18. S. C. Saxena and P. K. Tondon, in: Proceedings of the Symposium on Thermophysics, 4th ed. (1968), p. 398.
19. W. Van Dael and H. Gauwenbergh, Physica, 40, 165-181 (1968).
20. J. N. Peterson, T. P. Hahn, and E. W. Comings, AIChE J., 17, 289 (1971).
21. H. Cheng et al., Am. Inst. Chem. Eng. J., 8, 221 (1962).
22. A. G. Shashkov, E. V. Ivashkevich, and V. I. Aleinikova, Izv. Akad. Nauk BSSR, Ser. Fiz. Énerg. Nauk, No. 4 (1971).
23. J. Hirschfelder et al., Molecular Theory of Gases and Liquids, Wiley-Interscience (1964).
24. W. Hogervorst, Physica, 51, No. 1 (1971).
25. E. A. Mason, J. Chem. Phys., 23, 49 (1955).
26. O. P. Bahethi, R. S. Gambhir, and S. C. Saxena, Z. Naturforsch., 19a, 1478 (1963).

# AN EXPERIMENTAL STUDY OF THERMAL CONDUCTIVITY OF AROMATIC HYDROCARBONS AT HIGH TEMPERATURES AND PRESSURES

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UDC 536.6

Results are presented of an experimental study of thermal conductivity of aromatic hydrocarbons over a wide range of state parameters. Calculated equations which describe the experimental results well are obtained.

There are serious experimental difficulties connected with studying thermal conductivity at high pressures and temperatures. This evidently explains the fact that there is very limited information available in the literature on the thermal conductivity $\lambda$ of aromatic hydrocarbons at high temperatures and pressures. Data on the values of $\lambda$ for aromatic hydrocarbons at pressures up to 1500 kg/cm$^2$ are given only in [1]. Unfortunately even the experimental data of [1] encompass only temperatures below 200°C.

The present study offers results of an experimental investigation of thermal conductivity of m-xylol, n-xylol, o-xylol, and ethylbenzol in the temperature range 30-400°C and pressures to 1000 kg/cm$^2$. The thermal conductivity of benzol, toluol, and cumol were presented in [2-4].

The characteristics of the hydrocarbons studied are presented in Table 1. The monotonic heating method was employed. The theory of the method, experimental techniques, and device construction were described in [5-7].

The basic component of the apparatus is a cylindrical bicalorimeter, with a gap filled by the liquid to be studied. The inner cylinder (rod) is made of M1 copper. The operating surface of the rod was carefully ground, chrome plated, and polished. The outer cylinder is a massive copper block, in which a tube of 1Kh18N9T is pressed. In contrast to previous construction, a single seal with cone-shaped lip is used to maintain high pressure. The cone angle used is 60°. The bicalorimeter dimensions are as follows: internal diameter of copper block, 11.360 ± 0.005 mm; copper rod diameter, 10.320 ± 0.002 mm, length of bar measurement segment, 100 mm.

Experimental measurement of thermal conductivity reduces to measurement of the time delay of rod temperature relative to temperature of the block. For these measurements a class 0.001 R-345 potentiometer and 51-Sd stopwatch were used, while pressure was generated and measured by an MP-2500 piston manometer, class 0.05, and a set of reference manometers. All corrections essential to the method used [7] were introduced in calculating the thermal conductivity. The maximum calculated uncertainty comprises 2%. Reproducibility of experimental data obtained at one and the same state parameters lies within the limits ± 1%. Possible convection effects were checked by series of experiments at different heating rates (temperature differences). The good agreement of the results indicates the absence of convection. Moreover, for all measurements the product GrPr was significantly less than 1000. Due to the absence of information on absorption spectra the cor-

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TABLE 1. Characteristics of Hydrocarbons Studied

| Hydrocarbon | $M$ | $t_{boil}$, °C | $n_D^{20}$ | $d_4^{20}$ |
|---|---|---|---|---|
| m-Xylol | 106,16 | 138,7 | 1,4952 | 0,8622 |
| n-Xylol | 106,16 | 138,8 | 1,5005 | 0,8616 |
| o-Xylol | 106,16 | 145,1 | 1,5104 | 0,8908 |
| Ethylbenzol | 106,16 | 135,6 | 1,4864 | 0,8682 |

rection for radiation was not considered in thermal-conductivity measurements. The experimental results obtained are presented in Table 2. On their basis isobars were constructed, and for internal agreement of the latter, isotherms of corresponding sections were constructed. Figure 1 shows isobars and isotherms of ethylbenzol thermal conductivity. The isobars and isotherms for the other liquids studied have analogous forms.

The results obtained here agree well with the data of [1], with a divergence at low temperatures of about 1.5%, and about 3% for temperatures above 140°C.

Recently the Rivkin method [8] has been widely used for generalization of experimental data. In the P–t diagram lines of constant thermal conductivity are constructed, being straight lines described by the equation

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

Construction of lines $\lambda$ = const on the basis of our data revealed that these lines for the hydrocarbons studied are not straight, but curved, especially in the high-temperature region.

A shortcoming of Eq. (1) is the fact that the coefficients $a$ and b are functions of thermal conductivity; i.e., they are of an individual character for each liquid. In this relationship the Rivkin method is suitable for generalization and compilation of detailed tables for separate individual liquids. Generalization of the function $\lambda = F(P, t)$ for an individual liquid is a special case. In this respect it is of great interest to develop a method of calculating $\lambda = F(P, t)$ for an entire class of hydrocarbons on the basis of minimum information on the objects of study.

Analysis of the voluminous experimental material obtained herein has permitted constructing a generalized formula for calculating thermal conductivity of hydrocarbons of the aromatic series as a function of temperature and pressure in the form

$$\lambda_{P,t} = A(t) \exp\left(\frac{\sqrt{n_C}}{M^2} P\right), \tag{2}$$

where A is a universal coefficient, the temperature dependence of which is shown in Fig. 2.

A unique feature of the proposed formula is that it permits direct calculation of $\lambda = F(P, t)$ over a wide range of state parameters. The accuracy with which the proposed formula reflects the results obtained is evident from Fig. 3, where experimental data obtained at 200°C are compared with those calculated by this formula. There is a similar divergence at other temperatures.

With the aid of Eq. (2) one can calculate $\lambda = F(P, t)$ for hydrocarbons which have not been studied or are difficult to obtain, avoiding cumbersome and expensive experiments.

The majority of theoretical studies of the thermal-conductivity mechanism in liquids is connected with Bridgman's theory [9]. According to this theory, the liquid molecules occupy positions corresponding to their equilibrium states, forming a cubic lattice with a distance between neighboring molecules equal to $l = \sqrt[3]{M/N\rho}$.

According to Bridgman, the energy-transfer mechanism is that energy propagates along isothermal molecular chains at the speed of sound [10]. On this basis Bridgman established the well-known formula relating thermal conductivity to the speed of sound. This relationship is also established by the well-known formula of Borovik [11]. These formulas describe the temperature dependence of thermal conductivity properly, but quantitatively both give large deviations from experimental data.

On the basis of the experimental results on thermal conductivity obtained here and data available in the literature on the speed of sound in various liquids [12, 13] we have constructed the following relationship between the two quantities:

$$\frac{c}{\lambda\sqrt{n_C}} = 3950 - K(P)\, t, \tag{3}$$

where K(P) is a universal monotonically decreasing function of pressure (Fig. 4).

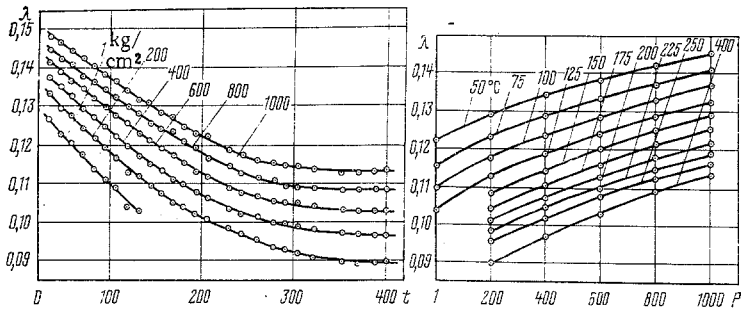


Fig. 1. Isobars and isotherms of the ethylbenzol thermal conductivity. λ, W/m·°C; t, °C; P, kg/cm².

TABLE 2. Experimental Values of Thermal Conductivity λ, W/m·°C, of Aromatic Hydrocarbons versus Temperature and Pressure

| t, °C | P, kg/cm² | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 200 | 400 | 600 | 800 | 1000 |
| | | | m-Xylol | | | |
| 33,1 | 0,1278 | 0,1347 | 0,1395 | 0,1447 | 0,1478 | 0,1583 |
| 45,2 | 0,1246 | 0,1314 | 0,1361 | 0,1416 | 0,1468 | 0,1504 |
| 56,9 | 0,1215 | 0,1290 | 0,1340 | 0,1393 | 0,1430 | 0,1470 |
| 70,0 | 0,1185 | 0,1261 | 0,1313 | 0,1364 | 0,1417 | 0,1458 |
| 82,1 | 0,1157 | 0,1229 | 0,1285 | 0,1342 | 0,1386 | 0,1427 |
| 94,3 | 0,1126 | 0,1195 | 0,1263 | 0,1315 | 0,1355 | 0,1404 |
| 106,0 | 0,1100 | 0,1174 | 0,1235 | 0,1294 | 0,1336 | 0,1383 |
| 118,8 | 0,1064 | 0,1145 | 0,1210 | 0,1270 | 0,1316 | 0,1360 |
| 130,9 | 0,1038 | 0,1120 | 0,1186 | 0,1241 | 0,1300 | 0,1336 |
| 143,2 | | 0,1093 | 0,1158 | 0,1214 | 0,1270 | 0,1321 |
| 155,0 | | 0,1074 | 0,1132 | 0,1190 | 0,1244 | 0,1289 |
| 168,1 | | 0,1049 | 0,1109 | 0,1166 | 0,1228 | 0,1286 |
| 180,3 | | 0,1026 | 0,1087 | 0,1142 | 0,1206 | 0,1260 |
| 193,2 | | 0,1008 | 0,1065 | 0,1117 | 0,1177 | 0,1238 |
| 205,1 | | 0,0998 | 0,1046 | 0,1105 | 0,1161 | 0,1207 |
| 230,0 | | 0,0969 | 0,1019 | 0,1076 | 0,1126 | 0,1176 |
| 242,3 | | 0,0957 | 0,1005 | 0,1061 | 0,1113 | 0,1162 |
| 259,9 | | 0,0945 | 0,0994 | 0,1049 | 0,1098 | 0,1154 |
| 278,1 | | 0,0931 | 0,0983 | 0,1040 | 0,1084 | 0,1139 |
| 290,0 | | 0,0918 | 0,0977 | 0,1033 | 0,1077 | 0,1130 |
| 303,2 | | 0,0913 | 0,0972 | 0,1026 | 0,1073 | 0,1124 |
| 320,8 | | 0,0906 | 0,0967 | 0,1019 | 0,1064 | 0,1118 |
| 352,2 | | 0,0900 | 0,0964 | 0,1014 | 0,1061 | 0,1110 |
| 368,7 | | 0,0897 | 0,0963 | 0,1011 | 0,1062 | 0,1110 |
| 387,1 | | 0,0899 | 0,0964 | 0,1012 | 0,1062 | 0,1106 |
| 399,4 | | 0,0899 | 0,0966 | 0,1014 | 0,1064 | 0,1108 |
| | | | n-Xylol | | | |
| 33,1 | 0,1262 | 0,1338 | 0,1402 | 0,1461 | | |
| 45,2 | 0,1244 | 0,1305 | 0,1374 | 0,1432 | 0,1432 | 0,1488 |
| 56,9 | 0,1201 | 0,1281 | 0,1348 | 0,1410 | 0,1460 | 0,1486 |
| 70,0 | 0,1182 | 0,1253 | 0,1320 | 0,1482 | 0,1444 | 0,1484 |
| 82,1 | 0,1145 | 0,1226 | 0,1284 | 0,1355 | 0,1406 | 0,1455 |
| 94,3 | 0,1126 | 0,1202 | 0,1278 | 0,1331 | 0,1395 | 0,1447 |
| 106,0 | 0,1089 | 0,1170 | 0,1246 | 0,1306 | 0,1371 | 0,1412 |
| 118,8 | 0,1066 | 0,1154 | 0,1214 | 0,1283 | 0,1360 | 0,1403 |
| 130,9 | 0,1037 | 0,1124 | 0,1197 | 0,1250 | 0,1325 | 0,1375 |
| 143,2 | | 0,1103 | 0,1161 | 0,1242 | 0,1291 | 0,1344 |
| 155,0 | | 0,1075 | 0,1146 | 0,1203 | 0,1275 | 0,1338 |
| 168,1 | | 0,1056 | 0,1128 | 0,1194 | 0,1244 | 0,1301 |
| 180,3 | | 0,1022 | 0,1092 | 0,1157 | 0,1227 | 0,1288 |
| 193,2 | | 0,1014 | 0,1081 | 0,1149 | 0,1205 | 0,1269 |
| 205,1 | | 0,0995 | 0,1057 | 0,1120 | 0,1196 | 0,1232 |
| 230,0 | | 0,0968 | 0,1036 | 0,1111 | 0,1169 | 0,1203 |
| 242,3 | | 0,0959 | 0,1028 | 0,1042 | 0,1143 | 0,1193 |
| 259,9 | | 0,0946 | 0,1007 | 0,1076 | 0,1136 | 0,1185 |
| 278,1 | | 0,0935 | 0,1006 | 0,1068 | 0,1122 | 0,1171 |
| 290,0 | | 0,0927 | 0,0993 | 0,1062 | 0,1121 | 0,1165 |
| 303,2 | | 0,0921 | 0,0985 | 0,1058 | 0,1116 | 0,1163 |
| 320,8 | | 0,0914 | 0,0988 | 0,1045 | 0,1114 | 0,1154 |
| 352,9 | | 0,0909 | 0,0977 | 0,1042 | 0,1102 | 0,1145 |
| 387,1 | | 0,0911 | 0,0982 | 0,1045 | 0,1096 | 0,1142 |
| 399,4 | | 0,0912 | 0,0984 | 0,1046 | 0,1098 | 0,1146 |

TABLE 2. Continued

| t, °C | P, kg/cm² | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 200 | 400 | 600 | 800 | 1000 |
| | | | o-Xylol | | | |
| 33,1 | 0,1284 | 0,1358 | 0,1406 | 0,1454 | 0,1495 | 0,1530 |
| 45,2 | 0,1248 | 0,1325 | 0,1388 | 0,1445 | 0,1481 | 0,1514 |
| 56,9 | 0,1222 | 0,1303 | 0,1363 | 0,1411 | 0,1454 | 0,1490 |
| 70,0 | 0,1187 | 0,1275 | 0,1336 | 0,1386 | 0,1436 | 0,1482 |
| 82,1 | 0,1166 | 0,1244 | 0,1307 | 0,1371 | 0,1420 | 0,1464 |
| 94,3 | 0,1133 | 0,1216 | 0,1285 | 0,1340 | 0,1395 | 0,1445 |
| 106,0 | 0,1108 | 0,1184 | 0,1255 | 0,1321 | 0,1374 | 0,1423 |
| 118,8 | 0,1071 | 0,1163 | 0,1230 | 0,1284 | 0,1346 | 0,1395 |
| 130,9 | 0,1056 | 0,1134 | 0,1207 | 0,1266 | 0,1324 | 0,1377 |
| 143,2 | | 0,1112 | 0,1170 | 0,1247 | 0,1305 | 0,1353 |
| 155,0 | | 0,1091 | 0,1149 | 0,1214 | 0,1281 | 0,1335 |
| 168,1 | | 0,1063 | 0,1136 | 0,1198 | 0,1262 | 0,1316 |
| 180,3 | | 0,1046 | 0,1116 | 0,1168 | 0,1240 | 0,1291 |
| 193,2 | | 0,1025 | 0,1096 | 0,1162 | 0,1218 | 0,1266 |
| 205,1 | | 0,1007 | 0,1082 | 0,1132 | 0,1198 | 0,1245 |
| 230,0 | | 0,0975 | 0,1041 | 0,1104 | 0,1163 | 0,1219 |
| 242,3 | | 0,0954 | 0,1012 | 0,1088 | 0,1147 | 0,1196 |
| 259,9 | | 0,0940 | 0,1008 | 0,1070 | 0,1126 | 0,1172 |
| 278,1 | | 0,0921 | 0,0976 | 0,1047 | 0,1120 | 0,1158 |
| 290,0 | | 0,0898 | 0,0972 | 0,1046 | 0,1101 | 0,1156 |
| 303,2 | | 0,0901 | 0,0968 | 0,1034 | 0,1094 | 0,1143 |
| 320,8 | | 0,0893 | 0,0968 | 0,1016 | 0,1075 | 0,1125 |
| 352,9 | | 0,0881 | 0,0955 | 0,1009 | 0,1063 | 0,1114 |
| 368,7 | | 0,0885 | 0,0948 | 0,1008 | 0,1060 | 0,1113 |
| 387,1 | | 0,0885 | 0,0950 | 0,1010 | 0,1058 | 0,1101 |
| 399,4 | | 0,0886 | 0,0954 | 0,1012 | 0,1062 | 0,1102 |
| | | | Ethylbenzol | | | |
| 33,1 | 0,1265 | 0,1329 | 0,1371 | 0,1415 | 0,1450 | 0,1481 |
| 45,2 | 0,1229 | 0,1294 | 0,1349 | 0,1388 | 0,1423 | 0,1469 |
| 56,9 | 0,1203 | 0,1275 | 0,1325 | 0,1364 | 0,1409 | 0,1444 |
| 70,0 | 0,1177 | 0,1244 | 0,1292 | 0,1434 | 0,1378 | 0,1425 |
| 82,1 | 0,1134 | 0,1209 | 0,1271 | 0,1318 | 0,1361 | 0,1405 |
| 94,3 | 0,1108 | 0,1189 | 0,1244 | 0,1295 | 0,1342 | 0,1383 |
| 106,0 | 0,1086 | 0,1164 | 0,1218 | 0,1274 | 0,1321 | 0,1364 |
| 118,8 | 0,1041 | 0,1128 | 0,1195 | 0,1252 | 0,1295 | 0,1338 |
| 130,9 | 0,1026 | 0,1116 | 0,1169 | 0,1228 | 0,1277 | 0,1316 |
| 143,2 | | 0,1093 | 0,1150 | 0,1209 | 0,1254 | 0,1304 |
| 155,0 | | 0,1069 | 0,1127 | 0,1191 | 0,1238 | 0,1278 |
| 168,1 | | 0,1048 | 0,1108 | 0,1167 | 0,1234 | 0,1269 |
| 180,3 | | 0,1036 | 0,1095 | 0,1152 | 0,1203 | 0,1243 |
| 193,2 | | 0,1017 | 0,1076 | 0,1126 | 0,1188 | 0,1221 |
| 205,1 | | 0,1006 | 0,1061 | 0,1114 | 0,1162 | 0,1219 |
| 230,0 | | 0,0981 | 0,1034 | 0,1086 | 0,1141 | 0,1185 |
| 242,3 | | 0,0968 | 0,1018 | 0,1075 | 0,1123 | 0,1170 |
| 269,9 | | 0,0949 | 0,1013 | 0,1064 | 0,1114 | 0,1158 |
| 278,1 | | 0,0936 | 0,0998 | 0,1055 | 0,1104 | 0,1154 |
| 290,0 | | 0,0928 | 0,0991 | 0,1049 | 0,1092 | 0,1143 |
| 303,2 | | 0,0916 | 0,0986 | 0,1044 | 0,1088 | 0,1140 |
| 320,8 | | 0,0906 | 0,0981 | 0,1038 | 0,1084 | 0,1133 |
| 352,2 | | 0,0897 | 0,0971 | 0,1032 | 0,1081 | 0,1126 |
| 368,7 | | 0,0893 | 0,0967 | 0,1028 | 0,1082 | 0,1128 |
| 387,1 | | 0,0895 | 0,0966 | 0,1028 | 0,1085 | 0,1133 |
| 399,4 | | 0,0896 | 0,0968 | 0,1030 | 0,1086 | 0,1134 |

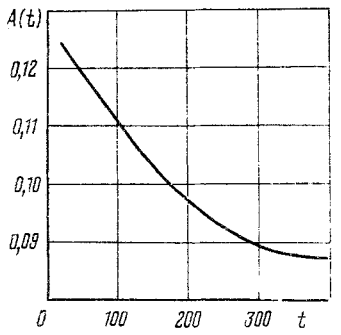


Fig. 2

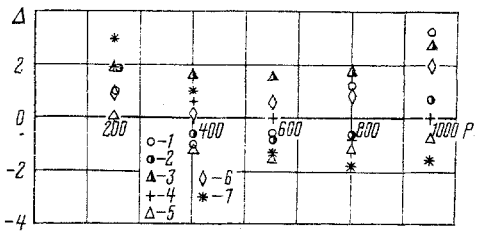


Fig. 3

Fig. 2. Temperature dependence of A = f(t) for aromatic hydrocarbons.

Fig. 3. Comparison of experimental data at 200°C and calculated thermal-conductivity values: 1) benzol; 2) toluol; 3) m-xylol; 4) n-xylol; 5) o-xylol; 6) ethylbenzol; 7) cumol. Δ, %.

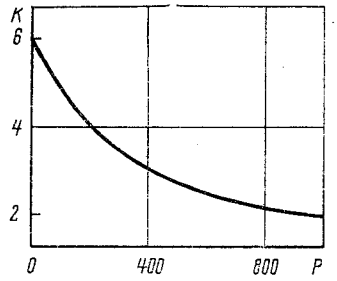


Fig. 4. Coefficient K versus pressure.

Equation (3) allows use of λ to calculate the speed of sound c over a wide range of temperature and pressure. Therefore, it can be considered a more accurate correlation of the thermal-conductivity coefficient with the speed of sound.

Analysis of data from the literature reveals that there is only scanty information available on c. Only in recent years have experiments been performed measuring c at high pressure [12, 13]. Unfortunately, those experiments encompass only a narrow temperature range, from room temperature to 120°C.

Comparison of speed of sound values calculated from Eq. (3) with available data for high pressures shows that the proposed formula describes the function $c = F(P, t)$ with sufficient accuracy. Average deviation of calculated values of c from experiment comprises about ± 1.3%, with a maximum of not more than ± 3%.

The proposed formula allows calculation of the speed of sound in aromatic hydrocarbons over the temperature range of 40-400°C at pressures to 1000 kg/cm$^2$.

## NOTATION

λ, thermal-conductivity coefficient; $n_C$, number of carbon atoms in molecule; M, mass of molecule; $\rho$, density of liquid; c, speed of sound.

## LITERATURE CITED

1. Yu. L. Rastorguev and V. V. Pugach, Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 8 (1970).
2. R. A. Mustafaev, D. M. Gabulov, and A. A. Abbasov, Izv. Vyssh. Uchebn. Zaved., Énerg., No. 7 (1975).
3. R. A. Mustafaev and D. M. Gabulov, Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 1 (1976).
4. R. A. Mustafaev, D. M. Gabulov, and A. A. Abbasov, Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 8 (1975).
5. R. A. Mustafaev and E. S. Platunov, Teplofiz. Vys. Temp., 10, No. 3 (1972).
6. R. A. Mustafaev, Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 11 (1973).
7. E. S. Platunov, Thermophysical Measurements in the Monotonic Regime [in Russian], Énergiya, Leningrad (1973).
8. S. L. Rivkin, Author's Abstract of Candidate's Dissertation, Moscow (1967).
9. P. W. Bridgman, Proc. Am. Acad., 59, 139 (1928).
10. G. Bridgman, Physics of High Pressure, Dover (1971).
11. E. P. Borovik, Zh. Éksp. Teor. Fiz., No. 1 (1948).
12. Yu. S. Shoitov and N. F. Otpushchennikov, in: Ultrasound and Physicochemical Properties of Materials [in Russian], Vol. 71, 4th ed., Kursk (1970).
13. B. S. Kir'yakov and N. F. Otpushchennikov, in: Ultrasound and Physicochemical Properties of Materials [in Russian], Vol. 7, 6th ed., Kursk (1972).