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Thermodynamic Data for Ligand Interaction with Protons and Metal Ions in Aqueous Solutions at High Temperatures

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Contents

I. Introduction

The chemistry of aqueous electrolyte solutions has been studied extensively within a narrow temperature range around 25 °C. Compilations of thermodynamic data are available[1-33] for a wide variety of aqueous reactions at ordinary temperatures (0–100 °C). Interest in aqueous solution chemistry at high-temperatures (above 100 °C, including the supercritical region) has increased steadily since the pioneering conductance studies by Noyes *et al.*[34-36] early in this century. Over the last three decades, there has been an increasing number of research articles published in the literature which contain either experimentally determined or estimated log K, ΔH, ΔS, and/or ΔCp values for ligand interaction with protons and metal ions in aqueous solutions for high temperatures and pressures. However, there are no reasonably complete compilations of thermodynamic data for high-temperature aqueous reactions in the literature. The following publications contain compilations of high-temperature thermodynamic data for a small number of reactions and/or descriptions of thermodynamic properties of high-temperature aqueous solutions.

(1) L. G. Sillén and A. E. Martell, *Stability Constants of Metal–Ion Complexes*, 1964.[4] This book and its supplement in 1971[8] compile log K, ΔH, and ΔS values for the interaction of inorganic and organic ligands with protons and metal ions. The majority of the data are limited to temperatures below 100 °C. High-temperature log K values are included for the ionization of H_2O, LiOH(aq), H_2SO_4(aq), HSO_4^-, DSO_4^-, KSO_4^-, $MgSO_4$(aq), UO_2SO_4(aq), $KHSO_4$(aq), H_2SO_3(aq), H_2S(aq), HS^-, H_2CO_3(aq), HCO_3^-, $PbCO_3$(aq), H_4SiO_4(aq), $H_3SiO_4^-$, HF(aq), HCl(aq), LiCl(aq), NaCl(aq), KCl(aq), RbCl(aq), CsCl(aq), $BaCl_2$(aq), $BaCl^+$, $ZnCl_2$(aq), HBr(aq), H_3PO_4(aq), and NH_4OH(aq). The literature is covered through 1968.

(2) H. C. Helgeson, "Thermodynamics of Complex Dissociation in Aqueous Solution at Elevated Temperatures", 1967.[37] Semiempirical equations are presented for the calculation of thermodynamic quantities for the dissociation of acids, bases, and metal complexes in aqueous solutions over the temperature range 0–370 °C. The approach used involves the separation of thermodynamic variables into hypothetical electrostatic and nonelectrostatic contributions. Thermodynamic quantities are compiled for the ionization of H_2O, HSO_4^-, KSO_4^-, H_2CO_3(aq), HCO_3^-, HCl(aq), NaCl(aq), KCl(aq), H_3PO_4(aq), NH_4OH(aq), CH_3CO_2H(aq), and HNO_3(aq) from 25 to 350 °C.

(3) H. C. Helgeson, "Thermodynamics of Hydrothermal Systems at Elevated Temperatures and Pressures", 1969.[38] This article contains estimated thermodynamic quantities for a wide variety of reactions involving aqueous species to high temperatures. The calculations involve entropy estimates, application of average heat capacities, and assumptions concerning the temperature dependence of thermodynamic variables, especially heat capacities, and the relative importance of electrostatic and nonelectrostatic interactions among the aqueous species in hydrothermal solutions. The results of such calculations (average heat capacities for aqueous species to 300 °C, entropies and enthalpies of formation for minerals and gases to 500 °C, and equilibrium constants for ionization, oxidation–reduction, and dissolution reactions to 300 °C) are presented in tables and diagrams.

(4) G. B. Naumov, B. N. Ryzhenko, and I. L. Khodakovskiy, *Handbook of Thermodynamic Data*, 1971 (Russian).[39] This handbook contains a compilation of thermodynamic data for a wide variety of chemical substances (solid compounds, gases, and aqueous species) and reactions. The thermodynamic quantities include Gibbs energy of formation, enthalpy

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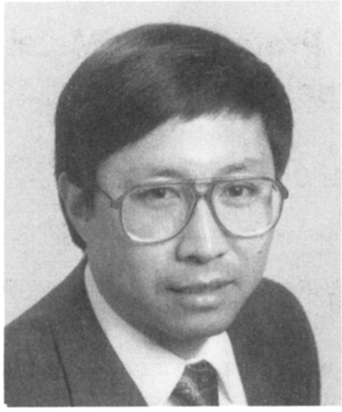

Xuemin Chen was born in Henan province, China. He received his B.S. degree in 1982 and his M.S. degree in 1985 with Professor Yun-Ti Chen in physical chemistry at Nankai University in Tianjin, China. After two years of teaching at Nankai University, he enrolled as a graduate student at Brigham Young University, where he obtained his Ph.D. degree in 1991 with Professor Reed M. Izatt in physical chemistry. He received the Loren C. and Maurine F. Bryner Award for outstanding graduate student and the Sigma Xi Award for the outstanding Ph.D. dissertation at BYU in 1991. Since 1992, he has been working as a postdoctoral research associate with Professors Reed M. Izatt and John L. Oscarson. He is a member of the American Chemical Society and Sigma Xi. His research interests include the design and construction of calorimeters, the use of calorimetry to determine thermodynamic quantities for reactions in solution over wide ranges of temperature and pressure, and the study of oxidation reactions in supercritical water.

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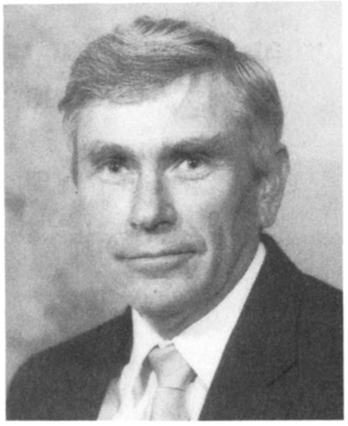

John L. Oscarson was born in Pleasant Grove, UT. He received his B.S. degree in chemical engineering at Brigham Young University in 1968. After three years as an officer in the U.S. Army, he attended the University of Michigan as a graduate student in the Department of Chemical Engineering. He received his masters degree in 1972 and his Ph.D. in 1985 with Dale E. Briggs. He has taught in the Department of Chemical Engineering at Brigham Young University since 1974. He received the Professor of the Year Award from his department in 1983. He has worked with Dr. Robert Mesmer's group at Oak Ridge National Laboratory and with the Nuclear Power Division at the Electric Power Research Institute. His research interests include the measurement and correlation of thermodynamic quantities associated with chemical reactions in high-temperature aqueous solutions, the effect of temperature on biologically important reactions, and the modeling of corrosion processes in high-temperature aqueous solutions.

of formation, entropy, heat capacity, partial molar volume, equilibrium constant, solubility, activity coefficent, and electrode potential. High-temperature thermodynamic data tabulated for aqueous species and/or reactions are the partial molar heat capacities, partial molar volumes, Gibbs energies of formation, Henry's law constants, solubility products, and dissociation constants.

(5) J. J. Christensen, L. D. Hansen, and R. M. Izatt, *Handbook of Proton Ionization Heats and Related Thermodynamic Quantities*, 1976.[13] This book is a compilation of enthalpy changes, ΔH, together with related thermodynamic quantities, $\log K$, ΔS, and ΔCp, where available for proton ionization reactions of approximately 600 acids, most of which are organic. Literature values through mid-1975 are tabulated under the headings of various acids. Also given in this book are methods and conditions of measurement and some brief remarks. The majority of the data are limited to temperatures at or around 25 °C. High-temperature data are included for the ionization of H_2O, H_2SO_4(aq), HNO_3(aq), H_3PO_4(aq), HCO_2H(aq), CH_3CO_2H(aq), oxalic acid, benzoic acid, glutamic acid, ammonium ion, and protonated amines (dipropylamine, triethylamine, aminocyclohexane, and 1-aminohexane).

(6) R. K. Freier, *Aqueous Solutions, Data for Inorganic and Organic Compounds*, 1976 and 1978.[40] This handbook (in two volumes) contains many thermodynamic data on aqueous solutions. Properties given are densities, solubilities, equilibrium constants, Gibbs energies of formation, electrochemical potentials, conductivities, pH values, species-composition diagrams, and vapor pressures. High-temperature $\log K$ values are included for a number of acid ionization and base protonation reactions. The most serious shortcoming of this handbook is the absence of specific references to the literature sources of the data. The bulk of the text is in German.

(7) H. E. Barner and R. V. Scheuerman, *Handbook of Thermochemical Data for Compounds and Aqueous Species*, 1978.[41] This book contains thermodynamic data (Gibbs energy of formation, enthalpy of formation, and entropy) for a wide variety of aqueous species from 25 to 300 °C. Most of the properties were calculated from data at 25 °C. The extrapolation of 25 °C data to high temperatures was done using the estimation procedures developed by Criss and Cobble[42–44] and Helgeson.[37,38]

(8) R. C. Murray, Jr. and J. W. Cobble, "Chemical Equilibria in Aqueous Systems at High Temperatures", 1980.[45] This review contains log K values up to 300 °C for the ionization of water and acids, the protonation of ammonia and amines, and the hydrolysis of metal ions. Methods of estimating thermodynamic quantities are described for chemical reactions in aqueous solutions to high temperatures. The materials in this review are included in a report to the Electric Power Research Institute in 1982.[46]

(9) T. M. Seward, "Metal Complex Formation in Aqueous Solutions at Elevated Temperatures and Pressures", 1981.[47] This article reviews the general topic of metal complexation in high-temperature aqueous solutions. Thermodynamic data are compiled for the formation of metal complexes at high temperatures. The majority of the data are log K values, most of which are presented graphically. The ligands include F^-, Cl^-, Br^-, I^-, OH^-, HS^-, S^{2-}, HCO_3^-, CO_3^{2-}, SO_4^{2-}, 1,10-phenanthroline, 5-nitro-1,10-phenanthroline, and 2,2′-bipyridyl. The effect of temperature on speciation and thermodynamic data is discussed.

(10) S. Arnorsson, S. Sigurdsson, and H. Svavarsson, "The Chemistry of Geothermal Waters in Iceland. I. Calculation of Aqueous Speciation from 0° to 370°C", 1982.[48] Thermodynamic data are incorporated into a computer program which has been developed to calculate the composition and aqueous speciation of geothermal reservoir waters to high-temperatures. Experimentally determined log K values to 350 °C are reviewed for about a dozen acid ionization and metal complexation reactions. Equations are given for the estimation of log K values as a function of temperature for about 50 aqueous reactions. The application of the computer program to geochemical systems is discussed.

(11) D. D. Perrin, *Ionization Constants of Inorganic Acids and Bases in Aqueous Solution*, 1982.[19] This book contains a compilation of equilibrium constants reported in the literature up to the end of 1980 for the ionization of inorganic acids, the protonation of inorganic bases, and the hydrolysis of metal ions in aqueous solution. About 250 acids, bases, and metal ions are included. The data are organized into a table, preceded by a brief introduction to the use of the table and a section on methods of measurement and calculation. There are approximately 1500 references listed alphabetically by author. The majority of the data are limited to ambient temperatures. High-temperature log K values are included for the ionization of H_2O, D_2O, HF(aq), HCl(aq), H_2S(aq), H_2SO_3(aq), H_2SO_4(aq), D_2SO_4(aq), HNO_3(aq), H_3PO_4(aq), H_2CO_3(aq), and H_4SiO_4(aq), the protonation of NH_3(aq), and the hydrolysis of Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Cr^{3+}, and Fe^{3+}.

(12) S. L. Phillips and L. F. Silvester, "A Data Base for Nuclear Waste Disposal for Temperatures up to 300°C", 1984.[49] A computerized data base is compiled of evaluated thermodynamic values for aqueous reactions associated with nuclear waste disposal. The data include hydrolysis and formation constants, solubilities of oxides and hydroxides, and Nernst potentials with emphasis on stability constants. Equations are given for the calculation of stability constants at various ionic strengths and to high-temperatures. Results are presented as tables for selected reactions involving uranium, amorphous silica, and actinides.

(13) R. S. Smith, C. J. Popp, and D. I. Norman, "The Dissociation of Oxy-Acids at Elevated Temperatures", 1986.[50] Experimental equilibrium constants are compiled for the ionization of H_2O, H_2CO_3(aq), HCO_3^-, HSO_4^-, H_3PO_4(aq), $H_2PO_4^-$, H_4SiO_4(aq), H_3BO_3(aq), and HNO_3(aq). The heat capacities of dissociation are evaluated at temperatures up to 300 °C using these ionization constants and a model similar to that developed by Helgeson.[37,38] The heat capacities calculated are independent of the entropies of dissociation and are the same for all acids of a given dissociation type (*i.e.*, 1st, 2nd, *etc.*). The heat capacities are used to calculate dissociation constants for the oxy-acids of Cr(III), N(III), S(IV), S(II), Se(IV), As(III), As(V), Te(VI), Cl(I), Cl(III), I(V), and C_1–C_3 aliphatic acids to 300 °C.

(14) B. N. Ryzhenko and O. V. Bryzgalin, "Dissociation of Acids under Hydrothermal Conditions", 1987.[51] This article presents equilibrium constants to 600 °C and 300 MPa for over 40 acid ionization reactions in aqueous solutions. These values are calculated using an electrostatic model for electrolytic dissociation.

(15) J. W. Cobble and S. W. Lin, "Chemistry of Steam Cycle Solutions: Properties", 1989.[52] This chapter contains high temperature log K values for chemical reactions important in the electric power industry. Most of the data were included in the 1980 review by Murray and Cobble.[45]

(16) R. E. Mesmer, D. A. Palmer, and J. M. Simonson, "Ion Association at High Temperatures and Pressures", 1991.[53] This chapter discusses ion association reactions in aqueous solutions at high temperatures and pressures. Included in this review are acid–base equilibria to 300 °C studied by electrochemical and electrical conductance measurements at the Oak Ridge National Laboratory since the late 1960s, correlation and extrapolation of thermodynamic quantities for the association reactions to form H_2O, NH_3(aq), HCl(aq), and NaCl(aq) to 800 °C, the evidence for association of electrolytes from calorimetric measurements, and metal complexation with ligands such as acetate, hydroxide, and chloride.

(17) R. J. Fernández-Prini, H. R. Corti, and M. L. Japas, "High-Temperature Aqueous Solutions: Thermodynamic Properties", 1992.[54] This book reviews theoretical treatments and experimental results for thermodynamic properties of water and aqueous solutions over wide ranges of temperature and pressure. The systems discussed include aqueous solutions of nonelectrolytes, electrolyte solutions, weak electrolytes, phase equilibria, chemical reactions, and dilute solutions near critical conditions. Calculation procedures based on statistical mechanical methods are described. These

procedures allow the calculation of thermodynamic properties of aqueous solutions using molecular parameters of the solutes or using adjustable coefficients.

In the present review, thermodynamic data (log K, ΔH, ΔS, and ΔCp) are compiled for the interaction of protons and metal ions with inorganic and organic ligands in high-temperature aqueous solutions. In preparing this review, we have made an extensive compilation of high temperature thermodynamic data reported in the literature through mid-1993. However, due to its size, only a small portion of the compiled data is published here. (At the end of the text portion of this review the reader will find information concerning options for acquiring the remaining data.) In addition to the data compilation, the nature of high-temperature aqueous solutions, the need for high-temperature thermodynamic data, and the experimental methods and estimation techniques used in obtaining thermodynamic data for high-temperature aqueous reactions are discussed in the present review.

II. Nature of High-Temperature Aqueous Solutions

Several models have been proposed[55–62] which give descriptions of both water and its electrolyte solutions under a wide variety of conditions. Excellent reviews are available[63–75] of various properties of water and aqueous solutions at high temperatures and pressures. Water is a highly complex solvent at ordinary temperatures. Raising the temperature of an aqueous electrolyte solution can be expected, and has been observed,[62–64] to have several significant effects on water structure and, hence, on the properties of the solution. These effects include a decrease in the dielectric constant of water, a decrease in the extent of hydrogen bonding, an increase in the volume of the hydration spheres around ionic species, an increase in the negative partial molar heat capacities of ionic species, and an increase in the degree of ion association. As temperature increases from 25 °C to the critical temperature (374 °C) of water, the ion product of water first increases then decreases above 250 °C.[70]

The dielectric constant is a key property that determines many aspects of the behavior of water as a solvent. The dielectric constant of water is a function of both temperature and pressure, decreasing as temperature increases and as pressure decreases. Along the vapor–liquid saturation line, the dielectric constant of liquid water changes from 78.5 at 25 °C to 13.1 at 350 °C.[76] As water is heated to supercritical conditions, there is a steady decrease in its dielectric constant. For example, the dielectric constant of water is only about 1.7 at 500 °C and 30 MPa.[77] Several authors have correlated the static dielectric constant of water over wide ranges of temperatures and pressures, including Bradley and Pitzer,[76] Uematsu and Franck,[77] Helgeson and Kirkham,[78] and Archer and Wang.[79] The formulation of Uematsu and Franck,[77] which is applicable from 0 to 550 °C and from 0 to 500 MPa, has been endorsed by the International Association for the Properties of Steam.[80] The formulation of Archer and Wang[79] not only gives a good representation of the available experimental dielectric constant, but also provides a good correlation of the first and second derivatives of the dielectric constant with respect to temperature and pressure.

The structure of water is determined largely by hydrogen bonding. A water molecule can participate in as many as four hydrogen bonds, one with each of the two protons and two more on the oxygen atom. The configuration with minimum energy occurs when all four bonds are tetrahedrally directed. Ice has a highly ordered lattice structure, with each oxygen atom being tetrahedrally coordinated by four other oxygen atoms. The structure that exists in the solid state persists into the liquid phase so that, at ambient temperatures, water still exhibits a high degree of structure. As temperature increases, the amount of hydrogen bonding in water decreases. An attempt has been made[81] to estimate the extent of hydrogen bonding in liquid water as a function of temperature up to 300 °C. The total number of hydrogen bonds at 300 °C was shown to be about 40% of that at 25 °C. Although the estimation may not be accurate, the trend illustrated by the estimation is certainly correct. The decrease in hydrogen bonding leads to a less ordered structure in water at higher temperatures.

The large permanent dipole of the water molecule and the responses of dielectric media to ionic species give rise to several important interactions, including electrostatic interactions of the ion–dipole, dipole–dipole, and dipole-induced dipole types, when an ionic compound is dissolved in water. The introduction of an ion into water causes at least local disturbances in the solvent structure as water molecules close to the ion respond to its charge by breaking away from the bulk liquid structure and orienting in the electric field of the ion. Of the many models which have been proposed for ions in water, the one that seems most appropriate and insightful over a wide range of temperature is the hydration model suggested by Frank and his co-workers.[60,61] This model describes the structure of water surrounding an ion in terms of three concentric regions: the primary hydration sphere, the secondary hydration sphere, and the bulk water. The primary hydration sphere is the innermost region which consists of water molecules tightly bound to the charged ion by electrostatic forces. The secondary hydration sphere is the intermediate region which consists of water molecules not in direct contact with the ion, but influenced by its charge. The outer region contains water having its normal liquid structure. This model has been supported by many experimental studies of aqueous electrolyte solutions.

Hydration spheres also form around neutral, but polar molecules. However, the number of water molecules in the hydration spheres around a neutral molecule is much smaller than that around an ion. As pointed out by Cobble,[63] the number of water molecules in the primary hydration sphere does not change much with temperature. However, the number of water molecules in the secondary hydration sphere is markedly affected by temperature. As the temperature of an electrolyte solution is increased, the volume of the secondary hydration sphere increases. As a result, the number of water molecules involved in the secondary hydration sphere increases in an accelerating fashion with temperature. The change in the volume of the secondary hydration sphere around an ion causes the ion to exert electrostatic forces on greater numbers of water molecules at higher temperatures.

Solute–solvent interactions have a great effect on chemical reactions which occur in aqueous solutions. When ions associate, their hydration spheres will overlap, and some water molecules will be released from the hydration spheres to the bulk liquid. In other words, the number of water molecules in the hydration spheres around the association product will be less than the sum of the numbers of water molecules in the hydration spheres around the constituent ions. Thus, thermodynamic quantities (log K, ΔH, ΔS, and ΔCp) for chemical reactions in aqueous solutions include the contribution due to the change in hydration. The entropy of the water in the primary hydration sphere is smaller than that of the bulk water because the dipoles are highly oriented and not free to rotate. The entropy of the water in the secondary hydration sphere is larger than that of the water in the primary hydration sphere, but it may be larger or smaller than that of the bulk water at lower temperatures, depending on the charge and size of the ion. For ion association reactions at ambient temperatures, the entropy change (ΔS) may be positive or negative, but the enthalpy change (ΔH) is most likely to be negative. The standard state Gibbs energy change (ΔG) for these reactions can be positive or negative. As a result, the association product may be thermodynamically less or more stable than the constituent ions. At low temperatures, most ion association reactions are either primarily or partially enthalpy driven.[24]

At higher temperatures, the structure of water is less ordered. The secondary hydration spheres of the ions are more structurally ordered than the thermally disrupted bulk water. As ions associate in an electrolyte solution, the number of water molecules bound in hydration spheres decreases, *i.e.*, dehydration occurs. The release of water molecules from the overlapping spheres makes the entropy change positive. Enthalpy changes for high-temperature ion association reactions are most likely to be positive, especially above 250 °C, since a considerable amount of energy is required to restore the released water molecules to the rotational, vibrational, and translational freedom which molecules have in the bulk water. Standard state Gibbs energy changes for ion association reactions become more negative as temperature increases, resulting in increased stability of the associated species, since the favorable entropy effect exceeds the unfavorable enthalpy effect at high temperatures. The magnitude of the entropy effect is such that ion association reactions in high-temperature aqueous solutions can be viewed as entropy-driven processes. As the temperature and pressure of the solution is brought close to the critical temperature and pressure of water, these effects increase dramatically.

The ionization of water is among the more important reactions in aqueous solution. An accurate knowledge of thermodynamic data for the ionization of water is required for the study of any aqueous reaction which is affected by hydrogen ion and/or hydroxide ion, *e.g.*, acid ionization, base protonation, and metal–ligand complexation. The ion product of water, K_w, has been determined accurately near 25 °C and 0.1 MPa. Numerous studies on the ionization of water at elevated temperatures and pressures have been made. The most accurate determination of K_w at elevated temperatures appears to be the potentiometric study of Sweeton *et al.*[82] up to 300 °C and 7.5 MPa. Marshall and Franck[70] have formulated an equation for calculating log K_w as a function of temperature and the density of water from 0 to 1000 °C and from 0.1 to 1000 MPa. The agreement between the log K_w values of Sweeton *et al.*[82] and those calculated from the Marshall–Franck equation[70] is excellent up to 250 °C, but as temperature increases, log K_w values calculated by the formulation decrease more rapidly than the potentiometric results. The log K_w values obtained by different investigators begin to show a discrepancy at 200 °C.[83] There are increasing uncertainties about log K_w as the critical temperature is approached. Although the formulation of Marshall and Franck has been endorsed by the International Association for the Properties of Steam,[84] it may not be accurate in the vicinity of the critical point. As pointed out by Lindsay,[72] the log K_w value at the critical temperature is not at all certain. Pitzer[85] has calculated K_w from mass spectrometric data on gas-phase hydration of the ions H^+ and OH^-, with results that are many powers of 10 lower than those calculated from the Marshall–Franck equation at very low densities. His calculation indicates that the Marshall–Franck equation may not give accurate K_w values at high temperatures and low pressures.

The log K_w values in the supercritical region used by Marshall and Franck[70] in deriving their equation were mainly from the conductance study of Quist,[86] who measured the electrical conductances of aqueous NH_4Br solutions to 800 °C and 400 MPa. However, as pointed out by Mesmer *et al.*,[87] the accuracy of these log K_w values was limited by the need to use equilibrium constants for the ionization of $NH_4Br(aq)$, $NH_4OH(aq)$, and $HBr(aq)$ in calculating K_w from the hydrolysis of NH_4Br. Ionization constants for $NH_4Br(aq)$ were not available and had to be estimated. Several approximations and assumptions were used by Quist[86] to calculate log K_w values. For example, Quist[86] assumed that the conductance of the hypothetically "unhydrolyzed" NH_4Br solution was equal to that of a KBr solution and the equilibrium constant for the ionization of $NH_4Br(aq)$ was the same as that for the ionization of $NaBr(aq)$. Quist[86] assigned an uncertainty of about 0.3–0.5 log unit to his log K_w values. Marshall and Franck[70] estimated the accuracy of their equation to be no better than ±0.03 to 0.1 log unit in log K_w at temperatures above 250 °C, with a higher estimate of ±0.05 to 0.3 log unit stated as the upper limit.

While log K values for the ionization of water have been studied extensively, calorimetrically determined ΔH values are available only at temperatures below 145 °C[88] and from 250 to 350 °C.[89,90] In their potentiometric determination of log K values, Sweeton *et al.*[82] also calculated ΔH, ΔS, and ΔCp values for the ionization of water from 0 to 300 °C along the vapor–liquid saturation line. Gates *et al.*[91] have calculated the heat capacity change for the ionization of water at the critical pressure of water (22.1 MPa) by differentiating the Marshall–Franck equation and showed that the ΔCp curve approaches minus infinity at the critical temperature of water (374 °C) as temperature increases. Gates *et al.*[91] also predicted very large and positive partial molar heat capacities for ionic species above the critical temperature of water. Although the Marshall–Franck equation they used may not be quantitatively reliable in the vicinity of the critical point, there are persuasive theoretical reasons to believe the conclusions of Gates *et al.*[91] The calculation of Pitzer[85] shows that ΔCp for the ionization of water at 427 °C and 22.1 MPa is a very large positive number and decreases with further increase of temperature.

III. Need for High-Temperature Thermodynamic Data

Chemical reactions in aqueous solutions at high temperatures are present in many industrial,[92-97] biochemical,[98-113] and geochemical[92,114-120] environments. There is a need to measure thermodynamic quantities (log K, ΔH, ΔS, and ΔCp) for these reactions. These data are important in understanding high-temperature aqueous chemistry. log K values define the extent of reactions, while ΔH, ΔS, and ΔCp values provide information about reaction-driving forces. Thermodynamic data for chemical reactions in high-temperature aqueous solutions are important in several scientific and industrial applications including geochemistry, biochemistry, oceanography, hydrometallurgy, electric power plant operation, water desalination, supercritical water oxidation, waste disposal, gas processing and production, and all industrial processes that are concerned with the use of high-temperature water and aqueous solutions.

A. Understanding High-Temperature Aqueous Chemistry

The importance of thermodynamic quantities in increasing our understanding of chemical reactions at ordinary temperatures is well known.[9,12,20,21,23,25-27,29-33] Without these quantities, knowledge of the reactions remains qualitative and accurate predictions of chemical behavior are not possible. The need for high-temperature thermodynamic data becomes apparent when one recognizes that the chemistry of aqueous electrolyte solutions at high temperatures differs considerably from that at 25 °C. The extent of chemical reactions in aqueous solutions changes markedly with temperature. At 25 °C, many ion association reactions do not occur to a measurable extent. Therefore, many ionic compounds can be considered to be strong electrolytes. As temperature increases, ion association becomes more significant. At 300 °C, only a few salts can be treated as strong electrolytes. As temperature approaches the critical temperature of water, all salts become weak electrolytes. The rapid changes in water properties with temperature result in large changes in thermodynamic quantities. Models and theories based on 25 °C data are often inaccurate to an unknown degree when applied to reactions at high temperatures. High-temperature thermodynamic data provide a quantitative foundation for the development of better models and theories for the chemistry of high-temperature aqueous solutions. The availability of these data also makes possible the testing of various estimation and extrapolation techniques.

B. Application to Biochemical Systems

Organisms capable of living at high temperatures, called thermophiles, have fascinated biologists and chemists for a long time. Over the past decades, a variety of living organisms have been found in many high-temperature environments which are widely distributed on the Earth.[98-113] The upper temperature limit for life in liquid water has not been identified, but it is likely to be somewhere between 110 and 200 °C.[103] Many amino acids are destroyed at temperatures above 250 °C.[121,122] The report of thermophilic bacteria growing at 250 °C[123] has been challenged.[124] The existence of living organisms at high temperatures poses interesting questions concerning how these organisms function in these environments and how the chemical behavior of biomolecules changes with temperature. The functioning of living organisms depends on their natural polymer components, such as nucleic acids and proteins, and reactive biomolecules, such as purines, pyrimidines, sugars, nucleosides, nucleotides, amino acids, and polypeptides. A knowledge of thermodynamic quantities for chemical reactions involving biomolecules in high-temperature aqueous solutions would be useful in the development and testing of hypotheses concerning how organisms function at high temperatures. Hypotheses based on firm data could lead to the identification of biochemical and physiological mechanisms by which organisms have adapted to high temperatures.

Thermodynamic quantities are available[6,9,11,25,30,31,33] in a small temperature range around 25 °C for chemical reactions involving some of the biomolecules mentioned above. However, experimental thermodynamic data above 100 °C for biochemical reactions are limited to the interaction of protons with a few amino acids.[125,126] In 1937, Wilson and Cannon[125] reported thermodynamic data for the protonation of glutamic acid at 78, 100, and 118 °C. Izatt *et al.*[126] have reported log K, ΔH, and ΔS values for the protonation of serveral amino acids up to 125 °C. The measurement of thermodynamic quantities for high-temperature reactions of biochemical significance represents an emerging field in chemistry. Investigation of high-temperature biochemical reactions has the potential to greatly expand the scope and impact of biotechnology. For instance, the study of the functionality of thermophilic organisms may lead to the discovery of catalytic enzymes that work at high-temperatures.[102,105]

Proteins play crucial roles in virtually all biological processes. Amino acids are the basic structural units of proteins. All proteins in all living species, from bacteria to humans, are constructed from the same set of primary amino acids. In conventional organisms, proteins are inactivated irreversibly by heat, but these components are stable in thermophiles. The basis for the high-temperature resistance of thermophiles is still unknown.

Over the last two decades, investigation of amino acid racemization in various biochemical systems has been an area of active research.[127-137] Amino acid racemization is markedly affected by temperature. The racemization half-lives of serine have been reported to be about 400 years at 25 °C and 4 days at 100 °C.[127] The rates of racemization are also influenced by pH and ionic strength. Since amino acid racemization is very slow at lower temperatures, most racemization studies are done at elevated temperatures. In the study of amino acid racemization, protonation constants are required to calculate the distribution of ionic species as a function of pH. It was found that the principal ionic species undergoing racemization is the one in which both the amino and carboxyl groups are protonated.[127] The racemization of alanine, phenylalanine, leucine, proline, and valine in aqueous solutions has been studied at 142 °C.[128] Since experimentally determined log K values are not available at elevated temperatures, the speciation in high-temperature amino acid solutions was estimated by extrapolation from the data at lower temperatures. This makes the racemization results less reliable.

There has been an increasing use of amino acid racemization in dating fossil materials as well as for determining the ages of living mammals.[127,128,138-141] The biochemical implication of racemization in living organisms has only begun to be investigated. Racemization in proteins may induce structural changes which in turn affect the functionality of the proteins.

C. Application to Industrial Processes

Preventing or minimizing corrosion in nuclear steam generators could lead to great savings for the electric power industry. Much effort has been made to identify the chemical species and reactions that are responsible for the corrosion. This effort has resulted in a much improved understanding of the corrosion processes. A considerable body of thermodynamic data has been accumulated for chemical reactions which occur at steam generator operating temperatures (250–330 °C). The availability of thermodynamic quantities for high-temperature chemical reactions would allow a much better control of the steam generator operation.

The most serious corrosion problems in the nuclear electric power industry occur in the steam power cycle. Water is used in the steam power cycle both as a thermodynamic working fluid and as a heat transfer and transport agent.[142,143] The majority of nuclear power plants use pressurized water reactors. In a pressurized water reactor system, high-temperature (300–330 °C), high-pressure (15–16 MPa) water is used to transport the heat of nuclear reactions from the reactor to a steam generator, where the energy of the pressurized water is transferred, through a heat exchanger, to water at lower pressures (5–7 MPa) to create superheated steam. The steam then passes through a steam turbine which drives a power generator to make electricity. The pressurized water from the reactor is contained within tubes which pass through a steam generator. The water to be converted to steam circulates within the steam generator, outside the tubes which contain the nuclear-heated water. Feedwater entering a steam generator is of high purity but becomes contaminated by leakages of small amounts of cooling water from condensers in the circulation system. Cooling waters are normally drawn from large natural water bodies such as rivers and therefore contain significant amounts of dissolved electrolytes. The concentration of contaminants in feedwater may be very low (ppb or even ppt range), but, with a large amount of feedwater entering the steam generator, transport and accumulation of contaminants can be significant.

Steam generators in nuclear power plants are usually constructed of iron and nickel alloys. The tubes inside the steam generator are made of nickel alloys. The support plates are made of carbon steel or stainless steel. The nickel alloy tubes pass through holes in a number of support plates, creating numerous small crevices between the tubes and the support plates within the steam generator. The locally higher-than-saturation temperature in the crevices created by poor heat transfer results in local boil-off of the water. The electrolytes become more concentrated, causing the pH of the solution to change. As a result, the solutions in the crevices become corrosive and attack the adjacent construction materials, causing corrosion which can perforate the nickel alloy tubes. When sufficient numbers of tubes have experienced severe corrosion, the steam generator has to be shut down for repairs or be replaced.

Corrosion problems cost the electric power industry billions of dollars each year. Finding methods to solve these problems is difficult because details of the chemistry involved in the corrosion processes are not fully understood. The concentrations and thermodynamic properties of the impurities change throughout the steam power cycle with temperature, pressure, phase of the solvent (water or steam), and reactions of the impurities with each other and with the construction materials. A necessary step toward obtaining better corrosion control is improved understanding of the chemical behavior of the substances present in the steam power cycle over the range of temperatures and pressures met in steam generators. An important part of this understanding involves a knowledge of chemical speciation and thermodynamic data for high-temperature chemical reactions.

Workers in the power industry have developed computer programs[144-147] to predict the composition of solutions that will be produced in steam generators as the processes described above occur. However, for such programs to predict the final compositions, the input data for the programs must include the equilibrium constants at the temperatures of interest for all the reactions which occur in the system. Many efforts have been made to estimate these equilibrium constants from available low-temperature data. However, relatively few systems have been studied *experimentally* at the generator operating temperatures. For the computer programs to be used effectively, it is necessary to determine experimentally log K values for chemical reactions and phase equilibria involving aqueous species at high temperatures. The availability of such quantities would allow reliable calculation of solution composition and species distribution among different phases. The determination of log K values as a function of temperature would allow the development of more reliable extrapolation techniques by which high-temperature data could be estimated from low-temperature data. Furthermore, the determination of such quantities could lead to the testing of current corrosion models and the development of new or modified models.

The above description represents the application of high-temperature thermodynamic data to only one of many industrial processes. Similar data are required for other processes involving the use of high-temperature aqueous systems. For example, high-temperature ΔH values are needed in order to design processes intended to be operated at high temperatures where heat transfer must be known. These processes include gas processing,[148-150] coal conversion,[151] waste treatment,[97,152] hydrometallurgy,[153] and oxidation processes in supercritical water.[154,155]

D. Application to Geochemical Systems

The application of thermodynamic data, especially log K values, to high temperature geochemical systems is evidenced by the large number of publications on the subject of high temperature aqueous reaction thermodynamics in geochemistry journals, *e.g.*, *Geochimica et Cosmochimica Acta*, *American Journal of Science*, and *Geochemistry International*, which is the English translation of the Russian journal *Geokhimiya*. Most of the early work on the determination of thermodynamic data for high-temperature aqueous reactions was concentrated on systems which are of primary interest in geochemistry.[114,115]

The interaction of water with minerals in hydrothermal systems can be formulated in terms of dissolution–precipitation processes that involve acid–base, oxidation–reduction, and complexation reactions. These processes result in a wide variety of aqueous species in hydrothermal solutions. The speciation and concentrations in solution must be known before metal transport and mineral precipitation can be understood, particularly under high-temperature and high-pressure conditions.

IV. Experimental Methods

A wide range of experimental techniques has been developed to study reactions in aqueous solutions at elevated temperatures and pressures. In general, five experimental methods have been used predominantly for the measurement of thermodynamic quantities for chemical reactions in high-temperature aqueous solutions. These methods are conductivity measurements, solubility measurements, spectroscopy, potentiometry, and calorimetry. High-temperature conductivity measurements can be traced back to the first decade of this century and have been widely used since the 1950s. Solubility measurements are mostly used under hydrothermal conditions by geochemists in determining the solubilities of minerals and, in some cases, the equilibrium constants for aqueous reactions. Spectroscopic techniques have been used at high temperatures in the study of reactions in a number of aqueous systems. High-temperature potentiometric cells have been constructed in several laboratories and successfully used to measure acidities of high temperature aqueous solutions and thus determine log K values for proton interactions with a variety of inorganic and organic ligands. Over the last several years, flow calorimetry has been extended to high temperatures to allow the determination of ΔH values and other thermodynamic quantities for chemical reactions in high-temperature aqueous solutions. Each of these methods has its own advantages and limitations.

A. Conductivity Measurements

One of the most convenient methods for determining ionization constants of an electrolyte is the measurement of its electrical conductance. By measuring the conductivities of a series of dilute solutions of an electrolyte and applying the theories of Onsager, Fuoss, and Shedlovsky,[156-161] not only can the ionization constants be obtained but also the limiting conductance values. High-temperature conductivity studies started with the exploratory work of Noyes *et al.*[34-36] early in this century. This group calculated the ionization constants of water to 306 °C, at saturation pressure of water, from electrical conductivity measurements on ammonium acetate solutions. Extension of these studies to higher temperatures and pressures was retarded by the difficulty in constructing the apparatus and the lack of materials with high strength and corrosion resistance.

The real breakthrough with respect to quantitative conductivity measurements of aqueous electrolyte solutions to high temperatures and pressures came in the 1950s when Fogo *et al.*[162,163] and Franck[164-166] independently constructed high-temperature conductance cells and determined the ionization constants of NaCl(aq), HCl(aq), KCl(aq), and KOH(aq) under supercritical water conditions. Since the early 1960s, Marshall, Quist, and others[86,167-183] at the Oak Ridge National Laboratory have made extensive conductivity measurements for a wide variety of aqueous electrolyte solutions, mostly at temperatures from 400 to 800 °C and pressures up to 400 MPa. The conductance apparatus and procedures for data analysis were described by Marshall and Frantz.[184]

An important observation common to all the systems studied is the strong tendency for ion association at high temperatures, especially in the supercritical region, even though the electrolytes may be completely dissociated in water at ordinary temperatures. In most conductivity studies, equilibrium constants are represented with a molar standard state. At the present time, it is not possible to assess properly the uncertainties in the log K values derived from conductivity measurements in supercritical water. In general, an uncertainty of about 0.2–0.5 log unit may be ascribed to these log K values. The major advantage of the conductivity measurements in determining ionization constants is that the method is presently the only one which has been successfully used to temperatures as high as 1000 °C. Conductivity measurements have also been used in the determination of log K values for the ionization of water by Fisher and Barnes[185] and by Bignold *et al.*[186] and the ionization of acids by Read,[187-190] Ellis,[191,192] and Ryzhenko[193-196] at temperatures up to 350 °C. The accuracy of the data below 350 °C is much better than that above 400 °C. Interested readers are referred to the review of Marshall and Frantz[184] for more information on this experimental technique and its use in determining high-temperature thermodynamic data by various investigators.

B. Solubility Measurements

Most of the information on metal ion hydrolysis and complexation at high temperatures is derived from solubility measurements, which are particularly applicable to systems where slightly soluble salts are present.[197-225] The extraction of thermodynamic information involves fitting experimental solubility data using solubility products, activity coefficients, and stability or hydrolysis constants over the whole range of conditions. Solubility studies are often tedious and inaccurate because of problems in sampling, analysis of low concentration solutions at high temperatures, slow equilibration kinetics, characterization of solid phases, existence of competitive reactions, and the control of experimental conditions. If the sampled solutions are analyzed at ambient temperatures, total concentrations can be obtained, but the speciation may not represent that actually present at high temperatures. For organic species which decompose at high temperatures, even though the rate of decomposition may be slow, the long time period required for equilibration makes this technique virtually inapplicable. The use of solubility measurements in determining thermodynamic quantities to high temperatures was illustrated by Seward[197] for the complexation of Ag^+ with Cl^-, by Marshall and Slusher[218,219] for the ionization of $HNO_3(aq)$, and by Lietzke *et al.*[225] for the ionization of HSO_4^-.

C. Spectroscopy

Vibrational (Raman) spectroscopy and electronic (UV–visible) spectroscopy have been used predominantly in the determination of concentrations of specific ionic or molecular species and equilibrium constants for reactions in high-temperature aqueous solutions. Various numerical methods have been developed to derive equilibrium constants from spectroscopic data.[226–233] General reviews on the construction and use of high-pressure and high-temperature spectroscopic cells have been given by Melveger *et al.*,[234] Ferraro and Basile,[235] Irish and Brooker,[230] Whalley,[236] and Buback and co-workers.[237,238]

The use of Raman spectroscopy in the study of ionic equilibria in aqueous solutions from 0 to 50 °C has been discussed by Young *et al.*[239] in 1959. Over the last three decades, Raman spectroscopy has been developed into a powerful tool for the identification of species and determination of equilibrium constants for reactions in high temperature aqueous solutions. Several high temperature Raman spectroscopic cells have been constructed[230,237,238,240–243] and an increasing number of systems have been studied up to 500 °C and 500 MPa.[244–258] Irish and co-workers[244–251] have made a series of investigations of reactions in high-temperature aqueous solutions by Raman spectroscopy. Raman spectroscopic studies are restricted to relatively high solute concentrations and to species with Raman-active bond stretching or vibrational modes. Since reliable estimations of activity coefficients are difficult at the high solute concentrations required by Raman spectroscopy, equilibrium constants are often expressed as concentration quotients. Raman spectroscopy is particularly useful in obtaining definite information about speciation. However, thermodynamic quantities determined by this method often contain relatively large errors.

Various high-temperature UV–visible spectrophotometric cells have been constructed since the late 1950s.[259–267] Several studies have been made by Lüdemann *et al.*[262,263,268,269] and Susak *et al.*[266,267,270] on the measurements of electronic spectra of transition metal complexes in high-temperature aqueous solutions. Some of these studies provided information on the molecular symmetry of the complexes, but no attempt was made to calculate stability constants. Ellis and Giggenbach[271] and Alexander *et al.*[265,272,273] are among the pioneers in the application of UV–visible spectrophotometry in determining thermodynamic data for reactions in aqueous solutions at elevated temperatures. Ellis and Giggenbach[271] reported the first ionization constant of H_2S to 276 °C. Alexander *et al.*[272,273] determined log K values for the interaction of some organic ligands with protons to 250 °C and with Fe(II) to 160 °C. Seward and Heinrich[274,275] reported thermodynamic quantities determined by UV spectrophotometry for the complexation of chloride ion with Pb(II) to 300 °C and with Fe(II) to 200 °C. The log K values for the formation of $PbCl^+$ and $PbCl_2(aq)$ were determined up to 200 °C by Yuchenko *et al.*[276] using the UV spectrophotometric data of Aksenova and Kolonin.[277]

Infrared spectra of concentrated aqueous LiCl, $NaClO_4$, and NaOH solutions have been measured up to 350 °C and 280 MPa.[278–280] Although some structural information was obtained, no thermodynamic data could be extracted from these IR spectroscopic studies.

Resonance techniques have also been developed for the study of high-temperature aqueous solutons. Wheat and Carpenter[281] reported association constants for $MnCl^+$ and $MnSO_4(aq)$ formation in aqueous solution determined by electron spin resonance (ESR) from 25 to 170 °C. The ESR method was described by Carpenter in 1983.[282] A high-temperature probe for nuclear magnetic resonance (NMR) experiments was constructed by DeFries and Jonas[283] for the study of transport and relaxation properties of water to 700 °C and 200 MPa.

D. Potentiometry

Potentiometry is one of the most convenient and useful techniques employed in the determination of equilibrium constants for proton–ligand interactions in aqueous solutions. At ordinary temperatures, log K values for various reactions have been determined using potentiometric cells with conventional electrodes. However, most of the electrodes which work at low temperatures fail to work at high temperatures. For example, the calomel electrode can only be used at temperatures below 70 °C due to the increased disproportionation of Hg_2Cl_2 at higher temperatures.[284] The use of the glass electrode is limited to temperatures below 150 °C because the degradation of glass is enormously accelerated at higher temperatures by aqueous solutions of extreme pH, particularly in the basic region.[284,285] Hydrogen electrode concentration cells have provided the best means for accurate measurements of acidity or log K at high temperatures. Their usefulness has been demonstrated for many systems at temperatures up to 300 °C.

The use of hydrogen electrode concentration cells for acidity measurements at high temperatures was pioneered principally at the Oak Ridge National Laboratory since the early 1970s.[286] These cells have been used extensively to obtain precise log K values for a large number of aqueous reactions, including the ionization of water[82,286–289] and heavy water,[290] the ionization of acids,[290–298] the protonation of bases,[299–302] and the hydrolysis and complexation of metal ions.[303–309] Other thermodynamic quantities (ΔH, ΔS, ΔCp, and ΔV) were also calculated from the dependence of log

K on temperature and pressure. A recent paper by Mesmer *et al.*[87] described this technique and summarized results for reactions studied prior to 1987. In most of these studies, NaCl was used as a supporting electrolyte for maintaining constant ionic strength and minimizing liquid junction potentials. The ionic strength is varied systematically to study salt effects and to permit calculation of log K values applicable at infinite dilution. Such cells have been operated in both titration[286,310] and flow[310,311] modes. The liquid junction potentials are approximated by the Henderson equation using limiting electrical conductances for all ions present. The liquid junction potential was often kept small (less than 1 mV) by the use of supporting electrolytes. Hydrogen electrode concentration cells have also been used by Matsushima and Okuwaki,[312] Macdonald *et al.*,[313-315] Becker and Bilal,[316-318] and Le Peintre[319] for pH or log K measurements at high temperatures.

The major advantage of potentiometry is that the acidity of the solution can be evaluated directly from the experimental data. This advantage makes this method particularly applicable to the study of acid-base equilibria and of complexation of metal ions with ligands. However, the use of a supporting electrolyte such as NaCl and the ignorance of possible associations of the constituent ions of the electrolyte with each other and with other ions present in the high-temperature solution may cause significant inaccuracy in the derived log K values, although the precision of the log K values may be very good (often about 0.01 log units). For systems where speciation is complicated by multiple equilibria, the derived log K values are dependent on the selection of reactions to be considered in data analysis. Since the reactions are studied in a hydrogen atmosphere, this method is not applicable to systems where species are present which are subject to reduction by hydrogen.

In addition to the hydrogen electrodes, three types of new pH sensors have been developed recently for operation in high-temperature aqueous environments,[320,321] including zirconia (ZrO_2) and yttria-doped zirconia ($ZrO_2-Y_2O_3$) electrodes, palladium hydride electrodes, and iridium oxide electrodes. Extensive investigations on the fabrication, calibration, testing, and use of high-temperature pH sensors and reference electrodes have been made by Macdonald,[322-332] Dobson,[333-335] Niedrach,[336-341] Danielson,[342-345] Nagy,[346,347] Lauks,[348-351] and their co-workers. While most of the new pH sensors are limited to use at temperatures below 300 °C, some of them are capable of operating in supercritical aqueous systems.[332] Although some high-temperature pH sensors have been used in a variety of laboratory and field applications, these electrodes are still under active investigation and many problems remain to be solved before they can be used routinely for pH measurements.

E. Calorimetry

Various types of calorimeters have been used at ambient temperature for the determination of thermodynamic quantities for reactions in solution. On the basis of how the reactions are initiated, solution calorimeters can be divided into batch, titration, and flow types. On the basis of how the heat changes are detected, solution calorimeters can be divided into adiabatic, heat conduction, isoperibol, and isothermal types. Excellent reviews are available[352-360] on the use of solution calorimeters in determining thermodynamic quantities under various conditions.

Many of the early solution calorimeters were designed to operate near ambient pressure and close to room temperature. There were no calorimetric data above 100 °C on aqueous systems until 1951 when Eigen and Wicke[361] made heat capacity measurements of aqueous solutions of NaCl, LiBr, and $MgCl_2$ up to 140 °C. In 1969, Gardner, Mitchell, and Cobble[362] described an enthalpy of solution calorimeter and measured enthalpies of solution of NaCl in water from 100 to 200 °C. From these data and earlier data below 100 °C, they calculated the standard partial molar heat capacities and entropies of aqueous NaCl from 0 to 200 °C. In 1973, Likke and Bromley[363] measured heat capacities from 80 to 200 °C for aqueous solutions of NaCl, KCl, $MgCl_2$, $MgSO_4$, and Na_2SO_4 using a bomb calorimeter described by Bromley and co-workers.[364] Perhaps the first measurement of enthalpies of reaction in aqueous solution above 100 °C was made by Olofsson and Olofsson[88] in 1973 when they determined the enthalpy of ionization of water up to 145 °C.

An important advance in high-temperature solution calorimetry came in 1980 with the use of flow calorimeters.[365] Two types of flow calorimeters have been developed for operation at high temperatures and pressures. One type is the heat capacity flow calorimeter[365-369] which is used to measure the heat capacities of fluids. The other type is the enthalpy of mixing flow calorimeter[365,370-377] which is used to measure the heats evolved or absorbed when two streams of fluid are mixed. The second type is also known as the enthalpy of reaction flow calorimeter if reaction(s) take(s) place in the calorimeter upon the mixing of fluids. If one of the streams contains only the solvent and the other contains a solution, the measured enthalpy of mixing is often called the enthalpy of dilution.

For the study of aqueous solutions or reactions at high temperatures, flow calorimetry has proven to be a useful technique. There are important advantages of using flow calorimeters for operations at high temperatures.[365-367] First, flow calorimetry is well suited to measurements involving fluid systems (liquid, gas, or supercritical) at high temperatures and pressures. Second, when only measurements of liquid systems are desired, flow calorimetry allows for easy elimination of the vapor phase, hence no correction for vaporization is needed. Third, because of the small diameter tubing used, relatively thin-walled tubing is strong enough to contain the solution at high pressures and, as a result, the calorimeter can be constructed with fast thermal response and high sensitivity. Fourth, experiments can be run consecutively without cooling and reloading the calorimeter. Finally, calorimetrically determined Cp and ΔH values are more reliable than those derived from other measurements.

1. Heat Capacity Measurements

Heat capacity data for aqueous solutions at high temperatures are useful for the calculation of various thermodynamic quantities to high temperatures for aqueous species and chemical equilibria involving aqueous species. At present the best method for making such measurements is by means of flow calorimetry. Use of flow calorimeters for the measurement of heat capacities of aqueous solutions at high temperatures and pressures was pioneered by Wood and Smith-Magowan[365,366] and by Rogers and Pitzer[367] in the early 1980s. More recently, Conti *et al.*[368] described a flow calorimeter which can be used for both heat capacity and enthalpy of mixing measurements at high temperatures. These calorimeters are based on the design principles outlined by Picker *et al.*[378] in 1971. During the past dozen years, heat capacity measurements have been made by flow calorimetry for high-temperature aqueous solutions of a number of electrolytes, including LiCl,[379] NaCl,[365,366,368,380–382] KCl,[383,384] $MgCl_2$,[385] $CaCl_2$,[386] $FeCl_2$,[387] $NiCl_2$,[388] NaBr,[389] Na_2SO_4,[367,368] $MgSO_4$,[390] NaOH,[368,391] and $NaAl(OH)_4$.[392] This technique has been extended to 450 °C and 40 MPa.[382,393] Results obtained for most electrolytes have shown that a very dramatic change occurs in the apparent molar heat capacity of the solute as the temperature approaches the critical temperature of water (374 °C). At a pressure of 32.2 MPa, which is above the critical pressure of water (22.1 MPa), the apparent molar heat capacity of 0.015 m NaCl becomes very large and negative as temperature increases toward the critical point and very large and positive as temperature decreases toward the critical point.[382,394] It was predicted[91,395,396] that the infinite dilution apparent molar heat capacity would approach infinity at the critical pressure as the temperature approaches the critical temperature. The results for $FeCl_2$ and $NiCl_2$ do not show the large negative values of apparent molar heat capacity characteristic of alkali and alkaline earth chlorides at high temperatures and low concentrations, indicating that transition metal chlorides are appreciably associated at high-temperatures.[387,388] It was pointed out by Mesmer *et al.*[53] that for systems where significant ion association exists the measured heat capacity may include contributions from the heat effects due to changes in relative species concentrations over the temperature range of an individual measurement. The use of high temperature flow calorimeters in determining heat capacities of aqueous electrolyte solutions has been reviewed by Wood[394] and will not be discussed in detail here. Interested readers are referred to the numerous publications in the literature[365–369,379–400] for further information.

Cobble *et al.*[62] reported infinite dilution partial molar heat capacities of aqueous NaCl and $BaCl_2$ up to 300 °C calculated from the experimentally measured enthalpies of solution of these salts in water. Tremaine *et al.*[401] measured apparent molar heat capacities of aqueous HCl up to 140 °C using a commercial Picker flow microcalorimeter. A drop calorimeter was used by Conti *et al.*[402–405] for the measurement of heat capacities of aqueous solutions of single electrolytes and of their mixtures to 220 °C. The use of the drop calorimeter was limited to concentrated solutions and the precision of the drop calorimeter is 10 times worse than that of the flow calorimeter constructed by the same research group.[368] Heat capacity measurements have been made by Luff with a differential scanning calorimeter (DSC) for concentrated phosphoric acid to 367 °C.[406]

2. Enthalpy of Dilution Measurements

Enthalpy of dilution data are important since they provide evidence for ion association in high-temperature aqueous solutions for electrolytes which are completely dissociated at ambient temperature. Enthalpy of dilution data can also be used to calculate the dependence of activity coefficients on temperature. Workers at the Oak Ridge National Laboratory have used a high-temperature flow calorimeter[372] for the measurement of enthalpies of dilution up to 400 °C and 40 MPa for a number of electrolytes, including NaCl,[372] HCl,[407,408] NH_4Cl,[409] $CaCl_2$,[410] and NaOH.[391] Simonson *et al.*[411] summarized the enthalpy of dilution results obtained prior to 1987. These data have been used to calculate the parameters in an "ion interaction" activity coefficient model developed by Pitzer and his co-workers.[76,412–427] The data for HCl[408] were also correlated with a "chemical equilibrium" activity coefficient model.[408,404] The calculation of activity coefficients from enthalpy of dilution data requires a sensitive calorimeter since enthalpies are needed at very low concentrations. The calculation process is complicated by the tendency of ions to associate at high-temperatures.

For a strong electrolyte, extrapolation of the enthalpy of dilution curve to infinite dilution gives a slope that is consistent with that predicted by the Debye–Hückel limiting law.[76,79] Due to increased ion association, the observed enthalpies of dilution at high temperatures deviate from the limiting law behavior. This deviation provides an evidence for ion association. However, calculation of log *K* and ΔH values for ion association reactions from enthalpies of dilution is not an easy task. The difficulty arises from the covariance of excess and reaction enthalpies, both of which are present in the experimental enthalpies of dilution.

Mayrath and Wood[375,429,430] have also made enthalpy of dilution measurements for aqueous solutions of NaCl, KCl, $MgCl_2$, Na_2SO_4, K_2SO_4, and $MgSO_4$ using their enthalpy of mixing flow calorimeter[365,375] which was operated up to 200 °C. Archer *et al.* measured the enthalpies of dilution of aqueous NaCl solutions,[431] as well as some aqueous surfactants,[431–434] up to 225 °C with an enthalpy of mixing flow calorimeter.[432] As will be discussed below, our research group has made extensive measurements[89,90,435–440] up to 350 °C on both enthalpies of dilution and enthalpies of reaction in an effort to determine thermodynamic quantities for reactions in high-temperature aqueous solutions.

3. Enthalpy of Reaction Measurements

For almost three decades, titration and flow calorimetric data collected when two solutions containing the reactants are mixed have been used by us to determine log *K*, ΔH, and ΔS values for chemical reactions in solution near ambient temperature.[441–459] The use of this technique has been extended in the last several years to the determination of log *K*, ΔH, ΔS, and ΔCp values for reactions in aqueous solutions up to 350 °C.[89,90,435–440] Three high-temperature enthalpy of mixing flow calorimeters[373,374,460] have been used in these studies. The reactions studied to date include ion association to form H_2O,[89,90] HCl(aq),[436,438,460] NaOH-

(aq),[89] HSO_4^-,[435] H_2SO_4(aq),[435] $NaSO_4^-$,[435] HCO_3^-,[440] H_2CO_3(aq),[440] $NaCO_3^-$,[440] CH_3CO_2H(aq),[436] CH_3CO_2Na(aq),[436] $MgCl^+$,[438,460] $CaCl^+$,[438,460] $NiCl^+$,[461] $CuCl^+$,[461] $NiNO_3^+$,[461] $CuNO_3^+$,[461] HNO_3(aq),[439,461] and $NaNO_3$(aq).[461] Thermodynamic quantities for the protonation of three alkanolamines in aqueous solutions have also been determined by flow calorimetry to 150 °C and extrapolated to 325 °C.[462] Recently, log K, ΔH, and ΔS values have been determined for the interaction of several amino acids with protons.[126] Izatt *et al.*[437] described the flow calorimetric technique and summarized results obtained prior to 1991.

The calculation of log K and ΔH values from calorimetric data is more complicated at higher temperatures. For reactions at high temperatures, the corrections due to activity coefficients for the species, the enthalpy changes due to dilution, and the log K and ΔH values for the reactions are needed to fit the observed heats. Since calorimetry is a bulk thermodynamic technique, it does not provide direct information on the species present in the solution. The assignment of speciation and the choice of reactions are more ambiguous at higher temperatures. Most ionic species associate at high temperatures so that reactions other than the one of interest may occur. The heat effects due to changing ionic strength during the course of the measurement are large at high temperatures, sometimes up to 50% of the total heat. It is impossible to carry out the reaction in a solution containing a high concentration of "inert electrolyte" to keep the ionic strength constant, since the constituent ions of the added salt will likely associate with each other and with the reactant ions at high temperatures. The activity coefficients of the electrolytes are significantly different from unity even at ionic strengths as low as 0.01, especially for multiply charged ions. As a result of these complications, great care must be exercised in the analysis of calorimetric data collected for aqueous reactions at high temperatures, and even then the values obtained are dependent on the activity coefficient model used and the assignment of reactions. It is usually necessary to collect data for both dilution and reaction runs at many temperatures and concentrations in order to calculate thermodynamically consistent log K and ΔH values. In addition, successful use of a given set of log K and ΔH values for each reaction in fitting all the enthalpy data collected by mixing different reactants provides confidence that these values are reasonably accurate for the particular reaction. For reactions which proceed to completion, ΔH values at infinite dilution can be determined directly from the measured enthalpies with appropriate corrections for dilutional enthalpies of the products and reactants, and log K values can be calculated from the temperature dependence of ΔH and reference log K values at lower temperatures.

V. Difficulties in High-Temperature Research

Despite the importance of high-temperature thermodynamic quantities in many applications, the available data for high temperature aqueous reactions are relatively few compared with the large data base at 25 °C. A number of difficulties combine to explain the lack of high-temperature thermodynamic data.

First, controlled experimentation at high temperatures and pressures is difficult and requires special equipment design. The solution under study must be heated up to the temperature of interest and maintained precisely at that temperature. The sensors used to measure the temperature must be calibrated so that they give accurate temperature readings. The solution must be kept at a constant pressure which exceeds the saturation vapor pressure of the solution at the system temperature so that evaporation does not occur. The solution must be contained in materials, usually metals or alloys, that can hold the high pressure and still provide resistance to corrosion by the solution at the high-temperature conditions. Few metals or alloys are inert in more than a small range of conditions (temperature, pressure, and solution pH). Dissolved oxygen must be removed from the solution due to its corrosive nature at high temperatures toward metal materials which are used in the construction of the equipment and may be in contact with the solution. Most of the equipment designs which work at low temperatures may fail to work at high temperatures.

Second, speciation in high-temperature aqueous solutions is much more complex and much less certain than that at 25 °C. Many ion association reactions which can be ignored at 25 °C may proceed to a significant extent at high temperatures. For example, the solution of a simple 2:1 salt MX_2 in high-temperature water could have many aqueous species including M^{2+}, X^-, MX^+, MX_2(aq), H^+, HX(aq), OH^-, $M(OH)^+$, $M(OH)_2$(aq), and $M(OH)_3^-$. The speciation in a solution of mixed electrolytes is even more complicated. The presence of neutral species adds a further complication in some cases, as some of the neutral species can be volatile and some may precipitate. The solubilities of most salts decrease rapidly as temperature increases.

Due to the difficulty of studying many reactions at the same time, it is desirable to neglect the species which are not present at significant concentrations. However, determining which species are important and which are not in high-temperature aqueous systems is not easy. Some incorrect thermodynamic quantities have resulted from the failure of investigators to take into account all of the important species present in the solution.

Because of the lack of strong, inert electrolytes at high temperatures, it is difficult to study chemical reactions in aqueous solutions with a constant ionic strength. Sodium chloride (NaCl) is one of only a few salts which may be treated as strong electrolytes up to 300 °C. But it is not inert in the sense that Na^+ and Cl^- can react with a variety of species in high-temperature aqueous solutions. The so-called strong acids and strong bases dissociate completely in water at room temperature, but only partially dissociate in water at high temperatures. Some salts of weak acids and bases may be strong electrolytes at 25 °C, but it is impossible to prepare a high-temperature solution that contains only the constituent ions because there will always be some degree of hydrolysis. Sodium trifluoromethanesulfonate (F_3CSO_3Na) is believed to be a very strong electrolyte to temperatures of at least 295 °C.[289] It is reported to be thermally stable in moderately acidic solutions[463] and in the presence of hydrogen.[289] Therefore, this salt may provide a better supporting ionic medium than sodium chloride.

Many reactions which can be ignored for kinetic reasons at 25 °C are likely to proceed rapidly at high temperatures. Systems involving aqueous transition metal ions are complicated because of their relatively high charge, their ability to form complexes, and their tendency to exist in more than one oxidation state. The much lower dielectric constant of water at high temperatures reduces its ability to stabilize highly charged species so that reactions which lead to a reduction in total charge are favored. These reactions include ion association or ion-pair formation, complexation between transition metal ions and anions, hydrolysis of cations, and proton interaction with negatively charged ligands. This effect makes it difficult to determine thermodynamic data from techniques which require pH buffers or supporting electrolytes.

Third, reliable models for activity coefficients are not well developed for high-temperature aqueous systems. As mentioned above, it is difficult to study chemical reactions in high-temperature aqueous solutions by adding a supporting electrolyte and maintaining the solution at a constant ionic strength. Therefore, activity coefficients are often needed to correct concentrations to activities for the species involved in the reaction. In high-temperature calorimetric studies, activity coefficient models are also used to make enthalpy of dilution corrections. At 25 °C, dilutional enthalpies typically contribute less than a few percent of the total enthalpy measured. At high temperatures, however, the dilutional enthalpies may contribute the majority of the total enthalpy. Excess thermodynamic properties, vapor pressures, and electrochemical cell data are needed to derive equations for activity coefficients.

Several activity coefficient models have been developed to describe the behavior of strong electrolytes in aqueous solutions. The model which has been used with the most success is the "ion interaction" model developed by Pitzer and co-workers.[76,412–427] This model has the advantage that it allows the calculation of the effect which ions have on water and on each other. The applicability of the Pitzer model to high-temperature aqueous solutions has been demonstrated in the correlation of various data for about 20 electrolytes.[427] The disadvantage of the Pitzer model is that so many interaction parameters must be fitted and it is easy to overfit the data, since available data are not sufficient for many systems. The utility of the Pitzer model is also limited by its poor extrapolation ability to high concentrations.

Recently, a modified form of the Pitzer model has been used by Archer[464,465] to represent thermodynamic properties for aqueous NaCl and NaBr solutions over wide ranges of temperature, pressure, and concentration. This modified Pitzer model includes an ionic strength dependent term in the third virial coefficient and thus improves the fit to experimental data.

Another model used with some success in representing activity coefficients is the Meissner model[466–468] as modified by Lindsay.[72] This model has fewer parameters and thus is less accurate than the Pitzer model. The parameters in the modified Meissner model have been fitted to NaCl data as a function of temperature along the vapor–liquid saturation line from 100 to 350 °C.[72] The major advantage of the modified Meissner model is its ability to extrapolate to high concentrations without introducing large errors. Sodium chloride is the most studied electrolyte at high temperatures, and it is one of only a few strong electrolytes up to 300 °C. It has been proposed[72] to use sodium chloride as the model substance for all 1:1 electrolytes at high temperatures as long as no ion association occurs.

High-temperature activity coefficient data are relatively few at the present time. The effect of ionic strength on the activity coefficients of neutral species is far more significant at high temperatures than at 25 °C. The deviation of neutral species from ideality can be estimated from the salting out effect, *i.e.*, the change in solubility of a nonelectrolyte when a salt is added to the solution. However, there are very few data on salting out effects in high-temperature salt solutions. Better activity coefficient models are needed to differentiate between the behavior of individual species as a function of temperature and concentration.

Finally, the rapid changes in water properties make it difficult to predict high-temperature thermodynamic quantities from low-temperature data. log K for any exothermic ion association reaction will inevitably go through a minimum as temperature increases, because above some temperature the changed solvating power of water toward ions must make the reaction endothermic. Estimation of high-temperature log K values is difficult, because it is not certain where the minimum would be. An even more serious problem can arise when dissolved species expected to predominate at high temperatures are undetectable at 25 °C or are only present at concentrations which are too low for them to be adequately characterized thermodynamically. The estimation of high-temperature log K data will be discussed in more detail in the next section.

VI. Estimation and Extrapolation Techniques

It is unlikely that there will ever be enough experimentally determined thermodynamic data for all the high-temperature aqueous reactions that are or will be found to be important in many theoretical and practical applications. Therefore, it is necessary to develop reliable estimation and extrapolation techniques to make possible the prediction of thermodynamic quantities that have not been studied experimentally.

A number of approaches are available for the extrapolation of low temperature log K values to high temperatures. Many of these approaches involve some assumptions about the heat capacity change (ΔCp) for a reaction. The simplest assumption is $\Delta Cp = 0$. For reactions with a change in total charge (*e.g.*, ion association), this assumption could lead to an error of several orders of magnitude in log K above 200 °C.[37] Clearly, the use of this assumption should be avoided for ion association reactions. However, for reactions with identical numbers of positive and negative charges on both sides of the equation, called "isocoulombic" reactions,[469] ΔCp values are often small over a wide range of temperature, and thus there is an approximately linear change of log K with $1/T$. This technique has been called the "isocoulombic reaction principle" [72,469] or the "principle of balance of identical like charges".[45]

Use of isocoulombic reactions represents a great improvement over non-isocoulombic reactions in extrapolation procedures for the estimation of log K values for aqueous reactions at temperatures far removed from the temperatures of the source data. Lindsay[72,469] has tested the applicability of this principle for various acid ionization and base protonation reactions. In most cases, the ionization of water was used in combination with the reaction to be evaluated to form the isocoulombic reaction. Water was chosen as the "model substance" because the ionization of water is the most extensively studied reaction which occurs in aqueous solutions.

The applicability of the isocoulombic reaction principle has been tested by us[89,435–440] for reactions studied up to 325 °C at Brigham Young University. It was found that equations based on this principle represent the data well for reactions where each charge on one side of the equation is balanced on the other side by a charge of the same sign and magnitude. However, such equations are not always as satisfactory at temperatures from 250 to 325 °C for reactions where two singly charged ions on one side of the equation are balanced by one doubly charged ion on the other side.[440] The deviation from the isocoulombic behavior may be explained by the difference in hydration effects between singly and doubly charged ions. The partial molar heat capacity of a doubly charged ion could not be expected to be close to twice that for a singly charged ion at very high temperatures.

Another assumption used in extrapolating log K is that ΔCp is constant over the temperature range involved. For many reactions, the only ΔCp values available are those at or near 25 °C, therefore, these values are often used for extrapolation in a temperature range. This assumption may still lead to large errors for ion association reactions, because it has been observed experimentally that ΔCp increases rapidly with temperature for these reactions. However, when applied to isocoulombic reactions, the assumption of constant ΔCp can make most of the corrections for the small curvature observed in a log K versus $1/T$ plot caused by assuming zero ΔCp. It was found[45,52] that log K values for many isocoulombic reactions can be adequately represented by an equation with the assumption that ΔCp is constant from 0 to 300 °C.

Harned and Robinson[470] proposed that the ΔCp change is proportional to the absolute temperature for some ionization reactions over a range of temperature. Khodakovskiy *et al.*[471] have used this assumption to extrapolate ionization constants for acids, Henry's law constants for gases, and solubility products for salts. This technique is generally acceptable for ionization reactions up to 200 °C.

High-temperature log K values can be calculated using ΔCp values estimated from the "entropy correspondence principle" proposed in 1964 by Criss and Cobble.[42–44] This principle states that the partial molar entropies of a class of ions at a higher temperature T are linearly related to the corresponding entropies at 25 °C. The average partial molar heat capacity of an ion between 25 °C and temperature T is calculated from its partial molar entropy. The average heat capacity change for a chemical reaction is obtained by subtracting the average partial molar heat capacities of the reactants from those of the products. This technique has been used for a number of aqueous systems[41–44,472–474] and was found to give reasonable results to about 200 °C.

In the late 1960s, Helgeson[37,38] proposed a method for the estimation of log K values for reactions in aqueous solutions at high temperatures. This method describes thermodynamic properties in terms of two parts: the electrostatic contribution and the nonelectrostatic contribution. The technique appears to be reliable to about 200 °C, but breaks down at higher temperatures. Since 1974, Helgeson and co-workers[78,475–497] have developed a theoretical basis and semiempirical equations for the prediction of various thermodynamic properties of aqueous species and reactions at high temperatures and pressures. Their work is aimed at providing geochemists with estimated data for use in understanding natural geological processes. Parameters used in the equations were obtained by correlating available experimental data, most of which are for temperatures below 300 °C. The nearly two decade evolution resulted in a computer software package for the calculation of thermodynamic properties of minerals, gases, aqueous species, and reactions from 0 to 1000 °C and 0.1 to 500 MPa.[498]

Many electrostatic models have been used by various investigators for the prediction of ion association in aqueous solutions over a wide range of temperature and pressure. Brady and Walther[499] have used a modified Fuoss[500] equation to calculate log K values for ion association reactions in supercritical aqueous solutions based on the electrostatics of the solution. Similar electrostatic approaches have been used by Gilkerson,[501] Mesmer *et al.*,[53] Walther and Schott,[502] and Ryzhenko, Bryzgalin, and co-workers.[51,503–505]

Anderson *et al.*[506] presented a "density model" for the estimation of thermodynamic quantities for reactions in aqueous solutions at high temperatures and pressures. This model is a simplification of the equation proposed by Marshall and Franck[70] for log K and the equations derived from the Marshall–Franck equation[70] by Gates *et al.*[91] and Mesmer *et al.*[53,87] for ΔH, ΔS, and ΔCp. The thermodynamic quantities are represented as a function of temperature and the density and coefficient of thermal expansion of water. The estimation procedure involves only the properties of water and values of log K, ΔH, and ΔCp for the reaction at reference conditions, usually 25 °C and 1 atm. This model has been shown to give reasonable results up to 300 °C.

The large changes in the properties of water make it difficult to predict high-temperature thermodynamic quantities. The potential for large error is always present when models and theories applicable at lower temperatures are applied to reactions at high temperatures, especially under supercritical water conditions. Most of the estimation and extrapolation techniques provide reasonably accurate results up to the 150–200 °C range. At the present time, it is very difficult to assess the accuracy of the thermodynamic values predicted near the critical temperature of water and in the supercritical region.

VII. High-Temperature Thermodynamic Data

Table 1 contains some thermodynamic data (log K, ΔH, ΔS, and ΔCp) for chemical reactions in aqueous solutions at high temperatures. As mentioned in section I, the data published here represent only a small portion (about one sixth) of the data we have compiled in preparing this review. The remaining data are available as supplementary material, and directions for obtaining the data are located at the end of the text portion of this review. The entire compilation consists of three parts as described below.

The first part of the compilation contains high temperature log K, ΔH, ΔS, and ΔCp values determined using the experimental methods discussed in section IV and estimated values based on some theoretical or empirical models or extrapolated from low-temperature data. Of those articles reporting thermodynamic data at elevated temperatures, most gave only log K values, some reported ΔH, ΔS, and/or ΔCp values calculated from basic thermodynamic relations, and about a dozen reported calorimetrically determined ΔH values. The thermodynamic quantities are tabulated as a function of temperature, pressure, and ionic strength. It is pointed out that above 200 °C estimated values may have significant errors for non-isocoulombic reactions.

The second part of the compilation is a table containing high-temperature log K values applicable at infinite dilution as a function of temperature and the density of water. Most of the log K values were determined by conductivity measurements under supercritical water conditions.

The third part is a compilation of equations representing thermodynamic quantities as a function of temperature, pressure, the density of water, and/or ionic strength. These equations are given in a table together with the conditions under which the equations can be used. The readers may use these equations to calculate thermodynamic values for the reactions at specific conditions of interest.

The compilation is limited to homogeneous aqueous reactions which do not involve the change of oxidation states, particularly to the ionization of acids, the protonation of bases, and the complexation of metal ions with inorganic and organic ligands. Thermodynamic data for heterogeneous equilibria, *e.g.*, dissolution of gases and solid minerals in water, and oxidation–reduction reactions are not included. Values appearing in theses, technical reports, books, or sources which are not in the open literature may not be included. It is not possible to claim completeness for the thermodynamic data. The authors would appreciate comments from interested readers concerning specific data sources absent from this compilation. Because of the uncritical nature of this compilation, the readers must be prepared to make their own evaluation of reliability for the thermodynamic data.

VIII. Suggestions for Future Work

Over the last three decades there has been an enormous expansion of research in all aspects of high-temperature aqueous solution chemistry. The importance of this field in practical applications and in fundamental understanding of chemical phenomena under extreme conditions has become evident. It is not the authors' intention to suggest direction for future research in all areas of high-temperature aqueous solution chemistry. The suggestions presented here are limited to several areas where reaction thermodynamics is important.

First, additional reliable thermodynamic data are needed for a variety of reactions in high-temperature aqueous solutions. The number of reactions studied at high temperatures is much less than that near room temperature. Calorimetrically determined high-temperature ΔH values are available only for a small number of reactions. A significant portion of the high-temperature thermodynamic properties reported in the literature was obtained by prediction or estimation based on theoretical or empirical models, or by extrapolation from data below 100 °C. Many important reactions need to be studied experimentally at high temperatures. These reactions include interaction in biochemical systems and complexation of metal ions with organic ligands. For most of the reactions studied at high temperatures, only log K values are reported. More ΔH, ΔS, and ΔCp values, especially those determined calorimetrically, are needed.

Second, thermodynamic quantities need to be determined over wider ranges of conditions (temperature, pressure, and concentration). Among the reactions studied at temperatures above 100 °C, the majority are limited to temperatures below 325 °C and to pressures not far above the saturation pressure of water. More systematic investigation of the pressure effects on reaction thermodynamics needs to be made for reactions in high-temperature aqueous solutions. Some of the most interesting changes in water properties occur near the critical point of water. It would be desirable to study reactions over the temperature range from about 325 to 425 °C. Measurements in this region should yield a wealth of important information for the development and testing of models for interactions among ions and solvent molecules. Most of the thermodynamic data above 400 °C are determined by conductivity measurements. Other experimental techniques currently used for measurements below 350 °C need to be improved or modified to extend their use to the supercritical region. More measurements in dilute solutions are needed so that better extrapolation of thermodynamic quantities to infinite dilution could be achieved. Such measurements require sensitive equipment.

Third, high-temperature thermodynamic data need to be determined with better accuracies. Because of the difficulties in experimental measurements and the uncertainties in estimation, most high temperature thermodynamic data contain relatively large errors. It appears at the present time that potentiometric and conductivity measurements provide reasonably precise log K values for some reactions at temperatures up to about 300 °C. Calorimetry should be preferred over other methods for the determination of ΔH and ΔCp values. In general, it is very difficult, if not impossible, to give a critical assessment of the accuracy for high-temperature thermodynamic data reported in the literature. For most reactions, there are considerable discrepancies among the thermodynamic values obtained by different investigators using various methods. Accurate determination of high-temperature thermodynamic data requires the development of sensitive instruments, careful design of experiments, explicit consideration of competing reactions and activity coefficients, and the use of reliable data analysis procedures.

Fourth, new or improved experimental techniques are needed to determine speciation in high-temperature aqueous solutions. Several spectroscopic techniques have been used to get direct evidence for the presence of certain species. These techniques include Raman, UV–visible, IR, and ESR. The use of hydrogen electrode concentration cells allows direct measurement of the hydrogen ion activity or concentration. The application of these spectroscopic and potentiometric techniques needs to be extended to higher temperatures. It would be desirable to develop novel methods to overcome the experimental difficulties and to incorporate the instrumentation which has been so successful in determining speciation at ambient temperature into high-temperature devices. New techniques for speciation determination may include high-temperature NMR, neutron and X-ray scattering analysis, ion chromatography, and potentiometry using ion-selective electrodes. Direct observation of the existence of certain species in high-temperature aqueous solution and significant changes in their concentrations would be very helpful in resolving ambiguities in the assignment of relative contributions of reaction thermodynamics and excess properties.

Finally, improved models for activity coefficients are needed, especially for multicharged ions and for mixed electrolyte solutions at high-temperatures. Additional measurements of various excess thermodynamic properties are required both for the development of new models and the testing of existing models and for the calculation of parameters. The need for better representation of activity coefficients becomes increasingly important as reactions above 325 °C are studied.

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Supplementary Material Free of Charge via Anonymous Ftp and Gopher. Additional high-temperature thermodynamic data for the interaction of protons and metal ions with inorganic and organic ligands (Tables 1 and 2), a listing of the equations used to derive the data (Table 3), and a complete list of references are available free of charge as supplementary material via anonymous ftp and gopher.

Ftp, the Internet file transfer protocol, allows individuals with Internet access to connect to the acsinfo server and download files. In order to use this feature, simply open an ftp session to acsinfo.acs.org, give the login id "anonymous", and enter your userid and hostname (in the form userid@hostname) as the password. Once logged in, work your way down the directory structure (/ChemicalReviews/v094) to reach the Izatt material. Files need to be transferred in the correct mode (binary or ASCII) in order to be received uncorrupted, and the mode varies depending on the file format. Please read the README file in the ChemicalReviews directory which contains details on the proper transfer modes as well as additional information on the sizes of the files and their available formats.

Gopher is a public-domain program developed at the University of Minnesota to navigate through the vast quantity of information available on the Internet. The gopher client software can be obtained for Macintosh, PC, and Unix computers via anonymous ftp from boombox.micro.umn.edu in the /pub/gopher directory. By default, running the gopher software will connect you to the University of Minnesota server. From there, you can select "Other Gopher and Information Servers", then "All the Gopher Servers in the World", and finally "Americal Chemical Society" to reach the ACS gopher server. From there, select "Publications" to find the supplementary material. Several other items of interest can also be found including copyright transfer forms and instructions to authors.

Table 1. log *K*, Δ*H*, Δ*S*, and ΔC_p Values for Reactions in aqueous Solution as a Function of Temperature, Pressure, and Ionic Strength

T, °C	*P*, MPa[a]	*I*, mol/kg[b]	log *K*[c]	Δ*H*, kJ/mol[c]	Δ*S*, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
$H^+ + OH^- = H_2O$								
100	Sat	0		-42.11			Cal	88
100	Sat	0	12.264	-42.05	122.1	182	Fit	90
100	Sat	0	12.264 ± 0.009	-42.03 ± 0.35	122.2 ± 1.0	174 ± 5	Pot	288
100	Sat	0	12.266	-42.025	122.2	183.0	Cal	68
100	Sat	0	12.27 ± 0.01	-42.3 ± 0.2	121 ± 1	167 ± 5	Pot	289
100	Sat	0.1 (KCl)	12.004 ± 0.006	-44.23 ± 0.35	111.3 ± 1.0	149 ± 4	Fit	82
100	Sat	0.1 (NaCl)	12.004 ± 0.006	-44.21 ± 0.35	111.3 ± 1.0	149 ± 4	Pot	288
100	Sat	0.5 (KCl)	11.903 ± 0.009	-46.02 ± 0.38	104.6 ± 1.1	125 ± 5	Fit	82
100	Sat	0.5 (NaCl)	11.883 ± 0.009	-46.33 ± 0.38	103.3 ± 1.1	122 ± 5	Pot	288
100	Sat	1.0 (F_3CSO_3Na)	11.90 ± 0.01	-46.9 ± 0.3	102 ± 1	110 ± 5	Pot	289
100	Sat	1.0 (KCl)	11.916 ± 0.009	-47.11 ± 0.41	101.9 ± 1.3	111 ± 4	Fit	82
100	Sat	1.0 (NaCl)	11.872 ± 0.010	-47.87 ± 0.14	99.0 ± 0.5	100 ± 4	Pot	288
100	Sat	3.0 (F_3CSO_3Na)	12.15 ± 0.02	-49.2 ± 0.4	101 ± 1	75 ± 9	Pot	289
100	Sat	3.0 (KCl)	12.074 ± 0.021	-50.92 ± 0.77	98.9 ± 2.4	75 ± 6	Fit	82
100	Sat	3.0 (NaCl)	12.044 ± 0.019	-52.30 ± 0.42	90.5 ± 1.3	34 ± 11	Pot	288
100	Sat	5.0 (F_3CSO_3Na)	12.41 ± 0.02	-51.5 ± 0.7	100 ± 2	43 ± 15	Pot	289
100	Sat	5.0 (NaCl)	12.306 ± 0.037	-56.07 ± 0.71	85.4 ± 2.2	-25 ± 18	Pot	288
100	Sat	7.0 (F_3CSO_3Na)	12.62 ± 0.02	-54.1 ± 1.0	96 ± 3	11 ± 21	Pot	289
110	Sat	0		-40.30		184	Cal	88
125	Sat	0		-37.46			Cal	88
125	Sat	0	11.914	-37.30	134.4	200	Fit	90
125	Sat	0	11.914 ± 0.009	-37.42 ± 0.37	134.1 ± 1.0	197 ± 5	Pot	288
125	Sat	0	11.916	-37.308	134.5	195.0	Cal	68
125	Sat	0.1 (KCl)	11.631 ± 0.009	-40.34 ± 0.41	121.4 ± 1.1	165 ± 5	Fit	82
125	Sat	0.1 (NaCl)	11.631 ± 0.009	-40.29 ± 0.41	121.5 ± 1.1	167 ± 5	Pot	288
125	Sat	0.5 (KCl)	11.512 ± 0.012	-42.79 ± 0.44	112.9 ± 1.3	135 ± 5	Fit	82
125	Sat	0.5 (NaCl)	11.489 ± 0.012	-43.14 ± 0.44	111.6 ± 1.3	135 ± 5	Pot	288
125	Sat	1.0 (KCl)	11.514 ± 0.012	-44.28 ± 0.49	109.2 ± 1.4	228 ± 5	Fit	82
125	Sat	1.0 (NaCl)	11.462 ± 0.010	-45.27 ± 0.19	105.7 ± 0.5	110 ± 4	Pot	288
125	Sat	3.0 (KCl)	11.634 ± 0.027	-49.11 ± 0.90	99.4 ± 2.8	71 ± 9	Fit	82
125	Sat	3.0 (NaCl)	11.587 ± 0.021	-51.46 ± 0.59	92.6 ± 1.5	34 ± 13	Pot	288
125	Sat	5.0 (NaCl)	11.807 ± 0.038	-56.82 ± 0.96	83.3 ± 2.6	-34 ± 21	Pot	288
130	Sat	0		-36.48		199	Cal	88
150	Sat	0		-32.27		223	Cal	88
150	Sat	0	11.64 ± 0.01	-32.7 ± 0.4	146 ± 1	227 ± 7	Pot	289
150	Sat	0	11.642 ± 0.012	-32.07 ± 0.40	147.1 ± 1.0	233 ± 13	Pot	288
150	Sat	0	11.644	-31.96	147.4	230	Fit	90
150	Sat	0	11.646	-32.188	146.9	217.8	Cal	68
150	Sat	0.1 (KCl)	11.334 ± 0.012	-35.89 ± 0.42	132.2 ± 1.3	192 ± 13	Fit	82
150	Sat	0.1 (NaCl)	11.335 ± 0.012	-35.78 ± 0.42	132.4 ± 1.3	195 ± 13	Pot	288
150	Sat	0.5 (KCl)	11.193 ± 0.015	-39.23 ± 0.44	121.6 ± 1.3	151 ± 11	Fit	82
150	Sat	0.5 (NaCl)	11.167 ± 0.015	-39.51 ± 0.44	120.4 ± 1.3	156 ± 11	Pot	288
150	Sat	1.0 (F_3CSO_3Na)	11.17 ± 0.01	-40.7 ± 0.3	118 ± 1	143 ± 7	Pot	289
150	Sat	1.0 (KCl)	11.181 ± 0.015	-41.25 ± 0.74	116.6 ± 1.4	126 ± 11	Fit	82
150	Sat	1.0 (NaCl)	11.121 ± 0.010	-42.31 ± 0.28	112.9 ± 0.7	127 ± 5	Pot	288
150	Sat	3.0 (F_3CSO_3Na)	11.36 ± 0.01	-45.1 ± 0.5	111 ± 1	95 ± 11	Pot	289
150	Sat	3.0 (KCl)	11.259 ± 0.033	-47.36 ± 1.21	103.6 ± 3.0	67 ± 14	Fit	82
150	Sat	3.0 (NaCl)	11.190 ± 0.021	-50.54 ± 0.84	94.7 ± 2.1	38 ± 14	Pot	288
150	Sat	5.0 (F_3CSO_3Na)	11.57 ± 0.01	-49.1 ± 0.7	105 ± 2	53 ± 17	Pot	289
150	Sat	5.0 (NaCl)	11.360 ± 0.039	-57.70 ± 1.42	81.1 ± 3.5	-39 ± 24	Pot	288
150	Sat	7.0 (F_3CSO_3Na)	11.72 ± 0.03	-53.7 ± 1.0	98 ± 3	12 ± 24	Pot	289
175	Sat	0	11.441 ± 0.012	-25.68 ± 0.42	161.7 ± 1.0	281 ± 15	Pot	288
175	Sat	0	11.442	-25.68	161.8	278	Fit	90
175	Sat	0.1 (KCl)	11.102 ± 0.012	-30.70 ± 0.42	144.1 ± 1.3	224 ± 14	Fit	82
175	Sat	0.1 (NaCl)	11.104 ± 0.012	-30.48 ± 0.42	144.6 ± 1.3	230 ± 14	Pot	288
175	Sat	0.5 (KCl)	10.943 ± 0.015	-35.23 ± 0.44	130.7 ± 1.3	167 ± 13	Fit	82
175	Sat	0.5 (NaCl)	10.907 ± 0.015	-35.30 ± 0.44	130.0 ± 1.3	179 ± 13	Pot	288
175	Sat	1.0 (KCl)	10.907 ± 0.018	-38.02 ± 0.54	124.0 ± 1.4	131 ± 14	Fit	82
175	Sat	1.0 (NaCl)	10.839 ± 0.011	-38.93 ± 0.40	120.6 ± 1.0	143 ± 5	Pot	288
175	Sat	3.0 (KCl)	10.937 ± 0.039	-45.84 ± 1.21	107.1 ± 3.4	51 ± 20	Fit	82
175	Sat	3.0 (NaCl)	10.842 ± 0.023	-49.58 ± 1.17	96.9 ± 2.8	38 ± 16	Pot	288
175	Sat	5.0 (NaCl)	10.954 ± 0.042	-58.83 ± 1.97	78.5 ± 4.7	-52 ± 27	Pot	288
200	Sat	0	11.29 ± 0.01	-18.7 ± 0.6	177 ± 1	341 ± 21	Pot	289
200	Sat	0	11.302 ± 0.012	-17.93 ± 0.79	178.4 ± 1.6	341 ± 30	Pot	288
200	Sat	0	11.303	-17.98	178.4	352	Fit	90
200	Sat	0.1 (KCl)	10.928 ± 0.012	-24.70 ± 0.70	157.0 ± 1.5	256 ± 29	Fit	82
200	Sat	0.1 (NaCl)	10.932 ± 0.012	-24.31 ± 0.71	157.9 ± 1.5	265 ± 29	Pot	288
200	Sat	0.5 (KCl)	10.727 ± 0.018	-30.98 ± 0.71	139.9 ± 1.3	170 ± 28	Fit	82
200	Sat	0.5 (NaCl)	10.701 ± 0.018	-29.71 ± 0.71	140.2 ± 1.6	195 ± 28	Pot	288
200	Sat	1.0 (F_3CSO_3Na)	10.69 ± 0.01	-32.6 ± 0.5	136 ± 1	174 ± 20	Pot	289
200	Sat	1.0 (KCl)	10.680 ± 0.021	-34.86 ± 0.84	130.8 ± 1.9	117 ± 28	Fit	82
200	Sat	1.0 (NaCl)	10.608 ± 0.012	-35.27 ± 0.54	128.5 ± 1.3	147 ± 6	Pot	288

Table 1 (Continued)

T, °C	*P*, MPa[a]	*I*, mol/kg[b]	log *K*[c]	Δ*H*, kJ/mol[c]	Δ*S*, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
200	Sat	3.0 (F_3CSO_3Na)	10.80 ± 0.01	-40.1 ± 0.9	122 ± 2	94 ± 21	Pot	289
200	Sat	3.0 (KCl)	10.656 ± 0.045	-45.10 ± 1.67	108.7 ± 4.1	2 ± 36	Fit	82
200	Sat	3.0 (NaCl)	10.536 ± 0.027	-48.83 ± 1.59	98.5 ± 3.7	18 ± 18	Pot	288
200	Sat	5.0 (F_3CSO_3Na)	10.95 ± 0.01	-46.6 ± 1.4	111 ± 3	34 ± 26	Pot	289
200	Sat	5.0 (NaCl)	10.582 ± 0.048	-60.50 ± 2.68	74.9 ± 6.3	-88 ± 30	Pot	288
225	Sat	0	11.222 ± 0.012	-8.53 ± 1.51	197.7 ± 3.0	415 ± 39	Pot	288
225	Sat	0	11.223	-8.02	198.8	474	Fit	90
225	Sat	0.1 (KCl)	10.804 ± 0.012	-17.98 ± 1.38	170.7 ± 2.8	281 ± 38	Fit	82
225	Sat	0.1 (NaCl)	10.811 ± 0.012	-17.24 ± 1.38	172.3 ± 2.8	297 ± 38	Pot	288
225	Sat	0.5 (KCl)	10.563 ± 0.018	-26.93 ± 1.34	148.2 ± 2.8	148 ± 36	Fit	82
225	Sat	0.5 (NaCl)	10.540 ± 0.018	-25.69 ± 1.34	150.2 ± 2.8	194 ± 36	Pot	288
225	Sat	1.0 (KCl)	10.490 ± 0.021	-32.48 ± 1.51	135.6 ± 3.1	65 ± 39	Fit	82
225	Sat	1.0 (NaCl)	10.418 ± 0.014	-31.80 ± 0.67	135.6 ± 1.5	128 ± 7	Pot	288
225	Sat	3.0 (KCl)	10.402 ± 0.054	-46.28 ± 2.64	106.2 ± 5.9	-109 ± 59	Fit	82
225	Sat	3.0 (NaCl)	10.261 ± 0.033	-48.99 ± 2.05	97.9 ± 4.6	-38 ± 20	Pot	288
225	Sat	5.0 (NaCl)	10.234 ± 0.058	-63.60 ± 3.43	68.2 ± 7.5	-166 ± 33	Pot	288
250	Sat	0	11.18 ± 0.01	2.5 ± 1.9	219 ± 4	545 ± 39	Pot	289
250	Sat	0	11.196 ± 0.015	2.97 ± 2.51	220.0 ± 5.0	511 ± 45	Pot	288
250	Sat	0	11.203	5.66	225.3	690	Cal	90
250	Sat	0.1 (KCl)	10.723 ± 0.015	-10.72 ± 2.34	184.8 ± 3.4	298 ± 41	Fit	82
250	Sat	0.1 (NaCl)	10.735 ± 0.015	-9.46 ± 2.34	187.4 ± 3.3	326 ± 41	Pot	288
250	Sat	0.5 (KCl)	10.429 ± 0.021	-23.93 ± 2.30	153.9 ± 3.4	85 ± 44	Fit	82
250	Sat	0.5 (NaCl)	10.416 ± 0.021	-21.09 ± 2.30	159.1 ± 3.4	169 ± 44	Pot	288
250	Sat	1.0 (F_3CSO_3Na)	10.38 ± 0.01	-24.8 ± 1.8	151 ± 4	124 ± 38	Pot	289
250	Sat	1.0 (KCl)	10.323 ± 0.024	-32.12 ± 2.64	136.2 ± 5.3	-49 ± 56	Fit	82
250	Sat	1.0 (NaCl)	10.259 ± 0.016	-29.16 ± 0.84	140.6 ± 1.9	73 ± 7	Pot	288
250	Sat	3.0 (F_3CSO_3Na)	10.39 ± 0.02	-38.0 ± 2.1	126 ± 4	-49 ± 39	Pot	289
250	Sat	3.0 (KCl)	10.156 ± 0.063	-51.43 ± 4.46	96.1 ± 9.3	-326 ± 103	Fit	82
250	Sat	3.0 (NaCl)	10.005 ± 0.042	-51.21 ± 2.55	93.7 ± 5.4	-150 ± 22	Pot	288
250	Sat	5.0 (F_3CSO_3Na)	10.45 ± 0.03	-48.5 ± 2.8	107 ± 6	-155 ± 44	Pot	289
250	Sat	5.0 (NaCl)	9.896 ± 0.072	-69.37 ± 4.27	56.9 ± 9.2	-310 ± 36	Pot	288
275	Sat	0	11.224 ± 0.027	17.46 ± 3.89	246.7 ± 7.5	661 ± 59	Pot	288
275	Sat	0	11.251	26.00	262.8	1121	Cal	90
275	Sat	0.1 (KCl)	10.676 ± 0.024	-3.05 ± 3.60	198.8 ± 7.0	319 ± 54	Fit	82
275	Sat	0.1 (NaCl)	10.695 ± 0.024	-0.88 ± 3.60	202.9 ± 7.1	368 ± 54	Pot	288
275	Sat	0.5 (KCl)	10.310 ± 0.030	-23.16 ± 3.68	155.1 ± 7.2	-32 ± 67	Fit	82
275	Sat	0.5 (NaCl)	10.316 ± 0.030	-17.45 ± 3.68	165.7 ± 7.1	121 ± 67	Pot	288
275	Sat	1.0 (KCl)	10.160 ± 0.036	-35.71 ± 4.44	129.4 ± 8.5	-254 ± 98	Fit	82
275	Sat	1.0 (NaCl)	10.117 ± 0.019	-28.49 ± 1.05	141.7 ± 2.2	-24 ± 8	Pot	288
275	Sat	3.0 (KCl)	9.892 ± 0.081	-63.98 ± 7.87	72.7 ± 15.6	-713 ± 195	Fit	82
275	Sat	3.0 (NaCl)	9.753 ± 0.053	-57.15 ± 3.14	82.4 ± 6.7	-342 ± 24	Pot	288
275	Sat	5.0 (NaCl)	9.551 ± 0.089	-79.96 ± 5.23	37.2 ± 10.9	-594 ± 40	Pot	288
300	Sat	0	11.301 ± 0.045	37.26 ± 5.65	281.4 ± 10.9	964 ± 93	Pot	288
300	Sat	0	11.382	60.14	322.8	2164	Cal	90
300	Sat	0.1 (KCl)	10.653 ± 0.042	5.72 ± 5.19	213.9 ± 9.8	404 ± 82	Fit	82
300	Sat	0.1 (NaCl)	10.683 ± 0.042	9.46 ± 5.19	220.9 ± 9.6	485 ± 84	Pot	288
300	Sat	0.5 (KCl)	10.187 ± 0.045	-25.88 ± 5.73	149.9 ± 10.7	-188 ± 120	Fit	82
300	Sat	0.5 (NaCl)	10.226 ± 0.045	-14.94 ± 5.73	169.9 ± 10.9	87 ± 120	Pot	288
300	Sat	1.0 (KCl)	9.975 ± 0.054	-45.81 ± 7.61	111.0 ± 14.3	-574 ± 190	Fit	82
300	Sat	1.0 (NaCl)	9.976 ± 0.023	-30.63 ± 1.26	137.5 ± 2.6	-149 ± 9	Pot	288
300	Sat	3.0 (KCl)	9.572 ± 0.117	-89.44 ± 14.64	27.2 ± 27.5	-1384 ± 390	Fit	82
300	Sat	3.0 (NaCl)	9.482 ± 0.066	-69.25 ± 3.77	60.7 ± 7.9	-651 ± 26	Pot	288
300	Sat	5.0 (NaCl)	9.177 ± 0.110	-98.74 ± 6.28	3.8 ± 13.0	-976 ± 44	Pot	288
325	Sat	0	11.638	130.5	441.0	5731	Cal	90
350	Sat	0	12.144	359.3	809.1	32885	Cal	90
			$D^+ + OD^- = D_2O$					
100	Sat	0	13.099 ± 0.020	-44.85 ± 0.79	130.6 ± 2.3	186 ± 11	Fit	290
100	Sat	1.0 (KCl)	12.717 ± 0.028	-38.99 ± 0.96	138.9 ± 2.7	150 ± 27	Fit	290
125	Sat	0	12.725 ± 0.024	-40.00 ± 0.75	143.1 ± 2.3	203 ± 17	Fit	290
125	Sat	1.0 (KCl)	12.282 ± 0.029	-35.15 ± 1.26	146.9 ± 3.3	162 ± 30	Fit	290
150	Sat	0	12.434 ± 0.027	-34.60 ± 0.84	156.3 ± 2.5	233 ± 26	Fit	290
150	Sat	1.0 (KCl)	11.910 ± 0.031	-30.79 ± 1.84	155.3 ± 4.5	188 ± 36	Fit	290
175	Sat	0	12.215 ± 0.028	-28.24 ± 1.30	170.8 ± 3.0	277 ± 33	Fit	290
175	Sat	1.0 (KCl)	11.590 ± 0.036	-25.65 ± 2.64	164.8 ± 6.3	226 ± 42	Fit	290
200	Sat	0	12.060 ± 0.030	-20.67 ± 2.13	187.0 ± 4.6	331 ± 46	Fit	290
200	Sat	1.0 (KCl)	11.312 ± 0.048	-19.41 ± 3.64	175.7 ± 8.4	276 ± 50	Fit	290
225	Sat	0	11.965 ± 0.036	-11.59 ± 3.31	205.9 ± 7.1	400 ± 54	Fit	290
225	Sat	1.0 (KCl)	11.069 ± 0.066	-11.80 ± 5.02	188.3 ± 10.9	339 ± 59	Fit	290
250	Sat	0	11.923 ± 0.049	-0.42 ± 4.60	227.2 ± 10.0	490 ± 67	Fit	290
250	Sat	1.0 (KCl)	10.852 ± 0.089	-2.38 ± 6.28	203.3 ± 13.8	418 ± 71	Fit	290
275	Sat	0	11.933 ± 0.070	13.39 ± 6.69	252.7 ± 13.0	636 ± 71	Fit	290
275	Sat	1.0 (KCl)	10.650 ± 0.120	9.62 ± 8.37	221.3 ± 17.2	540 ± 79	Fit	290
300	Sat	0	11.992 ± 0.098	32.64 ± 8.37	286.2 ± 16.7	933 ± 88	Fit	290
300	Sat	1.0 (KCl)	10.430 ± 0.150	25.52 ± 10.04	243.9 ± 20.5	749 ± 92	Fit	290

Table 1 (Continued)

T, °C	P, MPa[a]	I, mol/kg[b]	log K[c]	ΔH, kJ/mol[c]	ΔS, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
$Mg^{2+} + H_2O = Mg(OH)^+ + H^+$								
350	100	0	-5.38				Sol	208
350	200	0	-5.69				Sol	208
400	100	0	-4.77				Sol	208
400	200	0	-5.46				Sol	208
450	100	0	-3.94				Sol	208
450	200	0	-5.06				Sol	208
500	100	0	-2.60				Sol	208
500	200	0	-4.04				Sol	208
550	100	0	-0.77				Sol	208
550	200	0	-3.43				Sol	208
600	200	0	-3.97				Sol	208
$Ca^{2+} + H_2O = Ca(OH)^+ + H^+$								
100	50	0	-10.04				Sol	201
200	50	0	-8.20				Sol	201
300	50	0	-6.88				Sol	201
350	50	0	-6.35				Sol	201
$Fe^{2+} + H_2O = Fe(OH)^+ + H^+$								
100	Sat	0	-8.78 ± 0.35				Sol	198
150	Sat	0	-8.09 ± 0.25				Sol	198
200	Sat	0	-7.56 ± 0.20				Sol	198
250	Sat	0	-7.12 ± 0.20				Sol	198
300	Sat	0	-6.76 ± 0.23				Sol	198
$Fe^{2+} + 2H_2O = Fe(OH)_2(aq) + 2H^+$								
100	Sat	0	-17.15 ± 0.14				Sol	198
150	Sat	0	-15.44 ± 0.14				Sol	198
200	Sat	0	-14.09 ± 0.10				Sol	198
250	Sat	0	-12.99 ± 0.10				Sol	198
300	Sat	0	-12.09 ± 0.10				Sol	198
$Fe^{2+} + 3H_2O = Fe(OH)_3 + 3H^+$								
100	Sat	0	-28.11 ± 0.26				Sol	198
150	Sat	0	-25.63 ± 0.26				Sol	198
200	Sat	0	-23.68 ± 0.19				Sol	198
250	Sat	0	-22.10 ± 0.19				Sol	198
300	Sat	0	-20.80 ± 0.19				Sol	198
$Zn^{2+} + OH = Zn(OH)^+$								
100	Sat	0	7.40				Sol	217
150	Sat	0	8.04				Sol	217
200	Sat	0	8.70				Sol	217
250	Sat	0	9.4				Sol	217
300	Sat	0	10.1				Sol	217
$Zn^{2+} + 2OH^- = Zn(OH)_2(aq)$								
100	Sat	0	10.44				Sol	217
150	Sat	0	10.61				Sol	217
200	Sat	0	11.07				Sol	217
250	Sat	0	11.78				Sol	217
300	Sat	0	12.65				Sol	217
$Zn^{2+} + 3OH = Zn(OH)_3$								
100	Sat	0	13.49				Sol	217
150	Sat	0	13.92				Sol	217
200	Sat	0	14.57				Sol	217
250	Sat	0	15.44				Sol	217
300	Sat	0	16.45				Sol	217
$Zn^{2+} + 4OH = Zn(OH)_4^2$								
100	Sat	0	14.07				Sol	217
150	Sat	0	14.21				Sol	217
200	Sat	0	14.64				Sol	217
250	Sat	0	15.32				Sol	217
300	Sat	0	16.18				Sol	217
$Al^{3+} + H_2O = Al(OH)^{2+} + H^+$								
100	Sat	0	-3.00 ± 0.04	55.4 [illegible] 1.0	91 ± 3	0	Fit	309
100	Sat	0.1 (NaCl)	-3.49 ± 0.03	54.4 ± 1.0	79 ± 3	0	Fit	309
100	Sat	0.3 (NaCl)	-3.67 ± 0.03	53.1 ± 1.1	72 ± 3	0	Fit	309
100	Sat	1.0 (NaCl)	-3.93 ± 0.05	51.1 ± 1.4	62 ± 4	3 ± 20	Fit	309
100	Sat	5.0 (NaCl)	-4.01 ± 0.10	57.7 ± 4.8	78 ± 14	50 ± 30	Fit	309
125	Sat	0	-2.51 ± 0.04	55.4 ± 1.0	91 ± 3	0	Fit	309
125	Sat	0.1 (NaCl)	-3.05 ± 0.04	54.4 ± 1.0	79 ± 3	0	Fit	309
125	Sat	0.3 (NaCl)	-3.27 ± 0.04	53.1 [illegible] 1.1	71 ± 3	0	Fit	309
125	Sat	1.0 (NaCl)	-3.58 ± 0.05	51.1 ± 1.4	60 ± 4	3 ± 20	Fit	309
125	Sat	5.0 (NaCl)	-3.65 ± 0.13	59.2 ± 5.6	79 ± 16	60 ± 40	Fit	309
150	Sat	0	-2.08 ± 0.05	55.4 ± 1.0	91 ± 3	0	Fit	309
175	Sat	0	-1.70 ± 0.05	55.4 ± 1.0	91 ± 3	0	Fit	309

Table 1 (Continued)

T, °C	*P*, MPa[a]	*I*, mol/kg[b]	log *K*[c]	ΔH, kJ/mol[c]	ΔS, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
200	Sat	0	-1.36 ± 0.06	55.4 ± 1.0	91 ± 3	0	Fit	309
				$H^+ + F^- = HF(aq)$				
100	Sat	0	3.85 ± 0.01				Con	192
100	Sat	0	4.00				Sol	213
100	3.8	1.0 (NaCl)	3.40				Pot	316
100	28.4	1.0 (NaCl)	3.35				Pot	316
100	75.7	1.0 (NaCl)	3.29				Pot	316
110	4.0	1.0 (NaCl)	3.46				Pot	316
110	28.4	1.0 (NaCl)	3.42				Pot	316
110	78.3	1.0 (NaCl)	3.35				Pot	316
120	4.2	1.0 (NaCl)	3.53				Pot	316
120	29.8	1.0 (NaCl)	3.48				Pot	316
120	81.1	1.0 (NaCl)	3.41				Pot	316
125	Sat	0	4.09 ± 0.02				Con	192
130	4.4	1.0 (NaCl)	3.60				Pot	316
130	30.5	1.0 (NaCl)	3.55				Pot	316
130	83.0	1.0 (NaCl)	3.47				Pot	316
140	4.6	1.0 (NaCl)	3.67				Pot	316
140	30.5	1.0 (NaCl)	3.62				Pot	316
140	85.5	1.0 (NaCl)	3.52				Pot	316
150	Sat	0	4.34 ± 0.03				Con	192
150	4.8	1.0 (NaCl)	3.73				Pot	316
150	32.0	1.0 (NaCl)	3.69				Pot	316
150	88.0	1.0 (NaCl)	3.58				Pot	316
160	5.0	1.0 (NaCl)	3.80				Pot	316
160	32.0	1.0 (NaCl)	3.77				Pot	316
160	90.0	1.0 (NaCl)	3.64				Pot	316
170	5.2	1.0 (NaCl)	3.86				Pot	316
170	32.0	1.0 (NaCl)	3.83				Pot	316
170	93.4	1.0 (NaCl)	3.71				Pot	316
175	Sat	0	4.59 ± 0.04				Con	192
180	5.4	1.0 (NaCl)	3.91				Pot	316
180	32.0	1.0 (NaCl)	3.88				Pot	316
180	96.1	1.0 (NaCl)	3.77				Pot	316
190	5.6	1.0 (NaCl)	4.00				Pot	316
190	32.0	1.0 (NaCl)	3.94				Pot	316
190	99.4	1.0 (NaCl)	3.84				Pot	316
200	Sat	0	4.85				Sol	213
200	Sat	0	4.89 ± 0.04				Con	192
200	5.7	1.0 (NaCl)	4.07				Pot	316
200	35.7	1.0 (NaCl)	3.98				Pot	316
200	102.0	1.0 (NaCl)	3.89				Pot	316
210	35.7	1.0 (NaCl)	4.02				Pot	316
210	105.7	1.0 (NaCl)	3.96				Pot	316
220	35.7	1.0 (NaCl)	4.06				Pot	316
220	108.2	1.0 (NaCl)	3.99				Pot	316
230	35.7	1.0 (NaCl)	4.09				Pot	316
240	35.7	1.0 (NaCl)	4.10				Pot	316
250	Sat	0	5.40				Sol	213
250	39.6	1.0 (NaCl)	4.11				Pot	316
				$Rb^+ + F^- = RbF(aq)$				
303	50	0	1.55 ± 0.13				Con	488
303	100	0	1.43 ± 0.21				Con	488
303	150	0	1.33 ± 0.24				Con	488
303	200	0	1.26 ± 0.27				Con	488
356	50	0	1.76 ± 0.14				Con	488
356	100	0	1.64 ± 0.16				Con	488
356	150	0	1.57 ± 0.17				Con	488
356	200	0	1.48 ± 0.19				Con	488
356	250	0	1.43 ± 0.20				Con	488
356	300	0	1.37 ± 0.22				Con	488
400	50	0	1.82 ± 0.15				Con	488
400	100	0	1.70 ± 0.16				Con	488
400	150	0	1.61 ± 0.17				Con	488
400	200	0	1.54 ± 0.19				Con	488
400	250	0	1.50 ± 0.20				Con	488
400	300	0	1.46 ± 0.21				Con	488
400	350	0	1.42 ± 0.21				Con	488
460	50	0	3.07 ± 0.10				Con	488
460	100	0	1.94 ± 0.13				Con	488
460	150	0	1.81 ± 0.14				Con	488
460	200	0	1.71 ± 0.15				Con	488
460	250	0	1.66 ± 0.16				Con	488
460	300	0	1.61 ± 0.16				Con	488
460	350	0	1.56 ± 0.17				Con	488

Table 1 (Continued)

T, °C	*P*, MPa[a]	*I*, mol/kg[b]	log *K*[c]	Δ*H*, kJ/mol[c]	Δ*S*, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
460	400	0	1.53 ± 0.18				Con	488
502	100	0	2.22 ± 0.11				Con	488
502	150	0	1.97 ± 0.12				Con	488
502	200	0	1.86 ± 0.13				Con	488
502	250	0	1.78 ± 0.14				Con	488
502	300	0	1.75 ± 0.14				Con	488
502	350	0	1.70 ± 0.15				Con	488
502	400	0	1.66 ± 0.15				Con	488
606	100	0	3.46 ± 0.12				Con	488
606	150	0	2.50 ± 0.10				Con	488
606	200	0	2.14 ± 0.11				Con	488
606	250	0	1.95 ± 0.12				Con	488
606	300	0	1.86 ± 0.13				Con	488
606	350	0	1.79 ± 0.14				Con	488
606	400	0	1.74 ± 0.14				Con	488
718	150	0	3.33 ± 0.11				Con	488
718	200	0	2.66 ± 0.10				Con	488
718	250	0	2.28 ± 0.10				Con	488
718	300	0	2.07 ± 0.11				Con	488
718	350	0	1.93 ± 0.13				Con	488
718	400	0	1.87 ± 0.13				Con	488
801	150	0	4.00 ± 0.18				Con	488
801	200	0	3.12 ± 0.10				Con	488
801	250	0	2.61 ± 0.09				Con	488
801	300	0	2.31 ± 0.10				Con	488
801	350	0	2.12 ± 0.11				Con	488
801	400	0	2.02 ± 0.12				Con	488
				$H^+ + Cl^- = HCl(aq)$				
250	10.3	0	-0.49	108.4	198	629	Cal	438
275	10.3	0	0.37	103	195	1222	Cal	436
275	11.0	0	0.04	127.7	234	1003	Cal	438
300	10.3	0	0.87	141	263	1844	Cal	436
300	11.0	0	0.63	162.8	296	1989	Cal	438
320	12.8	0	1.37	184	336	2431	Cal	436
325	13.2	0	1.31	233.4	415	5220	Cal	438
400	50	0	2.98				Con	181
400	100	0	1.88				Con	181
400	150	0	1.37				Con	181
400	200	0	1.07				Con	181
400	250	0	0.83				Con	181
400	300	0	0.63				Con	181
400	350	0	0.46				Con	181
400	400	0	0.31				Con	181
450	50	0	5.60				Con	181
450	100	0	3.00				Con	181
450	150	0	2.27				Con	181
450	200	0	1.86				Con	181
450	250	0	1.56				Con	181
450	300	0	1.32				Con	181
450	350	0	1.12				Con	181
450	400	0	0.95				Con	181
500	50	0	8.59				Con	181
500	100	0	4.26				Con	181
500	150	0	3.19				Con	181
500	200	0	2.64				Con	181
500	250	0	2.26				Con	181
500	300	0	1.98				Con	181
500	350	0	1.74				Con	181
500	400	0	1.55				Con	181
550	50	0	10.55				Con	181
550	100	0	5.61				Con	181
550	150	0	4.13				Con	181
550	200	0	3.42				Con	181
550	250	0	2.96				Con	181
550	300	0	2.61				Con	181
550	350	0	2.33				Con	181
550	400	0	2.12				Con	181
600	50	0	11.90				Con	181
600	100	0	6.90				Con	181
600	150	0	5.06				Con	181
600	200	0	4.19				Con	181
600	250	0	3.63				Con	181
600	300	0	3.22				Con	181
600	350	0	2.90				Con	181
600	400	0	2.65				Con	181

Table 1 (Continued)

T, °C	P, MPa[a]	I, mol/kg[b]	log K[c]	ΔH, kJ/mol[c]	ΔS, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
650	50	0	12.93				Con	181
650	100	0	8.06				Con	181
650	150	0	5.97				Con	181
650	200	0	4.93				Con	181
650	250	0	4.30				Con	181
650	300	0	3.80				Con	181
650	350	0	3.44				Con	181
650	400	0	3.16				Con	181
700	50	0	13.81				Con	181
700	100	0	9.08				Con	181
700	150	0	6.83				Con	181
700	200	0	5.65				Con	181
700	250	0	5.15				Con	181
700	300	0	4.36				Con	181
700	350	0	3.96				Con	181
700	400	0	3.65				Con	181
$Li^+ + Cl^- = LiCl(aq)$								
401	50	0	1.17 ± 0.34				Con	488
442	50	0	2.44 ± 0.11				Con	488
442	100	0	1.16 ± 0.44				Con	488
494	100	0	1.97 ± 0.14				Con	488
494	150	0	1.38 ± 0.29				Con	488
494	200	0	0.89 ± 0.68				Con	488
547	100	0	2.74 ± 0.10				Con	488
547	150	0	1.82 ± 0.16				Con	488
547	200	0	1.28 ± 0.34				Con	488
594	100	0	3.63 ± 0.14				Con	488
594	150	0	2.33 ± 0.11				Con	488
594	200	0	1.70 ± 0.19				Con	488
594	250	0	1.25 ± 0.36				Con	488
692	150	0	3.50 ± 0.13				Con	488
692	200	0	2.56 ± 0.10				Con	488
692	250	0	1.99 ± 0.14				Con	488
692	300	0	1.57 ± 0.22				Con	488
692	350	0	1.10 ± 0.48				Con	488
795	150	0	4.67 ± 0.41				Con	488
795	200	0	3.50 ± 0.13				Con	488
795	250	0	2.77 ± 0.10				Con	488
795	300	0	2.28 ± 0.11				Con	488
795	350	0	1.88 ± 0.15				Con	488
795	400	0	1.50 ± 0.25				Con	488
$Na^+ + Cl^- = NaCl(aq)$								
405	50	0	1.61 ± 0.22				Con	488
405	100	0	1.20 ± 0.36				Con	488
405	150	0	0.90 ± 0.60				Con	488
405	200	0	0.68 ± 0.89				Con	488
457	50	0	3.16 ± 0.11				Con	488
457	100	0	1.65 ± 0.19				Con	488
457	150	0	1.33 ± 0.29				Con	488
457	200	0	1.10 ± 0.41				Con	488
457	250	0	0.83 ± 0.67				Con	488
457	300	0	0.67 ± 0.92				Con	488
507	100	0	2.18 ± 0.12				Con	488
507	150	0	1.63 ± 0.19				Con	488
507	200	0	1.35 ± 0.28				Con	488
507	250	0	1.06 ± 0.45				Con	488
507	300	0	0.98 ± 0.50				Con	488
507	350	0	0.86 ± 0.62				Con	488
507	400	0	0.70 ± 0.86				Con	488
555	100	0	2.90 ± 0.10				Con	488
555	150	0	2.04 ± 0.13				Con	488
555	200	0	1.70 ± 0.17				Con	488
555	250	0	1.46 ± 0.23				Con	488
555	300	0	1.27 ± 0.30				Con	488
555	350	0	1.11 ± 0.40				Con	488
555	400	0	0.97 ± 0.50				Con	488
594	100	0	3.56 ± 0.13				Con	488
594	150	0	2.35 ± 0.10				Con	488
594	200	0	1.87 ± 0.14				Con	488
594	250	0	1.57 ± 0.20				Con	488
594	300	0	1.33 ± 0.28				Con	488
594	350	0	1.12 ± 0.40				Con	488
594	400	0	1.01 ± 0.48				Con	488
606	100	0	3.74 ± 0.15				Con	488
606	150	0	2.47 ± 0.10				Con	488

Table 1 (Continued)

T, °C	*P*, MPa[a]	*I*, mol/kg[b]	log *K*[c]	Δ*H*, kJ/mol[c]	Δ*S*, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
606	200	0	1.95 ± 0.13				Con	488
606	250	0	1.66 ± 0.18				Con	488
606	300	0	1.45 ± 0.24				Con	488
606	350	0	1.28 ± 0.30				Con	488
606	400	0	1.20 ± 0.34				Con	488
709	100	0	5.02 ± 0.59				Con	488
709	150	0	3.51 ± 0.12				Con	488
709	200	0	2.68 ± 0.09				Con	488
709	250	0	2.18 ± 0.11				Con	488
709	300	0	1.86 ± 0.14				Con	488
709	350	0	1.60 ± 0.19				Con	488
709	400	0	1.44 ± 0.24				Con	488
812	150	0	4.52 ± 0.32				Con	488
812	200	0	3.48 ± 0.12				Con	488
812	250	0	2.83 ± 0.09				Con	488
812	300	0	2.40 ± 0.10				Con	488
812	350	0	2.06 ± 0.12				Con	488
812	400	0	1.81 ± 0.15				Con	488
				$K^+ + Cl^- = KCl(aq)$				
402	50	0	1.18 ± 0.45				Con	488
501	100	0	1.85 ± 0.16				Con	488
501	150	0	1.30 ± 0.32				Con	488
501	200	0	0.97 ± 0.55				Con	488
501	250	0	0.70 ± 0.92				Con	488
604	100	0	3.42 ± 0.12				Con	488
604	150	0	2.21 ± 0.11				Con	488
604	200	0	1.72 ± 0.17				Con	488
604	250	0	1.39 ± 0.27				Con	488
604	300	0	1.14 ± 0.40				Con	488
604	350	0	0.91 ± 0.61				Con	488
604	400	0	0.70 ± 0.91				Con	488
711	150	0	3.30 ± 0.11				Con	488
711	200	0	2.47 ± 0.10				Con	488
711	250	0	1.97 ± 0.14				Con	488
711	300	0	1.62 ± 0.20				Con	488
711	350	0	1.32 ± 0.30				Con	488
711	400	0	1.07 ± 0.46				Con	488
799	150	0	4.04 ± 0.20				Con	488
799	200	0	3.07 ± 0.10				Con	488
799	250	0	2.44 ± 0.10				Con	488
799	300	0	2.02 ± 0.13				Con	488
799	350	0	1.69 ± 0.18				Con	488
799	400	0	1.45 ± 0.25				Con	488
				$Rb^+ + Cl^- = RbCl(aq)$				
409	50	0	1.62 ± 0.22				Con	488
409	100	0	1.22 ± 0.34				Con	488
409	150	0	1.05 ± 0.44				Con	488
409	200	0	0.86 ± 0.60				Con	488
448	50	0	2.46 ± 0.11				Con	488
448	100	0	1.45 ± 0.25				Con	488
448	150	0	1.25 ± 0.32				Con	488
448	200	0	1.06 ± 0.42				Con	488
448	250	0	0.82 ± 0.67				Con	488
547	100	0	2.57 ± 0.10				Con	488
547	150	0	1.86 ± 0.15				Con	488
547	200	0	1.56 ± 0.20				Con	488
547	250	0	1.36 ± 0.26				Con	488
547	300	0	1.23 ± 0.32				Con	488
547	350	0	1.18 ± 0.34				Con	488
547	400	0	1.14 ± 0.35				Con	488
602	100	0	3.30 ± 0.11				Con	488
602	150	0	2.23 ± 0.11				Con	488
602	200	0	1.80 ± 0.15				Con	488
602	250	0	1.52 ± 0.22				Con	488
602	300	0	1.31 ± 0.29				Con	488
602	350	0	1.18 ± 0.35				Con	488
602	400	0	1.08 ± 0.42				Con	488
697	100	0	4.92 ± 0.53				Con	488
697	150	0	3.17 ± 0.10				Con	488
697	200	0	2.43 ± 0.10				Con	488
697	250	0	2.03 ± 0.12				Con	488
697	300	0	1.78 ± 0.15				Con	488
697	350	0	1.63 ± 0.18				Con	488
697	400	0	1.53 ± 0.26				Con	488
793	150	0	3.94 ± 0.17				Con	488

Table 1 (Continued)

T, °C	P, MPa[a]	I, mol/kg[b]	log K[c]	ΔH, kJ/mol[c]	ΔS, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
793	200	0	3.02 ± 0.10				Con	488
793	250	0	2.42 ± 0.10				Con	488
793	300	0	2.05 ± 0.12				Con	488
793	350	0	1.79 ± 0.16				Con	488
793	400	0	1.63 ± 0.18				Con	488
				$Cs^+ + Cl^- = CsCl(aq)$				
400	50	0	1.41 ± 0.28				Con	488
400	100	0	1.20 ± 0.34				Con	488
400	150	0	1.12 ± 0.37				Con	488
400	200	0	1.07 ± 0.40				Con	488
400	250	0	1.04 ± 0.41				Con	488
447	50	0	2.44 ± 0.11				Con	488
447	100	0	1.54 ± 0.22				Con	488
447	150	0	1.36 ± 0.26				Con	488
447	200	0	1.24 ± 0.30				Con	488
447	250	0	1.15 ± 0.34				Con	488
447	300	0	1.13 ± 0.35				Con	488
447	350	0	1.11 ± 0.36				Con	488
512	100	0	2.03 ± 0.13				Con	488
512	150	0	1.57 ± 0.20				Con	488
512	200	0	1.37 ± 0.26				Con	488
512	250	0	1.24 ± 0.31				Con	488
512	300	0	1.16 ± 0.34				Con	488
512	350	0	1.16 ± 0.34				Con	488
512	400	0	1.15 ± 0.34				Con	488
599	100	0	3.29 ± 0.11				Con	488
599	150	0	2.25 ± 0.11				Con	488
599	200	0	1.85 ± 0.14				Con	488
599	250	0	1.65 ± 0.18				Con	488
599	300	0	1.53 ± 0.20				Con	488
599	350	0	1.45 ± 0.22				Con	488
599	400	0	1.42 ± 0.22				Con	488
648	100	0	4.13 ± 0.20				Con	488
648	150	0	2.69 ± 0.09				Con	488
648	200	0	2.13 ± 0.11				Con	488
648	250	0	1.85 ± 0.14				Con	488
648	300	0	1.68 ± 0.17				Con	488
648	350	0	1.58 ± 0.19				Con	488
648	400	0	1.53 ± 0.20				Con	488
700	100	0	4.63 ± 0.37				Con	488
700	150	0	3.09 ± 0.10				Con	488
700	200	0	2.33 ± 0.10				Con	488
700	250	0	1.93 ± 0.13				Con	488
700	300	0	1.69 ± 0.17				Con	488
700	350	0	1.54 ± 0.20				Con	488
700	400	0	1.46 ± 0.22				Con	488
796	150	0	3.86 ± 0.16				Con	488
796	200	0	2.97 ± 0.09				Con	488
796	250	0	2.45 ± 0.10				Con	488
796	300	0	2.11 ± 0.12				Con	488
796	350	0	1.87 ± 0.14				Con	488
796	400	0	1.72 ± 0.16				Con	488
				$Ag^+ + Cl^- = AgCl(aq)$				
100	Sat	0	2.79				Sol	209
100	Sat	0	2.81	-9.33	28.8		Sol	216
100	Sat	0	2.88	-5.9	39		Sol	197
120	Sat	0	2.81	-10.33	27.4		Sol	216
140	Sat	0	2.71	-11.42	24.2		Sol	216
150	Sat	0	2.65				Sol	209
150	Sat	0	2.88	0	55		Sol	197
160	Sat	0	2.63	-12.59	21.3		Sol	216
200	Sat	0	2.59				Sol	209
200	Sat	0	2.87	2.0	59		Sol	197
250	Sat	0	2.63				Sol	209
250	Sat	0	3.07	36.6	130		Sol	197
300	Sat	0	2.78				Sol	209
300	Sat	0	3.52	73.6	200		Sol	197
350	Sat	0	3.05				Sol	209
350	Sat	0	4.21	121	280		Sol	197
				$Ag^+ + 2Cl^- = AgCl_2$				
100	Sat	0	4.57	-14.1	49.6		Sol	216
100	Sat	0	4.66				Sol	209
120	Sat	0	4.55	-15.7	47.2		Sol	216
140	Sat	0	4.48	-17.3	43.8		Sol	216
150	Sat	0	4.54				Sol	209

Table 1 (Continued)

T, °C	P, MPa[a]	I, mol/kg[b]	log K[c]	ΔH, kJ/mol[c]	ΔS, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
160	Sat	0	4.58	-19.0	43.8		Sol	216
200	Sat	0	4.54				Sol	209
250	Sat	0	4.65				Sol	209
300	Sat	0	4.89				Sol	209
350	Sat	0	5.27				Sol	209
$Ag^+ + 3Cl^- = AgCl_3^{2}$								
100	Sat	0	4.01				Sol	209
100	Sat	0	4.87	-2.68	86.1		Sol	216
120	Sat	0	4.70	-2.97	82.5		Sol	216
140	Sat	0	4.95	-3.26	86.9		Sol	216
150	Sat	0	3.66				Sol	209
200	Sat	0	3.46				Sol	209
$AgCl(aq) + Cl^- = AgCl_2$								
100	Sat	0	1.58	-1.6	26		Sol	197
150	Sat	0	1.57	3.8	38		Sol	197
200	Sat	0	1.93	0.3	58		Sol	197
250	Sat	0	1.77	4.8	43		Sol	197
300	Sat	0	1.89	29.8	88		Sol	197
350	Sat	0	2.89	77.9	170		Sol	197
$AgCl_2 + Cl^- = AgCl_3^{2}$								
100	Sat	0	-0.61	-12.2	-44		Sol	197
150	Sat	0	-0.72	-9.6	-36		Sol	197
200	Sat	0	-0.89	-3.6	-50		Sol	197
$Mg^{2+} + Cl^- = MgCl^+$								
250	10.3	0	1.86	72.7	175	549	Cal	438
275	11.0	0	2.22	89.6	206	1879	Cal	438
300	11.0	0	2.65	120.4	261	1751	Cal	438
325	13.2	0	3.17	182.6	366	4608	Cal	438
400	50	0	4.08				Con	180
400	100	0	2.65				Con	180
400	150	0	1.98				Con	180
400	200	0	1.91				Con	180
400	300	0	1.01				Con	180
400	400	0	0.60				Con	180
450	50	0	7.34				Con	180
450	100	0	3.94				Con	180
450	150	0	2.39				Con	180
450	200	0	2.45				Con	180
450	300	0	1.75				Con	180
450	400	0	1.26				Con	180
500	50	0	11.09				Con	180
500	100	0	5.43				Con	180
500	150	0	4.04				Con	180
500	200	0	3.32				Con	180
500	300	0	2.46				Con	180
500	400	0	1.90				Con	180
550	50	0	13.53				Con	180
550	100	0	7.07				Con	180
550	150	0	5.14				Con	180
550	200	0	4.21				Con	180
550	300	0	3.15				Con	180
550	400	0	2.51				Con	180
600	50	0	15.18				Con	180
600	100	0	8.64				Con	180
600	150	0	6.24				Con	180
600	200	0	5.10				Con	180
600	300	0	3.84				Con	180
600	400	0	3.09				Con	180
$Ca^{2+} + Cl^- = CaCl^+$								
250	10.3	0	1.85	82	192	388	Cal	438
275	11.0	0	2.24	94	214	618	Cal	438
300	11.0	0	2.67	115	252	1226	Cal	438
325	13.2	0	3.15	159	326	3219	Cal	438
400	50	0	4.14				Con	180
400	100	0	2.92				Con	180
400	150	0	2.35				Con	180
400	200	0	2.01				Con	180
400	300	0	1.53				Con	180
400	400	0	1.17				Con	180
450	50	0	6.94				Con	180
450	100	0	4.04				Con	180
450	150	0	3.23				Con	180
450	200	0	2.77				Con	180
450	300	0	2.17				Con	180

Table 1 (Continued)

T, °C	P, MPa[a]	I, mol/kg[b]	log K[c]	ΔH, kJ/mol[c]	ΔS, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
450	400	0	1.76				Con	180
500	50	0	10.15				Con	180
500	100	0	5.33				Con	180
500	150	0	4.14				Con	180
500	200	0	3.53				Con	180
500	300	0	2.80				Con	180
500	400	0	2.32				Con	180
550	50	0	12.25				Con	180
550	100	0	6.74				Con	180
550	150	0	5.10				Con	180
550	200	0	4.30				Con	180
550	300	0	3.41				Con	180
550	400	0	2.86				Con	180
600	50	0	13.66				Con	180
600	100	0	8.10				Con	180
600	150	0	6.05				Con	180
600	200	0	5.08				Con	180
600	300	0	4.00				Con	180
600	400	0	3.37				Con	180
$CaCl^+ + Cl^- = CaCl_2(aq)$								
400	50	0	1.92				Con	180
400	100	0	1.17				Con	180
400	150	0	0.82				Con	180
400	200	0	0.61				Con	180
400	300	0	0.31				Con	180
400	400	0	0.09				Con	180
450	50	0	3.70				Con	180
450	100	0	1.91				Con	180
450	150	0	1.41				Con	180
450	200	0	1.13				Con	180
450	300	0	0.76				Con	180
450	400	0	0.51				Con	180
500	50	0	5.73				Con	180
500	100	0	2.75				Con	180
500	150	0	2.02				Con	180
500	200	0	1.64				Con	180
500	300	0	1.19				Con	180
500	400	0	0.89				Con	180
550	50	0	7.07				Con	180
550	100	0	3.66				Con	180
550	150	0	2.65				Con	180
550	200	0	2.16				Con	180
550	300	0	1.60				Con	180
550	400	0	1.26				Con	180
600	50	0	7.98				Con	180
600	100	0	4.54				Con	180
600	150	0	3.27				Con	180
600	200	0	2.67				Con	180
600	300	0	2.00				Con	180
600	400	0	1.61				Con	180
$Mn^{2+} + Cl^- = MnCl^+$								
100	Sat	0	1.20 ± 0.02				ESR	281
120	Sat	0	1.57 ± 0.03				ESR	281
140	Sat	0	1.94 ± 0.03				ESR	281
170	Sat	0	2.30 ± 0.04				ESR	281
$Fe^{2+} + Cl^- = FeCl^+$								
100	Sat	0	0.21	18.6	54		UV	275
100	Sat	0	0.266	18.3	54	1900	Fit	308
150	Sat	0	0.648	28.5	80	2200	Fit	308
150	Sat	0	0.66	30.0	83		UV	275
200	Sat	0	0.67 ± 1.0				Sol	215
200	Sat	0	1.09	40.0	106	2400	Fit	308
200	Sat	0	1.10	43.1	112		UV	275
200	Sat	0	1.6				Sol	214
250	Sat	0	1.0 ± 1.0				Sol	215
250	Sat	0	1.58	52.8	131	2700	Fit	308
250	Sat	0	2.3				Sol	214
300	Sat	0	1.2 ± 1.0				Sol	215
300	Sat	0	2.10	66.9	157	2900	Fit	308
300	Sat	0	2.3				Sol	214
350	Sat	0	1.8 ± 1.0				Sol	215
$Pb^{2+} + Cl^- = PbCl^+$								
100	Sat	0	1.69	16.4	76	230	UV	274
100	Sat	0	1.84 ± 0.08	23.2 ± 7.9	97.5 ± 20.9		UV	276

Table 1 (Continued)

T, °C	P, MPa[a]	I, mol/kg[b]	log K[c]	ΔH, kJ/mol[c]	ΔS, J/K·mol[c]	ΔC$_p$, J/K·mol[c]	method[d]	ref
150	Sat	0	2.06	29.9	110	310	UV	274
150	Sat	0	2.23 ± 0.05	42.3 ± 8.4	141.8 ± 20.9		UV	276
200	Sat	0	2.56	47.5	150	400	UV	274
200	Sat	0	2.76 ± 0.06				UV	276
250	Sat	0	3.18	69.7	190	490	UV	274
300	Sat	0	3.89	97.0	240	600	UV	274
$Pb^{2+} + 2Cl^- = PbCl_2(aq)$								
100	Sat	0	2.62 ± 0.05				UV	274
150	Sat	0	3.18 ± 0.02				UV	274
200	Sat	0	4.00 ± 0.03				UV	274
250	Sat	0	4.98 ± 0.08				UV	274
300	Sat	0	6.26 ± 0.05				UV	274
$Pb^{2+} + 3Cl^- = PbCl_3$								
100	Sat	0	2.21 ± 0.05				UV	274
150	Sat	0	2.84 ± 0.05				UV	274
200	Sat	0	3.81 ± 0.05				UV	274
250	Sat	0	5.03 ± 0.10				UV	274
300	Sat	0	6.76 ± 0.06				UV	274
$PbCl^+ + Cl^- = PbCl_2(aq)$								
100	Sat	0	0.86 ± 0.08				UV	276
100	Sat	0	0.92	10.1	45	46	UV	274
150	Sat	0	1.12	15.5	58	180	UV	274
150	Sat	0	1.20 ± 0.16				UV	276
200	Sat	0	1.39	28.2	86	330	UV	274
200	Sat	0	1.86 ± 0.12				UV	276
250	Sat	0	1.79	49.5	130	520	UV	274
300	Sat	0	2.34	81.1	190	740	UV	274
$PbCl_2(aq) + Cl^- = PbCl_3$								
100	Sat	0	-0.49	4.95	3.9	89	UV	274
150	Sat	0	-0.38	7.13	9.5	36	UV	274
200	Sat	0	-0.27	12.3	21	210	UV	274
250	Sat	0	-0.06	31.8	60	610	UV	274
300	Sat	0	0.39	76.9	140	1200	UV	274
$Zn^{2+} + Cl^- = ZnCl^+$								
100	Sat	0	1.83	52.7	180	360	Sol	200
150	Sat	0	2.86	73.6	230	470	Sol	200
200	Sat	0	3.98	100	290	600	Sol	200
250	Sat	0	5.21	134	360	740	Sol	200
300	Sat	0	6.54	175	430	900	Sol	200
350	Sat	0	7.99	224	510	1100	Sol	200
$ZnCl^+ + Cl^- = ZnCl_2(aq)$								
100	Sat	0	0.06	-4.24	-10	81	Sol	200
150	Sat	0	0.04	3.81	9.8	240	Sol	200
200	Sat	0	0.18	19.3	44	380	Sol	200
250	Sat	0	0.49	41.6	89	510	Sol	200
300	Sat	0	0.98	69.9	140	620	Sol	200
350	Sat	0	1.60	104	200	720	Sol	200
$ZnCl_2(aq) + Cl^- = ZnCl_3$								
100	Sat	0	-0.59	-9.72	-35	-110	Sol	200
150	Sat	0	-0.81	-20.0	-63	-340	Sol	200
200	Sat	0	-1.20	-42.4	-110	-560	Sol	200
$ZnCl_3 + Cl^- = ZnCl_4^{2}$								
100	Sat	0	0.82	8.65	39	-200	Sol	200
150	Sat	0	0.85	14.1	52	450	Sol	200
200	Sat	0	1.37	56.2	140	1300	Sol	200
$Na^+ + Br^- = NaBr(aq)$								
399	50	0	1.28 ± 0.37				Con	488
399	100	0	0.93 ± 0.60				Con	488
399	150	0	0.66 ± 0.97				Con	488
441	50	0	2.24 ± 0.13				Con	488
441	100	0	1.33 ± 0.31				Con	488
441	150	0	1.07 ± 0.45				Con	488
441	200	0	0.82 ± 0.70				Con	488
501	100	0	1.92 ± 0.15				Con	488
501	150	0	1.41 ± 0.27				Con	488
501	200	0	1.16 ± 0.39				Con	488
501	250	0	0.97 ± 0.54				Con	488
501	300	0	0.84 ± 0.67				Con	488
557	100	0	2.72 ± 0.10				Con	488
557	150	0	1.86 ± 0.15				Con	488
557	200	0	1.45 ± 0.25				Con	488
557	250	0	1.24 ± 0.34				Con	488

Table 1 (Continued)

T, °C	P, MPa[a]	I, mol/kg[b]	log K[c]	ΔH, kJ/mol[c]	ΔS, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
557	300	0	1.02 ± 0.49				Con	488
557	350	0	0.88 ± 0.62				Con	488
557	400	0	0.76 ± 0.77				Con	488
600	100	0	3.28 ± 0.11				Con	488
600	150	0	2.14 ± 0.12				Con	488
600	200	0	1.65 ± 0.20				Con	488
600	250	0	1.29 ± 0.32				Con	488
600	300	0	0.99 ± 0.55				Con	488
600	350	0	0.76 ± 0.83				Con	488
698	100	0	4.78 ± 0.45				Con	488
698	150	0	3.16 ± 0.10				Con	488
698	200	0	2.38 ± 0.10				Con	488
698	250	0	1.93 ± 0.14				Con	488
698	300	0	1.62 ± 0.20				Con	488
698	350	0	1.38 ± 0.28				Con	488
698	400	0	1.18 ± 0.38				Con	488
809	150	0	4.26 ± 0.25				Con	488
809	200	0	3.26 ± 0.11				Con	488
809	250	0	2.61 ± 0.10				Con	488
809	300	0	2.19 ± 0.12				Con	488
809	350	0	1.87 ± 0.15				Con	488
809	400	0	1.63 ± 0.19				Con	488
				$K^+ + Br^- = KBr(aq)$				
402	50	0	1.24 ± 0.40				Con	488
402	100	0	0.85 ± 0.70				Con	488
447	50	0	2.35 ± 0.12				Con	488
447	100	0	1.25 ± 0.36				Con	488
447	150	0	1.08 ± 0.44				Con	488
447	200	0	0.85 ± 0.65				Con	488
503	100	0	1.87 ± 0.16				Con	488
503	150	0	1.35 ± 0.29				Con	488
503	200	0	1.04 ± 0.48				Con	488
503	250	0	0.78 ± 0.78				Con	488
596	100	0	3.16 ± 0.14				Con	488
596	150	0	2.08 ± 0.13				Con	488
596	200	0	1.61 ± 0.20				Con	488
596	250	0	1.38 ± 0.28				Con	488
596	300	0	1.09 ± 0.44				Con	488
596	350	0	0.90 ± 0.57				Con	488
596	400	0	0.82 ± 0.70				Con	488
692	100	0	4.61 ± 0.38				Con	488
692	150	0	2.97 ± 0.10				Con	488
692	200	0	2.23 ± 0.11				Con	488
692	250	0	1.79 ± 0.16				Con	488
692	300	0	1.50 ± 0.24				Con	488
692	350	0	1.26 ± 0.33				Con	488
692	400	0	1.05 ± 0.48				Con	488
798	150	0	3.88 ± 0.18				Con	488
798	200	0	2.89 ± 0.10				Con	488
798	250	0	2.28 ± 0.11				Con	488
798	300	0	1.88 ± 0.15				Con	488
798	350	0	1.54 ± 0.23				Con	488
798	400	0	1.24 ± 0.37				Con	488
				$Rb^+ + Br^- = RbBr(aq)$				
401	50	0	1.36 ± 0.32				Con	488
401	100	0	0.94 ± 0.57				Con	488
454	50	0	2.52 ± 0.11				Con	488
454	100	0	1.31 ± 0.33				Con	488
454	150	0	1.10 ± 0.43				Con	488
454	200	0	0.90 ± 0.59				Con	488
494	100	0	1.73 ± 0.19				Con	488
494	150	0	1.38 ± 0.27				Con	488
494	200	0	1.17 ± 0.37				Con	488
494	250	0	1.04 ± 0.45				Con	488
494	300	0	0.97 ± 0.50				Con	488
494	350	0	0.90 ± 0.57				Con	488
494	400	0	0.86 ± 0.60				Con	488
546	100	0	2.45 ± 0.10				Con	488
546	150	0	1.76 ± 0.17				Con	488
546	200	0	1.47 ± 0.24				Con	488
546	250	0	1.30 ± 0.29				Con	488
546	300	0	1.19 ± 0.34				Con	488
546	350	0	1.15 ± 0.36				Con	488
546	400	0	1.11 ± 0.38				Con	488
617	100	0	3.40 ± 0.12				Con	488

Table 1 (Continued)

T, °C	P, MPa[a]	I, mol/kg[b]	log K[c]	ΔH, kJ/mol[c]	ΔS, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
617	150	0	2.26 ± 0.11				Con	488
617	200	0	1.78 ± 0.16				Con	488
617	250	0	1.47 ± 0.24				Con	488
617	300	0	1.24 ± 0.34				Con	488
617	350	0	1.10 ± 0.42				Con	488
617	400	0	1.07 ± 0.43				Con	488
650	100	0	3.93 ± 0.18				Con	488
650	150	0	2.55 ± 0.10				Con	488
650	200	0	2.01 ± 0.13				Con	488
650	250	0	1.67 ± 0.18				Con	488
650	300	0	1.46 ± 0.24				Con	488
650	350	0	1.29 ± 0.30				Con	488
650	400	0	1.20 ± 0.34				Con	488
709	100	0	4.43 ± 0.31				Con	488
709	150	0	3.05 ± 0.10				Con	488
709	200	0	2.33 ± 0.11				Con	488
709	250	0	1.89 ± 0.15				Con	488
709	300	0	1.59 ± 0.20				Con	488
709	350	0	1.38 ± 0.27				Con	488
709	400	0	1.26 ± 0.33				Con	488
742	150	0	3.38 ± 0.12				Con	488
742	200	0	2.55 ± 0.10				Con	488
742	250	0	2.09 ± 0.12				Con	488
742	300	0	1.78 ± 0.17				Con	488
742	350	0	1.54 ± 0.22				Con	488
742	400	0	1.33 ± 0.29				Con	488
809	150	0	3.84 ± 0.17				Con	488
809	200	0	2.90 ± 0.10				Con	488
809	250	0	2.37 ± 0.11				Con	488
809	300	0	1.98 ± 0.14				Con	488
809	350	0	1.69 ± 0.18				Con	488
809	400	0	1.51 ± 0.23				Con	488
				$Cs^+ + Br^- = CsBr(aq)$				
414	50	0	1.62 ± 0.22				Con	488
414	100	0	1.32 ± 0.29				Con	488
414	150	0	1.23 ± 0.31				Con	488
414	200	0	1.12 ± 0.36				Con	488
414	250	0	1.10 ± 0.37				Con	488
414	300	0	1.08 ± 0.38				Con	488
462	50	0	3.01 ± 0.10				Con	488
462	100	0	1.54 ± 0.23				Con	488
462	150	0	1.40 ± 0.25				Con	488
462	200	0	1.28 ± 0.29				Con	488
462	250	0	1.21 ± 0.31				Con	488
462	300	0	1.20 ± 0.31				Con	488
509	50	0	4.72 ± 0.43				Con	488
509	100	0	1.98 ± 0.14				Con	488
509	150	0	1.57 ± 0.20				Con	488
509	200	0	1.38 ± 0.26				Con	488
509	250	0	1.26 ± 0.30				Con	488
509	300	0	1.21 ± 0.31				Con	488
632	100	0	3.58 ± 0.13				Con	488
632	150	0	2.40 ± 0.10				Con	488
632	200	0	1.92 ± 0.14				Con	488
632	250	0	1.68 ± 0.17				Con	488
632	300	0	1.51 ± 0.21				Con	488
632	350	0	1.42 ± 0.24				Con	488
632	400	0	1.38 ± 0.24				Con	488
712	100	0	4.58 ± 0.36				Con	488
712	150	0	3.00 ± 0.10				Con	488
712	200	0	2.23 ± 0.12				Con	488
712	250	0	1.78 ± 0.17				Con	488
712	300	0	1.49 ± 0.25				Con	488
813	150	0	3.80 ± 0.15				Con	488
813	200	0	2.91 ± 0.10				Con	488
813	250	0	2.38 ± 0.10				Con	488
813	300	0	2.01 ± 0.13				Con	488
813	350	0	1.73 ± 0.17				Con	488
813	400	0	1.55 ± 0.21				Con	488
				$Na^+ + I^- = NaI(aq)$				
406	50	0	1.12 ± 0.53				Con	488
406	100	0	1.03 ± 0.50				Con	488
406	150	0	0.86 ± 0.65				Con	488
406	200	0	0.78 ± 0.74				Con	488
457	50	0	2.57 ± 0.12				Con	488

Table 1 (Continued)

T, °C	P, MPa[a]	I, mol/kg[b]	log K[c]	ΔH, kJ/mol[c]	ΔS, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
457	100	0	1.23 ± 0.39				Con	488
457	150	0	1.00 ± 0.53				Con	488
457	200	0	0.87 ± 0.65				Con	488
457	250	0	0.77 ± 0.77				Con	488
508	100	0	1.95 ± 0.19				Con	488
508	150	0	1.33 ± 0.32				Con	488
508	200	0	1.10 ± 0.44				Con	488
508	250	0	0.94 ± 0.57				Con	488
508	300	0	0.86 ± 0.66				Con	488
508	350	0	0.78 ± 0.75				Con	488
605	100	0	3.12 ± 0.11				Con	488
605	150	0	1.97 ± 0.15				Con	488
605	200	0	1.47 ± 0.26				Con	488
605	250	0	1.16 ± 0.42				Con	488
605	300	0	0.98 ± 0.56				Con	488
605	350	0	0.70 ± 0.94				Con	488
702	100	0	4.69 ± 0.41				Con	488
702	150	0	2.92 ± 0.10				Con	488
702	200	0	2.13 ± 0.13				Con	488
702	250	0	1.67 ± 0.20				Con	488
702	300	0	1.36 ± 0.30				Con	488
702	350	0	1.07 ± 0.49				Con	488
702	400	0	0.85 ± 0.73				Con	488
796	150	0	3.79 ± 0.16				Con	488
796	200	0	2.80 ± 0.10				Con	488
796	250	0	2.21 ± 0.12				Con	488
796	300	0	1.83 ± 0.17				Con	488
796	350	0	1.51 ± 0.24				Con	488
796	400	0	1.27 ± 0.35				Con	488
				$K^+ + I^- = KI(aq)$				
404	50	0	0.96 ± 0.51				Con	488
404	100	0	0.83 ± 0.74				Con	488
446	50	0	2.18 ± 0.14				Con	488
446	100	0	1.19 ± 0.41				Con	488
446	150	0	0.98 ± 0.54				Con	488
446	200	0	0.82 ± 0.70				Con	488
503	100	0	1.72 ± 0.20				Con	488
503	150	0	1.26 ± 0.35				Con	488
503	200	0	1.08 ± 0.45				Con	488
503	250	0	0.92 ± 0.59				Con	488
503	300	0	0.73 ± 0.85				Con	488
543	100	0	2.15 ± 0.13				Con	488
543	150	0	1.47 ± 0.26				Con	488
543	200	0	1.16 ± 0.41				Con	488
543	250	0	0.97 ± 0.56				Con	488
543	300	0	0.82 ± 0.72				Con	488
647	100	0	3.67 ± 0.15				Con	488
647	150	0	2.36 ± 0.11				Con	488
647	200	0	1.76 ± 0.18				Con	488
647	250	0	1.41 ± 0.28				Con	488
647	300	0	1.14 ± 0.42				Con	488
647	350	0	0.93 ± 0.61				Con	488
647	400	0	0.78 ± 0.80				Con	488
711	100	0	4.54 ± 0.37				Con	488
711	150	0	2.89 ± 0.10				Con	488
711	200	0	2.18 ± 0.12				Con	488
711	250	0	1.68 ± 0.20				Con	488
711	300	0	1.31 ± 0.33				Con	488
711	350	0	0.93 ± 0.65				Con	488
744	150	0	3.14 ± 0.11				Con	488
744	200	0	2.31 ± 0.12				Con	488
744	250	0	1.79 ± 0.18				Con	488
744	300	0	1.44 ± 0.28				Con	488
744	350	0	1.08 ± 0.50				Con	488
744	400	0	0.80 ± 0.84				Con	488
803	150	0	3.64 ± 0.15				Con	488
803	200	0	2.69 ± 0.10				Con	488
803	250	0	2.09 ± 0.13				Con	488
803	300	0	1.67 ± 0.21				Con	488
803	350	0	1.24 ± 0.39				Con	488
				$Rb^+ + I^- = RbI(aq)$				
348	50	0	0.96 ± 0.55				Con	488
348	100	0	0.80 ± 0.71				Con	488
401	50	0	1.23 ± 0.40				Con	488
401	100	0	1.05 ± 0.46				Con	488

Table 1 (Continued)

T, °C	P, MPa[a]	I, mol/kg[b]	log K[c]	ΔH, kJ/mol[c]	ΔS, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
401	150	0	0.97 ± 0.51				Con	488
401	200	0	0.86 ± 0.61				Con	488
401	250	0	0.83 ± 0.63				Con	488
401	300	0	0.79 ± 0.67				Con	488
447	50	0	2.37 ± 0.12				Con	488
447	100	0	1.32 ± 0.32				Con	488
447	150	0	1.20 ± 0.35				Con	488
447	200	0	1.08 ± 0.41				Con	488
447	250	0	1.04 ± 0.44				Con	488
447	300	0	1.00 ± 0.47				Con	488
447	350	0	0.96 ± 0.49				Con	488
503	100	0	1.62 ± 0.22				Con	488
503	150	0	1.19 ± 0.39				Con	488
503	200	0	1.05 ± 0.47				Con	488
503	250	0	0.97 ± 0.52				Con	488
503	300	0	0.96 ± 0.52				Con	488
503	350	0	0.91 ± 0.55				Con	488
503	400	0	0.90 ± 0.56				Con	488
547	100	0	2.18 ± 0.13				Con	488
547	150	0	1.53 ± 0.24				Con	488
547	200	0	1.24 ± 0.35				Con	488
547	250	0	1.08 ± 0.44				Con	488
547	300	0	0.98 ± 0.51				Con	488
547	350	0	0.91 ± 0.57				Con	488
547	400	0	0.90 ± 0.57				Con	488
598	100	0	2.96 ± 0.10				Con	488
598	150	0	1.95 ± 0.15				Con	488
598	200	0	1.57 ± 0.22				Con	488
598	250	0	1.34 ± 0.29				Con	488
598	300	0	1.23 ± 0.34				Con	488
598	350	0	1.13 ± 0.39				Con	488
598	400	0	1.10 ± 0.40				Con	488
641	100	0	3.44 ± 0.12				Con	488
641	150	0	2.24 ± 0.12				Con	488
641	200	0	1.69 ± 0.19				Con	488
641	250	0	1.36 ± 0.30				Con	488
641	300	0	1.16 ± 0.40				Con	488
641	350	0	1.01 ± 0.50				Con	488
641	400	0	0.99 ± 0.51				Con	488
700	150	0	2.73 ± 0.10				Con	488
700	200	0	1.99 ± 0.14				Con	488
700	250	0	1.54 ± 0.23				Con	488
700	300	0	1.20 ± 0.39				Con	488
700	350	0	0.81 ± 0.81				Con	488
700	400	0	0.73 ± 0.92				Con	488
802	150	0	3.51 ± 0.13				Con	488
802	200	0	2.63 ± 0.10				Con	488
802	250	0	2.04 ± 0.14				Con	488
802	300	0	1.64 ± 0.21				Con	488
802	350	0	1.31 ± 0.33				Con	488
802	400	0	1.06 ± 0.51				Con	488
				$Cs^+ + I^- = CsI(aq)$				
401	50	0	1.27 ± 0.37				Con	488
401	100	0	1.17 ± 0.37				Con	488
401	150	0	1.15 ± 0.36				Con	488
401	200	0	1.10 ± 0.38				Con	488
401	250	0	1.06 ± 0.39				Con	488
448	50	0	2.29 ± 0.13				Con	488
448	100	0	1.43 ± 0.26				Con	488
448	150	0	1.23 ± 0.33				Con	488
448	200	0	1.15 ± 0.36				Con	488
448	250	0	1.11 ± 0.37				Con	488
448	300	0	1.10 ± 0.37				Con	488
503	100	0	1.82 ± 0.17				Con	488
503	150	0	1.45 ± 0.25				Con	488
503	200	0	1.36 ± 0.26				Con	488
503	250	0	1.30 ± 0.28				Con	488
503	300	0	1.27 ± 0.29				Con	488
503	350	0	1.24 ± 0.30				Con	488
503	400	0	1.21 ± 0.31				Con	488
607	100	0	3.11 ± 0.10				Con	488
607	150	0	2.07 ± 0.13				Con	488
607	200	0	1.67 ± 0.19				Con	488
607	250	0	1.45 ± 0.24				Con	488
607	300	0	1.32 ± 0.29				Con	488

Table 1 (Continued)

T, °C	P, MPa[a]	I, mol/kg[b]	log K[c]	ΔH, kJ/mol[c]	ΔS, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
607	350	0	1.27 ± 0.30				Con	488
607	400	0	1.26 ± 0.30				Con	488
661	100	0	3.80 ± 0.16				Con	488
661	150	0	2.50 ± 0.10				Con	488
661	200	0	1.96 ± 0.14				Con	488
661	250	0	1.65 ± 0.19				Con	488
661	300	0	1.47 ± 0.23				Con	488
661	350	0	1.36 ± 0.27				Con	488
661	400	0	1.33 ± 0.27				Con	488
708	100	0	4.32 ± 0.27				Con	488
708	150	0	2.92 ± 0.10				Con	488
708	200	0	2.24 ± 0.11				Con	488
708	250	0	1.87 ± 0.15				Con	488
708	300	0	1.62 ± 0.19				Con	488
708	350	0	1.47 ± 0.23				Con	488
708	400	0	1.41 ± 0.25				Con	488
762	100	0	4.95 ± 0.59				Con	488
762	150	0	3.26 ± 0.11				Con	488
762	200	0	2.47 ± 0.10				Con	488
762	250	0	2.04 ± 0.13				Con	488
762	300	0	1.72 ± 0.18				Con	488
762	350	0	1.52 ± 0.23				Con	488
762	400	0	1.38 ± 0.27				Con	488
798	150	0	3.51 ± 0.13				Con	488
798	200	0	2.66 ± 0.10				Con	488
798	250	0	2.18 ± 0.12				Con	488
798	300	0	1.85 ± 0.15				Con	488
798	350	0	1.62 ± 0.20				Con	488
798	400	0	1.43 ± 0.26				Con	488
				$H^+ + HS^- = H_2S(aq)$				
109	Sat	0	6.63				UV	271
167	Sat	0	6.92				UV	271
228	Sat	0	7.44				UV	271
276	Sat	0	7.82				UV	271
				$H^+ + SO_4^{2-} = HSO_4^-$				
100	Sat	0	2.855	34.8	148	259	Sol	222
100	Sat	0	2.987	38.23	159.8		Sol	225
100	Sat	0	2.99	38.3			Fit	245
100	Sat	0	3.061 ± 0.008	40.0 ± 0.3	165.9 ± 0.8	210.1 ± 9.5	Pot	297
100	Sat	0	3.08	38.7	163	200	Pot	312
100	Sat	0.1 (NaCl)	2.504 ± 0.006	36.3 ± 0.3	145.1 ± 0.8	164.0 ± 9.5	Pot	297
100	Sat	0.5 (NaCl)	2.135 ± 0.004	33.4 ± 0.3	130.5 ± 0.7	127.6 ± 9.4	Pot	297
100	Sat	1.0 (NaCl)	1.972 ± 0.004	31.7 ± 0.3	122.6 ± 0.6	107.4 ± 9.4	Pot	297
100	Sat	3.0 (NaCl)	1.775 ± 0.006	27.2 ± 0.3	106.9 ± 0.7	68.9 ± 9.3	Pot	297
100	Sat	5.0 (NaCl)	1.730 ± 0.005	24.2 ± 0.3	97.9 ± 0.7	48.1 ± 9.3	Pot	297
100	10	0.655	1.91	44.9			Ram	245
100	10	1.32	1.46	36.2			Ram	245
100	10	2.01	1.47				Ram	245
100	10	3.09	1.29	37.7			Ram	245
100	10	4.10	1.07	37.2			Ram	245
100	10	5.05	1.01				Ram	245
100	10	5.23	0.81				Ram	245
100	10	5.88	0.95				Ram	245
100	10	7.23	0.77				Ram	245
125	Sat	0	3.352	44.98	177.4		Sol	225
125	Sat	0	3.436 ± 0.007	45.4 ± 0.3	179.9 ± 0.9	222.7 ± 8.0	Pot	297
125	Sat	0	3.44	43.9	176	234	Pot	312
125	Sat	0.1 (NaCl)	2.840 ± 0.005	40.3 ± 0.3	155.7 ± 0.8	163.7 ± 7.9	Pot	297
125	Sat	0.5 (NaCl)	2.442 ± 0.003	36.5 ± 0.2	138.4 ± 0.6	117.1 ± 7.9	Pot	297
125	Sat	1.0 (NaCl)	2.261 ± 0.003	34.1 ± 0.2	129.0 ± 0.5	91.1 ± 7.8	Pot	297
125	Sat	3.0 (NaCl)	2.020 ± 0.005	28.6 ± 0.2	110.5 ± 0.5	41.8 ± 7.8	Pot	297
125	Sat	5.0 (NaCl)	1.946 ± 0.005	25.0 ± 0.2	99.9 ± 0.6	15.4 ± 7.8	Pot	297
150	Sat	0	3.534	48.1	181	272	Sol	222
150	Sat	0	3.728	52.22	194.6		Sol	225
150	Sat	0	3.73	52.2			Fit	245
150	Sat	0	3.809 ± 0.007	51.3 ± 0.4	194.2 ± 1.0	252.3 ± 5.6	Pot	297
150	Sat	0	3.81	50.6	192	287	Pot	312
150	Sat	0.1 (NaCl)	3.167 ± 0.005	44.6 ± 0.4	165.9 ± 0.9	176.7 ± 5.6	Pot	297
150	Sat	0.5 (NaCl)	2.735 ± 0.003	39.4 ± 0.3	145.4 ± 0.7	116.2 ± 5.6	Pot	297
150	Sat	1.0 (NaCl)	2.533 ± 0.003	36.3 ± 0.3	134.2 ± 0.6	82.4 ± 10.1	Pot	297
150	Sat	3.0 (NaCl)	2.244 ± 0.005	29.3 ± 0.3	112.3 ± 0.6	18.3 ± 5.6	Pot	297
150	Sat	5.0 (NaCl)	2.140 ± 0.004	25.0 ± 0.3	99.9 ± 0.7	-16.0 ± 5.6	Pot	297
150	2.31	0	3.56	57.36	204	264	Cal	435
150	10	0.655	2.78	50.9			Ram	245
150	10	1.32	2.15	40.4			Ram	245

Table 1 (Continued)

T, °C	*P*, MPa[a]	*I*, mol/kg[b]	log *K*[c]	Δ*H*, kJ/mol[c]	Δ*S*, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
150	10	2.01	2.18				Ram	245
150	10	3.09	1.86	44.4			Ram	245
150	10	4.10	1.85	47.0			Ram	245
150	10	5.05	1.65				Ram	245
150	10	5.88	1.59				Ram	245
150	10	7.23	1.49				Ram	245
150	10	8.61	1.46				Ram	245
175	Sat	0	4.113	59.87	212.1		Sol	225
175	Sat	0	4.18	58.6	211	361	Pot	312
175	Sat	0	4.182 ± 0.007	58.2 ± 0.4	209.8 ± 1.0	300.8 ± 9.0	Pot	297
175	Sat	0.1 (NaCl)	3.488 ± 0.006	49.2 ± 0.4	176.7 ± 0.9	201.6 ± 9.1	Pot	297
175	Sat	0.5 (NaCl)	3.015 ± 0.004	42.3 ± 0.3	152.1 ± 0.7	121.3 ± 9.1	Pot	297
175	Sat	1.0 (NaCl)	2.788 ± 0.004	38.2 ± 0.3	138.7 ± 0.6	76.1 ± 9.2	Pot	297
175	Sat	3.0 (NaCl)	2.446 ± 0.005	29.5 ± 0.3	112.6 ± 0.7	-9.4 ± 9.3	Pot	297
175	Sat	5.0 (NaCl)	2.309 ± 0.005	24.1 ± 0.3	98.0 ± 0.7	-55.1 ± 9.3	Pot	297
175	2.24	0	3.98	64.97	221	349	Cal	435
200	Sat	0	4.246	61.9	212	280	Sol	222
200	Sat	0	4.506	67.95	229.7		Sol	225
200	Sat	0	4.51	67.9			Fit	245
200	Sat	0	4.561 ± 0.008	66.4 ± 0.4	227.7 ± 1.0	370.4 ± 19.2	Pot	297
200	Sat	0	4.58	68.6	233	452	Pot	312
200	Sat	0.1 (NaCl)	3.804 ± 0.006	54.6 ± 0.4	188.3 ± 0.9	235.8 ± 19.2	Pot	297
200	Sat	0.5 (NaCl)	3.282 ± 0.004	45.4 ± 0.4	158.7 ± 0.8	125.5 ± 19.3	Pot	297
200	Sat	1.0 (NaCl)	3.027 ± 0.004	40.0 ± 0.4	142.4 ± 0.8	63.0 ± 19.4	Pot	297
200	Sat	3.0 (NaCl)	2.624 ± 0.005	28.7 ± 0.4	110.9 ± 0.9	-55.5 ± 19.5	Pot	297
200	Sat	5.0 (NaCl)	2.450 ± 0.005	22.0 ± 0.4	93.4 ± 1.0	-118.7 ± 19.5	Pot	297
200	2.31	0	4.41	75.05	243	462	Cal	435
200	10	0.655	3.54	57.7			Ram	245
200	10	1.32	2.71	45.2			Ram	245
200	10	2.01	2.77				Ram	245
200	10	3.09	2.55	51.9			Ram	245
200	10	4.10	2.35	58.2			Ram	245
200	10	5.05	2.20				Ram	245
200	10	5.23	1.90				Ram	245
200	10	5.88	2.25				Ram	245
200	10	7.23	1.66				Ram	245
200	10	8.61	1.60				Ram	245
225	Sat	0	4.905	76.48	247.3		Sol	225
225	Sat	0	4.951 ± 0.009	76.6 ± 0.9	248.7 ± 1.8	466.7 ± 33.4	Pot	297
225	Sat	0.1 (NaCl)	4.118 ± 0.007	60.9 ± 0.9	201.1 ± 1.8	276.6 ± 33.4	Pot	297
225	Sat	0.5 (NaCl)	3.537 ± 0.005	48.3 ± 0.9	164.8 ± 1.8	118.7 ± 33.5	Pot	297
225	Sat	1.0 (NaCl)	3.248 ± 0.005	41.1 ± 0.9	144.7 ± 1.9	28.5 ± 33.6	Pot	297
225	Sat	3.0 (NaCl)	2.775 ± 0.006	26.3 ± 1.0	106.0 ± 2.0	-142.9 ± 33.7	Pot	297
225	Sat	5.0 (NaCl)	2.560 ± 0.006	17.7 ± 1.0	84.7 ± 2.0	-234.7 ± 33.7	Pot	297
250	Sat	0	4.971	76.1	241	293	Sol	222
250	Sat	0	5.31	85.1			Fit	245
250	Sat	0	5.355 ± 0.012	89.6 ± 1.9	273.7 ± 3.7	606.3 ± 51.1	Pot	297
250	Sat	0.1 (NaCl)	4.432 ± 0.010	68.0 ± 1.9	214.9 ± 3.7	323.2 ± 51.4	Pot	297
250	Sat	0.5 (NaCl)	3.778 ± 0.009	50.7 ± 1.9	169.3 ± 3.8	84.5 ± 51.2	Pot	297
250	Sat	1.0 (NaCl)	3.447 ± 0.009	40.8 ± 1.9	143.9 ± 3.8	-53.0 ± 51.3	Pot	297
250	Sat	3.0 (NaCl)	2.892 ± 0.011	20.8 ± 2.2	95.2 ± 3.9	-316.5 ± 51.4	Pot	297
250	Sat	5.0 (NaCl)	2.629 ± 0.012	9.5 ± 2.0	68.6 ± 4.0	-459.0 ± 51.4	Pot	297
250	10	0.655	4.03	65.3			Ram	245
250	10	1.32	3.17	50.4			Ram	245
250	10	2.01	2.97				Ram	245
250	10	3.09	3.61				Ram	245
250	10	4.10	3.16	70.5			Ram	245
250	10	5.05	2.47				Ram	245
250	10	5.88	2.96				Ram	245
250	10	7.23	2.40				Ram	245
250	10	8.61	2.26				Ram	245
250	10.3	0	5.34	105.03	303	749	Cal	435
300	Sat	0	5.698	91.2	268	305	Sol	222
300	Sat	0	6.13				Fit	245
300	10	1.32	3.30				Ram	245
300	10	3.09	4.28				Ram	245
300	10	4.10	3.29				Ram	245
300	10	5.05	2.94				Ram	245
300	10	5.23	2.92				Ram	245
300	10	5.88	2.94				Ram	245
300	10	7.23	2.25				Ram	245
300	10	8.61	2.40				Ram	245
300	11.0	0	6.44	150.98	387	1097	Cal	435
320	12.8	0	6.94	174.42	427	1248	Cal	435
350	Sat	0	6.421	107.1	295	318	Sol	222

Table 1 (Continued)

T, °C	P, MPa[a]	I, mol/kg[b]	log K[c]	ΔH, kJ/mol[c]	ΔS, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
$Na^+ + SO_4^{2-} = NaSO_4$								
150	2.31	0	0.95	24.68	77	303	Cal	435
175	2.24	0	1.15	32.80	95	347	Cal	435
200	2.31	0	1.38	42.06	115	394	Cal	435
250	10.3	0	1.93	64.12	160	490	Cal	435
300	11.0	0	2.60	91.09	209	589	Cal	435
320	12.8	0	2.90	103.28	230	630	Cal	435
$K^+ + SO_4^{2-} = KSO_4$								
100	Sat	0	0.45				Pot	312
125	Sat	0	0.52				Pot	312
150	Sat	0	0.61				Pot	312
175	Sat	0	0.71				Pot	312
200	Sat	0	0.94				Pot	312
$Ca^{2+} + SO_4^{2-} = CaSO_4(aq)$								
150	Sat	0.513	1.32				Sol	221
150	Sat	2.01	0.86				Sol	221
150	Sat	5.90	0.73				Sol	221
250	Sat	0.505	1.84				Sol	221
250	Sat	2.00	1.22				Sol	221
250	Sat	5.93	0.96				Sol	221
350	Sat	1.99	1.78				Sol	221
350	Sat	5.95	1.36				Sol	221
$Mn^{2+} + SO_4^{2-} = MnSO_4(aq)$								
100	Sat	0	2.86 ± 0.05				ESR	281
120	Sat	0	3.08 ± 0.05				ESR	281
140	Sat	0	3.26 ± 0.09				ESR	281
170	Sat	0	3.76 ± 0.13				ESR	281
$H^+ + NO_3^- = HNO_3(aq)$								
100	Sat	0	-0.57				Sol	219
100	Sat	0	-0.59	29.3	67.4	172	Fit	219
125	Sat	0	-0.29				Sol	219
125	Sat	0	-0.31	33.9	79.1	184	Fit	219
150	Sat	0	-0.04	38.5	90.4	192	Fit	219
150	Sat	0	0.04				Sol	219
200	Sat	0	0.44				Sol	219
200	Sat	0	0.51	49.0	113.4	218	Fit	219
218	Sat	0	0.74	52.7	122	226	Fit	219
250	Sat	0	0.99	66.9	147	795	Fit	218
250	Sat	0	1.00	91.2	193.5	103	Cal	439
250	Sat	0	1.01				Sol	219
250	Sat	0	1.10	60.2	136	238	Fit	219
275	Sat	0	1.35	91.2	192	1130	Fit	218
275	Sat	0	1.42	102.6	214.3	1016	Cal	439
300	Sat	0	1.68	72.8	159	264	Fit	219
300	Sat	0	1.79	125.1	253	1590	Fit	218
300	Sat	0	1.82				Sol	219
300	Sat	0	1.92	152.5	302.8	3421	Cal	439
306	Sat	0	1.75	74.5	162	268	Fit	219
319	Sat	0	2.39	237.9	447.5	8040	Cal	439
325	Sat	0	2.35	171.1	331	2090	Fit	218
350	Sat	0	2.26	86.6	182	285	Fit	219
350	Sat	0	2.52				Sol	219
350	Sat	0	2.70				Sol	219
350	Sat	0	3.05	231.4	431	2720	Fit	218
350	Sat	0	3.22				Sol	219
350	Sat	0	3.34				Sol	219
360	Sat	0	3.37	260.2	477	3010	Fit	218
370	Sat	0	3.73	291.6	523	3305	Fit	218
$H^+ + HPO_4^{2-} = H_2PO_4^-$								
100	50	0	7.14				Ram, Pot	254
100	50	0.302 (NaCl)	6.43 ± 0.06				Ram, Pot	254
100	50	0.504 (NaCl)	6.33 ± 0.04				Ram, Pot	254
100	50	0.761 (NaCl)	6.21 ± 0.05				Ram, Pot	254
100	50	1.020 (NaCl)	6.11 ± 0.04				Ram, Pot	254
100	100	0	7.03				Ram, Pot	254
100	100	0.302 (NaCl)	6.32 ● 0.08				Ram, Pot	254
100	100	0.504 (NaCl)	6.20 ± 0.06				Ram, Pot	254
100	100	0.761 (NaCl)	6.13 ± 0.08				Ram, Pot	254
100	100	1.020 (NaCl)	6.07 ± 0.08				Ram, Pot	254
150	50	0	7.35				Ram, Pot	254
150	50	0.302 (NaCl)	6.52 ± 0.04				Ram, Pot	254
150	50	0.504 (NaCl)	6.39 ± 0.03				Ram, Pot	254
150	50	0.761 (NaCl)	6.27 ± 0.02				Ram, Pot	254

Table 1 (Continued)

T, °C	*P*, MPa[a]	*I*, mol/kg[b]	log *K*[c]	Δ*H*, kJ/mol[c]	Δ*S*, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
150	50	1.020 (NaCl)	6.18 ± 0.01				Ram, Pot	254
150	100	0	7.14				Ram, Pot	254
150	100	0.302 (NaCl)	6.32 ± 0.06				Ram, Pot	254
150	100	0.504 (NaCl)	6.20 ± 0.02				Ram, Pot	254
150	100	0.761 (NaCl)	6.13 ± 0.02				Ram, Pot	254
150	100	1.020 (NaCl)	6.04 ± 0.05				Ram, Pot	254
200	50	0	7.71				Ram, Pot	254
200	50	0.302 (NaCl)	6.72 ± 0.06				Ram, Pot	254
200	50	0.504 (NaCl)	6.55 ± 0.03				Ram, Pot	254
200	50	0.761 (NaCl)	6.42 ± 0.02				Ram, Pot	254
200	50	1.020 (NaCl)	6.31 ± 0.05				Ram, Pot	254
200	100	0	7.40				Ram, Pot	254
200	100	0.302 (NaCl)	6.46 ± 0.08				Ram, Pot	254
200	100	0.504 (NaCl)	6.28 ± 0.07				Ram, Pot	254
200	100	0.761 (NaCl)	6.22 ± 0.08				Ram, Pot	254
200	100	1.020 (NaCl)	6.12 ± 0.05				Ram, Pot	254
			$H^+ + H_2PO_4^- = H_3PO_4(aq)$					
100	0.1	0	2.57	14.0	87	105	Con	190
100	100	0	2.34	12.6	78	61	Con	190
100	200	0	2.15	11.5	72	40	Con	190
125	0.1	0	2.70	17.2	95	154	Con	190
125	Sat	0	2.70				Con	190
125	100	0	2.45	14.8	84	114	Con	190
125	200	0	2.24	13.2	76	100	Con	190
150	0.1	0	2.85	21.7	106	204	Con	190
150	Sat	0	2.84				Con	190
150	100	0	2.58	18.3	92	168	Con	190
150	200	0	2.36	16.5	84	160	Con	190
175	0.1	0	3.02	27.4	119	253	Con	190
175	Sat	0	3.02				Con	190
175	100	0	2.73	23.2	104	221	Con	190
175	200	0	2.51	21.2	95	220	Con	190
200	0.1	0	3.21	34.4	134	302	Con	190
200	Sat	0	3.20				Con	190
200	100	0	2.87	29.4	117	275	Con	190
200	200	0	2.64	27.5	108	280	Con	190
			$H_3PO_4(aq) + OH^- = H_2PO_4^- + H_2O$					
100	Sat	0	9.647 ± 0.015	-59.91 ± 0.75	24.0 ± 2.1	67 ± 21	Pot	295
100	Sat	0.1 (KCl)	9.691 ± 0.015	-59.79 ± 0.75	25.3 ± 2.1	68 ± 17	Pot	295
100	Sat	1.0 (KCl)	9.842 ± 0.018	-60.66 ± 0.92	25.9 ± 2.3	63 ± 21	Pot	295
125	Sat	0	9.127 ± 0.021	-58.31 ± 0.92	28.2 ± 2.6	63 ± 21	Pot	295
125	Sat	0.1 (KCl)	9.172 ± 0.015	-58.13 ± 1.13	29.6 ± 2.3	64 ± 17	Pot	295
125	Sat	1.0 (KCl)	9.315 ± 0.015	-59.12 ± 0.92	29.8 ± 2.1	59 ± 21	Pot	295
150	Sat	0	8.681 ± 0.024	-56.82 ± 1.26	31.8 ± 3.3	54 ± 21	Pot	295
150	Sat	0.1 (KCl)	8.727 ± 0.018	-56.63 ± 1.00	33.3 ± 2.5	55 ± 17	Pot	295
150	Sat	1.0 (KCl)	8.862 ± 0.012	-57.75 ± 0.92	33.2 ± 2.1	50 ± 21	Pot	295
175	Sat	0	8.294 ± 0.030	-55.64 ± 1.46	34.6 ± 3.6	42 ± 21	Pot	295
175	Sat	0.1 (KCl)	8.342 ± 0.021	-55.39 ± 1.13	36.1 ± 2.6	43 ± 17	Pot	295
175	Sat	1.0 (KCl)	8.468 ± 0.012	-56.65 ± 1.00	35.7 ± 2.3	38 ± 21	Pot	295
200	Sat	0	7.954 ± 0.036	-54.77 ± 1.63	36.5 ± 3.9	27 ± 42	Pot	295
200	Sat	0.1 (KCl)	8.004 ± 0.024	-54.50 ± 1.13	38.0 ± 2.6	28 ± 38	Pot	295
200	Sat	1.0 (KCl)	8.122 ± 0.015	-55.90 ± 1.21	37.4 ± 2.6	22 ± 29	Pot	295
225	Sat	0	7.652 ± 0.042	-54.32 ± 2.09	37.4 ± 4.6	9 ± 59	Pot	295
225	Sat	0.1 (KCl)	7.703 ± 0.027	-54.02 ± 1.59	39.0 ± 2.8	10 ± 93	Pot	295
225	Sat	1.0 (KCl)	7.813 ± 0.018	-55.56 ± 1.88	38.0 ± 4.0	4 ± 50	Pot	295
250	Sat	0	7.380 ± 0.048	-54.33 ± 3.14	37.4 ± 6.5	-10 ± 71	Pot	295
250	Sat	0.1 (KCl)	7.433 ± 0.027	-54.00 ± 2.72	39.1 ± 5.4	-9 ± 79	Pot	295
250	Sat	1.0 (KCl)	7.535 ± 0.027	-55.71 ± 3.22	37.8 ± 6.5	-15 ± 75	Pot	295
275	Sat	0	7.131 ± 0.057	-54.85 ± 4.90	36.5 ± 9.6	-31 ± 105	Pot	295
275	Sat	0.1 (KCl)	7.186 ± 0.036	-54.48 ± 4.56	38.2 ± 8.8	-30 ± 105	Pot	295
275	Sat	1.0 (KCl)	7.280 ± 0.042	-56.36 ± 5.19	36.6 ± 10.0	-37 ± 100	Pot	295
300	Sat	0	6.901 ± 0.072	-55.91 ± 7.32	34.6 ± 13.8	-54 ± 126	Pot	295
300	Sat	0.1 (KCl)	6.958 ± 0.051	-55.51 ± 7.03	36.4 ± 13.4	-52 ± 126	Pot	295
300	Sat	1.0 (KCl)	7.043 ± 0.066	-57.56 ± 7.95	38.6 ± 15.1	-59 ± 126	Pot	295
			$H_2PO_4^- + OH^- = HPO_4^{2-} + H_2O$					
100	Sat	0	4.933 ± 0.012	-52.65 ± 0.50	-46.7 ± 1.6	15 ± 21	Pot	295
100	Sat	0.1 (KCl)	5.214 ± 0.012	-51.20 ± 0.35	-37.4 ± 1.0	30 ± 17	Pot	295
100	Sat	1.0 (KCl)	5.578 ± 0.015	-50.43 ± 0.63	-28.4 ± 1.6	38 ± 17	Pot	295
125	Sat	0	4.471 ± 0.015	-52.26 ± 0.67	-45.6 ± 1.9	15 ± 21	Pot	295
125	Sat	0.1 (KCl)	4.768 ± 0.012	-50.44 ± 0.40	-35.4 ± 1.0	31 ± 17	Pot	295
125	Sat	1.0 (KCl)	5.139 ± 0.015	-49.45 ± 0.59	-25.8 ± 1.4	39 ± 17	Pot	295
150	Sat	0	4.068 ± 0.021	-51.96 ± 0.94	-44.9 ± 2.5	9 ± 21	Pot	295
150	Sat	0.1 (KCl)	4.379 ± 0.009	-49.71 ± 0.54	-33.6 ± 1.3	28 ± 17	Pot	295
150	Sat	1.0 (KCl)	4.760 ± 0.012	-48.49 ± 0.63	-23.5 ± 1.4	37 ± 17	Pot	295
175	Sat	0	3.710 ± 0.027	-51.86 ± 1.30	-44.7 ± 3.4	-1 ± 21	Pot	295

Table 1 (Continued)

T, °C	*P*, MPa[a]	*I*, mol/kg[b]	log *K*[c]	Δ*H*, kJ/mol[c]	Δ*S*, J/K·mol[c]	Δ*C*p, J/K·mol[c]	method[d]	ref
175	Sat	0.1 (KCl)	4.039 ± 0.009	-49.07 ± 0.63	-32.1 ± 1.5	24 ± 17	Pot	295
175	Sat	1.0 (KCl)	4.429 ± 0.012	-47.58 ± 0.67	-21.4 ± 1.5	36 ± 17	Pot	295
200	Sat	0	3.390 ± 0.036	-52.06 ± 1.84	-45.1 ± 4.6	-15 ± 25	Pot	295
200	Sat	0.1 (KCl)	3.739 ± 0.012	-48.48 ± 0.75	-30.8 ± 1.6	23 ± 17	Pot	295
200	Sat	1.0 (KCl)	4.139 ± 0.012	-46.63 ± 0.88	-19.3 ± 1.9	40 ± 17	Pot	295
225	Sat	0	3.101 ± 0.048	-52.62 ± 2.59	-46.3 ± 5.9	-31 ± 29	Pot	295
225	Sat	0.1 (KCl)	3.472 ± 0.012	-47.86 ± 0.92	-29.6 ± 2.0	28 ± 17	Pot	295
225	Sat	1.0 (KCl)	3.883 ± 0.012	-45.51 ± 1.09	-17.0 ± 2.3	51 ± 21	Pot	295
250	Sat	0	2.835 ± 0.060	-53.60 ± 3.77	-48.2 ± 7.9	-48 ± 38	Pot	295
250	Sat	0.1 (KCl)	3.234 ± 0.015	-47.04 ± 1.30	-28.0 ± 2.6	40 ± 21	Pot	295
250	Sat	1.0 (KCl)	3.659 ± 0.015	-43.97 ± 1.42	-14.0 ± 2.9	73 ± 42	Pot	295
275	Sat	0	2.588 ± 0.078	-55.04 ± 5.02	-50.9 ± 10.5	-68 ± 67	Pot	295
275	Sat	0.1 (KCl)	3.023 ± 0.018	-45.76 ± 0.75	-25.6 ± 3.9	64 ± 42	Pot	295
275	Sat	1.0 (KCl)	3.463 ± 0.021	-41.74 ± 2.22	-9.8 ± 4.2	107 ± 67	Pot	295
300	Sat	0	2.355 ± 0.100	-57.01 ± 6.90	-54.4 ± 13.8	-89 ± 88	Pot	295
300	Sat	0.1 (KCl)	2.836 ± 0.024	-43.77 ± 3.14	-22.0 ± 5.9	98 ± 71	Pot	295
300	Sat	1.0 (KCl)	3.296 ± 0.030	-38.52 ± 4.18	-4.1 ± 7.5	153 ± 126	Pot	295
			$D_2PO_4 + OD^- = DPO_4^2 + D_2O$					
100	Sat	0	5.285 ± 0.010	-53.63 ± 0.42	-42.6 ± 1.3	-11 ± 8	Pot	290
125	Sat	0	4.812 ± 0.010	-53.97 ± 0.54	-43.5 ± 1.5	-17 ± 19	Pot	290
150	Sat	0	4.392 ± 0.011	-54.48 ± 0.71	-44.6 ± 1.7	-21 ± 26	Pot	290
175	Sat	0	4.015 ± 0.011	-55.06 ± 0.71	-46.0 ± 1.7	-24 ± 33	Pot	290
200	Sat	0	3.674 ± 0.012	-55.65 ± 0.84	-47.3 ± 1.8	-25 ± 41	Pot	290
225	Sat	0	3.364 ± 0.012	-56.32 ± 1.63	-48.6 ± 3.3	-25 ± 59	Pot	290
250	Sat	0	3.080 ± 0.016	-56.94 ± 3.14	-49.8 ± 6.3	-25 ± 84	Pot	290
275	Sat	0	2.820 ± 0.031	-57.74 ± 5.44	-51.0 ± 10.0	-25 ± 109	Pot	290
300	Sat	0	2.579 ± 0.056	-58.16 ± 7.95	-51.9 ± 15.1	-21 ± 126	Pot	290
			$H^+ + CO_3^{2-} = HCO_3^-$					
100	Sat	0	10.120 ± 0.017	3.2 ± 1.2	202.3 ± 3.5	219 ± 19	Pot	292
100	Sat	0.1 (NaCl)	9.559 ± 0.015	-1.0 ± 1.2	180.4 ± 3.4	174 ± 19	Pot	292
100	Sat	0.5 (NaCl)	9.191 ± 0.017	-4.5 ± 1.1	164.0 ± 3.1	139 ± 15	Pot	292
100	Sat	1.0 (NaCl)	9.035 ± 0.019	-6.6 ± 1.0	155.4 ± 2.3	121 ± 17	Pot	292
100	Sat	3.0 (NaCl)	8.891 ± 0.028	-11.5 ± 0.9	139.3 ± 2.4	89 ± 25	Pot	292
100	Sat	5.0 (NaCl)	8.924 ± 0.048	-15.2 ± 1.0	130.0 ± 2.9	71 ± 38	Pot	292
125	Sat	0	10.171 ± 0.028	8.5 ± 1.5	216.2 ± 4.3	210 ± 21	Pot	292
125	Sat	0.1 (NaCl)	9.568 ± 0.026	3.1 ± 1.5	191.1 ± 4.2	156 ± 17	Pot	292
125	Sat	0.5 (NaCl)	9.166 ± 0.024	-1.3 ± 1.4	172.3 ± 3.9	115 ± 15	Pot	292
125	Sat	1.0 (NaCl)	8.989 ± 0.023	-3.9 ± 1.3	162.4 ± 2.6	94 ± 19	Pot	292
125	Sat	3.0 (NaCl)	8.797 ± 0.028	-9.7 ± 1.2	144.0 ± 3.1	55 ± 23	Pot	292
125	Sat	5.0 (NaCl)	8.796 ± 0.046	-13.9 ± 1.5	133.4 ± 3.5	34 ± 38	Pot	292
150	Sat	0	10.255 ± 0.039	13.7 ± 1.7	228.7 ± 4.6	203 ± 26	Pot	292
150	Sat	0.1 (NaCl)	9.606 ± 0.037	6.8 ± 1.6	199.9 ± 4.5	135 ± 26	Pot	292
150	Sat	0.5 (NaCl)	9.165 ± 0.033	1.3 ± 1.5	178.4 ± 4.1	84 ± 23	Pot	292
150	Sat	1.0 (NaCl)	8.966 ± 0.030	-2.0 ± 1.4	167.0 ± 3.0	57 ± 20	Pot	292
150	Sat	3.0 (NaCl)	8.725 ± 0.028	-8.9 ± 1.5	146.0 ± 3.6	9 ± 25	Pot	292
150	Sat	5.0 (NaCl)	8.689 ± 0.042	-13.7 ± 2.2	134.1 ± 4.9	-17 ± 39	Pot	292
175	Sat	0	10.365 ± 0.049	18.7 ± 1.8	240.3 ± 4.8	200 ± 45	Pot	292
175	Sat	0.1 (NaCl)	9.661 ± 0.046	9.8 ± 1.8	206.9 ± 4.6	106 ± 44	Pot	292
175	Sat	0.5 (NaCl)	9.177 ± 0.040	2.8 ± 1.6	182.0 ± 4.1	36 ± 42	Pot	292
175	Sat	1.0 (NaCl)	8.954 ± 0.036	-1.2 ± 1.4	168.8 ± 3.5	-1 ± 40	Pot	292
175	Sat	3.0 (NaCl)	8.661 ± 0.028	-9.5 ± 1.7	144.6 ± 4.0	-65 ± 40	Pot	292
175	Sat	5.0 (NaCl)	8.590 ± 0.042	-15.0 ± 3.0	131.0 ± 6.5	-99 ± 49	Pot	292
200	Sat	0	10.491 ± 0.056	23.7 ± 2.5	251.0 ± 5.9	202 ± 68	Pot	292
200	Sat	0.1 (NaCl)	9.725 ± 0.053	12.0 ± 2.5	211.4 ± 5.7	61 ± 48	Pot	292
200	Sat	0.5 (NaCl)	9.192 ± 0.046	2.8 ± 2.2	181.9 ± 5.0	-44 ± 65	Pot	292
200	Sat	1.0 (NaCl)	8.942 ± 0.040	-2.3 ± 2.0	166.3 ± 4.4	-97 ± 63	Pot	292
200	Sat	3.0 (NaCl)	8.592 ± 0.030	-12.5 ± 2.3	138.0 ± 5.0	-190 ± 60	Pot	292
200	Sat	5.0 (NaCl)	8.485 ± 0.043	-19.0 ± 3.9	122.2 ± 8.6	-237 ± 66	Pot	292
225	Sat	0	10.630 ± 0.063	28.9 ± 4.1	261.5 ± 8.7	212 ± 95	Pot	292
225	Sat	0.1 (NaCl)	9.788 ± 0.059	12.7 ± 4.0	212.8 ± 8.5	-8 ± 94	Pot	292
225	Sat	0.5 (NaCl)	9.196 ± 0.050	0.2 ± 3.7	176.5 ± 7.8	-170 ± 90	Pot	292
225	Sat	1.0 (NaCl)	8.914 ± 0.043	-6.6 ± 3.5	157.5 ± 7.2	-255 ± 90	Pot	292
225	Sat	3.0 (NaCl)	8.501 ± 0.035	-19.7 ± 3.6	123.2 ± 7.5	-400 ± 80	Pot	292
225	Sat	5.0 (NaCl)	8.355 ± 0.057	-27.6 ± 5.0	104.5 ± 11.4	-466 ± 88	Pot	292
250	Sat	0	10.777 ± 0.073	34.5 ± 6.6	272.0 ± 13.0	240 ± 120	Pot	292
250	Sat	0.1 (NaCl)	9.838 ± 0.069	11.3 ± 6.5	210.0 ± 13.0	-106 ± 120	Pot	292
250	Sat	0.5 (NaCl)	9.174 ± 0.059	-6.3 ± 6.2	164.0 ± 12.0	-370 ± 120	Pot	292
250	Sat	1.0 (NaCl)	8.852 ± 0.051	-16.0 ± 6.0	139.0 ± 12.0	-498 ± 120	Pot	292
250	Sat	3.0 (NaCl)	8.365 ± 0.046	-33.3 ± 5.7	96.0 ± 12.0	-720 ± 110	Pot	292
250	Sat	5.0 (NaCl)	8.176 ± 0.080	-43.0 ± 7.0	73.5 ± 15.4	-826 ± 114	Pot	292
250	12.4	0	11.09	53.7	315	462	Cal	440
275	12.4	0	11.36	66.0	337	515	Cal	440
300	12.4	0	11.66	79.5	362	572	Cal	440
325	12.4	0	11.99	94.6	388	631	Cal	440

Table 1 (Continued)

T, °C	*P*, MPa[a]	*I*, mol/kg[b]	log *K*[c]	Δ*H*, kJ/mol[c]	Δ*S*, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
$H^+ + HCO_3^- = CO_2(aq) + H_2O$								
100	0.1	0	6.42				Con	187
100	Sat	0	6.397 ± 0.012	12.72 ± 0.52	156.5 ± 1.6	278 ± 14	Pot	293
100	Sat	0.1 (NaCl)	6.122 ± 0.011	10.58 ± 0.51	145.5 [illegible] 1.5	253 ± 14	Pot	293
100	Sat	0.5 (NaCl)	5.952 ± 0.011	8.62 ± 0.48	137.1 ± 1.4	224 ± 15	Pot	293
100	Sat	1.0 (NaCl)	5.889 ± 0.011	7.29 ± 0.46	132.3 ± 1.3	200 ± 15	Pot	293
100	Sat	3.0 (NaCl)	5.873 ± 0.014	3.70 ± 0.60	122.3 ± 1.7	126 ± 19	Pot	293
100	Sat	5.0 (NaCl)	5.951 ± 0.024	0.75 ± 0.92	115.9 ± 2.4	58 ± 24	Pot	293
100	20	0	6.33				Con	187
100	40	0	6.24				Con	187
100	60	0	6.15				Con	187
100	80	0	6.07				Con	187
100	100	0	5.99				Con	187
100	120	0	5.91				Con	187
100	140	0	5.84				Con	187
100	160	0	5.76				Con	187
100	180	0	5.69				Con	187
100	200	0	5.62				Con	187
125	Sat	0	6.539 ± 0.015	19.88 ± 0.67	175.1 ± 1.9	297 ± 13	Pot	293
125	Sat	0.1 (NaCl)	6.242 ± 0.014	17.04 ± 0.66	162.3 ± 1.8	267 ± 13	Pot	293
125	Sat	0.5 (NaCl)	6.052 ± 0.013	14.31 ± 0.63	151.8 ± 1.7	233 ± 13	Pot	293
125	Sat	1.0 (NaCl)	5.974 ± 0.013	12.34 ± 0.61	145.4 ± 1.6	206 ± 13	Pot	293
125	Sat	3.0 (NaCl)	5.917 ± 0.014	6.75 ± 0.68	130.2 ± 1.7	120 ± 17	Pot	293
125	Sat	5.0 (NaCl)	5.960 ± 0.023	2.00 ± 0.92	119.1 ± 2.3	43 ± 23	Pot	293
150	0.1	0	6.76				Con	187
150	Sat	0	6.721 ± 0.018	27.70 ± 0.79	194.1 ± 2.1	330 ± 14	Pot	293
150	Sat	0.1 (NaCl)	6.399 ± 0.017	24.01 ± 0.79	179.3 ± 2.0	292 ± 14	Pot	293
150	Sat	0.5 (NaCl)	6.184 ± 0.015	20.36 ± 0.76	166.5 ± 1.9	251 ± 13	Pot	293
150	Sat	1.0 (NaCl)	6.088 ± 0.014	17.64 ± 0.75	158.3 ± 1.9	219 ± 13	Pot	293
150	Sat	3.0 (NaCl)	5.979 ± 0.015	9.74 ± 0.86	137.5 ± 2.1	120 ± 14	Pot	293
150	Sat	5.0 (NaCl)	5.975 ± 0.021	2.93 ± 1.16	121.3 ± 2.7	31 ± 21	Pot	293
150	20	0	6.66				Con	187
150	40	0	6.55				Con	187
150	60	0	6.45				Con	187
150	80	0	6.36				Con	187
150	100	0	6.27				Con	187
150	120	0	6.18				Con	187
150	140	0	6.09				Con	187
150	160	0	6.01				Con	187
150	180	0	5.94				Con	187
150	200	0	5.86				Con	187
175	Sat	0	6.938 ± 0.021	36.47 ± 0.88	214.2 ± 2.1	374 ± 22	Pot	293
175	Sat	0.1 (NaCl)	6.588 ± 0.019	31.68 ± 0.86	196.8 ± 2.1	322 ± 22	Pot	293
175	Sat	0.5 (NaCl)	6.344 ± 0.017	26.87 ± 0.82	181.4 ± 2.0	270 ± 21	Pot	293
175	Sat	1.0 (NaCl)	6.227 ± 0.016	23.27 ± 0.79	171.1 ± 1.9	231 ± 20	Pot	293
175	Sat	3.0 (NaCl)	6.053 ± 0.016	12.68 ± 0.98	144.2 ± 2.3	114 ± 19	Pot	293
175	Sat	5.0 (NaCl)	5.993 ± 0.021	3.51 ± 1.45	122.6 ± 3.3	12 ± 23	Pot	293
200	Sat	0	7.189 ± 0.023	46.49 ± 1.15	235.9 ± 2.5	430 ± 36	Pot	293
200	Sat	0.1 (NaCl)	6.804 ± 0.021	40.14 ± 1.13	215.1 ± 2.5	354 ± 36	Pot	293
200	Sat	0.5 (NaCl)	6.527 ± 0.018	33.80 ± 1.04	196.4 ± 2.3	282 ± 34	Pot	293
200	Sat	1.0 (NaCl)	6.384 ± 0.017	29.07 ± 0.97	183.7 ± 2.1	231 ± 33	Pot	293
200	Sat	3.0 (NaCl)	6.135 ± 0.017	15.27 ± 1.14	149.7 ± 2.5	89 ± 30	Pot	293
200	Sat	5.0 (NaCl)	6.008 ± 0.024	3.36 ± 1.78	122.1 ± 4.0	29 ± 32	Pot	293
200.1	0.1	0	7.24				Con	187
200.1	20	0	7.11				Con	187
200.1	40	0	6.99				Con	187
200.1	60	0	6.87				Con	187
200.1	80	0	6.75				Con	187
200.1	100	0	6.65				Con	187
200.1	120	0	6.55				Con	187
200.1	140	0	6.45				Con	187
200.1	160	0	6.36				Con	187
200.1	180	0	6.27				Con	187
200.1	200	0	6.19				Con	187
225	Sat	0	7.470 ± 0.024	58.09 ± 1.95	259.6 ± 4.0	500 ± 53	Pot	293
225	Sat	0.1 (NaCl)	7.045 ± 0.022	49.37 ± 1.91	234.0 ± 3.9	383 ± 53	Pot	293
225	Sat	0.5 (NaCl)	6.727 ± 0.019	40.86 ± 1.79	210.8 ± 3.7	279 ± 51	Pot	293
225	Sat	1.0 (NaCl)	6.555 ± 0.017	34.64 ± 1.67	195.0 ± 3.4	210 ± 50	Pot	293
225	Sat	3.0 (NaCl)	6.218 ± 0.019	16.87 ± 1.68	152.9 ± 3.5	31 ± 47	Pot	293
225	Sat	5.0 (NaCl)	6.016 ± 0.030	1.72 ± 2.35	118.6 ± 5.1	110 ± 47	Pot	293
250	Sat	0	7.783 ± 0.027	71.71 ± 3.33	286.1 ± 6.6	622 ± 73	Pot	293
250	Sat	0.1 (NaCl)	7.306 ± 0.025	59.30 ± 3.29	253.2 ± 6.5	436 ± 72	Pot	293
250	Sat	0.5 (NaCl)	6.939 ± 0.022	47.57 ± 3.14	223.8 ± 6.2	278 ± 71	Pot	293
250	Sat	1.0 (NaCl)	6.731 ± 0.020	39.29 ± 2.99	204.0 ± 5.9	179 ± 70	Pot	293
250	Sat	3.0 (NaCl)	6.293 ± 0.023	16.42 ± 2.83	151.9 ± 5.6	-58 ± 67	Pot	293
250	Sat	5.0 (NaCl)	6.005 ± 0.038	2.64 ± 3.38	109.9 ± 7.0	234 ± 66	Pot	293

Table 1 (Continued)

T, °C	*P*, MPa[a]	*I*, mol/kg[b]	log *K*[c]	Δ*H*, kJ/mol[c]	Δ*S*, J/K·mol[c]	Δ*C*$_p$, J/K·mol[c]	method[d]	ref
250	12.4	0	7.72	72.4	286	741	Cal	440
250.1	0.1	0	7.79				Con	187
250.1	20	0	7.62				Con	187
250.1	40	0	7.45				Con	187
250.1	60	0	7.31				Con	187
250.1	80	0	7.17				Con	187
250.1	100	0	7.05				Con	187
250.1	120	0	6.93				Con	187
250.1	140	0	6.82				Con	187
250.1	160	0	6.72				Con	187
250.1	180	0	6.61				Con	187
250.1	200	0	6.52				Con	187
275	Sat	0	8.125 ± 0.038	88.32 ± 5.30	316.7 ± 10.2	824 ± 96	Pot	293
275	Sat	0.1 (NaCl)	7.582 ± 0.037	70.07 ± 5.25	273.0 ± 10.1	530 ± 96	Pot	293
275	Sat	0.5 (NaCl)	7.153 ± 0.034	53.45 ± 5.08	234.4 ± 9.8	285 ± 95	Pot	293
275	Sat	1.0 (NaCl)	6.902 ± 0.032	42.19 ± 4.91	209.1 ± 9.4	137 ± 94	Pot	293
275	Sat	3.0 (NaCl)	6.347 ± 0.033	12.45 ± 4.62	144.2 ± 8.9	-194 ± 92	Pot	293
275	Sat	5.0 (NaCl)	5.961 ± 0.051	11.54 ± 5.04	93.1 ± 9.9	425 ± 94	Pot	293
275	12.4	0	8.09	93.1	325	916	Cal	440
300	Sat	0	8.498 ± 0.060	110.43 ± 7.95	355.4 ± 14.9	1300 ± 132	Pot	293
300	Sat	0.1 (NaCl)	7.864 ± 0.059	82.95 ± 7.89	295.3 ± 14.8	828 ± 131	Pot	293
300	Sat	0.5 (NaCl)	7.356 ± 0.056	58.68 ± 7.71	243.2 ± 14.4	433 ± 132	Pot	293
300	Sat	1.0 (NaCl)	7.052 ± 0.053	42.87 ± 7.53	209.8 ± 14.0	197 ± 134	Pot	293
300	Sat	3.0 (NaCl)	6.361 ± 0.052	3.25 ± 7.26	127.4 ± 13.5	-311 ± 146	Pot	293
300	Sat	5.0 (NaCl)	5.864 ± 0.071	27.42 ± 7.69	64.4 ± 14.5	646 ± 161	Pot	293
300	12.4	0	8.53	118.3	370	1105	Cal	440
325	12.4	0	9.03	148.4	421	1306	Cal	440
				$H^+ + H_3SiO_4^- = H_4SiO_4(aq)$				
100	Sat	0	9.10				Pot	294
100	Sat	0.1 (NaCl)	8.80				Pot	294
100	Sat	1.0 (NaCl)	8.52				Pot	294
100	Sat	3.0 (NaCl)	8.53				Pot	294
100	Sat	5.0 (NaCl)	8.64				Pot	294
125	Sat	0	8.98				Pot	294
125	Sat	0.1 (NaCl)	8.66				Pot	294
125	Sat	1.0 (NaCl)	8.35				Pot	294
125	Sat	3.0 (NaCl)	8.32				Pot	294
125	Sat	5.0 (NaCl)	8.40				Pot	294
130	Sat	0	8.88				Sol	220
150	Sat	0	8.86				Sol	220
150	Sat	0	8.90				Pot	294
150	Sat	0.1 (NaCl)	8.55				Pot	294
150	Sat	1.0 (NaCl)	8.20				Pot	294
150	Sat	3.0 (NaCl)	8.13				Pot	294
150	Sat	5.0 (NaCl)	8.18				Pot	294
175	Sat	0	8.85				Pot	294
175	Sat	0	8.85				Sol	220
175	Sat	0.1 (NaCl)	8.48				Pot	294
175	Sat	1.0 (NaCl)	8.09				Pot	294
175	Sat	3.0 (NaCl)	7.97				Pot	294
175	Sat	5.0 (NaCl)	7.97				Pot	294
200	Sat	0	8.85				Pot	294
200	Sat	0	8.86				Sol	220
200	Sat	0.1 (NaCl)	8.45				Pot	294
200	Sat	1.0 (NaCl)	8.00				Pot	294
200	Sat	3.0 (NaCl)	7.82				Pot	294
200	Sat	5.0 (NaCl)	7.77				Pot	294
225	Sat	0	8.89				Pot	294
225	Sat	0	8.91				Sol	220
225	Sat	0.1 (NaCl)	8.44				Pot	294
225	Sat	1.0 (NaCl)	7.94				Pot	294
225	Sat	3.0 (NaCl)	7.68				Pot	294
225	Sat	5.0 (NaCl)	7.58				Pot	294
250	Sat	0	8.96				Pot	294
250	Sat	0	9.04				Sol	220
250	Sat	0.1 (NaCl)	8.47				Pot	294
250	Sat	1.0 (NaCl)	7.88				Pot	294
250	Sat	3.0 (NaCl)	7.55				Pot	294
250	Sat	5.0 (NaCl)	7.39				Pot	294
275	Sat	0	9.07				Pot	294
275	Sat	0	9.23				Sol	220
275	Sat	0.1 (NaCl)	8.51				Pot	294
275	Sat	1.0 (NaCl)	7.84				Pot	294
275	Sat	3.0 (NaCl)	7.41				Pot	294
275	Sat	5.0 (NaCl)	7.17				Pot	294

Table 1 (Continued)

T, °C	*P*, MPa[a]	*I*, mol/kg[b]	log *K*[c]	ΔH, kJ/mol[c]	ΔS, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
300	Sat	0	9.22				Pot	294
300	Sat	0	9.48				Sol	220
300	Sat	0.1 (NaCl)	8.57				Pot	294
300	Sat	1.0 (NaCl)	7.78				Pot	294
300	Sat	3.0 (NaCl)	7.24				Pot	294
300	Sat	5.0 (NaCl)	6.92				Pot	294
325	Sat	0	9.76				Sol	220
350	Sat	0	10.06				Sol	220
$H_4SiO_4(aq) + OH^- = H_3SiO_4^- + H_2O$								
100	Sat	0	3.17 ± 0.02	-26.48 ± 0.46	-10.4 ± 1.3	49.4 ± 10.9	Pot	294
100	Sat	0.5 (NaCl)	3.29 ± 0.01	-26.78 ± 0.46	-8.9 ± 1.3	46.9 ± 10.9	Pot	294
100	Sat	1.0 (NaCl)	3.35 ± 0.01	-27.11 ± 0.46	-8.5 ± 1.3	44.4 ± 10.5	Pot	294
100	Sat	3.0 (NaCl)	3.52 ± 0.01	-28.28 ± 0.50	-8.5 ± 1.4	34.7 ± 10.0	Pot	294
100	Sat	5.0 (NaCl)	3.67 ± 0.02	-29.50 ± 0.63	-8.9 ± 1.6	25.1 ± 10.0	Pot	294
125	Sat	0	2.94 ± 0.02	-25.27 ± 0.38	-7.2 ± 1.0	49.4 ± 10.9	Pot	294
125	Sat	0.5 (NaCl)	3.06 ± 0.01	-25.61 ± 0.33	-5.9 ± 0.9	46.4 ± 10.9	Pot	294
125	Sat	1.0 (NaCl)	3.12 ± 0.01	-25.98 ± 0.33	-5.6 ± 0.9	43.9 ± 10.5	Pot	294
125	Sat	3.0 (NaCl)	3.27 ± 0.01	-27.45 ± 0.38	-6.4 ± 1.0	33.1 ± 10.0	Pot	294
125	Sat	5.0 (NaCl)	3.41 ± 0.01	-28.91 ± 0.54	-7.4 ± 1.3	21.8 ± 10.0	Pot	294
150	Sat	0	2.75 ± 0.02	-24.02 ± 0.50	-4.2 ± 1.2	49.4 ± 10.9	Pot	294
150	Sat	0.5 (NaCl)	2.86 ± 0.01	-24.48 ± 0.42	-3.1 ± 1.0	46.4 ± 10.9	Pot	294
150	Sat	1.0 (NaCl)	2.92 ± 0.01	-24.89 ± 0.38	-3.0 ± 0.9	43.1 ± 10.5	Pot	294
150	Sat	3.0 (NaCl)	3.06 ± 0.01	-26.65 ± 0.33	-4.4 ± 0.8	30.5 ± 10.0	Pot	294
150	Sat	5.0 (NaCl)	3.18 ± 0.01	-28.41 ± 0.54	-6.2 ± 1.3	18.4 ± 10.0	Pot	294
175	Sat	0	2.59 ± 0.02	-22.80 ± 0.67	-1.4 ± 1.6	49.4 ± 10.9	Pot	294
175	Sat	0.5 (NaCl)	2.70 ± 0.01	-23.30 ± 0.63	-0.4 ± 1.4	46.0 ± 10.9	Pot	294
175	Sat	1.0 (NaCl)	2.75 ± 0.01	-23.85 ± 0.54	-0.5 ± 1.3	42.3 ± 10.5	Pot	294
175	Sat	3.0 (NaCl)	2.88 ± 0.01	-25.94 ± 0.50	-2.8 ± 1.1	28.5 ± 10.0	Pot	294
175	Sat	5.0 (NaCl)	2.98 ± 0.01	-28.03 ± 0.67	-5.4 ± 1.5	14.6 ± 10.0	Pot	294
200	Sat	0	2.45 ± 0.02	-21.55 ± 0.92	1.3 ± 2.1	49.4 ± 10.9	Pot	294
200	Sat	0.5 (NaCl)	2.56 ± 0.01	-22.18 ± 0.84	2.1 ± 1.9	45.6 ± 10.9	Pot	294
200	Sat	1.0 (NaCl)	2.61 ± 0.01	-22.80 ± 0.79	1.7 ± 1.7	41.4 ± 10.5	Pot	294
200	Sat	3.0 (NaCl)	2.72 ± 0.01	-25.23 ± 0.67	-1.3 ± 1.5	25.9 ± 10.0	Pot	294
200	Sat	5.0 (NaCl)	2.81 ± 0.01	-27.70 ± 0.84	-4.8 ± 1.9	10.5 ± 10.0	Pot	294
225	Sat	0	2.33 ± 0.02	-20.33 ± 1.17	3.8 ± 2.6	49.4 ± 10.9	Pot	294
225	Sat	0.5 (NaCl)	2.44 ± 0.01	-21.05 ± 1.09	4.4 ± 2.3	45.2 ± 10.9	Pot	294
225	Sat	1.0 (NaCl)	2.48 ± 0.02	-21.76 ± 1.00	3.8 ± 2.2	40.6 ± 10.5	Pot	294
225	Sat	3.0 (NaCl)	2.58 ± 0.01	-24.60 ± 0.92	-0.1 ± 1.9	23.4 ± 10.0	Pot	294
225	Sat	5.0 (NaCl)	2.65 ± 0.02	-27.49 ± 1.09	-4.4 ± 2.3	6.3 ± 10.0	Pot	294
250	Sat	0	2.23 ± 0.03	-19.08 ± 1.42	6.3 ± 3.1	49.4 ± 10.9	Pot	294
250	Sat	0.5 (NaCl)	2.33 ± 0.02	-19.92 ± 1.34	6.6 ± 2.8	44.8 ± 10.9	Pot	294
250	Sat	1.0 (NaCl)	2.37 ± 0.02	-20.75 ± 1.26	5.8 ± 2.7	39.7 ± 10.5	Pot	294
250	Sat	3.0 (NaCl)	2.45 ± 0.02	-24.06 ± 1.13	1.0 ± 2.4	20.9 ± 10.0	Pot	294
250	Sat	5.0 (NaCl)	2.51 ± 0.02	-27.41 ± 1.30	-4.3 ± 2.8	1.7 ± 10.0	Pot	294
275	Sat	0	2.15 ± 0.03	-17.87 ± 1.67	8.6 ± 3.5	49.4 ± 10.9	Pot	294
275	Sat	0.5 (NaCl)	2.25 ± 0.02	-18.83 ± 1.59	8.7 ± 3.3	44.4 ± 10.9	Pot	294
275	Sat	1.0 (NaCl)	2.28 ± 0.02	-19.75 ± 1.51	7.6 ± 3.1	38.9 ± 10.5	Pot	294
275	Sat	3.0 (NaCl)	2.34 ± 0.02	-23.60 ± 1.38	1.8 ± 2.8	18.0 ± 10.0	Pot	294
275	Sat	5.0 (NaCl)	2.38 ± 0.03	-27.41 ± 1.55	-4.4 ± 3.2	-2.9 ± 10.0	Pot	294
300	Sat	0	2.08 ± 0.04	-16.61 ± 1.97	10.8 ± 4.0	49.4 ± 10.9	Pot	294
300	Sat	0.5 (NaCl)	2.17 ± 0.03	-17.70 ± 1.84	10.6 ± 3.7	43.5 ± 10.9	Pot	294
300	Sat	1.0 (NaCl)	2.20 ± 0.03	-18.79 ± 1.76	9.3 ± 3.6	38.1 ± 10.5	Pot	294
300	Sat	3.0 (NaCl)	2.24 ± 0.02	-23.18 ± 1.59	2.5 ± 3.2	15.1 ± 10.0	Pot	294
300	Sat	5.0 (NaCl)	2.26 ± 0.03	-27.53 ± 1.84	-4.8 ± 3.7	-7.5 ± 10.0	Pot	294
$H_3BO_3(aq) + OH = H_2BO_3 + H_2O$								
100	Sat	0	3.31	-38.95 ± 0.21	-41.0 ± 0.6	62.8 ± 3.3	Pot	296
125	Sat	0	2.98	-37.24 ± 0.25	-36.5 ± 0.6	74.1 ± 2.9	Pot	296
150	Sat	0	2.70	-35.23 ± 0.25	-31.7 ± 0.7	85.8 ± 3.3	Pot	296
175	Sat	0	2.46	-32.97 ± 0.25	-26.4 ± 0.7	97.5 ± 5.0	Pot	296
200	Sat	0	2.27	-30.38 ± 0.33	-20.8 ± 0.8	108.8 ± 6.7	Pot	296
225	Sat	0	2.11	-27.53 ± 0.46	-14.9 ± 1.0	120.5 ± 8.8	Pot	296
250	Sat	0	1.98	-24.35 ± 0.63	-8.74 ± 1.34	131.8 ± 10.9	Pot	296
275	Sat	0	1.87	-20.92 ± 0.92	-2.34 ± 1.80	143.5 ± 12.6	Pot	296
300	Sat	0	1.79	-17.20 ± 1.21	4.35 ± 2.34	157.7 ± 14.6	Pot	296
$H^+ + CrO_4^2 = HCrO_4$								
125	Sat	0	7.18 ± 0.03	24 ± 1	198 ± 4	197 ± 5	Pot	303
125	Sat	0.1 (NaCl)	6.59 ± 0.03	19 ± 1	174 ± 4	141 ± 5	Pot	303
125	Sat	0.5 (NaCl)	6.22 ± 0.03	15 ± 1	156 ± 4	95 ± 4	Pot	303
125	Sat	1.0 (NaCl)	6.07 ± 0.03	13 ± 1	148 ± 3	67 ± 8	Pot	303
125	Sat	3.0 (NaCl)	5.99 ± 0.04	8.1 ± 1.9	135 ± 5	1 ± 25	Pot	303
125	Sat	5.0 (NaCl)	6.09 ± 0.07	5.6 ± 3.3	131 ± 9	-48 ± 42	Pot	303
175	Sat	0	7.61 ± 0.05	36 ± 1	226 ± 4	281 ± 16	Pot	303
175	Sat	0.1 (NaCl)	6.92 ± 0.05	27 ± 1	193 ± 4	185 ± 14	Pot	303
175	Sat	0.5 (NaCl)	6.46 ± 0.04	20 ± 1	168 ± 3	107 ± 15	Pot	303
175	Sat	1.0 (NaCl)	6.27 ± 0.04	16 ± 1	156 ± 3	62 ± 11	Pot	303

Table 1 (Continued)

T, °C	*P*, MPa[a]	*I*, mol/kg[b]	log *K*[c]	Δ*H*, kJ/mol[c]	Δ*S*, J/K·mol[c]	Δ*C*$_p$, J/K·mol[c]	method[d]	ref
175	Sat	3.0 (NaCl)	6.10 ± 0.06	7.6 ± 3.1	134 ± 8	-37 ± 31	Pot	303
175	Sat	5.0 (NaCl)	6.14 ± 0.10	2.1 ± 5.4	122 ± 13	-105 ± 52	Pot	303
$H^+ + WO_4^{2-} = HWO_4^-$								
100	Sat	0	4.17 ± 0.16	26.29 ± 8.15	150 ± 19	258 ± 65	Pot	304
100	Sat	0.1 (NaCl)	3.70 ± 0.16	22.45 ± 8.16	131 ± 19	213 ± 65	Pot	304
100	Sat	0.5 (NaCl)	3.47 ± 0.16	20.27 ± 8.20	121 ± 19	180 ± 64	Pot	304
100	Sat	1.0 (NaCl)	3.37 ± 0.17	19.75 ± 8.26	117 ± 19	165 ± 64	Pot	304
100	Sat	3.0 (NaCl)	3.20 ± 0.24	21.17 ± 8.75	118 ± 20	142 ± 64	Pot	304
100	Sat	5.0 (NaCl)	3.14 ± 0.35	23.89 ± 9.54	124 ± 20	134 ± 67	Pot	304
150	Sat	0	4.71 ± 0.06	40.40 ± 5.15	186 ± 11	316 ± 65	Pot	304
150	Sat	0.1 (NaCl)	4.16 ± 0.06	33.83 ± 5.15	160 ± 11	248 ± 65	Pot	304
150	Sat	0.5 (NaCl)	3.88 ± 0.06	29.69 ± 5.17	144 ± 11	199 ± 64	Pot	304
150	Sat	1.0 (NaCl)	3.76 ± 0.07	28.22 ± 5.28	139 ± 11	176 ± 63	Pot	304
150	Sat	3.0 (NaCl)	3.61 ± 0.13	28.25 ± 6.35	136 ± 13	140 ± 65	Pot	304
150	Sat	5.0 (NaCl)	3.59 ± 0.23	30.44 ± 8.14	141 ± 16	127 ± 71	Pot	304
150	Sat	5.0 (NaCl)	4.36 ± 0.08	26.67 ± 10.97	134 ± 21	-443 ± 84	Pot	304
200	Sat	0	5.34 ± 0.04	58.68 ± 2.75	226 ± 6	423 ± 65	Pot	304
200	Sat	0.1 (NaCl)	4.68 ± 0.03	47.28 ± 2.70	189 ± 6	283 ± 65	Pot	304
200	Sat	0.5 (NaCl)	4.33 ± 0.03	39.63 ± 2.61	167 ± 5	181 ± 64	Pot	304
200	Sat	1.0 (NaCl)	4.18 ± 0.04	36.44 ± 2.78	157 ± 6	131 ± 63	Pot	304
200	Sat	3.0 (NaCl)	4.01 ± 0.08	33.84 ± 5.26	148 ± 10	53 ± 66	Pot	304
200	Sat	5.0 (NaCl)	4.02 ± 0.14	35.00 ± 8.58	151 ± 16	21 ± 77	Pot	304
250	Sat	0	6.07 ± 0.04	83.73 ± 3.09	276 ± 6	593 ± 65	Pot	304
250	Sat	0.1 (NaCl)	5.23 ± 0.03	60.90 ± 2.97	217 ± 6	243 ± 64	Pot	304
250	Sat	0.5 (NaCl)	4.77 ± 0.03	44.88 ± 2.68	177 ± 5	-15 ± 64	Pot	304
250	Sat	1.0 (NaCl)	4.57 ± 0.03	37.52 ± 2.80	159 ± 5	-144 ± 63	Pot	304
250	Sat	3.0 (NaCl)	4.35 ± 0.04	28.33 ± 6.35	137 ± 12	-352 ± 69	Pot	304
300	Sat	0	6.89 ± 0.06	122.11 ± 5.70	345 ± 11	1045 ± 65	Pot	304
300	Sat	0.1 (NaCl)	5.76 ± 0.05	70.61 ± 5.58	234 ± 10	170 ± 64	Pot	304
300	Sat	0.5 (NaCl)	5.09 ± 0.04	33.11 ± 5.27	155 ± 10	-497 ± 64	Pot	304
300	Sat	1.0 (NaCl)	4.80 ± 0.04	14.76 ± 5.31	118 ± 10	-845 ± 63	Pot	304
300	Sat	3.0 (NaCl)	4.45 ± 0.07	-12.61 ± 9.03	63 ± 17	-1442 ± 73	Pot	304
300	Sat	5.0 (NaCl)	4.43 ± 0.13	-22.70 ± 14.75	45 ± 28	-1731 ± 94	Pot	304
$H^+ + HCO_2^- = HCO_2H(aq)$								
100	Sat	0	3.951 ± 0.005	12.5 ± 0.3	109.1 ± 0.9	184 ± 5	Pot	298
100	Sat	0.1 (NaCl)	3.690 ± 0.004	12.3 ± 0.3	103.6 ± 0.8	183 ± 5	Pot	298
100	Sat	0.5 (NaCl)	3.554 ± 0.005	11.6 ± 0.3	99.1 ± 0.7	179 ± 5	Pot	298
100	Sat	1.0 (NaCl)	3.521 ± 0.006	10.7 ± 0.2	96.1 ± 0.6	175 ± 5	Pot	298
100	Sat	5.0 (NaCl)	3.764 ± 0.009	3.7 ± 0.5	82.0 ± 1.4	137 ± 5	Pot	298
150	Sat	0	4.233 ± 0.011	22.4 ± 0.5	134.0 ± 1.5	212 ± 6	Pot	298
150	Sat	0.1 (NaCl)	3.922 ± 0.009	22.1 ± 0.5	127.5 ± 1.4	210 ± 6	Pot	298
150	Sat	0.5 (NaCl)	3.735 ± 0.007	21.2 ± 0.5	121.6 ± 1.3	206 ± 6	Pot	298
150	Sat	1.0 (NaCl)	3.664 ± 0.007	20.1 ± 0.5	117.6 ± 1.2	200 ± 5	Pot	298
150	Sat	5.0 (NaCl)	3.714 ± 0.015	11.0 ± 0.7	97.2 ± 1.8	157 ± 5	Pot	298
200	Sat	0	4.591 ± 0.019	33.8 ± 0.8	159.3 ± 2.1	249 ± 6	Pot	298
200	Sat	0.1 (NaCl)	4.215 ± 0.018	33.5 ± 0.8	151.4 ± 2.0	246 ± 6	Pot	298
200	Sat	0.5 (NaCl)	3.962 ± 0.015	32.3 ± 0.8	144.1 ± 2.0	240 ± 6	Pot	298
200	Sat	1.0 (NaCl)	3.846 ± 0.014	30.8 ± 0.8	138.8 ± 1.8	233 ± 6	Pot	298
200	Sat	5.0 (NaCl)	3.683 ± 0.024	19.4 ± 0.9	111.5 ± 2.3	180 ± 6	Pot	298
$H^+ + CH_3CO_2^- = CH_3CO_2H(aq)$								
100	Sat	0	4.937 ± 0.005	10.66 ± 0.22	123.1 ± 0.7	153 ± 5	Fit	291
100	Sat	0	4.95				Con	191
100	Sat	0	4.95 ± 0.01				Con	185
100	Sat	0	4.96	11.0	124	120	Fit	188
100	Sat	0	4.96				Con	191
100	Sat	0.1 (NaCl)	4.684 ± 0.006	8.65 ± 0.22	112.9 ± 0.7	126 ± 5	Fit	291
100	Sat	0.5 (NaCl)	4.560 ± 0.010	6.65 ± 0.43	105.1 ± 1.1	100 ± 5	Fit	291
100	Sat	1.0 (NaCl)	4.533 ± 0.013	4.98 ± 0.53	100.1 ± 1.4	83 ± 5	Fit	291
100	Sat	3.0 (NaCl)	4.630 ± 0.012	-0.69 ± 0.53	86.8 ± 1.4	45 ± 5	Fit	291
100	Sat	5.0 (NaCl)	4.811 ± 0.018	-6.31 ± 0.83	75.2 ± 2.2	22 ± 7	Fit	291
125	0.1	0	5.06	14.1	132	134	Fit	188
125	Sat	0	5.047 ± 0.007	14.79 ± 0.30	133.8 ± 0.8	181 ± 7	Fit	291
125	Sat	0.1 (NaCl)	4.774 ± 0.006	12.01 ± 0.28	121.6 ± 0.8	145 ± 6	Fit	291
125	Sat	0.5 (NaCl)	4.629 ± 0.010	9.22 ± 0.47	111.8 ± 1.2	107 ± 5	Fit	291
125	Sat	1.0 (NaCl)	4.586 ± 0.012	7.05 ± 0.59	105.5 ± 1.5	83 ± 6	Fit	291
125	Sat	3.0 (NaCl)	4.628 ± 0.011	0.33 ± 0.55	89.4 ± 1.4	37 ± 6	Fit	291
125	Sat	5.0 (NaCl)	4.757 ± 0.017	-5.87 ± 0.87	76.3 ± 2.2	14 ± 8	Fit	291
150	0.1	0	5.18	17.9	142	174	Fit	188
150	Sat	0	5.180 ± 0.008	19.78 ± 0.46	145.9 ± 1.2	223 ± 9	Fit	291
150	Sat	0	5.20				Con	191
150	Sat	0	5.21				Con	191
150	Sat	0	5.21 ± 0.02				Con	185
150	Sat	0.1 (NaCl)	4.881 ± 0.007	15.94 ± 0.39	131.1 ± 1.0	173 ± 8	Fit	291
150	Sat	0.5 (NaCl)	4.710 ± 0.010	12.01 ± 0.51	118.6 ± 1.3	118 ± 7	Fit	291
150	Sat	1.0 (NaCl)	4.647 ± 0.013	9.13 ± 0.62	110.5 ± 1.5	84 ± 7	Fit	291

Table 1 (Continued)

T, °C	*P*, MPa[a]	*I*, mol/kg[b]	log *K*[c]	Δ*H*, kJ/mol[c]	Δ*S*, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
150	Sat	3.0 (NaCl)	4.633 ± 0.012	1.16 ± 56	91.5 ± 1.4	29 ± 7	Fit	291
150	Sat	5.0 (NaCl)	4.712 ± 0.018	-5.60 ± 0.87	77.0 ± 2.2	8 ± 11	Fit	291
175	0.1	0	5.33	23.0	153	239	Fit	188
175	Sat	0	5.334 ± 0.011	26.02 ± 0.69	160.2 ± 1.7	285 ± 12	Fit	291
175	Sat	0.1 (NaCl)	5.005 ± 0.009	20.72 ± 0.55	142.1 ± 1.3	215 ± 10	Fit	291
175	Sat	0.5 (NaCl)	4.802 ± 0.011	15.12 ± 0.55	125.7 ± 1.3	134 ± 10	Fit	291
175	Sat	1.0 (NaCl)	4.716 ± 0.014	11.26 ± 0.64	115.4 ± 1.5	87 ± 12	Fit	291
175	Sat	3.0 (NaCl)	4.643 ± 0.013	1.77 ± 0.57	92.8 ± 1.4	19 ± 11	Fit	291
175	Sat	5.0 (NaCl)	4.673 ± 0.021	-5.47 ± 0.88	77.3 ± 2.1	3 ± 18	Fit	291
200	0.1	0	5.49	30.1	169	330	Fit	188
200	Sat	0	5.51				Con	191
200	Sat	0	5.51				Con	191
200	Sat	0	5.515 ± 0.015	34.12 ± 1.00	177.7 ± 2.4	379 ± 16	Fit	291
200	Sat	0	5.54 ± 0.02				Con	185
200	Sat	0.1 (NaCl)	5.147 ± 0.012	26.74 ± 0.78	155.1 ± 1.8	278 ± 13	Fit	291
200	Sat	0.5 (NaCl)	4.904 ± 0.013	18.72 ± 0.66	133.4 ± 1.5	158 ± 17	Fit	291
200	Sat	1.0 (NaCl)	4.791 ± 0.016	13.45 ± 0.75	120.1 + 1.7	90 ± 21	Fit	291
200	Sat	3.0 (NaCl)	4.653 ± 0.015	2.06 ± 0.68	93.4 ± 1.5	2 ± 19	Fit	291
200	Sat	5.0 (NaCl)	4.639 ± 0.023	-5.52 ± 1.05	77.2 ± 2.4	-6 ± 30	Fit	291
225	0.1	0	5.68	39.8	189	447	Fit	188
225	Sat	0	5.727 ± 0.020	45.05 ± 1.44	200.1 ± 3.2	529 ± 23	Fit	291
225	Sat	0	5.74				Con	191
225	Sat	0	5.77				Con	191
225	Sat	0.1 (NaCl)	5.311 ± 0.016	34.62 ± 1.11	171.2 ± 2.5	375 ± 19	Fit	291
225	Sat	0.5 (NaCl)	5.015 ± 0.014	22.93 ± 1.00	142.1 ± 2.1	189 ± 30	Fit	291
225	Sat	1.0 (NaCl)	4.868 ± 0.017	15.61 ± 1.20	124.5 ± 2.5	85 ± 38	Fit	291
225	Sat	3.0 (NaCl)	4.662 ± 0.016	1.72 ± 1.11	92.7 ± 2.3	-33 ± 35	Fit	291
225	Sat	5.0 (NaCl)	4.605 ± 0.024	-5.91 ± 1.73	76.3 ± 3.6	-27 ± 54	Fit	291
250	0.1	0	5.91	52.7	214	590	Fit	188
250	Sat	0	5.978 ± 0.028	60.52 ± 2.09	230.1 ± 4.5	787 ± 36	Fit	291
250	Sat	0	5.99 ± 0.04				Con	185
250	Sat	0.1 (NaCl)	5.501 ± 0.021	45.38 ± 1.61	192.1 ± 3.4	538 ± 31	Fit	291
250	Sat	0.5 (NaCl)	5.136 ± 0.016	27.93 ± 1.84	151.7 ± 3.6	230 ± 55	Fit	291
250	Sat	1.0 (NaCl)	4.947 ± 0.019	17.41 ± 2.30	128.0 ± 4.5	61 ± 70	Fit	291
250	Sat	3.0 (NaCl)	4.665 ± 0.018	0.07 ± 2.13	89.4 ± 4.2	-114 ± 65	Fit	291
250	Sat	5.0 (NaCl)	4.571 ± 0.027	-7.12 ± 3.30	73.9 ± 6.5	-78 ± 98	Fit	291
275	Sat	0	6.282 ± 0.038	83.99 ± 3.11	273.5 ± 6.4	1292 ± 60	Fit	291
275	Sat	0.1 (NaCl)	5.725 ± 0.028	60.99 ± 2.48	220.9 ± 5.0	842 ± 55	Fit	291
275	Sat	0.5 (NaCl)	5.266 ± 0.022	33.77 ± 3.57	162.4 ± 6.8	279 ± 109	Fit	291
275	Sat	1.0 (NaCl)	5.021 ± 0.027	17.92 ± 4.52	128.8 ± 8.6	-26 ± 139	Fit	291
275	Sat	3.0 (NaCl)	4.653 ± 0.025	-4.71 ± 4.20	80.5 ± 8.0	-316 ± 129	Fit	291
275	Sat	5.0 (NaCl)	4.528 ± 0.037	-10.49 ± 6.40	67.6 ± 12.2	-220 ± 192	Fit	291
275	10.3	0	6.18	70	245	862	Cal	436
300	Sat	0	6.53 ± 0.05				Con	185
300	Sat	0	6.664 ± 0.052	123.68 ± 4.90	343.4 ± 9.5	2491 ± 116	Fit	291
300	Sat	0.1 (NaCl)	5.995 ± 0.039	85.87 ± 4.14	264.6 ± 7.9	1536 ± 116	Fit	291
300	Sat	0.5 (NaCl)	5.403 ± 0.037	40.09 ± 7.19	173.4 ± 13.1	331 ± 248	Fit	291
300	Sat	1.0 (NaCl)	5.081 ± 0.049	14.22 ± 9.16	122.1 ± 16.8	-317 ± 316	Fit	291
300	Sat	3.0 (NaCl)	4.609 ± 0.043	-17.71 ± 8.51	57.3 ± 15.6	-896 ± 293	Fit	291
300	Sat	5.0 (NaCl)	4.465 ± 0.065	-19.97	50.6 ± 23.4	-641 ± 432	Fit	291
300	10.3	0	6.52	97	293	1320	Cal	436
320	12.8	0	6.86	127	346	1748	Cal	436
350	Sat	0	7.46 ± 0.20				Con	185
			$Fe^{2+} + CH_3CO_2 = Fe(CH_3CO_2)^+$					
100	Sat	0	1.6 ± 0.2	21 ± 4	90 ± 10	100 ± 100	Pot	306
100	Sat	0	1.61 ± 0.10	17 ± 5	77 ± 13	130 ± 110	Fit	308
100	Sat	0.1 (F_3CSO_3Na)	1.20 ± 0.05	19 ± 5	80 ± 10	0 ± 100	Pot	306
100	Sat	0.1 (F_3CSO_3Na)	1.22 ± 0.06	21 ± 5	80 ± 12	150 ± 110	Fit	308
100	Sat	0.3 (F_3CSO_3Na)	0.82 ± 0.08	21 ± 6	72 ± 8	100 ± 100	Pot	306
100	Sat	0.5 (F_3CSO_3Na)	0.48 ± 0.12	30 ± 4	90 ± 10	210 ± 110	Fit	308
100	Sat	1.0 (F_3CSO_3Na)	0.74 ± 0.07	25 ± 3	81 ± 7	280 ± 110	Fit	308
100	Sat	1.0 (F_3CSO_3Na)	0.76 ± 0.08	14 ± 1	52 ± 4	100 ± 100	Pot	306
150	Sat	0	1.96 ± 0.10	25 ± 3	102 ± 9	260 ± 60	Fit	308
150	Sat	0	2.0 ± 0.2	29 ± 4	106 ± 8	250 ± 40	Pot	306
150	Sat	0.1 (F_3CSO_3Na)	1.55 ± 0.02	25 ± 3	89 ± 6	180 ± 50	Pot	306
150	Sat	0.1 (F_3CSO_3Na)	1.56 ± 0.02	32 ± 3	105 ± 6	270 ± 60	Fit	308
150	Sat	0.3 (F_3CSO_3Na)	1.20 ± 0.03	27 ± 4	86 ± 5	180 ± 60	Pot	306
150	Sat	0.5 (F_3CSO_3Na)	0.91 ± 0.08	43 ± 3	120 ± 6	330 ± 50	Fit	308
150	Sat	1.0 (F_3CSO_3Na)	1.06 ± 0.05	24 ± 2	77 ± 4	280 ± 50	Pot	306
150	Sat	1.0 (F_3CSO_3Na)	1.07 ± 0.04	42 ± 3	119 ± 7	400 ± 40	Fit	308
200	Sat	0	2.4 ± 0.1	44 ± 5	140 ± 10	420 ± 60	Pot	306
200	Sat	0	2.41 ± 0.13	43 ± 3	138 ± 8	390 ± 80	Fit	308
200	Sat	0.1 (F_3CSO_3Na)	1.94 ± 0.03	49 ± 2	140 ± 5	400 ± 70	Fit	308
200	Sat	0.1 (F_3CSO_3Na)	1.94 ± 0.04	37 ± 3	115 ± 7	290 ± 60	Pot	306
200	Sat	0.3 (F_3CSO_3Na)	1.61 ± 0.05	38 ± 3	111 ± 4	250 ± 60	Pot	306

Table 1 (Continued)

T, °C	*P*, MPa[a]	*I*, mol/kg[b]	log *K*[c]	Δ*H*, kJ/mol[c]	Δ*S*, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
200	Sat	0.5 (F_3CSO_3Na)	1.36 ± 0.06	63 ± 3	158 ± 6	440 ± 50	Fit	308
200	Sat	1.0 (F_3CSO_3Na)	1.45 ± 0.03	38 ± 2	109 ± 4	320 ± 60	Pot	306
200	Sat	1.0 (F_3CSO_3Na)	1.46 ± 0.03	64 ± 3	164 ± 6	500 ± 40	Fit	308
250	Sat	0	2.98 ± 0.14	66 ± 6	183 ± 12	520 ± 140	Fit	308
250	Sat	0	3.0 ± 0.1	69 ± 7	190 ± 10	700 ± 100	Pot	306
250	Sat	0.1 (F_3CSO_3Na)	2.39 ± 0.05	72 ± 5	183 ± 11	530 ± 130	Fit	308
250	Sat	0.1 (F_3CSO_3Na)	2.39 ± 0.06	51 ± 5	140 ± 10	400 ± 100	Pot	306
250	Sat	0.3 (F_3CSO_3Na)	2.06 ± 0.08	49 ± 6	132 ± 7	200 ± 200	Pot	306
250	Sat	0.5 (F_3CSO_3Na)	1.82 ± 0.05	88 ± 5	202 ± 9	560 ± 110	Fit	308
250	Sat	1.0 (F_3CSO_3Na)	1.87 ± 0.03	92 ± 2	211 ± 3	600 ± 110	Fit	308
250	Sat	1.0 (F_3CSO_3Na)	1.91 ± 0.05	49 ± 3	131 ± 6	200 ± 200	Pot	306
300	Sat	0	3.67 ± 0.16	95 ± 14	236 ± 25	650 ± 210	Fit	308
300	Sat	0	3.7 ± 0.2	110 ± 10	260 + 30	1800 ± 200	Pot	306
300	Sat	0.1 (F_3CSO_3Na)	2.8 ± 0.1	60 ± 10	160 ± 20	700 ± 200	Pot	306
300	Sat	0.1 (F_3CSO_3Na)	2.86 ± 0.10	101 ± 13	651 ± 196	530 ± 80	Fit	308
300	Sat	0.3 (F_3CSO_3Na)	2.5 ± 0.1	48 ± 8	130 ± 20	200 ± 200	Pot	306
300	Sat	0.5 (F_3CSO_3Na)	2.21 ± 0.07	118 ± 10	666 ± 173	570 ± 70	Fit	308
300	Sat	1.0 (F_3CSO_3Na)	2.17 ± 0.02	124 ± 8	258 ± 15	690 ± 180	Fit	308
300	Sat	1.0 (F_3CSO_3Na)	2.3 ± 0.1	38 ± 8	110 ± 20	-300 ± 300	Pot	306
$Fe^{2+} + 2CH_3CO_2^- = Fe(CH_3CO_2)_2(aq)$								
100	Sat	0	2.6 ± 0.2	30 ± 10	130 ± 20	200 ± 200	Pot	306
100	Sat	0.1 (F_3CSO_3Na)	1.9 ± 0.2	22 ± 10	100 ± 20	100 ± 200	Pot	306
100	Sat	0.3 (F_3CSO_3Na)	1.8 ± 0.1	20 ± 9	90 ± 20	100 ± 200	Pot	306
100	Sat	1.0 (F_3CSO_3Na)	1.5 ± 0.1	9 ± 6	50 ± 20	100 ± 200	Pot	306
150	Sat	0	3.2 ± 0.1	48 ± 7	180 ± 10	600 ± 100	Pot	306
150	Sat	0.1 (F_3CSO_3Na)	2.42 ± 0.09	39 ± 6	140 ± 10	500 ± 100	Pot	306
150	Sat	0.3 (F_3CSO_3Na)	2.22 ± 0.05	34 ± 5	120 ± 10	500 ± 100	Pot	306
150	Sat	1.0 (F_3CSO_3Na)	1.7 ± 0.1	22 ± 5	90 ± 10	400 ± 100	Pot	306
200	Sat	0	4.0 ± 0.1	87 ± 4	262 ± 9	1000 ± 100	Pot	306
200	Sat	0.1 (F_3CSO_3Na)	3.10 ± 0.08	70 ± 4	209 ± 8	800 ± 100	Pot	306
200	Sat	0.3 (F_3CSO_3Na)	2.84 ± 0.05	64 ± 3	189 ± 7	700 ± 100	Pot	306
200	Sat	1.0 (F_3CSO_3Na)	2.2 ± 0.1	49 ± 7	150 ± 20	600 ± 100	Pot	306
250	Sat	0	5.27 ± 0.09	147 ± 6	380 ± 9	1400 ± 200	Pot	306
250	Sat	0.1 (F_3CSO_3Na)	4.05 ± 0.06	110 ± 6	290 ± 10	900 + 200	Pot	306
250	Sat	0.3 (F_3CSO_3Na)	3.68 ± 0.05	100 ± 6	260 ± 10	700 ± 200	Pot	306
250	Sat	1.0 (F_3CSO_3Na)	2.8 ± 0.1	80 ± 10	200 ± 20	400 ± 200	Pot	306
300	Sat	0	6.82 ± 0.02	250 ± 20	530 + 30	2300 ± 300	Pot	306
300	Sat	0.1 (F_3CSO_3Na)	5.17 ± 0.04	170 ± 20	370 ± 30	1000 ± 300	Pot	306
300	Sat	0.3 (F_3CSO_3Na)	4.62 ± 0.09	130 ± 20	300 ± 30	400 ± 300	Pot	306
300	Sat	1.0 (F_3CSO_3Na)	3.5 ± 0.2	90 ± 20	200 ± 40	-400 ± 400	Pot	306
$Zn^{2+} + CH_3CO_2^- = Zn(CH_3CO_2)^+$								
100	Sat	0	2.3 ± 0.1	24 ± 3	109 ± 6	260 ± 28	Pot	307
100	Sat	0.1 (F_3CSO_3Na)	1.8 ± 0.1	21 ± 3	89 ± 6	225 ± 28	Pot	307
100	Sat	1.0 (F_3CSO_3Na)	1.25 ± 0.09	18 ± 3	72 ± 8	191 ± 29	Pot	307
150	Sat	0	2.8 ± 0.1	40 ± 4	149 ± 11	380 ± 40	Pot	307
150	Sat	0.1 (F_3CSO_3Na)	2.2 ± 0.1	34 ± 4	122 ± 10	300 ± 41	Pot	307
150	Sat	1.0 (F_3CSO_3Na)	1.6 ± 0.1	28 ± 5	97 ± 12	218 ± 42	Pot	307
200	Sat	0	3.5 ± 0.1	63 ± 7	200 ± 16	531 ± 57	Pot	307
200	Sat	0.1 (F_3CSO_3Na)	2.7 ± 0.1	51 ± 7	160 ± 16	382 ± 57	Pot	307
200	Sat	1.0 (F_3CSO_3Na)	2.1 ± 0.2	39 ± 7	123 ± 17	227 ± 58	Pot	307
250	Sat	0	4.3 ± 0.2	94 ± 10	262 ± 22	718 ± 76	Pot	307
250	Sat	0.1 (F_3CSO_3Na)	3.4 ± 0.2	72 ± 10	203 ± 22	471 ± 77	Pot	307
250	Sat	1.0 (F_3CSO_3Na)	2.5 ± 0.2	50 ± 10	145 ± 24	210 ± 78	Pot	307
300	Sat	0	5.3 ± 0.3	135 ± 14	337 ± 30	944 ± 101	Pot	307
300	Sat	0.1 (F_3CSO_3Na)	4.1 ± 0.3	98 ± 14	250 ± 30	565 ± 101	Pot	307
300	Sat	1.0 (F_3CSO_3Na)	3.0 ± 0.3	60 ± 15	162 ± 32	162 ± 102	Pot	307
$Zn^{2+} + 2CH_3CO_2^- = Zn(CH_3CO_2)_2(aq)$								
100	Sat	0	4.0 ± 0.1	39 ± 2	180 ± 4	414 ± 19	Pot	307
100	Sat	0.1 (F_3CSO_3Na)	3.14 ± 0.09	33 ± 2	149 ± 4	360 ± 18	Pot	307
100	Sat	1.0 (F_3CSO_3Na)	2.3 ± 0.1	28 ± 2	117 ± 5	303 ± 18	Pot	307
150	Sat	0	4.83 ± 0.09	64 ± 3	243 ± 7	603 ± 27	Pot	307
150	Sat	0.1 (F_3CSO_3Na)	3.85 ± 0.08	54 ± 3	202 ± 7	483 ± 27	Pot	307
150	Sat	1.0 (F_3CSO_3Na)	2.8 ± 0.1	44 ± 3	159 ± 7	354 ± 26	Pot	307
200	Sat	0	5.9 ± 0.1	100 ± 5	323 ± 11	843 ± 38	Pot	307
200	Sat	0.1 (F_3CSO_3Na)	4.72 ± 0.09	82 ± 4	263 ± 10	619 ± 38	Pot	307
200	Sat	1.0 (F_3CSO_3Na)	3.5 ± 0.1	63 ± 4	200 ± 10	379 ± 37	Pot	307
250	Sat	0	7.1 ± 0.1	149 ± 7	422 ± 15	1140 ± 51	Pot	307
250	Sat	0.1 (F_3CSO_3Na)	5.8 ± 0.1	116 ± 7	333 ± 15	769 ± 51	Pot	307
250	Sat	1.0 (F_3CSO_3Na)	4.3 ± 0.1	82 ± 7	238 ± 14	370 ± 50	Pot	307
300	Sat	0	8.7 ± 0.2	215 ± 10	542 ± 20	1499 ± 67	Pot	307
300	Sat	0.1 (F_3CSO_3Na)	6.9 ± 0.2	159 ± 10	410 ± 20	929 ± 67	Pot	307
300	Sat	1.0 (F_3CSO_3Na)	5.1 ± 0.2	99 ± 9	270 ± 19	316 ± 65	Pot	307
$Zn^{2+} + 3CH_3CO_2^- = Zn(CH_3CO_2)_3^-$								
100	Sat	0	4.7 ± 0.3	39 ± 2	193 ± 6	414 ± 19	Pot	307

Table 1 (Continued)

T, °C	P, MPa[a]	I, mol/kg[b]	log K[c]	ΔH, kJ/mol[c]	ΔS, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
100	Sat	0.1 (F_3CSO_3Na)	3.8 ± 0.3	33 ± 2	162 ± 6	360 ± 18	Pot	307
100	Sat	1.0 (F_3CSO_3Na)	3.0 ± 0.3	28 ± 2	131 ± 6	303 ± 18	Pot	307
150	Sat	0	5.5 ± 0.3	64 ± 3	257 ± 6	603 ± 27	Pot	307
150	Sat	0.1 (F_3CSO_3Na)	4.5 ± 0.3	54 ± 3	215 ± 6	843 ± 27	Pot	307
150	Sat	1.0 (F_3CSO_3Na)	3.5 ± 0.3	44 ± 3	172 ± 6	354 ± 26	Pot	307
200	Sat	0	6.6 ± 0.3	100 ± 5	337 ± 6	843 ± 38	Pot	307
200	Sat	0.1 (F_3CSO_3Na)	5.4 ± 0.3	82 ± 4	276 ± 6	619 ± 38	Pot	307
200	Sat	1.0 (F_3CSO_3Na)	4.2 ± 0.3	63 ± 4	213 ± 6	379 ± 37	Pot	307
250	Sat	0	7.9 ± 0.3	149 ± 7	435 ± 6	1140 ± 51	Pot	307
250	Sat	0.1 (F_3CSO_3Na)	6.5 ± 0.3	116 ± 7	346 ± 6	769 ± 51	Pot	307
250	Sat	1.0 (F_3CSO_3Na)	5.0 ± 0.3	82 ± 7	251 ± 6	370 ± 50	Pot	307
300	Sat	0	9.4 ± 0.3	215 ± 10	555 ± 6	1499 ± 67	Pot	307
300	Sat	0.1 (F_3CSO_3Na)	7.6 ± 0.3	159 ± 10	423 ± 6	929 ± 67	Pot	307
300	Sat	1.0 (F_3CSO_3Na)	5.8 ± 0.3	99 ± 9	283 ± 6	316 ± 65	Pot	307
			$H^+ + CH_3CH_2CO_2^- = CH_3CH_2CO_2H(aq)$					
100	Sat	0	5.07				Con	191
150	Sat	0	5.30				Con	191
200	Sat	0	5.64				Con	191
225	Sat	0	5.92				Con	191
			$H^+ + CH_3CH_2CH_2CO_2^- = CH_3CH_2CH_2CO_2H(aq)$					
100	Sat	0	5.09				Con	191
150	Sat	0	5.34				Con	191
200	Sat	0	5.70				Con	191
225	Sat	0	6.00				Con	191
			$H^+ + C_6H_5CO_2^- = C_6H_5CO_2H(aq)$					
100	Sat	0	4.35				Con	191
100	Sat	0	4.40	10.6	112	121	Con	188
100	20	0	4.35				Con	188
100	40	0	4.30				Con	188
100	60	0	4.25				Con	188
100	80	0	4.21				Con	188
100	100	0	4.16				Con	188
100	120	0	4.12				Con	188
100	140	0	4.08				Con	188
100	160	0	4.04				Con	188
100	180	0	4.00				Con	188
100	200	0	3.97				Con	188
125	0.1	0	4.50	13.9	121	149	Con	188
150	0.1	0	4.62	18.3	132	206	Con	188
150	Sat	0	4.55				Con	191
150.2	20	0	4.56				Con	188
150.2	40	0	4.49				Con	188
150.2	60	0	4.43				Con	188
150.2	80	0	4.37				Con	188
150.2	100	0	4.32				Con	188
150.2	120	0	4.27				Con	188
150.2	140	0	4.22				Con	188
150.2	160	0	4.17				Con	188
150.2	180	0	4.12				Con	188
150.2	200	0	4.08				Con	188
175	0.1	0	4.77	24.4	146	290	Con	188
200	0.1	0	4.95	33.0	164	401	Con	188
200	Sat	0	4.85				Con	191
200.2	20	0	4.88				Con	188
200.2	40	0	4.81				Con	188
200.2	60	0	4.73				Con	188
200.2	80	0	4.66				Con	188
200.2	100	0	4.60				Con	188
200.2	120	0	4.54				Con	188
200.2	140	0	4.48				Con	188
200.2	160	0	4.42				Con	188
200.2	180	0	4.37				Con	188
200.2	200	0	4.31				Con	188
225	0.1	0	5.16	44.7	188	540	Con	188
225	Sat	0	5.05				Con	191
250	0.1	0	5.41	60.2	219	707	Con	188
251	20	0	5.29				Con	188
251	40	0	5.18				Con	188
251	60	0	5.08				Con	188
251	80	0	4.99				Con	188
251	100	0	4.91				Con	188
251	120	0	4.84				Con	188
251	140	0	4.77				Con	188
251	160	0	4.71				Con	188
251	180	0	4.64				Con	188

Table 1 (Continued)

T, °C	P, MPa[a]	I, mol/kg[b]	log K[c]	ΔH, kJ/mol[c]	ΔS, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
251	200	0	4.58				Con	188
			$NH_4^+ + OH^- = NH_3(aq) + H_2O$					
100	0.1	0	4.84	11.5	124	170	Con	189
100	Sat	0	4.84				Fit	185
100	Sat	0	4.856 ± 0.014	11.00 ± 0.71	122.4 ± 2.1	212 ± 8	Pot	300
100	Sat	0.1 (KCl)	4.587 ± 0.013	8.91 ± 0.67	111.7 ± 2.0	187 ± 8	Pot	300
100	Sat	0.5 (KCl)	4.420 ± 0.014	7.28 ± 0.63	104.1 ± 1.8	165 ± 9	Pot	300
100	Sat	1.0 (KCl)	4.351 ± 0.017	6.28 ± 0.71	100.1 ± 2.0	149 ± 12	Pot	300
100	Sat	3.0 (KCl)	4.284 ± 0.044	4.14 ± 1.92	93.1 ± 5.3	103 ± 31	Pot	300
100	100	0	4.44	9.2	110	160	Con	189
100	200	0	4.10	7.6	99	139	Con	189
125	0.1	0	4.96	15.7	134	170	Con	189
125	Sat	0	4.96				Fit	185
125	Sat	0	4.976 ± 0.019	16.65 ± 0.92	137.1 ± 2.5	243 ± 13	Pot	300
125	Sat	0.1 (KCl)	4.685 ± 0.017	13.89 ± 0.88	124.7 ± 2.4	214 ± 13	Pot	300
125	Sat	0.5 (KCl)	4.502 ± 0.016	11.63 ± 0.79	115.4 ± 2.2	187 ± 13	Pot	300
125	Sat	1.0 (KCl)	4.422 ± 0.018	10.21 ± 0.84	110.3 ± 2.2	168 ± 15	Pot	300
125	Sat	3.0 (KCl)	4.330 ± 0.044	6.86 ± 1.51	100.1 ± 3.9	115 ± 34	Pot	300
125	100	0	4.53	13.6	121	180	Con	189
125	200	0	4.19	11.7	109	180	Con	189
150	0.1	0	5.10	20.1	145	190	Con	189
150	Sat	0	5.11				Fit	185
150	Sat	0	5.128 ± 0.024	23.22 ± 1.00	153.1 ± 2.7	285 ± 16	Pot	300
150	Sat	0.1 (KCl)	4.814 ± 0.022	19.71 ± 1.00	138.7 ± 2.6	249 ± 15	Pot	300
150	Sat	0.5 (KCl)	4.610 ± 0.019	16.65 ± 0.96	127.6 ± 2.5	216 ± 13	Pot	300
150	Sat	1.0 (KCl)	4.516 ± 0.020	14.73 ± 0.96	121.3 ± 2.4	193 ± 14	Pot	300
150	Sat	3.0 (KCl)	4.393 ± 0.044	9.96 ± 1.46	107.6 ± 3.5	131 ± 33	Pot	300
150	100	0	4.65	18.4	133	200	Con	189
150	200	0	4.28	16.4	121	200	Con	189
175	0.1	0	5.26	25.7	158	260	Con	189
175	Sat	0	5.311 ± 0.028	31.00 ± 1.05	170.9 ± 2.6	338 ± 20	Pot	300
175	Sat	0.1 (KCl)	4.969 ± 0.026	26.40 ± 1.00	154.1 ± 2.6	288 ± 20	Pot	300
175	Sat	0.5 (KCl)	4.741 ± 0.022	22.43 ± 0.96	140.8 ± 2.4	244 ± 18	Pot	300
175	Sat	1.0 (KCl)	4.633 ± 0.022	19.83 ± 1.00	133.0 ± 2.4	215 ± 18	Pot	300
175	Sat	3.0 (KCl)	4.470 ± 0.042	13.39 ± 1.76	115.4 ± 3.9	140 ± 38	Pot	300
175	100	0	4.80	23.5	144	200	Con	189
175	200	0	4.42	21.3	132	190	Con	189
200	0.1	0	5.43	33.2	174	350	Con	189
200	Sat	0	5.47				Fit	185
200	Sat	0	5.525 ± 0.031	40.21 ± 1.21	190.8 ± 2.8	401 ± 31	Pot	300
200	Sat	0.1 (KCl)	5.151 ± 0.028	34.10 ± 1.17	170.7 ± 2.6	328 ± 31	Pot	300
200	Sat	0.5 (KCl)	4.895 ± 0.024	28.83 ± 1.05	154.6 ± 2.3	264 ± 27	Pot	300
200	Sat	1.0 (KCl)	4.768 ± 0.023	25.40 ± 1.05	144.9 ± 2.3	225 ± 26	Pot	300
200	Sat	3.0 (KCl)	4.559 ± 0.040	16.82 ± 2.30	122.8 ± 4.8	130 ± 40	Pot	300
200	100	0	4.96	28.7	156	210	Con	189
200	200	0	4.56	25.6	141	160	Con	189
225	0.1	0	5.64	43.5	195	480	Con	189
225	Sat	0	5.68				Fit	185
225	Sat	0	5.770 ± 0.031	51.17 ± 2.01	213.2 ± 4.1	477 ± 59	Pot	300
225	Sat	0.1 (KCl)	5.357 ± 0.028	42.76 ± 1.92	188.4 ± 3.9	362 ± 58	Pot	300
225	Sat	0.5 (KCl)	5.067 ± 0.025	35.52 ± 1.67	168.3 ± 3.4	268 ± 55	Pot	300
225	Sat	1.0 (KCl)	4.918 ± 0.023	30.92 ± 1.59	156.2 ± 3.1	211 ± 52	Pot	300
225	Sat	3.0 (KCl)	4.654 ± 0.039	19.58 ± 3.10	128.4 ± 6.2	85 ± 56	Pot	300
225	100	0	5.14	33.9	166	210	Con	189
225	200	0	4.72	28.8	148	100	Con	189
250	0.1	0	5.89	57.4	222	640	Con	189
250	Sat	0	5.91				Fit	185
250	Sat	0	6.047 ± 0.032	64.27 ± 3.47	238.6 ± 6.7	574 ± 102	Pot	300
250	Sat	0.1 (KCl)	5.584 ± 0.029	52.17 ± 3.35	206.7 ± 6.5	393 ± 101	Pot	300
250	Sat	0.5 (KCl)	5.252 ± 0.025	42.01 ± 3.01	180.8 ± 5.9	248 ± 97	Pot	300
250	Sat	1.0 (KCl)	5.077 ± 0.023	35.69 ± 2.80	165.4 ± 5.4	164 ± 95	Pot	300
250	Sat	3.0 (KCl)	4.747 ± 0.043	20.63 ± 4.27	130.3 ± 8.5	-12 ± 94	Pot	300
250	100	0	5.31	38.9	176	200	Con	189
250	200	0	4.86	30.2	151	10	Con	189
275	Sat	0	6.17				Fit	185
275	Sat	0	6.355 ± 0.039	80.33 ± 5.56	268.2 ± 10.6	724 ± 115	Pot	300
275	Sat	0.1 (KCl)	5.827 ± 0.037	62.51 ± 5.44	225.6 ± 10.3	437 ± 112	Pot	300
275	Sat	0.5 (KCl)	5.441 ± 0.032	47.74 ± 4.98	191.3 ± 9.5	210 ± 108	Pot	300
275	Sat	1.0 (KCl)	5.233 ± 0.029	38.83 ± 4.69	171.0 ± 8.9	82 ± 106	Pot	300
275	Sat	3.0 (KCl)	4.825 ± 0.054	18.41 ± 6.02	126.0 ± 11.6	-175 ± 113	Pot	300
300	0.1	0	6.55	99.5	299	1070	Con	189
300	Sat	0	6.47				Fit	185
300	Sat	0	6.694 ± 0.058	101.67 ± 8.37	305.3 ± 15.8	1013 ± 155	Pot	300
300	Sat	0.1 (KCl)	6.079 ± 0.056	74.68 ± 8.24	246.7 ± 15.2	560 ± 137	Pot	300
300	Sat	0.5 (KCl)	5.622 ± 0.051	52.68 ± 7.70	199.6 ± 14.2	198 ± 130	Pot	300

Table 1 (Continued)

T, °C	P, MPa[a]	I, mol/kg[b]	log K[c]	ΔH, kJ/mol[c]	ΔS, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
300	Sat	1.0 (KCl)	5.371 ± 0.047	39.71 ± 7.36	172.1 ± 13.6	-5 ± 138	Pot	300
300	Sat	3.0 (KCl)	4.870 ± 0.075	11.30 ± 8.95	112.9 ± 16.6	-407 ± 203	Pot	300
325	Sat	0	6.83				Fit	185
350	0.1	0	7.50	166.3	410	1630	Con	189
350	Sat	0	7.30				Fit	185
$H^+ + L(aq) = HL^+$ (L = Diglycolamine)								
100	Sat	0	7.64	-51.1	9.3	-12.2	Cal	462
125	Sat	0	7.19	-51.4	8.5	-12.2	Cal	462
150	Sat	0	6.79	-51.7	7.8	-12.2	Cal	462
$H^+ + L(aq) = HL^+$ (L = Diethanolamine)								
100	Sat	0	7.37	-44.4	22.2	-35.5	Cal	462
125	Sat	0	6.96	-45.3	19.9	-35.5	Cal	462
150	Sat	0	6.62	-46.1	17.7	-35.5	Cal	462
$H^+ + L(aq) = HL^+$ (L = *N*-Methyldiethanolamine)								
100	Sat	0	7.25	-39.8	32.1	-62.6	Cal	462
125	Sat	0	6.89	-41.4	28.1	-62.6	Cal	462
150	Sat	0	6.57	-42.9	24.3	-62.6	Cal	462
$HL^+ + OH^- = L(aq) + H_2O$ (L = Morpholine)								
100	Sat	0	5.178 ± 0.012	0.02 ± 0.59	99.2 ± 1.7	241 ± 15	Pot	299
125	Sat	0	5.204 ± 0.015	6.28 ± 0.73	115.5 ± 2.0	265 ± 13	Pot	299
150	Sat	0	5.278 ± 0.018	13.35 ± 0.84	132.6 ± 2.2	299 ± 13	Pot	299
175	Sat	0	5.394 ± 0.021	21.34 ± 0.88	150.9 ± 2.1	341 ± 25	Pot	299
200	Sat	0	5.549 ± 0.022	30.50 ± 1.09	170.7 ± 2.3	392 ± 23	Pot	299
225	Sat	0	5.740 ± 0.021	41.05 ± 1.92	192.3 ± 3.8	452 ± 42	Pot	299
250	Sat	0	5.965 ± 0.023	53.30 ± 3.43	215.9 ± 6.7	531 ± 100	Pot	299
275	Sat	0	6.222 ± 0.034	67.78 ± 5.44	243.1 ± 10.5	649 ± 96	Pot	299
300	Sat	0	6.512 ± 0.057	86.61 ± 8.37	275.3 ± 15.9	862 ± 159	Pot	299
$HL^+ + OH^- = L(aq) + H_2O$ (L = Cyclohexylamine)								
100	Sat	0	3.780 ± 0.032	19.12 ± 0.67	123.6 ± 1.8	199 ± 13	Pot	299
125	Sat	0	6.969 ± 0.031	24.35 ± 0.79	137.1 ± 2.1	220 ± 15	Pot	299
150	Sat	0	4.179 ± 0.031	30.21 ± 0.96	151.4 ± 2.3	252 ± 19	Pot	299
175	Sat	0	4.407 ± 0.030	37.03 ± 1.38	167.0 ± 3.1	295 ± 31	Pot	299
200	Sat	0	4.655 ± 0.029	45.10 ± 2.30	184.5 ± 5.0	351 ± 54	Pot	299
225	Sat	0	4.924 ± 0.033	54.64 ± 3.72	204.2 ± 7.9	418 ± 59	Pot	299
250	Sat	0	5.214 ± 0.048	66.11 ± 5.86	226.4 ± 11.7	515 ± 100	Pot	299
275	Sat	0	5.527 ± 0.074	80.75 ± 8.37	253.1 ± 16.7	669 ± 130	Pot	299
300	Sat	0	5.863 ± 0.111	101.25 ± 12.55	288.7 ± 23.4	1004 ± 255	Pot	299
$(HOCH_2)_3CNH_2(aq) + H^+ = (HOCH_2)_3CNH_3^+$								
100	Sat	0	6.462 ± 0.011	-44.1 ± 0.4	5.5 ± 1.3	29 ± 9	Pot	302
100	Sat	0.1 (NaCl)	6.476 ± 0.008	-44.2 ± 0.4	5.4 ± 1.2	28 ± 8	Pot	302
100	Sat	0.5 (NaCl)	6.533 ± 0.009	-44.8 ± 0.4	5.1 ± 1.3	23 ± 9	Pot	302
100	Sat	1.0 (NaCl)	6.605 ± 0.011	-45.4 ± 0.2	4.7 ± 0.8	18 ± 8	Pot	302
100	Sat	5.0 (NaCl)	7.177 ± 0.038	-50.7 ± 0.8	1.4 ± 2.5	-25 ± 20	Pot	302
150	Sat	0	5.742 ± 0.015	-43.1 ± 0.7	8.2 ± 1.8	14 ± 19	Pot	302
150	Sat	0.1 (NaCl)	5.753 ± 0.015	-43.3 ± 0.7	7.9 ± 2.0	12 ± 19	Pot	302
150	Sat	0.5 (NaCl)	5.800 ± 0.017	-44.0 ± 0.7	7.0 ± 1.9	7 ± 18	Pot	302
150	Sat	1.0 (NaCl)	5.858 ± 0.012	-45.0 ± 0.6	5.8 ± 1.5	0 ± 15	Pot	302
150	Sat	5.0 (NaCl)	6.324 ± 0.041	-52.7 ± 1.5	-3.6 ± 3.8	-55 ± 27	Pot	302
200	Sat	0	5.183 ± 0.022	-42.7 ± 1.6	9.1 ± 3.6	3 ± 35	Pot	302
200	Sat	0.1 (NaCl)	5.192 ± 0.021	-42.9 ± 1.5	8.7 ± 3.5	2 ± 34	Pot	302
200	Sat	0.5 (NaCl)	5.226 ± 0.024	-44.0 ± 1.5	7.0 ± 3.5	-5 ± 11	Pot	302
200	Sat	1.0 (NaCl)	5.269 ± 0.018	-45.4 ± 1.4	5.0 ± 3.2	-14 ± 19	Pot	302
200	Sat	5.0 (NaCl)	5.616 ± 0.051	-56.2 ± 3.0	-11.2 ± 6.9	-83 ± 34	Pot	302
$(HOCH_2)_3CN(CH_2CH_2OH)_2(aq) + H^+ = (HOCH_2)_3CN(CH_2CH_2OH)_2H^+$								
100	Sat	0	5.445 ± 0.007	-30.6 ± 0.4	22.2 ± 1.1	-35 ± 8	Pot	301
100	Sat	0.1 (NaCl)	5.471 ± 0.006	-30.8 ± 0.4	22.1 ± 1.1	-35 ± 8	Pot	301
100	Sat	0.5 (NaCl)	5.554 ± 0.005	-31.7 ± 0.4	21.5 ± 1.1	-35 ± 8	Pot	301
100	Sat	1.0 (NaCl)	5.646 ± 0.005	-32.7 ± 0.4	20.6 ± 1.0	-35 ± 8	Pot	301
100	Sat	5.0 (NaCl)	6.240 ± 0.006	-40.7 ± 0.4	10.4 ± 1.0	-35 ± 8	Pot	301
125	Sat	0	5.172 ± 0.010	-31.6 ± 0.6	19.7 ± 1.7	-40 ± 9	Pot	301
125	Sat	0.1 (NaCl)	5.196 ± 0.009	-31.8 ± 0.6	19.6 ± 1.6	-40 ± 9	Pot	301
125	Sat	0.5 (NaCl)	5.272 ± 0.008	-32.6 ± 0.6	19.1 ± 1.6	-40 ± 9	Pot	301
125	Sat	1.0 (NaCl)	5.355 ± 0.007	-33.6 ± 0.6	18.1 ± 1.5	-40 ± 9	Pot	301
125	Sat	5.0 (NaCl)	5.878 ± 0.008	-41.7 ± 0.5	7.9 ± 1.5	-40 ± 9	Pot	301
$Fe^{2+} + 3L(aq) = FeL_3^{2+}$ (L = 2,2′-Bipyridine)								
100	Sat	0	12.95[e]				UV	273
107	Sat	0	12.59[e]				UV	273
120	Sat	0	12.13[e]				UV	273
140	Sat	0	11.40[e]				UV	273
160	Sat	0	10.49[e]				UV	273
$H^+ + L(aq) = HL^+$ (L = 1,10-Phenanthroline)								
100	Sat	0	4.274 ± 0.009[e]	-14.8[e]	42.7[e]		UV	272

Table 1 (Continued)

T, °C	P, MPa[a]	I, mol/kg[b]	log K[c]	ΔH, kJ/mol[c]	ΔS, J/K·mol[c]	ΔC_p, J/K·mol[c]	method[d]	ref
107	Sat	0	4.266 ± 0.008[e]	-14.8[e]	42.7[e]		UV	272
125	Sat	0	4.21 ± 0.01[e]	-14.9[e]	42.3[e]		UV	272
150	Sat	0	4.02 ± 0.01[e]	-15.1[e]	41.8[e]		UV	272
175	Sat	0	3.96 ± 0.01[e]	-15.3[e]	41.4[e]		UV	272
200	Sat	0	3.84 ± 0.02[e]	-15.4[e]	41.0[e]		UV	272
225	Sat	0	3.79 ± 0.02[e]	-15.7[e]	40.6[e]		UV	272
250	Sat	0	3.68 ± 0.10[e]	-15.9[e]	40.6[e]		UV	272
$H^+ + L(aq) = HL^+$ (L = 5-Nitro-1,10-phenanthroline)								
107	Sat	0	2.83 ± 0.01[e]	-11.5[e]	24.7[e]		UV	272
125	Sat	0	2.79 ± 0.01[e]	-11.1[e]	25.2[e]		UV	272
150	Sat	0	2.68 ± 0.01[e]	-10.8[e]	25.9[e]		UV	272
175	Sat	0	2.62 ± 0.04[e]	-10.5[e]	26.7[e]		UV	272
$H^+ + L(aq) = HL^+$ (L = 2,9-Dimethyl-1,10-phenanthroline)								
107	Sat	0	5.14 ± 0.01[e]	-17.7[e]	52[e]		UV	272
125	Sat	0	4.97 ± 0.01[e]	-20.1[e]	46[e]		UV	272
150	Sat	0	4.83 ± 0.01[e]	-23.5[e]	37[e]		UV	272
175	Sat	0	4.69 ± 0.02[e]	-27.0[e]	29[e]		UV	272[a]

[a] Pressure: Sat = the saturation pressure of water. Saturation pressure is assumed if the pressure was not stated in the original paper. [b] Ionic strength (with medium in parentheses): Infinite dilution (I = 0) is assumed if the ionic strength was not stated in the original paper. [c] Thermodynamic quantities: If not otherwise specified (see footnote e), log K, ΔH, ΔS, and ΔC_p values are based on a molal standard state for solute species. The standard state of the solvent (H_2O) is pure water on a mole fraction basis. The standard state of the solute species is the hypothetical 1 molal solution. The standard states are assumed as such if they were not stated in the original paper. The values are applicable at the ionic strengths indicated. The uncertainties are those in the original reference. A conversion factor of 1 cal = 4.1840 J and the gas constant R = 8.31441 J/K·mol are used when the original data need to be converted. [d] Methods: Cal = calorimetry, Con = conductivity, ESR = electron spin resonance, Fit = fit to thermodynamic data from different sources, Pot = potentiometry, Ram = Raman spectroscopy, Sol = solubility, UV = ultraviolet-visible spectrophotometry. [e] The standard state of solute species is the hypothetical 1 molar solution.

IX. References

(1) Yatsimirskii, K. B.; Vasil'ev, V. P. *Instability Constants of Complex Compounds*; Pergamon Press: New York, 1960 (translated from Russian).

(2) Kortum, G.; Vogel, W.; Andrussow, K. *Dissociation Constants of Organic Acids in Aqueous Solution*; Butterworths: London, 1961.

(3) Albert, A.; Serjeant, E. P. *Ionization Constants of Acids and Bases*; Wiley: New York, 1962.

(4) Sillén, L. G.; Martell, A. E. *Stability Constants of Metal-Ion Complexes*; Special Publication 17; The Chemical Society, Burlington House: London, 1964.

(5) Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution*; Butterworths: London, 1965.

(6) Phillips, R. *Chem. Rev.* **1966**, *66*, 501–527.

(7) Perrin, D. D. *Dissociation Constants of Inorganic Acids and Bases in Aqueous Solution*; IUPAC Chemical Data Series 19; Butterworths: London, 1969.

(8) Sillén, L. G.; Martell, A. E. *Stability Constants of Metal-Ion Complexes, Supplement No. 1*; Special Publication 25; The Chemical Society, Burlington House: London, 1971.

(9) Izatt, R. M.; Christensen, J. J.; Rytting, J. H. *Chem. Rev.* **1971**, *71*, 439–481.

(10) Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution. Supplement*; IUPAC Chemical Data Series 12; Pergamon Press: Oxford, 1972.

(11) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum Press: New York, 1974 (Vol. 1); 1975 (Vol. 2); 1977 (Vol. 3); 1976 (Vol. 4); 1982 (Vol. 5); and 1989 (Vol. 6).

(12) Christensen, J. J.; Eatough, D. J.; Izatt, R. M. *Chem. Rev.* **1974**, *74*, 351–384.

(13) Christensen, J. J.; Hansen, L. D.; Izatt, R. M. *Handbook of Proton Ionization Heats and Related Thermodynamic Quantities*; Wiley-Interscience: New York, 1976.

(14) Anderegg, G. *Critical Survey of Stability Constants of EDTA Complexes*; IUPAC Chemical Data Series 14; Pergamon Press: Oxford, 1977.

(15) McBryde, W. A. E. *A Critical Review of Equilibrium Data for Proton and Metal Complexes of 1,10-Phenanthroline, 2,2′-Bipyridyl and Related Compounds*; IUPAC Chemical Data Series 17; Pergamon Press: Oxford, 1978.

(16) Perrin, D. D. *Stability Constants of Metal-Ion Complexes. Part B: Organic Compounds*; IUPAC Chemical Data Series 22; Pergamon Press: Oxford, 1979.

(17) Serjeant, E. P.; Dempsey, B. *Ionization Constants of Organic Acids in Aqueous Solution*; IUPAC Chemical Data Series 23; Pergamon Press: Oxford, 1979.

(18) Bond, A. M.; Hefter, G. T. *Critical Survey of Stability Constants and Related Thermodynamic Data of Fluoride Complexes in Aqueous Solution*; IUPAC Chemical Data Series 27; Pergamon Press: Oxford, 1980.

(19) Perrin, D. D. *Ionization Constants of Inorganic Acids and Bases in Aqueous Solution*, 2nd ed.; IUPAC Chemical Data Series 29; Pergamon Press: Oxford, 1982.

(20) Stary, J.; Liljenzin, J. O. *Pure Appl. Chem.* **1982**, *54*, 2557–2592.

(21) Anderegg, G. *Pure Appl. Chem.* **1982**, *54*, 2693–2758.

(22) Högfeldt, E. *Stability Constants of Metal-Ion Complexes, Part A. Inorganic Ligands*; IUPAC Chemical Data Series 21; Pergamon Press: Oxford, 1982.

(23) Tuck, D. G. *Pure Appl. Chem.* **1983**, *55*, 1477–1528.

(24) Christensen, J. J.; Izatt, R. M. *Handbook of Metal Ligand Heats and Related Thermodynamic Quantities*, 3rd ed.; Marcel Dekker: New York, 1983.

(25) Pettit, L. D. *Pure Appl. Chem.* **1984**, *56*, 247–292.

(26) Paoletti, P. *Pure Appl. Chem.* **1984**, *56*, 491–522.

(27) Izatt, R. M.; Bradshaw, J. S.; Nielson, S. A.; Lamb, J. D.; Christensen, J. J. *Chem. Rev.* **1985**, *85*, 271–339.

(28) Smith, R. M.; Martell, A. E. *Sci. Total Environ.* **1987**, *64*, 125–47.

(29) Beck, M. T. *Pure Appl. Chem.* **1987**, *59*, 1703–1720.

(30) Kiss, T.; Sóvágó, I.; Gergely, A. *Pure Appl. Chem.* **1991**, *63*, 597–638.

(31) Smith, R. M.; Martell, A. E.; Chen, Y. *Pure Appl. Chem.* **1991**, *63*, 1015–1080.

(32) Izatt, R. M.; Krystyna, P.; Bradshaw, J. S.; Bruening, R. L. *Chem. Rev.* **1991**, *91*, 1721–2085.

(33) Sóvágó, I.; Kiss, T.; Gergely, A. *Pure Appl. Chem.* **1993**, *65*, 1029–1080.

(34) Noyes, A. A. *The Electrical Conductivity of Aqueous Solutions*; Publication 63; Carnegie Institute of Washington: Washington, DC, 1907.

(35) Noyes, A. A.; Kato, Y.; Sosman, R. B. *J. Am. Chem. Soc.* **1910**, *32*, 159–178.

(36) Noyes, A. A.; Kato, Y.; Sosman, R. B. *Z. Phys. Chem.* **1910**, *73*, 1–24.

(37) Helgeson, H. C. *J. Phys. Chem.* **1967**, *71*, 3121–3136.

(38) Helgeson, H. C. *Am. J. Sci.* **1969**, *267*, 729–804.

(39) Naumov, G. B.; Ryzhenko, B. N.; Khodakovskiy, I. L. *Handbook of Thermodynamic Data*; Atomizdat: Moscow, 1971 (Russian).

(40) Freier, R. K. *Aqueous Solutions, Data for Inorganic and Organic Compounds*; Walter de Gruyter: Berlin, 1976 (Vol. 1); and 1978 (Vol. 2).

(41) Barner, H. E.; Scheuerman, R. V. *Handbook of Thermochemical Data for Compounds and Aqueous Species*; John Wiley and Sons: New York, 1978.

(42) Criss, C. M.; Cobble, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 5385–5390.

(43) Criss, C. M.; Cobble, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 5390–5393.

(44) Cobble, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 5394–5401.

(45) Murray, R. C., Jr.; Cobble, J. W. in *Proceedings of the 41st International Water Conference*; Engineers Society of Western Pennsylvania: Pittsburgh, PA, 1980; pp 295–310.

(46) Cobble, J. W.; Murray, R. C., Jr.; Turner, P. J.; Chen, K. *High-Temperature Thermodynamic Data for Species in Aqueous*

Solution; EPRI Report NP-2400, Electric Power Research Institute: Palo Alto, CA, 1982.
(47) Seward, T. M. in *Chemistry and Geochemistry of Solutions at High Temperatures and Pressures*; Rickard, D. T.; Wickman, F. E., Eds.; Pergamon Press: Oxford, 1981; pp 113–132.
(48) Arnorsson, S.; Sigurdsson, S; Svavarsson, H. *Geochim. Cosmochim. Acta* **1982**, *46*, 1513–1532.
(49) Phillips, S. L.; Silvester, L. F. *High Temp.-High Press.* **1984**, *16*, 81–91.
(50) Smith, R. S.; Popp, C. J.; Norman, D. I. *Geochim. Cosmochim. Acta* **1986**, *50*, 137–142.
(51) Ryzhenko, B. N; Bryzgalin, O. V. *Geochem. Int.* **1987**, *24*, No. 8, 122–127.
(52) Cobble, J. W.; Lin, S. W. In *The ASME Handbook on Water Technology for Thermal Power Systems*; Cohen, P., Ed.; The American Society of Mechanical Engineers: New York, 1989; Chapter 8, pp 545–658.
(53) Mesmer, R. E.; Palmer, D. A.; Simonson, J. M. In *Activity Coefficients in Electrolyte Solutions*, 2nd ed.; Pitzer, K. S., Ed.; CRC Press: Boca Raton, FL, 1991; Chapter 8, pp 491–529.
(54) Fernández-Prini, R. J.; Corti, H. R.; Japas, M. L. *High-Temperature Aqueous Solutions: Thermodynamic Properties*; CRC Press: Boca Raton, FL, 1992.
(55) *Water: A Comprehensive Treatise*; Franks, F., Ed.; Plenum Press: New York, 19721982; Vols. 1–7.
(56) Eisenberg, D.; Kauzmann, W. *The Structure and Properties of Water*; Oxford University Press: Oxford, 1969.
(57) Ben-Naim, A. *Water and Aqueous Solutions: Introduction to a Molecular Theory*; Plenum Press: New York, 1974.
(58) *Water and Aqueous Solutions: Structure, Thermodynamics and Transport Processes*; Horne, R. A., Ed.; Wiley-Interscience: New York, 1972.
(59) Kavanau, J. L. *Water and Solute-Water Interactions*; Holden-Day: San Francisco, 1964.
(60) Frank, H. S.; Evans, M. W. *J. Chem. Phys.* **1945**, *13*, 507–532.
(61) Frank, H. S.; Wen, W.-Y. *Discuss. Faraday Soc.* **1957**, 133–140.
(62) Cobble, J. W.; Murray, R. C., Jr.; Sen, U. *Nature* **1981**, *291*, 566–568.
(63) Cobble, J. W. *Science* **1966**, *150*, 1479–1485.
(64) Franck, E. U. *Endeavour* **1968**, *27*, 55–59.
(65) Marshall, W. L. *Rec. Chem. Prog.* **1969**, *30*, 61–84.
(66) Franck, E. U. *Pure Appl. Chem.* **1970**, *24*, 13–30.
(67) Todheide, T. In *Water: A Comprehensive Treatise*; Franks, F., Ed.; Plenum Press: New York, 1972; Vol. 1.
(68) Olofsson, G.; Hepler, L. G. *J. Solution Chem.* **1975**, *4*, 127–143.
(69) Marshall, W. L. *Chemistry* **1975**, *48*, 6–12.
(70) Marshall, W. L.; Franck, E. U. *J. Phys. Chem. Ref. Data* **1981**, *10*, 295–304.
(71) Hamann, S. D. In *Chemistry and Geochemistry of Solutions at High Temperatures and Pressures*; Rickard, D. T., Wickman, F. E., Eds.; Pergamon Press: Oxford, 1981; pp 89–111.
(72) Lindsay, W. T., Jr. In *The ASME Handbook on Water Technology for Thermal Power Systems*; Cohen, P., Ed.; The American Society of Mechanical Engineers: New York, 1989; Chapter 7, pp 341–544.
(73) Fine, R. A.; Millero, F. J. *J. Chem. Phys.* **1973**, *59*, 5529–5536.
(74) Gregorio, P.; Merlini, C. *Termotecnica* **1969**, *23*, 41–54.
(75) Halbach, H.; Chatterjee, N. D. *Contrib. Mineral. Petrol.* **1982**, *79*, 337–345.
(76) Bradley, D. J.; Pitzer, K. S. *J. Phys. Chem.* **1979**, *83*, 1599–1603.
(77) Uematsu, M.; Franck, E. U. *J. Phys. Chem. Ref. Data* **1980**, *9*, 1291–1306.
(78) Helgeson, H. C.; Kirkham, D. H. *Am. J. Sci.* **1974**, *274*, 1089–1198.
(79) Archer, D. G.; Wang, P. *J. Phys. Chem. Ref. Data* **1990**, *19*, 371–411.
(80) *Release on Static Dielectric Constant of Water Substance*; International Association for the Properties of Steam, 1977.
(81) Haggis, G. H.; Hasted, J. B.; Buchanan, T. J. *J. Chem. Phys.* **1952**, *20*, 1452–1465.
(82) Sweeton, F. H; Mesmer, R. E.; Baes, C. F., Jr. *J. Solution Chem.* **1974**, *3*, 191–214.
(83) Turner, D. J. In Proceedings: 1987 Symposium on Chemistry in High-Temperature Water; Izatt, R. M., Oscarson, J. L., LindH, G. C., Eds.; EPRI Report NP-6005; Electric Power Research Institute: Palo Alto, CA, 1990.
(84) *Release on the Ion Product of Water Substance*; International Association for the Properties of Steam, 1980.
(85) Pitzer, K. S. *J. Phys. Chem.* **1982**, *86*, 4704–4708.
(86) Quist, A. S. *J. Phys. Chem.* **1970**, *74*, 3396–3402.
(87) Mesmer, R. E.; Marshall, W. L.; Palmer, D. A.; Simonson, J. M.; Holmes, H. F. *J. Solution Chem.* **1988**, *17*, 699–718.
(88) Olofsson, G; Olofsson, I. *J. Chem. Thermodyn.* **1973**, *5*, 533–539.
(89) Chen, X.; Gillespie, S. E.; Oscarson, J. L.; Izatt, R. M. *J. Solution Chem.* **1992**, *21*, 803–824.
(90) Chen, X.; Oscarson, J. L.; Gillespie, S. E.; Cao, H.; Izatt, R. M. *J. Solution Chem.* in press.
(91) Gates, J. A.; Wood, R. H.; Quint, J. R. *J. Phys. Chem.* **1982**, *86*, 4948–4951.
(92) *High Temperature High Pressure Electrochemistry in Aqueous Solutions*; Jones, D. de G., Staehle, R. W., Eds.; National Association of Corrosion Engineers: Houston, TX, 1976.
(93) *Thermodynamics of Aqueous Systems with Industrial Applications*; Newman, S. A., Ed.; ACS Symposium Series 133; American Chemical Society: Washington, DC, 1980.
(94) *Chemical Thermodynamics in Steam Power Cycles Data Requirements*; Jonas, O., White, H. J., Jr., Eds.; NBS Report NBSIR 85-3205, National Bureau of Standards, Office of Standard Reference Data: Gaithersburg, MD, 1985.
(95) Zemaitis, J. F., Jr.; Clark, D. M.; Rafal, M.; Scrivner, N. C. *Handbook of Aqueous Electrolyte Thermodynamics*; American Institute of Chemical Engineers: New York, 1986.
(96) *The ASME Handbook on Water Technology for Thermal Power Systems*; Cohen, P., Ed.; The American Society of Mechanical Engineers: New York, 1989.
(97) *Standard Handbook of Hazardous Waste Treatment and Disposal*; Freeman, H. M., Ed.; McGraw-Hill Book Company: New York, 1989.
(98) Stetter, K. O. *Nature* **1982**, *300*, 258–260.
(99) Grassel, J. F. *Science* **1985**, *229*, 713–717.
(100) Jannasch, H. W.; Mottl, M. J. *Science* **1985**, *229*, 717–725.
(101) Laubier, L.; Desbruyères, D. *Endeavour* **1985**, *9*, 67–76.
(102) Pool, R. *Science* **1990**, *247*, 158–160.
(103) Brock, T. D. *Science* **1985**, *230*, 132–138.
(104) Huber, R.; Kurr, M.; Jannasch, H. W.; Stetter, K. O. *Nature* **1989**, *342*, 833–834.
(105) Borman, S. *Chem. Eng. News* **1991**, *69*, No. 44, 31–34.
(106) Tunnicliffe, V. *Am. Sci.* **1992**, *80*, 336–349.
(107) Miller, S. L.; Bada, J. L. *Nature* **1988**, *334*, 609–611.
(108) Jones, W. J.; Leigh, J. A.; Mayer, F.; Woese, C. R.; Wolfe, R. S. *Arch. Microbiol.* **1983**, *136*, 254–261.
(109) Jones, W. J.; Stugard, C. E.; Jannasch, H. W. *Arch. Microbiol.* **1989**, *151*, 314–318.
(110) Fiala, G.; Stetter, K. O. *Arch. Microbiol.* **1986**, *145*, 56–61.
(111) Jannasch, H. W.; Wirsen, C. O.; Molyneaux, S. J.; Langworthy, T. A. *Appl. Environ. Microbiol.* **1988**, *54*, 1203–1209.
(112) Zhao, H.; Wood, A. G.; Widdel, F.; Bryant, M. P. *Arch. Microbiol.* **1988**, *150*, 178–183.
(113) Zillig, W.; Holz, I.; Janekovic, D.; Klenk, H.-P.; Imsel, E.; Trent, J.; Wunderl, S.; Forjaz, V. H.; Coutinho, R.; Ferreira, T. *J. Bact.* **1990**, *172*, 3959–3965.
(114) Ellis, A. J.; Fyfe, W. S. *Rev. Pure Appl. Chem.* **1957**, *7*, 261–316.
(115) Helgeson, H. C. *Complexing and Hydrothermal Deposition*; Pergamon Press: New York, 1964.
(116) Marshall, W. L. *Chem. Geol.* **1972**, *10*, 59–68.
(117) *Chemistry and Geochemistry of Solutions at High Temperatures and Pressures*; Rickard, D. T., Wickman, F. E., Eds.; Pergamon Press: Oxford, 1981.
(118) Eugster, H. P. *Am. Mineral.* **1986**, *71*, 655–673.
(119) *Hydrothermal Experimental Techniques*; Ulmer, G. C., Barnes, H. L., Eds.; John Wiley & Sons: New York, 1987.
(120) *Water-Rock Interaction*; Kharaka, Y. K., Maest, A. S., Eds.; A. A. Balkema: Rotterdam, 1992.
(121) White, R. H. *Nature* **1984**, *310*, 430–432.
(122) Dernhardt, G.; Lüdemann, H. D.; Jaenicke, R.; Konig, H.; Stetter, K. O. *Naturwissenschaften* **1984**, *71*, 583–586.
(123) Baross, J. A.; Deming, J. W. *Nature* **1983**, *303*, 423–426.
(124) Trent, J. D.; Chastain, R. A.; Yayanos, A. A. *Nature* **1984**, *307*, 737–740.
(125) Wilson, H.; Cannon, R. K. *J. Biol. Chem.* **1937**, *119*, 309–331.
(126) Izatt, R. M.; Oscarson, J. L.; Gillespie, S. E.; Wang, P.; Renuncio, J. A. R.; Pando, C. Manuscripts in preparation.
(127) Bada, J. L. In *Chemistry and Biochemistry of the Amino Acids*; Barrett, G. C., Ed.; Chapman and Hall: New York, 1985; Chapter 13, pp 399–414.
(128) Bada, J. L.; Shou, M.-Y. In *Biogeochemistry of Amino Acids*; Hare, P. E., Hoering, T. C., King, K., Eds.; Wiley: New York, 1980; pp 235–255.
(129) Bada, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 1371–1373.
(130) Goodfriend, G. A.; Meyer, V. R. *Geochim. Cosmochim. Acta* **1991**, *55*, 3355–3367.
(131) Bada, J. L.; Protsch, R. *Proc. Natl. Acad. Sci. U.S.A.* **1973**, *70*, 1331–1334.
(132) Bada, J. L.; Schroeder, R. A. *Earth Planet. Sci. Lett.* **1972**, *15*, 1–11.
(133) Goodfriend, G. A. *Geochim. Cosmochim. Acta* **1991**, *55*, 293–302.
(134) Kvenvolden, K. A.; Peterson, E.; Wehmiller, J.; Hare, P. E. *Geochim. Cosmochim. Acta* **1973**, *37*, 2215–2225.
(135) Wehmiller, J.; Hare, P. E. *Science* **1971**, *173*, 907–911.
(136) Rafalska, J. K.; Engel, M. H.; Lanier, W. P. *Geochim. Cosmochim. Acta* **1991**, *55*, 3669–3675.
(137) Zumberge, J. E. *Geochim. Cosmochim. Acta* **1979**, *43*, 1443–1448.
(138) Kimber, R. W. L.; Hare, P. E. *Geochim. Cosmochim. Acta* **1992**, *56*, 739–743.
(139) Bada, J. L. *Ann. Rev. Earth Planet. Sci.* **1985**, *13*, 241–268.
(140) Kimber, R. W. L.; Griffin, C. V. *Geochim. Cosmochim. Acta* **1987**, *51*, 839–846.
(141) Goodfriend, G. A. *Geology* **1987**, *15*, 698–700.
(142) Cohen, P. *Water Coolant Technology of Power Reactors*; Gordon and Breach: New York, NY, 1969.
(143) Cohen, P. In Proceedings: 1987 Symposium on Chemistry in High-Temperature Water; Izatt, R. M., Oscarson, J. L., LindH, G. C.,

Eds.; EPRI Report NP-6005; Electric Power Research Institute: Palo Alto, CA, 1990.

(144) Chen, C. M.; Theuss, C. J. *Chemistry of Corrosion-Production Salts in Light Water Reactors*; EPRI Report NP-2298; Electric Power Research Institute: Palo Alto, CA, 1982.

(145) Leibovitz, J.; Shoemaker, C. E.; Snyder, G. R. *HITCH Computer Code: Chemistry and pH Estimates of Concentrated Aqueous Solutions*; EPRI Report NP-2388; Electric Power Research Institute: Palo Alto, CA, 1982.

(146) Oscarson, J. L.; Christensen, J. J.; Izatt, R. M. In Proceedings: 1987 Symposium on Chemistry in High-Temperature Water; Izatt, R. M., Oscarson, J. L., LindH, G. C., Eds.; EPRI Report NP-6005; Electric Power Research Institute: Palo Alto, CA, 1990; Paper 4b.

(147) Rafal, M.; Sanders, S. J. In Proceedings: 1987 Symposium on Chemistry in High-Temperature Water; Izatt, R. M., Oscarson, J. L., LindH, G. C., Eds.; EPRI Report NP-6005; Electric Power Research Institute: Palo Alto, CA, 1990; Paper 4k.

(148) Astarita, G.; Savage, D. W.; Bisio, A. *Gas Treating with Chemical Solvents*; Wiley: New York, 1983.

(149) Mather, A. E.; Deshmukh, R. D. In *Thermodynamics of Aqueous Systems with Industrial Applications*; Newman, S. A., Ed.; ACS Symposium Series 133; American Chemical Society: Washington, DC, 1980; pp 49–60.

(150) Albright, M. A.; Forbes, D. A.; Wiener, L. D. In *Thermodynamics of Aqueous Systems with Industrial Applications*; Newman, S. A., Ed.; ACS Symposium Series 133; American Chemical Society: Washington, DC, 1980; pp 317–321.

(151) Mason, D. M.; Kao, R. In Thermodynamics of Aqueous Systems with Industrial Applications; Newman, S. A., Ed.; ACS Symposium Series 133; American Chemical Society: Washington, DC, 1980; pp 107–138.

(152) Atkins, W. T.; Seward, W. H.; Takach, H. J. In *Thermodynamics of Aqueous Systems with Industrial Applications*; Newman, S. A., Ed.; ACS Symposium Series 133; American Chemical Society: Washington, DC, 1980; pp 15–47.

(153) Barner, H. E.; Kust, R. N. In *Thermodynamics of Aqueous Systems with Industrial Applications*; Newman, S. A., Ed.; ACS Symposium Series 133; American Chemical Society: Washington, DC, 1980; pp 625–641.

(154) Shaw, R. W.; Brill, T. B.; Clifford, A. A.; Eckert, C. A.; Franck, E. U. *Chem. Eng. News* **1991**, *69*, No. 51, 26–39.

(155) Modell, M. In *Standard Handbook of Hazardous Waste Treatment and Disposal*; Freeman, H. M., Ed.; McGraw-Hill Book Company: New York, 1989; Chapter 8.

(156) Onsager, L.; Fuoss, R. M. *J. Phys. Chem.* **1932**, *36*, 2689–2778.

(157) Fuoss, R. M.; Onsager, L. *J. Phys. Chem.* **1957**, *61*, 668–682.

(158) Fuoss, R. M.; Onsager, L.; Skinner, J. F. *J. Phys. Chem.* **1965**, *69*, 2581–2594.

(159) Shedlovsky, T. *J. Franklin Inst.* **1938**, *225*, 739–743.

(160) Fuoss, R. M.; Shedlovsky, T. *J. Am. Chem. Soc.* **1949**, *71*, 1496–1498.

(161) Fuoss, R. M. *J. Solution Chem.* **1978**, *7*, 771–782.

(162) Fogo, J. K.; Copeland, C. S.; Benson, S. W. *Rev. Sci. Instrum.* **1951**, *22*, 765–769.

(163) Fogo, J. K.; Benson, S. W.; Copeland, C. S. *J. Chem. Phys.* **1954**, *22*, 212–216.

(164) Franck, E. U. *Z. Phys. Chem.* **1956**, *8*, 92–106.

(165) Franck, E. U. *Z. Phys. Chem.* **1956**, *8*, 107–126.

(166) Franck, E. U. *Z. Phys. Chem.* **1956**, *8*, 192–206.

(167) Franck, E. U.; Savolainen, J. E.; Marshall, W. L. *Rev. Sci. Instrum.* **1962**, *33*, 115–117.

(168) Quist, A. S.; Franck, E. U.; Jolley, H. R.; Marshall, W. L. *J. Phys. Chem.* **1963**, *67*, 2453–2459.

(169) Quist, A. S.; Marshall, W. L.; Jollry, H. R. *J. Phys. Chem.* **1965**, *69*, 2726–2735.

(170) Quist, A. S.; Marshall, W. L. *J. Phys. Chem.* **1965**, *69*, 2984–2987.

(171) Quist, A. S.; Marshall, W. L. *J. Phys. Chem.* **1966**, *70*, 3714–3725.

(172) Quist, A. S.; Marshall, W. L. *J. Phys. Chem.* **1968**, *72*, 684–703.

(173) Quist, A. S.; Marshall, W. L. *J. Phys. Chem.* **1968**, *72*, 1545–1552.

(174) Quist, A. S.; Marshall, W. L. *J. Phys. Chem.* **1968**, *72*, 2100–2105.

(175) Quist, A. S.; Marshall, W. L. *J. Phys. Chem.* **1968**, *72*, 3122–3128.

(176) Dunn, L. A.; Marshall, W. L. *J. Phys. Chem.* **1969**, *73*, 723–728.

(177) Quist, A. S.; Marshall, W. L. *J. Phys. Chem.* **1969**, *73*, 978–985.

(178) Quist, A. S.; Marshall, W. L. *J. Chem. Eng. Data* **1970**, *15*, 375–376.

(179) Yeatts, L. B.; Marshall, W. L. *J. Phys. Chem.* **1972**, *76*, 1053–1062.

(180) Frantz, J. D.; Marshall, W. L. *Am. J. Sci.* **1982**, *282*, 1666–1693.

(181) Frantz, J. D.; Marshall, W. L. *Am. J. Sci.* **1984**, *284*, 651–667.

(182) Marshall, W. L. *J. Chem. Phys.* **1987**, *87*, 3639–3643.

(183) Marshall, W. L. *J. Chem. Eng. Data* **1987**, *32*, 221–226.

(184) Marshall, W. L.; Frantz, J. D. In *Hydrothermal Experimental Techniques*; Ulmer, G. C., Barnes, H. L., Eds.; John Wiley & Sons: New York, 1987; Chapter 11.

(185) Fisher, J. R.; Barnes, H. L. *J. Phys. Chem.* **1972**, *76*, 90–99.

(186) Bignold, G. J.; Brewer, A. D.; Hearn, B. *Trans. Faraday Soc.* **1971**, *67*, 2419–2430.

(187) Read, A. J. *J. Solution Chem.* **1975**, *4*, 53–70.

(188) Read, A. J. *J. Solution Chem.* **1981**, *10*, 437–450.

(189) Read, A. J. *J. Solution Chem.* **1982**, *11*, 649–664.

(190) Read, A. J. *J. Solution Chem.* **1988**, *17*, 213–224.

(191) Ellis, A. J. *J. Chem. Soc.* **1963**, 2299–2310.

(192) Ellis, A. J. *J. Chem. Soc.* **1963**, 4300–4304.

(193) Ryzhenko, B. N. *Geochemistry* **1963**, 151–164.

(194) Ryzhenko, B. N. *Geochemistry* **1963**, 463–479.

(195) Ryzhenko, B. N. *Dokl. Akad. Nauk SSSR* **1963**, *149*, 639–641.

(196) Ryzhenko, B. N. *Geochem. Int.* **1965**, *2*, 196–200.

(197) Seward, T. M. *Geochim. Cosmochim. Acta* **1976**, *40*, 1329–1341.

(198) Tremaine, P. R.; LeBlanc, J. C. *J. Solution Chem.* **1980**, *9*, 415–442.

(199) Gammons, C. H.; Barnes, H. L. *Geochim. Cosmochim. Acta* **1989**, *53*, 279–290.

(200) Ruaya, J. R.; Seward, T. M. *Geochim. Cosmochim. Acta* **1986**, *50*, 651–661.

(201) Seewald, J. S.; Seyfried, W. E., Jr. *Geochim. Cosmochim. Acta* **1991**, *55*, 659–669.

(202) Hayashi, K.; Sugaki, A.; Kitakaze, A. *Geochim. Cosmochim. Acta* **1990**, *54*, 715–725.

(203) Fahlquist, L. S.; Popp, R. K. *Geochim. Cosmochim. Acta* **1989**, *53*, 989–995.

(204) Shenberger, D. M.; Barnes, H. L. *Geochim. Cosmochim. Acta* **1989**, *53*, 269–278.

(205) Wood, S. A.; Vlassopoulos, D. *Geochim. Cosmochim. Acta* **1989**, *53*, 303–312.

(206) Ziemniak, S. E.; Jones, M. E.; Combs, K. E. S. *J. Solution Chem.* **1989**, *18*, 1133–1152.

(207) Lietzke, M. H.; Marshall, W. L. *J. Solution Chem.* **1986**, *15*, 903–917.

(208) Walter, J. V. *Geochim. Cosmochim. Acta* **1986**, *50*, 733–739.

(209) Zotov, A. V.; Levin, K. A.; Khodakovskiy, I. L.; Kozlov, V. K. *Geochem. Int.* **1986**, *23*, No. 9, 103–116.

(210) Kurovskaya, N. A.; Malinin, S. D. *Geochem. Int.* **1983**, *20*, No. 1, 13–27.

(211) Marshall, W. L.; Chen, Chen-Tung A. *Geochim. Cosmochim. Acta* **1982**, *46*, 367–370.

(212) Dadze, T. P.; Sorokhin, V. I.; Nekrasov, I. Ya. *Geochem. Int.* **1981**, *18*, No. 5, 142–152.

(213) Richardson, C. K.; Holland, H. D. *Geochim. Cosmochim. Acta* **1979**, *43*, 1313–1325.

(214) Crerar, D. A.; Susak, N. J.; Borcsik, M.; Schwarts, S. *Geochim. Cosmochim. Acta* **1978**, *42*, 1427–1437.

(215) Crerar, D. A.; Barnes, H. L. *Econ. Geol.* **1976**, *71*, 772–794.

(216) Ivanenko, V. V.; Pamfilova, L. A. *Geochem. Int.* **1975**, *12*, No. 2, 216–225.

(217) Khodakovskiy, I. L.; Yelkin, A. Ye. *Geochem. Int.* **1975**, *12*, No. 5, 127–133.

(218) Marshall, W. L.; Slusher, R. *J. Inorg. Nucl. Chem.* **1975**, *37*, 2165–2170.

(219) Marshall, W. L.; Slusher, R. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1191–1202.

(220) Seward, T. M. *Geochim. Cosmochim. Acta* **1974**, *38*, 1651–1664.

(221) Kalyanaraman, R.; Yeatts, L. B.; Marshall, W. L. *J. Chem. Thermodyn.* **1973**, *5*, 899–909.

(222) Marshall, W. L.; Jones, E. V. *J. Phys. Chem.* **1966**, *70*, 4028–4040.

(223) Marshall, W. L.; Slusher, R.; Jones, E. V. *J. Chem. Eng. Data* **1964**, *9*, 187–191.

(224) Ellis, A. J. *Am. J. Sci.* **1963**, *261*, 259–267.

(225) Lietzke, M. H.; Stoughton, R. W.; Young, T. F. *J. Phys. Chem.* **1961**, *65*, 2247–2249.

(226) Ramette, R. W. *J. Chem. Educ.* **1967**, *44*, 647–654.

(227) Gans, P.; Irving, H. *J. Inorg. Nucl. Chem.* **1972**, *34*, 1885–1890.

(228) McBryde, W. A. E. *Talanta* **1974**, *21*, 979–1004.

(229) Leggett, D. J.; McBryde, W. A. E. *Anal. Chem.* **1975**, *47*, 1060–1065.

(230) Irish, D. E.; Brooker, M. H. In *Advances in Infrared and Raman Spectroscopy*; Clark, R. J. H., Hester, R. E., Eds.; Heyden: London, 1976; Vol. 2, Chapter 6.

(231) Leggett, D. J. *Talanta* **1977**, *24*, 535–542.

(232) Brooker, M. H.; DeYoung, B. S. *J. Solution Chem.* **1980**, *9*, 279–288.

(233) Leggett, D. J. *Am. Lab.* **1982**, *14*, 29–37.

(234) Melveger, A. J.; Brasch, J. W.; Lippincott, E. R. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Marcel Dekker: New York, 1972; pp 51–72.

(235) Ferraro, J. R.; Basile, L. J. *Appl. Spectrosc.* **1974**, *28*, 505–516.

(236) Whalley, E. In *High Pressure Chemistry*; Kelm, H., Ed.; Reidel: New York, 1978; pp 127–157.

(237) Buback, M. In *Chemistry and Geochemistry of Solutions at High Temperatures and Pressures*; Rickard, D. T., Wickman, F. E., Eds.; Pergamon Press: Oxford, 1981; pp 345–360.

(238) Buback, M.; Crerar, D. A.; Koplitz, L. M. V. In *Hydrothermal Experimental Techniques*; Ulmer, G. C., Barnes, H. L., Eds.; John Wiley & Sons: New York, 1987; Chapter 14.

(239) Young, T. F.; Haranville, L. F.; Smith, H. M. In *The Structure of Electrolytic Solutions*; Hamer, W. J., Ed.; Wiley and Chapman and Hall: New York, 1959; pp 35–63.

(240) Irish, D. E.; Jarv, T.; Ratcliffe, C. I. *Appl. Spectrosc.* **1982**, *36*, 137–140.

(241) Eckel, R.; Buback, M.; Strobl, G. R. *Colloid Polym. Sci.* **1981**, *259*, 326–334.

(242) Marley, N. A.; Ott, M.; Feary, B. L.; Benjamin, T. M.; Rogers, P. S. Z.; Gaffney, J. S. *Rev. Sci. Instrum.* **1988**, *59*, 2247–2253.

(243) Marshall, W. L.; Begun, G. M. *J. Chem. Soc., Faraday Trans. 2* **1989**, *85*, 1963–1978.

(244) Irish, D. E.; Jarv, T. *Faraday Discuss. Chem. Soc.* **1977**, *64*, 95–101.
(245) Dawson, B. S. W.; Irish, D. E.; Toogood, G. E. *J. Phys. Chem.* **1986**, *90*, 334–341.
(246) Yang, M. M.; Crerar, D. A.; Irish, D. E. *J. Solution Chem.* **1988**, *17*, 751–762.
(247) Anderson, B. G.; Irish, D. E. *J. Solution Chem.* **1988**, *17*, 763–775.
(248) Semmler, J.; Irish, D. E. *J. Solution Chem.* **1988**, *17*, 805–824.
(249) Yang, M. M.; Crerar, D. A.; Irish, D. E. *Geochim. Cosmochim. Acta* **1989**, *53*, 319–326.
(250) Murata, K; Irish, D. E.; Toogood, G. E. *Can. J. Chem.* **1989**, *67*, 517–524.
(251) Semmler, J.; Irish, D. E.; Ozeki, T. *Geochim. Cosmochim. Acta* **1990**, *54*, 947–954.
(252) Kruus, P.; Hayes, A. C.; Adams, W. A. *J. Solution Chem.* **1985**, *14*, 117–128.
(253) Marley, N. A.; Gaffney, J. S. *Appl. Spectrosc.* **1990**, *44*, 469–476.
(254) Haufe, P. *J. Solution Chem.* **1985**, *14*, 73–85.
(255) Pessall, N.; Dunlap, A. B.; Feldman, D. W. *Corrosion* **1977**, *33*, 130–144.
(256) Pan, P.; Wood, S. A. *Geochim. Cosmochim. Acta* **1991**, *55*, 2365–2371.
(257) Pan, P.; Wood, S. A. *J. Solution Chem.* **1993**, *22*, 163–172.
(258) Schulz, K. R. Ph.D. Dissertation, University of Karlsruhe, Karlsruhe, Germany, 1974.
(259) Waggener, W. C. *Rev. Sci. Instrum.* **1959**, *30*, 788–793.
(260) James, D. W. Smith, G. P. *Appl. Spectrosc.* **1966**, *20*, 317–319.
(261) Griffiths, T. R.; Lee, F., Wijayanayake, R. H. *J. Sci. Instrum.* **1967**, *44*, 876–878.
(262) Lüdemann, H. D.; Franck, E. U. *Ber. Bunsen-Ges. Phys. Chem.* **1967**, *71*, 455–460.
(263) Lüdemann, H. D.; Mahon, W. A. J. *High Temp.-High Press.* **1969**, *1*, 215–220.
(264) Giggenbach, W. F. *J. Phys. E: Sci. Instrum.* **1971**, *4*, 148–149.
(265) Alexander, R. D.; Dudeney, A. W. L.; Irving, R. J. *J. Phys. E* **1974**, *7*, 522–524.
(266) Susak, N. J. Ph.D. Dissertation, Princeton University, Princeton, NJ, 1981.
(267) Susak, N. J.; Crerar, D. A.; Forseman, T. C.; Haas, J. L., Jr. *Rev. Sci. Instrum.* **1981**, *52*, 110–113.
(268) Lüdemann, H. D.; Franck, E. U. *Ber. Bunsen-Ges. Phys. Chem.* **1968**, *72*, 514–523.
(269) Scholz, B.; Lüdemann, H. D.; Franck, E. U. *Ber. Bunsen-Ges. Phys. Chem.* **1972**, *76*, 406–409.
(270) Susak, N. J.; Crerar, D. A. *Geochim. Cosmochim. Acta* **1985**, *49*, 555–564.
(271) Ellis, A. J.; Giggenbach, W. *Geochim. Cosmochim. Acta* **1971**, *35*, 247–260.
(272) Alexander, R. D.; Dudeney, A. W. L.; Irving, R. J. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1075–1080.
(273) Alexander, R. D.; Buisson, D. H.; Dudeney, A. W. L.; Irving, R. J. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1081–1088.
(274) Seward, T. M. *Geochim. Cosmochim. Acta* **1984**, *48*, 121–134.
(275) Heinrich, C. A.; Seward, T. M. *Geochim. Cosmochim. Acta* **1990**, *54*, 2207–2221.
(276) Yuchenko, E. N.; Kolonin, G. R.; Shironosova, G. P.; Aksenova, T. P. *Russ. J. Inorg. Chem.* **1976**, *21*, 1682–1685.
(277) Aksenova, T. P.; Kolonin, G. R. In *Eksperiment v Mineralogii i Petrografii* (*Collected Papers*); Zharikov, V. A., Ed.; Nauka: Moscow, 1975; pp 135–139.
(278) Valyashko, V. M.; Buback, M. Franck, E. U. *Z. Naturforsch.* **1980**, *35a*, 549–555.
(279) Valyashko, V. M.; Buback, M. Franck, E. U. *Z. Naturforsch.* **1981**, *36a*, 1169–1176.
(280) Charuel, M. Ph.D. Dissertation, University of Karlsruhe, Karlsruhe, Germany, 1975.
(281) Wheat, C. G.; Carpenter, R. *J. Solution Chem.* **1988**, *17*, 467–480.
(282) Carpenter, R. *Geochim. Cosmochim. Acta* **1983**, *47*, 875–885.
(283) DeFries, T. H.; Jonas, J. *J. Magn. Reson.* **1979**, *35*, 111–119.
(284) Galster, H. *pH Measurement: Fundamentals, Methods, Applications, Instrumentation*; VCH: Weinheim, Germany, 1991.
(285) Baes, C. F., Jr.; Meyer, N. J. *Inorg. Chem.* **1962**, *1*, 780–789.
(286) Mesmer, R. E.; Baes, C. F., Jr.; Sweeton, F. H. *J. Phys. Chem.* **1970**, *74*, 1937–1942.
(287) Busey, R. H.; Mesmer, R. E. *J. Solution Chem.* **1976**, *5*, 147–152.
(288) Busey, R. H.; Mesmer, R. E. *J. Chem. Eng. Data* **1978**, *23*, 175–176.
(289) Palmer, D. A.; Drummond, S. E. *J. Solution Chem.* **1988**, *17*, 153–164.
(290) Mesmer, R. E.; Herting, D. L. *J. Solution Chem.* **1978**, *7*, 901–913.
(291) Mesmer, R. E.; Patterson, C. S.; Busey, R. H.; Holmes, H. F. *J. Phys. Chem.* **1989**, *93*, 7483–7490.
(292) Patterson, C. S.; Busey, R. H.; Mesmer, R. E. *J. Solution Chem.* **1984**, *13*, 647–661.
(293) Patterson, C. S.; Slocum, G. H.; Busey, R. H.; Mesmer, R. E. *Geochim. Cosmochim. Acta* **1982**, *46*, 1653–1663.
(294) Busey, R. H.; Mesmer, R. E. *Inorg. Chem.* **1977**, *16*, 2444–2450.
(295) Mesmer, R. E.; Baes, C. F., Jr. *J. Solution Chem.* **1974**, *3*, 307–322.
(296) Mesmer, R. E.; Baes, C. F., Jr.; Sweeton, F. H. *Inorg. Chem.* **1972**, *11*, 537–543.
(297) Dickson, A. G.; Wesolowski, D. J.; Palmer, D. A.; Mesmer, R. E. *J. Phys. Chem.* **1990**, *94*, 7978–7985.
(298) Bell, J. L. S.; Wesolowski, D. J.; Palmer, D. A. *J. Solution Chem.* **1993**, *22*, 125–136.
(299) Mesmer, R. E.; Hitch, B. F. *J. Solution Chem.* **1977**, *6*, 251–261.
(300) Hitch, B. F.; Mesmer, R. E. *J. Solution Chem.* **1976**, *5*, 667–680.
(301) Wesolowski, D. J.; Palmer, D. A. *J. Solution Chem.* **1989**, *18*, 545–559.
(302) Palmer, D. A.; Wesolowski, D. *J. Solution Chem.* **1987**, *16*, 571–581.
(303) Palmer, D. A.; Wesolowski, D.; Mesmer, R. E. *J. Solution Chem.* **1987**, *16*, 443–463.
(304) Wesolowski, D.; Drummond, S. E.; Mesmer, R. E.; Ohmoto, H. *Inorg. Chem.* **1984**, *23*, 1120–1132.
(305) Mesmer, R. E.; Baes, C. F., Jr. *Inorg. Chem.* **1971**, *10*, 2290–2296.
(306) Palmer, D. A.; Drummond, S. E. *J. Phys. Chem.* **1988**, *92*, 6795–6800.
(307) Giordano, T. H.; Drummond, S. E. *Geochim. Cosmochim. Acta* **1991**, *55*, 2401–2415.
(308) Palmer, D. A.; Hyde, K. E. *Geochim. Cosmochim. Acta* **1993**, *57*, 1393-1408.
(309) Palmer, D. A.; Wesolowski, D. J. *Geochim. Cosmochim. Acta* **1993**, *57*, 2929–2938.
(310) Mesmer, R. E.; Sweeton, F. H.; Hitch, B. F.; Baes, C. F., Jr. In *High Temperature High Pressure Electrochemistry in Aqueous Solutions*; Jones, D. de G., Staehle, R. W., Eds.; National Association of Corrosion Engineers: Houston, TX, 1976; pp 365–374.
(311) Sweeton, F. H.; Mesmer, R. E.; Baes, C. F., Jr. *J. Phys. E: Sci. Instrum.* **1973**, *6*, 165–168.
(312) Matsushima, Y.; Okuwaki, A. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3344–3346.
(313) Macdonald, D. D.; Butler, P.; Owen, D. *J. Phys. Chem.* **1973**, *77*, 2474–2479.
(314) Macdonald, D. D.; Butler, P.; Owen, D. *Can. J. Chem.* **1973**, *51*, 2590–2595.
(315) Macdonald, D. D.; Owen, D. *Can. J. Chem.* **1973**, *51*, 2747–2749.
(316) Becker, P.; Bilal, B. A. *J. Solution Chem.* **1983**, *12*, 573–580.
(317) Becker, P.; Bilal, B. A. *Fresenius Z. Anal. Chem.* **1984**, *317*, 118–120.
(318) Becker, P.; Bilal, B. A. *J. Solution Chem.* **1985**, *14*, 367–374.
(319) Le Peintre, M. M. *Bull. Soc. Fr. Electr.* **1960**, *8*, 584–591.
(320) Bourcier, W. L.; Ulmer, G. C.; Barnes, H. L. In *Hydrothermal Experimental Techniques*; Ulmer, G. C., Barnes, H. L., Eds.; John Wiley & Sons: New York, 1987; Chapter 7.
(321) Macdonald, D. D.; Cragnolino, G. A. In *The ASME Handbook on Water Technology for Thermal Power Systems*; Cohen, P., Ed.; The American Society of Mechanical Engineers: New York, 1989; Chapter 9.
(322) Macdonald, D. D.; Hettiarachchi, S.; Lenhart, S. J. *J. Solution Chem.* **1988**, *17*, 719–732.
(323) Macdonald, D. D.; Wentrcek, P. R.; Scott, A. C. *J. Electrochem. Soc.* **1980**, *127*, 1745–1751.
(324) Tsuruta, T.; Macdonald, D. D. *J. Electrochem. Soc.* **1981**, *128*, 1199–1203.
(325) Tsuruta, T.; Macdonald, D. D. *J. Electrochem. Soc.* **1982**, *129*, 1221–1225.
(326) Hettiarachchi, S.; Macdonald, D. D. *J. Electrochem. Soc.* **1984**, *131*, 2206–2207.
(327) Hettiarachchi, S.; Kedzierzawski, P.; Macdonald, D. D. *J. Electrochem. Soc.* **1985**, *132*, 1866–1870.
(328) Macdonald, D. D.; Scott, A. C.; Wentrcek, P. R. *J. Electrochem. Soc.* **1979**, *126*, 908–911.
(329) Macdonald, D. D.; Scott, A. C.; Wentrcek, P. R. *J. Electrochem. Soc.* **1979**, *126*, 1618–1624.
(330) Hettiarachchi, S.; Macdonald, D. D. *J. Electrochem. Soc.* **1987**, *134*, 1307–1308.
(331) Macdonald, D. D. *Corrosion* **1978**, *34*, 75–84.
(332) Macdonald, D. D.; Hettiarachchi, S.; Song, H.; Makela, K.; Emerson, R.; Ben-Haim, M. *J. Solution Chem.* **1992**, *21*, 849–881.
(333) Dobson, J. V.; Dagless, M. N.; Thirsk, H. R. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 749–763.
(334) Dobson, J. V.; Dagless, M. N.; Thirsk, H. R. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 764–772.
(335) Dobson, J. V. *J. Electroanal. Chem.* **1972**, *35*, 129–135.
(336) Niedrach, L. W. *J. Electrochem. Soc.* **1980**, *127*, 2122–2130.
(337) Niedrach, L. W. *Science* **1980**, *207*, 1200–1202.
(338) Niedrach, L. W. *J. Electrochem. Soc.* **1982**, *129*, 1445–1449.
(339) Niedrach, L. W. *Adv. Ceram. Sci.* **1984**, *12*, 672–684.
(340) Niedrach, L. W. *J. Electrochem. Soc.* **1986**, *133*, 1521–1521.
(341) Niedrach, L. W.; Stoddard, W. H. *Corrosion* **1985**, *41*, 45–51.
(342) Danielson, M. J.; Koski, O. H.; Meyers, J. *J. Electrochem. Soc.* **1985**, *132*, 2037–2038.
(343) Danielson, M. J.; Koski, O. H.; Meyers, J. *J. Electrochem. Soc.* **1985**, *132*, 296–301.
(344) Danielson, M. J. *Corrosion* **1979**, *35*, 200–204.
(345) Danielson, M. J. *Corrosion* **1983**, *39*, 202–203.
(346) Nagy, Z.; Yonco, R. M. *J. Electrochem. Soc.* **1986**, *133*, 2232–2235.
(347) Cahan, B. D.; Nagy, Z.; Genshaw, M. A. *J. Electrochem. Soc.* **1972**, *119*, 64–69.
(348) Lauks, I.; Yuen, M. F.; Dietz, T. *Sens. Actuators* **1983**, *4*, 375–379.
(349) Katsube, T.; Lauks, I. R.; van der Speigel, J.; Zemel, J. N. *Jpn. J. Appl. Phys.* **1983**, *22*, 469–472.

(350) Katsube, T.; Lauks, I. R.; Zemel, J. N. *Sens. Actuators* **1982**, *2*, 399–410.

(351) Yuen, M. F.; Lauks, I.; Dautremont-Smith, W. C. *Solid State Ionics* **1983**, *11*, 19–19.

(352) Sturtevant, J. M. In *Physical Methods of Chemistry*; Weissberger, A.; Rossiter, B. W., Eds.; Wiley-Interscience: New York, 1971; Vol. 1, Chapter 7.

(353) Eatough, D. J.; Lewis, E. A.; Hansen, L. D. In *Analytical Solution Chemistry*; Grime, K., Ed., Wiley: New York, 1985; Chapter 5.

(354) Izatt, R. M.; Redd, E. H.; Christensen, J. J. *Thermochim. Acta* **1983**, *64*, 355–372.

(355) Oscarson, J. L.; Izatt, R. M.; Christensen, J. J. *Thermochim. Acta* **1986**, *100*, 271–282.

(356) Hansen, L. D.; Eatough, D. J. *Thermochim. Acta* **1983**, *70*, 257–268.

(357) Wadsö, I. *Thermochim. Acta* **1985**, *88*, 35–48.

(358) Zielenkiewicz, W.; Margas, E.; Hatt, J. *Thermochim. Acta* **1985**, *88*, 387–390.

(359) Kuessner, A. *Thermochim. Acta* **1987**, *119*, 59–79.

(360) Oscarson, J. L.; Izatt, R. M. in *Physical Methods of Chemistry: Determination of Thermodynamic Properties*, 2nd ed.; Rossiter, B. W., Baetzold, R. C., Eds.; John Wiley & Sons: New York, 1992; Vol. 6, Chapter 7.

(361) Eigen, M.; Wicke, E. *Z. Elektrochem.* **1951**, *55*, 354–363.

(362) Gardner, W. L.; Mitchell, R. E.; Cobble, J. W. *J. Phys. Chem.* **1969**, *73*, 2025-2032.

(363) Likke, S.; Bromley, L. A. *J. Chem. Eng. Data* **1973**, *18*, 189–195.

(364) Bromley, L. A.; Diamond, A. E.; Salami, E.; Wilkins, D. G. *J. Chem. Eng. Data* **1973**, *18*, 189–195.

(365) Wood, R. H.; Smith-Magowan, D. In *Thermodynamics of Aqueous Systems with Industrial Applications*; Newman, S. A., Ed.; ACS Symposium Series 133; American Chemical Society: Washington, DC, 1980; pp 569–581.

(366) Smith-Magowan, D.; Wood, R. H. *J. Chem. Thermodyn.* **1981**, *13*, 1047–1073.

(367) Rogers, P. Z. S.; Pitzer, K. S. *J. Phys. Chem.* **1981**, *85*, 2886–2895.

(368) Conti, G.; Gianni, P.; Papini, A.; Matteoli, E. *J. Solution Chem.* **1988**, *17*, 481–497.

(369) White, D. R.; Downes, C. J. *J. Solution Chem.* **1988**, *17*, 733–750.

(370) Christensen, J. J.; Hansen, L. D.; Izatt, R. M.; Eatough, D. J.; Hart, R. M. *Rev. Sci. Instrum.* **1981**, *52*, 1226–1231.

(371) Christensen, J. J.; Izatt, R. M. *Thermochim. Acta* **1984**, *73*, 117–129.

(372) Busey, R. H.; Holmes, H. F.; Mesmer, R. E. *J. Chem. Thermodyn.* **1984**, *16*, 343–372.

(373) Christensen, J. J.; Brown, P. R.; Izatt, R. M. *Thermochim. Acta* **1986**, *99*, 159–168.

(374) Oscarson, J. L.; Chen, X.; Gillespie, S. E.; Izatt, R. M. *Thermochim. Acta* **1991**, *185*, 51–61.

(375) Mayrath, J. E.; Wood, R. H. *J. Chem. Thermodyn.* **1982**, *14*, 15–26.

(376) Randzio, S.; Tomaszkiewicz, I. *J. Phys. E: Sci. Instrum.* **1980**, *13*, 1292–1296.

(377) Tomaszkiewicz, I.; Randzio, S. *J. Phys. E: Sci. Instrum.* **1985**, *18*, 92–94.

(378) Picker, P.; Leduc, P. A.; Philip, P. R.; Desnoyers, J. E. *J. Chem. Thermodyn.* **1971**, *3*, 631–642.

(379) White, D. E.; Gates, J. A.; Wood, R. H. *J. Chem. Thermodyn.* **1987**, *19*, 1037–1045.

(380) Rogers, P. S. Z.; Duffy, C. J. *J. Chem. Thermodyn.* **1989**, *21*, 595–614.

(381) Gates, J. A.; Tillett, D. M.; White, D. E.; Wood, R. H. *J. Chem. Thermodyn.* **1987**, *19*, 131–146.

(382) White, D. E.; Wood, R. H.; Biggerstaff, D. R. *J. Chem. Thermodyn.* **1988**, *20*, 159–168.

(383) White, D. E.; Ryan, M. A.; Armstrong, M. C.; Gates, J. A.; Wood, R. H. *J. Chem. Thermodyn.* **1987**, *19*, 1023–1030.

(384) Pabalan, R. T.; Pitzer, K. S. *J. Chem. Eng. Data* **1988**, *33*, 354–362.

(385) White, D. E.; Gates, J. A.; Tillet, D. M.; Wood, R. H. *J. Chem. Eng. Data* **1988**, *33*, 485–490.

(386) White, D. E.; Doberstein, A. L.; Gates, J. A.; Tillett, D. M.; Wood, R. H. *J. Chem. Thermodyn.* **1987**, *19*, 251–259.

(387) Wood, R. H.; White, D. E.; Davis, W. E.; Thompson, P. T. *J. Chem. Eng. Data* **1988**, *33*, 301–306.

(388) Smith-Magowan, D.; Wood, R. H.; Tillett, D. M. *J. Chem. Eng. Data* **1982**, *27*, 335–342.

(389) White, D. E.; Gates, J. A.; Wood, R. H. *J. Chem. Thermodyn.* **1987**, *19*, 493–503.

(390) Phutela, R. C.; Pitzer, K. S. *J. Phys. Chem.* **1986**, *90*, 895–901.

(391) Simonson, J. M.; Mesmer, R. E.; Rogers, P. S. Z. *J. Chem. Thermodyn.* **1989**, *21*, 561–584.

(392) Caiani, P.; Conti, G.; Gianni, P.; Matteoli, E. *J. Solution Chem.* **1989**, *18*, 447–461.

(393) Biggerstaff, D. R.; Wood, R. H. *J. Phys. Chem.* **1988**, *92*, 1994–2000.

(394) Wood, R. H. *Thermochim. Acta* **1989**, *154*, 1–11.

(395) Wood, R. H.; Quint, J. R. *J. Chem. Thermodyn.* **1982**, *14*, 1069–1076.

(396) Levelt Sengers, J. M. H.; Everhart, C. M.; Morrison, G. *Chem. Eng. Commun.* **1986**, *47*, 315–328.

(397) White, D. E.; Wood, R. H. *J. Solution Chem.* **1982**, *11*, 223–236.

(398) Rogers, P. S. Z.; Pitzer, K. S. *J. Phys. Chem. Ref. Data* **1982**, *11*, 15–81.

(399) White, D. R.; Downes, C. J. *J. Phys. E: Sci. Instrum.* **1989**, *22*, 79–81.

(400) Wood, R. H.; White, D. E.; Gates, J. A.; Albert, H. J.; Biggerstaff, D. R.; Quint, J. R. *Fluid Phase Equilib.* **1985**, *20*, 283–296.

(401) Tremaine, P. R.; Sway, K.; Barbero, J. A. *J. Solution Chem.* **1986**, *15*, 1–22.

(402) Conti, G.; Festa, C.; Gianni, P.; Tiné, M. R. *Gazz. Chim. Ital.* **1984**, *114*, 7–14.

(403) Conti, G.; Gianni, P.; Tiné, M. R. *Thermochim. Acta* **1985**, *85*, 159–162.

(404) Conti, G.; Gianni, P.; Tiné, M. R. *J. Solution Chem.* **1986**, *15*, 349–362.

(405) Conti, G.; Gianni, P.; Tiné, M. R. *Thermochim. Acta* **1989**, *145*, 61–75.

(406) Luff, B. B. *J. Chem. Eng. Data* **1981**, *26*, 70–74.

(407) Holmes, H. F.; Busey, R. H.; Simonson, J. M.; Mesmer, R. E.; Archer, D. G.; Wood, R. H. *J. Chem. Thermodyn.* **1987**, *19*, 863–890.

(408) Simonson, J. M.; Holmes, H. F.; Busey, R. H.; Mesmer, R. E.; Archer, D. G.; Wood, R. H. *J. Phys. Chem.* **1990**, *94*, 7675–7681.

(409) Thiessen, W. E.; Simonson, J. M. *J. Phys. Chem.* **1990**, *94*, 7794–7800.

(410) Simonson, J. M.; Busey, R. H.; Mesmer, R. E. *J. Phys. Chem.* **1985**, *99*, 557–560.

(411) Simonson, J. M.; Holmes, H. F.; Mesmer, R. E.; Busey, R. H. In Proceedings: 1987 Symposium on Chemistry in High Temperature Water; Izatt, R. M., Oscarson, J. L., LindH, G. C., Eds.; EPRI Report NP-6005; Electric Power Research Institute: Palo Alto, CA, 1990; Paper 3a.

(412) Pitzer, K. S. *J. Phys. Chem.* **1973**, *77*, 268–277.

(413) Pitzer, K. S.; Mayorga, G. *J. Phys. Chem.* **1973**, *77*, 2300–2308.

(414) Pitzer, K. S.; Mayorga, G. *J. Phys. Chem.* **1974**, *78*, 2698–2698.

(415) Pitzer, K. S.; Mayorga, G. *J. Solution Chem.* **1974**, *3*, 539–546.

(416) Pitzer, K. S.; Kim, J. J. *J. Am. Chem. Soc.* **1974**, *96*, 5701–5705.

(417) Pitzer, K. S. *J. Solution Chem.* **1975**, *4*, 249–265.

(418) Pitzer, K. S.; Silvester, L. F. *J. Solution Chem.* **1976**, *5*, 269–278.

(419) Pitzer, K. S. *Acc. Chem. Res.* **1977**, *10*, 371–377.

(420) Silvester, L. F.; Pitzer, K. S. *J. Solution Chem.* **1978**, *7*, 327–337.

(421) Pitzer, K. S. In *Activity Coefficients in Electrolyte Solutions*; Pytkowicz, R. M., Ed.; CRC Press: Boca Raton, FL, 1979; Vol. 1, Chapter 7.

(422) Bradley, D. J.; Pitzer, K. S. *J. Phys. Chem.* **1983**, *87*, 3798–3798.

(423) Pitzer, K. S. *J. Phys. Chem.* **1983**, *87*, 2360–2364.

(424) Phutela, R. C.; Pitzer, K. S. *J. Solution Chem.* **1986**, *15*, 649–662.

(425) Pitzer, K. S. In *Thermodynamic Modeling of Geological Materials: Minerals, Fluids and Melts*; Carmichael, I. S. E., Eugster, H. P., Eds.; Mineralogical Society of America: Washington, DC, 1987; pp 97–142.

(426) Yang, J.-Z.; Pitzer, K. S. *J. Solution Chem.* **1988**, *17*, 909–924.

(427) Pitzer, K. S. In *Activity Coefficients in Electrolyte Solutions*, 2nd ed.; Pitzer, K. S., Ed.; CRC Press: Boca Raton, FL, 1991; Chapter 3.

(428) Archer, D. G.; Wood, R. H. *J. Solution Chem.* **1985**, *14*, 757–780.

(429) Mayrath, J. E.; Wood, R. H. *J. Chem. Thermodyn.* **1982**, *14*, 563–576.

(430) Mayrath, J. E.; Wood, R. H. *J. Chem. Eng. Data* **1983**, *28*, 56–59.

(431) Archer, D. G. *J. Solution Chem.* **1986**, *15*, 727–742.

(432) Archer, D. G.; Albert, H. J.; White, D. E.; Wood, R. H. *J. Colloid Interface Sci.* **1984**, *100*, 68–81.

(433) Archer, D. G. *J. Solution Chem.* **1986**, *15*, 581–596.

(434) Archer, D. G. *J. Solution Chem.* **1987**, *16*, 347–365.

(435) Oscarson, J. L.; Izatt, R. M.; Brown, P. R.; Pawlak, Z.; Gillespie, S. E.; Christensen, J. J. *J. Solution Chem.* **1988**, *17*, 841–863.

(436) Oscarson, J. L.; Gillespie, S. E.; Christensen, J. J.; Izatt, R. M.; Brown, P. R. *J. Solution Chem.* **1988**, *17*, 865–885.

(437) Izatt, R. M.; Gillespie, S. E.; Chen, X.; Oscarson, J. L. *Pure Appl. Chem.* **1991**, *63*, 1419–1426.

(438) Gillespie, S. E.; Oscarson, J. L.; Chen, X.; Izatt, R. M.; Pando, C. *J. Solution Chem.* **1992**, *21*, 761–788.

(439) Oscarson, J. L.; Gillespie, S. E.; Izatt, R. M.; Chen, X.; Pando, C. *J. Solution Chem.* **1992**, *21*, 789–801.

(440) Chen, X.; Gillespie, S. E.; Oscarson, J. L.; Izatt, R. M. *J. Solution Chem.* **1992**, *21*, 825–848.

(441) Hansen, L. D.; Christensen, J. J.; Izatt, R. M. *J. Chem. Soc., Chem. Commun.* **1965**, 36–37.

(442) Christensen, J. J.; Izatt, R. M.; Hansen, L. D. *Rev. Sci. Instrum.* **1965**, *36*, 779–783.

(443) Christensen, J. J.; Izatt, R. M.; Hansen, L. D.; Partridge, J. A. *J. Phys. Chem.* **1966**, *70*, 2003–2010.

(444) Christensen, J. J.; Wrathall, D. P.; Izatt, R. M. *Anal. Chem.* **1968**, *40*, 175–181.

(445) Christensen, J. J.; Wrathall, D. P.; Oscarson, J. L.; Izatt, R. M. *Anal. Chem.* **1968**, *40*, 1713–1717.

(446) Izatt, R. M.; Eatough, D. J.; Snow, R. L.; Christensen, J. J. *J. Phys. Chem.* **1968**, *72*, 1208–1213.

(447) Christensen, J. J.; Johnston, H. D.; Izatt, R. M. *Rev. Sci. Instrum.* **1968**, *39*, 1356–1359.

(448) Christensen, J. J.; Rytting, J. H.; Izatt, R. M. *J. Chem. Soc. A* **1969**, 861–862.

(449) Christensen, J. J.; Ruckman, J.; Eatough, D. J.; Izatt, R. M. *Thermochim. Acta* **1972**, *3*, 203–218.

(450) Eatough, D. J.; Christensen, J. J.; Izatt, R. M. *Thermochim. Acta* **1972**, *3*, 219–232.

(451) Eatough, D. J.; Izatt, R. M.; Christensen, J. J. *Thermochim. Acta* **1972**, *3*, 233–246.

(452) Christensen, J. J.; Gardner, J. W.; Eatough, D. J.; Izatt, R. M.; Watts, P. J.; Hart, R. M. *Rev. Sci. Instrum.* **1973**, *44*, 481–484.

(453) Christensen, J. J.; Hansen, L. D.; Eatough, D. J.; Izatt, R. M.; Hart, R. M. *Rev. Sci. Instrum.* **1976**, *47*, 730–734.

(454) Izatt, R. M.; Terry, R. E.; Haymore, B. L.; Hansen, L. D.; Dalley, N. K.; Avondet, A. G.; Christensen, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 7620–7626.

(455) Izatt, R. M.; Terry, R. E.; Hansen, L. D.; Avondet, A. G.; Bradshaw, J. S.; Dalley, N. K.; Haymore, B. L.; Christensen, J. J. *Inorg. Chim. Acta* **1978**, *30*, 1–8.

(456) Izatt, R. M.; Lamb, J. D.; Izatt, N. E.; Rossiter, B. E. Jr.; Christensen, J. J.; Haymore, B. L. *J. Am. Chem. Soc.* **1979**, *101*, 6273–6276.

(457) Eatough, D. J.; Izatt, R. M.; Christensen, J. J. In *Biochemical and Clinical Applications of Thermometric and Thermal Analysis*; Jesperson, N., Ed.; Elsevier Press: New York, NY, 1982; pp 3–38.

(458) Izatt, R. M.; Clark, G. A.; Lamb, J. D.; King, J. E.; Christensen, J. J. *Thermochim. Acta* **1986**, *97*, 115–126.

(459) Izatt, R. M.; Oscarson, J. L.; Gillespie, S. E.; Grimsrud, H.; Renuncio, J. A. R.; Pando, C. *Biophys. J.* **1992**, *61*, 1394–1401.

(460) Izatt, R. M.; Oscarson, J. L.; Gillespie, S. E.; Chen, X. *Determination of Thermodynamic Data for Modelling Corrosion*; EPRI Report NP-5708; Electric Power Research Institute: Palo Alto, CA, 1992; Vol. 4.

(461) Izatt, R. M.; Oscarson, J. L.; Gillespie, S. E.; Chen, X. *Determination of Thermodynamic Data for Modelling Corrosion*; EPRI Report NP-5708; Electric Power Research Institute: Palo Alto, CA, 1992; Vol. 5.

(462) Oscarson, J. L.; Wu, G.; Faux, P. W.; Izatt, R. M.; Christensen, J. J. *Thermochim. Acta* **1989**, *154*, 119–127.

(463) Fabes L.; Swaddle, T. W. *Can. J. Chem.* **1975**, *53*, 3053–3059.

(464) Archer, D. G. *J. Phys. Chem. Ref. Data* **1991**, *20*, 509–555.

(465) Archer, D. G. *J. Phys. Chem. Ref. Data* **1992**, *21*, 793–829.

(466) Meissner, H. P.; Tester, J. W. *Ind. Eng. Chem. Proc. Des. Dev.* **1972**, *11*, 128–133.

(467) Meissner, H. P.; Kusik, C. L.; Tester, J. W. *AIChE J.* **1972**, *18*, 661–662.

(468) Meissner, H. P. In *Thermodynamics of Aqueous Systems with Industrial Applications*; Newman, S. A., Ed.; ACS Symposium Series 133; American Chemical Society: Washington, DC, 1980; pp 495–511.

(469) Lindsay, W. T., Jr. In *Proceedings of the 41st International Water Conference*; Engineers Society of Western Pennsylvania: Pittsburgh, PA, 1980; pp 284–294.

(470) Harned, H. S.; Robinson, R. A. *Trans. Faraday Soc.* **1940**, *36*, 973–978.

(471) Khodakovskiy, I. L.; Ryzhenko, B. N.; Naumov, G. B. *Geochem. Int.* **1968**, *5*, 1200–1219.

(472) Readnour, J. M.; Cobble, J. W. *Inorg. Chem.* **1969**, *8*, 2174–2182.

(473) Stephens, H. P.; Cobble, J. W. *Inorg. Chem.* **1971**, *10*, 619–625.

(474) Criss, C. M. In *Proceedings of the 41st International Water Conference*; Engineers Society of Western Pennsylvania: Pittsburgh, PA, 1980; pp 311–317.

(475) Helgeson, H. C.; Kirkham, D. H. *Am. J. Sci.* **1974**, *274*, 1199–1261.

(476) Helgeson, H. C.; Kirkham, D. H. *Am. J. Sci.* **1976**, *276*, 97–240.

(477) Walther, J. V.; Helgeson, H. C. *Am. J. Sci.* **1977**, *277*, 1315–1351.

(478) Helgeson, H. C.; Delany, J. M.; Nesbitt, H. W.; Bird, D. K. *Am. J. Sci.* **1978**, *278-A*, 1–229.

(479) Walther, J. V.; Helgeson, H. C. *Am. J. Sci.* **1980**, *280*, 575–606.

(480) Helgeson, H. C.; Kirkham, D. H.; Flowers, G. C. *Am. J. Sci.* **1981**, *281*, 1249–1516.

(481) Helgeson, H. C. In *Chemistry and Geochemistry of Solutions at High Temperatures and Pressures*; Rickard, D. T., Wickman, F. E., Eds.; Pergamon Press: Oxford, 1981; pp 133–177.

(482) Helgeson, H. C. *Am. J. Sci.* **1982**, *282*, 1144–1149.

(483) Bowers, T. S.; Helgeson, H. C. *Geochim. Cosmochim. Acta* **1983**, *47*, 1247–1275.

(484) McKenzie, W. F.; Helgeson, H. C. *Geochim. Cosmochim. Acta* **1984**, *48*, 2167–2177.

(485) Helgeson, H. C. *Am. J. Sci.* **1985**, *285*, 845–855.

(486) Jackson, K. J.; Helgeson, H. C. *Econ. Geol.* **1985**, *80*, 1365–1378.

(487) Oelkers, E. H.; Helgeson, H. C. *Geochim. Cosmochim. Acta* **1988**, *52*, 63–85.

(488) Oelkers, E. H.; Helgeson, H. C. *J. Phys. Chem.* **1988**, *92*, 1631–1639.

(489) Shock, E. L.; Helgeson, H. C. *Geochim. Cosmochim. Acta* **1988**, *52*, 2009–2036.

(490) Tanger, J. C. IV; Helgeson, H. C. *Am. J. Sci.* **1988**, *288*, 19–98.

(491) Shock, E. L.; Helgeson, H. C.; Sverjensky, D. A. *Geochim. Cosmochim. Acta* **1989**, *53*, 2157–2183.

(492) Shock, E. L.; Helgeson, H. C. *Geochim. Cosmochim. Acta* **1990**, *54*, 915–945.

(493) Oelkers, E. H.; Helgeson, H. C. *Geochim. Cosmochim. Acta* **1991**, *55*, 1235–1251.

(494) Shock, E. L.; Oelkers, E. H.; Johnson, J. W.; Sverjensky, D. A.; Helgeson, H. C. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 803–826.

(495) Helgeson, H. C. *Appl. Geochem.* **1992**, *7*, 291–308.

(496) Helgeson, H. C. *Geochim. Cosmochim. Acta* **1992**, *56*, 3191–3207.

(497) Pokrovskii, V. A.; Helgeson, H. C. In *Water-Rock Interaction*; Kharaka, Y. K.; Maest, A. S., Eds.; A. A. Balkema: Rotterdam, 1992; pp 1021–1024.

(498) Johnson, J. W.; Oelkers, E. H.; Helgeson, H. C. *Comput. Geosci.* **1992**, *18*, 899–947.

(499) Brady, P. V.; Walther, J. V. *Geochim. Cosmochim. Acta* **1990**, *54*, 1555–1561.

(500) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059–5061.

(501) Gilkerson, W. R. *J. Phys. Chem.* **1970**, *74*, 746–750.

(502) Walther, J. V.; Schott, J. *Nature*, **1988**, *332*, 635–638.

(503) Bryzgalin, O. V. *Geochem. Int.* **1986**, *23*, No. 2, 84–95.

(504) Ryzhenko, B. N.; Bryzgalin, O. V.; Artamkina, I. Yu.; Spasennykh, M. Yu.; Shapkin, A. I. *Geochem. Int.* **1985**, *22*, No. 9, 138–144.

(505) Bryzgalin, O. V. *Geochem. Int.* **1989**, *26*, No. 10, 63–70.

(506) Anderson, G. M.; Castet, S.; Schott, J.; Mesmer, R. E. *Geochim. Cosmochim. Acta* **1991**, *55*, 1769–1779.