

Thermal conductivity of liquids: Mixtures

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THERMAL CONDUCTIVITY OF LIQUIDS: MIXTURES

1. INTRODUCTION

This Item presents recommended values of binary mixing parameters, α required for the estimation of thermal conductivities of miscible, two-component liquid mixtures from Equation (4.1). The thermal conductivities of liquid multicomponent systems may be found by an extension of the procedure described in Section 4.1 for two-component mixtures.

An extensive survey of measurements reported in the literature for the thermal conductivities of 173 single phase, two-component liquid mixtures was undertaken. 1500 data points were analysed for 164 of these, and optimum values for the binary mixing parameter were determined by fitting to a simple expression, Equation (4.1). Equation (4.1) was found to be as reliable as equations derived from more complicated models, but does require the thermal conductivities of the pure components to be known. In this Item, multiphase systems such as emulsions, immiscible liquid-liquid, and solid-liquid systems have been excluded.

Quantities are expressed in SI units and conversion factors to other units are provided in Section 3.

Section 4 describes the procedure for determining the thermal conductivity of binary and multicomponent liquid systems. A description of the contents of the tables in Section 7 is provided in Section 5.

In Section 6, References 1 to 6 are sources of supplementary information. Reference 2 is a comprehensive summary of the data available up to 1973 and these sources are reproduced here for convenience. They have been supplemented with more recent data sources for one- and two-component systems, Derivations 38 to 83.

Since this Item was first published in 1988, ESDU has undertaken a comprehensive review of measurements of liquid thermal conductivities of pure fluids. The results are summarised as Tables and in equation form in a series of Data Items from 1983 onwards; these Items are listed under Derivations 54, 56 and 61 to 83. Where appropriate, the reader is referred to these as sources of pure component data.

Table 7.1 gives recommendations for assigning mixing parameters to some specific classes of mixture. They should be used when no optimised mixing parameters are available from Table 7.2. In addition to assigned and optimised values of α , Table 7.2 also contains comparisons of experimental data with Equation (4.1) for unoptimised, assigned and optimised values of α . An alphabetical list of the two-component systems in Table 7.2 is given in Appendix A. Tables 7.3 to 7.7 give values of thermal conductivity for binary aqueous mixtures of methanol, ethanol, propan-1-ol, propan-2-ol and acetone from $-50\text{ }^{\circ}\text{C}$ to $180\text{ }^{\circ}\text{C}$ or $200\text{ }^{\circ}\text{C}$ over the whole composition range.

2. NOTATION

N	number of points	—
r.m.s.	denotes root mean square	
t	celsius temperature	$^{\circ}\text{C}$
w	weight fraction of mixture component	—
α	non-dimensional binary mixing parameter in Equations (4.1) and (4.2)	—
Δ	denotes property difference	
λ	thermal conductivity	mW/m K

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Subscripts

1, 2, 3	denote mixture component
1, 3	denote mixture of components 1 and 3
asgn	denotes assigned value in Table 7.1
calc	denotes value calculated from Equation (4.1)
exp	denotes experimental value
mix	denotes mixture
opt	denotes optimum value
unopt	denotes unoptimised value.

3. CONVERSION FACTORS

$$\begin{aligned}
 1 \text{ mW/m K} &= 0.8598 \times 10^{-3} \text{ kcal/m h } ^\circ\text{C}^* \\
 &= 2.3885 \times 10^{-6} \text{ cal/cm s } ^\circ\text{C}^* \\
 &= 0.5778 \times 10^{-3} \text{ Chu/ft h } ^\circ\text{C}^* \\
 &= 0.5778 \times 10^{-3} \text{ Btu/ft h } ^\circ\text{F}^* \\
 &= 6.9335 \times 10^{-3} \text{ Btu in/ft}^2 \text{ h } ^\circ\text{F}^*.
 \end{aligned}$$

* The values used for the calorie and British Thermal Unit are International Table values.

4. THERMAL CONDUCTIVITY OF LIQUID MIXTURES

4.1 Thermal Conductivity of Two-component Systems

For most systems, measurements have been made at either a small number of concentrations or only at one temperature. This makes graphical interpolation or extrapolation difficult or even impossible. It was shown in Derivation 36, however, that a simple expression, Equation (4.1) can predict values of reasonable accuracy at all concentrations. Equation (4.1) contains an empirical correction factor, a binary mixing parameter, α apparently not substantially dependent on temperature, that can be estimated by fitting to experimental data. The experimental data were represented best, with Equation (4.1) expressed in terms of weight fractions rather than mole or volume fractions.

Equation (4.1) has the following simple form:

$$\lambda_{\text{mix}} = \lambda_1 w_1 + \lambda_2 w_2 - \alpha(\lambda_2 - \lambda_1)(1 - \sqrt{w_2})w_2 \quad (4.1)$$

in which $\lambda_2 > \lambda_1$ and α , λ and w denote the binary mixing parameter, thermal conductivity and weight fraction composition respectively. The term containing α is essentially a correction factor to the simple additive expression, that can be derived from Equation (4.1) by setting α to zero.

In general, for virtually all cases investigated, Equation (4.1) with $\alpha = 1$ gives improved predictions of thermal conductivity over the simple additive rule ($\alpha = 0$) for each mixture. When α is unknown, therefore, or cannot be estimated it may be taken as equal to 1.

Analysis of experimental data from the literature has been carried out, to determine optimum values for α that best represent all the observed thermal conductivity values over the entire experimental temperature ranges. The results are given in Table 7.2, where maximum differences between thermal conductivities from Equation (4.1) and experiment for optimum and unoptimised values of α (α set to unity) are given.

Some mixtures have slightly negative values of α but as the results with α set to zero were not significantly worse, the simple additive rule is preferred in these cases.

When the difference, $(\lambda_2 - \lambda_1)$ between the thermal conductivities of the pure components is less than about 40 mW/m K, the optimum value of α determined from fitting to data becomes increasingly erratic. The values found are reported, but observation of the maximum differences between thermal conductivities from Equation (4.1) and experiment with α set to unity indicates that unity is equally acceptable.

Where the pure component liquid thermal conductivities were not reported, an analysis was not conducted. As the accuracy of different measuring procedures was rather variable, it was considered that values for the pure component thermal conductivities, derived from alternative sources would corrupt the analysis.

An attempt has been made to codify the results into simple rules for given types of binary mixtures. These values of α , α_{asgn} , given in Table 7.1 are recommended for use where similar mixtures are encountered and no optimised values are available from Table 7.2.

More confidence pertains to the results for aqueous systems than to the remainder because the pure component values of thermal conductivity differ widely; the values of $(\lambda_2 - \lambda_1)$ exceed 300 mW/m K in all cases. Values for aqueous mixtures of methanol, ethanol, propan-1-ol, propan-2-ol and acetone are given in Tables 7.3-7.7.

Data for aqueous mixtures of glycols and glycerol, calculated from Equation (4.1) are tabulated in ESDU 78033 (superseded by ESDU 99013, Derivation 76). Best results were obtained for these mixtures with a value of α between 0.42 and 0.83. Optimum values of α , α_{opt} and the pure component thermal conductivities were used to determine the mixture thermal conductivities for temperatures from -50°C to 250°C over the whole composition range.

4.2 Thermal Conductivity of Multicomponent Systems

The thermal conductivities of a multicomponent mixture may be predicted by grouping the components into binary pairs. For a binary pair, 1,3, Equation (4.1) becomes:

$$\lambda_{1,3} = \lambda_1 \left(\frac{w_1}{w_1 + w_3} \right) + \lambda_3 \left(\frac{w_3}{w_1 + w_3} \right) - \alpha(\lambda_3 - \lambda_1) \left(1 - \sqrt{\frac{w_3}{w_1 + w_3}} \right) \left(\frac{w_3}{w_1 + w_3} \right). \quad (4.2)$$

where $\lambda_3 > \lambda_1$. For a two-component system, Equation (4.1) can be recovered from Equation (4.2) by setting $w_1 + w_3$ to unity.

For a four-component mixture, the components are grouped into two binary pairs, the thermal conductivities of which are calculated from Equation (4.2). Subsequently the two binary pairs are combined according to Equation (4.2) with $\alpha = 1$.

For a ternary, the two components with the smallest and largest values of thermal conductivity are combined; subsequently this pair is combined with the third component. Since the concentration of a binary pair 1,3 can be represented as $(1 - w_2)$ and taking $\alpha = 1$, then

$$\text{if } \lambda_{1,3} < \lambda_2: \lambda_{\text{mix}} = \lambda_{1,3}(1 - w_2) + \lambda_2 w_2 - (\lambda_2 - \lambda_{1,3})(1 - \sqrt{w_2}) w_2. \quad (4.3)$$

$$\text{if } \lambda_{1,3} > \lambda_2: \lambda_{\text{mix}} = \lambda_2 w_2 + \lambda_{1,3}(1 - w_2) - (\lambda_{1,3} - \lambda_2)1 - \sqrt{(1 - w_2)}(1 - w_2). \quad (4.4)$$

Example

The above procedure may be illustrated with the following example. Usmanov (Derivation 43) measured the thermal conductivity of a ternary mixture consisting of 20% w/w dimethyl formamide, 20% w/w aminoethanol, and 60% w/w aniline at 30 °C as 173.0 mW/m K. The pure component values were reported as 178.5, 234.0 and 164.0 mW/m K. The weight fractions of aniline and aminoethanol in an equivalent binary mixture are 0.6/0.8 and 0.2/0.8 so that

$$\text{from Equation (4.2): } \lambda_{1,3} = 164 \times 0.75 + 234 \times 0.25 - 70(1 - \sqrt{0.25})0.25 = 127.75;$$

$$\text{from Equation (4.3): } \lambda_{\text{mix}} = 172.75 \times 0.8 + 178.5 \times 0.2 - 5.8(1 - \sqrt{0.2})0.2 = 173.3.$$

5. NOTES ON DERIVATION AND EXPLANATION OF TABLES

Derivations 25, 28, 38, 43 and 60 have been included to give sources of data on ternary mixtures. The effect of pressure is reported in Derivations 40, 46, 51, 53 and 58.

Table 7.1 gives rules for assigning preferred values of binary mixing parameters, α_{asgn} according to the chemical characteristics of the mixture components. These assigned values are derived from comparisons of experimental data with Equation (4.1). If no optimised values of α are available from Table 7.2, assigned values should be used in Equation (4.1). If neither are available or $(\lambda_2 - \lambda_1) < 40$ mW/m K, α should be set to the unoptimised value, unity.

In Table 7.2 assigned (Table 7.1) and optimum values of α , α_{asgn} and α_{opt} respectively, for 173 binary mixtures are given, together with comparisons between experiment and Equation (4.1) for unoptimised (α_{unopt}), assigned (α_{asgn}) and optimum (α_{opt}) values of α . The comparisons are in terms of percentage differences, defined as:

$$\Delta\lambda\% = \frac{\lambda_{\text{exp}} - \lambda_{\text{calc}}}{\lambda_{\text{calc}}} \times 100 \quad (5.1)$$

Also listed are the number of experimental data points, and the associated temperature or temperature range. The maximum differences reported for the binary mixtures in Table 7.2 are the largest values of the percentage differences calculated from Equation (5.1). This is the worst case. Had r.m.s. values been reported, Equation (4.1) would have appeared to be even more satisfactory.

Tables 7.3 to 7.7 give the thermal conductivity of binary aqueous mixtures of methanol, ethanol, propan-1-ol, propan-2-ol and acetone. Data for aqueous mixtures of ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, di- α -propylene glycol and glycerol are reported in ESDU 99013, Derivation 76.

Appendix A contains an alphabetical listing of the binary mixtures given in Table 7.2. Links to the data sources in the Derivation are also given here so that the reader may, if desired refer to the original measurements.

6. REFERENCES AND DERIVATION

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The references given are recommended sources of information supplementary to that in this Item.

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The derivation lists all sources of data found in the literature since the survey in 1973 (Reference 2) and includes the sources contained in that survey.

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