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THERMAL CONDUCTIVITY OF HYDROCARBONS IN THE NAPHTHENE GROUP UNDER HIGH PRESSURES

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UDC 536.23

The thermal conductivity of hydrocarbons in the naphthene group has been experimentally determined. An equation is now proposed for calculating the thermal conductivity over the given temperature and pressure ranges.

The thermal conductivity of seven hydrocarbons in the naphthene group (cyclopentane, cyclohexane, ethyl cyclohexane, trans-1,2-dimethyl cyclohexane, cis-1,3-dimethyl cyclohexane, trans-1,4-dimethyl cyclohexane, and cyclohexene) was measured by the method of coaxial cylinders at temperature from 20 to 180°C and under pressures from 0.1 to 150 MPa. The construction of the test equipment and the measuring procedure have already been described [1]. The maximum error of a λ determination was ±1.5%.

The experimentally determined values of the thermal conductivity are given in Table 1.

Only a few published data are available on the thermal conductivity of hydrocarbons in the naphthene group. For cyclopentane, e.g., only one value of λ and the magnitude of its derivative $(\partial\lambda/\partial t)_p$ are given. A comparison of the data in [2] with the results of this study indicates that there the value of the thermal conductivity at 20°C is 2.5% higher and the value of the temperature coefficient at this temperature $\alpha + (1/\lambda_{20})(d\lambda/dt)_p$ is 11.7% lower.

The thermal conductivity of cyclohexane was studied by several authors, the results having been surveyed and analyzed in another report [3]. Its thermal conductivity under atmospheric pressure was studied most thoroughly by Filippov [4] and Mukhamedzyanov [5]. The value of λ_{30} in [4] is 4.7% higher and the value of α is 25% lower than according to the data of this study.

The values in [5] are consistently higher than those obtained in this study: 2.5% at 20°C, 5.1% on the average, and 7.0% maximum. The temperature coefficient α for cyclohexane in [5] is 30% higher.

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TABLE 1. Experimentally Determined Values of the Thermal Conductivity of Hydrocarbons in the Naphthene Group (λ, W/(m•K); t, °C; P, MPa)

t	P	λ	t	P	λ	t	P	λ
Cyclopentane								
22,91	0,1	0,1267	60,21	78,5	0,1464	120,0	120,1	0,1466
22,69	20,1	0,1361	60,18	99,5	0,1529	139,9	149,9	0,1556
22,60	39,2	0,1430	60,06	119,2	0,1592	141,2	40,1	0,1119
22,42	58,8	0,1505	60,06	147,6	0,1673	140,9	78,0	0,1280
22,39	78,5	0,1572	83,77	3,9	0,1067	140,9	98,6	0,1357
22,36	98,6	0,1628	83,59	20,1	0,1162	140,8	118,2	0,1427
22,35	117,7	0,1679	83,13	39,1	0,1252	140,7	145,1	0,1505
22,32	143,2	0,1749	83,23	58,8	0,1337	163,4	42,2	0,1084
40,36	0,1	0,1200	83,14	79,4	0,1409	163,2	58,4	0,1164
40,20	20,6	0,1299	82,91	99,5	0,1475	163,0	78,5	0,1249
40,05	39,2	0,1379	82,88	118,2	0,1538	162,9	98,1	0,1316
39,92	60,3	0,1452	82,85	146,1	0,1621	162,8	116,7	0,1389
39,89	78,5	0,1521	101,7	19,6	0,1107	162,6	147,1	0,1478
39,76	99,0	0,1582	101 3	39,7	0,1211	181,3	58,4	0,1131
39,74	117,7	0,1633	101,2	79,4	0,1372	181,2	78,9	0,1218
39,71	149,1	0,1720	101,0	117,7	0,1496	181,0	98,1	0,1290
60,54	18,6	0,1225	100,8	147,6	0,1581	181,1	115,7	0,1346
60,39	40,2	0,1321	120,1	39,9	0,1162	180,9	148,6	0,1454
60,25	57,9	0,1395	120,0	80,0	0,1328			
Cyclohexane								
25,27	0,1	0,1177	60,22	20,1	0,1157	121,8	39,2	0,1093
25,34	10,3	0,1221	60,07	38,3	0,1227	121,6	58,8	0,1169
25,33	19,6	0,1244	59,95	58,8	0,1286	121,3	78,5	0,1236
24,81	27,5	0,1271	59,89	78,5	0,1350	121,4	98,1	0,1295
31,34	0,1	0,1153	59,85	98,1	0,1391	121,2	116,7	0,1344
30,99	10,3	0,1197	59,83	107,9	0,1420	121,1	145,6	0,1414
31,42	19,6	0,1224	80,02	0,1	0,1020	142,2	46,1	0,1097
31,37	28,4	0,1252	80,35	19,6	0,1110	141,8	58,4	0,1138
31,33	34,3	0,1272	80,26	38,3	0,1181	141,7	78,5	0,1205
31,31	39,2	0,1285	79,95	57,4	0,1244	141,3	98,6	0,1262
31,28	44,1	0,1295	79,72	78,5	0,1303	140,9	118,2	0,1322
42,54	0,1	0,1128	79,88	98,1	0,1358	141,3	145,1	0,1393
42,46	19,6	0,1204	79,66	118,7	0,1411	162,8	58,4	0,1107
42,24	38,3	0,1264	79,59	129,0	0,1439	162,8	58,4	0,1109
42,19	58,8	0,1326	100,7	18,6	0,1059	162,7	78,5	0,1180
42,18	58,8	0,1327	100,8	19,6	0,1064	162,7	98,1	0,1235
49,55	0,1	0,1103	100,6	38,3	0,1140	162,6	117,7	0,1294
49,62	10,3	0,1147	100,6	58,4	0,1206	162,4	145,1	0,1364
49,66	20,1	0,1180	100,4	78,5	0,1271	182,1	57,9	0,1076
49,65	29,4	0,1211	100,2	99,1	0,1326	181,8	98,1	0,1216
49,71	40,2	0,1244	100,1	118,2	0,1380	181,7	117,2	0,1275
49,69	49,0	0,1273	100,1	133,4	0,1416	181,6	144,2	0,1338
49,72	67,7	0,1343	122,1	26,0	0,1046			
60,38	0,1	0,1077	121,8	26,0	0,1053			
Ethyl cyclohexane								
24,74	0,1	0,1092	61,84	79,4	0,1256	120,4	38,7	0,1047
24,48	21,1	0,1163	61,74	98,6	0,1296	120,2	58,8	0,1113
24,36	40,7	0,1216	61,66	118,7	0,1344	120,1	79,9	0,1173
24,24	80,4	0,1309	61,53	149,0	0,1405	120,0	98,1	0,1224
24,10	118,2	0,1385	80,72	19,1	0,1041	119,9	116,2	0,1270
24,09	135,3	0,1412	80,61	40,2	0,1113	119,7	146,1	0,1334
41,68	0,1	0,1056	80,41	59,4	0,1169	139,7	58,4	0 1083
41,50	19,6	0,1125	80,22	78,9	0,1228	139,5	78,9	0,1150
41,28	39,7	0,1179	80,20	98,6	0,1272	139,4	118,2	0 1248
41,23	58,4	0,1228	80,07	119,2	0,1319	139,3	144,7	0,1312
41,10	79,4	0,1280	79,99	148,6	0,1375	160,9	78,0	0,1123
41,07	99,1	0,1323	101,6	19,6	0,1010	160,7	98,1	0,1181
Ethyl cyclohexane								
41,05	118,2	0,1365	101,6	21,1	0,1017	160,7	118,2	0,1232
41,03	145,1	0,1413	101,5	40,2	0,1081	160,6	146,1	0,1297
62,40	0,1	0,1012	101,3	59,8	0,1143	182,2	29,0	0,0925
62,27	7,9	0,1039	101,3	79,9	0,1202	181,7	79,4	0,1109
62,09	19,6	0,1083	101,0	98,1	0,1245	181,6	98,1	0,1159
62,04	40,2	0,1146	101,0	118,7	0,1298	181,5	117,7	0,1210
61,92	58,4	0,1200	100,9	147,1	0,1354	181,4	145,1	0,1275

TABLE 1. (Continued)

t	P	λ	t	P	λ	t	P	λ
				1,2-Dimethyl cyclohexane				
25,36	0,1	0,1060	61,16	21,6	0,1056	100,8	114,7	0,1249
25,26	20,6	0,1123	60,71	49,5	0,1146	121,0	17,2	0,0941
25,02	39,2	0,1178	60 71	79,4	0,1220	120,7	39,2	0,1023
24,97	59,3	0,1226	60,53	110,3	0,1290	120,5	58,4	0,1083
24,82	79,9	0,1272	60,51	132,4	0,1335	120,9	78,5	0,1142
24,73	98,1	0,1309	80,32	0,1	0,0941	120,2	98,1	0,1192
24,70	120,6	0,1354	79,90	29,9	0,1056	120,1	117,7	0,1239
24,66	146,1	0,1397	79,73	48,5	0,1114	139,1	24,5	0,0945
41,09	0,1	0,1023	79,69	68,7	0,1172	138,4	80,4	0,1120
40,78	20,6	0,1093	79,57	89,2	0,1219	138,3	116,7	0,1213
40,68	40,2	0,1150	79,55	109,8	0,1262	138,2	138,3	0,1269
40,57	58,8	0,1204	79,42	131,4	0,1311	160,9	39,2	0 0967
40,46	79,4	0,1249	101,7	0,1	0,0901	160,7	57,9	0,1034
40,43	100,5	0,1294	101,5	19,6	0,0982	160,6	78,9	0,1097
40,41	118,7	0,1334	101,1	48,1	0,1073	160,5	99,1	0,1151
40,29	139,3	0,1368	100,9	70,6	0,1144	160,4	119,6	0,1207
61,32	0,1	0,0986	100,8	92,7	0,1200	160,4	151,0	0,1272
				1,3-Dimethyl cyclohexane				
28,70	0,1	0,1022	59,68	98,6	0,1247	119,2	147,1	0,1293
28,54	20,6	0,1092	59,60	118,2	0,1295	140,8	32,9	0,0957
28,45	39,2	0,1147	59,47	146,6	0 1348	140,5	58,4	0,1041
28,36	59,3	0,1202	80,27	7,4	0,0949	140,3	79,9	0,1105
28,23	79,4	0,1244	79,77	61,8	0,1128	140,2	98,1	0,1155
28,21	97,6	0,1285	79,52	108,9	0,1247	140,2	117,7	0,1208
28,08	117,7	0,1328	79,41	140,7	0,1316	140,0	147,1	0,1268
27,95	150,5	0,1384	103,5	17,2	0,0948	163,9	40 7	0,0956
41,00	0,1	0,0994	103,4	18,6	0,0953	163,8	41,2	0,0960
40,66	20,6	0,1065	103,1	40,7	0,1032	163,6	58,4	0,1018
40,54	39,2	0,1126	103,0	58,6	0,1088	163,5	78,5	0,1080
40,46	58,4	0,1174	102,9	78,5	0,1145	163,4	97,6	0,1136
40,34	79,9	0,1233	102,8	99,5	0,1200	163,2	117,7	0,1187
40,21	99,5	0,1271	102,7	117,7	0,1244	163,1	148,6	0,1257
40,19	117,7	0,1312	102,6	146,6	0,1309	183,1	51,5	0,0980
40,06	146,1	0,1363	120,0	24,5	0,0947	183,1	58,4	0,1001
60,37	0,1	0,0954	119,8	39,2	0,1002	182,9	78,0	0,1059
60,19	19,6	0,1030	119,6	58,4	0,1067	182,7	97,6	0,1118
59,94	39,7	0,1095	119,5	78,9	0,1124	182,6	117,2	0,1173
59,79	57,9	0,1152	119,4	98,1	0,1178	182,5	147,6	0,1238
59,67	80,9	0,1207	119,3	117,2	0,1225			
				1,4-Dimethyl cyclohexane				
25,66	0,1	0,1035	81,11	0,1	0,0918	123 4	147,1	0,1294
25,45	21,1	0,1107	80,80	19,1	0 0997	140,5	21,6	0,0915
25,36	39,7	0,1160	80,68	39,2	0,1065	140,5	23,1	0,0922
25,23	59,5	0,1214	80,59	58,4	0,1124	140,2	40,2	0,0987
25,12	79,4	0,1258	80,45	79,4	0,1184	140,1	58,4	0,1046
25,08	99,1	0,1301	80,36	99,5	0,1242	139,9	78,5	0,1108
25,05	118,2	0,1340	80,28	117,7	0,1289	139,8	97,6	0,1161
				1,4-Dimethyl cyclohexane				
24,93	146,6	0,1389	80,26	138,3	0,1330	139,8	116,7	0,1210
43,81	0,1	0,0994	99,73	5,9	0,0918	139,7	149,1	0,1283
43,45	38,6	0,1125	99,41	19,9	0,0968	162,5	30,9	0,0926
43,36	58,8	0,1183	99,29	40,2	0,1043	162,2	58,8	0,1023
43,30	78,9	0,1235	99,12	58,4	0,1098	162,1	78,5	0,1084
43,18	98,1	0,1276	99,01	78,5	0,1156	161,9	99,5	0,1142
43,07	117,7	0,1322	98,90	98,1	0,1208	161,8	117,4	0,1193
43,05	141,2	0,1365	98,78	118,2	0,1258	161,7	149,1	0,1262
60,42	0,1	0,0960	98,75	147,8	0,1316	182,6	36,8	0,0929
60,12	20,1	0,1038	124,2	16,2	0,0916	182,6	39,2	0,0940
59,99	39,2	0,1101	124,2	16,7	0,0917	182,3	58,4	0,0998
59,93	58,4	0,1149	123,9	39,0	0,1002	182,1	78,5	0,1064
59,69	78,8	0,1209	123,8	57,9	0,1062	182,0	97,1	0,1122
59,61	99,1	0,1256	123,6	79,4	0,1130	182,0	117,7	0,1175
59,58	116,7	0,1298	123,5	98,1	0 1178	181,8	147,6	0,1245
59,45	148,1	0 1361	123,4	117,2	0,1228			

TABLE 1. (Continued)

t	P	λ	t	P	λ	t	P	λ
				Cyclohexene				
25,13	0,1	0,1286	79,79	0,1	0,1129	120,2	100,0	0,1389
24,87	19,6	0,1356	80,10	11,8	0,1180	120,1	117,2	0,1433
24,84	40,2	0,1422	80,15	14,2	0,1185	120,0	145,6	0,1507
24,76	57,9	0,1473	79,93	38,3	0,1282	139,4	0,422	0,0965
24,62	79,9	0,1529	79,84	58,4	0,1344	139,3	8,8	0,1009
24,6	99,1	0,1572	79,74	78,5	0,1408	139,1	20,6	0,1069
24,5	117,7	0,1615	79,62	99,5	0,1464	138,9	39,2	0,1148
24,48	147,6	0,1671	79,53	118,2	0,1516	138,8	58,8	0,1222
38,77	0,1	0,1231	79,42	147,6	0,1579	138,7	77,5	0,1282
38,53	21,1	0,1312	101,0	0,169	0,1082	139,1	100,0	0,1325
38.45	39,1	0,1377	101,3	23,5	0,1175	139,1	150,0	0,1486
38,33	60,3	0,1429	101,1	39,2	0,1238	164,5	1,0	0,0918
38,29	79,4	0,1483	101,0	57,9	0,1303	164,7	42,7	0,1119
38,27	98,1	0,1527	100,9	77,5	0,1364	164,7	48,5	0,1142
38,23	117,2	0,1565	100,8	94,1	0,1412	164,7	58,4	0,1176
38,16	147,8	0,1636	100,8	117,2	0,1478	164,5	78,5	0,1250
60,36	0,1	0,1172	100,6	146,6	0,1548	164,5	97,6	0,1306
60,01	20,6	0,1260	120,5	0,277	0,1017	164,3	118,2	0,1366
60,01	39,7	0,1323	121,0	8,8	0,1047	164,2	147,6	0,1448
59,90	58,9	0,1383	120,9	9,8	0,1062	181,0	1,5	0,0887
59,82	80,4	0,1443	120,8	22,6	0,1119	181,1	52,0	0,1125
59,76	99,1	0,1491	120,6	39,2	0,1188	181,1	80,0	0,1228
59,64	120,1	0,1542	120,4	58,4	0,1256	179,9	121,0	0,1355
59,57	147,6	0,1604	120,3	78,0	0,1324	180,9	147,1	0,1422

Ya. M. Naziev and his colleagues measured the thermal conductivity λ of cyclohexane in the liquid phase and in the vapor phase [3] over the 20-360°C temperature range and under pressures up to 50 MPa. The values of λ under atmospheric pressure are almost the same in [2] and in [4]. The values of $(\partial\lambda/\partial P)_t$ in [3] are higher than those obtained in this study, 26.7% at 20°C and 15% at 80°C. It is to be noted that in [3] the values of λ for cyclohexane at 20°C were obtained under a pressure of 50 MPa, much higher than the melting pressure P_{melt}. The 20°C isotherm plotted on the basis of the data in [3] does not contain any singularities in the trend of λ associated with the phase transition from liquid to solid [5], this phase transition itself not having been recorded during the λ measurements in [3]. For this reason, the readings taken in [3] at low temperatures and under high pressures are questionable.

Recommended values of the thermal conductivity of cyclohexane, over wide ranges of temperature and pressure, are given in [6]. The value of λ at 30°C and under atmospheric pressure recommended in [6] is 4.3% higher than λ_{30} obtained in this study, while the temperature coefficient α is 23% higher. The differences at high pressures are almost the same as with those in [3], taken as the basis for compiling the table of recommended λ values at high pressures.

In another study [7] the thermal conductivity of cyclohexane was measured over the 20-350°C temperature range under pressures up to 30 MPa. A comparison of the data in [7] with the results of this study indicates differences not exceeding 1-2% for the 20-80°C temperature range at atmospheric pressure and a 3% higher value of the temperature coefficient α in [7]. The values of $(\partial\lambda/\partial P)_t$ in [7] are 8.9% higher at 30°C and 14% higher at 180°C than those obtained in this study.

The thermal conductivity of ethyl cyclohexane was also measured before [8]. A comparison of the data in [8] with the results of this study indicates that the values there for 20°C and atmospheric pressure are 3.0% higher than the values obtained here, while the values of $(\partial\lambda/\partial P)_t$ at 180°C are 30% higher.

The characteristic λ—T and λ—P section diagrams for cyclohexane, as an example, are shown in Fig. 1. The spread of experimental points about the average curves does not exceed 0.7%. According to this graph, the λ-isobars for hydrocarbons have a small curvature and are convex toward the temperature axis. As the temperature rises, $(\partial\lambda/\partial t)_P$ decreases. At atmospheric pressure, however, one can assume that $(\partial\lambda/\partial t)_{P_0} \approx$ const (within experimental accuracy) from T_{boil} down to a point a few degrees higher than T_{melt}. This greatly simplifies the analysis of experimental data, inasmuch as the temperature dependence of the thermal conductivity can be expressed as

$$\lambda_{t,P_0} = \lambda_{t_0,P_0}[1 - \alpha(t - t_0)], \quad (1)$$

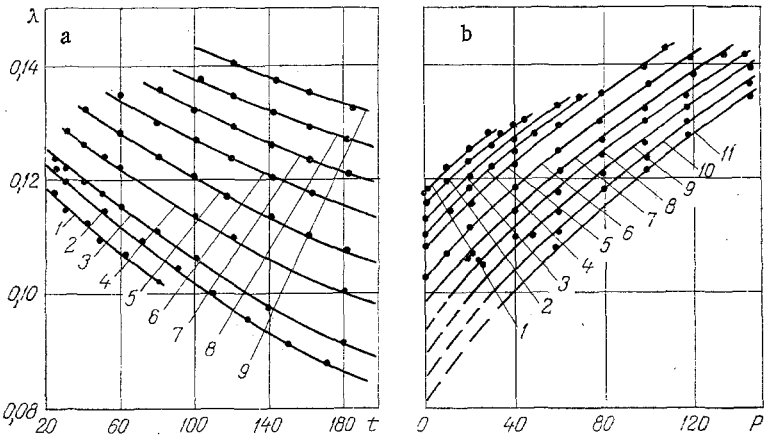

Fig. 1. Isobars (a) and isotherms (b) of the thermal conductivity of cyclohexane: a: 1) 0.098; 2) 9.8; 3) 19.6; 4) 40.0; 5) 53.8; 6) 78.5; 7) 98.0; 8) 117.7; 9) 140 MPa; b: 1) 25.2; 2) 31.3; 3) 42.2; 4) 49.7; 5) 60.0; 6) 80.0; 7) 100.4; 8) 121.4; 9) 141.5; 10) 152.6; 11) 181.8°C. λ, W/(m•K); t, °C; P, MPa.

where

$$\alpha = \frac{1}{\lambda_{t_0, P_0}} \left(\frac{\partial \lambda}{\partial t} \right)_{P_0}.$$

A processing of the experimental data has yielded empirical relations for λ_{20,P_0} and α for hydrocarbons in the naphthene group, viz.

$$\lambda_{20,P_0} = 0.3193 - 0{,}1038 \lg M, \tag{2}$$

$$\alpha = -1{,}998 \cdot 10^{-3} + 3.636\,\alpha_\rho, \tag{3}$$

where $\alpha_\rho = (1/\rho_{20})(\partial\rho/\partial t)_{P_0}$ (K^{-1}) is the temperature coefficient of density. The average errors of λ_{20,P_0} and α calculation according to expressions (2) and (3) are, respectively, 1.8 and 1.0%, the maximum errors 3 and 1.6%.

The isotherms of the thermal conductivity are convex toward the pressure axis. One can assume that $(\partial\lambda/\partial P)_t \approx$ const, within experimental accuracy, over the pressure range from 0.1 to 50 MPa and that, therefore,

$$\lambda_{t,P} = \lambda_{t,P_0} + \left(\frac{\partial \lambda}{\partial P} \right)_t^{av} (P - P_0). \tag{4}$$

The lines of constant thermal conductivity (λ = const) in P–T coordinates have also a small curvature. Such a section through the λ–P–T surface offers no substantial advantage over a λ–T section from the standpoint of empirical data representation.

The availability of extensive experimental data on the thermal conductivity of hydrocarbons under high pressures has made it possible to evaluate existing methods of calculating the pressure dependence of the thermal conductivity. An analysis has revealed that most of these methods are based on the fundamental relation between thermal conductivity and density, thus either P–ρ–T data or the equation of state being needed for calculating the pressure dependence of the thermal conductivity for liquid hydrocarbons.

These authors have made an attempt to derive an equation for $\lambda = f(P)$ which would be based on experimental data on λ and would not require P–ρ–T data for a given substance.

An analysis of isotherms of the thermal conductivity and of the density of hydrocarbons has revealed that they are identical in shape, the temperature dependence and the pressure dependence of the relative thermal conductivity $\Delta\lambda/\lambda_P = (\lambda_P - \lambda_0)/\lambda_P$ being analogous to those of the relative compression $\Delta v/v_0 = (v_0 - v_P)/v_0$ (Fig. 2). As the relative compression of a hydrocarbon increases, its thermal conductivity becomes more pressure dependent. As the boiling temperature rises, $\Delta v/v_0$ and thus also $\Delta\lambda/\lambda_P$ decrease.

It is well known [9-12] that the isothermal variation on the density of a liquid at $\tau < 0.9$ and $\rho \geqslant 2\rho_{cr}$ can very accurately be described by the Tait equation. Methods of

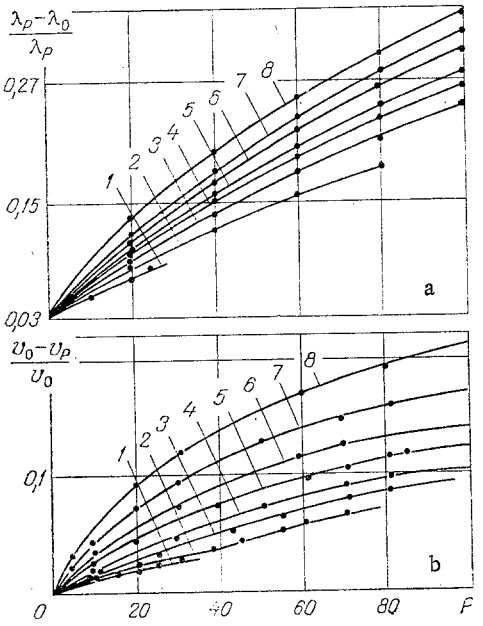

Fig. 2. Isotherms of the relative thermal conductivity (a) and the relative specific volume (b) of cyclohexane: 1) 25; 2) 50; 3) 75; 4) 100; 5) 125; 6) 150; 7) 175; 8) 200°C. λ_P, λ_0, W(m•K); v_0, v_P, m^3/kg; P, MPa.

optimizing the values of the coefficients in the Tait equation and extending them to liquid hydrocarbons have been proposed in other studies [13-17].

Since the isotherms of the relative thermal conductivity and those of the density of hydrocarbons in the naphthene group follow the same trend, the same approach has been used in deriving a generalized equation of heat conduction for this group of hydrocarbons.

For calculating the isothermal variation of the thermal conductivity, the equation

$$\lambda_P = \lambda_0 \Big/ \left[1 - A_\lambda \ln \frac{P + B_\lambda(t)}{P_0 + B_\lambda(t)}\right] \tag{5}$$

was used, with coefficients A_λ and $B_\lambda(t)$ evaluated through processing of experimental data.

First the experimental data on the thermal conductivity of hydrocarbons in the naphthene group were processed according to a special program, for the purpose of an evaluation of the coefficients A_λ and $B_\lambda(t)$. The optimum values of A_λ and $B_\lambda(t)$ were assumed to correspond to the minimum of the quadratic functional, viz.,

$$\left(\frac{\partial S_\lambda}{\partial A_\lambda}\right)_{B_\lambda(t)} = 0, \tag{6}$$

$$S_\lambda = \sum_{i=1}^{n} W_{i,\lambda}^2 \lambda_{t,P}^{\exp} - \left[\lambda_{t,P_0} \Big/ \left(1 - A_\lambda \ln \frac{P + B_\lambda(t)}{P_0 + B_\lambda(t)}\right)\right]^2, \tag{7}$$

with $W_i = 1/\sigma_i \lambda_{t,P}^{\exp}$.

An analysis has revealed that A_λ = const and $B_\lambda(t)$ does not depend on the pressure but only on the temperature for each hydrocarbon, over the entire range of values of the state variables in this study.

Then the coefficients $B_\lambda(t)$ were averaged over an isotherm, on the basis of the number of experimental points along the various segments of an isotherm and on the basis of the pressure step, according to the expression

$$\bar{B}_\lambda(t) = \left[B_1(P_1 - P_2) + \sum_{i=2}^{n-1} B_i(P_{i-1} - P_{i+1}) + B_n(P_{n-1} - P_n)\right] / 2(P_1 - P_n), \tag{8}$$

with n denoting the number of experimental points and B_i being the value of B at the i-th experimental point.

With the optimum values of coefficients A_λ and $B_\lambda(t)$ and with experimental data on $\lambda_0 = f(t)$, Eq. (5) very accurately describes the pressure dependence of the thermal conductivity of hydrocarbons.

An analysis of Eq. (5) and of A_λ values for the seven hydrocarbons in the naphthene group indicates that one can, without a noticeable loss in accuracy, assume that $\overline{A}_\lambda$ = idem for this group of substances. Processing of the array of experimental data has yielded $\overline{A}_\lambda$ = 0.1969 and the corresponding optimum $\overline{B}_\lambda(t)$ values for these hydrocarbons. The rms error of $\lambda_{t,P}$ calculation was 0.34%, the maximum error was 1.7%.

The coefficients $\overline{B}_\lambda(t)$ were found to be decreasing functions of the temperature. They were generalized by one variant of the similitude method, with the critical temperature and the value of $\overline{B}_\lambda(t) = \overline{B}_{\lambda,\tau=0.6}$ at $T = 0.6T_{cr}$ used as parameters.

Processing of the $\overline{B}_\lambda(t)$ data has yielded the generalized equation

$$B_\lambda^* = -2{,}13037 + 0.86530\,\tau + \frac{1{,}5723}{\tau}, \qquad (9)$$

where $B_\lambda^* = \overline{B}_\lambda(t)/\overline{B}_{\lambda,\tau=0.6}$ and $\tau = T/T_{cr}$, for calculating the temperature coefficient in Eq. (5) for hydrocarbons in the naphthene group.

In order to calculate $\overline{B}_\lambda(t)$ according to Eq. (9), it is necessary to have at least one experimental value of $\lambda_{t,P}$ under pressure or data on $B_{\lambda,\tau=0.6}$ for obtaining of which can be recommended the empirical expression

$$B_{\lambda,\tau=0,6} = -247{,}3 - 0{,}00496\,M^2 + 171{,}05\lg M. \qquad (10)$$

Calculations of $\lambda_{t,P}$ made by these authors for hydrocarbons in the naphthene group according to Eq. (5), also using Eqs. (1), (9), and (10), show a mean error of 0.5% and a maximum error not exceeding 1.75%.

NOTATION

λ, thermal conductivity; λ_{20} and λ_{30}, values of the thermal conductivity at 20 and 30°C, respectively; λ_{t_0,P_0}, thermal conductivity at t_0, P_0; $\lambda_{t,P}$, thermal conductivity at temperature t and under pressure P; $\Delta\lambda$, change in thermal conductivity; P, pressure; P_{melt}, melting pressure; P_0, atmospheric pressure; t_0, 20°C temperature; T, t, temperature; T_{cr}, critical temperature; α, temperature coefficient of thermal conductivity; α_ρ, temperature coefficient of density; ρ, density; ρ_{20}, density at 20°C; ρ_{cr}, critical density; M, molar mass; $\tau = T/T_{cr}$, referred temperature; v, specific volume; v_0, specific volume at 20°C; Δv, change in specific volume; A_λ, a coefficient; $B_\lambda(t)$, a function of the temperature; S_λ, a quadratic functional; $W_{i,\lambda}$, weight of the i-th experimental point; σ_i, error of the i-th experimental value of thermal conductivity; $\overline{B}_{\lambda,\tau=0.6}$, value of $B_\lambda(t)$ at $T = 0.6T_{cr}$; and $B_\lambda^* = \overline{B}_\lambda(t)/B_{\lambda,\tau=0.6}$, referred value of coefficient $B_\lambda(t)$.

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MEASUREMENT OF DYNAMIC VISCOSITY OF BINARY MIXTURES OF BUTYL ALCOHOL AND BUTYRALDEHYDE

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We present measured values of the viscosity of binary mixtures of butyl alcohol and butyraldehyde of various concentrations at temperatures from 288 to 500°K and pressures from 0.1 to 50 MPa.

Among the various materials of great practical importance for the chemical, petroleum refining, power, and gas industries, an important place is occupied by alcohols, aldehydes, and their binary liquid solutions.

We have measured the viscosity of binary solutions of n-butyl alcohol and n-butyraldehyde of various concentrations in the liquid state over a wide range of temperatures and pressures.

The n-butyl alcohol used in the mixtures was freed of contaminants by the method described in [1]. Particular attention was paid to the removal of moisture from the alcohol. The purity of the alcohol was 99.96% by weight. The butyraldehyde was also purified by the method of [1], and precautionary measures were taken to prevent contact of the butraldehyde with the air. The purified aldehyde was kept in a dark environment. We estimate its purity as 99.97% by weight. The binary liquid mixtures were made before the viscosity was measured.

The dynamic viscosity was measured by the capillary viscometer method developed by Golubev [2, 3] at temperatures from 288 to 500°K and pressures from 0.1 to 50 MPa.

The viscometer capillary had a radius $r = 1.724 \cdot 10^{-4}$ m, the volume of the measuring tank was $v = 206.607 \cdot 10^{-4}$ m^3, and the length of the capillary was $l = 772.94 \cdot 10^{-4}$ m. The

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