THERMAL CONDUCTIVITY AND SPECIFIC HEAT OF n-DECANE AT VARIOUS TEMPERATURES AND PRESSURES

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Results are shown of experiments in which the thermal conductivity and the specific heat at constant pressure of n-decane were measured under pressures from 1 to 140 bars and at temperatures from 40 to 330°C.

Only a few studies have been made concerning the thermophysical properties of liquid n-decane under high pressures. The thermal conductivity of n-decane under pressure was measured by various test methods [1-3], namely: with a double calorimeter (transient method), with a hot wire, and with a spherical probe.

In [1] the test range of pressures was 0.98-392 bars and the temperature range was 20-171°C. In [2] these ranges were somewhat wider, namely, $p = 0.98$-490 bars and $t = 20$-200°C. In [3], where a spherical probe was used, the temperature ranged from 4.4 to 171.2°C and the pressure up to 346 bars. Unlike in [1, 2], here the measurements covered both liquid and gaseous n-decane.

Liquid decane under atmospheric pressure was studied by many researchers [4, 5]. A survey of the references listed here indicates wide discrepancies in the results, in some specific cases up to 20%.

Only meager data are available on the specific heat of decane at constant pressure. There are no data to be found in the technical literature pertaining to high-pressure measurements, while the test data obtained under atmospheric pressure [6, 7] refer to a very narrow temperature range.

In this article the authors will show the results of thermal conductivity and specific heat measurements pertaining to n-decane at temperatures from 40 to 330°C and pressures from 1 to 140 bars. The specific heat per volume c_p' of n-decane under high pressures was considered first.

Both λ and c_p' were measured compositely, by the method of monotonic heating in a calorimeter which we had developed earlier [8, 9]. The basic dimensions of the coaxial cylinders were the same as in [8]. The tests were performed along isobars and in about 10°C temperature steps. Both λ and c_p were then calculated according to well-known equations [8, 9], with corrections to account for the variability of the physical properties and for the heating rate of the system.

The heating rate during the test was varied over the range $b = 59$-104 deg/h, and the temperature drop across the tested layer of liquid was $\theta = 2.97$-4.97°C in the solid cylinder or $\theta' = 1.89$-4.23°C in the hollow cylinder.

During monotonic heating in a calorimeter, the top test pressure and temperature are very much limited by the choice of material for the autoclave, since experience has shown that during heating the temperature field becomes increasingly nonuniform along both the cylinder height and circumference. All components in our apparatus were made of copper and this ensured the best possible thermal mode of operation. The test pressure is also limited by the feasibility of maintaining it constant in large volumes of compressed air throughout the experiment, in order to measure c_p'. For these reasons, the pressure in our tests did not exceed 140 bars.

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TABLE 1. Thermal Conductivity λ (W/m · deg) and Specific Heat per Volume at Constant Pressure c_p' (J/m^3 · deg) of n-Decane (Average values)

t, °C	p, bars						
	1,01	10	25	50	75	100	140
				λ			
40	0,1349	0,1354	0,1361	0,1373	0,1383	0,1392	0,1407
60	0,1299	0,1305	0,1312	0,1326	0,1336	0,1345	0,1362
80	0,1251	0,1258	0,1265	0,1280	0,1290	0,1300	0,1319
100	0,1205	0,1212	0,1220	0,1235	0,1247	0,1258	0,1278
120	0,1161	0,1168	0,1176	0,1192	0,1206	0,1218	0,1238
140	0,1118	0,1125	0,1133	0,1150	0,1166	0,1180	0,1200
160	0,1075	0,1083	0,1092	0,1111	0,1127	0,1142	0,1164
180	0,0222	0,1042	0,1052	0,1073	0 1090	0,1106	0,1130
200	0,0240	0,1002	0,1012	0,1036	0,1054	0,1070	0,1097
220	0,0259	0,0962	0,0973	0,1000	0,1018	0,1034	0,1065
240	0,0278	0,0923	0,0935	0,0964	0,0983	0,1000	0,1033
260	0,0299	0,0882	0,0897	0,0929	0,0949	0,0968	0,1004
280	0,0321	0,0839	0,0859	0,0895	0,0919	0,0940	0,0978
300	0,0343	0,0374	0,0819	0,0860	0,0890	0,0915	0,0954
320	0,0366	0,0391	0,0776	0,0824	0,0860	0,0892	0,0932
				$c_p' \cdot 10^6$			
40	1,575	1,573	1 570	1,566	1,562	1,558	1,552
60	1,580	1,577	1,574	1,570	1,565	1,561	1,555
80	1,588	1,584	1,580	1,575	1,569	1,565	1,558
100	1,600	1,595	1,589	1,581	1,573	1,569	1,561
120	1,616	1,610	1,600	1,588	1,578	1,574	1,565
140	1,637	1,627	1,614	1,596	1,586	1,581	1,571
160	1,675	1,645	1,629	1,607	1,596	1,590	1,578
180	—	1,666	1,646	1,622	1,609	1,602	1,588
200	—	1,696	1,670	1,642	1,627	1,617	1,601
220	—	1,735	1,704	1,672	1,655	1,640	1,616
240	—	1,790	1,755	1,710	1,688	1,668	1,636
260	—	1,870	1,816	1,758	1,730	1,705	1,665
280	—	2,010	1,910	1,825	1,787	1,755	1,707
300	—	—	2,052	1,925	1,868	1,820	1,759
320	—	—	2,310	2,045	1,958	1,892	1,818

The results of our measurements are shown in Table 1 with rounded off temperature and pressure values. The estimated maximum error is ±2% for λ and ±3% for c_p.

Our values are compared with those obtained by others under atmospheric pressure in Fig. 1, where a wide discrepancy with the data from [2, 3] can be seen (up to 13 and 17%, respectively). There is a close agreement in the temperature coefficient of thermal conductivity according to us and to [2].

The absolute values of λ according to [1] come close to ours, although the values of its temperature coefficient differ.

Our data agree fairly well with those in [5] (the values in [5] are 3.0-4.5% lower).

A comparison between our values with those in [1-3] for high pressures shows that in [1] the values for $p = 100$ bars are only 2% lower at $t = 45°C$ and 1% higher at $t = 171°C$; in [2] the values for $p = 100$ bars are 12% lower at 40°C and 13.5% lower at $t = 200°C$; in [3] the values for $p = 140$ bars are 11% lower at $t = 38°C$ and 18% lower at $t = 171°C$.

An analysis of the data in [10] on the thermal conductivity of liquids would indicate that the values in [2, 3] are much too high also for other representatives of the paraffin series. The values in [1] agree closely with those in [10]. They agree fairly well with most recent data on the thermal conductivity of n-heptane [11].

Such a wide discrepancy between our data and those in [2, 3] is, apparently, due to the fundamental differences between the methods used for measuring the thermal conductivity.

It is to be noted that existing experimental methods of measuring still leave much to be desired. As of today, many problems have not yet been solved.

A comparison between our c_p values and those in other sources [6, 7] has shown that ours are slightly higher (by approximately 0.8%).

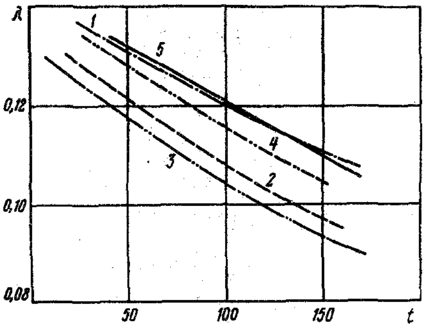

Fig. 1

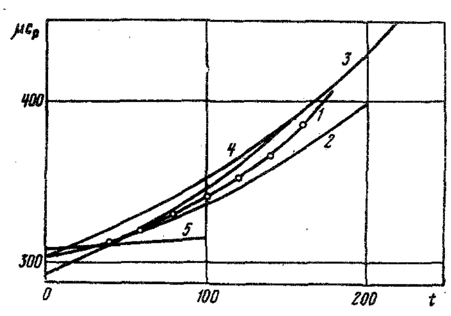

Fig. 2

Fig. 1. Comparison between thermal conductivity data for n-decane under atmospheric pressure, λ (W/m · deg): 1) according to Abas-zade and Guseinov; 2) according to Rastorguev, Bogatov, and Grigor'ev; 3) according to Carmichael and Sage; 4) according to Mukhamedzyanov, Usmanov, and Tarzimanov; 5) according to Naziev and Aliev.

Fig. 2. Comparison between measured and calculated values of thermal conductivity for n-decane: 1) test data; 2) Eq. (1); 3) Eq. (3); 4) Eq. (2); 5) Eq. (4).

For determining the temperature dependence of c_p for n-alkanes, various researchers have proposed the following formulas:

the Sokolov equation [12]

$$\mu c_p = \mu c_1 + \mu^{\frac{3}{4}} \frac{(T - 0.5\,T_{cr})}{\left[T\,(T_{cr} - T)\right]^{\frac{1}{2}}} \cdot \frac{T}{T_{cr}}, \text{ cal/mole}\cdot\text{deg}, \tag{1}$$

with μc_1 determined from the equation

$$\mu c_1 = -8.318 + 2.6n; \tag{1a}$$

the Hadden equation [13]

$$c_p = a + bT_r + cT_r^2 + dT_r^3 + m(\Delta a + \Delta bT_r + \Delta cT_r^2 + \Delta dT_r^3), \text{ cal/g}\cdot\text{deg}; \tag{2}$$

the Naziev equation [14]

$$\mu c_p = \mu c_1 + 0.086\mu\,(\mu - 14)\,\frac{T - T_1}{L}, \text{ cal/mole}\cdot\text{deg}, \tag{3}$$

with $\mu c_1 = -1.00 + 0.52\mu$;

the Anghelescu equation [15]

$$\frac{\mu c_p}{n - 2} = (-0.082 + 0.074n)\,\theta + (9.072 + 0.012n), \text{ cal/mole}\cdot\text{deg}, \tag{4}$$

where $\theta = (T - T_m)/(T_{cr} - T_m)$. (4a)

The constants in Eq. (2) for n-alkanes are a = 0.84167; b = 1.47040; c = 1.67165; d = 0.59198; Δa = −0.003826; Δb = 0.000747; Δc = 0.041126; Δd = −0.013950.

Formulas (1)-(4), after a proper conversion, were applied to the c_p of n-decane under atmospheric pressure. The calculated results are shown and compared with test data in Fig. 2.

It is quite evident here that Eq. (1) yields a close agreement with test results at low temperatures. As the temperature rises, the discrepancy becomes much wider (a −6% difference at t = 174°C). The error of Eq. (2) is maximum at moderate temperatures (+70% at t = 100°C). The error of Eq. (3) is relatively smaller (maximum +3% at t = 120°C).

According to Eq. (4), c_p should be a linear function of the temperature and its temperature coefficient should be small. Tests have not confirmed this, as we see in Fig. 2.

On the basis of our c_p data, we recommend a more accurate empirical equation:

$$\mu c_p = A + BT_r + CT_r^2 + DT_r^3, \text{ J/mole} \cdot \text{deg},$$

with A = −64.63, B = 1367, C = −1833, and D = 932.

NOTATION

λ	is the thermal conductivity of a substance;
c_p, c'_p, and μc_p	are the specific heat per mass, per volume, and per mole, respectively;
T_{cr}	is the critical point;
T_m	is the melting point;
T_b	is the boiling point;
n	is the total number of all atoms in a molecule;
m	is the number of carbon atoms in a molecule;
$T_1 = 0.5\ T_{cr}$;	
$T_r = T/T_b$;	
L	is the heat of evaporation, per mole;
A, B, C, D, a, b, c, d, Δa, Δb, Δc, and Δd	are constants in the equations.

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