Standard Reference Data for the Thermal Conductivity of Liquids

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The available experimental liquid-phase thermal conductivity data for water, toluene, and n-heptane have been examined with the intention of establishing standard reference values along the saturation line. The quality of available data is such that for toluene and water new standard reference values can be proposed with confidence limits better than ±1.0% for most of the normal liquid range. For n-heptane there are insufficient reliable experimental data for the system to be treated as a primary reference standard, so a lower quality correlation has been developed which yields a set of secondary reference data with confidence limits of ±1.5% for most of the normal liquid range.

Key words: concentric cylinders; convection; n-heptane; radiation effect; reference materials; standard reference data; thermal conductivity; transient hot wire; toluene; water.

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1. Introduction

The thermal conductivity of liquids has proved to be one of the most difficult thermophysical properties to measure accurately. As a consequence it was not until 1951 that any proposal was made for standard reference data for this fluid property. At that time Riedel suggested that liquid toluene be adopted as a standard reference material and proposed a set of standard reference values. Subsequent measurements did little to substantiate the proposed values or to halt the apparent systematic downward trend of the thermal conductivity of toluene with time which is illustrated in Fig. 1 (Ref. 2) for a temperature of 293.15 K. The inherent difficulty in the measurement of the thermal conductivity arises from the fact that it is impossible to decouple the process of heat conduction from convection, in experiments performed in a gravitational field, and radiative heat transfer under any conditions. Since 1951, and most especially since 1977, technological advances, and in particular the development of the transient hot-wire technique, have brought about an improvement in the precision of measurement of about an order of magnitude.1-7

The latest set of general recommendations for thermal conductivity standards are set out in a document8 published in 1981, which originates from the recommendations accepted in 1977, by the Commission on Physicochemical Measurements and Standards of the Physical Chemistry Division of the International Union of Pure and Applied Chemistry (IUPAC). These recommendations were primarily for use in industrial calibrations, and because they are based upon experimental data prior to 1973 they do not include the most recent and most accurate results. In the specific case of liquid water a more recent set of recommendations is contained in the formulation of the properties of water substance approved by the International Association for the Properties of Steam (IAPS) in 1977 and amended in 1982.9

Internationally accepted standard reference materials for thermal conductivity serve two purposes: first, they provide a means of confirming the accuracy of any new absolute apparatus and the reproducibility of existing equipment. Second, they provide a means of determining a constant or group of constants in the working equation of an instrument which is to be operated in a relative manner. In view of the rapid developments in the measurement of the thermal conductivity of liquids in the last few years it seems that the time is appropriate for a complete reappraisal of standard reference values for this property. The present paper provides the results of such a reappraisal for the liquids toluene, water, and n-heptane carried out in 1985 under the auspices of the International Union of Pure and Applied Chemistry. The reappraisal takes the form of a critical analysis of the experimental measurements of the thermal conductivity of these liquids which permits the available data to be characterized as primary or secondary according to their estimated accuracy. In general, primary data are those obtained in an instrument for which a full working equation for the experimental technique is given, together with a complete set of corrections. In addition, it is essential that there should be a demonstration that the results are free from significant effects from heat transfer mechanisms other than the process of pure conduction. The final primary data set is used where it is adequate to form a correlation between the thermal conductivity and temperature along the saturation line of each fluid, and leads to a series of recommended standard reference values. For toluene and water the available data permits recommendations of the thermal conductivity with an estimated accuracy of ±1.0%. For n-heptane the data are less consistent and the recommendations have a correspondingly greater uncertainty which precludes their inclusion as primary reference standards.

It is worthy of note that benzene was initially included in our study. However, no results are presented here because the literature data available are too discordant to permit any
definitive statement. It is important to record here this situation is representative of the current state for most liquid systems. The standard reference data given in this paper should form the first step towards the establishment of a large body of more consistent data.

2. Experimental Techniques

The experimental methods used to measure the thermal conductivity of fluids may be divided into two groups: steady-state and transient methods. The presence of the earth’s gravitational field makes instruments of either type prone to convective heat transport while radiative energy transport is also an inevitable addition to conductive transfer. Isolation of the pure conductive energy transport requires either that experimental conditions render the effects of the other modes of transfer negligible or that a complete mathematical description of the process, permitting corrections to be applied to experimental data, be available. As exact solutions of the hydrodynamic equations describing convection are not known, the latter course is impractical and extremely careful design of an instrument is therefore necessary to ensure that the effects of convective flow upon the measurement are negligible. This is particularly true for instruments of the steady-state variety where the effects of convection can only be rendered small by the use of specially selected arrangements of parallel plates and coaxial cylinders which require careful alignment and construction. For transient methods the time scale of the measurement must be such that the elements of the fluid do not attain a velocity sufficient to unduly perturb the conductive energy flow. Such a time scale can always be found for these instruments by ensuring that the measurement is completed before the onset of convection, so that the effect is eliminated entirely.

Whilst it has been possible to make the effect of convective energy transfer negligible for both classes of instruments, only very recently has it been possible to make accurate corrections for the radiative contribution. In the case where the fluid does not contribute directly or indirectly to the radiation process through absorption, the radiative energy transport associated with the measurement of thermal conductivity (transient or steady state) is easily treated. However, if the fluid absorbs and emits radiation the problem is complex because the radiative and conductive energy fluxes are coupled and the situation is described by an integro-partial differential equation. A number of solutions of the coupled radiation–conduction equations for steady-state instruments have been proposed. However, in most work these solutions have not been employed in an analysis of the thermal conductivity data because of their complexity and because of the absence of the necessary optical characteristics of the fluids under the conditions of interest. Fischer and Obermeier reported the results of a careful experimental and theoretical study of the contribution of radiative heat transfer to the measurement of the thermal conductivity of liquids in a steady-state concentric cylinder apparatus. Experiments carried out with annular layer thicknesses of 2, 4, and 7 mm over the temperature range 253–473 K showed that the radiation contribution to the measured thermal conductivity varied with layer thickness, temperature, and the liquid being studied. The radiation contribution was calculated for each of the different layer thicknesses and the experimental data corrected to yield a “radiation-free” value. The radiation-free values obtained in this way for different layer thicknesses differed from each other by less than ±1.5% for toluene, benzene, and n-heptane among others. Measurements on water showed no variation of the apparent thermal conductivity with layer thickness, within the experimental precision, implying that the radiation contribution is very small.

The results of Fischer and co-workers have a number of important implications. In some of their measurements the contribution of radiation to the measured thermal conductivity was as much as 40%. In such cases the correction of the data to radiation-free values adds a significant amount to the uncertainty in the final data. For this reason, in cases where radiation is significant we adopt the policy that the best accuracy attainable with a steady-state technique is one of ±1.5%. At the present time the careful work of Fischer and his collaborators, as well as their apparatus, is unique. Consequently, from the viewpoint of standard reference values for thermal conductivity their results must, for the moment, be considered with circumspection awaiting independent confirmation. Moreover we are forced to conclude that all steady-state measurements for such fluids to which no correction has been applied are burdened with a far greater uncertainty and must be ignored. There seems little doubt that radiation makes some contribution to the large discrepancies observed between different measurements of the thermal conductivity of toluene (Fig. 1). It is important to note that the same discord has not been observed for the thermal conductivity of water which must, in part, be because radiation contributes only a small amount to the overall heat transfer process for this liquid.

Until recently the situation for transient methods of measurement with regard to radiation was the same, but the work of Wakeham and co-workers now makes it possible to apply a complete set of corrections for the transient hot-wire technique which turn out to be very small. In view of the fact that the same instrument avoids the effects of convection completely and possesses a full working equation.

![Graph](image_url)

**Fig. 1.** The apparent thermal conductivity of toluene as a function of year of measurement.

it is undoubtedly the preferred technique of measurement. An assessment of the accuracy of measurements made with the transient hot-wire technique is therefore based on somewhat different criteria. The principal points considered in the evaluation of the accuracy are as follows:

First, one of two methods must be used to compensate for the fact that the wires employed are necessarily of finite length rather than infinite as assumed in the model of the instrument. Either two wires must be used, resulting in an ideal wire with length equal to the difference between the wires, or potential leads at either end of a single wire must be employed. Both of these methods require corrections. For two wires a correction must be made owing to the difference of resistance per unit length of the wires, whereas for the potential leads thermal conduction down the leads must be considered.

Secondly, for measurements on electrically conducting fluids the wire must be coated with some insulating material, for which a correction to the heat capacity of the line source must be made, or an alternating heating current must be employed if the measurements are performed with a bare wire.

3. Standard Reference Materials

Until very recently a necessary condition for fluids to be selected as standard reference materials has been that the contribution of radiation to the thermal conductivity measurements should be very small, due to the absence of any reliable analysis of this component of the measured value. However, the work of Nieto de Castro et al. suggests that this may no longer be a necessary condition albeit a desirable one. Nieto de Castro and Wakeham have suggested that materials should be selected following a series of transient hot-wire measurements which will reveal whether radiation plays a significant role or not. The work of Fischer and co-workers shows that whilst it is now possible to calculate radiation-free thermal conductivity values from the results of steady-state measurements, subject to availability of spectroscopic data, the corrected data have an uncertainty of the order of ±1.5%−2.0% for fluids of interest in this study at ambient temperatures. Thus, if the results of steady-state measurements are to be used in the determination of recommended thermal conductivity values of standard reference materials the requirement of a very small radiative contribution is still valid.

The role of radiation does not constitute the complete set of conditions to be satisfied by standard materials. In 1961 Ziebland suggested the following criteria for standard materials for liquid thermal conductivity:

(a) The temperature interval between the freezing point and the normal boiling point, i.e., the extent of the liquid range, must be large and include some thermometric fixed point.

(b) The liquid should be nontoxic and noncorrosive with respect to the usual engineering materials.

(c) It should be obtainable at reasonably low cost and guaranteed high purity.

Two further criteria have been added by Nieto de Castro and Wakeham:

(d) A series of liquids covering as wide a range of thermal conductivity as possible should be selected.

(e) Reliable values of liquid densities for the saturated and compressed liquids should be available in the literature, allowing reliable extrapolation of high-pressure data to the saturation line.

On the basis of the preceding conditions, Nieto de Castro and Wakeham proposed the following liquids as standard reference materials: iso-octane, n-heptane, toluene, methanol, and water with methanol–water mixtures bridging the large gap in thermal conductivity between these two fluids. For the present work iso-octane and methanol were found unsatisfactory because of the problems of purity and the lack of reliable density data. In addition, simply to ensure high accuracy in the recommended values we have introduced the following condition in this work:

(f) The primary data subset for standard reference materials must have a maximum uncertainty ±1.5% at ambient temperatures.

After a literature survey and evaluation of available experimental data it was found that only for toluene and water could all of these conditions for primary standard reference materials be met. Whilst the data available for n-heptane satisfy all of the above conditions the limited degree of overlap of the different data sets leads to apparent discontinuities in those regions.

4. Experimental Data

In order to establish standard reference values for the thermal conductivity the most reliable experimental data must be collected by making critical assessments of the measurement techniques employed and the precision obtained. To assist in the assessment it is convenient to define two categories of experimental data:

(1) Primary data—these are the results of measurements carried out with an instrument of high precision for which a complete working equation and a detailed knowledge of all corrections are available.

(2) Secondary data—these are the results of measurements which are of inferior accuracy to primary data. The inferior accuracy may arise from operation at extreme conditions or incomplete characterization of the apparatus.

Although the division of experimental data into these categories is somewhat subjective, the following recommendations have been employed as a means of identifying primary data:

(i) Measurements must have been made with a primary experimental apparatus, i.e., a complete working equation must be available.

(ii) The form of the working equation should be such that sensitivity of thermal conductivity to the principal variables does not magnify the random errors of measurement.

(iii) All principal variables should be measurable to a high degree of precision.

(iv) The published work should include some description of purification methods and a guarantee of purity.

(v) The data reported must be unsmoothed data. Whilst graphs and fitted equations are useful summaries for the reader, they are not sufficient for standardization purposes.
The lack of accepted values of the thermal conductivity of standard reference materials implies that only absolute and not relative measurement results can be considered.

Explicit quantitative estimates of the uncertainty of reported values should be given, taking into account the precision of the experimental measurements and possible systematic errors.

Owing to the desire to produce high-accuracy reference values, limits have been imposed on the accuracy, as determined by the present authors, of the primary data sets. For primary standard reference materials the accuracy of primary data is required to be better than $\pm 1.5\%$.

Among the more general results of the application of these criteria to the available experimental data is the rejection from the primary data set of all values obtained with steady-state techniques for liquids other than water. This follows from the results of Fischer et al.\textsuperscript{16–19} discussed earlier.

As most equipment operates along the saturation line or at a pressure of 0.1 MPa the standard reference values refer to these conditions. In practice there is no distinction between the values for the two conditions over the range of conditions of interest here. This is illustrated by the experimental data of Nieto de Castro et al.\textsuperscript{20} for toluene at 308 K which shows that a change in pressure from 9 to 15 atm causes a change in thermal conductivity of less than $\pm 0.2\%$. Consequently the difference between the thermal conductivity at the saturation line and at 0.1 MPa is less than 0.05\% and is insignificant.

### 4.1. Primary Data

A summary of the primary data for each system, together with their estimated uncertainty, is given in Table 1. The statistical treatment of the data is described in Sec. 5.2.

The reasons for the assigned accuracies in Table 1 are outlined below.

#### a. Toluene

The accuracy of the transient hot-wire technique is illustrated by the very good agreement between the results from absolute instruments at three different research centers.\textsuperscript{21,24} The measurements cover almost the entire "normal" liquid range. In their earlier work Nieto de Castro et al.\textsuperscript{24} were not aware of the need to correct for differences in the resistance per unit length of the two platinum wires and the original claimed accuracy of their results has thus been reevaluated at $\pm 1.0\%$. The later work of Nieto de Castro et al.\textsuperscript{20} using the instrument at Imperial College (London) has been extrapolated from high pressures to yield values at the saturation line\textsuperscript{23} and the extrapolated data has been assigned an accuracy of $\pm 1.0\%$. The results of Nagasaka and Nagashima\textsuperscript{2} have also been assigned an accuracy of 1.0\%. In part this is because the liquid used was taken straight from the supplier at a purity of 99\% and used without further purification. In addition, the precision of the temperature measurements is slightly inferior to that of the other instruments and no corrections have been made for heat conduction down the potential leads used to monitor the temperature change of the bare wire. Thus, with the benefit of hindsight the accuracy we estimate for these three sets of transient hot-wire results is worse than that originally claimed for them. There is little doubt that if new measurements were carried out in the three instruments superior accuracy could be achieved but the effort does not seem justified at present.

A final set of transient hot-wire data for toluene has been reported by Pittman.\textsuperscript{25} The data in this set above 340 K have an estimated accuracy which falls outside our allowed

### Table 1. Primary experimental data sources for thermal conductivity

<table>
<thead>
<tr>
<th>Literature source</th>
<th>Technique</th>
<th>Temp. range</th>
<th>Number of data pts</th>
<th>Assigned accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y. Nagasaka et al. (Ref. 7)</td>
<td>THW\textsuperscript{a}</td>
<td>274–355</td>
<td>5</td>
<td>$\pm 1.0$</td>
</tr>
<tr>
<td>C. A. Nieto de Castro et al. (Ref. 24)</td>
<td>THW</td>
<td>293–323</td>
<td>14</td>
<td>$\pm 1.0$</td>
</tr>
<tr>
<td>C. A. Nieto de Castro et al. (Refs. 20 and 21)</td>
<td>THW</td>
<td>308–360</td>
<td>5</td>
<td>$\pm 1.0$</td>
</tr>
<tr>
<td>J. F. T. Pittman (Ref. 6)</td>
<td>THW</td>
<td>189–326</td>
<td>45</td>
<td>$\pm 1.5$</td>
</tr>
<tr>
<td>Y. Nagasaka et al. (Ref. 26)</td>
<td>THW</td>
<td>274−354</td>
<td>5</td>
<td>$\pm 0.5$</td>
</tr>
<tr>
<td>F. J. Dietz (Ref. 25)</td>
<td>THW</td>
<td>304−371</td>
<td>4</td>
<td>$\pm 0.5$</td>
</tr>
<tr>
<td>L. Riedel (Ref. 1)</td>
<td>CC\textsuperscript{b}</td>
<td>353</td>
<td>2</td>
<td>$\pm 1.5$</td>
</tr>
<tr>
<td>L. Riedel (Ref. 27)</td>
<td>CC</td>
<td>274–353</td>
<td>13</td>
<td>$\pm 1.5$</td>
</tr>
<tr>
<td>Yu. L. Rastorguev et al. (Ref. 28)</td>
<td>CC</td>
<td>295–370</td>
<td>22</td>
<td>$\pm 1.5$</td>
</tr>
<tr>
<td>E. Schmidt et al. (Ref. 29)</td>
<td>PP\textsuperscript{c}</td>
<td>293–357</td>
<td>8</td>
<td>$\pm 1.5$</td>
</tr>
<tr>
<td>Y. Nagasaka et al. (Ref. 7)</td>
<td>THW</td>
<td>274–365</td>
<td>7</td>
<td>$\pm 1.0$</td>
</tr>
<tr>
<td>C. A. Nieto de Castro et al. (Ref. 24)</td>
<td>THW</td>
<td>279−315</td>
<td>15</td>
<td>$\pm 1.0$</td>
</tr>
<tr>
<td>J. F. T. Pittman (Ref. 6)</td>
<td>THW</td>
<td>191–330</td>
<td>13</td>
<td>$\pm 1.5$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}THW—transient hot-wire technique.

\textsuperscript{b}CC—concentric cylinder technique.

\textsuperscript{c}PP—parallel-plate technique.
range of ± 1.5% and they are therefore excluded. However, the data at lower temperatures have an estimated error of ± 1.5% and are included.

b. Water

The steady-state results included in the primary data set are those of Riedel, 1,27 Rastorguev et al.,28 and Schmidt and Leidenfrost29 and they all have been assigned the best attainable accuracy for steady-state experiments of ± 1.5%. The data of Nagasaka et al.26 are the results of measurements made using a transient hot-wire apparatus with two insulated wires and in view of the relative ease with which water can be highly purified these data are assigned the accuracy claimed, i.e., ± 0.5%. Dietz25 used two bare wires in a transient hot-wire apparatus driven by alternating current instead of insulated wire and direct current employed by Nagasaka et al. The data have also been reported in the open literature30 but smoothed values are given there so that the original data from the doctoral thesis of Dietz25 has been used. The random scatter of data from this source is slightly worse than that for Nagasaka et al. and thus the data have been assigned an accuracy of ± 1.2%.

c. n-Heptane

For the reasons outlined in the toluene section it is not possible to include any measurements made with steady-state instruments for n-heptane. The primary data sets used are therefore from the same sources that provided transient hot-wire data for toluene 6-7,24, the accuracies assigned to each set of data are therefore the same as for toluene. Within these sets the results of Menashe and Wakeham3 are of high accuracy but do not extend below a pressure of 50 MPa. These values must therefore be extrapolated to the saturation line, a process which over such a large pressure interval introduces an unacceptably large possibility for error. Consequently these particular results cannot be included in the preparation of recommended values along the saturation line. The exclusion of this set of results means that only three sets remain which have but a small temperature range of overlap which makes the development of a correlation difficult. For this reason we propose that the data for n-heptane can serve as the basis of a secondary standard which we define as one where the data are good enough to allow a statement of the values of the thermal conductivity but where the uncertainty band is somewhat larger than that set for a primary standard.

5. Correlation Procedures and Results

5.1. Equation Forms

The experimental thermal conductivity data have been fitted to two functional forms:

\[ \lambda = b_0 + b_1 T, \]  
\[ \lambda = b_0 + b_1 T + b_2 T^2. \]

In Eqs. (1) and (2), \( \lambda \) is the thermal conductivity and \( T \) the absolute temperature. The data have been fitted to these equations using the method of least squares with weighting factors reflecting the accuracy of the data given in Table 1.

5.2. Weighting Methods

In assigning relative weights to the different data sets we have made the usual assumption that the estimated precision is approximately three times the standard deviation of the data in an imaginary distribution of measurements repeated an infinite number of times. With the further assumption that the error in the independent variable \( T \) is negligible the weighting factors \( w_i \) for the functional form,

\[ \lambda = \sum_{i=0}^{n} b_i T^i, \]  
are
\[ w_i = \left( \frac{3}{\Delta \lambda_i} \right)^2, \]

where \( w_i \) is the weighting factor and \( \Delta \lambda_i \) is the estimated absolute error in the value of the thermal conductivity \( \lambda_i \).

If the error in \( \lambda_i \) is expressed as a relative error then
\[ w_i' = \left[ \frac{3}{\lambda_i (\Delta \lambda_i)^2} \right]^2, \]

with \( (\Delta \lambda_i)' \) the relative error in \( \lambda_i \) and \( w_i' \) the relative weighting factor.

5.3. Primary Correlations

In order to establish recommended standard reference values for the thermal conductivity over a range of temperatures we have first established correlations for the thermal conductivity as a function of temperature. From these correlations we recommend values for the thermal conductivity at 298.15 K and 0.1 MPa and they are given in Table 2. Then using the convention of the IAPS formulations for the transport properties of water substance \(^9,32\) we have expressed the correlation in terms of the dimensionless variables \( \lambda^* \) and \( T^* \), defined as follows:

\[ T^* = T/298.15 \]

and

\[ \lambda^*(T^*) = \lambda(T)/\lambda(298.15). \]

Here, \( \lambda(298.15) \) is the adopted standard value for the thermal conductivity at 298.15 K and 0.1 MPa given in Table 2.

| Table 2. Recommended thermal conductivities at 298.15 K and 0.1 MPa |
|--------------------|--------------------|--------------------|
| Toluene             | Water              | n-Heptane          |
| \( \lambda(298.15)/W m^{-1} K^{-1} \) | \( \lambda(298.15)/W m^{-1} K^{-1} \) | \( \lambda(298.15)/W m^{-1} K^{-1} \) |
| 1.301 ± 0.0013      | 0.6067 ± 0.0061    | 0.1228 ± 0.0018    |

STANDARD REFERENCE DATA FOR THE THERMAL CONDUCTIVITY OF LIQUIDS

Fig. 2. The deviations of the primary data for the thermal conductivity of toluene from the correlation of Eq. (8).

Fig. 4. The deviations of the primary data for the thermal conductivity of water from the correlation of Eq. (10).

a. Toluene

For the representation of the thermal conductivity of toluene from its normal freezing point to the upper limit of the experimental data (360 K) it is necessary to adopt the quadratic form of Eq. (2), whereas over the limited temperature range 230 K < T < 360 K, where the experimental data are of higher quality, the linear representation of Eq. (1) is adequate. Thus we have produced two correlations: a linear, higher accuracy, correlation covering the limited temperature range 230 K < T < 360 K and a quadratic correlation covering the range 189 K < T < 360 K which is of slightly inferior quality. The two correlations are given in reduced form in Eqs. (8) and (9), respectively.

\[ \lambda^* = 1.681 \, 82 - 0.682 \, 022 T^* \quad 230 \, K < T < 360 \, K, \quad \text{(8)} \]

\[ \lambda^* = 1.452 \, 10 - 0.224 \, 229 T^* - 0.225 \, 873 (T^*)^2, \quad 189 \, K < T < 360 \, K. \]

The maximum deviation of the primary experimental data from Eq. (8) is 1.3% with a standard deviation of 0.00067 W/(m K). The maximum deviation of the primary data from Eq. (9) is 1.5% with a standard deviation of \( \pm 0.00089 \, \text{W/(m K)} \). Deviation plots of the primary data from the correlations represented by Eqs. (8) and (9) are given in Figs. 2 and 3, respectively. The weighted standard deviations for the correlation of the uncorrected data are 1.09 and 1.34 for the linear and quadratic correlations, respectively.

b. Water

The reduced thermal conductivity of water as a function of the reduced temperature is described over the entire normal liquid range by the quadratic equation,

\[ \lambda^* = -1.265 \, 23 + 3.704 \, 837 T^* - 1.439 \, 557 (T^*)^2, \quad 274 \, K < T < 370 \, K, \]

where the variables \( T^* \) and \( \lambda^* \) are defined in Eqs. (6) and (7), respectively. The maximum deviation of the primary data from the correlation is 1.1% with a standard deviation of \( \pm 0.0028 \, \text{W/(m K)} \). The deviations of the primary data from the correlation are plotted in Fig. 4 where it is clearly shown that all data are reproduced within their assigned experimental uncertainty. The weighted standard deviation for the correlation of the uncorrected data is 1.04.

5.4. Secondary Correlation

a. \( n \)-Heptane

The reduced thermal conductivity of \( n \)-heptane as a function of the reduced temperature is described by the linear equation,

\[ \lambda^* = 1.730 \, 26 - 0.729 \, 932 T^*, \quad 191 \, K < T < 365 \, K, \]

with the reduced parameters defined as before. The maximum deviation of the primary data from the correlation is 1.4% with a standard deviation of \( \pm 0.00067 \, \text{W/(m K)} \), and a weighted standard deviation for the correlation of the uncorrected data of 1.8. Deviations of the primary data from the correlation are shown in Fig. 5. The large deviations occur for data with an assigned accuracy of 1.0%, so that not all of the data are reproduced by the above equation to within their experimental uncertainty. This is because although
Fig. 5. The deviations of the primary data for the thermal conductivity of n-heptane from the correlation of Eq. (11).

the data of Nagashima et al. and that of Nieto de Castro et al. have the same slope, their absolute values differ by about 2% and extend over different temperature ranges with a different density of points. Obviously no correlation can reconcile these differences. Thus, we are forced to conclude that pending further measurements for this system, the correlation for n-heptane can be adapted only as a secondary standard and that the accuracy of data generated with Eq. (11) can be no better than ± 1.5%.

5.5. Tabulations

As outlined earlier the recommended values of the thermal conductivity of the three liquids studied here, at 298.15 K and 0.1 MPa, are given in Table 2. Tables 3–5 give recommended values for the thermal conductivity along the saturation line for toluene, water, and n-heptane, respectively. The recommended values are given to four significant figures but it should be emphasized that the uncertainties in the tabulated data should be taken from Secs. 5.3 and 5.4.

<table>
<thead>
<tr>
<th>Table 3. Recommended thermal conductivities for toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T ) K</td>
</tr>
<tr>
<td>230.00</td>
</tr>
<tr>
<td>240.00</td>
</tr>
<tr>
<td>250.00</td>
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<tr>
<td>260.00</td>
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<tr>
<td>270.00</td>
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<th>Table 5. Recommended thermal conductivities for n-heptane</th>
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Fig. 6. The deviations of the secondary data for the thermal conductivity of toluene from the correlation of Eq. (8).
5.6. Comparison of Correlations with Secondary Data

The correlations outlined in the preceding section should ideally reproduce all of the secondary data if the latter are assigned a realistic experimental uncertainty. This, however, would be a very difficult and tedious task and would not serve any important purpose. We therefore content ourselves with a plot of the deviation of these secondary data from the correlation for each fluid.

These deviation plots are given in Figs. 6–8 and include only the data for which the deviations are less than ±5%. A compilation of all literature data sources for which we were able to obtain copies is given in the Appendix, which includes a brief summary of each.

5.7. Comparison of Literature Correlations with This Work

The correlations produced in this work are compared with previous correlations in Figs. 9 and 10 for the systems toluene and water, respectively.

Inspection of Fig. 9 shows a systematic deviation between the present correlation and the recommended values of TPRC that increases with increasing temperature. This is as expected for toluene, because the TPRC recommendations are based on the results of steady-state experiments which the work of Fischer et al.1-7 shows are prone to errors from radiation contributions.

The agreement between the correlation for water in this work and the recommendations of previous studies is considerably better than the case for toluene. The IAPS recommendations deviate from this correlation by ±0.6% at most, which is well within the mutual uncertainties of both works, although Fig. 10 shows that the slopes are slightly different. This may well arise from the fact that as the IAPS work covers the whole fluid range it is consequently influenced by a data set that is of slightly inferior quality to that used in this work. The maximum deviation of the TPRC recommendations from this correlation is 0.5%, which is quite different from the results for toluene, emphasizing the absence of radiation problems for this fluid. The worst deviations in Fig. 10 are for the IUPAC recommendations, where at low temperatures it amounts to −1.75%. Although this is within the mutual uncertainties of the two works the deviation is systematic at the low end of the temperature region.
This may well be due to the effect of including in the present correlation the very high-accuracy data from transient hot-wire experiments which were not available for the earlier work.

5.6. Cautions for Use of the Tabulated Recommended Thermal Conductivities

As mentioned earlier, recommended standard values serve two purposes: (i) they act as a test of the accuracy of new absolute instruments, and (ii) they are a means of calibrating instruments for which the full working equation is not available. It is for the latter use that caution must be used, as the use of the reference standard for the calibration of such instruments may lead to erroneous results for other systems, where the radiation contributions to the measured thermal conductivity will be different. Thus it is stressed that any relative instrument should be calibrated with at least two fluids with very different thermal conductivities and radiation properties, such as the primary fluids in this study, toluene and water. It is emphasized that the tabulated values calculated from Eqs. (8) and (10) are radiation free, i.e., true thermal conductivities.

6. Conclusions

Standard reference data for thermal conductivity are proposed for the systems toluene, water, and n-heptane over the normal liquid range. These recommendations are based on the most accurate available literature data up to and including 1985, and as such are considered to be of higher accuracy than any correlations presently available in the literature.

However, in view of the recent improvements in both the theory and experimental techniques, further experimental work should allow even more accurate correlations to be determined for all of the systems studied here. Thus it is envisaged that the recommendations for Standard Reference Data will be periodically updated as new experimental data become available.

Inspection of the thermal conductivities in Tables 2–5 reveals that there is a considerable gap in magnitude of the thermal conductivities for water and those for toluene and n-heptane. This suggests the need for experiments to be carried out on fluids with thermal conductivities in this void area. Possible systems to satisfy this need are methanol and methanol–water mixtures, using transient hot-wire techniques as this will make apparent any problems due to absorption of radiation. Further it is obvious that a liquid of low thermal conductivity be included in future recommendations of Standard Reference Data for use in calibrating instruments used in industry for such materials. At present there are insufficient accurate data to permit any fluid of this category to be included. Again, industrial operations frequently require a calibration material for use at elevated temperatures. The present correlations do not really address this need, but the available experimental information is just too sparse to permit any definite statements about this important area at present.

7. Acknowledgments

The work described in this paper has been carried out under the auspices of the Sub-committee on Transport Properties of Commission I.2 of the International Union of Pure and Applied Chemistry. The authors are grateful to the members of the sub-committee for their valuable advice. The authors are also indebted to Y. Nagasaka and J. Watson for enlightening discussions and comments. We take this opportunity to thank Mrs. P. Brown for her invaluable assistance in our literature search. Partial financial support for the work was provided by the United Kingdom Department of Trade and Industry.

8. References

Appendix. Results of the Literature Survey of the Thermal Conductivity of Toluene, Water, and n-Heptane

This is a summary of all the thermal conductivity data sources, for the liquids of interest to this study, of which it was possible to obtain copies. It is our intention that this summary serve as a foundation on which any future work may be based and consequently it is as extensive as possible, even though it is apparent that the results of most experimental work prior to 1970 are in error.

For each reference excluded from the primary database a summary is given of the systems studied of interest to us and the temperature and pressure range covered together with the estimation of the experimental accuracy of the original authors themselves. If any information is missing from the summary it is because it was not reported or because of translation difficulties. The references are in alphabetical order by first author and are arranged chronologically within this order.

Paper in Russian, no statement of uncertainty.

Toluene 273–493 K 0.1–4.3 MPa

Calorimeter. Paper in Russian.

Correlation of thermal conductivity of water and steam as a function of temperature and pressure—contains table of recommended values.

IAPS release of the international tables and equations for the thermal conductivity of water and steam.

Transient hot-wire apparatus.

Abstract only.

Flat plate cell.


Apparatus for multiproperty measurement, thermal conductivity, thermal diffusivity, thermal activity, and heat capacity.


Transient optical methods.


Correlations for prediction of thermal conductivity.

Calorimeter.

Calorimeter.

Calorimeter.

Calorimeter.

Concentric cylinder rotating about a horizontal axis to avoid convection. Layer thickness of 4 mm used and radiative transfer ignored for pure water.

Concentric cylinder apparatus. Equation only for data.


Hot-wire apparatus.

Parallel-plate apparatus. Graphical representation of experimental results.


Multilayer concentric cylinder apparatus.

Hot-wire apparatus.


Transient hot-wire apparatus.


Transient hot-wire, ac and dc mode. Instrument operating in both ac and dc mode used to measure the thermal conductivity of toluene with a maximum difference of 0.5%. Scatter with ac mode 0.3% and with dc mode 0.6%. Data in table of smoothed data.


Transient hot-wire apparatus with ac current. Smoothed values in table.

Paper in Russian. Calibrated instrument.

Parallel-plate apparatus.

Hot wire, ac current. Referred to an earlier paper for experimental details.


Instrument for multiproperty measurement. Paper in Russian.

Toluene 293–643 K 0.1–30 MPa
Concentric cylinder rotating about a horizontal axis. Dissertation in German.
Toluene 253–473 K \(P_{\text{sat}}\) ± 2.0% Water 273–473 K \(P_{\text{sat}}\) ± 2.0%
\(\text{Heptane} 253–473 K \ P_{\text{sat}}\) ± 2.0%
Concentric cylinder rotating about a horizontal axis. Graphical and least-squares representation only.
Toluene 253–473 K \(P_{\text{sat}}\) ± 2.0% Water 273–473 K \(P_{\text{sat}}\) ± 2.0%
\(\text{Heptane} 253–473 K \ P_{\text{sat}}\) ± 2.0%
Transient hot-wire apparatus. Only graphical representation of experimental results.
\(\text{Heptane} 260–328 K 0.1–1.0 \text{ GPa}\) ± 2.0%
Parallel plate apparatus. Paper in German.
Water 298 K ± 0.5%
A.36 V. V. Frontsev, Zavod. Lab. 22, 812 (1956).
Yofe's optical method. Paper in Russian.
Water 293 K 293 K
Yofe's optical method. Paper in Russian.
Water 293 K 293 K
Concentric cylinder apparatus.
Water 313–430 K ± 1.5%
Transient laser source.
Water 293 K
A.40 R. Goldschmidt, Phys. Z. 12, 417 (1911).
Hot-wire apparatus.
Toluene 194–287 K 273 K
Steady-state hot wire. Standard deviation of experimental results 1.9% and no discussion of convective or radiative energy transfer.
Toluene 298–373 K 0.1–250 MPa ± 2.0% \(\text{Heptane} 298–373 K 0.1–250 \text{ MPa}\) ± 2.0%
Flat-plate method. Paper in German.
\(\text{Heptane} 276–278 K\)
Hot-wire apparatus.
Water 286 K
Transient hot-wire apparatus.
Toluene 298–334 K ± 0.25%
Hot-wire apparatus.
Water 291 K
Toluene 273–365 K 2.6%
Steady-state hot-wire apparatus.
Toluene 323 K ± 5.0% Water 323 K ± 5.0%
Hot-wire apparatus. Graphical and least-squares representations of the data. Thesis in German.
Water 293 K n-Heptane 183–323 K
Graphical representation only.
\(\text{Heptane} 223–225 K\)
Parallel-plate apparatus. Graphical representation of data.
Transient hot-wire apparatus.
Transient hot-wire. Relative method—instrument calibrated with toluene data.
Water 273–353 K 0.1 MPa ± 2.0%
Transient hot-wire. Single wire with potential leads, no discussion of radiative contribution or conduction down the potential leads.
Paper in Russian.
Water 293–473 K
Paper in Russian.
Concentric cylinder apparatus.
Steady-state multipurpose instrument. Graphical representation of data only.
Review with recommended values.
Transient hot-wire apparatus.
Water 181–396 K \(P_{\text{sat}}\) ± 0.7–1.5% A.61 A. M. Mamedov, Inzh. Fiz. Zh. 34, 465 (1978).
Transient hot-wire apparatus. Graphical and least-squares representation of experimental results.
Recommended values for water from 1977 IAPWS release.
Transient hot-wire—extrapolated to 0.1 MPa. n-Heptane 308–348 K 0.3–500 MPa ± 0.3%

Concentric cylinder apparatus. Abstract only.

Water 273–472 K 0–100 MPa ± 1.0%


Toluene 273–353 K


Proposed standard reference materials and data.

Toluene 178–413 K $P_{\text{sat}}$ ± 1.0%

Water 283–313 K 0.1 MPa ± 0.5%


Steady-state hot-wire apparatus: single-wire annular test as coaxial cylinder apparatus.

Toluene 283–313 K 0.1 MPa

Water 283–313 K 0.1 MPa


Concentric cylinder apparatus. Paper in German.

$n$-Heptane 298–353 K 0.1–100 MPa


Parallel-plate apparatus. Paper in German.

Water 298 K


Parallel-plate apparatus. Graphical representation of results.

Toluene 298 K


Parallel-plate apparatus.

Water 298 K


Abstract of deposited paper—in Russian.

Toluene 303 K


Thermal comparator. Graphical representation of results.

$n$-Heptane 303 K


Concentric cylinder apparatus. Graphical representation of data only.

Water 313–433 K ± 1.5%


[Transl. of Tekhnologia 17, 77 (1970).]

Concentric cylinder apparatus.

Water 295–454 K 0.1–200 MPa ± 1.6%


Concentric cylinder apparatus.

Water 259–483 K 0.1–200 MPa ± 1.5%


Concentric cylinder apparatus. Graphical representation of data only.

Water 293–373 K ± 1.0%


Water 303–385 K


Toluene 293–413 K

Water 293–413 K

$n$-Heptane 293–413 K


Concentric cylinder apparatus. Only temperature coefficients given.

Toluene


Concentric cylinder apparatus.

Water 273–373 K ± 1.0%


Parallel-plate, concentric cylinder, and concentric sphere apparatus. Deviation between the three different types of instruments <0.5%.

Toluene 193–353 K ± 1.0%

Water 293–353 K ± 1.0%


Transient hot-wire apparatus.

Toluene 298 K


Parallel-plate apparatus. One temperature point plus slope given.

$n$-Heptane 306–350 K ± 1.5%


Toluene 239 K


Presentation of IAPS release of the thermal conductivity of water and steam.


Parallel-plate apparatus. Graphical representation only of experimental results.

Toluene 293–353 K

Water 273–353 K


Concentric sphere apparatus. Graphical representation of experimental results.

Toluene 193–333 K 0.1 MPa ± 2.0%

Water 308–373 K 0.1 MPa ± 2.0%


Concentric cylinder apparatus.

Water 303–363 K 0.1 MPa


Concentric cylinder apparatus.

Toluene 303–348 K

Water 303–348 K


Concentric cylinder apparatus. Reports data from other papers.

$n$-Heptane 303–333 K


Transient hot-wire apparatus. Paper in Russian.

Toluene 293–453 K ± 1.5%


Toluene 298–350 K

Water 315–351 K


Graphical representation of data only.

$n$-Heptane 293–443 K


Laser flash apparatus. Graphical representation of experimental results.

Toluene 283–353 K

Water 283–353 K


Transient hot-wire apparatus.

Water 273–373 K 0.1–4.87 MPa ± 1.5%


Transient hot-wire apparatus.

Water 273–373 K 0.1 MPa ± 1.5%


Water 274–283 K


Transient hot-wire apparatus.

Toluene 273–313 K
Water 298 K


Transient hot-wire apparatus.

Water 273-315 K


Concentric cylinder apparatus.

Toluene 708 K


Concentric sphere apparatus.

Toluene 273-373 K $P_{\text{atm}}$


Radial temperature waves method. No results given.

Toluene


Abstract only.


Concentric cylinder apparatus.

Toluene 293-343 K $\pm$ 2.0%

Water 280-315 K $\pm$ 2.0%


Concentric cylinder apparatus.

Toluene 273-353 K 0.1 MPa $\pm$ 2.0%


Transient hot-wire apparatus. Graphical and least-squares representation of results.

Toluene 173-383 K $P_{\text{atm}}$


Transient hot-wire apparatus.

Water 303-370 K $\pm$ 0.5%


Concentric cylinder and hot-wire instruments.

n-Heptane 293-371 K


Paper in German. No details of experimental apparatus.

Water 274-314 K 0.1 MPa


Concentric cylinder apparatus.

Water 297-366 K $\pm$ 1.85%


Formulation of equation for thermal conductivity of water and steam.


Concentric cylinder apparatus. Formulation of standard.

Toluene 268-385 K 0.1-0.4 MPa $\pm$ 1.0%-3.0%