# Thermal Conductivity of Five Normal Alkanes in the Temperature Range 283–373 K at Pressures up to 250 MPa

Y. Tanaka,<sup>1</sup> Y. Itani,<sup>1,2</sup> H. Kubota,<sup>1</sup> and T. Makita<sup>1</sup>

Received February 12, 1988

Experimental data on the thermal conductivity of five liquid *n*-alkanes—hexane, heptane, octane, decane, and dodecane—are presented in the temperature range from 283 to 373 K at pressures up to 250 MPa or the freezing pressures. The measurements were performed on an absolute basis by an automated transient hot-wire apparatus. The uncertainty of the reported data is estimated to be within  $\pm 1$ %. The thermal conductivity of each alkane decreases almost linearly with rising temperature at a constant pressure and increases with increasing pressure at a constant temperature. Both the temperature coefficient of the thermal conductivity  $|(\partial \lambda/\partial T)_P|$  and the pressure coefficient  $(\partial \lambda/\partial P)_T$  decrease with increasing carbon number of alkanes. The experimental results were correlated with temperature and pressure by a similar expression to the Tait equation. It is also found that both the dense hard-sphere model presented by Menashe et al. and the modified significant structure theory proposed by Prabhuram and Saksena provide good representations of the present experimental results.

**KEY WORDS:** alkane; correlation; decane; dodecane; heptane; hexane; octane; thermal conductivity; transient hot-wire method.

## **1. INTRODUCTION**

Accurate thermophysical property data of fluids are required over wide ranges of temperature and pressure in the designs of various processes and plants. However, reliable information is unexpectedly scarce on the thermal conductivity of these fluids, especially under high pressures. Even if available, there exists a sizable discrepancy among the literature values

<sup>&</sup>lt;sup>1</sup> Department of Chemical Engineering, Kobe University, Kobe 657, Japan.

<sup>&</sup>lt;sup>2</sup> Present address: Asahi Chemical Industry Co., Ltd., 2767-11 Niihama, Kojima-shiou, Kurashiki City, 711, Japan.

obtained by different researchers. Although several empirical estimation methods have been presented, they are often based on the earlier measurements before the development and refinement of the transient hotwire technique. Therefore, there is an urgent need for accurate and systematic measurements in order to improve technological designs and to develop the estimation techniques. The present investigation is undertaken in order to measure accurately the thermal conductivity of five *n*-alkanes over wide range of temperature and pressure.

## 2. EXPERIMENTAL

The measurements have been performed on an absolute basis by a transient hot-wire apparatus, fully described elsewhere [1], with an uncertainty less than 1%. A new set of platinum wires ( $20 \mu m$  in diameter and 150 mm long) was installed for the present measurements. Each of the experimental measurements has been subjected to the analysis proposed by Nieto de Castro et al. [2] to determine whether there is a significant radiative contribution to the thermal conductivity. After the analysis, it is concluded that the experimental results reported here are radiation-free values. The sample liquids were supplied by Tokyo Chemical Industry Co., Ltd., and Wako Pure Chemical Industries, Ltd. The reported purities were better than 99%. Before each measurement, the samples were purified by fractional distillation and degassing.

The density of heptane has been taken from the experimental results of Ozawa et al. [3]. For other alkanes the density data of Dymond et al. [4] were used. For the purpose of interpolation the Tait equation was employed, which provided a satisfactory description of the density values.

#### **3. EXPERIMENTAL RESULTS**

The experimental results for *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, and *n*-dodecane are presented in Tables I to V, respectively. Each table contains thermal conductivity at seven nominal temperatures from 283.15 to 373.15 K. Even if the thermostatic bath temperature  $T_b$  remained constant throughout a series of measurements as a function of pressure, the reference temperature  $T_r$  would change owing to the change of the thermal diffusivity. In this work, the reference temperature is generally 0 to 1.5 K higher than the bath temperature and is given by the following equation:

$$T_{\rm r} = T_{\rm b} + \{\Delta T_{\rm w}(t_1) + \Delta T_{\rm w}(t_2)\}/2 \tag{1}$$

where  $\Delta T_{w}$  is the temperature rise of the wire, and  $t_{1}$  and  $t_{2}$  are the initial and the final instants in the linear part of the experimental  $\Delta T$  vs ln t line.

	-
P (MPa)	$(\mathbf{W} \cdot \mathbf{m}^{-1} \cdot \mathbf{K}^{-1})$
$T_{\rm nom} = 283.$	15 K (10°C)
0.10	0.1218
$T_{nom} = 298.$	15 K (25°C)
0.10	0.1168
25.01	0.1293
50.00 75.02	0.1384 0.1472
100.00	0.1539
125.01 150.03	0.1606 0.1666
174.98	0.1728
199.98 225.01	0.1783 0.1823
250.00	0.1823
$T_{\rm norm} = 313$ .	15 K (40°C)
0.10	0.1119
$T_{\rm nom} = 323.$	15 K (50°C)
0.10	0.1096
25.13 50.02	0.1216 0.1309
74.98	0.1406
100.01 125.02	0.1479 0.1550
149.99	0.1550
175.02 199.98	0.1669
225.01	0.1727 0.1773
250.00	0.1824
$T_{\rm nom} = 333.$	15 K (60°C)
0.10	0.1055
	15 K (75°C)
24.99 49.98	0.1134 0.1236
75.01	0.1336
100.01 125.00	0.1419 0.1484
149.99	0.1559
175.02 200.00	0.1617 0.1679
225.01	0.1732
250.00	0.1772
	15 K (100°C)
24.99 50.02	0.1066 0.1174
75.01	0.1269
100.01 125.00	0.1359 0.1436
149.99	0.1503
175.02 199.98	0.1568 0.1626
225.01	0.1681
250.00	0.1733

Table I. Thermal Conductivity of n-Hexane

· · · · · · · · · · · · · · · · · · ·	
P (MPa)	$(\mathbf{W} \cdot \mathbf{m}^{\lambda_{nom}} \mathbf{K}^{-1})$
$T_{\rm nom} = 283$	.15 K (10°C)
0.10	0.1290
$T_{\rm nom} = 298$	.15 K (25°C)
0.10 24.92	0.1246 0.1345
50.09	0.1441
74.91 100.08	0.1515 0.1595
124.90 150.06	0.1666 0.1730
174.88 200.05	0.1783 0.1826
$T_{\rm nom} = 313$ 0.10	0.15 K (40°C) 0.1201
	.15 K (50°C)
0.10 24.92	0.1180 0.1283
50.09 74.91	0.1372 0.1452
100.08 124.90	0.1545 0.1614
150.06	0.1683
174.88 200.05	0.1736 0.1798
224.87 250.03	0.1846 0.1891
$T_{\rm nom} = 348$	3.15 K (75°C)
0.10	0.1116
24.92 50.09	0.1212 0.1335
74.91 100.08	0.1415 0.1496
124.90	0.1575 0.1647
150.06 174.88	0.1714
200.05 225.04	0.1784 0.1831
250.03	0.1886
	15 K (100°C)
24.92 50.09	0.1153 0.1278
74.91 100.08	0.1347 0.1457
124.90	0.1540 0.1631
174.88	0.1705
200.05 224.87	0.1769 0.1822
250.03	0.1856

Table II. Thermal Conductivity of *n*-Heptane

	-
P (MPa)	$(\mathbf{W}\cdot \overset{\lambda_{\mathrm{nom}}}{\mathbf{m}^{-1}}\mathbf{K}^{-1})$
Tnom	$= 283.15 \text{ K} (10^{\circ}\text{C})$
0.10 0.10 24.92 50.09 74.91 100.08 124.90 150.06 174.88 200.05	0.1303 0.1399 0.1483 0.1549 0.1621 0.1681 0.1736 0.1791 0.1835
$T_{\rm nom}$	$= 298.15 \text{ K} (25^{\circ}\text{C})$
$\begin{array}{c} 0.10\\ 24.92\\ 50.09\\ 74.91\\ 100.08\\ 124.90\\ 150.06\\ 174.88\\ 200.05\end{array}$	$\begin{array}{c} 0.1262\\ 0.1371\\ 0.1454\\ 0.1526\\ 0.1597\\ 0.1657\\ 0.1722\\ 0.1777\\ 0.1823\end{array}$
$T_{norm}$	$_{\rm h} = 323.15 \ {\rm K} \ (50^{\circ})$
$\begin{array}{c} 0.10\\ 24.94\\ 50.09\\ 74.91\\ 100.08\\ 124.90\\ 150.06\\ 174.88\\ 200.05\end{array}$	$\begin{array}{c} 0.1202\\ 0.1315\\ 0.1398\\ 0.1475\\ 0.1553\\ 0.1617\\ 0.1686\\ 0.1746\\ 0.1794 \end{array}$
$T_{nom}$	$= 333.15 \text{ K} (60^{\circ}\text{C})$
0.10	0.1173
$T_{\rm nom}$	$= 348.15 \text{ K} (75^{\circ}\text{C})$
$\begin{array}{c} 0.10\\ 24.92\\ 50.09\\ 74.91\\ 100.08\\ 124.90\\ 150.06\\ 174.88\\ 200.05\end{array}$	$\begin{array}{c} 0.1130\\ 0.1245\\ 0.1349\\ 0.1433\\ 0.1511\\ 0.1590\\ 0.1657\\ 0.1721\\ 0.1776\end{array}$
$T_{\rm nom} =$	= 373.15 K (100°C)
0.10 24.92 50.09 74.91 100.08 124.90 150.06 174.88 200.05	$\begin{array}{c} 0.1083\\ 0.1196\\ 0.1292\\ 0.1377\\ 0.1472\\ 0.1553\\ 0.1624\\ 0.1681\\ 0.1755\end{array}$

Table III. Thermal Conductivity of n-Octane

P (MPa)	$(\mathbf{W} \cdot \overset{\lambda_{nom}}{\mathbf{m}^{-1}} \mathbf{K}^{-1})$
Т	$= 283.15 \text{ K} (10^{\circ}\text{C})$
0.10 24.92 50.09 74.91 100.08 124.90 150.06 174.88	0.1347 0.1430 0.1503 0.1581 0.1635 0.1691 0.1739 0.1790
$T_{\rm nom}$	= 298.15 K (25°C)
0.10 24.92 50.09 74.91 100.08 124.90 150.06 174.88 200.05	$\begin{array}{c} 0.1311\\ 0.1398\\ 0.1476\\ 0.1549\\ 0.1612\\ 0.1672\\ 0.1726\\ 0.1726\\ 0.1779\\ 0.1826\end{array}$
$T_{\rm nom}$	$= 313.15 \text{ K} (40^{\circ}\text{C})$
0.10	0.1275
$T_{\rm nom}$	$= 323.15 \text{ K} (50^{\circ}\text{C})$
$\begin{array}{c} 0.10\\ 24.92\\ 50.09\\ 74.91\\ 100.08\\ 124.90\\ 150.06\\ 174.88\\ 200.05\end{array}$	$\begin{array}{c} 0.1256\\ 0.1341\\ 0.1434\\ 0.1512\\ 0.1581\\ 0.1642\\ 0.1709\\ 0.1752\\ 0.1806\end{array}$
$T_{\rm nom}$	= 348.15 K (75°C)
$\begin{array}{c} 0.10\\ 24.92\\ 50.09\\ 74.91\\ 100.08\\ 124.90\\ 150.06\\ 174.88\\ 200.05\end{array}$	0.1189 0.1307 0.1388 0.1476 0.1546 0.1615 0.1674 0.1733 0.1784
$T_{\rm nom}$ =	= 373.15 K (100°C)
0.10 24.92 50.09 74.91 100.08 124.90 150.06 174.88 200.05	$\begin{array}{c} 0.1129\\ 0.1242\\ 0.1333\\ 0.1428\\ 0.1513\\ 0.1578\\ 0.1637\\ 0.1698\\ 0.1763\end{array}$

Table IV.	Thermal	Conductivity	of <i>n</i> -Decane
-----------	---------	--------------	---------------------

P (MPa)	$(\mathbf{W} \cdot \mathbf{m}^{\lambda_{nom}} \mathbf{K}^{-1})$
$T_{\rm nom} = 283.$	15 K (10°C)
0.10	0.1385
$T_{\rm nom} = 298.$	15 K (25°C)
0.10	0.1356
24.92	0.1433
50.09 74.91	0.1502 0.1566
100.08	0.1633
124.90 150.06	0.1686 0.1742
164.89	0.1770
$T_{\rm nom} = 313.$	15 K (40°C)
0.10	0.1325
24.92 50.09	0.1403 0.1474
74.91	0.1543
100.08 124.90	0.1614 0.1666
150.06	0.1724
174.88	0.1781
200.05	0.1830
	15 K (50°C)
0.10 24.92	0.1299 0.1374
50.09	0.1456
74.91 100.08	0.1525 0.1592
124.90	0.1651
150.06 174.88	0.1707 0.1767
200.05	0.1815
$T_{\rm nom} = 348.$	15 K (75°C)
0.10	0.1250
24.92 50.09	0.1329 0.1413
74.91	0.1487
100.08 124.90	0.1558 0.1625
150.06	0.1625
174.88 200.05	0.1743
	0.1790
$T_{\rm nom} = 373.1$	
0.10 24.92	0.1188 0.1273
50.09 74.01	0.1371
74.91 100.08	0.1447 0.1523
124.90	0.1587
150.06 174.88	0.1647 0.1700
200.05	0.1761

Table V. Thermal Conductivity of n-Dodecane

337

Consequently, small temperature corrections were made to refer all the experimental thermal conductivities to common nominal temperatures  $T_{\text{nom}}$ . These corrections have been applied by means of a linear relation:

$$\lambda(P, T_{\text{nom}}) = \lambda(P, T_{\text{r}}) + (\partial \lambda / \partial T)_{P, T_{\text{nom}}} (T_{\text{nom}} - T_{\text{r}})$$
(2)

The derivative  $(\partial \lambda / \partial T)_{P, T_{nom}}$  has been evaluated with the assumption that the thermal conductivity of the liquids is a linear function of temperature at a constant pressure. Since the correction does not exceed 0.15% in any case, it is estimated that the additional uncertainty introduced into the tabulated thermal conductivity is negligible.

## 3.1. Temperature Dependence of Thermal Conductivity

The temperature dependence of the thermal conductivity of alkanes at atmospheric pressure are illustrated in Fig. 1, together with the experimen-

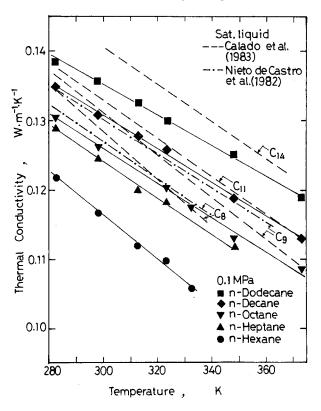


Fig. 1. Comparison of the thermal conductivity of normal alkanes at atmospheric pressure or saturated vapor pressures.

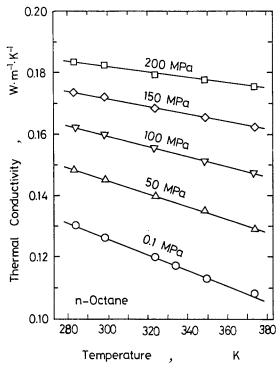


Fig. 2. Temperature dependence of the thermal conductivity of *n*-octane at various pressures.

tal data of Nieto de Castro et al. [5] and Calado et al. [6] for octane, nonane, undecane, and tetradecane at the saturated vapor pressures. The thermal conductivity of each alkane decreases almost linearly with rising temperature. Although there exist considerable inconsistences between the literature values [5, 6] and ours, the thermal conductivity of alkanes studied in each group increases with increasing carbon number at a

Substance	$(\mathbf{W} \cdot \mathbf{m}^{-1} \cdot \mathbf{K}^{-1})$	$10^4 b$ (W · m <sup>-1</sup> · K <sup>-2</sup> )	Mean dev. (%)	Max dev (%)
n-Hexane	0.2119	-3.185	0.25	0.57
n-Heptane	0.2041	- 2.665	0.20	0.47
n-Octane	0.2004	-2.486	0.33	0.73
n-Decane	0.2032	-2.418	0.14	0.41
n-Dodecane	0.2006	-2.183	0.20	0.33

Table VI. Empirical Coefficients in Eq. (3)

constant temperature. The absolute value of the temperature coefficient of  $\lambda$ , on the other hand, decreases with carbon number.

The thermal conductivity of each alkane investigated in this work can be expressed by a linear function of temperature as follows:

$$\lambda_0 = a + bT, \qquad 283 \text{ K} \leqslant T \leqslant 373 \text{ K} \tag{3}$$

where  $\lambda_0$  is the thermal conductivity in  $W \cdot m^{-1} \cdot K^{-1}$  and T is the temperature in K (see Table VI). Figure 2 illustrates typically the temperature dependence of the thermal conductivity of octane at various pressures. The temperature coefficient  $(\partial \lambda / \partial T)_P$  is always negative and nearly constant independently of temperature. The absolute value of  $(\partial \lambda / \partial T)_P$  decreases with increasing pressure. The behavior of other alkanes is generally similar to that of octane.

## 3.2. Pressure Dependence of Thermal Conductivity

The pressure dependences of the thermal conductivity of heptane and octane are typically illustrated in Figs. 3 and 4, respectively, as well as the

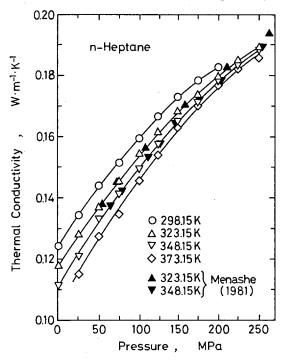


Fig. 3. Isothermal pressure dependence of the thermal conductivity of *n*-heptane.

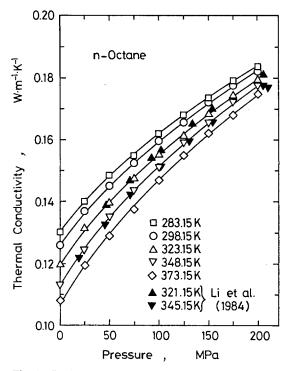


Fig. 4. Isothermal pressure dependence of the thermal conductivity of *n*-octane.

experimental data of Menashe and Wakeham [7] for heptane and those of Li et al. [8] for octane. It is found that the present results agree with these data within the mutual experimental uncertainties. As for decane and dodecane, there exist few experimental data under high pressures. Although the data of Rastorguev et al. [9] for decane are about 5% lower systematically than the present values, those of Mustafaev [10] for dodecane agree with our data within the experimental uncertainty.

The thermal conductivity of alkanes investigated increases with increasing pressure. Along an isotherm the pressure derivative is always positive and becomes larger with rising temperature and decreases with increasing pressure. In order to compare the pressure dependence of thermal conductivity as a function of temperature, it is convenient to use the relative thermal conductivity defined as  $\lambda/\lambda_0$ , where  $\lambda$  and  $\lambda_0$  are the thermal conductivities at high pressure and atmospheric pressure, respectively. Figure 5 is a plot of the relative thermal conductivity becomes larger with rising temperature. This may mean that the isotherms in Figs. 3 and 4 will intersect

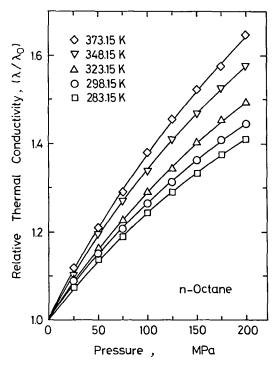


Fig. 5. Isothermal pressure dependence of the relative thermal conductivity of *n*-octane.

mutually at high pressures and the temperature coefficient  $(\partial \lambda / \partial T)_P$  will invert from negative to positive.

The relative thermal conductivity of alkanes investigated at 323.15 K is illustrated as a function of pressure in Fig. 6. The relative thermal conductivity of alkanes increases with decreasing carbon number at a constant temperature. Therefore, the thermal conductivities of lower alkanes would become higher ultimately than those of higher alkanes at very high pressures, although the thermal conductivities of the former are generally lower than those of the latter at atmospheric pressure as seen in Fig. 1.

## 3.3. Density Dependence of Thermal Conductivity

The thermal conductivity of n-octane is plotted against density in Fig. 7. The thermal conductivity increases with increasing density. The density dependence of thermal conductivity is almost independent of temperature in the experimental range of this work. The density derivative is always positive and increases with both increasing density and increasing carbon number of alkanes.

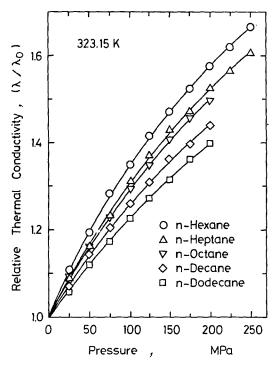


Fig. 6. Comparison of the relative thermal conductivity for normal alkanes at 323.15 K.

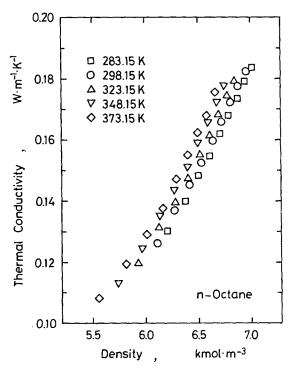


Fig. 7. Isothermal density dependence of the thermal conductivity of *n*-octane.

#### 4. DISCUSSION

#### 4.1. Empirical Correlation with Pressure and Temperature

As is well known, the isothermal variation of liquid density with pressure is well represented by the Tait equation. Recently, it was also found [11] that the effects of pressure on several thermophysical properties of fluids such as sound velocity, dielectric constant, viscosity, and thermal conductivity could be correlated by an expression similar to the Tait equation. Thus, the present experimental results were correlated with pressure and temperature by the following equation:

$$[\lambda - \lambda_0(T)]/\lambda = A \ln\{[B(T) + P]/[B(T) + P_0]\}$$
(4)

where  $\lambda_0(T)$  is the thermal conductivity at a reference pressure  $P_0$  (=0.1 MPa) and P is the pressure in MPa. The empirical coefficients A and B were determined by the method of least squares. Although the optimum coefficients could be determined for each isotherm, it is more convenient to treat A as a specific constant for an alkane and B as a function of temperature as follows:

$$B(T) = B_1 + B_2 T + B_3 T^2$$
(5)

where B(T) is in MPa and T is in K. The empirical coefficients thus obtained are listed in Table VII together with the deviations of experimental data from Eq. (4). The value of  $\lambda_0(T)$  can be calculated by Eq. (3). Equations (3) to (5) enable us to calculate the thermal conductivity of normal alkanes studied within the experimental uncertainty.

## 4.2. Correlation with Density by Dense Hard-Sphere Theory

Based on the hard-sphere theory of Dymond [12], Menashe et al. [13] derived a reduced thermal conductivity as follows:

$$\lambda' = (\lambda/\lambda^{0})(V/V_{0})^{2/3}$$
  
= 1.936 × 10<sup>7</sup> \lambda V^{2/3} (M/RT)^{1/2} / (1 + 0.352 C\_{v,int}^{0}/R) (6)

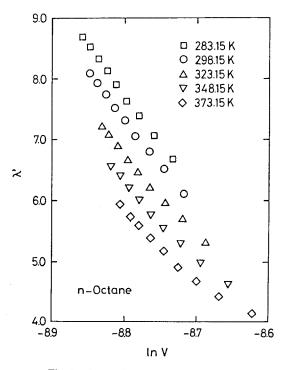
where  $\lambda^0$  is the thermal conductivity of dilute gas,  $V_0$  the molar volume of close packing for hard spheres (the effective molecular core volume), M the molecular weight, R the gas constant, and  $C_{v,int}^0$  the internal part of the molar heat capacity at zero density. The quantity  $\lambda'$  against ln V for octane is plotted typically in Fig. 8. The slope is almost equal for each isotherm. Therefore these isotherms can be superimposed into a single curve merely

Substance	A	B <sub>1</sub> (MPa)	$10 B_2$ (MPa · K <sup>-1</sup> )	$\frac{10^4 B_3}{(\mathrm{MPa} \cdot \mathrm{K}^{-2})}$	Mean dev. (%)	Max. dev. (%)
<i>n</i> -Hexane	0.190	144.3	-4.664	3.824	0.39	1.33
n-Heptane	0.216	94.36	-0.02209	4.14	0.55	2.30
n-Octane	0.207	250.4	-9.225	9.280	0.29	1.50
n-Decane	0.204	289.8	-10.80	11.08	0.25	1.07
n-Dodecane	0.239	302.4	-9.141	7.661	0.21	1.06

Table VII. Empirical Coefficients in Eqs. (4) and (5)

by imposing relative shifts along the ln V axis only. In order to construct these plots for octane, the volume  $V_0$  at 298.15 K was fixed arbitrarily and tentatively to 1.0000, and shifts of the lines  $\lambda'$  vs ln V at other temperatures were applied to achieve coincidence. As seen in Fig. 9 the agreement is quite good. The quantity ln  $\lambda'$  can be expressed by a linear equation of  $\ln(V/V_0)$  independently of temperature as follows:

$$\ln \lambda' = c + d \ln(V/V_0) \tag{7}$$



**Fig. 8.** Plots of  $\lambda'$  vs ln V for *n*-octane.

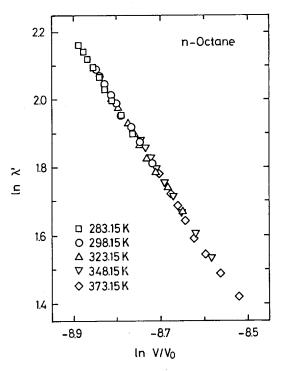


Fig. 9. Plots of  $\ln \lambda'$  vs  $\ln(V/V_0)$  for *n*-octane.

According to Menashe et al. [13] the thermal conductivity of normal alkanes with an odd number of carbon atoms  $(C_3, C_7-C_{13})$  and  $C_6$  and  $C_8$  alkanes could be represented by a single equation the same as Eq. (7). Therefore it is worthwhile to examine whether this equation is also valid for other alkanes studied in the present work. Consequently, it was confirmed that the reduced thermal conductivity of all alkanes investigated could be represented satisfactorily by Eq. (7) in a manner similar to the

Substance	с	d	Mean dev. (%)	Max. dev (%)
<i>n</i> -Hexane	- 16.90	-2.084	0.19	1.13
n-Heptane	-16.92	-2.119	0.41	1.90
n-Octane	-16.44	-2.094	0.30	1.86
n-Decane	-16.84	-2.191	0.23	0.72
n-Dodecane	-15.87	-2.122	0.29	1.22

Table VIII. Empirical Coefficients in Eq. (7)

$T(\mathbf{K})$	n-Hexane	n-Heptane	n-Octane	n-Decane	n-Dodecane
283.15			1.0288	1.0203	
298.15	1.0000	1.0000	1.0000	1.0000	1.0000
313.15					0.9815
323.15	0.9605	0.9530	0.9634	0.9607	0.9652
348.15	0.9206	0.9227	0.9259	0.9267	0.9315
373.15	0.8923	0.8822	0.8965	0.8997	0.9058

**Table IX.** Ratios of  $V_0(T)/V_0$  (298.15) in Eq. (7)

case of octane by imposing relative shifts along the ln V axis, only adopting  $\lambda'$  against the ln V curve at 298.15 K as a reference. The optimum coefficients in Eq. (7) and the ratios of the molar volumes V(T)/V (298.15 K) for each alkane are listed in Tables VIII and IX, respectively, as well as the deviations of experimental data from Eq. (7). It was also found that Eq. (7) could be a universal correlating equation for all normal alkanes studies here by taking heptane as the reference substance and reproduce all

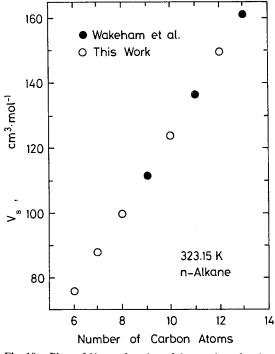


Fig. 10. Plots of  $V_s$  as a function of the number of carbon atoms at 323.15 K.

experimental data with a mean deviation of 0.3% and a maximum of 2.02%.

## 4.3. Correlation with Density by Modified Significant Structure Theory

Taking the liquid state for mixtures of gas and randomly distributed clusters of distorted microcrystals, Prabhuram and Saksena [14] derived the following expression for the liquid thermal conductivity:

$$\lambda = CT^{4/7} (V - V_{\rm s})^{-2/7} (V_{\rm s}/V)^2 \tag{8}$$

where V and  $V_s$  are the molar volume of the liquid and that of the quasicrystalline solid, and C is a specific constant of a substance independent of temperature and pressure.

In this work C and  $V_s$  of each alkane were determined by the method of least squares at each constant temperature. As a result, it was found that

Substance	Temp. (K)	$10^6 V_{\rm s}$ (m <sup>3</sup> ·mol <sup>-1</sup> )	Mean dev. (%)	Max. dev (%)
<i>n</i> -Hexane	298.15	76.44	0.34	0.67
	323.15	75.59	0.33	0.86
	348.15	74.90	0.35	0.84
	373.15	74.52	0.38	0.95
<i>n</i> -Heptane	298.15	88.93	0.29	0.72
	323.15	87.90	0.40	1.26
	348.15	87.43	0.57	2.52
	373.15	86.40	0.79	1.94
n-Octane	283.15	101.02	0.25	0.57
	298.15	100.58	0.20	0.51
	323.15	99.83	0.23	0.46
	348.15	99.21	0.43	0.84
	373.15	98.53	0.72	2.03
n-Decane	283.15	125.43	0.20	0.61
	298.15	124.77	0.07	0.17
	323.15	123.92	0.23	0.76
	348.15	123.19	0.19	0.49
	373.15	122.41	0.44	1.12
n-Dodecane	298.15	150.49	0.39	1.26
	313.15	150.03	0.36	1.47
	323.15	149.61	0.26	1.35
	348,15	149.11	0.36	1.78
	373.15	148.47	0.34	1.89

Table X. Empirical Coefficients in Eq. (8)

Temp. (K)	$e (m^3 \cdot mol^{-1})$	$\int (\mathbf{m}^3 \cdot \mathbf{mol}^{-1})$	$g (m^3 \cdot mol^{-1})$	Mean dev. (%)	Max. dev (%)
298.15	9.69	10.62	0.0922	0.67	1.56
323.15	8.34	10.72	0.0866	0.57	1.97
348.15	8.24	10.60	0.0940	0.82	3.69
373.15	10.14	10.00	0.1267	0.74	2.83

Table XI. Empirical Coefficients in Eq. (9)

C is almost constant for each alkane independently of temperature, whereas  $V_s$  depends on both substance and temperature. Therefore C was fixed constant at the mean value  $C = 8.138 \times 10^{-4}$ , and  $V_s$  was redetermined based on the experimental data. The values of  $V_s$  thus obtained are given in Table X as well as the deviations of experimental data from Eq. (8). As shown in Fig. 10,  $V_s$  at a constant temperature varies quite systematically with the carbon number of alkanes. The value of  $V_s$  is given by the following equation as a function of the carbon number  $N_c$  for each isotherm:

$$V_s = (e + fN_c + gN_c^2) \times 10^{-6}$$
<sup>(9)</sup>

The optimum coefficients in Eq. (9) and the deviations of experimental data from Eqs. (8) and (9) are given in Table XI. It was found that Eqs. (8) and (9) reproduce the present experimental results and those of Wakeham and co-workers [15, 16] with mean deviations of 0.7 and 1.5%, respectively. As shown in Table X,  $V_s$  changes very slightly and quite systematically with the temperature. Therefore, this method is useful for the correlation of liquid thermal conductivity of alkanes. It is expected to be developed into an excellent generalized correlation method by further consideration on other normal alkanes [17].

#### 5. CONCLUSION

The thermal conductivity of five normal alkanes  $C_6$ ,  $C_7$ ,  $C_8$ ,  $C_{10}$ , and  $C_{12}$  has been measured by the transient hot-wire method in the temperature range from 283 to 373 K under pressures up to 250 MPa. The experimental data are correlated with temperature, pressure, and density by several empirical and semitheoretical equations over the entire temperature and pressure ranges of this work. At this stage accumulations of experimental data on the thermal conductivity of organic liquids under high pressures are quite scarce in the literature, and even where available,

there exist remarkable scatters and inconsistencies among the literature values. However, it is well established that there is an urgent need for accurate thermal conductivity data on organic liquids in order to improve the technological applications, estimation techniques, and understanding of molecular aspects of heat transfer in liquids. The authors hope that the present work may contribute to a systematic and generalized investigation of the thermal conductivity of liquids.

#### REFERENCES

- 1. H. Kashiwagi, T. Hashimoto, Y. Tanaka, H. Kubota, and T. Makita, Int. J. Thermophys. 3:201 (1982).
- C. A. Nieto de Castro, S. F. Y. Li, G. C. Maitland, and W. A. Wakeham, Int. J. Thermophys. 4:311 (1983).
- S. Ozawa, N. Ooyatsu, M. Yamabe, S. Honmo, and Y. Ogino, J. Chem. Thermodyn. 12:51 (1980).
- 4. J. H. Dymond, J. Robertson, and J. D. Isdale, J. Chem. Thermodyn. 14:51 (1982).
- 5. C. A. Nieto de Castro, J. M. N. A. Fareleira, J. C. G. Calado, and W. A. Wakeham, in *Proc. 8th Symp. Thermophys. Prop.*, J. V. Sengers, ed. (ASME, New York, 1982), p. 247.
- J. C. G. Calado, J. M. N. A. Fareleira, C. A. Nieto de Castro, and W. A. Wakeham, Int. J. Thermophys. 4:193 (1983).
- 7. J. Menashe and W. A. Wakeham, Ber. Bunsenges. Phys. Chem. 85:340 (1981).
- 8. S. F. Y. Li, G. C. Maitland, and W. A. Wakeham, Ber. Bunsenges. Phys. Chem. 88:32 (1984).
- 9. Yu. L. Rastorguev, G. F. Bogatov, and B. A. Grigor'ev, *Izv. vyssh. ucheb. Zaved. Neft'i* Gaz. 12:69 (1969).
- 10. R. A. Mustafaev, Fluid Mech. Soviet Res. 3:133 (1974).
- 11. T. Makita, Netsu Bussei 1:19 (1987).
- 12. J. H. Dymond, Physica 75:100 (1974).
- 13. J. Menashe, M. Mustafa, M. Sage, and W. A. Wakeham, in Proc. 8th Symp. Thermophys. Prop., J. V. Sengers, ed. (ASME, New York, 1982), p. 254.
- 14. Prabhuram and M. P. Saksena, Indian J. Pure Appl. Phys. 19:717 (1981).
- 15. J. Menashe and W. A. Wakeham, Ber. Bunsenges. Phys. Chem. 86:541 (1982).
- 16. M. Mustafa, M. Sage, and W. A. Wakeham, Int. J. Thermophys. 3:217 (1982).
- 17. A. M. F. Palavra, W. A. Wakeham, and M. Zalaf, Int. J. Thermophys. 8:305 (1987).