Thermodynamic Properties of Aqueous Sulfuric Acid

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ABSTRACT: Thermodynamic properties of aqueous sulfuric acid were modeled with the Pitzer equation. Both the second dissociation constant K_2 for sulfuric acid and the Pitzer parameters were fitted simultaneously. The most accurately considered experimental data including electrochemical cell, osmotic, enthalpy, and vapor pressure data at temperature range (0 to 170) °C were used in the assessment. After variations of the used experimental data and the temperature dependency of the Pitzer parameters, the thermodynamic values for the bisulfate dissociation in aqueous sulfuric acid at 25°C were re-evaluated. The obtained values for the dissociation reaction are (11.00 ± 0.27) and (25.11 ± 0.80) kJ·mol^{-1} for Gibbs energy and enthalpy change, respectively, yielding to 0.0119 for K_2. The obtained thermodynamic values for the cell reactions are in good agreement with CODATA and NBS literature values as well as with other Pitzer based thermodynamic models for aqueous sulfuric acid. The best model selected by using the obtained new thermodynamic data was further tested and compared to the recent Pitzer models with excellent agreement as well as with good extrapolating capabilities with respect to temperature and acid concentration. The total number of fitted terms in Pitzer parameters is eight.
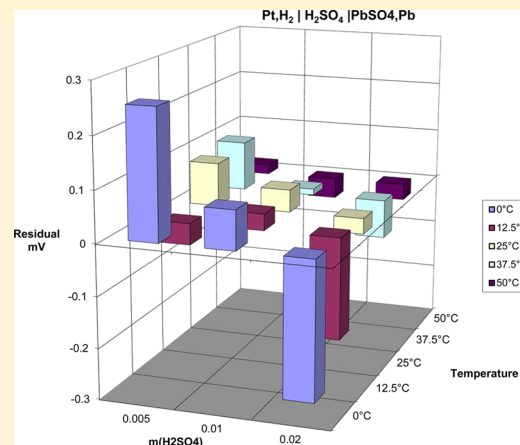
INTRODUCTION

Sulfuric acid is an important chemical for industry widely used in phosphate fertilizer and pigment production, steel pickling, and other hydrometallurgical applications, and the production of organic chemicals, explosives, etc.[1] Its thermodynamically related properties have been extensively studied especially at 298.15 K and summarized by Clegg et al.[2]

The thermodynamic modeling of sulfuric acid is complicated by the incomplete dissociation of sulfuric acid

$$HSO_4^- = SO_4^{2-} + H^+ \quad K_2 = a(SO_4^{2-})a(H^+)/a(HSO_4^-) \tag{1}$$
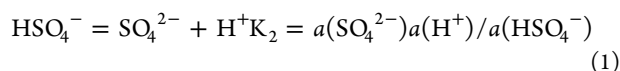
There are several different equations available in the literature for the value of the second dissociation constant of sulfuric acid as a function of temperature. Thermodynamic properties for reaction 1 derived from these equations are listed in Table 1.

Pitzer et al.[5] have modeled the thermodynamic behavior of aqueous sulfuric acid using the activity coefficient model, named after Pitzer[11] himself, from (0 to 55) °C up to 6 m sulfuric acid solution. After that, several other thermodynamic models for aqueous sulfuric acid have been generated with the Pitzer equation (Table 2) or by local composition models (Table 3).

The concentration range for Pitzer models is up to 6 mol H$_2$SO$_4$ per 1 kg water, that is, 6 m, except for mole fraction scale models where the weight fraction of sulfuric acid is from 0 to 0.8. As can been seen from Table 2 the total number of excess parameters and fitted terms has increased during years beyond the level of practical usability.

In general, the local composition models have fewer parameters than Pitzer models, but they are focused on speciation and vapor pressure. The gas phase is assumed ideal in most cases. Available electrochemical data are usually ignored. Thus, these models do not describe so accurately the behavior of sulfuric acid in dilute regions but are more accurate in higher concentrations where the bisulfate ion dominates. A more detailed discussion on thermodynamic models for aqueous sulfuric acid can be found elsewhere.[18]

In 2012, Sippola[19] found out that only four Pitzer parameters with a simple temperature dependency of $(a + b/T)$ is sufficient to present the stoichiometric osmotic and activity coefficients equally well as the more complicated models by Clegg et al.[2] and Clegg and Brimblecombe[15] in the temperature range (0 to 55) °C up to 6 m sulfuric solution. Several different K_2 equations were found to be able to present the studied experimental data equally well. An extension of the temperature range does not change the situation.[18]

The importance of choosing the best K_2 equation for sulfuric acid is a key factor for the further development of model for multicomponent aqueous systems where sulfuric acid is involved. According to the philosophy of CALPHAD method,[20,21] the binary systems should be modeled first and critically evaluate the available thermodynamic data before any ternary or higher order

Table 1. Thermodynamic Properties Related to the K_2 of Sulfuric Acid

| authors | year | temperature range | ΔH_{298} | ΔS_{298} | $\Delta C_{p,298}$ | K_2 |
		°C	J·mol^{-1}	J·K^{-1}·mol^{-1}	J·K^{-1}·mol^{-1}	
Lietzke et al.[3]	1961	25 to 225	−20 546	−106.95	−209	0.01030
Marshall and Jones[4]	1966	25 to 350	−16 128	−92.15	−239	0.01029
Pitzer et al.[5]	1977	5 to 55	−23 490	−116.67	0	0.01050
Young et al.[6]	1978	5 to 55	−21 693	−110.91	−192	0.01017
Young et al.[6]	1978	5 to 55	−22 238	−112.33	−238	0.01068
Matsushima and Okuwaki[7]	1988	25 to 200	−24 140	−119.01	−218	0.01030
Dickson et al.[8]	1988	50 to 250	−22 756	−113.92	−275	0.01086
Hovie and Hepler[9]	1990	10 to 55	−23 496	−116.80	−265	0.01036
Clegg et al.[2]	1994	0 to 50	−22 756	−114.21	−275	0.01050
Knopf et al.[10]	2003	−93 to 200	−18 555	−100.06	−206	0.01058

Table 2. Pitzer Interaction Models for Aqueous Sulfuric Acid

author(s)	year	modifications[a]	temperature range (°C)	no. parameters	total no. terms	equation for K_2
Pitzer et al.[5]	1977		5 to 55	4	8	Pitzer[5]
Reardon and Beckie[12]	1987	U	5 to 55	4	9	Pitzer[5]
Sippola[13]	1992	U	5 to 55	4	8	Okuwaki[7]
Holmes and Mesmer[14]	1992		25 to 200	5	17	Dickson[8]
Clegg et al.[2]	1994	UA	0 to 55	9	32	Dickson[8,b]
Clegg and Brimblecombe[15]	1995	M	−70 to 55	10	40	Dickson[8,b]
Knopf et al.[10]	2003	A	−90 to 200	10	34	Knopf[10]
Christov and Moller[16]	2004	U	0 to 200	5	20	Dickson[8]
Friese and Ebel[17]	2010	M	−70 to 55	11	66	Dickson[8,b]

[a]U = unsymmetrical mixing terms; A = Archer extension; M = mole fraction scale. [b]Modified to yield 0.01050 at 25 °C.

Table 3. Local Composition Models for Aqueous Sulfuric Acid

author(s)	year	model	temperature	concentration	number of excess parameters and (terms within)
Liu and Grén[24,a]	1991	Liu−Harvey−Prausnitz	25 °C	(1 to 76) mol·kg^{-1}	2
Bosen and Engels[25,a]	1998	NRTL	(0 to 240) °C	w = 0 to 0.96	10 (17)
Messnaoui and Bounahmidi[26]	2006	eNRTL	(25 to 75) °C	(1 to 7) mol·kg^{-1}	4 (6)
Bollas et al.[27]	2010	eNRTL (refined)	25 °C	(0 to 50/65) mol·kg^{-1}	10
Que et al.[28]	2011	eNRTL (symmetric)	(0 to 500) °C	w = 0 to 1	18 (30)
Simonin et al.[29]	2006	MSA-NRTL	25 °C	(0.1 to 6.0) mol·kg^{-1}	6
Simonin et al.[30,b]	2004	MSA (BIMSA)	25 °C	(0.1 to 27) mol·kg^{-1}	6
Campos et al.[31]	2006	UNIQUAC	(0 to 150) °C	w = 0 to 1	7 (15)

[a]Complete dissociation of sulfuric acid is assumed. [b]The bisulfate ion is considered via equilibrium only. No ion specific parameters are used.

systems is modeled. Choosing the best K_2 equation is thus a crucial step in this process.

The scope of this article is to generate a practical Pitzer model with reasonable number of parameters and terms to model the thermodynamic properties of the H$_2$SO$_4$−H$_2$O system in a wide temperature range.

Theory. In aqueous solutions the chemical potential of the solvent, that is water, is defined as

$$\mu_w = \mu_w^\circ + RT \ln(a_w) \tag{2}$$

where the standard state is pure water at the temperature and pressure of the solution. For the solutes the chemical potential is

$$\mu_i = \mu_i^\circ + RT \ln(a_i) = \mu_i^\circ + RT \ln(m_i) + RT \ln(\gamma_i) \tag{3}$$

where m_i is the molality and γ_i is the activity coefficient of the solute.

Since the concentration is expressed in molalities, the standard state is hypothetical, 1 m ideally dilute solution at the temperature and pressure of the solution.

The practical osmotic coefficient (ϕ) is generally used in aqueous systems instead of the activity of water:

$$\varphi = -\left(\frac{1000}{M_w \sum m_i}\right) \ln a_w \tag{4}$$

where M_w is the molecular weight of water in g·mol^{-1}.

Electrolytes dissociate in aqueous solutions

$$M_{\nu+}X_{\nu-} = \nu_+ M^{z+} + \nu_- X^{z-} \tag{5}$$

and the chemical potential of the electrolyte is defined to be equal to the sum of chemical potentials of ions:

$$\mu(M_{\nu+}X_{\nu-}) \equiv \nu_+ \mu(M^{z+}) + \nu_- \mu(X^{z-}) \tag{6}$$

This applies also in the case of incomplete dissociation of the electrolyte.

Thus, from eqs 3 and 6 follows for any electrolyte:

$$\mu^\circ(M_{\nu+}X_{\nu-}) = \nu_+ \mu^\circ(M^{z+}) + \nu_- \mu^\circ(X^{z-}) \tag{7}$$

and

$$a_{MX} = m_{MX}\gamma_{MX} = (m_M\gamma_M)^{\nu+}(m_X\gamma_X)^{\nu-} \tag{8}$$

If the electrolyte dissociates completely, the molalities of ions can be calculated from

$$m_M = \nu_+ m_{MX} \tag{9}$$

$$m_X = \nu_- m_{MX} \tag{10}$$

Thus, from eq 8 for completely dissociated electrolyte applies

$$m_{MX}\gamma_{MX} = (\nu_\pm m)^\nu (\gamma_\pm)^\nu \tag{11}$$

$$\nu = \nu_+ + \nu_- \tag{12}$$

$$\nu_\pm^\nu = (\nu_+)^{\nu+}(\nu_-)^{\nu-} \tag{13}$$

$$\gamma_\pm^\nu = (\gamma_M)^{\nu+}(\gamma_X)^{\nu-} \tag{14}$$

where the term $\gamma_\pm$ is generally called the mean activity coefficient of the electrolyte.

Inserting eq 11 to eq 3 we get eq 15 for the chemical potential of completely dissociated electrolyte:

$$\mu_i = \mu_i^\circ + \nu RT \ln(\nu_\pm m_i \gamma_\pm) \tag{15}$$

Applying eq 3 for sulfuric acid we obtain

$$\mu_{H_2SO_4} = \mu_{H_2SO_4}^\circ + RT \ln(a_{H_2SO_4}) = \mu_{H_2SO_4}^\circ + RT \ln(m)$$
$$+ RT \ln(\gamma_{H_2SO_4}) \tag{16}$$

where m is the molality of sulfuric acid and

$$\mu^\circ(H_2SO_4) = 2\mu^\circ(H^+) + \mu^\circ(SO_4^{2-}) \tag{17}$$

Assuming complete dissociation eqs 8−10, 15, and 16 yield the following expressions for activity and the stoichiometric activity coefficient for sulfuric acid:

$$a_{H_2SO_4} = m\gamma_{H_2SO_4} = (m_H\gamma_H)^2(m_{SO_4}\gamma_{SO_4}) = 4m^3\gamma_\pm^3 \tag{18}$$

and furthermore

$$\gamma_\pm^3 = (m_H\gamma_H)^2(m_{SO_4}\gamma_{SO_4})/4m^3 \tag{19}$$

On the other hand, if the incomplete dissociation of sulfuric acid in eq 1 is considered, the following relationship with the activity of sulfuric acid is obtained:

$$a_{H_2SO_4} = m\gamma_{H_2SO_4} = (m_H\gamma_H)^2(m_{SO_4}\gamma_{SO_4}) = K_2 m_H \gamma_H m_{HSO_4}\gamma_{HSO_4} \tag{20}$$

and furthermore

$$a_{H_2SO_4} = K_2 m^2 (1 - \alpha^2)\gamma_H\gamma_{HSO_4} \tag{21}$$

where α is the degree of dissociation of the bisulfate ion.

■ COMPUTATIONAL METHODS

Pitzer Equation. Pitzer[11] introduced an interaction model for excess Gibbs energy of aqueous solutions which is based on virial coefficients similar to the gas phase. After recombining virial coefficients and changing moles to molalities (m), the excess Gibbs energy divided by gas constant (R), absolute temperature (T), and mass of solvent (w_w) is

$$\frac{G^{E,m}}{w_w RT} = f(I) + 2\sum_c\sum_a m_c m_a[B_{ca} + (\sum_c m_c z_c)C_{ca}]$$
$$+ \sum_{c<c'}\sum m_c m_{c'}[2\Phi_{cc'} + \sum_a m_a \psi_{cc'a}]$$
$$+ \sum_{a<a'}\sum m_a m_{a'}[2\Phi_{aa'} + \sum_c m_c \psi_{aa'c}]$$
$$+ 2\sum_n\sum_c m_n m_c \lambda_{nc} + 2\sum_n\sum_a m_n m_a \lambda_{na} \tag{22}$$

where c refers to a cation, a to an anion, and n to a neutral species. B_{ca} and C_{ca} are interaction parameters for the cation c and the anion a and $\Phi_{cc'}$ and $\Phi_{aa'}$ for two different cations and anions, respectively. z_i is the charge of the ion.

Parameters $\psi_{cc'a}$ and $\psi_{aa'c}$ are for interactions between three ions, and λ_{nc} and λ_{na} are parameters for interactions between an electrically neutral species and a cation or an anion, respectively. Function $f(I)$ describes the long-range forces between ions and is dependent on temperature and ionic strength defined as

$$I = 1/2\sum_i m_i z_i^2 \tag{23}$$

Assuming C, λ, and ψ to be independent of concentration, the equations for activity and osmotic coefficients for cation M, anion X, and neural species N are obtained with appropriate differentiation from eq 22 and summarized in eqs 24 to 31

$$\ln\gamma_M = \left(\frac{\partial G^{E,m}/RT}{\partial n_M}\right)_{T,p,n_w,n_i,i\neq M} = z_M^2(f'(I)/2)$$
$$+ \sum_a m_a[2B_{Ma} + ZC_{Ma}] + z_M\sum_c\sum_a m_c m_a C_{ca}$$
$$+ z_M^2\sum_c\sum_a m_c m_a B'_{ca} + \sum_c m_c[2\Phi_{Mc} + \sum_a m_a \psi_{Mca}]$$
$$+ z_M^2\sum_{c<c'}\sum m_c m_{c'}\Phi'_{cc'} + z_M^2\sum_{a<a'}\sum m_a m_{a'}\Phi'_{aa'}$$
$$+ \sum_{a<a'}\sum m_a m_{a'}\psi_{Maa'} + 2\sum_n m_n\lambda_{nM} \tag{24}$$

where the prime symbol (′) indicates a derivative by ion strength and Z is defined as $Z = \sum_i m_i |z_i|$.

$$\ln\gamma_X = \left(\frac{\partial G^{E,m}/RT}{\partial n_X}\right)_{T,p,w_w,n_i,i\neq X} = z_X^2(f'(I)/2)$$
$$+ \sum_c m_c[2B_{cX} + ZC_{cX}] + |z_X|\sum_c\sum_a m_c m_a C_{ca}$$
$$+ z_X^2\sum_c\sum_a m_c m_a B'_{ca} + \sum_a m_a[2\Phi_{Xa} + \sum_c m_c \psi_{Xac}]$$
$$+ z_X^2\sum_{c<c'}\sum m_c m_{c'}\Phi'_{cc'} + z_X^2\sum_{a<a'}\sum m_a m_{a'}\Phi'_{aa'}$$
$$+ \sum_{c<c'}\sum m_c m_{c'}\psi_{cc'X} + 2\sum_n m_n\lambda_{nX} \tag{25}$$

$$\ln\gamma_N = \left(\frac{\partial G^{E,m}/RT}{\partial n_N}\right)_{T,p,w_w,n_i,i\neq N}$$
$$= 2\sum_c m_c\lambda_{Nc} + 2\sum_a m_a\lambda_{Na} \tag{26}$$

and for the osmotic coefficient

$$(\phi - 1) = -\left(\frac{1}{\sum_i m_i}\right)\left(\frac{\partial G^{E,m}/RT}{\partial w_w}\right)_{T,p,n_i}$$

$$= \left(\frac{2}{\sum_i m_i}\right)\left\{If^\phi(I) + \sum_c \sum_a m_c m_a [B_{ca}^\phi + ZC_{ca}]\right.$$

$$+ \sum_{c<c'} \sum m_c m_{c'}[\Phi_{cc'}^\phi + \sum_a m_a \psi_{cc'a}] + \sum_{a<a'} \sum m_a m_{a'}$$

$$\times [\Phi_{aa'}^\phi + \sum_c m_c \psi_{aa'c}] + \sum_n \sum_c m_n m_c \lambda_{nc}$$

$$\left. + \sum_n \sum_a m_n m_a \lambda_{na}\right\} \tag{27}$$

where

$$f^\phi(I) = \frac{1}{2}[f' - f(I)/I] \tag{28}$$

$$B_{ca}^\phi = B_{ca} + IB' \tag{29}$$

$$\Phi_{cc'}^\phi = \Phi_{cc'} + I\Phi_{cc'}' \tag{30}$$

$$\Phi_{aa'}^\phi = \Phi_{aa'} + I\Phi_{aa'}' \tag{31}$$

Pitzer[11] considered three different forms for Debye−Hückel functions $f^\phi(I)$ and concluded that the following one is superior

$$f^\phi = -A_\phi\left[\frac{\sqrt{I}}{(1 + b\sqrt{I})}\right] \tag{32}$$

where b is a constant, 1.2, independent of electrolyte type. Solving f from eq 28 yields

$$f = -A_\phi \frac{4I}{b} \ln(1 + b\sqrt{I}) \tag{33}$$

and

$$f'/2 \equiv f^\gamma = -A_\phi\left(\frac{\sqrt{I}}{(1 + b\sqrt{I})} + \frac{2}{b}\ln(1 + b\sqrt{I})\right) \tag{34}$$

For parameter B_{ca}^ϕ Pitzer chose the following concentration dependency

$$B_{ca}^\phi = \beta^{(0)} + \beta^{(1)}\exp(-\alpha_1\sqrt{I}) + \beta^{(2)}\exp(-\alpha_2\sqrt{I}) \tag{35}$$

where α_1 and α_2 are constants, dependent on the electrolyte type, and β's are electrolyte specific Pitzer parameters. Thus, from eq 29 follows

$$B_{ca} = \beta^{(0)} + \beta^{(1)}g(\alpha_1\sqrt{I}) + \beta^{(2)}g(\alpha_2\sqrt{I}) \tag{36}$$

$$B_{ca}' = \beta^{(1)}g'(\alpha_1\sqrt{I}) + \beta^{(2)}g'(\alpha_2\sqrt{I}) \tag{37}$$

where

$$g(x) = 2(1 - (1 + x)e^{-x})/x^2$$

$$g'(x) = -2(1 - (1 + x + x^2/2)e^{-x})/x^2$$

Values for constants α_1 and α_2 depend on electrolyte type and are listed in Table 4.[11,19,22,23]

Table 4. Numerical Constants in the Original Pitzer Ion Interaction Model

electrolyte type $(\nu_+ - |\nu_-|)$	α_1	α_2
$1 - N$, $N - 1$	2.0	$\beta^{(2)}$ not used
$2 - 2$	1.4	12
higher values	2.0	50

Applying the ionic solution theory, Pitzer concluded that the concentration dependency for the interaction parameter for like sign ions is

$$\Phi_{ij} = \theta_{ij} + {}^E\theta_{ij}(I) \tag{38}$$

where θ_{ij} is a Pitzer parameter for short-range interactions between two like sign ions and ${}^E\theta_{ij}$ is a parameter for long-range interactions depending on ion strength only.[32] So from eq 30 follows

$$\Phi_{ij}^\phi = \theta_{ij} + {}^E\theta_{ij}(I) + I{}^E\theta_{ij}'(I) \tag{39a}$$

$$\Phi_{ij}' = {}^E\theta_{ij}'(I) \tag{39b}$$

According to Friedman's mixed electrolyte theory[33] for equal charge ions, ${}^E\theta_{ij}$ terms are zero. For unequal but like charge ions these terms can be calculated from the complex integral, which must be calculated numerically. Pitzer derived an approximation method to calculate it analytically. After testing experimental data of 15 different ternary systems Pitzer concluded that ${}^E\theta_{ij}$ terms can practically be omitted.[32]

When modeling brine systems, Harvie and Weare[34] discovered that including ${}^E\theta_{ij}$ terms improves the model significantly, so they included these parameters in their model, calculated the integrals numerically and fitted them as Chebyshev expansions accurate to six significant figures. Nowadays, ${}^E\theta_{ij}$ terms are usually included in the Pitzer model either by Chebyshev expansions or the approximation by Pitzer.

Instead of C_{MX}, Pitzer parameter C_{MX}^ϕ, which is defined as $2|z_M z_X|^{1/2}C$, is generally listed since it will generalize the osmotic coefficient equation for single electrolyte solution as follows.

$$(\phi - 1) = -\left(\frac{1}{\sum_i m_i}\right)\left(\frac{\partial G^{E,m}/RT}{\partial w_w}\right)_{T,p,n_i}$$

$$= \left\{|z_+ z_-|f^\phi(I) + m\left(\frac{2\nu_M\nu_X}{\nu}\right)B_{MX}^\phi\right.$$

$$\left. + m^2\left(\frac{2(\nu_M\nu_X)^{3/2}}{\nu}\right)C^\phi\right\} \tag{40}$$

where $\nu = \nu_+ + \nu_-$.

A more detailed description of the Pitzer model can be found elsewhere.[11,35−37]

Experimental Data Used in the Assessment. Previously[18] it was discovered that there was little difference in the predicted values for stoichiometric osmotic and activity coefficients between studied K_2 equations when only Gibbs energy related experimental data were used in the assessment. Therefore, enthalpy data were included in the used experimental data. Moreover, since the standard heat of the dissociation reaction of bisulfate ion varies from one equation to another, the equation for dissociation reaction itself was included in the assessment.

Table 5. Experimental Data Included and Excluded in the Evaluation

| measurements		temperature range	$m_{\text{H}_2\text{SO}_4}$	excluded molalities	estimated experimental accuracy
		°C	mol·kg⁻¹	mol·kg⁻¹	
cell A[38]	Pt, H$_2$|H$_2$SO$_4$|PbSO$_4$, Pb, Hg	0 to 50	0.001 to 0.02	all data < 0.005	1.0 mV
cell B[39]	Pt, H$_2$|H$_2$SO$_4$|Hg$_2$SO$_4$, Hg	5 to 55	0.1003 to 5.767	5.767 (5 °C); 7.972 (all)	1.0 mV
cell C[40]	Pt, H$_2$|H$_2$SO$_4$|PbO$_2$, PbSO$_4$, Pt	5 to 55	0.1 to 6.095	7.199 (all)	0.5 mV
isopiestic data[41]	critical evaluation of several isopiestic measurements	25	0.1 to 6.0	0.1 (25 °C) > 6.0 (all)	$\Delta\phi = 0.005$
isopiestic data[14]	isopiestic measurements at ≈ 110 °C, ≈ 140 °C, and ≈ 170 °C	110 to 170	0.5 to 5.6		$\Delta a_{\text{w}} = 1\ \%$
vapor pressure data[42]	vapor pressure data	25 to 130	$w = 0.1$ to 0.35	all data $w > 0.35$	$\Delta a_{\text{w}} = 2\ \%$
heat of solution[15]	relative apparent heat of solution	25	0.1 to 6.0	all data > 6.0	$\Delta L^{\phi} = 10\ \%$
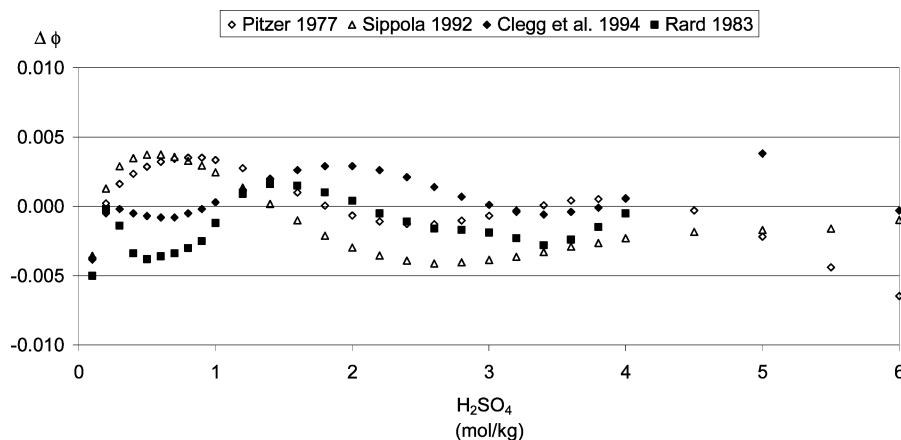
Figure 1. Deviation of the calculated[2,5,13,44] values of the stoichiometric osmotic coefficient for aqueous sulfuric acid compared to Rard et al.'s[41] critically evaluated data at 25 °C. Filled markers indicate the values listed in the corresponding reference. Unfilled markers indicate the values calculated from the parameters given in each source.

The experimental data used for the evaluation were chosen to be the most accurate considered ones and are listed in Table 5.

For cell A all data below 0.005 mol·kg⁻¹ was measured using a platinum bright electrode instead of platinum black one due to experimental difficulties and was thus excluded.[38] Pitzer et al.[5] have also considered data for the cell A below 0.005 mol·kg⁻¹ as unreliable. International volts were changed to absolute volts following Clegg et al.[2]

For cell B the measurement of 5.767 mol·kg⁻¹ at 5 °C differs clearly from the other measurements and was excluded from the fit. No apparent reason to exclude a priori the other six measurements was found. All data within the selected concentration range (0 to 6.1) mol·kg⁻¹ was included for cell C as was done by Clegg et al.[2] in their work, too.

According to Clegg et al.[2] the solubility of PbSO$_4$ must be taken into consideration only for sulfuric acid concentrations below 0.04 mol·kg⁻¹. For cell A, the lead sulfate concentrations approximated by Shrawder and Cowperweite[38] were assumed to be present. To cover the effect of soluble lead sulfate the Pitzer parameters for PbSO$_4$ determined by Paige et al.[43] were included in the model for this cell. Similar treatment is not necessary for cells B and C due to a greater sulfuric acid concentration.[2]

The experimental accuracy was evaluated for cells A and B to be 1.0 mV and for cell C as 0.5 mV, which are about 3 times the standard deviations obtained for these cells in earlier evaluations.[5,13] Experimental accuracy is an estimation for a

range within the true value of measured quantity lies. It does not describe the experimental error of an individual experiment or set of experiments.

The cell potential for each cell A and B can be calculated from stoichiometric activity coefficients of sulfuric acid based on a complete dissociation.

$$E = E^0 - (RT/2F)\ln(a_{\text{H}_2\text{SO}_4}) = E^0 - (RT/2F)$$
$$\ln(4m^3\gamma_{\pm}^3) \tag{41a}$$

In addition to the cell C the activity of water is needed[5]

$$E = E^0 + (RT/2F)\ln(a_{\text{H}_2\text{SO}_4}/a_{\text{w}}^2)$$
$$= E^0 + (RT/2F)\ln(4m^3\gamma_{\pm}^3/a_{\text{w}}^2) \tag{41b}$$

The electrochemical force (E^{o}) for cells A to C was expressed as a function of temperature:

$$\Delta_{\text{r}}G^{\circ} = -zFE^0 = A_E + B_ET + C_ET\ln(T) \tag{42}$$

where A_E–C_E are cell specific parameters.

In 1976 Rard et al. published isopiestic data[41] at 25 °C based on critical evaluation of several experimental data sets for osmotic coefficient or vapor pressure by several authors. Their data up to 6 mol·kg⁻¹ was included in the assessment except the lowest value of 0.1 mol·kg⁻¹ concentration was excluded since it deviates as much as the announced accuracy[41] 0.5 % from the

Table 6. Experimental Data Sets

data set	cell data[38−40] (0 to 55) °C	isopiestic data[41] 25 °C	apparent heat of solution data[15] 25 °C	isopiestic data[14] (110 to 170) °C	vapor pressure data[42] (25 to 130) °C
1	x	x			
2	x	x	x		
3	x	x	x	x	
4	x	x	x	x	x

corrected values of Rard[44] published in 1983. The stoichiometric osmotic coefficients are estimated to be correct within ± 0.005 which is also in line with previously modeled values, as can been seen in Figure 1. Instead of the stoichiometric osmotic coefficient, the activity of water was used as experimental data in fitting. The experimental accuracy for water activity was calculated from the corresponding accuracy for stoichiometric osmotic coefficient estimated by Rard et al.,[41] that is, 0.005 for each data point.

Isopiestic data from Holmes and Mesmer[14] at temperatures of (383.46, 413.19, and 443.42) K were all included in the assessment, while data at 473.21 K were reserved for testing the model's extrapolating capability. Again the activity of water was used as experimental data instead of stoichiometric osmotic coefficients. The accuracy of water activity was estimated to be 1 %.

Previously[18] vapor pressure data by Vermeulen,[45] Tarasenkov,[46] and Collins,[42] were critically evaluated against Holmes and Mesmer's isopiestic data[14] and Collins[42] data was found the most reliable in line with the Bosen and Engels's results.[25] The reported saturated vapor pressures for pure water agree within 0.2 % with the recent IAPWS 95 equation by Wagner and Pruss[47] with obtained standard deviation of 0.04 %. Instead of the actual experimental data, the relative pressures published in Table 2 in the Collins article[42] were used in the temperature range of the measurements, thus excluding values at 20 °C and all values above 130 °C.

In precise modeling of aqueous sulfuric acid the nonideality of gas phase cannot be ignored over 50 °C temperatures.[18] The vapor over sulfuric acid consists of practically water in the concentration and temperature ranges considered in this work. Thus, any sulfur species in the gas phase can be ignored, and the activity of water can be calculated from relative pressures and fugacity coefficients:

$$a_w = (\phi_w/\phi_w^*)(p_w/p_w^*) \tag{43}$$

where ϕ is fugacity coefficient of water in gas phase, p is pressure, and the star ($*$) refers to pure water. Fugacity coefficients were estimated using the second virial coefficient

$$\ln \phi = BP/RT \tag{44}$$

The second virial coefficients (B) were obtained from the Wagner−Pruss equation[47] using Fluidcal software.[48] The relative pressures were taken from Table 2 in Collins's article.[42] The accuracy of water activity calculated from Collins's data[42] was estimated to be 2 %.

The relative apparent heat of solution data from model of Clegg and Brimblecombe[15] was considered to be accurate within 10 %. Their data were chosen to present enthalpy experimental data since it agrees quite well with experimental data by Wu and Young[49] at 25 °C. Experimental relative apparent heat of solution is not available at other temperatures to our knowledge.

Fitted Parameters. The second dissociation constant for sulfuric acid was modeled with the following equation:

$$\Delta_r G^\circ = -RT \ln(K_2) = A_K + B_K T + C_K T \ln(T/K) \tag{45}$$

where A_K (J·mol^{-1}), B_K (J·K^{-1}·mol^{-1}), and C_K (J·K^{-1}·mol^{-1}) are fitted parameters. The relationships between these parameters and thermodynamic properties of the dissociation reaction of bisulfate ion at 25 °C are

$$\Delta_r H^\circ = A_K + C_K \cdot 298.15 \text{ K} \tag{46}$$

$$\Delta_r S^\circ = -(B_K + C_K(1 + \ln(298.15))) \tag{47}$$

$$\Delta_r C_p = -C_K \tag{48}$$

Previously,[19] it was found that only four Pitzer parameters, namely, $\beta^{(0)}$ and C^ϕ for H$^+$/SO$_4^{2-}$ interaction and parameters $\beta^{(0)}$ and $\beta^{(1)}$ for H$^+$/HSO$_4^-$ interaction, are sufficient to describe the thermodynamic behavior aqueous sulfuric acid with simple temperature dependency of $a + b/T$.

Also the effect of reducing the temperature dependency of the parameter $\beta^{(0)}$ for H$^+$/SO$_4^{2-}$ only to b/T as well as adding a cT term to the temperature dependency of the parameter $\beta^{(0)}$ for H$^+$/HSO$_4^-$ as suggested with previous results with NPL Pitzer model[50,50,51] were tested.

Methods. MTDATA[52,53] version 4.81 was used for parameter fitting. MTDATA is a general tool for calculating thermodynamic equilibrium and other thermodynamic properties for solutions or pure substances. It is using the Gibbs energy minimization technique to solve thermodynamic equilibrium and includes several pure substance databases and a number of excess Gibbs energy models for different kind of solutions. It also has an assessment module to fit model parameters from experimental data.

The objective function (OF) used in MTDATA for parameter fitting is

$$\text{OF} = \sum_{i=1}^{N} w_i[(C_i - E_i)/U_i]^2 \tag{49}$$

where w_i = weight of the experimental value, C_i = calculated value, E_i = experimental value, and U_i = uncertainty.

All weights for the included experimental data in eq 49 were set to 1 except the rejected values.

The excess Gibbs energy was modeled using the Pitzer equation with unsymmetrical mixing terms built in MTDATA. The Pitzer model in MTDATA calculates unsymmetrical mixing terms with Chebyshev expansions introduced by Harvie and Weare.[34] It was found earlier[19] that MTDATA version 4.81 included these terms only if the corresponding θ parameter was included in the specific input file. Thus, a zero value for this parameter was used in assessment.

The goodness of the assessments for each experimental data set is estimated by standard deviations (SD), also known as root-mean-square-error (RMSE), defines as

$$\text{SD} = \sqrt{\sum_{i=1}^{N} \frac{(C_i - E_i)^2}{N}} \tag{50}$$

Table 7. Tested Experimental Data Sets in the Assessments

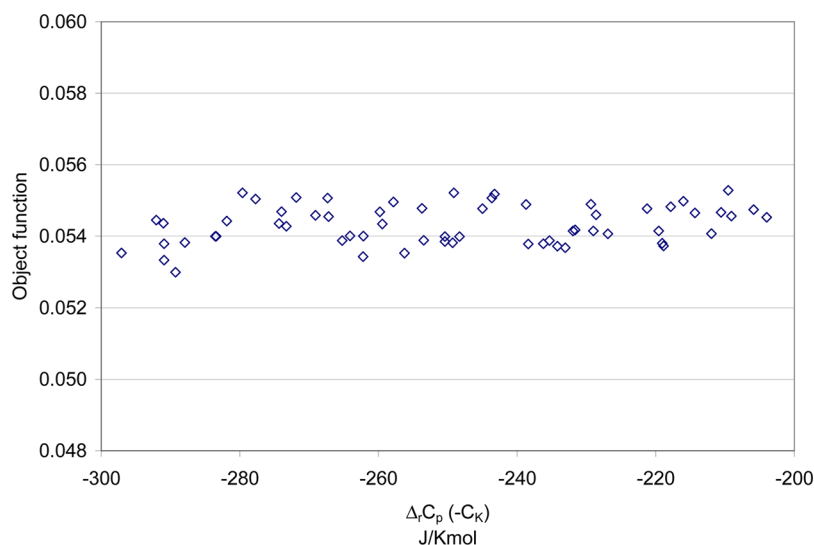|		all parameters	$\beta^{(0)}(\text{H}^+/\text{SO}_4{}^{2-})$	$\beta^{(0)}(\text{H}^+/\text{HSO}_4{}^-)$
assessment	experimental data	$a + b/T$	b/T	$a + b/T + cT$
1	Set 1 (E_{0-55}, $a_{w,25}$)	x		
2	Set 2 (E_{0-55}, $a_{w,25}$, $^{\phi}L_{25}$)	x		
3	Set 3 (E_{0-55}, $a_{w,25}$, $^{\phi}L_{298}$, $a_{110-170}$)	x		
4	Set 4 (E_{0-55}, $a_{w,25}$, $^{\phi}L_{25}$, $a_{110-170}$, p_{25-130})	x		
5	Set 1 (E_{0-55}, $a_{w,25}$)		x	
6	Set 2 (E_{0-55}, $a_{w,25}$, $^{\phi}L_{25}$)		x	
7	Set 3 (E_{0-55}, $a_{w,25}$, $^{\phi}L_{298}$, $a_{110-170}$)		x	
8	Set 4 (E_{0-55}, $a_{w,25}$, $^{\phi}L_{25}$, $a_{110-170}$, p_{25-130})			x
9	Set 2 (E_{0-55}, $a_{w,25}$, $^{\phi}L_{25}$)		x	x
10	Set 4 (E_{0-55}, $a_{w,25}$, $^{\phi}L_{25}$, $a_{110-170}$, p_{25-130})		x	x

Figure 2. Value of the object function in assessment 1 as a function of the heat capacity change of the second dissociation constant (67 best values).

where i goes over all experimental points (N) with nonzero weights in the experimental set.

Instead of standard deviation, the mean absolute percentage error (MAPE), also known as the absolute average relative deviation (AARD %), is used when the focus is on relative deviation:

$$\text{MAPE} = \frac{100}{N}\left(\sum_{i=1}^{N}\frac{|C_i - E_i|}{E_i}\right) \tag{51}$$

■ RESULTS AND DISCUSSION

Data sets. The experimental data were organized in different data sets shown in Table 6.

Assessments. Several different combinations of the experimental data set and parameters with different temperature dependences were tested during the assessment. The used combinations are listed in Table 7.

During the assessment it was found out that results are extremely sensitive to the initial values of the parameters $A_K - C_K$ for the second dissociation constant K_2 (eq 45). Assuming that the heat capacity change in reaction 1 in range of (-200 to -300) $\text{J·K}^{-1}\cdot\text{mol}^{-1}$ (see Table 1), the initial value of C_K was varied from 200 to 300 with steps of 1 $\text{J·K}^{-1}\cdot\text{mol}^{-1}$. So, each assessment was evaluated with 100 different initial parameter values, leading to 1000 in the total number of fits.

During the assessment, it was found that several K_2 equations can describe the experimental data set 1 almost equally well. The

obtained values for objective function as a function of ΔC_p derived from fitted K_2 equations are shown in Figure 2. It was also found that the obtained Gibbs energy changes ($\Delta G^{\text{o}}{}_{298}$) for the cell reactions at 25 °C will vary linearly with the corresponding value of the dissociation reaction at 25 °C (Figure 3).

Thus, the following relationship was found between the Gibbs energy change of cell reaction and that of the dissociation reaction:

$$\Delta G^{\text{o}}{}_{298}(\text{cell reaction})$$

$$= a + b\Delta G^{\text{o}}{}_{298}(\text{dissociation reaction})$$

$\Delta G^{\text{o}}{}_{298}$ for the dissociation reaction varies from (10.9 to 11.1) kJ·mol^{-1}, and the corresponding K_2 values are from 0.0113 to 0.0123.

A similar relation can be found also between enthalpy and entropy changes at 25 °C. The obtained linear parameters and their correlations are listed in Table 8. The parameters were generated from the results of assessment 1.

The reason for this linear relationship can be understood if we apply eq 21 instead of 18 for the equations of electrochemical cell potentials, yielding to cells A and B

$$E = E^0 - (RT/2F)\ln(a_{\text{H}_2\text{SO}_4}) = E^0 - (RT/2F)\ln(K_2)$$

$$- (RT/2F)\ln(m^2(1-\alpha^2)\gamma_{\text{H}}\gamma_{\text{HSO}_4}) \tag{52}$$
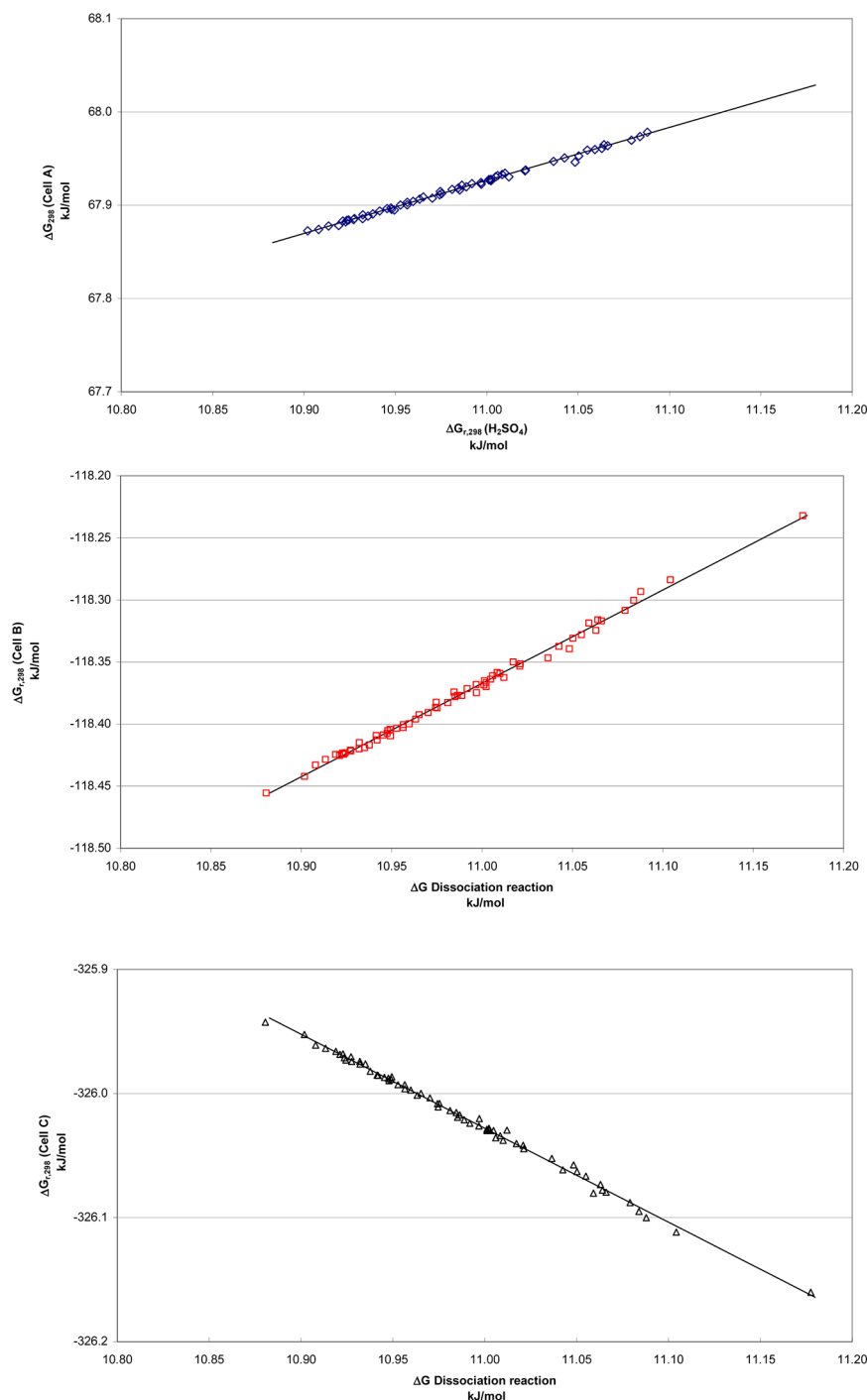
and to cell C

Figure 3. Gibbs energy changes for the cell reaction as a function of Gibbs energy change in second dissociation reaction of sulfuric acid for cell A (a), cell B (b), and cell C (c) in assessment 1.

$$E = E^0 + (RT/2F)\ln(a_{H_2SO_4}/a_w^2)$$

$$= E^0 + (RT/2F)\cdot\ln(K_2) + (RT/2F)$$

$$\times \ \ln\left(\frac{m^2(1-\alpha^2)\gamma_H\gamma_{HSO_4}}{a_w^2}\right) \tag{53}$$

The first two terms are function of temperature only. Thus, any change in K_2 can be compensated with a change in E^0.

The linear relationships between Gibbs energy changes in cell reactions and that of bisulfate dissociation reaction do not

disappear even when more experimental Gibbs energy related data on higher temperatures or enthalpy data at 25 °C are included in the assessment. However, that does not apply for enthalpy and entropy changes as can be seen in Figures 4 to 6.

The best objective values for each assessment are shown in Table 9.

The following conclusions can be made from Table 9:

(1) The temperature dependency of the $\beta^{(0)}(H^+/SO_4^{2-})$ parameter can be reduced to b/T in the temperature range (5 to 55) °C (data set 1). At higher temperatures the temperature dependency of $a + b/T$ for this parameter is required (data set 3).

Table 8. Linear Correlation Parameters between the Thermodynamic Properties of the Dissociation Reaction of Bisulfate and Cell Reactions from Assessment 1

| estimated property	property of the second dissociation reaction of sulfuric acid	$a/(\text{kJ·mol}^{-1})$	b	correlation
$\Delta_r G^{\circ}_{298}$ (cell A)	$\Delta_r G^{\circ}_{298}$	61.673	0.5685	−0.998
$\Delta_r G^{\circ}_{298}$ (cell B)	$\Delta_r G^{\circ}_{298}$	−126.650	0.7530	−0.998
$\Delta_r G^{\circ}_{298}$ (cell C)	$\Delta_r G^{\circ}_{298}$	−317.699	−0.7572	0.998
$\Delta_r H^{\circ}_{298}$ (cell A)	$\Delta_r H^{\circ}_{298}$	25.028	0.6090	−0.982
$\Delta_r H^{\circ}_{298}$ (cell B)	$\Delta_r H^{\circ}_{298}$	−146.286	0.8042	−0.992
$\Delta_r H^{\circ}_{298}$ (cell C)	$\Delta_r H^{\circ}_{298}$	−326.420	−0.8068	0.992
		$a/(\text{J·K}^{-1}\text{·mol}^{-1})$	b	
$\Delta_r S^{\circ}_{298}$ (cell A)	$\Delta_r S^{\circ}_{298}$	−120.860	0.6135	−0.984
$\Delta_r S^{\circ}_{298}$ (cell B)	$\Delta_r S^{\circ}_{298}$	−63.429	0.8086	−0.992
$\Delta_r S^{\circ}_{298}$ (cell C)	$\Delta_r S^{\circ}_{298}$	−31.572	−0.8108	0.993
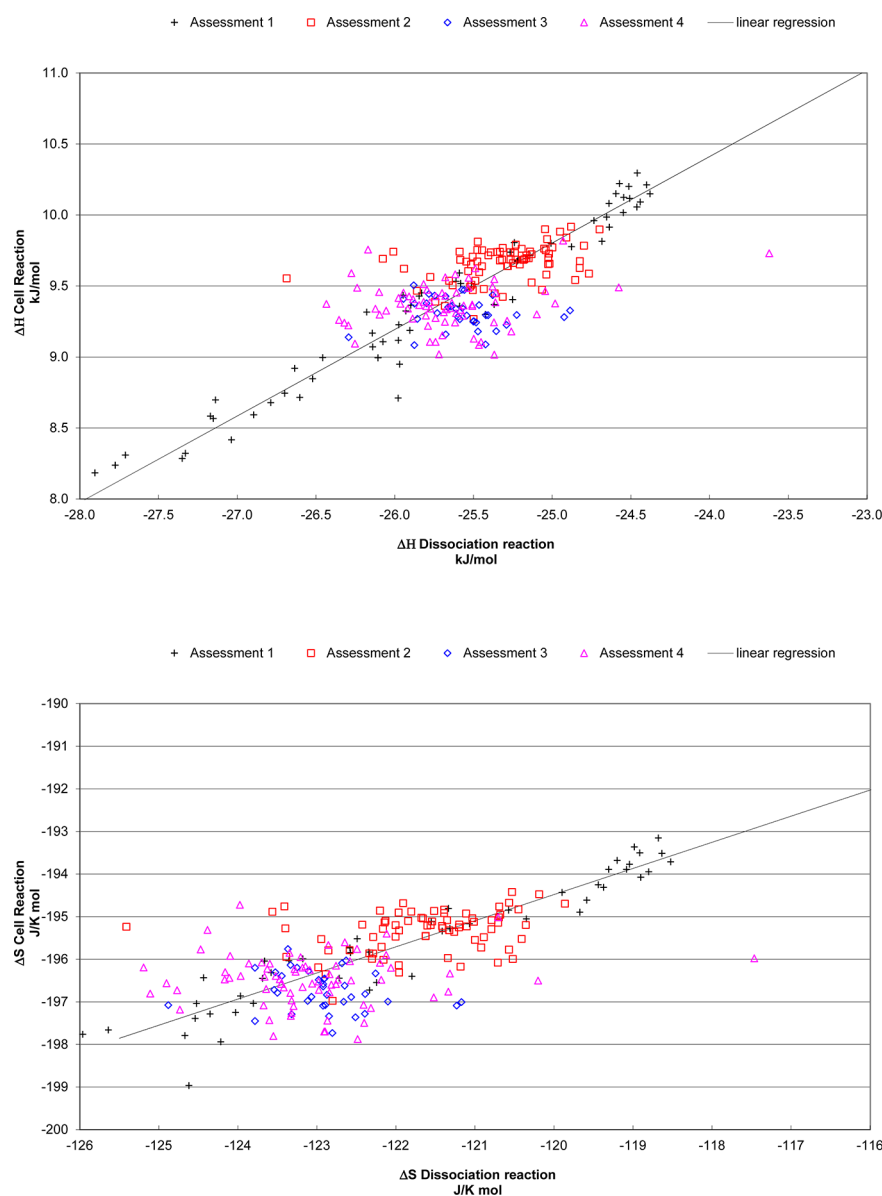
Figure 4. Enthalpy (a) and entropy (b) changes of the cell reaction for cell A as a function of the corresponding change in the second dissociation reaction of sulfuric acid. The line is regressed from the results of assessment 1.

(2) Adding a cT-term to the temperature dependency of the $\beta^{(0)}(\text{H}^+/\text{HSO}_4^-)$ parameter will improve the assessment at higher temperatures (assessments 4 and 8), but it is not required in the temperature range (5 to 55) °C (assessments 2 and 9). At higher temperatures this addition succeeds in reducing the temperature dependency of the $\beta^{(0)}(\text{H}^+/\text{SO}_4^{2-})$ parameter back to b/T (assessments 8 and 10).
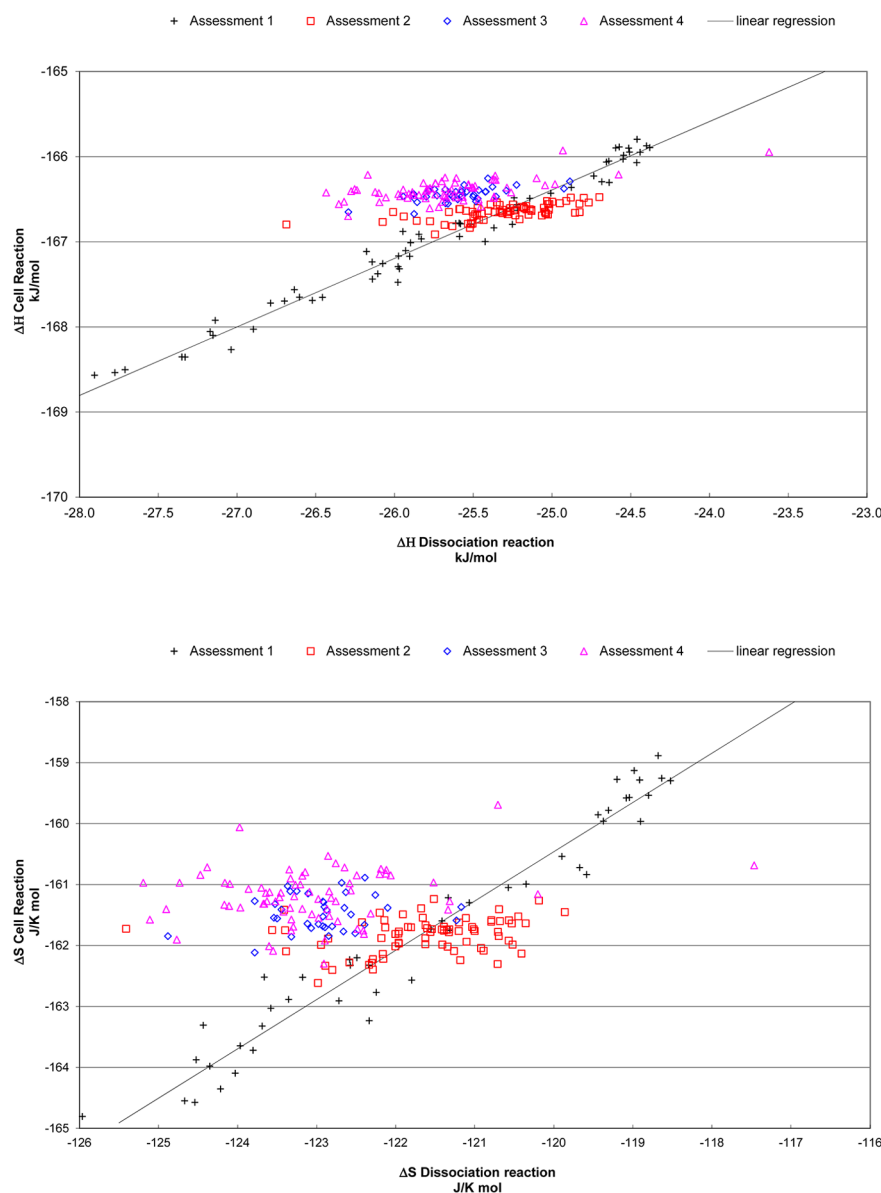
Figure 5. Enthalpy (a) and entropy (b) changes of the cell reaction for cell B as a function of the corresponding change in the second dissociation reaction of sulfuric acid. The line is regressed from the results of assessment 1.

(3) The best assessment to describe the thermodynamic properties at temperature range (0 to 55) °C is assessment 6, since it includes only seven terms to describe the temperature dependency of the four Pitzer parameters used.

(4) Extending the model to higher temperatures, the following combination of temperature dependences will improve the assessment (data set 4): for interaction with H^+/SO_4^{2-}, $\beta^{(0)}$ as b/T and C^ϕ as $a + b/T$; for interaction with H^+/SO_4^-, $\beta^{(0)}$ as $a + b/T + cT$ and $\beta^{(1)}$ as $a + b/T$.

Thermodynamic Properties. Thermodynamic properties of the second dissociation reaction of sulfuric acid as well as the electrochemical cells at 25 °C are derived from the temperature range (0 to 55) °C, that is from the assessment 6 with data set 2. The obtained values are average values of 78 fits with OF values from 0.049 to 0.055, and the fitted heat capacity change in the second dissociation reaction varies from (202 to 303) $J \cdot K^{-1} \cdot mol^{-1}$ (Figure 7). The error estimate is either three times the standard deviation or half of the difference between the obtained maximum and minimum values. The smaller value is selected.

The obtained thermodynamic properties for the dissociation reaction of bisulfate ion as well as the thermodynamic properties of the cell reactions at 298.15 K (25 °C) are listed in Table 10.

Values calculated from CODATA and NBS thermodynamic tables[54,55] and from the recent article of Clegg et al.[2] are also included in Table 10 as well as the average of 75 fits obtained for assessment 10 with data set 4, covering the temperature range from (0 to 170) °C.

Except enthalpy and entropy changes for the second dissociation reaction for sulfuric acid, the obtained values are in excellent agreement with the literature values. Extending the data up to 170 °C does change the situation.

In 1977, Pitzer et al.[5] modeled the thermodynamic behavior of aqueous sulfuric acid using the activity coefficient model, named after Pitzer[11] himself, from (0 to 55) °C up to 6 m sulfuric acid solution. As a result, they obtained two different sets of Pitzer parameters and K_2 equations describing the behavior of aqueous sulfuric acid equally well. The corresponding values for K_2 at 25 °C were 0.0105 and 0.0120, respectively.
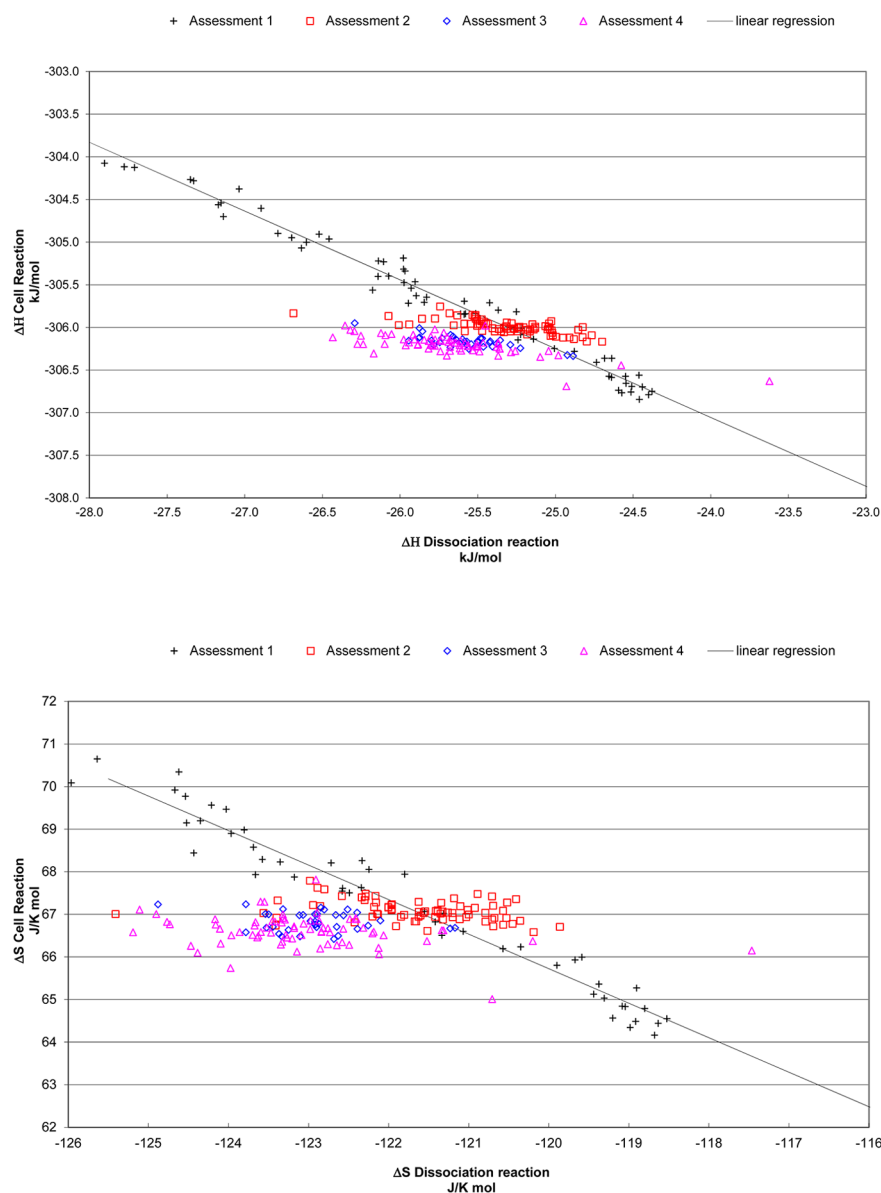
Figure 6. Enthalpy (a) and entropy (b) changes of the cell reaction for cell C as a function of the corresponding change in the second dissociation reaction of sulfuric acid. The line is regressed from the results of assessment 1.

Table 9. Best Values of the Objective Function for Each Studied Assessment

assessment		all parameters $a + b/T$	$\beta^{(0)}(\mathrm{H}^+/\mathrm{SO}_4^{2-})$ b/T	$\beta^{(0)}(\mathrm{H}^+/\mathrm{HSO}_4^-)$ $a + b/T + cT$	objective function best value
1	data set 1 (E_{0-55} $a_{w,25}$)	x			0.053
5			x		0.054
2	data set 2 (E_{0-55} $a_{w,25}$, $^\phi L_{25}$)	x			0.049
6			x		0.049
9			x	x	0.052
3	data set 3 (E_{0-55} $a_{w,25}$, $^\phi L_{25}$, $a_{110-170}$)	x			0.056
7			x		0.070
4	data set 4 (E_{0-55} $a_{w,25}$, $^\phi L_{25}$, $a_{110-170}$, p_{25-130})	x			0.052
8				x	0.037
10			x	x	0.037

The standard potentials at 25 °C for the cells (A−C), Pt,H$_2$|H$_2$SO$_4$|PbSO$_4$,Pb (A), Hg, Pt,H$_2$|H$_2$SO$_4$|Hg$_2$SO$_4$,Hg (B), and Pt,H$_2$|H$_2$SO$_4$|PbO$_2$,PbSO$_4$,Pt (C), and the thermodynamic properties for sulfuric acid at 25 °C are summarized in Table 11

The values of the alternate set by Pitzer et al.[5] coincide with this work.

Thermodynamic Model for Aqueous Sulfuric Acid. Thirteen different fits in assessment 10 (data set 4, (0 to 170) °C)
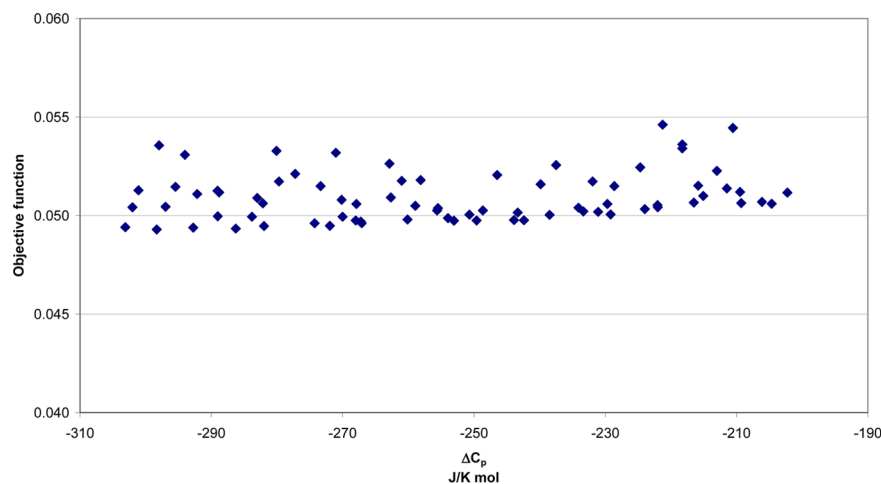
Figure 7. Value of the object function in the assessment 6 as a function of the heat capacity change in the dissociation reaction of bisulfate ion (78 best fits).

Table 10. Obtained Thermodynamic Properties for Sulfuric Acid and Cells A to C at 298.15 K

property	this work assessment 6 (0 to 55) °C	Clegg et al.[2]	CODATA key values[54]	NBS tables[56]	this work assessment 10 (0 to 170) °C
		H$_2$SO$_4$			
$\Delta_r G°_{298}$ (kJ·mol^{-1})	11.00 ± 0.27	11.30	11.31	11.37	(10.94)
$\Delta_r H°_{298}$ (kJ·mol^{-1})	−25.11 ± 0.80	−22.76	−22.44	−21.93	(−25.78)
$\Delta_r S°_{298}$ (J·K^{-1}·mol^{-1})	−121.12 ± 1.87	−114.21	−113.2	−111.7	(123.16)
		Cell A^a			
$E°$ (mV)	−352.0 ± 0.5	−352.77	−351.9	−349.7	(−351.8)
$\Delta_r G°_{298}$ (kJ·mol^{-1})	67.92 ± 0.10	68.08	67.90	67.48	(67.89)
$\Delta_r H°_{298}$ (kJ·mol^{-1})	9.68 ± 0.26	9.74	10.66	10.70	(9.44)
$\Delta_r S°_{298}$ (J·K^{-1}·mol^{-1})	−195.35 ± 1.09	−195.66	−191.99	−190.45	(−196.04)
$\Delta_r C_p°_{298}$ (J·K^{-1}·mol^{-1})	−359 ± 30	348.57		−398.6	(−368)
		Cell B			
$E°$ (mV)	613.4 ± 0.7	612.36	612.7	615.0	(613.6)
$\Delta_r G°_{298}$ (kJ·mol^{-1})	−118.37 ± 0.14	−118.17	−118.22	−118.68	(−118.41)
$\Delta_r H°_{298}$ (kJ·mol^{-1})	−166.61 ± 0.18	−166.75	−166.25	−166.15	(−166.68)
$\Delta_r S°_{298}$ (J·K^{-1}·mol^{-1})	−161.80 ± 0.74	−162.94	−161.08	−159.20	(−161.88)
$\Delta_r C_p°_{298}$ (J·K^{-1}·mol^{-1})	−395 ± 41	−363.71		−397.7	(404)
		Cell C^b			
$E°$ (mV)	1689.5 ± 0.7	1691.0	1689.1	1686.8	(1689.3)
$\Delta_r G°_{298}$ (kJ·mol^{-1})	−326.02 ± 0.14	−326.32	−325.95	−325.50	(−325.98)
$\Delta_r H°_{298}$ (kJ·mol^{-1})	−306.03 ± 0.15	−305.92	−304.89	−304.93	(−306.01)
$\Delta_r S°_{298}$ (J·K^{-1}·mol^{-1})	67.04 ± 0.52	68.42	70.62	69.01	(66.99)
$\Delta_r C_p°_{298}$ (J·K^{-1}·mol^{-1})	433 ± 48	424.69		449.3	(446)

^{a}Thermodynamic values for reaction Pb(s) = Pb(Hg) are taken from Bates et al.[57] ^{b}Thermodynamic values for PbO$_2$ are from NBS tables.[56]

Table 11. Thermodynamic Properties for Sulfuric Acid and Cells A to C at 25 °C

property	Pitzer et al.[5] adopted set	this work	Pitzer et al.[5] alternate set
$K_{2,298}$	0.0105	0.0119	0.0120
$\Delta_r G°_{298}$ (kJ·mol^{-1})	11.295	11.00 ± 0.27	10.96^a
$\Delta_r H°_{298}$ (kJ·mol^{-1})	−23.49	−25.11 ± 0.80	(−25.6)^b
$\Delta_r S°_{298}$ (J·K^{-1}·mol^{-1})	−116.67	−121.12 ± 1.87	(−122.6)^c
$E°$(A) (mV)	−352.8	−352.0 ± 0.5	−351.75
$E°$(B) (mV)	612.42	613.4 ± 0.7	613.54
$E°$(C) (mV)	1690.38	1689.5 ± 0.7	1689.27

^{a}Calculated from K_2. ^{b}Calculated from Pitzer.[58] ^{c}Calculated as $\Delta S_{298} = (\Delta H_{298} − \Delta G_{298})/T$.

qualify for the thermodynamic values obtained and are listed in Table 10 with $\Delta C_p°_{298}$ varying from (−220 to −289) J·K^{-1}·mol^{-1}.

The closest fit and thus the best one is a fit with $\Delta_r C_p$ value near −276 J·K^{-1}·mol^{-1} (fit 10.276). The equation of K_2 for this fit is

$$\Delta_r G° = −RT \ln(K_2) = 57092.9(\text{J·mol}^{-1}) − 1724.98(\text{J·K}^{-1}\cdot\text{mol}^{-1})\cdot T + 275.667(\text{J·K}^{-1}\cdot\text{mol}^{-1})\cdot T \ln(T/\text{K}) \quad (54)$$

Obtained Pitzer parameters for this fit are listed in Table 12. The thermodynamic properties for the second dissociation reaction of

Table 12. Pitzer Parameters for Our Model

Pitzer parameter	interaction	a	$b/(T/\text{K})$	c (T/K)
$\beta^{(0)}$	H$^+$/SO$_4^{2-}$		12.04250	
C^ϕ	H$^+$/SO$_4^{2-}$	0.137684	−30.395	
$\beta^{(0)}$	H$^+$/HSO$_4^-$	0.24106	22.0454	−3.5118·10^{-4}
$\beta^{(1)}$	H$^+$/HSO$_4$	0.333982	39.296	

Table 13. Thermodynamic Properties of Sulfuric Acid and Cells A to C at 25 °C Obtained by Our Model

property	our model	estimated range, this work
$K_{2,298}$	0.0115	
$\Delta_r G°_{298}$ (kJ·mol⁻¹)	11.08	11.00 ± 0.27
$\Delta_r H°_{298}$ (kJ·mol⁻¹)	−25.10	−25.11 ± 0.80
$\Delta_r S°_{298}$ (J·K⁻¹·mol⁻¹)	−121.33	−121.12 ± 1.87
$\Delta_r C_p°_{298}$ (J·K⁻¹·mol⁻¹)	−275.67	
$E°(A)$ (mV)	−352.24	−352.0 ± 0.5
$E°(B)$ (mV)	613.08	613.4 ± 0.7
$E°(C)$ (mV)	1689.84	1689.5 ± 0.7

sulfuric acid as well as for electrochemical cells A to C are shown in Table 13.

The quality of our model (fit 10.276) is summarized in Table 14 where the standard and maximum deviations are reproduced. For comparison, the same values obtained with the K_2 equation by Hepler and Hovey using the same data set, and Pitzer parameters are also listed. Moreover, the values obtained previously by Sippola[18] using the K_2 equation by Hepler and Hovey (Hepler A) with the same data set but without the heat of solution data, $^\phi L$, are included in Table 14, too. In case of Hepler A the Pitzer parameters used were the same as in our model, but the temperature dependency was $a + b/T$ for all of the parameters.

The values of the objective function with the K_2 equation from Dickson et al.[8] and Knopf et al.[10] are 0.062 and 0.18, respectively. This confirms the estimated[18] superiority of the K_2 equation by Hepler and Hovey over these two other equations.

Stoichiometric Osmotic and Activity Coefficients. The standard and maximum deviations for predicted stoichiometric osmotic coefficient in this work at 25 °C, compared to the values obtained by models[2,15] of Clegg et al. and of Clegg and Brimblecombe, are in both cases 0.002 and 0.004, respectively. Results at (0 and 50) °C are also in good agreement with the model of Clegg and Brimblecombe (Figure 8)

The standard and the maximum deviations for stoichiometric activity coefficients at 25 °C compared to the model of Clegg et al.[2] are 0.003 and 0.008, respectively. Results at (0 and 50) °C are also in good agreement with standard deviations 0.003 and 0.002,

respectively (Figure 9). The mean absolute percentage (maximum) errors at (0, 25, and 50) °C are 0.96 % (2.12 %), 1.67 % (2.06 %), and 1.23 % (1.96 %), respectively.

The largest differences are at around 0.01 m sulfuric acid solution. However, the extrapolated values to more dilute solution are in good agreement with the results of the Clegg et al.[2] (see Table 15).

Relative Apparent Molal Enthalpy. Even though the enthalpy data were included in the assessment only at 25 °C our new model can predict the relative apparent molal enthalpy $^\phi L$ also at (0 and 50) °C quite well (Figure 10).

The standard deviations at temperatures (0, 25, and 50) °C are (493, 293, and 1180) J·mol⁻¹, respectively, and the mean absolute errors are 3.3 %, 1.1 %, and 3.6 %, respectively. The maximum error is below 7 % at all temperatures.

Our model successfully extrapolates the apparent relative enthalpy also to the dilute region as displayed in Figure 11.

Electrochemical Cell Potential. Calculating the standard cell potential for the cell $Hg_2SO_4,Hg|H_2SO_4|PbO_2,PbSO_4$, not included in the assessment, using the corresponding values of the cells B and C in Table 10 yields a value of $E° = 1076.1$ mV which is in agreement with the value of 1077.5 mV obtained by Clegg et al.[2] The corresponding value for our model from Table 13 is (1689.84 − 613.08) mV, that is, 1076.76 mV.

The calculated electrochemical potentials by our model agree within 1 mV with the experimental data except two points which were considered unreliable by Clegg et al.[2] (see Figure 12). The calculated values are about 0.52 mV higher in average, which are in excellent agreement with measured values when considering that neither the standard potential nor the experimental data were included in the assessment.

Thus, the standard potential for the cell $Hg_2SO_4,Hg|H_2SO_4|PbO_2,PbSO_4$ can be evaluated to be (1076.76 − 0.52) mV, yielding to 1076.24 mV which is in excellent agreement with the value of 1076.1 mV calculated from the obtained standard potentials for the cells B and C (Table 10). Thus, the obtained values for standard potentials of the cells B and C are internally consistent within 0.2 mV which is remarkably less than 1.0 mV achieved by Clegg et al.[2] in their assessment including all these cells.

Table 14. Obtained Standard and Maximum Deviations for Three Different Thermodynamic Models for Aqueous Sulfuric Acid

K_2	standard deviation			maximum deviation		
	this work	Hepler	Hepler (A)	this work	Hepler	Hepler (A)
data set 4	yes	yes	no $^\phi L_{25}$ data	yes	yes	no $^\phi L_{25}$ data
reference	this work	this work	Sippola[18]	this work	this work	Sippola[18]
cell A (mV)	0.12	0.21	0.22	−0.27	−0.44	−0.47
cell B (mV)	0.27	0.27	0.27	−0.76	−0.76	−0.91
cell C (mV)	0.14	0.14	0.17	−0.32	−0.31	0.40
$\phi_{25°C}$	0.00061	0.00100	0.00096	0.0019	0.0019	0.0019
$\phi_{110°C}$	0.005	0.009	0.009	−0.008	−0.011	0.017
$\phi_{140°C}$	0.004	0.011	0.015	−0.007	−0.014	0.022
$\phi_{170°C}$	0.006	0.012	0.020	0.016	−0.016	0.031
$\phi_{w=0.1}$	0.027	0.032	0.017	−0.024	−0.052	−0.024
$\phi_{w=0.2}$	0.031	0.033	0.029	−0.038	−0.050	−0.038
$\phi_{w=0.25}$	0.013	0.013	0.013	−0.021	−0.019	−0.021
$\phi_{w=0.3}$	0.017	0.016	0.019	−0.027	−0.022	−0.027
$\phi_{w=0.35}$	0.018	0.017	0.021	−0.032	−0.024	−0.032
$^\phi L_{25}$(J·mol⁻¹)	291	617	1831[a]	−578	767	2172[a]
OF (data set 4)	0.039	0.052	0.092			

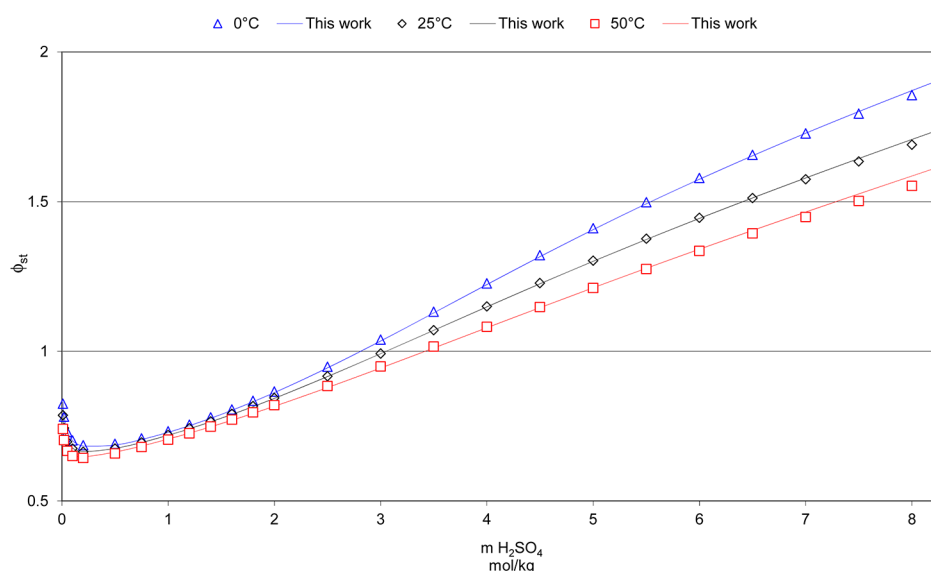[a]Data not included in the assessment.

Figure 8. Calculated stoichiometric osmotic coefficients (lines) by our model compared to the results from model of Clegg and Brimblecombe[15] at three temperatures of 0 °C (blue), 25 °C (black), and 50 °C (red). Calculated values over 6 mol·kg^{-1} are extrapolated.
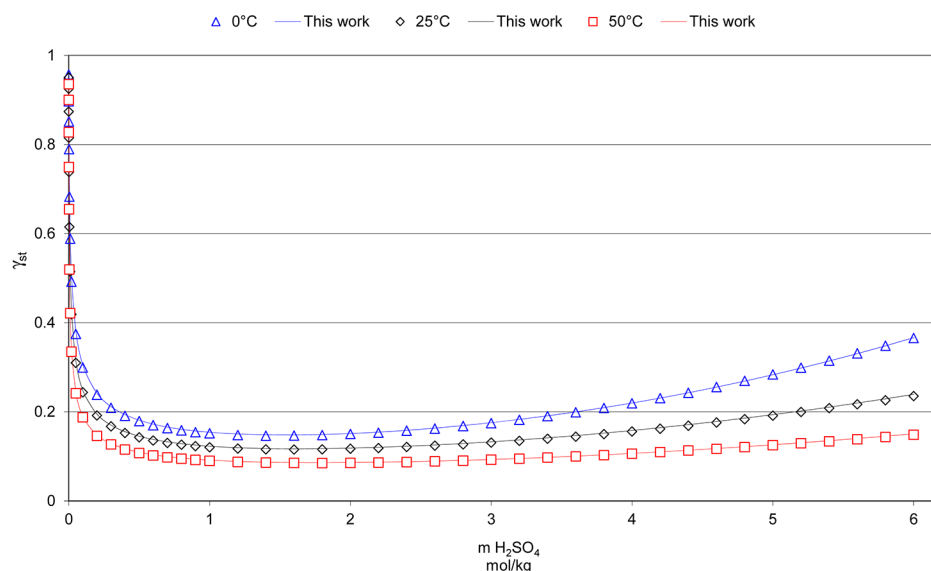

Figure 9. Calculated stoichiometric activity coefficient (lines) by our model compared to the model of Clegg et al.[2] at three temperatures: 0 °C (blue), 25 °C (black), and 50 °C (red).

Table 15. Predicted Stoichiometric Activity Coefficients for Sulfuric Acid at Dilute Solutions Compared to the Values Obtained by Clegg at al.[2,a]

molality	0 °C		25 °C		50 °C	
mol·kg^{-1}	this work	Clegg et al.[2]	this work	Clegg et al.[2]	this work	Clegg et al.[2]
0.0001	0.9577	0.9569	0.9507	0.9500	0.9329	0.9353
0.0002	0.9386	0.9373	0.9268	0.9253	0.9025	0.9003
0.0005	0.9000	0.8971	0.8768	0.8737	0.8285	0.8273
0.001	0.8565	0.8515	0.8200	0.8152	0.7511	0.7492
0.002	0.7966	0.7895	0.7447	0.7384	0.6569	0.6547
0.005	0.6925	0.6827	0.6225	0.6146	0.5217	0.5192
0.01	0.5997	0.5888	0.5225	0.5145	0.4237	0.4213

^{a}The predicted values below 0.005 are extrapolated.

Extrapolating Capability by Temperature. The extrapolating ability of our model by temperature is first tested against the osmotic data measured by Holmes and Mesmer[14] at 200 °C and not used in the parameter optimization but reserved for validation. The predicted values are 0.009 higher in average than the actually measured ones (Figure 13). The mean absolute
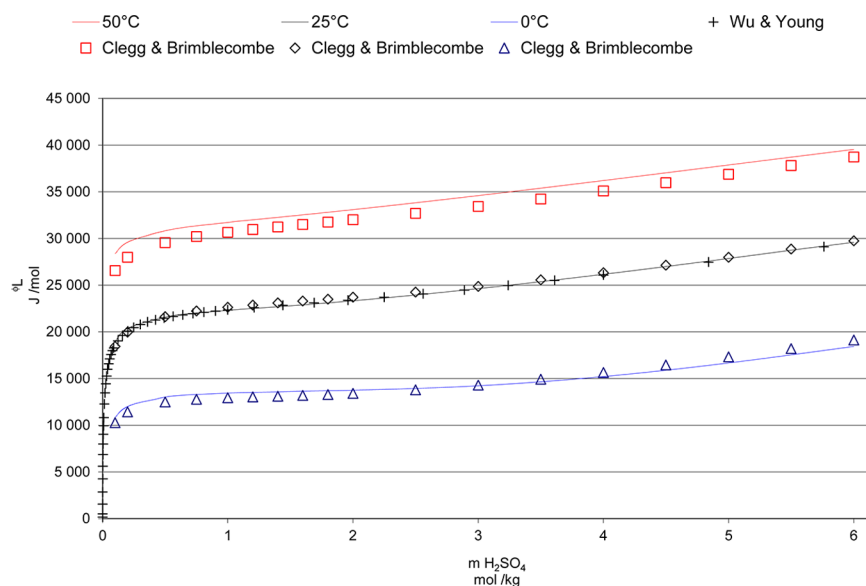
Figure 10. Relative apparent molal enthalpy predicted by our model (lines) compared to the model of Clegg and Brimblecombe[15] at three temperatures: 0 °C (blue), 25 °C (black), and 50 °C (red), experimental data at 25 °C by Wu and Young[49] is also shown (crosshairs).
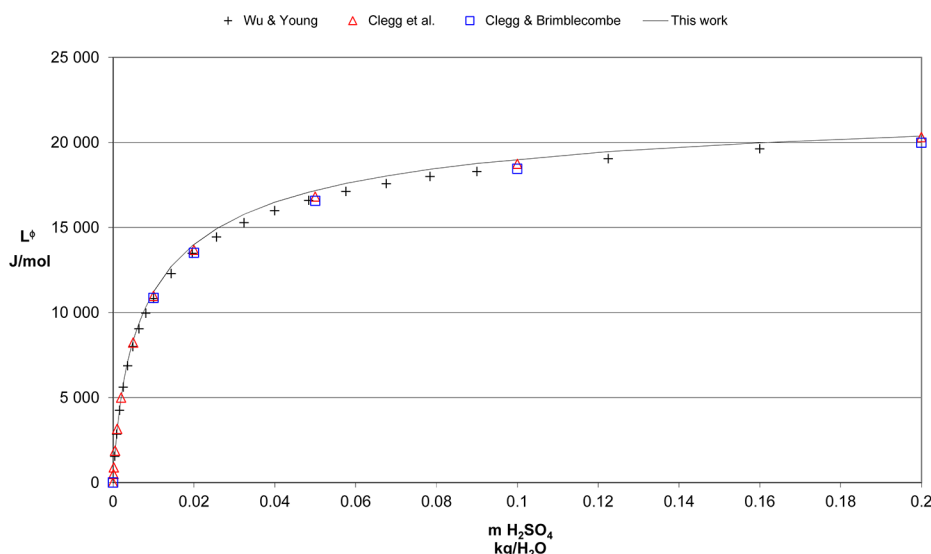

Figure 11. Relative apparent molal enthalpy predicted by our model (line) at 25 °C compared to experimental data by Wu and Young[49] and models of Clegg et al.[2] and Clegg and Brimblecombe.[15] Predicted values below 0.1 are extrapolated.

percentage error (MAPE) is 1.45 %, and the maximum absolute error is 2.69 %.

Second, the extrapolating abilities were tested with the osmotic coefficient at −20 °C calculated by Clegg and Brimblecombe.[15] As can been seen from Figure 14, our model can extrapolate the stoichiometric osmotic coefficient reasonably well when considering that the lowest temperature used in the assessment was 0 °C.

■ **CONCLUSIONS**

As a summary the following conclusions can be made:

(1) Several different K_2 equations consisting only four Pitzer parameters with a simple temperature dependency can describe the thermodynamic behavior of aqueous sulfuric acid up to 6 m solution in the temperature range (0 to 170) °C with good to excellent extrapolation capabilities (Figures 13 and 14).

(2) The predicted thermodynamic values at 25 °C for the electrochemical cells and the thermodynamic properties of the second dissociation reactions are linearly correlated if the assessment is made using only the Gibbs energy related data over a temperature range from (0 to 55) °C.

(3) Thus, the correct value of the second dissociation constant of sulfuric acid at 25 °C cannot be predicted only from the experimental electrochemical data from the temperature range from (0 to 55) °C.

(4) Extending the temperature range and including enthalpy data in the assessment will break this linear dependency for enthalpy and entropy change, and thus, the values for the standard Gibbs energy, enthalpy, and entropy change at 25 °C for the second dissociation constant of sulfuric acid can be estimated with a reasonable accuracy at 25 °C but not for the heat capacity change which lies from (−220 to −289) $J \cdot K^{-1} \cdot mol^{-1}$.
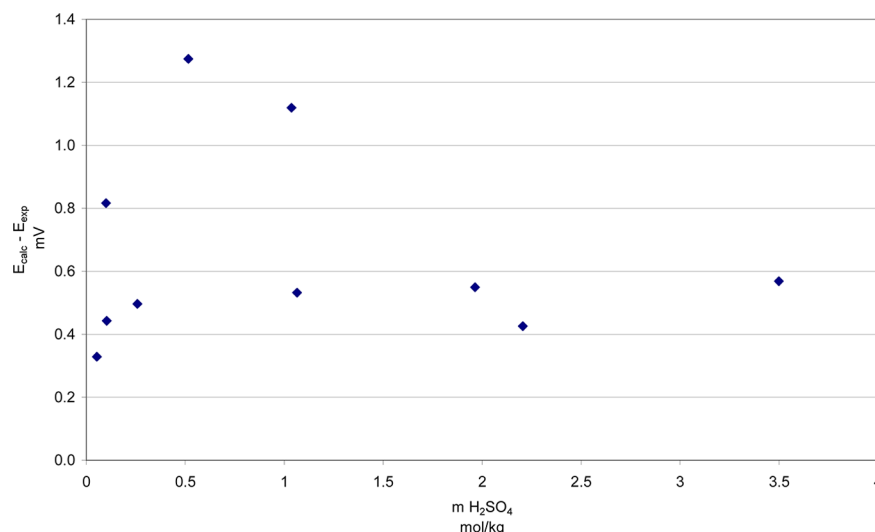
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Figure 12. Deviations between the predicted and measured values for the electrochemical cell $Hg_2SO_4,Hg|H_2SO_4|PbO_2,PbSO_4$ by our model at 25 °C. International volts are assumed for the experimental data and are converted to absolute volts by multiplying 1.00033. Neither the experimental data nor the used standard electrochemical potential (1 076.76) mV for this cell were included in the assessment.
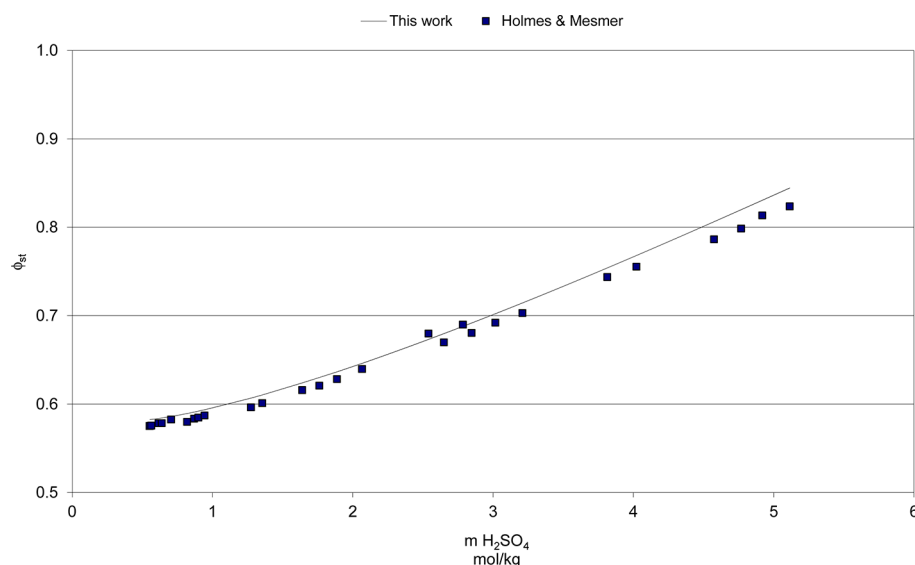

Figure 13. Calculated stoichiometric osmotic coefficient (line) by our model at 473.21 K ($\approx$ 200 °C) compared to experimental data by Holmes and Mesmer.[14]

(5) The obtained thermodynamic values for the second dissociation reaction of sulfuric acid differ from the currently best estimated values. The obtained value for the K_2 at 25 °C is around 0.0119, whereas the current values lie between from 0.0102 to 0.0108. However, the predicted stoichiometric osmotic and activity coefficients are in good agreement with the literature values (Figures 8 and 9 and Table 15).

(6) The obtained thermodynamic properties for the electrochemical cells are in agreement with literature values (Table 10). Moreover, our model for aqueous sulfuric acid (Table 12) selected using these properties is capable to predict the measured potentials of the electrochemical cell $Hg_2SO_4,Hg|H_2SO_4|PbO_2,PbSO_4$ at 25 °C within 0.52 mV. The data were not included in the assessment but reserved for validation (Figure 12).

(7) The obtained standard potentials for cells B and C are internally consistent, within the experimental accuracy.

■ DISCUSSION

In 1975, Pitzer[58] modeled the behavior of dilute aqueous sulfuric acid solutions with the experimental data for the cell $Pt,H_2|H_2SO_4|PbSO_4,Pb$ (A). He used Debye−Huckel like term for the activity coefficients similar to the one used in the Pitzer equation.

$$\ln \chi_i = -A_\phi z_i^2 \left(\frac{\sqrt{I}}{(1 + b\sqrt{I})} + \frac{2}{b} \ln(1 + b\sqrt{I}) \right) \quad (55)$$

Pitzer varied the value of b from 0.8 to 3.0 and iterated the values of K_2 for the sulfuric acid and the standard potential (E°) for the cell. The best fit was obtained with the value of 2.0, yielding to the value of 0.0122 for K_2, but the minimum was very broad so the best value for b cannot, according to Pitzer, be determined. He also found that the value of b does not affect considerably the values of the standard potential or stoichiometric coefficients, but the effect on the variation of K_2 is substantial. Pitzer concluded that there is an intrinsic redundancy between K_2 and b which
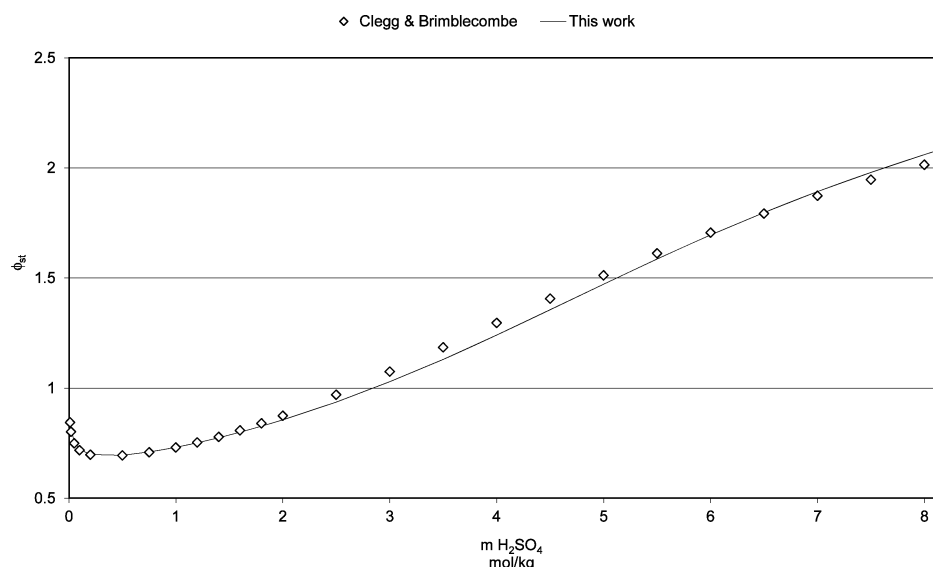
Figure 14. Calculated stoichiometric osmotic coefficient at −20 °C (solid line) compared to values obtained by the model of Clegg and Brimblecombe.[15] Calculated values over 6 mol·kg^{-1} are extrapolated.

Table 16. Standard Deviations Electrochemical Cells A to C and Osmotic Coefficient at 25 °C (Data Set 1) with Different K_2 Equations[a]

cell	this work	Pitzer[5] (1977)	Dickson[8] (1990)	Okuwaki[7] (1988)	Hepler[9] (1990)	Clegg[2] (1994)	Knopf[10] (2003)
A	0.11	0.16	0.20	0.21	0.22	0.22	0.28
B	0.27	0.27	0.28	0.27	0.26	0.27	0.29
C	0.13	0.15	0.13	0.13	0.13	0.13	0.14
ϕ_{25}	0.0008	0.0011	0.0008	0.0009	0.0009	0.0009	0.0008
objective function	0.059	0.078	0.071	0.068	0.072	0.073	0.088

[a]The data for other K_2 equations are from ref 19.

cannot be solved from the electrochemical data used. He continued the analysis with b equal to 1.2, yielding to the values of 0.0136 for K_2 and about −6 kcal·mol^{-1} for the enthalpy change ($\Delta H°$) at 25 °C. We recalculated the value of $\Delta H°$ from his data as −25.6 kJ·mol^{-1}. Pitzer estimated that $E°$ is (−351.3 ± 0.3) mV.

In 1977 Pitzer et al.[5] modeled aqueous sulfuric acid system and obtained two equally good models yielding to K_2 values 0.0103 and 0.0120. They preferred the lower value.

All of these results agree with our findings that the second dissociation constant of sulfuric acid cannot be predicted solely from electrochemical cell data. The reason for this redundancy is due to linear dependency between $E°$ and K_2 (see eqs 52 and 53), which was also confirmed by assessments with assessment 1 (Table 8) using data set 1 (Table 6). The obtained linear dependency between cell and the second dissociation reactions are shown in Figures 3 to 6. The concurrent fit of K_2 and Pitzer parameters with data set 1 yield to K_2 values from 0.0113 to 0.0123 which are higher than currently estimated, that is from 0.0102 to 0.0108 (Table 1).

After several hundreds of successful fits varying used experimental data and Pitzer parameter temperature dependencies with different second dissociation constants, new thermodynamic values for the second dissociation reaction of sulfuric acid as well as the cell reactions are obtained (Table 10). These values deviate slightly from the current "best" thermodynamic values for aqueous sulfuric[2,54,55] acid as well as the standard electrochemical cell potentials at 25 °C.[2,54,55]

To test these new thermodynamic values we chose the closest fit from assessment 10 covering the temperature range from (0 to 170) °C consisting only four Pitzer parameters with eight temperature dependency terms and tested its capacity. The results are as follows: (1) Our model can represent the data of cells A to C with standard deviations of (0.12, 0.27, and 0.14) mV, respectively, as well as the osmotic coefficients measured by Holmes and Mesmer at temperature range (100 to 170) °C with standard deviation of 0.006 or better. The standard deviation of relative apparent molal enthalpy at 25 °C is only 291 J·mol^{-1} (Table 14). (2) The predicted activity and osmotic coefficients are in line with corresponding values obtained with the more complicated models[2,15] (Figures 8 and 9). This also applies when extrapolated in dilute concentrations (Table 15). (3) The extrapolating capability up to 200 °C and down to −20 °C is excellent (Figures 13 and 14). (4) The relative apparent molal enthalpy can be also extrapolated to (0 and 50) °C with reasonable accuracies, that is, better than 4 %.

As a final test we compared the K_2 of our model with other K_2 equations using the same temperature dependencies for Pitzer parameters ($a + b/T$) and the same experimental data (data set 1).

As can see from Table 16 the K_2 equation from our model has a lower objective function value than any of the other K_2 equations. Especially, it can model dilute solution (cell A), where the relative concentration of SO_4 is highest, most precisely.

The K_2 equation obtained in this work will also be tested in the future with new NPL Pitzer model, which has been shown to be capable to model sulfuric acid up to 80 wt % sulfuric acid[51] and predict the solubility of $FeSO_4$ in aqueous sulfuric acid solution up to anhydrous $FeSO_4$[59] We also encourage other modelers to test our new K_2 equation.

The question about correct ΔC_p for dissociation reaction remains still open. Our results indicates that it will lie from $(-220$ to $-289)$ $J \cdot K^{-1} \cdot mol^{-1}$. Unfortunately, MTDATA does not support using solution heat capacity data as in parameter estimation.

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Notes

The authors declare no competing financial interest.

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