# The Thermal Conductivity and Thermal Diffusivity of Liquid *n*-Alkanes: $C_nH_{2n+2}$ (*n*=5 to 10) and Toluene

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Experimental values of the thermal conductivity  $\lambda$  and the thermal diffusivity  $\kappa$  of six pure liquid *n*-alkanes ( $C_n H_{2n+2}$ ; n = 5 to 10) and toluene are presented in the temperature range of -20 to 70°C under atmospheric or saturation pressure. Measurements were made with the transient hot-wire method, and in the analysis, the temperatures  $T_{\lambda}$  and  $T_{\kappa}$  (associated with both  $\lambda$  and  $\kappa$ ) were used. In the present work, the values of thermal diffusivity were corrected by the factors  $k_r$  (=1.0076 to 0.9892) for data sets obtained with different configurations of the experiment, in which the factors were determined by reference to the thermal diffusivity of *n*-heptane [ $\kappa = \lambda_s/(c_p \rho)_s$ ] at 298.15 K calculated from the volumic heat capacity ( $c_p \rho$ )<sub>s</sub> as a reference material for heat capacity and the experimentally obtained thermal conductivity  $\lambda_s$ . The uncertainty of the data is estimated to be 0.48% for the thermal conductivity (absolutely measured) and about 1.8% for the thermal diffusivity (with a coverage factor of  $k_p = 2$ ; p = 95%).

**KEY WORDS:** decane; heptane; hexane; hydrocarbons; liquids; *n*-alkanes; nonane; octane; pentane; reference materials; specific heat capacity; thermal conductivity; thermal diffusivity; toluene; transient hot-wire method.

# **1. INTRODUCTION**

The thermophysical properties of liquid *n*-alkanes ( $C_nH_{2n+2}$ ) are important for improving the design of chemical plants, as well as for improving the energy efficiency of chemical processes. The authors have previously introduced procedures to measure simultaneously and absolutely the thermal

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conductivity and thermal diffusivity with the transient hot-wire (THW) method [1]. Results were reported for *n*-alkanes  $C_n H_{2n+2}$  (*n* = 5 to 10) in the temperature range of -20 to 70°C under atmospheric or saturation pressure [2, 3]. The temperature  $T_m = T_0 + (\frac{1}{2}) \{ \Delta T(t_i) + \Delta T(t_f) \}$  was referred to for the thermal conductivity data [4], and the initial equilibrium (bath) temperature  $T_0$  for the thermal diffusivity data, following a commonly used procedure [5]. One of the authors previously reported that the measured thermal diffusivity depended on the heating rate of the wire,  $Q_0$  (or the heating parameter  $Q_0/(4\pi\lambda)$ ) [1], and introduced two temperatures,  $T_{\lambda}$ and  $T_{\rm r}$ , referred to for the thermal conductivity and thermal diffusivity data [6]. The previous results are reanalyzed using  $T_i$  and  $T_r$  (along with the results for toluene). Those for toluene were obtained at the same time as the others to confirm the system, but they had not yet been reported. The system and experimental procedures are described in detail elsewhere [6]. Furthermore, the small diameter of the wire ( $\approx 15 \,\mu m$ ) is required to the obtain thermal diffusivity and is determined metrologically by the mass and the density of the piece of Pt wire. However, some systematic difference was found among the thermal diffusivity values in the data for different hot wires when employing this diameter. Therefore, the thermal diffusivity values were corrected by factors  $k_{\rm f}$  (=1.0076 to 0.9892) for a reason described in detail below.

## 2. MEASUREMENT PROCEDURE

#### 2.1. THW Model

To summarize the system, the actual model of the THW method is practically described by a transfer function having a feedback loop as shown in Fig. 1 [i.e., the heating rate of the wire,  $q(t) = Q_0(1 + A \Delta T(t) + B \Delta T^2(t) + \cdots)$ ,  $t \ge 0$ ], where A and B are fixed by the temperature dependence of the wire resistance and the circuit arrangement including the type of power supply. The temperature rise of the wire  $\Delta T(t)$  [inverse-Laplace transformation



Fig. 1. Equivalent diagram for the transient hotwire method with a feedback loop.  $F(\lambda, \sqrt{(s/\kappa)} a)$  is the ideal transfer function involving both  $\lambda$  and  $\kappa$  as parameters,  $\beta(s)$  is a feedback transfer function,  $Q_0/s$ is the step input of heat generation in the wire, and  $\Theta(s)$  is the corresponding temperature rise. of  $\Theta(s)$ ] (if  $\lambda$  and  $\kappa$  are not dependent on the temperature) is as follows [1, 6]:

$$dT(t) = \left(\frac{Q_0}{4\pi\lambda}\right) \left\{ \ln\frac{4\kappa t}{a^2 C} + \frac{a^2}{2\kappa t} \left(\frac{k-1}{k} \ln\frac{4\kappa t}{a^2 C} + 1\right) - \frac{a^2}{4\kappa_W t} + \frac{\lambda}{2\lambda_W} - \left(\frac{a^2}{4\kappa t}\right)^2 \left[ 3\left(1 - \frac{1}{k}\right)^2 \left(\ln\frac{4\kappa t}{a^2 C}\right)^2 + \left(1 + \frac{4}{k} - \frac{6}{k^2}\right) \left(\ln\frac{4\kappa t}{a^2 C}\right) - \left(\frac{\pi}{2} + \frac{3}{2}\right) + \frac{\pi^2 + 4}{k} - \frac{\pi^2}{2k^2} \right] + \cdots \right\} + A\left(\frac{Q_0}{4\pi\lambda}\right)^2 \left\{ \left(\ln\frac{4\kappa t}{a^2 C}\right)^2 + \frac{a^2}{\kappa t} \left(\ln\frac{4\kappa t}{a^2 C} + 1\right) - \frac{\pi^2}{6} + \cdots \right\} + A^2\left(\frac{Q_0}{4\pi\lambda}\right)^3 \left\{ \left(\ln\frac{4\kappa t}{a^2 C}\right)^3 - \frac{\pi^2}{2} \ln\frac{4\kappa t}{a^2 C} + 2\zeta(3) + \cdots \right\} + B\left(\frac{Q_0}{4\pi\lambda}\right)^3 \left\{ \left(\ln\frac{4\kappa t}{a^2 C}\right)^3 - \frac{\pi^2}{3} \ln\frac{4\kappa t}{a^2 C} + 2\zeta(3) + \cdots \right\}$$
(1)

where  $\lambda$  and  $\kappa$  are the thermal conductivity and thermal diffusivity of the sample, and  $\lambda_w$  and  $\kappa_w$  are those of the wire material (platinum), *a* is the radius of the wire ( $\approx 7.5 \,\mu$ m), *k* is the ratio of the volumic heat capacities (at constant pressure) of the sample and wire materials  $[c_p \rho/(c\rho)_w]$ , etc. [1, 6]. The higher-order term proportional to  $[4\kappa t/(a^2C)]^2$  is small in the present case, but it is significant for an experiment for lower-density substances or when using a hot-wire sensor having a relatively thick wire.

### **2.2.** Effective Temperatures $T_{\lambda}$ and $T_{\kappa}$ to be Referred to $\lambda$ and $\kappa$

When the temperature dependence of the thermal conductivity of the sample is  $\chi$  and that of the volumic heat capacity is  $\phi$ ,

$$\lambda = \lambda_0 (1 + \chi \, \Delta T) \tag{2}$$

$$c_p \rho = (c_p \rho)_0 \left( 1 + \phi \, \Delta T \right) \tag{3}$$

$$\kappa = \lambda/(c_p \rho) = \kappa_0 \{ 1 + (\chi - \phi) \, \varDelta T \}$$
(4)

where  $\lambda_0$ ,  $(c_p \rho)_0$ , and  $\kappa_0$  are the properties at  $T = T_0$ .

Then  $T_{\lambda}$  and  $T_{\kappa}$  are derived as follows:

$$T_{\lambda} = T_0 + \Delta T_{\lambda} = T_0 + \{1 + (\phi/\chi)\} \Delta T_{\rm m} - (\chi - \phi)(Q_0/4\pi\lambda_0)^2 \ln 4$$
 (5)

and

$$T_{\kappa} = T_0 + \Delta T_{\kappa} = T_0 + \{(\chi + \phi)/(\chi - \phi)\} \{ \Delta T_{\rm m} \ln(4\kappa_0 \cdot {\rm s}/a^2 {\rm C}) - (\frac{1}{2})(Q_0/4\pi\lambda_0) \times [(\ln 4\kappa_0 \cdot {\rm s}/a^2 {\rm C})^2 - (\ln t_{\rm i}/{\rm s})(\ln t_{\rm f}/{\rm s})] \} + (Q_0/4\pi\lambda_0) \ln 4$$
(6a)

or, as another equivalent expression,

$$T_{\kappa} = T_{0} + \Delta T_{\kappa} = T_{0} + \{(\chi + \phi)/(\chi - \phi)\}\{(\frac{1}{2})(Q_{0}/(4\pi\lambda_{0}))^{-1} \Delta T_{m}^{2} - (\frac{1}{8})(Q_{0}/(4\pi\lambda_{0}))\ln(t_{f}/t_{i})\} + (Q_{0}/4\pi\lambda_{0})\ln 4$$
(6b)

where

$$\Delta T_{\rm m} = \left(\frac{1}{2}\right) \left\{ \Delta T(t_{\rm i}) + \Delta T(t)_{\rm f} \right\}$$
(7)

The temperature  $T_{\lambda}$  is different by the small factor  $(\phi/\chi) \Delta T_{\rm m} - (\chi - \phi)$  $(Q_0/(4\pi\lambda_0))^2 \ln 4$  from the temperature  $T_{\rm m} = T_0 + \Delta T_{\rm m}$ . The magnitude of the heat capacity coefficient,  $\phi$ , for *n*-alkanes is rather small in comparison to the  $\chi$  for thermal conductivity. Also, the factor  $(\chi - \phi)(Q_0/(4\pi\lambda_0))^2 \ln 4$  can be neglected in the practical experiment. Therefore, the substitution of  $T_{\rm m}$  for the temperature  $T_{\lambda}$  is not such a serious problem. However,  $\Delta T_{\kappa}$  is larger [i.e., roughly  $\Delta T_{\kappa} \approx \Delta T_{\lambda} \ln(4\kappa \cdot s/(a^2C)) = \Delta T_{\rm m} \ln(4\kappa \cdot s/(a^2C))]$  for  $\phi \approx 0$  [under the present experimental conditions,  $\ln(4\kappa \cdot s/(a^2C)) \approx 7.5$ -8.0)], and so the use of the temperature  $T_{\kappa} = T_0 + \Delta T_{\kappa}$  in place of  $T_0$  is more significant. The relationships of both correction temperatures,  $\Delta T_{\kappa}$  and  $\Delta T_{\lambda}$ , is in correspondence with  $d\kappa/\kappa \approx d\lambda/\lambda \ln(4\kappa \cdot s/(a^2C))$ , the propagation of uncertainty: Eq. (12). That is, if  $d\lambda \to \chi \Delta T_{\lambda}\lambda$ , then,  $d\kappa \approx \chi \Delta T_{\kappa} \lambda \ln(4\kappa \cdot s/(a^2C))$ .

#### 2.3. Practical System for Measurements

The system and procedures for the experiment have been improved but remain almost the same as those reported previously [1]. In brief, they are as follows.

(a) Two hot-wire (four-terminal resistance) sensors (designated cells AC and BD) are employed, with platinum wires  $15 \,\mu\text{m}$  in diameter, which are installed as an arm of the double bridge. The potential leads are connected to the hot wire with a platinum wire  $10 \,\mu\text{m}$  in diameter. The effective

diameter of the platinum wire 2a is determined from the measured mass, length, and density, and the effective length of the hot-wire resistances is about 106 mm.

(b) The time range of the data sampling is normally between  $t_i$  (initial)  $\cong 0.030$  s and  $t_f$  (final)  $\cong 0.98$  s, and the number of data is 20 (i.e., sampling interval, 0.05 s; integration time, 0.02 s). For minimizing systematic errors of the results, it is very important to consider the terms deviating from the simplified equation  $\Delta T = (Q_0/(4\pi\lambda)) \ln(4\kappa t/(a^2C))$  in the working equation, for realizing a practical model with a feedback loop, accompanying the terms proportional to the feedback factors A,  $A^2$ , and B as shown in Eq. (1) [1, 6].

(c) The effect of the radiation heat transfer is regarded as a part of the ordinary heat conduction phenomena by carriers such as phonons, electrons, and molecules [6].

## 3. RESULTS AND COMPARISONS WITH OTHER DATA

The experiments are usually made using three heating rates  $Q_0$  at a controlled bath temperature  $T = T_0$  between -18 and  $70^{\circ}$ C. To avoid bringing into the results systematic differences resulting from the cells and the configuration of the experiment, the measurements were carried out with two cells, AC and BD, as usual [1]. Data for a regular configuration are designated set A for cell AC, and those for a inverted position, set C: similarly, the regular position for cell BD is associated with set B and the inverted position is for set D. The thermal conductivity results are considered reliable. However, for the thermal diffusivity, some slight systematic differences between groups were observed, although they come within 1% or so of the mean data in the respective sets. One of the major components of the systematic deviation is considered to result from the uncertainty of the diameter of the wire and its nonuniformity. Therefore, using the heat capacity value  $c_n \rho$  of *n*-heptane as a standard reference material for thermal diffusivity measurements, the cells were calibrated using the values of *n*-heptane:  $c_n = 2.2429 \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$  and  $\rho = 679.46 \text{ kg} \cdot \text{m}^{-3}$  at T =298.15 K [7], and the relationship  $\kappa = \lambda/(c_n \rho)$  (where  $\lambda_{298.15 \text{ K}}$  was determined from the results by an experiment made separately for calibration [6]). Then the correction factor  $k_{\rm f}$  for thermal diffusivity is introduced as follows:

> Set A data:  $k_{\rm f} = 1.00561$ Set B data:  $k_{\rm f} = 0.98917$ Set C data:  $k_{\rm f} = 1.00765$ Set D data:  $k_{\rm f} = 0.99181$

Measured thermal diffusivity data are multiplied by  $k_{\rm f}$  for the respective groups. These adjustments are about +0.7% for the AC cell and -1.0% for the BD cell. This is equivalent to an adjustment for the radius of the wire by about +0.35% for the AC cell and -0.5% for the BD cell.

Most *n*-alkanes used in the measurements were supplied by Wako Pure Chemical Industries Ltd., Japan, while *n*-hexane and toluene were supplied by Kishida Chemical Co. The purities were as follows: *n*-pentane, 98% special reagent; *n*-hexane, 98% spectroscopy special reagent; *n*-heptane, 99% spectroscopy special reagent; *n*-octane, 98% special reagent, *n*-nonane, 98% special reagent; *n*-decane, 99% special reagent; and toluene, 99% spectroscopy special reagent. Residual water was removed by means of a molecular sieve.

The experiments were carried out at three heating rates  $Q_0$  at a bath temperature  $T_0$  for respective settings of the cells (This means 12 data points at a temperature  $T_0$ .) Figures 2a and b show the data and the respective correlation lines for toluene, and Figs. 3a and b show all the data and respective correlations. The coefficients of these equations are listed in Table I in terms of the following formulas:

$$\lambda(\mathbf{W} \cdot \mathbf{m}^{-1} \cdot \mathbf{K}^{-1}) = \lambda_0(\mathbf{W} \cdot \mathbf{m}^{-1} \cdot \mathbf{K}^{-1}) - A[T(\mathbf{K}) - 273.15]$$
(8)

and

$$\kappa(10^{-8} \,\mathrm{m}^2 \cdot \mathrm{s}^{-1}) = \kappa_0(10^{-8} \,\mathrm{m}^2 \cdot \mathrm{s}^{-1}) - B[T(\mathrm{K}) - 273.15] \tag{9}$$

where the numbers in parentheses following the coefficients in Table I are the numerical values of the standard uncertainties referred to in the corresponding last digits of the quoted results for the intercept and slope. The data presented in Tables II to VIII are summarized as the mean of four

Material	N (data)	$\lambda_0 \left( W \!\cdot\! m^{-1} \!\cdot\! K^{-1} \right)$	$A(10^{-4})$	$\kappa_0 (10^{-8}\mathrm{m}^2\cdot\mathrm{s}^{-1})$	$B(10^{-2})$
Toluene	84	0.13763(4)	-2.848(11)	9.572(15)	-2.048(40)
<i>n</i> -Pentane	48	0.12073(5)	-3.785(21)	8.557(15)	-2.590(44)
<i>n</i> -Hexane	84	0.12504(5)	-3.347(14)	8.522(10)	-2.281(25)
<i>n</i> -Heptane	96	0.12856(4)	-3.112(11)	8.434(09)	-1.946(25)
<i>n</i> -Octane	84	0.13173(3)	-2.932(08)	8.522(08)	-1.913(21)
<i>n</i> -Nonane	60	0.13374(2)	-2.729(05)	8.493(10)	-1.757(25)
<i>n</i> -Decane	60	0.13599(2)	-2.568(06)	8.424(10)	-1.519(24)

Table I. Coefficients of Eqs. (8) and  $(9)^a$ 

<sup>*a*</sup> The numbers in parentheses following the coefficients are the numerical values of the standard uncertainties referred to in the corresponding last digits.



Fig. 2. Measured values for toluene: (a) thermal conductivity; (b) thermal diffusivity. Values were adjusted by factors  $k_{\rm f}$ .

results (sets A, B, C, and D obtained experimentally with an equivalent heating rate  $Q_0$ ) to reduce the number of data.

The properties of toluene obtained at 298.15 K are as follows:  $\lambda = 0.13051 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ ,  $\kappa = 9.060 \times 10^{-8} \text{ m}^2 \cdot \text{s}^{-1}$ ,  $c_p \rho = 1.441 \text{ MJ} \cdot \text{m}^{-3} \cdot \text{K}^{-1}$ ,  $c_p = 1.671 \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ , and  $c_m = 153.9 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ . The thermal conductivity value is consistent with  $\lambda = 0.1311 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  (the IUPAC value [9] with a confidence limit of 1%) and  $\lambda = 0.13088 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  (obtained previously by the first author using another measurement system [1]). The



Fig. 3. Measured values for *n*-alkanes  $C_nH_{2n+2}$  (*n*=5 to 10): (a) thermal conductivity, (b) thermal diffusivity. Values were adjusted by factors  $k_f$ .

thermal diffusivity is different by 1% from that reported previously [1], and this may be caused by adopting the temperature  $T_{\kappa}$  in the analysis. The specific and molar heat capacities are almost consistent with the values  $c_p = 1.707 \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$  and  $c_m = 157.29 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  [8] and, also, with  $c_p = 1.692 \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$  (presented previously [1]) within the estimated uncertainty (see Section 4).

Figures 4 to 9 show the deviations for *n*-alkanes of the measured thermal conductivity data and other data [9-16] from Eq. (8), and Fig. 10 shows those of the thermal diffusivity data from Eq. (9).

$T_0$ (°C)	$T_{\lambda}$ (°C)	$\lambda \left(W \!\cdot\! m^{-1} \!\cdot\! K^{-1}\right)$	$T_{\kappa}$ (°C)	$\kappa (10^{-8} \mathrm{m}^2 \cdot \mathrm{s}^{-1})$	$Q_0/(4\pi\lambda)(\mathrm{K})$
23.7469	24.5242	0.13039	26.1041	8.921	0.1285
23.7466	25.0998	0.13033	27.8786	8.979	0.2219
23.7459	25.4445	0.13015	28.8986	8.901	0.2808
4.1031	4.8336	0.13628	6.3412	9.352	0.1195
4.1017	5.3635	0.13607	7.9793	9.352	0.2056
4.1027	5.7047	0.13595	9.0283	9.355	0.2609
-12.7003	-11.9988	0.14117	-10.5052	9.829	0.1120
-12.7000	-11.4903	0.14101	-8.9081	9.836	0.1926
-12.7020	-11.1750	0.14080	-7.9339	9.776	0.2443
43.2860	44.1179	0.12506	45.8075	8.620	0.1374
43.2870	44.7266	0.12489	47.6546	8.611	0.2375
43.2855	45.1036	0.12478	48.7970	8.586	0.3003
54.5137	55.3734	0.12189	57.0912	8.348	0.1438
54.5134	56.0031	0.12177	59.0189	8.397	0.2465
54.5145	56.4019	0.12162	60.2134	8.372	0.3130
23.4219	24.2032	0.13075	25.8106	8.999	0.1279
23.4222	24.8566	0.13064	27.8644	9.103	0.2313
23.4225	25.3241	0.13049	29.2851	9.047	0.3083
40.5045	41.3312	0.12586	43.0186	8.672	0.1361
40.5057	42.0064	0.12572	45.0924	8.703	0.2455
40.5056	42.4986	0.12555	46.5816	8.664	0.3271

Table II. Experimenal Data for Toluene: Means of Four Results<sup>a</sup>

Table III. Experimental Data for *n*-Pentane: Means of Four Results<sup>*a*</sup>

$T_0$ (°C)	$T_{\lambda}$ (°C)	$\lambda(W\!\cdot\!m^{-1}\!\cdot\!K^{-1})$	$T_{\kappa}$ (°C)	$\kappa (10^{-8}\mathrm{m}^2\cdot\mathrm{s}^{-1})$	$Q_0/(4\pi\lambda)$ (K)
23.1470	24.0578	0.11146	26.0285	7.838	0.1426
23.1464	24.7875	0.11122	28.3479	7.829	0.2564
23.1470	25.2227	0.11104	29.7045	7.788	0.3254
4.1519	5.0827	0.11863	7.1387	8.367	0.1436
4.1524	5.6654	0.11833	8.9894	8.313	0.2344
4.1517	6.0796	0.11821	10.3160	8.302	0.2987
-15.2601	-14.4682	0.12635	-12.6889	8.831	0.1209
-15.2593	-13.8648	0.12618	-10.6969	8.878	0.2112
-15.2602	-13.4744	0.12595	-9.4350	8.832	0.2713
30.5845	31.5749	0.10897	33.7556	7.641	0.1533
30.5847	32.2864	0.10871	36.0431	7.633	0.2629
30.5848	32.7958	0.10859	37.6891	7.637	0.3408



**Fig. 4.** Deviations of measured values of the thermal conductivity of *n*-pentane and other results [10] from Eq. (8) with coefficients from Table I.

<i>T</i> <sub>0</sub> (°C)	$T_{\lambda}$ (°C)	$\lambda \left( W \cdot m^{-1} \cdot K^{-1} \right)$	$T_{\kappa}$ (°C)	$\kappa (10^{-8} \mathrm{m}^2 \cdot \mathrm{s}^{-1})$	$Q_0/(4\pi\lambda)$ (K)
24.4282	25.2944	0.11639	27.2332	7.894	0.1442
24.4298	25.9215	0.11610	29.2651	7.861	0.2481
24.4290	26.3200	0.11593	30.5541	7.835	0.3147
6.2821	7.0869	0.12236	8.9026	8.301	0.1331
6.2826	7.6644	0.12238	10.7865	8.285	0.2283
6.2813	8.0387	0.12230	12.0157	8.271	0.2900
-14.0773	-13.3403	0.12998	-11.6625	8.786	0.1211
-14.0768	-12.8091	0.12970	-9.9179	8.777	0.2079
-14.0775	-12.4664	0.12952	-8.7906	8.770	0.2642
42.5886	43.5194	0.11031	45.5820	7.465	0.1562
42.5884	44.1870	0.11010	47.7358	7.469	0.2679
42.5891	44.6138	0.10994	49.1033	7.431	0.3396
23.5154	24.3744	0.11673	26.2978	7.835	0.1430
23.5152	25.0744	0.11640	28.5697	7.815	0.2593
23.5159	25.5863	0.11625	30.2302	7.807	0.3441
51.1794	52.1367	0.10767	54.2520	7.257	0.1610
51.1813	52.9071	0.10737	56.7203	7.213	0.2902
51.1812	53.4810	0.10719	58.5649	7.179	0.3867
61.7126	62.7056	0.10444	64.8878	7.045	0.1678
61.7129	63.5039	0.10415	67.4425	7.024	0.3024
61.7132	64.0933	0.10391	69.3256	6.977	0.4019

Table IV. Experimental Data for *n*-Hexane: Means of Four Results<sup>a</sup>



Fig. 5. Deviations of measured values of the thermal conductivity of n-hexane and other results [11, 12] from Eq. (8) with coefficients from Table I.

Table V. Experimental Data for <i>n</i> -Heptane	: Means of Four Results <sup>a</sup>
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$T_0$ (°C)	$T_{\lambda}$ (°C)	$\lambda \left( W \!\cdot\! m^{-1} \!\cdot\! K^{-1} \right)$	$T_{\kappa}$ (°C)	$\kappa (10^{-8}\mathrm{m}^2\cdot\mathrm{s}^{-1})$	$Q_0/(4\pi\lambda)$ (K)
-12.2095	-11.4172	0.13236	-9.6296	8.600	0.1204
-12.2107	-10.8607	0.13209	-7.7996	8.614	0.2045
-12.2106	-10.4556	0.13199	-6.4482	8.635	0.2645
3.3213	4.1515	0.12737	6.0124	8.297	0.1268
3.3212	4.7629	0.12709	8.0175	8.311	0.2189
3.3218	5.1620	0.12696	9.2948	8.273	0.2805
18.7133	19.6125	0.12235	21.6186	7.996	0.1376
18.7129	20.2663	0.12190	23.7869	7.973	0.2354
18.7127	20.7161	0.12189	25.2413	7.923	0.3043
34.0466	35.0203	0.11762	37.2868	7.769	0.1448
34.0462	35.6632	0.11727	39.3791	7.677	0.2426
34.0464	36.1616	0.11709	41.0175	7.651	0.3176
49.7688	50.7879	0.11258	53.0866	7.335	0.1549
49.7683	51.5154	0.11252	55.4883	7.357	0.2640
49.7694	51.9870	0.11240	57.0356	7.360	0.3348
61.8953	62.9499	0.10921	65.3200	7.133	0.1607
61.8962	63.7237	0.10902	67.8678	7.157	0.2766
61.8946	64.2108	0.10884	69.4418	7.120	0.3516
23.7782	24.6753	0.12082	26.6544	7.841	0.1385
23.7783	25.3947	0.12062	28.9855	7.859	0.2482
23.7789	25.9787	0.12035	30.8191	7.787	0.3402
14.8034	15.6732	0.12376	17.6115	8.055	0.1333
14.8038	16.3742	0.12345	19.8780	8.035	0.2405
14.8039	16.8936	0.12327	21.5335	7.993	0.3211



Fig. 6. Deviations of measured values of the thermal conductivity of *n*-heptane and other results [1, 9-11, 13, 14] from Eq. (8) with coefficients from Table I.

$T_0$ (°C)	$T_{\lambda}$ (°C)	$\lambda \left( W \!\cdot\! m^{-1} \!\cdot\! K^{-1} \right)$	$T_{\kappa}$ (°C)	$\kappa (10^{-8}\mathrm{m}^2\cdot\mathrm{s}^{-1})$	$Q_0/(4\pi\lambda)(\mathrm{K})$
23.9356	24.7361	0.12433	26.4147	7.945	0.1294
23.9355	25.3915	0.12422	28.4889	7.983	0.2328
23.9361	25.7619	0.12410	29.6341	7.956	0.2927
34.1890	35.0492	0.12143	36.8679	7.808	0.1381
34.1893	35.6895	0.12121	38.8648	7.795	0.2407
34.1890	36.0809	0.12106	40.0727	7.767	0.3044
47.8307	48.7119	0.11743	50.5393	7.496	0.1435
47.8315	49.4143	0.11724	52.7227	7.519	0.2562
47.8312	49.8105	0.11717	53.9583	7.525	0.3198
62.2410	63.1888	0.11327	65.1418	7.241	0.1550
62.2404	63.8954	0.11314	67.3357	7.274	0.2688
62.2400	64.3175	0.11299	68.6155	7.240	0.3387
-14.5962	-13.8690	0.13593	-12.3150	8.763	0.1159
-14.5993	-13.3560	0.13572	-10.7029	8.734	0.1984
-14.5968	-13.0141	0.13564	-9.6266	8.741	0.2519
-1.7705	-1.0107	0.13209	0.5976	8.501	0.1219
-1.7708	-0.4611	0.13191	2.3163	8.493	0.2098
-1.7721	-0.1063	0.13175	3.4143	8.459	0.2676
11.5112	12.3082	0.12804	13.9738	8.211	0.1290
11.5117	12.8734	0.12790	15.7363	8.229	0.2194
11.5112	13.2421	0.12779	16.8751	8.210	0.2794

Table VI. Experimental Data for n-Octane: Means of Four Results<sup>a</sup>

$T_0$ (°C)	$T_{\lambda}$ (°C)	$\lambda (W \cdot m^{-1} \cdot K^{-1})$	$T_{\kappa}$ (°C)	$\kappa (10^{-8} \mathrm{m}^2 \cdot \mathrm{s}^{-1})$	$Q_0/(4\pi\lambda)$ (K)
-15.0425	-14.3301	0.13766	-12.8298	8.688	0.1143
-15.0423	-13.8211	0.13744	-11.2456	8.675	0.1958
-15.0426	-13.4832	0.13739	-10.1772	8.697	0.2490
4.8575	5.6126	0.13228	7.1864	8.345	0.1220
4.8557	6.1703	0.13209	8.9210	8.349	0.2118
4.8565	6.5301	0.13200	10.0362	8.345	0.2694
22.4876	23.2940	0.12738	24.9545	8.020	0.1314
22.4879	23.8756	0.12724	26.7499	8.038	0.2252
22.4884	24.2541	0.12708	27.9079	8.020	0.2867
46.5630	47.4383	0.12081	49.2425	7.681	0.1423
46.5588	48.0194	0.12061	50.9836	7.584	0.2404
46.5399	48.4343	0.12045	52.2843	7.581	0.3115
62.2008	63.1050	0.11650	64.9148	7.307	0.1503
62.2009	63.7763	0.11640	66.9731	7.317	0.2594
62.2010	64.1840	0.11620	68.1605	7.293	0.3292

Table VII. Experimental Data for *n*-Nonane: Means of Four Results<sup>*a*</sup>

$T_0$ (°C)	$T_{\lambda}$ (°C)	$\lambda(W\!\cdot\!m^{-1}\!\cdot\!K^{-1})$	$T_{\kappa}$ (°C)	$\kappa (10^{-8}\mathrm{m}^2\cdot\mathrm{s}^{-1})$	$Q_0/(4\pi\lambda)$ (K)
23.4813	24.3201	0.12975	26.1864	7.987	0.1287
23.4817	25.0145	0.12963	28.4694	8.043	0.2330
23.4817	25.5044	0.12947	30.0366	7.998	0.3087
5.7986	6.5919	0.13433	8.3681	8.254	0.1212
5.7984	7.2394	0.13417	10.4919	8.283	0.2189
5.7996	7.7178	0.13405	12.0518	8.276	0.2912
-14.9659	-14.2268	0.13961	-12.5546	8.585	0.1121
-14.9651	-13.6257	0.13945	-10.5883	8.580	0.2029
-14.9664	-13.1803	0.13931	-9.1321	8.562	0.2706
44.1005	44.9991	0.12453	46.9954	7.710	0.1379
44.1007	45.7274	0.12431	49.3499	7.706	0.2493
44.1012	46.2678	0.12410	51.0737	7.670	0.3330
62.4669	63.4139	0.11968	65.4917	7.403	0.1466
62.4677	64.1753	0.11944	67.9065	7.362	0.2652
62.4675	64.7469	0.11931	69.7281	7.351	0.3539

Table VIII. Experimental Data for *n*-Decane: Means of Four Results<sup>*a*</sup>



Fig. 7. Deviations of measured values of the thermal conductivity of n-octane and other results [10, 11, 15, 16] from Eq. (8) with coefficients from Table I.

Naturally, the specific heat capacities at constant pressure  $c_p$  can be derived from the thermal conductivity  $\lambda$ , the thermal diffusivity  $\kappa$ , and the density  $\rho$  using the equation  $\kappa = \lambda/(c_p \rho)$ . The density and molar mass of the sample were obtained from the literature [8]. Table IX lists the values determined for the properties at a nominal temperature of 298.15 K together with other literature values. The various (volumic,  $c_p \rho$ ; specific,



Fig. 8. Deviations of measured values of the thermal conductivity of *n*-nonane and other results [15] from Eq. (8) with coefficients from Table I.

Table IX. Comparisons of the	Present Data at 2	25°C (= 298.15 K	) and at 101.325 ]	Pa with Other Da	ita [7–9, 17–19]	
	<i>n</i> -Pentane	<i>n</i> -Hexane	<i>n</i> -Heptane	<i>n</i> -Octane	<i>n</i> -Nonane	<i>n</i> -Decane
	(72.151) <sup>a</sup>	(86.178)	(100.206)	(114.233)	(128.260)	(142.287)
<b>Present results</b> $1 (\mathbf{W}, \dots -1, \mathbf{V} - 1)$	11177	11667	0 12078	012440	103610	0 12057
x (w m $x$ ) x (10 <sup>-8</sup> m <sup>2</sup> · s <sup>-1</sup> )	7 910	7 952	7 947	0.12440 8 044	8 053	8 044
$c_{-D}$ (MJ·m <sup>-3</sup> ·K <sup>-1</sup> )	1.407	1.467	1.521	1.547	1.576	1.611
$c_n^{PT}$ ( <b>kJ</b> · <b>kg</b> <sup>-1</sup> · <b>K</b> <sup>-1</sup> )	2.264	2.241	2.239	2.214	2.208	2.218
$c_{m}^{r} (\mathbf{J} \cdot \mathbf{mol}^{-1} \cdot \mathbf{K}^{-1})$	163.4	193.1	224.3	252.9	283.2	315.5
$\rho$ (kg·m <sup>-3</sup> ) in TRC [8]	621.3	654.84	679.46	698.62	713.75	726.35
$(1/\lambda)(d\lambda/dT) (\mathbf{K}^{-1})$	$-3.41 \times 10^{-3}$	$-2.87 \times 10^{-3}$	$-2.59 \times 10^{-3}$	$-2.36 \times 10^{-3}$	$-2.15 \times 10^{-3}$	$-1.98 \times 10^{-3}$
$(1/\kappa)(\mathrm{d}\kappa/\mathrm{d}T)(\mathrm{K}^{-1})$	$-3.42 \times 10^{-3}$	$-2.87 \times 10^{-3}$	$-2.53 \times 10^{-3}$	$-2.44 \times 10^{-3}$	$-2.23 \times 10^{-3}$	$-1.94 \times 10^{-3}$
Other data (with, respectively, the same units)						
IUPAC value [9], $\lambda$			0.1228			
A general eq., $[17] \lambda$	0.1125	0.1175	0.1217	0.1254	0.1287	0.1317
<b>TPRC</b> data [19], <i>λ</i>	0.1182	0.1235	0.1270	0.1321	0.1362	0.1388
JSME data [18], $\lambda$	0.119	0.123	0.127	0.130		
JSME data [18], $\kappa$	8.26	8.28	8.32	8.35		
TPRC [19], $c_p$	2.348	2.273	2.245	2.219	2.217	2.209
JSME data [18], $c_p$	2.319	2.269	2.246	2.226		
Kagaku Binran $[7]$ , $c_{\rm m}$	171.5	195.0	224.74	254.1	284.4	314.5
TRC [8], $c_{\rm m}$		195.48	224.98	254.15	284.45	314.54
<b>TPRC</b> [19], $c_{\rm m}$	169.4	195.9	224.9	253.5	284.4	314.4
IUPAC [9], $(1/\lambda)(d\lambda/dT)$			$-2.45 \times 10^{-3}$			
TPRC [19], $(1/\lambda)(d\lambda/dT)$	$-2.68 \times 10^{-3}$	$-1.96 \times 10^{-3}$	$-1.81 \times 10^{-3}$	$-2.17 \times 10^{-3}$	$-2.24 \times 10^{-3}$	$-2.36 \times 10^{-3}$
<b>TPRC</b> [19], $(1/c_p)(dc_p/dT)$	$2.48 \times 10^{-3}$	$1.87 \times 10^{-3}$	$1.62 \times 10^{-3}$	$1.39 \times 10^{-3}$	$1.55 \times 10^{-3}$	$1.48 \times 10^{-3}$
TRC [8], $(1/\rho)(\dot{d}r/dT)$	$-1.57 \times 10^{-3}$	$-1.37 \times 10^{-3}$	$-1.26 \times 10^{-3}$	$-1.16 \times 10^{-3}$	$-1.11 \times 10^{-3}$	$-1.06 \times 10^{-3}$

# The Thermal Conductivity and Thermal Diffusivity of Liquid n-Alkanes

<sup>*a*</sup> Molar mass  $(g \cdot mol^{-1})$  in parentheses.



Fig. 9. Deviations of measured values of the thermal conductivity of *n*-decane and other results [12, 16] from Eq. (8) with coefficients from Table I.

 $c_p$ ; and molar,  $c_m$ ) heat capacities are considered to be consistent with most values in the literature.

Figure 11 shows the thermal conductivity values and their temperature dependences at 298.15 K. Values  $(\nabla)$  which Wada et al. [17] measured or selected from various reports were converted to those at 298.15 K from 273.15 K using the respective temperature dependences presented there, while the dashed-dotted line was calculated by a generalized equation, which they derived at the same time, as a function of the variables:  $\theta(^{\circ}C) = T(K) - 273.15$  (temperature) and *n* (the carbon number). Figure 12 shows the thermal diffusivity and specific heat capacity values at 298.15 K. It is interesting that the thermal diffusivity of *n*-alkanes seems to be constant with the number of carbon atoms *n* (in an ordinary temperature range). This is a behavior clearly different from that for the thermal conductivity. In addition, the specific heat capacity does not seem to be strongly dependent on the number of carbon atoms, although the molar or volumic heat capacity is linearly dependent on the number *n* (i.e., their molar mass).

#### 4. EVALUATIONS OF UNCERTAINTY

The evaluation of the uncertainty components of the measurement may be made using the simple working formula,

$$\Delta T = (Q_0/(4\pi\lambda))\ln(t/s) + (Q_0/4\pi\lambda)\ln(4\kappa s/(a^2C))$$
(10)



Fig. 10. Deviations of measured values of the thermal diffusivity of *n*-alkanes from the respective fitted formulas. Values were corrected by factors  $k_{\rm f}$ .

The uncertainty in the thermal conductivity can be evaluated as [1, 6]

$$\frac{\delta\lambda}{\lambda} = \frac{\delta Q_0}{Q_0} + \frac{\delta(dR_W/dT)}{dR_W/dT} + \frac{\delta(\Delta T_f - \Delta T_i)}{\Delta T_f - \Delta T_i} + \frac{\delta\tau(t_f - t_i)}{(t_f t_i)\ln(t_f/t_i)} + \left(\frac{\delta\lambda}{\lambda}\right)_{\text{material}} + \left(\frac{\delta\lambda}{\lambda}\right)_{\text{other terms}}$$
(11)

where  $\delta(*)$  is the uncertainty of the term (\*),  $R_{\rm w}$  is the resistance of the hotwire sensor, and  $\delta\tau$  is the ambiguity of the time lag of both trigger signals to the bridge and the digital voltmeter. The magnitude of the respective components, contributing as a random part or a systematic part, is almost the same as or lower than those discussed previously [1]. The first component is 0.17%, in terms of the standard uncertainty (as a random part;



Fig. 11. Values of the thermal conductivity (together with those referred to in Ref. 17) and temperature dependence at 298.15 K vs n (number of carbon atoms).

type A), the second is  $\approx 0.05\%$  (a systematic part; type A), the third is  $\approx 0.05\%$  (a random part; type A), the fifth (sample material) is  $\approx 0.10\%$  (a random part; type B), and the other components including the potential lead, the sampling time-step distribution, etc., are  $\approx 0.04\%$  (a random part; mixed types A and B). Overall, the combined standard uncertainty is about 0.24% evaluated as the root-sum-square of various components.



Fig. 12. Values of the thermal diffusivity and specific heat capacity at 298.15 K vs *n* (number of carbon atoms).

For the measurement of the thermal diffusivity, since the adjustment of the diameter of the wire has been made for respective configurations, the original uncertainty  $(2\delta a/a)$  is replaced by the term  $(\delta \kappa/\kappa)_{cal}$ , and the uncertainty is evaluated as in Ref. 6:

$$\delta\kappa/\kappa = (\delta\kappa/\kappa)_{\text{cal}} + \delta(\Delta T)_0 / (Q_0 / (4\pi\lambda)) + (\delta\lambda/\lambda)^* \ln(4\kappa s / (a^2 C))$$
$$+ (\delta\kappa/\kappa)_{\text{material}}$$
(12)

In this formula, the first term cannot be evaluated exactly but is tentatively said to be 0.3% (a systematic part; type B) [6], the second term  $[\delta(\Delta T)_0,$ the initially remaining deflection in terms of temperature, originating from an inadequate balance in the bridge at temperature  $T_0$ ] is about 0.5% (a random part; type B). According to the third term, the subcomponents  $\delta Q_0/Q_0$  and  $(\delta \lambda/\lambda)_{\text{material}}$  in Eq. (11) practically do not affect  $\delta \kappa/\kappa$ , therefore,  $(\delta \lambda/\lambda)^*$  is 0.084%. This term is estimated to be 0.67% [ln(4 $\kappa$ s/ ( $a^2$ C))  $\approx$  8] (a random part; type A). The last term ( $\delta \kappa/\kappa$ )<sub>material</sub> is practically the same as  $(\delta \lambda/\lambda)_{\text{material}}$  and is 0.10% (a random part; type B). Finally, the overall uncertainty is estimated to be 0.90%, computed as the root-sum-square of subcomponents.

# 5. DISCUSSION AND CONCLUSIONS

The original data (including those on toluene) are reported together with the temperatures  $T_{\lambda}$  and  $T_{\kappa}$  referred to the two measured properties. Thermal diffusivity data did not scatter noticeably among the respective sets A to D, but slight systematic differences were observed among the groups; consequently, the factors  $k_{\rm f}$  (0.9892 to 1.0076) for the thermal diffusivity were introduced for minimizing the systematic differences. The various (volumic,  $c_p \rho$ ; specific,  $c_p$ ; molar,  $c_m$ ) heat capacities were derived at the nominal temperature 298.15 K from the ratio of thermal conductivity to thermal diffusivity  $\lambda/\kappa$ , the density  $\rho$ , and the molar mass  $M_{\rm m}$  [8]. The derived  $c_p$  and  $c_m$  are consistent with values from the literature [7, 8] within about 1%. The thermal conductivities were compared with literature values [9, 18, 19] and those calculated from a generalized correlation [17], although the uncertainty of the other data is unknown except for *n*-heptane.

The present system is regarded to be satisfactory for simultaneously and accurately measuring thermal conductivity and thermal diffusivity values. The thermal conductivity of toluene is consistent with those of IUPAC and also data obtained previously by the authors [1], and the heat capacities  $c_p$  and  $c_m$  derived from  $c_p \rho = \lambda/\kappa$  do not conflict with the literature values [7, 8]. In conclusion, empirical equations for the thermal conductivity and thermal diffusivity of the liquid pure *n*-alkanes ( $C_nH_{2n+2}$ ; n = 5 to 10) are reported, with an uncertainty of 0.5% for the thermal conductivity and 1.8% for the thermal diffusivity and the heat capacity (respectively, with a level  $k_p = 2$ , p = 95%).

# REFERENCES

- 1. H. Watanabe, Metrologia 33:101 (1996).
- 2. H. Watanabe and D. J. Seong, in Proc. 5th ATPC (1998), pp. 119, 135.
- H. Watanabe and D. J. Seong, in *Proc. 19th JSTP* (Japan Soc. Thermophys. Prop., 1998), p. 123.
- 4. J. J. Healy, J. J. de Groot, and J. Kestin, Physica 83C:392 (1976).
- C. A. Nieto de Castro, B. Taxis, H. M. Roder, and W. A. Wakeham, *Int. J. Thermophys.* 9:293 (1988).
- 6. H. Watanabe, Metrologia 39 (2002), to appear.
- 7. Chem. Soc. Japan (ed.), Kagaku Binran II, Chemical Handbook (Maruzen, Tokyo, 1993), p. 229.
- K. N. Marsh, B. E. Gammon, R. C. Wilhoit, C. A. Baxter, M. Frenkel, A. Das, N. M. Gadalla, A. M. Ferguson, and A. S. Rodgers (eds.), *TRC Thermodynamics Tables (Hydrocarbons)* (Texas A&M University System, College Station), Vol. 1, p. a1010 [for density and molar mass], Vol. 10, pp. vc1001–vc1561 [for molar heat capacity].
- C. A. Nieto de Castro, S. F. Y. Li, A. Nagashima, R. D. Trengove, and W. A. Wakeham, J. Phys. Chem. Ref. Data 15:1073 (1986).
- 10. J. F. T. Pittman, Ph.D. thesis (Imperial Coll. Sci. Tech. London, London, 1968).
- 11. H. Watanabe and P. Qiu, in Proc. 18th JSTP (Japan Soc. Thermophys. Prop., 1997), p. 429.
- M. J. Assael, E. Charitidou, C. A. Nieto de Castro, and W. A. Wakeham, Int. J. Thermophys. 8:663 (1987).
- C. A. Nieto de Castro, J. C. G. Calado, and W. A. Wakeham, in Proc. 7th Symp. Thermophys. Prop. (1977), p. 730.
- 14. Y. Nagasaka and A. Nagashima, Ind. Eng. Chem. Fundam. 20:216 (1981).
- J. C. G. Calado, J. M. N. A. Fereleira, and C. A. Nieto de Castro, *Int. J. Thermophys.* 4:193 (1983).
- C. A. Nieto de Castro, J. C. G. Calado, and W. A. Wakeham, *High Temp. High Press*. 11:551 (1979).
- 17. Y. Wada, Y. Nagasaka, and A. Nagashima, Int. J. Thermophys. 6:251 (1985).
- 18. Jpn. Soc. Mech. Eng. (ed.), JSME Data Book: Thermophysical Properties of Fluids (1983).
- Y. S. Touloukian and T. Makita (eds.), in *Thermophysical Properties of Matter*, TPRC Data Series (Plenum, New York, 1970), Vol. 3, pp. 164, 211, 214, 230, 233, 236 [for thermal conductivity], Vol. 6, p. 25a [for specific heat capacity].