Aqueous Speciation of Arsenic in Sulfuric Acid and Cupric Sulfate Solutions

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Physicochemical data for arsenic speciation calculations, and the development and application of an equilibrium model were determined numerically and experimentally to simulate the speciation of arsenic and copper in aqueous sulfuric acid solutions. Results show that concentrations of dissolved species depended highly on temperature, acidity, and solution concentration. A range of species can be formed, depending on pH and temperature. In acidic solutions, the principal ones are: HSO_4^-, H^+, Cu^{2+}, $CuSO_{4(aq)}$, $H_3AsO_{3(aq)}$, *and* $H_3AsO_{4(aq)}$; *arsenic ions are present in low concentrations. Association degrees increase with temperature and concentration, the solutes being partially dissociated. Calculations of metal solubilities, pH, and ionic conductivity showed good agreement with experimental data. The model can be applied to study the aqueous speciation in industrial copper hydrometallurgical solutions, as well as to define and to evaluate purification strategies for the treatment of industrial effluents.*

Introduction

Arsenic is found as an impurity in the hydrometallurgical processing of many copper and gold ores. Leaching of such ores produces intermediate compounds or byproducts, which often result in arsenic dissolution and the subsequent need to remove it from solution in an environmentally acceptable manner. This is done in order to satisfy quality control as well as effluent standards.

Arsenic has the tendency to accumulate in industrial metallurgical circuits reaching high concentration levels, which affect the metal production performance (Noguchi et al., 1992). In order to prevent this situation, dissolved arsenic compounds must be periodically removed from aqueous liquors. Totsuka et al. (1986) mentioned the necessity of periodic arsenic removal from copper electrolytes to prevent the occurrence of high As concentration levels in electrorefining cells. Arsenic concentration should be kept below 4–6 g/L in order to produce good cathodes; it can be removed in the form of the Cu_3As intermetallic compound at liberator tanks with insoluble anodes. From a technical point of view, arsenic could be removed from aqueous liquors by operations such as chemical precipitation, absorption, ion exchange, solvent extraction, crystallization, membrane or electrolytic processes (Dewalens et al., 1975; Totsuka et al., 1986; Robins, 1988; Monhemius and Swash, 1999; Piret, 1999; Cifuentes et al., 1999, 2002; Nishimura et al., 2000; Welham et al., 2000). However, there is still no established technology for arsenic removal from industrial circuits in the copper industry, because of the high treatment cost. As a consequence, industrial companies apply different methodologies for arsenic control.

The distribution of arsenic compounds in hydrometallurgical liquors and in environmental aquatic systems has been studied by Price and Davenport (1981), Itagaki and Nishimura (1986), Robins (1988), Nishimura et al. (1988), Fernández et al. (1992), Pokrovski et al. (1996), Vink (1996), Edwards et al. (1998), Langmuir et al. (1999), and Welham et al. (2000). Arsenic can be present in acid solutions as reduced arsenite [As(III)] or oxidized arsenate [As(V)] compounds, such as $H_3AsO_{3(aq)}$, $H_3AsO_{4(aq)}$, $H_2AsO_4^-$. Bisulfate (HSO_4^-) and arsenic acid (H_3AsO_4) predominate up to pH ~2, where deprotonation occurs and sulfate (SO_4^{2-}) and dihydrogen arsenate ($H_2AsO_4^-$) ions become predominant species. For ar-

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senite, the major species is H_3AsO_3 at all acidic pH values. As(V) is much more soluble than As(III) in water, their solubilities as 25°C being 570 g/L and 15 g/L, respectively (Nishimura and Tozawa, 1986).

In previous articles, Casas et al. (1999, 2000) applied the models proposed by Davies (1962) and Pitzer (1991) to simulate the nonideality of the aqueous solution containing copper sulfate and sulfuric acid and to calculate the effective equilibrium constants and activity coefficients in the 15 to 80°C range. These models are useful to calculate the speciation in diluted systems with more than one component or in simple concentrated solutions. In the first case, ion−cation electrostatic interactions can be better evaluated by using a simplification of the Debye-Hückel theory. In the latter case, high concentrations produce binary and ternary interactions between solutes and solvent. This requires a large number of model parameters to represent all the involved phenomena, and only solutions containing two to four species can be properly modeled for a range of temperatures and concentrations. In the case of electrolytic solutions at moderate concentrations (0.3 to 1.5 molal), the main models that could be applied are extended Debye-Hückel (Helgeson et al., 1981; Wolery, 1992), Bromley-Zemaitis (Zemaitis et al., 1986; Rafal et al., 1994), and specific interaction (Wang et al., 1997; Grenthe and Plyasunov, 1997).

This article examines the speciation of metallurgically relevant systems formed by As(III), As(V), and Cu(II) in aqueous sulfuric acid solutions using critically reviewed thermodynamic data for the calculation of equilibrium constants. Ionic activities are calculated using the extended Debye-Hückel equation, evaluated as a function of solution ionic strength, and the speciation model is solved using the EQ3/6 thermodynamic code (Wolery, 1996). Simulations of copper and arsenic solubilities, as well as aqueous metal speciation, are studied in the 0−100°C and 0.01−1.0-m ranges. The results are compared with our own experimental data and the results published by other workers.

Experimental studies were carried out at moderate concentrations, because data are scarce in these conditions and they are necessary to understand the solution speciation. Motivation for this study was originated in current research on the application of electrodialysis to solutions occurring in copper electrometallurgy (Cifuentes et al., 2002). Knowledge of the ionic equilibrium of these solutions is important in order to understand the processes, to optimize the productive operations, as well as to define the control strategies for impurities and contaminants present in the resulting liquid effluents.

There are very few published data regarding the speciation of the As-$CuSO_4$-H_2SO_4-H_2O system, typical of operations such as copper leaching and electrorefining. This is because the experimental determination of the speciation of electrolyte systems presents considerable difficulties, for example, the lack of analytical techniques for *in situ* determination of some ions and metallic complexes at different temperatures and concentrations, and the very high cost of modern laboratory equipment. In this sense, the main contribution of this work is the combination of experimental measurements (metal solubility, solute concentration, ionic conductivity, and pH) and the application of a thermodynamic model to establish the solution speciation in real conditions.

Modeling

Modeling the aqueous speciation

The aqueous speciation in electrolyte systems can be determined by the application of a thermodynamic model that consists of a set of defined species, components, and reactions occurring in aqueous solution (Casas et al., 2000; Cifuentes et al., 2002), plus a set of equilibrium relationships and mass-balance equations for each defined component. A detailed speciation modeling methodology is presented by Stumm and Morgan (1996). The main relationships are

Equilibrium

$$K_{ri} = \prod_{j=1}^{N_{sp,n}} a_j^{\pm \nu_j} \tag{1}$$

Mass balance

$$TOT\,X_j = \sum_{i=1}^{N_{sp}} \nu_i m_i \tag{2}$$

where K_{ri} is the equilibrium constant of the reaction for the formation of the ith species; m_i, a_i, and $\pm\nu$ are the molal concentration, the activity, and the stoichiometric coefficient (+ for products and − for reactants) of the ith species, respectively; and $TOT\,X_j$ is the total molal concentration of the jth component. Activity and concentration are related by $a_i = m_i \gamma_i$, where γ_i is the activity coefficient of the ith species (see units in Notation section).

In order to exclude density changes with temperature, all calculations include molal concentrations (m), that is, moles of solute per kilogram of water, thus allowing a comparison of solute concentrations at different temperatures.

In the present work, the extended Debye-Hückel activity coefficient model is applied in order to study the speciation of copper and arsenic in sulfuric acid solutions. A simplification of Helgeson's model (Helgeson et al., 1981) is proposed as

$$\log \gamma_i = -\frac{A_\gamma z_i^2 \sqrt{I}}{1 + \mathring{a}_i B_\gamma \sqrt{I}} + \dot{B}\cdot I \tag{3}$$

Equation 3 is also known as a B-dot equation; $\mathring{a}_i$ is the hard-core diameter of the species i; z_i is the charge of the ith species; A_γ and B_γ are Debye-Hückel parameters; and I is the solution ionic strength. This model has three temperature-dependant parameters (A_γ, B_γ, and $\dot{B}$), as shown later in Table 3, and one parameter for each of the solvated species, the "hard-core diameter" ($\mathring{a}$). This is a modification of the classic Debye-Hückel model and it is valid for binary interactions. In order to correct the activity coefficient for those cases where molecular interactions—other than electrostatic ones —come into play, the same value in the B-dot parameter is included for all participating species. The model is valid for aqueous electrolyte solutions with moderate ionic strength values. The validity range for this model has been reported up to $I = 1$ molal (Wolery, 1992; Parkhurst, 1995; Cifuentes et al., 2002). The term $\dot{B}\cdot I$ represents a correction for molecular interactions. The extended Debye-Hückel model has been used by Helgeson and coworkers (Helgeson et al., 1981) and introduced in several speciation codes and geochemical software, such as: MINTEQA2 (Allison et al., 1991), EQ3/6 (Wolery, 1992), and PHREEQC (Parkhurst, 1995).

In the systems considered in this work, only moderate concentrations were used in order to prevent copper or arsenic precipitation. These systems present electrostatic (long-range) interactions and molecular (short-range) interactions between dissolved species; however, their effect is small in the studied concentration ranges, given that water activity is about 0.98 and the ionic strength of the solution is 0.85 molal (see Table 3). These considerations justify the use of the B-dot model. The use of other models like the ones mentioned earlier, could allow better evaluation of short-range molecular interactions between solutes and solvent; however, these models require a large amount of experimental data in order to obtain numerous interaction parameters. Such data are unavailable.

The equilibrium speciation model consists of an algebraic nonlinear system (Eqs. 1 to 4), which can be solved by geochemical codes such as the EQ3/6 software (Wolery, 1996). This code implements a multidimensional Newton-Raphson numerical algorithm and allows the calculation of the aqueous speciation in the presence of minerals and dissolved gaseous species for a wide range of pH, temperature, saturation pressure, and concentration values. In the EQ3/6 code the activity of water is evaluated as a function of temperature, ionic strength, and solution composition. To solve the model, the code requires the values of standard equilibrium constants as a function of temperature for dissolution, complexation, and hydrolysis reactions of minerals, neutral solutes, and complex species.

Thermochemistry of Arsenic in H_2O-H_2SO_4-$CuSO_4$ System

Databases

Several thermodynamic databases are available to obtain species, reactions and thermodynamic properties for minerals and aqueous electrolytes: Baes and Mesmer (1981), NBS (Wagman et al., 1982), MINTEQA2 (Allison et al., 1991), Data0.com (Wolery, 1996), NIST database (Smith et al., 1998), Slop98.dat (Shock et al., 1998), Aspen Plus; HSC Chemistry (Roine, 2002), Web Sites (Bale, 2002). Databases are usually comprehensive, but there are differences among them with respect to the reported values for the thermochemical properties of many minerals, aqueous ions, and metallic complexes. This is due to difficulties in the chemical analysis of solutions with several components at high concentrations and temperatures; it is also due to the diversity of the experimental and mathematical techniques and equilibrium models currently used.

Model formulation

The model formulation that represents the aqueous speciation in the As-Cu-H_2O-H_2SO_4 system is summarized in Table 1 as a "speciation tableau." The aqueous species were selected from the literature (Wagman et al., 1982; Wolery, 1996; Stumm and Morgan, 1996). In Table 1 the reactions are represented as stoichiometric combinations of components, for example, the reaction of dissolution for arsenious oxide (arsenolite) is

$$As_2O_3(s) + 3H_2O \leftrightarrow 2H_2AsO_3^- + 2H^+$$

Table 1. Stoichiometry for the Main Species, as a Function of Components in the As(III)-As(V)-H_2SO_4-$CuSO_4$-H_2O System, and Hard-Core Diameters for Ionic Species

	Components						
Species	H_2O	SO_4^{2-}	H^+	$H_2AsO_3^-$	$H_2AsO_4^-$	Cu^{2+}	å (Å)
HSO_4^-	0	1	1	0	0	0	4.0
$CuSO_{4(aq)}$	0	1	0	0	0	1	—
$CuHSO_4^+$	0	1	1	0	0	1	4.0*
$CuOH^+$	1	0	−1	0	0	1	4.0
$Cu_2(OH)_2^{2+}$	2	0	−2	0	0	2	6.0
$H_3AsO_{3(aq)}$	0	0	1	1	0	0	—
$H_3AsO_{4(aq)}$	0	0	1	0	1	0	—
$H_4AsO_3^+$	0	0	2	1	0	0	4.0
$As_2O_{3(S)}$	−3	0	2	2	0	0	
$As_2O_{5(S)}$	−3	0	2	0	2	0	
$CuSO_4 \cdot 5H_2O_{(S)}$	−5	1	0	0	0	1	
$CuSO_4 \cdot 3H_2O_{(S)}$	−3	1	0	0	0	1	
å (Å)	—	4.0	9.0	4.0	4.0	6.0	

Source: Wolery, 1992.

*The hard-core diameter (å) for $CuHSO_4^+$ was estimated using data for monovalent cations reported in the EQ3/6 database documentation (Wolery, 1996).

The standard equilibrium constant for this reaction at 25°C is

$$K_{eq,25°C} = [H_2AsO_3^-]^2 * [H^+]^2 / a_w^3 = 10^{-19.84} \quad (6)$$

The system can be evaluated by the following set of mass-balance equations for each defined component, according to Eq. 2

$$Cu(II) = [Cu^{2+}] + [CuSO_{4(aq)}] + [CuHSO_4^+] + m[Cu_m(OH)_n^-] \quad (7)$$

$$As(III) = [H_2AsO_3^-] + [H_3AsO_{3(aq)}] + [H_4AsO_3^-] \quad (8)$$

$$As(V) = [H_2AsO_4^-] + [H_3AsO_{4(aq)}] \quad (9)$$

$$H(tot) = 2[H_2O] + [H^+] + [HSO_4^-] + [MeHSO_4^{n+}] - n[Me(OH)_n^-] + 4^*[H_4AsO_3^+] - 2^*([H_2AsO_3^-] + [H_2AsO_4^-]) + 3^*([H_3AsO_{4(aq)}] + [H_3AsO_{3(aq)}]) \quad (10)$$

$$SO_4(tot) = [SO_4^{2-}] + [HSO_4^-] + [MeHSO_4^{n+}] + q[Me_p(SO_4)_{q(aq)}] + r[Me(SO_4)_r^-] + [MeSO_4^+] \quad (11)$$

where Me represents a metal such as Cu or As. To solve the balance equations, five concentrations must be fixed in advance: those of Cu^{2+}, $H_2AsO_3^-$, $H_2AsO_4^-$, H^+, and SO_4^{2-}, which correspond to selected system components.

Table 2. Equilibrium Constants of Dissociation Reactions Represented in Table 1 as a Function of Temperature

Species	Log K_d (Molal Basis)				Ref.
	°C	25°C	60°C	100°C	
Water, H_2O	−14.94	−14.00	−13.03	−12.26	*
Bisulfate ion, HSO_4^-	−1.72	−1.98	−2.44	−3.00	*
Aqueous cupric sulfate, $CuSO_{4(aq)}$	−2.23	−2.40	−2.68	−3.03	**
Cupric bisulfate ion, $CuHSO_4^+$	−1.38	−2.34	−3.45	−4.46	†
Cupric hydroxide ion, $CuOH^+$	8.66	7.93	7.09	6.33	*
Dicupric hydroxide ion, $Cu_2(OH)_2^{2+}$	11.58	10.41	9.03	7.74	††
Arsenious acid, $H_3AsO_{3(aq)}$	−9.69	−9.23	−8.76	−8.40	*, ‡
Arsenic acid, $H_3AsO_{4(aq)}$	−2.18	−2.27	−2.43	−2.63	*
$H_4AsO_3^+$	−9.40	−8.94	−8.45	−8.10	‡‡
Arsenolite, α-$As_2O_{3(S)}$	−21.25	−19.84	−18.25	−16.95	§
Claudetite, β-$As_2O_{3(S)}$	−21.16	−19.77	−18.36	−17.30	§
Arsenic pentaoxide, $As_2O_{5(S)}$	2.67	2.16	1.38	0.46	§§
Chalcanthite, $CuSO_4 \cdot 5H_2O_{(S)}$	−2.54	−2.46	−2.50	−2.51	‖
Bonattite, $CuSO_4 \cdot 3H_2O_{(S)}$	−1.48	−1.69	−2.05	−2.53	‖ ‖

*Calculated with SUPCRT'92 Johnson et al. (1992) and the upgrade database "SLOP98.dat" from Shock (1998).

**Reference data from Stumm and Morgan (1996) for the equilibrium constant of magnesium sulfate [$MgSO_{4(aq)}$].

†Reference data from Smith et al. (1998) for the equilibrium constant of ferrous bisulfate [$FeHSO_4^+$].

††Reference data from Stumm and Morgan (1996), extrapolated using heat-capacity integration procedure with HSC-Chemistry (Roine, 2002).

‡Reference data from Langmuir et al. (1999).

‡‡Reference data from Langmuir et al. (1999) for the equilibrium constant of arsenious acid [H_3AsO_3(aq)].

§Reference data from EQ3/6 database (Wolery, 1996) and mathematical regression of arsenolite solubility data in water at various temperatures.

§§Reference data from Wagman et al. (1982), extrapolated using heat-capacity integration method.

‖Reference data from HSC-Chemistry database (Roine, 2002) and mathematical regression of chalcanthite solubility data in water at various temperatures.

‖ ‖Calculated with HSC-Chemistry (Roine, 2002), heat capacity integration method.

Model parameters

In the present work, the equilibrium constant approach is adopted because standard equilibrium constants are the key parameters for the speciation model. There are two ways of estimating equilibrium constants as a function temperature. The first one is based on direct or indirect concentration measurements; the second one is to evaluate the partial molal properties of aqueous species as a function of temperature and pressure (based on measurements and calculations), which permits the calculation of the free energy for reactions involving these species. Knowledge of the free energy of the reaction leads to the calculation of its equilibrium constant.

For example, the equilibrium constant for the metal complex formation can be obtained by measuring the concentration of dissolved species and then calculating the activity quotients using an activity coefficient model

$$n\text{Me}^+ + m\text{L}^- \leftrightarrow \text{Me}_n\text{L}_m^{+n-m}, \qquad K_{\text{eq}} = \frac{a_{\text{Me}_n L_{\text{m}}^{+m-m}}}{a_{Me^+}^n \cdot a_{L^-}^m} \tag{12}$$

where Me^+ represents a metal ion (cation) and L^- is a ligand (anion). Alternatively, the equilibrium constant at a given temperature and pressure can be obtained through calculation using the Gibbs free energy of reaction as

$$K_{\text{eq}} = \exp\left\{-\frac{\Delta G_{P,T}}{RT}\right\} \tag{13}$$

The Gibbs free energy for each species that participates in the chemical reaction is a thermochemical property that can be obtained in various ways, for example, it has been determined by using different regression methods and experimental techniques. For example, Helgeson et al. (1981) proposed an equation of state (EOS) model for electrolyte solutions, where standard thermodynamic properties such as entropy, enthalpy, and Gibbs free energy of dissolved species were derived from both volume and heat-capacity relationships, which are functions of the system's temperature and pressure.

In this work, model data are partly based on reported equilibrium constants for metal complexes and mineral dissolution/precipitation reactions. When no data are available, either Helgeson's model for electrolytic solutions (Helgeson et al., 1981; Johnson et al., 1992; Sverjensky et al., 1997) or a heat-capacity integration model (Roine, 2002) are used to estimate the equilibrium constants at various temperatures. Most standard equilibrium constants as a function of temperature were estimated from copper sulfate and arsenic (III) oxide solubility data for the 0–100°C temperature range. These are presented in Table 2 and the parameters for the extended Debye-Hückel model as a function of temperature are presented in Table 3.

Experimental Methodology

Experimental work to study the As(III)-As(V)-H_2SO_4-$CuSO_4$-H_2O system was carried out at room temperature (18 ± 1°C). A set of solutions formed by binary and ternary mix-

Table 3. Extended Debye-Hückel Parameters as a Function of Temperature

Parameter	Temperature (°C)			
	0	25	60	100
A_γ (kg$^{0.5}$/mol$^{0.5}$)	0.4939	0.5114	0.5465	0.5995
B_γ (kg$^{0.5}$/mol$^{0.5}$/Å)	0.3253	0.3288	0.3346	0.3421
$\dot{B}$ (kg/mol)	0.0394	0.0410	0.0438	0.0460

Source: EQ3/6 software, Wolery, 1996.

tures were prepared using 0–0.16 M $CuSO_4$, 0.3–0.5 M H_2SO_4, and 0–0.1 M As (see details in Table 5). Solutions were equilibrated in agitated beakers and then liquid samples were taken and filtered. Chemical analyses were performed to determine the solution concentration; pH and ionic conductivity were measured.

The analytical procedure was as follows: distilled water was used throughout, and the stock solution of sulfuric acid was prepared by dilution of the concentrated analytical reagent (Mallinkrodt: SP, ACS, USA, H_2SO_4 96.1%). The concentration of the stock solution was determined by titration with a standard solution of sodium hydroxide 0.1 M. The copper sulfate was prepared from cupric sulfate pentahydrate (Fluka, $CuSO_4 \cdot 5H_2O$ 99%) and dissolved arsenic was prepared from arsenious oxide (Fluka, As_2O_3 99%). The concentration of dissolved Cu(II), As(III), and As(V) was determined by atomic absorption spectroscopy using a Perkin-Elmer 1100B spectrophotometer and hydride generator equipment. The values of pH and the electrochemical potential of the solution (E_h) were measured with a Cole Parmer model 5982-10 meter, using a combination electrode with calomel for the pH and a silver/silver chloride combination electrode for the E_h determination (values against SHE). The pH at low ranges was measured with a differential probe from Great Lakes Instruments (Schott). Finally, the ionic conductivity of the solution was determined with a Jenco model 1,671 meter that works in the range 0–200 mS/cm, using a No. 104 platinum cell.

Results and Discussion

The developed model was used to simulate the speciation (that is, the distribution and concentration of dissolved species) in aqueous solutions that contain sulfuric acid, cupric sulfate, and dissolved arsenic in the 0–100°C temperature range, 0.0–1.0 m H_2SO_4, 0.0–1.0 m As, and 0.0–4.0 m Cu concentration ranges. The results are presented as distribution diagrams (see Figures 1 to 9), where the concentration of each species is a function of temperature, pH, and the concentration of the remaining species. Model calculations are compared with our own experimental data and the results published by other workers.

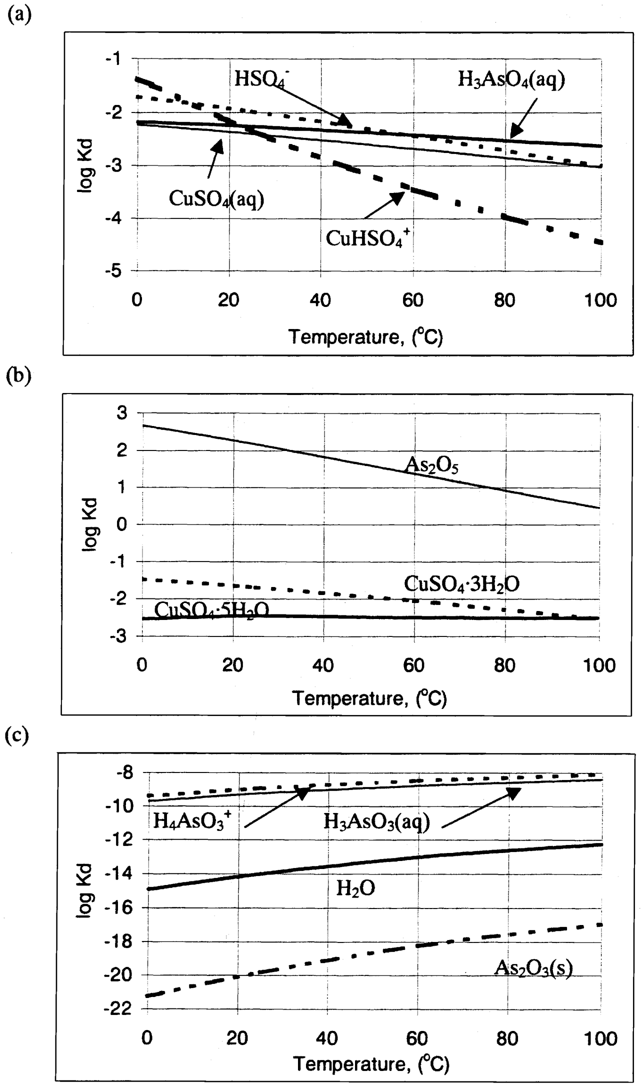

Figure 1. Equilibrium constants as a function of temperature for both aqueous and mineral species shown in Table 2.

Model calibration

The model was first calibrated using equilibrium constants for each reaction and thermochemical parameters that were revised and carefully compared with available properties and information contained in databases (SUPCRT'92, EQ3/6, and HSC-Chemistry) and in the literature (Wagman et al., 1982; Arnorsson et al., 1982; Allison et al., 1991; Robins, 1988; Nishimura et al., 1988; Stumm and Morgan, 1996). Thermochemical properties, such as entropy, enthalpy, and free energy of ions and dissolved complexes, at reference conditions (25°C, 1 atm, and infinite dilution), are available from chemical handbooks and databases (Smith et al., 1998; Shock, 1998; Lide, 1999; Roine, 2002; Bale, 2002, and so on). These properties were extrapolated to standard conditions (1 atm and infinite dilution) in order to estimate equilibrium constants in the 0 to 100°C range. Helgeson's model (SUPCRT'92; Johnson et al., 1992) with the upgraded "Slop98.dat" database (Shock et al., 1998) was used. In the absence of parameters for this model, a heat-capacity integration method (HSC-Chemistry; Roine, 2002) was applied.

Standard equilibrium constants for the dissociation reaction involving species with a few or incomplete thermochemical data have been estimated by adjusting them to fit the speciation model to experimental solubility results of arsenolite (α-As_2O_3), claudetite (β-As_2O_3), chalcanthite ($CuSO_4 \cdot 5H_2O$), and bonattite ($CuSO_4 \cdot 3H_2O$), in water in the temperature range 0–100°C. Results are reported in Table 2 and Figure 1. In this graphic, a great variation of equilibrium constant values with temperature is observed for the majority of the species in the studied range.

In comparison, those compounds participating in reactions with large equilibrium constant values exhibit low stability and tend to undergo dissociation or dissolution. For example, the stability of arsenic acid (H_3AsO_4) and both aqueous and mineral copper compounds increases with temperature. On the other hand, the stability of arsenolite (As_2O_3), arsenious

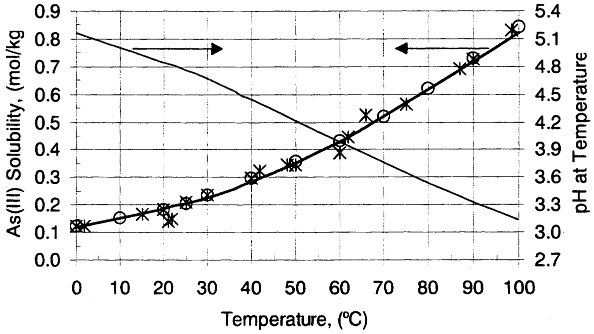

Figure 2. Solubility of arsenolite (α-As_2O_3) in water and equilibrium pH as a function of temperature.

Experimental data from; (O): Lide (1999), and (∗): Pokrovski et al. (1999), and (—): calculated values using EQ3/6 software (Wolery, 1996).

acid (H_3AsO_3), and $H_4AsO_3^+$ ions present the opposite tendency. The stability of As_2O_5 increases very little with temperature in the studied range.

Solubility data for copper and arsenic minerals were used in order to calibrate model parameters as a function of temperature. The reported species and estimated values for equilibrium constants mentioned earlier were carefully revised and then introduced in the "data0.dat" database used by the EQ3/6 software. The upgraded database was used in calculations of the aqueous speciation of As-Cu-H_2SO_4 systems. The list of incorporated species, stoichiometric, and equilibrium constants in the database are shown in Tables 1 and 2.

Solubility and speciation calculations

This section presents solubility calculations, aqueous speciation, and model comparisons for copper and arsenic solubility in aqueous sulfuric acid solutions. Solubility calculations were carried out in order to calibrate and to validate the speciation model (see Table 4 and Figures 2 to 7).

Arsenic Solubility in Water. Figure 2 shows the experimental and calculated values for arsenolite solubility in water within the 0–100°C temperature range. As(III) is dissolved mainly as arsenious acid $H_3AsO_{3(aq)}$, which remains undissociated. The stability of this species increases with temperature, changing its relative arsenic concentration from 97% to 100% at 0°C and 100°C, respectively. Solution pH decreases with temperature from 5.2 to 3.2 at 0°C and 100°C, respectively. This is a consequence of high increases in arsenolite solubility. The arsenious acid concentration in solution increases from 0.12 m at 0°C to 0.82 m at 100°C, and the solution becomes more concentrated in H^+ ions.

Copper Solubility in Water. The results for copper solubility and speciation calculations are shown in Figure 3. Figure 3a shows the experimental and calculated values for chalcanthite solubility in water in the 0–100°C temperature range.

Copper is dissolved mainly as cupric sulfate [$CuSO_{4(aq)}$], an undissociated species. The dissolved copper concentration increases with temperature from 0.8 m at 0°C to 4.7 m at 100°C. The solution pH decreases with temperature from 4.6 at 0°C to 3.7 at 100°C as a consequence of an increase in the concentration of hydrolyzed compounds represented as $Cu_a(OH)_b^{+2a-b}$. At temperatures higher than 95°C, chalcanthite is unstable and transforms to bonattite. This experimentally observed change in the solid phase (Linke, 1958) is well predicted by the model using the EQ3/6 software.

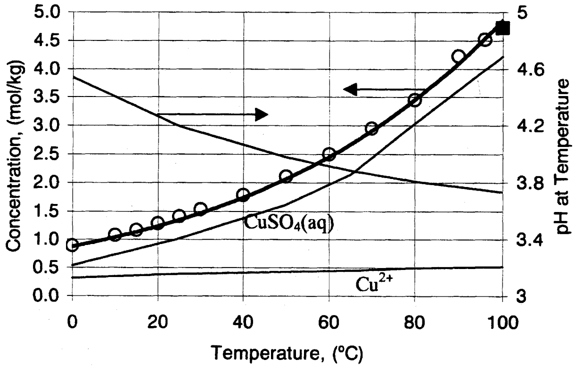

Figure 3a. Experimental and calculated solubility of chalcanthite ($CuSO_4 \cdot 5H_2O$) in water and calculated equilibrium speciation as a function of temperature.

Experimental data from Lide (1999) and Linke, 1958, (O: $CuSO_4 \cdot 5H_2O$; ■: $CuSO_4 \cdot 3H_2O$). Calculated values using EQ3/6 software (Wolery, 1996), (—).

Figure 3b shows the calculated equilibrium concentration of the main species formed from chalcanthite dissolution in water as a function of temperature. The stability of $CuSO_{4(aq)}$ increases with temperature. Its relative concentration increases from 62% at 0°C to about 88% at 100°C. On the other hand, the relative concentration of sulfate ion decreases from 38% to 12% at the same temperature.

Figures 2 and 3 show that the association degree of complex species in solution increases with temperature. The use of the thermodynamic model allows the prediction of the As(III) and Cu(II) solubilities in water. Calculations are in good agreement with experimental data throughout the studied temperature range.

Speciation of Arsenic and Copper in Aqueous Sulfuric Acid Solutions. This section presents results obtained by the application of the speciation model in order to study and to

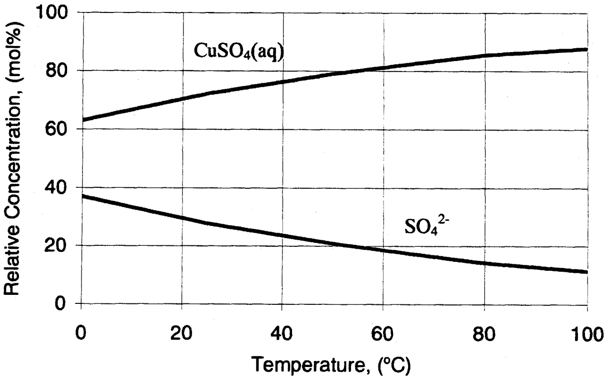

Figure 3b. Calculated equilibrium concentration of main aqueous sulfate species formed from chalcanthite dissolution in water as a function of temperature.

Table 4. Calculated Speciation at 25°C for an Aqueous Solution Containing 0.5 m H_2SO_4, 0.2 m $CuSO_4$, 0.1 m H_3AsO_3, and 0.1 m H_3AsO_4

Species	Conc. (mol/kg of Water)
HSO_4^-	0.532
H^+	0.420
Cu^{2+}	0.104
$H_3AsO_{4(aq)}$	0.098
$H_3AsO_{3(aq)}$	0.079
SO_4^{2-}	0.072
$CuSO_{4(aq)}$	0.066
$CuHSO_4^+$	0.030
$H_4AsO_3^+$	0.021
$H_2AsO_4^-$	0.002
pH	0.483
Water activity	0.977
Ionic strength	0.854

analyze concentration and temperature effects on the distribution and concentration of the species present in the As(III)-As(V)-H_2SO_4-$CuSO_4$-H_2O system. The electrolyte composition is 0.5 m H_2SO_4, 0.2 m $CuSO_4$, 0.1 m H_3AsO_3, and 0.1 m H_3AsO_4. The studied ranges are 10–80°C for temperature and 0.0–1.0 molal for each solute. The latter range was selected in order to prevent the formation of precipitates and also to study nonideal solutions with concentrations similar to those found in the industrial hydrometallurgy of copper.

Table 4 presents a summary of model calculations for the speciation of the studied solution at 25°C. Results indicate that sulfuric acid and copper sulfate are partially dissociated and the arsenic acids are mostly nondissociated. It is possible to say that the studied solution is highly nonideal, due to its concentration, high acidity (pH $\approx$ 0.5), and high ionic strength ($I \approx 0.9$ molal). The ionic species with higher concentrations are HSO_4^-, H^+, and Cu^{2+}, and the neutral species with lower concentrations are $H_3AsO_{4(aq)}$, $H_3AsO_{3(aq)}$, and $CuSO_{4(aq)}$ (see details in Table 4).

Temperature Effects. Relative concentration and solution pH for arsenic, copper, and sulfate species as a function of temperature are presented in Figures 4a to 4c. These figure parts represent the calculated speciation for an aqueous solution containing 0.5 m H_2SO_4, 0.2 m $CuSO_4$, 0.1 m H_3AsO_3, and 0.1 m H_3AsO_4, in the 10–80°C temperature range.

Figure 4a shows the pH and relative concentrations of dissolved arsenic species as a function of temperature. The solution pH increases with temperature from pH = 0.45 at 10°C to pH = 0.61 at 80°C, due to an increase in the association degree of compounds present in solution, for example, bisulfates (see Figures 4b and 4c). The relative concentrations of arsenic and arsenious acids were 49% and 40%, respectively, these being the main dissolved arsenic species. These values are not affected by temperature changes in the studied range, and remain practically constant. Other arsenic compounds are present in concentrations lower than 10%.

Figure 4b shows the relative concentration of dissolved copper species as a function of temperature. The concentrations of Cu^{2+} and $CuSO_{4(aq)}$ decrease with temperature, and the concentration of copper bisulfate ($CuHSO_4^+$) increases with temperature. Copper sulfate is partially dissociated, the relative concentration of cupric ions being 55% at 0°C and 30% at 80°C. Notice that, in this case, there is an increase in the stability of copper bisulfate. The formation of this species is favored by high solution acidity and temperatures in the 50–80°C range (see Figure 4c).

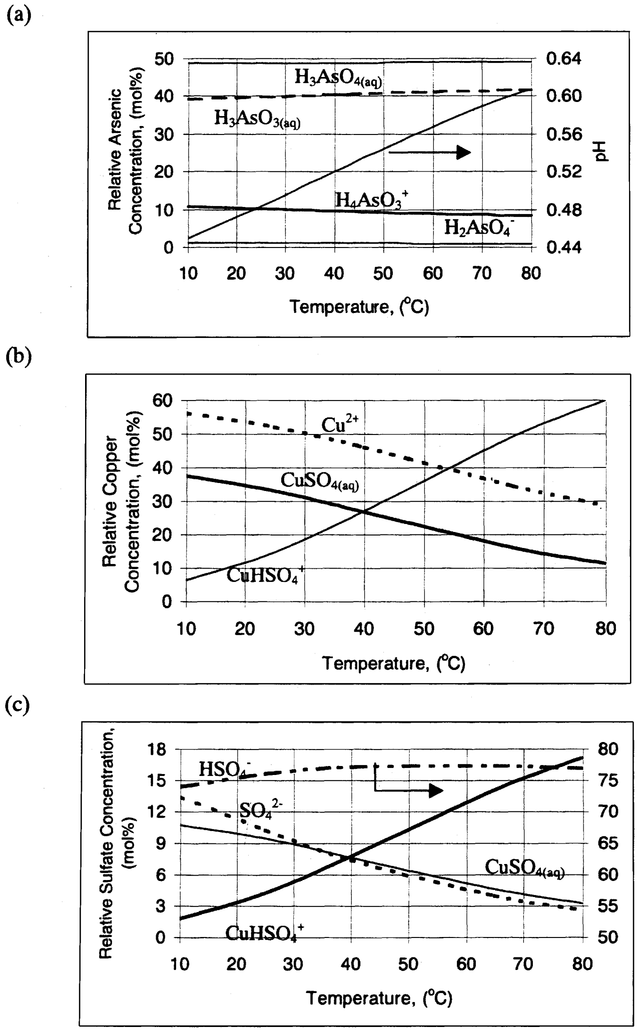

Figure 4. Calculated speciation as a function of temperature for an aqueous solution containing 0.5 m H_2SO_4, 0.2 m $CuSO_4$, 0.1 m H_3AsO_3, and 0.1 m H_3AsO_4.

(a) Relative arsenic concentration; (b) relative copper concentration; (c) relative sulfate concentration.

Figure 4c shows the relative concentrations of dissolved sulfate species as a function of temperature. The concentrations of SO_4^{2-} and $CuSO_{4(aq)}$ decrease with temperature and the concentrations of HSO_4^- and $CuHSO_4^+$ increase with temperature. The dissociation degree of sulfate is low and decreases with temperature, for example, the relative concentration of SO_4^{2-} is 13.5% at 0°C and 3% at 80°C. Bisulfate is the main sulfate-derived species and its relative concentration increases with temperature from 74% at 0°C to 77% at 80°C.

Concentration Effects. The pH value and the concentrations of arsenic, copper and sulfate species as a function of

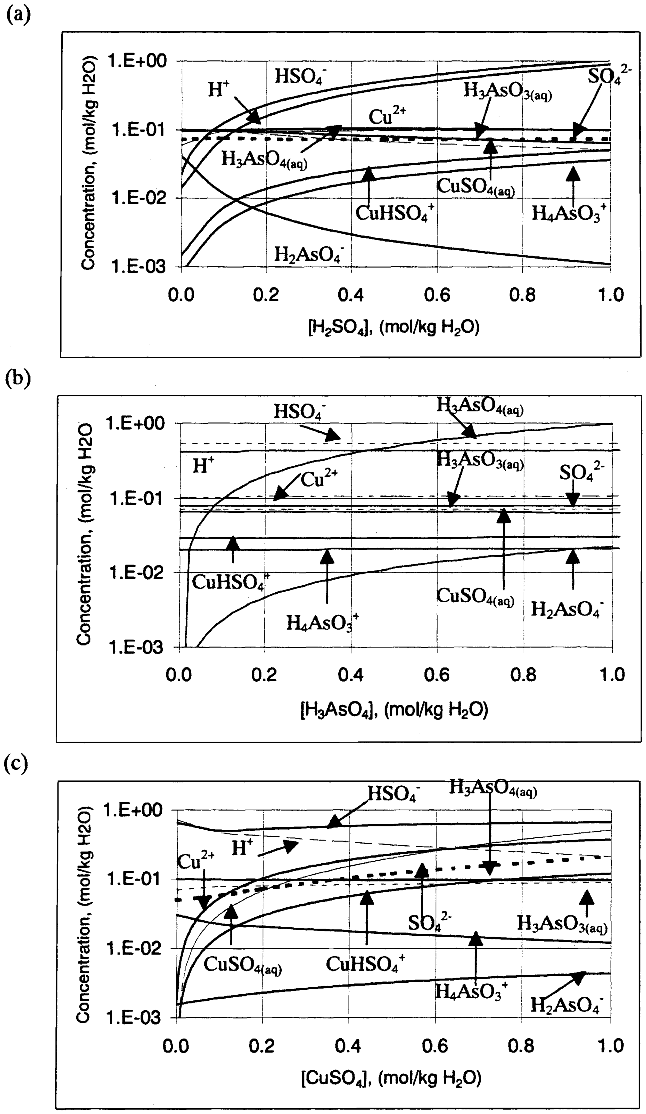

Figure 5. Calculated speciation at 25°C as a function of added solute concentration.

The analytical solution composition for the three cases is shown in Table 4.

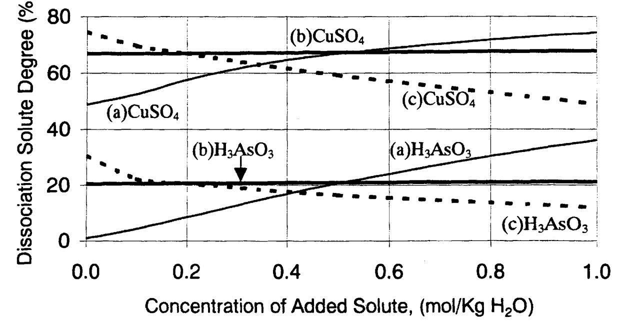

Figure 6. Calculated dissociation degree of $CuSO_4$ and H_3AsO_3 at 25°C as a function of added solute concentration.

The analytical solution composition for the three cases is shown in Table 4. Added solutes (a) H_2SO_4; (b) H_3AsO_4; (c) $CuSO_4$.

temperature are presented in Figures 5 and 6. These figures present the calculated speciation and pH at 25°C as a function of added solute concentration in the 0.0–1.0 molal range. They refer to an aqueous solution containing 0.5 m H_2SO_4, 0.2 m $CuSO_4$, 0.1 m H_3AsO_3, and 0.1 m H_3AsO_4.

Figure 5a shows the concentrations of the main dissolved species as a function of added sulfuric acid concentration. The concentrations of $HSO_4{}^-$, H^+, $CuHSO_4{}^+$, and $H_4AsO_3{}^+$ increase with the amount of added acid. The concentrations of Cu^{2+}, $CuSO_{4(aq)}$, $H_3AsO_{3(aq)}$, $H_3AsO_{4(aq)}$, and $SO_4{}^2$ remain constant with increasing sulfuric acid concentration. However, the concentration of $H_2AsO_4^-$ decreases with increasing acid concentration.

Figure 5b shows the concentration of the main dissolved species as a function of the concentration of added arsenic acid. The concentration of As(V) species increases with the amount of added acid, while the concentration of all other dissolved species remains practically constant. This behavior indicates that arsenic acid exhibits a low dissociation degree, which corresponds to a weak electrolyte.

Figure 5c shows the concentration of the main dissolved species as a function of the concentration of added cupric sulfate. The concentration of the H^+ ion decreases due to bisulfate formation, which is in turn a result of the increase in the sulfate content of the solution. Decreasing the H^+ ion concentration produces an increase in the dissociation degree of arsenic acid as well as an increase in the concentration of $H_2AsO_4{}^-$.

Figure 6 shows the calculated dissociation degree of $CuSO_4$ and H_3AsO_3 at 25°C as a function of added solute concentration for all three cases shown in Figures 5a to 5c. Cupric sulfate is highly dissociated as Cu^{2+} species in acid solutions. The degree of dissociation ranges from 50% to 75% for $CuSO_4$, from 1% to 38% for H_3AsO_3, and from 0.5% to 4.3% for H_3AsO_4, depending on the solution composition. For the case of the $CuSO_4$ and H_3AsO_3, the dissociation degree increases with the addition of sulfuric acid, stays relatively constant with the addition of arsenic acid, and decreases with the addition of cupric sulfate. The dissociation degree for H_3AsO_4 showed the opposite trend when sulfuric acid or cupric sulfate were added to the solution. The dissociation degree decreases with the addition of sulfuric acid, due to its higher stability compared with bisulfate species.

Figure 7 shows the calculated pH at 25°C as a function of the added solute concentration for all three cases shown in Figure 5. A significant decrease in pH from 1.8 to 0.2 is observed when sulfuric acid concentration increases from 0.0 to 1.0 molal. In the case of the addition of H_3AsO_4, the pH remains constant at a value close to 0.5. As mentioned before, this behavior is explained by the acid's low dissociation degree. The addition of cupric sulfate produces a pH increase from 0.3 to 0.8 as a result of the increase in bisulfate ion concentration, according to the results mentioned earlier. In all cases, a higher solute concentration produces an increase in bisulfate concentration and a decrease in H^+ concentration compared with a pure sulfuric acid solution. For example, the calculated pH of the studied solution was 0.48 compared with pH = 0.38 for a pure sulfuric acid solution (0.5 molal and 25°C).

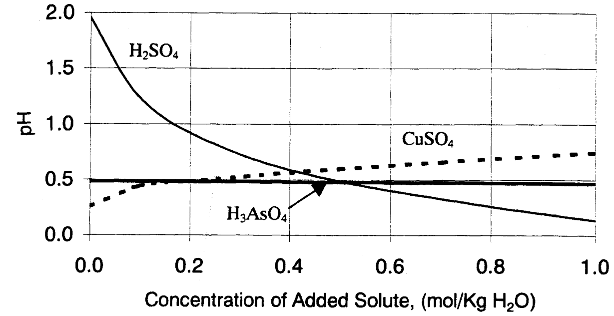

Figure 7. Calculated pH at 25°C as a function of added solute concentration. The analytical solution composition for the three cases is shown in Table 4.

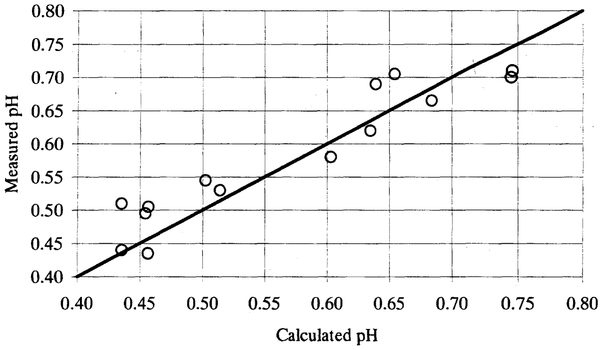

Figure 8. Experimental and calculated pH for the As(III)-As(V)-H_2SO_4-$CuSO_4$-H_2O system at 18 ± 1°C.

Model validity

A comparison of experimental results and results calculated by the speciation model is presented in this section. Due to the limited availability of experimental data for the studied systems, the model can be validated only for a restricted range of conditions. However, a different set of experimental results for solubility, pH, and ionic conductivity was used in order to validate the model predictions presented in Figures 1 to 7.

Speciation data for the studied system are far from complete. Because of difficulties in chemical analysis, there are few studies regarding moderate concentrations, and most of the work has been focused on copper and arsenic speciation in natural waters, and determination of metal solubility in water and concentrated sulfuric acid solutions (Linke, 1958; Price and Davenport, 1981; Nishimura and Tozawa, 1986; Nishimura et al., 1988; Robins, 1988; and Stumm and Morgan, 1996).

The experimental and calculated results for pH and ionic conductivity of the solution are shown in Table 5 and Figures 8 and 9. The calculations were carried out with the EQ3/6 software using the extended Debye-Hückel correlation for calculating the ionic activities, in order to validate the model predictions.

Table 5 shows the experimental data and calculated values for pH and ionic conductivity for the As(III)-As(V)-H_2SO_4-$CuSO_4$-H_2O system at room temperature (18 ± 1°C). Figure 8 shows experimental and calculated pH values. As expected, pH decreases with increasing acid concentration, but some differences between measured and calculated values are evident. The calculated pH values present a standard deviation of 0.05 pH units, that is, ±5–10% when compared to measured results. Greater differences are observed in a solution with high acidity and pH values lower than 0.5.

An indirect determination of speciation is carried out by ionic conductivity measurements and calculations produced by the thermodynamic speciation model (Casas et al., 2000). The conductivity of the solution was calculated as

$$\kappa = \frac{F^2}{RT} \sum_{i}^{NI} z_i^2 C_i D_{ef,i} \tag{14}$$

Table 5. Experimental and Calculated Data for the As(III)-As(V)-H_2SO_4-$CuSO_4$-H_2O System at 18 ± 1°C

[$CuSO_4$] (mol/L)	[H_2SO_4] (mol/L)	H_3AsO_3 (mol/L)	H_3AsO_4 (mol/L)	E_h (mV)	pH (*)	Calc. pH	Conduct. (mS/cm)	Calc. Conduct. (mS/cm)
0	0.495	0	0	724.8	0.51	0.31	170.9	171.9
0	0.299	0	0	690.0	0.69	0.49	108.1	107.7
0	0.000	0.091	0.012	419.3	5.78	5.78	0.015	1.6
0	0.000	0.046	0.006	415.2	5.81	5.81	0.011	1.0
0	0.337	0.023	0.005	696.3	0.58	0.63	124.1	117.2
0	0.302	0.003	0.002	708.2	0.62	0.66	108.7	108.7
0	0.482	0.023	0.004	692.3	0.44	0.47	169.1	163.8
0	0.495	0.003	0.003	711.6	0.44	0.47	169.3	171.7
0.158	0.302	0.025	0.001	633.9	0.71	0.64	104.5	104.8
0.032	0.285	0.020	0.007	636	0.67	0.65	108.0	102.4
0.158	0.290	0.003	0.002	630.4	0.70	0.64	101.3	104.4
0.031	0.302	0.004	0.001	641.2	0.71	0.65	102.9	108.6
0.153	0.490	0.025	0.001	637.4	0.53	0.47	158.2	162.1
0.031	0.500	0.025	0.001	649.4	0.51	0.47	168.0	168.6
0.157	0.490	0.003	0.002	640.3	0.55	0.50	158.8	166.3
0.032	0.487	0.003	0.002	648.1	0.50	0.47	168.7	169.3

*Average value between differential and combination pH electrodes.

where κ is the solution conductivity measured with a conductivity cell (mS/cm), F is Faraday's constant, R is the ideal gas constant, T is the absolute temperature, NI is the number of ionic species, and z_i, C_i, and $D_{ef,i}$, are the ionic charge, the molar concentration, and the effective diffusivity of the ith ionic species in solution, respectively.

At present, no theoretical methods are available for predicting the conductivity of concentrated solutions that contain several ions, therefore, the use of Eq. 14 demands knowledge of ion concentrations and their diffusivities in aqueous solution. Ionic concentrations can be calculated with the help of speciation models, and the effective diffusivity ($D_{ef,i}$) must be determined via mathematical regression from experimental data for multicomponent solutions. In this work, the estimated values for ionic diffusivities were 0.5, 1.1, 1.3, 6.7, 0.9, 0.9, and 0.9 ($\times 10^{-9}$ m^2/s) for Cu^{2+}, SO_4^{2-}, HSO_4^-, H^+, $CuHSO_4^+$, $H_2AsO_4^-$, and $H_4AsO_3^+$, respectively. Lide (1999) reported similar orders of magnitude for these diffusivities in diluted solutions.

Measurements and calculations of the ionic conductivity for various solution compositions are shown in Table 5 and Figure 9. There is good agreement between experimental and predicted values. Measuring both the ionic conductivity and the analytical concentration provides greater reliability than measurements carried out with pH electrodes. The standard deviation between experimental and calculated values was about 3–5%, depending on solution acidity. Major differences were observed in more concentrated solutions.

The conductivity of the solution is mainly determined by the concentration of hydrogen ion (H^+), because this ion has the highest mobility. Ionic conductivity increases with acidity and decreases with increasing copper sulfate concentration. This phenomenon was explained by Casas et al. (2000).

Comparison of experimental and calculated results show that the model has been qualitatively and quantitatively validated, that is, the predicted species distribution and solution concentrations are correct for H_2SO_4, $CuSO_4$, H_3AsO_4, and H_3AsO_3 in the 0.0–1.0 m concentration range and 0–80°C temperature range.

Validation of the model could not be extended to a wider range of solution concentrations due to the generation of precipitates of copper and arsenic. Possible precipitates in more concentrated solutions could be: arsenolite As_2O_3, diarsenic tetraoxide As_2O_4, $Cu(AsO_2)_2$, $CuHAsO_4 \cdot H_2O$; basic cupric arsenate Cu_2AsO_4OH; $Cu_3(AsO_4)_2 \cdot 6H_2O$ and lammerite $Cu_3(AsO_4)_2$. As(III) species exhibit a much lower solubility than As(V) species (Robins, 1988; Nishimura et al., 1988). Considerable difficulties were found in carrying out quantitative chemical analysis in high-acidity solutions. The presented model includes only the long-range interactions between anions and cations; the presence of additional molecular and ionic solute interactions that appear at higher concentrations is not included and requires further work and the use of a wider range of activity coefficient models.

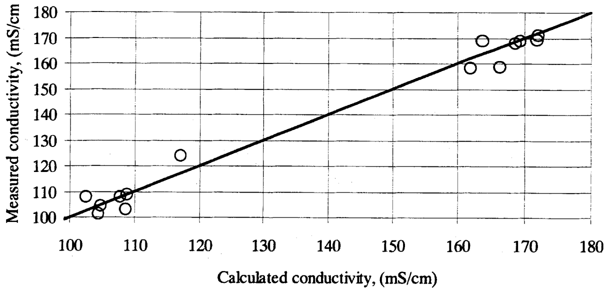

Figure 9. Experimental and calculated ionic conductivity for the As(III)-As(V)-H_2SO_4-$CuSO_4$-H_2O system at 18 ± 1°C.

Conclusions

The experimental data and thermodynamic model described in this work allow the prediction of As(III) and Cu(II) solubilities in water as well as the speciation for aqueous sulfuric acid systems. Calculations are in good agreement with experimental data throughout the studied concentration and temperature ranges. The solubility of both As_2O_3 and $CuSO_4 \cdot 5H_2O$ increases markedly with temperature between 0 and 100°C. Ionic conductivity and pH values for the As-Cu-H_2SO_4-H_2O system were predicted at 18°C with a standard deviation of 3 to 10%, depending on solution concentration.

The association degree of complex species in solution increases with temperature and concentration, the solutes being partially dissociated. Results show that the concentration of dissolved species for arsenic and copper was highly dependent on temperature, acidity, and concentration. Several species can be formed at various pH and temperature values, the principal ones being HSO_4^-, H^+, Cu^{2+}, $CuSO_{4(aq)}$, $H_3AsO_{3(aq)}$, and $H_3AsO_{4(aq)}$.

Arsenic speciation depends on both the pH value and the redox potential of the solution. The undissociated arsenious and arsenic acids are the main species predicted by the model in sulfuric acid solutions. The main ionic species of As(III) and As(V) are $H_4AsO_3^+$ (or AsO^+) and $H_2AsO_4^-$ (AsO_3^-), respectively. However, the concentration of ionic species is lower than the concentration of uncharged species because the dissociation degree of arsenic species is in the 10–20% range. The presence of cations, anions, and neutral arsenic species could be the cause of several observed phenomena in metallurgical processing, such as absorption, migration, diffusion, and molecular interactions in solution.

A rigorous methodology was applied to model validation. First, the model was calibrated using solubility data; then, it was validated on the basis of measurements for pH and conductivity. Three sets of data were independently determined. Additionally, the activity of water was taken into account, which introduced a 1–5% deviation from ideal behavior. Finally, a critically reviewed and upgraded thermochemical database was used. This validation strategy represents a clear improvement on previous works.

Acknowledgments

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Notation

a = activity, mol/kg of water
$\mathring{a}$ = hard-core diameter of solvated species, Å

A_γ = Debye-Hückel parameter, $kg^{0.5}/mol^{0.5}$
B_γ = Debye-Hückel parameter, $kg^{0.5}/mol^{0.5}/\text{Å}$
$\dot{B}$ = B-dot parameter, kg/mol
Cp = heat capacity, J/mol/K
F = Faraday's constant, 96,485 coulomb/equivalent
G = Gibbs free energy, kJ/mol
H = enthalpy, kJ/mol
I = ionic strength, moles/kg of water
K = equilibrium constant of formation reaction, molal
m = molal concentration, moles of solute/kg of water
N = number of species
n = number of moles
R = ideal gas constant, 8.3173 J/mol/K
S = entropy, J/mol/K
T = temperature, K
TOT X = total concentration, mol/kg of water
X = free concentration, mol/kg of water
z_i = charge of ionic species

Greek letters

γ = activity coefficient
ν = stoichiometric coefficient
Ω = number of moles of water making up a mass of 1 kg, 55.51 mol/kg

Subscripts and superscripts

a = anion
c = cation or component
ef = effective
i = species index
j = component index
P = pressure, bar
r = reaction
sp = species
w = water
o = thermodynamic standard state

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