at higher temperatures and their close agreement with other works, Ziebland discounted Goldschmidt's result and suggested that a change in the temperature coefficient of the conductivity might occur below the range of his own measurements. It has been seen that this is found in the present work and the smoothed value at 193.2 K is 1.3 % below Riedel's. After allowance for a small radiative component in Riedel's result, this is probably consistent with his estimated accuracy of 1 %. The small influence of radiation and convection errors at low temperatures in the present measurements is shown by the weak dependence of the effective conductivity on time in figure 5. This, and the agreement with Riedel's result, suggests that the low temperature determinations are reliable, and that the temperature coefficient does become less negative below 230 K.

5.6. *Conclusions*

Data have been obtained on the thermal conductivity of liquid toluene under saturation pressure at temperatures from just above the freezing-point to about 12 K above the normal boiling-point. No previous single investigation has covered this range, existing data being particularly sparse below about 150 K and above 360 K, which was clearly undesirable in a fluid which has been recommended as a thermal conductivity standard. The recently demonstrated importance of radiative transfer in thermal conductivity measurement on certain fluids at normal temperatures reinforces the case for toluene as a standard. Its properties fall conveniently in the range which makes the apparent conductivity dependent on the cell design, and measurements on toluene can therefore be used to test the susceptibility of a technique to radiation errors.

The present technique has been shown to be capable of accuracies at least as high as the steady-state methods which have previously been used for some of the most careful measurements and internal evidence and comparison with previous results suggest that the present values for toluene are true, radiation-free conductivities which are substantially free from error (at least below 340 K), although one or two anomalous relationships with previous data have been noted, which point to the need for further work.

Thanks are due to the Science Research Council for a grant for the apparatus.

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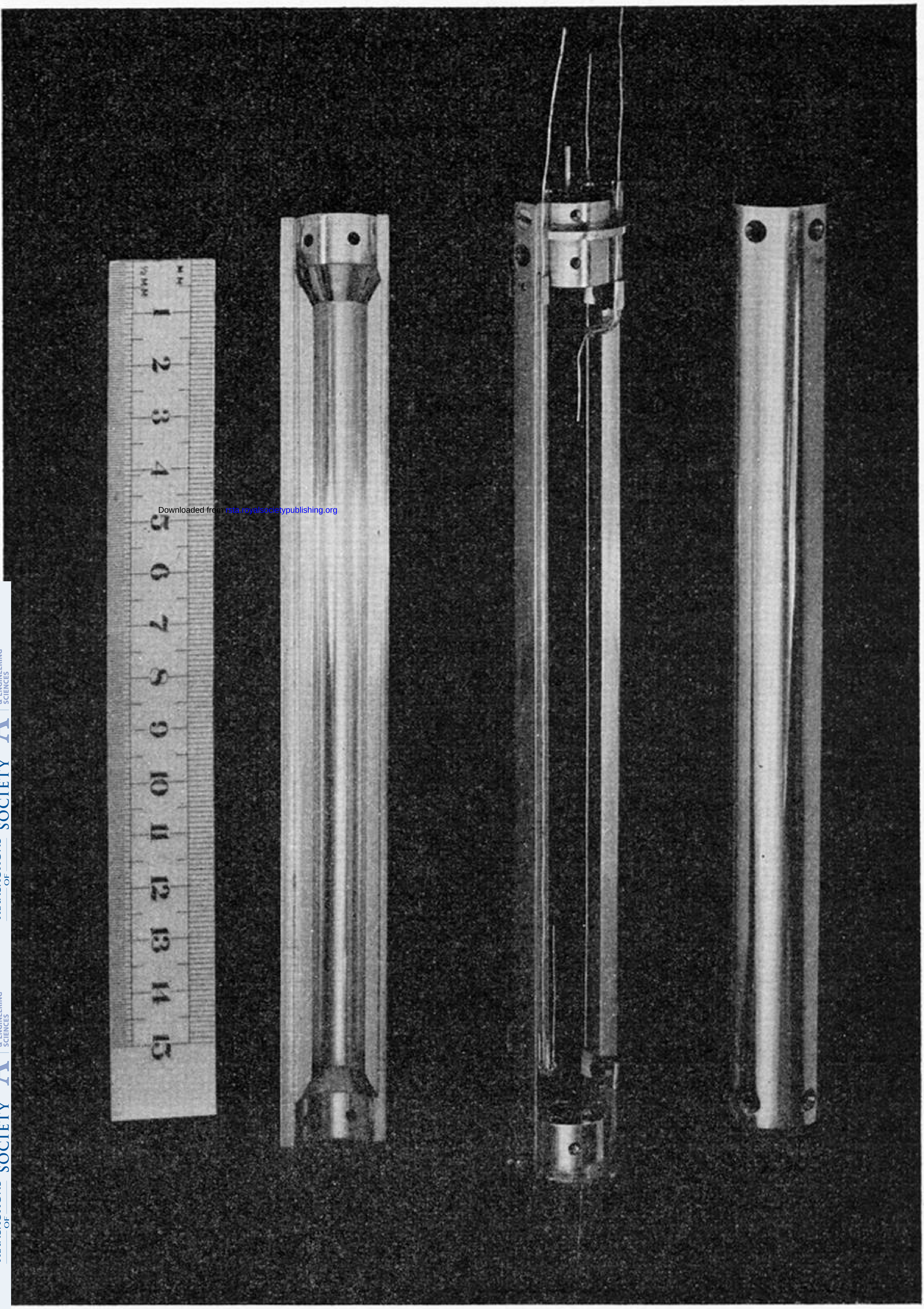
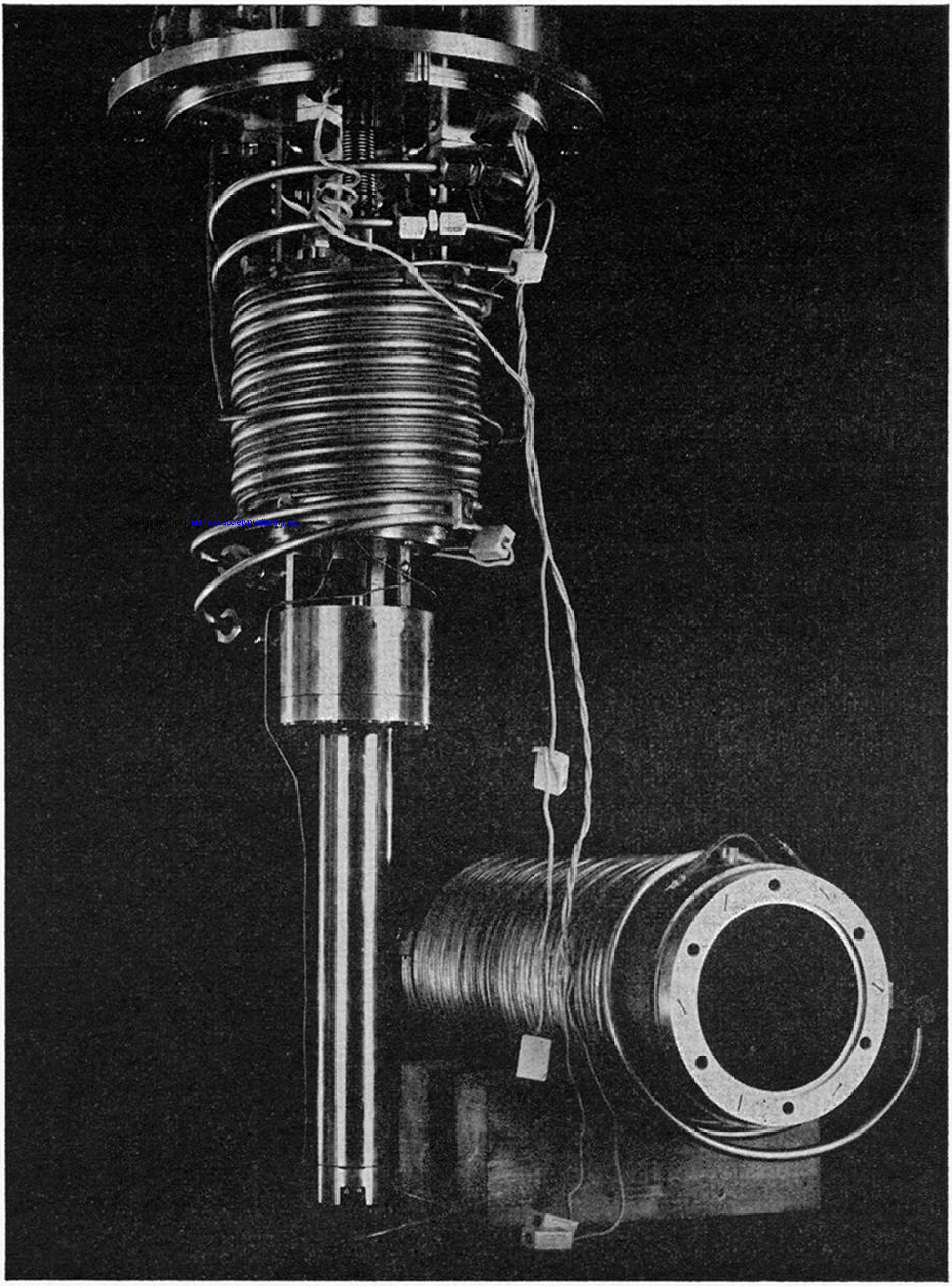


FIGURE 1. Thermal conductivity cell frame with side pieces.



IGURE 2. The thermostat block suspended from the top plate of the vacuum vessel. The lower half of the block is removed to show the pressure vessel.