EXPERIMENTAL STUDY OF THE THERMAL CONDUCTIVITY OF TOLUENE AT HIGH PRESSURES

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The experimental apparatus used for determining the thermal conductivity of toluene at temperatures of 0-180°C and pressures of 0.098-49.0 MN/m^2 is described, and some of the results are presented. Computing relationships providing an excellent representation of the experimental data are derived.

The thermal conductivity of toluene was measured by the heated-filament method using the apparatus depicted in Fig. 1. In the experiments we used a measuring cell of the No. 3 type, the construction of which was described in full detail in [1]. The measuring cell 4 was placed in the autoclave 3, made of Kh17N13M2T steel. In order to smooth out the temperature field of the autoclave and reduce the temperature gradient along it, the autoclave was placed in a massive copper cylinder 5, with a gap of 1 mm between the two, the whole then being immersed in the thermostatting liquid of the thermostat 6 (TS-24 type). As thermostatting liquid we used spindle oil. In order to eliminate the vibration of the measuring cell during the operation of the thermostat, the autoclave and copper cylinder were fixed rigidly to the main wall. The temperature in the thermostat was stabilized by means of a specially manufactured thermal regulator coupled to a pulse-width modulator based on the Gouy principle [2]. This stabilization system reduced the temperature fluctuations in the thermostat to ±0.005 deg in experiments up to 160°C; at higher temperatures the fluctuations increased slightly to ±0.01 deg. The temperature fluctuations within the autoclave were much smaller than those within the thermostat on account of the thermal inertia of the copper-cylinder–air-gap–autoclave system. The temperature gradient along the measuring cell was monitored by means of a three-junction differential thermocouple, and in the experiments at 180°C never exceeded $0.1 \cdot 10^{-3}$deg/mm.

The pressure in the autoclave was created by way of a bellows separating vessel 9, using a hydraulic press, and was measured with a piston manometer 1 of the MP-600 type (class 0.05). The position of the bellows in the separating vessel was checked by reference to the motion of a core set in the bottom of the bellows, aided by an induction coil 8 and a secondary electronic instrument 7 of the ÉPID type.

The experimental value of the pressure was corrected for the effect of the rigidity of the bellows; this was determined by comparing the readings of the piston manometer MP-600 with those of a standard class 0.4 manometer 13, which was only connected for the calibration purposes. Low pressures (up to 5 MN/m^2) were created in the autoclave by means of nitrogen, for which purpose a special line was provided, connecting the autoclave 3 through the expander 16 to the nitrogen cylinder 11.

The measuring cables were taken out of the high-pressure zone through a gland seal extending into the low-temperature region.

The autoclave and bellows separating vessel were filled with the test liquid by means of the glass vessels 14 and 15 with the vacuum pump 2 connected. The rarefaction created by the vacuum pump, equal to 10^{-2} mm Hg, ensured the reliable filling of the apparatus with liquid, without any air bubbles being admitted. The line joining the piston manometer 1 to the separating vessel 14 was also filled under vacuum. The product was removed from the apparatus through a special valve. After the removal of the product, the apparatus was repeatedly washed with petroleum ether, and then air, purified in a zeolite filter 10 and heated to 300°C in an electric furnace 12, was blown through.

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TABLE 1. Experimental Values of the Thermal Conductivities (W/m · deg) of Toluene

t_{av}, °C	λ	t_{av}, °C	λ	t_{av}, °C	λ	t_{av}, °C	λ	t_{av}, °C	λ	t_{av}, °C	λ	t_{av}, °C	λ	t_{av}, °C	λ
P=0,098	MN/m^2	99,36	0,1085	78,65	0,1182	P=19,6	MN/m^2	113,49	0,1156	P=34,3	MN/m^2	95,10	0,1250	113,08	0,1227
3,12	0,1342	107,02	0,1063	75,27	0,1189	30,69	0,1333	129,10	0,1127	30,59	0,1378	98,37	0,1241	129,46	0,1196
4,47	0,1338	P=0,98	MN/m^2	95,58	0,1140	33,36	0,1328	130,86	0,1119	33,20	0,1373	109,97	0,1221	132,02	0,1190
19,32	0,1298	115,87	0,1042	99,10	0,1132	54,47	0,1276	152,73	0,1076	54,32	0,1323	113,14	0,1215	154,91	0,1150
21,06	0,1294	118,99	0,1034	108,44	0,1109	57,39	0,1268	154,68	0,1073	57,25	0,1317	130,05	0,1179	157,07	0,1148
25,81	0,1281	P=4,9	MN/m^2	110,40	0,1104	75,14	0,1225	P=29,4	MN/m^2	74,93	0,1275	132,67	0,1173	177,25	0,1108
27,59	0,1278	33,53	0,1278	128,61	0,1063	78,54	0,1215	30,61	0,1364	78,18	0,1268	154,33	0,1134	176,33	0,1114
30,87	0,1267	30,82	0,1283	130,15	0,1059	95,44	0,1178	33,25	0,1360	95,28	0,1234	156,06	0,1131	P=49,0	MN/m^2
33,60	0,1260	57,61	0,1212	153,12	0,1004	98,95	0,1171	54,36	0,1308	98,59	0,1226	176,82	0,1096	30,46	0,1421
36,55	0,1253	54,64	0,1221	154,85	0,1001	110,23	0,1144	57,25	0,1303	109,81	0,1198	178,33	0,1093	33,06	0,1414
38,44	0,1248	75,34	0,1166	P=14,7	MN/m^2	114,00	0,1136	75,00	0,1260	113,12	0,1194	P=44,1	MN/m^2	54,16	0,1368
39,05	0,1245	78,71	0,1159	30,74	0,1314	129,20	0,1106	78,25	0,1253	130,09	0,1160	30,50	0,1408	56,97	0,1357
44,46	0,1231	95,67	0,1117	33,42	0,1312	130,99	0,1100	95,43	0,1214	132,04	0,1154	33,10	0,1401	74,79	0,1319
46,72	0,1225	99,27	0,1107	54,52	0,1258	153,29	0,1054	98,75	0,1208	152,57	0,1117	54,22	0,1354	78,00	0,1314
54,69	0,1202	109,77	0,1085	57,45	0,1249	155,29	0,1050	109,89	0,1182	154,42	0,1113	57,04	0,1347	94,95	0,1282
57,69	0,1193	106,98	0,1088	75,22	0,1207	P=24,5	MN/m^2	113,26	0,1175	P=39,2	MN/m^2	74,84	0,1304	98,24	0,1273
60,04	0,1188	128,29	0,1038	78,56	0,1198	30,65	0,1348	128,84	0,1144	30,55	0,1389	78,04	0,1298	110,31	0,1247
62,71	0,1184	130,03	0,1030	95,49	0,1161	33,31	0,1343	130,27	0,1141	33,15	0,1385	95,01	0,1268	113,58	0,1250
69,10	0,1164	152,84	0,0978	99,02	0,1153	54,42	0,1291	152,62	0,1094	54,47	0,1335	98,35	0,1257	133,82	0,1206
72,01	0,1160	154,31	0,0976	110,32	0,1124	57,32	0,1284	154,47	0,1090	57,60	0,1329	109,75	0,1234	154,76	0,1169
75,42	0,1142	P=9,8	MN/m^2	114,09	0,1115	75,07	0,1240			74,88	0,1290			156,98	0,1165
78,81	0,1139	30,78	0,1296	129,26	0,1080	78,34	0,1233			78,09	0,1284			176,86	0,1132
86,11	0,1120	33,48	0,1294	131,07	0,1076	95,47	0,1196							179,97	0,1129
88,18	0,1114	54,58	0,1241	153,08	0,1027	98,88	0,1187								
95,76	0,1095	57,52	0,1234	154,44	0,1023	110,02	0,1165								

TABLE 2. Comparison Between the Experimental Thermal Conductivities of Toluene (W/m · deg) and Those Calculated from Eqs. (4) and (7)

p, MN/m^2	Temperature, °C							Temperature, °C						
	20			60				100		140			180	
	λ_{ex}	$\lambda_{(4)}$	$\lambda_{(7)}$	λ_{ex}	$\lambda_{(4)}$	$\lambda_{(7)}$	λ_{ex}	$\lambda_{(4)}$	$\lambda_{(7)}$	λ_{ex}	$\lambda_{(4)}$	$\lambda_{(7)}$	λ_{ex}	$\lambda_{(4)}$	$\lambda_{(7)}$
0,098	0,1297	0,1295	0,1300	0,1189	0,1186	0,1190	0,1082	0,1081	0,1083	—	—	—	—	—	—
4,9	0,1313	0,1313	0,1317	0,1207	0,1207	0,1207	0,1106	0,1106	0,1103	0,1010	0,1014	0,1008	—	—	—
9,8	0,1330	0,1330	0,1334	0,1227	0,1226	0,1223	0,1129	0,1129	0,1122	0,1035	0,1040	0,1031	—	—	—
14,7	0,1344	0,1346	0,1348	0,1244	0,1245	0,1240	0,1148	0,1151	0,1142	0,1056	0,1065	0,1055	—	—	—
19,6	0,1360	0,1366	0,1363	0,1260	0,1263	0,1254	0,1167	0,1170	0,1160	0,1081	0,1085	0,1077	—	—	—
24,5	0,1374	0,1377	0,1378	0,1277	0,1279	0,1270	0,1185	0,1188	0,1178	0,1101	0,1105	0,1098	0,1023	0,1032	0,1031
29,4	0,1390	0,1391	0,1393	0,1295	0,1295	0,1287	0,1204	0,1206	0,1197	0,1119	0,1123	0,1119	0,1042	0,1052	0,1054
34,3	0,1405	0,1406	0,1407	0,1309	0,1311	0,1304	0,1221	0,1223	0,1214	0,1140	0,1142	0,1141	0,1064	0,1071	0,1074
39,2	0,1415	0,1419	0,1420	0,1322	0,1326	0,1321	0,1238	0,1239	0,1233	0,1160	0,1159	0,1157	0,1090	0,1088	0,1094
44,1	0,1432	0,1432	0,1434	0,1340	0,1340	0,1336	0,1253	0,1254	0,1250	0,1177	0,1175	0,1176	0,1108	0,1105	0,1113
49,0	0,1441	0,1444	0,1449	0,1354	0,1354	0,1351	0,1269	0,1269	0,1270	0,1194	0,1191	0,1193	0,1128	0,1121	0,1131

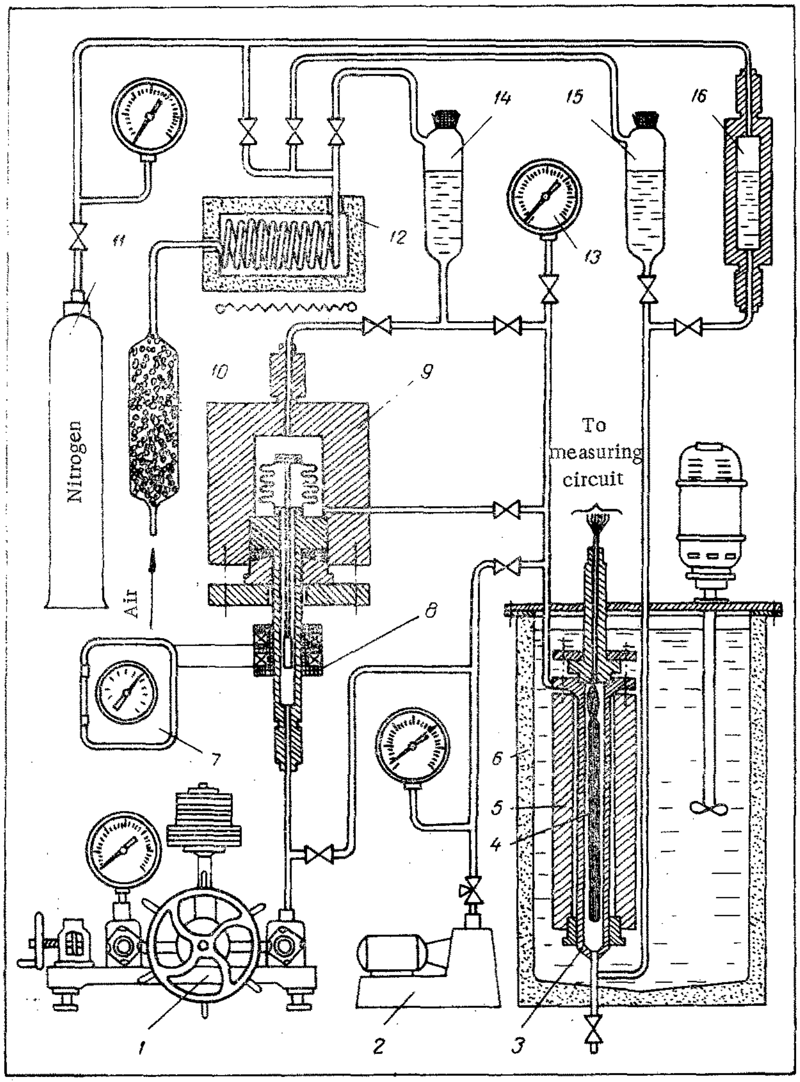

Fig. 1. Arrangement of the experimental apparatus.

The measuring part of the apparatus was made on the usual potentiometric principle. The internal resistance thermometer, which also served as a heater, was supplied from a 4TZhN-250 storage battery. The thermometer circuit incorporated a 1 Ω standard coil taken from an electrical resistance of the R-321 type (class 0.01). The electrical measurements were made with an R307 potentiometer and an M17/2 mirror galvanometer. A current of 1.5 mA was passed through the external resistance thermometer, the source of this being a heater battery of the 1.28-NVMTs-525 type (Deviz brand). The thermometer circuit incorporated a standard 10 Ω coil taken from an electrical resistance of the R-321 type (class 0.01), and the electrical measurements were made with the help of an R306 potentiometer and an M17/2 mirror galvanometer. In order to eliminate the effect of parasitic thermo-emf in the thermometric circuits, all the measurements were carried out with currents flowing in opposite directions. The current circuits were reversed by means of oil switches.

In calculating the thermal conductivity, all the corrections associated with the heated-filament method were introduced; these were set out in detail in [1].

In the experiments we used toluene of the "Scintillation toluene – high purity" type, as standardized by the All-Union State Standard 1318-57 ($\rho_4^{20} = 0.8669$, $n_D^{20} = 1.4969$). The thermal conductivity was measured along isotherms in steps of 4.9 MN/m^2 for two values of the temperature drop in the liquid layer and a criterion product GrPr < 1000. Experiments were carried out both as the pressure was being raised to its maximum value and also as it was being reduced from the maximum to atmospheric pressure. Altogether 173 experimental points were obtained. The maximum relative error in the experimental data was estimated at ±1.3%. The scatter in the experimental points was no greater than 0.8%. The results of our measurements of the thermal conductivity of toluene are presented in Table 1.

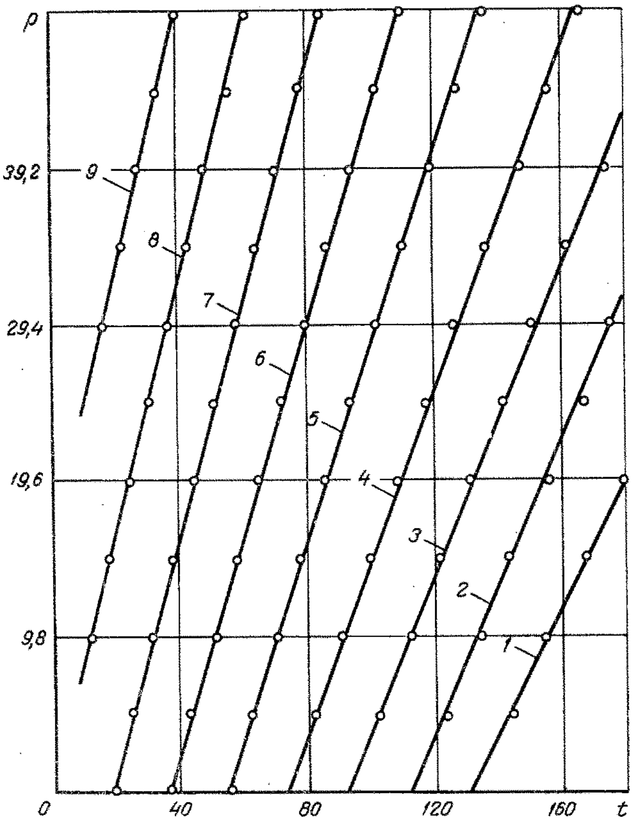

Fig. 2. The p–t sections of the λ–p–t-surface of toluene (p in MN/m², t in °C): 1) λ = 0.100; 2) 0.105; 3) 0.110; 4) 0.115; 5) 0.120 ; 6) 0.125; 7) 0.130; 8) 0.135; 9) 1.140.

TABLE 3. Density of Toluene (kg/m³) as a Function of Temperature and Pressure

t, °C	p, MN/m²										
	0,098	4,9	9,8	14,7	19,6	24,5	29,4	34,3	39,2	44,1	49,0
20	865,1	869,5	873,0	876,1	879,0	882,0	885,2	888,1	890,8	893,5	896,1
30	857,5	861,5	865,0	868,2	871,3	874,5	877,6	880,7	883,6	886,7	889,3
40	849,1	853,1	856,7	860,1	863,5	868,0	870,0	873,2	876,3	879,5	882,4
50	840,8	844,6	848,2	851,8	855,4	858,7	862,1	865,8	869,0	872,2	875,4
60	832,1	835,8	839,6	843,5	847,2	850,5	849,3	858,0	861,6	865,0	868,8
70	822,9	826,8	830,8	835,0	838,7	842,3	846,4	850,3	854,2	857,8	861,3
80	813,1	817,5	821,7	826,2	830,3	834,1	838,5	842,5	846,6	850,3	854,1
90	803,1	807,8	812,6	817,5	821,8	825,3	830,4	834,7	838,9	842,8	846,8
100	792,8	797,8	803,2	808,3	813,0	817,4	822,1	826,6	831,0	835,4	839,3
110	782,4	787,7	793,5	798,9	804,0	808,9	813,9	818,5	823,0	827,7	831,8
120	771,6	778,5	783,5	789,6	794,9	800,1	805,6	810,2	814,8	819,2	824,2
130	767,0	773,5	780,1	785,7	791,2	797,0	799,7	801,9	806,5	811,7	816,6
140	751,8	756,2	763,5	770,5	776,6	782,4	788,5	793,7	798,3	803,7	808,8
150	737,3	745,1	753,3	760,8	767,2	773,3	779,7	785,2	790,0	795,5	800,8
160	725,3	733,8	743,1	750,7	757,7	764,1	770,8	776,6	781,6	787,2	792,5
170	712,7	722,2	732,3	740,7	748,1	755,0	761,8	767,7	773,0	778,7	784,0
180	689,6	710,7	721,1	730,3	738,3	745,5	752,6	758,8	764,4	770,2	775,5

In order to establish the general laws relating the thermal conductivity of toluene to temperature and pressure, and to derive an analytical relationship of the λ = f(p, t) type, we analyzed the experimental data and plotted λ–t, λ–p and p–t sections of the λ–p–t-surface of toluene. On analyzing the resultant sections, we may draw the following simple conclusion: The thermal conductivity of toluene falls with rising temperature and increases with rising pressure. The isotherms and isobars of thermal conductivity constitute slightly curved lines. The isobars are bent downward toward the temperature axis and the isotherms upward, away from the pressure axis. The effect of pressure on the thermal conductivity increases with rising pressure. Thus at 20°C

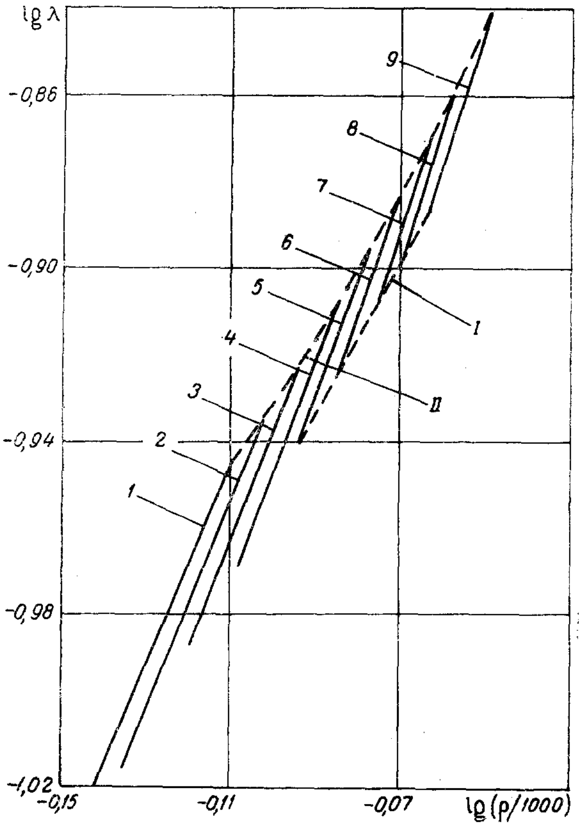

Fig. 3. The log λ −log (ρ/1000) relationship for toluene: 1) 180°C; 2) 160°C; 3) 140; 4) 120; 5) 100; 6) 80; 7) 60; 8) 40; 9) 20°C; I) p = 0.98; II) p = 49.0 MN/m².

$$\left(\frac{\partial\lambda}{\partial p}\right)_t^{\mathrm{av}} = 294\cdot 10^{-6}\,\frac{\mathrm{W\cdot m^2}}{\mathrm{m\cdot deg\cdot MN}},$$

and at 180°C

$$\left(\frac{\partial\lambda}{\partial p}\right)_t^{\mathrm{av}} = 429\cdot 10^{-6}\,\frac{\mathrm{W\cdot m^2}}{\mathrm{m\cdot deg\cdot MN}}.$$

The p−t sections of the λ−p−t-surface are of particular interest; in these sections the lines of constant thermal conductivity are straight, within the limits of experimental error (Fig. 2), and may be described by the equation

$$p = a + bt. \tag{1}$$

For the coefficients a and b we obtained the following expressions by the method of least squares

$$a = 40828\lambda^2 - 8153\lambda + 358, \tag{2}$$

$$b = 11.81\lambda - 0.7993. \tag{3}$$

After substituting (2) and (3) into (1), we obtain an equation for calculating the thermal conductivity of toluene as a function of temperature and pressure:

$$\lambda_{t,p} = 0.0998 - 0.000145t + \sqrt{0.209\cdot 10^{-7}t^2 - 0.929\cdot 10^{-5}t + 0.244\cdot 10^{-4}p + 1.212\cdot 10^{-3}}. \tag{4}$$

Table 2 compares the experimental data relating to the thermal conductivity of toluene with those calculated from Eq. (4). The deviations are no greater than 1.0%.

In order to extrapolate experimental data relating to the thermal conductivity of organic liquids at atmospheric pressure, the following well-known relationship is often employed [3]

$$\lambda_t = B\left(\frac{\rho_t}{1000}\right)^{4/3}. \tag{5}$$

In order to use this equation for pressures above atmospheric, it is essential to possess p−ρ−t-data. So far as we know, the literature contains no such data for toluene. We therefore made an attempt at obtaining p−ρ−t-data for toluene by calculation. For calculating the density of toluene as a function of temperature and pressure, we used the law of corresponding states in its most general form

$$\pi = F(\varphi, \tau). \tag{6}$$

The computing method was as follows. First we verified the law of corresponding states at atmospheric pressure for several aromatic hydrocarbons: benzene, m-xylene, p-xylene, o-xylene, and toluene; we did likewise for n-hexane and n-heptane. We then found the $\rho/\rho_{\mathrm{cr}} = f_1(T/T_{\mathrm{cr}})$ relationship. The critical parameters ρ_{cr} and T_{cr} were taken from [4] and the density data from [5]. In generalized coordinates, the data relating to m-xylene, toluene, n-heptane, and n-hexane lay on a single common curve. Those relating to benzene, o-xylene, and p-xylene, however, deviated seriously from this curve. We then verified the law of corresponding states for n-hexane [6], n-heptane [7], and m-xylene [8] over the pressure range 0.098-49 MN/m² and the temperature range 20-200°C. As at atmospheric pressure, the densities of these compounds lay accurately on the generalized curves, the deviations never exceeding ±0.5%.

Subsequently we took m-xylene as standard substance, since reliable experimental data regarding the p−ρ−t-relationship were available for this compound [8]. In addition to this, m-xylene and toluene have neighboring values of the Hirschfelder and Guldberg similarity criteria.

Using the experimental data, we plotted the isochoric, isobaric, and isothermal sections of the surface of state of m-xylene, and matched the data in these sections. Since the density values were only given up to 20 MN/m² in [8], we extrapolated the density of m-xylene to a pressure of 49 MN/m².

Then the smoothed experimental data taken from the curves of the isobaric section were expressed in generalized coordinates $\pi = p/p_{cr} - \varphi = \rho/\rho_{cr}$ along the isotherms $\tau = T/T_{cr}$. For m-xylene we took the following values of the critical parameters: $p_{cr} = 3.43$ MN/m^2, $T_{cr} = 619.13$°K; $\rho_{cr} = 285$ kg/m^3.

Assuming that the law of corresponding states was valid for m-xylene and toluene, for specified values of π and τ we found $\varphi = \rho/\rho_{cr}$, and then calculated the reference values of the density of toluene, from which we plotted the isobaric, isothermal, and isochoric sections of the ρ–ρ–t-surface. For toluene we took the following critical parameters: $p_{cr} = 3.92$ MN/m^2; $T_{cr} = 593.93$°K; $\rho_{cr} = 289$ kg/m^3.

The calculated densities of toluene for various temperatures and pressures are presented in Table 3.

The resultant data enabled us to calculate the isothermal compressibility of toluene $\beta_T = (1/v_0)(\partial v/\partial p)_{t=25°}$, the value of which agreed closely with the data of [9].

We see from Fig. 3 that the coefficient B and the power index n associated with the $\rho/1000$ in Eq. (5) are not constant but depend on the temperature. With increasing pressure the isobars become curved, particularly in the high-temperature region. Only at atmospheric pressure is $(\partial \log \lambda/\partial \log \rho)_p = \text{const}$. However, for the whole of the pressure range studied the isotherms are straight lines, $n = (\partial \log \lambda/\partial \log \rho)_t$ being constant for these. With increasing temperature n diminishes, as a result of which the isotherms approach one another in the region close to the solid state. Analysis of the experimental data, expressed in terms of the isotherms in Fig. 3, yields the following expression for n:

$$n = 3.252 - 5.03 \cdot 10^{-3} t.$$

The coefficient B changes very little with temperature; its value may be regarded as constant and equal to B = 0.2070.

Then the computing equation for calculating the thermal conductivity of toluene in terms of the density over a wide range of variation of the determining parameters may be written in the following way:

$$\lambda_{t,p} = 0.2070 \left(\frac{\rho_{t,p}}{1000} \right)^{3.256 - 5.03 \cdot 10^{-3} t} \tag{7}$$

Table 2 compares the experimental data relating to the thermal conductivity of toluene with those calculated by means of Eq. (7). The deviations never exceed 1.0%.

NOTATION

ρ	is the density;
n_D^{20}	is the refractive index;
Gr	is the Grashof criterion;
Pr	is the Prandtl criterion;
λ	is the thermal conductivity;
p	is the pressure;
t	is the temperature;
T	is the absolute temperature;
B, a, b, n	are the empirical coefficients;
π	is the reduced pressure;
φ	is the reduced density;
τ	is the reduced temperature;
β_T	is the isothermal compressibility;
v	is the specific volume.

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