THERMAL CONDUCTIVITY OF ORGANIC LIQUIDS

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A new instrument and technique for determining the thermal conductivity of liquids by the coaxial cylinder method are described. Experimental values of the thermal conductivity, obtained over a broad temperature interval, are compared with the results of other investigators.

This paper presents the results of an experimental investigation of the thermal conductivity of toluene, n-heptyl alcohol, dimethylformamide, and formamide.

The thermal conductivity of toluene was measured by the absolute method of coaxial cylinders on the temperature interval 20–200° C, that of the other liquids on the interval 20–160° C. The measuring cell of the experimental apparatus is shown in Fig. 1. It consists of two, coaxially arranged copper cylinders 7 and 8. The inner cylinder 8 is 180 mm long and 12.51 ± 0.003 mm in diameter. A hole 3 mm in diameter was drilled along the axis of the cylinder to accommodate an electric heater 9. This heater is made of nichrome wire 0.15 mm in diameter uniformly wound onto a porcelain tube. It is insulated from the cylinder by a layer of fiberglas and fluoroplastic. Two copper leads, 0.18 mm in diameter, whose resistance was accurately measured, were soldered to the ends of the heater.

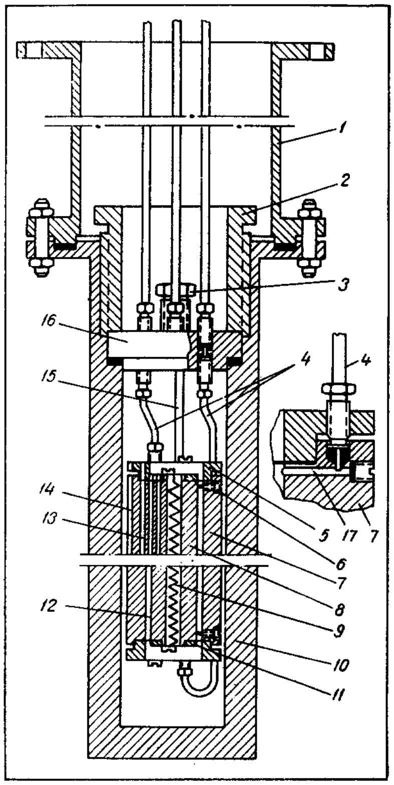

Fig. 1. Diagram of measuring cell.

The outer cylinder 7 has an inside diameter of 14.09 ± 0.005 mm. The working surfaces of the inner and outer cylinders were chromed and polished. Coaxiality of the cylinders was achieved by means of six textolite spacers, secured in brass screws 6, and two centering inserts, which were removed from the annular gap 12 after the screws had been tightened. The uniformity of the gap was checked with a special set of gauges. The eccentricity of the cylinders did not exceed 0.015 mm. Fluoroplastic rings 0.23 mm thick were placed over the ends of the cylinders, against which they were compressed by flanges 5 and 11.

The annular gap of the measuring cell was filled with the test liquid through thin-walled stainless capillaries 4 and holes 17 drilled in the wall of the outer cylinder 7. The temperature difference in the liquid layer was measured with a three-junction differential nichrome-constantan thermocouple using thermoelectrodes 0.15 mm in diameter. Three holes (13), 1.5 mm in diameter and 90 mm deep, were drilled in cylinders 7 and 8 to receive the thermocouples. The thermocouple electrodes and the heater leads were carried out of the autoclave through a gland 3.

The measuring cell was suspended on insulators 15 from cover 16 of autoclave 10, which was made of 2Cr13 steel. Cover 16 of the autoclave was secured by means of nut 2. The gap between the autoclave and the measuring cells was about 2 mm. The autoclave was placed in the bath of a TS-24 constant-temperature apparatus and attached to its cover by means of a thin flanged cylinder 1. The temperature in the TS-24 was maintained constant correct to ±0.02° C by means of a thermostat similar to that described in [1]. There was practically no fluctuation of the temperature at the surface of the outer cylinder 7, as monitored by the thermocouple inserted in channel 14. Dry spindle oil was used as the thermostating liquid. The necessary pressure was created in the apparatus by nitrogen. This relieved the pressure on the fluoroplastic rings. To eliminate convective nitrogen currents in the autoclave and at the ends of the measuring cell, the cavities of the autoclave were filled with loose fiberglass.

The heater of the measuring cell was powered by a group of ZhN-100 batteries. The current in the heat circuit was determined from the voltage drop across a R321 standard resistance coil. The voltage drop across the coil and the electric heater was measured with a PPTV-1 potentiometer. The thermocouple emf was measured with a R306 potentiometer.

The thermal conductivity of the test liquid was calculated from the equation

$$\lambda = \frac{IU \ln \frac{d_2}{d_1}}{2\pi l \Delta t_c}, \tag{1}$$

where $\Delta t_c = \Delta t_m - \Delta t_t + \Delta t$.

The differential thermocouple correction Δt_d depends on the positioning of the thermocouple junctions and the thermal conductivity of the cylinder material and the test liquid. In the experiments the correction Δt_t at a temperature of 30° C was 0.18% of the calculated temperature difference Δt_c for toluene and 0.49% for formamide. The correction for the heat losses along the thermocouple leads was negligibly small and disregarded in calculating the thermal conductivity.

To calculate the correction Δt for the heat losses from the ends of the measuring cell we constructed the heat balance equation for an element of length dx. As the coordinate origin we took a point on the axis of the cylinders at a distance $l/2$ from the ends and as the reference temperature we took the temperature of the outer cylinder:

$$\frac{IU}{l}\,dx = \left\{-\lambda_{op}F\,\frac{dt}{dx} - \left[-\lambda_{op}F\,\frac{d}{dx}\left(t - \frac{dt}{dx}\,dx\right)\right]\right\} + \frac{2\pi\lambda t}{\ln\frac{d_2}{d_1}}\,dx. \tag{2}$$

The left-hand side of Eq. (2) determines the amount of heat released by an element dx of the inner cylinder, while the right-hand side characterizes the amount of heat passing through the cross section of the cylinder in the direction of the end and transported by heat conduction through the layer of material investigated.

After transformations we obtain a second-order ordinary linear differential equation:

$$\frac{d^2t}{dx^2} - At + B = 0, \tag{3}$$

where

$$A = \frac{2\pi\lambda}{\lambda_{cop} F \ln \frac{d_2}{d_1}}; \quad B = \frac{IU}{\lambda_{cop} F l}.$$

The solution of Eq. (3) with boundary conditions

$$x = 0, \quad \frac{dt}{dx} = 0;$$

$$x = \frac{l}{2}, \quad \frac{dt}{dx} = \frac{2\pi\lambda_p \delta_p t}{\lambda_{cop} F \ln \frac{d_2}{d_1}} + \frac{3\lambda_t F_t t}{\lambda_{cop} F \delta} + \frac{F_\text{п}}{\lambda_{cop} F \left(\frac{\delta_{fl}}{\lambda_{fl}} + \frac{\delta_{fib}}{\lambda_{fib}}\right)} (t - t_{cp})$$

has the form

$$t = \frac{B}{A} - \left\{\left\{\frac{B}{A}\left[\frac{F_p}{\lambda_{cop} F \left(\frac{\delta_{fl}}{\lambda_{fl}} + \frac{\delta_{fib}}{\lambda_{fib}}\right)} + \frac{2\pi\lambda_{fl}\delta_{fl}}{\lambda_{fl} F \ln \frac{d_2}{d_1}} + \frac{3\lambda_{tex} F_{tex}}{\lambda_{cop} F \delta}\right] - \frac{F_r t_w}{\lambda_{cop} F \left(\frac{\delta_{fl}}{\lambda_{fl}} + \frac{\delta_{fib}}{\lambda_{fib}}\right)}\right\} \operatorname{ch}(\sqrt{A} x) \Bigg/ \left\{\sqrt{A} \operatorname{sh}\left(\sqrt{A} \frac{l}{2}\right) + \left[\frac{F_p}{\lambda_{cop} F \left(\frac{\delta_{fl}}{\lambda_{fl}} + \frac{\delta_{fib}}{\lambda_{fib}}\right)} + \frac{2\pi\lambda_{fl}\delta_{fl}}{\lambda_{cop} F \ln \frac{d_2}{d_1}} + \frac{3\lambda_{tex} F_{tex}}{\lambda_{cop} F \delta}\right] \operatorname{ch}\left(\sqrt{A} \frac{l}{2}\right)\right\}\right\}. \quad (4)$$

The first term of Eq. (4) characterizes the temperature at the surface of the inner cylinder in the absence of heat losses, and the second the magnitude of the correction Δt.

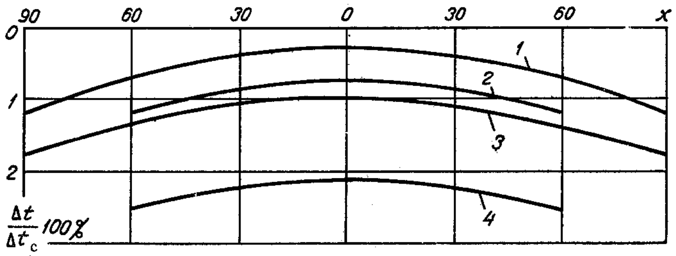

Fig. 2. Relative correction for heat losses from the ends as a function of the length of the cylinders.

The graphs in Fig. 2 represent the ratio $\Delta t/\Delta t_c$ and the length of the cylinder l for the measuring cells used in our research (l = 180 mm, d_1 = 12.51 mm) and in [2] (l = 120 mm, d_1 = 13.99 mm). Curves 1 and 2 were constructed for formamide, and curves 3 and 4 for toluene. To check the accuracy of the correction Δt we conducted special experiments on measuring cells with different thicknesses of the end rings and l/d ratios. The good agreement (within the limits of experimental accuracy) of the data obtained in these experiments indicates the accuracy of the absolute value of the correction introduced. In our experiments (at x = 0) the correction for toluene did not exceed 1% and that for formamide 0.33%.

Considerable attention was paid to the question of eliminating convective heat transfer in the test liquid. In a vertical cylindrical layer, convection may take place at large temperature gradients in both the axial and radial directions. As calculations and special measurements showed, the temperature gradient along the length of the inner cylinder was inconsiderable and in the experiments did not exceed $1 \cdot 10^{-4}$ deg/mm.

Table 1. Experimental Data on the Thermal Conductivity of the Liquids Investigated

Toluene		n-Heptyl alcohol		Dimethylformamide	
t, °C	λ, W/m · deg	t, °C	λ, W/m · deg	t, °C	λ, W/m · deg
26.0	0.134	35.5	0.151	32.3	0.186
31.2	0.132	66.4	0.145	69.8	0.176
44.5	0.129	87.8	0.143	106.9	0.166
45.3	0.130	108.4	0.136	143.1	0.156
45.4	0.129	146.7	0.130	26.9	0.185
47.7	0.129	162.9	0.126	41.0	0.182
56.7	0.127	163.1	0.126	42.3	0.182
64.6	0.125	24.6	0.151	60.1	0.177
77.1	0.122	31.3	0.150	60.4	0.176
97.6	0.116	32.7	0.150	80.6	0.170
114.8	0.112	43.6	0.146		
126.2	0.109	52.6	0.146		
145.6	0.105	62.1	0.144		
154.5	0.102	79.4	0.141		
165.5	0.101	89.8	0.138		
173.9	0.098	94.2	0.138		
184.7	0.096	Formamide			
192.2	0.094	54.0	0.352		
201.7	0.092	83.2	0.348		
21.6	0.135	109.5	0.341		
25.4	0.132	151.0	0.341		
38.0	0.130	43.2	0.351		
39.0	0.130	52.3	0.347		
40.6	0.129				
59.3	0.125				
61.0	0.124				
76.8	0.120				
77.3	0.120				
80.3	0.120				
84.0	0.119				

The bracketed data were obtained on the apparatus described in [2].

The temperature gradient in the layer of test liquid is usually selected from the condition $GrPr \leq 1000$. In a number of studies [3–5] made in recent years it has been shown that in small cylindrical gaps (δ = 1–4 mm) convection takes place at GrPr values considerably greater than 1000. This is confirmed by our special experiments, in which no convection was detected at GrPr = 1750. In our investigations of the thermal conductivity of toluene, n-heptyl alcohol, dimethylformamide, and formamide, the values of GrPr did not exceed 600, and the temperature gradient in the layer was 1.2–1.8 deg.

The correction for the change in the linear dimensions of the measuring cell in the experiments at 200° C was about 0.3%.

Since problems of radiative heat transfer in liquids have not been very thoroughly studied, we did not introduce corrections for radiation.

As the calculations showed, in our experiments the total error in calculating the corrections did not exceed ±0.2%.

Below, we present the results of an investigation of the thermal conductivity of toluene, n-heptyl alcohol, dimethylformamide, and formamide on the types of apparatus described in this paper and in [2]. An error analysis showed that the maximum error in measuring the thermal conductivity of the liquids investigated does not exceed ±1%.

In recent years alone, there have been at least ten studies of the thermal conductivity of toluene [2, 3, 5, 6–14]. This is because toluene can be successfully employed as a standard in instrument testing and relative methods of measuring thermal conductivity. However, the discrepancies among even the recent experimental data are quite large, and at temperatures above the boiling point the thermal conductivity of toluene is almost uninvestigated. Therefore, the accumulation of reliable experimental material and the extension of the region of investigation of the thermal conductivity of toluene are urgent tasks.

As the test liquid we selected toluene from the Khar'kov Chemical Reagent Plant designated "toluene, scintillation. Special purity" (Soviet standard GOST 1318–57).

In the experiments up to the boiling point the pressure in the apparatus was kept equal to 0.4 MN/m^2 and at higher temperatures several MN/m^2 above saturation pressure. A pressure correction was not introduced in calculating the thermal conductivity of the toluene.

Table 1 presents the results of an experimental investigation of the thermal conductivity of toluene. It also includes the experimental data on the thermal conductivity of n-heptyl alcohol, dimethylformamide, and formamide. On the temperature interval investigated, the thermal conductivity of these liquids is described by the equation

$$\lambda_t = \lambda_{30}[1 - \alpha(t - 30)]. \quad (5)$$

Values of λ_{30} and α and of ρ_4^{20} and n_D^{20} for the liquids investigated are presented in Table 2. The deviation of our experimental data from the values calculated from Eq. (5) does not exceed 1%.

Table 2. Characteristics of the Liquids Investigated

Liquid	ρ_4^{20}	n_D^{20}	λ_{30}, W/m · deg	$\alpha \cdot 10^3$, $\frac{1}{deg}$
Toluene	0.8670	1.4969	0.132_8	1.84
n-Heptyl alcohol	0.8236	1.4249	0.152	1.28
Dimethylformamide	0.9459	1.4305	0.185	1.38
Formamide	1.1360	1.4480	0.355	0.39

We have compared our experimental data on toluene with the data of other investigators. Thus, Ziebland's data [7] at a temperature of 20° are in good agreement with our own, while at 112° C the discrepancy reaches 4.2%. It should be noted that elsewhere [8] Ziebland and Burton present values for the thermal conductivity of toluene at three temperatures which, within the limits of accuracy of the experiment, coincide with our data. Good agreement (up to ±1%) is observed between our data and the data presented in [5, 6, 9–12]. The data of [14] are lower than ours by, on the average, 2%.

The thermal conductivity of n-heptyl alcohol was investigated in [15, 16] on the temperature interval 30–100° C. These data are 7.5% higher than our own.

Our values for the thermal conductivity of dimethylformamide are, on the average, 5.2% higher than those obtained in [17]. As far as we know, nothing has been published on the thermal conductivity of formamide.

NOTATION

λ is the thermal conductivity, W/m · deg
I is the current in the heater circuit, A
U is the voltage drop across the heat, V
d_1 is the outside diameter of the inner cylinder, mm
d_2 is the inside diameter of outer cylinder, mm
l is the length of the cylinder, m
Δt_c is the calculated temperature difference, deg
Δt_m is the measured temperature difference, deg
Δt_d is the thermocouple correction, deg
Δt is the correction for heat losses from ends of measuring cell, deg
F_r is the surface area of the fluoroplastic ring, m^2
F_{tex} is the cross-sectional area of the centering spacers, m^2
F is the cross-sectional area of the inner cylinder, m^2
δ is the thickness of the layer of test liquid, m
δ_{fl} is the thickness of the fluoroplastic ring, m
δ_{fib} is the thickness of the layer of fiberglas at the ends of the cylinder, m
λ_{cop} is the thermal conductivity of copper, W/m · deg
λ_{fl} is the thermal conductivity of fluoroplastic, W/m · deg
λ_{fib} is the thermal conductivity of fiberglas, W/m · deg
λ_{tex} is the thermal conductivity of textolite, W/m · deg
x is the distance from the center of the cylinder to the location of the thermocouple, m;
Gr is the Grashof number
Pr is the Prandtl number
α is the temperature coefficient of thermal conductivity, deg^{-1}.
t_w is the temperature of the autoclave wall, °C
ρ_4^{20} is the density
n_D^{20} is the index of refraction

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