

Tests of Equations for the Electrical Conductance of Electrolyte Mixtures: Measurements of Association of NaCl (Aq) and Na₂SO₄ (Aq) at High Temperatures

Andrei V. Sharygin,[†] Ilham Mokbel,[‡] Caibin Xiao,[§] and Robert H. Wood*

Department of Chemistry and Biochemistry and Center for Molecular and Engineering Thermodynamics, University of Delaware, Newark, Delaware 19716

Received: July 19, 2000

A review of requirements for equations to calculate the conductivity of a mixture of ions in low dielectric constant solvents (i.e., water at high temperatures) shows that there are conceptual difficulties with all current equations. To explore whether these difficulties limit our ability to predict mixtures, four models for the activity coefficients, two models for the conductivity of a single strong electrolyte, and an equation for the change in equivalent conductivity on mixing single strong electrolytes were chosen. These equations were then tested on the theoretical equation of Turq et al. (*J. Phys. Chem.* **1995**, *99*, 822–827) for three ion mixtures. Next the equations were tested on a single 1–1 electrolyte, NaCl (aq) at 652.6 K and 22.75 MPa measured by Gruskiewicz and Wood (*J. Phys. Chem. B* **1997**, *101*, 61549–6559) and new measurements at 623.9 K and 19.79 MPa. Then it was tested with new measurements on Na₂SO₄ (aq) from 300 to 574 K because, in water at high temperatures, this salt produces a solution containing six different ions (Na⁺, SO₄²⁻, NaSO₄⁻, HSO₄⁻, H⁺, OH⁻). The equations were able to reproduce the experimental data. Values of equilibrium constants, *K*, for the dissociation of NaCl and NaSO₄⁻ and equivalent conductances Λ_0 derived by a least-squares fit agreed with reported data determined by other methods, showing that conductivity measurements can yield accurate equilibrium constants in complex mixtures of ions. The values of *K* and Λ_0 were not very sensitive to changes in (1) the single electrolyte conductance equation, (2) assumed values of Λ_0 for minor species, or (3) equilibrium constants for minor reactions. Uncertainty in the activity coefficient model was the largest contributor to uncertainty in *K* and Λ_0 . This method should allow rapid and accurate measurements of the equilibrium constant for any reaction, which changes the number of ions in solution. The equilibrium constants for many reactions of this type are unknown in water at high temperatures.

1. Introduction

A new flow conductance apparatus from this laboratory has demonstrated unprecedented speed, precision, and sensitivity when measuring aqueous solutions near the critical point of water.^{1,2} In principle this apparatus can be used to measure equilibrium constants for any reaction that changes the number of ions in solution. Many of these reactions (acid, base, hydrolysis, and complexing) have not been measured at high temperatures. However, equations that accurately calculate the conductance of a reacting mixture of ions are needed to analyze the experimental conductance measurements. This article explores whether the use of this apparatus and the application of a mixture equation allows the measurement of equilibria in complex electrolyte mixtures at high temperatures. Our equation for the conductance of a reacting mixture of electrolytes has three components: (1) a model for the activity coefficients of the ions so that the equilibrium concentrations of free ions in a reacting mixture can be calculated from the equilibrium constants for the reactions; (2) an equation for the equivalent conductivity of a single strong electrolyte as a function of concentration; (3) a mixing rule that predicts the conductance

of a mixture of strong electrolytes from the conductance of the single electrolytes. We start with a brief review of equations for each of these components and discuss the difficulty with these equations at high temperatures. Next we compare our equations with the three-ion mixture equations of Durand-Vidal et al.³ We then test these equations using our experimental results for sodium chloride and sodium sulfate. In this article a promising single electrolyte model and four activity coefficient models are tested using our mixture model against our data. For NaCl we also compare our model with a well-established conductance equation. In sodium sulfate, hydrolysis and association reactions produce many different ionic species so the mixture equation is necessary.

Sodium sulfate was chosen for this study because its association and hydrolysis in aqueous solutions at elevated temperatures are of great importance in many industrial processes such as material transport, solid deposition, and corrosion in steam generators and electric power boilers. Sodium sulfate is a common product of hydrothermal waste destruction by supercritical water oxidation. Na₂SO₄ (aq) is also an important constituent of natural subsurface brines and sea floor vent fluids. In addition, Na₂SO₄ (aq) is a prime representative of 1–2 charge-type electrolytes, and it is therefore an important candidate for study in our high-temperature aqueous chemistry program. The association of Na₂SO₄ (aq) has been investigated previously;^{4–10} however, the information is limited at temperatures greater than 473 K.

[†] Present address: Congoleum Corporation, Research & Development, P.O. Box 3127, 861 Sloan Avenue, Mercerville, New Jersey 08619.

[‡] Present address: Université Claude Bernard, Laboratoire de Chimie Analytique 1, Lyon, France.

[§] Present address: Oak Ridge National Laboratory, P.O. Box 2008, Bldg. 4500S, MS-6110, Oak Ridge, Tennessee 37831-6110.

2. Mixture Conductance Equations

2.1. Activity Coefficient Model. First, we will examine the activity coefficient model, which is necessary for our mixture calculation. In calculating the equilibrium concentrations of ions in a reacting mixture, we need the equilibrium constants for the reactions and a model for the activity coefficients of the ions as a function of the ionic strength. Two models were tested. The first is the Bjerrum model for activity coefficient, (γ_{\pm}), which is essentially the extended Debye–Hückel equation for an ion with the assumption that all ions within the Bjerrum distance are ion-paired and do not contribute to the screening of other ions.

The Debye–Hückel limiting law is:

$$\ln \gamma_{\pm} = -|z_+ z_-| A_{\gamma} I_c^{1/2} / (1 + B a I_c^{1/2}) \quad (1)$$

where z_+ and z_- are the charges of cation and anion, respectively; A_{γ} is the Debye–Hückel slope; $I_c = 1/2 \sum c_i z_i^2$ is the ionic strength; $B = 2 N_A e^2 / (\epsilon_0 \epsilon k_B T)^{1/2}$, where N_A is the Avogadro's number, e is the electronic charge, and ϵ_0 and ϵ are the dielectric constants of vacuum and solvent, respectively. The distance of closest approach, a , was set equal to the Bjerrum distance following the recommendation of Justice¹¹:

$$a = \sigma_{Bj} = |z_+ z_-| e^2 / (8 \pi \epsilon_0 \epsilon_R k T) \quad (2)$$

The activity coefficients of the undissociated electrically neutral species were assumed to equal unity in all conditions. The other model we tested is the mean spherical approximation (MSA) for the activity coefficient¹²:

$$\ln \gamma_i = \ln \gamma_i^{\text{el}} + \ln \gamma_i^{\text{HS}} \quad (3)$$

where γ_i^{el} is the electrostatic part and γ_i^{HS} is the hard sphere part.

There are conceptual difficulties with these activity models at high temperatures. The Bjerrum model, eq 1, is not consistent with the Gibbs–Duhem relation unless a is the same for all cation–anion interactions. When ions with different charges are present, the Bjerrum distance varies with the product $z_i z_j$ (eq 2). The MSA equations are for a system of hard-sphere ions that are additive ($\sigma_{ij} = (\sigma_i + \sigma_j)/2$). However, the Bjerrum distances of closest approach for cation and anion are nonadditive. Also one might expect that all distances of closest approach are approximately the sums of the ionic radii except for cation–anion interactions, which should be about equal to the Bjerrum distance (because the ions are considered as paired inside this distance).¹¹ Because of these conceptual difficulties we empirically tried four activity coefficient models. In the Bj model, the Bjerrum equation (eq 1) was used with a equal to Bjerrum distance for a 1–1 electrolyte. In the MSA models, there were two simple choices for the diameters of the species: either the ionic diameters (σ_{HS}) or the Bjerrum distances for an interaction with an ion of equal and opposite charge (eq 2 with $z_+ = z_- = z$). This gives the correct Bjerrum distances for 1–1 and 2–2 interaction, but for the 1–2 interaction it is too high (by 25%). Also the like-charged diameters are too high and the diameter is zero when $z = 0$. Because of this, for $z = 0$ we always used the hard-sphere diameters. These considerations led us to try three approximations: MSA.HS.HS, MSA.Bj.Bj, and MSA.HS.Bj, where for instance, MSA.HS.Bj indicates $\gamma_{\text{MSA}}^{\text{HS}}$ calculated with σ_{HS} and $\gamma_{\text{MSA}}^{\text{el}}$ is calculated with σ_{Bj} for ions and σ_{HS} for neutrals.

2.2. Equation for a Single Strong Electrolyte. In previous work^{1,2} we used the FHFP equation of Fuoss and Hsia¹³ as adapted by Fernández-Prini,¹⁴ and this was able to describe precisely the concentration dependence of symmetric electrolytes. The concentration dependence of the equivalent conductance, Λ , and the specific conductance, κ , of a 1–1 electrolyte are expressed by the FHFP equation as

$$\kappa = N \Lambda = N(\Lambda_0 - S N^{1/2} + E N \ln N + J_1 N + J_2 N^{3/2}) \quad (4)$$

where N is the actual, (equilibrium) equivalent concentration of the electrolyte in the solution ($N = c z_+ = c |z_-|$) calculated from the equilibrium constants and the activity coefficient model; Λ_0 is the limiting equivalent conductance of the electrolyte; S , E , and J_1 are calculated following the equations given by Fernández-Prini,¹⁴ with viscosities from Watson et al.,¹⁵ dielectric constants from Archer and Wang,¹⁶ and other water properties from Hill.¹⁷ To obtain the best estimates of Λ_0 and the equilibrium constant, the parameter J_2 usually is treated as a fitting parameter, although its theoretical value can be approximated with the FHFP model.¹¹ The FHFP equation worked well for the alkali halides at high temperatures, and it has been used successfully by many authors.^{1,2,18,19}

Recently, Turq and co-workers^{3,12,20,21} have derived a series of conductance equations for electrolytes of any charge type starting from the same continuum hydrodynamic equations as the FHFP equation but with the more accurate MSA pair distribution function and a solution of the equations using a Green's function. Their equations fit experimental results on aqueous solutions near room temperature with an accuracy of about 1% to very high concentrations indicating that they may be very useful at high temperatures. However, Bianchi et al.²² report that there are some problems in fitting very accurate data at low concentrations. According to Turq et al.¹² (TBBK model), the specific and equivalent conductances of an individual ion, κ_i and Λ_i , are related to the limiting equivalent conductance of the ion at infinite dilution $\Lambda_{i,0}$ by

$$\kappa_i = \Lambda_i c_i = \Lambda_{i,0} c_i (1 + \delta \nu_i^{\text{el}} / \nu_i^0) \cdot (1 + \delta X/X) \quad (5)$$

where $\delta \nu_i^{\text{el}}$ is the electrophoretic term, and $\delta X/X$ is the relaxation term, and c_i is the actual equilibrium equivalent concentration of the i th ion from the equilibrium calculation (see below). The electrophoretic effect expresses the hydrodynamic drag of one ion in the velocity field of the others. The relaxation term describes the effect of the distortion of the ion atmosphere (in the linear response approximation) by the perturbation of the external force. Besides the temperature and the dielectric permittivity of the solvent, the only parameters necessary to evaluate both the electrophoretic and relaxation terms are the ionic radii r_i and the limiting, equivalent conductances of the single ions. The total equivalent conductance is equal to the sum of the equivalent conductances of individual ions:

$$\Lambda = \sum_i \Lambda_i \quad (6)$$

Analytical expressions for the relaxation and electrophoretic terms are given in detail by Turq et al.¹² and will not be repeated here. However, note $(x - \kappa_q)$ in eq 35 should be $(x + \kappa_q)$.²³

The TBBK model is appropriate for strong electrolytes (symmetric and asymmetric) within the limitations of continuum hydrodynamics. However, when association is introduced and when the Bjerrum distance is much greater than the hard-sphere

diameter, both the TBBK and FHP models are no longer appropriate, because the equations have just one distance parameter when two distances are necessary to describe the interactions. The first distance is the contact distance (distance of closest approach) between an anion and a cation, and this is the distance that determines the hydrodynamic effects. The second distance is the distance at which an ion pair no longer contributes to the conductivity. In this work we have followed Justice¹¹ and used the Bjerrum distance as a good approximation for this distance. Clearly, if ions closer than the Bjerrum distance are considered to be ion-paired, then the ion atmosphere around an ion is limited to distances outside the Bjerrum distance. Thus, ion atmospheres and the relaxation of ion atmospheres should be calculated with the Bjerrum distance. In aqueous solutions near the critical point, these two distances are not close to each other, so in this article both equations are treated as empirical representations of the experimental data, and the best one is chosen on the basis of accuracy and number of adjustable parameters. In principle, the approach of Turq et al.¹² does not need to consider association reactions at all but this would require a much more accurate model for the pair correlation function of a strongly associating electrolyte. Higher order terms in the conductance equation would also be required.

In the TBBK equation, Λ is a function of the individual diameters. We tried two approximations: TBBK.HS and TBBK.Bj. In the, hard-sphere approximation, TBBK.HS, the ionic diameters were used: $\sigma_{ij} = (\sigma_i + \sigma_j)/2$. In the Bjerrum approximation, TBBK.Bj, the ionic diameters were used, except for interactions of oppositely charged ions, where the Bjerrum distance was used. Fortunately, the TBBK results are relatively insensitive to this choice.

2.3. Mixing Rule. A review of the literature on mixing rules reveals many different recommendations of essentially the same rule, although for different properties and with varying refinements. Young and co-workers^{24,25} noticed that volumes and enthalpies of mixing two salts of the same charge type with a common ion at constant ionic strength are generally much smaller than for mixtures without a common ion (sometimes called Young's rule). Reilly and Wood²⁶ generalized this to allow predictions of multicomponent mixtures of different charge types using the fact that any mixture can be formed using only common-ion mixtures and applied the resulting equation to volumes, heats, and free energies. If one takes the equation of Reilly and Wood²⁶ for the excess free energy per kilogram of water for a general multicomponent mixture and applies it to the specific conductance but neglecting volume changes of mixing so that the molality can be replaced by the molar concentration, then, one finds for the specific conductance of the mixture:

$$\begin{aligned} \kappa [I_c] = & \sum_{M=1}^{N_c} \sum_{X=1}^{N_a} \{c_{M^z M^c X} |z_X| (z_M - z_X)\} \kappa_{MX}^0 [I_c] / (2NI_c) + \\ & RT / (4N) \sum_{M < N} \sum_{X=1}^{N_a} c_{M^z M^c N^z N^c X} |z_X| (z_M - z_X) \cdot (z_N - z_X) g_{M,N}^X + \\ & RT / (4N) \sum_{X < Y=1}^{N_a} \sum_{M=1}^{N_c} c_X |z_X| c_Y |z_Y| c_{M^z M^c} (z_M - z_X) \cdot (z_M - z_Y) g_{XY}^M \end{aligned} \quad (7)$$

where c is the concentration of an ion and z is its charge; subscripts M and N denote cations and X and Y denote anions; N_c and N_a are the numbers of cations and anions in the mixture, respectively; $\kappa_{MX}^0 [I_c]$ is the specific conductance of the pure

salt MX at molar ionic strength $I_c = 1/2 \sum_i c_i z_i^2$; and N is the equivalent concentration, $N = \sum c_M z_M = \sum c_X |z_X|$. The values of $g_{M,N}^X$ are obtained by fitting experimental results on the common-ion mixture of MX with NX . Thus, the first term in eq 7 represents the prediction if only single salts have been measured and the second term, if only two-salt, common-ion mixtures have been measured. Equation 7 can be simplified if we use the equivalent concentration of the pure salt MX at the same ionic strength: $N_{MX}^0 = 2I_c / (z_M - z_X)$ and define: $k_{M,N}^X = (z_M - z_X) \cdot (z_N - z_X) g_{M,N}^X / 4$ with equivalent fractions: $x_M = c_M z_M / N$ and $x_Y = c_Y |z_Y| / N$ and $\Lambda_{o,MX} [I_c] = \kappa_{MX}^0 [I_c] / N_{MX}^0$. Then, the final result is:

$$\begin{aligned} \kappa [I_c] = & N \sum_{M=1}^{N_c} \sum_{X=1}^{N_a} x_M x_X \Lambda_{o,MX} [I_c] + \\ & RTN^2 \sum_{M < N} \sum_{Y=1}^{N_a} x_M x_N x_Y k_{M,N}^Y + RTN^2 \sum_{X < Y} \sum_{Y=1}^{N_a} x_X x_Y x_M k_{XY}^M \end{aligned} \quad (8)$$

This multicomponent rule provides a rational choice of what salts are mixed to form a general mixture based on forming the mixture with only common-ion mixtures.

Wu et al.²⁷ tested Young's cross square rule by applying it to conductances of mixtures and found that the rule is obeyed quite accurately at high concentrations $\{I = (1 \text{ to } 4) \text{ mol} \cdot \text{kg}^{-1}\}$. This rule is closely related to eq 8.²⁶ Although small errors are made in predicting the Debye–Onsager limiting slope, the rule worked well on both with experimental data and in theoretical calculations. Wu et al.²⁷ concluded that "It seems likely that Reilly–Wood analysis of electrolyte mixtures at equilibrium has a counterpart for transport properties in electrolyte mixtures."

Later on, Miller²⁸ tested a variety of mixing rules on the common-ion mixture of NaCl with MgCl_2 . Miller²⁸ estimated the specific conductance of a mixture using the specific conductance of its constituent binary systems through a linear mixing rule:

$$k = \sum_i a_{iL'} \cdot \kappa_{iL} + \delta_{LL'} \quad (9)$$

where $a_{iL'}$ denotes the solute fraction of the i th binary solution, which can be the molar, equivalent, or ionic strength fraction, and the subscript L' indicates an arbitrary choice of composition; κ_{iL} is the specific conductance of the i th binary solution, which has the same type of binary evaluation concentration L as the mixture; $\delta_{LL'}$ is the deviation of the linear mixing rule from the experimental value. The value of $\delta_{LL'}$ depends on both the binary evaluation strategy L and the choice of composition fraction L' , although the experimental value of κ depends only on concentration. Using the NaCl – MgCl_2 – H_2O system as an example, Miller²⁸ compared the deviations $\delta_{LL'}$ resulting from nine possible combinations of L and L' . He found that $\delta_{LL'}$ is the smallest among all the combinations for low-concentration mixtures when both L and L' are the ionic strength, that is, using the ionic strength fraction and the specific conductance of the constituent binary systems that have the same ionic strength as the mixture in the linear approximation. This mixing rule, referred to below as the "constant ionic strength mixing rule," is the same as eq 8 for this two-salt common-ion mixture when neglecting the $k_{\text{Na,Mg}}^{\text{cl}}$ term. Equation 8 generalizes this rule to any mixture.

More recently, Anderko and Lencka²⁹ presented a mixing rule in terms of the equivalent conductance of ion M in the pure salt MX at constant ionic strength, $\Lambda_{o,M(X)} [I]$. Their equation

can be written as

$$\kappa[I_c] = N \sum_{M=1}^{N_c} \sum_{X=1}^{N_a} x_M x_X (\Lambda_{oM(X)}[I_c] + \Lambda_{oX(M)}[I_c]) = N \sum_{M=1}^{N_c} \sum_{X=1}^{N_a} x_M x_X \Lambda_{oMX}[I_c] \quad (10)$$

and is identical with the first term in eq 8. At present we can only use the first term in eq 8 because we lack common-ion mixture data, which allow the determination of the $\kappa_{M,N}^X$ parameter. The fact that the first term is recommended by many authors led us to explore its utility.

3. Experimental Section

The flow-type, high-temperature, high-pressure conductance apparatus and the associated operating procedures have previously been described in detail by Zimmerman et al.¹ The apparatus underwent minor modifications as reported by Gruskiewicz and Wood.² The conductance apparatus with platinum–rhodium tubing in the hot zone was used to measure aqueous solutions of NaCl and Na₂SO₄ at a given temperature and pressure. The conductance cell consisted of a platinum–rhodium cup, which served as an outer electrode and a sapphire insulator with a hole in the center through which the inner electrode passed into the center of the cup. The resistances, measured at (1 and 10) KHz frequencies using a 1654 General Radio impedance comparator, were extrapolated linearly to infinite frequency as a function of the inverse of the square root of the frequency. The resistances of measured solutions ranged from 30 Ω to 1.2 kΩ. All measured resistances were corrected for the lead resistance, which was less than 1% of the resistance for the most concentrated solution.

The temperature was measured with a Rosemont platinum resistance standard (Model 162 CE) and a Leeds and Northrup Mueller bridge (model G-2) with a manufacturer's stated accuracy of ±0.01K. The temperature stability varied from 0.02 to 0.5 K during a typical series of six measurements. The solution was introduced inside of the conductance apparatus using an HPLC pump (Waters, Division of Millipore, Inc., model 590), which was operated at a constant flow rate of $8.3 \cdot 10^{-3} \text{ cm}^3 \cdot \text{s}^{-1}$. At high temperatures nine experiments were made with two different flow rates to ensure that the thermal equilibration was complete. These experiments showed that the solutions, flowing into the cell, were well equilibrated with the block, because the difference in measured conductances at different flow rates was within the experimental uncertainties. The temperature gradient between the inlet tubing and the conductance block was also measured periodically with an iron–constantan thermocouple. The voltage across the thermocouple was never greater than 5 μV corresponding in temperature to about 0.1 K. The pressure was measured using a Digiquartz pressure transducer (ParoScientific, Inc.; model 760-6) with an accuracy of ± 0.01 MPa. The temperature and pressure were recorded immediately after a stable reading of resistance, corresponding to a sample plateau, was achieved.

The cell constant was determined by a series of five measurements on dilute aqueous solutions of KCl (with molalities from 10^{-4} to $10^{-2} \text{ mol} \cdot \text{dm}^{-3}$) at $T = 298.15 \text{ K}$. The measurements of the cell constant were made from two stock solutions of KCl. The first stock solution was prepared by mass from certified A.C.S. grade KCl (Fisher Scientific Co.; maximum impurity was mass fraction 10^{-4} of Br⁻) and distilled and deionized water. The salt was dried for 24 h at $T = 573 \text{ K}$,

cooled in a desiccator, and diluted by mass with conductivity water to the initial molality. The second solution was prepared from granular KCl, analytical reagent (Mallinckrodt Inc.) using the same procedure. All apparent masses were corrected for buoyancy. A conversion of molalities to molar concentrations was done using the densities of KCl (aq) at $T = 298.15 \text{ K}$ taken from Jones and Ray³⁰ and MacInnes and Dayhoff.³¹

The cell constant at $T = 298.15 \text{ K}$ and $p = 0.1 \text{ MPa}$ was calculated to be $(0.2090 \pm 0.0004) \text{ cm}^{-1}$ using equations given by Justice¹¹ and Barthel et al.³² for KCl (aq). Calculated cell constants agreed within 0.15% over the complete range of concentrations. The cell constant was also determined at $p = 25.3 \text{ MPa}$ and $T = 298.15 \text{ K}$ to ensure that bubbles did not form inside the cell. The high-pressure value of the cell constant, calculated using the results of Fisher and Fox³³ at these conditions, agreed with room pressure result within 0.1%. The cell constant was also determined after all measurements were completed and found to be lower by 1.9% than the initial value. Similar changes in the cell constant were reported previously by Zimmerman et al.¹ and Gruskiewicz and Wood.² These changes are probably caused by small changes of the cell dimensions with time because of annealing at high temperatures. It was concluded previously² that, although the changes in the cell constant directly influence the conductance results, the calculated equilibrium constants are not significantly affected (<0.1%). The cell constant at elevated temperatures was calculated from the known thermal expansion of the platinum cup, inner electrode, and sapphire insulator. The corrections are small (about 0.4% at $T = 623 \text{ K}$).

Stock solutions were prepared from A.C.S. reagent-grade anhydrous sodium sulfate (Fisher Scientific Co.; largest impurities were mass fraction 10^{-4} of Ca²⁺ and mass fraction 10^{-4} of Mg²⁺), which was dried in a vacuum oven for 16 h at $T = 453 \text{ K}$, cooled in a desiccator, and diluted with distilled and deionized water. The solutions were prepared by mass, and all weights were corrected for air buoyancy. The concentration of each stock solution was checked by measuring conductance at room temperature immediately after all experiments were completed. The conductance results at $T = 298.15 \text{ K}$ were in good agreement with the reported results^{9,34} for Na₂SO₄ (aq). A stock solution of sodium chloride had been prepared by mass from A.C.S. grade NaCl (Fisher Scientific Co.; largest impurity, mass fraction 10^{-4} of Br⁻) and conductivity water. The conductivity water used in all measurements and preparations of stock solutions was distilled, then passed through four deionization cartridges (Barnstead/Thermolyne Co., E-pure system, model D4641), and had a resistivity of $18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$. The solvent conductance was measured at each temperature and pressure.

4. Tests of the Equations

To test these equations a nonlinear least-squares fit of the measured conductivity divided by the stoichiometric salt concentration was performed to derive values for some of the equilibrium constants and some of the limiting conductances. The specific conductance was calculated by first solving for the equilibrium concentrations of all species in solution using the equilibrium constant for each reaction, the activity coefficient model, and the stoichiometric molalities of the salts in solution. This was done by solving for the extent of each reaction using a Newton–Raphson method with line search.³⁵ Then the specific conductances were calculated using the mixture equation and either the TBBK or FHFP equations. The Levenberg–Marquand algorithm was used for the least-squares fit.³⁵ Hard-sphere

TABLE 1: Experimental Specific Conductances κ_{exp} of NaCl (aq)^a

T (K)	p (MPa)	$m \cdot 10^5$ (mol·kg ⁻¹)	$c \cdot 10^5$ (mol·dm ⁻³)	$(\kappa_{\text{exp}} - \kappa_s)/c$ (S·cm ² ·mol ⁻¹)
$\rho_s = 596.4 \text{ kg}\cdot\text{m}^{-3}; \kappa_s = 2.4 \times 10^{-4} \text{ S}\cdot\text{m}^{-1}$				
623.87	19.79	24.66	14.71	1153
623.87	19.79	107.3	64.02	1106
623.86	19.79	261.8	156.20	1055
623.86	19.79	518.5	309.60	1001
623.85	19.79	1106.0	661.50	928

^a Measured conductances of NaCl (aq), κ_{exp} , were corrected for the solvent conductance, κ_s , and reported here as $(\kappa_{\text{exp}} - \kappa_s)/c$, which is essentially equal to the equivalent conductance of NaCl (aq), assuming there is no hydrolysis.

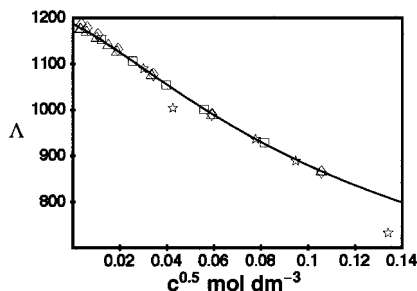


Figure 1. Equivalent conductance Λ of NaCl (aq) as a function of $c^{1/2}$: \square , present results at $T = 624 \text{ K}$ and $\rho_s = 597 \text{ kg}\cdot\text{m}^{-3}$; Δ , Gruszkiewicz and Wood results² at $T = 620 \text{ K}$ and $\rho_s = 600 \text{ kg}\cdot\text{m}^{-3}$; \diamond , Gruszkiewicz and Wood results² at $T = 632 \text{ K}$ and $\rho_s = 600 \text{ kg}\cdot\text{m}^{-3}$; \star , Ho et al. results³⁷ at $T = 623 \text{ K}$ and $\rho_s = 600 \text{ kg}\cdot\text{m}^{-3}$; $-$, least-squares fit of the TBBK equation¹² to the experimental points from Table 1.

diameters were calculated from the ionic radii of Marcus.³⁶ For ionic diameters of complex ions, we used the combining rule: $\sigma[\text{NaSO}_4^{2-}]^3 = \sigma[\text{Na}^+]^3 + \sigma[\text{SO}_4^{2-}]^3$. The calculations were corrected for slight changes in pressure and temperature during the run using the procedure of Zimmerman et al.¹ In all cases, the corrections caused negligible changes in the results of the fit. Corrections for changes in the density with concentration were negligible.

4.1. Test with Durand-Vidal et al.³ Equation for Three-Ion Mixtures. The validity of the linear mixing rule (eq 10) is unknown for mixtures at high temperatures and low steam densities where the electrostatic interaction is much stronger than at ambient conditions. To test our mixture equations at those conditions, we calculated the concentration dependence of the equivalent conductance of a model ionic mixture of three ions with charges: 1+, 2+, and 1- and the limiting conductances equal to (700,1800,600) S·cm²·mol⁻¹ at $T = 673 \text{ K}$ and $p = 28 \text{ MPa}$. For concentrations below 0.01 mol·dm⁻³, the conductance calculated from the three-ion mixture equation given by Durand-Vidal et al.³ agreed within 1% with that calculated using the present mixture equations.

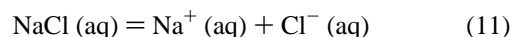
4.2. Test with NaCl Measurements. Next, we tested our equations using the present and literature conductance results for NaCl (aq). The experimental results for NaCl (aq) at $T = 623.9 \text{ K}$ and $\rho_s = 596.4 \text{ kg}\cdot\text{m}^{-3}$ are listed in Table 1. Figure 1 shows a comparison of the present experimental results for NaCl (aq) with the results of Gruszkiewicz and Wood² from this laboratory and Ho et al.³⁷ at different temperatures and pressures but about the same density of water: $\rho_s \approx 600 \text{ kg}\cdot\text{m}^{-3}$. The values of Λ do not have a strong dependence on temperature at this density, and they are in good agreement except for two of five results of Ho et al.,³⁷ which deviate by more than the expected error. Least-squares fit of these measurements confirm that the values of Λ_0 and K_d are essentially the same at the

TABLE 2: Results of the Fit of the Conductance Equations to the NaCl (aq) Data

conductance equation	activity	$\log K_d^a$	$\Lambda_0(\text{NaCl})^b$	AAD ^c	$J_2 \cdot 10^{-6}^d$
$T = 623.9 \text{ K}; p = 19.79 \text{ MPa}; \rho_s = 596 \text{ kg}\cdot\text{m}^{-3}$					
TBBK.Bj	Bjerrum	-1.37(7) ^e	1184(10)	0.28	
	MSA.HS.HS	-1.44(3)	1187(5)	0.12	
	MSA.HS.Bj	-1.38(7)	1184(10)	0.26	
	MSA.Bj.Bj	-1.34(10)	1183(13)	0.35	
TBBK.HS	Bjerrum	-1.33(8)	1184(10)	0.28	
	MSA.HS.HS	-1.40(4)	1187(5)	0.14	
	MSA.HS.Bj	-1.34(8)	1184(10)	0.27	
	MSA.Bj.Bj	-1.30(10)	1183(13)	0.35	
FHFP.Calc	Bjerrum	-1.44(3)	1189(5)	0.14	
	MSA.HS.HS	-1.50(1)	1192(2)	0.05	
	MSA.HS.Bj	-1.44(3)	1189(4)	0.12	
	MSA.Bj.Bj	1.41(5)	1187(8)	0.27	
FHFP.Fit	Bjerrum	-1.49(3)	1191(2)	0.02	0.11(2)
	MSA.HS.HS	-1.49(3)	1191(2)	0.02	0.16(2)
	MSA.HS.Bj	-1.49(3)	1191(2)	0.02	0.12(2)
	MSA.Bj.Bj	-1.49(3)	1191(2)	0.02	0.09(2)
$T = 652.6 \text{ K}; p = 22.75 \text{ MPa}; \rho_s = 200.0 \text{ kg}\cdot\text{m}^{-3}$					
All	All	-5.03(8)	1106(30)	3.0 to 4.3	

^a K_d is the equilibrium constant of the dissociation reaction 11 (molal standard state). ^b Units: S·cm²·mol⁻¹. ^c AAD, average absolute deviation from the fit in percent. ^d Units: S·dm^{9/2}·cm²·mol^{-5/2}. ^e The numbers in parentheses are the uncertainties of the last digit.

three temperatures. Because NaCl is a charge symmetric salt, both the TBBK¹² and FHFP^{13,14} equations are applicable. The limiting equivalent conductance of NaCl (aq) for the FHFP model was calculated using eq 4, and for the TBBK model using eqs 5 and 6. Solution densities were calculated from the apparent molal volume at infinite dilution, V_φ^0 , using equations given by Sedlbauer et al.³⁸ The dissociation constant, K_d (1 mol·kg⁻¹ standard state), for reaction:



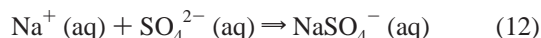
and Λ_0 (NaCl) were obtained by a least-squares fit to the conductance data. The mean activity coefficients, γ_{\pm} , were calculated from either eq 1 (Bjerrum) or from eq 4 (MSA).

Table 2 gives the results of the least-squares fit of our NaCl measurement at 623.9 K and of the measurements of Gruszkiewicz and Wood at 652.6 K.² At 623.9 K, all combinations of models give reasonable accurate results for $\log K$ and Λ_0 and accurate fits to the data. As expected, best fits were obtained with the three-parameter conductance equation (FHFP with J_2 fit). With this equation the results were independent of the activity model presumably because the extra parameter compensates for differences in the activity model. The FHFP equation with J_2 calculated was the best two-parameter conductance equation, and MSA.HS.HS was the best activity model.

At $T = 652.6 \text{ K}$, and $\rho_s = 200 \text{ kg}\cdot\text{m}^{-3}$ all combinations of conductance equations and activity models gave essentially identical fits to the data. The values of $\log K_d$ differed by less than 0.01 and Λ_0 varied by less than 1 S·cm²·mol⁻¹ with average absolute deviations of the fits varying from 3.0 to 4.3%. The MSA.HS.HS activity model gave slightly better fits. Except for the highest concentrations, the deviations of the experimental points from the fit were essentially independent of the model and did not vary systematically with concentration indicating that the experimental errors increase to about 3% at this low density.

4.3. Test with Na₂SO₄ Measurements. The electrical conductances of aqueous solutions have been extensively studied and reviewed for the past several decades. However, most of

the theoretical treatments and experimental investigations have been directed toward systems containing only a single cation–anion pair. Solutions of Na₂SO₄ must be treated as mixed electrolytes, because association of sulfate ion with sodium ion



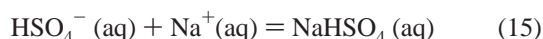
as well as hydrolysis of sulfate ion



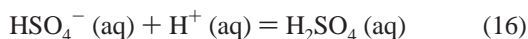
will occur resulting in a solution that is slightly basic. Reaction 13 was studied extensively by different authors.^{39–46} According to their results, the extent of hydrolysis increases with increasing temperature. When the concentration of OH[−] produced by reaction 13 is very low, it is necessary to account for the additional OH[−] produced by the dissociation of water:



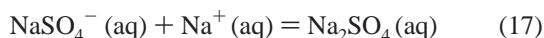
In this study we neglected association of univalent anions: for instance, the association of HSO₄[−] ion, formed by reaction 13 which can result in two new products, that is,



and



Also we can have further association of NaSO₄[−]



which should be important at lower water densities. Even neglecting reactions 15, 16, and 17, there are six ionic species present in solution: Na⁺, SO₄^{2−}, NaSO₄[−], HSO₄[−], H⁺, and OH[−].

The experimental specific conductances of Na₂SO₄(aq), κ_{exp} , without a correction for impurities and specific conductances of solvent (water), κ_s , at each temperature and pressure are listed in Table 3. The specific conductance of water represented less than 3% of the total conductance at the lowest concentration measured at all temperatures and pressures, so solvent conductance corrections are small. In a salt that produces acidic or basic solutions, a correction must be made for the change in self-ionization of the solvent when the salt is added. It was assumed that the solvent conductance was due to the equal amounts of H⁺(aq) and OH[−](aq) and to the conductance of an unknown “salt” MX that is neither acidic nor basic: $\kappa_s = \kappa_{MX} + c_s(\text{H}^+) \cdot \{\Lambda(\text{H}^+) + \Lambda(\text{OH}^-)\}$, where $c_s(\text{H}^+)$ is the concentration of H⁺ in the solvent calculated from the ionization constant of water. We used the conductance equations of TBBK model¹² to calculate the molar conductance of the solution, including conductances $\Lambda(\text{H}^+)$ and $\Lambda(\text{OH}^-)$, which are produced by the ionization of water. The stoichiometric specific conductance of a solution of Na₂SO₄ in pure water (including H⁺ and OH[−]), κ , should then be equal to the experimental specific conductance minus the specific conductance of the unknown salt MX, that is,

$$\kappa = \kappa_{\text{exp}} - \kappa_{MX} \quad (18)$$

The molar concentrations that are listed in Table 3 were calculated from molalities using the differences between the densities of pure solvent (from the Hill equation of state for

TABLE 3: Experimental Specific Conductance κ_{exp} of Na₂SO₄(aq)^a

<i>T</i> (K)	<i>p</i> (MPa)	<i>m</i> ·10 ⁵ (mol·kg ^{−1})	<i>c</i> ·10 ⁵ (mol/dm ³)	κ_{exp}/c (S·cm ² ·mol ^{−1})
$\rho_s = 996.55 \text{ kg}\cdot\text{m}^{-3}; \kappa_s = 2.5\cdot 10^{-5} \text{ S}\cdot\text{m}^{-1}$				
300.12	0.11	13.12	13.08	265.1
300.10	0.15	28.53	28.43	261.2
300.08	0.14	56.52	56.33	257.3
300.08	0.14	388.1	386.7	238.0
300.07	0.14	689.3	686.9	229.1
300.06	0.14	1225.	1220.	219.2
300.05	0.14	1709.	1703.	212.8
$\rho_s = 819.8 \text{ kg}\cdot\text{m}^{-3}; \kappa_s = 5.0\cdot 10^{-4} \text{ S}\cdot\text{m}^{-1}$				
526.48	28.21	13.51	11.07	1791
526.48	28.15	26.79	21.96	1751
526.40	28.15	53.81	44.11	1695
526.14	28.15	355.8	291.8	1419
526.06	28.15	620.9	509.4	1308
526.02	28.12	1429.	1173.	1140
$\rho_s = 745.97 \text{ kg}\cdot\text{m}^{-3}; \kappa_s = 3.9\cdot 10^{-4} \text{ S}\cdot\text{m}^{-1}$				
573.90	27.70	23.93	17.85	1983
573.93	27.71	47.46	35.41	1893
573.93	27.72	331.4	247.3	1453
573.94	27.72	637.9	476.1	1282
573.95	27.73	1032.	770.8	1162
573.96	27.74	1470.	1098.	1080
$\rho_s = 720.5 \text{ kg}\cdot\text{m}^{-3}; \kappa_s = 4.0\cdot 10^{-4} \text{ S}\cdot\text{m}^{-1}$				
573.89	13.24	28.19	20.31	1983
573.92	13.24	56.36	40.62	1866
573.93	13.24	324.5	233.9	1413
573.95	13.24	658.3	474.7	1217
573.98	13.25	1037.	747.8	1099
574.00	13.25	1611.	1163.	996

^a Experimental specific conductances divided by concentration (*c* is in moles of Na₂SO₄ per liter) are reported here without a correction for impurities. ρ_s is the average value of density of pure solvent (water) at experimental *T* and *p* calculated using the equation of state for water by Hill; κ_s is the experimental specific conductance of water).

H₂O¹⁷) and those of solution estimated assuming a linear dependence of the solution density on molality and using the experimental densities of Na₂SO₄(aq) obtained at *T* = 300 K from Chen et al.⁴⁷ and at *T* = (526–574) K from Obsil et al.⁴⁸

The values of equilibrium constants for reactions 13 and 14 are required to analyze our experimental conductance results for Na₂SO₄(aq) using the constant ionic strength mixing rule (eq 8) and the TBBK equation (eqs 5 and 6). The equilibrium constants for the hydrolysis of SO₄^{2−}, K_H , (reaction 13) and the ionization of water, K_w , (reaction 14) were calculated from the Helgeson–Kirkham–Flowers (HKF) revised equations of state⁴⁹ using the SUPCRT92 software package.⁵⁰ The HKF model, which is based on the Born equation for a charged sphere in a dielectric continuum, predicts the standard thermodynamic properties of aqueous electrolytes to *T* = 623 K. The combined experimental results of Marshall and Jones,³⁹ Lietzke et al.,⁴⁰ Ryzhenko,⁴¹ Readnour and Cobble,⁴² and Davies et al.⁴³ for the dissociation of the bisulfate ion together with K_w were used for prediction of the K_H by the HKF model. More recently, Oscarson et al.,¹⁰ Dawson et al.,⁴⁴ Dickson et al.,⁴⁵ and Matsushima and Okuwaki⁴⁶ reported values of equilibrium constant for reaction 13 to temperatures up to 593 K. The deviation between these recent results and the prediction using the HKF model is shown in Figure 2. The values of Dawson et al.⁴⁴ agreed with the HKF model within the experimental uncertainties. Results of Oscarson et al.¹⁰ are lower by 0.2 log units at *T* = 423 K and higher by 0.4 log units at *T* = 593 K than those from the HKF model. There is a systematic difference between the HKF model and probably the most reliable potentiometric results of Dickson et

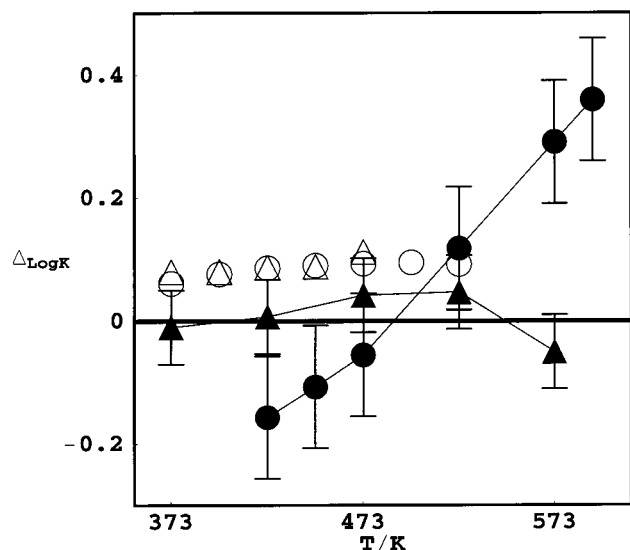


Figure 2. Deviation between experimental results for the Log K (reaction 13) and the HKF model^{49,50} as a function of temperature: ○, Dickson et al.⁴⁵; ●, Oscarson et al.¹⁰; △, Matsushima and Okuwaki⁴⁶; ▲, Dawson et al.⁴⁴ The estimated errors of results of Dickson et al.⁴⁵ and Matsushima and Okuwaki⁴⁶ are equal to the size of the points. The lines were added to aid the eye.

al.⁴⁵ and Matsushima and Okuwaki⁴⁶ at temperatures from 373 to 523 K, but the difference is small: < 0.1 log units. Because the HKF model does not produce a significant error, it was used in the treatment of our results. In the following calculations, the equilibria 15 through 17 were neglected. This leaves two cations and four anions in the solution for a total of eight salts in the mixture equation. The auxiliary data used in fitting the present results is given in Table 4.

We treat the equilibrium constant for reaction 12, K_a , and the limiting conductance Λ_0 of $1/2\text{SO}_4^{2-}$ as the two adjustable parameters. The limiting conductances for the other ions in equilibrium were calculated from reported data interpolated with Marshall's equation⁵¹ (see Table 4). In each iteration step during the least-squares fitting, three chemical equilibrium equations {reactions 12, 13, and 14} were solved for the extent of reaction using the activity coefficient model. Then, the ionic strength and the equivalent concentration of the mixture were calculated. Finally, the equivalent conductances for each ion in all possible binary solutions that have the same ionic strength as the mixture were calculated from the TBBK equation, and the conductance mixture equation was used to calculate the conductivity.

The results of the least-squares fits with the various models is given in Table 5. The TBBK conductance equation with either hard-sphere (HS) or Bjerrum (Bj) radii works very well with no real advantage for either set of radii. The different activity models give larger differences. On average, the MSA.HS.Bj model is the best, especially at high temperatures. For fitting the NaCl data the MSA.HS.HS was best at 623.9 K. We tentatively accept the MSA.HS.Bj model because it gives the best fits to the Na_2SO_4^- data and use the average of the parameters obtained with the TBBK.HS and TBBK.Bj equations. As an error estimate, we used the largest of (1) the two 95% confidence limits or (2) the difference between the two results. Table 6 gives our final values with error estimates.

Figure 3 gives a plot of the calculated equivalent conductances of the various ions in solution at 573.9 K, 27.7 MPa, and 746 $\text{kg}\cdot\text{m}^{-3}$. At this high temperature, the hydrolysis of SO_4^{2-} is quite large, so our result at this temperature is a good test of our mixture equations. This figure raises the question of whether

inaccuracies in the assumed values for $\lambda_0(\text{Na}^+)$, $\lambda_0(\text{HSO}_4^-)$, $\lambda_0(1/2\text{SO}_4^{2-})$, $\lambda_0(\text{OH}^-)$, $\lambda_0[\text{H}^+]$, K_H and K_W could cause large systematic errors in our results (see Table 4). We checked this by increasing the auxiliary values by 10% one at a time and refitting the data. This check showed that, as expected, the ratio $\Delta\lambda_0(\text{Na}^+)/\Delta\lambda_0(1/2\text{SO}_4^{2-})$ was near 1.0 because at low concentrations (mostly Na^+ and SO_4^{2-} ions in solution) the conductance is proportional to $\lambda_0(\text{Na}^+) + \lambda_0(1/2\text{SO}_4^{2-})$ and only the sum of these two is measured by the experiment. The values found for this ratio were: -1.004 , -1.07 , -1.06 , and -0.88 (in order of decreasing water density). Because of this strong correlation we report only the value of $\lambda_0(\text{Na}^+) + \lambda_0(1/2\text{SO}_4^{2-})$ in Table 6, because only the sum was determined. The values of $\Delta\lambda_0(1/2\text{SO}_4^{2-})$ for the 10% changes in $\lambda_0(\text{NaSO}_4^-)$, $\lambda_0(\text{HSO}_4^-)$, and $\lambda_0(\text{OH}^-)$ were small but not always negligible at the three lowest densities. The values were (0.9, 7, and 15) $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ for 10% changes in $\lambda_0(\text{NaSO}_4^-)$; (-1.5 , -4 , and -5) $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ for 10% changes in $\lambda_0(\text{HSO}_4^-)$; and (-3.3 , -8 , and -8) $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ for 10% changes in $\lambda_0(\text{OH}^-)$. The values of $\Delta\lambda_0(1/2\text{SO}_4^{2-})$ for 10% changes in the other parameters was negligible ($< 20\%$ of our error estimate). The values of $\Delta\text{Log } K_a$ for a change of 10% in $\lambda_0(\text{Na}^+)$ or $\lambda_0(\text{NaSO}_4^-)$ were 0.07, 0.05, 0.03 and 0.03 for 10% changes in $\lambda_0(\text{Na}^+)$ and 0.08, 0.06, 0.03, and 0.02 for 10% changes in $\lambda_0(\text{NaSO}_4^-)$ in order of decreasing density. In all other cases, the changes in log K_a were negligible ($< 20\%$ of our error estimates). From these tests we conclude that systematic errors from the choice of auxiliary data are small.

5. Discussion

The main objective of this study was to see if our equations could give accurate values of equilibrium constants from conductance data. There have been several investigations of the equilibrium constants for the association of Na_2SO_4 (aq). Oscarson et al.¹⁰ used a flow calorimetry results to calculate log K_a values at temperatures from 423 to 593 K. Styrikovich et al.⁴ used the conductance measurements of Samoilov and Men'shikova⁵ to estimate the equilibrium constants for reaction 12 at $\rho_s = 900\text{--}460 \text{ kg}\cdot\text{m}^{-3}$ without making corrections for hydrolysis. A sodium-selective glass electrode was used by Pokrovski et al.⁶ to measure the association constants of Na_2SO_4^- (aq) at $T = (323\text{--}473) \text{ K}$ and estimate the parameters for the HKF model to $T = 623 \text{ K}$. At $T = 298.15$, there are also calorimetric results of Izatt et al.⁸ and conductance measurements of Jenkins and Monk⁷ and Fisher and Fox.⁹ The NaSO_4^- association constants for reaction 12 from all reported results are compared with the present values of log K_a in Figure 5 and Table 6. The deviation between the experimental results and a calculation using the parameters of Pokrovski et al.⁶ for the HKF model is also shown in Figure 5. The present results are in reasonable agreement with the calculated values at all densities. The model of Pokrovski is in somewhat better agreement with the present data than the model of McCollom and Shock⁵² (see Table 6). The values of Styrikovich et al.⁴ are higher than the calculation by 0.6 log units at $\rho_s = 900 \text{ kg}\cdot\text{m}^{-3}$ and lower by 0.15 log units at $\rho_s = 600 \text{ kg}\cdot\text{m}^{-3}$. The results of Oscarson et al.³ are lower than the calculated values at densities $\rho_s = 920\text{--}860 \text{ kg}\cdot\text{m}^{-3}$ and in agreement within the estimated uncertainties from $\rho_s = 800\text{--}670 \text{ kg}\cdot\text{m}^{-3}$. This comparison confirms that the parameters of Pokrovski et al.⁶ for the HKF model give good estimates of log K values at the temperatures to at least 573 K and can be used for geochemical predictions.

The comparison of our values of $[\lambda_0(\text{Na}^+) + \lambda_0(1/2\text{SO}_4^{2-})]$ with reported values is not as satisfying. The 3.5% difference

TABLE 4: Auxiliary Parameters Used in Fitting the Conductance Results for Na₂SO₄ (aq)^a

<i>T</i> (K)	<i>p</i> (MPa)	Λ ₀ (Na ⁺)	Λ ₀ (HSO ₄ ⁻)	Λ ₀ (NaSO ₄ ⁻)	Λ ₀ (OH ⁻)	Λ ₀ (H ⁺)	<i>b</i> ^b	Log [<i>K</i> _H] ^c	Log [<i>K</i> _w] ^d
300.1	0.14	52.37	53.64	53.64	205.0	359.0	127.8	-11.93	-13.932
526.3	28.2	373.8	356.2	356.2	750.7	871.9	158.0	-5.853	-10.019
573.9	27.7	438.5	420.0	420.0	744.8	893.3	169.2	-5.116	-11.095
573.9	13.2	453.6	435.7	435.7	750.0	894.1	191.0	-5.113	-11.250

^a The ionic radii (Angstroms) were: Na⁺, 0.95; SO₄²⁻, 2.3; NaSO₄⁻, 2.355; HSO₄⁻, 2.3; H⁺, 1.4; OH⁻, 1.4. Units of Λ₀ = S·cm²·mol⁻¹. The equivalent conductances were interpolated from reported values using the density dependence of Marshall's equation.⁵¹ The data for Λ₀ at 300.1 K were from Robinson and Stokes⁵³ except for Λ₀ (HSO₄⁻). All other values of Λ₀ were taken from Marshall⁵¹ except for OH⁻ which was from Bianchi et al.,¹⁹ Wright et al.,⁵⁴ and Ho and Palmer.⁵⁵ Also Λ₀(NaSO₄⁻) was assumed equal to Λ₀(HSO₄⁻). ^b The densities were calculated by ρ = ρ_s + *b*·*m*. The value of *b* (kg²·mol⁻¹·m⁻³) was interpolated from the densities of Chen et al.⁴⁷ at 300.1 K and Obsil et al.⁴⁸ at 526 and 573 K. ^c *K*_H, the hydrolysis constant for SO₄²⁻ (eq 13) in the molality standard state, was calculated using SUPCRT 92.⁵⁰ ^d *K*_w, the water ionization constant (eq 14) in the molality standard state, was calculated using SUPCRT 92.⁵⁰ The use of other equations does not significantly change the results.

TABLE 5: Results of the Fit of the Conductance Equations to the Na₂SO₄ (aq) Data

conductance equation	activity model	Log <i>K</i> _a ^a	λ ₀ (1/2SO ₄ ²⁻) ^b	AAD ^c
<i>T</i> = 300.1 K; <i>p</i> = 0.14 MPa; density = 996.5 kg·m ⁻³				
TBBK.Bj	Bjerrum	0.85(3) ^d	82.2(2)	0.08
	MSA.HS.HS	0.85(3)	82.2(2)	0.08
	MSA.HS.Bj	0.75(6)	82.0(4)	0.16
	MSA.Bj.Bj	0.64(10)	81.9(6)	0.28
TBBK.HS	Bjerrum	0.77(3)	82.2(2)	0.08
	MSA.HS.HS	0.77(3)	82.2(2)	0.08
	MSA.HS.Bj	0.67(6)	82.1(4)	0.15
	MSA.Bj.Bj	0.56(10)	81.9(6)	0.25
<i>T</i> = 526.3 K; <i>p</i> = 28.16 MPa; density = 819.8 kg·m ⁻³				
TBBK.Bj	Bjerrum	1.99 (4)	556(8)	0.32
	MSA.HS.HS	2.04 (6)	558(13)	0.56
	MSA.HS.Bj	1.85 (4)	549(7)	0.36
	MSA.Bj.Bj	1.69(15)	542(23)	1.15
TBBK.HS	Bjerrum	1.95 (4)	555(7)	0.28
	MSA.HS.HS	2.00 (6)	557(11)	0.50
	MSA.HS.Bj	1.81 (4)	548(7)	0.37
	MSA.Bj.Bj	1.65(16)	541(23)	1.15
<i>T</i> = 573.9 K; <i>p</i> = 27.72 MPa; density = 746.0 kg·m ⁻³				
TBBK.Bj	Bjerrum	2.54 (6)	677(29)	0.79
	MSA.HS.HS	2.61(10)	692(52)	1.34
	MSA.HS.Bj	2.38 (1)	651(2)	0.05
	MSA.Bj.Bj	2.19(13)	626(40)	1.32
TBBK.HS	Bjerrum	2.50 (6)	672(24)	0.68
	MSA.HS.HS	2.58(10)	687(46)	1.22
	MSA.HS.Bj	2.34 (1)	648(4)	0.12
	MSA.Bj.Bj	2.15(14)	624(42)	1.39
<i>T</i> = 573.9 K; <i>p</i> = 13.2 MPa; density = 720.5 kg·m ⁻³				
TBBK.Bj	Bjerrum	2.76(14)	724(78)	1.62
	MSA.HS.HS	2.84(19)	754(121)	2.30
	MSA.HS.Bj	2.59 (7)	681(31)	0.77
	MSA.Bj.Bj	2.40 (7)	642(25)	0.68
TBBK.HS	Bjerrum	2.72(12)	716(68)	1.47
	MSA.HS.HS	2.81(18)	745(109)	2.13
	MSA.HS.Bj	2.55 (6)	676(25)	0.63
	MSA.Bj.Bj	2.36(80)	638(28)	0.80

^a *K*_a is the equilibrium constant for association of Na⁺ with SO₄²⁻ reaction 12 (molal standard state). ^b Units: S·cm²·mol⁻¹. ^c AAD, average absolute deviation from the fit in percent. ^d Numbers in parentheses are the estimated 95% confidence limits of the last digit of the calculated values; i.e., 0.85(3) is 0.85 ± 0.03.

from the Robinson and Stokes⁵³ values at room temperature is disappointing because we fit our conductance data to within an average deviation of 0.16% at this temperature. Perhaps, the TBBK conductance equation or the mixture equation are responsible for this difference. At the three higher temperatures, the λ₀(Na⁺) + λ₀(1/2SO₄²⁻) values of Marshall are 11–18% higher than our present values. This large disagreement is very surprising and needs further investigation but it seems unlikely that our limiting equivalent conductance is wrong by this much.

We conclude that the TBBK equation together with the constant ionic strength mixing rule allows the calculation of *K*_a

TABLE 6: Comparison of Final Results with Reported Values for Na₂SO₄ (aq)

<i>T</i> (K)	<i>p</i> (MPa)	Log [<i>K</i> _a] ^a			λ ₀ (Na ⁺) + λ ₀ (1/2SO ₄ ²⁻)	
		present result	PSS ^b	MS ^c	present result	literature
300.1	0.14	0.70(8) ^f	0.92	0.71	134.4 (4)	137.2 ^d
526.3	28.2	1.83(4)	2.03	2.13	922.0 (7)	1087.0 ^e
573.9	27.7	2.36(4)	2.54	2.66	1088.0 (4)	1236.0 ^e
573.9	13.2	2.57(7)	2.69	2.82	1132.0(31)	1253.0 ^e

^a *K*_a is the equilibrium constant for reaction 12. ^b Calculated from Pokrovski et al.⁶ ^c Calculated from McCollom and Shock.⁵² ^d The numbers in parentheses are the uncertainties of the last digit. ^e Value of Robinson and Stokes⁵³ interpolated with Marshall's equation.⁵¹ ^f Value from Marshall's equation⁵¹ with linear interpolation of his ρ_s.

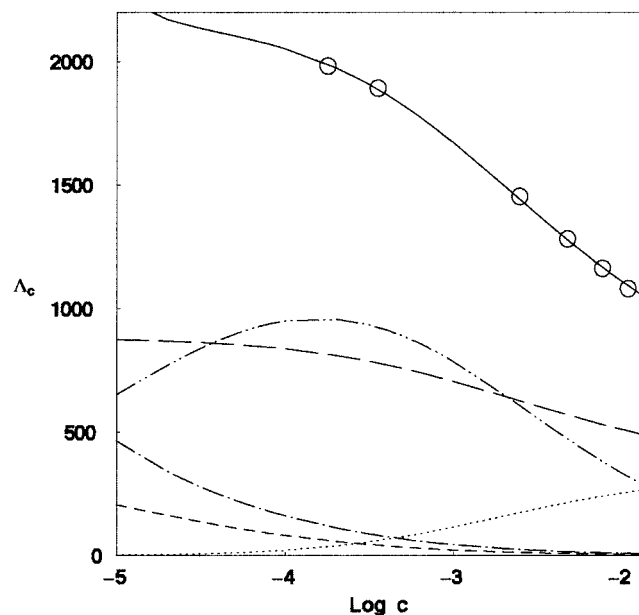


Figure 3. Contributions of various ions to the molar equivalent conductance (Λ(*i*) = κ(*i*)/(2*c*_{ST}) as a function of logarithm of molar stoichiometric concentration, *c*_{ST}, at *T* = 573.9 K and *p* = 27.7 MPa: ○, Λ (Na⁺); -·-·-, Λ(1/2SO₄²⁻); ····, Λ(NaSO₄⁻); - - -, Λ(OH⁻); - - -, Λ(HSO₄⁻). Total equivalent conductance, Λ_c = Σ_{*i*}κ(*i*)/(2*c*_{ST}): ○, experimental; —, least-squares⁵¹ fit of the TBBK equation¹² to the experimental results.

and [λ₀(Na⁺) + λ₀(1/2SO₄²⁻)] from conductance measurements on Na₂SO₄ (aq) across a wide temperature range from 300 to 573 K with reasonable accuracy. The temperature range can be extended to near critical and supercritical temperatures if reliable results for all side reactions (eqs 13–17) are known. When more and better data are available it will probably be worthwhile to compare the TBBK equation with other equations in the literature. For the present this is not likely to help very much because the main source of uncertainty is the activity model.

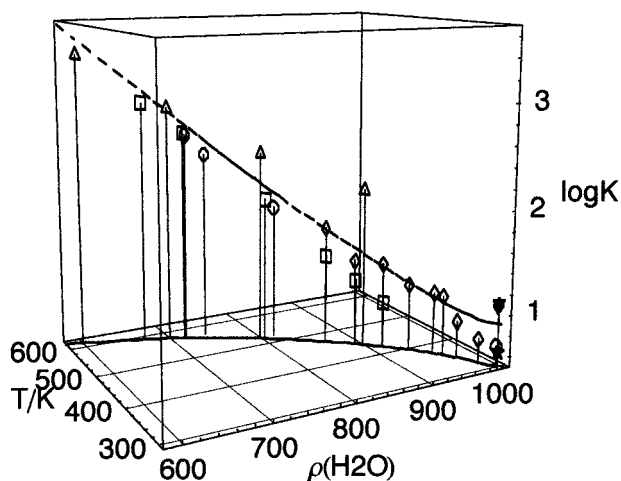


Figure 4. Logarithm of association constant for reaction 12 as a function of temperature and water density: \circ , present results; \square , Oscarson et al.¹⁰; \triangle , Styrikovich et al.⁴; \diamond , Pokrovski et al.⁶; ∇ , Jenkins and Monk⁷; \star , Izatt et al.⁸; \blacklozenge , Fisher and Fox⁹; ---, calculated using Pokrovski et al.⁶ parameters for the HKF model^{49,50} at saturation pressure. The curved full line is the boundary of the two-phase region for water calculated using the equation of the state of Hill.¹⁷

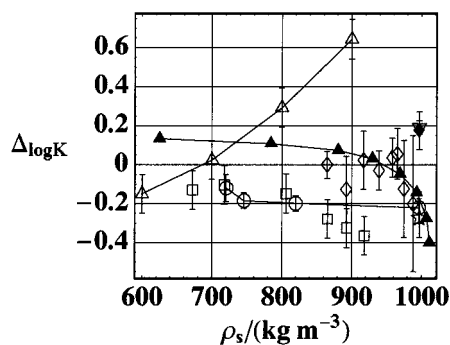


Figure 5. Deviation between the experimental results for the logarithm of association constant for reaction 12 and a calculation using Pokrovski et al.⁶ parameters for the HKF model^{49,50} as a function of water density. Symbol assignments are the same as in Figure 4 except the additional: \blacktriangle , McCullom and Shock.⁵² The lines were added to aid the eye.

Acknowledgment. This research was supported by the National Science Foundation under grant no. CHE9725163 and by the Department of Energy under grant no. DEFG02-89ER-14080. The authors are indebted to Jean-Claude Justice, Pierre Turq, Olivier Bernard, Roberto Fernandez-Prini, and Horacio Corti for many helpful discussions of conductance equations.

References and Notes

- Zimmerman, G. H.; Gruskiewicz, M. S.; Wood, R. H. *J. Phys. Chem.* **1995**, *99*, 11612–11625.
- Gruskiewicz, M. S.; Wood, R. H. *J. Phys. Chem. B* **1997**, *101*, 6549–6559.
- Durand-Vidal, S.; Turq, P.; Bernard, O. *J. Phys. Chem.* **1996**, *100*, 17345–17350.
- Styrikovich, M. A.; Martynova, O. I.; Belova, Z. S.; Men'shikova, V. L. *Dokl. Akad. Nauk SSSR* **1968**, *182*, 644–646.
- Samoilov, Yu. F.; Men'shikova, V. L. Report of Scientific-Technical Conference on the Results of Scientific Research during 1966–67. Heat and Power Section. *Technology of Water and Fuel Subsection*; Martynova, O. I., Ed.; Moscow, 1967; pp 71–81.
- Pokrovski, G. S.; Schott, J.; Sergeev, A. S. *Chem. Geol.* **1995**, *124*, 253–265.
- Jenkins, I. L.; Monk, C. B. *J. Am. Chem. Soc.* **1950**, *72*, 2695–2698.
- Izatt, R. M.; Eatough, D.; Christensen, J. J.; Bartholomew, C. H. *J. Chem. Soc. (A)* **1969**, 45–47.
- Fisher, F. H.; Fox, A. P. *J. Solution Chem.* **1975**, *4*, 225–236.
- Oscarson, J. L.; Izatt, R. M.; Brown, P. R.; Pawlak, Z.; Gillespie, S. E.; Christensen, J. J. *J. Solution Chem.* **1988**, *17*, 841–863.
- Justice, J. C. In *Comprehensive Treatise of Electrochemistry*; Conway, B. E., Bockris, J. O'M., Yeager, E., Eds.; Plenum Press: London, 1983; Vol. 5, Chapter 3, p 310.
- Turq, P.; Blum, L.; Bernard, O.; Kunz, W. *J. Phys. Chem.* **1995**, *99*, 822–827.
- Fuoss, R. M.; Hsia, K. L. *Proc. Natl. Acad. Sci. U.S.A.* **1967**, *8*, 1550–1557.
- Fernández-Prini, R. *Trans. Faraday Soc.* **1969**, *65*, 3311.
- Watson, J. T. R.; Basu, R. S.; Sengers, J. V. *J. Phys. Chem. Ref. Data* **1980**, *9*, 1255.
- Archer, D. G.; Wang, P. *J. Phys. Chem. Ref. Data* **1990**, *19*, 371–411.
- Hill, P. G. *J. Phys. Chem. Ref. Data* **1990**, *19*, 1233–1274.
- Ho, P. C.; Palmer, D. A. *Geochim. Cosmochim. Acta* **1997**, *61*, 3027–3040.
- Bianchi, H.; Corti, H. R.; Fernández-Prini, R. *J. Solution Chem.* **1994**, *23*, 1203–1212.
- Bernard, O.; Kunz, W.; Turq, P.; Blum, L. *J. Phys. Chem.* **1992**, *96*, 3833–3840.
- Chiah A.; Turq, P.; Bernard, O.; Barthel, J. M. G.; Blum, L. *Ber. Bunsen-Ges. Phys. Chem.* **1994**, *98*, 1516–1525.
- Bianchi, H. L.; Dujovne, I.; Fernández-Prini, R. *J. Solution Chem.* **2000**, *29*, 237–252.
- Bernard, O. Personal communication.
- Young, T. F.; Smith, M. B. *J. Phys. Chem.* **1954**, *58*, 716–724.
- Wu, Y. C.; Smith, M. B.; Young, T. F. *J. Phys. Chem.* **1965**, *69*, 1868–1872.
- Reilly, P. J.; Wood, R. H. *J. Phys. Chem.* **1969**, *73*, 4292–4297.
- Wu, Y. C.; Koch, W. F.; Zong, E. C.; Friedman, H. L. *J. Phys. Chem.* **1988**, *92*, 1692–1695.
- Miller, D. G. *J. Phys. Chem.* **1996**, *100*, 1220–1226.
- Anderko, A.; Lencka, M. M. *Ind. Eng. Chem. Res.* **1997**, *36*, 1932–1943.
- Jones, G.; Ray, W. A. *J. Am. Chem. Soc.* **1937**, *59*, 187–198.
- MacInnes, D. A.; Dayhoff, M. O. *J. Am. Chem. Soc.* **1952**, *74*, 1017–1020.
- Barthel, J.; Feuerlein, F.; Neuder, R.; Wachter, R. *J. Solution Chem.* **1980**, *9*, 209–219.
- Fisher, F. H.; Fox, A. P. *J. Solution Chem.* **1979**, *8*, 627–634.
- Weingärtner, H.; Price, W. E.; Edge, A. V. J.; Mills, R. *J. Phys. Chem.* **1993**, *97*, 6289–6291.
- Press, W. H.; Vetterling, W. T. *Numerical Recipes in Fortran 90: The Art of Parallel Scientific Computing*, 2nd ed.; Cambridge University Press: Cambridge, 1996.
- Marcus, Y. *Ion Solvation*, Wiley: New York, 1985.
- Ho, P. C.; Palmer, D. A.; Mesmer, R. E. *J. Solution Chem.* **1994**, *23*, 997–1018.
- Sedlbauer, J. S.; Yezdimer, E. M.; Wood R. H. *J. Chem Thermodyn.* **1998**, *30*, 3–12.
- Marshall, W. L.; Jones, E. V. *J. Phys. Chem.* **1966**, *70*, 4028–4040.
- Lietzke, M. H.; Stoughton, R. W.; Young T. F. *J. Phys. Chem.* **1961**, *65*, 2247–2249.
- Ryzenko, B. N. *Geochem. Int.* **1964**, *1*, 8–13.
- Readnour, J. M.; Cobble, J. W. *Inorg. Chem.* **1969**, *8*, 2174–2182.
- Davies, C. W.; Jones, H. W.; Monk, C. B. *Trans. Faraday Soc.* **1952**, *48*, 921–928.
- Dawson, B. S. W.; Irish, D. E.; Toogood, G. E. *J. Phys. Chem.* **1986**, *90*, 334–341.
- Dickson, A. G.; Wesolowski, D. J.; Palmer, D. A.; Mesmer, R. E. *J. Phys. Chem.* **1990**, *94*, 7978–7985.
- Matsushima, Y.; Okuwaki, A. *Bull. Chem. Soc. Jpn.* **1998**, *61*, 3344–3346.
- Chen, C. T. A.; Chen, J. H.; Millero, F. J. *J. Chem. Eng. Data* **1980**, *25*, 307–310.
- Obsil, M.; Majer, V.; Hefter, G. T.; Hynek, V. *J. Chem. Eng. Data* **1997**, *42*, 137–142.
- Tanger, J. C. IV; Helgeson, H. C. *Am. J. Sci.* **1988**, *288*, 19–98.
- Johnson, J. W.; Oelkers, E. H.; Helgeson, H. C. *Comput. Geosci.* **1992**, *18*, 899–947.
- Marshall, W. L. *J. Chem. Phys.* **1987**, *87*, 3639–3643.
- McCullom, T. M.; Shock, E. L. *Geochim. Cosmochim. Acta* **1997**, *61*, 4375–4391.
- Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*; Academic Press: New York, 1955.
- Wright, J. M.; Lindsay, W. T. Jr.; Druga, T. R. *WAPD-TM-204, UC-4 Chemistry, TID-4500*, 16th ed.; Bettis Atomic Power Laboratory: 1961.
- Ho, P. C.; Palmer, D. A. *J. Chem. Eng. Data* **1998**, *43*, 162–170.
- Mesmer, R. E.; Marshall, W. L.; Palmer, D. A.; Simonson, J. M.; Holmes, H. F. *J. Solution Chem.* **1988**, *17*, 699–718.