EXPERIMENTAL INVESTIGATION OF THE THERMAL CONDUCTIVITY OF ORGANIC FLUIDS AT LOW TEMPERATURES

V. P. Brykov, G. Kh. Mukhamedzyanov,
and A. G. Usmanov

UDC 532.529.5

A description is given of an experimental apparatus for measuring the thermal conductivity of fluids at low temperatures by using a heated filament. Results are given of the measurement of the thermal conductivity of propane, n-butane, n-pentane, n-hexane, n-heptane, n-octane, n-nonane, n-decane, hexene-1, heptene-1, toluene, and isoprene, from the melting point to +100°C. The results obtained are generalized using the entropy method.

The study of the thermal conductivity for homologous series of organic compounds in a wide range of temperatures covering the whole region of the liquid state from melting to boiling is of some interest. No study has been made of a considerable part of this temperature range lying below 0°C, including the interesting region close to the melting point, for most of the organic fluids.

To make these measurements, an experimental apparatus has been developed using the absolute method with a heated filament. The use of this method requires a steady temperature field of a cylindrical shape, and it must be maintained to a high accuracy. In our apparatus for low temperatures (from 0° to −190°C), this problem is solved using a cryostat (Fig. 1) based on a Swenson temperature control device [5]. A heat exchanger 1 made of copper tubing 6 mm in diameter is wound around a hollow copper cylinder 2. The thermostat copper core 3, 58 mm in diameter and 350 mm long, is mounted inside the cylinder. Four manganin heating elements 7: a main element (600 Ω) for accurate temperature control and three compensating elements (200 Ω each) for eliminating the temperature gradient over the core, are wound around the core. The temperature field is controlled by five copper–constantan thermocouples 11. The low-temperature section of the cryostat is insulated by a high-vacuum jacket.

The cryostat is cooled and its temperature is controlled in the following way. Liquid nitrogen is supplied from the Dewar flask into the heat exchanger and evaporates. The vapors formed are partly heated and are pumped out by a vacuum pump. The evacuation rate of the nitrogen is accurately controlled by a vacuum needle valve 9. This valve is used for an approximate setting of the required temperature, and a slight excess cooling off is produced which is later compensated by selecting the magnitude of the heating current in the main heater. The temperature drop over the length of the operating section of the core 3 does not exceed 0.07°C at the lowest temperature of −190°C, is constant in time, and is easily eliminated by means of the compensating heaters. The heaters are fed and controlled by U1139 regulators. With this construction of the cryostat it is possible to maintain any temperature within a range from 0 to −190°C with an accuracy of 0.01°C. Temperatures up to +100°C were produced and maintained by a water thermostat.

The thermal conductivity was measured using a molybdenum glass pipe with a thickness of the fluid layer of 0.419 mm. The remaining dimensions of the pipe and the other experimental details are described in [9].

The maximum calculated error of the experiment does not exceed 2%. The main corrections were calculated using conventional methods. The correction for radiation loss on measuring the thermal conductivity of the fluids was not taken into account because of the absence of any reliable method of determining it for

---

S. M. Kirov Chemical and Technological Institute, Kazan'. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 18, No. 1, pp. 82-89, January, 1970. Original article submitted February 28, 1969.

© 1972 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for $15.00.

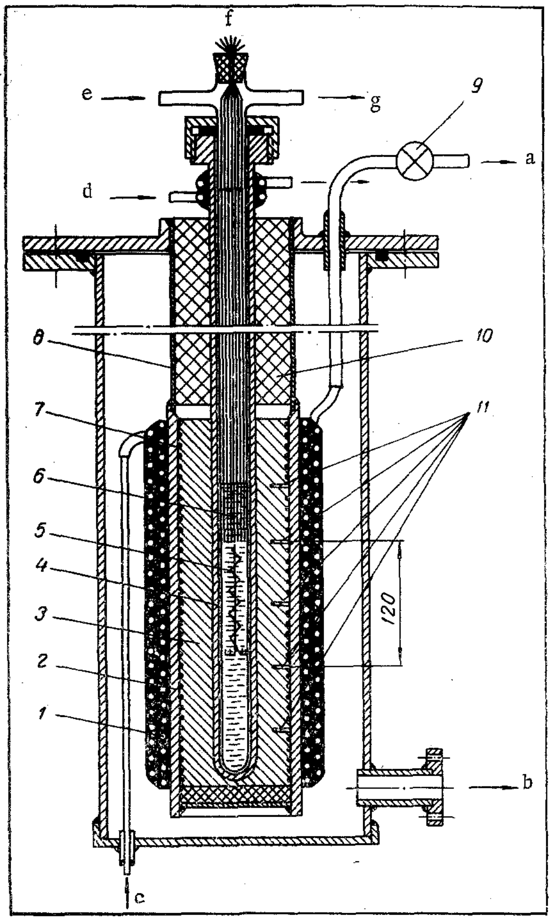

Fig. 1. Cryostat: 1) heat exchanger; 2) copper cylinder; 3) core; 4) autoclave of stainless steel; 5) measuring pipe; 6) test liquid; 7) heater; 8) thin-wall throat ($\delta = 0.3$ mm, $l = 350$ mm); 9) needle valve; 10) throat insulation (plastic foam); 11) thermocouples; a) to vacuum pump; b) to high-vacuum installation; c) liquid nitrogen; d) water for junction thermostating; e) liquid filling; f) to measuring system; g) to vacuum pump before filling.

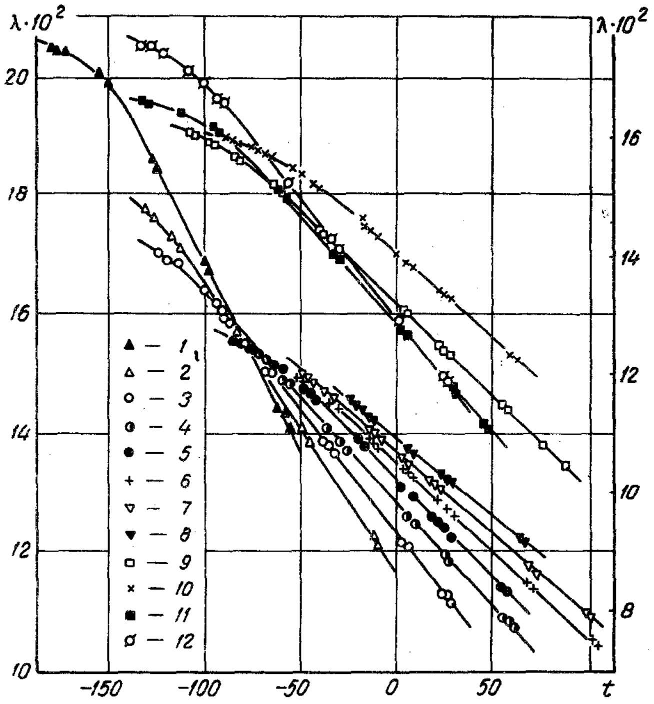

Fig. 2. Thermal conductivity λ (W/m • deg) as a function of temperature t(°C). 1) Propane; 2) n-butane; 3) n-pentane; 4) n-hexane; 5) n-heptane; 6) n-octane; 7) n-nonane; 8) n-decane; 9) heptene-1 10) toluene; 11) hexene-1; 12) isoprene. Left scale for toluene, hexene-1, heptene-1, isoprene.

this particular method of measuring the thermal conductivity, and also because of the absence of any data on the absorption spectra of the investigated materials at different temperatures. Apart from that, of the low temperature at which our main measurements were taken, one cannot expect that the radiation component of the thermal conductivity will have a substantial effect on the result of the measurement. Chemically pure materials were used in the experiments.

The described apparatus was used for making control measurements of the thermal conductivity of water, benzene, liquid oxygen, and gaseous air. The results obtained were in good agreement with those in the literature [3].

The results of the measurements of the thermal conductivity of 12 organic fluids at atmospheric pressure are given in Fig. 2. Rounded values are given in Table 1. The deviations of the experimental points from the mean line are not greater than 0.5%. For most of the materials the range of the investigations covered the whole region of the liquid state from the melting point to the boiling point.

It can be seen from the graphs that the temperature dependence of the thermal conductivity is linear in the greater section of the liquid state. However, on approaching the melting point, a marked deviation from linearity towards a decrease in the temperature coefficient is observed. These deviations are very marked for light hydrocarbons which have a low melting point. For propane, isoprene, hexene-1, heptene-1, and toluene they reach 5-7%. For heavy hydrocarbons, beginning with n-octane, with a relatively high melting point, this effect is insignificant.

Values for the thermal conductivity of most of the investigated materials at temperatures below 0°C were obtained for the first time.

TABLE 1. Rounded Values for the Thermal Conductivity of Organic Fluids $-\lambda \cdot 10^4$, W/m·deg

t,°C	Propane	n-Butane	n-Pentane	n-Hexane	n-Heptane	n-Octane	n-Nonane	n-Decane	Hexane-1	Heptene-1	Toluene	Isoprene
+100						1050	1089					
+ 90						1080	1116			1037		
+ 80						1110	1144			1069		
+ 70						1140	1172			1100		
+ 60					1130	1170	1199	1230	1076	1131	1233	
+ 50					1162	1200	1227	1257	1111	1163	1261	
+ 40					1194	1230	1255	1284	1147	1195	1290	
+ 30			1106	1182	1226	1260	1283	1311	1183	1225	1319	**1176**
+ 20			1147	1217	1259	1290	1310	1337	1218	1256	1348	**1216**
+ 10			1189	1251	1292	1320	1338	1364	1254	1288	1377	**1256**
+ 0		1166*	1230	1288	1324	1350	1366	1388	1290	1320	1406	**1296**
—10		1214	1272	1322	1357	1380	1394	1415	1326	1351	1435	**1336**
—20		1263	1312	1357	1390	1410	1421	1440	1361	1382	1464	**1376**
—30		1312	1354	1392	1422	1440	1448	1460	1397	1413	1492	**1416**
—40		1360	1396	1427	1454	1470	1472		1433	1445	1519	**1456**
—50	1374	1410	1438	1462	1487	1490	1494		1469	1476	1538	**1496**
—60	1439	1458	1480	1498	1515				1505	1507	1558	**1536**
—70	1502	1507	1521	1533	1536				1540	1537	1576	**1576**
—80	1565	1556	1563	1568	1552				1575	1560	1594	**1616**
—90	1629	1605	1605	1597	1562				1605	1581	1603	**1656**
—100	1693	1654	1647						1627	1598		**1689**
—110	1756	1703	1677						1643	1610		**1717**
—120	1820	1752	1695						1653			**1738**
—130	1884	1780							1660			**1750**
—140	1947											**1758**
—150	1991											
—160	2021											
—170	2042											
—180	2054											

*The value of the thermal conductivity refers to a temperature of − 0.5 °C.

The comparison of our values for the thermal conductivity of the fluids with the data published earlier shows that our measurements on toluene are in good agreement with the experimental results obtained by Reidel [8] and Venart [7]. They are 2% higher than the data obtained by Poltz [6] (without taking into account the radiation correction), agree with the experimental values for the thermal conductivity obtained by V. Z. Geller and Yu. L. Rastorguev [4] at 30°C, and are 2% lower than the results of these authors at 60°C. This discrepancy may be due to the great influence of the radiation component of the thermal conductivity on the measured results obtained by these authors at a fluid thickness $\delta = 0.675$ mm.

The values for the thermal conductivity of saturated hydrocarbons, calculated by Ya. M. Naziev [10] using Predvoditelev's equation and the theory of corresponding states, are, by and large, higher than our data. This can apparently be explained by the fact that most of these values for λ have been found by extrapolation of the results of the measurements obtained in a comparatively narrow temperature range in a completely unexplored region of the liquid state.

Apart from that, the values for the thermal conductivity of the higher hydrocarbons, beginning with n-hexane, are determined from Ya. M. Naziev's own data, obtained in ordinary conditions, which are higher than the measured values obtained by most of the investigators [2, 11, 12, 13].

The increase in the calculated temperature coefficient of thermal conductivity on approaching the melting point is doubtful. The experiment shows the opposite.

The experimental results were generalized using the following functional relationship

$$\frac{q}{q_{\Delta S}} = \varphi\left(\frac{S_1 - S}{R}\right). \qquad (1)$$

Since it is impossible to select a single origin for the calculation of the entropy S_1 for all investigated materials in the liquid state, the treatment was carried out for different values of S_1. For propane and n-butane it was chosen to be equal to 168 kJ/kmol·deg, for n-pentane, n-hexane, n-heptane, heptene-1, and toluene, equal to 251 kJ/kmol·deg, and for n-octane, n-nonane, and n-decane equal to 378 kJ/kmol·deg. The scaling factor for the entropy ΔS was assumed to be equal to 4.2 kJ/kmol·deg for all materials.

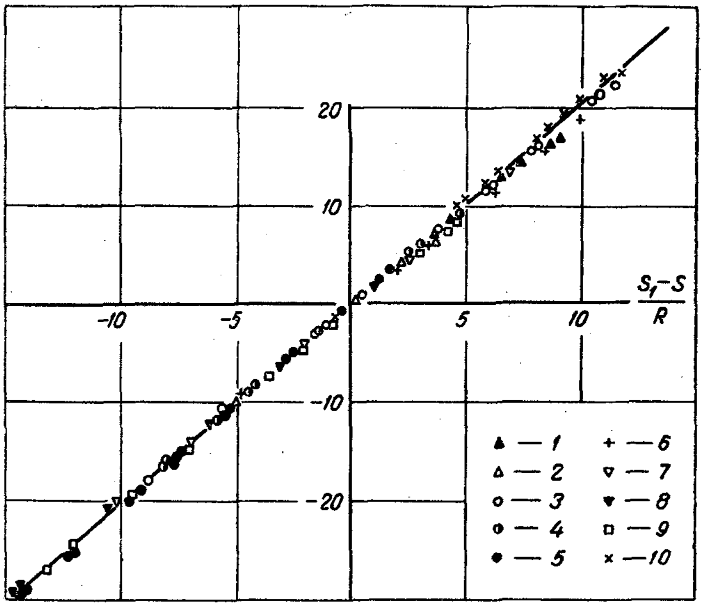

Fig. 3. Generalized relationship $q/q_{\Delta S} = \varphi((S_1 - S)/R)$: 1) propane; 2) n-butane; 3) n-pentane; 4) n-hexane; 5) n-heptane; 6) n-octane; 7) n-nonane; 8) n-decane; 9) heptene-1; 10) toluene.

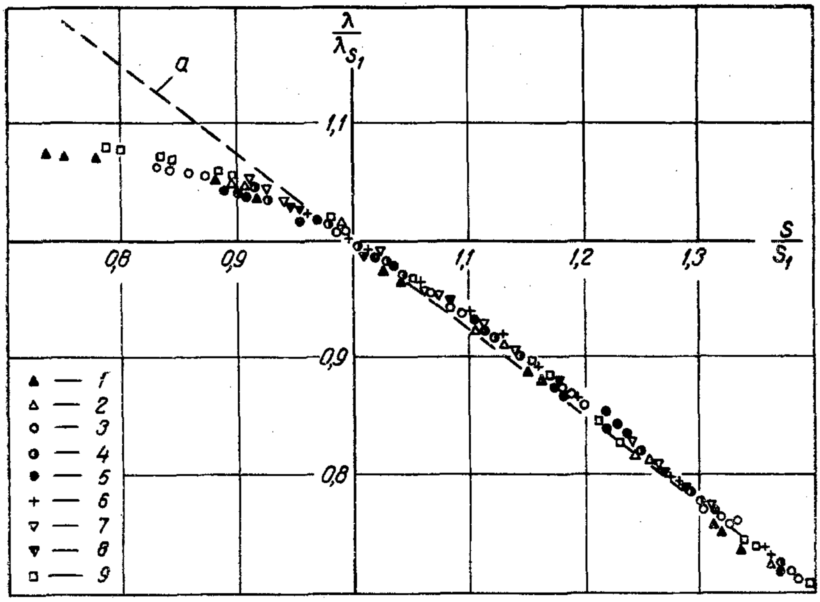

Fig. 4. Generalized relationship for liquid thermal conductivities $\lambda/\lambda_{S_1} = \psi(S/S_1)$: 1) propane; 2) n-butane; 3) n-pentane; 4) hexane; 5) n-heptane; 6) n-octane; 7) n-nonane; 8) n-decane; 9) heptene-1; a) corresponds to equation (4).

The generalized results are given in Fig. 3. From Fig. 3 it can be seen that the scatter of the experimental points from the average straight line described by the equation

$$\frac{q}{q_{\Delta S}} = 2.03\left(\frac{S_1 - S}{R}\right) \qquad (2)$$

is substantial only near the melting points.

The use, on generalization, of relationships of the form

$$\frac{\lambda}{\lambda_{S_1}} = \psi\left(\frac{S}{S_1}\right), \tag{3}$$

suggested earlier [2] on the basis of the treatment of experimental data on the thermal conductivity of a number of fluids in a comparatively narrow temperature range, gives good results (Fig. 4) only on selecting the origin for the entropy S_1 in the region near the given temperatures. Strictly speaking, the generalized relationship is nonlinear, especially near the melting points. However, in most cases of the liquid state at atmospheric pressure, the relationship (3) is approximately linear, and on choosing S_1 in a temperature region $\tau = 0.6$ takes the form

$$\frac{\lambda}{\lambda_{S_1}} = \left(1.75 - 0.75\frac{S}{S_1}\right), \tag{4}$$

recommended in [2]. The choice of S_1 at other values of τ also leads to a single relationship, but in this case the numerical coefficients in equation (4) are different.

On using a more general functional relationship (1), the mentioned limitations on the choice of S_1 are eliminated. It is only necessary to use a common value for all materials if possible. It should be noted that the generalization of the experimental data in the form of the relationship (3) is not identical with the treatment using the equation

$$\frac{\lambda}{\lambda_1} = \psi\left(\frac{T}{T_1}\right) \tag{5}$$

on choosing $T_1 = 0.6\ T_{\text{boil}}$ as the corresponding point of the state of the liquid. The use of equation (5) for the generalization of the experimental values of the thermal conductivity for saturated hydrocarbons gives a marked scatter of the experimental points, particularly for the lower members of this series. On using the relationship (3), as it is shown in Fig. 4, the slight scatter of the points is only observed near the melting point. The correcting influence of the variable thermal capacity C_p entering into the entropy is particularly noticeable on comparing the results of the treatment using these two methods when the origin for the entropy S_1 in Eq. (3) and the corresponding point in Eq. (5) is chosen at the boiling point.

NOTATION

λ	is the thermal conductivity, W/m · deg;
$q/q_{\Delta S}$	is the relative heat flux;
$q_{\Delta S}$	is the scale heat flux, W/m^2;
S_1	is the initial value of entropy, kJ/kmol · deg;
S	is the current value of entropy, kJ/kmol · deg;
R	is the universal gas constant, kJ/kmol · deg.

LITERATURE CITED

1. A. G. Usmanov, Heat Transfer and Thermal Modeling [in Russian], Izd. AN SSSR (1959).
2. G. Kh. Mukhamedzyanov and A. G. Usmanov, Heat and Mass Transfer [in Russian], Énergiya, 7 (1966); 7 (1963); Inzh.-Fiz. Zh., 13, No. 2 (1967); Transact. of KKhTI, 32 (1964); Izv. Vuzov, Neft' i Gaz, No. 4 (1965); No. 1 (1967); No. 4 (1967).
3. N. B. Vargaftik, Handbook on the Physical Properties of Gases and Liquids, Fizmatgiz (1963).
4. V. Z. Geller and Yu. L. Rastorguev, Teploénergetika, 7 (1968).
5. C. A. Swenson and R. H. Stahl, Rev. Sei. Instrum., 25, 608 (1954).
6. H. Poltz and R. Jugel, Int. J. Heat Mass Transfer, 10, 1075 (1967).
7. J. E. S. Venart, Chem. and Engng. Data, 10, 3 (1965).
8. L. Riedel, Chem.-Ing.-Technik, 13 (1951).
9. V. P. Brykov, G. Kh. Mukhamedzyanov, and A. G. Usmanov, Transact. of KKhTI, Vol. 39 (1968).
10. Ya. M. Naziev, Izv. Vuzov, Neft' i Gaz, No. 4 (1966).
11. V. P. Frontas'ev and M. Ya. Gusakov, Zh. Tekh. Fiz., No. 10 (1959).
12. L. P. Filippov, Vestnik MGU, No. 12 (1954).
13. D. K. H. Briggs, Ind. Eng. Chem., 49, 3, 418 (1957).