THERMAL CONDUCTIVITY OF HIGHER SATURATED n-HYDROCARBONS OVER WIDE RANGES OF TEMPERATURE AND PRESSURE

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Results are shown of an experimental study concerning the thermal conductivity of n-alkanes over a wide range of values of the state variables. Numerical formulas are derived which agree closely with the test data.

Since a few years ago the thermal conductivity of liquids has been measured by transient methods with, for example, spherical or cylindrical double calorimeters [1-3]. These methods do not account for the temperature dependence of thermophysical properties, neither is the testing time (at high temperatures) much shorter than that required in steady-state methods and, furthermore, they do not yield in a single test the temperature characteristic of thermal conductivity. In this respect, monotonic heating methods are most effective for measurements over a wide temperature range. These methods are more convenient than others, because they make it unnecessary during measurements over a wide temperature range to repeatedly establish a steady state, and also because they make it possible over an essentially unlimited temperature range to determine the temperature characteristic of thermal conductivity $\lambda(T)$ from a single test.

This experimental study was concerned with the thermal conductivity of higher n-alkanes (n-hexadecane, n-heptadecane, n-octadecane, and n-nonadecane). The tests covered the 40-420°C temperature range as well as pressures up to 500 kg/cm^2. The characteristics of the tested hydrocarbons are given in Table 1. The measurements were made by a monotonic heating method which had been developed for this purpose. The theoretical principle of this method, the test procedure, and the apparatus design have all been described earlier in [4, 5].

The main component of the apparatus was a double calorimeter consisting of two coaxial cylinders. The inner cylinder (rod) was made of grade M1 copper. The active rod surfaces were carefully ground, chrome plated, and polished. The outer cylinder was tube of grade 1Kh18N9T stainless steel pressed into a massive copper block. The basic dimensions of this double calorimeter are given in [5]. The gap between both cylinders was filled with the test liquid. The gap, uniform over the entire rod surface, was maintained by means of specially calibrated quartz balls pressed into the rod. For calculations we used the formula

$$\lambda(\bar{t}) = \frac{b_r N(t)}{(\vartheta_h - \vartheta_0)} (1 + \Delta\sigma_r + \Delta\sigma_\Phi + \Delta\sigma_\vartheta) - \Delta\lambda. \tag{1}$$

With $\bar{t} = t_r(\tau) + 1/2\vartheta_h(\tau)$; $N(t) = hC_r/\bar{F}$; a correction $\Delta\sigma_r = C/2C_r$ for the heat capacity of the rod; a correction $\Delta\sigma_\Phi = [-\Delta\sigma_r(\Delta F_{tr}/3\bar{F}) + 1/8(\Delta F_{tr}/\bar{F})^2]$ for the curvature of the rod; a correction $\Delta\sigma_\vartheta = 1/6[\Delta\sigma_r \cdot (2k_\vartheta - k_r)\bar{\vartheta}_h - 1/2n_\lambda\bar{\vartheta}_h^2]$ for nonlinearity; a correction $\Delta\lambda(t)$ for heat leakage through fasteners in contact with the liquid layer, with $\Delta F_{tr} = F_t - F_r$, and the relative temperature coefficients $k_\vartheta = (1/\vartheta_h)(d\vartheta_h/dt)$; $k_r = (1/C)(dC/dt)$; $n_\lambda = (1/2\lambda)(d^2\lambda/dt^2)$.

The form of the correction terms suggests that $\Delta\sigma_r$ can be estimated analytically from rough data on the thermal capacity of the liquid layer, while correction terms $\Delta\sigma_\Phi$ and $\Delta\sigma_\vartheta$ amounting to $8 \cdot 10^{-4}$ and $7 \cdot 10^{-4}$, respectively (for the given instrument design and the far from critical test mode) may be omitted in the calculation. With the thermocouples installed permanently, correction ϑ_0 depends only on the temperature level and on the heating rate and, therefore, is determined in calibration tests as an "instrument

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TABLE 1. Characteristics of Tested Hydrocarbons

n-Hexadecane	$\rho_4^{20}=0,7736$	$n_D^{20}=1,4344$	$t_{boil}=287,5$ °C
n-Heptadecane	$\rho_4^{30}=0,7714$	$n_D^{30}=1,4330$	$t_{boil}=302,5$ °C
n-Octadecane	$\rho_4^{50}=0,7622$	$n_D^{50}=1,4272$	$t_{boil}=318,2$ °C
n-Nonadecane	$\rho_4^{50}=0,7761$	$n_D^{50}=1,4296$	$t_{boil}=332,2$ °C

TABLE 2. Rounded Values of Thermal Conductivity $\lambda \cdot 10^4$ (W/m · deg as a function of temperature and pressure, for four saturated n-hydrocarbons)

t, °C	P, kg/cm²												
	1	100	200	300	400	500	1	50	100	200	300	400	500
	n-Hexadecane						n-Heptadecane						
40	1400	1441	1476	1505	1532	1555	1427	1446	1465	1500	1529	1556	1582
60	1364	1407	1439	1468	1495	1519	1391	1412	1431	1466	1495	1523	1550
80	1323	1367	1401	1430	1458	1483	1352	1373	1396	1430	1462	1492	1521
100	1284	1329	1365	1396	1426	1454	1314	1333	1359	1394	1427	1458	1488
120	1245	1292	1329	1362	1394	1425	1282	1297	1328	1365	1398	1430	1460
140	1204	1256	1295	1330	1363	1396	1240	1262	1290	1330	1365	1398	1429
160	1168	1224	1265	1303	1336	1372	1201	1226	1254	1295	1333	1367	1401
180	1132	1192	1235	1276	1312	1346	1161	1190	1220	1263	1304	1340	1377
200	1095	1160	1206	1249	1289	1325	1125	1155	1187	1232	1275	1315	1348
220	1062	1132	1181	1228	1273	1311	1088	1125	1158	1207	1254	1293	1330
240	1034	1111	1163	1215	1262	1298	1059	1099	1135	1183	1234	1277	1317
260	1008	1090	1145	1199	1249	1286	1030	1075	1112	1166	1219	1264	1305
280		1072	1131	1186	1237	1275	1005	1056	1097	1153	1206	1253	1293
300		1052	1118	1174	1225	1265		1039	1080	1138	1197	1243	1286
320		1036	1104	1163	1214	1257		1022	1067	1127	1182	1232	1278
340		1025	1092	1153	1205	1250		1006	1055	1118	1174	1225	1272
360		1015	1084	1145	1196	1244		996	1043	1106	1165	1216	1264
380		1008	1078	1138	1189	1239		985	1032	1097	1156	1210	1260
400		1002	1074	1132	1182	1234		978	1026	1093	1151	1204	1254
420		995	1069	1127	1176	1230		973	1020	1087	1148	1202	1250
	1	100	200	300	400	500	1	50	100	200	300	400	500
	n-Octadecane						n-Nonadecane						
40	1448	1487	1519	1549	1578	1605	1470	1489	1506	1540	1570	1598	1625
60	1414	1456	1487	1518	1547	1575	1435	1454	1472	1504	1534	1562	1591
80	1378	1422	1453	1484	1514	1543	1400	1421	1439	1472	1503	1532	1561
100	1343	1388	1421	1454	1484	1512	1364	1385	1405	1439	1471	1501	1530
120	1308	1354	1390	1424	1455	1485	1330	1352	1372	1408	1441	1472	1502
140	1273	1321	1362	1396	1429	1461	1295	1317	1339	1377	1412	1443	1474
160	1237	1290	1332	1368	1400	1433	1259	1286	1308	1346	1382	1416	1448
180	1202	1260	1302	1339	1375	1409	1224	1253	1279	1319	1357	1393	1427
200	1167	1228	1274	1315	1352	1386	1190	1221	1250	1292	1333	1372	1408
220	1134	1198	1252	1294	1332	1368	1159	1192	1224	1272	1315	1355	1394
240	1102	1172	1228	1274	1314	1352	1129	1164	1201	1251	1297	1341	1382
260	1073	1151	1208	1257	1229	1339	1100	1140	1180	1232	1281	1326	1368
280	1043	1130	1189	1241	1286	1327	1074	1117	1160	1216	1268	1316	1358
300	1017	1110	1174	1226	1275	1318	1049	1098	1142	1200	1255	1305	1351
320		1095	1162	1215	1264	1308	1024	1075	1125	1186	1244	1295	1345
340		1082	1150	1204	1255	1302		1062	1110	1175	1232	1286	1338
360		1071	1138	1193	1248	1295		1049	1095	1166	1223	1279	1332
380		1060	1128	1182	1239	1289		1035	1082	1154	1215	1272	1325
400		1050	1120	1174	1230	1284		1020	1070	1145	1206	1264	1318
420		1044	1114	1167	1223	1279		1007	1060	1140	1198	1257	1313

constant." Correction $\Delta\lambda(t)$ is also an "instrument constant" in the case of a permanent test setup.

A special feature of formula (1) is that it has been derived with the temperature characteristic of thermal conductivity $\lambda(t)$ taken into account and it is quite suitable for determining this characteristic from a single test.

In accordance with the formula, the determination of $\lambda(t)$ for a liquid reduces to a measurement of the heating rate $b_r(\tau)$ of the rod and the temperature drop ϑ_h across the layer.

The temperatures were measured with Nichrome–constantan thermocouples (electrodes 0.2 mm in diameter) which had been precalibrated at the D. I. Mendeleev VNIIM. The heating rate and the temperature drop were measured with a model R-306 class 0.015 low-resistance potentiometer, a model M17/4 mirror galvanometer, and a model 51SD stop watch graduated in 0.1 sec. The pressure was produced and measured with a model MP-600 loading piston manometer and a set of class 0.2 standard manometers.

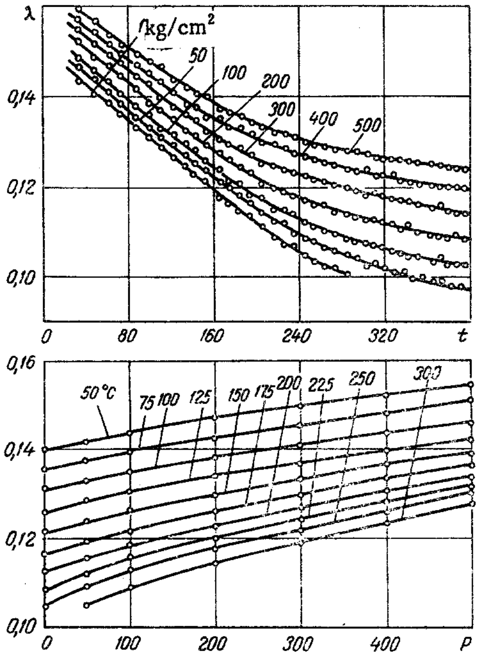

Fig. 1

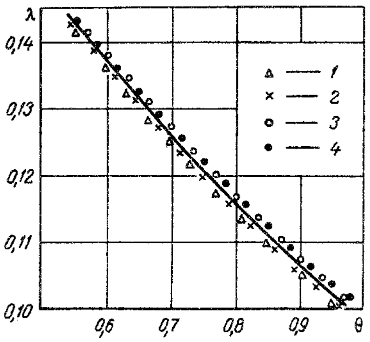

Fig. 2

Fig. 1. Thermal conductivity λ (W/m · deg) of n-heptadecane as a function of the temperature t (°C) and the pressure P (kg/cm²).

Fig. 2. Universal curve of thermal conductivity λ (W/m · deg) as a function of the referred temperature $\theta = T/T_{\text{boil}}$, for: 1) n-hexadecane; 2) n-heptadecane; 3) n-octadecane; 4) n-nonadecane.

Measurements were made at various heating rates, so that the temperature drop across the liquid layer could be varied within 3-8°C limits. The absence of convection was ascertained by measurements at various heating rates. Rounded values of the λ(t) characteristics are given in Table 2 for the four tested hydrocarbons. The maximum relative measurement error was estimated at ±2%. The repeatability of test data taken at the same values of the state variables was within 0.8-1.0%. Isobars were then plotted on the basis of these data and, for their intercorrelation, isotherms were also plotted by appropriate point matching. The isobars and the isotherms of thermal conductivity are shown in Fig. 1 for n-heptadecane. The isobars and the isotherms of thermal conductivity for n-hexadecane, n-octadecane, and n-nonadecane are analogous.

An analysis of the data shows that the thermal conductivity of hydrocarbons decreases with rising temperature and increases with rising pressure. The effect of pressure becomes more appreciable at higher temperatures, which causes the isobars of thermal conductivity to bend for all hydrocarbons. The isobars and the isotherms of thermal conductivity are not straight lines. They are slightly bent curves, the isobars bending downward to the temperature axis and the isotherms bending upward from the pressure axis.

The test data pertaining to the thermal conductivity of all four hydrocarbons, as a function of the pressure along isotherms, can be described rather accurately by the equation

$$\lambda = \lambda_0 + k(P - P_0), \tag{2}$$

with λ_0 denoting the thermal conductivity at $P = P_0$; P_0 denoting the atmospheric pressure; and P denoting the applied pressure. The coefficient $k = (\partial\lambda/\partial P)_T$ at various temperatures can be calculated according to the equation

$$k = k_0 + A(t - t_0),$$

where $k_0 = k_{t=t_0} = 3.2 \cdot 10^{-5}$ and $A = 8 \cdot 10^{-8}$.

Modern theory of the liquid state yields no analytical relation for calculating the thermophysical properties. It is worthwhile, therefore, to develop semiempirical and empirical methods of calculating the thermophysical properties. Several formulas have been proposed recently for calculating the thermal conductivity of liquids. The authors usually aimed at establishing some empirical relations for the thermal conductivity of individual hydrocarbons, without attempting to cover various hydrocarbon groups by a single formula. Another common drawback of these formulas is that they are either approximations covering a narrow temperature range or are complicated and contain quantities the determination of which requires a design of special experiments.

Test data pertaining to the thermal conductivity of liquids are usually generalized by functional relations in the form

$$\frac{\lambda_{p,t}-\lambda_t}{\lambda_{pc,tc}-\lambda_{tcr}}=f_1\left(\frac{\rho}{\rho_{cr}}\right);\quad \frac{\lambda_{p,t}}{\lambda_{pc,tc}}=f_2(\pi,\tau);$$
$$\frac{\lambda_t}{\lambda_{tcr}}=f_3(\tau);\quad \frac{\lambda_t}{\lambda_1}=f_4(\tau).$$

In order to be able to use them, one must know the values of λ_{pc}, λ_{tc}, and λ_1. Unfortunately, these values cannot be found in the technical literature for most liquids and, especially, for saturated n-hydrocarbons.

In order to generalize data on the thermal conductivity of normal liquids, the author has established in [7] that under atmospheric pressure there exists a single functional relation between the thermal conductivity and the referred temperature $\tau = t/t_{cr}$. An excellent total correlation can be obtained if the boiling point T_{boil} of a liquid is used as the reference temperature and $\theta = T/T_{boil}$. The thermal conductivity data for the four liquid hydrocarbons fit then along a straight line in $\lambda = f(\theta)$ coordinates. In Fig. 2 are shown the results of an evaluation of these thermal conductivity data for higher n-alkanes, in λ, θ coordinates. According to the graph, the data fit closely on a single curve represented by the equation

$$\lambda_t = 0.2289-0.1822\theta+0.0511\theta^2. \tag{3}$$

Equation (3) yields the thermal conductivity of higher n-alkanes directly, over the entire range of liquid state. The discrepancy between test values of λ and those calculated according to formula (3) is less than 1% over the entire temperature range. Only at $\theta = 0.95$ is the discrepancy maximum and almost 2%.

An analysis of the obtained experimental material on the thermal conductivity of saturated n-hydrocarbons under high pressures has yielded a universal formula for this thermal conductivity as a function of both temperature and pressure:

$$\lambda_{p,t}=\left[\lambda_{\theta=0.5}+5.5\cdot 10^{-5}(P-P_0)\right]\frac{A}{\sqrt{\theta}},\quad A=0.0875\theta+0.648. \tag{4}$$

Here $\lambda_{\theta=0.5} = 0.148$ is the thermal conductivity at $\theta = 0.5$.

The special feature of formulas (3) and (4) is that their coefficients are common for all the tested hydrocarbons and that they yield directly the thermal conductivity of higher n-alkanes (n-hexadecane, n-heptadecane, n-octadecane, and n-nonadecane) over a wide range of values of the state variables.

NOTATION

C_r	is the thermal capacity of copper rod;
h, $\bar{F}$	are the thickness and mean cross section of liquid layer;
b_r	is the heating rate of rod;
$\bar{\vartheta}_h$	is the mean-over-the-surface temperature drop across the liquid layer;
ϑ_0	is the correction for thermocouple readings of the temperature drop $\bar{\vartheta}_h$;
F_t, F_r	are the surface area of tube and of rod, respectively, contiguous to the liquid;
λ_t, ρ_t	are the thermal conductivity and density under atmospheric pressure and at temperature t;
$\lambda_{p,t_{cr}}$	is the thermal conductivity under pressure P and temperature t;
λ_{p_c,t_c}	is the thermal conductivity at critical point;
ρ_{cr}	is the density at critical point;
λ_1	is the thermal conductivity under atmospheric pressure and at $t = 0.5\ t_{cr}$;
$\tau = t/t_{cr}$;	
$\pi = P/P_{cr}$.	

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