EXPERIMENTAL INVESTIGATION OF THE THERMAL CONDUCTIVITY OF TOLUENE

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The procedure of measurements of the thermal conductivity of toluene by the heated filament method is described and the results measured in four measuring cells in the temperature range of 0-130°C are presented. The effect of gap thickness on the heat transfer in liquids is discussed.

The thermal conductivity of toluene in liquid state has been measured by many authors [1-38] by different methods. However, only a small number of the works [7, 11-13, 30] are devoted to an independent investigation of the thermal conductivity of toluene. In many of the works toluene is used only for checking experimental equipment and finalizing the experimental procedure.

At present such special investigations have acquired a nature of urgency in connection with work being done on standardization of materials, since only these investigations will make it possible to make an objective approach to the estimate of the reliability of the experimental material. The results of an experimental investigation of the thermal conductivity of toluene in the temperature range of 0-130°C are presented below. In the second part of this article the data on the thermal conductivity of toluene in the temperature range 20-200°C and at pressures of 0.098-49 MN/m^2 will be presented. In these investigations an exceptional care was taken in developing the procedure of organizing and conducting the experiment.

EXPERIMENTAL METHOD

The stationary method of heated filament, which has been fairly well developed, was chosen for the measurement of the thermal conductivity of toluene. Four measuring cells were prepared, which differed in construction, geometrical dimensions, the type of glass, and the step of winding of the resistance thermometers on the glass capillaries.

The characteristics of the measuring cells are given in Table 1, and those of the construction are given in Fig. 1.

For the convenience of centering filament 1 in the glass capillary 2 with $d_i < 1$ mm (cells No. 1, 3, 4) a light metal frame 3 (Fig. 1a) was used, in which the capillary was centered with respect to the filament by eight centering screws 4. This construction of the cell made it possible to achieve very small eccentricities and avoided the need of using centering devices which appreciably reduce the transfer cross section of the capillary, thereby making its filling difficult

In measuring cell No. 2 (Fig. 1b) the platinum filament 1 was centered inside the glass capillary 2 with the use of special centering devices 3, which were mounted in brass sleeves 4 with a small gap. The sleeves were fixed to the capillary with the stop screws 5. Glass capillary insulators with inner diameter ~0.12 mm were mounted along the axis of the centering devices. The filament was soldered at the bottom capillary, passed through the capillary above, and was fixed to a tungsten spring.

Platinum wire of mark "Pobeda," annealed beforehand twice at 1000°C, was used for preparing the resistance thermometers of all the four measuring cells. The diameter of the filament was determined

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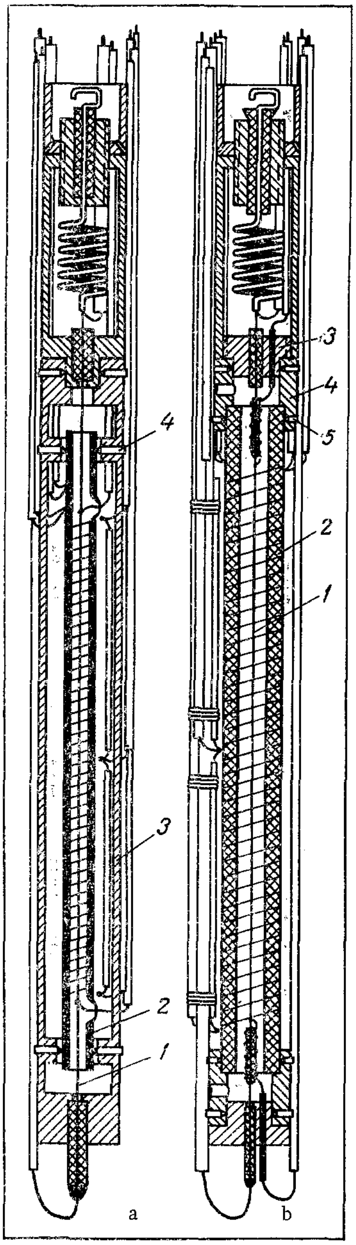

Fig. 1. Diagrams of the measuring cells: a) cells No. 1, 3, 4; b) cell No. 2.

by three independent methods: by BMI microscope with an error of ±0.003 mm, by a lever micrometer with 0.002 mm division, and by weighing one meter of platinum wire on ADV-200 analytical balances. The outer diameter of the capillaries and their rectilinearity were checked on a BMI microscope in two mutually perpendicular planes. The inner diameter of the capillaries was determined by filling them with mercury and then weighing them. This was repeated many times. The uniformity of the inner diameter along the length was checked by displacing a column of mercury along the capillary and measuring its length on a MIR-12 microscope. The maximum deviation of the inner diameter from the average value was 0.02%. The measuring part of the filament in each cell was limited by two seals of platinum potential wire of diameter 0.06 mm. The potential leads to the filament were soldered by gold and were lead out of the capillaries through an opening made in such a way that the junction was at a segment of the capillary with undeformed geometry. For taking out the potential leads of cell No. 2 thin-walled glass capillaries were put on the filament; the potential leads were first wound on these capillaries and then taken out through capillary insulators placed on the centering devices.

For "aging" the platinum resistance thermometers after assembly the measuring cells were heated to 300°C and then cooled to 0°C and this process was repeated four times. As was found later, this mode of "aging" ensured a good stability of the thermometers in the range 20-200°C. After checking the eccentricity on a BMI microscope all the thermometers of the measuring cells were calibrated at three reference points (melting point of ice, boiling points of water and naphthalene). Besides, the thermometers were periodically checked at these reference points in a thermostat in the range 20-200°C by a standard platinum resistance thermometer.

In the assembled form the measuring cells were 200 mm in length and about 10 mm in diameter. They were placed in a glass case which was later dropped in an autoclave made of stainless steel. In order to produce a uniform temperature field along the length of the measuring cell the autoclave was completely immersed in thermostatting liquid of the thermostat TS-24. The autoclave was rigidly secured to the main wall in order to eliminate vibrations during the operation of the thermostat. The temperature in the thermostat was regulated with the use of a specially constructed thermoregulator operating in conjunction with a wide-pulse modulator based on Hui's principle [39]. This scheme ensured that during the experiments the temperature was held constant at 160°C with an accuracy of ±0.005°C. The measurements by the platinum resistance thermometers were carried out by the usual potentiometer scheme. Potentiometers of type R306 and R307, mirror galvanometers M17/2 and standard resistance coils R321 were used in the measurements.

The measuring cells were checked with water and air. The thermal conductivity of water was measured at 0°C in a Dewar vessel with melting ice and at 30°C in a thermostat. At higher temperatures the thermal conductivity of water was not measured, since electrical connection developed between the resistance thermometers. The thermal conductivity of air was measured in the temperature range 0-180°C. The divergence between the obtained values of thermal conductivities of water and air and the corresponding values found in [40, 41] does not exceed 0.8%. The coefficient of thermal conductivity for water, air, and also toluene was computed from the formula

$$\lambda = \frac{(IU - Q_{\mathrm{e}} - Q_{\mathrm{r}}) \ln \frac{d_{\mathrm{c}}}{d_1}}{2\pi l (\Delta t_{\mathrm{mes}} - \Delta t_{\mathrm{gl}} \pm \Delta t_{\mathrm{cal}})}. \quad (1)$$

TABLE 1. Characteristics of the Measuring Cells

Denomination	Measuring cell			
	No. 1	No. 2	No. 3	No. 4
Type of capillary glass	Skhodninskii	Klinskii	Pyrex	Skhodninskii
Inner diameter of the glass capillary d_i, mm	0.796	1.890	0.941	0.816
Outer diameter of capillary, d_o, mm	1.818	3.830	1.683	1.852
Diameter of platinum filament of inner resistance thermometer, d_1, mm	0.100	0.100	0.100	0.100
Length of measuring segment, l, mm	110.68	111.71	99.95	103.21
Diameter of platinum wire of outer resistance thermometer, d_2, mm	0.10	0.10	0.10	0.10
Thickness of the layer of investigated material, δ, mm	0.348	0.895	0.421	0.358
Resistance of inner thermometer at 0°C, R_0^i, Ω	1.49206	1.41267	1.27644	1.30899
Resistance of outer thermometer at 0°C, R_0^o, Ω	10.10495	8.38531	5.51506	6.36503
Ratio R_{100}^o/R_0^o	1.39124	1.39114	1.39102	1.39103
Ratio R_{100}^i/R_0^i	1.39124	1.39148	1.39102	1.39102
Value of geometrical constant A, m^{-1}	2.98	4.206	3.57	3.24
Eccentricity a, mm	0.017	0.030	0.020	0.035

The computed values of the thermal conductivity pertained to the average temperature over the section of the gap

$$t_{av} = t_1 - \frac{(\Delta t_{mes} - \Delta t_{gl} \pm \Delta t_{cal})}{2} \left\{ 2 - \left[\frac{2}{1 - \left(\frac{d_1}{d_c}\right)^2} - \frac{1}{\ln \frac{d_c}{d_1}} \right] \right\}. \qquad (2)$$

The correction Q_e for the leakage of heat from the ends of the measuring cells was introduced by the well-known procedure [42]. In the experiments it did not exceed 0.3% for water, 1.1% for air, and 0.5% for toluene. The radiation correction Q_r was taken into consideration only in the computation of the thermal conductivity of air. It was 2.7% at 180°C. The correction for the eccentricity was insignificant ($<0.2\%$) and was introduced in the final result.

In order to calculate Δt_{gl} it is necessary to have data on the thermal conductivity of glass as a function of temperature.

For measuring cells No. 1, 2, and 4 the thermal conductivity of glass was computed from the formula [43]

$$\lambda_{gl} = 0.756(1 + 0.0012\ t_{gl}), \qquad (3)$$

while for cell No. 3 it was computed from the formula

$$\lambda_{gl} = 1.037(1 + 0.0011\ t_{gl}). \qquad (4)$$

The calibration correction Δt_{cal} determines the difference in the readings of the inner and outer thermometers at different temperatures and reflects the effect of tension of the spring, which varies with temperature and time. A large amount of experimental data obtained during prolonged operation of the measuring cells showed that the calibration corrections are very stable with time and change with temperature according to a definite law for each cell. The dependence of the calibration correction on the temperature is shown in Fig. 2 for the operation of measuring cell No. 3 during 11 months.

Obviously it is assumed that the outer resistance thermometer measures the temperature of the outer surface of the glass capillary. If this problem is considered rigorously, then it should be noted that theoretically this is possible only for infinitely small thickness of the platinum wire. In reality the diameter of the wire is comparable with the outer diameter of the capillary; in this case even for a very high coefficient of thermal conductivity of platinum the resistance thermometer would indicate the temperature of the boundary layer. In order to obtain a qualitative estimate of this temperature difference four measuring cells with different diameters of the glass capillaries and different spacing of winding of the resistance thermometers were prepared. The measurements of the thermal conductivity of water, air, and toluene with these cells showed that this effect is apparently very small and lies within the limits of the error of measurements.

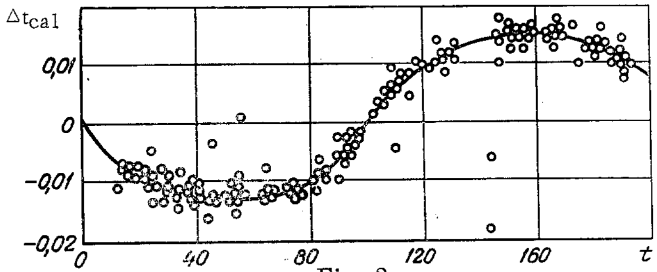

Fig. 2

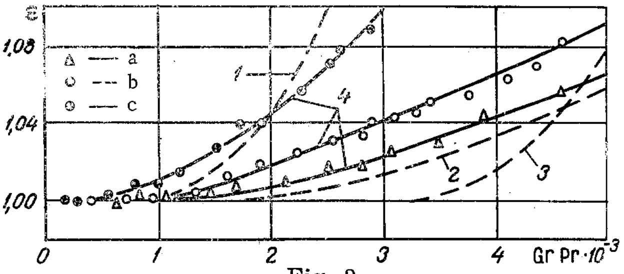

Fig. 3

Fig. 2. Dependence of the calibration correction Δt_{cal} (°C) on temperature (°C) for cell No. 3.

Fig. 3. Dependence of the convection coefficient ε on the product GrPr: 1) from Kraussold's equation; 2) from Berkengeim's equation; 3) from data of [47]; 4) from our data: a) for cell No. 1; b) for cell No. 2; c) for cell No. 2 in the presence of insignificant vibration.

In conducting the experiments considerable attention was devoted to the elimination of natural convection in the liquid layer and the convection due to the vibrations of the equipment. In vertical gaps the convection may arise not only due to a large temperature gradient in the radial direction, but also due to the temperature differential along the height of the liquid layer. The uniformity of the temperature field along the height of the measuring cell was controlled in the experiments by a three-junction differential thermocouple. In the first experiments the temperature gradient along the height reached a value of $0.2 \cdot 10^{-4}$ deg/mm. To eliminate this the top of the thermostat was further insulated with a thick asbestos layer; as a result the gradient was reduced to 0 and only at 180°C it reached $0.1 \cdot 10^{-4}$ deg/mm.

Kraussold [44] has shown that natural convection in vertical gaps begins at $(\mathrm{GrPr}) \geq 1000$. Recent works [45–47] on the investigation of natural convection in cylindrical gaps of small diameter displace this threshold toward larger values of GrPr.

In order to determine the threshold of occurrence of convection in our experiments special investigations were carried out in measuring cells No. 1 and 2 for different temperature differentials in the liquid layer and for different values of $(\mathrm{GrPr}) \leq 4500$. The dependence of the convection coefficient $\varepsilon = \lambda_{eff}/\lambda$ on the product GrPr is shown in Fig. 3 for cells No. 1 and 2.

In the experiments with cell No. 2 ($d_i = 1.89$ mm) the convection started at $(\mathrm{GrPr}) = 540$. It was found later that the lowering of the threshold for the onset of convection was caused by a small vibration of the equipment.

After taking special measures (installation of shock absorbers and additional weight on the thermostat motor) the convection in cell No. 2, placed in the thermostat, started at $(\mathrm{GrPr}) = 1000$.

It was interesting to check the effect of small vibrations in the measurement of thermal conductivity of toluene. For this purpose the rigid connection of the autoclave together with the measuring cell No. 2 was removed and the unit was secured to the lid of the thermostat. The results of this experiment are presented in Fig. 4. It was found that in the presence of vibrations the thermal conductivity of toluene increased by 1.7% and the temperature coefficient decreased from 0.002 to 0.00156 deg^{-1}. The results obtained in this experiment are in good agreement with those of many other investigations.

In cell No. 1 ($d_i = 0.796$ mm) convection started at $(\mathrm{GrPr}) \geq 1000$, but it developed considerably more slowly, i.e., in this case the walls of the capillary apparently have a restricting effect.

In view of this all the experiments for the determination of thermal conductivities of water, air, and toluene were conducted at $(\mathrm{GrPr}) < 1000$.

An analysis of the quantities occurring in Eq. (1) showed that the maximum relative error of the experimental results in cells No. 1, 3, and 4 is ±1.3%, and in cell No. 2 ±1.5%. In the measurements of the thermal conductivity of air the error increases up to ±2%.

RESULTS AND DISCUSSION

The toluene chosen for the investigation was designated "Scintillation toluene; special purity," in accordance with GOST (All-Union State Standard) 1318-57 ($\rho_4^{20} = 0.8669$; $n_D^{20} = 1.4969$). The presence of

TABLE 2. Experimental Values of the Coefficient of Thermal Conductivity of Toluene (W/m · deg)

t_{av}, °C	λ	t_{av}, °C	λ	t_{av}, °C	λ
		Cell No. 2		60,04	0,1188
Cell No. 1		3,81	0,1370	62,71	0,1184
		4,63	0,1368	69,10	0,1164
27,20	0,1275	25,98	0,1312	72,01	0,1162
27,42	0,1273	26,90	0,1308	75,42	0,1142
27,65	0,1271	50,11	0,1249	78,81	0,1139
30,13	0,1269	51,82	0,1243	86,11	0,1120
31,21	0,1266	74,32	0,1185	88,18	0,1114
54,26	0,1207	75,98	0,1182	95,76	0,1095
55,23	0,1202	101,79	0,1114	99,36	0,1085
55,73	0,1201	102,16	0,1113	107,02	0,1063
56,26	0,1198	Cell No. 3		115,87*	0,1042
59,51	0,1190	3,12	0,1342	118,99*	0,1034
59,55	0,1189	4,47	0,1338	Cell No. 4	
59,77	0,1188	19,32	0,1298		
61,40	0,1184	21,06	0,1294	3,53	0,1337
76,91	0,1146	25,81	0,1281	4,68	0,1335
81,44	0,1133	27,59	0,1278	31,67	0,1265
84,87	0,1128	30,87	0,1267	34,12	0,1258
90,14	0,1110	33,60	0,1260	58,03	0,1194
93,66	0,1100	36,55	0,1253	61,14	0,1188
100,14	0,1086	38,44	0,1248	72,89	0,1142
101,49	0,1078	39,05	0,1245	74,16	0,1139
106,04*	0,1070	44,46	0,1231	97,34	0,1087
118,43*	0,1040	46,72	0,1225	99,10	0,1083
123,63*	0,1025	54,69	0,1202	109,79*	0,1056
130,91*	0,1005	57,69	0,1193	113,81*	0,1048

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*In the experiments the pressure was maintained equal to 0.98 Mn/m^2.

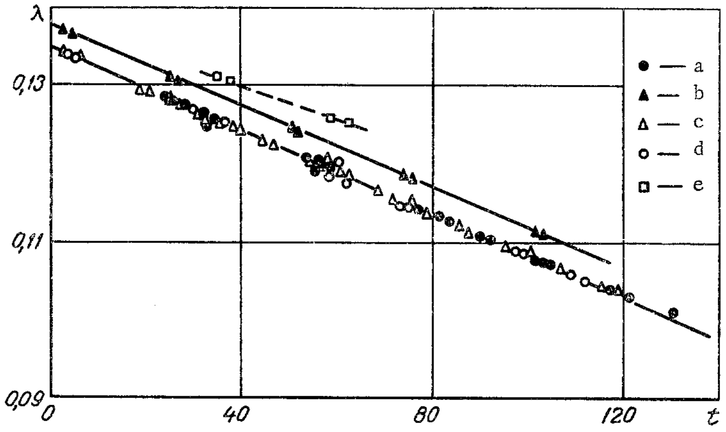

Fig. 4. Dependence of the coefficient of thermal conductivity (W/m ·deg) of toluene on temperature (°C): a) for cell No. 1; b) for cell No. 2; c) for cell No. 3; d) for cell No. 4; e) for cell No. 2 in the presence of vibrations.

impurities in the sample was checked on a KhT-63 chromatograph before and after the experiments. No impurities were detected. The experimental data on the thermal conductivity of toluene are presented in Table 2 and also in the form of graphs in Fig. 4.

It is evident from an inspection of Fig. 4 that the values of the coefficient of thermal conductivity of toluene, obtained in measuring cells No. 1, 3, and 4 with almost the same thickness of the liquid layer, are in good agreement with each other. The scatter of the data is not more than 0.7%. However, these results appear to be underestimated compared to those of other investigators [1-3, 7, 9, 10, 26, 30-32] by 3-6% on the average.

The experimental data obtained in measuring cells No. 1, 3, and 4 are described by the equation

$$\lambda_t = 0.127\,[1 - 0.0021\,(t - 30)]. \tag{5}$$

with error less than 1%. At the same time in cell No. 2, in which the gap is 2.5 times larger than in the others, the obtained values of the thermal conductivity are higher than in the cells with small gap by 2.3%.

The difference was not observed in the experiments with water and air. The thermal conductivity of toluene was then measured in a Dewar vessel and in a hypsometer. The experiments confirmed the results obtained earlier. Hence, this increase can not be explained by vibrations. The experimental procedure also excluded natural convection. Then it can apparently be assumed that the thermal conductivity depends on the thickness of the liquid layer, which does not occur in the computational equation. This assumption is not new, since similar phenomena were noticed by Dick and McCready [48], Sutherland [49], and Poltz [12, 13] in the measurement of the thermal conductivity of liquids by the slab method. The explanations offered were different. In the discussion of [48] Bonilla assumed that in all probability this is a result of radiation. Sutherland explained the increase in the thermal conductivity with the increase in the thickness of the liquid layer as due to the orienting effect of the metallic surfaces on the molecules of the liquid; the degree of this influence changes with the gap thickness. Poltz investigated this phenomenon especially; he assumed that in liquids with weak infrared absorption the heat transfer in the layer can occur also due to radiation. He showed that the radiative component in the process of heat transfer through the toluene layer can reach 5-7% and may increase with temperature. In [50] he has presented an equation for the computation of the radiative component as a function of the absorption coefficient of the medium, the degree of blackness of the surfaces, and temperature for the case of a plane layer of infinite dimensions. The derivation of the equation for a cylindrical layer encounters great mathematical difficulties. In view of this it is not possible to estimate the radiative component. It must be mentioned that the increase in the thermal conductivity of liquids, having weak infrared absorption, with the increase in the thickness of the layer is of special interest and needs to be checked carefully. All the more so, as our analysis of a large volume of experimental data on the thermal conductivity of toluene [1-38] has shown that there is a tendency toward an increase of the thermal conductivity with the increase in the gap thickness. This is particularly clear for plane and cylindrical gaps (with $d_i \approx d_o$).

Our results obtained on measuring cells No. 1, 3, and 4 differ from those of Poltz and Jugel [13] by 1.7% for the gap with 0.4581 mm thickness and exactly coincide with their results extrapolated to zero gap. The values of the thermal conductivity of toluene, obtained in [4] by the filament method, are overestimated compared to ours by 2%. It is interesting to note that the results of [4], as also ours, are found to be underestimated on the average by 3-6% compared to those of other investigators, obtained on equipment using the method of plane layer and coaxial cylinders.

NOTATION

R	is the electrical resistance;
λ	is the coefficient of thermal conductivity;
I	is the current intensity in the filament circuit;
U	is the voltage drop in the filament;
t	is the temperature;
Δt	is the temperature difference;
Q	is the heat flux;
l	is the length of the measuring segment;
d	is the diameter;
A	is the geometrical constant of the measuring cell;
a	is the eccentricity;
Gr	is the Grashof number;
Pr	is the Prandtl number;
n	is the refractive index;
ρ	is the density;
δ	is the layer thickness;
ε	is the convection coefficient.

Subscripts

i	denotes inner;
o	denotes outer;
av	denotes average;
eff	denotes effective;
m	denotes measured;
cal	denotes calibration;

gl denotes glass;
r denotes radiative;
e denotes ends;
0 denotes 0°C;
4 denotes 4°C;
20 denotes 20°C;
100 denotes 100°C;
D denotes green line of sodium;
1 denotes inner thermometer;
2 denotes outer thermometer.

LITERATURE CITED

1. E. Schmidt and W. Leidenfrost, Chem. Ing. Tech., 26, 35 (1954).
2. L. Riedel, Chem. Ing. Tech., 23, 321 (1951).
3. L. Riedel, Forschung, 11, 340 (1940).
4. B. Zudzinowicz, R. Cambell, and J. Adams, J. Chem. Engng. Data, 9, 79 (1964).
5. H. Ziebland and J. Burton, J. Chem. Engng. Data, 6, 579 (1961).
6. D. Briggs, Ind. Engng. Chem., 49, 418 (1957).
7. H. Ziebland, Int. J. Heat and Mass Transfer, 2, 273 (1961).
8. H. F. Weber, Repert. d. Phys., 22, 116 (1886).
9. J. Venart, J. Sci. Instr., 41, 727 (1964).
10. J. Venart, J. Chem. Engng. Data, 10, 239 (1965).
11. A. Challoner and R. Powell, Proc. Roy. Soc., A238, 90 (1956).
12. H. Poltz, Int. J. Heat and Mass Transfer, 8, 609 (1965).
13. H. Poltz and R. Jugel, Int. J. Heat and Mass Transfer, 10, 1075 (1967).
14. V. Schrock and E. Starkman, Rev. Sci. Instr., 29, 625 (1958).
15. J. Horrocks and E. McLaughlin, Proc. Roy. Soc., A273, 259 (1963).
16. A. Challoner, H. Gundry, and R. Powell, Proc. Roy. Soc., A245, 259 (1958).
17. R. Tufeu, B. Neidre, and R. Johannin, C.R. Acad. Sci., 262, 229 (1966).
18. R. Goldschmidt, Phys. Zeit., 12, 417 (1911).
19. A. Davis, Phil. Mag., 47, 972 (1924).
20. A. Kardos, Z. Ver. Deut. Ing., 77, 1158 (1933).
21. H. Tautz and H. Lippmann, Plast und Kauts., 9, 595 (1962).
22. J. F. Smith, Ind. Engng. Chem., 22, 1246 (1930).
23. A. K. Abas-Zade, Dokl. Akad. Nauk AzSSR, 3, No. 1 (1947); Dokl. Akad. Nauk SSSR, 68, 665 (1949).
24. A. K. Abas-Zade and M. F. É'fendiev, Az. Neft. Khoz., No. 12 (1965).
25. S. V. Starodubtsev, R. A. Akbaev, and B. S. Mazitov, Dokl. Akad. Nauk UzSSR, 4, 21 (1966).
26. N. B. Vargaftik, Izvestiya VTI, No. 8 (1949).
27. V. P. Frontas'ev, Zavodskaya Laboratoriya, No. 7 (1956).
28. V. P. Frontas'ev and M. Ya. Gusakov, Zh. Tekh. Fiz., 29, 1275 (1959).
29. G. N. Skrynnikova, Candidate's Dissertation [in Russian], LGU (1954).
30. V. Z. Geller, Candidate's Dissertation [in Russian], MEI (1968).
31. O. B. Tsvetkov, Candidate's Dissertation [in Russian], Leningrad (1965).
32. G. Kh. Mukhamedzyanov, Candidate's Dissertation [in Russian], KKhTI (1964).
33. P. V. Bridgmen, Fiz. Vys. Davl., ONTI (1935).
34. Z. I. Geller and Yu. L. Rastorguev, Chemistry and Technology of Fuel and Oil [in Russian], No. 10 (1958).
35. Z. I. Geller, Yu. L. Rastorguev, and Yu. A. Ganiev, Izv. Vuzov SSSR, Neft' i Gaz, No. 6 (1965).
36. L. T. Krasivskaya, Report, Ural Polytechnical Institute, 81, 78 (1959).
37. L. P. Filippov, Bull. MGU, Phys.-Math. and Natural Sciences Series, No. 9 (1953).
38. B. I. Brounshtein and V. R. Zharkova, Report VNIINKhP, 5, 39 (1962).
39. J. G. Becsey and J. A. Bierlein, Rev. Sci. Instr., 38, 556 (1967).
40. M. P. Bukalovich, Thermophysical Properties of Water and Water Vapor [in Russian], Mashizdat, Moscow (1967).
41. A. A. Vasserman, Ya. Z. Kazavchinskii, and V. A. Rabinovich, Thermophysical Properties of Air and Its Components [in Russian], Nauka, Moscow (1966).
42. D. L. Timrot and N. B. Vargaftik, Izvestiya VTI, No. 9 (1935).

43. N. B. Vargaftik, Thermophysical Properties of Materials [in Russian], Gosénergoizdat, Moscow (1956).
44. H. Kraussold, Forschung, 5, 186 (1934).
45. R. V. Shingarev, Candidate's Dissertation [in Russian], VTI, Moscow (1952).
46. A. A. Berkengeim, Inzh.-Fiz. Zh., 10, 459 (1966).
47. Yu. L. Rastorguev and V. Z. Geller, Inzh.-Fiz. Zh., 13, 16 (1967).
48. M. F. Dick and D. W. McCready, Trudy ASME, 76, 831 (1954).
49. R. Sutherland, R. Davies, and W. Seyer, Ind. Engng. Chem., 51, 585 (1959).
50. H. Poltz, Int. J. Heat and Mass Transfer, 8, 515 (1965).