

Electrolytes. Properties of Solutions. Methods for Calculation of Multicomponent Systems and Experimental Data on Thermal Conductivity and Surface Tension

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ELECTROLYTES. PROPERTIES OF SOLUTIONS. METHODS FOR CALCULATION OF MULTICOMPONENT SYSTEMS AND EXPERIMENTAL DATA ON THERMAL CONDUCTIVITY AND SURFACE TENSION

Methods for calculation of the thermal conductivity and surface tension of multicomponent electrolyte solutions with minimum errors are presented. Related equations for calculation of the thermal conductivity of water at the saturation line in the temperature range 0–350°C, the activity of water, and the water vapor pressure over pure water in the temperature range 0–350°C and over a solution at the saturation line are also considered. Calculation coefficients for many electrolytes, obtained as a result of mathematical processing by the methods of regression analysis of experimental data available from the literature and measured by the author, are given. The material is illustrated by examples of calculation.

Tables of experimental data on the thermal conductivity and surface tension are presented for wide ranges of the mass contents of electrolytes in aqueous solutions, the temperatures, and pressures. The data were obtained as a result of mathematical processing of available reported information and experimental results determined by the author. The material is processed on computer.

This book gives data for a great number of electrolytes, which are most widely used in modern chemical technology, and is intended for scientific workers and engineers of chemical industry and allied industries.

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Foreword

This book is the continuation of a number of the author's works dealing with study, representation, and methods of calculation of the physicochemical properties of binary and multicomponent electrolyte solutions [1–5].

Compared to [3], this book contains substantially revised and enlarged data on thermal conductivity, new experimental data on the surface tension of electrolyte solutions, and coefficients for calculation of the thermal conductivity and vapor pressure over a solution for many electrolytes. The coefficients are obtained as a result of mathematical processing of available experimental data by the methods of regression analysis. Experimental data for the most widely used electrolytes are given for high temperatures and pressure ranges.

Section I gives the methods for calculation of thermal conductivity and various coefficients for a wide range of electrolytes, which allow one to calculate multicomponent solutions with high accuracy. New regression equations for calculation of the thermal conductivity of water in the range 0–350°C, which are necessary for determination of the thermal conductivity of solutions, are proposed. An equation for calculation of the surface tension of binary and multicomponent systems, based on data on the water activity, is also presented. Approximation expressions for calculation of the vapor pressure over pure water and a solution, which are used to find the water activity, are also given.

The list of electrolytes in Section II is significantly longer than in [3] (see table index for Section II), and the data for the same electrolytes were revised. The logic sequence of reference data is identical to that in [3], and the maximum temperature range and mass content in a solution are given for each electrolyte. Considerable attention is given to high-temperature studies. Experimental data for many electrolytes were additionally obtained by the author, using original experimental techniques, which should make this book popular.

The following system of references is used in [1–3] and the next books [4, 5]. The complete references are given for each property and each electrolyte, and the absence of references means that original data are presented. Many data were refined by the author's experimental studies, and not all data from the references were mathematically processed.

The author will gratefully accept all comments and wishes of the reader.

Section I

1.1 Calculation of the Thermal Conductivity of Multicomponent Electrolyte Solutions

The thermal conductivity of multicomponent electrolyte solutions can be calculated by the formula [1–3]

$$\lambda = \lambda_0 \left(1 + \sum_{i=1}^k \beta_i c_i \right) \quad (1.1)$$

where λ is the thermal conductivity of solution, W/(m·K); λ_0 is the thermal conductivity of water, W/(m·K); β_i are coefficients obtained as a result of mathematical processing by the methods of regression analysis of available experimental data on thermal conductivity (Table 1.3); c_i is the mass content of electrolyte in the solution, %; and k is the number of components in the solution.

The thermal conductivity of water from 0 to 135°C is approximated by the polynomial

$$\lambda_0 = 10^{-3} (L_0 + L_1 T_* + L_2 T_*^{1.5} + L_3 T_*^{2.5} + L_4 T_*^3) \quad (1.2)$$

where

$$\begin{aligned} L_0 &= 560.971778 & L_1 &= 178.153112 & L_2 &= 59.731618 \\ L_3 &= -245.008302 & L_4 &= 124.973313 \end{aligned}$$

from 135 to 350°C, by the polynomial

$$\lambda_0 = 10^{-3} (L_0 + L_1 T_*^{2.5} + L_2 T_*^{3.5} + L_3 T_*^4 + L_4 T_*^5) \quad (1.3)$$

where

$$\begin{aligned} L_0 &= 689.135856 & L_1 &= -12.717225 & L_2 &= 32.337897 \\ L_3 &= -23.977428 & L_4 &= 2.002973 \end{aligned}$$

with the root-mean-square error of calculation $S_\lambda = 0.29 \text{ W/(m}\cdot\text{K)}$ and the mean relative error of calculation $\Delta = 0.03\%$.

In all instances, $T_* = 0.01t$, where t is the temperature, $^\circ\text{C}$.

Example. Calculate the thermal conductivity of a $\text{CaCl}_2\text{-NaCl-H}_2\text{O}$ solution at $t = 50.8^\circ\text{C}$ and the mass content of CaCl_2 15.75% and of NaCl 5.25%. The experimental thermal conductivity of the solution is $0.612 \text{ W/(m}\cdot\text{K)}$ [6].

According to formula (1.2), the thermal conductivity of water is

$$T_* = 0.01 \cdot 50.8 = 0.508$$

$$\begin{aligned} \lambda_0 &= 10^{-3} (560.971778 + 178.153112 \cdot 0.508 + 59.731618 \cdot 0.508^{1.5} \\ &\quad - 245.008302 \cdot 0.508^{2.5} + 124.973313 \cdot 0.508^3) = 0.644 \text{ W/(m}\cdot\text{K)} \end{aligned}$$

Coefficients β_i from Table 1.3 are $-2.0856 \cdot 10^{-3}$ for CaCl_2 and $-1.9004 \cdot 10^{-3}$ for NaCl . According to equation (1.1), the thermal conductivity of the solution is

$$\lambda_0 = 0.644 (1 - 2.0856 \cdot 10^{-3} \cdot 15.75 - 1.9004 \cdot 10^{-3} \cdot 5.25) = 0.617 \text{ W/(m}\cdot\text{K)}$$

The mean relative error of calculation is 0.82%.

1.2 Calculation of the Surface Tension of Multicomponent Solutions

The surface tension of a multicomponent solution can be calculated by the formula [1–3]

$$\sigma = \sigma_0 + 0.049(1 - a_w) \quad (1.4)$$

where σ is the surface tension of the multicomponent electrolyte solution, N/m ; σ_0 is the surface tension of water, N/m ; and a_w is the activity of water in the multicomponent solution.

The surface tension everywhere over the region of existence of water can be calculated from the data in [7] with high accuracy:

$$\sigma_0 = B \left(\frac{T_0 - T}{T_0} \right)^m \left[1 + b \left(\frac{T_0 - T}{T_0} \right) \right] \quad (1.5)$$

where

$$B = 235.6 \cdot 10^{-3} \quad T_0 = 647.15 \quad m = 1.256 \quad b = -0.625$$

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