# TEMPERATURE DEPENDENCE OF THE SPECIATION OF COPPER AND IRON IN ACIDIC ELECTROLYTES

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A alidated speciation models and revised thermodynamic data have been used to establish the temperature dependence of the concentrations of all the main species in aqueous  $Cu(II)-H_2SO_4$  and  $Fe(II)-Fe(III)-H_2SO_4$  solutions in the 25-65°C temperature range. Mathematical relationships have been derived for the temperature dependence of the equilibrium constants for the relevant reactions and also for the species concentrations in a well specified set of conditions. These relationships have been developed in order to use them as components of complex temperature-dependent models in hydrometallurgy, but they are also useful as stand-alone predictors of equilibrium data in the studied systems.

Keywords: speciation; thermodynamics; copper; iron; catholyte; anolyte; hydrometallurgy.

## INTRODUCTION

Copper electrowinning (EW) cells based on reactive electrodialysis (RED) have recently been developed (Cifuentes *et al.* 2004a, b, 2005). These cells consist of two compartments: one for cathode and catholyte and one for anode and anolyte. They are separated by an anion membrane which hinders cation transport between the catholyte (aqueous Cu(II)–H<sub>2</sub>SO<sub>4</sub>) and anolyte (aqueous Fe(II)–Fe(III)–H<sub>2</sub>SO<sub>4</sub>). The cathodic reaction is Cu<sup>2+</sup> +  $2e \rightarrow Cu^0$  and the anodic reaction is Fe<sup>2+</sup>  $\rightarrow$  Fe<sup>3+</sup> + e.

In order to develop a temperature-dependent model of the operation of these cells, it is necessary, among other things, to establish the dependence on temperature of the speciation, i.e., the determination of the species present in solution and their concentrations.

Work on the speciation of cupric sulphate and ferrous/ ferric sulphate in aqueous sulphuric acid solutions has been carried out (Casas *et al.*, 2000, 2003, 2005a) via experiments and thermodynamic modelling. These models are concentration-dependent, so that, in principle, it is possible to predict speciations for any given composition within their ranges of validity. Given the availability of thermodynamic data for a range of temperatures, it then becomes feasible to derive mathematical relationships for the dependence of the concentration of all the main species in catholyte and anolyte as functions of temperature. The aim of the present work is to use validated thermodynamic models and updated data in order to determine the temperature dependence of the relevant equilibrium constants and species concentrations of aqueous Cu(II)–  $H_2SO_4$  and Fe(II)–Fe(III)– $H_2SO_4$  solutions for a set of well specified conditions. These relationships could then be used as straightforward predictive tools and also as components of more complex mathematical models.

#### SPECIATION MODELS

The aqueous speciation in multi-component ionic systems can be determined by the application of a thermodynamic model which consists of a set of defined species, components and reactions, plus a set of equilibrium relationships and mass balance equations for each defined component. The formalism is a system of non-linear algebraic equations which is solved by a multi-dimensional Newton-Raphson method. This calculation methodology was presented in previous articles (Casas *et al.*, 2000, 2003). The electrolyte speciation in concentrated aqueous solutions can be determined using appropriate equilibrium constants and ionic activity coefficient models derived from Debye-Hückel theory (Casas *et al.*, 2003, 2005a, b).

For the aqueous  $Cu(II)-H_2SO_4$  speciation model, thermodynamic data (including equilibrium constants) were taken from databases such as NBS, Data0.com, NEA, Aspen Plus and HSC Chemistry (Casas *et al.*, 2000). Data for solubility, pH and electrical conductivity for the studied solutions were taken from the literature. The model was first calibrated using solubility data and then it

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was validated on the basis of independent pH and conductivity data. The ranges of validity for the model are, for concentration,  $0-50 \text{ g L}^{-1}$  Cu and  $0-200 \text{ g L}^{-1}$  sulphuric acid; for temperature,  $15-65^{\circ}$ C.

The aqueous Fe(II)-Fe(III)-H<sub>2</sub>SO<sub>4</sub> speciation model was developed by the same authors (Casas et al., 2003, 2005a) and it is similar to the already described model. The validation methodology was as follows: first, the model was defined by selecting an appropriate ion activity model and a list of main species according to the published literature and measurements obtained by laser Raman spectroscopy. Second, the model was calibrated using revised equilibrium constant values for the selected iron species and the supporting electrolyte (sulphuric acid). Solubility data as a function of pH was used to obtain the equilibrium constant for the  $FeH(SO_4)_2^0$  species. Third, a comparison between conductivity measurements and model calculations was used to validate the model. Its ranges of validity are, for concentration,  $0-72.5 \text{ g L}^{-1}$  Fe and  $0-215 \text{ g L}^{-1}$ sulphuric acid; for temperature, 25-65°C.

Both models were developed in MATLAB (2002) software and run on a personal computer.

## **RESULTS AND DISCUSSION**

## **Temperature Dependence of Equilibrium Constants**

Thermodynamic equilibrium constants (standard formation constants,  $K_{\rm f}^0$ ) were taken from the literature or calculated at various temperatures by a methodology described elsewhere (Casas *et al.*, 2000, 2003, 2005a, b). The corresponding formation reactions are:

Anolyte:

$$\begin{aligned} H^{+} + SO_{4}^{2-} \Leftrightarrow HSO_{4}^{-} \\ Fe^{2+} + H^{+} + SO_{4}^{2-} \Leftrightarrow FeHSO_{4}^{+} \\ Fe^{2+} + SO_{4}^{2-} \Leftrightarrow FeSO_{4}^{0} \\ Fe^{3+} + H^{+} + SO_{4}^{2-} \Leftrightarrow FeHSO_{4}^{2+} \\ Fe^{3+} + 2SO_{4}^{2-} \Leftrightarrow Fe(SO_{4})_{2}^{-} \\ Fe^{3+} + SO_{4}^{2-} \Leftrightarrow FeSO_{4}^{+} \\ Fe^{3+} + H^{+} + 2SO_{4}^{2-} \Leftrightarrow FeH(SO_{4})_{2}^{0} \\ Fe^{3+} + H^{+} + 2SO_{4}^{2-} \Leftrightarrow FeH(SO_{4})_{2}^{0} \end{aligned}$$

Catholyte:

$$H^{+} + SO_{4}^{2-} \Leftrightarrow HSO_{4}^{-}$$
$$Cu^{2+} + SO_{4}^{2-} \Leftrightarrow CuSO_{4}^{0}$$

Data for the temperature dependence of the equilibrium constants are presented in Table 1.

From these data, mathematical relationships were determined for nine relevant reactions. An expression of the form

$$\log (K_{\rm f}^0) = A + B/T(K) + C \log (T(K)) + DT(K)$$
(1)

Table 1. Equilibrium (standard formation) constants for the main species in aqueous  $Cu(II)-H_2SO_4$  and  $Fe(II)-Fe(III)-H_2SO_4$  solutions in the 25–65°C range.

Species	$\frac{\log K_{\rm f}^0}{25^{\circ}{\rm C}}$	$\frac{\log K_{\rm f}^0}{35^{\circ}\rm C}$	$\begin{array}{c} \text{Log } K_{\text{f}}^{0} \\ 45^{\circ}\text{C} \end{array}$	$\begin{array}{c} \text{Log } K_{\rm f}^0 \\ 55^{\circ} \text{C} \end{array}$	$\begin{array}{c} \text{Log } K_{\text{f}}^{0} \\ 65^{\circ}\text{C} \end{array}$
Anolyte					
$HSO_4^-$	1.98	2.12	2.26	2.36	2.52
FeHSO <sub>4</sub> <sup>+</sup>	1.08	1.42	1.74	1.97	2.33
FeSO <sub>4</sub> <sup>0</sup>	2.25	2.33	2.40	2.48	2.73
$Fe(SO_4)_2^-$	5.38	6.33	7.22	7.95	8.54
FeHSO <sub>4</sub> <sup>2+</sup>	2.48	2.90	3.29	3.64	3.94
FeSO <sub>4</sub> <sup>+</sup>	4.04	4.34	4.63	4.91	5.20
$FeH(SO_4)_2^0$	8.10	8.90	9.70	10.60	11.60
$Fe_2(SO_4)_3^0$	4.36	5.07	5.77	6.43	7.22
Catholyte					
$HSO_4^-$	1.98	2.12	2.26	2.36	2.52
$CuSO_4^0$	2.36	2.46	2.56	2.63	2.74

proved appropriate to represent this dependence in all cases, with a correlation coefficient ranging from 0.96 to 1.00.

The parameters A, B, C and D, plus the corresponding correlation coefficients, are given in Table 2. The  $K_{\rm f}^0$  values increase with increasing temperature for all species.

The plots of log  $(K_{\rm f}^0)$  versus temperature all look linear, despite the fact that the *A*, *B*, *C* and *D* parameters in Table 2 are not zero. This due to a compensation effect between the various parameter values. Only one plot (the one corresponding to  $HSO_4^-$ ) is presented as an example in Figure 1.

#### **Temperature Dependence of Species Concentrations**

In order to determine the temperature dependence of species concentrations, the above described models were run for the following concentrations: catholyte: 1.95 m sulphuric acid (191 g L<sup>-1</sup>), 0.472 m Cu(II) (30 g L<sup>-1</sup>); anolyte: 1.95 m sulphuric acid (191 g L<sup>-1</sup>), 1.03 m Fe(II) (57.5 g L<sup>-1</sup>) and 0.03 m Fe(III) (1.7 g L<sup>-1</sup>) and for the following temperatures: 25, 30, 35, 40, 45, 50, 55, 60 and 65°C. These concentration and temperature values were chosen because they have been used for the experimental development of the copper electrowinning cell based on reactive electrodialysis (Cifuentes *et al.*, 2004a, b, 2005) mentioned above.

Table 3 shows the results for the speciations of catholyte and anolyte at various temperatures. In the conditions

*Table 2.* Mathematical relationships for the temperature dependence of equilibrium (standard formation) constants in aqueous Cu(II)–H<sub>2</sub>SO<sub>4</sub> and Fe(II)–Fe(III)–H<sub>2</sub>SO<sub>4</sub> solutions in the 25–65°C range.

Species	Α	В	С	D	$R^2$
Anolyte					
$HSO_4^-$	0.3954	0.9962	-1.1263	0.0147	0.999
FeHSO <sub>4</sub> <sup>+</sup>	0.4207	0.9964	-1.7603	0.0359	0.998
FeSO <sub>4</sub> <sup>0</sup>	0.8398	0.9990	-0.8950	0.0120	0.959
$Fe(SO_4)_2^-$	-1.9709	0.9812	-7.8709	0.0905	0.995
FeHSO <sub>4</sub> <sup>2+</sup>	0.3844	0.9961	-1.9330	0.0441	0.999
FeSO <sub>4</sub> <sup>+</sup>	0.0157	0.9938	-2.2090	0.0319	1.000
$FeH(SO_4)_2^0$	0.0118	0.9938	-3.7223	0.0981	0.997
$\operatorname{Fe}_2(\operatorname{SO}_4)_3^0$	0.0508	0.9941	-3.5299	0.0819	0.999
Catholyte					
$HSO_4^-$	0.3954	0.9962	-1.1263	0.0147	0.999
$CuSO_4^0$	0.6184	0.9976	-0.4955	0.0100	0.998

Relationship:  $\log (K_f^0) = A + B/T(K) + C \log (T(K)) + DT(K)$ .



Figure 1. Logarithm of the equilibrium constant of formation for bisulphate ion versus temperature.

studied, the dominant species in the catholyte were  $HSO_4^-$ ,  $H^+$ ,  $Cu^{2+}$  and  $CuSO_4^0$ , and in the anolyte, they were  $HSO_4^-$ ,  $H^+$ ,  $Fe^{2+}$ ,  $SO_4^{2-}$ ,  $FeHSO_4^+$ ,  $FeSO_4^0$  and  $FeH(SO_4)_2^0$ . Both solutions present a high buffer capacity due to the existence of bisulphate ions ( $HSO_4^-$ ) as main species.

In these solutions copper produces one cation (Cu<sup>2+</sup>) and one neutral species (CuSO<sub>4</sub><sup>0</sup>), whereas iron produces five cations (Fe<sup>2+</sup>, Fe<sup>3+</sup> FeHSO<sub>4</sub><sup>+</sup>, FeHSO<sub>4</sub><sup>2+</sup> and FeSO<sub>4</sub><sup>+</sup>), one anion (Fe(SO<sub>4</sub>)<sub>2</sub><sup>-</sup>) and three neutral species (FeSO<sub>4</sub><sup>0</sup>, FeH(SO<sub>4</sub>)<sub>2</sub><sup>0</sup>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub><sup>0</sup>).

The existence of all these species in the studied solutions has been demonstrated by various analytical methods, including laser Raman spectroscopy (Casas *et al.*, 2000, 2003, 2005a, b; Stumm and Morgan, 1996).

The thermodynamic speciation model predicted a decrease in the concentration of  $H^+$  and  $SO_4^{2-}$  in both catholyte and anolyte. It also predicted a decrease in the concentration of Fe<sup>2+</sup>, Fe<sup>3+</sup>, FeSO<sub>4</sub><sup>0</sup>, FeHSO<sub>4</sub><sup>2+</sup>, FeSO<sub>4</sub><sup>+</sup> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in the anolyte with increasing temperature from 25°C to 65°C (see Table 3). This is due to ion association to form more stable species.

The concentration of cupric ions  $(Cu^{2+})$  in the catholyte increases with temperature and decreases with the concentration of  $SO_4^{2-}$  because of the latter's tendency to form associated species such as  $CuSO_4^0$ . On the other hand, the concentration of FeHSO<sub>4</sub><sup>+</sup> in the anolyte and of HSO<sub>4</sub><sup>-</sup> in the catholyte increase with temperature. FeH $(SO_4)_2^0$  concentrations in the anolyte remain fairly constant with increasing temperature, whereas the concentrations of HSO<sub>4</sub><sup>-</sup> and of Fe $(SO_4)_2^-$  in the anolyte first increase and then decrease with increasing temperature.

From the data in Table 3, relationships were obtained for all the main species in catholyte ( $Cu(II)-H_2SO_4$ ) and anolyte ( $Fe(II)-Fe(III)-H_2SO_4$ ). All the concentrations are expressed as molalities (moles of solute per kg of water) and the temperatures used in the thermo-chemical relationships are in K. All the relationships are represented by an expression of the form

$$c_{j}$$
(mol kg<sup>-1</sup>) =  $A'_{j} + B'_{j} T(K)$   
+  $C'_{i} T(K)^{2} + D'_{i} T(K)^{3}$  (2)

Table 4 gives values for the parameters (A', B', C' and D') and for the corresponding correlation coefficients. In some cases the concentration varies linearly with temperature, so C' and D' are equal to zero. When the dependence is quadratic, D' equals zero. When the dependence is cubic, no parameters equal zero.

Concentration variations with temperature are linear for all species in the catholyte. In the anolyte, they are quadratic for  $SO_4^{2-}$ , H<sup>+</sup>, FeHSO<sub>4</sub><sup>2+</sup>, FeSO<sub>4</sub><sup>0</sup> and FeSO<sub>4</sub><sup>+</sup>, whereas the remaining species exhibit a cubic dependence on temperature.

As an example of a linear relationship, the temperature dependence of the concentration of the cupric ion ( $Cu^{2+}$ ) in the catholyte is shown in Figure 2. As an example of a

Table 3. Aqueous speciation for Cu(II)–H<sub>2</sub>SO<sub>4</sub> and Fe(II)–Fe(III)–H<sub>2</sub>SO<sub>4</sub> solutions in the 25–65°C range.

		Concentration (mol kg $^{-1}$ )					
Species	25°C	35°C	45°C	55°C	65°C		
Anolyte							
H <sup>+</sup>	1.32	1.26	1.21	1.18	1.01		
$SO_4^{2-}$	$1.35 \times 10^{-1}$	$1.06 \times 10^{-1}$	$8.38 \times 10^{-2}$	$7.02 \times 10^{-2}$	$5.22 \times 10^{-3}$		
Fe <sup>2+</sup>	$7.04 \times 10^{-1}$	$7.05 \times 10^{-1}$	$7.03 \times 10^{-1}$	$6.87 \times 10^{-1}$	$2.63 \times 10^{-1}$		
Fe <sup>3+</sup>	$1.60 \times 10^{-6}$	$5.05 \times 10^{-7}$	$1.85 \times 10^{-7}$	$3.83 \times 10^{-8}$	$9.20 \times 10^{-10}$		
$HSO_4^-$	2.50	2.53	2.55	2.55	2.19		
FeHSO <sub>4</sub> <sup>+</sup>	$4.73 \times 10^{-2}$	$7.43 \times 10^{-2}$	$1.10 \times 10^{-1}$	$1.42 \times 10^{-1}$	$6.67 \times 10^{-1}$		
FeSO <sub>4</sub> <sup>0</sup>	$2.79 \times 10^{-1}$	$2.50 \times 10^{-1}$	$2.17 \times 10^{-1}$	$2.02 \times 10^{-1}$	$1.00 \times 10^{-1}$		
FeHSO <sub>4</sub> <sup>2+</sup>	$3.14 \times 10^{-5}$	$1.93 \times 10^{-5}$	$1.28 \times 10^{-6}$	$4.73 \times 10^{-6}$	$1.11 \times 10^{-6}$		
$Fe(SO_4)_2^-$	$2.77 \times 10^{-4}$	$4.62 \times 10^{-4}$	$7.70 \times 10^{-4}$	$5.71 \times 10^{-4}$	$2.47 \times 10^{-5}$		
FeSO <sub>4</sub>	$1.26 \times 10^{-4}$	$6.02 \times 10^{-5}$	$3.23 \times 10^{-5}$	$1.02 \times 10^{-5}$	$3.36 \times 10^{-7}$		
$FeH(SO_4)_2^0$	$2.96 \times 10^{-2}$	$2.95 \times 10^{-2}$	$2.92 \times 10^{-2}$	$2.94 \times 10^{-2}$	$3.00 \times 10^{-2}$		
$Fe_2(SO_4)_3^0$	$1.74 \times 10^{-14}$	$3.85 \times 10^{-15}$	$1.09 \times 10^{-15}$	$1.10 \times 10^{-16}$	$1.230 \times 10^{-18}$		
Ion strength	3.61	3.56	3.51	3.45	2.47		
Catholyte							
$H^+$	1.70	1.67	1.64	1.63	1.58		
$SO_4^{2-}$	$9.32 \times 10^{-2}$	$7.08 \times 10^{-2}$	$5.42 \times 10^{-2}$	$4.51 \times 10^{-2}$	$2.87 \times 10^{-2}$		
Cu <sup>2+</sup>	$3.44 \times 10^{-1}$	$3.52 \times 10^{-1}$	$3.61 \times 10^{-1}$	$3.68 \times 10^{-1}$	$3.75 \times 10^{-1}$		
$HSO_4^-$	2.20	2.23	2.26	2.27	2.32		
$CuSO_4^0$	$1.28 \times 10^{-1}$	$1.20 \times 10^{-1}$	$1.11 \times 10^{-1}$	$1.04 \times 10^{-1}$	$9.70 \times 10^{-2}$		
Ion strength	2.82	2.80	2.78	2.77	2.71		

<sup>a</sup>Anolyte composition:  $[H_2SO_4] = 1.95$  m, [Fe(II)] = 1.03 m, and [Fe(III)] = 0.03 m.

<sup>b</sup>Catholyte composition:  $[H_2SO_4] = 1.95$  m, and [Cu(II)] = 0.472 m.

Species	A'	B'	C'	D'	$R^2$
Anolyte					
$SO_4^{2-}$	-3.55	$2.62 \times 10^{-02}$	$-4.53 \times 10^{-05}$		0.9582
Fe <sup>3+</sup>	$1.96 \times 10^{-03}$	$-1.79 \times 10^{-05}$	$5.46 \times 10^{-08}$	$5.55 \times 10^{-11}$	0.9977
Fe <sup>2+</sup>	1022.85	-9.84	$3.21 \times 10^{-02}$	$-3.37 \times 10^{-05}$	0.9863
$\rm H^+$	-11.00	$8.43 \times 10^{-02}$	$-1.43 \times 10^{-04}$		0.9512
$HSO_4^-$	881.46	-8.48	$2.73 \times 10^{-02}$	$2.92 \times 10^{-05}$	0.9837
FeHSO <sub>4</sub> <sup>+</sup>	-1225.87	11.79	$-3.78 \times 10^{-02}$	$4.04 \times 10^{-05}$	0.9862
FeSO <sub>4</sub>	-7.73	$5.41 \times 10^{-02}$	$-9.14 \times 10^{-05}$		0.9505
$Fe(SO_4)_2^-$	1.12	$-1.10 \times 10^{-02}$	$3.60 \times 10^{-05}$	$-3.92 \times 10^{-08}$	0.9725
FeHSO <sub>4</sub> <sup>2+</sup>	$3.02 \times 10^{-03}$	$-1.82 \times 10^{-05}$	$2.74 \times 10^{-08}$		0.9373
FeSO <sub>4</sub> <sup>+</sup>	$9.49 \times 10^{-03}$	$-5.65 \times 10^{-05}$	$8.41 \times 10^{-08}$		0.9914
$FeH(SO_4)_2^0$	-1.44	$-1.43 \times 10^{-02}$	$-4.63 \times 10^{-05}$	$5.00 \times 10^{-08}$	0.9740
$Fe_2(SO_4)_3^0$	$2.89 \times 10^{-11}$	$-2.64 \times 10^{-13}$	$8.09 \times 10^{-16}$	$-8.27 \times 10^{-19}$	0.9957
Catholyte					
$\mathrm{H}^{+}$	2.53	$-2.80 \times 10^{-03}$			0.9655
$SO_4^{2-}$	0.55	$-1.55 \times 10^{-03}$			0.9803
Cu <sup>2+</sup>	0.11	$7.80 \times 10^{-04}$			0.9974
$HSO_4^-$	1.37	$2.80 \times 10^{-03}$			0.9655
$CuSO_4^0$	0.36	$-7.80 \times 10^{-04}$			0.9974

Table 4. Mathematical relationships for species concentration as a function of temperature in aqueous  $Cu(II)-H_2SO_4$  and  $Fe(II)-Fe(III)-H_2SO_4$  solutions in the 25–65°C range.

Relationship:  $c_i (\operatorname{mol} \operatorname{kg}^{-1}) = A'_i + B'_i T(K) + C'_i T(K)^2 + D'_i T(K)^3$ .





Figure 2. Cupric ion concentration versus temperature.

*Figure 3.*  $Fe(SO_4)_2^-$  ion concentration versus temperature.

non-linear plot, the temperature dependence of the concentration of  $Fe(SO_4)_2^-$  in the analyte is shown in Figure 3.

From Table 4 it should be noted that as  $Cu^{2+}$  concentration in the catholyte increases,  $CuSO_4^0$  concentration

diminishes with temperature with the same absolute value for the slope. On the other hand, as the  $HSO_4^-$  concentration in the catholyte increases, the hydrogen ion concentration decreases with the same absolute value for the slope.

#### CONCLUSIONS

The above results show that it is possible to obtain mathematical expressions for the temperature dependence of equilibrium constants and species concentrations for a number of species belonging to aqueous  $Cu(II)-H_2SO_4$  and  $Fe(II)-Fe(III)-H_2SO_4$  solutions for a set of well defined conditions.

The obtained relationships can be used on their own as predictors of species concentrations as functions of temperature for copper and iron species in the studied electrolytes, but they can also be used as components of more complex mathematical models in hydrometallurgy. Additionally, the methodology proposed here can be used for other electrolytes.

## NOMENCLATURE

A, A'	parameters in equations (1) and (2)
B, B'	parameters in equations (1) and (2)
C, C'	parameters in equations (1) and (2)
c <sub>i</sub>	concentration of <i>j</i> th species, mol kg <sup><math>-1</math></sup>
D, D'	parameters in equations (1) and (2)
$K_{\rm f}^0$	equilibrium constant of formation
Т	absolute temperature, K

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### ACKNOWLEDGEMENTS

This work was funded by the National Committee for Science and Technology (CONICYT, Chile) via FONDECYT projects No. 101 0138 and No. 103 0530. Continued support from the Departments of Mining Engineering, Universidad de Chile, and Metallurgical Engineering, Universidad de Santiago, are gratefully acknowledged. Financial support from Placer Dome to the Chair of Environmental Studies in Mining is also acknowledged.