Accurate Determination of Thermal Conductivities

D. G. GILLAM, LARS ROMBÉN, HANS-ERIK NISSEN and
OLE LAMM

Division of Physical Chemistry, Royal Institute of Technology, Stockholm, Sweden

The electrical method for measuring thermal conductivities, introduced by Stålhane and Pyk [1] and Eucken and Englert [2], has been put on a sound basis and the accuracy increased, for both solids and liquids, up to about $\pm$ 0.3 %. The principle is that of the classical methods for gases in which the temperature of an electrically heated wire, immersed in the medium, is measured over a suitable time interval. The temperature of the wire is determined continuously by a resistance measurement, not over the whole length of the wire but only over a central section. In this way undesired conduction effects at the ends of the cell and the corrections for them can be neglected. Also, because unsteady state conditions are used, no correction is required for the temperature discontinuity at the wire-medium interface. A number of precautions and arrangements, necessary for accurate work, have been examined in detail, in order to adapt the method for precision routine measurements.

The method can be used for solids, whose melting points are not too high, by pouring the liquified substance directly into the cell, care being taken to see that no gas bubbles settle out on the wire due to incomplete degasification. In the case of liquids, high accuracy is obtained for fluids of sufficiently high viscosity or sufficiently low thermal dilatation, as will be described in a following paper.

THE HOT WIRE PRECISION METHOD

1. General principles

Thermal conductivities, apart from their undoubted industrial importance, can also be used to throw light upon the structure of the substances studied and the mechanism by which heat is transmitted through them. The two main difficulties of this work are, first, to insulate the substance in such a way that heat will flow only in the desired direction and, second, to avoid errors in the temperature measurements due to the temperature jump which exists between the substance under investigation and the temperature measuring device. Accurate methods fall into two groups — those in which uni-dimensional heat conduction is investigated (generally steady state), proper care being taken with the insulation of the substance to ensure correct
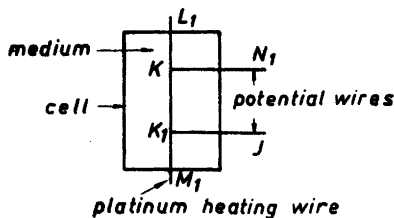
platinum heating wire

Fig. 1. Principle of the hot wire method.

boundary conditions, and those in which two-dimensional heat conduction is studied (both steady and unsteady state). With the former group and likewise with the steady state methods in the latter group, the insulation and temperature jump errors are likely to be appreciably large. Both of these errors can be avoided by using instead a certain two-dimensional unsteady state method. The principles of this method were first laid down by Stålhane and Pyk [1]. It was first used for accurate measurements by Eucken and Englert [2] but the cell and electrical system used by them were inconvenient and have been considerably simplified in the present work. Heat was provided by passing an electrical current through a thin platinum wire immersed in the medium and situated in the axis of the cylindrical glass containing vessel (Fig. 1).

As soon as current passed through the wire, the temperature of the wire increased but the rate of increase decreased as heat was conducted away by the medium. From a resistance determination on the platinum wire (*i.e.* a temperature determination at the axis) at various times during the passage of the current, the thermal conductivity could be calculated. Moreover by measuring the resistance of the section KK_1 only, using the potential wires shown in the diagram, it was possible to assume strictly two-dimensional heat conductivity and thus there was no necessity for applying a correction for the three-dimensional heat flow at the ends as is usual in methods of this type. Platinum, because of its superior resistance qualities, *e.g.* resistance stability over long time periods and freedom from corrosion, can be considered to be the most suitable material for the wire.

The mechanical design of Eucken and Englert's cell [2] was felt to be unnecessarily complicated and it was thought preferable to construct a simpler cell (Fig. 2) which could be easily filled with liquids and also solids whose melting points were not too high.

The diameter of this simpler cell was 3 cm, the length of the KK_1 section was 10 cm and the distances from the points K and K_1 to the ends of the cell were 4 cm. The lengths of the platinum sections of the potential wires were about 4 cm. Thermo-pure platinum was used for the central wire and chemical pure platinum for the potential wires.

The difficulty of making a neat join between the platinum wires was overcome by the use of a small spot welder. The welding current is rather critical; too small currents will not give sufficient heat for welding whilst too high currents will completely burn away the wires at the welding point. With practice, a strong, right-angle join could be made between the potential wires and the central wire without any bead formation at the point of union. The four ends of the platinum wire system were then each sealed into short copper wires, using a small reducing gas-oxygen flame and pushing the platinum wire into the molten
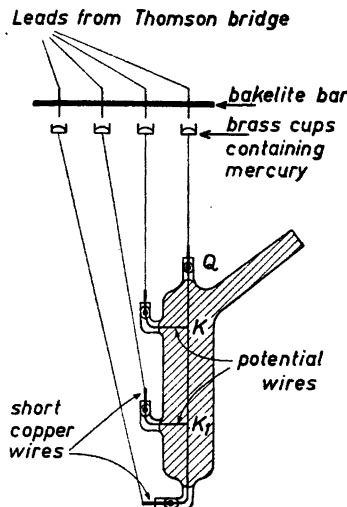
Fig. 2. Pyrex cell designed for the method.

copper bead. The wires were carefully moved into the cell by attaching cotton threads to the copper wires and pulling each section into the correct side arm. Both the copper and the platinum wires were sealed into the side arms — a small cavity containing the copper-platinum join being left unsealed. Thus the cell was made vacuum tight and the platinum wire system protected from mechanical breakage. The final operation was to straighten the central platinum wire in order to get a true cylindrical heat flow during the experiment. This was accomplished by inverting the cell and attaching a 50 g weight to the lower end of the side arm Q (cf. Fig. 2) and heating very gently in the middle of this side arm. As the glass began to melt, the weight brought the platinum wire straight. To each of the four short copper wires were soldered long copper wires to the other ends of which were soldered brass cups containing mercury. The cell was connected into the bridge by lowering the bakelite bar. This convenient method also gave freedom from variable contact potentials and resistances at the connection points. The cell was placed in a thermostat bath ($\pm$ 0.005° C) which was filled with transformer oil in order to insulate the cell leads.

With solids, the filling of the cells required care because of the ability of solid organic compounds to dissolve large amounts of air — both in the solid and fluid states. Moreover the difficulty is that many of them dissolve more air in the liquid state and thus on solidification air bubbles are formed in the solid which tend to become attached to the central platinum wire and thus alter completely the heat flow properties of the medium. To overcome this, the solid was alternately melted and frozen several times under vacuum in a large container until all the air bubbles had escaped — it was then melted again and poured carefully into the cell.

2. Electrical circuit

A Kelvin bridge was used to determine the resistance of the KK_1 section and thus the temperature of this platinum wire section (Fig. 3). The Kelvin bridge is usually used for measuring constant resistances and therefore, since the resistance of the platinum wire is continuously changing when the heating
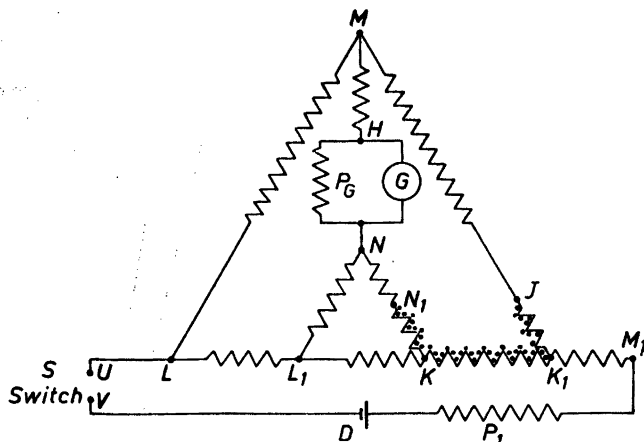
Fig. 3. *Kelvin bridge used for the resistance measurements. G: galvanometer. The resistances of the platinum wire sections situated inside the cell are represented by L_1K, KK_1, K_1M_1, N_1K and JK_1 (cf. Figs. 1 and 2).*

current is passing through it, the bridge method must be modified in order to determine a continuously varying resistance.

The battery D was used to supply current to the bridge and also to pass the heating current through the axial platinum wire during the experiment. The section KK_1 was that part of the platinum wire which was used to measure the temperature at the centre of the conductivity cell whilst N_1K and JK_1 correspond to the potential wires which were connected to the end points of this section. The two end sections of the central platinum wire are included in the parts of the bridge denoted by L_1K and K_1M_1.

It is necessary to make the central wire as thin as possible to make the heating effect large. Thus the resistance change will be large and hence an increase in accuracy will result. From the practical point of view, e.g. mechanical strength and possibility of manipulating the wire etc., 0.1 mm diameter platinum wire was the thinnest possible to use. It was necessary that the potential wires should also be thin so that there would be a negligible disturbance of the two-dimensional heat flow from the central wire. The practical limit to the diameter was about 0.05 mm and it was proved that the disturbance of the heat flow from the axial wire into the medium was small with such a diameter. Because the potential wires were so thin, it was necessary to ensure that only small currents were passed through them. For this reason, ML consisted of a fixed resistance of 100 ohm whilst NK was made up of a fixed resistance of 50 ohm (NN_1) in series with the upper platinum potential wire (N_1K) in Fig. 1. Because the conditions for bridge balancing are:

$$\frac{MK_1}{ML} = \frac{NK}{NL_1} = \frac{KK_1}{LL_1}$$

and $KK_1/LL_1 = 1.25$ (LL_1 consisted of a fixed resistance of 1 ohm), it is seen that NL_1 will be about 40 ohm and MK_1 about 125 ohm. This also guaranteed that the maximum possible changes in the resistances of the potential wires during the experiment due to the temperature alterations were not sufficient to disturb the balance of the bridge. A Leeds and Northrup potentiometer was set up so that the potential differences across LL_1 and KK_1 could be measured. Using these potential differences, the values of the heating current and the KK_1 resistance at the start of the experiment (both required for the calculation of the thermal conductivity) could be computed.

Since the bridge galvanometer deflection can vary continuously, this gives the idea for the measurement of a resistance varying with time. Assuming first that the bridge has been balanced, then, if one of the resistances, say KK_1, is altered, the galvanometer will be deflected from its zero position and for each value of the resistance there will be a corresponding value of the galvanometer scale reading. Thus from a calibration curve of the galvanometer scale against the cell resistance KK_1, the resistance and thus the temperature of the central platinum wire can be determined during the whole of the experiment. However, it would be clearly impossible to use the cell resistance KK_1 for this calibration because of its variation with the passage of current and therefore it was necessary to use instead a continuously adjustable resistance whose value was independent of the current and could also be altered by previously determined small steps. This resistance will be referred to as the ''calibration resistance''. It is also clear that the initial value of this calibration resistance should be equal to the cell resistance KK_1 (at $t = 0$, i.e. before it is altered by the passage of current) and that, for the calibration using the calibration resistance to correspond to the cell resistance, it is necessary that the other elements in the bridge circuit should be the same in both cases. Now ML, NL_1 and LL_1 can be kept the same but this is not possible for MK_1 and NK since parts of these resistances lie within the cell itself (i.e. the two potential wires form part of MK_1 and NK). This difficulty can be overcome by placing switches in the circuit so that the parts N_1K, KK_1 and JK_1 (i.e. the cell resistance and its potential wires) can be replaced by the calibration resistance and new N_1K, JK_1 resistances (represented by the dotted lines, see Fig. 3). If this new system is balanced by adjusting the new N_1K and JK_1 resistances and using the same values for ML, NL_1, MJ and LL_1 as before, then, because of the balance conditions, the values obtained for the new N_1K and JK_1 will be identical with those obtained previously for N_1K and JK_1 when the cell resistances were contained in the circuit. Thus the bridge circuit containing the calibration resistance can be made identical with that containing the cell and therefore the calibration curve of KK_1 resistance against scale reading, obtained with the calibration resistance, will also apply for the cell.

3. Bridge adjustments performed during an actual experiment

When current flows through the central platinum wire, its temperature rises as a logarithmic function of the time. Thus its resistance rises logarithmically and hence also the galvanometer scale deflection (Fig. 4).
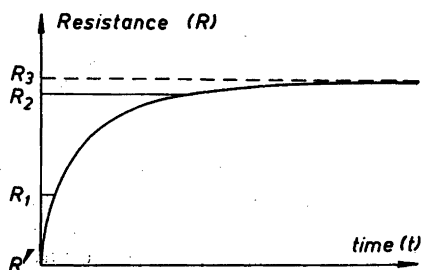

Fig. 4. Resistance versus time for a wire surrounded by a conducting medium and heated by a constant electric current.

The time taken for the resistance increase from the initial KK_1 value, R', to the value R_1, is very short and the accuracy of the measurements in this region is small because of both the rapid resistance change and the lack of accuracy of the time determinations. The region from R_2 to R_3 is useless because the resistance change is too small to permit accurate determinations. Thus the middle region from R_1 to R_2 is the most suitable one for the measurements. This immediately suggests the possibility of altering MJ and NL_1 (see Fig. 3) so that the bridge is balanced when KK_1 is placed at the value R_1 and using such a heating current that the maximum galvanometer scale deflection is reached when the KK_1 resistance has increased to the value R_2. In this way the galvanometer's sensitivity can be used to the greatest advantage. For the experimental currents necessitated by the sensitivity of the galvanometer used here, the resistance R_1 was reached after about 4 sec.

A. In practice the value R_1 was found by trial and error (and MJ and NL_1 were altered so as to obtain balance). One outcome of this procedure was that the galvanometer circuit should not be closed during the experiment until 4 sec after the heating current has been switched on — this was to avoid galvanometer scale deflections in the negative direction which, because of the galvanometer hysteresis, would make inapplicable the previous calibration of galvanometer scale *versus* KK_1 resistance.

B. A similar procedure was adopted when the calibration resistance and its potential leads were placed in the circuit in order to determine the calibration curve — the KK_1 value for the calibration resistance was made equal to R_1 and the same values for MJ and NL_1 were used as were found in A. In this way, (1) the calibration curve started from the same KK_1 value as that from which the measurements were begun, (2) the other elements in the bridge, e.g. MJ, JK_1, NK, ML, LL_1, NL_1 were the same during the actual experiment with the cell and during the calibration, and thus (3) the calibration curve of galvanometer scale reading *versus* KK_1 resistance was applicable to the scale deflections obtained during the experiment.

An optical system was designed so that the galvanometer scale and a chronometer could be photographed simultaneously. Thus it was possible to calculate the resistance of the central platinum wire during the experiment as a function of time. The order in which the bridge adjustments were carried out in practice is summarized as follows:

1) The cell was connected into the bridge (*cf*. Fig. 3) and MJ and NL_1 were adjusted so that balance was obtained.

2) The calibration resistance was connected into the bridge and its KK_1 section was made equal to the KK_1 section of the cell resistances using the Leeds and Northrup potentiometer mentioned in section 2.

3) With the calibration resistance in the bridge, N_1K and JK_1 were adjusted so that balance was obtained.

4) With the cell in the bridge, the value of R_1 was found by trial and error (and MJ and NL_1 were altered to obtain balance, see A. above) after choosing a heating current such that the maximum galvanometer deflection was reached when the KK_1 cell resistance had increased to the value R_2.

5) The calibration resistance was connected into the bridge and its KK_1 section was made equal to the value R_1 found in (4). Using the values for MJ,

NL_1 and the heating current found in (4), the calibration curve was obtained by altering KK_1 stepwise from R_1 to R_2, photographing the scale after each alteration and plotting the scale values obtained against the KK_1 resistance.

6) The cell was then connected in and the heating current switched on. The galvanometer scale and the chronometer were photographed simultaneously about 20 times during the passage of current. Using the calibration curve, the resistance corresponding to each galvanometer scale reading could be obtained. Thus the resistance (and hence the temperature) of the central platinum wire could be calculated as a function of the time during the whole of the experiment.

In (1), (2), (3), (4) the potential placed across the bridge was chosen (using the resistance P_1, Fig. 3) sufficiently large to make the adjustment accurate enough but sufficiently small so that the resistances in the bridge were not appreciably altered.

Great care had to be taken with the design of the switches used to replace the cell resistances by the calibration resistance and its potential leads. All common types of switches were found to give much trouble due to their contact potentials and resistances. Because of the variability of these contact phenomena, it was difficult to maintain the balance of the bridge over long periods of time. All of the switches were therefore specially designed so that contact was made and broken between an amalgamated copper rod and mercury — the contact resistance and potential being negligible in that case.

Now the calibration curve was obtained when the galvanometer was stationary. Therefore a correction must be applied to each scale reading determined during the experiment since the galvanometer is then in motion and possesses a finite oscillation period. Moreover since the galvanometer speed varies during the experiment, the correction will also vary from point to point on the scale. However, instead of correcting each scale value, it is shown in the next section that a great simplification results if the correction is applied to the time values.

4. Galvanometer theory

The equation of motion for the galvanometer is

$$K_0 \frac{d^2\Phi}{dt^2} + \left(p_0 + \frac{q^2}{R_T}\right) \frac{d\Phi}{dt} + D\Phi = q\ I(t) \tag{1}$$

where

Φ = angle of deflection of the mirror
    = 1/2 (angle of deflection of the light beam)
K_0 = moment of inertia of the rotating system
$-p_0 \dfrac{d\Phi}{dt}$ = moment on the mirror due to air resistance
q = the dynamical galvanometer constant
R_T = total resistance of the galvanometer circuit
$-D\Phi$ = elastic torque
$I(t)$ = current through the galvanometer (a function of time).

The constants in this equation were calculated from experimental determinations of the following experimentally observable galvanometer properties:

statical galvanometer constant, oscillation period, logarithmic decrement and critical damping resistance.

Instead of the independent variable Φ, it is more convenient to use the deflection, x, on the galvanometer scale where $x = 10^2 \cdot 2\Phi$ (x is in cm). The equation of motion was found to be

$$2.44 \cdot 10^{-3} \frac{\mathrm{d}^2 x}{\mathrm{d}t^2} + \left(1.77 \cdot 10^{-3} + \frac{10.3}{R_\mathrm{T}}\right) \frac{\mathrm{d}x}{\mathrm{d}t} + x = 0.96 \cdot 10^7 \ I(t) = x_0(t) \quad (2)$$

where $x = x(t)$, a function of time, is obtained from the experimental film, and thus using equation (2) the value of $x_0(t)$ can be found. Hence every point of the experimentally found, $x(t)$ *versus* time, curve must be corrected using this equation. To avoid the time consuming numerical work, a zero time correction was tried instead. Equation (2) can be written as

$$x_0(t) = x + P \frac{\mathrm{d}x}{\mathrm{d}t} + Q \frac{\mathrm{d}^2 x}{\mathrm{d}t^2} \quad (3)$$

Now the right hand side represents the first three terms in a Taylor expansion if $Q = 1/2 \ P^2$. This condition can be satisfied since the value of P can be altered by changing R_T. If the terms in the Taylor expansion after the first three are neglected, equation (3) can be written

$$x_0(t) = x(t + P) \quad (4)$$

Thus instead of correcting all of the x values determined experimentally, it is only necessary to subtract the constant term P from all of the time values. Hence the galvanometer correction can be expressed by adding a positive term to the zero time. The resistance value, R_T, to make this simple correction possible is obtained from $Q = 1/2 \ P^2$, which gives $R_\mathrm{T} = 150$ ohm. Therefore, by arranging that the *total* resistance in the galvanometer circuit should have this value, the correction to be applied because of the finite oscillation time of the galvanometer can be expressed as a correction, P, in the zero time where $P = \sqrt{2 \ Q} = 0.07$ sec. It can also be shown that the remainder term neglected above is negligible.

It is the sensitivity of the galvanometer which mainly determines the minimum heating current which can be used. Using the minimum current for the substances so far studied, it was found that the time required for the KK_1 resistance to increase from R' to R_2 (*i.e.* the experimental time length) was in all cases about 60 sec. It is of course possible to use higher currents by making a compensatory increase in the galvanometer series resistance MH, *cf.* Fig. 3 (and placing a certain resistance P_G in parallel with the galvanometer so that the condition, $Q = 1/2 \ P^2$, is still valid). Moreover in practice slightly greater currents than the minimum were used for reasons of experimental convenience. By suitably increasing the galvanometer series resistance it is possible to obtain the same scale deflection as when the minimum current is used and in addition it results that the experimental time length will also be about 60 sec. However, if the current becomes too large, it may exceed the safe heating limit for some of the resistance elements in the bridge and also, in the case of liquids, it may be large enough to produce convection. In order that

Fig. 5. Relay system for the simultaneous operation of the bridge current switch and the camera shutter.
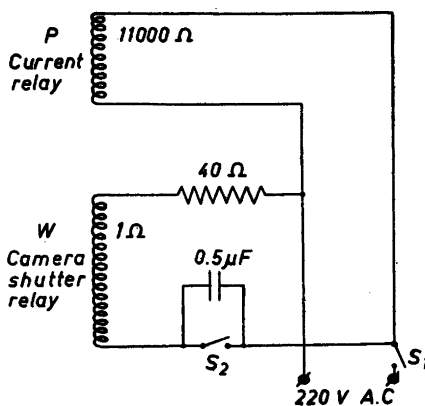
the assumption of an infinite two dimensional medium should be valid, it is necessary to make the diameter of the cell greater than a certain minimum value. Using the experimental time length of 60 sec, a diameter of 3 cm was found to be suitable for the substances so far studied.

5. Zero time determination

The time determination was obtained by photographing a chronometer. To determine the absolute value t, the zero time when current first began passing through the cell must also be determined. To do this the relay P which switched on the current in the bridge circuit was connected in parallel with the relay W which operated the camera shutter. The circuit is shown in Fig. 5.

Passage of current through the electromagnetic relay P caused contact to be made between two mercury pools, one of which was in contact with the lead U and the other with the lead V (see Fig. 3). This type of relay was ideal for high precision electrical work because no contamination of the surfaces, by which contact was made and broken, took place. When current passed through the relay W, the camera shutter release was depressed and a photograph taken. The experiment was started thus: First switch S_2 was closed and then S_1 thrown. Both relays were therefore activated, *i.e.* the bridge current switched on and a photograph of the chronometer taken simultaneously. Switch S_2 was then opened and afterwards closed every time it was desired to photograph the galvanometer scale to obtain the scale reading. The zero time was the time shown by the chronometer in the first photograph.

However, the zero time must be corrected for the small time difference between the relays, *e.g.* the first photograph was actually taken 0.02 sec before the bridge current was switched on. This value remained constant to within $\pm$ 0.005 sec over a six months' period of daily operation. The time difference was determined using a Cossar double beam oscilloscope and placing a photomultiplier inside the camera. The pulse obtained from the photomultiplier, when the camera shutter opened, deflected one of the oscilloscope beams vertically whilst the passage of current through the switch S (Fig. 3),

when it was closed, was used to deflect the other beam vertically. A horizontal pulse was applied to both beams simultaneously during the interval when the two vertical pulses were registered. Thus by comparing the resulting wave trace with a sinusoidal time base curve, the time difference between the two operations could be determined.

6. Theory of the hot wire method

The two-dimensional solution of the heat conductivity equation, given by Eucken and Englert, assuming an infinite medium and an infinitely thin heating wire is

$$\lambda = \frac{Q}{4\pi} \cdot \frac{\Delta \ln t}{\Delta T} \tag{5}$$

(λ = thermal conductivity of the medium, t = time,
Q = heat liberated by the heating wire in cal/cm/sec,
T = temperature of the wire.)

Ideally, Q should remain constant during the experiment. However, in practice, the resistance of the heating wire alters due to its temperature change and thus Q actually varies with time. The necessary correction to eq. (5) was calculated as follows:

If Q is constant, then the temperature $T(t)$ at a certain point in the medium is

$$T(t) = Q \ f(t) \tag{6}$$

where $f(t)$ is a function of t.

However, if Q is dependent on t (and therefore written $Q(t)$), then the temperature $T_0(t)$, at the point under consideration, will be given by

$$T_0(t) = \frac{\delta}{\delta t} \int_0^t Q(\tau) f(t-\tau) d\tau \tag{7}$$

(this is known as Duhamel's integral [3]).

The battery potential is denoted by E. This voltage is put across the central platinum wire (with resistance R_J at $t=0$, this is the resistance over the *whole* length $L_1 M_1$, cf. Fig. 1) and, in series with it, a constant resistance R_K (equal to the resistance P_1 plus the resistance LL_1, cf. Fig. 3). Then, if $T_0(t)$ is the temperature at the boundary surface between the wire and the medium, the variable amount of heat liberated during the experiment $Q(t)$ is given by

$$Q(t) = \frac{0.2389}{l} \cdot R'(1 + \alpha \ T_0(t)) \cdot \left[\frac{E}{R_K + R_J(1 + \alpha \ T_0(t))} \right]^2 \tag{8}$$

where R' ohm is the resistance of the KK_1 section of the wire at $t = 0$, l cm is the length of this section and α the temperature coefficient of this resistance. Equation (8) can be written

$$Q(t) = \frac{0.2389 \ R'}{l} \left(\frac{E}{R_K + R_J} \right)^2 \cdot (1 + \alpha \ T_0(t)) \ (1 + \frac{\alpha R_J}{R_K + R_J} \ T_0(t))^{-2}$$

which, remembering that $\alpha T_0(t) < 0.01$, becomes

$$Q(t) = \frac{0.2389\ R'}{l} \left(\frac{E}{R_K + R_J}\right)^2 \left(1 + \frac{R_K - R_J}{R_K + R_J} \cdot \alpha \cdot T_0(t)\right) \qquad (9)$$

We now assume that the value $Q = \dfrac{0.2389\ R'}{l} \left(\dfrac{E}{R_K + R_J}\right)^2$, $i.\ e.$ the heat liberated at the start of the experiment, is the one which is to be used in equation (5) for the calculation of $\bar{\lambda}$. Now the wire temperatures $T(t)$, which would be obtained with this ideal constant heat generation Q, can be calculated by applying a correction to the actual wire temperatures $T_0(t)$ obtained during the experiment, as is seen in the following:

Putting $\eta = \dfrac{R_K - R_J}{R_K + R_J}$, equation (9) becomes

$$Q(t) = Q(1 + \alpha\eta\ T_0(t))$$

Placing this value for $Q(t)$ in equation (7), we get the following value for the temperature of the wire

$$T_0(t) = \frac{\delta}{\delta t} \int_0^t [Q + \alpha\eta\ Q\ T_0(\tau)] f(t-\tau)\ \mathrm{d}\tau$$

which, using eq (6), gives

$$T_0(t) = T(t) + \alpha\eta\ \frac{\delta}{\delta t} \int_0^t T_0(\tau)\ T(t-\tau)\ \mathrm{d}\tau \qquad (10)$$

The second term on the right hand side is only a small correction and hence in it $T_0(\tau)$ can be replaced by $T(\tau)$. For small values of $r^2/4at$ it can be shown that

$$\frac{\delta^2}{\delta t^2} \int_0^t T(\tau)\ T(t-\tau)\ \mathrm{d}\tau = \frac{\delta}{\delta t}\ [T(t)]^2 \qquad (11)$$

which gives

$$\frac{\delta}{\delta t} \int_0^t T(\tau)\ T(t-\tau)\ \mathrm{d}\tau = [T(t)]^2 - \text{constant} \qquad (12)$$

Equation (10) then becomes

$$T(t) = T_0(t) - \alpha\ \eta\ [T(t)]^2 + \text{constant} \qquad (13)$$

Now, equation (13) shows that the correction is nonlinear and thus ought to be made separately for each experimental point used for the determination of the thermal conductivity. However, in the temperature range used in the present experiments, the correction term is small and does not change greatly. Thus the correction can be made more simply as follows:

From equation (13), using the delta symbol for the changes in the variables and dropping the notation for the independent variable t, we have

$$\Delta T = \Delta T_0 - \alpha\eta \Delta T^2 \simeq \Delta T_0 - \alpha\eta \Delta T_0^2$$

Now if T_1 is the temperature of the central platinum wire when resistance measurements are begun and if T_2 is the temperature at the end of the resistance

measurements (*i.e.* T_1 and T_2 correspond respectively to R_1 and R_2 which are the end points of the experimental resistance range in Fig. 4) then

$$\frac{\triangle T}{\triangle T_0} = 1 - \alpha\eta \ \frac{\triangle T_0^2}{\triangle T_0} = 1 - \alpha\eta \ \left(\frac{T_2^2 - T_1^2}{T_2 - T_1}\right) = 1 - \alpha\eta \ (T_2 + T_1)$$

Thus $\dfrac{\triangle T}{\triangle T_0} = 1 - 2 \ \alpha\eta T_c$ (14) where T_c is the mean temperature. For the experimental evaluation of this correction factor it is more convenient if T_c is expressed in terms of resistances which can be measured during the experiment. Now $\alpha T_c = \dfrac{1}{R'} \ [R'(1 + \alpha T_c) - R']$.

If the resistance of the central platinum wire is R_c when its temperature is T_c then $R_c = R'(1 + \alpha T_c)$.

Therefore $\alpha T_c = \dfrac{1}{R'} \ [R_c - R']$

and

$$\frac{\triangle T}{\triangle T_0} = \frac{R' - 2\eta(R_c - R')}{R'} \tag{15}$$

This correction equation is used as follows: In the experiment $\dfrac{\triangle\ln t}{\triangle T_0}$ is actually measured but, according to equation (5), $\dfrac{\triangle\ln t}{\triangle T}$ is required. Equation (5) can be written:

$$\lambda = \frac{Q}{4\pi} \cdot \frac{\triangle\ln t}{\triangle T_0} \cdot \frac{\triangle T_0}{\triangle T}$$

and using equation (15)

$$\lambda = \frac{Q}{4\pi} \cdot \frac{\triangle\ln t}{\triangle T_0} \cdot \frac{R'}{R' - 2\eta(R_c - R')} \tag{16}$$

If I amp is the current through the central platinum wire at $t = 0$ and R ohm the resistance of the KK_1 section of this wire during the experiment, then

$$\lambda = \frac{R'I^2}{4\pi l} \cdot 0.2389 \cdot \alpha \ R' \cdot \frac{\triangle\ln t}{\triangle x} \cdot \frac{\triangle x}{\triangle R} \cdot \frac{R'}{[R' - 2\eta(R_c - R')]} \tag{17}$$

Using equation (17), it is seen that the thermal conductivity, λ, can be calculated from determinations of the slope of the calibration curve, $\dfrac{\triangle x}{\triangle R}$, and the slope of the experimentally-determined galvanometer scale reading *versus* ln time curve, $\dfrac{\triangle\ln t}{\triangle x}$. All of the other quantities in this equation are constants and can be obtained from direct potentiometric measurements on the particular cell used.

7. Correction for the differing heat capacities of the heating wire and of the medium

In the theoretical case, heat is generated in a mathematical line and then flows out into the medium. However, in the method used here, heat is generated in a thin cylinder of radius 0.005 cm. In order to apply the theory of the

theoretical case, it is therefore necessary to assume that, if the heat generated is the same, the heat flow in the medium for radial distances $r \gg 0.005$ cm is the same in both cases (assumption A).

Now, in the theoretical case, the medium situated in the region $r < 0.005$ cm will take up a certain amount of heat depending on its heat capacity. However, this amount of heat will be different to that taken up by the platinum wire in the actual case because of the wire's different heat capacity. The correction to be applied will now be estimated.

If we assume a constant amount of heat Q cal/cm/sec generated in the platinum wire, then the amount $c_1\gamma_1\pi r_2^2 \; T_0'(t)$ is taken up by the wire and the rest $Q_1(t)$ streams out from the wire into the medium, where

$$Q_1(t) = Q - c_1 \; \gamma_1 \pi \; r_2^2 \; T_0'(t) \tag{18}$$

(c_1 = specific heat of platinum, γ_1 = density of platinum, r_2 = radius of the wire (0.005 cm), $T_0(t)$ = temperature of the wire and $T_0'(t) = \dfrac{\delta}{\delta t} \; [T_0(t)]$).

The platinum wire is now replaced by a hypothetical wire of the same specific heat (c) and density (γ) as the medium. If we again assume a constant heat supply, Q, then the part streaming out from the wire is, to a first approximation,

$$Q_2(t) = Q - c\gamma\pi r_2^2 T_0'(t) \tag{19}$$

Using this value for $Q_2(t)$ and the notation of Duhamel's integral (equation (7)), we find that the temperature of this hypothetical wire, and hence the temperature $T(t)$ at $r = 0.005$ cm in the medium in the theoretical case (this follows from assumption A above), is given by an expression

$$T(t) = \frac{\delta}{\delta t} \int_0^t [Q - c\gamma\pi r_2^2 T_0'(\tau)] \; f(t-\tau) \; \mathrm{d}\tau \tag{20}$$

Substituting the value for Q from equation (18), we get

$$T(t) = \frac{\delta}{\delta t} \int_0^t Q_1(\tau) \; f(t-\tau)\mathrm{d}\tau + \frac{\delta}{\delta t} \int_0^t (c_1\gamma_1-c\gamma)\pi r_2^2 \; T_0'(\tau) \; f(t-\tau) \; \mathrm{d}\tau \tag{21}$$

Now the first term on the R.H.S. is the temperature $T_0(t)$ of the platinum wire and hence, putting $\beta = (c_1\gamma_1-c\gamma) \; \dfrac{\pi r_2^2}{Q}$ and neglecting second order terms, we can write

$$T(t) = T_0(t) + \beta \; \frac{\delta^2}{\delta t^2} \int_0^t T_0(\tau) \; T_0(t-\tau) \; \mathrm{d}\tau \tag{22}$$

Using equation (11), we find

$$T(t) = T_0(t) + \beta \; \frac{\delta}{\delta t} \; [T_0(t)]^2$$

$$i.e. \; T(t) = T_0(t) + 2\beta \; T_0(t) \; T_0'(t) \tag{23}$$

This can be written as a Taylor expansion

$$T(t) = T_0(t + 2\beta \ T_0(t)) \qquad (24)$$

since the remainder term which has been neglected is negligible. Thus the correction for the differing heat capacities of the wire and the medium can be expressed by adding a correction term τ_3 to the zero time where

$$\tau_3 = 2\beta \ T_0(t) \qquad (25)$$

The numerical evaluation of τ_3 can be performed sufficiently accurately as follows:

For ideal two-dimensional heat flow with a constant amount, Q, of heat liberated at a mathematical line in an infinite medium, the temperature at a point r cm from the line is given by

$$T(t) = \frac{Q}{4\pi\lambda} \int_0^t (e^{-r^2/4a\tau}/\tau)d\tau \qquad (26)$$

where $a = \dfrac{\lambda}{c\gamma}$.

For small values of $r^2/4at$, i. e. for relatively large time values, equation (26) becomes

$$T(t) = \frac{Q}{4\pi\lambda} \ (\ln t + \ln \frac{4a}{r^2} - \gamma') \qquad (27)$$

where γ' is Euler's constant (0.5772).

Now $T_0(t)$, the temperature of the wire, is given sufficiently accurately by equation (27) on putting $r = r_2$. During the experiments log t increased from 0.5 to 1.5 and could be taken equal to 1.0 for the calculation of τ_3 since the resultant error was small. Thus

$$T_0(t) = \frac{Q}{4\pi\lambda} \ (\ln \frac{4a}{r_2^2} + 1.7) \qquad (28)$$

Putting this value for $T_0(t)$ in equation (25), substituting the value for β and noting that $c_1\gamma_1 = 0.64$ for platinum, we get

$$\tau_3 = \frac{r_2^2}{2\lambda} \ (0.64 - c\gamma) \ (\ln \frac{4a}{r_2^2} + 1.7) \qquad (29)$$

For all solutions studied, τ_3 was found to be small due to the thinness of the heating wire, e. g. $\tau_3 = +\ 0.03$ (naphthalene), -0.02 (water), -0.01 (glycerol) sec. This correction was combined with the two other zero time corrections given above, i. e.

(1) the time difference between the current and camera shutter relays (p. 649).
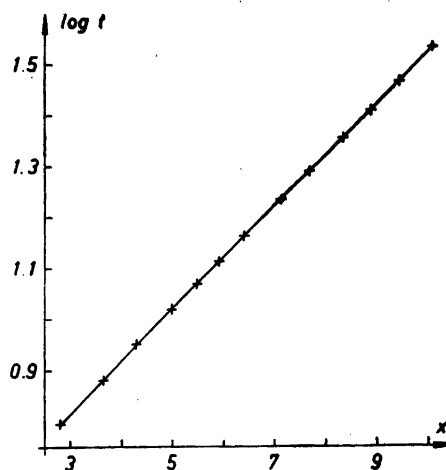(2) the zero time correction due to the inertia of the galvanometer (p. 648).

Fig. 6. x (the galvanometer scale reading) as a function of log t for a diphenylmethane/ naphthalene mixture. Temp.: 20.0° C, I = 0.28 amp.

EXPERIMENTAL

In equation (17), a and l were determined for each cell before it was used for experiments while I, R' and R_c were determined during the experiment using the Leeds and Northrup potentiometer mentioned in section 2. $\frac{\Delta x}{\Delta R}$ was determined from the calibration curve giving the scale reading (x cm) as a function of the KK_1 resistance (R ohm). This curve was almost exactly linear — its mean slope was used for the value of $\frac{\Delta x}{\Delta R}$ and the slight curvature was corrected for by adding small corrections to the x values obtained during the experiment and used for the determination of $\frac{\Delta \ln t}{\Delta x}$.

Initially experiments were carried out on a homogeneous mixture of diphenylmethane and naphthalene containing 2.6 % of the former. Fig. 6 is a plot of x *versus* log t obtained during a typical experiment on this mixture.

The slope of the line was denoted by k. Because it is difficult to see how accurately the line fits the points with such a graph, a simultaneous plot (Fig. 7) of k log $t-x$ *versus* x was always made (with a scale for k log $t-x$ which was 10 times larger than that for x).

By inspection of this latter graph (which should be a horizontal line if the graph of x *versus* log t is linear) it could be seen whether the deviations from linearity fell within the experimental error.

Values obtained from independent measurements for the thermal conductivity, $\lambda \cdot 10^6$, of the mixture of diphenylmethane and naphthalene were: 835, 836, 839, 836, 834, 837, 835, 838, 840, using heating currents from 0.22 amp to 0.28 amp.
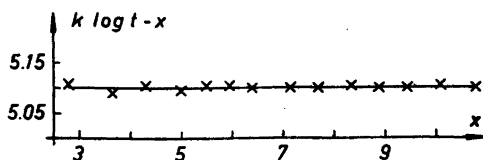

Fig. 7. k log t—x versus x for the same experiment as in Fig. 6. k = 9.92, λ = 0.000835.

The errors in the quantities used in equation (17) were:

$$I^2, \pm 0.1 \%; \quad \frac{\triangle x}{\triangle R}, \pm 0.3 \%; \quad \frac{\triangle \ln t}{\triangle x}, \pm 0.1 \%; \quad l, \pm 0.05 \%$$

The errors in the resistances used in this equation were negligible and thus the total experimental error was about $\pm$ 0.5 %. Various other errors such as the heat lost from the central heating wire through the potential wires and by radiation, the error resulting from the cross-sectional unevenness of the central wire and others were investigated and found to be negligible. As seen from the above results and also from results on experiments with water and aqueous solutions, at temperatures not too far from the maximum density point, and highly viscous liquids such as glycerine (a following paper), it was possible in practice to reproduce thermal conductivities to within $\pm$ 0.3 %.

REFERENCES

1. Stålhane, B. and Pyk. S. *Tekn. Tidskr.* **61** (1931) 389.
2. Eucken, A. and Englert, H. *Z. ges. Kälte-Ind.* **45** (1938) 109.
3. Carslaw, H. S. and Jaeger, J. C. *Conduction of Heat in Solids*, Oxford 1947, p. 18, § 10.