THE THERMAL CONDUCTIVITY OF ORGANIC MATERIALS NEAR THE MELTING POINT.

BY J. H. READ AND D. M. G. LLOYD.

(*Communicated by* PROF. W. E. GARNER.)

.Though there have been numerous measurements of the thermal conductivity of liquids and of solids and of the dependence of thermal conductivity on temperature, few measurements have been carried out at, or near, the melting point. The behaviour of solid and liquid sulphur has been investigated with the aid of a special apparatus,[1] but even in this case it proved impracticable to take measurements at the melting point. Measurements of specific heat near the melting points of organic materials, such as those of Ubbelohde on long-chain paraffins,[2] have been of value in interpreting the phenomenon of melting and for the theory of liquid structure, so that it seemed likely that measurements of thermal conductivity should provide additional information. The difficulty of constructing an apparatus suitable both for solids and for liquids and capable of operation during the very considerable volume changes near the melting point has been overcome, and this paper is mainly devoted to the experimental technique involved, though some interesting results are described.

Experimental.

It was clear that most of the thermal conductivity apparatuses previously described [3] were quite unsuited to the present investigation. With solids, the main difficulty is the elimination of air-gaps and temperature discontinuities between the sample and the surfaces across which the temperature gradient is applied. It is important that the structure of a polycrystalline, anisotropic specimen should be capable of examination and specification.

[1] Kaye and Higgins, *Proc. Roy. Soc. A*, 1929, **122**, 633.
[2] Ubbelohde, *Trans. Faraday Soc.*, 1938, **34**, 282.
[3] See the useful summaries in *Archiv. Technisches Messen*, May 1943, V9213-3, and Hutchinson, *Trans. Faraday Soc.*, 1945, **41**, 87.

25 *

722 THERMAL CONDUCTIVITY OF ORGANIC MATERIALS

For liquids, the " hot-wire " method of Goldschmidt,[4] of which a convenient modification has recently been described,[5] is one of the most reliable, and it was therefore adapted to measurements on solids. In principle, a very thin platinum wire is embedded axially in a cylinder of the material under test, which is immersed in a thermostat. Passage of an electric current through the wire raises its temperature, setting up a temperature gradient through the sample. The heat supplied by the wire is readily calculated from the resistance and current ; the resistance also gives the temperature of the wire, provided that the temperature coefficient of resistance is known. Hence the thermal conductivity of the sample may be calculated.

Preparation of Test Pieces.—Initially, cylinders of the material under test were cast with the platinum wire embedded axially, and immersed directly in the thermostat ; but by this means measurements could only be carried out at temperatures below the melting point.

The apparatus employed for obtaining readings over the melting-point is shown in Fig. 1. A length of platinum wire (A) of 0·05 mm. diam. (only the best quality, such as Johnson, Matthey's " thermo-pure " variety, is suitable) was soldered between two brass end-pieces, the lower of which (B) was ground to fit a hole in the bakelite plug (C), which was tightly held in the thin-walled cylindrical brass container (D), of 1 cm. internal diam. The upper end-piece (E) was held by a set-screw (not shown in Fig. 1) in a brass collar (F) itself screwed to the flange (G) which was soldered to the outside of the tube. The collar, and so the end-piece, was insulated from the flange and tube by Bakelite washers (H) of such design as to eliminate as far as possible, the distortion and splitting that so readily occur with an apparatus intended for use over a wide temperature range, and to make possible their easy replacement. The flange was threaded on the outside, and a wide brass funnel (I) could be screwed to it. The apparatus was filled, after heating in the oven, by pouring the molten material into the funnel, whence it ran by feeding holes into the tube. Cooling began near the bottom so any cavities were filled up by liquid flowing downwards from the reservoir, which cooled last. In practice, two cylinders were cast separately, one containing a wire 11 cm. long, and the other a wire 3 cm. long. These were then inserted into opposite arms of the measuring bridge, so as to eliminate end-effects. The thermal conductivity of the brass sheath was so great that the temperature gradient across its walls could be neglected.
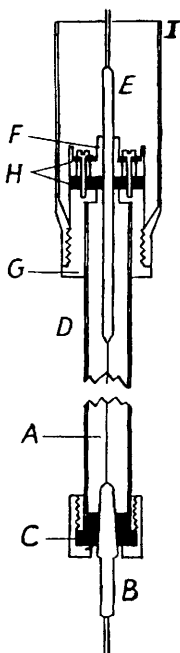
This apparatus is, of course, suitable for liquids in general, but, for ordinary purposes, simpler and better modifications of Goldschmidt's original apparatus have been described.[5]

The Measuring Bridge.—The modified Wheatstone bridge shown in Fig. 2 was employed. The same current, supplied from accumulators in series with a rheostat, was used both for heating the platinum wire and for making the measurement of resistance. The ratio arms (A and B) were made equal, and the long and short platinum wires (C and D) were inserted in the other two arms of the bridge. The temperature gradient was measured directly by including in the same arm as the shorter embedded wire, a resistance thermometer (E) wound of thick platinum wire and immersed in the thermostat liquid. Its resistance was, as nearly as possible, equal to the difference in resistance between the two embedded wires. When current was passed, thus heating the thin embedded wires but not appreciably raising the temperature of the thick wire in the bath, the circuit was balanced with the aid of a calibrated rheostat (F), adjustable to 0·001 ohm, and a galvanometer (G) connected through a reversing switch. The current was measured with a calibrated ammeter (H) included in the bridge circuit, the resistance of the ammeter and also that of all lead-wires being permanently balanced by a constant compensating resistance (N) in the opposite arm of the bridge.

FIG. 1.

[4] Goldschmidt, *Physik. Z.*, 1911, **12**, 417.
[5] Hutchinson, *loc. cit.*

The accuracy of the method depends upon the sensitivity of the rheostat, and the precision with which the temperature is controlled in the thermostat bath. Fluctuations of more than 0·05° c. in the bath made it impossible to obtain a sharp balance point. An adjustable Sun-Vic thermoregulator was used in conjunction with a hot-wire vacuum switch. With careful setting the bath temperature could be controlled to 0·05°-0·01° c., but more rigid control is desirable. Considerable difficulty was encountered over the variable contact resistance of the slider of the rheostat, and the circuit could be improved by inserting the rheostat (F) between (C) and (D), increasing its sensitivity by the use of a much longer and thicker slide wire and by connecting the slider to the galvanometer.

It is, of course, desirable, especially in the neighbourhood of the melting point, that the whole sample should be as nearly as possible at the same temperature ; it is therefore preferable to obtain increased sensitivity by improving the measuring apparatus rather than by imposing large temperature gradients.

If T is the temperature of the bath corresponding to a steady temperature T' at the centre of the cylinder, R_1^0 and $R_1^{T'}$, and R_2^0 and R_2^T the resistances
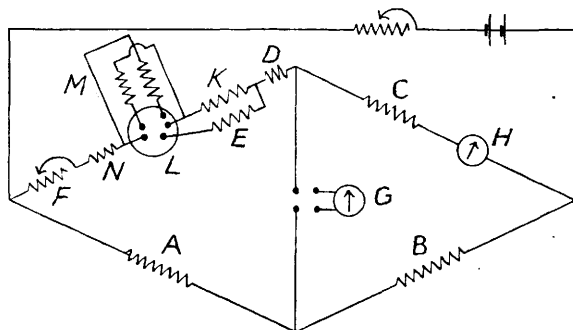

FIG. 2.

respectively of the embedded wire at 0° c. and T' °c., and of the immersed resistance thermometer at 0° c. and $T°$ c., and α the temperature coefficient of resistance of pure platinum, it follows from definition that :.

$$T' = \frac{R_1^{T'} - R_1^0}{\alpha R_1^0} \text{ and } T = \frac{R_2^T - R_2^0}{\alpha R_2^0}$$

whence, if
$$R_2/R_1 = k$$

$$\Delta T = T' - T = \frac{\Delta R - R_1^{T'}(1 - k)}{\alpha R_2^0} \qquad . \qquad . \qquad . \quad (1)$$

where $\Delta R = R_1^{T'} - R_2^T$, i.e. the reading of the sensitive rheostat. It will be noted that αR_2^0 is a constant, and that the second term of (1) disappears if $R_1 = R_2$ (when $k = 1$). In practice, it was not possible to solder the platinum wires with an accuracy of more than 0·5 mm., so that the second term of eqn. (1) remained as a correction, and it was necessary to measure directly $R_1^{T'}$, the absolute resistance of the hot wire, a figure which was also required for the calculation of the input of heat.

When steady conditions have been established, the thermal conductivity is given by the formula : [6]

$$K = \frac{0·239 \ I^2 . R_1^{T'} \log_e \frac{r_2}{r_1}}{2\pi l . \Delta T} \qquad . \qquad . \qquad . \quad (2)$$

where r_1 and r_2 are the respective radii of the platinum wire and of the specimen, and l the difference in length of the two embedded wires, and I the current.

Measuring Procedure.—It was found that when the sample and its embedded wire were heated, the resistance of the wire increased but not exactly in

[6] Carslaw, *The Mathematical Theory of the Conduction of Heat in Solids* (London, 1921), 114.

the manner to be expected.   If, from the measured values of the resistance at in-creasing temperatures, the resistance of the wire was calculated for a fixed temperature (e.g. o° c.) by means of the temperature coefficient of resistance, α, values were obtained which were not quite constant.   Though this deviation was very small, it was thought better not to rely on a single reading and a simple substitution in eqn. (2), a procedure which demands that the resistance of the embedded wire at o° c. remain constant (quite small deviations lead to appreci-able errors in the calculated value of K), but to eliminate error in the following manner.

Eqn. (1) and (2) were combined and written in the form :

$$\frac{\Delta R}{R_1}T' = \alpha R_2^0 \left(\frac{0 \cdot 239 \log_e \frac{r_2}{r_1}}{2\pi l K} \right) I^2 + (1 - k). \qquad . \qquad . \qquad (3)$$

Hence when readings were taken for different values of the current, a plot of $\frac{\Delta R}{R_1}T'$ against I^2 gave a straight line, from the slope of which K could readily be calculated.   Currents of 50-150 ma. were usually employed, corresponding to temperature gradients of $1 \cdot 5° - 8 \cdot 5°$ c. for a typical sample of liquid TNT and to gradients of about half these values for solid TNT.

Values of K calculated in the fashion described were independent of slight fluctuations in R_1^0, and the extent of such small variations could be checked

TABLE I.

TNT (S.P. $= 80 \cdot 4°$ c.).		Palmitic Acid (M.P. $\sim 58°$ c.).	
Temp. °c.	$k (= R_2/R_1)$.	Temp. °c.	$k (= R_2/R_1)$.
25	0·9760	18	0·9789
35	0·9758	25	0·9795
45	0·9757	35	0·9791
55	0·9754	45	0·9785
65	0·9745	55	0·9783
75	0·9724	60	0·9787
110	0·9737	65	0·9789
90	0·9750	75	0·9787
80	0·9757	85	0·9784

by reading off the intercepts, $l - k$, from the graphs.   The extent of the variations over typical runs is shown in Table I.

It is significant that the only measurable change in the value of k occurred near the melting point, where there is a large change in the volume of the sample. It is also noteworthy that the change in k was greater with TNT, which gives a dense casting with hard well-formed crystals, than with palmitic acid with its soft ill-defined crystals, which would tend to adhere to the wire less firmly. Indeed with palmitic acid, the trend of the results is hardly significant.

The specially-purified platinum employed for the experiment behaved very nearly as a perfectly elastic solid up to a linear extension of 0·23 %.   Over a temperature range of 80° c., the linear expansion of the brass case, relative to that of the wire, was 0·08 %, i.e. well within the elastic limit of the platinum. The change in resistance that might be ascribed to alteration in geometrical dimensions was negligible.

The expansion of the solid TNT over the range 20°-80° c. might be enough to deform the wire, but because of the confinement of the TNT to the case and the radial arrangement of the crystals, the main result of the expansion must have been, apart from local effects, an increased pressure on the wire.   Owing to the temperature gradient across the sample, the wire at the centre was sheathed with a liquid cushion during the melting of the great bulk of the solid.   Though the pressure was probably not relieved immediately melting started because of the blockage of the feeder holes by solid TNT, such a cushion would tend to transmit the pressure evenly to the wire.

An estimate of the upper limit of the pressure in the cylinder may be made

from the pressure necessary to disrupt the cylinder ; since the cylinder did not disrupt, and was probably not even stretched beyond the elastic limit, this figure obviously cannot have been reached.

Different types of brass have tensile strengths varying between 22 and 50 kg./mm.². Using these values it may be calculated that the critical bursting pressure for the cylinders lay between 400 and 1000 atm. Consequently 1000 atm. may be taken as an upper limit to the pressure and it is improbable that it at any time exceeded 500 atm., this being the pressure required to stretch the brass beyond an elastic limit of 25 kg./mm.².

Bridgman [7] found that the resistance of pure platinum decreased with increase in pressure, a pressure of 500 atm. corresponding approximately to a drop in resistance of 0·1 %. However, a drop in the value of k, representing an *increase* in the resistance of the embedded wires, was observed, so that it appears that the pressure at the centre was quickly released, or was not excessive. Bridgman also found that there was little variation of the pressure coefficient of resistance with temperature, and concludes that the temperature coefficient of resistance is nearly independent of pressure.

The very slight rise in resistance may have been caused by local straining of the wire. The results in Table I are recorded in the order of measurement, which took place at intervals of about ½ hr., and it will be seen that with TNT,
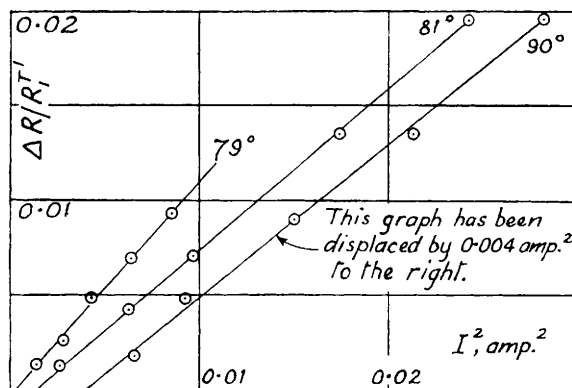

FIG. 3.

even after liquefaction and the complete release of pressure and local tension, total recovery of the wire was slow.

This discussion has been given, because, although the experimental technique eliminated errors arising from *slight* changes in k, it is clearly of importance to understand what happened to the embedded platinum wire during temperature change.

When measuring the change of thermal conductivity with temperature, measurements on solids were always carried out during rise of temperature to avoid the possible splitting away of the sample from the wire that might occur during cooling and contraction. Measurements on liquids could clearly be carried out during either rise or fall of temperature. The apparatus came to equilibrium within a few minutes after the setting of the bath temperature, and measurements with different currents were made at 5 min. intervals, 20 min. being allowed between changes in the temperature of the bath. Thermoelectric effects were avoided by eliminating, as far as possible, bimetallic junctions, and their effect was nullified by reversing the connections when balancing the circuit, and averaging the two settings of the sensitive rheostat. The curves of Fig. 3 obtained for TNT at different temperatures by the procedure described, show how accurately eqn. (3) is obeyed. It should, however, be mentioned that for currents below 25-50 ma. the straight line relationship appeared to hold no longer and that very erratic results were obtained. It was thought that this effect was caused by imperfections in the measuring apparatus.

Calibration of Apparatus.—It was possible, by measuring the dimensions of the test pieces and platinum wires with a travelling microscope, to calculate

[7] Bridgman, *The Physics of High Pressure* (London, 1931), 268.

absolute values for the thermal conductivity. Absolute measurements of TNT cylinders immersed directly in a water-bath, and determinations on castings encased in our apparatus with the brass sheaths, as described above, were sufficiently close in view of the differing structures of the polycrystalline blocks.

It was found, however, when the thermal conductivities of a series of liquids was measured in our apparatus, that, although the relative values agreed sufficiently well with the results of previous workers, the absolute values were somewhat high ; the results which follow were calculated on the basis of Bates' figure of $3 \cdot 10 \times 10^{-4}$ cal./sec. cm. °C. for chloroform at 20° C.[8]

Distilled water and carefully dried B.D.H. Analar materials were used. In view of the difficulty of measuring the thermal conductivities of liquids and of the uncertainty of published results, it is considered that agreement was sufficiently good to justify the use of the instrument for determining changes with temperature in the conductivity of the same sample, though the apparatus, in its present form, is not suited to exact determination of the absolute conductivities of different liquids. Chloroform was used as standard as it was the liquid studied most in our apparatus, and gave most reproducible results.

That the curves of $\Delta R/R_1^{T'} - I^2$ (Fig. 3) were straight lines is a demonstration that the method is fundamentally sound, for, if convection currents had been set up, eqn. (3) would no longer have held, and the plots would have been curvilinear (as actually happened when large temperature gradients were deliberately

TABLE II.—K IN CAL./SEC. CM. °C. ; TEMP., 20° C.

Material.	K Observed $\times 10^{-4}$.	K Literature. $\times 10^{-4}$.
Chloroform . . .	3·10	3·10 Bates
Carbon disulphide . . .	3·77	3·85 I.C.T.
Ether	3·23	3·30 ,,
Ethyl alcohol	3·81	4·35 ,,
Ethyl iodide	2·37	2·65 ,,
Water	13·1	14·0 ,,

imposed). The calibration constant obtained from the measurements on chloroform was applied in calculating the results that follow.

Results.

The variation with temperature of the thermal conductivity of TNT is shown in Fig. 4. The TNT was of the quality known as Grade I, of setting-point 80·4° C., and consisting almost entirely of 2 : 4 : 6-trinitro-toluene.

Owing to the decision to use at least 5 different heating currents for each determination, the experiments were long drawn-out and it was impossible to obtain all the data during one run, so that the results of Fig. 4 were drawn from several experiments, as shown by the circles, triangles, etc. It has already been explained that the measurements on solid samples were always carried out during rise of temperature. The use of different currents was also a safeguard against the occurrence of convection, as revealed by curvature of the $\Delta R/R_1^{T'} - I^2$ plots. For solid TNT, the numerical results of different determinations varied by some 15 %, as was not surprising in view of variations in crystal structure of successive castings.

The striking feature of all the curves for solid TNT was the sharp drop in thermal conductivity near the melting point. It is not known just how low the conductivity fell, because the readings were taken discontinuously at arbitrary temperatures, but values were obtained below those subsequently recorded for liquid TNT. The temperatures plotted as abscissæ are those of the thermostat bath, as measured to the nearest 1/10° with a mercury-in-glass thermometer calibrated at the N.P.L. ; the temperatures at the centre of the cylinders were from 1°-4° C. higher, depending upon the heating current, and fell away exponentially towards the perimeter. In view of the large expansion of TNT during heating and of the resulting increased pressure inside the cylinders, the melting point may have been raised. It is, however, clear that the drop

[8] Bates, *Ind. Eng. Chem.*, 1941, **33**, 375.

occurred substantially at the melting point itself. Owing to the temperature gradient across the cylinders and to the slowness with which a mass of solid melts when heated only slightly above its melting point, it is probable that the condition of the sample at bath temperatures just below the melting -point was that of a liquid surrounded by a solid annulus. Even if the liquid sheath were very thin, such a sample would behave more like a liquid than a solid, because the fall in temperature across the samples takes place very largely in the region nearest the heating wire.

Measurements carried out during the cooling of liquid TNT revealed little variation of thermal conductivity with temperature in the region more than $5°$ c. bath temperature above the melting point ; below this temperature there was evidence of a downward trend in thermal conductivity, but it did not prove possible to establish any sudden drop at the melting point, possibly because the TNT at the outside began to solidify before the material round the wire, in which practically the entire temperature drop occurs, was sufficiently near the melting point. (Once solidification was observed, the experiment was discontinued because of the possibility of entrapping air bubbles in the sample during the marked contraction associated with solidification, which would vitiate any results obtained then.) It should be added that the incipient fall in conductivity shown in the figure depended to a marked extent on the previous
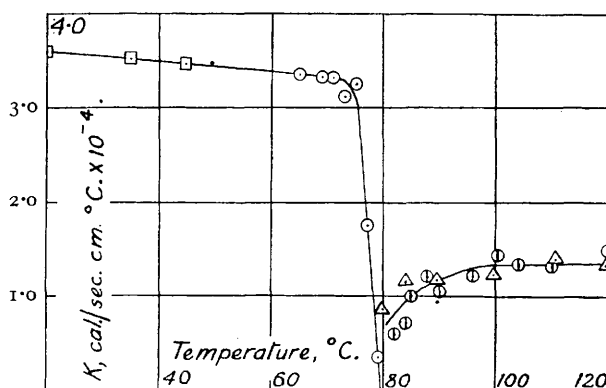

FIG. 4.

history of the sample and was probably related to the number of crystal nuclei present in the liquid. Experiments on pure specimens of α-nitro-naphthalene and vanillin gave very similar results.

Experiments were also carried out on a sample of palmitic acid. B.D.H. material was used and not specially purified ; it did not melt sharply, but became " mushy " at about $55°$ c. In this case a maximum in thermal conductivity was obtained near the melting point. Further experiments on a purified sample are required in this case ; the present result is quoted to show that the results obtained with the other materials were not simply conditioned by the apparatus and method of measurement.

Discussion.

The occurrence of abnormally low values of thermal conductivity near the melting point of cast samples of TNT prompts the question as to whether the effect was a gross one, conditioned perhaps by convection currents within the partially melted block or by cracks in a solid annulus, or whether it was conditional upon changes in the lattice or in the internal state of the molecules. Convection was unlikely, both because straight lines were obtained for the plot of $\Delta R/R_1 T' - I^2$ and because convection currents should help to dissipate heat and therefore to *increase* the apparent conductivity. A more probable explanation is that the pressure set up by the expansion of the melting TNT fractured the crystalline part of the block, thus multiplying areas of temperature discontinuity. Neither

of these explanations is altogether convincing; moreover, it remains to account for the incipient fall in conductivity observable after complete liquefaction and subsequent cooling to a temperature *above* the set point. In the case of palmitic acid, which melted indefinitely, it is possible that fragments of solid material dropped through the liquid, setting up currents and thus accounting for the apparent maximum in thermal conductivity.

The persistence of some form of solid structure into the liquid state has been widely discussed, among others by Stewart,[9] Frenkel,[10] and Malkin,[11] who have brought forward interesting X-ray and thermal evidence. The downward turn of the thermal conductivity-temperature curve at temperatures just above the melting point would seem to provide new evidence for a structure in that region markedly different from that of the liquid at higher temperatures.

It is possible that the decrease in conductivity observed both just below and just above the melting point is due to the material behaving neither as a true solid nor as a true liquid in the respective cases, but that in one case premelting and in the other case presetting might be occurring locally at numerous points giving rise to a mosaic-like structure with very frequent interfaces separating regions differing in local degrees of order. The presence of such interfaces and consequent discontinuities might well be a contributing factor to the decrease in thermal conductivity observed here.

Ubbelohde has shown that paraffins and various other long-chain compounds, even when very highly purified, are subject to a sharp rise in specific heat before the melting point is reached and that the enhanced specific heat most probably persists for some degrees above the melting point. The general relation between thermal conductivity and specific heat is that

$$K = c\rho\lambda\mu \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (5)$$

where c is the specific heat, ρ the density, and λ and μ are the wavelength and mean free path of the elastic heat waves. It is tempting to compare the maximum in the thermal conductivity curve for palmitic acid with Ubbelohde's specific heat data, but such correlation is not straightforward, and must, in any case, await conductivity data for purer material.

It is realised that the data put forward are incomplete, but, as the apparatus has been dismantled for the present, it seemed appropriate to publish an account of the work which had been carried out. Further experiments, preferably with more than one type of apparatus, are required to establish finally that the thermal conductivity-temperature plot cannot be represented by a step-shaped curve and that the minimum suggested by the present experiments is generally characteristic.

[9] Stewart, *Rev. Mod. Physics*, 1930, **2**, 116.
[10] Frenkel, *Trans. Faraday Soc.*, 1937, **33**, 58.
[11] Malkin, *J. Chem. Soc.*, 1939, 1141; 1939, 103; 1937, 1409; 1936, 1628; 1934, 666.

Summary.

An apparatus has been constructed for the measurement of thermal conductivity near the melting point of organic solids, and has been calibrated with liquids for which data are already available. Repeated measurements have revealed an abrupt discontinuity in the thermal conductivity of TNT at the melting point and suggest that a minimum in conductivity exists under the conditions of experiment. The interpretation of these results is briefly discussed.

Department of Chemistry,
The University,
Sheffield, 10.

Department of Chemistry,
The University,
Birmingham, 15.