Introduction

**Need for Thermophysical Data for Aqueous Systems
at High Temperatures and High Pressures**

Water, the most important solvent in nature, has surprising properties as a reaction medium in its supercritical state [1]. The remarkable anomalous properties of supercritical fluids are widely used in industry. Supercritical fluids are of fundamental importance in geology and mineralogy (for hydrothermal synthesis), in chemistry, in the oil and gas industries (e. g., in tertiary oil recovery), and for some new separation techniques, especially in supercritical fluid extraction. Supercritical water is used for the destruction of hazardous wastes and has been explored as a solvent medium to carry out chemical reactions or biological degradations without char formation. Although our understanding of the thermophysical properties of water and aqueous systems at ambient conditions has improved significantly, it is far from sufficient to even conjecture the behavior of aqueous systems in the highly compressible conditions (near-critical and supercritical conditions) that are currently of great scientific and practical interest. Aqueous solutions at high temperatures and high pressures play a major role in both natural and industrial processes and in waste disposal, which is, in a sense, both industrial and natural [2]. While surface and oceanic waters are near room temperature, similar aqueous solutions are present at high temperature and high pressure in deep geological formations. Aqueous systems also arise in steam-power generation, geothermal power plants, hydrothermal synthesis, seawater desalination processes, and other industrial operations at high temperatures and high pressures. Thus, there is great practical interest in the thermodynamic properties of aqueous salt solutions at these conditions. Aqueous systems play a significant role not only in chemical industry and technological processes, but also in nature as geothermal systems and in the biological processes of living organisms. The oceans and underground waters are the largest reservoirs of aqueous electrolyte solutions.

The dominant solutes are often simple electrolytes such as NaCl, $CaCl_2$, $MgCl_2$, and Na_2SO_4 with lesser amounts of potassium salt, carbonates, borates, etc. H_2O +

NaCl systems are very important in many geological processes. NaCl is the primary solution in most hydrothermal and metasomatic fluids. The two-phase region for this system is of particular interest because phase separation is an important process in many hydrothermal systems and, in particular, seafloor geothermal systems [3, 4]. Seawater circulates in these systems between the seafloor and the top subsurface magma chamber, with hydrostatic pressures ranging from 10 to 60 MPa. The H_2O + NaCl system can serve as a model for other ionic salts. The importance of $CaCl_2$ in deep brines of the Earth's crust and its reactivity in fluid-rock interaction is becoming increasingly recognized. The thermodynamic properties of H_2O + $CaCl_2$ systems are important in understanding these interactions and deep-seated geochemical processes. *Ca* is the second most important cation after *Na*. At salinities in excess of about 30wt%, *Ca* becomes the most abundant cation, and such brines are widespread in the deeper parts of many sedimentary basins. Groundwaters encountered in deep wells drilled in crystalline rocks also commonly are highly saline brines in which *Ca* is the dominant cation, exceeding *Na* by a factor of 2–3 by weight basis. The Russian super-deep well in the Kola Peninsula produced a brine rich in *Ca*. That *Ca*-rich brines have been mobilized in hydrothermal processes related to ore deposition is clearly shown by compositions of fluid inclusions trapped within hydrothermally deposited minerals in ore deposits. *Ca*-rich brines also play an important role in seafloor hydrothermal systems at mid-ocean ridges. In addition, $CaCl_2$ is the premier example of an electrolyte of the 2:1 charge type, and its aqueous solution has been much used as an isopiestic standard.

Na^+ and SO_4^{2-} are important components of natural fluids, and a knowledge of their aqueous solution thermodynamic properties is important in understanding various geochemical processes, such as those related to evaporite formation, subsurface brines, seafloor vents, geothermal energy production, and mineral scaling problems. In addition, aqueous Na_2SO_4 solution is a good example of a 1:2 charge type electrolyte.

In this book, special attention is focused on the thermodynamic properties of aqueous systems in the supercritical region. Supercritical water (SCW) (i.e., water at temperatures and pressures above its critical point, T_C = 647.1 K; P_C = 22.1 MPa) has recently become subject to growing scientific interest due to its crucial role in a variety of natural processes, as well as because of emerging promising technological applications (supercritical water oxidation, SCWO, for the environmentally-friendly destruction of toxic and hazardous wastes).

SCWO technology is an emerging technology for the destruction of civilian and military hazardous wastes. One of the important applications of SCWO for waste treatment is in the handling of solids that can be present at high temperatures and high pressures. Sodium sulfate is one of the most commonly encountered salts in prospective applications of SCWO. Development of effective strategies for applying SCWO technology to the destruction of hazardous materials requires knowledge of the thermodynamic properties of aqueous salt solutions near the critical point.

Due to the large compressibility under supercritical conditions, small changes in pressure can produce substantial changes in density, which, in turn, affect diffusivity, viscosity, dielectric, and solvation properties, thus dramatically influencing the kinetics and mechanisms of chemical reactions in water. The properties of water change markedly when it is approaching temperatures and pressures near, or above, the critical point

(22.1 MPa and 647.1 K). The ionic product falls by many orders of magnitude and the dielectric constant is reduced to values (about 2 at 25 MPa and 723 K) typical of organic solvents. It is possible to sustain a flame in supercritical water by injecting oxygen into an aqueous solution of methane [1]. This is to allow the use of SCWO as a means for hazardous waste destruction, including chemical weapons and the clean-up of nuclear processing sites. SCWO is the oxidation of organics, in the presence of a high concentration of water, at temperatures and pressures above the critical point of water. The oxidation is usually conducted at temperatures from 673 K to 723 K and at pressures of 25 MPa. SCWO offers significant improvements over conventional methods of oxidation because the effluents are clean. The gaseous effluent can be discharged directly to the atmosphere without scrubbing, the solids can be reused or landfilled, and the water reused. Significant problems in the practical development of SCW destruction facilities are considerable experimental difficulties and the lack of detailed knowledge of the thermodynamic and transport properties of supercritical fluids at the molecular level. The advantages of SCWO arise primarily from the unusual properties exhibited by water under supercritical conditions. The density decreases rapidly in the range of 573 K to 673 K. The solubility of organics in SCW is typified by that of benzene and pentane. Between 533 K and 573 K, benzene solubility increases from a few percent to completely miscible. In general, organics and water are miscible in all proportions above the critical temperature of pure water. Gases such as oxygen are completely miscible with SCW. The solubility of salts (for example NaCl) in SCW at a pressure of 25 MPa and a temperature of 723 K decreases sharply. The residual solubility is on the order of 100 ppm. This is not surprising because inorganics are practically insoluble in SCW. One of the most serious obstacles in developing industrial-scale supercritical water technologies is the lack of fundamental understanding of many aspects of the supercritical fluid state itself, and particularly the behavior of supercritical aqueous systems. Therefore, additional experimental and theoretical studying of the thermophysical properties of aqueous systems at high temperatures and high pressures is very important to many industrial processes such as emerging technologies of hazardous waste destruction (supercritical water oxidation processes), for understanding mechanisms and kinetics of chemical reactions in supercritical water, design calculations, heat and mass transfer, fluid flow, developments and utilization of geothermal energy, etc. Understanding various geochemical and industrial processes requires a thorough knowledge of thermodynamic properties of aqueous electrolyte solutions.

Supercritical fluids have been proposed as solvent or reaction media for a number of technological applications such as coal conversion [5], organic synthesis [6], destructive oxidation of hazardous wastes (SCWO process) [7–11], enhanced oil recovery [12], activated carbon regeneration [13], formation of inorganic films and powders [14], supercritical chromatography [15], organic reaction rate modification [16], precipitation polymerization [17], etc. Thermodynamic properties of hydrocarbons in water at high temperatures and high pressures are of considerable interest in a number of industrial applications such as and petroleum chemistry (reservoir fluids, enhanced oil recovery-in tertiary oil recovery), environmental protection (removal of hydrocarbons from waste waters, fate of hydrocarbons in geological fluids), organic chemistry (formation of petroleum), geology and mineralogy (for hydrothermal synthesis), new separation techniques, biological degradations without char formation [5–22], etc. SCW is receiving

increased interest as an alternative to organic solvents [10]. SCW has the capability of dissolving both non-polar and polar, solutes since its dielectric constant can be adjusted from a room temperature value of 80 to a value 5 at its critical point. Therefore, water can solubilize most non-polar organic compounds, including most hydrocarbons and aromatics starting at 473 K to 523 K and extending to the critical point [23, 24]. Low-polarity organic pollutants, such as polycyclic aromatic hydrocarbons (PAH), typically have very low solubility in water at ambient conditions because of water's high polarity (dielectric constant, $\varepsilon = 80$). However, the dielectric constant of water can be drastically lowered by raising the temperature of the water under moderate pressure to effect dramatic increases (to percent levels) in the solubility of low-polarity organics. For example, sub-critical water at 523 K and 5 MPa has $\varepsilon = 27$, which allowed quantitative extractions of PAH in 15 min from soil and urban air particulars. Decreasing the polarity of water by sequentially raising the extraction temperature from 323 K to 523 K (sub-critical water), and finally to 673 K (SCW if $P > 22.1$ MPa), allowed class-selective extractions of polar organics (chlorinated phenols), low-polarity organics (PAH), and nonpolar organics (n-alkanes) to be performed. Hawthorne et al. [25–28] used sub-critical and supercritical water for quantitative extraction of organics from environmental solids.

The properties of water + hydrocarbon systems are also of fundamental importance in geology and mineralogy, i.e., in the geothermal processes, which form oil reservoirs, and in the oil and gas industries. Furthermore, water + hydrocarbon systems may serve as model systems that are useful in the development of processes such as the hydrolysis of plastic, synthetic fibers, or polycarbonates for recycling [30] and the destruction of hazardous wastes [7–11]. Water + toluene mixtures are also used for extraction processes [29]. Fundamental understanding of some of these technologically important applications of SCW might be substantially improved through comprehending the solvation structures around solutes dissolved in SCW. Design and control of systems for supercritical fluid extractions requires pure-component and mixture thermodynamic properties and molecular-based understanding of the mechanism underlying the supercritical solubility enhancement. The efficient utilization of the possibilities offered by supercritical fluid solubility requires an accurate and detailed knowledge of the fluid thermodynamic properties, particularly *PVTx* relation to the near-critical mixtures.

Water-hydrocarbon mixtures are important in a wide range of industrial processes, including coal gasification, oil recovery, steam distillation, steam reforming, and combustion. It is crucial to understand *PVTx* behavior for water + hydrocarbon systems at high temperatures and high pressures for supercritical process design. Understanding the thermodynamic behavior of the water + hydrocarbon mixtures and water + salt solutions near the critical point of pure water would well serve supercritical technological processes at high temperatures and high pressures. Much attention has been focused also on the water + hydrocarbon systems because of their fundamental importance to understanding specific interaction between polar (water) and non-polar (hydrocarbon) molecules. *PVTx* measurements are crucial to the comprehension of many important phenomena taking place in supercritical aqueous solutions.

To use water + hydrocarbon systems effectively, it is necessary to know their fundamental *PVTx* relationship and other derived properties. The sparing solubility of

oil, gas, and water mixtures at the earth's surface may very well present an entirely different mutual relationship when subject to high underground pressure and temperature. The present technological advancement in the use of high temperature and high pressure in chemical industries would be well served by an understanding of the phase and *PVTx* relations in water + hydrocarbon mixtures. *PVTx* data for water + hydrocarbon systems provide additional information on the effects of temperature, pressure, and composition on the thermodynamic behavior in such systems, which could lead to improved understanding of processes near the solvent critical point. However, *PVTx* data for the water + hydrocarbon systems under supercritical conditions are scarce.

In addition to being of practical interest (primarily in the nuclear industries), the thermodynamic properties of heavy water and its mixtures with light water are interesting from a modeling point of view. Because of the similarity of the molecules, the mixture properties are very nearly ideal. Reproducing the small nonidealities is a challenge for modelers. In addition, the presence of the isotope exchange equilibrium involving HDO adds an extra complication, but does so in a way that has less impact on the phase diagram than is observed in most reacting systems.

The thermodynamic behavior of dilute mixtures in the vicinity of the solvent (water) critical point is of considerable practical and theoretical importance. Much of the theoretical work on supercritical solubility has focused upon relating the infinite dilution properties, for example, negatively and positively diverging solute partial molar volume in mixtures in the immediate vicinity of the solvent critical point and path-dependence solvent properties in near-critical systems [31–42].

To develop a reliable equation of state for fluids and fluid mixtures, various thermodynamic properties data are required. Among them, isochoric heat capacity data C_V is one of the important thermodynamic properties of fluids and provides a strong test of the reliability of the *PVT* equation of state. Calorimetric ($C_V VT$) measurements to develop an equation of state are very important, especially near the critical and phase transition points where real curvature of *P–T* isochores is essential. The accurate calculation of the caloric and acoustic properties from a *PVT* equation of state strongly depends on accurate determination of the *PVT* data and temperature derivatives $(\partial P/\partial T)_\rho$ and $(\partial^2 P/\partial T^2)_\rho$. These derivatives directly relate to caloric and acoustic properties. As a rule, thermal properties (*PVT*) do not correctly reproduce the values and qualitative behavior of caloric (C_V, C_P, S, H) and acoustic (sound of velocity, W) properties of real fluids because the calculation depends upon the $(\partial P/\partial T)_\rho$ and second $(\partial^2 P/\partial T^2)_\rho$ temperature derivatives of the pressure. Reliable isochoric heat capacity measurements yield valuable, accurate, and direct information about second temperature derivatives $(\partial^2 P/\partial T^2)_\rho$ of the pressure, which cannot be correctly determined solely on the basis of *PVT* measurements. It is almost impossible to accurately extract $(\partial^2 P/\partial T^2)_\rho$ from thermal (*PVT*) measurements. If, however, measurements of $C_V VT$ are available, use of well-known thermodynamic relations can yield a *PVT* equation of state that is capable of reproducing caloric (C_V, C_P, S, H) and thermal (*PVT*) properties within the experimental uncertainties of the measurements. The role of calorimetric, particularly isochoric heat capacity ($C_V VT$), measurements to develop an equation of state, especially near the critical and supercritical regions, is very important. Isochoric heat capacity measurements are often used to develop a fundamental equation of state. Detailed com-

parisons of the experimental data on isochoric heat capacity are necessary to establish an accurate *PVT* equation of state because they contain direct information on second temperature derivatives of pressure $(\partial^2 P/\partial T^2)_\rho$. An accurate equation for $P(VT)$ should describe all thermodynamic (thermal, caloric, and acoustic) properties within their experimental uncertainties.

There is a very important theoretical aspect of near-critical and supercritical phenomena in ionic systems such as H_2O + NaCl. For these systems, the P_C–x and T_C–x critical lines show rapid changes in slope near the critical point of pure water. The derivatives dT_C/dx and dP_C/dx govern the thermodynamic (crossover) behavior of fluid mixtures near the critical point of one of the components. Thermodynamic properties of dilute aqueous salt solutions (ionic solutions) are difficult to determine accurately from experiment due to simultaneous occurrence of long-ranged density-composition fluctuations and long-ranged Coulomb interactions, which translates into a rapid change in the slope of the T_C–x and P_C–x critical lines. More precise experimental C_{Vx} data are needed to confirm the basic ideas of the modern crossover theory of the critical phenomena in ionic systems. Therefore, new experimental C_{Vx} data for H_2O + NaCl near the critical point of pure water may prove to be very important in the development of new theoretical equations of state that will more correctly predict the thermodynamic behavior of ionic solutions near the solvent critical point (pure water), and to improve existing models for aqueous electrolyte solutions.

Much attention has been focused on the H_2O + NaCl system because of its fundamental importance to the understanding of electrolyte behavior and its importance in many geological and industrial processes. The development of an equation of state depends on experimental data, from which empirical parameters can be obtained. NaCl is a good example of a 1:1 charge-type electrolyte. Theoretical modeling of the H_2O + NaCl system will serve as an example for other ionic systems of 1:1 charge-type electrolytes.

Water and alcohol are complicated highly associated, H-bonding liquids that are a challenge to study experimentally and theoretically. Therefore, their mixtures are far more complex liquid systems. If a small amount of alcohol is added to water, the water structure becomes enhanced in a way similar to when a non-polar solute is dissolved in water. Water + alcohol mixtures show many unusual properties, often quite different from those observed for the pure components of the mixture. Alcohol has highly polar molecules and interacts strongly with water in a hydrogen-bonded network. A knowledge of the *PVTx* properties of water + alcohol mixtures over wide temperature and pressure ranges is necessary in understanding the role of hydrogen bonding and other non-electrostatic effects in solvation. Methanol and ethanol and their aqueous solutions are of interest for various applications, such as transport and storage of hydrogen, natural refrigerants, and working fluids in new power cycles. The properties of aqueous methanol and ethanol mixtures as a function of temperature, pressure, and composition are scarce in the literature, especially in the near-critical and supercritical conditions.

A thorough knowledge of the thermodynamic and transport properties of hot aqueous salt solutions that transport heat and the vapors that drive turbines to produce electricity is essential. An understanding of the transport properties of water + salt solutions is needed in many industrial applications, such as design calculation, heat and

mass transfers, and fluid flow, developments and utilization of geothermal and ocean thermal energy, etc. Thermal conductivity is important in the prediction of heat- and mass-transfer coefficients under both laminar and turbulent regimes. Thermal conductivity data are also required for calculating flow, heat transfer, and mass transfer rates in various pieces of industrial equipment. For engineering utility, reliable methods for the estimation of the thermal conductivity of solutions over wide ranges of concentration, temperature, and pressure would be extremely valuable. To understand and control those processes that use electrolyte solutions, it is necessary to know their thermodynamic and transport properties. However, the lack of reliable data over wide temperature, pressure, and concentration ranges makes it necessary to estimate the missing properties by empirical and semi-empirical methods. Therefore, new experimental data on the thermal conductivity of aqueous systems at high temperatures and high pressures are needed to improve and extend the range of validity of avaliable estimation and correlation methods that are capable of reproducing the experimental thermal conductivity data and to develop more reliable prediction techniques of thermal conductivity behavior at high temperatures, high pressures, and high concentrations.

Aqueous solutions of electrolytes are also very important in physical chemistry and biophysical systems. For example, data on geothermal brines and sea water, which can be considered as mixtures of aqueous solutions of $NaCl$, KCl, $CaCl_2$, $MgCl_2$ etc., are needed for geothermal and ocean thermal energy utilization devices and for desalination of sea water. Aqueous LiBr solution is widely used in absorption refrigerators for air conditioning. However, measurements of the thermal conductivity of aqueous salt solutions have so far been limited to rather narrow ranges of temperature, pressure, and concentration with less than satisfactory accuracy.

Only limited experimental thermal conductivity data of water + salt solutions over a wide range of temperatures, pressures, and concentrations are available in the literature. Measurements of the thermal conductivity of aqueous salt solutions at high temperatures and high pressures are very scarce. Almost all of the previous thermal conductivity measurements for aqueous salt solutions were performed at atmospheric pressure and low temperatures (up to 373 K).

There is an ongoing demand for new reliable thermodynamic and transport properties data on the properties of aqueous solutions that cover a wide temperature and pressure range, especially in the near-critical and supercritical conditions.

For the study of the properties of aqueous systems, in most cases the properties of pure water are required. Therefore, we critically analyzed all of the available experimental, *PVT*, isochoric heat capacity, and thermal conductivity data sets for pure light and heavy water near the critical point and in the supercritical conditions. Selected and recommended data are presented in the Appendix for easy access.

Due to the lack of experimental data, all the necessary design and safety calculations have been upon estimated thermophysical property values. Very limited experimental data are available on aqueous salt solution and aqueous hydrocarbons at near-critical and supercritical conditions. Therefore, the designers and scientists who require information about thermodynamic and transport properties for high-temperature and high-pressure aqueous solutions must rely on the avaliable estimation techniques. The main goals of this book are to provide readers with a review of the avaliable ex-

perimental data sets on the thermodynamic and transport properties of aqueous systems at high temperatures and high pressures, give critical analyses of the estimation, correlation, and prediction methods, select more reliable data sets, and offer recommendations for scientific and applied use.

The main objective of the book is to provide new, reliable experimental thermodynamic (volumetric, *PVTx* and caloric, C_VTx) and transport (thermal conductivity) properties for aqueous systems, such as pure light and heavy water, their mixtures, aqueous hydrocarbons, aqueous salt, and aqueous alcohol solutions in near subcritical and near supercritical conditions, which can be used as prospective media in the emerging technologies of hazardous waste destruction, such as SCWO processes.