



doi:10.1016/j.gca.2003.08.017

Chemical equilibrium model of solution behavior and solubility in the H-Na-K-OH-Cl-HSO₄-SO₄-H₂O system to high concentration and temperature

CHRISTOMIR CHRISTOV* and NANCY MOLLER

Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093-0340, USA

(Received March 31, 2003; accepted in revised form August 15, 2003)

Abstract—This paper describes a chemical model that calculates solute and solvent activities and solid-liquid equilibria in the H-Na-K-OH-Cl-HSO₄-SO₄-H₂O system from dilute to high solution concentration within the 0° to 250°C temperature range. All binary and ternary subsystems are included in the model parameterization. The model is validated by comparing predictions with experimental data, primarily in higher order systems, not used in the parameterization process. Limitations of the model due to data insufficiencies are discussed.

The Harvie and Weare (*GCA* **44**, 981, 1980) solubility modeling approach, incorporating their implementation of the concentration-dependent specific interaction equations of Pitzer (*J. Phys. Chem.* **77**, 268, 1973), is employed. This model expands the variable temperature Na-K-Cl-SO₄-H₂O model of Greenberg and Moller (*GCA* **53**, 2503, 1989) by including acid (H₂SO₄, HCl) and base (NaOH, KOH) species. Temperature functions for the chemical potentials of 5 acidic (sodium bisulfate, sodium sesquisulfate, mercallite, potassium sesquisulfate and misenite) and 6 basic (4 sodium hydroxide hydrates and 2 potassium hydroxide hydrates) solid phases are determined. Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

Chemical models that predict solid-liquid-gas equilibria close to experimental accuracy over broad ranges of composition and temperature have wide applicability. They can simulate the complex changes that occur in nature and can replicate conditions that are difficult or expensive to duplicate in the laboratory. Such models can be powerful predictive and interpretive tools to study the geochemistry of natural waters and mineral deposits, solve environmental problems and optimize industrial processes.

Harvie and Weare (1980) showed that Pitzer's (1973) specific interaction description of aqueous solutions could be extended to construct accurate models of solubilities in complex brines (Na-K-Ca-Mg-Cl-SO₄-H₂O system) at 25°C and that such models could be successfully applied to the interpretation of important natural fluid processes (Harvie et al., 1980). See also Brantley et al. (1984) and Felmy and Weare (1986). Harvie et al. (1984) (HMW) significantly expanded the compositional flexibility of the 25°C model by parameterizing carbonate and acid-base (HCl, H₂SO₄, H₂CO₃, NaOH, KOH, Ca(OH)₂, Mg(OH)₂) interactions in the H-Na-K-Ca-Mg-OH-Cl-HSO₄-SO₄-HCO₃-CO₃-H₂O-CO₂(g) system.

The model described here extends the HMW description of acid-base reactions in the H-Na-K-OH-Cl-HSO₄-SO₄-H₂O aqueous system to a broad temperature range. It incorporates the variable temperature (0° to 250°C) solubility models of Moller (1988) and Greenberg and Moller (1989) for interactions in the Na-K-Ca-Cl-SO₄-H₂O system. The TEQUIL model of Moller et al. (1998) (see our interactive Web site at <http://geochem.uscd.edu/>) also expands the Moller (1988) and Greenberg and Moller (1989) parameterizations to include H-Cl and Na-OH (low concentration only) interactions, Ca-H-

HCO₃-CO₃ equilibria as well as amorphous silica and calcite solubilities. By including a comprehensive description of the HSO₄⁻/SO₄²⁻ (in addition to HCl), NaOH and KOH specific interactions as well as eleven acidic and basic solid phases, the present model broadens the TEQUIL carbonate-free, acid-base description to treat systems at very low and very high pH.

The parameterization established here (Tables 2–4) can be used to calculate acid (HCl, H₂SO₄) and base (NaOH, KOH) equilibria in the H-Na-K-OH-Cl-HSO₄-SO₄-H₂O system and to assess the effect of compositional, pH and temperature changes on these equilibria. Interactions of these acids and bases can play significant roles in the behavior of many natural and industrial fluids. Their influence on hydrolysis, buffering and ionization in aqueous solutions makes them of interest in physiochemical studies (e.g., Holmes and Mesmer, 1998). Sulfuric acid is an important component of atmospheric aerosols, notably in the stratosphere, and of natural acidic brines (Clegg et al., 1994). The bisulfate anion HSO₄⁻ is a common constituent of a variety of process streams (Holmes and Mesmer, 1993). Sodium hydroxide and hydrochloric acid are some of the most commonly used laboratory chemicals, both rank among the top chemicals manufactured per year in the United States. The model presented here also forms a useful base for developing expanded variable temperature models that describe additional important acid-base reactions, such as carbonate and metal-hydroxide equilibria. The addition of calcium and carbonate interactions to the present model will be discussed in future publications.

Several authors (e.g., Pabalan and Pitzer, 1987; Clegg et al., 1998; Millero and Pierrot, 1998; Marion, 2001, 2002; Koenigsberger, 2001) have constructed variable temperature models that include some of the acid and/or base subsystems within the H-Na-K-OH-Cl-HSO₄-SO₄-H₂O system. Pabalan and Pitzer (1987) evaluated hydroxide solution interaction parameters using solubility data from 0°–200°C in the NaOH-NaCl-Na₂SO₄-H₂O quaternary system but did not include solubilities of

* Author to whom correspondence should be addressed (nweare@ucsd.edu).

hydroxide solid phases or acid interactions. The mole-fraction model of Clegg et al. (1998) includes a comprehensive representation of activities and solubilities in the H-Na-SO₄-Cl-H₂O system to high concentration at 25°C. The multispecies chemical equilibrium model of Millero and Pierrot (1998) extends to 50°C and describes acid-base solute reactions using parameters taken mostly from the literature but does not include solid phase behavior. Marion constructed models that include NaOH and KOH interactions (Marion, 2001) and HCl and H₂SO₄ interactions (Marion, 2002) to predict brine chemistry at low temperatures ($T \leq 25^\circ\text{C}$) with special focus on subzero temperatures. With the exception of $\Psi_{\text{H,K,HSO}_4}$, Marion's mixing parameters are the same as those of Harvie et al. (1984). The Koenigsberger (2001) model successfully calculates water dissociation in NaCl solutions (H-Na-Cl-OH-H₂O system) from 25° to 250°C. He uses temperature extrapolations of the 25°C Na-OH and H-Cl single electrolyte parameters from Pitzer and Mayorga (1973) and temperature independent (25°C) acid and base mixing parameters from Pitzer and Kim (1974). He does not include acid/base solid phases. The model presented here includes a comprehensive description of all acid/base solute interactions and solid phase solubilities in the H-Na-K-OH-Cl-HSO₄-SO₄-H₂O system to high temperature over a very broad concentration range to low and high pH.

Model parameterization is discussed below. Activity data (emf, osmotic, activity coefficient) are used when available to evaluate solution parameters for low and moderate acid or base concentration (see Table 1). However, for some subsystems (e.g., H₂SO₄-K₂SO₄-H₂O) solubility measurements are the only data we found. In others, solubility data broaden the temperature range of parameterization. The chemical potentials of the five acidic and six basic solid phases reported here (see Table 4) are established in temperature ranges where the maximum acid or base concentrations are below specified upper limits.

2. THEORETICAL BACKGROUND AND APPROACH

2.1. Pitzer Equations and Single Ion Expressions

The specific interaction approach for describing aqueous solutions to high concentration introduced by Pitzer (1973) represents a significant advance in physical chemistry that has facilitated the construction of accurate thermodynamic models. Harvie and Weare (1980) showed that this approach could be expanded to accurately calculate solubilities in complex brines and to predict the behavior of natural fluids (Harvie et al., 1980).

In this study, the model framework incorporates the ionic strength-dependent specific interaction equations for the osmotic coefficient and activity coefficients of the various solutes as described in Harvie and Weare (1980), Harvie et al. (1984) and Felmy and Weare (1986) (Appendix A). The Harvie and Weare expressions yield values for single ion activity coefficients (e.g., γ_{H^+} ; see Appendix A, Eqn. 1A). Although single ion activities do not have physical significance, these expressions combine properly into the measurable sums and differences that preserve the ionic strength dependence of the original Pitzer expressions.

It is sometimes desirable to report single ion activities de-

finied by convention. As long as only the mean activity coefficients are used in any comparison with the experimental data the choice of convention is arbitrary (Appendix B). Single ion activities produced by the Harvie-Weare convention are not directly comparable with other conventional values of single ion activities. However, single ion activity values determined directly by the Harvie-Weare formulation or activity values defined by other conventions, such as that of MacInnes (1961) (Appendix B), calculate the same final equilibrium species distribution.

2.2. Chemical Potentials, Equilibrium Constants, and Solubility Calculations

In our variable temperature modeling approach, the standard chemical potentials (μ°/RT) of the independent ions, such as H⁺, OH⁻ and SO₄²⁻, are set equal to zero. When species are related by equilibrium reactions, the dependent standard chemical potentials are determined from equilibrium data. For example, using this reference system, the standard chemical potential, $\mu^\circ_{\text{HSO}_4(\text{aq})}/RT$, for the bisulfate ion can be expressed in terms of the equilibrium constant, $K_2 = (a_{\text{SO}_4} \cdot a_{\text{H}})/a_{\text{HSO}_4}$, for the dissociation of HSO₄⁻ → SO₄²⁻ + H⁺, as:

$$\begin{aligned} \ln K_2 &= -1/RT [\mu^\circ_{\text{SO}_4(\text{aq})} + \mu^\circ_{\text{H}(\text{aq})} - \mu^\circ_{\text{HSO}_4(\text{aq})}] \\ &= \mu^\circ_{\text{HSO}_4(\text{aq})}/RT. \quad (1) \end{aligned}$$

Similarly, referencing the standard chemical potentials to the independent ions in solution (in this model H⁺, Na⁺, K⁺, Cl⁻, SO₄²⁻, OH⁻), the chemical potentials of solid phases, such as halite (NaCl(s)), that do not contain water or dependent species, such as HSO₄⁻, are equal to the logarithm of the solubility products ($\ln K_s$). Calculation of the chemical potential of solid phases, such as NaHSO₄ · H₂O(s), must include the HSO₄⁻ and water standard chemical potentials. For example, with $\mu^\circ_{\text{Na}^+}/RT$ set equal to 0, $\ln K_s(\text{NaHSO}_4 \cdot \text{H}_2\text{O}(\text{s})) = \mu^\circ_{\text{NaHSO}_4 \cdot \text{H}_2\text{O}(\text{s})}/RT - \mu^\circ_{\text{H}_2\text{O}}/RT - \mu^\circ_{\text{HSO}_4}/RT$. Note that to compare chemical potentials given in Table 4 with those reported using other reference systems (e.g., Harvie et al., 1984), the nonzero standard chemical potentials of the independent ions must be considered.

2.3. Temperature Dependence

Temperature dependence is built into the model by establishing temperature functions for model parameters as described in Moller (1988). The temperature dependent equations for the acid-base parameters presented here are determined by adjusting selected constants in the following equation:

$$\begin{aligned} \text{Parameter}(T) &= a_1 + a_2T + a_3T^2 + a_4T^3 + a_5/T + a_6 \ln T \\ &+ a_7/(T - 263) + a_8/(680 - T). \quad (2) \end{aligned}$$

Note that the a_4T^3 term in Eqn. 2 is not included in the temperature dependence form used in Moller (1988), Greenberg and Moller (1989) and Moller et al. (1998). It is used here only for some binary interaction parameters in the NaHSO₄-H₂O and H₂SO₄-H₂O systems when necessary to obtain correct temperature variation.

Table 1. Data used to parameterize acid-base interactions in the H-Na-K-OH-Cl-HSO₄-SO₄-H₂O system.

Parameter	Data
Binary interactions	
H ⁺ , Cl ⁻	e.m.f. and activity coefficient data in the HCl-H ₂ O system
Na ⁺ , OH ⁻	e.m.f., K _w and solubility data in the NaOH-NaCl-H ₂ O system; osmotic data in the NaOH-H ₂ O system
K ⁺ , OH ⁻	Osmotic and activity coefficient data in the KOH-H ₂ O system
H ⁺ , HSO ₄ ⁻	Osmotic data in the H ₂ SO ₄ -H ₂ O system; K ₂ data
H ⁺ , SO ₄ ²⁻	
Na ⁺ , HSO ₄ ⁻	
K ⁺ , HSO ₄ ⁻	Osmotic data in the NaHSO ₄ -H ₂ O, Na ₂ SO ₄ -NaHSO ₄ -H ₂ O and Na ₂ SO ₄ -H ₂ SO ₄ -H ₂ O systems; solubility data in the Na ₂ SO ₄ -H ₂ SO ₄ -H ₂ O system
K ⁺ , HSO ₄ ⁻	Solubility data in the K ₂ SO ₄ -H ₂ SO ₄ -H ₂ O system
Mixing parameters	
SO ₄ ²⁻ , HSO ₄ ⁻	Osmotic data in the H ₂ SO ₄ -H ₂ O system; K ₂ data
H ⁺ , SO ₄ ²⁻ , HSO ₄ ⁻	e.m.f. data in the HCl-H ₂ SO ₄ -H ₂ O system; K ₂ data in NaCl solutions; solubility data in the Na-H-Cl-SO ₄ -H ₂ O system
Cl ⁻ , HSO ₄ ⁻	
H ⁺ , Cl ⁻ , SO ₄ ²⁻	e.m.f. and solubility data in the NaCl-NaOH-H ₂ O system; K _w data in NaCl solutions
H ⁺ , Cl ⁻ , HSO ₄ ⁻	
Na ⁺ , Cl ⁻ , HSO ₄ ⁻	
OH ⁻ , Cl ⁻	
Na ⁺ , OH ⁻ , Cl ⁻	Solubility data in the KCl-HCl-H ₂ O system; K _w data in KCl solutions;
K ⁺ , H ⁺	
K ⁺ , H ⁺ , Cl ⁻	Activity coefficient and solubility data in the NaCl-HCl-H ₂ O system
Na ⁺ , H ⁺	
Na ⁺ , H ⁺ , Cl ⁻	Osmotic data in the Na ₂ SO ₄ -H ₂ SO ₄ -H ₂ O and Na ₂ SO ₄ -NaHSO ₄ -H ₂ O systems; solubility data in the Na ₂ SO ₄ -H ₂ SO ₄ -H ₂ O system
Na ⁺ , H ⁺ , HSO ₄ ⁻	
Na ⁺ , H ⁺ , SO ₄ ²⁻	Solubility data in the K ₂ SO ₄ -H ₂ SO ₄ -H ₂ O ternary system
Na ⁺ , SO ₄ ²⁻ , HSO ₄ ⁻	
K ⁺ , H ⁺ , HSO ₄ ⁻	
K ⁺ , H ⁺ , SO ₄ ²⁻	Solubility data in the KCl-KOH-H ₂ O system
K ⁺ , SO ₄ ²⁻ , HSO ₄ ⁻	
K ⁺ , OH ⁻ , Cl ⁻	
OH ⁻ , SO ₄ ²⁻	Solubility data in the Na ₂ SO ₄ -NaOH-H ₂ O system
Na ⁺ , OH ⁻ , SO ₄ ²⁻	Solubility data in the K ₂ SO ₄ -KOH-H ₂ O system
K ⁺ , OH ⁻ , SO ₄ ²⁻	
Na ⁺ , K ⁺ , OH ⁻	Solubility data in the NaOH-KOH-H ₂ O system and in the quaternary Na-K-OH-Cl-H ₂ O system

3. MODEL PARAMETERIZATION

Since the Pitzer equations we use are expansions of the excess Gibbs free energy to third virial coefficient terms, only binary and ternary data are required to fully parameterize a model of higher order systems (see Harvie and Weare, 1980). At constant temperature and pressure, the solution model parameters to be evaluated are $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^φ for each cation-anion pair; θ for each unlike cation-cation or anion-anion pair; Ψ for each triple ion interaction where the ions are all not of the same sign (Appendix A). The system under study here does not include neutral species interactions; therefore all λ 's and ζ 's (see Felmy and Weare, 1986) are set equal to zero. The parameter values for each system are determined by least square analyses as described in detail in Harvie (1981). When speciation reactions are important, such as in the redistribution of SO₄²⁻ and H⁺ into HSO₄⁻, the least square problem is no longer linear, and a chemical equilibrium problem must be solved for each step in the nonlinear least squares analysis. To solve this problem, we use the free energy minimization algorithm described in Harvie et al. (1987). For application to nonideal multiphase equilibria, this method is equivalent to, but more stable than, methods based on the iterative substitution method of solving the mass action equations.

In constructing the model of the H-Na-K-OH-Cl-HSO₄-SO₄-H₂O system, the temperature functions of the ion interaction parameters and solid phase chemical potentials for the Na-K-Cl-SO₄-H₂O system were taken from Moller (1988) and Greenberg and Moller (1989). The standard chemical potentials of the independent ionic species, H⁺, Na⁺, K⁺, Cl⁻, OH⁻, SO₄²⁻, are all set equal to zero from 0° to 250°C. The temperature function for the bisulfate ion potential (see Table 4) is based on the work of Dickson et al. (1990). The temperature function for $\mu^\circ_{\text{H}_2\text{O}}/RT$ (Table 4) is taken from Moller (1988) as adapted from the Busey and Mesmer (1978) study. The temperature function for the Debye-Huckel constant, A^φ (limiting law slope for osmotic coefficient) (see Table 4 and Eqn. 2A), is taken from Pitzer et al. (1984) as adapted by Moller (1988). From 0° to 100°C (P = 0.1 MPa), the maximum difference between the A^φ values calculated by the equation given in Moller and by the more recent equation of Archer and Wang (1990) is 0.0003 (0.136%). At 175°C (P = 1.0 MPa), the max diff is 0.0042 (0.74%).

Evaluations of temperature functions for the remaining model parameters are discussed in the sections below. They are the binary solution model parameters, $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^φ , for the ion interactions: H-HSO₄, H-SO₄, H-Cl, Na-HSO₄, Na-OH, K-HSO₄ and K-OH (see Table 2); the mixed solution model parameters, θ and Ψ , for ion interactions in the common-ion acid and base ternary solutions: HCl-NaCl-H₂O, NaOH-NaCl-H₂O, H₂SO₄-HCl-H₂O, H₂SO₄-Na₂SO₄-H₂O, NaOH-Na₂SO₄-H₂O, HCl-KCl-H₂O, KOH-KCl-H₂O, H₂SO₄-K₂SO₄-H₂O, KOH-K₂SO₄-H₂O and NaOH-KOH-H₂O (see Table 3); the standard chemical potentials of the aqueous bisulfate ion (HSO₄⁻(aq)) and of eleven sodium and potassium acid and base solid phases (see Table 4) contained within the H-Na-K-Cl-OH-HSO₄-SO₄-H₂O system.

Table 2. Values of the temperature function (Eqn. 2) fitting constants for the single electrolyte interaction parameters.^a

Parameter	Constants						
	a ₁ (-)	a ₂ (T)	a ₃ (T ²)	a ₄ (T ³)	a ₅ (1/T)	a ₇ (1/(T - 263))	a ₈ (1/(680 - T))
$\beta^{(0)}$ (Na,H ₂ SO ₄) (0-225°C)	9.47999871d-01	-5.59737012d-03	1.18646053d-05	-8.60598682d-09	0.	0.	0.
$\beta^{(1)}$ (Na,H ₂ SO ₄) (0-225°C)	-5.98712856d00	3.18347572d-02	-4.08067492d-05	5.42698272d-09	0.	0.	0.
C ^φ (Na,H ₂ SO ₄) (0-225°C)	-1.55052543d-01	1.05510017d-03	-2.40340258d-06	1.82204715d-09	0.	0.	0.
$\beta^{(0)}$ (Na,OH) (0-250°C)	7.48451133d-01	-1.04785158d-03	0.	0.	-9.88884052d01	0.	0.
$\beta^{(1)}$ (Na,OH) (0-250°C)	1.20222953d00	-1.29580589d-03	0.	0.	-2.06111999d02	0.	0.
C ^φ (Na,OH) (0-250°C)	-9.11316056d-02	1.18266752d-04	0.	0.	1.73000563d01	0.	0.
$\beta^{(0)}$ (K,H ₂ SO ₄) ^b (0-75°C)	-3.00000000d-04	0.	0.	0.	0.	0.	0.
$\beta^{(1)}$ (K,H ₂ SO ₄) (0-75°C)	4.80794533d00	0.	0.	0.	-1.34573451d03	0.	0.
C ^φ (K,H ₂ SO ₄) (0-75°C)	2.21417968d-02	-1.66609598d-05	0.	0.	-4.95021084d00	0.	0.
$\beta^{(0)}$ (K,OH) (0-169.94°C)	-5.90638934d-01	7.87878491d-04	0.	0.	1.47009407d02	0.	0.
$\beta^{(1)}$ (K,OH) (0-169.94°C)	1.26574698d01	-1.71311828d-02	0.	0.	-2.15113077d03	0.	0.
C ^φ (K,OH) (0-169.94°C)	1.36927121d-01	-2.02214588d-04	0.	0.	-2.23159846d01	0.	0.
$\beta^{(0)}$ (H,Cl) (0- 250°C)	5.20980985d-02	6.26911217d-04	-2.17745839d-06	0.	0.	1.00115257d-01	4.87979143d01
$\beta^{(1)}$ (H,Cl) (0- 250°C)	2.19549623d+00	-7.77644382d-03	1.84693733d-05	0.	0.	-4.06503624d-01	-4.61357568d02
C ^φ (H,Cl) (0- 250°C)	0.	0.	0.	0.	0.	0.	0.
$\beta^{(0)}$ (H ₂ SO ₄) (0-200°C)	-1.48303709d00	1.77928136d-02	-6.29550580d-05	7.03841000d-08	0.	0.	0.
$\beta^{(1)}$ (H ₂ SO ₄) (0-200°C)	0.	0.	0.	0.	0.	0.	0.
C ^φ (H ₂ SO ₄) (0-200°C)	-2.54119885d00	2.14343886d-02	-5.70137550d-05	4.80658000d-08	0.	0.	0.
$\beta^{(0)}$ (H,H ₂ SO ₄) (0-200°C)	1.05070838d00	-6.32093298d-03	1.61005730d-05	-1.45994000d-08	0.	0.	0.
$\beta^{(1)}$ (H,H ₂ SO ₄) (0-200°C)	2.02496163d-01	1.60079716d-03	-2.68455000d-06	0.	0.	0.	0.
C ^φ (H,H ₂ SO ₄) (0-200°C)	0.	0.	0.	0.	0.	0.	0.

^a The temperature range of unsaturated solution data used in evaluation and validation of the acid-base parameters is given. The constant a₆ is equal to zero for all above parameters. Note that $\beta^{(1)}$ (K,H₂SO₄) and C^φ(K,H₂SO₄) are determined using solubility data in the K₂SO₄-H₂SO₄-H₂O system only.

^b Parameter determined by Harvie et al. (1984).

3.1. Sodium Acid-Base Systems

3.1.1. Evaluation of Parameters in the HCl-NaCl-H₂O Ternary

Mesmer and Holmes (1992) report mean HCl activity coefficient values in the HCl-H₂O system to 300°C and to 7 m (to 2 m at 350°C) (see also Leitzke et al., 1965; Holmes et al., 1987; Simonson et al., 1990). In the present study, temperature functions for the binary H-Cl interaction parameters, $\beta^{(0)}$ and $\beta^{(1)}$, are established by fitting the mean activity coefficients for HCl recommended by Mesmer and Holmes (1992) from 25°C to 300°C and the 0°-60°C data of Leitzke and Stoughton (1964). $\beta^{(2)}$ is set equal to zero. When we vary C^φ along with $\beta^{(0)}$ and $\beta^{(1)}$, agreement with these data is not significantly improved; therefore C^φ is also set equal to zero.

Model agreement with the experimental mean HCl activity coefficients recommended by Mesmer and Holmes is excellent from 25° to 300°C. In Figure 1, we compare model (solid lines) and experiment (symbols) from 0° to 250°C. Agreement with the 0°-60°C mean HCl activity coefficient data of Leitzke and Stoughton (1964) is also very good (see 0° curve in Fig. 1). Calculations of our earlier TEQUIL model (Moller et al., 1998) diverge from the data above ~175°C (see dashed lines in Fig. 1). This finding is not surprising since the HCl-H₂O parameterization in TEQUIL is based upon the electrochemical data of Greeley et al. (1960). These data, taken using AgCl electrodes, are known to suffer from the increased solubility of AgCl above temperatures of approximately 175°C.

In the TEQUIL model, the $\theta_{Na,H}$ and $\Psi_{Na,H,Cl}$ mixing parameters for the ternary NaCl-HCl-H₂O system are determined

Table 3. Values of the temperature function (Eqn. 2) fitting constants for the ternary solution mixing parameters.^a

Parameter	Constants						
	a ₁ (-)	a ₂ (T)	a ₃ (T ²)	a ₅ (1/T)	a ₆ (lnT)	a ₇ (1/(T - 263))	a ₈ (1/(680 - T))
$\Psi_{\text{Na,K,OH}}^b$ (0–100°C)	1.09189587d00	-1.60450254d-03	0.	-1.84024816d+02	0.	0.	0.
$\theta_{\text{Na,H}}$ (0– 97°C)	4.81363462d-02	0.	0.	-4.05430635d00	0.	0.	0.
$\Psi_{\text{Na,H,Cl}}$ (0– 85.7°C)	-1.45623335d-02	0.	0.	3.59308925d00	0.	0.	0.
$\Psi_{\text{Na,H,SO}_4}$ (0–97°C)	4.76203879d-03	0.	0.	2.47901813d00	0.	0.	0.
$\Psi_{\text{Na,H,HSO}_4}$ (0–97°C)	-1.46329100d-02	0.	0.	0.	0.	0.	0.
$\theta_{\text{K,H}}$ (0– 87.2°C)	2.02786744d-01	0.	0.	-5.58760313d01	0.	0.	0.
$\Psi_{\text{K,H,Cl}}$ (0– 87.2°C)	-8.03290665d-01	2.12457757d-05	0.	4.36421594d01	1.11869143d-01		
$\Psi_{\text{K,H,SO}_4}$ (0–75°C)	1.29877062d-01	0.	0.	-4.04666908d01	0.	0.	0.
$\Psi_{\text{K,H,HSO}_4}$ (0–75°C)	3.47636881d-02	0.	0.	-1.85961875d01	0.	0.	0.
$\theta_{\text{Cl,OH}}$ (0– 250°C)	1.10485703d-01	0.	0.	-4.93613455d01	0.	0.	0.
$\Psi_{\text{Na,Cl,OH}}$ (0–250°C)	1.27601977d01	3.66503385d-03	0.	-3.55227032d02	-2.21051220d00	3.23085637d-03	-2.71988632d01
$\Psi_{\text{K,Cl,OH}}$ (0–180°C)	-3.53984523d-03	2.02193825d-05	0.	-1.70410062d00	0.	0.	0.
$\theta_{\text{SO}_4,\text{OH}}$ (0– 250°C)	2.30121677d-01	-1.22733042d-03	7.77608349d-07	0.	0.	0.	2.10214125d01
$\Psi_{\text{Na,SO}_4,\text{OH}}$ (0–250°C)	1.01804141d-01	-7.29640874d-05	0.	-2.53105985d01	0.	0.	0.
$\Psi_{\text{K,SO}_4,\text{OH}}$ (0–100°C)	1.31440594d-01	0.	0.	-4.20903077d01	0.	0.	0.
$\theta_{\text{SO}_4,\text{HSO}_4}^c$ (0–200°C)	-3.65022515d-01	9.96042215d-04	0.	1.11361517d01	0.	-5.70637657d-01	-2.75132804d01
$\Psi_{\text{H,SO}_4,\text{HSO}_4}^c$ (0–200°C)	0.	0.	0.	0.	0.	0.	0.
$\Psi_{\text{Na,SO}_4,\text{HSO}_4}$ (0–97°C)	-1.03380870d-01	1.40454833d-04		1.98974337d01	0.	0.	0.
$\Psi_{\text{K,SO}_4,\text{HSO}_4}$ (0–75°C)	0.	0.	0.	0.	0.	0.	0.
$\Psi_{\text{H,Cl,SO}_4}$ (0–250°C)	0.	0.	0.	0.	0.	0.	0.
$\theta_{\text{Cl,HSO}_4}$ (0–250°C)	0.	0.	0.	0.	0.	0.	0.
$\Psi_{\text{H,Cl,HSO}_4}$ (0–250°C)	0.	0.	0.	0.	0.	0.	0.
$\Psi_{\text{Na,Cl,HSO}_4}$ (0–250°C)	0.	0.	0.	0.	0.	0.	0.
$\Psi_{\text{K,Cl,HSO}_4}$ (0–100°C)	0.	0.	0.	0.	0.	0.	0.

^a The constant a_4 is equal to zero for all above parameters. The temperature range of data used in evaluation and validation of the acid-base parameters is given.

^b The mixing $\Psi_{\text{Na,K,OH}}$ parameter is determined using solubility data in the NaOH-KOH-H₂O system from 0°C to 25°C and in the quaternary Na-K-OH-Cl-H₂O system at 100°C.

^c The mixing $\theta_{\text{SO}_4,\text{HSO}_4}$ and $\Psi_{\text{H,SO}_4,\text{HSO}_4}$ parameters are determined using osmotic data in the unsaturated H₂SO₄-H₂O system from 0°C to 200°C.

from emf and activity data for low concentration NaCl-HCl-H₂O solutions (Harned and Mannweiler, 1935). To treat solubility calculations of highly soluble acid minerals, in this study we establish temperature functions for the important $\theta_{\text{Na,H}}$ and $\psi_{\text{Na,H,Cl}}$ mixing parameters from solubility data as well as from HCl mean activity coefficients in aqueous NaCl solutions calculated by Mesmer and Holmes (1992). The Mesmer and Holmes model includes a temperature function for the mixing

parameter, $\theta_{\text{Na,H}}$, but sets $\psi_{\text{Na,H,Cl}}$ equal to zero. In establishing their model, Mesmer and Holmes fit the experimental results of Leitzke et al. (1965) from 25° to 175°C and from 0.4 to 1 *m* ionic strength. We use solubility measurements in saturated ternary solutions up to 10 *m* HCl to characterize the high concentration behavior of $\theta_{\text{Na,H}}$ and $\psi_{\text{Na,H,Cl}}$. Several sets of halite solubility data for the NaCl-HCl-H₂O ternary system were found from 0°C to 80°C (Linke, 1965; Zdanovskii et al.,

Table 4. Values of the temperature function (Eq. 2) fitting constants^a for A^φ, lnK_w, lnK₂ and for the standard chemical potentials^b of solid phases.

Parameter	Constant						
	a ₁ (-)	a ₂ (T)	a ₃ (T ²)	a ₅ (1/T)	a ₆ (lnT)	a ₇ (1/(T - 263))	a ₈ ((1/(680 - T))
A ^φ ^c	3.36901532d-01	-6.32100430d-04	1.92118597d-06	9.14252359d00	-1.35143986d-02	2.26089488d-03	4.52586464d01
lnK _w ^c (μ°/RT H ₂ O(aq))	1.04031130d03	4.86092851d-01	-2.32009393d-04	-3.26224352d04	-1.90877133d02	-5.35204850d-01	5.20549183d01
lnK ₂ ^d (μ°/RT HSO ₄ ⁻ (aq))	1.295096d03	5.705525d-01	-2.573487d-04	-3.053648d04	-2.359648d02	0.	0.
Sodium bisulfate (NaHSO ₄ · H ₂ O) (0–25°C)	1.23935627d04	3.40413743d00	0.	-3.44916799d05	-2.15603853d03	0.	0.
Sodium sesquisulfate (Na ₂ SO ₄ · NaHSO ₄) (0–97°C)	-2.65259618d04	-1.39944227d01	6.29673293d-03	5.66780781d05	4.95581018d03	0.	0.
Sodium hydroxide tetrahydrate (NaOH · 4H ₂ O) (0–5.1°C)	-1.84754242d01	0.	0.	-3.12866712d04	0.	0.	0.
Na ₂ (OH) ₂ · 7H ₂ O (5.1–15.9°C)	-3.70420458d01	0.	0.	-5.28096129d04	0.	0.	0.
Sodium Hydroxide Dihydrate (NaOH · 2H ₂ O) (5–12.9°C)	7.75421478d00	0.	0.	-1.82495306d04	0.	0.	0.
Sodium Hydroxide Monohydrate (NaOH · H ₂ O) (12–65.2°C)	-1.79875159d01	2.49197550d-02	0.	-2.00561996d03	0.	0.	0.
Mercallite (KHSO ₄) (0–75°C)	1.12579904d01	-1.62096380d-02	0.	-2.87658734d03	0.	0.	0.
Potassium Sesquisulfate (K ₂ SO ₄ · KHSO ₄) (0–75°C)	-1.08587834d04	-7.57563186d00	4.21750544d-03	1.80712508d05	2.12867851d03	0.	0.
Misenite (K ₂ SO ₄ · 6KHSO ₄) (0–50°C)	2.77108296d04	1.36889050d01	-6.16592651d-03	-6.44740044d05	-5.10849887d03	0.	0.
Potassium Hydroxide Dihydrate (KOH · 2H ₂ O) (0–33°C)	4.04200613d00	-1.26427660d-03	0.	-1.71197284d04	0.	0.	0.
Potassium Hydroxide Monohydrate (KOH · H ₂ O) (0–70°C)	2.43736648d02	-3.65075674d-01	0.	-4.53215736d04	0.	0.	0.

^a The constant a₄ is equal to zero for all above parameters. The temperature range of mineral crystallization indicated by the solubility data is given.

^b Standard chemical potentials are referenced to the independent ions in solution.

^c See Moller (1988).

^d We use the values of K₂ (the molal equilibrium quotients, Q₂ = [H⁺] [SO₄²⁻]/[HSO₄], approach K₂ at infinite dilution) from the Dickson et al. (1990) model to describe the temperature variation of the HSO₄⁻ standard chemical potential from 0° to 250°C. Our temperature function for lnK₂ is essentially the same as that given by Dickson et al. (1990).

1973). Above 80°C, we found only the Potter and Clyne (1980) study of halite solubility in aqueous HCl (one data point at 85.68°C). In these data correlations, our evaluations of the binary parameters for aqueous HCl (see above) and NaCl (see Greenberg and Moller, 1989) and of the halite standard chemical potential (Greenberg and Moller, 1989) are used.

Our model (see Tables 2–4) reproduces the activity, emf and osmotic data in the HCl-NaCl-H₂O system to concentrations above 7 m HCl from 0° to 200°C. Halite solubilities in the NaCl-HCl-H₂O system calculated with the model are also in excellent agreement with the available (0°C to 80°C) solubility data for the NaCl-HCl-H₂O system up to 10 m HCl (sigma equals 0.084). See Greenberg and Moller (1989) for a definition

of sigma. In Figure 2, we compare model and experiment at 0°C and 80°C. The model predicts reasonable halite solubilities in the HCl-NaCl-H₂O ternary system to 200°C. This extrapolation (from 80° to 200°C) must be validated by comparison with new solubility experimental data.

3.1.2. Evaluation of Parameters in the NaOH-NaCl-H₂O Ternary

The NaOH-H₂O binary solution interaction parameters and the $\theta_{\text{Cl,OH}}$ and $\Psi_{\text{Na,Cl,OH}}$ mixing parameters are evaluated from data in this ternary. In the TEQUIL model, these parameters are determined from relatively low concentration data that include

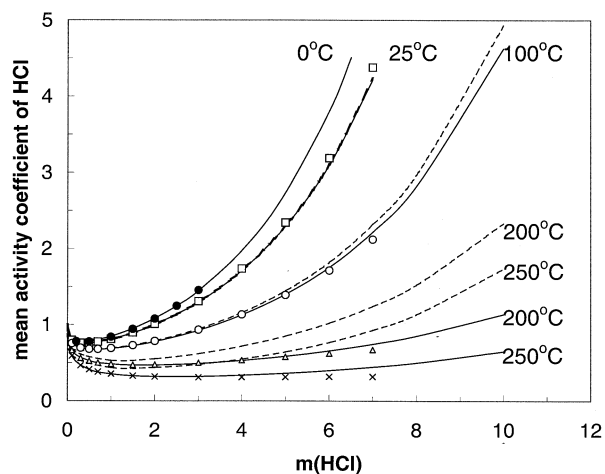


Fig. 1. Comparison of mean HCl activity coefficients in HCl-H₂O solutions calculated by the model (solid lines) with the data (symbols) from 0°C to 250°C ($T = 0^\circ\text{C}$, Leitzke and Stoughton (1964); $T = 25^\circ\text{--}250^\circ\text{C}$, reference values of Mesmer and Holmes, 1992). The dashed lines represent predictions of the TEQUIL model (Moller et al., 1998).

emf measurements in the NaOH-NaCl-H₂O system (0° to 70°C: Akerlof and Kegeles, 1940; 0°–60°C: Harned and Manweiler, 1935) as well as water dissociation data from 0°C to 250°C (Busey and Mesmer, 1978) in aqueous NaCl (0–5 *m*).

To better reflect the high concentration behavior of the mixed NaOH-NaCl-H₂O system, we include measurements of halite solubility in this ternary as well as the above low concentration data in our parameterization of $\theta_{\text{Cl,OH}}$ and $\Psi_{\text{Na,Cl,OH}}$. The halite solubility data, which range from 0°C to 200°C and up to 10 *m* NaOH, are taken from compilations by Linke (1965), Zdanovskii et al. (1973) and Silcock (1979). Osmotic coefficient data for binary NaOH-H₂O solutions are used to help define the concentration variation of $\beta_{\text{NaOH}}^{(0)}$, $\beta_{\text{NaOH}}^{(1)}$

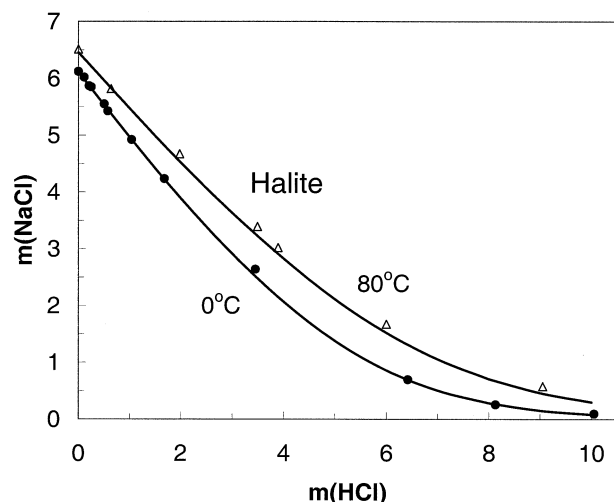


Fig. 2. Comparison of calculated (solid lines) and experimental (symbols, Linke, 1965; Silcock, 1979; Zdanovskii et al., 1973) halite solubility as a function of HCl concentration in the NaCl-HCl-H₂O system at 0°C and 80°C.

and C_{NaOH}° with temperature. The osmotic coefficient data sets included are: Hamer and Wu's (1972) recommended values to 8 *m* NaOH at 25°C, Simonson et al.'s (1989) recommended values to 6 *m* NaOH from 0°C to 250°C and Holmes and Mesmer's (1998) measurements up to 7.3 *m* NaOH at 110.10°C, 139.97°C and 169.94°C. Simonson et al. (1989) calculated osmotic coefficients on the basis of measured data for the molar enthalpy of dilution of NaOH(aq). Holmes and Mesmer (1998) determined osmotic coefficients directly from isopiestic measurements of sodium hydroxide solutions, using NaCl(aq) as the isopiestic standard. There is good agreement between both sets of osmotic coefficient data (Holmes and Mesmer, 1998).

Four mixing parameters ($\theta_{\text{Cl,OH}}$, $\Psi_{\text{Na,Cl,OH}}$, $\theta_{\text{Na,H}}$ and $\Psi_{\text{Na,H,Cl}}$) and nine binary solution parameters (for the HCl-H₂O, NaOH-H₂O and NaCl-H₂O systems) can describe water dissociation in aqueous solutions containing Na⁺, H⁺, Cl⁻ and OH⁻. Of these, only the binary NaOH-H₂O parameters and the mixing parameters, $\theta_{\text{Cl,OH}}$ and $\Psi_{\text{Na,Cl,OH}}$, have not been determined in our previous work. Temperature functions for the H-Cl binary interaction parameters and for the mixing parameters, $\theta_{\text{Na,H}}$ and $\Psi_{\text{Na,H,Cl}}$, have been determined above. The temperature functions for the Na-Cl binary interaction parameters and for the halite chemical potential are taken from Greenberg and Moller (1989). $\Psi_{\text{Na,H,OH}}$ and $\Psi_{\text{OH,Cl,H}}$ are set equal to zero.

The model's parameterization for the binary NaOH-H₂O system (Table 2) gives very good agreement with the data for unsaturated NaOH-H₂O binary solutions. The sigma value for the fit to the osmotic NaOH-H₂O data sets from 0° to 250°C is 0.022. The calculated dependence of NaOH mean activity coefficients vs. temperature and molality in binary NaOH-H₂O solutions is in good agreement with values recommended by Holmes and Mesmer (1998) from 0.1 to 5 *m* and from 0° to 250°C (see Fig. 3). At 0°C, the difference between model and experiment is within 10% at high molality (5 *m*). Petrenko and Pitzer (1997) report mean activity coefficient data for NaOH from 0° to 250°C. Their lowest NaOH concentration is 5 *m*. Our agreement with the Petrenko and Pitzer (1997) data at 5 *m* and 6 *m* is very good.

Temperature functions for the standard chemical potentials of four sodium hydroxide hydrates, NaOH · nH₂O(s) ($n = 4, 3.5, 2, 1$) (see Table 4), are evaluated from solubility data in the NaOH-H₂O system using our evaluation of the Na-OH binary interaction parameters. Solubility data from 0° to 65°C are taken from Linke (1965), Zdanovskii (1973) and Rollet and Cohen-Adad (1964). According to Rollet and Cohen-Adad, NaOH · 4H₂O(s) is stable from below 0° to 5.1°C where it undergoes a peritectic phase transformation to NaOH · 3.5H₂O(s). The 3.5 hydrate congruently melts at 15.9°C and has a eutectic point with NaOH · 2H₂O(s) at 6.2°C (Rollet and Cohen-Adad). Note that data presented in Linke give 5° for this eutectic temperature. Rollet and Cohen-Adad report that the peritectic temperature for the transformation of the dihydrate to the monohydrate is 12.9°C and that NaOH · H₂O(s) undergoes congruent melting at 62°C. Figure 4 shows that our model with the temperature functions for the chemical potentials given in Table 4 can reproduce this complicated cooling curve to high concentration (NaOH ≈ 64 *m*) although the Na-OH binary parameters in our model are determined using activity data only

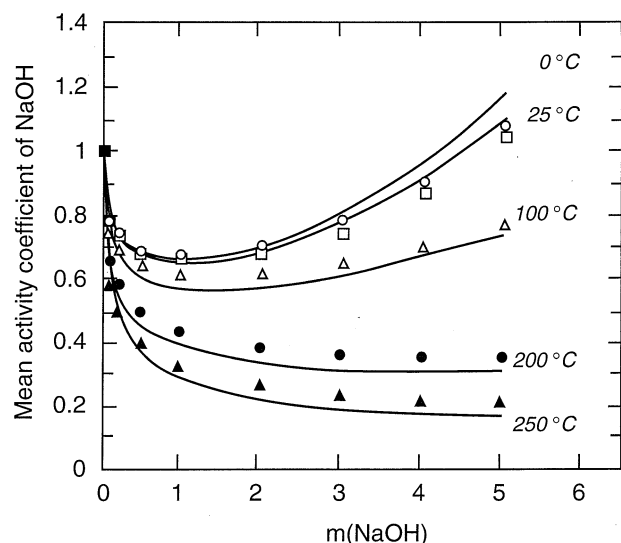


Fig. 3. Comparison of mean NaOH activity coefficients in NaOH-H₂O solutions calculated by the model (solid lines) with the recommended values of Holmes and Mesmer (1998) from 0°C to 250°C (0°, open squares; 25°, open circles; 100°, open triangles; 200°, solid circles; 250°, closed triangles).

up to 8 m NaOH. A discrepancy exists between model and experiment for the NaOH·3.5H₂O-NaOH·2H₂O coexistence point, the model reaching eutectic equilibrium at $\approx 2.8^\circ\text{C}$ instead of 5°–6.2°C.

The model's agreement with the data for unsaturated NaOH-

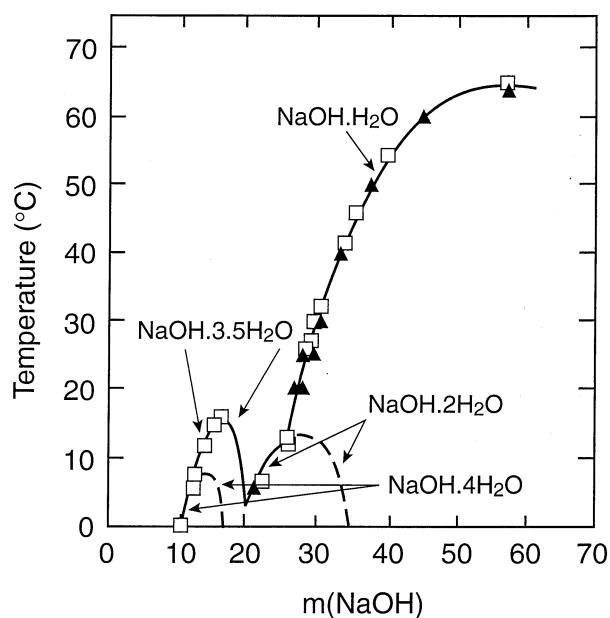


Fig. 4. Comparison of calculated (solid line) and experimental (Rollet and Cohen-Adad, 1964, open square; Linke, 1965, solid triangle) solubility of the NaOH·nH₂O (n = 1, 2, 3.5 and 4) solid phases in the NaOH-H₂O system as a function of temperature (0° to $\approx 65^\circ\text{C}$). Dashed lines are the predicted metastable equilibria for NaOH·4H₂O (disallowing crystallization of NaOH·3.5H₂O) and for NaOH·2H₂O (disallowing crystallization of NaOH·H₂O).

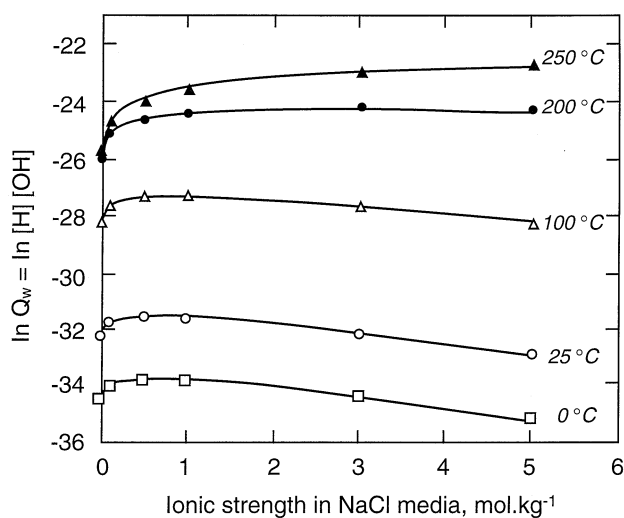


Fig. 5. Comparison of calculated (solid lines) water dissociation constant values ($\ln Q_w$) in aqueous NaCl solutions with the data from 0°C to 250°C (symbols: Busey and Mesmer, 1978).

NaCl-H₂O ternary solutions is excellent. The emf data of Akerlof and Kegeles (1940) and of Harned and Mannweiler (1935) are fit with sigma values of 0.041 and 0.030, respectively. The agreement with the water dissociation data of Busey and Mesmer (1978) from 0°C to 250°C and to 5 m NaCl (Fig. 5) is also excellent (sigma equals 0.034). The model predictions of halite solubility in NaOH-NaCl-H₂O solutions are in excellent agreement with the experimental data from 0° to 200°C and to ≈ 12 m NaOH (Fig. 6).

3.1.3. Evaluation of Parameters in the H₂SO₄-Na₂SO₄-H₂O Ternary

Aqueous solutions of H₂SO₄ contain hydrogen, bisulfate, and sulfate ions and can be described by nine solution model

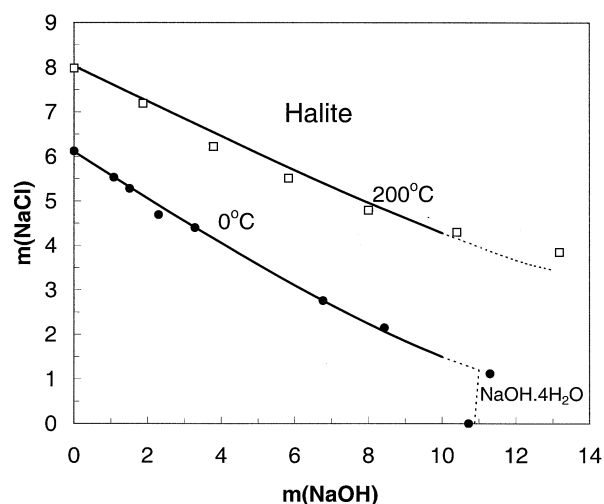


Fig. 6. Comparison of calculated (solid lines) and experimental (symbols, Linke, 1965; Silcock, 1979; Zdanovskii et al., 1973) halite solubility as a function of NaOH concentration in the NaCl-NaOH-H₂O system at 0°C and 200°C. The dashed lines represent extrapolations of the model parameterization.

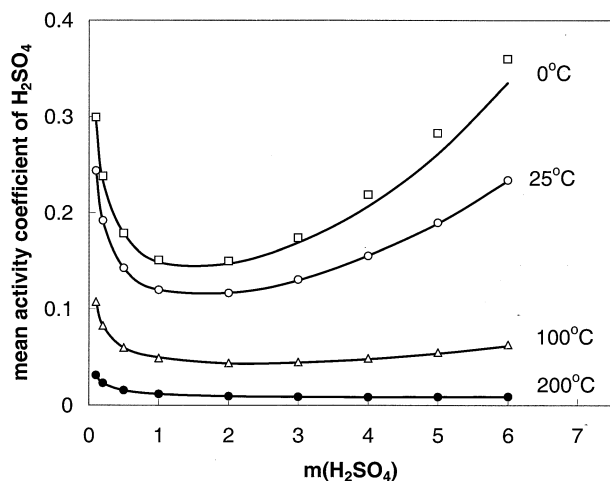


Fig. 7. Comparison of mean H_2SO_4 activity coefficients in H_2SO_4 - H_2O solutions calculated by the model (solid lines) with the model predictions of Clegg et al. (1994) at 0°C and the recommended values of Holmes and Mesmer (1992) from 25°C to 200°C . Above 4.096 m H_2SO_4 , the activity coefficient values at 0°C are extrapolations of the Clegg et al. (1994) model.

parameters: $\beta^{(0)}$, $\beta^{(1)}$ and C^φ for the H-HSO_4 and H-SO_4 interactions, μ°/RT (HSO_4^-) and the $\theta_{\text{HSO}_4,\text{SO}_4}$ and $\Psi_{\text{H,HSO}_4,\text{SO}_4}$ mixing parameters. Using their isopiestic results from 110.31°C to 200.06°C , along with the low temperature H_2SO_4 - H_2O model of Pitzer et al. (1977) from 25° to 55°C and the 25°C H_2SO_4 - H_2O data of Rard (1983), Holmes and Mesmer (1992) constructed an ion-interaction model for the H_2SO_4 - H_2O system from 25° to 200°C for concentrations up to 6 m H_2SO_4 . Their temperature function for the standard chemical potential of the HSO_4^- (aq) species ($\ln K_2$; see Eqn. 1) is taken from the work of Dickson et al. (1990).

We use the values of K_2 (the molal equilibrium quotients, $Q_2 = [\text{H}^+][\text{SO}_4^{2-}]/[\text{HSO}_4^-]$, approach K_2 at infinite dilution) from the Dickson et al. (1990) model to describe the temperature variation of the HSO_4^- standard chemical potential from 0° to 250°C . The functional form of our equation for $\ln K_2$ (Table 4) is the same and the temperature coefficients are nearly the same as in Dickson et al. (1990). The temperature function in Table 4 gives $\log K_2$ values from 0° to 250°C which differ from the Dickson et al. values by 0.00048 log units or less. Temperature functions for the H-HSO_4 ($\beta^{(0)}$ and $\beta^{(1)}$) and H-SO_4 ($\beta^{(0)}$ and C^φ) solution parameters (Table 2) are generated from the cubic power functions of Holmes and Mesmer (1992). With these parameters evaluated, a temperature function for $\theta_{\text{SO}_4,\text{HSO}_4}$ (Table 3) is established by fitting the 0°C osmotic coefficient values in Table 9 of Clegg et al. (1994) and the calculated osmotic coefficients from 25° – 200°C in Table 5 of Holmes and Mesmer (1992). $\psi_{\text{H,SO}_4,\text{HSO}_4}$ can be set equal to zero.

Model calculations of mean H_2SO_4 activity coefficients agree well with the data from 0° to 200°C and to 6.0 m H_2SO_4 (Fig. 7). Activity coefficients reported by Holmes and Mesmer (1992) from 25° to 200°C are fit with a sigma value of 0.0041 . The 0°C osmotic coefficient values predicted by the model of Clegg et al. (1994; Table 9) are fit with a sigma value of 0.0226 . The difference between model and reported activity coeffi-

cients for the H_2SO_4 - H_2O system is greatest (within $\approx 7\%$) at 0°C and $5, 6\text{ m}$ (Fig. 7). However, note that above 4.096 m H_2SO_4 , the Clegg et al. values are extrapolations of their model.

Using the temperature functions evaluated above for the $\text{HCl-H}_2\text{O}$ binary parameters and that of Moller (1988) for the $\theta_{\text{SO}_4,\text{Cl}}$ mixing parameter, the parameters, $\theta_{\text{HSO}_4,\text{Cl}}$, $\Psi_{\text{H,HSO}_4,\text{Cl}}$ and $\Psi_{\text{H,SO}_4,\text{Cl}}$ are evaluated in this ternary common ion system. We found that zero values for all three parameters give very good agreement with the emf data for the H_2SO_4 - $\text{HCl-H}_2\text{O}$ system. These data, which are available from 0° to 50°C , are those of Davies et al. (1952) from 5° to 50°C , Nair and Nancollas (1958) between 0° and 45°C , and Storonkin et al. (1967) at 25°C . The first two sets of experiments are confined to low concentrations ($I < 1\text{ m}$) while the data of Storonkin are up to ionic strengths of almost 4. The model fits the data of Davies et al. (1952) with a sigma value of 0.0096 and of Nair and Nancollas (1958) with a sigma value of 0.0029 . The agreement with the 25°C data of Storonkin et al. (1967) is also very good ($\sigma = 0.0251$).

Testing of our model (Tables 2–4) shows that it is in good agreement with solubility data in the Na-H-Cl-SO_4 - H_2O reciprocal system and with data for the molal equilibrium quotient $Q_2 = \{[\text{H}][\text{SO}_4]\}/[\text{HSO}_4]$ in NaCl media from 0° to 250°C .

Holmes and Mesmer (1994) established an ion-interaction model for the Na-H-HSO_4 - SO_4 - H_2O system from 25° to 225°C using their (Holmes and Mesmer, 1993, 1994) isopiestic studies from 110.31° to 225.05°C along with the 25°C isopiestic data of Rard (1989) and data for pure H_2SO_4 aqueous solutions (Holmes and Mesmer, 1992). Clegg et al. (1998) constructed a model of the Na-H-HSO_4 - SO_4 - H_2O system for 25°C using the mole-fraction modeling approach (Pitzer and Simonson, 1986; Clegg et al., 1992). There are six possible mixing parameters ($\theta_{\text{Na,H}}$, $\Psi_{\text{Na,H,HSO}_4}$, $\Psi_{\text{Na,H,SO}_4}$, $\theta_{\text{SO}_4,\text{HSO}_4}$, $\Psi_{\text{Na,SO}_4,\text{HSO}_4}$, and $\Psi_{\text{H,SO}_4,\text{HSO}_4}$) for the Na_2SO_4 - H_2SO_4 - H_2O system. Holmes and Mesmer (1994) found good agreement with the experimental data to high temperature when they varied only $\theta_{\text{SO}_4,\text{HSO}_4}$ and $\Psi_{\text{Na,SO}_4,\text{HSO}_4}$. The authors note that because of lack of data, the NaHSO_4 - H_2O binary and the mixing parameterization are not well defined for the entire temperature interval between 25°C and approximately 110°C (the lower temperature limit of their experimental results). They did not extend their model to 0°C .

In this study, we use the isopiestic data of Rard (1989, 1992) at 25°C and of Holmes and Mesmer for the H_2SO_4 - H_2O (Holmes and Mesmer, 1992), NaHSO_4 - H_2O (Holmes and Mesmer, 1993) and Na_2SO_4 - NaHSO_4 - H_2O (Holmes and Mesmer, 1994) systems at temperatures above 100°C as well as solubility data from 0°C to 82.5°C to establish temperature functions for the NaHSO_4 - H_2O binary solution interaction parameters, the mixing parameters, $\Psi_{\text{Na,H,HSO}_4}$, $\Psi_{\text{Na,H,SO}_4}$ and $\Psi_{\text{Na,SO}_4,\text{HSO}_4}$, and the chemical potentials of the solid phases: $\text{NaHSO}_4 \cdot \text{H}_2\text{O}(\text{s})$ and $\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4(\text{s})$ from 0°C to 225°C . Many inconsistencies are found in the solubility data for the Na_2SO_4 - H_2SO_4 - H_2O system (see Bukshtein et al., 1953; Linke, 1965; Zdanovskii, 1973). However, general support is found from the data for the existence of four stable solid phases: mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) (0° – 32°C), sodium bisulfate ($\text{NaHSO}_4 \cdot \text{H}_2\text{O}$) (0° – 25°C), thenardite (Na_2SO_4) (20° – 97°C), and sodium sesquisulfate ($\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4$) (0° – 97°C) in the 0° to 100°C temperature range for

H_2SO_4 concentrations up to 8 *m*. Harvie et al. (1984) chose not to include the $\text{NaHSO}_4 \cdot \text{H}_2\text{O}(\text{s})$ solid phase in their 25°C isothermal model. We have included it here because of its prominent appearance in the data below 25°C.

In our data correlations, we retain the temperature dependence established above for $\beta^{(0)}$ and $\beta^{(1)}$ for the H-HSO_4 interactions, $\beta^{(0)}$ and C^φ for H-SO_4 interactions, $\theta_{\text{SO}_4, \text{HSO}_4}$ and $\theta_{\text{Na}, \text{H}}$. We keep $\Psi_{\text{H}, \text{SO}_4, \text{HSO}_4}$ equal to zero. The temperature functions of Greenberg and Moller (1989) for the $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ binary solution parameters are used from 0°–250°C. Holmes and Mesmer (1994) use the $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ model of Holmes and Mesmer (1986) in which α has a value of 1.4 at high temperature ($T > 110^\circ\text{C}$) and a value of 2.0 for lower temperatures. In our models, α is 2.0 for the Na_2SO_4 electrolyte over the entire temperature range (Appendix B). The temperature functions for the chemical potentials of the mirabilite and thenardite solid phases are taken from Greenberg and Moller (1989) (see also Moller, 1988). We found that a constant value of -0.01463 could be assigned to the $\Psi_{\text{Na}, \text{H}, \text{HSO}_4}$ mixing parameter.

Predictions of the model (Tables 2–4) for the $\text{Na-H-HSO}_4\text{-SO}_4\text{-H}_2\text{O}$ system agree with the Holmes and Mesmer (1993) recommended osmotic data in the $\text{NaHSO}_4\text{-H}_2\text{O}$ system from 25° to 225°C and to 6 *m* NaHSO_4 with a sigma value of 0.0082. The model fits the experimental osmotic data for the $\text{Na}_2\text{SO}_4\text{-NaHSO}_4\text{-H}_2\text{O}$ system of Holmes and Mesmer (1994) from 110°C to 225°C and to ≈ 4.6 *m* NaHSO_4 with a sigma value of 0.0149. At 25°C, the model fits the Rard (1989, 1992) data for $\text{Na}_2\text{SO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ solutions up to 8 *m* of H_2SO_4 with a sigma of 0.015. The osmotic data of Holmes and Mesmer (1986) for $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ from 0° to 225°C and to 3 *m* are fit with a sigma value of 0.0229.

Solubilities predicted by the model in the $\text{Na}_2\text{SO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ system (e.g., Fig. 8) from 0° to 82.5°C agree well with the experimental solubility data for mirabilite ($\sigma = 0.070$), thenardite ($\sigma = 0.046$) and sodium sesquisulfate ($\sigma = 0.055$). The sigma value for the fit to the sodium bisulfate data is 0.097. Model calculations of the $\text{NaHSO}_4 \cdot \text{H}_2\text{O}(\text{s})$ saturation curve at 0°C are for the most part at lower H_2SO_4 concentrations than the data. At 25°C (Fig. 8a), model calculations for this salt are within the spread of the data (all eutonic points) to ~ 8 *m* H_2SO_4 . Using the mole fraction approach, the Clegg et al. (1998) model agrees with the data to higher H_2SO_4 concentrations (see their fig. 27). At 82.5°C (Fig. 8b), there is only one data point for sodium bisulfate. The two sets of solubility data found above 82.5°C (Zdanovskii, 1973 at 97°C and 120°C) are not used because they are not consistent with solubility data at lower temperatures or because of their very high sulfuric acid molality. Model extrapolation allows reasonable solubility predictions for $\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4(\text{s})$ and thenardite in the $\text{Na}_2\text{SO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ system to high sulfuric acid molality (≈ 15 *m*) to 200°C. When new experimental data are available, these extrapolations can be validated.

3.1.4. Evaluation of Parameters in the $\text{NaOH-Na}_2\text{SO}_4\text{-H}_2\text{O}$ Ternary

Temperature functions for the mixing parameters, $\theta_{\text{SO}_4, \text{OH}}$ and $\psi_{\text{Na}, \text{SO}_4, \text{OH}}$, are established in this study using experimental solubility data in the ternary $\text{Na-OH-SO}_4\text{-H}_2\text{O}$ system up to 8 *m* NaOH at temperatures from 0° to 250°C. The solubility data

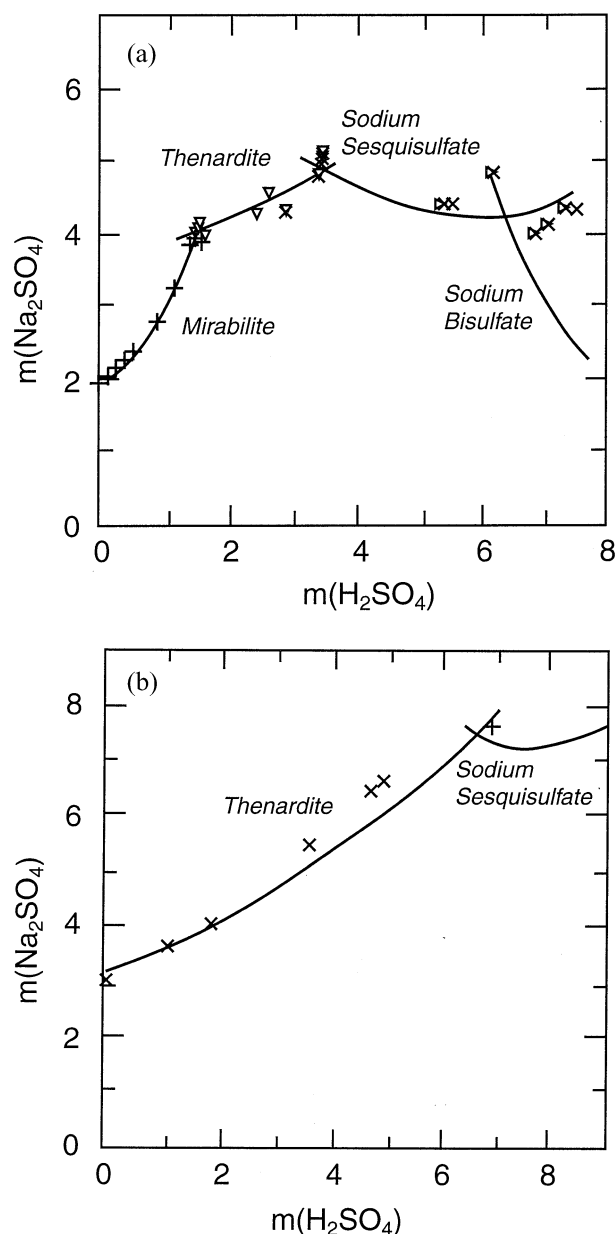


Fig. 8. Comparison of calculated (solid lines) and experimental (Linke, 1965; Silcock, 1979; Zdanovskii et al., 1973) solubilities in the $\text{Na}_2\text{SO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ system. (a) 25°C; Symbols: mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) (+), thenardite (Na_2SO_4) (down facing triangles), sodium sesquisulfate ($\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4$) (x) and sodium bisulfate ($\text{NaHSO}_4 \cdot \text{H}_2\text{O}$) (right facing triangles). (b) 82.5°C; Symbols: thenardite (x) and sodium sesquisulfate ($\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4$) (+).

are taken from Zdanovskii et al. (1973) and Silcock (1979). According to the literature, the phase diagrams for the ternary system consist of crystallization fields of mirabilite (from 0° to 30°C), thenardite (from 0° to 250°C) and very narrow fields of crystallization of sodium hydroxide hydrates, $\text{NaOH} \cdot n\text{H}_2\text{O}$, that appear at very high NaOH concentration. In our data correlations, we use the experimental data for mirabilite and thenardite saturation only. The temperature functions for the Na-SO_4 binary parameters and for the chemical potentials of

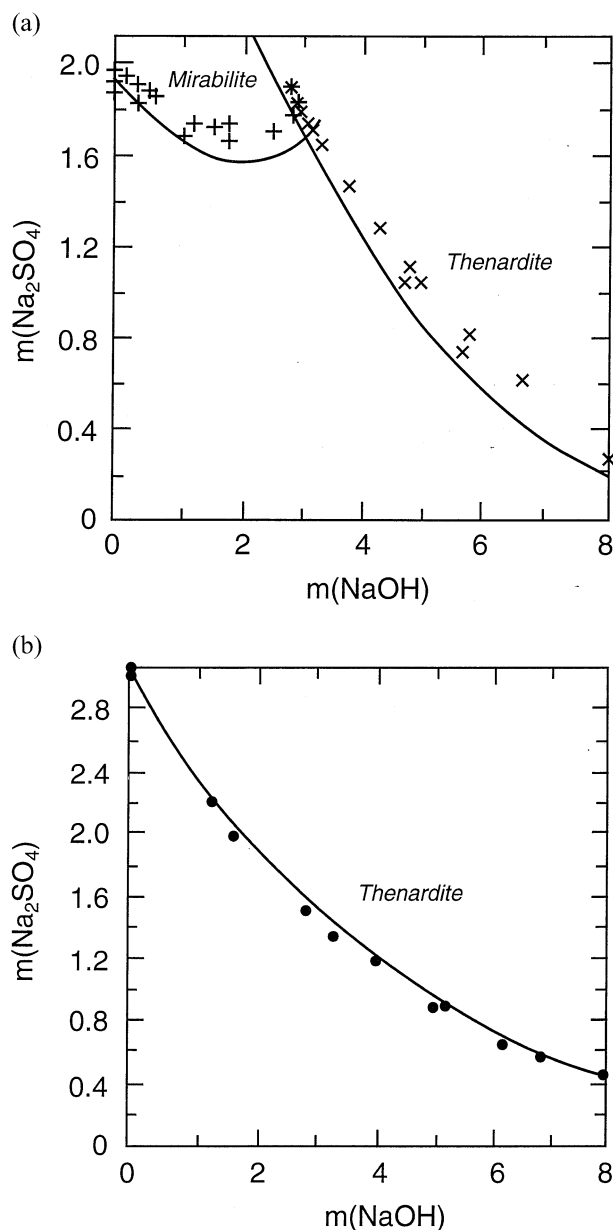


Fig. 9. Comparison of calculated (solid lines) and experimental (Zdanovskii et al., 1973) solubility of mirabilite and thenardite in the Na₂SO₄-NaOH-H₂O system. (a): 25°C; Symbols: mirabilite (Na₂SO₄·10H₂O) (+) and thenardite (Na₂SO₄) (x). (b) 100°C; Symbols: thenardite (Na₂SO₄) (closed circle).

mirabilite and thenardite are taken from Moller (1988) and Greenberg and Moller (1989). The resulting temperature functions for the $\theta_{\text{SO}_4, \text{OH}}$ and $\psi_{\text{Na}, \text{SO}_4, \text{OH}}$ mixing parameters are given in Table 3.

Good agreement between model (Tables 2–4) predictions and the experimental data in the ternary system is obtained from 0° to 200°C and up to 8 *m* NaOH (Fig. 9). Including the 250°C data in our evaluation of $\theta_{\text{SO}_4, \text{OH}}$ and $\psi_{\text{Na}, \text{SO}_4, \text{OH}}$ slightly degrades the agreement of the model and the 25°C Na-OH-SO₄-H₂O solubility data, particularly for mirabilite-

thenardite coexistence, relative to that for the 25°C isothermal model of Harvie et al. (1984). However, note that our model fits the closest mirabilite-thenardite invariant data point within 7%.

At 250°C, calculated thenardite solubilities in high $m_{\text{NaOH}} + m_{\text{Na}_2\text{SO}_4}$ solutions agree with the data of Schroeder et al. (1935) to 4 *m* NaOH, but at higher molalities they are lower than experimentally determined. Note that in the 200–300°C temperature range, the behavior of high concentration NaOH-Na₂SO₄-H₂O solutions changes. From 0° to 200°C, the ternary solubility of thenardite decreases with increasing concentration of sodium hydroxide up to 8 *m* NaOH. However, the ternary data of Schroeder et al. (1935) show that thenardite solubility decreases at 250°C up to 4 *m* NaOH and then is approximately constant from 4 to ~8 *m* NaOH. At 300°C, they report that the solubility of thenardite increases with increasing NaOH concentration. To define the unusual behavior of thenardite in the NaOH-Na₂SO₄-H₂O system, Pabalan and Pitzer give different temperature functions for the model parameters from 0° to 180°C (Pabalan and Pitzer, 1987) and from 150° to 300°C (Pabalan and Pitzer, 1988). We could not reproduce this complicated behavior at 250°C by readjusting the $\theta_{\text{OH}, \text{SO}_4}$ and $\psi_{\text{Na}, \text{OH}, \text{SO}_4}$ mixing parameters without degrading the fit to the low molality data (from 1–4 *m* OH). Consequently, our model (Tables 2–4) predictions of the thenardite solubility at 250°C in the NaOH-Na₂SO₄-H₂O system and in the NaOH-NaCl-Na₂SO₄-H₂O system (see below) are restricted to 0–4 *m* NaOH.

3.2. Potassium acid-base systems

In this section, we establish temperature functions for the solution parameters describing potassium-acid/base interactions and for the chemical potentials of the potassium-acid/base solid phases in the H-Na-K-OH-Cl-HSO₄-SO₄-H₂O system. There is less flexibility in fitting the data for the potassium acid-base system because we accept our evaluations determined above for the HCl-H₂O and H₂SO₄-H₂O parameters and for the mixing parameters, $\theta_{\text{Cl}, \text{OH}}$, $\theta_{\text{SO}_4, \text{OH}}$ and $\theta_{\text{SO}_4, \text{HSO}_4}$, common to both the potassium and sodium acid-base systems. We also accept the model of Greenberg and Moller (1989) for the K-Cl-SO₄-H₂O system. Therefore, the only potassium mixing parameters determined here are: $\theta_{\text{K}, \text{H}}$, $\Psi_{\text{K}, \text{OH}, \text{Cl}}$, $\Psi_{\text{K}, \text{OH}, \text{SO}_4}$, $\Psi_{\text{K}, \text{HSO}_4, \text{SO}_4}$, $\Psi_{\text{K}, \text{H}, \text{Cl}}$, $\Psi_{\text{K}, \text{H}, \text{SO}_4}$ and $\Psi_{\text{K}, \text{H}, \text{HSO}_4}$. In the H-K-OH-Cl-HSO₄-SO₄-H₂O system, the activity data for unsaturated solutions and the solubility data are more sparse than for the corresponding sodium solutions. Note that the K-acid-base parameters in the TEQUIL model (see Moller et al., 1998) are given values equal to those for the corresponding sodium parameters. Pabalan and Pitzer (1987) did not determine temperature functions for the binary KOH-H₂O solution parameters and for the ternary $\Psi_{\text{K}, \text{OH}, \text{Cl}}$ and $\Psi_{\text{K}, \text{OH}, \text{SO}_4}$ parameters.

3.2.1. Evaluation of Parameters in the KOH-KCl-H₂O Ternary

Holmes and Mesmer (1998) carried out isopiestic studies of the KOH-H₂O binary system at 110.10°C, 139.97°C and 169.94°C and up to 6.75 *m* KOH. Using their osmotic coeffi-

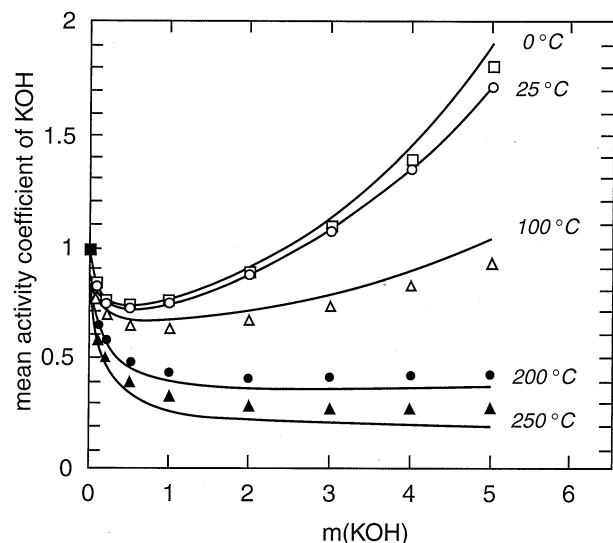


Fig. 10. Comparison of mean KOH activity coefficients in KOH-H₂O solutions calculated by the model (solid lines) with the recommended values of Holmes and Mesmer (1998) from 0°C to 250°C (0°, open squares; 25°, open circles; 100°, open triangles; 200°, solid circles; 250°, closed triangles).

cient data as well as lower temperature activity coefficient and osmotic data found in the literature, Holmes and Mesmer (1998) report mean activity coefficients of KOH from 0° to 250°C and to 5 m KOH. To extend our model to lower temperatures, we use the osmotic coefficient data of Hamer and Wu (1972) and those reported in Mikulin (1968) at 25°C as well as the activity coefficient data (from emf measurements) of Harned and Cook (1937) at 0°, 10° and 20°C and of Akerlof and Bender (1948) at 0°, 10°, 20°, 30°, 40°, 50°, 60° and 70°C. The maximum KOH concentration used in the parameter evaluation process is 8 m. Variable temperature expressions determined for $\beta_{\text{KOH}}^{(0)}$, $\beta_{\text{KOH}}^{(1)}$, and C_{KOH}^{ϕ} that give the best agreement ($\sigma = 0.0125$) with these osmotic and activity data from 0° to 169.94°C are given in Table 2.

In Figure 10, we compare the calculated temperature and molality dependence of mean KOH activity coefficients in binary KOH-H₂O solutions with experiment. With the exception of the 4 and 5 m points at 200°C, the calculated activity coefficients are within 10% of those recommended by Holmes and Mesmer (1998) from 0.1 to 5 m and from 0° to 200°C. The activity coefficients data at 200°C recommended by Balej (1996) (not shown) appear to be incorrect. At 250°C, KOH activity coefficient values are approximately constant in the 3–5 molality range. Our calculated value (0.22) in this range is somewhat lower than that (0.26) recommended by Holmes and Mesmer.

According to solubility data (Rollet and Cohen-Adad, 1964; Linke, 1965; Zdanovskii, 1973), KOH · 2H₂O(s) crystallizes from saturated binary KOH-H₂O solutions from 0° to ~32.5–33°C and the monohydrate KOH.H₂O(s) crystallizes in the 33° to 99°C temperature range. A temperature function for the standard chemical potential of the potassium hydroxide dihydrate (see Table 4) is determined by fitting these binary solubility data. The temperature function for the chemical potential

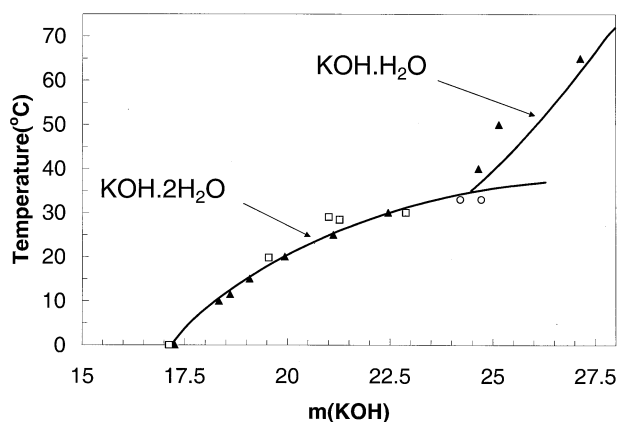


Fig. 11. Comparison of calculated (solid line) and experimental (open square, Rollet and Cohen-Adad, 1964; solid triangle, Linke, 1965) solubility of potassium hydroxide dihydrate (KOH · 2H₂O(s)) and monohydrate (KOH · H₂O(s)) in the KOH-H₂O system from 0°C to ~72°C. The experimental KOH · 2H₂O(s) + KOH · H₂O(s) invariant point is indicated by the open circles.

of the monohydrate (Table 4) is established on the basis of solubility data in the binary KOH-H₂O system (32.5°–65.3°C; Linke, 1965) and in the ternary NaOH-KOH-H₂O system (0°–25°C). Although our KOH-H₂O solution parameters are evaluated from data only up to 8 m KOH, Figure 11 shows that the model agrees well with the KOH · nH₂O(s) solubility data in this binary to 72°C and 28 m. The predicted KOH · 2H₂O(s) + KOH · H₂O(s) invariant point (34°C and 24.4 m) is close to the experimental point.

Using the solution parameter evaluations for the KOH-H₂O system, the $\Psi_{\text{K,OH,Cl}}$ mixing parameter is evaluated from solubility data in the ternary KOH-KCl-H₂O system from 0° to 180°C and to 8 m KOH. According to these data, only the sylvite solid phase crystallizes in this concentration and temperature range. The solubility data are taken from Zdanovskii et al. (1973) and Silcock (1979). In our data correlation, we use the temperature dependent equation for the mixing parameter, $\theta_{\text{Cl,OH}}$, determined above in the NaOH-NaCl-H₂O system. The temperature functions for the KCl-H₂O binary parameters and sylvite chemical potential are taken from Greenberg and Moller (1989). The resulting temperature function for $\Psi_{\text{K,OH,Cl}}$ (Table 3) provides an excellent fit of the experimental data for sylvite solubility in the KOH-KCl-H₂O system from 0° to 180°C to 8 m KOH. The fit over this temperature range is also good to higher KOH molalities (~17 m). At high temperatures, where the divergence of model and experiment is greatest, agreement is within 11% (e.g., 150°C curve in Fig. 12). Note that the binary K-OH solution parameters were determined from activity data in KOH-H₂O solutions only up to 8 m KOH.

3.2.2. Evaluation of Parameters in the HCl-KCl-H₂O Ternary

We use the water dissociation data of Sweeton et al. (1974) in potassium chloride solutions along with available sylvite solubility data in the ternary HCl-KCl-H₂O system to evaluate

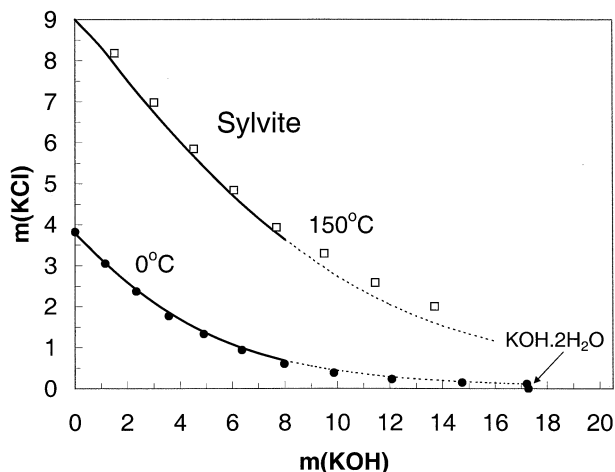


Fig. 12. Comparison of calculated (solid lines) and experimental (symbols, Zdanovskii et al., 1973) solubility of sylvite (KCl) as a function of KOH concentration in the KCl-KOH-H₂O system at 0°C and 150°C. The dashed lines represent extrapolations of the model parameterization. At 0°C, saturation of KOH · 2H₂O is also shown.

the mixing parameters, $\theta_{K,H}$ and $\Psi_{K,H,Cl}$. The solubility data, up to 10.5 *m* HCl, are taken from Linke (1965) and Zdanovskii et al. (1973) (0° to 50°C) and from Potter and Clynnne (1980) (25.19° to 87.19°C). The K_w data range from 0°C to 250°C and from 0.02 to 2.68 *m* KCl. Nine binary solution parameters for the KCl-H₂O, KOH-H₂O and HCl-H₂O systems and four mixing parameters, $\theta_{K,H}$, $\theta_{Cl,OH}$, $\Psi_{K,OH,Cl}$ and $\Psi_{K,H,Cl}$, can be used to describe water dissociation data in potassium chloride solutions. The temperature functions for the KCl-H₂O binary parameters and the sylvite chemical potential are taken from Greenberg and Moller (1989). All other parameters, except $\theta_{K,H}$ and $\Psi_{K,H,Cl}$, have already been evaluated in this study using data in other systems (see above and Tables 2–4).

The resulting model is in very good agreement with the sylvite solubility data from 0° to 87.19°C in the ternary HCl-KCl-H₂O system ($\sigma = 0.054$). In Figure 13, we compare model predictions and the experimental solubility isotherms for the HCl-KCl-H₂O system at 0°, 50° and 87.19°C. The model extrapolates well (dashed lines) to at least HCl ≈ 15 *m*. The highest HCl concentration used in fitting the data in this ternary is 10.5 *m*. The agreement with the Q_w data in aqueous KCl solutions of Sweeton et al. (1974) from 0°C to 250°C is also very good (Fig. 14).

3.2.3. Evaluation of Parameters in the H₂SO₄-K₂SO₄-H₂O Ternary

As in the case of the H₂SO₄-Na₂SO₄-H₂O system, the thermodynamic analysis of the potassium sulfate-sulfuric acid system is complicated by the fact that many model parameters can define the solid-liquid equilibria in this system. The model parameters that can be adjusted to fit the data in the potassium system are the salt chemical potentials, $\mu^\circ(\text{HSO}_4^-)/RT$ and the binary solution parameters for the H-SO₄, H-HSO₄, K-SO₄ and K-HSO₄ interactions as well as the six mixing parameters: $\theta_{K,H}$, θ_{SO_4,HSO_4} , Ψ_{K,H,HSO_4} , Ψ_{K,H,SO_4} , Ψ_{H,SO_4,HSO_4} and Ψ_{K,SO_4,HSO_4} . Many of these parameters have already been

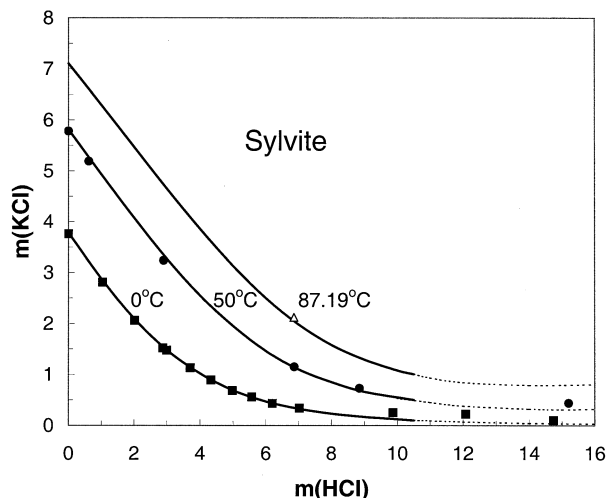


Fig. 13. Comparison of calculated (solid lines) and experimental (symbols: Zdanovskii et al., 1973; Potter and Clynnne, 1980) solubility of sylvite (KCl) as a function of HCl concentration in the KCl-HCl-H₂O system at 0°, 50° and 87.19°C. The dashed lines represent extrapolations of the model parameterization.

determined using data in other systems. The temperature functions for the K₂SO₄-H₂O binary parameters and for the chemical potential of arcanite (K₂SO₄) are taken from Greenberg and Moller (1989). The binary solution parameters for the H-SO₄, and H-HSO₄ interactions and the mixing parameters, $\theta_{K,H}$, θ_{SO_4,HSO_4} and Ψ_{H,SO_4,HSO_4} have been evaluated previously in this study and presented in Tables 2 and 3. The remaining parameters that need to be evaluated from data in the H₂SO₄-K₂SO₄-H₂O ternary are the K-HSO₄ binary parameters, the Ψ_{K,H,HSO_4} , Ψ_{K,H,SO_4} and Ψ_{K,SO_4,HSO_4} mixing parameters and the chemical potentials of the acid salts: mercallite (KHSO₄), potassium sesquisulfate (K₂SO₄ · KHSO₄) and misenite (K₂SO₄ · 6KHSO₄).

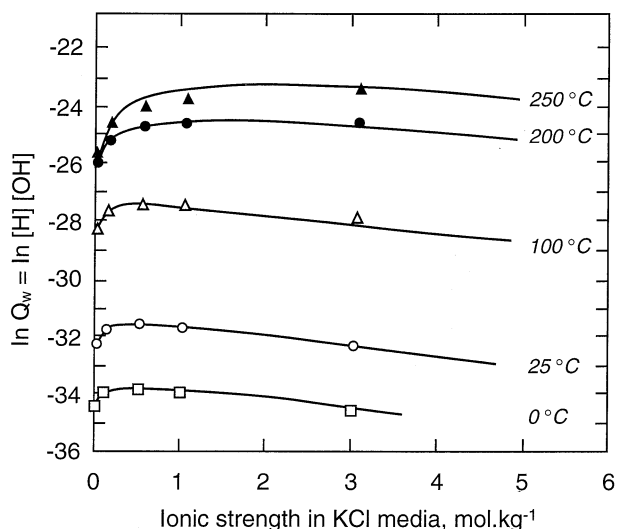


Fig. 14. Comparison of calculated (solid lines) water dissociation constant values ($\ln Q_w$) in aqueous KCl solutions with the data from 0°C to 250°C (symbols: Sweeton et al., 1974).

Data for the H_2SO_4 - K_2SO_4 - H_2O system are scarce. The only data we found are solubility measurements (Silcock, 1979; Linke, 1965) from 0° to 75°C . These have considerable differences in some of the solid phases crystallizing from saturated solutions. Therefore, we removed inconsistent solubility data and made some assumptions about the nature of the solid phases with unknown or debated compositions. The data used to evaluate the six solution parameters and three salt chemical potentials range from 0° to 50°C and to 9 m .

Good agreement with experiment from 0° to 50°C is attained keeping $\beta_{\text{KHSO}_4}^{(0)}$ constant at the same value (-0.0003) determined by Harvie et al. (1984) in their comprehensive 25°C parameterization of the H_2SO_4 - K_2SO_4 - H_2O system and also keeping $\Psi_{\text{K}_2\text{SO}_4, \text{H}_2\text{SO}_4}$ constant (0.0). In Figure 15, we compare the model (Tables 2–4) and experimental solubilities at 0° and 50°C . The fit to the data from 0°C to 75°C has a sigma value of 0.193, the relatively large value reflecting the poor agreement of the model with the available data at 75°C above 4 m H_2SO_4 . However, note that these 75°C data appear to be inconsistent with the data at lower temperatures. Crystallization of an unreported double salt with different stoichiometry than that of misenite appears likely at this temperature.

Using the evaluation of the K - HSO_4 binary parameters established here, the 25°C osmotic data of Mikulin (1968) from 0.1 to 4 m KHSO_4 (not used in the model parameterization) are fit very well with a sigma value of 0.0179. Extrapolation of our parameterization established by solubility data in the H_2SO_4 - K_2SO_4 - H_2O system also gives good agreement with the KHSO_4 - H_2O osmotic data at high temperature. The isopiestic data of Holmes and Mesmer (1996) from 110.31°C to 200.06°C and from 0.6 to 6.3 m (not used in model parameterization) are fit with a sigma value of 0.0834. The extrapolated model also yields reasonable solubility isotherms to temperatures above 75°C . At 120°C , the model predicts crystallization of arcanite, potassium sesquisulfate and mercallite up to 10 m H_2SO_4 . At 150°C , it predicts that arcanite and potassium sesquisulfate are the stable phases up to 13 m H_2SO_4 . Only arcanite is predicted to crystallize at 200°C . New data are needed to better describe this system and to verify our assumptions.

3.2.4. Evaluation of Parameters in the KOH - K_2SO_4 - H_2O Ternary

Arcanite solubility data in the KOH - K_2SO_4 - H_2O system at 0° , 25° , 50° and 75°C (Zdanovskii et al., 1973) and up to 8 m KOH are used to establish the temperature dependence of the $\Psi_{\text{K}_2\text{SO}_4, \text{KOH}}$ mixing parameter. The temperature functions for the K_2SO_4 - H_2O binary parameters and for the arcanite standard chemical potential are taken from Greenberg and Moller (1989). The pure electrolyte KOH - H_2O binary parameters and the $\theta_{\text{SO}_4, \text{OH}}$ mixing parameter needed to describe equilibria in this system have been previously determined (Tables 2 and 3). Data correlation yields the temperature function for $\Psi_{\text{K}_2\text{SO}_4, \text{KOH}}$ given in Table 3. Model calculations of arcanite solubilities in KOH - K_2SO_4 - H_2O solutions from 0° to 75°C are in good agreement with experimental data. In Figure 16, we compare model and experiment at 0° and 50°C . Extrapolation of the model provides reasonable predictions of arcanite solubility in the KOH - K_2SO_4 - H_2O to 250°C and to 13 m KOH . The extrapolation is tested at 100°C by comparing model pre-

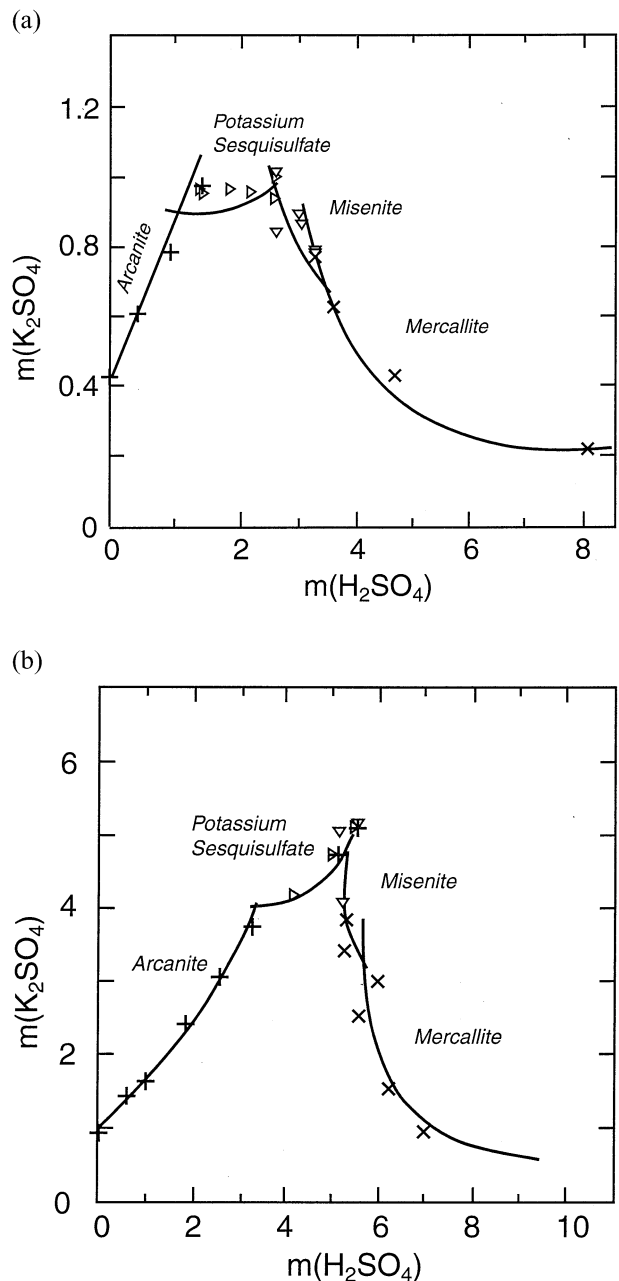


Fig. 15. Comparison of calculated (solid lines) and experimental (Zdanovskii et al., 1973; Silcock, 1979) solubility of arcanite (K_2SO_4) (+), potassium sesquisulfate ($\text{K}_2\text{SO}_4 \cdot \text{KHSO}_4$) (right facing triangles), misenite ($\text{K}_2\text{SO}_4 \cdot 6\text{KHSO}_4$) (down facing triangles) and mercallite (KHSO_4) (x) in the K_2SO_4 - H_2SO_4 - H_2O system. (a) 0° . (b) 50°C .

dictions and experimental solubilities in the Na - K - OH - SO_4 - H_2O system.

3.2.5. Evaluation of Parameters in the Na - K - OH - H_2O Ternary

Ternary sodium-potassium-hydroxide interactions are typically neglected (i.e., $\Psi_{\text{Na}, \text{K}, \text{OH}} = 0.0$) in thermodynamic mod-

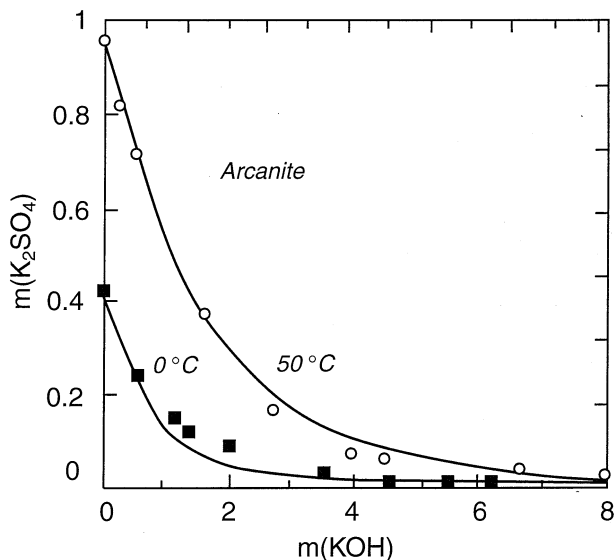


Fig. 16. Comparison of calculated (solid lines) and experimental (symbols: Zdanovskii et al., 1973) solubility of arcanite as a function of KOH concentration in the K_2SO_4 -KOH- H_2O system at 0° and $50^\circ C$.

els of the acid-base seawater system described in the literature (e.g., see Harvie et al., 1984; Pabalan and Pitzer, 1987; Moller et al., 1998; Marion, 2001). Accurate parameterization of the NaOH-KOH- H_2O system is difficult. We could not find activity data for unsaturated ternary solutions in the literature. Solubility measurement is complicated by the fact that saturation in the ternary and binary solutions even at $25^\circ C$ occurs at very high concentrations that increase with temperature. The few ternary solubility data found (Silcock, 1979; Portnova and Itkina, 1969b) for determination of the $\Psi_{Na,K,OH}$ mixing parameter are only for a very narrow temperature range (0° – $25^\circ C$) and are often conflicting. The data of Portnova and Itkina (1969a) at $150^\circ C$ is excluded in our parameterization because of the very high concentration ($>60 m$ OH) of saturated solutions. Therefore, we can only estimate $\Psi_{Na,K,OH}$ parameter values in this study.

The solubility data in the ternary at 20° and $25^\circ C$ show isotherms consisting of crystallization fields for $KOH \cdot 2H_2O(s)$, $NaOH \cdot H_2O(s)$ and $KOH \cdot H_2O(s)$. At $0^\circ C$, solid solution mixtures of $NaOH \cdot H_2O$ and $KOH \cdot H_2O$ are reported in addition to the above hydroxide solid phases. Note that the solubility data for the NaOH- H_2O system indicate that $NaOH \cdot 4H_2O(s)$ is the stable solid phase at $0^\circ C$. Removing some of the obviously inconsistent data and assuming crystallization of simple salts only (and not of solid solutions), we use these solubility data to establish a temperature function for $\Psi_{Na,K,OH}$ and for the chemical potential of potassium hydroxide monohydrate in the 0° – $25^\circ C$ temperature range. To extend the parameterization of $\Psi_{Na,K,OH}$ to higher temperature, we use the solubility data (halite + sylvite coexistence points) of Ginzburg and Markel (1969) in the quaternary Na-K-OH-Cl- H_2O reciprocal system. The temperature function for the $\theta_{Na,K}$ mixing parameter is taken from Greenberg and Moller (1989). Temperature functions for the NaOH- H_2O and KOH- H_2O binary parameters and for the chemical potentials of the solid phases: $NaOH \cdot H_2O(s)$, $NaOH \cdot 4H_2O(s)$, $KOH \cdot H_2O(s)$ (in the

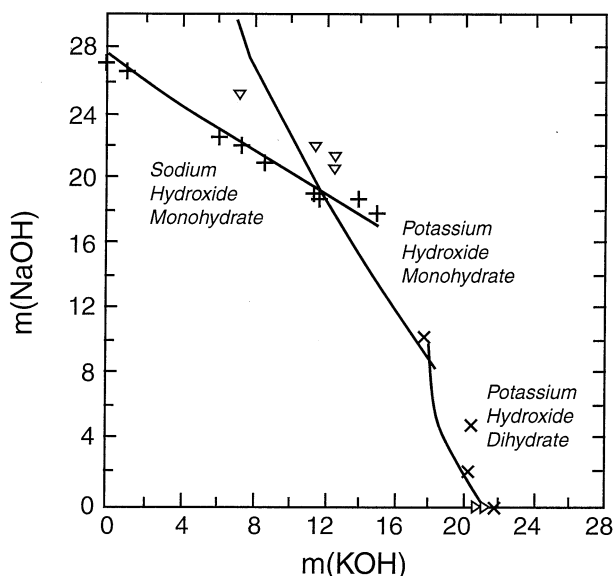


Fig. 17. Comparison of calculated (solid lines) and experimental (Portnova and Itkina, 1969b) solubility isotherms in the NaOH-KOH- H_2O system at $25^\circ C$. Symbols: sodium hydroxide monohydrate ($NaOH \cdot H_2O$) (+); potassium hydroxide monohydrate ($KOH \cdot H_2O$) (down facing triangles); potassium hydroxide dihydrate ($KOH \cdot 2H_2O$) (x); pure water solubility of potassium hydroxide dihydrate (right facing triangles) (see also Fig. 11).

32.5° – $65.3^\circ C$ temperature range) and $KOH \cdot 2H_2O(s)$ have been established using other data in this study.

Model agreement with the available solubility data at $25^\circ C$ (Fig. 17) is good if our prediction is correct that the potassium hydroxide monohydrate data points at $25^\circ C$ are for metastable equilibrium. The model also predicts that the sodium hydroxide monohydrate data points at high $mKOH$ ($>12 m$) are for metastable equilibrium. Agreement with the ternary solubility data at 0° and $20^\circ C$ is generally not good. The disagreement at $0^\circ C$ between the model and the data for $NaOH \cdot 4H_2O$ and $KOH \cdot 2H_2O$ saturation is removed if the $KOH \cdot H_2O$ solid phase is assumed to precipitate instead of the dihydrate. This might explain some of the discrepancy about the nature of the solid phases in the data below $25^\circ C$.

In the temperature range from 25° to $100^\circ C$, $\Psi_{Na,K,OH}$ varies little. However, the model is not expected to reproduce high temperature solubility calculations in this ternary system because the very high hydroxide concentrations extend beyond the molality limits of our binary hydroxide parameterizations ($64 m$ NaOH and $28 m$ KOH; Figs. 4 and 11).

4. TESTING AND APPLICATIONS

In this section, we validate our acid-base model of the H-Na-K-Cl-OH- HSO_4 - SO_4 - H_2O system by comparing model calculations with experimental data not used in the model parameterization. With one exception (extension of $\Psi_{Na,K,OH}$ to high temperature) the model is parameterized from the data in binary and common-ion ternary systems. Therefore, when data are available in more complex mixed aqueous solutions comparisons are made to these data. Several tests of the model by comparison with data not used in the model parameteriza-

tion have been described above for binary and ternary systems (e.g., KOH-KCl-H₂O and H₂SO₄-K₂SO₄-H₂O).

4.1. Acid Systems

In our model parameterization, the temperature functions for $\theta_{K,H}$ and $\Psi_{K,H,Cl}$ are defined by water dissociation data in KCl solutions and by solubility data in the KCl-HCl-H₂O ternary. The model agreement with the low concentration (0.01–1.35 *m* HCl) ternary emf data of Harned and Hamer (1933) (0° to 60°C), Leitzke and O'Brien (1968) (25° to 125°C), Chan et al. (1979) (25°C) and Macaskill et al. (1978) (5° to 45°C), which are not used in the model parameterization, is excellent (sigma values for these four data sets are: 0.042, 0.030, 0.010 and 0.011).

Chan et al. (1979) report emf measurements for the quaternary HCl-KCl-NaCl-H₂O system at 25°C. These measurements, which are for a total molality of 1 *m*, provide a good test of our low concentration predictions in this system. Jiang (1996) measured this system also at 25°C at higher total molalities (4–6 *m*). Our model is in excellent agreement with the two data sets (total sigma value of 0.053).

Compositions of quaternary H-Na-K-Cl-H₂O solutions in equilibrium with the minerals, halite + sylvite, are found in literature at 20° and 60°C (Zdanovskii et al., 1973). Model calculations are compared with these experimental solubility data, which are not used in the model parameterization, in Figure 18. The agreement between predictions and experiment is excellent up to 18 *m* HCl at 20°C and up to 15 *m* HCl at 60°C. Note that parameterization of the HCl-NaCl-H₂O and the HCl-KCl-H₂O system used data with a maximum HCl concentration of 10 *m* and 10.5 *m*, respectively.

In our model parameterization, we use the Dickson et al. (1990) calculations of molal equilibrium quotients, Q₂, for bisulfate dissociation ($Q_2 = [H^+][SO_4^{2-}]/[HSO_4^-]$) only at infinite dilution to establish the temperature variation of the HSO₄⁻ standard chemical potential from 0° to 250°C. The ability to reproduce the Dickson et al. data in the H-Na-Cl-HSO₄-SO₄-H₂O system to 5 *m* NaCl from 25° to 250°C and their extrapolated 0°C values to 1 *m* (Fig. 19) tests the reliability of extrapolations of the temperature functions for several of the parameters describing the Na-H-Cl-HSO₄-SO₄-H₂O system. For example, the temperature functions for the mixing parameters, $\theta_{Na,H}$ and $\Psi_{Na,H,Cl}$, are derived from solubility data in the NaCl-HCl-H₂O system from 0° to 80°C and activity coefficient data in this system from 25° to 175°C, which are available only to 1 *m* NaCl. Also, zero values were given to $\theta_{HSO_4,Cl}$, $\Psi_{H,HSO_4,Cl}$ and $\Psi_{H,SO_4,Cl}$ on the basis of emf data in the HCl-H₂SO₄-H₂O system that ranged only from 10° to 50°C.

The TEQUIL model (Moller et al., 1998) does not include H-HSO₄-SO₄ interactions. Using the relationship, $Q_2/[H^+] = [SO_4^{2-}]/[HSO_4^-]$, model calculations, such as shown in Figure 19, can be used to estimate the solution conditions when it is necessary to include the HSO₄⁻ ↔ H⁺ + SO₄²⁻ equilibrium. For example, calculations in 1 *m* NaCl solutions containing H₂SO₄ at room temperature show that HSO₄⁻ formation is small ($[SO_4^{2-}]/[HSO_4^-] > 10$) for pH > 2. At higher temperatures, HSO₄⁻ becomes a weaker acid and a more significant solute in these solutions at higher pH values (e.g., pH < 4

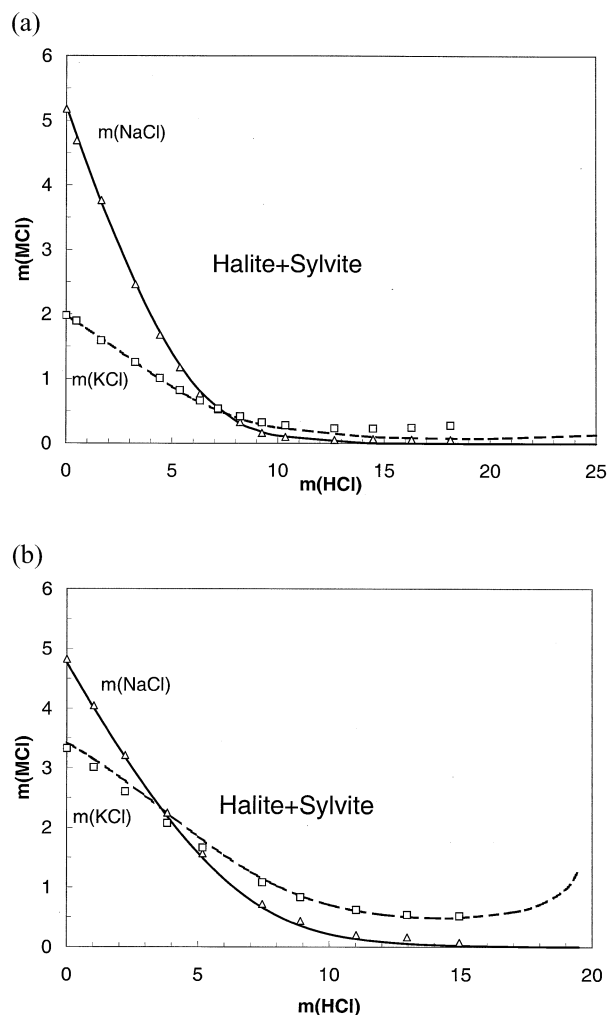


Fig. 18. The calculated NaCl (solid line) and KCl (dashed line) composition of a H-Na-K-Cl-H₂O solution in equilibrium with halite and sylvite is compared with the experimental data of Zdanovskii et al. (1975) (Δ , *m*(NaCl); open square, *m*(KCl)) on a *m*(MCl) vs. *m*(HCl)(M = Na, K) diagram. (a) 20°C. (b) 60°C.

at 200°C). Therefore the inclusion of this species in this model provides a significant generalization of the TEQUIL model for application to acid waters.

Korf and Shatrovskaya (1940; see Zdanovskii et al., 1975, p. 263) studied solubility in the reciprocal HCl-H₂SO₄-NaCl-Na₂SO₄-H₂O system at 25°C. The authors report crystallization of the stable salts occurring in corresponding ternary solutions at 25°C (halite, thenardite, mirabilite, NaHSO₄ · H₂O(s) and Na₂SO₄ · NaHSO₄(s)) as well as two additional salts: NaHSO₄(s) and Na₂SO₄ · NaHSO₄ · H₂O(s). The model predictions are in excellent agreement with the experimental univariant points: halite + thenardite, halite + NaHSO₄ · H₂O(s), halite + Na₂SO₄ · NaHSO₄(s) and Na₂SO₄ · NaHSO₄(s) + NaHSO₄ · H₂O(s) as well as with all the invariant ternary points (Fig. 20). The predicted thenardite + mirabilite univariant curve gives higher sodium concentrations than the experimental data. Model and experiment are also in excellent agreement for the invariant point: halite + NaHSO₄ · H₂O(s) + Na₂SO₄

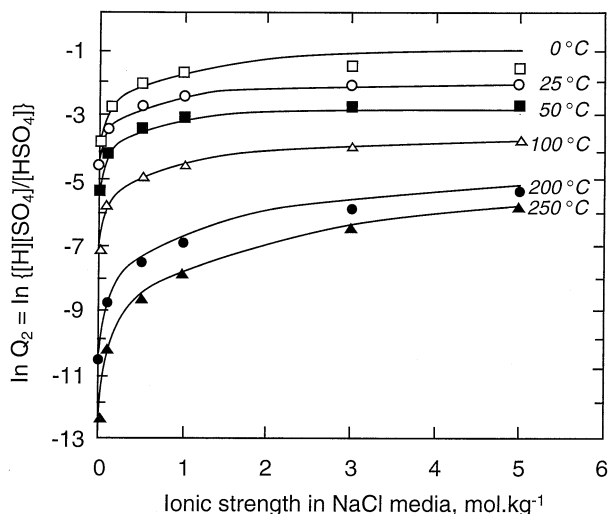


Fig. 19. Comparison of calculated (solid lines) $\ln Q_2$ ($Q_2 = ([H^+][SO_4^{2-}])/[HSO_4^-]$) values and the recommended data (symbols) of Dickson et al. (1990) in the H_2SO_4 -NaCl- H_2O system as a function of NaCl concentration from 0° to 250°C.

· $NaHSO_4(s)$ (Fig. 20). Data for the invariant point: halite + thenardite + $Na_2SO_4 \cdot NaHSO_4(s)$ could not be found; however the model is in good agreement (slightly higher hydrogen concentration) with the invariant point predicted by the HMW model (see open triangle in Fig. 20). Note that the agreement of

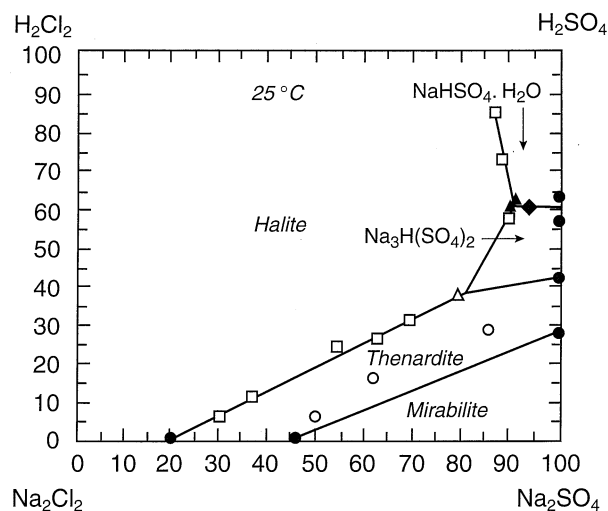


Fig. 20. Comparison of the calculated (solid lines) phase diagram for the reciprocal HCl - H_2SO_4 - $NaCl$ - Na_2SO_4 - H_2O system at 25°C with the data of Korf and Shatrovskaya (1940; see Zdanovskii et al., 1975, p. 263). The open squares denote the experimental univariant halite equilibria: halite + thenardite, halite + $Na_2SO_4 \cdot NaHSO_4(s)$ and halite + $NaHSO_4 \cdot H_2O(s)$. The open circles denote the experimental univariant thenardite + mirabilite equilibria. The closed diamond denotes the experimental univariant $NaHSO_4 \cdot H_2O(s)$ + $Na_2SO_4 \cdot NaHSO_4(s)$ equilibria. The solid circles denote experimental invariant points in the ternary systems: H_2SO_4 - Na_2SO_4 - H_2O and Na_2SO_4 - $NaCl$ - H_2O . The closed triangles denote the experimental invariant point, halite + $NaHSO_4 \cdot H_2O(s)$ + $Na_2SO_4 \cdot NaHSO_4(s)$, in the HCl - H_2SO_4 - $NaCl$ - Na_2SO_4 - H_2O system. The open triangle is the invariant halite + thenardite + $Na_2SO_4 \cdot NaHSO_4(s)$ point predicted by the HMW model.

the Clegg et al. (1998) mole fraction model with the data (including the thenardite + mirabilite univariant data) in this reciprocal system (see their fig. 23) is very similar to that of our ion interaction model.

Many inconsistencies are found in the solubility data for the Na_2SO_4 - H_2SO_4 - H_2O system. The excellent fit to $NaHSO_4 \cdot H_2O(s)$ and $Na_2SO_4 \cdot NaHSO_4(s)$ data in the H - Na - Cl - HSO_4 - SO_4 - H_2O system provides strong support for (1) our assessment of the stable solid phases in the ternary, and particularly for including the single water hydrate, $NaHSO_4 \cdot H_2O(s)$; (2) Use of zero values for the mixing parameters: $\theta_{HSO_4,Cl}$, $\Psi_{H,HSO_4,Cl}$, $\Psi_{H,SO_4,Cl}$ and $\Psi_{Na,HSO_4,Cl}$.

Multicomponent data in the K - H - Cl - HSO_4 - SO_4 - H_2O and H - Na - K - HSO_4 - SO_4 - H_2O systems could not be found for model validation.

4.2. Base Systems

Evaluation of the $\Psi_{K,OH,Cl}$ interaction parameter includes only solubility data in the KOH - KCl - H_2O ternary. To test how our model extrapolates to low concentration, we compare model predictions with the emf data of Harned and Hamer (1933) for unsaturated K - Cl - OH - H_2O solutions. The Harned and Hamer data, which range from 0° to 60°C, are for 0.1 *m* KOH and 0 to 3.5 *m* KCl . The model agrees well with these data (sigma equal to 0.0482).

There are solubility data in the literature for the quaternary Na - OH - Cl - SO_4 - H_2O system from 25° to 250°C that are not used in model parameterization. Data for two-salt equilibrium for halite, mirabilite and thenardite in Na - OH - Cl - SO_4 - H_2O solutions are given in Zdanovskii et al. (1975) at 25° and 50°C, Itkina (1962) at 100°C and by Itkina and Kohova (1960) at 150°C. Invariant three-salt equilibria data for halite + thenardite + $NaOH \cdot H_2O(s)$ are available only at 30°C (Zdanovskii et al., 1975). According to the data in Zdanovskii et al., the three-salt coexistence occurs at very high OH^- concentration ($>28 m$) at 30°C. Model calculations are in good agreement with these two and three salt equilibrium data over the entire 25°–150°C temperature range. In Figure 21, we compare calculated (solid lines) phase diagrams for the Na - OH - Cl - SO_4 - H_2O system with the data at 25° and 150°C. Solution compositions are projected from the H_2O corner. The solid circles denote the experimental univariant points in the Na - OH - Cl - SO_4 - H_2O system, while the open circles represent experimental invariant points in the common ion ternary systems. In the temperature range from 25° to 50°C, the model predicts that the invariant point $NaCl(s)$ + $Na_2SO_4(s)$ + $NaOH \cdot H_2O(s)$ exists at very high OH^- molality ($\approx 28 m$ at 25°C, and 36 *m* at 50°C) (not shown in figures). This is in good agreement with experimental results at 30°C (Zdanovskii et al., 1975). According to the experimental data of Itkina and Kohova (1960) and Itkina (1962) at 100°C $< T \leq 150^\circ C$, a triple salt with composition $mNaCl \cdot nNa_2SO_4 \cdot kNaOH$ crystallizes in the Na - OH - Cl - SO_4 - H_2O system at high OH^- concentration ($\sim 14 m$ $NaOH$). The authors cannot determine the values of stoichiometric coefficients *m*, *n* and *k*. For that reason we did not include this triple salt in our model. However, we do note that in this system changes in our predicted thenardite + halite surface at high temperature ($T \geq 100^\circ$) and high OH^- molality are consistent with crystallization of some new solid phase (Figs. 21b, 22a).

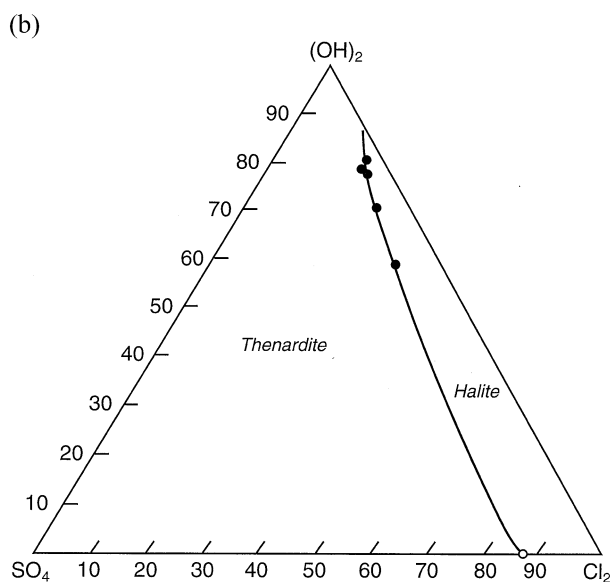
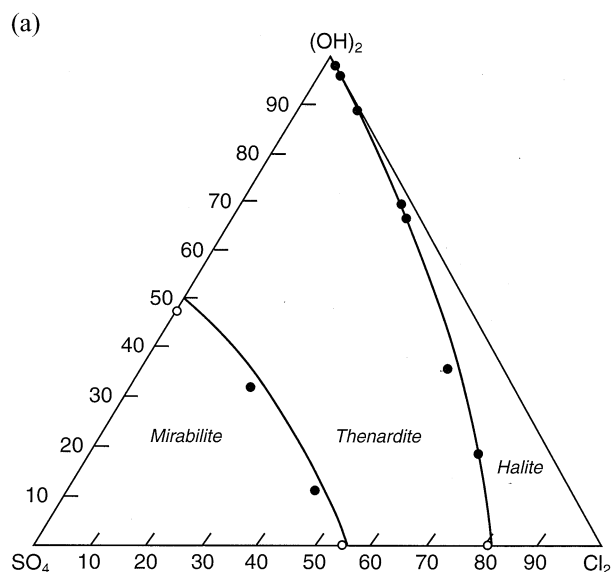


Fig. 21. (a) Comparison of calculated (solid lines) and experimental (Zdanovskii et al., 1975) mirabilite + thenardite and thenardite + halite coexistence in the Na-Cl-OH-SO₄-H₂O system at 25°C. The solid circles denote the quaternary univariant points; the open circles denote ternary invariant points. (b) Comparison of calculated (solid lines) and experimental (Itkina and Kohova, 1960) thenardite + halite coexistence in the Na-Cl-OH-SO₄-H₂O system at 150°C. The solid circles denote the quaternary univariant points; the open circles denotes the ternary invariant point.

Schroeder et al. (1935) studied the solubility of thenardite in the Na-OH-Cl-SO₄-H₂O system at 200° and 250°C. The authors determined the composition of the solutions in equilibrium with thenardite at fixed molalities of NaOH ($m \approx 0.8, 1.5, 3.0$ and 6.3) and varying concentrations of NaCl. Figure 22 compares thenardite solubilities calculated with the model (dashed lines) and the experimental data of Schroeder et al. (closed triangles) at 200° and 250°C, respectively. The agreement at 200°C is excellent for the entire composition range of

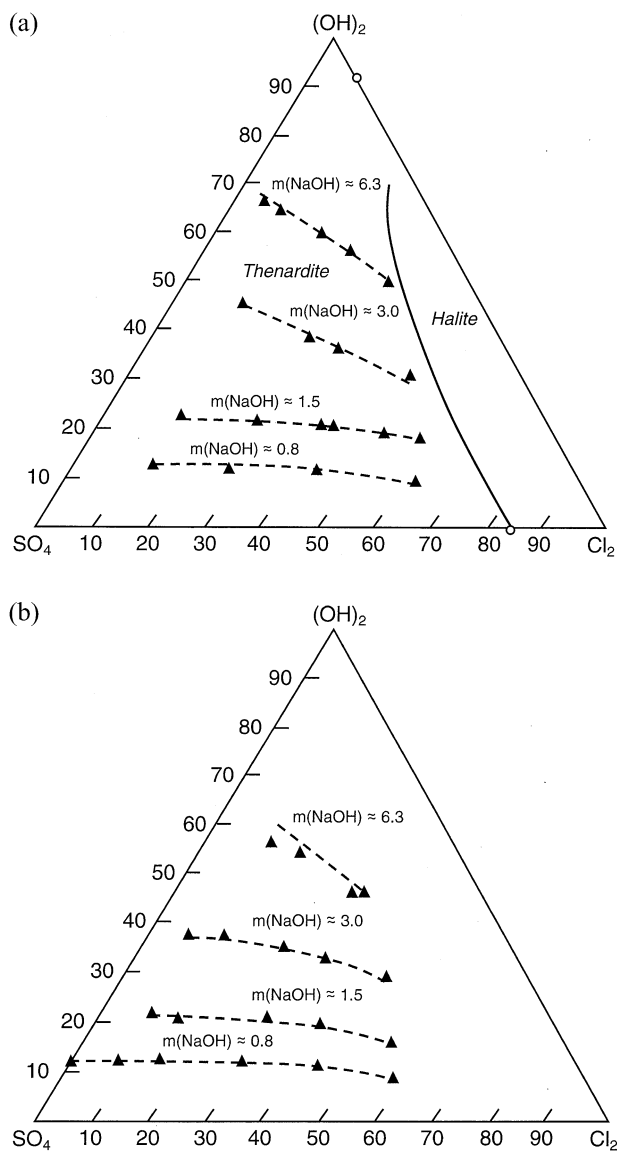


Fig. 22. Comparison of calculated (dashed lines) single thenardite salt solubility in the Na-Cl-OH-SO₄-H₂O system at fixed NaOH molality ($m(\text{NaOH}) = 0.8, 1.5, 3.0,$ and 6.3 , approximately) with the experimental data (solid triangle) of Schroeder et al. (1935). (a) 200°C. The open circles denote the ternary invariant points and the solid line denotes the calculated thenardite + halite coexistence equilibria. (b) 250°C.

the experiments. The solid line in Figure 22a represents calculated halite + thenardite coexistence in the Na-OH-Cl-SO₄-H₂O system. The open circles represent data for invariant two-salt coexistence in the ternary systems. Note that it was shown above that extrapolation of the model reproduces experimental halite solubilities in the NaOH-NaCl-H₂O ternary to 200°C and 10 m NaOH. Therefore model predictions do not extend to the invariant halite + NaOH(s) datum on the NaOH-NaCl-H₂O edge of the 200°C diagram in Figure 22a. The calculated thenardite solubilities at 250°C and 0.8, 1.5, and 3.0 m_{NaOH} are also in excellent agreement with the data (Fig. 22b). At 6.3 m_{NaOH} , the agreement is excellent for the low sulfate

solutions. The temperature function for the $\Psi_{\text{Na,OH,Cl}}$ ternary mixing parameter is determined using solubility data in the NaCl-NaOH-H₂O ternary system from 0° to 200°C. The agreement obtained between predicted and experimental solubilities at 250°C at high values of $m_{\text{NaOH}} + m_{\text{NaCl}}$, where $\Psi_{\text{Na,OH,Cl}}$ becomes important, validates the extrapolation of the $\Psi_{\text{Na,OH,Cl}}$ temperature function to 250°C. The small discrepancy between model and experiment in low chloride solutions (Fig. 22b) at 250°C and 6.3 *m* NaOH is not surprising since our parameterization of the common ion ternary Na-OH-SO₄-H₂O system at 250°C calculates lower solution Na₂SO₄ concentrations at the thenardite saturation than experiment above 4 *m* NaOH.

Solubility data for the Na-K-OH-Cl-H₂O and Na-K-OH-SO₄-H₂O reciprocal systems were found only for 100°C (Ginzburg and Markel, 1969). The solubility data for chloride system are used in this work to extend the temperature function for $\Psi_{\text{Na,K,OH}}$ above 25°C. Model calculations of halite + sylvite coexistence are compared with these data in Figure 23a. The data of Ginzburg and Markel (1969) for the sulfate quaternary at 100°C are not used in model parameterization. Model calculations of thenardite + glasserite and arcanite + glasserite coexistence curves in the Na-K-OH-SO₄-H₂O reciprocal system at 100°C are compared with these data in Figure 23b. The data of Ginzburg and Markel (1969) for ternary invariant and quaternary univariant thenardite + glasserite, and arcanite + glasserite points are represented by solid circles. The open circle on the Na-K-SO₄-H₂O edge denotes the ternary invariant arcanite + glasserite point recommended by Zdanovskii et al. (1973). In our model, the variable temperature $\Psi_{\text{K,OH,SO}_4}$ parameterization is determined from solubility data in the ternary K-OH-SO₄-H₂O system from 0° to 75°C only. The agreement between the calculated phase diagram and experimental data in the Na-K-OH-SO₄-H₂O system is good and shows that the $\Psi_{\text{K,OH,SO}_4}$ parameterization can be extrapolated at least to 100°C and to 30 *m* OH⁻.

According to the experimental data of Ginzburg and Markel (1969), thenardite + glasserite and arcanite + glasserite saturated solutions exhibit unusual behavior at high OH⁻ molality. At ~11–13 *m* OH⁻, the potassium ion-concentration in the two-salt saturated solutions drops sharply. The model predicts this decrease of K⁺ concentration in the two-salt saturated solutions at high OH⁻ molality. The largest difference between model and experiment occurs for some of the arcanite + glasserite coexistence points for which the model predicts potassium concentrations that are ~13% lower than experiment (Fig. 23b).

5. SUMMARY AND RESTRICTIONS

We show here that the ion interaction approach as implemented by Harvie and Weare (1980) accurately calculates solubilities and solution activities in the acid/base H-Na-K-Cl-OH-SO₄-HSO₄-H₂O system within the 0° to 250°C temperature range to high solution concentration within experimental uncertainty (for exceptions see text). The behavior of bisulfate formation in multicomponent acidic solutions, solid/solution equilibria involving very soluble acid sulfate (Figs. 8 and 20) and solid-liquid equilibria in NaOH and KOH solutions (Figs. 6, 12, and 21) are well described to high temperature and concentration. The extension of our earlier variable temperature

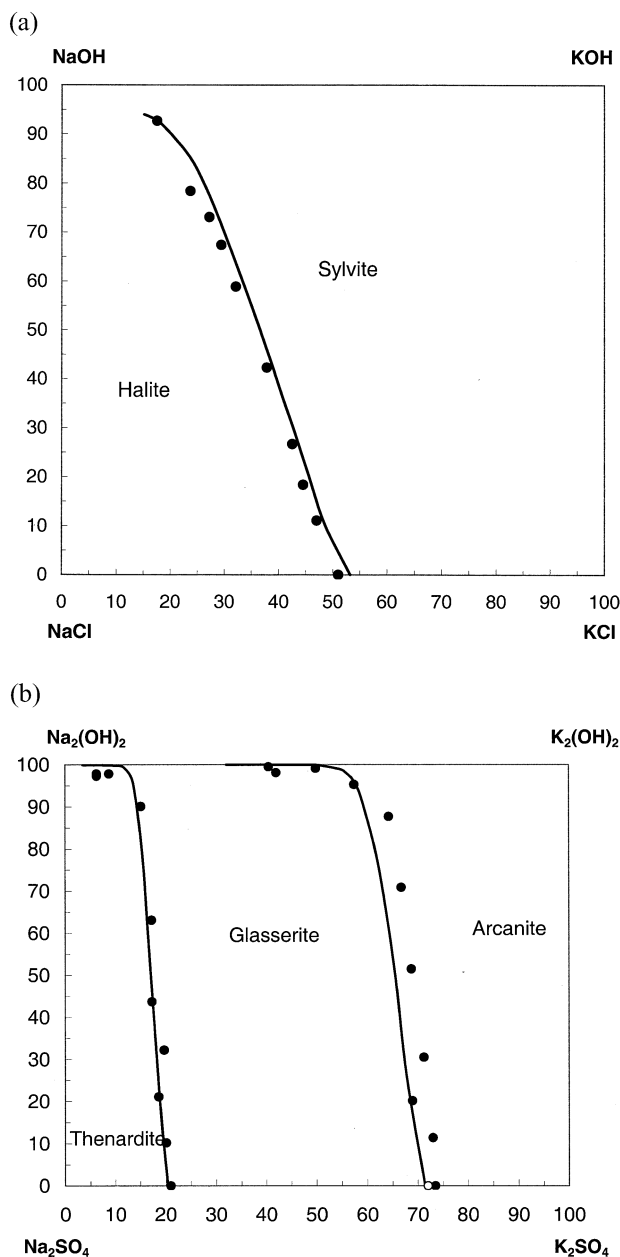


Fig. 23. (a) Comparison of calculated (solid line) and experimental (solid circles: Ginzburg and Markel, 1969) halite + sylvite univariant phase equilibria in the Na-K-Cl-OH-H₂O reciprocal system at 100°C. (b) Comparison of calculated (solid lines) and experimental (solid circles: Ginzburg and Markel, 1969) thenardite + glasserite and arcanite + glasserite univariant equilibria in the Na-K-OH-SO₄-H₂O reciprocal system at 100°C. The open circle on the Na-K-SO₄-H₂O edge denotes the experimental arcanite + glasserite ternary invariant point (Zdanovskii et al., 1973).

acid-free models to include H₂SO₄, HCl, NaOH and KOH interactions broadens the natural fluid and industrial applications to include pH dependent behavior.

Temperature functions for the chemical potentials (referenced to the independent ions in the solutions) of 11 acid and base sodium and potassium salts are established here (see Table 4) from solubility data in corresponding binary and ternary

Table 5. Standard molar Gibbs free energies of formation, $\Delta_f G_m^\circ$, of acid/base salts at $T = 298.15$.

Salt composition	$\Delta_f G_m^\circ / (\text{kJ} \cdot \text{mol}^{-1})$				
	This study		Harvie et al. (1984) ^c	Clegg et al. (1998)	Wagman et al. (1982)
	(I) ^a	(II) ^b			
NaHSO ₄ · H ₂ O	-1244.65			-1244.1	
Na ₂ SO ₄ · Na ₂ HSO ₄	-2278.57	-2278.58	-2279.52	-2278.9	
KHSO ₄	-1035.96	-1035.15	-1035.08		
K ₂ SO ₄ · KHSO ₄	-2359.08	-2356.70	-2356.86		
K ₂ SO ₄ · 6KHSO ₄	-7539.79	-7533.45	-7533.73		
NaOH · H ₂ O	-619.26				-629.338
NaOH · 2H ₂ O	-866.18				-873.091
NaOH · 3.5H ₂ O	-1235.00				-1236.36
NaOH · 4H ₂ O	-1354.11				-1356.64
KOH · H ₂ O	-640.21				-645.1
KOH · 2H ₂ O	-888.28				-887.3

^a Calculated using standard chemical potentials for independent ions in solution from Wagman et al. (1982).

^b Calculated using standard chemical potentials for independent ions in solution from Robie et al. (1979).

^c Calculated using standard chemical potentials for ions in solution from Robie et al. (1979).

solutions. Table 5 gives the standard molar Gibbs free energy of formation ($\Delta_f G_m^\circ$) of the acid/base solid phases at 25°C calculated from the salt potentials and from the equilibrium constants of water (lnK_w) and of bisulfate dissociation (lnK₂) given in Table 4 using the reference data for aqueous species given in Wagman et al. (1982) and Robie et al. (1979). The $\Delta_f G_m^\circ$ values are in good agreement with those given in Harvie et al. (1984) for acid salts (Na₂SO₄ · Na₂HSO₄(s), KHSO₄(s), K₂SO₄ · KHSO₄(s), K₂SO₄ · 6KHSO₄(s)). The difference is 0.94 kJ · mol⁻¹ or less. The $\Delta_f G_m^\circ$ value for Na₂SO₄ · NaHSO₄(s) obtained here using a molality-based ion interaction model agrees to within 0.33 kJ · mol⁻¹ with the result of Clegg et al. (1998) using a mole fraction-based model. The Gibbs energy of formation for NaHSO₄ · H₂O(s) also agrees very well with the result of Clegg et al. (1998) but differs from that recommended by Wagman et al. (1982) by 13.05 kJ · mol⁻¹. The Gibbs energies of formation for the hydroxide salts (NaOH · nH₂O(s) n = 1, 2, 3.5, 4; KOH · nH₂O(s) n = 1, 2) differ from those recommended by Wagman et al. (1982) by similar amounts (10.16 kJ · mol⁻¹, or less). Note that the predicted activities are for very high concentration hydroxide solutions. For example, the NaOH · H₂O(s) solubility in water is ≈ 30 m at 25°C. Also note that, according to the experimental solubility data in the binary and complex systems we consider here, NaOH · 4H₂O(s), NaOH · 3.5H₂O(s) and NaOH · 2H₂O(s) are not stable solid phases at 25°C.

Good agreement with both the experimental activity and solubility data as a function of temperature is achieved with temperature-independent or zero values of twelve acid parameters, $\beta^{(0)}_{\text{K,HSO}_4}$, $\beta^{(1)}_{\text{H,SO}_4}$, $C^{\circ}_{\text{H,Cl}}$, $C^{\circ}_{\text{H,HSO}_4}$, $\theta_{\text{HSO}_4,\text{Cl}}$, $\Psi_{\text{H,HSO}_4,\text{Cl}}$, $\Psi_{\text{H,SO}_4,\text{Cl}}$, $\Psi_{\text{Na,H,HSO}_4}$, $\Psi_{\text{Na,HSO}_4,\text{Cl}}$, $\Psi_{\text{K,Cl,HSO}_4}$, $\Psi_{\text{K,SO}_4,\text{HSO}_4}$ and $\Psi_{\text{H,SO}_4,\text{HSO}_4}$.

Since the model has been parameterized for all the constituent binary and ternary common ion systems in the H-Na-K-Cl-OH-SO₄-HSO₄-H₂O system, it can, in principle, be applied to all compositions in the H-Na-K-Cl-OH-SO₄-HSO₄-H₂O system. However, there are several restrictions of the acid-base model due to: (1) lack of activity data for some binary (e.g., KHSO₄-H₂O) and ternary (e.g., K₂SO₄-KHSO₄-H₂O; NaOH-

KOH-H₂O) unsaturated solutions, (2) lack of solubility data in some ternary systems at high temperature, (3) disagreement in the literature about the nature and composition of the solid phases crystallizing from saturated binary (NaOH-H₂O) and ternary (K₂SO₄-H₂SO₄-H₂O; NaOH-KOH-H₂O) solutions, (4) very high concentrations of solutions in equilibrium with sodium- and potassium-hydroxide solid phases, (5) unusual solubility behavior indicated by the available experimental data for some solid phases (thenardite, mercurite, misenite, potassium sesquisulfate) in binary (Na₂SO₄-H₂O) and/or in ternary (Na₂SO₄-NaOH-H₂O and K₂SO₄-H₂SO₄-H₂O) solutions at different temperatures. These problems are discussed in section 3.

When data are available, extrapolations of the model to concentration and temperature ranges and compositions not used in the model parameterization are tested. Testing indicates excellent model reliability. Examples have been given for successful extrapolation of binary system parameters to very high concentrations (to 64 m in the NaOH-H₂O system; to 28 m in the KOH-H₂O system). Such extensive extrapolative capability may not occur in ternary and higher order systems. Testing has shown that the parameterization of the KCl-KOH-H₂O system extrapolates well from 8 m to 17 m KOH and that the $\Psi_{\text{K,OH,SO}_4}$ temperature function established in the KOH-K₂SO₄-H₂O system from data to 8 m KOH and 75°C can be extrapolated to fit data in the Na-K-OH-SO₄-H₂O system at 100°C to 30 m OH. New experimental data will be required to validate model extrapolations in temperature and composition ranges not studied here.

Acknowledgments—This work has been supported by the U.S. Department of Energy, Assistant Secretary Energy Efficiency and Renewable Energy under DOE Idaho Operations Financial Assistance Award DE-FG07-99ID13745/DE-FG36-99ID13745. We wish to thank Professor John H. Wear for his advice and many helpful comments. We also thank Associate Editor Dr. David J. Wesolowski, Dr. Joseph A. Rard and two anonymous reviewers for their constructive suggestions.

Associate editor: D. J. Wesolowski

REFERENCES

- Akerlof G. and Kegeles G. (1940) Thermodynamics of concentrated aqueous solutions of sodium hydroxide. *J. Am. Chem. Soc.* **62**, 620–640.
- Akerlof G. and Bender P. (1948) Thermodynamics of aqueous solutions of potassium hydroxide. *J. Am. Chem. Soc.* **70**, 2366–2369.
- Archer D. and Wang P. (1990) The dielectric constant of water and Debye-Huckel limiting law slope. *J. Phys. Chem. Ref. Data* **19**, 371–411.
- Balej J. (1996) Activity coefficients of aqueous solutions of NaOH and KOH in wide concentration and temperature ranges. *Collect. Czech. Chem. Commun.* **61**, 1549–1562.
- Brantley S., Crerar D., Moller N., and Weare J. (1984) Geochemistry of marine evaporate: Bocana de Virilla, Peru. *J. Sed. Pet.* **54**, 447–462.
- Bukhshtein V. M., Valyashko M. G. and Pel'sh A. D., eds. (1953) *Spravochnik po rastvorimosti solevykh sistem*. Vols. 1 and 2. Izd. Vses. Nauch.-Issled. Inst. Goz., Goskhimizdat., Moscow-St. Petersburg, 1270 p.
- Busey R. and Mesmer R. (1978) Thermodynamic quantities for the ionization of water in sodium chloride media. *J. Chem. Eng. Data* **23**, 175–176.
- Chan C.-Y., Khoo K., and Lim T. (1979) Specific ionic interactions in the quaternary systems HCl-NaCl-KCl-water and HCl-NH₄Cl-KCl-water at 25°C. *J. Solution Chem.* **8**, 41–52.
- Clegg S., Pitzer K. S., and Brimblecombe P. (1992) Thermodynamics of multicomponent, miscible, ionic solutions. 2. Mixtures including unsymmetrical electrolytes. *J. Phys. Chem.* **96**, 9470–9479.
- Clegg S., Rard J., and Pitzer K. (1994) Thermodynamic properties of 0–6 mol · kg⁻¹ aqueous sulphuric acid from 273.15 to 328.15 K. *J. Chem. Soc. Faraday Trans.* **90**, 1875–1894.
- Clegg S., Brimblecombe P., and Wexler A. S. (1998) Thermodynamic Model of the System H⁺-NH₄⁺-Na⁺-SO₄²⁻-NO₃⁻-Cl⁻-H₂O at 298.15 K. *J. Phys. Chem. A* **102**, 2155–2171.
- Davies C. W., Jones H. W., and Monk C. B. (1952) E.M.F. studies of electrolytic dissociation, Part 1. Sulphuric acid in water. *Trans. Faraday Soc.* **48**, 921–928.
- Dickson A. (1984) pH scales and proton-transfer reactions in saline media such as sea water. *Geochim. Cosmochim. Acta* **48**, 2299–2308.
- Dickson A., Wesolowski D., Palmer D., and Mesmer R.O. (1990) Dissociation constant of bisulfate ion in aqueous sodium chloride solutions to 250°C. *J. Phys. Chem.* **94**, 7978–7985.
- Felmy A. and Weare J. (1986) The prediction of mineral solubilities in natural waters: Application to Searles Lake, California. *Geochim. Cosmochim. Acta* **50**, 2771–2783.
- Ginzburg D. and Markel S. (1969) Solubility in K₂, Na₂/CO₃, (OH)₂-H₂O, K₂, Na₂/SO₄, (OH)₂-H₂O, and K, Na/Cl, OH-H₂O systems at 100°C. *Russ. J. Inorg. Chem.* **14**, 1099–1105.
- Greeley R. S., Smith W. T., Jr., Stoughton R. W., and Leitzke M. H. (1960) Electromotive force studies in aqueous solutions at elevated temperatures. I. The standard potential of the silver-silver-chloride electrode. *J. Phys. Chem.* **64**, 652–657.
- Greenberg J. and Moller N. (1989) The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-K-Ca-Cl-SO₄-H₂O system to high concentration from 0 to 250°C. *Geochim. Cosmochim. Acta* **53**, 2503–2518.
- Hamer W. and Wu Y.-C. (1972) Osmotic coefficients and mean activity coefficients of univalent electrolytes in water at 25°C. *J. Phys. Chem. Ref. Data* **1**, 1047–1099.
- Harned H. and Hamer W. (1933) The ionization constant of water and the dissociation of water in potassium chloride solutions from electromotive forces of cells without liquid junction. *J. Am. Chem. Soc.* **55**, 2194–2201.
- Harned H. and Mannweiler G. (1935) The thermodynamics of ionized water in sodium chloride solutions. *J. Am. Chem. Soc.* **57**, 1873–1876.
- Harned H. and Cook M. (1937) The thermodynamics of aqueous potassium hydroxide solutions from electromotive force measurements. *J. Am. Chem. Soc.* **59**, 496–500.
- Harvie C. (1981) Theoretical investigations in geochemistry and atom surface scattering. Ph.D. thesis. University of California, San Diego.
- Harvie C. and Weare J. (1980) The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-Cl-SO₄-H₂O system from zero to high concentration at 25°C. *Geochim. Cosmochim. Acta* **44**, 981–997.
- Harvie C., Weare J., Hardie L., and Eugster H. (1980) Evaporation of seawater: Calculated mineral sequences. *Science* **208**, 498–500.
- Harvie C., Moller N., and Weare J. (1984) The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O system from zero to high concentration at 25°C. *Geochim. Cosmochim. Acta* **48**, 723–751.
- Harvie C., Greenberg J., and Weare J. (1987) A chemical equilibrium algorithm for highly non-ideal multiphase systems: Free energy minimization. *Geochim. Cosmochim. Acta* **51**, 1045–1057.
- Holmes H. and Mesmer R. (1986) Thermodynamics of aqueous solutions of the alkali metal sulfates. *J. Solution Chem.* **15**, 495–518.
- Holmes H., Busey R., Simonson J., Mesmer R., Archer D., and Wood R. (1987) The enthalpy of dilution of HCl(aq) to 648 K and 40 Mpa: Thermodynamic properties. *J. Chem. Thermodynamics* **19**, 863–890.
- Holmes H. and Mesmer R. (1992) Isopiestic studies of H₂SO₄(aq) at elevated temperatures. Thermodynamic properties. *J. Chem. Thermodynamics* **24**, 317–328.
- Holmes H. and Mesmer R. (1993) Isopiestic studies of NaHSO₄(aq) at elevated temperatures. Thermodynamic properties. *J. Chem. Thermodynamics* **25**, 99–110.
- Holmes H. and Mesmer R. (1994) An isopiestic study of {(1-y)NaHSO₄ + yNa₂SO₄} (aq) at elevated temperatures. *J. Chem. Thermodynamics* **26**, 581–594.
- Holmes H. and Mesmer R. (1996) An isopiestic study of aqueous solutions of the alkali metal hydrogensulfates at elevated temperatures. *J. Chem. Thermodynamics* **28**, 67–81.
- Holmes H. and Mesmer R. (1998) Isopiestic molalities for aqueous solutions of the alkali metal hydroxides at elevated temperatures. *J. Chem. Thermodynamics* **30**, 311–326.
- Itkina L. (1962) Interaction of sodium sulfate and chloride in sodium hydroxide solutions at 25–150°C. *Russ. J. Inorg. Chem.* **7** (1), 184–193.
- Itkina L. and Kohova V. (1960) 150°C solubility isotherm of the Na₂SO₄-NaCl-NaOH system. *Russ. J. Inorg. Chem.* **5** (9), 2102–2111.
- Jiang C. (1996) Activity coefficients of hydrochloric acid in concentrated electrolyte solutions. 2. HCl+BaCl₂+KCl+H₂O, HCl+LiCl+KCl+H₂O, and HCl+NaCl+KCl+H₂O at 298.15 K. *J. Chem. Eng. Data* **41**, 117–120.
- Koenigsberger E. (2001) Prediction of electrolyte solubilities from mineral thermodynamic information. *Monatshfte Chem.* **132**, 1363–1386.
- Leitzke M. and O'Brien H., Jr. (1968) Electromotive force studies in aqueous solutions at elevated temperatures. X. The thermodynamic properties of HCl-KCl, HCl-RbCl, HCl-CsCl, HCl-MgCl₂, HCl-CaCl₂, HCl-SrCl₂, and HCl-AlCl₃ mixtures. *J. Phys. Chem.* **72**, 4408–4414.
- Leitzke M. and Stoughton R. (1964) The activity coefficients of hydrochloric acid and sodium chloride in hydrochloric acid-sodium chloride mixtures. *J. Tennessee Acad. Sci.* **39**, 3–7.
- Leitzke M., Hupf H., and Stoughton R. (1965) Electromotive force studies in aqueous solutions at elevated temperatures. VI. The thermodynamic properties of NaCl-HCl mixtures. *J. Phys. Chem. Ref. Data* **69**, 2395–2399.
- Linke W. (1958, 1965) *Solubilities Inorganic and Metal-Organic Compounds*. 4th ed. Vols. 1 and 2. American Chemical Society.
- Macaskill J., Vega C., and Bates R. (1978) Activity coefficients of hydrochloric acid in HCl-KCl-H₂O mixtures at ionic strengths up to 1.5 mol · kg⁻¹ and temperatures from 5 to 45°C. *J. Chem. Eng. Data* **23**, 314–316.
- MacInnes P. (1961) *Principles of Electrochemistry*. Dover.
- Marion G. (2001) Carbonate mineral solubility at low temperatures in the Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O system. *Geochim. Cosmochim. Acta* **65**, 1883–1896.
- Marion G. (2002) A molal-based model for strong acid chemistry at low temperatures (<200 to 298 K). *Geochim. Cosmochim. Acta* **66**, 2499–2516.
- Mesmer R. and Holmes H. (1992) pH, definition and measurement at high temperatures. *J. Solution Chem.* **21**, 725–744.

- Mikulin G. (1968) *Voprosy Fizicheskoi Khimii Electrolytov*. Izd. Khimiya.
- Millero F. and Pierrot D. (1998) A chemical equilibrium model for natural waters. *Aquat. Geochem.* **4**, 153–199.
- Moller N. (1988) The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-Ca-Cl-SO₄-H₂O system to high temperature and concentration. *Geochim. Cosmochim. Acta* **52**, 821–837.
- Moller N., Greenberg J., and Weare J. (1998) Computer modeling for geothermal systems: Predicting carbonate and silica scale formation, CO₂ breakout and H₂S exchange. *Transport Porous Media* **33**, 173–204.
- Nair V. S. K. and Nancollas G. H. (1958) Thermodynamics of ion association. Part V. Dissociation of the bisulphate ion. *J. Chem. Soc.* 4144–4147.
- Pabalan R. and Pitzer K. S. (1987) Thermodynamics of concentrated electrolyte mixtures and the prediction of mineral solubilities to high temperatures for mixtures in the system Na-K-Mg-Cl-SO₄-OH-H₂O. *Geochim. Cosmochim. Acta* **51**, 2429–2443.
- Pabalan R. and Pitzer K. S. (1988) Heat capacity and other thermodynamic properties of Na₂SO₄(aq) in hydrothermal solutions and the solubilities of sodium sulfate minerals in the system Na-Cl-SO₄-OH-H₂O to 300°C. *Geochim. Cosmochim. Acta* **51**, 2393–2404.
- Petrenko S. and Pitzer K. S. (1997) Thermodynamics of aqueous NaOH over the complete composition range and to 523 K and 400Mpa. *J. Phys. Chem. B* **101**, 3589–3595.
- Pitzer K. S. (1973) Thermodynamics of electrolytes. I. Theoretical basis and general equations. *J. Phys. Chem.* **77**, 268–277.
- Pitzer K. S. and Mayorga G. (1973) Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent. *J. Phys. Chem.* **77**, 2300–2308.
- Pitzer K. S. and Kim J. (1974) Thermodynamics of electrolytes. IV. Activity and osmotic coefficients for mixed electrolytes. *J. Am. Chem. Soc.* **96**, 5701–5707.
- Pitzer K. S., Roy R., and Silvester L. (1977) Thermodynamics of electrolytes. 7. Sulfuric acid. *J. Am. Chem. Soc.* **99**, 4930–4936.
- Pitzer K. S., Peiper J. C., and Busey R. H. (1984) Thermodynamic properties of aqueous sodium chloride solutions. *J. Phys. Chem. Ref. Data* **13**, 1–102.
- Pitzer K. S. and Simonson J. M. (1986) Thermodynamics of multicomponent, miscible, ionic systems: Theory and equations. *J. Phys. Chem.* **90**, 3005–3009.
- Portnova S. and Itkina L. (1969a) The KOH-NaOH-H₂O system at 150°C. *Russ. J. Inorg. Chem.* **14** (1), 137–138.
- Portnova S. and Itkina L. (1969b) Solubility polytherm of the KOH-NaOH-H₂O system. *Russ. J. Inorg. Chem.* **14** (8), 1148–1150.
- Potter R. W., II and Clynne M. A. (1980) Solubility of NaCl and KCl in aqueous HCl from 20 to 85°C. *J. Chem. Eng. Data* **25**, 50–51.
- Rard J. (1983) Isopiestic determination of the osmotic coefficients of aqueous H₂SO₄ at 25°C. *J. Chem. Eng. Data* **28**, 384–387.
- Rard J. (1989) Isopiestic determination of the osmotic and activity coefficients of {(1 - y)H₂SO₄ + yNa₂SO₄} (aq) at the temperature 298.15 K I. Results for y = 0.5 (NaHSO₄) and y = 0.55595, 0.70189, and 0.84920. *J. Chem. Thermodynamics* **21**, 539–560.
- Rard J. (1992) Isopiestic determination of the osmotic and activity coefficients of {(1 - y)H₂SO₄ + yNa₂SO₄} (aq) at the temperature 298.15 K II. Results for y = (0.12471, 0.24962, and 0.37439). *J. Chem. Thermodynamics* **24**, 45–66.
- Robie R., Hemingway B., and Fisher J. (1979) Corrected reprint of Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar pressure and at high temperatures. *USGS Bull.* 1452.
- Rollet A.-R. and Cohen-Adad R. (1964) Les systems eau-hydroxide alcalin. *Rev. Chim. Min.* **1**, 451.
- Schroeder W., Gabriel A., and Partridge E. (1935) Solubility equilibria of sodium sulfate at temperatures 150 to 350°C. I. Effect of sodium hydroxide and sodium chloride. *J. Am. Chem. Soc.* **57**, 1539–1546.
- Silcock H. (1979) *Solubilities of Inorganic and Organic Compounds*. Pergamon Press.
- Simonson J., Mesmer R., and Rogers P. (1989) The enthalpy of dilution and apparent molar heat capacity of NaOH(aq) to 523K and 40 Mpa. *J. Chem. Thermodynamics* **21**, 561–584.
- Simonson J., Holmes H., Busey R., Mesmer R., Archer D., and Wood R. (1990) Modeling of the thermodynamics of electrolyte solutions to high temperatures including ion association. Application to hydrochloric acid. *J. Phys. Chem.* **94**, 7675–7681.
- Storonkin A. V., Shul'ts M. M., Lagunov M. D., and Okatov M. A. (1967) Aqueous solutions of strong electrolytes. IV. Activity of hydrogen chloride in the hydrochloric acid-sulphuric acid-water system and of sodium chloride in the sodium chloride-sodium sulphate-water system. *Russ. J. Phys. Chem.* **41**, 541–543.
- Sweeton F., Mesmer R., and Baes C., Jr. (1974) Acidity measurements at elevated temperatures. VII. Dissociation of water. *J. Solution Chem.* **3**, 191–214.
- Wagman D. D., Evans W. H., Parker V. B., Schumm I. H., Bailey S. M., Churney K. L., and Nuttall R. L. (1982) The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C₁ and C₂ organic substances in SI units. *J. Phys. Chem. Ref. Data* **11**, 1–392.
- Zdanovskii A., Soloveva E., Liahovskaia E., Shestakov N., Shleimovich P. and Abutkova L. (1973, 1975) *Spravochnik po rastvorimosti solevykh system*. Vols. I-1, I-2, II-1 and II-2. Izd. Khimya.

APPENDIX A

Specific Interaction Model Equations

Since the specific interaction approach of Pitzer (1973) and model equations for the osmotic and activity coefficients described in Harvie and Weare (1980) have been discussed in detail in many publications, we give only the expression for the activity coefficient of the hydrogen ion, $\gamma_{(H^+)}$ here.

$$\gamma_{(H^+)} = z_{H^+}^2 F + \sum_a m_a (2B_{Ha} + ZC_{Ha}) + \sum_c m_c (2\varphi_{Hc} + \sum_a m_a \Psi_{Hca}) + \sum_{a < a'} \sum m_a m_{a'} \Psi_{aa'H} + |z_{H^+}| \sum_c \sum_a m_c m_a C_{ca} \quad (1A)$$

The subscripts c and a refer to cations and anions and the summations are over the total number of cations or anions. The double summation index, $a < a'$, denotes the sum over all distinguishable pairs of dissimilar anions. In Eqn. 1A, B and φ represent measurable combinations of the second virial coefficients. C and Ψ represent measurable combinations of the third virial coefficients. B and C are parameterized from single electrolyte data, and φ and Ψ are parameterized from two salt mixed system data.

The function F is the sum of the debye-huckel term,

$$-A^\varphi [\sqrt{I}/(1 + b\sqrt{I}) + (2/b)(\ln(1 + b\sqrt{I}))], \quad (2A)$$

and terms with the derivatives of the second virial coefficients with respect to ionic strength (see HMW, 1984). In Eqn. 2A, b is a universal empirical constant assigned to be equal to 1.2. A^φ (Debye-Huckel limiting law slope for osmotic coefficient) is a function of temperature, density and the dielectric constant of water (see Moller, 1988).

For the interaction of any cation M and any anion X, Pitzer assumes that in Eqn. 1A B has the ionic strength dependent form:

$$B_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} g(\alpha_1 \sqrt{I}) + \beta^{(2)}_{MX} g(\alpha_2 \sqrt{I}), \quad (3A)$$

where $g(x) = 2[1 - (1 + x)e^{-x}]/x^2$ with $x = \alpha_1 \sqrt{I}$ or $\alpha_2 \sqrt{I}$. In our model expressions, α is a function of electrolyte type and does not vary with concentration or temperature. Following Harvie et al. (1984), when either cation or anion for an electrolyte is univalent we set α_1 equal to 2.0 and omit the $\beta^{(2)}$ term. For 2–2 or higher valence pairs, α_1 equals 1.4 and α_2 equals 12. The modified form, assigned by Pitzer, for these higher valence species accounts for their increased tendency to associate in solution. The C_{MX} third virial coefficients (see Eqn. 1A) are assumed to be ionic strength independent. However, some terms containing C_{MX} parameters have a concentration dependence given by Z, as:

$$Z = \sum m_i |z_i|, \quad (4A)$$

where m is the molality of species i and z is its charge.

In Eqn. 1A, the φ terms account for interactions between two ions i and j of like charges. In the expression for φ ,

$$\varphi_{ij} = \theta_{ij} + {}^E\theta_{ij} \quad (I), \quad (5A)$$

θ_{ij} is the only adjustable parameter. The ${}^E\theta_{ij} \quad (I)$ term accounts for electrostatic unsymmetric mixing effects that depend only on the charges of ions i and j and the total ionic strength. See the equations for calculating these terms in the appendix of Harvie and Weare (1980).

The Ψ_{ijk} parameters, which are used for each triple ion interaction where the ions are not all of the same sign, are assumed in this work to be independent of ionic strength. Their inclusion is generally important for describing solubilities in concentrated multicomponent systems.

APPENDIX B

Single Ion Activity and pH

The chemical potential, μ_s , of a neutral salt (a measurable quantity) is defined as:

$$\mu_s = \nu_a \mu_a + \nu_c \mu_c, \quad (1B)$$

where the stoichiometric coefficient, ν_a , is the number of anions in the salt and ν_c is the number of cations. Using the activity definition, Eqn. 1B can be written in terms of ion activity coefficients as:

$$\mu_s = \nu_a \mu_a^\circ + \nu_c \mu_c^\circ + RT \ln m_a^{\nu_a} m_c^{\nu_c} + RT \ln \gamma_a^{\nu_a} \gamma_c^{\nu_c}. \quad (2B)$$

The last term contains the non-ideal contributions. Because single ion activity coefficients cannot be measured, the mean activity coefficient, γ_{\pm}^v , is defined as:

$$\gamma_{\pm}^v = \gamma_a^{\nu_a} \gamma_c^{\nu_c}. \quad (3B)$$

The mean activity coefficient, γ_{\pm} , defined by Eqn. 3B can be measured and is often reported.

For convenience, Harvie and Weare (1980) rearranged the Pitzer equations for the derivatives of G_{ex}/RT into three separate expressions for modeling the osmotic coefficient and the activity coefficients of cations and anions. The model values for single ion activities and activity coefficients, such as $\gamma_{(H^+)}$ in Eqn. 1A, and single ion chemical potentials are not measurable quantities. These expressions do however combine properly into the measurable sums and differences that preserve the ionic strength dependence of the original second and third virial coefficient Pitzer expressions. For example, it is the measurable γ_{\pm}^v quantity (Eqn. 3B) that is compared with experimental data in the model parameterization process.

Since it is often desirable to report single ion activities, particularly

in attempts to relate pH cell measurements with solution properties, they are defined by convention. Consider the expression given in Eqn. 3B for the measurable mean activity coefficient quantity. If the value of one single ion activity coefficient is defined, then the other in the product can be calculated from the mean activity coefficient. As long as only the mean activity coefficients are used in any comparison with the experimental data, the choice of convention is arbitrary. We often use the MacInnes convention in our modeling codes. In this convention, the activity coefficients of the chloride ion is defined as the mean activity coefficient of a KCl solution of the same ionic strength (see MacInnes, 1961; Harvie et al., 1984). These conventional values of single ion activities are not directly comparable with the Pitzer model single ion activities produced directly by the Harvie-Weare formulation. However, single ion activity coefficients values determined directly by the Harvie-Weare formulation or by convention (e.g., MacInnes) will calculate the same final equilibrium species distribution. For example, the acid dissociation equilibrium: $\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{2-}$ can be expressed as:

$$K2 = \{(\gamma_H \gamma_{\text{SO}_4})/\gamma_{\text{HSO}_4}\} \{([\text{H}][\text{SO}_4])/\text{HSO}_4\} = \{\Pi\} \{Q\}, \quad (4B)$$

where γ_i are the single ion activity coefficients predicted by the Harvie-Weare formulation, Π is the activity coefficient product and Q is the concentration product. If a new conventional activity coefficient is defined for a single ion species, γ_i^{new} (e.g., using the MacInnes convention), by the equation:

$$\gamma_i^{\text{new}} = C^{z_i} \gamma_i, \quad (5B)$$

where C is a constant defined by the convention that is the same for all species and z_i is the charge of species i , then it can be seen that Π^p equals Π . Note that the z_i exponent (e.g., $z_H = +1$ and $z_{\text{SO}_4} = -2$) causes the plus and minus charged species to be treated differently in Eqn. 5B.

Because of the common use of pH cell measurements and because they are the only data available for parameterizing models of some aqueous systems (e.g., see HMW), it would be useful to directly relate pH data and the acid/base properties (e.g., $\ln a_H$) predicted by this model (and other equilibrium models). However, the activity of H^+ is a single ion property and, therefore, cannot be uniquely defined. In addition, the correspondence of thermodynamic quantities, which depend on reversible properties of the system, with cell measurements that depend on both irreversible and reversible properties is not exact. Harvie et al. (1984) have discussed in some detail the approximations involved in relating such pH cell measurements with an equilibrium property of a system. Dickson (1984) has assessed the problems with theoretical interpretation of various approaches defining pH scales.