INVESTIGATING THE THERMAL CONDUCTIVITY OF POLYATOMIC ALCOHOLS

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We present the description of a new experimental installation and of a new method of investigating the thermal conductivity of liquids. We measure the thermal conductivity of water and of toluene. We have derived new experimental data on the thermal conductivity of glycerin, ethylene glycol, diethylene and triethylene glycol, in the temperature range 30-165°C.

As follows from [1-4], the thermal conductivity of glycerin has been measured by numerous investigators, but for a very narrow temperature range (0-100°C) and primarily at only one or two-three temperature points. Little effort has been devoted to investigating the thermal conductivity of ethylene glycol [5-8], and of diethylene glycol [8]. Data on the thermal conductivity of triethylene glycol, to the best of our knowledge, are entirely absent from the literature.

To investigate the thermal conductivity of the above-cited liquids, we chose a steady-state coaxial-cylinder method. The metering cell of the experimental installation is shown in Fig. 1. It consists of two coaxially positioned copper cylinders 1 and 2. The inside cylinder 1 ends in the lower portion of a hemisphere, and it exhibits a diameter of 22.45 ± 0.005 mm and the cylindrical portion is 236 mm long. An orifice with a diameter of 4.5 mm is drilled into the cylinder axis, and this hole is designed to hold electrical heater 3. The heater is made of constantan wire that is 0.2 mm in diameter; it is wound onto a thin porcelain tube and insulated from the cylinder by means of Fiberglas. Current and potential wires 0.35 mm in diameter have been soldered to the ends of the heater. Outside cylinder 2 is 287 mm long, its outside diameter is 67 mm and the inside diameter of the working section is 24.07 ± 0.008 mm. Insert 4 with a hemispherical surface at the end is placed from the bottom into the outside cylinder. The insert has been run in well to the seating surface of the cylinder and is held tight to that surface by means of shaped flange 5. The working surfaces of the inside and outside cylinders, as well as the hemispherical surface of the inserts,

TABLE 1. Experimental Data on the Thermal Conductivity of Water and Toluene

Water						Toluene		
p, MN/m^2	t, °C	λ, W/m deg	p, MN/m^2	t, °C	λ, W/m •deg	p, MN/m^2	t, °C	λ, W/m • deg
0	36,4	0,626	0,90	92,3	0,670	0	34,4	0,130
0	36,4	0,625	0,90	92,3	0,671	0	34,4	0,130
0,83	36,4	0,623	0	93,5	0,678	0	46,8	0,127
0,83	36,3	0,623	0,84	93,5	0,672	0	46,9	0,124
0	40,2	0,623	0	96,5	0,678	0	47,2	0,126
0	59,9	0,654	0	96,6	0,676	0	51,4	0,125
0,90	59,9	0,654	0,90	103,0	0,678	0	70,8	0,120
0	67,0	0,656	0,84	105,3	0,681	0	86,0	0,117
0	67,0	0,658	0,87	110,1	0,683	0	91,5	0,114
0,84	69,4	0,657	0,87	110,1	0,682	0	92,0	0,114
0	69,4	0,660	0,90	119,5	0,680	0	94,5	0,114
0	69,4	0,662	0,90	119,5	0,681	0,90	94,4	0,116
0,93	89,3	0,675	0,87	128,7	0,682	0,96	118,3	0,108
0	89,7	0,673	0,90	143,2	0,681	0,40	141,2	0,103
0	89,7	0,672	0,96	161,3	0,676	0,40	141,5	0,103
0,90	89,7	0,676	0,96	161,3	0,674	0,96	142,0	0,103

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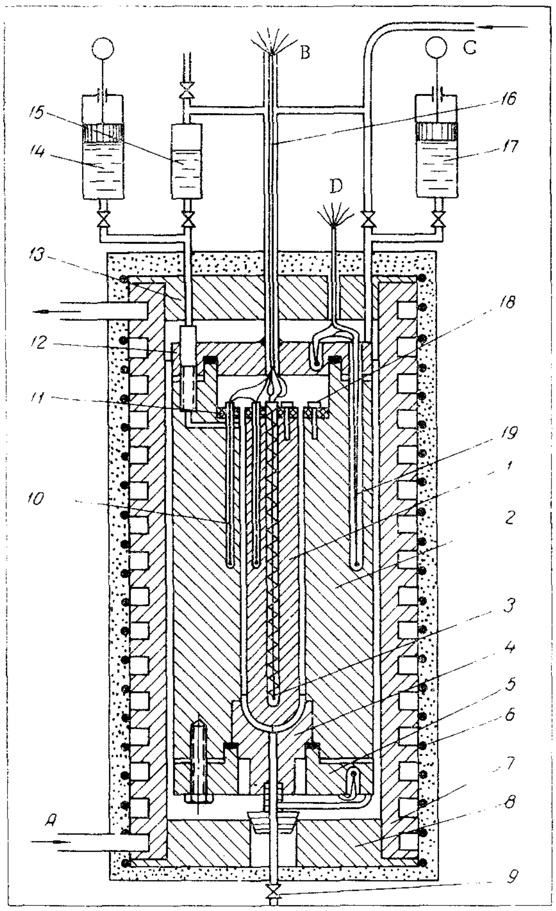

Fig. 1. Overall view of the measuring cell and the thermostating jacket: 1) inside cylinder; 2) outside cylinder; 3) electric heater; 4) insert; 5) flange; 6) cube; 7) brass cylinder of thermostating jacket; 8 and 13) massive brass stoppers; 9) valve; 10) three-junction differential thermocouple; 11 and 18) flanges clamping teflon spacer; 12) lid; 14 and 17) injectors; 15) expansion vessel; 16) tube for wire leads and nitrogen supply; A) from the thermostat; B) from the nitrogen tank; C, D) to the metering circuit.

have been chrome-coated and polished. The cylinders are made coaxial by means of seven porcelain spacers 1.8 mm in diameter. The uniformity of the clearance is checked by means of a calibrated wire thickness-gauge device. The measurements showed that the magnitude of the eccentricity does not exceed 0.01 mm. A teflon spacer that is 0.35 mm thick is mounted in the upper portion of the metering cell. It is pressed against the ends of the cylinders by means of flanges 11 and 18.

To permit the installation of the three-junctioned differential thermocouple in the outside and inside cylinders, as many as three orifices 2.7 mm in diameter have been drilled to a depth of 124 mm. The orifices have been drilled into the cylinders at angles of 120°, they are positioned opposite each other, and the ends come as close as 1-1.5 mm to the working surfaces of the cylinders. The thermal electrodes of the differential thermocouple, as well as the current and potential wiring of the electric heater are contained in the thin-walled stainless-steel tube 16, soldered to lid 12, and they are led out to the metering circuit through the packing gland.

The measuring cell is housed in the thermostating jacket which is 485 mm long. The thermostating jacket (Fig. 1) is made from the stainless-steel tube 6 into which a massive brass cylinder 7 is pressed; a rectangular thread-like channel has been cut into the outside surface of that brass cylinder. A U8 thermostat pump is used to pump the thermostating liquid – axle grease – along these channels from the bottom to the top. During the experiments, the temperature of the thermostating liquid was maintained by the thermostat to within ± 0.05°. The temperature fluctuation at the surface of the outside cylinder 2 in this case, monitored by means of a specially installed thermocouple, were virtually nonexistent.

The thermostating jacket is also electrically heated, and the heater here is intended for use in experiments at temperatures above 180°C. The thermostating jacket carries three heaters: one main heater and two backup heaters. The power for the main heater is 650 W and the backup heaters are rated at 250 W each. To maintain a more uniform temperature field within the measuring cell, the ends of the thermostating jacket are covered with removable massive brass stoppers 8 and 13. To reduce the loss of heat the thermostating jacket is insulated from the ambient medium by means of a thick layer of asbestos.

In the experiments, the temperature gradient through the height of the measuring cell was monitored by means of two (an upper and a lower) differential thermocouples 19. At a temperature of 165°C the temperature difference across the core and the ends of the measuring cell did not exceed 0.02°C. The liquid being investigated is poured into the measuring cell by means of injectors 14 and 17, connected to thin-walled capillaries made of stainless steel. Prior to the filling operation, both the measuring cell and the liquid being investigated were heated to temperatures of 70-80°C. The material is drained out of the installation through valve 9. After the experiments the measuring cell is flushed with distilled water, and then with warm dry air.

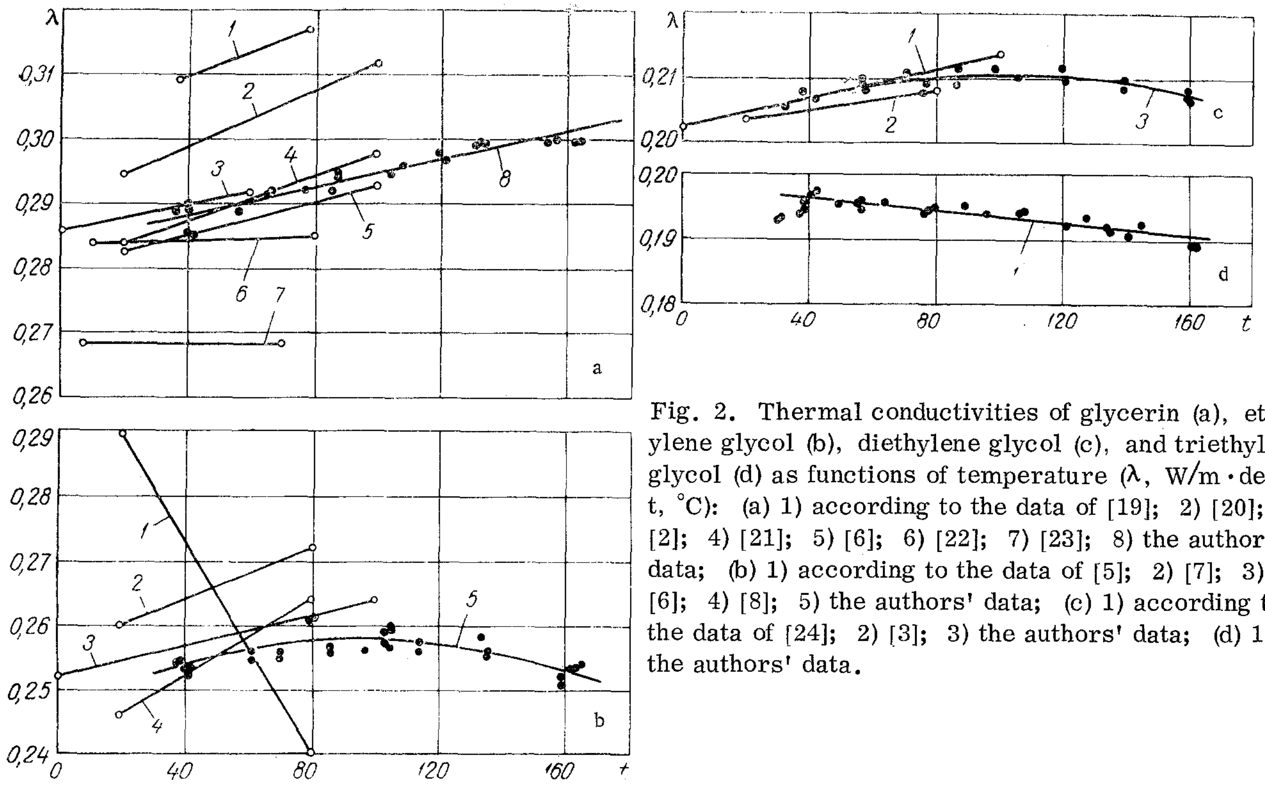

Fig. 2. Thermal conductivities of glycerin (a), ethylene glycol (b), diethylene glycol (c), and triethylene glycol (d) as functions of temperature (λ, W/m • deg; t, °C): (a) 1) according to the data of [19]; 2) [20]; 3) [2]; 4) [21]; 5) [6]; 6) [22]; 7) [23]; 8) the authors' data; (b) 1) according to the data of [5]; 2) [7]; 3) [6]; 4) [8]; 5) the authors' data; (c) 1) according to the data of [24]; 2) [3]; 3) the authors' data; (d) 1) the authors' data.

The required pressure is thus achieved within the installation through the use of nitrogen, for which purpose provision is made for a special line connecting the measuring cell through expander 15 with the nitrogen tanks. The nitrogen line is also connected to tube 16, as a result of which the Teflon spacer of the measuring cell is relieved of pressure.

The power for the electric heater of the measuring cell is taken from a TZhN-250 storage battery. The current in the heater circuit is determined from the voltage drop across a standard R-321 resistance coil. The voltage drop across the standard coil and across the electric heater were measured by means of a UPL-60 potentiometer through a DN-1 voltage divider.

The temperature difference across the layer of the liquid being investigated was determined by means of a three-junction differential Nichrome–constantan thermocouple 10. The emf of the thermocouple was measured with the same potentiometer. The error in the measurement of the temperature difference in these experiments did not exceed ± 0.01°.

The thermal conductivity was measured at each temperature level at atmospheric pressure and at a pressure of 0.7-1.0 MN/m^2 and at various temperature differences across the layer (1.0-3.5°). The product GrPr did not exceed 1000 during the experiments.

We estimate the maximum relative error in measuring the thermal conductivity with the above-described installation at 1.5%.

The thermal conductivity of the investigated liquids was calculated by means of the equation

$$Q - \Sigma Q_{\text{loss}} = \frac{2\pi\lambda l \Delta t}{\ln \frac{D}{d}} + \frac{\pi\lambda\Delta t}{\frac{1}{d} - \frac{1}{D}}, \tag{1}$$

whence

$$\lambda = \frac{UI - \Sigma Q_{\text{loss}}}{A\Delta t}, \tag{2}$$

TABLE 2. Thermal Conductivities of Glycerin, Ethylene Glycol, Diethylene Glycol, and Triethylene Glycol, W/m · deg

Designation	Temperature, °C						
	40	60	80	100	120	140	160
Glycerin	0,288	0,290	0,293	0,295	0,297	0,299	0,301
Ethylene glycol	0,253	0,256	0,257	0,258	0,257	0,255	0,253
Diethylene glycol	0,207	0,209	0,210	0,210	0,210	0,209	0,208
Trethylene glycol	0,196	0,195	0,194	0,194	0,193	0,192	0,191

where

$$A = \pi \left(\frac{2l}{\ln \frac{D}{d}} + \frac{Dd}{D-d} \right).$$

In the calculation of the thermal conductivity we introduce the correction factors for the installation for the differential thermocouple, for the change in the geometric dimensions of the measuring cell as a consequence of temperature, and for the loss of heat from the end of the inside cylinder and through the centering spacers.

Because of the great thermal conductivity of copper, the magnitude of the correction factor for the installation of the thermocouple, as demonstrated by calculation, ranged within 0.2% of Δt. The correction factor for the loss of heat from the end of the inside cylinder did not exceed 0.25%, while that through the spacers amounted to 0.4% of Q.

The quantity A is a function of the geometric dimensions of the measuring cell and varies with a changing temperature. At a temperature of 165° C the correction factor for the variation in geometric dimensions in the measuring cell amounts to 0.25% of $A_{20} = 38.70$ m.

To refine the experimental methods using the above-described installation, we measure the thermal conductivities of distilled water and toluene. The measurement results are presented in Table 1.

The data on the thermal conductivity of water are in good agreement with the data of [2, 4, 9]. The differences do not exceed 1.2%.

The data on the thermal conductivity of toluene for the temperature range under consideration and with an error not exceeding 1.4% are described by the equation

$$\lambda_t = \lambda_{30} \left[1 - \alpha (t - 30) \right],$$

where $\lambda_{30} = 0.130$ W/m · deg and $\alpha = 0.00189$ 1/deg.

The thermal-conductivity values which we derived for toluene at 30° C were understated in comparison with the data of [10-14] by 0.8-2.3%, and by 3.0-4.6% in comparison with the data of [2, 15-17]. However, the temperature coefficient of thermal conductivity is higher by 8.5% than in [17], and lower by 27% than in [16].

We also compared our data on the thermal conductivity of toluene with the data of [10-13, 15, 16], derived exclusively by the coaxial-cylinder method. The comparison demonstrated that in this case the difference between the coefficients of thermal conductivity for toluene and their temperature coefficients remain approximately the same as indicated earlier. Here it was noted that with an increase in the thickness of the clearance there is a tendency toward an increase in thermal conductivity. Apparently, this can be explained either by the appearance of convection in the layer, something which had not been observed by this investigator, or as indicated by Poltz [18], by the influence of radiation.

After testing the installation with water and toluene, we measured the thermal conductivities of glycerin, ethylene glycol, diethylene glycol, and triethylene glycol. For each substance, in the subject temperature range, we obtained from 40 to 50 experimental points. Approximately half of the points were derived in tests at atmospheric pressure, with the remaining half derived at pressures of 0.7-1.0 MN/m^2. No correction was introduced for pressure in the calculation of the thermal conductivity.

We attempted to choose liquids with a high degree of purity for the test. Thus the tests were conducted with distilled dynamite glycerin for which $\rho_4^{20} = 1.2557$ and $n_D^{20} = 1.4715$. Hungarian ethylene glycol was rated as chemically pure, with $\rho_4^{20} = 1.1127$ and $n_D^{20} = 1.4309$. The diethylene glycol produced by the Khar'kov Chemical Reagent Plant, laboratory pure, was rated at $\rho_4^{20} = 1.1165$ and $n_D^{20} = 1.4447$. The triethylene glycol produced in the German Democratic Republic was rated for laboratory purposes, with $\rho_4^{20} = 1.1225$ and $n_D^{20} = 1.4549$. These substances were not additionally refined or purified.

Figure 2 shows the thermal conductivities of these liquids as a function of temperature. The scattering of the experimental points with respect to the averaging lines does not exceed 1.5%. For purposes of comparison, the figures also show the experimental data of other investigators.

From Fig. 2a we see that the thermal conductivity of glycerin in this range of temperatures increases with a rise in temperature. A similar relationship at temperatures below 80-100° C was also derived by numerous other investigators. However, according to the data of [22] and [23], the thermal conductivity of glycerin is virtually independent of temperature.

The experimental values which we derived for the thermal conductivity of glycerin are in good agreement with the data of [2, 6, 21], and the differences do not exceed 1.2%; however, they differ substantially from the data of [19, 20, 23]. Thus, at a temperature of 60° C the experimental data from [19] and [20] are overstated in comparison with ours by 8.3 and 4.7%, respectively, while the data of [23] are understated by 7.5%. In this case there is an increase in the difference with a rise in temperature. The data from [19] differ from the data of [23] by 14.5% at a temperature of 60° C.

Particular attention should be devoted to the temperature relationship between the thermal conductivity of ethylene glycol and that of diethylene glycol. We see from Fig. 2b, c that the thermal conductivities of these liquids with a rise in temperature initially increase, attaining a maximum at some point in the temperature region of 80-120° C, subsequently diminishing. It is impossible to establish more precisely the region of transition for the thermal-conductivity curves through the maximum because of the relatively low accuracy of the experimental data (a measurement error of ± 1.5%). In this paper we will also be unable to establish the region at which the temperature curve for the glycerin passes through the maximum. It lies somewhere above a temperature of 165° C, but it is apparently below the normal boiling point for glycerin. The thermal conductivities of ethylene glycol and of diethylene glycol were also studied by other investigators [5-8], but primarily for the temperature range 20-80° C. The cited authors established a linear relationship between the thermal conductivity and temperature for this temperature interval. According to the data of [8, 24] the thermal conductivities of ethylene glycol and of diethylene glycol increase with a rise in temperature, whereas according to the data of [5] the thermal conductivity of these liquids diminishes.

The results which we derive from the measurement of the thermal conductivity of ethylene glycol in the temperature range from 40 through 100° C is in good agreement with the data of [6, 8], and the differences do not exceed 2.3%. The data of [7] for a temperature of 80° C are higher than our data by 5.4%. However, the data of [5] are in doubt, since they differ significantly from our measurements and results, and those derived by other authors [6, 7], not only in terms of the magnitude of thermal conductivity, but also in terms of the temperature relationship.

Triethylene glycol in relation to thermal conductivity behaved as a normal liquid and we have noted no anomalies in its behavior. The thermal conductivity of triethylene glycol diminishes with a rise in temperature (Fig. 2d).

Table 2 shows smoothed data with respect to the thermal conductivity of glycerin, ethylene glycol, diethylene glycol, and triethylene glycol.

NOTATION

Q	is the quantity of heat liberated by the heater, W;
ΣQ_{loss}	is the loss of heat through the inside cylinder, W;
λ	is the coefficient of thermal conductivity for the liquid being investigated, W/m · deg;
U	is the voltage drop across the heater, V;
I	is the current strength in the heater circuit, A;
Δt	is the theoretical temperature difference across the layer, deg;
l	is the length of the cylindrical portion of the inside cylinder, m;
D	is the inside diameter of the outside cylinder, m;

d	is the outside diameter of the inside cylinder, m;
A	is the instrument constant, m;
α	is the temperature coefficient of thermal conductivity, 1/deg;
t	is the temperature, °C;
p	is the pressure, MN/m^2.

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