Hydrogen Ion Activities and Species Distribution in Mixed Metal Sulfate Aqueous Systems

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The activity of the hydrogen ion (H^+) is estimated in sulfuric acid aqueous solutions of concentrations 0.25 to 2.0 mol·L^{-1} at temperatures 298 to 373 K (25 to 100°C). This is done by following an existing "extended Debye-Hückel" equation, which was originally developed only for the case of pure H_2SO_4 solutions at ambient temperature. The same equation is applied for the evaluation of the activity of H^+ in mixed metal sulfate solutions, particularly for the aqueous system H_2SO_4-$ZnSO_4$-$FeSO_4$-$Fe_2(SO_4)_3$. The estimation of the activity of H^+ by this method requires the knowledge of the molality of free H^+ ions and the true ionic strength (in molal scale). Consequently, an algorithm is advanced for the calculation of species concentrations in such mixed solutions. Estimated pH values agree very well with experimentally measured ones.

Introduction

The importance of the hydrogen ion activity (a_{H^+}) in many hydrochemical systems of industrial interest is very well-known. Particularly in hydrometallurgy, the activity of H^+ is a key parameter that may determine equilibria in precipitation reactions (Demopoulos et al., 1987), or dissolution rates of certain compounds (Majima and Awakura, 1981). This becomes more apparent in moderately to highly acidic solutions where the value of the activity of H^+, the so-called *effective concentration* of H^+, differs significantly from its analytical concentration.

Unfortunately, the experimental determination of the activity of H^+ by means of a pH-meter and two suitable electrodes is too difficult—if not impossible—in concentrated hot acid solutions. The glass electrode which is commonly used for pH measurements does not give steady and reproducible potential readings when it is immersed in such solutions. The presence of any solid particles or any immiscible organic droplets may give rise to other unexpected errors. Strictly speaking, even when a stable pH measurement is achieved, the obtained pH value is a relative indicator of acidity (or alkalinity) and does not necessarily coincide with the real values of $-\log [H^+]$ or $-\log a_{H^+}$ (Bates, 1973).

The present work was initiated for the treatment of data of zinc ferrite dissolution in industrial H_2SO_4 solutions containing relatively high concentrations of $ZnSO_4$ and $Fe_2(SO_4)_3$ (Filippou and Demopoulos, 1992). The negative effect of the two latter electrolytes on the kinetics of zinc ferrite dissolution could not be related to any mass-transfer mechanism. It was presumed that those electrolytes decrease the rate of zinc ferrite dissolution by lowering the driving force of the reaction, the activity of H^+. It was therefore necessary to prove this in a quantitative manner by first estimating the activity of H^+ in sulfuric acid solutions and, then, by relating the rate of the reaction to this value. As is shown in the following paragraphs, the determination of species distribution in relatively concentrated H_2SO_4-$ZnSO_4$-$FeSO_4$-$Fe_2(SO_4)_3$ solutions had also to be undertaken for the ultimate estimation of the hydrogen ion activity in these mixed sulfate solutions.

Activity of H^+

Activity of H^+ in pure H_2SO_4 solutions

The experimental measurement of single-ion activities in electrolyte solutions is by principle impossible (Bockris and Reddy, 1970). Nevertheless, single-ion activities can in chloride solutions be estimated by a formulation which assumes that the anion (Cl^-) is not hydrated (Bates et al., 1970; Jansz, 1983). Similarly, Das (1988) tacitly assumed that the sulfate (SO_4^{2-})

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and the bi-sulfate (HSO_4^-) ions are not hydrated to come with the following "extended Debye-Hückel" type of equation for the activity coefficient of the hydrogen ion (γ_{H^+}) in sulfuric acid solutions:

$$\log \gamma_{H^+} = -\frac{A\sqrt{I_m}}{1+5.66B\sqrt{I_m}} + 0.04785 I_m + \text{scale effect}, \qquad (1)$$

where A and B are the temperature dependent Debye-Hückel coefficients (Bockris and Reddy, 1970), and I_m the true ionic strength of the solution on molal basis. If n is the total number of ionic species in the solution, and m_i is the molality (mols per kg of solvent) of the species i with ionic charge z_i, then $I_m = 1/2\ \Sigma_{i=1}^{n}\ m_i z_i^2$.

The "scale effect" in Eq. 1 is a simple function that Das used to convert the activity coefficient of H^+ from mole fraction scale to molal scale. It can be calculated as:

$$\text{scale effect} = -\log\left[1 + \frac{0.018\sum_{i=1}^{n} m_i}{1-0.018hm_{H^+}}\right], \qquad (2)$$

where h is the hydration number of the hydrogen ion. Das accepted the value $h = 4$, that is, the proton is surrounded by four water molecules in the form $H^+ \cdot 4H_2O$.

From Eqs. 1 and 2, it becomes obvious that in order to estimate the activity of H^+ in H_2SO_4 solutions, one needs the values of m_{H^+} and I_m. The latter values can be obtained only by considering species equilibria and determining the distribution of species, that is, by performing *speciation* [another term which is also used to describe the determination of species distribution in aqueous solutions is *chemical modeling* (Bassett and Melchior, 1990)] for the solution in question.

The dissociation of H_2SO_4 in an aqueous environment takes place in two consecutive steps:

$$H_2SO_4 \overset{K_1}{\rightleftharpoons} H^+ + HSO_4^-, \qquad (R1)$$

$$HSO_4^- \overset{K_2}{\rightleftharpoons} H^+ + SO_4^{2-}. \qquad (R2)$$

Hence, the species that exist in a pure solution of sulfuric acid are: $H_2SO_4^0$, H^+, HSO_4^- and SO_4^{2-}. Awakura et al. (1990) recently calculated from activity data the equilibrium constant K_1 to be in the order of 1 to 10 at ambient temperature. However, most of the experimental and theoretical work of the past, which has been compiled by IUPAC (Perrin, 1982), has shown this constant to be much higher, in the order of 10^3. For this reason, many researchers—including Das—have assumed that the first dissociation of H_2SO_4 to H^+ and HSO_4^- is complete for any kind of thermodynamic analysis concerning sulfuric acid solutions.

In fact, Das, in order to derive Eq. 1, used data for the degree of second dissociation of H_2SO_4 at 298 K which had originated from a study of Pitzer et al. (1977). The data and the ion-ion interaction theoretical approach of Pitzer and his co-workers were also used by Dickson et al. (1990) in their extensive investigation of the dissociation constant of the bisulfate ion for temperatures as high as 523 K. The work of Dickson and his coworkers resulted in a series of equations which include:

$$\log K_2^0 = p_1 + p_2/T + p_3 \ln T + p_4 T + p_5 T^2, \qquad (3)$$

$$\log K_2 = \log K_2^0 - \frac{4f_1}{\ln 10} + p_6\frac{I_m}{T} + f_2(p_7 T + p_8/T) + p_9\left(\frac{I_m^2}{T}\right), \qquad (4)$$

$$f_1 = -f_3\left\{\frac{\sqrt{I_m}}{1+1.2\sqrt{I_m}} + \frac{2\ln(1+1.2\sqrt{I_m})}{1.2}\right\}, \qquad (5)$$

$$f_2 = 1-(1+2\sqrt{I_m})\exp\{-2\sqrt{I_m}\}, \qquad (6)$$

$$\begin{aligned} f_3 = {} & p_{10} + p_{11}T + p_{12}T^2 + p_{13}T^3 + p_{14}\exp\left\{\frac{T-543}{10}\right\} \\ & + p_{15}/(T-253) + p_{16}/(588-T) + p_{17}/(588-T)^2 \\ & + p_{18}/(588-T)^3 + p_{19}/(588-T)^4 + p_{20}/(588-T)^5. \qquad (7) \end{aligned}$$

All the ps in the above equations are parameters that were determined experimentally by Dickson and his coworkers (Table 1).

Equation 3 gives the value of the thermodynamic equilibrium constant for step R2:

$$K_2^0 = \frac{a_{H^+}a_{SO_4^{2-}}}{a_{HSO_4^-}} \qquad (8)$$

which, as known, is a function of T only. The combination of the rest of the equations gives the value of the mass equilibrium constant of Step R2. That is, the molality quotient:

$$K_2 = \frac{m_{H^+}m_{SO_4^{2-}}}{m_{HSO_4^-}}. \qquad (9)$$

Equations 3-7 give K_2 within an error of ±0.04 log units. When compared to some similar equations developed by Marshall and Jones (1966), Eqs. 3-7 may look quite complicated. However, Marshall and Jones, while working on the solubility of calcium sulfate, ignored the presence of the neutral aqueous species $CaSO_4^0$ which exists in significant quantities at high temperatures. Therefore, it was considered more appropriate to use Dickson's formulas.

In order to determine the amount of each individual species (H^+, HSO_4^- and SO_4^{2-}) in a pure sulfuric acid solution at a given $[H_2SO_4]$ and temperature, one can make a first guess of their concentration values in molar and molal basis. For instance, at first, it might be assumed that the bisulfate ion dissociates completely. Then, one can find an estimate of I_m, and from Eqs. 3-7 get the value of K_2. For reasons of convenience, one may evaluate the corresponding mass stability constant of the bisulfate ion (HSO_4^-) on molar basis β_2 as:

$$\beta_2 = \frac{1/K_2}{\rho - 0.001\sum_{i=1}^{n} c_i M_i}, \qquad (10)$$

where ρ is the solution density in kg/L^{-1}, c_i the concentration

Table 1. p Parameters of Dickson et al. (1990)

Parameter	Value
p_1	562.7097
p_2	$-13{,}273.75$
p_3	-102.5154
p_4	0.2477538
p_5	-1.117033×10^{-4}
p_6	-57.07583
p_7	-1.144759×10^{-3}
p_8	46.72816
p_9	2.499849
p_{10}	0.413070
p_{11}	-1.04397×10^{-3}
p_{12}	2.64092×10^{-6}
p_{13}	-9.96723×10^{-11}
p_{14}	5.98066
p_{15}	1.39987×10^{-2}
p_{16}	18.4374
p_{17}	-554.596
p_{18}	7,684.77
p_{19}	$-54{,}091$
p_{20}	154,381

of the species i in $\mathrm{mol\cdot L^{-1}}$ (molarity), and M_i the molecular weight of the same species in $\mathrm{g\cdot mol^{-1}}$. (It can be easily shown that for any aqueous equilibrium, the mass equilibrium constant expressed in terms of molarities (β) and the one expressed in terms of molalities (K) have the same value (but not the same units) only at infinite dilution. That particular value is the *thermodynamic stability constant* and is indicated as β^0, or K^0.)

After the evaluation of β_2, a system of three equations with three unknowns is set up:

$$\beta_2=\frac{[\mathrm{HSO_4^-}]}{[\mathrm{H^+}][\mathrm{SO_4^{2-}}]}, \tag{11}$$

$$[\mathrm{SO_4^{2-}}]_{\mathrm{tot}}=[\mathrm{SO_4^{2-}}]+[\mathrm{HSO_4^-}], \tag{12}$$

$$0=[\mathrm{H^+}]-[\mathrm{HSO_4^-}]-2[\mathrm{SO_4^{2-}}]. \tag{13}$$

The three unknowns in the system are the species concentrations $[\mathrm{H^+}]$, $[\mathrm{SO_4^{2-}}]$, and $[\mathrm{HSO_4^-}]$. Equation 12 represents the sulfate mass balance, while with Eq. 13 the condition of solution electroneutrality is fulfilled. Hydroxide ($\mathrm{OH^-}$) ions have not been taken into account in the above system, since their concentration is negligible in very acidic solutions.

By solving the above system, new estimates of the concentration of the species and the true ionic strength are obtained. With a new value for I_m, a new β_2 can be calculated and the procedure can be repeated in an iterative mode until I_m is evaluated within satisfactory small error such as 10^{-3}. A simple computer program was written to facilitate those repetitive calculations.

In this manner, the values of $m_{\mathrm{H^+}}$ and I_m were estimated for sulfuric acid solutions of various sulfate concentrations. Through Eqs. 2 and 1, the activity coefficient of $\mathrm{H^+}$ was also evaluated and, finally, its activity $a_{\mathrm{H^+}}$ was calculated as:

$$a_{\mathrm{H^+}}=\gamma_{\mathrm{H^+}}m_{\mathrm{H^+}}. \tag{14}$$

Table 2. Activity of $\mathrm{H^+}$ in Aqueous Solutions of 0.25 to 2.0 $\mathrm{mol\cdot L^{-1}}$ $\mathrm{H_2SO_4}$ at 298 K

$(\mathrm{H_2SO_4})$ $\mathrm{mol\cdot L^{-1}}$	$\log a_{\mathrm{H^+}}$	$\log a_{\mathrm{H^+}}$ as by Das (1988)
0.25	-0.66	—
0.50	-0.37	-0.34
0.75	-0.20	—
1.00	-0.06	0.01
1.25	0.04	—
1.50	0.14	—
1.75	0.22	0.41
2.00	0.29	0.57

The results which are shown on Table 2, compare quite well with those of Das, at least for ionic strength less than 1.5 $\mathrm{mol\cdot kg^{-1}}$. Nonetheless, at ionic strengths greater than 1.5 $\mathrm{mol\cdot kg^{-1}}$, a significant deviation appears between the activity values given by Das and those of the present work even though the values of the activity coefficient still compare very well. The reason for this is the fact that Das got the value of $m_{\mathrm{H^+}}$ directly from bisulfate dissociation data tabulated by Pitzer et al. (1977), while in the present study this was done by using Eqs. 3-7 and solving the system of Eqs. 11-13. Pitzer's data could have been used in this work as well for $T=298$ K and there would not be any difference with Das' results. This approach, however, is impossible at temperatures higher than 298 K because such data do not exist. For this reason, it was absolutely necessary to resort to Eqs. 3-7 and 11-13.

Activity of H^+ in mixed metal sulfate solutions

Since Eq. 1 has a generic form, it can be assumed that with that equation and known values of $m_{\mathrm{H^+}}$ and I_m, it is possible to calculate $a_{\mathrm{H^+}}$ even in the case of mixed metal sulfate solutions. However, in order to obtain the necessary values of $m_{\mathrm{H^+}}$ and I_m, a nonlinear system with many more unknowns than that of Eqs. 11-13 will have to be solved. In the case of an aqueous solution containing $\mathrm{ZnSO_4}$, $\mathrm{FeSO_4}$, $\mathrm{Fe_2(SO_4)_3}$ and $\mathrm{H_2SO_4}$, which is of particular interest to zinc hydrometallurgy and is analyzed as a case study here, a system of 27 equations with 27 unknowns has to be set up and solved. These 27 unknowns are all the possible simple or complexed ions that exist in this aqueous system (Table 3), with the exception of $\mathrm{H_2O}$. This system can become even bigger if solid-liquid equilibria are taken into account. Such equilibria that could have been incorporated in the present speciation calculations have been left out, because at the high acidities of interest (pH generally less than 2.0), practically no solid phase precipitates.

Collection of Thermodynamic Data. To evaluate the distribution of species in an aqueous system at temperatures higher than 298 K, a complete set of thermodynamic data is required for every single species that may exist in that specific system.

For the particular system which has been under consideration, most of the necessary thermodynamic data were collected from the computer database of F*A*C*T (Bale et al., 1991) and were checked against the latest compilation of the U.S. National Bureau of Standards (Wagman et al., 1982). For a number of these species, more careful examination of the thermodynamic data was done by performing cross-examination with some other publications. Moreover, missing values of enthalpies (ΔH) and entropies (S) had to be estimated for many compounds by resorting to some other sources of information.

Table 3. Species and Thermodynamic Data for the Aqueous System $ZnSO_4$-$FeSO_4$-$Fe_2(SO_4)_3$-H_2SO_4*

Species	$\Delta G^0_{f,\,298\,K}$ $kJ\cdot mol^{-1}$	$\Delta H^0_{f,\,298\,K}$ $kJ\cdot mol^{-1}$	$S^0_{298\,K}$ $J\cdot K^{-1}\cdot mol^{-1}$	$C_p=\mathcal{A}+10^{-3}\times\mathcal{B}T+10^5\times\mathcal{C}T^{-2}$ $J\cdot K^{-1}\cdot mol^{-1}$			Ref.
				$\mathcal{A}$	$\mathcal{B}$	$\mathcal{C}$	
H^+	0	0	0	0			
OH^-	−157.29	−230.12	−10.88	506.38	−1,181.34	−246.02	(**)
H_2O	−237.18	−285.85	69.96	75.44			(**)
SO_4^{2-}	−744.63	−909.18	20.08	874.6	−1,759.7	−519.98	(**)
HSO_4^-	−756.01	−887.01	131.8	−547.29	1,342.16	266.78	(**)
Zinc Species							
Zn^{2+}	−147.06	−153.97	−112.1	2.77	−39.14	34.6	(**)
$ZnOH^+$	−330.1	[−357]	[5]				(**)
$Zn(OH)_2^0$	−522.73	−133.47	−133.5	−251.04			(†)
$Zn(OH)_3^-$	−694.22	[−844]	[107]				(**)
$Zn(OH)_4^{2-}$	−858.52	[−1,078]	[−218]				(**)
$ZnSO_4^0$	−904.9	−1,047.3	5.02				(**)
Iron (II) Species							
Fe^{2+}	−78.9	−89.12	−137.65	−1.08	1.21	39.97	(**)
$FeOH^+$	−277.4	−324.68	−29.29	−29.79	270.61	26.64	(**)
$Fe(OH)_2^0$	−441.0	−540.5	29.1				(**)
$Fe(OH)_3^-$	−615.05	−783.82	29.9				(**)
$Fe(OH)_4^{2-}$	−769.86	−1,009.74	24.5				(**)
$FeSO_4^0$	−823.43	−998.3	−117.6				(†)
$FeHSO_4^+$	−838.92	−937.69	137.57				(‡)
Iron (III) Species							
Fe^{3+}	−4.6	−48.5	−315.9	79.09	−219.35	15.4	(‡)
$FeOH^{2+}$	−229.41	−290.8	−142.0	19.4	−21.22	29.4	(‡)
$Fe(OH)_2^+$	−446.4	−543.80	−29.29				(‡)
$Fe(OH)_3^0$	−660.0	−795.73	75.4				(‡)
$Fe(OH)_4^-$	−830.0	−1,050.4	25.5				(‡)
$Fe_2(OH)_2^{4+}$	−466.97	−611.38	−355.64	124.68	−619.0	14.0	(‡)
$FeSO_4^+$	−772.8	−931.78	−129.7	37.7	317.0	−1.0	(‡)
$Fe(SO_4)_2^-$	−1,524.65	−1,828.39	−43.07				(‡)
$Fe_2(SO_4)_3^0$	−2,243.0	−2,825.04	−571.53				(‡)
$FeHSO_4^{2+}$	−768.38	−894.29	−18.68				(‡)

*Values in square brackets have been computed for the first time in this work.
**Bale et al. (1991).
†Wagman et al. (1982).
‡Papangelakis and Demopoulos (1990).

These estimated values are given along with the ones taken from compilations in Table 3.

Zinc Species. The only zinc aqueous compounds for which complete thermodynamic data exist are: Zn^{2+}, $Zn(OH)_2^0$, and $ZnSO_4^0$. The values of the standard heat of formation ($\Delta H^0_{f,298\,K}$), and absolute entropy ($S^0_{298\,K}$) for other zinc-hydroxyl complexes were obtained by analyzing some information provided by Reichle et al. (1975). These authors have examined the equilibria between zinc-hydroxyl ions [$ZnOH^+$, $Zn(OH)_2^0$, $Zn(OH)_3^-$, and $Zn(OH)_4^{2-}$], and have estimated equilibrium constants for temperatures ranging from 285.5 to 348 K. They, however, have declined to list values of $\Delta H^0_{f,298\,K}$ and $S^0_{298\,K}$ because of some uncertainties in their experimental work regarding solid-liquid equilibria.

Having, though, no other alternative source of such information, the heat of formation of the zinc-hydroxyl complexes was evaluated from plots of ln β^0 vs. $(1/T)$, with values of β^0 taken from the work of Reichle and his co-workers. For short ranges of temperature such as 298-373 K, the standard enthalpy of reaction, ΔH^0, can be taken approximately constant and then Van't Hoff's differential equation can be integrated to give (Denbigh, 1981):

$$\ln \beta_T^0 = -\frac{\Delta H^0}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)+\ln \beta_{T_0}^0 \qquad (15)$$

where

β_T^0 = thermodynamic equilibrium constant at temperature T
$\beta_{T_0}^0$ = same constant at temperature $T_0 = 298$ K
R = universal gas constant (8.31434 $J\cdot mol^{-1}\cdot K^{-1}$)

Thus, a plot of ln β^0 vs. $(1/T)$ for a given equilibrium should result in a straight line with a slope of $(-\Delta H^0/R)$. For example, for the reaction

$$Zn^{2+} + OH^- \rightleftharpoons ZnOH^+$$

from a plot ln β^0 vs. $(1/T)$ (Figure 1), it is estimated that

$$\frac{\Delta H^0}{R} = 3{,}270 \text{ K}$$

which gives

$$\Delta H^0_{T_0} \equiv \Delta H^0 = 27 \text{ kJ}\cdot\text{mol}^{-1}.$$

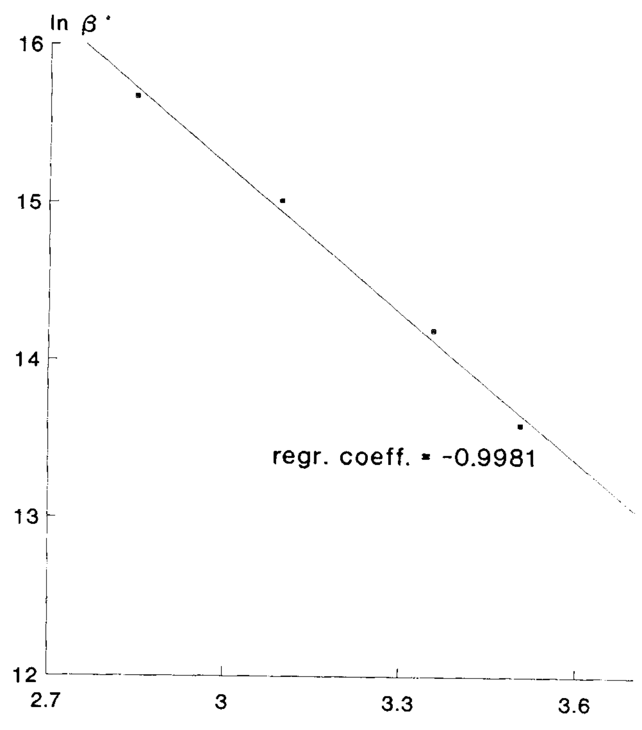

Figure 1. Characteristic Van't Hoff plot for the formation reaction of $ZnOH^+$.

Subsequently, the standard heat of formation of $ZnOH^+$ was calculated as:

$$\Delta H^0_{f,T_0}[\mathrm{ZnOH}^+] = \Delta H^0_{T_0} + \Delta H^0_{f,T_0}[\mathrm{Zn}^{2+}] + \Delta H^0_{f,T_0}[\mathrm{OH}^-]$$
$$= -357\ \mathrm{kJ \cdot mol^{-1}}.$$

In a similar way, the heats of formation of the remaining zinc-hydroxyl complexes, that is, $Zn(OH)_3^-$, and $Zn(OH)_4^{2-}$, were estimated.

Because the formation processes for ions in solutions are defined in terms of oxidation-reduction processes, the standard entropy for the same zinc-hydroxyl ions was evaluated accordingly (Wagman et al., 1982):

$$S^0_T = \frac{\Delta H^0_{f,T} - \Delta G^0_{f,T}}{T} + \sum_{e} S^0_{e,T} - \left(\frac{z}{2}\right) S^0_T[\mathrm{H_2},\ 1\ \mathrm{atm}]. \quad (16)$$

The subscript *e* in the sum of the above equation indicates the elements from which the same species is formed.

Beyond these species already known to exist in zinc sulfate solutions, Fedorov et al. (1973) in a potentiometric study of $ZnSO_4$-$LiClO_4$ aqueous solutions have speculated over the existence of a number of zinc sulfato-complexes of the type $Zn(SO_4)_n^{2-2n}$ with $n = 2, \ldots, 5$. On the other hand, Burkov and his co-workers (1978) have discussed the possible existence of poly-nuclear zinc-hydroxyl complexes such as Zn_2OH^{3+}. Such poly-sulfato and poly-nuclear zinc complexes have not been considered in the present work since their existence has not been confirmed by any other investigator through different experimental techniques. Finally, zinc oxy-anions and hydroxy-anions of the type ZnO_2^{2-} and $HZnO_2^-$ were also ignored because they are thermodynamically equivalent to $Zn(OH)_4^{2-}$ and $Zn(OH)_3^-$, respectively.

Iron(II) Species. The necessary information about these species was taken from the thermodynamic database of F*A*C*T (Bale et al., 1991) and the U.S. N.B.S. (National Bureau of Standards) compilation (Wagman et al., 1982).

It is worth mentioning at this point that Tremaine and LeBlanc (1980), while examining the solubility of magnetite at high temperatures (up to 573 K), derived certain thermodynamic values for Fe^{2+} and its hydroxy complexes. These values are slightly different from those listed in Table 3. However, the values of enthalpies, entropies, and so on, given by these authors were computed after assuming that the free energy of formation of Fe^{3+} is equal to $-16.7\ \mathrm{kJ \cdot mol^{-1}}$, which is not considered to be consistent with the F*A*C*T or N.B.S. data (Papangelakis and Demopoulos, 1990). For this reason, Tremaine and LeBlanc's data were not used.

Iron(III) Species. The thermodynamic values for the Fe(III) species are the same with those collected in a previous study on the chemistry of the oxidative dissolution of arsenopyrite (Papangelakis and Demopoulos, 1990).

In addition to these species, the possible existence of a neutral compound of the type $FeSO_4HSO_4^0$ was ignored. The possible existence of this species was put forth by Lister and Rivington (1955) to accommodate their colorimetric study of ferric sulfate solutions. But, even the more recent studies on the structure of ferric sulfate complexes like that carried out by Magini (1979) fail to prove the existence of this complex. Magini, from his side, has speculated over the possible formation of complexes like $Fe(SO_4)_n^{3-2n}$ with $n \geq 3$. For these last ferric poly-sulfato complexes there do not exist any thermodynamic data.

Thermodynamic Equilibrium Constants at Elevated Temperatures. Any equilibrium (reaction) can be written in the general form:

$$\sum_{i=1}^{n} \nu_i N_i = 0 \quad (17)$$

with ν_i being the stoichiometric coefficient of the species N_i (negative for the reactants). (In this work, all reactions are written in the direction of complex formation from its primary components (see Table 4).) Of course, the thermodynamic equilibrium constant at any temperature is obtained from the value of the standard free energy of reaction ΔG^0_T as:

$$\beta^0_T = \exp\left(-\frac{\Delta G^0_T}{RT}\right). \quad (18)$$

Consequently, the value of ΔG^0_T can be computed at temperatures higher than 298 K only when the standard entropy change of the reaction is known at $T_0 = 298$ K ($\Delta S^0_{T_0}$) together with the heat capacity functions for all reactants and products. Should this be the case, then:

$$\Delta G^0_T = \Delta G^0_{T_0} - (T - T_0)\Delta S^0_{T_0}$$
$$+ \int_{T_0}^{T} \Delta C_p(T)\,dT - T\int_{T_0}^{T} \frac{\Delta C_p(T)}{T}\,dT \quad (19)$$

where

$$\Delta C_p(T) = \sum_{i=1}^{n} \nu_i C_{p,i}(T) \tag{20}$$

and $C_{p,i}(T)$ is the heat capacity function of the reactant or product i (Table 3).

Alternatively, if for some species participating in one equilibrium the function $C_p(T)$ is unknown, a close approximate of the value of β_T^0 can be obtained directly by "Helgeson's extrapolation" (Helgeson, 1967). By this method, a very good approximate of β_T^0 can be estimated at temperatures as high as 423 K (Jackson and Helgeson, 1985) provided that the standard enthalpy of reaction is also known at $T_0 = 298$ K ($\Delta H_{T_0}^0$):

$$\ln \beta_T^0 \approx \frac{\Delta S_{T_0}^0}{RT} \left[T_0 - \theta_1 \left\{ 1 - \exp\left[\exp(\theta_2 + \theta_3 T) + \theta_4 + \frac{T - T_0}{\theta_5} \right] \right\} \right] - \frac{\Delta H_{T_0}^0}{RT}. \tag{21}$$

In this last equation, all θs are constants which have the following values: $\theta_1 = 218.3$ K; $\theta_2 = -12.741$; $\theta_3 = 0.01875$ K^{-1}; $\theta_4 = -7.84 \times 10^{-4}$; and $\theta_5 = 219$ K.

Mass Stability Constants. Aqueous equilibria in relatively concentrated solutions cannot be described adequately with the use of thermodynamic equilibrium constants. The thermodynamic equilibrium constant β^o, which is defined as a product of activities, may be far different from the mass equilibrium constant β that is defined as a product of molar concentrations. To get the value of β at ionic strength considerably higher than zero, a simple equation similar to Eq. 1 can be used as has been proposed by Vasil'ev (1962):

$$\log \beta_T = \log \beta_T^0 + \frac{A \Delta z^2 \sqrt{I_c}}{1 + 1.6\sqrt{I_c}} + b I_c, \tag{22}$$

where $\Delta z^2 = \Sigma_{i=1}^n \nu_i z_i^2$, I_c the ionic strength on molar basis ($I_c = 1/2\ \Sigma_{i=1}^n c_i z_i^2$), and b is an arbitrary constant.

The constant b, which is different for every equilibrium, can be determined by plotting the quantity:

$$q \equiv \log\left(\frac{\beta_{T_0}}{\beta_{T_0}^0}\right) - \frac{A \Delta z^2 \sqrt{I_c}}{1 + 1.6\sqrt{I_c}}$$

against I_c (Figure 2). This has been done for almost all the equilibria in the system analyzed in this work, and estimated values of b are listed in Table 4. The necessary values of β at different I_c for the estimation of the parameter b were taken from the tables of Smith and Martell (1976) and Martell and Smith (1982). Only in one case another source was used; β values were taken from Liddell and Bautista (1981) for the reaction of $FeHSO_4^+$ formation.

However, for some of the equilibria, values of β vs. I_c are not available and, therefore, plots like those on Figure 2 could not be made. The mass stability constant of these equilibria was taken as equal to the thermodynamic one. Moreover, Vasil'ev's equation was not used for two other equilibria. For the dissociation of HSO_4^-, Eqs. 3-7 were used. Also, for the equilibrium:

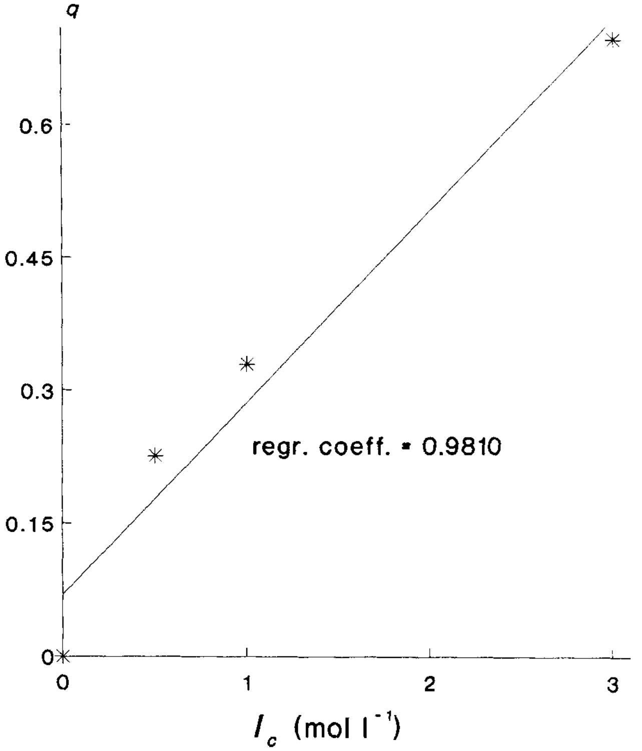

Figure 2. Characteristic Vasil'ev plot for the determination of the *b* parameter for the $FeSO_4^+$ complex formation.

b is estimated by linear regression equal to 0.216±0.030.

$$Zn^{2+} + SO_4^{2-} \rightleftharpoons ZnSO_4^0$$

the data β vs. I_c do not fit well Vasil'ev's equation. For this equilibrium, Davies' modified form of the Debye-Hückel equation was used:

$$\log K_7 = \log K_7^0 + A \Delta z^2 \left(\frac{\sqrt{I_m}}{1 + \sqrt{I_m}} - 0.2 I_m \right) \tag{23}$$

That last equation has been originally used by Nair and Nancollas (1958) to determine the thermodynamic stability constant of $ZnSO_4^0$ by extrapolating from high ionic strength to $I_m = 0$. Here, it is used for the opposite purpose. The mass stability constant on molal basis K was converted to the one on molar basis β by an equation similar to Eq. 10.

Numerical Solution. As already mentioned, the determination of species' concentrations in a sulfate solution of Zn, Fe(II) and Fe(III) requires solving a system of 27 equations with 27 unknowns. The equations of this system include the 22 equilibrium constants which are listed in Table 4. In addition to these 22 equations, another 5 equations have to be considered to complete the system. These include:

(i) The sulfate mass-balance:

$$0 = [SO_4^{2-}]_{tot} - [SO_4^{2-}] - [HSO_4^-] - [ZnSO_4^0] - [FeSO_4^0] - [FeHSO_4^+] - [FeSO_4^+] - 2[Fe(SO_4)_2^-] - 3[Fe_2(SO_4)_3^0] - [FeHSO_4^{2+}]; \tag{24}$$

Table 4. Equilibria in the Aqueous System $ZnSO_4$-$FeSO_4$-$Fe_2(SO_4)_3$-H_2SO_4, the Mass Equilibrium Constants on Molar Basis (β) and the Parameter b of Eq. 22

Equilibrium	β	b
$H^+ + OH^- \rightleftharpoons H_2O$	$\beta_1 = \frac{1}{\beta_w} = \frac{1}{[H^+][OH^-]}$	0.219
$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$	$\beta_2 = \frac{[HSO_4^-]}{[H^+][SO_4^{2-}]}$	(*)
$Zn^{2+} + OH^- \rightleftharpoons ZnOH^+$	$\beta_3 = \frac{[ZnOH^+]}{[Zn^{2+}][OH^-]}$	−0.087
$Zn^{2+} + 2OH^- \rightleftharpoons Zn(OH)_2^0$	$\beta_4 = \frac{[Zn(OH)_2^0]}{[Zn^{2+}][OH^-]^2}$	−0.163
$Zn^{2+} + 3OH^- \rightleftharpoons Zn(OH)_3^-$	$\beta_5 = \frac{[Zn(OH)_3^-]}{[Zn^{2+}][OH^-]^3}$	0.403
$Zn^{2+} + 4OH^- \rightleftharpoons Zn(OH)_4^{2-}$	$\beta_6 = \frac{[Zn(OH)_4^{2-}]}{[Zn^{2+}][OH^-]^4}$	1.113
$Zn^{2+} + SO_4^{2-} \rightleftharpoons ZnSO_4^0$	$\beta_7 = \frac{[ZnSO_4^0]}{[Zn^{2+}][SO_4^{2-}]}$	(*)
$Fe^{2+} + OH^- \rightleftharpoons FeOH^+$	$\beta_8 = \frac{[FeOH^+]}{[Fe^{2+}][OH^-]}$	0.587
$Fe^{2+} + 2OH^- \rightleftharpoons Fe(OH)_2^0$	$\beta_9 = \frac{[Fe(OH)_2^0]}{[Fe^{2+}][OH^-]^2}$	(†)
$Fe^{2+} + 3OH^- \rightleftharpoons Fe(OH)_3^-$	$\beta_{10} = \frac{[Fe(OH)_3^-]}{[Fe^{2+}][OH^-]^3}$	(†)
$Fe^{2+} + 4OH^- \rightleftharpoons Fe(OH)_4^{2-}$	$\beta_{11} = \frac{[Fe(OH)_4^{2-}]}{[Fe^{2+}][OH^-]^4}$	(†)
$Fe^{2+} + SO_4^{2-} \rightleftharpoons FeSO_4^0$	$\beta_{12} = \frac{[FeSO_4^0]}{[Fe^{2+}][SO_4^{2-}]}$	0.274
$Fe^{2+} + H^+ + SO_4^{2-} \rightleftharpoons FeHSO_4^+$	$\beta_{13} = \frac{[FeHSO_4^+]}{[Fe^{2+}][H^+][SO_4^{2-}]}$	0.145
$Fe^{3+} + OH^- \rightleftharpoons FeOH^{2+}$	$\beta_{14} = \frac{[FeOH^{2+}]}{[Fe^{3+}][OH^-]}$	0.277
$Fe^{3+} + 2OH^- \rightleftharpoons Fe(OH)_2^+$	$\beta_{15} = \frac{[Fe(OH)_4^+]}{[Fe^{3+}][OH^-]^2}$	0.652
$Fe^{3+} + 3OH^- \rightleftharpoons Fe(OH)_3^0$	$\beta_{16} = \frac{[Fe(OH)_3^0]}{[Fe^{3+}][OH^-]^3}$	1.049
$Fe^{3+} + 4OH^- \rightleftharpoons Fe(OH)_4^-$	$\beta_{17} = \frac{[Fe(OH)_4^-]}{[Fe^{3+}][OH^-]^4}$	1.249
$2Fe^{3+} + 2OH^- \rightleftharpoons Fe_2(OH)_2^{4+}$	$\beta_{18} = \frac{[Fe_2(OH)_2^{4+}]}{[Fe^{3+}]^2[OH^-]^2}$	0.492
$Fe^{3+} + SO_4^{2-} \rightleftharpoons FeSO_4^+$	$\beta_{19} = \frac{[FeSO_4^+]}{[Fe^{3+}][SO_4^{2-}]}$	0.216
$Fe^{3+} + 2SO_4^{2-} \rightleftharpoons Fe(SO_4)_2^-$	$\beta_{20} = \frac{[Fe(SO_4)_2^-]}{[Fe^{3+}][SO^{2-}]^2}$	−0.100
$2Fe^{3+} + 3SO_4^{2-} \rightleftharpoons Fe_2(SO_4)_3^0$	$\beta_{21} = \frac{[Fe_2(SO_4)_3^0]}{[Fe^{3+}]^2[SO^{2-}]^3}$	(†)
$Fe^{3+} + H^+ + SO_4^{2-} \rightleftharpoons FeHSO_4^{2+}$	$\beta_{22} = \frac{[FeHSO_4^{2+}]}{[Fe^{3+}][H^+][SO_4^{2-}]}$	−0.247

[*] The mass equilibrium constant on molar basis, β, of these reactions has been evaluated differently (see text).

[†] Due to lack of sufficient data, for these equilibria it has been assumed that $\beta = \beta^0$.

(ii) The zinc mass-balance:

$$\begin{aligned}0 = {} & [Zn^{2+}]_{tot} - [Zn^{2+}] - [ZnOH^+] - [Zn(OH)_2^0] \\ & - [Zn(OH)_3^-] - [Zn(OH)_4^{2-}] - [ZnSO_4^0]; \quad (25)\end{aligned}$$

(iii) The ferrous mass-balance:

$$\begin{aligned}0 = {} & [Fe^{2+}]_{tot} - [Fe^{2+}] - [FeOH^+] - [Fe(OH)_2^0] \\ & - [Fe(OH)_3^-] - [Fe(OH)_4^{2-}] - [FeSO_4^0] - [FeHSO_4^+]; \quad (26)\end{aligned}$$

(iv) The ferric mass-balance:

$$\begin{aligned}0 = {} & [Fe^{3+}]_{tot} - [Fe^{3+}] - [FeOH^{2+}] - [Fe(OH)_2^+] - [Fe(OH)_3^0] \\ & - [Fe(OH)_4^-] - 2[Fe_2(OH)_2^{4+}] - [FeSO_4^+] - [Fe(SO_4)_2^-] \\ & - 2[Fe_2(SO_4)_3^0] - [FeHSO_4^{2+}]; \quad (27)\end{aligned}$$

(v) The electroneutrality principle:

$$\begin{aligned}0 = {} & [H^+] - [OH^-] - 2[SO_4^{2-}] - [HSO_4^-] + 2[Zn^{2+}] + [ZnOH^+] \\ & - [Zn(OH)_3^-] - 2[Zn(OH)_4^{2-}] + 2[Fe^{2+}] + [FeOH^+] \\ & - [Fe(OH)_3^-] - 2[Fe(OH)_4^{2-}] + [FeHSO_4^+] + 3[Fe^{3+}] \\ & + 2[FeOH^{2+}] + [Fe(OH)_2^+] - [Fe(OH)_4^-] + 4[Fe_2(OH)_2^{4+}] \\ & + [FeSO_4^+] - [Fe(SO_4)_2^-] + 2[FeHSO_4^{2+}]. \quad (28)\end{aligned}$$

By using the expressions for the mass stability constants which are given on the second column of Table 4, the concentrations of all species in Eqs. 24–28 can be defined in terms of the concentration of five *key components*, namely $[H^+]$, $[SO_4^{2-}]$, $[Zn^{2+}]$, $[Fe^{2+}]$ and $[Fe^{3+}]$. Consequently, Eqs. 24–28 can be rewritten in terms of the concentrations of these components forming a system of five equations that define five F functions. The whole problem is reduced to finding the roots of this 5 × 5 system:

$$\begin{aligned}F_1 = {} & [SO_4^{2-}]_{tot} - [SO_4^{2-}] - \beta_2[H^+][SO_4^{2-}] - \beta_7[Zn^{2+}][SO_4^{2-}] \\ & - \beta_{12}[Fe^{2+}][SO_4^{2-}] - \beta_{13}[Fe^{2+}][H^+][SO_4^{2-}] - \beta_{19}[Fe^{3+}][SO_4^{2-}] \\ & - 2\beta_{20}[Fe^{3+}][SO_4^{2-}]^2 - 3\beta_{21}[Fe^{3+}]^2[SO_4^{2-}]^3 \\ & - \beta_{22}[Fe^{3+}][H^+][SO_4^{2-}] = 0, \quad (29)\end{aligned}$$

$$\begin{aligned}F_2 = {} & [Zn^{2+}]_{tot} - [Zn^{2+}] - \beta_3\beta_w \frac{[Zn^{2+}]}{[H^+]} - \beta_4\beta_w^2 \frac{[Zn^{2+}]}{[H^+]^2} \\ & - \beta_5\beta_w^3 \frac{[Zn^{2+}]}{[H^+]^3} - \beta_6\beta_w^4 \frac{[Zn^{2+}]}{[H^+]^4} - \beta_7[Zn^{2+}][SO_4^{2-}] = 0, \quad (30)\end{aligned}$$

$$\begin{aligned}F_3 = {} & [Fe^{2+}]_{tot} - [Fe^{2+}] - \beta_8\beta_w \frac{[Fe^{2+}]}{[H^+]} - \beta_9\beta_w^2 \frac{[Fe^{2+}]}{[H^+]^2} \\ & - \beta_{10}\beta_w^3 \frac{[Fe^{2+}]}{[H^+]^3} - \beta_{11}\beta_w^4 \frac{[Fe^{2+}]}{[H^+]^4} - \beta_{12}[Fe^{2+}][SO_4^{2-}] \\ & - \beta_{13}[Fe^{2+}][H^+][SO_4^{2-}] = 0, \quad (31)\end{aligned}$$

$$\begin{aligned}F_4 = {} & [Fe^{3+}]_{tot} - [Fe^{3+}] - \beta_{14}\beta_w \frac{[Fe^{3+}]}{[H^+]} - \beta_{15}\beta_w^2 \frac{[Fe^{3+}]}{[H^+]^2} \\ & - \beta_{16}\beta_w^3 \frac{[Fe^{3+}]}{[H^+]^3} - \beta_{17}\beta_w^4 \frac{[Fe^{3+}]}{[H^+]^4} - 2\beta_{18}\beta_w^2 \frac{[Fe^{3+}]^2}{[H^+]^2} \\ & - \beta_{19}[Fe^{3+}][SO_4^{2-}] - \beta_{20}[Fe^{3+}][SO_4^{2-}]^2 - 2\beta_{21}[Fe^{3+}][SO_4^{2-}]^3 \\ & - \beta_{22}[Fe^{3+}][H^+][SO_4^{2-}] = 0, \quad (32)\end{aligned}$$

$$\begin{aligned}F_5 = {} & [H^+] - \frac{\beta_w}{[H^+]} - 2[SO_4^{2-}] - \beta_2[H^+][SO_4^{2-}] + 2[Zn^{2+}] \\ & + \beta_3\beta_w \frac{[Zn^{2+}]}{[H^+]} - \beta_5\beta_w^3 \frac{[Zn^{2+}]}{[H^+]^3} - 2\beta_6\beta_w^4 \frac{[Zn^{2+}]}{[H^+]^4} \\ & + 2[Fe^{2+}] + \beta_8\beta_w \frac{[Fe^{2+}]}{[H^+]} - \beta_{10}\beta_w^3 \frac{[Fe^{2+}]}{[H^+]^3} - 2\beta_{11}\beta_w^4 \frac{[Fe^{2+}]}{[H^+]^4} \\ & + \beta_{13}[Fe^{2+}][H^+][SO_4^{2-}] + 3[Fe^{3+}] + 2\beta_{14}\beta_w \frac{[Fe^{3+}]}{[H^+]} \\ & + \beta_{15}\beta_w^2 \frac{[Fe^{3+}]}{[H^+]^2} - \beta_{17}\beta_w^4 \frac{[Fe^{3+}]}{[H^+]^4} + 4\beta_{18}\beta_w^2 \frac{[Fe^{3+}]^2}{[H^+]^2} \\ & + \beta_{19}[Fe^{3+}][SO_4^{2-}] - \beta_{20}[Fe^{3+}][SO_4^{2-}] \\ & + 2\beta_{22}[Fe^{3+}][H^+][SO_4^{2-}] = 0. \quad (33)\end{aligned}$$

This system of Eqs. 29–33 is a nonlinear one and it can be solved only by a numerical iterative method. In this case, the F functions are treated as *residuals*, the absolute values of which have to be minimized and set as close to zero as possible. Lee and Tavlarides (1985), for example, used the Secant iterative method to minimize the respective Fs for the determination of species distribution in the system $Fe_2(SO_4)_3$-H_2SO_4. Another method is the Newton-Raphson one, which is generally much faster than the Secant method. Both these methods, though, may not coverage to a solution set or, as mathematicians would say, to a *solution vector* (Press et al., 1989). They also require a "good first guess" of the solution vector. To ensure convergence and to avoid negative roots, the method used here is the Newton-Raphson one as modified by I and Nancollas (1972).

The computational method that is presented in Figure 3 consists of two loops—one nested into the other. (The source code of the computer program has been written for the Microsoft Fortran (Microsoft Corporation, 1989), which is compatible—with only a few extensions—to the standard Fortran 77. This computer program is available from the authors upon request.) In brief, it has as follows.

(i) *Initial Guesses.* First guesses for the values of the key components' concentrations are obtained by assuming complete dissociation of the electrolytes. In other words, the initial guesses can be:

$$\begin{aligned}[H^+]^{(0)} & = 2[H_2SO_4]_{free} \\ & = 2\left([SO_4^{2-}]_{tot} - [Zn^{2+}]_{tot} - [Fe^{2+}]_{tot} - \frac{3}{2}[Fe^{3+}]_{tot}\right),\end{aligned}$$

$$[SO_4^{2-}]^{(0)} = [SO_4^{2-}]_{tot},$$

$$[Zn^{2+}]^{(0)} = [Zn^{2+}]_{tot},$$

$$[Fe^{2+}]^{(0)} = [Fe^{2+}]_{tot},$$

$$[Fe^{3+}]^{(0)} = [Fe^{3+}]_{tot}.$$

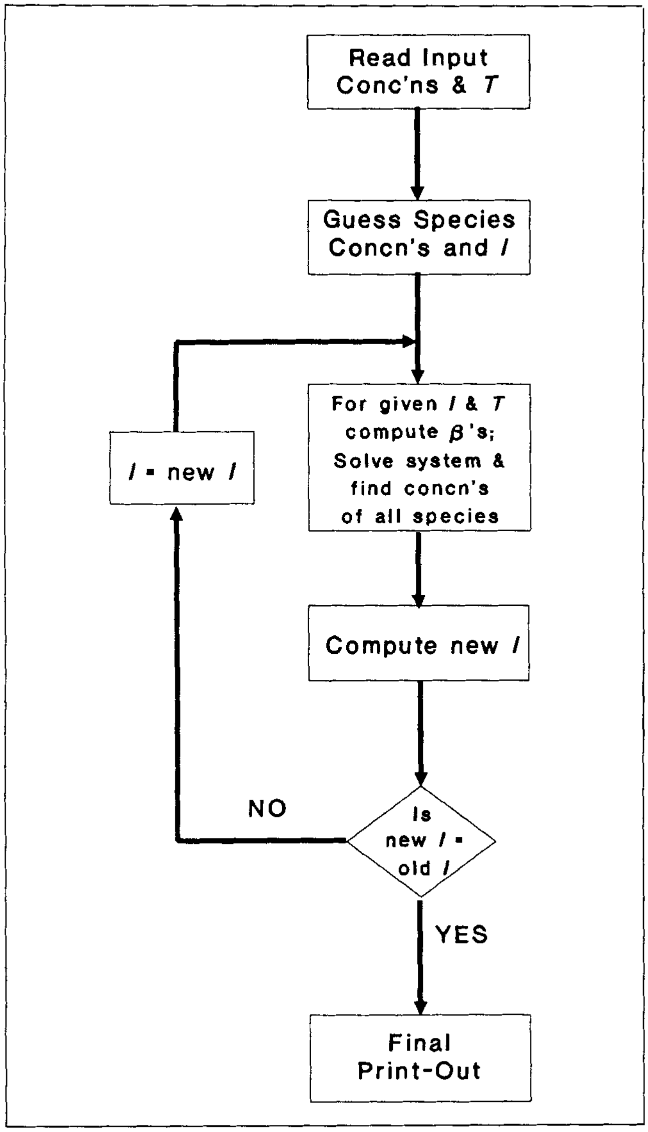

Figure 3. Conceptual flowchart of the computational procedure.

The initial value of the ionic strength on molar basis, $I_c^{(0)}$, is computed accordingly. Also, the value of $I_m^{(0)}$ must be computed at this point. One way to estimate $I_m^{(0)}$ for moderately concentrated solutions is by taking the solution density equal to 1 kg/L^{-1}.

Alternatively, the value of ρ for pure binary solutions such as H_2SO_4-H_2O, $ZnSo_4$-H_2O, and so on, can be found in handbooks (Washburn, 1928), but density data do not exist for all kinds of solutions compositions and temperatures. Here, the density of a mixed sulfate solution was estimated by a simple linear function that was derived by regression of tabulated binary-solution data (Washburn, 1928; Lide, 1991, 1992):

$$\rho = 1.15382 - 5.5\times10^{-4}T + 6.6748\times10^{-2}[H_2SO_4]_{\text{free}} + 0.181436[Zn^{2+}]_{\text{tot}} + 0.158354[Fe^{3+}]_{\text{tot}} + 0.396312[Fe^{3+}]_{\text{tot}}, \text{ in } kg\cdot L^{-1}.$$

This simple equation gives a very good estimate for binary solutions and temperatures less than 373 K (error in ρ less than 1%). For more complex solutions this equation may introduce a slightly higher error, but still such an estimate is far better than assuming ρ equal to 1 $kg\cdot L^{-1}$. For example, with the above empirical equation, it is estimated that a solution of $[Zn^{2+}]_{\text{tot}}$ 0.66 $mol\cdot L^{-1}$ and $[SO_4^{2-}]_{\text{tot}}$ 0.95 $mol\cdot L^{-1}$ at 298 K has $\rho = 1.135$ $kg\cdot L^{-1}$. The density of the same solution can be estimated by applying "Young's Rule" (Teng and Lenzi, 1975) to existing binary solution data (Washburn, 1928). With the second method ρ is estimated equal to 1.137 $kg\cdot L^{-1}$ (less than 1% difference).

(ii) *System Solution.* For given ionic strengths ($I^{(0)}$) and temperature T, mass equilibrium constants β_T can be computed as described in the section discussing mass stability constants. To get new values of the five key components, first the partial derivatives of the F residuals with respect to the key components' concentrations are computed:

$$\left.\frac{\partial F_1}{\partial [H^+]}\right|_{[H^+]^{(0)}}$$

Then, the following system is solved by matrix inversion for the unknown corrections $\delta[H^+]$, $\delta[SO_4^{2-}]$, $\delta[Zn^{2+}]$, $\delta[Fe^{2+}]$, and $\delta[Fe^{3+}]$:

$$\begin{bmatrix} \frac{\partial F_1}{\partial[H^+]} & \frac{\partial F_1}{\partial[SO_4^{2-}]} & \cdots & \frac{\partial F_1}{\partial[Fe^{3+}]} \\ \frac{\partial F_2}{\partial[H^+]} & \frac{\partial F_2}{\partial[SO_4^{2-}]} & \cdots & \frac{\partial F_2}{\partial[Fe^{3+}]} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial F_5}{\partial[H^+]} & \frac{\partial F_5}{\partial[SO_4^{2-}]} & \cdots & \frac{\partial F_5}{\partial[Fe^{3+}]} \end{bmatrix} \cdot \begin{bmatrix} \delta[H^+] \\ \delta[SO_4^{2-}] \\ \delta[Zn^{2+}] \\ \delta[Fe^{2+}] \\ \delta[Fe^{3+}] \end{bmatrix} = \begin{bmatrix} -F_1 \\ -F_2 \\ \vdots \\ -F_5 \end{bmatrix}. \tag{34}$$

In a "pure" Newton-Raphson iterative procedure, the values of $[H^+]$, for example, are updated as:

$$[H^+]^{(1)} = [H^+]^{(0)} + \delta[H^+]$$

If, however, the corresponding relative correction $\alpha_{H^+}^{(1)} = \delta[H^+]/[H^+]^{(0)}$ is less than -1, then the new value of $[H^+]$, $[H^+]^{(1)}$, will be negative. To avoid negative roots for the system of Eqs. 29-33, I and Nancollas (1972) suggested the use of an exponential root updating formula like:

$$[H^+]^{(1)} = [H^+]^{(0)}\exp\{\alpha_{H^+}^{(1)}\}$$

Another pitfall lies in the above equation. If $\alpha_{H^+}^{(1)} \ll 0$, then $[H^+] \approx 0$ and fatal computational errors may occur because the value of $[H^+]$ appears in the denominator of many fractions in Eqs. 29-33. To avoid this problem as well as the previous one of negative roots, the root updating function was selected to be:

$$[H^+]^{(1)} = \begin{cases} [H^+]^{(0)} + \delta[H^+] & \text{when } \alpha_{H^+}^{(1)} > -1 \\ [H^+]^{(0)}/3 & \text{otherwise.} \end{cases} \tag{35}$$

Certainly, this root updating scheme is slower than the exponential method, but it eliminates the possibility of "divide-by-zero" problems. As for the values of the concentrations of the rest of the key components, these are indeed updated by I and Nancollas' exponential formula, since they do not appear at the denominator of any fraction in Eqs. 29-33.

(iii) *End of Iterations.* After the concentrations of the key components are updated, a check is performed to see whether it is worth continuing the search for a solution. If the sum:

$$\Upsilon^{(1)} = \sum_{j=1}^{5} |F_j|$$

is smaller than an acceptable error level there is no need to repeat the procedure. If not, the F functions must be re-evaluated along with their partial derivatives using the solution set which has been obtained after the first iteration (solution vector$^{(1)}$). Then, matrix inversion (Eq. 34) is repeated and Eq. 35 is used to get a new set of values (solution vector$^{(2)}$) for concentrations of the key components. The procedure has to be repeated again and again until Υ is sufficiently small ($< 10^{-6}$, in this work). When this is true, then, by using the definitions of the mass stability constants (Table 4), the concentrations of the rest of the species can be evaluated.

(iv) *Ionic Strength Correction.* When a complete set of concentration values has been obtained, the updated value(s) of I can be calculated and compared to what it had been assumed in the previous cycle. This procedure defines a second loop that is external to (ii) and (iii). If the absolute difference between the present and the previous values of Is is not big ($< 10^{-3}$, in this work), the speciation computational effort is over. In an opposite situation, the updated Is (I_m and I_c) become the current ionic strength values and the whole procedure from step (ii) is repeated. The whole computational effort is over only when the ionic strength values are within the acceptable predefined error level.

At the end of the speciation calculations, the necessary values of m_{H^+} are I_m known. The calculation of the activity coefficient of H^+ and, ultimately, the calculation of the hydrogen activity can be easily made with Eqs. 1-2 and Eq. 14.

Results from such calculations are presented in Table 5. Speciation diagrams that were produced complementary to those calculations are also presented in Figures 4-6. It is worth noting here that in these figures the pH (that is the computed value of $-\log a_{H^+}$) lies well within the acidic region. Metal ions are known to hydrolyze strongly to solid hydroxides even at moderately acidic or neutral pH, but solid-liquid equilibria have not been taken into account in the present calculations.

Experimental Evidence

In the introduction section, it was mentioned that what one measures as pH with a pH-meter is an indicator of relative acidity rather than the exact value of $-\log a_{H^+}$. However, a pH-meter or a potential measuring device in general remains today the most convenient way for studying the thermodynamics (equilibria, activities, and so on) of aqueous electrolytes. For this reason, pH measurements were taken with several aqueous sulfate solutions.

The pH-meter which was used was a Fisher Accumet 825MP with digital display and automatic temperature compensation probe. Attached to this pH-meter there was a combination glass/calomel electrode (Fisher Accu-pHast). According to the manufacturer, this electrode has an overall accuracy of ±0.05 pH-units from 0 to 95°C at pH = 4.

Table 5. Calculated Values of α_{H^+}

Solution Composition (mol·L^{-1})				a_{H^+}		
$[SO_4^{2-}]_{tot}$	$[Zn^{2+}]_{tot}$	$[Fe^{2+}]_{tot}$	$[Fe^{3+}]_{tot}$	298 K	323 K	373 K
0.25	0	0	0	0.220	0.208	0.195
0.50	0	0	0	0.424	0.404	0.382
1.00	0	0	0	0.863	0.831	0.791
1.50	0	0	0	1.367	1.325	1.268
2.00	0	0	0	1.959	1.907	1.834
0.50	0.25	0	0	0.159	0.132	0.087
1.00	0.50	0	0	0.311	0.267	0.195
2.00	1.00	0	0	0.677	0.614	0.514
0.50	0	0.25	0	0.102	0.067	0.027
0.50	0	0	0.25	0.073	0.056	0.022
1.00	0.50	0.10	0	0.198	0.154	0.088
2.00	1.00	0.25	0	0.336	0.270	0.174
3.00	2.00	0.50	0	0.099	0.057	0.017
1.00	0.50	0	0.10	0.185	0.147	0.076
2.00	1.00	0	0.25	0.305	0.245	0.130
3.00	2.00	0	0.50	0.070	0.047	0.018
3.00	2.00	0.10	0.50	0.031	0.019	0.009

Similar solutions are often encountered in zinc electrolytic plants.

Beakers containing solutions of unknown pH were immersed into a water bath together with ones containing standard (buffer) solutions. The temperature of the bath was maintained

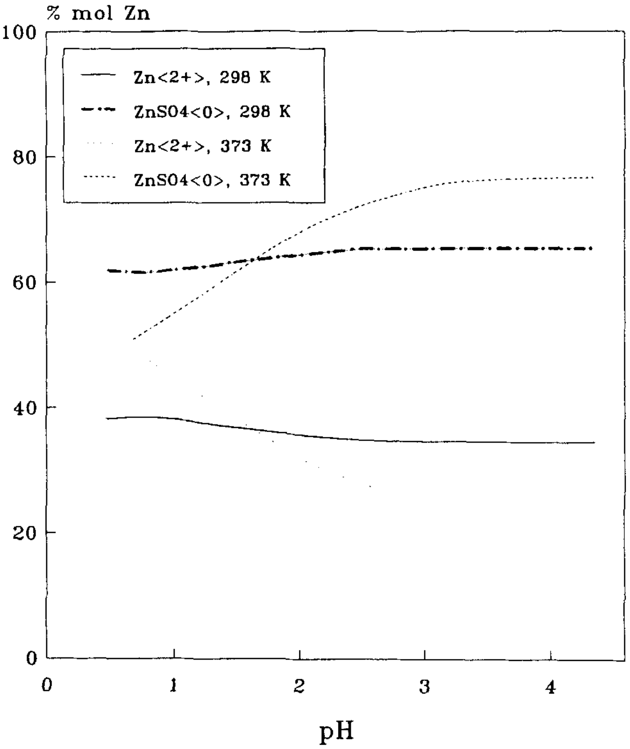

Figure 4. Zinc sulfate speciation diagram at 298 and 373 K.

The total zinc concentration is 0.5 mol·L^{-1} and the value of pH ($-\log a_{H^+}$) has been adjusted by varying the total sulfate concentration.

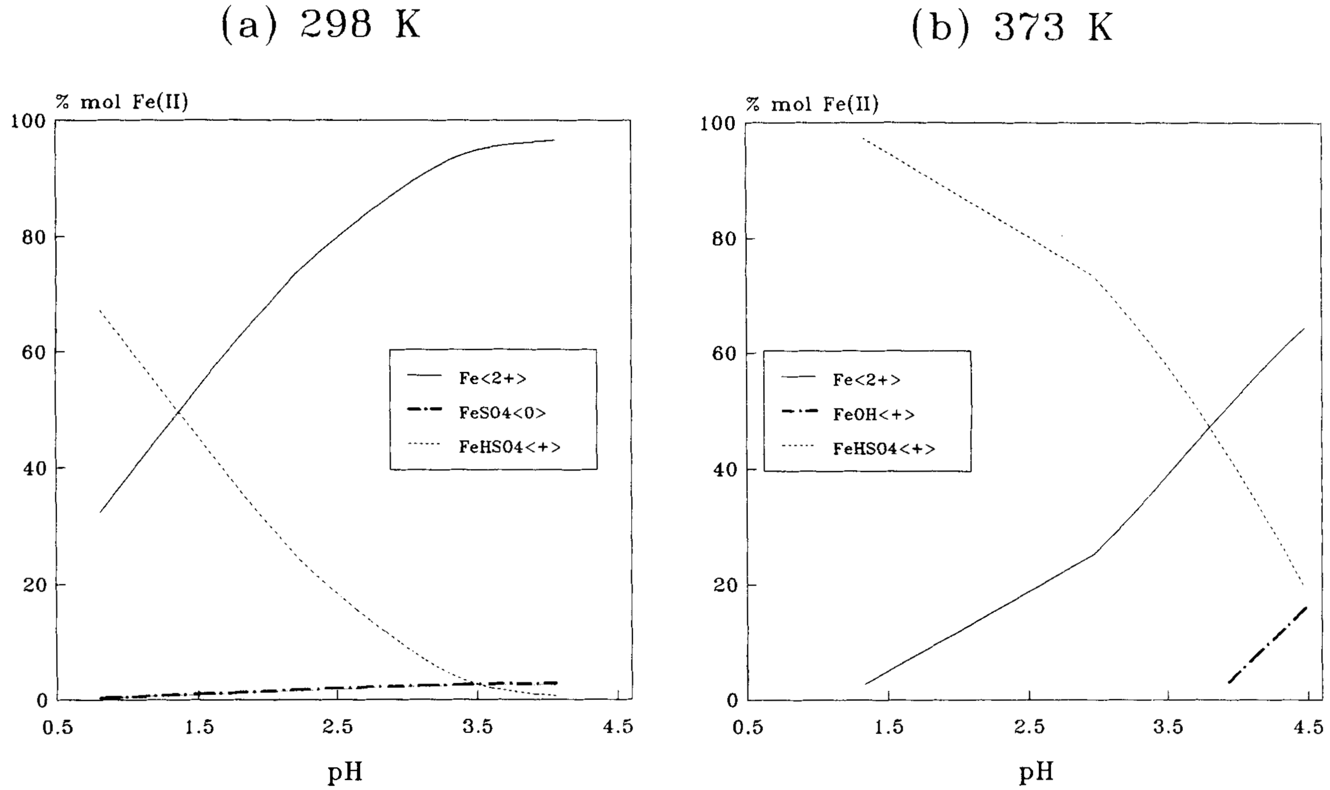

Figure 5. Ferrous sulfate speciation diagram at 298 (a) and 373 K (b).

The total ferrous concentration is 0.5 mol·L^{-1}, and the value of pH ($-\log a_{H^+}$) has been adjusted by varying the total sulfate concentration.

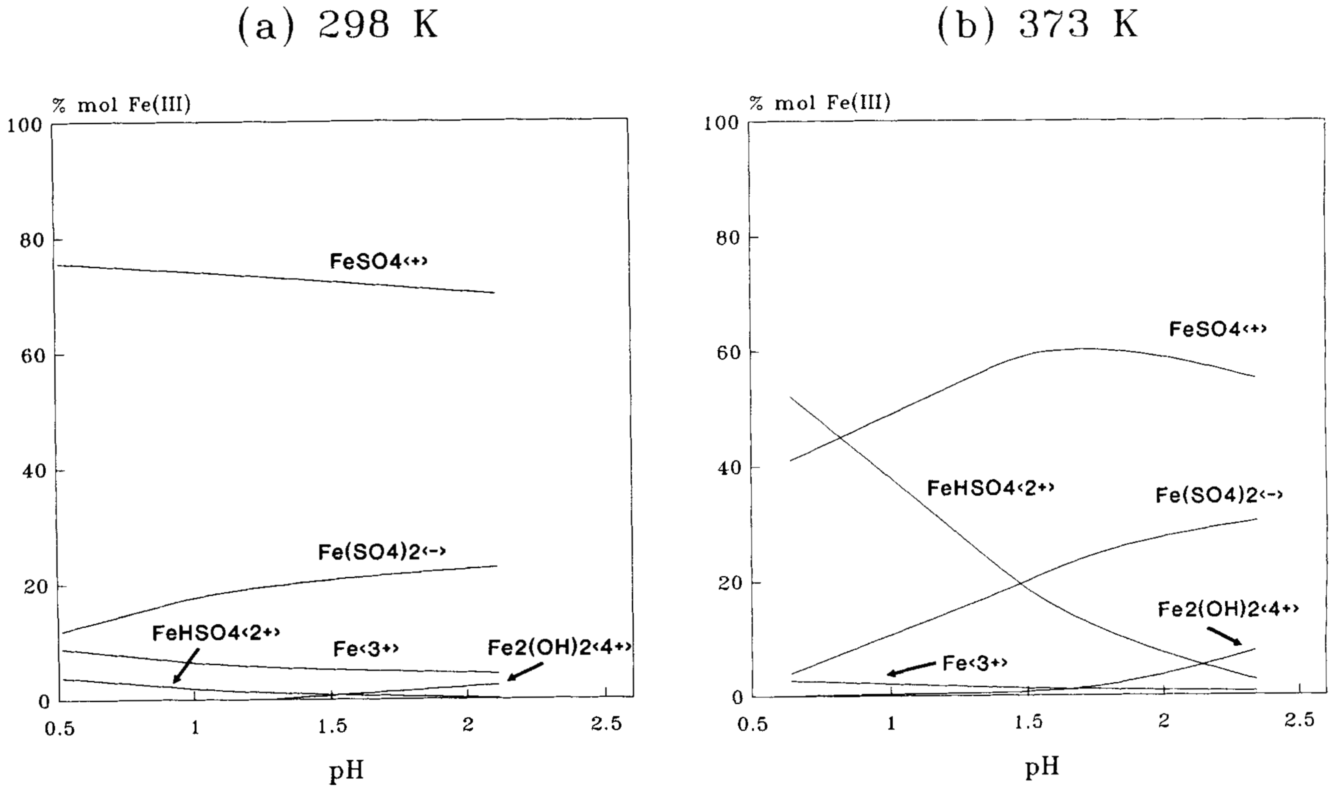

Figure 6. Ferric sulfate speciation diagram at 298 (a) and 373 K (b).

The total ferric concentration is 0.5 mol·L^{-1}, and the value of pH ($-\log a_{H^+}$) has been adjusted by varying the total sulfate concentration.

Table 6. Fisher Buffer Solutions Used for Calibration of the pH-Meter*

Buffer pH at 298 K	Basic Components
1.00	HCl, KCl
2.00	HCl, KCl
4.00	K-H-phthalate
7.00	KH_2PO_4, NaOH

*The exact composition of these solutions is not obtainable (proprietary data), but the manufacturer acknowledges that they are rather dilute solutions ("their total molarity is 0.05").

constant at 298 K (±1 K) with a temperature circulator. Calibration of the pH-meter was performed between measurements using the buffer solutions, which in fact, were Fisher certified ones of relatively low ionic strength (Table 6). Each measurement was taken only when 20 min had passed since the immersion of the electrode into the unknown or buffer solution. This waiting time was deemed necessary so as to have a stable reading at the pH-meter.

In Table 7 several pH measurements have been listed and are compared to the ones predicted by the computational procedure described in the section on numerical solution. In most of these solutions, excellent agreement exists between measured pH values and computed ones (as $-\log a_{H^+}$). Small discrepancies can be attributed to experimental errors such as the accuracy of the electrode. The only solutions for which the differences between measured and computed pH might not be considered negligible are the ones which contain solely $ZnSO_4$. The predicted pH values for the $ZnSO_4$ solutions is higher by 0.5 pH units than the measured ones because the hydrolysis of Zn^{2+} to solid zinc hydroxide has not been taken into account.

The reader may also notice that in the last table, there have not been included any pH measurements at ionic strengths higher than 0.25 $mol \cdot L^{-1}$. In fact, such measurements were attempted, but the results were not reliable. The electrode was not providing stable readings (it was "drifting"), and there was a severe problem of proper calibration. Unfortunately, the known standard solutions, like the Fisher buffers used here, are not suitable for calibration when the solution to be measured has high ionic strength and pH much lower than 1.

It is worth mentioning at this point the speciation work of Mihaylov and Distin (1993) for the aqueous system $Ga_2(SO_4)_3$-H_2SO_4. These authors have also used Eqs. 1-2 to get the activity of H^+, and their predictions were confirmed by an excellent agreement between measured and computed pH (as $-\log a_{H^+}$) values.

Lastly, the values of a_{H^+} were used to get the order of the zinc ferrite dissolution in sulfuric acid (Filippou and Demopoulos, 1992a). It has been found that indeed the zinc ferrite dissolution rate is proportional to $(a_{H^+})^{0.54}$. The 0.54 order of the ferrite dissolution reaction has been explained also theoretically (Filippou and Demopoulos, 1993) and this is another confirmation—indirect, though—of the validity of the present approach for the estimation of a_{H^+} in aqueous sulfate systems.

Comparison to Previous Work

Hydrogen ion activities have never been estimated before in mixed metal sulfate aqueous solutions. Therefore, this discussion has to be restricted to speciation calculations and diagrams produced by other investigators in the past.

For the case of $ZnSO_4$ solutions, it seems that there do not exist many speciation diagrams. In one of the few relevant publications, Long and Angino (1977) have constructed speciation diagrams for Zn and other base metals in freshwater, seawater and brine at room temperature. These authors have determined that the most dominant Zn species at low pH is Zn^{2+} when the total metal concentration is in the range of 10 ppm. This finding seems to be in contrast to the speciation diagram of Figure 4, but it can be explained by the fact that Long and Angino included in their speciation some other species as well: Cl^-, CO_3^{2-} and HCO_3^-. Certainly the presence of these negatively charged species alters the zinc ion distribution.

More recently, Larsen and Linkson (1993) constructed potential-pH ("Pourbaix") diagrams for the system Zn-SO_2-H_2O at temperatures as high as 473 K. Their work confirms that at pH generally less than 3, Zn^{2+} is the most dominant species. Nevertheless, these authors ignored the neutral species $ZnSO_4^0$ and their estimated thermodynamic values for the Zn-OH species differ significantly from the ones given in Table 3.

Table 7. Measured vs. Computed pH ($-\log a_{H^+}$) Values for Various Solutions at 298 K

Solution Composition ($mol \cdot L^{-1}$)				pH		I computed	
$[SO_4^{2-}]_{tot}$	$[Zn^{2+}]_{tot}$	$[Fe^{2+}]_{tot}$	$[Fe^{3+}]_{tot}$	Comp.	Meas.	I_c, $mol \cdot L^{-1}$	I_m, $mol \cdot kg^{-1}$
0.010	0	0	0	1.87	1.88	0.021	0.021
0.100	0	0	0	1.01	0.98	0.145	0.146
0.250	0	0	0	0.66	0.70	0.325	0.330
0.050	0.025	0	0	1.62	1.59	0.099	0.100
0.050	0.050	0	0	5.88	5.34	0.118	0.119
0.100	0.100	0	0	5.84	5.22	0.216	0.219
0.050	0	0.025	0	1.67	1.60	0.126	0.127
0.063	0	0	0.025	1.60	1.57	0.078	0.078
0.050	0.013	0.013	0	1.65	1.61	0.112	0.113
0.056	0.013	0	0.013	1.62	1.59	0.088	0.089
0.056	0	0.013	0.013	1.64	1.59	0.101	0.102
0.054	0.008	0.008	0.008	1.61	1.60	0.100	0.101

Many more speciation diagrams have been published for the iron species. In the case of ferrous sulfate solutions, Davison (1979) has examined the accuracy of the stability constants of $FeOH^+$ and $FeSO_4^0$ at 298 K. His revised values for these stability constants are 1-1.5 orders of magnitude higher than the ones computed by the thermodynamic data of Table 3. Davison did not consider some other species which are listed in Table

3, but he came to the conclusion that the most dominant ferrous species in natural waters which contain some sulfate ions is the Fe^{2+} at pH values around 7. Nonetheless, despite the differences between Davison and the work presented here, the findings of this author can be confirmed also by the present speciation diagrams (Figure 5).

Tremaine and LeBlanc (1980) have also produced speciation diagrams of Fe^{2+} species. They have shown that in the absence of sulfate ions, Fe^{2+} dominates at pH generally lower than 6 and temperatures as high as 573 K. This is certainly not in disagreement with the results of the present work.

Speciation of ferric aqueous compounds may well be the most widely examined case to date. Many of the speciation diagrams that have been constructed do not seem to agree with each other. Differences in databases used and individual decisions as how to take into account ionic strength effects are believed to be the most frequent source of these variations (May and Murray, 1991). For example, Dousma et al. (1979) and Pouillon and Doyle (1987) have apparently used a "nominal" (or "formal") ionic strength, that is, an ionic strength value corresponding to complete electrolyte dissociation for their speciation calculations in the ferric sulfate aqueous system. This is obviously incorrect since the stability constants depend on the value of the true ionic strength of the solution, I_m or I_c. The true solution ionic strength cannot really be a fixed quantity when the pH varies.

The above remark applies also in the case of ferrous-ferric speciation diagrams produced by Liddell and Bautista (1981) and by Senanayake and Muir (1988). Only in speciation diagrams for ferric sulfate solutions produced by Lee and Tavlarides (1985) and by Wu and Yu (1991) the ionic strength effect has been really taken into account. The approach of these authors to the speciation problem is almost the same as the one used here and, not surprisingly, their results are almost identical to those in Figure 6.

Conclusion

In this publication, an attempt to evaluate hydrogen ion activities through speciation in plain or mixed-metal sulfate aqueous solutions was described. First, with the aid of an existing extended Debye-Hückel type of equation, the value of the hydrogen ion activity coefficient was computed at temperatures ranging from 298 to 373 K and total sulfate concentration up to 2.0 $mol \cdot L^{-1}$.

Then, the same equation was also used for mixed metal sulfate solutions. In particular, hydrogen ion activities were estimated for the mixed aqueous system $ZnSO_4$-$FeSO_4$-$Fe_2(SO_4)_3$-H_2SO_4. In order to evaluate the molality of hydrogen ion and the true solution ionic strength, it was necessary to undertake speciation work from which speciation diagrams were constructed. To this end, a comprehensive algorithm was built which accounts for I and T effects on stability constants.

The results of the computational effort were confirmed by several pH measurements and by an extensive review of previously published speciation work. It was found that there exists a very good agreement between computed and measured pH values at ambient temperature. Finally, most of the previously published speciation work for similar systems provides an additional affirmation of the validity of the present work.

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Notation

a = activity
$\mathcal{A}$ = coefficient of C_p polynominal, $J \cdot mol^{-1} \cdot K^{1}$
b = Vasil'ev's constant (Eq. 22)
$\mathcal{B}$ = coefficient of C_p polynomial, $10^3\ J \cdot mol^{-1} \cdot K^{-2}$
c = molar concentration, $mol \cdot L^{-1}$
$\mathcal{C}$ = coefficient of C_p polynomial, $10^5\ J \cdot K \cdot mol^{-1}$
C_p = heat capacity, $J \cdot mol^{-1} \cdot K^{-1}$
f = Dickson's auxiliary functions (Eqs. 3-7)
F = residual functions (Eqs. 24-28 or 29-33)
G = free energy, $J \cdot mol^{-1}$ or $kJ \cdot mol^{-1}$
H = enthalpy, $J \cdot mol^{-1}$ or $kJ \cdot mol^{-1}$
I = ionic strength, $mol \cdot L^{-1}$ or $mol \cdot kg^{-1}$
K = equilibrium constant on molal basis
m = molal concentration, $mol \cdot kg^{-1}$
p = Dickson's parameters (Eqs. 3-7 and Table 1)
q = auxiliary function for the estimation of b
R = universal gas constant, 8.31434 $J \cdot mol^{-1} \cdot K^{-1}$
S = entropy, $J \cdot mol^{-1} \cdot K^{-1}$
T = temperature, K
z = ionic charge

Greek letters

β = equilibrium constant on molar basis
γ = activity coefficient
δ = correction (Eq. 34)
Δ = change
θ = Helgeson's parameters (Eq. 21)
Υ = sum of residual functions F

Subscripts and superscripts

c = on molar scale
f = formation
i = species indicator
j = residual function indicator
m = on molal scale
n = total number of species
tot = total
T = at temperature T
0 = standard

Other symbol

[ ] = concentration, $mol \cdot L^{-1}$

Literature Cited

Awakura, Y., K. Koyama, Y. Takegawa, and H. Majima, "Determination of the Association Constant of Sulfuric Acid," *Metall. Trans. B*, **21B**, 689 (1990).

Bale, C. W., A. D. Pelton, and W. T. Thompson, *Facility for the Analysis of Chemical Thermodynamics* (*F*A*C*T*), Thermofact Ltd./Ltée & McGill Univ., Montreal (1991).

Bassett, R. L., and D. C. Melchior, "Chemical Modeling of Aqueous Systems: An Overview," *Chemical Modeling of Aqueous Systems II*, D. C. Melchior and R. L. Bessett, eds., Am. Chem. Soc., Washington, DC, p. 1 (1990).

Bates, R. G., B. R. Staples, and R. A. Robinson, "Ionic Hydration and Single Ion Activities in Unassociated Chlorides at High Ionic Strengths," *Anal. Chemistry*, **42**, 867 (1970).

Bates, R. G., *Determination of pH. Theory and Practice*, 2nd ed., Wiley, New York, pp. 15 and 59 (1973).

Bockris, J. O'M., and A. K. N. Reddy, *Modern Electrochemistry*, Vol. 1, Plenum Press, New York, p. 175 (1970).

Burkov, K. A., L. A. Garmash, and L. S. Lilich, "Hydrolysis of Zinc Ions at Different Temperatures," *Russ. J. of Inorg. Chemistry*, **23**, 1770 (1978).

Davison, W., "Soluble Inorganic Ferrous Complexes in Natural Waters," *Geochimica et Cosmochimica Acta*, **43**, 1693 (1979).

Das, K., "Single Ion Activities in Aqueous Sulfuric Acid Solutions: A New Extra-Thermodynamic Assumption," *J. of Solution Chemistry*, **17**, 327 (1988).

Demopoulos, G. P., P. Kondos, and V. G. Papangelakis, "Prediction of Solubilities in Chemical Compound Precipitation Systems," *Int. Symp. on Crystallization and Precipitation*, G. L. Strathdee, M. O. Klein, and L. A. Melis, eds., Metallurgical Soc. of CIM and Pergamon Press, Saskatoon, Canada, p. 231 (1987).

Denbigh, K., *The Principles of Chemical Equilibrium*, 4th ed., Cambridge University Press, Cambridge, p. 143 (1981).

Dickson, A. G., D. J. Wesolowski, D. A. Palmer, and R. E. Mesmer, "Dissociation Constant of Bisulfate Ion in Aqueous Sodium Chloride Solutions to 250°C," *J. of Phys. Chemistry*, **94**, 7978 (1990).

Dousma, J., D. den Ottelander, and P. L. de Bruyn, "The Influence of Sulfate Ions on the Formation of Iron(III) Oxides," *J. Inorg. Nucl. Chemistry*, **41**, 1565 (1979).

Fedorov, V. A., G. E. Chernikova, M. A. Kuznechikhina, and V. E. Mironov, "Effect of the Ionic Medium and Temperature on the Formation of Sulphato-Complexes of Zinc and Cadmium and Calculations of their Thermodynamic Stability Constants," *Russ. J. of Inorg. Chemistry*, **18**, 337 (1973).

Filippou, D., and G. P. Demopoulos, "A Reaction Kinetic Model for the Leaching of Industrial Zinc Ferrite Particulates in Sulphuric Acid Media," *Can. Metall. Quart.*, **31**, 41 (1992a).

Filippou, D., and G. P. Demopoulos, "On the Variable Dissolution Kinetics of Zinc Ferrite in Acid Media," *Can. J. of Chem. Eng.*, **71**, 790 (1993).

Helgeson, H. C., "Thermodynamics of Complex Dissociation in Aqueous Solutions at Elevated Temperatures," *J. of Phys. Chemistry*, **71**, 3121 (1967).

I, Ting-Po, and G. H. Nancollas, "EQUIL—A General Computational Method for the Calculation of Solution Equilibria," *Anal. Chemistry*, **44**, 1940 (1972).

Jackson, K. J., and H. C. Helgeson, "Chemical and Thermodynamic Constraints on the Hydrothermal Transport and Deposition of Tin: I. Calculation of the Stability of Cassiterite at High Pressures and Temperatures," *Geochimica et Cosmochimica Acta*, **49**, 1 (1985).

Jansz, J. J. C., "Estimation of Ionic Activities in Chloride Systems at Ambient and Elevated Temperatures," *Hydrometall.*, **11**, 13 (1983).

Larsen, D. M., and P. B. Linkson, "Thermodynamics of the Zinc-Sulfur Dioxide-Water System," *Metall. Trans. B*, **23B**, 409 (1993).

Lee, C. K., and L. L. Tavlarides, "Ionic Equilibria in Ferric Sulfate-Sulfuric Acid Solutions," *Polyhedron*, **4**, 47 (1985).

Lide, D. R., ed., *CRC Handbook of Chemistry and Physics*, 72nd ed., CRC Press, Boca Raton, FL, p. 15:19 (1991-92).

Liddell, K. C., and R. G. Bautista, "A Partial Equilibrium Chemical Model for the Dump Leaching of Chalcopyrite," *Metall. Trans. B*, **12B**, 627 (1981).

Lister, M. W., and D. E. Rivington, "Ferric Sulphate Complexes, and Ternary Complexes with Thiocyanate Ions," *Can. J. of Chemistry*, **33**, 1591 (1955).

Long, D. T., and E. E. Angino, "Chemical Speciation of Cd, Cu, Pb, and Zn in Mixed Freshwater, Seawater, and Brine Solutions," *Geochimica et Cosmochimica Acta*, **41**, 1183 (1977).

Magini, M., "Solute Structuring in Aqueous Iron(III) Sulphate Solutions: Evidence for the Formation of Iron(III)-Sulphate Complexes," *J. of Chem. Phys.*, **70**, 317 (1979).

Majima, H., and Y. Awakura, "Measurement of the Activity of Electrolytes and the Application of Activity to Hydrometallurgical Studies," *Metall. Trans. B*, **12B**, 141 (1981).

Marshall, W. L., and E. V. Jones, "Second Dissociation Constant of Sulfuric Acid from 25 to 350° Evaluated from Solubilities of Calcium Sulfate in Sulfuric Acid Solutions," *J. of Phys. Chemistry*, **70**, 4028 (1966).

Martell, A. E., and R. M. Smith, *Critical Stability Constants*, Vol. 5, 1st Suppl., Plenum Press, New York (1982).

May, P. M., and K. Murray, "JESS, A Joint Expert Speciation System: I. Raison d'Être," *Talanta*, **38**, 1409 (1991).

Microsoft Corporation, *Microsoft FORTRAN*, Version 5.0. Redmond, CA (1989).

Mihaylov, I. O., and P. Distin, "Solvent Extraction of Gallium with D2EHPA from Acidic Sulphate Solutions—Equilibria and Complexation," *Can. Metall. Quart.*, **32**, 21 (1993).

Nair, V. S. K., and G. H. Nancollas, "Thermodynamics of Ion Association: IV. Magnesium and Zinc Sulphates," *J. Chem. Soc.*, 3706 (1958).

Papangelakis, V. G., and G. P. Demopoulos, "Acid Pressure Oxidation of Arsenopyrite: I. Reaction Chemistry," *Can. Metall. Quarterly*, **29**, 1 (1990).

Perrin, D. D., ed., "Ionisation Constants of Inorganic Acids and Bases," *IUPAC Chem. Data Series*, 2nd ed., No. 29, Pergamon Press, Oxford, p. 103 (1982).

Pitzer, K. S., R. N. Roy, and L. F. Silvester, "Thermodynamics of Electrolytes. 7. Sulfuric Acid," *J. of the Am. Chem. Soc.*, **99**, 4930 (1977).

Pouillon, D., and F. M. Doyle, "Software for Computation of Aqueous Phase Species Distribution and Solvent Extraction with Liquid Cation Exchangers," *Metall. Trans. B*, **18B**, 743 (1987).

Press, W. H., B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes; the Art of Scientific Computing (Fortran Version)*, Cambridge University Press, Cambridge, p. 240 (1989).

Reichle, R. A., K. G. McCurdy, and L. G. Hepler, "Zinc Hydroxide: Solubility Product and Hydroxy-Complex Stability Constants from 12.5-75°C," *Can. J. of Chemistry*, **53**, 3841 (1975).

Senanayake, G., and D. M. Muir, "Speciation and Reduction Potentials of Metal Ions in Concentrated Chloride and Sulfate Solutions Relevant to Processing Base Metal Sulfides," *Metall. Trans. B.*, **19B**, 37 (1988).

Smith, R. M., and A. E. Martell, *Critical Stability Constants*, Vol. 4, Plenum Press, New York (1976).

Teng, T.-T., and F. Tenzi, "Density Predictions of Multicomponent Aqueous Solutions from Binary Data," *Can. J. of Chem. Eng.*, **53**, 673 (1975).

Tremaine, P. R., and J. C. LeBlanc, "The Solubility of Magnetite and the Hydrolysis and Oxidation of Fe^{2+} in Water to 300°C," *J. of Solution Chemistry*, **9**, 415 (1980).

Vasil'ev, V. P., "Influence of Ionic Strength on the Instability Constants of Complexes," *Russ. J. of Inorg. Chemistry*, **7**, 924 (1962).

Wagman, D. D., W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Baley, K. L. Churney, and R. L. Nuttall, "The NBS Tables of Chemical Thermodynamic Properties," *J. Physical and Chem. Ref. Data*, **11** (Suppl. 2), 2-21 (1982).

Washburn, E. W., ed., *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, Vol. III, McGraw-Hill, New York, p. 51 (1928).

Wu, Z., and S. Yu, "Ionic Equilibria in Fe(III)-H_2SO_4-Na_2SO_4 Aqueous Solution System," *Acta Metall. Sinica*, **27**, B6, in Chinese with English abstract (1991).

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