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A molal-based model for strong acid chemistry at low temperatures (<200 to 298 K)

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Abstract—Geochemical processes occurring in cold environments on Earth, Mars, and Europa have elicited considerable interest in the application of geochemical models to subzero temperatures. Few existing geochemical models explicitly include acid chemistry and those that do are largely restricted to temperatures $\geq 0^\circ\text{C}$ or rely on the mole-fraction scale rather than the more common molal scale. This paper describes (1) use of the Clegg mole-fraction acid models to develop a molal-based model for hydrochloric, nitric, and sulfuric acids at low temperatures; (2) incorporation of acid chemistry and nitrate minerals into the FREZCHEM model; (3) validation and limitations of the derived acid model; and (4) simulation of hypothetical acidic brines for Europa.

The Clegg mole-fraction acid models were used to estimate activities of water and mean ionic activity coefficients that serve as the database for estimating molal Pitzer-equation parameters for HCl (188 to 298 K), HNO_3 (228 to 298 K), and H_2SO_4 (208 to 298 K). Model eutectics for HNO_3 and H_2SO_4 agree with experimental measurements to within $\pm 0.2^\circ\text{C}$. In agreement with previous work, the experimental freezing point depression (fpd) data for pure HCl at subzero temperatures were judged to be flawed and unreliable. Three alternatives are discussed for handling HCl chemistry at subzero temperatures. In addition to defining the solubility of solid-phase acids, this work also adds three new nitrate minerals and six new acid salts to the FREZCHEM model and refines equilibria among water ice, liquid water, and water vapor over the temperature range from 180 to 298 K. The final system is parameterized for Na-K-Mg-Ca-H-Cl- SO_4 - NO_3 -OH- HCO_3 - CO_3 - CO_2 - H_2O .

Simulations of hypothetical MgSO_4 - H_2SO_4 - H_2O and Na_2SO_4 - MgSO_4 - H_2SO_4 - H_2O brines for Europa demonstrate how freezing can convert a predominantly salt solution into a predominantly acid solution at subzero temperatures. This result has consequences for the effects of salinity, acidity, and temperature as limiting factors for potential life on Europa. Strong acidity would limit life-forms to highly acidophilic organisms. Copyright © 2002 Elsevier Science Ltd

1. INTRODUCTION

Geochemical processes occurring in cold environments on Earth, Mars, and Europa have elicited considerable interest in the application of geochemical models to subzero temperatures (Spencer et al., 1990; Marion, 1997; Marion and Farren, 1999; Morse and Marion, 1999; Kargel et al., 2000). Several models published in recent years describe chloride and sulfate mineral solubilities in concentrated brines using the Pitzer equations over temperatures ranging from -60 to 250°C (e.g., Harvie et al., 1984; Pabalan and Pitzer, 1987; Greenberg and Møller, 1989; Møller, 1988; Plummer et al., 1988; Spencer et al., 1990; He and Morse, 1993; Millero and Pierrot, 1998; Møller et al., 1998; Marion and Farren, 1999; Marion, 2001). With respect to these cited models, only the Harvie et al. (1984), Plummer et al. (1988), Millero and Pierrot (1998), Møller et al. (1998), and Marion (2001) models explicitly include acid chemistry; but, with the exception of Marion (2001), these models are restricted to temperatures $\geq 0^\circ\text{C}$. Strong acid chemistry on Earth is especially relevant to cold stratospheric aerosol chemistry (Molina et al., 1993; Carslaw et al., 1995, 1997; Fahey et al., 2001) and acid mine drainage problems (Nordstrom et al., 2000) including permafrost-affected sites (Elberling, 2001). There is also evidence that solid-phase sulfuric acid may be present on the icy surface of Europa (Carlson, 1999).

Simon Clegg and his colleagues have written several papers

in recent years on hydrochloric, nitric, and sulfuric acids using the Pitzer approach (Clegg and Brimblecombe, 1988a, 1988b, 1990a, 1990b, 1995; Clegg et al., 1994, 1998; Carslaw et al., 1995, 1997). These seminal papers are based on an extensive review of the experimental data for osmotic coefficients, vapor pressure measurements, electromotive force measurements, degrees of dissociation of the HSO_4^- ion, differential heats of dilution, heat capacities, freezing points, solubilities, and partial molal enthalpies of water. The papers cover temperatures ranging from <200 K to 328 K and up to 40 m total solute molality. However, these models are based on the mole-fraction scale instead of the more common molal scale. A problem with the Clegg mole-fraction models is that they are primarily developed for aerosol chemistry and, to date, are only parameterized for a limited chemistry that includes the cations: H, Na, and NH_4 , and the anions: Br, Cl, NO_3 , and SO_4 (<http://www.hpcl.uea.ac.uk/~770/aim.html>). This restricts their direct application to narrow chemistries using the mole-fraction scale. The Clegg mole-fraction models are also computationally inefficient for incorporation into other models (Carslaw et al., 1995).

The objectives of this work were to (1) use the Clegg mole-fraction acid models as a database to develop a molal-based model for hydrochloric, nitric, and sulfuric acids at low temperatures; (2) incorporate acid chemistry and nitrate minerals into the FREZCHEM model; (3) validate and discuss the limitations of the derived acid model; and (4) apply the model to simulate hypothetical acidic brines for Europa.

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2. MATERIAL AND METHODS

2.1. Pitzer Equation Parameterization

It is conventional to define the activity of a species (a_i) by the relation:

$$\mu_i = \mu_i^0 + RT \ln(a_i) \quad (1)$$

where μ_i is the chemical potential of species i , and μ_i^0 is the standard chemical potential of species i . In turn, the activity is related to molality of species i (m_i) by

$$a_i = \gamma_i m_i \quad (2)$$

where γ_i is the activity coefficient of species i . In this work, the solubility product (K_{sp}) or the ion activity product (IAP) for a solid phase such as $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ is calculated by

$$K_{sp} \text{ (or IAP)} = (\gamma_{\text{H}^+}) (m_{\text{H}^+}) (\gamma_{\text{NO}_3^-}) (m_{\text{NO}_3^-}) (a_{\text{H}_2\text{O}(l)})^3 \quad (3)$$

where γ values and $a_{\text{H}_2\text{O}(l)}$ (activity of liquid water) are estimated with the Pitzer equations, and m_i values are measured. In the model, the calculated IAP is compared to the solubility product (K_{sp}) to ascertain whether a solution is undersaturated ($\text{IAP} < K_{sp}$), saturated ($\text{IAP} = K_{sp}$), or supersaturated ($\text{IAP} > K_{sp}$).

The osmotic coefficient of a solution (related to the activity of liquid water) and the ion activity coefficients of chemical species in concentrated solutions can be estimated with the Pitzer equations, which have been presented in several recent papers (e.g., Harvie et al., 1984; Plummer et al., 1988; Spencer et al., 1990; Pitzer, 1991, 1995; Clegg et al., 1994; Marion and Farren, 1999). Therefore, this presentation will not be repeated here. To estimate the osmotic coefficient and ion activity coefficients using the Pitzer approach requires knowing the following interaction parameters: $\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$, $\beta_{ca}^{(2)}$ (for di-valent salts), C_{ca}^{ϕ} , Θ_{cc} , (or Θ_{aa}) and Ψ_{ca} (or Ψ_{caa}) for the appropriate solution phase ions, where c is a cation and a is an anion. The only significant departure in this paper from the "standard" Pitzer approach was that Clegg et al. (1994) were followed in making C_{ca}^{ϕ} a function of two independent parameters, $C_{ca}^{(0)}$ and $C_{ca}^{(1)}$, for sulfuric acid. See Clegg et al., 1994 (pp. 1891 to 1893) for definition of these terms.

Pitzer-equation parameters and solubility products were estimated isothermally using a previously described algorithm (Marion and Farren, 1999). Initially, literature values or zero were assumed for the parameters. The algorithm optimizes parameters sequentially and iterates through the parameter set until no further improvement is possible (Marion and Farren, 1999). These isothermal constants were then fitted to equations of the form:

$$P(T)_j = a_{1j} + a_{2j}T + a_{3j}T^2 + a_{4j}T^3 + \frac{a_{5j}}{T} + a_{6j} \ln(T) + a_{8j}T^4 \quad (4)$$

where P_j is the j^{th} Pitzer-equation parameter or \ln (solubility product) and T is temperature (K). To maintain numbering consistency with previous work (Marion and Farren, 1999; Marion, 2001), a new term ($a_{8j}T^4$) was defined in this paper to accommodate higher order polynomials; and a previously defined term (a_{7j}/T^2) was not used.

In a few cases, goodness-of fit of the model to the databases was estimated by the standard error of estimate (SE), which is given by

$$SE(\%) = \left\{ \sum \left[\left(\frac{M_i - E_i}{E_i} \right) 100 \right]^2 / n \right\}^{0.5} \quad (5)$$

where M_i is the model estimate of a property [e.g., $a_{\text{H}_2\text{O}(l)}$, γ_{\pm} , or $\ln(\text{IAP})$] and E_i is the corresponding experimental measurement [e.g., $a_{\text{H}_2\text{O}(l)}$, γ_{\pm} , or $\ln(K_{sp})$], and n is the number of observations.

2.2. Acid and Nitrate Databases

The databases for acid chemistry were developed from the mole-fraction models of Simon Clegg and his colleagues (Clegg and Brimblecombe 1990a, 1990b; 1995; Carslaw et al., 1995). These mole-fraction models were used to estimate the activity of liquid water (a function of the osmotic coefficient) and mean molal ion activity coef-

ficients (γ_{\pm}) as functions of temperature and composition to acid concentrations sufficiently high (8 to 12 m) to define the eutectic composition at subzero temperatures. It was necessary to include both water activities and mean ion activity coefficients in the databases to accurately model these acid chemistries. Using a single set of measurements (either water activities or mean ion activity coefficients) sometimes lead to a poor fit to the other unspecified variable. This is probably a consequence of the linear dependency of the Pitzer-equation parameters, which allows more than one set of Pitzer-equation parameters to fit the databases equally well. Specifying both water activities and mean ion activity coefficients lead to a better constrained model. Molal activity coefficients can be determined directly from mole-fraction activity coefficients (see Clegg and Brimblecombe, 1990a, 1995). For nitric and sulfuric acids, computer programs based on published papers were used to estimate the water activities and mean ion activity coefficients (Clegg and Brimblecombe, 1990a, 1995). For hydrochloric and mixed nitric-sulfuric acids, the Internet-based Atmospheric Inorganic Model (AIM) (at <http://www.hpcl.uea.ac.uk/~770/aim.html>) was used to estimate water activities and mean ion activity coefficients. Databases for nitrate parameters were based on osmotic and mean ion activity coefficients at 25°C, solubility data, and fpd data (Linke, 1965; Robinson and Stokes, 1970). Databases for mixed acid-salt systems were largely based on mineral solubilities (Bukhshtein et al., 1953; D'Ans and Freund, 1960; Linke, 1965; Marshall and Jones, 1966).

2.3. FREZCHEM Model

An objective of this work was to produce solubility products and Pitzer-equation parameters that can be incorporated seamlessly into the FREZCHEM model (Marion and Grant, 1994; Mironenko et al., 1997; Marion and Farren, 1999; Marion, 2001). The FREZCHEM model as presently structured has 50 solid phases including ice, nine chloride minerals, 12 sulfate minerals, 14 carbonate minerals, five new solid-phase acids, three new nitrate minerals, and six new acid-salts (Table 1). Solubility products for chloride minerals, the equilibrium constant for ice, the Debye-Hückel parameter, and 22 Pitzer-equation parameters dealing with chloride interactions were taken primarily from Spencer et al. (1990). Solubility products for sulfate minerals and 25 Pitzer-equation parameters dealing with sulfate interactions were taken primarily from Marion and Farren (1999). Solubility products for bicarbonate-carbonate minerals and 55 Pitzer-equation parameters dealing with bicarbonate, carbonate, and hydroxide interactions were taken primarily from Marion (2001). Solubility products for acids, nitrate minerals, and acid-salts and Pitzer-equation parameters dealing with acid and nitrate interactions were estimated in this work.

3. RESULTS

Parameterization of binary and ternary chemistries will be given in this section. First, water ice-liquid water- water vapor equilibria will be presented, followed by acid chemistries, then nitrate minerals, and finally acid-salt systems.

3.1. Water Ice-Liquid Water-Water Vapor Equilibria

Equilibria among water ice, liquid water, and water vapor are critical for model development because these relations can be used as a base for model parameterization. For example, given a fpd measurement for a specific solution, one can calculate directly the activity of liquid water (or osmotic coefficient) that can then be used as data to parameterize the model (Clegg and Brimblecombe, 1995). These phase relations also allow one to estimate in a model the properties of one phase (e.g., gas) based on the calculated properties of another phase (e.g., aqueous), or to control one phase (e.g., aqueous) based on the known properties of another phase (e.g., gas) (see Section 3.5).

Table 1. Solid Phases in the FREZCHEM Model.

1. H ₂ O(cr,I) (ice)
2. NaCl(cr) (halite)
3. NaCl·2H ₂ O(cr) (hydrohalite)
4. KCl(cr) (sylvite)
5. MgCl ₂ ·6H ₂ O(cr) (bischofite)
6. MgCl ₂ ·8H ₂ O(cr)
7. MgCl ₂ ·12H ₂ O(cr)
8. CaCl ₂ ·6H ₂ O(cr) (antarcticite)
9. KMgCl ₃ ·6H ₂ O(cr) (carnallite)
10. CaCl ₂ ·2MgCl ₂ ·12H ₂ O(cr) (tachyhydrite)
11. Na ₂ SO ₄ (cr) (thenardite)
12. Na ₂ SO ₄ ·10H ₂ O(cr) (mirabilite)
13. K ₂ SO ₄ (cr) (arcanite)
14. MgSO ₄ ·H ₂ O(cr) (kieserite)
15. MgSO ₄ ·6H ₂ O(cr) (hexahydrate)
16. MgSO ₄ ·7H ₂ O(cr) (epsomite)
17. MgSO ₄ ·12H ₂ O(cr)
18. CaSO ₄ (cr) (anhydrite)
19. CaSO ₄ ·2H ₂ O(cr) (gypsum)
20. Na ₂ SO ₄ ·3K ₂ SO ₄ (cr) (aphthitalite)
21. Na ₂ SO ₄ ·MgSO ₄ ·4H ₂ O(cr) (bloedite)
22. MgSO ₄ ·K ₂ SO ₄ ·6H ₂ O(cr) (picromerite)
23. NaHCO ₃ (cr) (nahcolite)
24. Na ₂ CO ₃ ·7H ₂ O(cr)
25. Na ₂ CO ₃ ·10H ₂ O(cr) (natron)
26. NaHCO ₃ ·Na ₂ CO ₃ ·2H ₂ O (trona)
27. KHCO ₃ (cr) (kalicinite)
28. MgCO ₃ (cr) (magnesite)
29. MgCO ₃ ·3H ₂ O(cr) (nesquehonite)
30. MgCO ₃ ·5H ₂ O(cr) (lansfordite)
31. 3MgCO ₃ ·Mg(OH) ₂ ·3H ₂ O(cr) (hydromagnesite) ^a
32. CaCO ₃ (cr) (calcite)
33. CaCO ₃ (cr) (aragonite)
34. CaCO ₃ (cr) (vaterite)
35. CaCO ₃ ·6H ₂ O(cr) (ikaite)
36. CaMg(CO ₃) ₂ (cr) (dolomite)
37. HCl·3H ₂ O(cr)
38. HCl·6H ₂ O(cr)
39. HNO ₃ ·3H ₂ O(cr)
40. H ₂ SO ₄ ·4H ₂ O(cr)
41. H ₂ SO ₄ ·6.5H ₂ O(cr)
42. NaNO ₃ (cr) (soda niter)
43. KNO ₃ (cr) (niter)
44. NaNO ₃ ·Na ₂ SO ₄ ·2H ₂ O(cr) (darapskite) ^b
45. Na ₃ H(SO ₄) ₂ (cr)
46. NaHSO ₄ ·H ₂ O(cr)
47. K ₃ H(SO ₄) ₂ (cr)
48. K ₃ H ₃ (SO ₄) ₄ (cr)
49. K ₈ H ₆ (SO ₄) ₇ ·H ₂ O(cr) (misenite) ^b
50. KHSO ₄ (cr) (mercallite)

^a There is some controversy with respect to the “correct” chemical formula for hydromagnesite. Some prefer the formula: 4MgCO₃·Mg(OH)₂·4H₂O (e.g., Drever, 1997, Königsberger et al., 1999).

^b These salts are sometimes written with one fewer water of hydration.

Incorporation of strong acids into the FREZCHEM model extended the lower temperature range from 219 K (the eutectic of seawater) to 187 K [the eutectic of HCl·3H₂O(cr)]. As fpd data were used to define water activities at low temperatures, it became apparent that the equation defining the equilibrium of ice and liquid water at temperatures below ≈228 K (Spencer et al., 1990) did not fit the fpd data well. This necessitated a re-evaluation of the relationship.

For liquid water and ice at equilibrium:

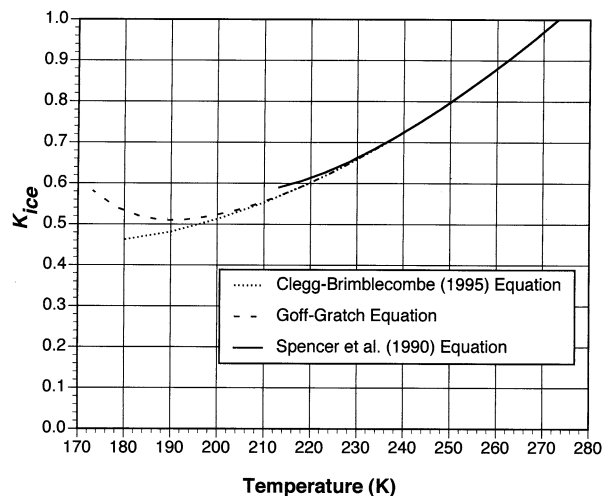


Fig. 1. Three equations for the equilibrium constant of water ice in equilibrium with liquid water (K_{ice}) for temperatures ranging from 180 to 273 K.

$$\mu_i = \mu_i^\circ + RT \ln(a_{H_2O(cr,l)}) = \mu_w = \mu_w^\circ + RT \ln(a_{H_2O(l)}) \quad (6)$$

where μ_i and μ_w are the chemical potentials of ice and liquid water, μ_i° and μ_w° are the standard chemical potentials, and $a_{H_2O(cr,l)}$ and $a_{H_2O(l)}$ are the activities of water in the form of ice and liquid water. Eqn. 6 can be rearranged to yield:

$$\frac{\mu_i^\circ - \mu_w^\circ}{RT} = \ln\left(\frac{a_{H_2O(l)}}{a_{H_2O(cr,l)}}\right) = \frac{-\Delta_{fus}G^\circ}{RT} = \ln(K_{ice}) \quad (7)$$

where $\Delta_{fus}G^\circ$ is the standard Gibbs energy of fusion ($\mu_w^\circ - \mu_i^\circ$) and K_{ice} is the equilibrium constant for liquid water in equilibrium with ice. At equilibrium with respect to pure ice, $a_{H_2O(cr,l)} = 1.0$. The following therefore applies:

$$a_{H_2O(l)} = \exp\left(\frac{-\Delta_{fus}G^\circ}{RT}\right) = K_{ice} \quad (8)$$

The activity of liquid water in equilibrium with pure ice is equal to the equilibrium constant (K_{ice}) at a given temperature. In turn, the activity of liquid water in equilibrium with pure ice can be estimated from

$$a_{H_2O(l)} = \frac{P_{H_2O(cr,l)}}{P_{H_2O(l)}} = K_{ice} \quad (9)$$

where $P_{H_2O(cr,l)}$ and $P_{H_2O(l)}$ are the partial pressures of water vapor above pure ice and pure liquid water, respectively. In this derivation, the water vapor was assumed to behave as an ideal gas, which allows substitution of partial pressures for fugacities. To estimate K_{ice} , the partial pressures of water above pure ice and pure liquid water must therefore be specified.

The equation used in the FREZCHEM model to define K_{ice} , the Spencer et al. (1990) equation, begins to significantly depart from the Goff-Gratch (List, 1951; McDonald, 1965) and the Clegg-Brimblecombe (Clegg and Brimblecombe, 1995) equations at temperatures below 228 K (Fig. 1). Similarly the Goff-Gratch equation significantly departs from the Clegg-Brimblecombe equation at temperatures below 208 K. The Goff-

Table 2. Equilibrium Constants^a Derived in this Work or Taken from the Literature (Footnoted).

	Equation Parameters						
	a ₁	a ₂	a ₃	a ₄	a ₅	a ₆	a ₈
Gas-Solution Phase Equilibria							
H ₂ O	9.053594e1	-7.215505e-1	2.112659e-3	-2.254724e-6			
HCl ^b	7.812179e1	-3.696246e-1	6.735943e-4	-5.006380e-7			
HNO ₃ ^c	3.94005278e2	1.31442311e-1	-4.20928363e-5		-3.0203522e3	-7.1001998e1	
H ₂ SO ₄	1.718120e2	-6.503309e-1	6.909049e-4				
Solution Phase Equilibria							
H ₂ SO ₄ -SO ₄ ^d	1.2956527e3	5.704742e-1	-2.57206e-4		-3.056394e4	-2.360504e2	
Solution-Solid Phase Equilibria							
Ice(I,cr)	1.833946e0	-1.787269e-3	6.212940e-5	-2.884752e-8			
HCL·3H ₂ O(cr) ^e	5.142350e0	1.630170e-2					
HCl·6H ₂ O(cr) ^e	4.367384e0	3.637139e-3					
HNO ₃ ·3H ₂ O(cr)	-1.270087e1	7.050180e-2					
H ₂ SO ₄ ·4H ₂ O(cr)	-7.103329e1	6.235489e-1	-1.279573e-3				
H ₂ SO ₄ ·6.5H ₂ O(cr)	-8.947832e1	7.407673e-1	-1.477903e-3				
NaNO ₃ (cr)	7.016265e2	-9.648812e0	5.093224e-2	-1.227837e-4			1.144431e-7
KNO ₃ (cr)	-4.652079e1	2.575014e-1	-3.431593e-4				
NaNO ₃ ·Na ₂ SO ₄ ·2H ₂ O(cr)	1.419947e2	-1.119580e0	2.168240e-3				
Na ₃ H(SO ₄) ₂ (cr)	-2.122993e3	2.296880e1	-8.282936e-2	9.946746e-5			
NaHSO ₄ ·H ₂ O(cr)	6.581474e2	-6.926105e0	2.431396e-2	-2.830635e-5			
K ₂ H(SO ₄) ₂ (cr)	4.561655e1	-4.356452e-1	8.546984e-4				
K ₂ H ₃ (SO ₄) ₄ (cr)	-3.552640e1	6.711111e-2					
K ₈ H ₆ (SO ₄) ₇ ·H ₂ O(cr)	9.591803e1	-9.575202e-1	1.841905e-3				
KHSO ₄ (cr)	-1.019832e1	3.865551e-2					
MgSO ₄ ·H ₂ O(cr)	1.306284e2	-8.440640e-1	1.356205e-3				

^a All equations in this table are presented as $\ln(K) = a_1 + a_2T + \dots$ (Eqn. 4), except for Ice, which is presented as $K_{\text{ice}} = a_1 + a_2T + \dots$

^b Derived from the mole fraction equation of Carlsaw et al., 1995.

^c Derived from the mole fraction equation of Clegg and Brimblecombe, 1990a.

^d Derived from the mole fraction equation of Clegg and Brimblecombe, 1995.

^e These equations can only be used with the "variable parameter model." See text discussion.

Gratch equations directly estimate $P_{\text{H}_2\text{O}(\text{cr},\text{I})}$ and $P_{\text{H}_2\text{O}(\text{l})}$ (the vapor pressures above pure water ice and pure supercooled liquid water, respectively), to temperatures as low as -100°C (List, 1951; McDonald, 1965; Clegg and Brimblecombe, 1995), which allows a direct calculation of K_{ice} (Eqn. 9). The Clegg-Brimblecombe equation is based on $P_{\text{H}_2\text{O}(\text{cr},\text{I})}$ (180 to 273 K) and $P_{\text{H}_2\text{O}(\text{l})}$ (213 to 273 K) estimated from the Goff-Gratch equations supplemented with $P_{\text{H}_2\text{O}(\text{l})}$ estimates from Clegg and Brimblecombe (1995, p. 47) for temperatures ranging from 180 to 220 K; the latter estimates were calculated from an extrapolated equation based on vapor pressures, enthalpies, and heat capacities. The coldest experimental fpd datum used by Clegg and Brimblecombe (1995) in developing their sulfuric acid model was 6.0188 m H₂SO₄ at 201.94 K, which has an experimentally estimated $a_{\text{H}_2\text{O}(\text{l})}$ equal to 0.518. The estimated $a_{\text{H}_2\text{O}(\text{l})}$ for the Goff-Gratch and Clegg-Brimblecombe equations at this temperature are 0.526 and 0.521, respectively (Fig. 1). Similarly at 203.93 K (5.9528 m H₂SO₄), the experimentally estimated $a_{\text{H}_2\text{O}(\text{l})}$ is 0.526 (Clegg and Brimblecombe, 1995), while the estimated $a_{\text{H}_2\text{O}(\text{l})}$ for the Goff-Gratch and Clegg-Brimblecombe equations at this temperature are 0.531 and 0.528, respectively. Since the Clegg-Brimblecombe equation for K_{ice} (Fig. 1, Table 2) is most consistent with the experimental fpd data at temperatures below 223 K, this model was used in all subsequent analyses to define the activity of water in equilibrium with ice at specific temperatures.

An equilibrium constant for liquid water-water vapor ($K =$

$a_{\text{H}_2\text{O}(\text{l})}/P_{\text{H}_2\text{O}(\text{l})}$) was estimated, where $a_{\text{H}_2\text{O}(\text{l})}$ is the activity of water in the liquid phase and $P_{\text{H}_2\text{O}(\text{l})}$ is the gas partial pressure above liquid water. For temperatures ≥ 273.15 K, K was estimated using the Goff-Gratch equation for $P_{\text{H}_2\text{O}(\text{l})}$ (McDonald, 1965) assuming a pure liquid water system; in this case, $a_{\text{H}_2\text{O}(\text{l})} = 1.0$; therefore, $K = 1.0/P_{\text{H}_2\text{O}(\text{l})}$. For temperatures from 180 to 273.15 K, K was estimated using the published values of $P_{\text{H}_2\text{O}(\text{l})}$ above pure liquid water from Clegg and Brimblecombe (1995). The resulting water equilibrium equation (Table 2) is valid for temperatures ranging from 180 to 298 K.

3.2. The HCl-H₂O System

The AIM model was used to estimate the activity of water and mean ion activity coefficients in HCl solutions ranging in composition from 0.01 to 12 m and in temperature from 188 to 298 K in 10 K increments for a total of 624 model-generated datapoints [26 compositions \times 12 temperatures \times 2 data sets (water activities and activity coefficients)]. Estimated Pitzer-equation binary parameters include $C_{\text{H},\text{Cl}}^\phi$, $\beta_{\text{H},\text{Cl}}^{(0)}$, and $\beta_{\text{H},\text{Cl}}^{(1)}$ (Table 3). The Henry's Law constant for HCl ($K_{\text{H}} = a_{\text{HCl}(\text{aq})}/P_{\text{HCl}(\text{g})}$) was derived from the mole-fraction equation of Carlsaw et al. (1995) (their Eqn. 22) and is valid for temperatures ranging from 183 to 298 K (Table 2).

The standard error of the model in reproducing the AIM model water activities and mean ion activity coefficients is 1.6% ($n = 624$). Goodness-of-fit for water activities at +25 and

Table 3. Binary and Temperature-Dependent Ternary Pitzer-Equation Parameters Derived in this Work or Taken from the Literature (Footnoted).

Pitzer-equation Parameter	Equation Parameter						
	a_1	a_2	a_3	a_4	a_5	a_6	a_8
$C_{H,Cl}^{\phi}$	-2.786190e-3	1.735035e-5	-5.937631e-8				
$B_{H,Cl}^{(0)}$	3.561220e-1	-5.305245e-4					
$B_{H,Cl}^{(1)}$	-7.420199e0	1.158740e-1	-6.666408e-4	1.685445e-6			-1.564321e-9
C_{H,NO_3}^{ϕ}	1.264791e-1	-8.808517e-4	1.469263e-6				
$B_{H,NO_3}^{(0)}$	-1.019608e0	8.052811e-3	-1.414706e-5				
$B_{H,NO_3}^{(1)}$	-6.829838e0	7.588276e-2	-2.843828e-4	3.695995e-7			
$C_{H,SO_4}^{(0)}$	-5.315201e-1	8.619821e-3	-5.145710e-5	1.350347e-7			-1.314709e-10
$C_{H,SO_4}^{(1)}$	-7.766817e2	1.164255e1	-6.537128e-2	1.626702e-4			-1.513403e-7
$B_{H,SO_4}^{(0)}$	1.388618e1	-2.200263e-1	1.31476e-3	-3.475869e-6			3.420786e-9
$B_{H,SO_4}^{(1)}$	-1.679737e2	2.609701e0	-1.526685e-2	3.984122e-5			-3.908818e-8
$C_{H,HSO_4}^{(0)}$	9.773929e-2	-1.148641e-3	4.422169e-6	-5.765707e-9			
$C_{H,HSO_4}^{(1)}$	1.099940e2	-1.969903e0	1.289248e-2	-3.672285e-5			3.850406e-8
$B_{H,HSO_4}^{(0)}$	-6.888679e-1	1.195453e-2	-4.667571e-5	5.878913e-8			
$B_{H,HSO_4}^{(1)}$	-3.815780e2	6.261241e0	-3.789588e-2	1.006085e-4			-9.906089e-8
C_{Na,NO_3}^{ϕ}	0.00						
$B_{Na,NO_3}^{(0)}$	7.088889e-1	-5.599812e-3	1.085000e-5				
$B_{Na,NO_3}^{(1)}$	8.312979e1	-6.161264e-1	1.133400e-3				
C_{K,NO_3}^{ϕ}	6.669e-2	-2.0505e-4					
$B_{K,NO_3}^{(0)}$	-2.948e-1	7.326e-4					
$B_{K,NO_3}^{(1)}$	-6.2735	2.1149e-2					
C_{Mg,NO_3}^{ϕ}	-2.062e-2						
$B_{Mg,NO_3}^{(0)}$	5.207e-1	-5.1525e-4					
$B_{Mg,NO_3}^{(1)}$	2.9242e0	-4.4925e-3					
C_{Ca,NO_3}^{ϕ}	-2.014e-2						
$B_{Ca,NO_3}^{(0)}$	3.687e-1	-5.295e-4					
$B_{Ca,NO_3}^{(1)}$	4.1485e0	-9.1875e-3					
C_{Na,HSO_4}^{ϕ}	0.00						
$B_{Na,HSO_4}^{(0)}$	4.54e-2						
$B_{Na,HSO_4}^{(1)}$	-6.7010e0	2.5352e-2					
C_{K,HSO_4}^{ϕ}	0.00						
$B_{K,HSO_4}^{(0)}$	-3.0e-4						
$B_{K,HSO_4}^{(1)}$	1.004759e2	-7.127881e-1	1.262349e-3				
C_{Mg,HSO_4}^{ϕ}	3.075223e0	-2.094837e-2	3.566667e-5				
$B_{Mg,HSO_4}^{(0)}$	1.175741e0	-2.374627e-3					
$B_{Mg,HSO_4}^{(1)}$	-4.091076e2	2.838782e0	-4.902359e-3				
C_{Ca,HSO_4}^{ϕ}	0.00						
$B_{Ca,HSO_4}^{(0)}$	6.19e-2						
$B_{Ca,HSO_4}^{(1)}$	2.602e0						
C_{Na,SO_4}^{ϕ}	1.470571e1	-2.293478e-1	1.350491e-3	-3.537708e-6			3.466102e-9
$B_{Na,SO_4}^{(0)}$	-3.447035e1	5.312162e-1	-3.119749e-3	8.181394e-6			-8.022815e-9
$B_{Na,SO_4}^{(1)}$	5.161188e1	-8.245243e-1	4.902233e-3	-1.280795e-5			1.252258e-8
Ψ_{Na,H,NO_3}	-7.707985e-2	2.482609e-4					
Ψ_{K,H,NO_3}	-2.089075e0	1.399737e-2	-2.360221e-5				
θ_{NO_3,HSO_4}	4.151797e0	-4.445727e-2	1.573030e-4	-1.876457e-7			
$\Psi_{NO_3,HSO_4,H}$	-6.187135e0	9.307292e-2	-5.252546e-4	1.316116e-6			-1.233392e-9
θ_{NO_3,SO_4}	2.559033e0	-1.679067e-2	2.892045e-5				
$\Psi_{NO_3,SO_4,H}$	-3.756770e-1	3.241125e-3	-8.920938e-6	7.367910e-9			
$\Psi_{NO_3,Cl,Na}$	-5.773862e-1	3.940840e-3	-6.800000e-6				
$\Psi_{NO_3,Cl,K}$	-1.065548e0	6.957931e-3	-1.142531e-5				
$\Psi_{NO_3,SO_4,Na}$	-2.222887e-1	1.031300e-3	-1.00e-6				
$\Psi_{NO_3,SO_4,K}$	-4.715997e0	3.156712e-2	-5.304224e-5				
$\Psi_{NO_3,SO_4,Mg}$	-2.9392e-1	9.60e-4					
Ψ_{Na,Ca,NO_3}	-3.481452e-2	1.285714e-4					
Ψ_{K,Mg,NO_3}	-6.494e-1	2.000e-3					
Ψ_{K,Ca,NO_3}	-9.011042e-1	2.944255e-3					
Ψ_{K,H,SO_4}^b	-1.4967e0	5.456e-3					
Ψ_{Mg,H,HSO_4}^c	-4.525314e-2	7.995736e-5					
$\Psi_{SO_4,HSO_4,Mg}^c$	-7.656214e-1	2.487100e-3					

^a From Pitzer, 1991.

^b These equations are only valid between 0 and 25°C. At subzero temperatures, use $B_{K,HSO_4}^{(1)} = -0.0371$ and $\Psi_{K,HSO_4} = -0.0064$.

^c These equations are only valid between 0 and 25°C. At subzero temperatures, use $C_{Mg,HSO_4}^{\phi} = 0.0143$, $B_{Mg,HSO_4}^{(0)} = 0.5315$, $B_{Mg,HSO_4}^{(1)} = 0.5361$, $\Psi_{Mg,H,HSO_4} = -0.0234$, and $\Psi_{SO_4,HSO_4,Mg} = -0.0884$.

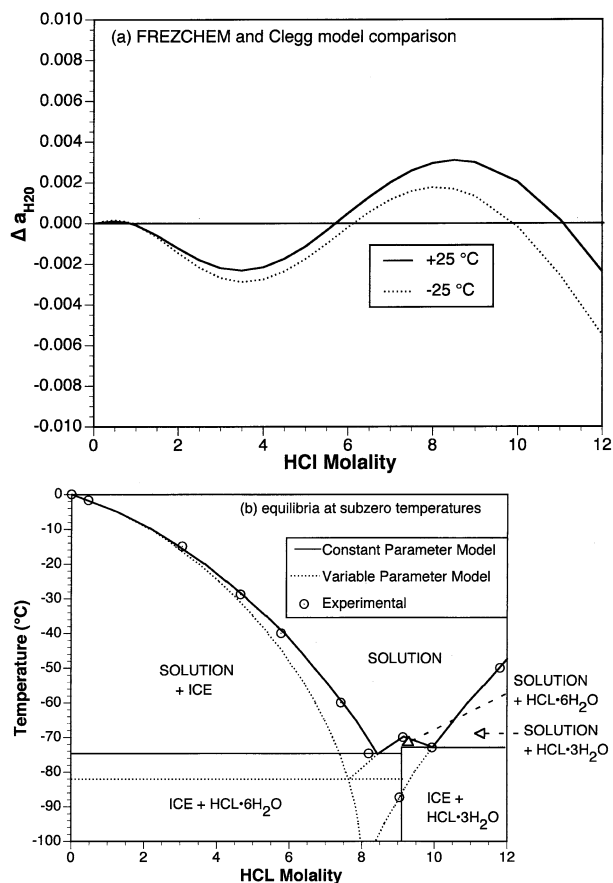


Fig. 2. Hydrochloric acid solutions. (a) The difference in the activity of water (Δa_{H_2O}) between the Clegg mole-fraction model (database) and the derived molal model at 25 and -25°C . (b) Model and experimental estimates of equilibria at subzero temperatures.

-25°C is shown in Figure 2a. The magnitude of the standard error is greater for hydrochloric acid than for either nitric or sulfuric acids.

Application of the hydrochloric acid binary parameters at subzero temperatures to predict ice equilibria (variable parameter model, Fig. 2b) shows a major deviation from the experimental data. In the parameterization of their hydrochloric acid model, Carslaw et al. (1995) rejected all the fpd data below -4°C (≈ 1 m HCl) because these data were inconsistent with presumably better data at higher temperatures. As a consequence, their model does not fit the experimental data very well at subzero temperatures. Since subzero temperatures are the temperatures of most interest in many applications of the FREZCHEM model (Marion, 1997; Marion and Farren, 1999; Marion et al., 1999; Morse and Marion, 1999; Kargel et al., 2000), this issue needs to be addressed.

One strategy that appears to work is to replace the temperature-dependent binary hydrochloric acid parameters (Table 3) with their values at 298.15 K ($C^{\phi} = -0.00289$, $\beta^{(0)} = 0.1979$, and $\beta^{(1)} = 0.1766$) and keep these parameters constant with temperature (constant parameter model, Fig. 2b). The result is a much better fit to the experimental fpd and solubility data at subzero temperatures.

To determine if the “constant parameter” fit is fortuitous,

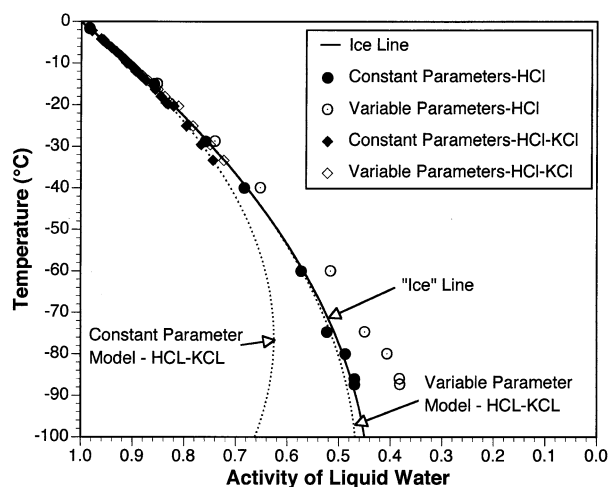


Fig. 3. Model and experimental estimates of equilibria at subzero temperatures for HCl-H₂O and HCl-KCl-H₂O systems.

mixed HCl-chloride salt fpd data (Bukshstein et al., 1953) were used to test the two HCl models for thermodynamic consistency. These HCl-chloride salt fpd data were not used in deriving ternary Pitzer parameters (See Section 3.7.1) and, therefore, constitute an independent database for testing the two models. These “datapoints” (Fig. 3) are partly experimental (fpd, Y axis) and partly model-derived (activity of liquid water, X axis) based on experimentally measured solution concentrations. As was the case for the previous HCl plots (Fig. 2b), for pure HCl, the constant parameter model (closed circles) better fit the theoretical “Ice” line (Clegg-Brimblecombe equation, Fig. 1) than the variable parameter model (open circles) (Fig. 3). The fit to the mixed HCl-KCl database, however, is much better for the variable parameter model (open diamonds) than for the constant parameter model (closed diamonds) at temperatures $< -20^\circ\text{C}$ (cf., the model equations to the theoretical “Ice” line, Fig. 3). Similarly for a mixed HCl-NaCl solution at -14.6°C , the calculated activities of water for the constant and variable parameter models are 0.8699 and 0.8665, respectively; the theoretical activity of water in equilibrium with pure ice at -14.6°C is 0.8672 (Fig. 1), which is nearer to the variable parameter estimate. Similar results were found for HCl-CaCl₂ mixtures. In all cases, the HCl-chloride salt mixtures were in better agreement with the variable parameter model than the constant parameter model.

These results lend support to the argument made by Carslaw et al. (1995) that there is something fundamentally flawed with the pure HCl data. Most of the pure HCl data at temperatures below -4°C date back to the work of Roloff in 1893 and Pickering in 1895 (cited in Linke, 1965), and it may not have been appreciated at that time that there are “right” and “wrong” ways to conduct these experiments to prevent significant incorporation of HCl into the ice (Simon Clegg, personal communication, 2001).

If there is significant incorporation of HCl into the ice, then Eqn. 8 is invalid. Instead, we have

$$a_{H_2O(l)} = K_{ice} a_{H_2O(cr,l)} \quad (10)$$

For dilute solutions, Raoult’s Law states that the vapor pressure

(activity) of a pure phase (e.g., ice) will always be lowered by a small addition of a solute (e.g., HCl) (Pitzer, 1995). Assuming the validity of Raoult's Law, then the $a_{\text{H}_2\text{O}(l)}$ in the presence of an impure ice phase ($a_{\text{H}_2\text{O}(cr,I)} < 1.00$) will be less than the $a_{\text{H}_2\text{O}(l)}$ for a pure ice phase ($a_{\text{H}_2\text{O}(cr,I)} = 1.00$). If we compare the water activities calculated with the variable parameter model for the pure HCl data (open circles) to the mixed HCl-KCl data (open diamonds) or the "Ice" line (Fig. 3), we see that the pure HCl calculated water activities are always less than the HCl-KCl water activities or the "Ice" line, which is in the direction expected if there was an impure ice phase in the HCl experiments. If we assume that the variable parameter model accurately calculates the $a_{\text{H}_2\text{O}(l)}$, then Eqn. 10 can be used to estimate $a_{\text{H}_2\text{O}(cr,I)}$, which varies monotonically in value from 1.000 at 0.0 m HCl to 0.804 at 9.04 m HCl (-86 to -87.4°C , Fig. 3).

If we assume that the experimental HCl concentrations in equilibrium with $\text{HCl}\cdot 3\text{H}_2\text{O}$ or $\text{HCl}\cdot 6\text{H}_2\text{O}$ (Linke, 1965; Kirgintsev et al., 1972) were accurately measured, even though displaced in some cases by the activity of impure ice, then these measurements can be used to estimate solubility products for solid phase $\text{HCl}\cdot 3\text{H}_2\text{O}$ and $\text{HCl}\cdot 6\text{H}_2\text{O}$ (Table 3). Then in the presence of a pure ice phase, application of these solubility products with the variable parameter model causes a displacement of the $\text{HCl}\cdot \text{H}_2\text{O}$ -Ice eutectic from -74.7°C with 8.19 m HCl to -82.1°C with 7.64 m HCl (Fig. 2b). Similarly, the metastable $\text{HCl}\cdot 3\text{H}_2\text{O}$ -Ice eutectic is displaced from -86.0°C (or -87.4°C) with 9.04 m HCl to -108.3°C with 8.00 m HCl; this latter eutectic is beyond the range of the database used to parameterize the model.

From the above analyses, there are, at least, three alternatives for defining equilibria among ice, HCl solutions, and HCl solid phases. First, one can use the constant parameter model which fits the data well at subzero temperatures (Figs. 2b and 3); but this fit is probably fortuitous. Second, one can use the variable parameter model without solid phases; but this leaves the model open-ended at low temperatures (i.e., no sink or eutectic for HCl). Third, one can use the variable parameter model with solid phases; but the eutectic for $\text{HCl}\cdot 6\text{H}_2\text{O}$ -Ice, in this case, is hypothetical (-82.1°C at 7.64 m HCl).

At this time, the variable parameter model with solid phases is probably the most prudent choice to quantify HCl properties at subzero temperatures. However, only future experimental work will clearly resolve the problems associated with HCl chemistry at subzero temperatures.

3.3. The HNO_3 - H_2O System

The Clegg-Brimblecombe (1990a) mole-fraction model was used to estimate the activity of water and mean molal ion activity coefficients in nitric acid solutions ranging in composition from 0.01 to 9.0 m and in temperature from 228 to 298 K in 5 K increments for a total of 750 model-generated data-points (25 compositions \times 15 temperatures \times 2 datasets). Pitzer-equation parameters estimated include the binary parameters $C_{\text{H},\text{NO}_3}^\phi$, $\beta_{\text{H},\text{NO}_3}^{(0)}$, and $\beta_{\text{H},\text{NO}_3}^{(1)}$ (Table 3). The Henry's Law constant for HNO_3 (molal-based) was derived from the mole-fraction equation of Clegg and Brimblecombe (1990a) (their Eqn. 40) and is valid for temperatures ranging from 213 to 393 K (Table 2). The solubility product for $\text{HNO}_3\cdot 3\text{H}_2\text{O}$ (Table 2)

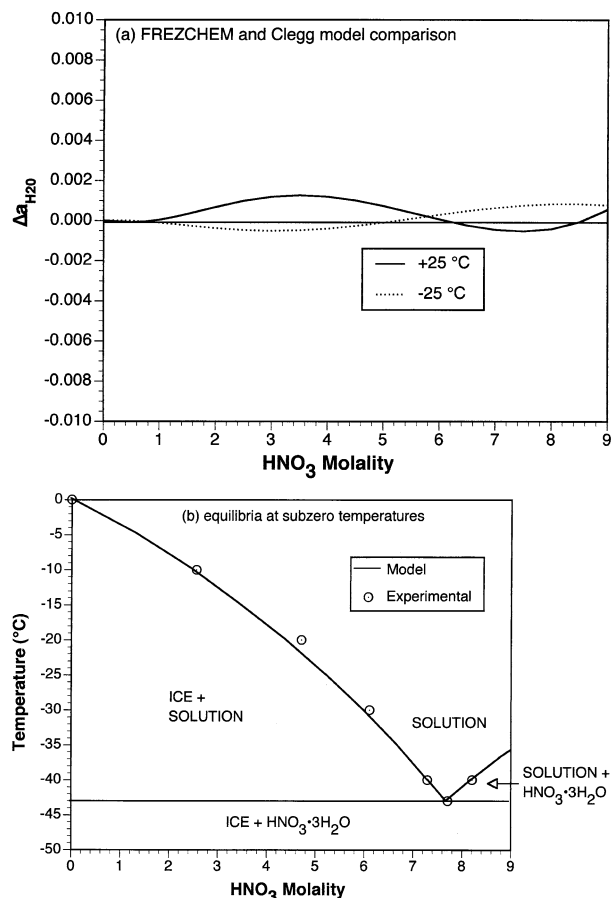


Fig. 4. Nitric acid solutions. (a) The difference in the activity of water ($\Delta a_{\text{H}_2\text{O}}$) between the Clegg mole-fraction model (database) and the derived molal model at 25 and -25°C . (b) Model and experimental estimates of equilibria at subzero temperatures.

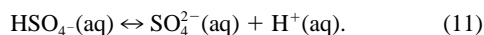
was estimated from solubility data (Linke, 1965) and the derived HNO_3 Pitzer-equation binary parameters (Table 3).

The standard error of the derived model in reproducing the water activities and mean activity coefficients of the Clegg and Brimblecombe (1990a) model is 0.36% ($n = 750$). Goodness-of-fit for water activities at $+25$ and -25°C is shown in Figure 4a. The nitric acid model has a significantly lower standard error (0.36%) than the hydrochloric acid model (1.6%) (cf., Figs. 2a and 4a).

Predictions of ice equilibria with nitric acid are in good agreement with the experimental data (Fig. 4b). The predicted eutectic for $\text{HNO}_3\cdot 3\text{H}_2\text{O}$ -Ice occurs at a composition of 7.68 m at a temperature of -43.2°C , which is in excellent agreement with the experimental composition of 7.71 m at a temperature of -43.0°C (Fig. 4b) (Linke, 1965).

3.4. The H_2SO_4 - H_2O System

The sulfuric acid system is more complex than either hydrochloric or nitric acids because of the presence of the bisulfate ion (HSO_4^-), which doubles the number of parameters that must be estimated. The equilibrium for sulfate-bisulfate is governed by the reaction:



The molal-based equation used to define this equilibrium (Table 2) was derived from the mole-fraction equation of Clegg and Brimblecombe (1995) (their Eqn. 26); this equation is assumed to be valid over temperatures ranging from <200 to 328 K (Clegg and Brimblecombe, 1995).

The Clegg and Brimblecombe (1995) mole-fraction model for sulfuric acid was used to estimate the activity of water and the degree of dissociation [$\alpha = \text{SO}_4^{2-}/(\text{SO}_4^{2-} + \text{HSO}_4^-)$] in sulfuric acid solutions ranging in composition from 0.01 to 8.0 m and in temperature from 208 to 298 K in 5 K increments for a total of 950 model-generated datapoints (25 compositions \times 19 temperatures \times 2 datasets). The Pitzer-equation parameters were estimated directly from the water activities and indirectly by comparing model-calculated ion activity products (IAP) for Eqn. 11 to the thermodynamic equilibrium constant (K). The IAP was calculated from α , which gives the molal concentrations, and model activity coefficients. This model-generated database was used to estimate the temperature-dependent binary Pitzer-equation parameters for sulfuric acid: $C_{\text{H}_2\text{SO}_4}^{(0)}$, $C_{\text{H}_2\text{SO}_4}^{(1)}$, $\beta_{\text{H}_2\text{SO}_4}^{(0)}$, $\beta_{\text{H}_2\text{SO}_4}^{(1)}$, $C_{\text{H}_2\text{SO}_4}^{(0)}$, $C_{\text{H}_2\text{SO}_4}^{(1)}$, $\beta_{\text{H}_2\text{SO}_4}^{(0)}$, and $\beta_{\text{H}_2\text{SO}_4}^{(1)}$ (Table 3). The solubility products for $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4 \cdot 6.5\text{H}_2\text{O}$ (Table 2) were estimated from solubility data (Linke, 1965) and the derived H_2SO_4 Pitzer-equation binary parameters (Table 3).

While sulfuric acid is considered a non-volatile acid (Carslaw et al., 1995), some attempts have been made to measure the partial pressure of sulfuric acid ($P_{\text{H}_2\text{SO}_4(\text{g})}$) over aqueous solutions (e.g., Ayers et al., 1980). A Henry's Law constant for sulfuric acid ($K_{\text{H}} = a_{\text{H}_2\text{SO}_4(\text{aq})}/P_{\text{H}_2\text{SO}_4(\text{g})}$) (Table 2) was derived from $a_{\text{H}_2\text{SO}_4(\text{aq})}$ estimated with the newly acid-parameterized FREZCHEM model and $P_{\text{H}_2\text{SO}_4(\text{g})}$ estimated from the AIM model over temperatures ranging from 213 to 298 K.

The standard error of the derived model in reproducing the water activities and the natural logarithm of the bisulfate equilibrium (Eqn. 11) of the Clegg and Brimblecombe (1995) model is 0.29% ($n = 950$). Goodness-of-fit for water activities at +25 and -25°C is shown in Fig. 5a. The error magnitude for sulfuric acid is similar to nitric acid and less than hydrochloric acid (cf., Figs. 2a, 4a, and 5a).

Predictions of ice and solid-phase sulfuric acid equilibria with sulfuric acid solutions are in excellent agreement with the experimental measurements (Linke, 1965; Clegg and Brimblecombe, 1995) (Fig. 5b). The predicted eutectic for $\text{H}_2\text{SO}_4 \cdot 6.5\text{H}_2\text{O}$ -Ice occurs at a composition of 5.68 m at a temperature of -62.0°C , which is in excellent agreement with experimental measurements of 5.68 m at a temperature of -62.0°C (Linke, 1965).

3.5. Mixed Acid Systems

Mixtures of HCl with aqueous H_2SO_4 or HNO_3 can be satisfactorily modeled by assigning values of 0.0 to ternary interaction parameters (Carslaw et al., 1995; Clegg et al., 1998). In this work, values of 0.0 were assigned to $\Psi_{\text{Cl},\text{SO}_4,\text{H}}$ and $\Psi_{\text{Cl},\text{NO}_3,\text{H}}$; a literature value of 0.013 was assigned to $\Psi_{\text{Cl},\text{HSO}_4,\text{H}}$ (Pitzer, 1991). The only acid system where ternary

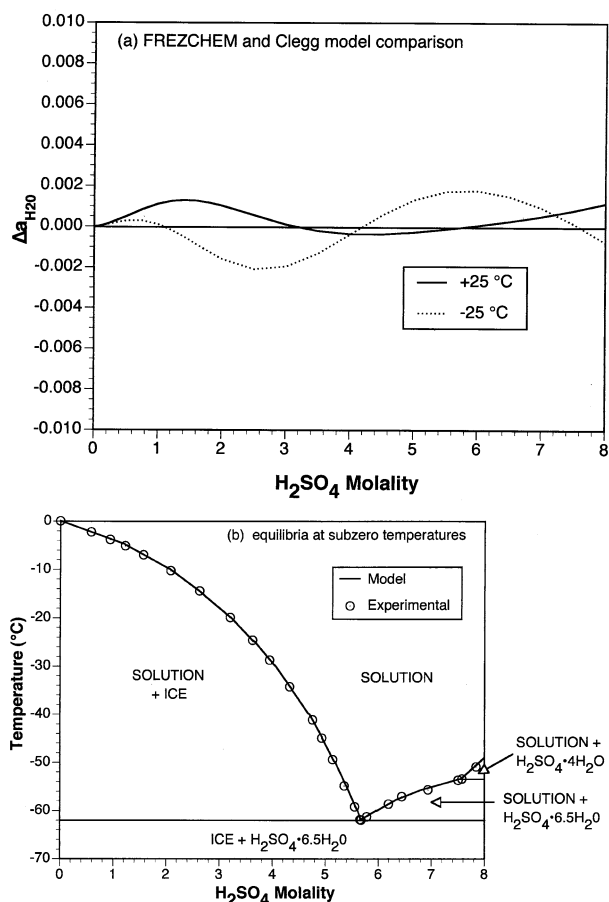


Fig. 5. Sulfuric acid solutions. (a) The difference in the activity of water ($\Delta a_{\text{H}_2\text{O}}$) between the Clegg mole-fraction model (database) and the derived molal model at 25 and -25°C . (b) Model and experimental estimates of equilibria at subzero temperatures.

interaction parameters are critical is the $\text{H}-\text{NO}_3-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ system.

The database for estimating the $\text{HNO}_3-\text{HSO}_4-\text{SO}_4$ ternary interaction parameters was generated with the mole-fraction AIM model. Acid concentrations ranged from 0.01 to 8.0 m H_2SO_4 and from 0.01 to 5.0 m HNO_3 , and temperatures ranged from 208 to 298 K in 10 K increments. Both water activities and " α " values were used in deriving the ternary parameters. See the previous $\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ discussion for how " α " values were used. The total number of model-generated datapoints for this analysis was 400 (20 compositions \times 10 temperatures \times 2 datasets). Estimated temperature-dependent ternary parameters included: $\theta_{\text{NO}_3,\text{HSO}_4}$, $\theta_{\text{NO}_3,\text{SO}_4}$, $\Psi_{\text{NO}_3,\text{HSO}_4,\text{H}}$, and $\Psi_{\text{NO}_3,\text{SO}_4,\text{H}}$ (Table 3).

The standard error of the derived model in reproducing the water activities and natural logarithm of the bisulfate equilibrium (Eqn. 11) of the AIM model is 0.59% ($n = 400$). A good dataset for evaluating the model fit is the fpd data of Carpenter and Lehrman (1925). The model calculations, using the experimental stoichiometric concentrations and the model binary and ternary parameters, provide a reasonably good estimate of the activity of water in equilibrium with ice for these mixed $\text{HNO}_3-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ systems (Fig. 6). The calculated eutectic for this

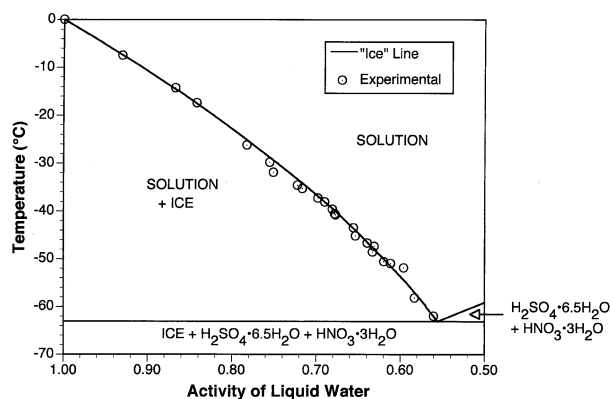


Fig. 6. Model and experimental estimates of equilibria at subzero temperatures for sulfuric-nitric acid solutions.

system is 0.654 m HNO₃ and 5.350 m H₂SO₄ at a temperature of -63.1°C (1.1°C lower than the pure H₂SO₄ system, Fig. 5b). No experimental determination of this equilibrium is available for comparison.

The FREZCHEM model is structured to input acidity directly by explicitly specifying the hydrogen and acid anion (Cl, NO₃, SO₄) concentrations or indirectly by specifying the atmospheric concentrations of acids ($P_{\text{HCl(g)}}$, $P_{\text{HNO}_3\text{(g)}}$, $P_{\text{H}_2\text{SO}_4\text{(g)}}$), which are then equilibrated with the solution phase. For an acidic system ($\text{pH} < 4.5$), electrostatic charge balance requires that:

$$[\text{H}^+] + [\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] = [\text{Cl}^-] + [\text{NO}_3^-] + [\text{HSO}_4^-] + 2[\text{SO}_4^{2-}] \quad (13a)$$

This equation can be rewritten as

$$[\text{H}^+] + \Delta_i = \frac{K_{\text{HCl}} P_{\text{HCl(g)}}}{\gamma_{\text{H}} \gamma_{\text{Cl}}} [\text{H}^+] + \frac{K_{\text{HNO}_3} P_{\text{HNO}_3\text{(g)}}}{\gamma_{\text{H}} \gamma_{\text{NO}_3}} [\text{H}^+] + \frac{K_{\text{H}_2\text{SO}_4} P_{\text{H}_2\text{SO}_4\text{(g)}}}{K_{\text{HSO}_4} \gamma_{\text{HSO}_4} \gamma_{\text{H}}} [\text{H}^+] + \frac{2K_{\text{H}_2\text{SO}_4} P_{\text{H}_2\text{SO}_4\text{(g)}}}{(\gamma_{\text{H}})^2 \gamma_{\text{SO}_4}} [\text{H}^+]^2 \quad (13b)$$

where $\Delta_i = [\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}]$, which are “non-acid” cations estimated by the existing FREZCHEM model, and $P_{\text{HA(g)}}$ are acid gas partial pressures with $K_{\text{HA}} = a_{\text{HA(aq)}}/P_{\text{HA(g)}}$. The model calculates the activity coefficients (γ) and the equilibrium constants (K), and the $P_{\text{HCl(g)}}$, $P_{\text{HNO}_3\text{(g)}}$, and $P_{\text{H}_2\text{SO}_4\text{(g)}}$ are gas partial pressures specified as input to the model. This leaves only the $[\text{H}^+]$ concentration as an unknown that is then solved for by successive approximations. By this means, the model can use gas-phase properties to constrain the solution phase.

3.6. Nitrate Salt Systems

Incorporation of nitric acid into the model served as a baseline for considering nitrate salts. In this work, NaNO₃ (soda niter), KNO₃ (niter), and NaNO₃·Na₂SO₄·2H₂O (darapskite) were selected as the most likely nitrate salts to be found in natural environments (Palache et al., 1951; Garrels and Christ, 1965). Since calcium nitrate and magnesium nitrate salts are rare in nature, they were excluded.

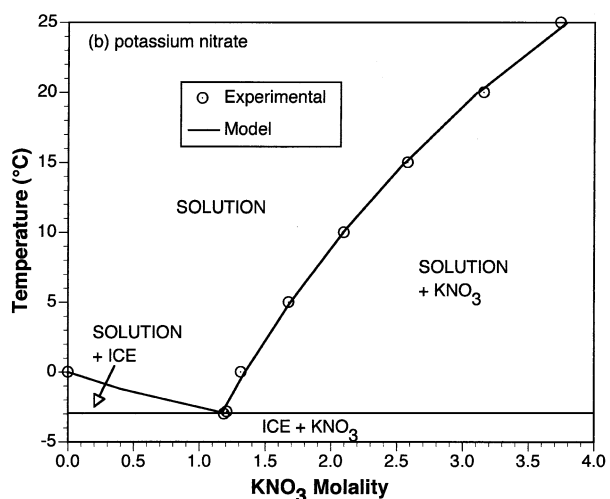
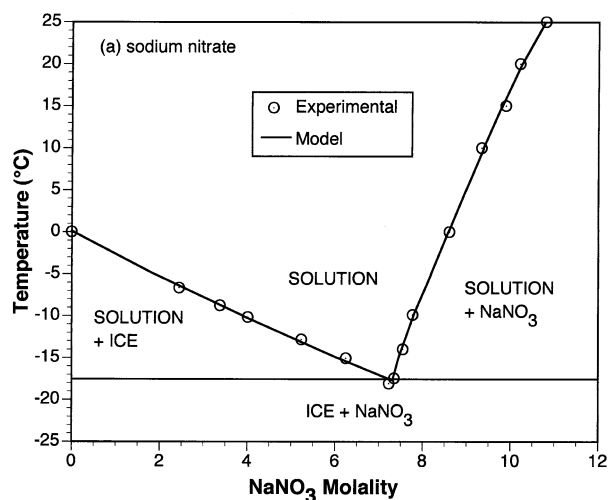


Fig. 7. Model and experimental estimates of equilibria as a function of temperature and concentration for (a) sodium nitrate, and (b) potassium nitrate.

Binary Pitzer-equation parameters for Na-NO₃ interactions were estimated from mean activity coefficient and osmotic coefficient data at 25°C , solubility data over a range of temperatures, and fpd data at subzero temperatures (Linke, 1965; Hamer and Wu, 1972). An iterative process was used. First the mean activity coefficient, osmotic coefficient, and fpd data were used to estimate binary parameters. Second, the binaries were used to estimate the NaNO₃ solubility product. Third, the solubility data were incorporated into the analysis with the solubility product. This was repeated until successive estimates of the parameters provided no further improvement. Temperature-dependent binary parameters for $C_{\text{Na,NO}_3}^{\phi}$, $\beta_{\text{Na,NO}_3}^{(1)}$, and $\beta_{\text{Na,NO}_3}^{(0)}$ are listed in Table 3, and the NaNO₃ solubility product is listed in Table 2. The model provides a good fit to the experimental solubility and fpd data (Fig. 7a). The model estimate of the eutectic occurs at a molality of 7.30 m NaNO₃ at a temperature of -17.6°C , in reasonably good agreement with two experimental estimates that place the molalities between 7.23 and 7.35 m NaNO₃ with temperatures between -17.5 and -18.1°C (Fig. 7a) (Linke, 1965).

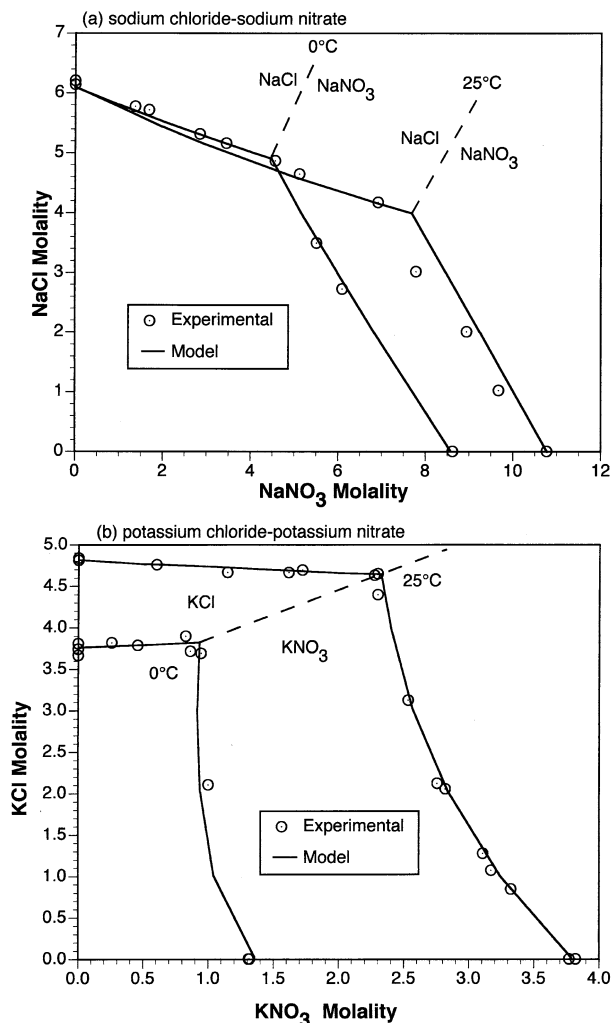


Fig. 8. Model and experimental estimates of solubilities at 0 and 25 °C for (a) sodium chloride-sodium nitrate, and (b) potassium chloride-potassium nitrate.

Temperature-dependent binary Pitzer-equation parameters for K-NO₃ interactions were estimated from mean activity coefficient and osmotic coefficient data at 25°C, solubility data over a range of temperatures, and fpd data at subzero temperatures (Linke, 1965; Hamer and Wu, 1972) in an iterative manner similar to that used for NaNO₃ (see above). These binary parameters (Table 3) were used, in turn, with niter solubility data to estimate a solubility product for niter (Table 2). The model provides a good fit to the solubility and fpd data (Fig. 7b). Two experimental estimates of the eutectic place the molalities between 1.19 and 1.21 m KNO₃ with temperatures between -2.84 and -3.0°C (Linke, 1965), while the model predicts a KNO₃ molality of 1.18 m at a temperature of -2.9°C (Fig. 7b).

The ternary parameter, $\Psi_{\text{Cl,NO}_3,\text{Na}}$, was estimated from NaCl-NaNO₃ solubility data at 0, 20, and 25°C (Linke, 1965) (Table 3). The solubility data at 0 and 25°C completely overlap in the region where NaCl is the precipitating salt (Fig. 8a). In this case, the fit of the model to the experimental solubility data

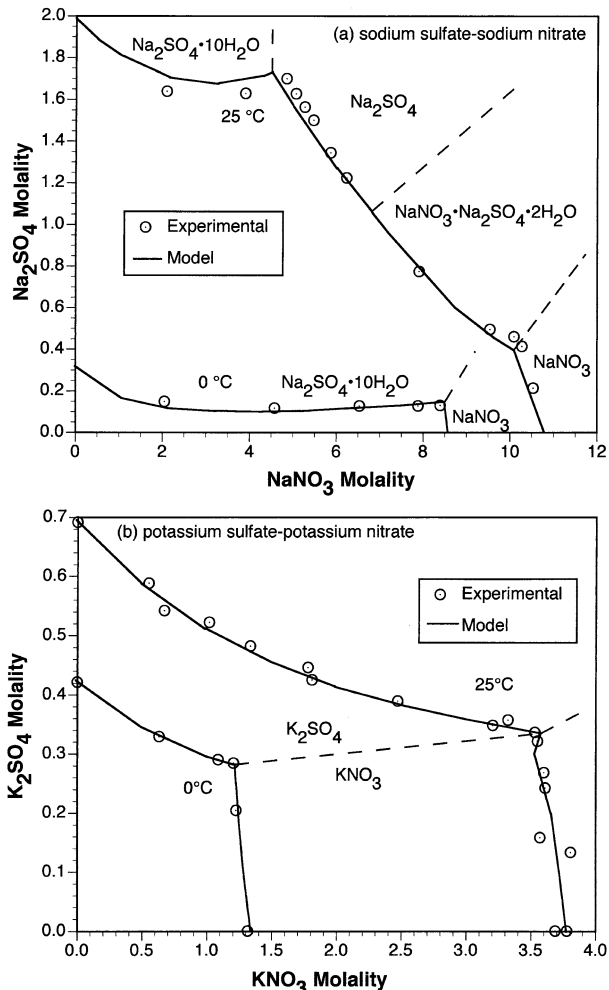


Fig. 9. Model and experimental estimates of solubilities at 0 and 25 °C for (a) sodium sulfate-sodium nitrate, and (b) potassium sulfate-potassium nitrate.

is better at 0°C (SE = 2.1%) than at 25°C (SE = 6.7%). Attempts to refine $\Psi_{\text{Cl,NO}_3,\text{Na}}$ to improve the fit at 25°C were unsuccessful. Any adjustment of $\Psi_{\text{Cl,NO}_3,\text{Na}}$ to improve the fit to the NaCl solubility data resulted in a poorer fit to NaNO₃ solubility data and vice versa.

The ternary parameter, $\Psi_{\text{Cl,NO}_3,\text{K}}$, was estimated from KCl-KNO₃ solubility data at 0, 10, 18.5, 20.5, and 25°C (Linke, 1965) (Table 3). In this case, the fit of the model to the experimental data is equally good at 0 and 25°C (Fig. 8b).

The ternary parameter, $\Psi_{\text{NO}_3,\text{SO}_4,\text{Na}}$, was estimated from Na₂SO₄-NaNO₃ solubility data at 0, 20, and 25°C (Linke, 1965) (Table 3). The model provides a reasonable fit to the experimental data at 0 and 25°C (Fig. 9a). The calculated eutectic for this system occurs at -17.7°C with 0.031 m Na₂SO₄ and 7.30 m NaNO₃, in reasonably good agreement with an experimental evaluation that places the eutectic at -17.8°C with 0.014 m Na₂SO₄ and 7.13 m NaNO₃ (Linke, 1965).

The ternary parameter, $\Psi_{\text{NO}_3,\text{SO}_4,\text{K}}$, was estimated from K₂SO₄-KNO₃ solubility data at 0 and 25°C (Linke, 1965) (Table 3). In this case, the model matches the experimental data

Table 4. A Summary of the Temperature-Independent Ternary Pitzer-Equation Parameters Derived in this Work or Taken from the Literature (Footnoted).

Cations(c,c')	$\theta_{cc'}$	$\Psi_{cc'}\text{Cl}$	$\Psi_{cc'}\text{SO}_4$	$\Psi_{cc'}\text{HSO}_4$	$\Psi_{cc'}\text{NO}_3$
H, Na	0.036 ^a	-0.0037	—	-0.0129 ^a	— ^b
H, K	0.005 ^a	-0.0114	— ^b	-0.0303	— ^b
H, Mg	0.10 ^a	-0.0077	—	— ^b	—
H, Ca	0.092 ^a	-0.0142	—	—	—
Na, K	— ^c	— ^c	— ^d	—	-0.0012 ^a
Na, Mg	— ^c	— ^c	— ^d	—	-0.0099
Na, Ca	— ^d	— ^c	— ^d	—	— ^b
K, Mg	— ^c	— ^c	— ^d	—	— ^b
K, Ca	— ^c	— ^c	— ^d	—	— ^b

Anions (a,a')	$\theta_{aa'}$	$\Psi_{aa'}\text{H}$	$\Psi_{aa'}\text{Na}$	$\Psi_{aa'}\text{K}$	$\Psi_{aa'}\text{Mg}$	$\Psi_{aa'}\text{Ca}$
Cl, NO ₃	0.016 ^a	—	— ^b	— ^b	0.0046	-0.0409
Cl, HSO ₄	-0.006 ^a	0.013 ^a	-0.006 ^a	—	—	—
NO ₃ , HSO ₄	— ^b	— ^b	—	—	—	—
SO ₄ , HSO ₄	—	—	-0.0094 ^a	-0.0677 ^a	— ^b	—
SO ₄ , NO ₃	— ^b	— ^b	— ^b	— ^b	— ^b	-0.2281
NO ₃ , HCO ₃	—	—	0.0061	—	—	—
NO ₃ , CO ₃	—	—	0.0132	0.0075	—	—

^a From Pitzer, 1991.

^b See Table 3.

^c See Spencer et al., 1990.

^d See Marion and Farren, 1999.

equally well at 0 and 25°C (Fig. 9b). The calculated eutectic temperature is -3.3°C with 0.268 m K₂SO₄ and 1.028 m KNO₃, in good agreement with an experimental evaluation that places the temperature at -3.3°C with 0.270 m K₂SO₄ and 1.019 m KNO₃ (Linke, 1965).

Pitzer-equation binary parameters for Mg-NO₃ and Ca-NO₃ were derived from the temperature-dependent equations of Pitzer (1991) (Table 3). In addition, the literature contains a scattering of solubility data over temperatures ranging from 0 to 25°C (Linke, 1965) that were used to estimate the following ternary interaction parameters: $\Psi_{\text{Na,Mg,NO}_3}$, $\Psi_{\text{Na,Ca,NO}_3}$, $\Psi_{\text{K,Mg,NO}_3}$, $\Psi_{\text{K,Ca,NO}_3}$, $\Psi_{\text{NO}_3,\text{Cl,Mg}}$, $\Psi_{\text{NO}_3,\text{Cl,Ca}}$, $\Psi_{\text{NO}_3,\text{SO}_4,\text{Mg}}$, $\Psi_{\text{NO}_3,\text{SO}_4,\text{Ca}}$, $\Psi_{\text{NO}_3,\text{HCO}_3,\text{Na}}$, $\Psi_{\text{NO}_3,\text{CO}_3,\text{Na}}$, and $\Psi_{\text{NO}_3,\text{CO}_3,\text{K}}$ (Tables 3 and 4).

3.7. Acid-Salt Systems

3.7.1. HCl-Chloride Salt Systems

Ternary interaction parameters for HCl with NaCl, KCl, Mg(Cl)₂, and Ca(Cl)₂ salts were estimated from solubility data between 0 and 25°C. In contrast to nitric and sulfuric acids, hydrochloric acid ternary parameters show no significant temperature dependence. The calculated values for $\Psi_{\text{Na,H,Cl}}$, $\Psi_{\text{K,H,Cl}}$, $\Psi_{\text{Mg,H,Cl}}$, and $\Psi_{\text{Ca,H,Cl}}$ are -0.0037, -0.0114, -0.0077, and -0.0142, respectively (Table 4). These values are similar to those of Harvie et al. (1984), which are -0.004, -0.011, -0.011, and -0.015, respectively. Goodness-of-fit (not presented) is similar to Harvie et al. (1984, their Fig. 4a).

Abundant fpd data for mixed HCl-chloride salt systems were not used in estimating the Ψ values. Instead, these data were used to test the two HCl models (see Fig. 3 and the accompanying discussion).

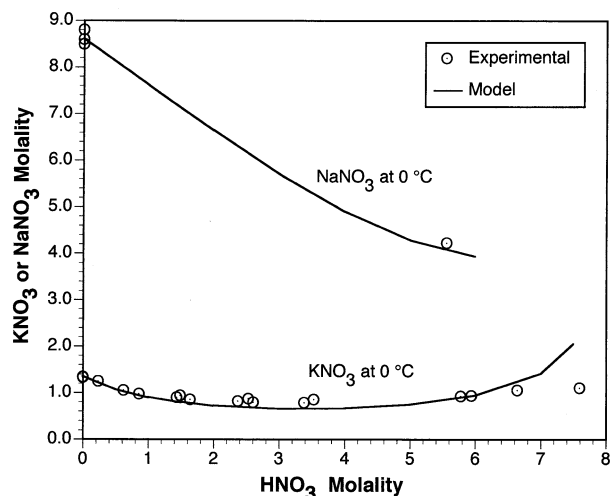


Fig. 10. Model and experimental estimates of potassium nitrate and sodium nitrate solubilities at 0 °C as a function of nitric acid concentration.

3.7.2. HNO₃-Nitrate Salt Systems

There are only limited data available for nitrate salt solubilities in nitric acid at molalities <8 m [for NaNO₃, n = 5; for KNO₃, n = 25 (Linke, 1965)]. Nevertheless, temperature-dependent values for $\Psi_{\text{Na,H,NO}_3}$ and $\Psi_{\text{K,H,NO}_3}$ were estimated from data over temperatures ranging from 0 to 25°C (Table 3). Only for KNO₃ in HNO₃ at 0°C is there an adequate database (n = 15). In this case, the model fits the experimental data reasonably well up to 6 m HNO₃, after which there is a significant discrepancy between the model and the experimental data (Fig. 10).

This discrepancy illustrates a problem with the FREZCHEM model as it is presently structured. The problem is accurately calculating activity coefficients in some cases where the activity coefficients become very small. For example, the calculated activity coefficients for the K⁺ ion in 6.0, 7.0, and 7.5 m HNO₃ (Fig. 10) are 0.0278, 0.0161, and 0.0114, respectively. In this case and others cited below, the model does not always accurately estimate activity coefficients in concentrated solutions. This causes the model to be inaccurate or, at times, to figuratively “blow up.” Where the nitric acid concentration is 8.0 m (Fig. 10), for example, the model predicts that KNO₃ is infinitely soluble, a result that is inconsistent with experimental measurements. These results indicate that care must be taken in applying the FREZCHEM model and interpreting the output across a broad range of compositions and temperatures (see further discussion in Section 5. Limitations).

3.7.3. H₂SO₄-Sulfate Salt Systems

There is abundant solubility data on mixed Na₂SO₄-H₂SO₄ systems for temperatures ranging from -30 to 25°C (Linke, 1965). Data at 0, 5, 12.5, 14, 23, and 25 °C were used to estimate a temperature-dependent equation for $\beta_{\text{Na}_2\text{SO}_4}^{(1)}$. All other binary and ternary parameters needed to define equilibrium in this system were either taken from the literature or previously defined in this work (Tables 3 and 4). The only

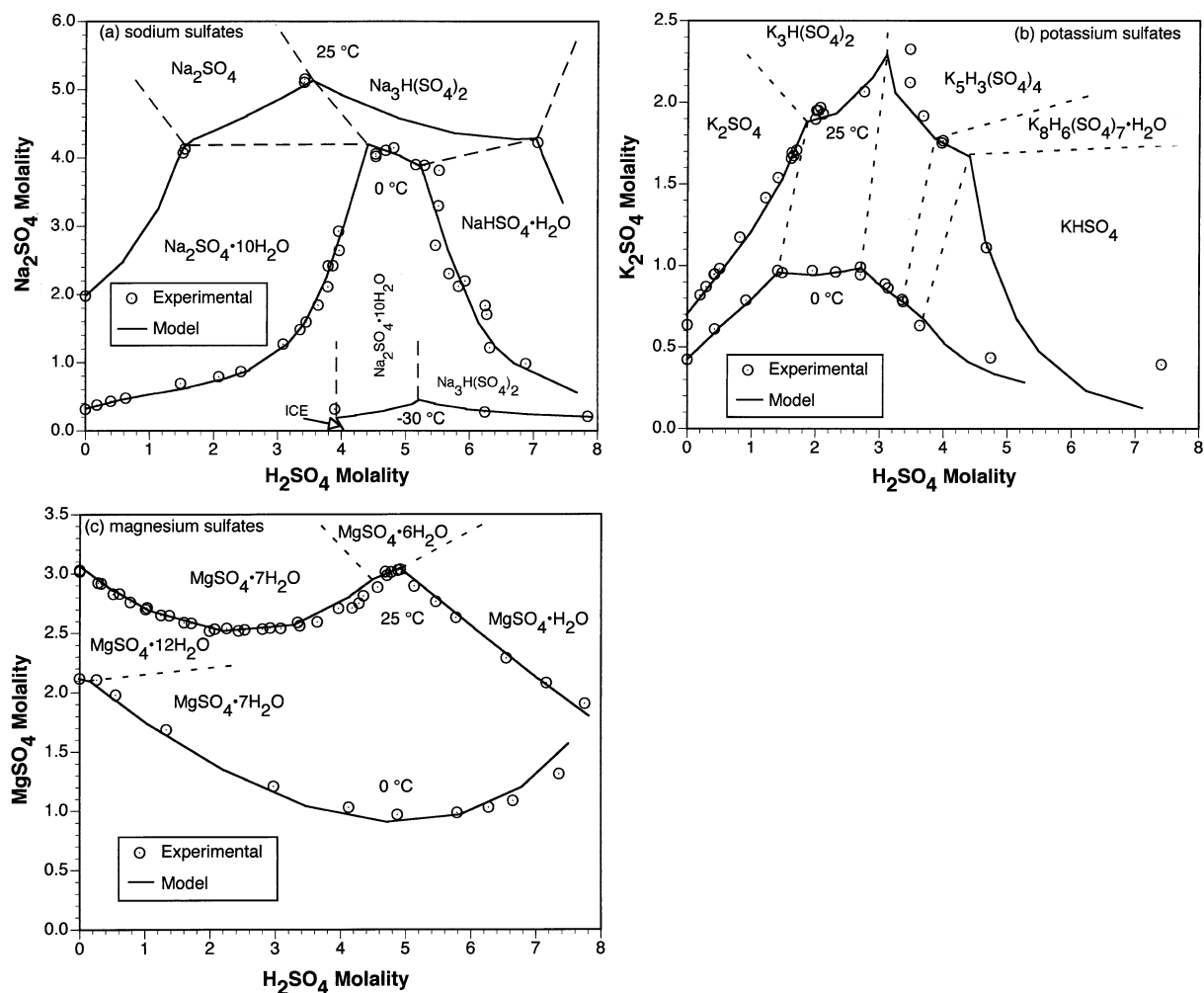


Fig. 11. Model and experimental estimates of sulfate salt solubilities as a function of sulfuric acid concentration for (a) sodium sulfate, (b) potassium sulfate, and (c) magnesium sulfate.

exceptions are the binary Na-SO₄ parameters ($C_{\text{Na}_2\text{SO}_4}^\phi$, $\beta_{\text{Na}_2\text{SO}_4}^{(0)}$, and $\beta_{\text{Na}_2\text{SO}_4}^{(1)}$), which were modified from a previous model (Marion and Farren, 1999). As was the case for the previously mentioned KNO₃-HNO₃ system (Fig. 10), it was difficult to estimate Na₂SO₄-H₂SO₄ parameters because the calculated activity coefficients for the sulfate ion become very small (e.g., $\gamma_{\text{SO}_4} = 0.0028$ where Na₂SO₄ and Na₃H(SO₄)₂ are in equilibrium at 25°C) (Fig. 11a). To address this problem, it was necessary to modify the previous binary equations for Na-SO₄ interaction parameters by re-estimating the parameter set at 25°C based on activity coefficient data that extended the model fit from 2 m to 4 m Na₂SO₄ (saturation \approx 2 m) (Robinson and Stokes, 1970). This new parameter set at 25°C was then integrated into the previously defined model to produce new equations for $C_{\text{Na}_2\text{SO}_4}^\phi$, $\beta_{\text{Na}_2\text{SO}_4}^{(0)}$, and $\beta_{\text{Na}_2\text{SO}_4}^{(1)}$ (Table 3). This modification significantly improves the fit to the experimental data at 25°C (Fig. 11a) without significantly altering the previously defined equilibria (Marion and Farren, 1999). For example, the revised model predicts that mirabilite equilibrium for a pure Na₂SO₄ solution occurs at 1.987 m Na₂SO₄, while the older version predicts equilibrium at 1.967 m Na₂SO₄; both

calculated molalities fall within the range of published values for this equilibrium, which ranges from 1.9 to 2.0 m Na₂SO₄ (Marion and Farren, 1999). Solubility products for mirabilite and thenardite were taken from a previous paper (Marion and Farren, 1999). Solubility products for Na₃H(SO₄)₂ and NaHSO₄·H₂O were estimated from mineral solubility data (Bukhshtein et al., 1953; Linke, 1965) and the Pitzer equation parameters used in this work (Tables 3 and 4).

The model provides an excellent fit to the experimental data at -30, 0, and 25°C (Fig. 11a). There are only three datapoints at -30°C, all of which represent equilibrium with respect to Na₃H(SO₄)₂. Two of these points fall on the model equilibrium line for Na₃H(SO₄)₂ at -30°C (Fig. 11a). The third observation at 0.311 m Na₂SO₄ and 3.90 m H₂SO₄ is a metastable equilibrium (Linke, 1965), which agrees qualitatively with the model that predicts the stable equilibrium in the vicinity of this datapoint is an ice-mirabilite mixture at 0.189 m Na₂SO₄ and 3.93 m H₂SO₄ (Fig. 11a).

Solubility data for arcanite in K₂SO₄-H₂SO₄ systems at 0, 18, and 25°C (Bukhshtein et al., 1953; Linke, 1965) and a solubility product for arcanite from a previous paper (Marion

and Farren, 1999) were used to estimate $\beta_{\text{K,HSO}_4}^{(1)}$, $\Psi_{\text{K,H,SO}_4}$, and $\Psi_{\text{K,H,HSO}_4}$ (Tables 3 and 4). All other parameters needed to define equilibria in this system were taken from the literature or previously defined in this work (Tables 3 and 4). This analysis was complicated by the fact that the solid phases precipitating are not always specifically identified. For example, experimental work at 0°C indicates that there are two unidentified phases between $\text{K}_3\text{H}(\text{SO}_4)_2$ and KHSO_4 (Bukshstein et al., 1953; Linke, 1965). Based on data at other temperatures, an assumption was made that these two phases are $\text{K}_5\text{H}_3(\text{SO}_4)_4$ and $\text{K}_8\text{H}_6(\text{SO}_4)_7 \cdot \text{H}_2\text{O}$. With this K-H- HSO_4 - SO_4 parameterization and experimental salt solubilities, solubility products for $\text{K}_3\text{H}(\text{SO}_4)_2$, $\text{K}_5\text{H}_3(\text{SO}_4)_4$, $\text{K}_8\text{H}_6(\text{SO}_4)_7 \cdot \text{H}_2\text{O}$, and KHSO_4 were calculated (Table 2).

The model provides a reasonable fit to the experimental data at 0 and 25°C (Fig. 11b). Note that the stability field for $\text{K}_5\text{H}_3(\text{SO}_4)_4$ at 25°C in Figure 11b is hypothetical based on extrapolation of the solubility product from lower temperatures (0 and 18°C). The datapoints that fall in the $\text{K}_5\text{H}_3(\text{SO}_4)_4$ stability field are actually $\text{K}_8\text{H}_6(\text{SO}_4)_7 \cdot \text{H}_2\text{O}$ solubility data. At 25°C, the model underestimates the solubility of KHSO_4 at high H_2SO_4 molalities (>6m); again the problem is that the K^+ ion activity coefficient is not accurately modeled in this case (see also Fig. 10).

The only temperature-dependent parameters estimated for this system were $\beta_{\text{K,HSO}_4}^{(1)}$ and $\Psi_{\text{K,H,SO}_4}$. These derived parameters do not extrapolate well to subzero temperatures, causing the model to “blow up.” For all extrapolations to subzero temperatures, the values for the latter Pitzer-equation parameters at 0°C should be used. These assumptions lead to declining K salt solubilities similar to the Na salt solubilities (Fig. 11a) at subzero temperatures.

Solubility data at 0, 13, and 25°C (D’Ans and Freund, 1960) for MgSO_4 salts in H_2SO_4 were used to estimate binary ($C_{\text{Mg,HSO}_4}^\phi$, $\beta_{\text{Mg,HSO}_4}^{(0)}$, $\beta_{\text{Mg,HSO}_4}^{(1)}$) and ternary ($\Psi_{\text{Mg,H,HSO}_4}$, $\Psi_{\text{SO}_4,\text{HSO}_4,\text{Mg}}$) Pitzer-equation parameters (Table 3). With these equations and others previously defined, a solubility product for kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) was estimated at 0, 13, and 25°C and added to the model mineral database (Table 2).

The model fits the experimental data for the MgSO_4 - H_2SO_4 system reasonably well, with the exception of high H_2SO_4 molalities at 0°C (Fig. 11c). The latter discrepancy is again due to an inaccurate model parameterization in a region where an activity coefficient is low ($\gamma_{\text{SO}_4} = 0.033$). The model predicts a small stability field for hexahydrate between epsomite and kieserite at 25°C. The model also predicts a small stability field for $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ at 0°C. According to the model, the $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ -epsomite equilibrium at 0°C occurs at 0.16 m H_2SO_4 and 2.09 m MgSO_4 , in good agreement with an experimental estimate of 0.26 m H_2SO_4 and 2.10 m MgSO_4 (D’Ans and Freund, 1960).

As was the case for K_2SO_4 - H_2SO_4 , the MgSO_4 - H_2SO_4 Pitzer-equation parameters also do not extrapolate well to subzero temperatures. As a consequence, the parameter values for 0°C should be used for all subzero temperatures until such time as experimental measurements can better constrain the model at subzero temperatures. The consequences of these assumptions on subzero simulations will be illustrated below under “Application to Europa.”

Data at 25°C for the CaSO_4 - H_2SO_4 system (Marshall and

Jones, 1966) were used to estimate $\beta_{\text{Ca,HSO}_4}^{(0)}$ and $\beta_{\text{Ca,HSO}_4}^{(1)}$ (Table 3). The fit of the model to the experimental data (not presented) is similar to Harvie et al. (1984, their Fig. 4e). While this parameterization works well at 25°C, these parameters might vary at lower temperatures.

4. VALIDATION

The fit of model calculations to experimental data (Figs. 2b, 3, 4b, 5b, 6 to 11) and the ability of the model to simulate critical equilibria such as peritectics and eutectics are a test of the internal consistency of the experimental data and the derived model. Because the special focus of this work is to develop a model for subzero temperatures, the fit of the model to data at subzero temperatures is especially important. The model estimates of eutectic temperatures agree with experimental measurements to within $\pm 0.2^\circ\text{C}$ for six cases either presented in graphs (Figs. 4b, 5b, 7a, 7b) or discussed in the text ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ - NaNO_3 -Ice and K_2SO_4 - KNO_3 -Ice). While these fits are encouraging, they do not constitute validation, which requires a comparison of the model output to independent data.

Of the data presented so far, only Figure 3 and the accompanying discussion compare the model to independent data (fpd data for HCl-chloride salt systems) not explicitly used in the parameterization. In that case, the data were used to test which of two models for HCl parameterization is more accurate. From this analysis, the pure fpd HCl database at subzero temperatures was found to be flawed and unreliable, in agreement with Carslaw et al. (1995).

Many of the comparisons between model calculations and experimental data are for mineral solubilities (Figs. 7 to 11). The ability of the model to accurately predict solution properties at molalities lower than mineral saturation is also important. Estimates were made of the mean activity coefficients at 0.1 and 1.0 m NaNO_3 , KNO_3 , $\text{Mg}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, HCl, and HNO_3 at 25°C and compared to experimental estimates compiled by Robinson and Stokes (1970). In all 12 cases, the model mean activity coefficients, which range from 0.34 to 0.80, agree to within $\pm 1.2\%$ with the experimental data. The average deviation is -0.19% .

The FREZCHEM acid model can be compared to the Harvie et al. (1984) (HMW) model at 25°C. The HMW model (evaluated using the TEQUIL version at <http://geotherm.ucsd.edu/tequil/tequil.html>) predicts a water activity of 0.4812 and a *K* (bisulfate equilibrium) of 0.0105 at 25°C in 8.0 m H_2SO_4 . This results in good agreement with the Clegg model (0.4816 and 0.0105) and the FREZCHEM model (0.4829 and 0.0105). All three models are able to reproduce the primary databases [mean activity coefficients and water activities (or osmotic coefficients)] to within model error bars (e.g., Fig. 5a).

The distribution of species (H^+ , HSO_4^- , SO_4^{2-}) is, however, quite different between the Clegg and FREZCHEM models and the HMW model. For example, at 8.0 m H_2SO_4 at 25°C, α [$= \text{SO}_4^{2-}/(\text{HSO}_4^- + \text{SO}_4^{2-})$] is equal to 0.2399 in the Clegg model, 0.2370 in the FREZCHEM model, and 0.0594 in the HMW model. The ionic strength of this solution is 11.79 m for the FREZCHEM model, 11.84 m for the Clegg model, and 8.95 m for the HMW model. These differences are due to different parameterizations.

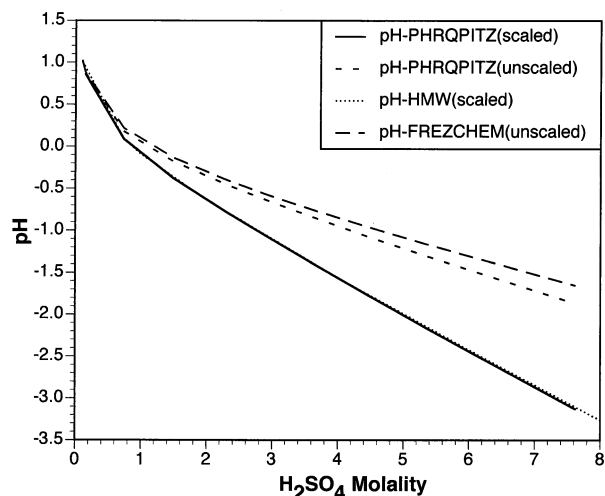


Fig. 12. A comparison of calculated pH values among the PHRQPITZ, HMW, and FREZCHEM models.

Another factor that influences calculated single ion activities is the convention used to define activity coefficients. In the FREZCHEM and Clegg models, the activity coefficients are calculated directly from the Pitzer equations. In the HMW model, the MacInnis convention is used to “scale” Pitzer activity coefficients (Harvie et al., 1984; Plummer et al., 1988; Nordstrom et al., 2000). This results in very different single ion activities, especially at high concentrations, even though all the models accurately predict experimentally measurable quantities such as mean activity coefficients and water activities.

These differences in parameterization and convention have consequences for estimating pH [$= -\log(a_{H^+})$] in concentrated acid solutions. For example, in Nordstrom et al. (2000), the PHRQPITZ model (Plummer et al., 1988) was used to calibrate concentrated sulfuric acid solutions for pH. The sulfuric acid chemistry in PHRQPITZ is based on the HMW model; therefore, the scaled pH values for the PHRQPITZ and HMW models are identical (Fig. 12). A comparison of unscaled pH values calculated with the FREZCHEM and PHRQPITZ (Nordstrom et al., 2000) models shows a small discrepancy that widens as pH drops (Fig. 12). This is due to a different parameterization. For example, the calculated pH values at 7.622 m H_2SO_4 are -1.66 for the FREZCHEM model and -1.87 for the PHRQPITZ model (unscaled); in contrast, the scaled pH of this solution calculated with either the PHRQPITZ or HMW models is -3.13 (Fig. 12). Since single ion activities cannot be unambiguously measured (Babcock, 1963), there is no definitive method to ascertain which of these models is more accurate in estimating pH. Nevertheless, the results of these comparisons (Fig. 12) point out the importance of conventions used to define activity coefficients and the importance of specific parameterizations when comparing model predictions.

5. LIMITATIONS

There are several limitations of the low-temperature acid model developed in this work that need to be considered in applying the model and interpreting the results. These limitations are due to (1) some poor datasets, (2) a paucity of data

especially at subzero temperatures, and (3) inherent problems in the model parameterization.

First, while the chemistries of pure HNO_3-H_2O (Fig. 4b), $H_2SO_4-H_2O$ (Fig. 5b), and $HNO_3-H_2SO_4-H_2O$ (Fig. 6) systems are unambiguously defined to their eutectics, this is not the case for $HCl-H_2O$ (Figs. 2b and 3). For pure HCl , much of the *fpd* data at subzero temperatures are flawed and unreliable. At present, the best alternative is to use the variable parameter model (with or without solid phase acids; see previous discussion) based on the work of Carslaw et al. (1995). This model is consistent with mixed HCl -chloride salt databases for $NaCl$, KCl , and $CaCl_2$ (Fig. 3).

The second limitation is that there are several cases where parameters are only defined for the temperature range from 0 to $25^\circ C$, and some of these parameters do not extrapolate well to subzero temperatures (e.g., $K_2SO_4-H_2SO_4-H_2O$ and $MgSO_4-H_2SO_4-H_2O$; see previous discussions). In the latter cases, this poor extrapolation is because some of the parameter equations are highly curvilinear. In these circumstances, using the $0^\circ C$ parameters at all subzero temperatures seems most prudent as this assumption leads to trends consistent with the experimental data for other similar systems (cf., Figs. 11a and 13a). For the nitrate salts, the coldest temperatures in the experimental databases are the eutectics for $NaNO_3$ -Ice ($-17.6^\circ C$, Fig. 7a), KNO_3 -Ice ($-2.9^\circ C$, Fig. 7b), $NaNO_3-Na_2SO_4$ -Ice ($-17.7^\circ C$), and $KNO_3-K_2SO_4$ -Ice ($-3.3^\circ C$). How well these nitrate Pitzer-equation parameters or the nitrate solubility products extrapolate to lower temperatures is an open question. On the other hand, there are parameters that were estimated for the temperature range from 0 to $25^\circ C$ that are, nevertheless, valid to much lower temperatures. For example, the ternary parameters for the HCl - KCl - H_2O system were estimated from data for the temperature range from 0 to $25^\circ C$ and are valid to at least $-33^\circ C$ (Fig. 3). In this particular case, the ternary parameters demonstrated no temperature dependence in the 0 to $25^\circ C$ range, which may account for their accurate extrapolation to lower temperatures.

Last, there are a number of instances where the model predicts poorly in certain ranges (e.g., Figs. 8a, 9a, 10, 11b, 11c). These problem areas are generally associated with regions where the activity coefficients are rapidly becoming smaller. This rapid change in activity coefficients is not just an artifact of the model but occurs with experimental data as well. For example, the datapoints in the stability field of $K_5H_3(SO_4)_4$ at $25^\circ C$ (Fig. 11b) are becoming vertically asymptotic. This rapid rise in solubility is caused by a rapid decline in the activity coefficients, a phenomenon not always predicted well by the model.

6. APPLICATION TO EUROPA

The near infrared mapping spectrometer (NIMS) satellite reflectance spectra from the “nonicy” regions of Europa’s surface indicate the presence of highly distorted water absorption bands suggesting the presence of bound water in compounds such as hydrated salts or acids (McCord et al., 1998, 1999; Carlson et al., 1999). The leading hypotheses to explain the surficial salt (or acid) assemblages on Europa are that salts (or acids) are forming from brines such as (1) $MgSO_4-Na_2SO_4-H_2O$ (the neutral hypothesis), (2) $Na_2SO_4-Na_2CO_3-H_2O$ (the

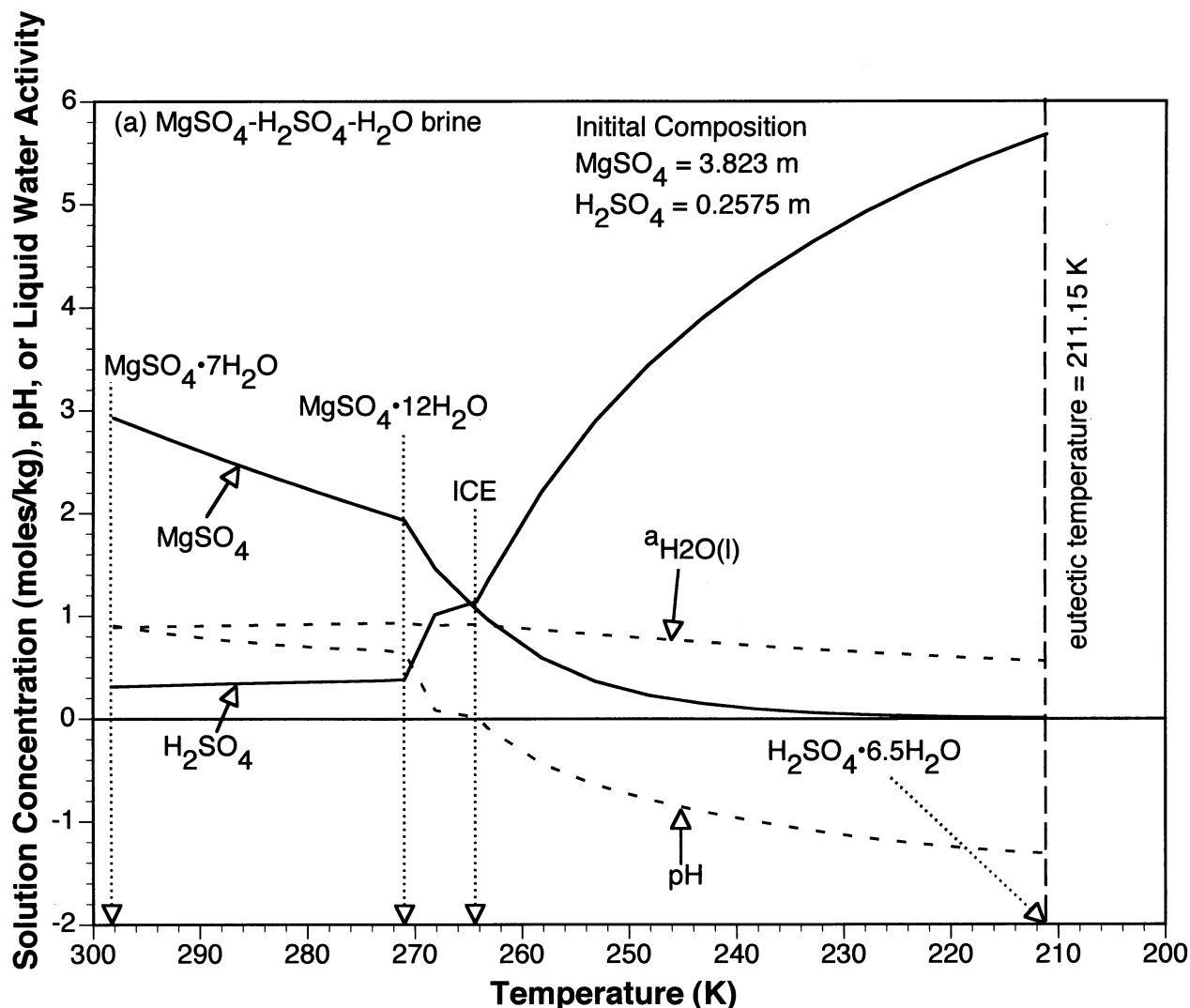


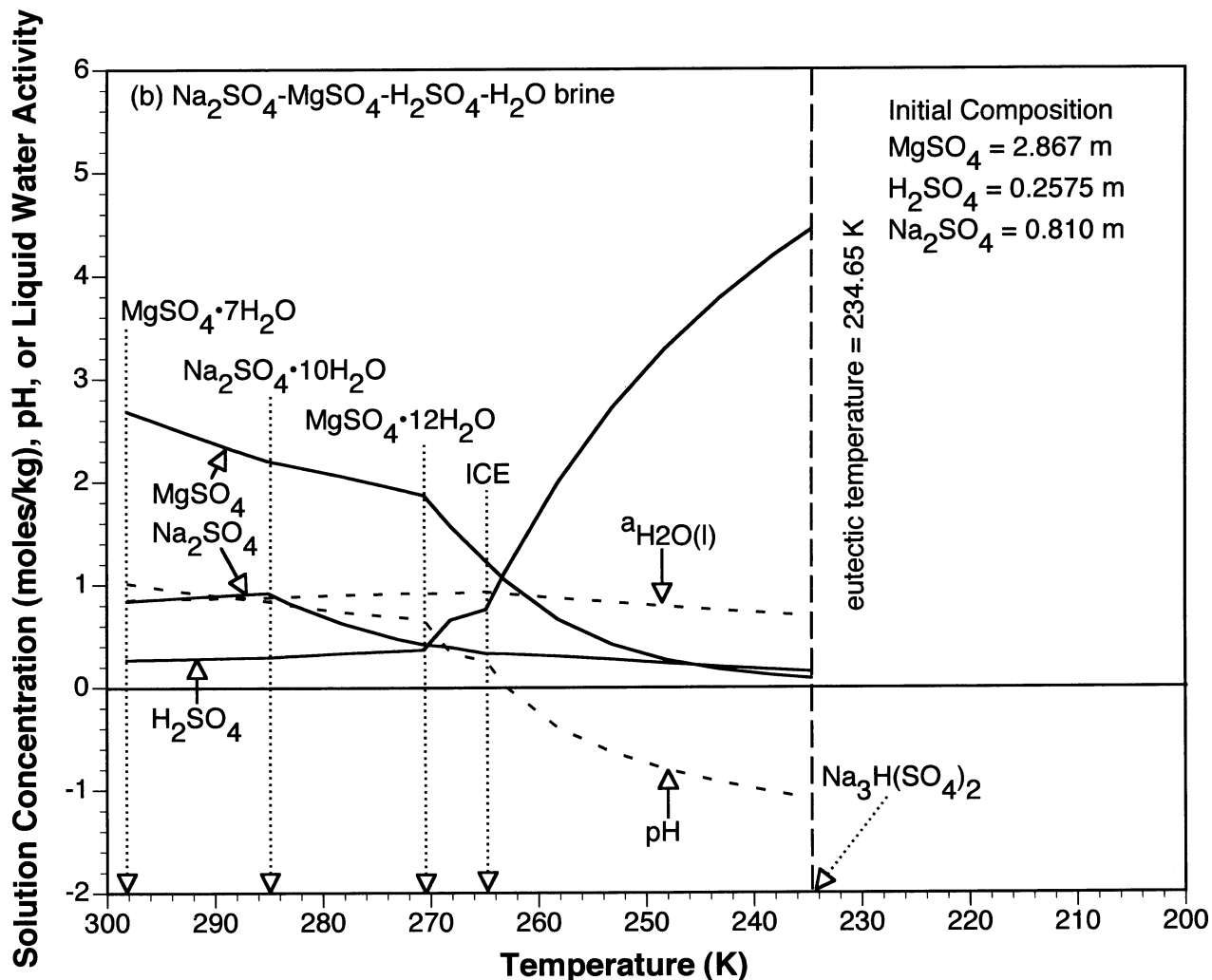
Fig. 13. Simulation of hypothetical brines for Europa. (a) a $\text{MgSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ brine, and (b) a $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ brine. Dashed arrows indicate the temperature where the solid phases begin to precipitate.

alkaline hypothesis), and (3) $\text{MgSO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ (the acid hypothesis) (McCord et al., 1998, 1999; Carlson et al., 1999; Kargel et al., 2000). In previous work, we examined the first (Kargel et al., 2000) and second (Marion, 2001) of these hypotheses. In this paper, we examine the third hypothesis as an example of how the acid model can be applied.

Incorporation of acid chemistry into the FREZCHEM model allows examination of the role of acids on the freezing process to their eutectics. A hypothetical $\text{MgSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ solution based on low temperature leaching of chondritic material to produce MgSO_4 and high-temperature devolatilization and venting of SO_2 into the ocean to produce H_2SO_4 was developed for Europa (Kargel et al., 2001). This hypothetical solution is 67.32% H_2O , 30.98% MgSO_4 , and 1.70% H_2SO_4 (Kargel et al., 2001). In molal units, this initial solution is 3.823 m MgSO_4 and 0.2575 m H_2SO_4 . The model predicts that this solution is supersaturated with respect to epsomite at 298 K (Fig. 13a). As temperature decreases, epsomite is eventually replaced by

$\text{MgSO}_4\cdot 12\text{H}_2\text{O}$ around 271 K, and ice starts forming around 264 K. Formation of the latter two highly hydrated solid phases causes a rapid rise of H_2SO_4 and a rapid decline of MgSO_4 (Fig. 13a). The eutectic temperature and composition ultimately reached by this system is essentially the same as that reached for pure H_2SO_4 (Fig. 5b) because the predicted concentration of MgSO_4 approaches zero at the eutectic.

We also simulated a $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ system by partitioning the salt content (30.98%) into Na_2SO_4 (25%) and MgSO_4 (75%) components that are representative of carbonaceous chondrites (J.S. Kargel, pers. comm., 2001). In this case, the initial solution concentrations are 0.810 m Na_2SO_4 , 2.867 m MgSO_4 , and 0.2575 m H_2SO_4 . The patterns for MgSO_4 and H_2SO_4 concentrations with decreasing temperature are similar for both simulations (Figs. 13a and 13b). The presence of sodium leads initially to the precipitation of mirabilite ($\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$), which is eventually largely replaced by $\text{Na}_3\text{H}(\text{SO}_4)_2$ under highly acidic conditions at subzero temper-



atures (Fig. 13b). According to model calculations, the equilibrium salt assemblage at the eutectic (234.65 K) includes 2.867 mol of $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$, 0.515 mol of $\text{Na}_3\text{H}(\text{SO}_4)_2$, and 0.0375 mol of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. An alternative sink for hydrogen in the presence of sodium leads to a much higher eutectic temperature (234.65 K) (Fig. 13b) compared to the non-sodium case where the ultimate hydrogen sink is solid-phase sulfuric acid at 211.15 (Fig. 13a).

Because of the differential solubilities of salts such as Na_2SO_4 and MgSO_4 compared to H_2SO_4 as a function of temperature, freezing can convert a predominantly salt solution into a predominantly acid solution (Fig. 13). If the surficial salts on Europa are forming from an acid brine, then these results have implications for potential life on Europa.

The presence of a putative liquid ocean on Europa has focused a great deal of attention on the possibility of life on this body (Gaidos et al., 1999; Chyba, 2000; Kargel et al., 2000). At 298 and 273 K, the calculated activities of water (a measure of salinity) are 0.888 and 0.928, respectively, for the MgSO_4 - H_2SO_4 - H_2O system (Fig. 13a) and 0.850 and 0.909, respectively, for the Na_2SO_4 - MgSO_4 - H_2SO_4 - H_2O system (Fig. 13b). These calculated water activities are well within the tolerance

range of halophilic organisms, whose lower limit for water activity is approximately 0.6 (Mazur, 1980; Kushner, 1981). Only at temperatures $< 220 \text{ K}$ does the activity of liquid water drop below 0.6 (Fig. 13a). So salinity, per se, should not limit life in such a salty-acidic brine.

For solid-phase sulfuric acid to form requires a minimum sulfuric acid concentration of 5.68 m (pH = -1.31) at a temperature of 211 K or a higher acid concentration at a higher temperature (Fig. 5b). While life can exist in the dormant stage to temperatures approaching absolute zero, active life requires temperatures $\geq 253 \text{ K}$ (Vogel, 1999; Rivkina et al., 2000). Furthermore, organic life, as we know it, cannot tolerate sulfuric acid concentrations of 5.7 m (reagent grade sulfuric acid $\approx 18 \text{ m}$). The most tolerant acidophilic organisms can tolerate pH values around 0 (acid concentrations around 1 m) (Schleper et al., 1995; Robbins et al., 2000). In the simulations, this acidity is reached around $263 \pm 1 \text{ K}$ (Fig. 13). The conditions necessary for solid-phase sulfuric acid to have formed on the icy surface of Europa are incompatible with life (too cold and too acid). On the other hand, surficial depositions could have formed exogenically or as the result of flash freezing of more dilute acidic brines emanating from cracks in the European

surface. If solid-phase sulfuric acid is forming on the European surface as the result of endogenic processes, then this would limit life-forms to highly acidophilic organisms.

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