Standard Reference Data for the Thermal Conductivity of Water

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New experimental data on the thermal conductivity of liquid water along the saturation line have been obtained recently, using the bare and coated transient hot wire technique, with high accuracy. The quality of the data is such that new standard reference values can be proposed with confidence limits of 0.7% at a 95% confidence level. These data and the correlation herein presented revise a previous correlation endorsed by IUPAC. *©1995 American Institute of Physics and American Chemical Society.*

Key words: liquid; reference material; standard reference data; thermal conductivity; water.

Contents

1. Introduction 1377
2. Experimental Techniques 1378
3. Experimental Data 1378
    3.1. Primary Data 1379
4. Correlation Procedures and Results 1379
    4.1. Equation Form 1379
    4.2. Correlation 1379
    4.3. Tabulations 1379
    4.4. Comparison with Previous SRD Correlation. 1380
    4.5. Cautions for Use of the Tabulated Recommended Thermal Conductivities 1380
5. Conclusions 1381
6. Acknowledgements 1381
7. References 1381

List of Tables

1. Primary sources of experimental data for thermal conductivity 1379
2. Recommended thermal conductivites for water .. 1380

List of Figures

1. The Standard Reference Data recommended for water along the saturation line, together with the primary data selected 1380
2. Deviations of primary data for water from the Standard Reference Data for water given by Eq. 4 ... 1380
3. Deviations of the SRD correlation proposed in Ref. 1 and of the equation recommended by IAPS in Ref. 20 and 21 from the Standard Reference Data for water given by Eq. 4 1380

1. Introduction

In recent papers[1,2] we have proposed standard reference data for the thermal conductivity of liquid toluene, liquid water, liquid benzene and liquid n-heptane for most of the normal liquid range. The available data in the literature were assessed by a careful analysis of the experimental methods and equipment used and divided in primary and secondary data. The primary data were used to develop correlations for the thermal conductivity of toluene, water and benzene, along the saturation line as a function of temperature. This effort[1,2] was developed under the auspices of the Subcommittee on Transport Properties of the Commission on Thermodynamics of the International Union of Pure and Applied Chemistry and published later as a part of a complete set of recommendations on the different physical properties of fluids by IUPAC[3].

Since then new data of high quality, which also extend the temperature range of the available data, have been published for water[4–7] and it is now possible to review the correlations proposed earlier. We will report in this paper revised correlations and revised standard reference data for water. The accuracy of the present correlations is better than the earlier ones[1].

2. Experimental Techniques

The experimental methods used for the measurement of thermal conductivity can be divided in two groups: steady state and transient. The thermal conductivity can also be obtained indirectly from the measurement of the thermal diffusivity, a technique specially valuable near the critical region and at high temperatures. For an overall discussion of the experimental techniques for the measurement of the thermal conductivity of liquids the reader is referred to recent monographs on the subject[8,9].

The transient hot wire technique is now accepted as the most accurate method for the measurement of the thermal conductivity of electrically non-conducting fluids, with the exception of regions of the phase diagram in the vicinity of the critical point and at very low densities in the gaseous phase[9]. However, a large number of fluids are electrically conducting including polar liquids such as water and the refrigerants, inorganic melts, electrolyte solutions, molten metals and molten semiconductors. We will extend the discussion presented in an earlier paper[1] to include additional experimental techniques and their application to electrically conducting fluids, particularly water. In the previous paper we indicated that those transient hot wire instruments that use bare wires, acting simultaneously as a resistance thermometer and as a heating element, could not be used directly for these types of fluids, because several problems are encountered[10], and these are:

1. The contact between the bare metallic wire and the conducting liquid provides a secondary path for the flow of current into the cell and the heat generation in the wire becomes, therefore, ambiguous.
2. Polarisation of the liquid occurs at the surface of the wire, degrading the electrical resistance between the wires and the cell walls.
3. The electrical system is effectively in contact with the metallic cell and the combined resistance/capacitance effect distorts the small voltage signals in the wire.

The solutions presented so far to overcome these problems can be grouped into three categories. In the first place an ac bridge can be used. This was the case in the work of Dietz *et al.*[11] who measured the thermal conductivity of water between 304 and 371 K, chosen as primary data set in Ref. 1 with an accuracy of 1.2%. Another solution is the use of an electrically insulating coat on the wires. This solution was pioneered by Nagasaka *et al.*[12], who used a polyester coating on a platinum wire. This work was chosen as primary data in our previous correlation, as it includes values for the thermal conductivity of water between 274 and 354 K. A third solution is to use a tantalum wire which is anodised in an acid solution to produce a very thin layer of a uniform and non brittle tantalum oxide. This solution was pioneered by Alloush *et al.*[13], and was used for the most recent sets of data on the thermal conductivity of water[4–7], shown to be accurate to within 0.5%. Finally a fourth solution has been developed by Nieto de Castro *et al.*[14] for chlorobenzene by using a dc polarisation voltage in the bridge. This polarisation voltage establishes compact double layers near the surfaces in the electrical field. The double layers may contain solvated ions, with a charge that is opposite to that of the metallic surface which they surround, in order to maintain the charge neutrality in the solution. The compact double layers effectively shield the ions in the bulk liquid from the electrical charges which are present on the wire surface. This last technique has recently been applied to the measurement of the thermal conductivity of environmentally acceptable refrigerants, which are extremely good solvents and polar, by Laesecke *et al.*[15] The technique has been now fully investigated and discussed by Perkins *et al.*[16] It was proved that it could achieve an accuracy better than 1%. However no data on water has been obtained with this last technique.

3. Experimental Data

In this work we use the recommendations previously made by Nieto de Castro *et al.*[1] for the selection of primary and secondary data. The primary data are the results carried out with an instrument of high precision for which a complete working equation and a detailed knowledge of all corrections are available. On the other hand, the experimental results which are of inferior accuracy to primary data due to operation at extreme conditions or incomplete characterization of the apparatus are classified as secondary data.

The primary data was identified using the following criteria[1] :

(i) Measuremments 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 shoould be such that sensitivity of thermal conductivity to the principal variables does not magnify the random errors of measurement,
(iii) All principal varibles should be measureable 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.
(vi) 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.
(vii) Explicit quantitative estimates of uncertainty of reported values should be given, taking into account the precision of the experimental measurements and possible systematic errors.

Owing to the quality of the new experimental data the limit that has been imposed in the accuracy of the primary data was 0.5%.

3.1. Primary Data

A summary of primary data for water, together with their estimated accuracy is given in Table 1. The statistical treatment of data is the same adopted in Refs. 1 and 2. In this table we have maintained the accuracies assigned in Ref. 1 for those new sets of data that are included in the revised correlations[12,17]. For the new sets of data the accuracy assigned is that claimed by the authors, since most equipments operate along the saturation line of the liquids or at a pressure of 0.1 MPa and the standard reference values refer to these conditions. In practice there is no distinction between the values of the thermal conductivity over the range of conditions presented here.

Nearly all of the experimental values were presented with the temperatures assigned to IPTS 68. The exception are the data of Ramires *et al.*[7] which were measured on the ITS 90. The differences in temperature scales over the temperature range used in this work are never bigger than 40 mK, the effect in the reported thermal conductivities is never bigger than 0.00002 $W\ m^{-1}K^{-1}$, well beyond the accuracy of the reported data. Therefore the correlations presented in section 4 can be considered to be on the ITS 90.

4. Correlation Procedures and Results

4.1. Equation Form

The experimental thermal conductivity data have been fitted to a quadratic functional form:

$$\lambda=b_0+b_1T+b_2T^2 \qquad (1)$$

where λ is the thermal conductivity and T the absolute temperature. The data have been fit to these equation using the method of least squares with weighting factors reflecting the accuracy of the data given in Table 1. The assumptions made in Ref. 1 to assign relative weights to the different data sets were adopted here.

4.2. Correlations

In order to establish recommended standard reference data we use a correlation to take account of the differences between the various sets of primary data. This correlation relates the thermal conductivity as a function of temperature. From these correlations we recommend for the thermal conductivity of water at 298.15 K and 0.1 MPa the value:

$$\lambda\ (298.15,\ 0.1\ \text{MPa}) = 0.6065 \pm 0.0036\ W\ m^{-1}\ K^{-1}$$

It is worth noting that these values do not depart from the previous[1] ones by more than 0.06 %, but have a much smaller uncertainty.

Using the convention of the IAPS formulation for the transport properties of the water substance developed by Sengers *et al.*[18,19] we have expressed the correlation in terms of dimensionless variables λ^* and T^* defined as

$$T^*=T/298.15 \qquad (2)$$

$$\lambda^*=\lambda(T)/\lambda(298.15) \qquad (3)$$

where $\lambda(298.15)$ is the adopted standard value of the thermal conductivity of water at 298.15 K and 0.1 MPa, given above.

The data used in the new correlation calculation are represented in Fig. 1. 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:

$$\lambda^*=-1.48445+4.12292T^*-1.63866T^{*2} \text{ for } 274\leq T\leq 370\text{ K} \quad (4)$$

Equation (4) is also plotted in Fig. 1. The maximum deviation of the primary experimental data is 0.7% with a standard deviation of 0.0020 $W\ m^{-1}\ K^{-1}$. The deviations of the primary data from the correlation are presented in Fig. 2, where it is clearly shown that most of the data are reproduced within their assigned experimental uncertainty.

4.3. Tabulations

Table 2 shows the recommended values for the thermal conductivity of water at 0.1 MPa. These values can be used as saturation line values in the temperature range considered as

TABLE 1. Primary sources of experimental data for thermal conductivity

Literature source	Technique	Temp. range	Number of data pts.	Assigned accuracy %
Y. Nagasaka *et al.* (Ref. 17)	TCHW	274 - 354 K	5	0.5
M.J. Assael *et al.* (Ref. 4)	TCHW	300 - 335 K	12	0.5
W.A. Wakeham *et al.* (Refs. 5,6)	TCHW	300 - 345 K	4	0.5
M.L.V. Ramires *et al.* (Ref. 7)	TCHW	298 - 365 K	38	0.5

TCHW - Transient coated hot wire technique.

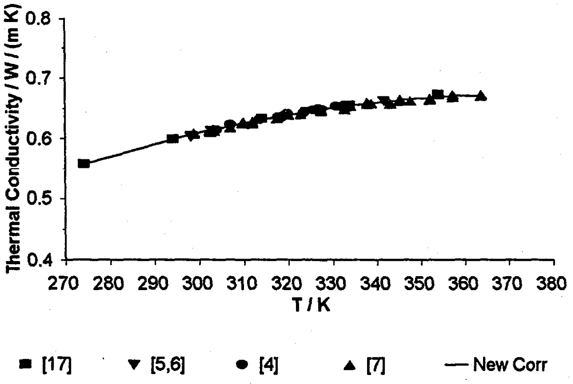

FIG. 1. The standard reference data recommended for water along the saturation line, together with the primary data selected.

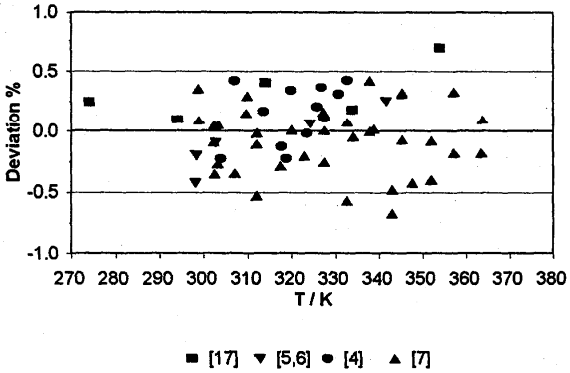

FIG. 2. Deviations of primary data for water from the standard reference data for water given by Eq. 4.

TABLE 2. Recommended thermal conductivities for water

T/K	λ/W/(m K)
275.00	0.5606
280.00	0.5715
285.00	0.5818
290.00	0.5917
295.00	0.6009
300.00	0.6096
305.00	0.6176
310.00	0.6252
315.00	0.6322
320.00	0.6387
325.00	0.6445
330.00	0.6499
335.00	0.6546
340.00	0.6588
345.00	0.6624
350.00	0.6655
355.00	0.6680
360.00	0.6700
365.00	0.6714
370.00	0.6723
	±0.0036

discussed in section 3.1, by taking $T=T_{sat}$ and obtaining p_{sat} and ρ_{sat} from an equation of state [18] or using recommendations of Ref. 19.

The recommended values are given to four significant digits but it should be emphasised that the uncertainties in the tabulated data are based on the analysis presented in section 4.2. We estimate the accuracy of the tabulated standard reference data for water to be 0.7 % at a 95 % confidence level (two standard deviations).

4.4. Comparison With Previous Standard Reference Data Correlations

The correlations produced in this work are compared in Fig. 3, for water, with the previously standard reference correlation proposed in Ref. 1 and with the equation for the thermal conductivity of water recommended by IAPS in Ref. 20 and 21.

The analysis of Fig.3 shows that the deviations between the three correlations for water do not deviate by more than 0.9 % in the entire temperature range. The departure are smaller than 0.5% for temperatures below 360 K. The largest deviations are found in the temperature range where more accurate data have become available.

Although the correlations agree within their mutual uncertainties, we recommend the use of the new one because of the higher accuracy of the primary data set.

4.5. Cautions in the Use of the Tabulated Recommended Thermal Conductivities

As already stated in Refs.1 and 2, some care must be taken by any user of the tabulated recommended thermal conductivities. These values serve two main purposes: (i) They act as the test of the accuracy of new absolute instruments, and (ii) they are means of calibrating instruments for which the full working equation is not available. Relative instruments must be calibrated with two standards, of very different thermal

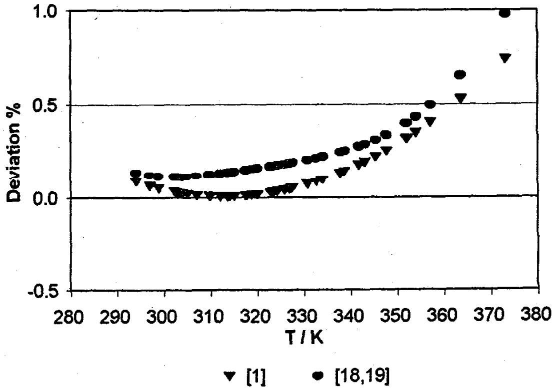

FIG. 3. Deviations of the SRD correlation proposed in Ref. 1 and of the equation recommended by IAPS in Ref. 20 and 21 from the standard reference data for water given by Eq. 4.

conductivity and radiative properties, because the effect of the radiative heat transfer in the measurements might be different from that observed in the instruments used for the data acquisition herein selected. It has been shown that the transient hot wire technique yields radiation free values. However this may not be the case in other instruments, specially those operating in steady-state mode.

5. Conclusions

New standard reference data for the thermal conductivity of water based on ITS 90 are proposed, which cover the normal liquid range along the saturation line. These recommendations are based on previously selected as well as on new highly accurate data obtained with transient hot wire instruments where the wires were coated in the case of water.

The correlation presented here is considered to have an accuracy higher than the correlations presently available in the literature.

6. Acknowledgments

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