A MODIFICATION OF THE MEASURING CELL FOR THE INVESTIGATION OF THE THERMAL CONDUCTIVITY OF LIQUIDS AND GASES BY THE HOT-WIRE METHOD

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Inzhenerno-Fizicheskii Zhurnal, Vol. 13, No. 1, pp. 16–23, 1967

UDC 536.22:536.23

The construction of an instrument for measurements by the absolute hot-wire method is described. The thermal conductivity of toluene, benzene, carbon tetrachloride, and air in the temperature range 20–160° C was measured to an accuracy of 1%. Natural convection in the cylindrical gap ($\delta = 0.675$ mm) when the measuring cell is vertical occurs when GrPr ≥ 3400.

Hot-wire instruments with glass capillaries can be used to determine thermal conductivity (λ) with an error of ±1.5–2.5% [1–3]. A considerable part of the error (up to 1%) is due to the fact that the temperature gradient in the capillary wall cannot be determined exactly. To avoid this error, Zenkevich [4] in an investigation of λ of petroleum fuels and oils replaced the glass capillary by a nickel one, which also acted as the external resistance thermometer. However, since he could not measure accurately the internal diameter of the capillary and the eccentricity of the wire, Zenkevich determined the thermal conductivity by a relative method in a small temperature range (20–100° C).

The instrument which we propose is based on the absolute hot-wire method and can provide measurements of the thermal conductivity of liquids and gases with an error of less than 1% at temperatures up to 200° C and pressures of 10 MN/m^2 or more.

The external resistance thermometer is a thin-walled nickel capillary (Ni ≈ 99.7%, Mg = 0.1%, Cu = = 0.1%), which was selected from a large number of capillaries of a batch. In the selection of the capillary we paid particular attention to its straightness, uniform wall thickness, and absence of ellipticity. The linear dimensions of the capillaries were measured to an accuracy of 3 μ on a large BMI instrument microscope. The outer diameter (d_3) of the capillaries was measured in two mutually perpendicular planes at eight points along the capillaries. The capillary used in the instrument had $d_3 = 1.550 \pm 0.003$ mm and its deviation from straightness did not exceed 0.01 mm.

The internal diameter (d_2) of the nickel capillary was determined by the relative method on a special stand (Fig. 1) with the aid of a previously calibrated glass capillary. The glass (3) and nickel (4) capillaries were attached to a clear plastic plate and connected to one another by a hole. When the capillaries were in position the system was thoroughly washed with petroleum ether, flushed with air, and filled with purified mercury. A syringe (2) was used to move the mercury in the capillaries. The movement of the mercury in the glass capillary was measured to an accuracy of ±1 μ with a KM-6 cathetometer (5), and in the nickel capillary to an accuracy of ±10 μ bv an electric probe. The probe consisted of a micrometer head (1) on which was soldered a 0.08 mm platinum wire insulated with glass straw. When the probe touched the mercury meniscus an electrical circuit was made and the galvanometer needle was deflected. From the change in mercury level in the capillaries and the known diameter of the glass capillary we determined d_2 of the nickel capillary at steps of 10 mm over the entire length of the measuring section. We obtained $d_2 = 1.450 \pm 0.003$ mm.

To check the stand method we measured the diameters of two glass capillaries previously calibrated by the usual method. The experiments and an analysis of the errors showed that the proposed method gave the internal diameter of the capillaries to an accuracy of ±3 μ.

The construction of the measuring cell is shown in Fig. 2. A platinum wire (3) ("Pobeda" grade platinum of diameter 0.100 ± 0.001 mm), which is both the heater and the internal resistance thermometer, is stretched along the axis of the nickel capillary (10). The diameter of the wire was measured by two independent methods: by a microscope and by weighing one meter of the platinum wire on an ADV-200 analytical balance. Before the wire was fixed in position it was baked twice at 1000° C. The measuring section of the wire was demarcated by the two seals of the potential leads (5 and 13). The length of the measuring section was 122.1 mm. The potential leads were of 0.06 mm platinum wire and were silver-soldered to the wire by means of a special micro-torch. The diameter of the joints did not exceed 0.2 mm. The wire was kept under constant tension by a tungsten spring (2) held in a frame (1).

Both the potential and current leads of the capillary were made of nickel wire, which ensured the absence of a thermal emf at the points of connection of the leads. The potential leads (not shown in the figure) were made of 0.07 mm wire, and the current leads (4 and 12) of 0.2 mm wire. To create a radial temperature field on the ends of the measuring cell and to reduce heat loss the ends of the nickel capillary were enclosed in tight-fitting 20 mm long glass tubes (6 and 11).

Coaxiality of the wire and capillary is usually achieved by the use of various centering devices (beads, rings, etc.), which considerably reduce the through section and make it difficult to fill the capillary, especially with viscous liquids. For convenient centering of the wire in our instrument the capillary

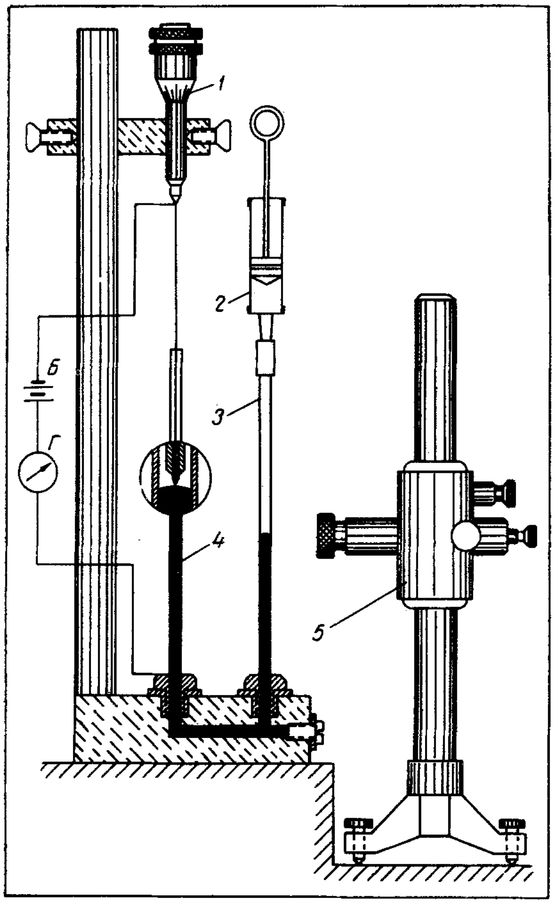

Fig. 1. Diagram of stand for determination of inside diameter of nickel capillary.

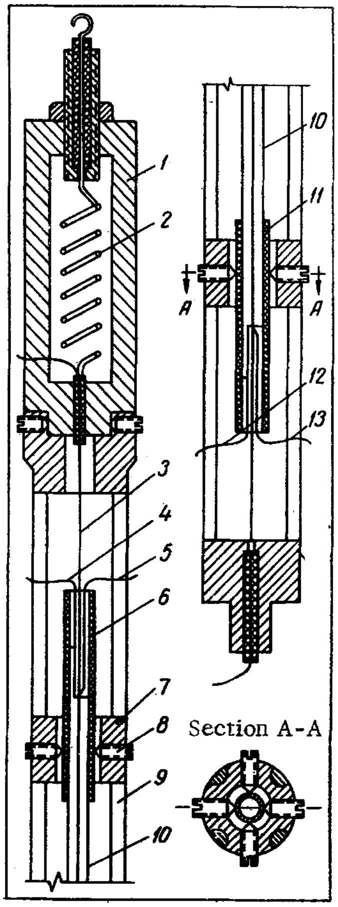

Fig. 2. Diagram of measuring cell.

was mounted in a light frame made of steel spokes (9) and collars (7) with adjusting screws (8). The wire was centered by mounting the measuring cell on the stage of the BMI instrument microscope so that the wire, held under tension by a 12 g weight, was aligned with the horizontal axis of the objective. The microscope stage was then moved through a step (15 mm) and the eccentricity of the wire was checked from the external diameter of the capillary. The measurements were made in two mutually perpendicular planes with forward and backward motion of the microscope stage. A correction was introduced for the curvature of the capillary. The mean eccentricity of the wire, checked twice, was 0.03 mm.

After assembly of the measuring cell the resistance thermometers were "aged" and were then calibrated from two reference points (melting ice and boiling water) and against a standard resistance thermometer in a thermostat in the range 20–200° C. The relationship between the resistance of a nickel thermometer and temperature is given by

$$R_t = R_0(1 + At + Bt^2), \tag{1}$$

where $R_0 = 0.036183$ ohm, $A = 5.279 \cdot 10^{-3}$ 1/deg, $B = 7.162 \cdot 10^{-6}$ 1/deg^2. The resistance of the internal thermometer $R_0 = 1.55356$ ohm, $R_{100}/R_0 = 1.39121$, $A = 3.971 \cdot 10^{-3}$ 1/deg, $B = -5.852 \cdot 10^{-7}$ 1/deg^2.

After calibration of the resistance thermometers, followed by a check of the centering of the wire, we put the measuring cell into a stainless-steel autoclave, which fitted with a clearance of 1 mm into a massive copper block 300 mm long.

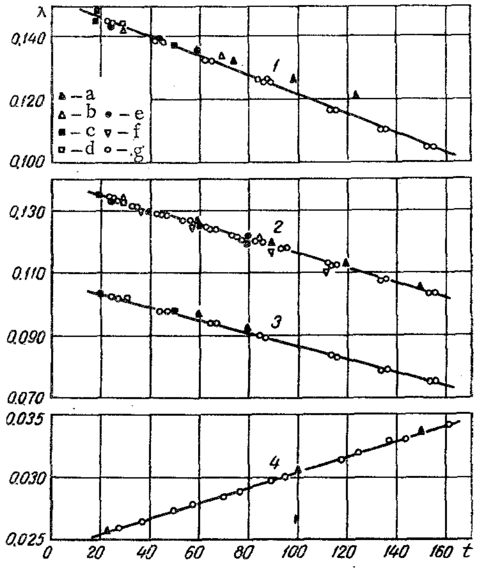

Fig. 3. Plots of thermal conductivity (W/m · deg) of benzene (1), toluene (2), carbon tetrachloride (3), and air (4) against temperature (° C): a) Data of [8]; b) [5]; c) [6]; d) [7]; e) [9]; f) [10]; g) our data.

A uniform temperature field along the measuring cell was secured by completely submerging the copper blocks in the constant temperature liquid of the TS-24 thermostat. The constant-temperature liquid was water or No. 5 silicone fluid. The temperature of the thermostat bath was kept constant to within ±0.05° C by a regulator. The temperature fluctuations in the autoclave due to inertia of the copper block + air gap + autoclave system did not exceed ±0.005° C.

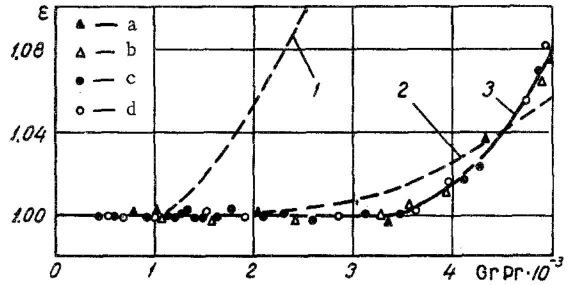

Fig. 4. Convection coefficient ε as function of product GrPr: 1) From Kraussold's equation; 2) from Berkengeim's equation; 3) from our data; a) carbon tetrachloride; b) n-hexane; c) toluene; d) benzene.

The temperature gradient along the autoclave was measured by a differential thermocouple, the junctions of which were located at the ends of the measuring section. At the maximum experimental temperature of 160° C it was not more than 0.02° C.

The autoclave was filled with the investigated liquid by means of medical syringes. Air bubbles adsorbed by the walls of the autoclave and the measuring cell were removed by repeated pumping of the liquid. The required pressure in the autoclave was produced by nitrogen. The system could also be filled under vacuum. The leads from the autoclave were brought out through special seals tested at a pressure of 15 MN/m^2.

The electrical circuits of the external and internal resistance thermometers were fed from 3- and 6-V ZhN-60 storage batteries, respectively. The current in the circuit of the external thermometer was chosen to ensure no heating of the capillary and in the experiments it did not exceed 50 mA. The calibration current in the circuit of the internal thermometer was less than 3 mA, and the working current did not exceed 500 mA.

The electrical resistance of the thermometers was determined from the current and potential difference on the measuring sections. The potential difference on the measuring sections of the wire, capillary, and terminals of the class 0.01 standard resistance coils was measured with UPL-60-2 and R-330 potentiometers. The resistance of the nickel capillary in the experiments and during its calibration were measured with an R-330 potentiometer (the scale division of the last decade was 0.1 μV) to an accuracy of $2 \cdot 10^{-6}$ ohm, which corresponds to a temperature accuracy of ±0.01° C. The effect of the thermal emf during the measurements was excluded by reversing the electric circuits of the thermometers.

Table 1

Experimental Values of Thermal Conductivity of Toluene

I, A	U, V	Δt_{meas}, deg	Δt_{cal}, deg	P, MN/m^2	t_{exp}, °C	λ, W/M · deg
0.29976	0.51241	3.99	+0.01	0.1	23.9	0.1340
0.34334	0.58630	5.24	+0.01	0.1	25.0	0.1338
0.42348	0.73301	8.12	0.00	0.1	27.4	0.1333
0.29811	0.52795	4.17	0.00	0.1	33.6	0.1317
0.34122	0.60367	5.47	0.00	0.1	34.7	0.1314
0.30416	0.55871	4.60	0.00	0.1	44.3	0.1289
0.35931	0.66265	6.46	0.00	0.1	45.8	0.1286
0.38011	0.68316	7.03	+0.01	0.1	46.3	0.1286
0.28504	0.53932	4.25	0.00	0.1	53.0	0.1262
0.34707	0.65658	6.31	0.00	0.1	54.8	0.1260
0.27502	0.54237	4.19	0.00	0.1	63.8	0.1242
0.33514	0.65880	6.22	0.00	0.1	65.4	0.1240
0.37574	0.74349	7.82	+0.03	0.1	66.5	0.1240
0.26340	0.53506	4.03	0.00	0.1	73.2	0.1220
0.27337	0.55091	4.31	0.00	0.1	73.9	0.1219
0.32412	0.66945	6.24	—0.01	0.1	76.3	0.1215
0.26779	0.55576	4.36	—0.03	0.1	84.1	0.1199
0.30823	0.57827	5.22	—0.03	0.1	85.5	0.1198
0.27112	0.54668	4.41	—0.01	0.1	92.7	0.1175
0.31161	0.63184	5.84	—0.01	0.1	94.1	0.1178
0.26148	0.59005	4.80	0.00	0.3	114.1	0.1122
0.30536	0.69096	6.57	0.00	0.3	115.4	0.1121
0.31122	0.70437	6.82	0.00	0.3	115.7	0.1121
0.22632	0.53827	4.00	—0.03	0.5	133.7	0.1071
0.27676	0.65576	5.95	—0.03	0.5	135.1	0.1070
0.23808	0.59294	4.78	—0.02	0.5	154.0	0.1035
0.27674	0.68157	6.38	—0.02	0.5	155.1	0.1035

Table 2

Thermal Conductivity and Brief Description of Investigated Products

Product	Density ρ_4^{20}	Refractive index n_D^{20}	Thermal conductivity at 30°C, λ_{30}, W/(m · deg)	Temperature coefficient of thermal conductivity a, 1/deg
Toluene, C_7H_8	0.8670	1.4969	0.1328	0.00179
Benzene, C_6H_6	0.8782	1.5015	0.1434	0.00218
Carbon tetrachloride CCl_4	1.5930	1.4605	0.1010	0.00208
Air	—	—	0.0260	0.00231

To take into account the effect of variations in tension of the spring with temperature and time on the readings of the internal resistance thermometer we calibrated the latter against the external thermometer before each experiment. The correction to the initial calibration of the wire did not exceed ±0.03° C. To test for the absence of convection we carried out experiments with two different temperature drops in the layer of investigated liquid. The steady state was reached 30–40 min after the start of the experiment.

The thermal conductivity was determined from the equation

$$\lambda = \frac{IU \ln \frac{d_2}{d_1}}{2\pi l (\Delta t_{\text{meas}} \pm \Delta t_{\text{cal}})}. \qquad (2)$$

In the calculation of λ we introduced corrections for heat removal from the ends of the measuring cell and for eccentricity of the wire, which did not exceed 0.3 and 0.1%, respectively. In view of the logarithmic law of temperature variation in a cylindrical gap the obtained thermal conductivity values were referred to the mean-integral temperature of the layer.

In the experiments we measured the thermal conductivity of air, toluene, benzene, and carbon tetrachloride in the temperature range 20–160° C. The purity of the liquids was determined by means of a KhT-63 chromatograph with a flame ionization detector. The chromatographic analysis showed that the benzene and carbon tetrachloride contained no impurities, while the toluene, analytically pure according to GOST 5739-51, contained less than 0.06% impurities.

Since toluene, in view of its properties, can be used as a standard liquid for the calibration and testing of instruments for the determination of λ, it was investigated particularly carefully. We obtained 45 experimental points for the thermal conductivity of toluene in the range 22–155° C, and 27 of these are given in Table 1. The purity of the toluene was determined not only before the start of the experiments, but after they had ended. The chromatographic analysis confirmed that its purity was unaffected by the experiments.

A brief description of the investigated products and their thermal conductivity at 30° C are given in Table 2. This table also gives the temperature coefficients of the thermal conductivity.

Calculations showed that the systematic error in the measurement of λ of liquids did not exceed 0.4%. The maximum random error was found from Eq. (2). It did not exceed 0.5% in the determination of the temperature drop in the liquid layer and 0.02% in the determination of the heat flow. Thus, the maximum relative error of the experimental data is ~1%. The scatter of the experimental points did not exceed this value.

The thermal conductivity of all the investigated liquids decreased with increase in temperature, whereas that of air increased, and in the investigated temperature range is given to an accuracy of 0.7% by the equation

$$\lambda = \lambda_{30}[1 \pm \alpha(t - 30)]. \qquad (3)$$

In the graphs of Fig. 3 we compare our experimental data with the most reliable values obtained for toluene, benzene, carbon tetrachloride, and air by other researchers [5–10]. As the graphs show, our experimental values of λ are in good agreement with the data of other researchers (they differ from the most reliable data [5, 6, 10] by not more than 1% on the average) and satisfy Ziebland's equation [10] to within 1–2%. The only exception was benzene, for which we found a slightly different behavior of the thermal conductivity from that found in [5]. Since the data of [5] were subsequently [8] extrapolated to the region of higher temperatures the difference between our experimental values of λ of benzene and the values of [8] at 125° C is 6%.

In the measurements of λ of liquids we noted that there was no convection in the cylindrical gap ($\delta = 0.675$ mm) with the measuring cell in the vertical position when GrPr ≫ 1000. In view of this we carried out special investigations to determine the critical values of GrPr for liquids with well-investigated, but substantially different, physical properties. The liquids we chose were toluene, benzene, carbon tetrachloride (see Table 2) and n-hexane ($\rho^{20}_4 = 0.6594$, $\eta_{20} = 0.00031$ N·sec/m²).

The experiments were carried out with different temperature drops in the layer of investigated liquid and at GrPr values up to 5000. The experimental data were treated by the well-known method [11]. The graph (Fig. 4) shows the convection coefficient $\varepsilon = \lambda_{\text{eff}}/\lambda$ plotted against the product GrPr. The graph indicates that natural convection in the investigated layer ($\delta = 0.675$ mm) of liquid in the vertical position begins at GrPr = 3400, which is 3.4 times greater than the value suggested by Kraussold and Mikheev. Schmidt and Leidenfrost [12] came to similar conclusions. They measured the thermal conductivity of liquids by the cylindrical-layer method ($\delta = 2$ and 4 mm) with GrPr ≤ 4000. The convection coefficient ε was less than 2%, which corresponded to the accuracy of their experiments. Shingarev [13] thinks that convective heat transfer in narrow gaps begins when GrPr = 2500.

When this paper was ready for publication there appeared Berkengeim's work [14], which showed that in cylindrical layers with a gap width of 1.5–6.6 mm natural convection begins when GrPr ≥ 1700.

Thus, the conducted investigations showed that in tubes of small diameter and small cylindrical gaps natural convection begins in the layer when GrPr ≫ 1000. This can be used to increase the accuracy of measurement of thermal conductivity by increasing the temperature drop in the layer of investigated liquid. Despite the fact that the developed instrument can give reliable values of λ when GrPr ≤ 3400, the values of GrPr in the experiments did not exceed 1700.

NOTATION

R_0, R_{100}, and R_t are the electrical resistances at temperatures 0, 100, and t° C, respectively; A and B are the coefficients of the thermometric equation; λ is the thermal conductivity of the investigated substance; I is the current in the wire circuit; U is the voltage drop in the wire; Δt_{meas} is the measured temperature difference; Δt_{cal} is the correction for initial calibration of the wire; t_{exp} is the mean temperature of the experiment; P is the absolute pressure; d_1 is the outside diameter of the wire; d_2 is the inside diameter of the capillary; d_3 is the outside diameter of the capillary; l is the length of the measuring section; λ_{eff} is the effective thermal conductivity; Gr is the Grashof number; Pr is the Prandtl number; δ is the thickness of the layer.

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