Foreword

Because of the rapid development of various branches of engineering, there has been a burgeoning interest in obtaining information on the thermodynamic properties of numerous pure fluids and fluid mixtures with which researchers and practical engineers deal when solving various scientific and application problems. Science and engineering projects cannot be implemented without data on the properties of materials involved in their particular processes. Modern physics only rarely makes it possible to accurately calculate fluid properties. Therefore, experiment is the principal source of information for the great majority of properties of most common fluids and fluid mixtures.

For many years, a vast amount of experimental data on the thermodynamic properties of gases, liquids, and their mixtures has been obtained in various research laboratories over the world. Russian researchers have made significant contributions to this sea of data. Unfortunately, they are frequently under-represented in other countries scholarly works, because much of their data is published in sources that are difficult for foreign readers to access. This book corrects the situation to a certain degree. It considers experimental techniques in the study of thermal ($PVTx$), caloric (C_VVTx), and transport (λPTx) properties of aqueous systems (light and heavy water, their mixtures, hydrocarbons, alcohols, aqueous salt, aqueous hydrocarbon, and aqueous alcohol solutions) within a broad range of independent thermodynamic variables (VT, PT), including near-critical and supercritical regions. The experimental thermodynamic (PVT), (C_VVT), and transport (λPT) properties results for pure light and heavy water, hydrocarbons, and alcohols, and the ($PVTx$), (C_VVTx), and (λPTx) results for binary aqueous salt, aqueous hydrocarbon, and aqueous alcohol solutions at high temperatures and high pressures obtained in the Thermopysical Division of the Dagestan Scientific Center of the Russian Academy of Sciences are presented and evaluated.

Experimental methods of determining thermodynamic, (PVT) and (C_VVT), and transport, (λPT), properties of aqueous systems at high temperatures and high pressures are considered in Chapters 1 to 3. A brief survey of apparatuses is given here; the main components, their characteristic features, and the experimental procedures are described. The experimental data sets obtained using these apparatuses are given in the Appendices, and the main sources of the uncertainties of the measurements are estimated. Special attention is paid to problems with the experimental studies of near-critical and supercritical states.

It is well known that the development of new methods and improvement of existing techniques of theoretical calculation of determining thermodynamic properties of fluids and fluid mixtures requires reliable experimental data. Because of the existence of such data, practical methods of the use of equations of state have been developed extensively in the last two decades. A detailed analysis of the modern theoretical crossover models for prediction of thermodynamic properties of aqueous systems in, and beyond, the critical region is given in Chapter 2. Here, the crossover theory has been used in comparison with the derived experimental data sets for pure light and heavy water, and their mixtures, in the near-critical and supercritical regions and to estimate the consistency of various data sets. The crossover equations of state considered in this book are the kinds of instruments for studying thermodynamic behavior of the near-critical and supercritical aqueous systems needed for supercritical technological processes.

Almost all available sources of data for $PVTx$, C_VVTx, and λPTx of aqueous systems have been collected, evaluated, corrected, and converted to the ITS-90 temperature scale. Critical analyses are presented as to the uncertainty of each data source, along with comparisons with other sources. The reliability of these data are estimated on the bases of detailed comparisons with accurate equations of state (IAPWS-95 formulation for light water, IAPWS-98 formulation for heavy water, crossover equations of state, multiparametric equations of state) and literature data. Special attention has been focused on the thermodynamic properties of aqueous systems in the near-critical and supercritical conditions. The most reliable ($PVTx$, C_VVTx, and λPTx) data for light and heavy water, and aqueous systems are selected and recommended for scientific and technological applications.

The book is organized as follows. In Chapter 1, useful information is given for $PVTx$ measurements of pure light and heavy water, pure hydrocarbons, aqueous hydrocarbon and aqueous salt solutions in the near-critical and supercritical regions, and on the coexistence curve. In this chapter, the analyses of the avaliable types (multiparameter, MBWR, fundamental, IAPWS-95 formulation, virial, scaling, and crossover) of the equations of state for pure components, aqueous hydrocarbon, and aqueous salt solutions are presented. The experimental apparatuses for $PVTx$ measurements of the high-temperature and high-pressure aqueous system are described. The data derived from $PVTx$ measurements of thermodynamic (excess, apparent, and partial molar volumes, the Krichevskii parameter) and structural (DCFI and TCFI) properties for dilute aqueous systems near the solvent (pure water) critical point are considered.

Chapter 2 presents a brief review of the calorimetric methods for determining the isochoric heat capacity of light and heavy water, their mixtures, aqueous hydrocarbon, aqueous salt, and aqueous alcohol solutions in the near-critical and supercritical conditions. There is a detailed description of the method of quasi-static thermograms for measurement of the phase transition temperature T_S near the critical point in calorimetric (C_VVTx) experiments. The likely sources of systematic and nonsystematic uncertainties are considered for each method. This chapter also contains tables that include information on experimental sources, methods of measurements, uncertainties of measured results, temperature and density ranges of measurements, and a list of sources. Detailed comparisons of various experimental data sets for isochoric heat capacity with crossover equations of state and IAPWS-95 and IAPWS-85 for light and heavy water, their mixtures, and aqueous salt solutions are presented.

In Chapter 3, the thermal conductivity data sources for light and heavy water, and aqueous salt solutions at high temperatures and high pressures are reviewed, including brief descriptions of the methodology, known sources of uncertainties, boundaries of study, and uncertainty estimates for different thermodynamic states. More reliable data sets are selected and recommended for scientific and technological applications. Various correlation and prediction techniques for thermal conductivity of aqueous salt solutions are discussed. All of the avaliable experimental data sets for thermal conductivity of light and heavy water, and 25 aqueous salt solutions were critically analyzed, and their reliability and consistency were estimated. Selected data sets are recommended on the bases of detailed comparisons with the IAPWS-98 formulation for light and heavy water, and various correlation equations and prediction techniques for salt solutions. The deviation plots, deviations statistics, and analyses of the character and distribution of the deviations for various thermal conductivity data sets are presented. The quality of data and their consistency are graphically demonstrated in the deviation plots.

In the Appendix, we have presented tables of original extended experimental data ($PVTx$, C_VVTx, and λPTx) for pure light and heavy water, pure hydrocarbons, alcohols, their mixtures, aqueous salt solutions, aqueous hydrocarbon mixtures, and aqueous alcohol solutions at high temperatures and high pressures, including two- and one-phase regions, near-critical and supercritical regions, and properties at saturation. More detailed comparisons with fundamental equations of state and deviation plots for each system are given. A discussion of the accuracy of these data is also included.

This book is designed for specialists in molecular physics, chemical technology, and chemical and power engineering, as well as researchers, lecturers, postgraduates, and students in technical colleges and universities. We hope that the results presented in this book will be useful to a wide circle of researchers and practionists working in various fields of science and technology.