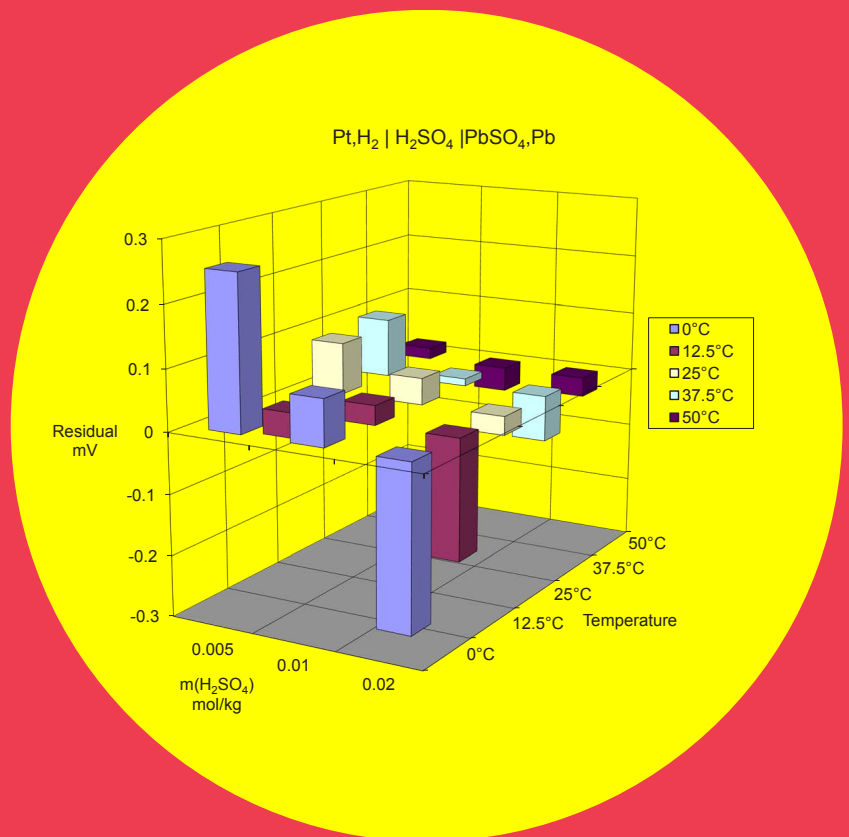


Thermodynamic Modelling of Aqueous Sulfuric Acid

Hannu Sippola



Thermodynamic Modelling of Aqueous Sulfuric Acid

Hannu Sippola

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Abstract

Aqueous sulfuric acid is an important chemical not only for the industry but also with respect to the environment. A need for a simple thermodynamic model is obvious. The purpose of this thesis was to create a thermodynamic model for aqueous sulfuric acid with a reasonable number of parameters.

A key factor in modelling aqueous sulfuric acid is the correct value for the second dissociation constant, K_2 . In this thesis it was discovered that several equations describing K_2 can model aqueous sulfuric acid equally well. The reason for this was identified as the equilibrium between sulfate (SO_4^{2-}) and bisulfate (HSO_4^-) ions which creates an internal redundancy in the thermodynamic description. Thus, the equation for K_2 must be included in the assessment of aqueous sulfuric acid.

The thermodynamic properties of aqueous sulfuric acid were modelled with the Pitzer equation. Both the second dissociation constant K_2 for sulfuric acid and Pitzer parameters were fitted simultaneously. After variation of the experimental data used and the temperature dependencies of the Pitzer parameters, it was found that only four Pitzer parameters with eight fitted terms are required to cover the thermodynamic properties of aqueous sulfuric acid over a temperature range of 0–170°C. The obtained thermodynamic properties are in good agreement with literature values as well as with other Pitzer based and more complex thermodynamic models for aqueous sulfuric acid. The recent version of Pitzer equation, NPL Pitzer, was also tested. It was found to be capable of predicting activity and osmotic coefficient using only five parameters up to 80w% solution over a wide temperature range.

Keywords Thermodynamic properties, Pitzer model, Activity coefficient, Osmotic coefficient, Electrochemical cell

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Tekijä

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Väitöskirjan nimi

Rikkihappo-vesiliuoksen termodynaaminen mallinnus

Julkaisija Kemian tekniikan korkeakoulu**Yksikkö** Metallurgisten prosessien termodynamiikka ja mallinnus**Sarja** Aalto University publication series DOCTORAL DISSERTATIONS 44/2015**Tutkimusala** Kemiallinen termodynamiikka**Käsikirjoituksen pvm** 01.12.2014**Väitöspäivä** 15.04.2015**Julkaisuluvan myöntämispäivä** 18.03.2015**Kieli** Englanti **Monografia** **Yhdistelmäväitöskirja (yhteenvedo-osa + erillisartikkelit)****Tiivistelmä**

Rikkihappo on merkittävä kemikaali sekä teollisuuden että ympäristön suojelun kannalta, joten tarve yksinkertaiselle termodynaamiselle mallille on ilmeinen. Tämän väitöskirjan tavoitteena oli luoda rikkihapon vesiliuokselle termodynaaminen malli, jossa käytettävien malliparametrien lukumäärä on kohtuullinen.

Merkittävä seikka rikkihapon vesiliuoksen mallintamisessa on toisen dissosioitumisvakion, K_2 , arvo. Tässä väitöskirjassa havaittiin, että rikkihapon vesiliuos voidaan mallittaa yhtä hyvin usealla eri dissosioitumisvakion yhtälöllä. Syyksi paljastui bisulfaatti- (HSO_4^-) ja sulfaatti- (SO_4^{2-}) ionien välinen tasapaino, joka lisää termodynaamiseen kuvaukseen sisäisen riippuvuuden. Dissosioitumisvakion yhtälö on siksi otettava mukaan parametrien sovitukseen.

Rikkihapon vesiliuos mallinnettiin Pitzerin yhtälön avulla. Sekä K_2 -yhtälö että Pitzerin parametrit sovitettiin yhtä aikaa. Vaihtelemalla sovitukseen mukaan otettuja kokeellisia tuloksia ja parametrien lämpötilariippuvuutta havaittiin, että rikkihapon vesiliuoksen termodynaamiseen kuvaukseen lämpötila-alueella 0–170°C tarvitaan vain neljä Pitzerin parametria, joissa on yhteensä kahdeksan sovitettavaa termiä. Mallilla lasketut termodynaamiset ominaisuudet ovat sopusoinnussa sekä kirjallisuudesta löytyneiden että muilla monimutkaisemmilla Pitzer malleilla laskettujen arvojen kanssa. Lisäksi tutkittiin äskettäin kehitetyn NPL Pitzer yhtälön soveltuvuutta ja havaittiin, että sen avulla voidaan kuvata sekä aktiivisuuserroin että osmoottinen kerroin laajalla lämpötila-alueella vain viidellä parametrilla aina 80p% rikkihappoon asti.

Avainsanat Termodynaamiset ominaisuudet, Pitzerin yhtälö, aktiivisuuserroin, osmoottinen kerroin, sähkökemiallinen kenno

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Preface

This thesis was carried out at the Metallurgical and Thermodynamic Modelling (TDM) Research Group at Aalto University during the years 2009 to 2014.

First, I would like to thank Professor Pekka Taskinen for the opportunity to carry out this thesis in his laboratory as well as the financial support he has actuated. His advice and profound discussions with him on thermodynamics has inspired me a lot.

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Third, I would like thank Dr. David Lloyd for proofreading my compendium.

The financial support from Finland Centennial Foundation Fund for the Association of Finnish Steel and Metal Producers and Outokumpu Foundation are gratefully acknowledged.

Last but not least I would like to express my deep gratitude to my dear wife Merja for allowing me to spend my summer holidays as well as taking unpaid leave to satisfy my scientific ambitions. Without her patience and support this thesis would not ever have been finished.

Espoo, 11 September 2014
Hannu Sippola

List of Publications

This thesis consists of a compendium and the following Publications which are referred to in the text by their Roman Numbers

- I. Hannu Sippola, Critical evaluation of the 2nd dissociation constants for aqueous sulfuric acid, *Thermochemica Acta*, 532(2012), 65–77.
doi:10.1016/j.tca.2011.04.030
- II. Hannu Sippola, Critical Evaluation of the Second Dissociation Constants for Aqueous Sulfuric Acid over a Wide Temperature Range, *Journal of Chemical and Engineering Data*, 58(2013), 3009–3032.
doi: 10.1021/je4004614
- III. Hannu Sippola, Thermodynamic modelling of concentrated sulfuric acid solutions, *Calphad*, 38(2012), 168–176.
doi: 10.1016/j.tca.2011.04.030
- IV. Hannu Sippola and Pekka A. Taskinen, Thermodynamic Properties of Aqueous Sulfuric Acid, *Journal of Chemical and Engineering Data*, 59(2014), 2389–2407.
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Author's Contribution

Publication 1: "Critical evaluation of the 2nd dissociation constants for aqueous sulfuric acid."

The author is the sole author

Publication 2: "Thermodynamic modelling of concentrated sulfuric acid solutions."

The author is the sole author

Publication 3: "Critical Evaluation of the Second Dissociation Constants for Aqueous Sulfuric Acid over a Wide Temperature Range."

The author is the sole author

Publication 4: "Thermodynamic Properties of Aqueous Sulfuric Acid."

The author processed the data, analysed the results and wrote the manuscript.

List of Symbols and Abbreviations

A_ϕ	Temperature dependent Debye–Hückel constant,
a_i	Activity of solute i
A_E, B_E, C_E	Fitted cell specific parameters for (eq.54)
A_K, B_K, C_K	Fitted parameters for the 2 nd dissociation constant (eqs.58-61)
a_w	Activity of water
b	Constant 1.2 in Pitzer model
B	Second virial coefficient (in eq.56)
B_{ca}	Interaction parameter between cation c and anion a
B_{ca}^ϕ	Osmotic interaction parameter between cation c and anion a
C_{ca}	Pitzer parameter between cation c and anion a
C_{ca}^ϕ	Osmotic Pitzer parameter between cation c and anion a
C_i	Predicted value (eq.56)
E	Electrochemical cell potential (V)
E_i	Experimental value (eq.56)
E°	Standard electrochemical cell potential, (V)
F	Faraday constant, 96487 (C/mol)
f, f'	Debye–Hückel functions in Pitzer model
G^E	Excess Gibbs energy of solution (J/mol)
${}^\phi H$	Apparent molal enthalpy (J/mol)
H°	Enthalpy in standard state (J/mol)
H^E	Excess enthalpy of solution (J/mol)
H^{id}	Ideal enthalpy of solution (J/mol)
H_{sol}	Enthalpy of solution (J/mol)
H_w^*	Enthalpy of pure water

Introduction

I	Ion strength (mol/kg)
I'	Modified ion strength (mol/kg)
K ₂	Second dissociation constant of sulfuric acid
ϕ_L	Relative apparent molal enthalpy (J/mol)
m'	Modified molality (mol/kg)
m	Molality (mol/kg)
M _w	Molecular weight of water (g/mol)
n _i	Amount in moles (mol/kg)
OF	Object function (eq.56)
p _w *	Pressure of pure water (Pa)
p _w	Partial pressure of water (Pa)
R	Gas constant 8.31451 J/K mol
T	Temperature (K)
U _i	Uncertainty of experimental value (eq.56)
w _i	Weight of the experimental value (eq.56)
ϕ_Y	Apparent molal property
Y*	Any thermodynamic property of solvent (water)
Y _{sol}	Any thermodynamic property of solution
Z _i	Charge of ion
w	Weight fraction (tables 5 and 6)
w _w	Amount of water (kg)
α	Degree of dissociation of bisulfate ion
α_1, α_2	Electrolyte specific constants in Pitzer model
$\beta^{(0)}, \beta^{(1)}, \beta^{(2)}$	Pitzer parameters between cation and anion
$\Delta_r C_p^\circ$	Standard heat capacity change in reaction (J/K mol)
$\Delta_r G^\circ$	Standard Gibbs energy change in reaction (J/mol)
$\Delta_r H^\circ$	Standard enthalpy change in reaction (J/mol)
$\Delta_r S^\circ$	Standard entropy change in reaction (J/K mol)
$E_{\theta_{ij}}$	Long range parameter between two different cations or anions

ϕ	Osmotic coefficient
ϕ	Fugacity coefficient (in eqs. 54 and 55)
Φ_{cc}, Φ_{aa}	Interaction parameter between two cations or anions
λ_{nc}	Interaction parameter between neural species and cation
λ_{na}	Interaction parameter between neural species and anion
ν	Sum of stoichiometric coefficients, $\nu = (\nu_+ + \nu_-)$
ν^\pm	Mean stoichiometric coefficient of ions
ν_+, ν_-	Stoichiometric coefficients of cation (+) or anion (-)
θ_{ij}	Pitzer parameters between two different cations or anions
ψ	Pitzer parameter between three different ions
μ_i	Chemical potential of solute i
μ_i°	Chemical potential of solute i in standard state
γ_i	Activity coefficient of solute i
γ_\pm	Mean active coefficient

Superscript

o	Standard state
E	Excess
id	Ideal
'	Partial derivate by ion strength

Subscripts

a	Anion
c	Cation
i,j	Species
n	Neutral
w	Water
r	Reaction
sol	Solution
\pm	Mean

Abbreviations

AARD	Average Absolute Relative Deviation
BIMSA	BInding Mean Spherical Approximation
CODATA	Committee for DATA on science and technology
HKF	Helgeson–Kirkham–Flowers
MSA	Mean Spherical Approximation
MTDATA	Thermodynamic software
NBS	National Bureau of Standards
NPL	National Physical Laboratory
NRTL	Non Random Two Liquid
SLE	Solid–Liquid Equilibrium
UNIQUAC	UNIversal QUAsiChemical Model
VLE	Vapour–Liquid Equilibrium
eNRTL	Electrolyte NRTL model

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1. Introduction

Sulfuric acid[†] is one of the most widely used chemicals in industry. It is produced by oxidizing sulfur dioxide to sulfur trioxide which is then absorbed to aqueous sulfuric acid where it reacts with water to form more sulfuric acid. Sulfur dioxide is either produced by burning elemental sulfur or it is formed as a secondary product for example in nonferrous metal smelters processing sulfide ores.¹

The largest single consumer is the fertilizer industry where it is used to produce phosphoric acid, which is further used to manufacture superphosphate and other fertilizers. It is also used as an acidic dehydrating media in organic and petrochemical processes as well as in TiO₂ and hydrochloric acid production. In the metal processing industry it is used in steel pickling or leaching copper and other metals in hydrometallurgical processes. Dilute sulfuric acid is a preferred electrolyte in metal electro winning and electroplating due to its high conductivity and chemical stability. It is also less corrosive than hydrochloric acid. Only a tiny fraction of sulfuric acid is used in lead–acid batteries which are the most familiar products to ordinary people.¹

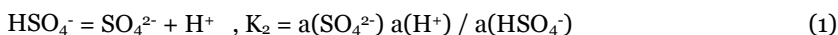
However, most of the sulfuric acid used does not enter the market in finished products but instead ends up as spent acid creating an environmental problem. In the past typical methods to solve this problem was direct dumping in the sea or in a dumping area as neutralized calcium sulfate, i.e., gypsum. Nowadays, regeneration of spent acid is the only acceptable method even though the cost of regenerated acid greatly exceeds the “normal” sulfuric acid production costs.¹

[†] Recommended name for sulphuric acid as well as other sulphur species by IUPAC. As editorial of Nature Chemistry 1(2009) titled as “So long sulphur” express the situation: “It is not a question of American or Oxford Spelling. It is a given name – and ‘correcting’ such a name to a different spelling is wholly inappropriate”

1.1 Background and research environment

Thermodynamically related properties of aqueous sulfuric acid have been extensively studied especially at 298.15 K and summarized by Clegg et al.². Its properties at lower temperatures have recently gained attention due to its impact on aerosols in the stratosphere and troposphere².

In moderate temperatures and concentrations sulfuric acid behaves like a strong acid and dissociates in aqueous solutions completely to hydrogen and bisulfate ions. However, bisulfate ion does not dissociate further completely to hydrogen and sulfate ions. This incomplete dissociation of sulfuric acid complicates the thermodynamic modelling of sulfuric acid.



The importance of choosing the best equation for the second dissociation constant (K_2) of sulfuric acid is a key factor for the further development of models for multicomponent aqueous systems where sulfuric acid is involved.

According to the philosophy of the Calphad Method^{3, 4} binary systems should be modelled first using critically evaluated thermodynamic data before any ternary systems is modelled. For sulfuric acid choosing the best K_2 equation is a crucial step in this process.

There are several thermodynamic models available in the literature for thermodynamic description of aqueous sulfuric acid^{I,II}. The focus of the first models has been on proper description of activity and osmotic coefficients. More recent models have enlarged the focus to vapour pressure, heat capacity and other enthalpy related properties. Consequently, the number of used excess parameters has increased as well as the complexity of the temperature dependency of these parameters attaining the level which make these recent models practically unusable for further development in ternary or higher order thermodynamic systems.

1.2 Objectives and scope

The aim of this study and objectives of this thesis were:

1. Create a thermodynamic description for aqueous sulfuric acid with a reasonable number of Pitzer parameters.
2. Test the existing equations for the second dissociation constant for sulfuric acid.
3. Identify the best equation for the second dissociation constant of sulfuric acid.
4. Identify the most important parameters of the Pitzer model to describe the thermodynamic properties of the $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ system.
5. Test the ability of the new version of the Pitzer ion interaction model, NPL Pitzer, to thermodynamically describe aqueous sulfuric acid.

1.3 Research approach and process

In the beginning the following decisions were made:

- The Pitzer equation⁵⁻¹⁰ was selected as the excess Gibbs energy model.
- All experimental data would be obtained from literature. No experimental research would be performed.
- Temperature range is limited to moderate temperatures. Thus, the pressure dependency of activity coefficients as well as the volumetric properties of ions can be excluded which will keep the used model simple.
- MTDATA^{11,12} was selected as a thermodynamic modelling tool since it is the only thermodynamic software containing the NPL variant of the Pitzer equation.

The Pitzer equation is the only activity coefficient model which has been applied to a broad range of modelling applications by researchers who are independent of the model originator(s).¹³ Several hundred binary electrolyte–water systems have been modelled with it especially at 25°C temperature¹³⁻¹⁸. It has been used to model solubilities in complicated geochemical systems from 25°C to high pressures and temperatures¹⁹⁻²⁶ as well as systems which are important for industry and environment protection.²⁷⁻³² There are also several computer programs available for thermodynamic calculations which include Pitzer activity coefficient model.^{11,13, 33-34, 35}. Other activity coefficient models used in aqueous systems are discussed and compared in author's licentiate thesis³⁶. Newest local composition models are discussed elsewhere^{37, 38}. Models used for modelling of aqueous sulfuric acid are discussed in Chapter 2.

Following the Calphad methodology the first step was a critical literature evaluation of existing experimental thermodynamic data on sulfuric acid – water system. After that the most common K_2 -equations for the second dissociation of sulfuric acid were selected for testing. Since aqueous sulfuric acid solutions contains three species: H^+ , SO_4^{2-} and HSO_4^- there are at least eight Pitzer parameters available for the description of the non-ideal behaviour of aqueous sulfuric acid. Not all of them are needed for a proper thermodynamic model. Thus, several parameter combinations were tested. The schema of the research process is presented in figure 1.

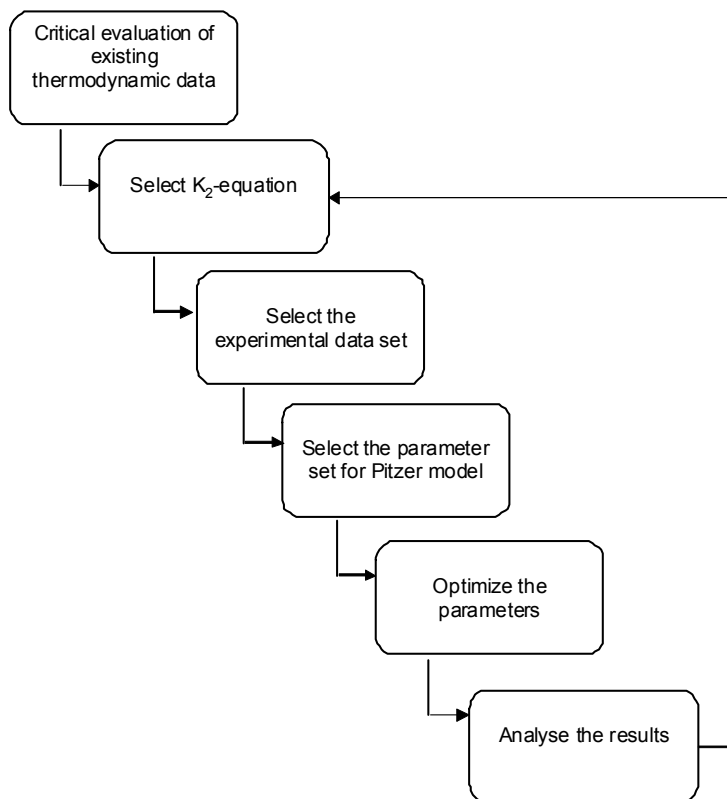


Figure 1. Schema of research process.

In Publication I six different K_2 -equations were tested at temperature range from 0 to 55°C with four different Pitzer parameter sets consisting of two four parameter and two five parameter sets. Four of the studied K_2 -equations were found to fit equally well the experimental data including electrochemical cell and isopiestic data. No significant differences between three of the studied parameter sets were found. However, one of the studied K_2 -equations was found to have excellent extrapolating capabilities of osmotic coefficient to up to 140°C temperature.^I

The temperature range was extended up to 170°C in Publication II by including isopiestic and vapour pressure data. Also the number of parameter sets were increased to 14 including three four parameter, nine five parameter and two six parameter sets. The best parameter set was identified consisting of only four parameters. Increasing the number of parameters above four does not improve the assessment. Four K_2 -equations were studied but significant differences between fitted values were not found. However, one of the four K_2 -equations was found to predict the relative apparent molal enthalpy with reasonable accuracy in the temperature range from 0 to 50°C even though no enthalpy or heat capacity data was used in the assessment.^{II}

So far only Gibbs energy related experimental data was used in the assessments. Relative apparent molal enthalpy data at 25°C was included in

the experimental data used. Since the standard heat of the dissociation reaction of bisulfate ion varies from one equation to another, predefined K_2 -equations were dismissed and the K_2 -equation itself was included in the assessment. The four Pitzer parameters identified in Publication II were used.^{IV}

Ten different assessments were made varying the experimental data used and the temperature dependency of the chosen Pitzer parameters. As a result the thermodynamic properties of the second dissociation reaction of sulfuric acid as well as the thermodynamic properties of the three studied electrochemical cells at 25 °C were obtained. These values were then utilised to identify the best combination of studied Pitzer parameters for aqueous sulfuric acid at temperature range from 0 to 170°C (Sippola model). The predicted values of activity and osmotic coefficient as well as apparent relative molal enthalpy by Sippola model at temperature range from 0 to 50°C up to six molal sulfuric acid solution are in good agreement with values obtained with more complicated Pitzer models^{2, 39} for aqueous sulfuric acid. The extrapolating capabilities of the new model with respect to temperature and concentration over 6 molal sulfuric acid solution are also good.^{IV}

The capabilities of NPL Pitzer model were studied in Publication III. Several sets of Pitzer parameters with four different K_2 -equations were studied. K_2 -equations were the same equations as studied in Publication II. The used experimental data was the same as in Publication I but covering temperature range from 0 to 55 °C up to 15 molal solution. A five NPL Pitzer parameter set was found to be able to predict the osmotic coefficient up 40 molal solution. There were little differences between studied K_2 equations.^{III}

1.4 New scientific contribution

Following the Calphad methodology the thermodynamic properties of aqueous sulfuric acid including the second dissociation constant K_2 were critically evaluated as well as the capabilities of a new version of the Pitzer equation, NPL Pitzer. The main discoveries are:^{I-IV}

1. The most crucial Pitzer parameters for sulfuric acid in temperature range from 0 to 170°C are:
 - a. C^ϕ for H^+ and SO_4^{2-} interaction
 - b. $\beta^{(0)}$ and $\beta^{(1)}$ for H^+ and HSO_4^- interaction
 - c. For the NPL Pitzer model the θ parameter describing the interaction between SO_4^{2-} and HSO_4^- ions is also needed.
2. Only four Pitzer parameters are required to model aqueous sulfuric acid in temperature range from 0 to 170°C. Increasing the number of parameters is not justified.
3. The thermodynamic modelling of aqueous sulfuric acid is complicated due to the internal redundancy found earlier by several researchers. The reason for this redundancy was identified as the equilibrium between bisulfate and sulfate ions.
4. Consequently, several equations for the second dissociation constant, K_2 , for this equilibrium, are able to describe the Gibbs energy related data equally well. A linear relationship between thermodynamic properties of the electrochemical cells and those of aqueous sulfuric acid is formed. The enthalpy change in the dissociation reaction and the equilibrium amounts of bisulfate and sulfate ions have a remarkable contribution to the enthalpy of the solution. Thus, a predefined equation for the second dissociation constant, K_2 should not be used in the assessment. On the contrary it must be included in the assessment as an adjustable parameter.
5. Applying this strategy new thermodynamic properties of aqueous sulfuric acid as well as the electrochemical cells used in the assessment were obtained. They are in excellent agreement with literature except the thermodynamic values for sulfuric acid which deviate somewhat from the values currently considered best. These new values for standard electrochemical potential are internally consistent and explain the currently existing 1.0 mV discrepancy between electrochemical cell potentials.
6. Using these new thermodynamic values a thermodynamic model for aqueous sulfuric acid is generated covering the temperature range from 0 to 170°C and up to 6 m solution which is considered as the maximum concentration for the Pitzer equation. The obtained model can predict the thermodynamic properties of aqueous sulfuric acid including enthalpy related data equally well as more complicated models using only four parameters with simple temperature dependencies. The total number of fitted terms is excess parameters is only eight.

7. The NPL Pitzer equation was found to be able to predict the osmotic coefficient of aqueous sulfuric acid up to 40 m (80 w%) solution in temperature range from 0 to 50°C. The total number of parameters needed is five.

Modelling acidic sulfate solutions has been complicated due to complex models of sulfuric acid with an extensive number of model parameters. This hindrance has now been removed with a simple thermodynamic model covering a large temperature range with reliable extrapolation capabilities.

1.5 Practical applications

An increasing amount of low grade mineral deposits as well as secondary raw materials from landfill sites (landfill mining) or from waste treatment plants are going to be exploited in the near future. Lower grades and an increasing price of energy will favour hydrometallurgical processes. Sulfuric acid is a major candidate as a solvent. However, environmental and energy requirements are constantly increasing which generates demands for cleaner and more energy-efficient technology. Treatment of effluents such as spent sulfuric acid or acidic mine drainage will be an important factor in process design. Thermodynamic modelling is a basic tool when analysing the process alternatives and optimising the process conditions.

A practicable thermodynamic description of the sulfuric acid –water system is essential for the modelling of acidic sulfate solutions required in process optimization and waste management. As demonstrated in this thesis the Pitzer equation and its NPL variant are able to predict the thermodynamic behaviour of aqueous sulfuric acid with a reasonable number of parameters thus, enabling the modelling of more complex acidic sulfate solutions and the planning of new treatment methods for them in the future. Limiting the number of model parameters used also improves the extrapolating capabilities which enable digitalization of industrial production by including the thermodynamic calculation as a new element in online automation or expert systems.

2. Excess Gibbs energy models

2.1 Pitzer models

The Pitzer ion interaction model⁵⁻¹⁰ has proved to be the most accurate activity coefficient model up to moderate concentrations in aqueous solutions^{36, 40-42}. The unsymmetrical mixing terms for ions with like sign but with unequal magnitude are not included in the original Pitzer ion interaction model.

However, Harvie et al.^{19, 20} discovered that these terms improve their model for the Na–K–Mg–Ca–H–Cl–SO₄–OH–HCO₃–CO₃–CO₂–H₂O–system and introduced them in their modification of the Pitzer interaction model. They calculated these terms numerically and fitted them as Chebyshev expansions accurate to six significant figures.

In 1977 Pitzer et al.⁴³ modelled the thermodynamic behaviour of aqueous sulfuric acid using the activity coefficient model, named after Pitzer⁵ himself, from 0 to 55 °C up to 6 m sulfuric acid solution. They found out that two different sets of the model parameters and second dissociation constants (K_2) can describe the experimental data equally well.

Reardon and Beckie⁴⁴ included unsymmetrical mixing terms in their model for the H₂SO₄–FeSO₄–H₂O system. For aqueous sulfuric acid they used the same set of Pitzer parameters with a slightly different temperature dependency and the same dissociation constant K_2 obtained by Pitzer et al.⁴³ and were able to model the solubility of iron sulfate in aqueous sulfuric acid solutions in the temperature range from 0 to 60 °C up to 5 m acid solution.

Dickson et al.⁴⁵ determined in 1990 by electrochemical cell experiments the value of the second dissociation constant K_2 over a temperature range from 50 °C to 250 °C. They used the K_2 -equation derived by Pitzer et al.⁴³, the standard enthalpy of the dissociation reaction at 25 °C and the heat capacity change of reaction 1 between 10 to 55 °C determined by Hovie and Hepler⁴⁶ to extend their equation for K_2 down to 10 °C. However, Hovie and Hepler⁴⁶ values for the heat capacity change in the dissociation reaction are partly based on the K_2 values previously determined by Pitzer et al.⁴³.

In 1992 Holmes and Mesmer⁴⁷ used their own isopiestic data over a temperature range from 110 to 200 °C, the equation of Dickson et al.⁴⁵ for the dissociation constant K_2 , and the stoichiometric osmotic coefficients from Pitzer et al.⁴³ in the temperature range of from 25 to 50 °C to generate their own model for the H₂SO₄–H₂O system. Isopiestic measurements in the concentration range from 0.35 to 4.36 mol/kg at 25 °C by Rard⁴⁸ as well as

isopiestic values at 50 °C from 0.5 to 4.2 m solution, obtained in a personal communication in 1990 by Palmer and Sweeton, were also included in their assessment. Holmes and Mesmer considered the unsymmetrical mixing terms an unnecessary complication.

In 1994 Clegg et al.² examined thoroughly the available thermodynamics related experiments in the literature for the H₂SO₄–H₂O system and used only those experimental values in their modelling they considered the most reliable. They used the K₂ equation by Dickson et al.⁴⁵ but shifted its value at 25 °C from 0.010865 down to more accurate considered value of 0.01050, defined earlier by Pitzer et al.⁴³. Archer's extension⁴⁹ for the third virial coefficients was included in the Pitzer model as well as the unsymmetrical mixing terms but they calculated the latter ones using an approximating method introduced by Pitzer⁸ instead of numerical integration. The temperature and concentration ranges for their model are from 0 to 55 °C and from 0 to 6 mol/kg, respectively. The total number of fitted terms in Pitzer interaction parameters is 32.

Later in 1995, Clegg and Brimblecombe³⁹ extended the temperature and concentration range using the mole fraction based version of Pitzer ion interaction model⁵⁰⁻⁵² to describe the thermodynamic behaviour of the H₂SO₄–H₂O system from <200 K to 328 K (55 °C) up to a sulfuric acid concentration of 40 mol/kg. They retained the shifted version of the K₂–equation from Dickson et al.⁴⁵. The total number of terms in 8 fitted parameters for the interactions between the ions is quite high, 40. The isopiestic measurements for sulfuric acid at 323.15 K earlier referred to as personal communications with Palmer and Sweeton used in all these three assessments were published in 1996⁵³.

Recently, Christov and Møller²⁴ chose to use the unshifted equation for K₂ from Dickson et al.⁴⁵ when modelling the H₂SO₄–H₂O system from 0 to 250°C. They did not use any experimental data directly in their assessment. The interaction parameters $\beta^{(0)}$ and C^ϕ for H⁺–SO₄²⁻ interaction as well as $\beta^{(0)}$ and $\beta^{(1)}$ for H⁺–HSO₄⁻ were generated from the cubic power functions of Holmes and Mesmer⁴⁷. However, the total number of terms in these cation–anion parameters is increased by two up to 15. Unlike Holmes and Mesmer, the unsymmetrical mixing terms are included in their model which may be the reason for the increase in the number of temperature dependency terms in cation–anion parameters. Unfortunately, Christov and Møller do not specify how the parameter generation process was performed. The higher order parameter θ between SO₄²⁻ and HSO₄⁻ was assessed from the published values for the stoichiometric osmotic coefficients in the concentration range from 0.1 to 6.0 mol/kg by Holmes and Mesmer⁴⁷ over a temperature range from 25 to 200°C and by Clegg et al.² at 0 °C, while the ternary parameter ψ between H⁺, SO₄²⁻ and HSO₄⁻ was set to zero at all temperatures. The total number of nonzero terms in five Pitzer interaction parameters is 20.

There are only a few Pitzer models outside 25 °C for the H₂SO₄–H₂O system, which are independent from the 1977 model of Pitzer et al.⁴³.

In 1992, the author³⁶ developed a model for the $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ system from the same electrochemical cell data used by Pitzer et al.⁴³, but using the equation of Matsushima and Okuwaki⁵⁴ for K_2 determined from electrochemical cell measurements in the temperature range from 25 to 250 °C. The author was able to describe the solubility of iron sulfate up to 50 w% sulfuric acid in the temperature range from 0 to 100 °C. The author used Harvie et al.¹⁹ modification of the Pitzer model, that is, unsymmetrical mixing terms were included.

Recently, Knopf et al.⁵⁵ constructed a model from their own Raman spectroscopy data in a temperature range from 180 to 326 K, i.e., about from -93 to 53 °C, heat capacity and enthalpy data by Giaugue et al.⁵⁶ in a temperature range from 15 to 300 K, cell measurements by Harned and Hamer⁵⁷ over a temperature range from 0 to 60 °C and dissociation constants in the temperature range from 50 to 200 °C by Dickson et al.⁴⁵, and by Marshall and Jones⁵⁸ from calcium sulfate solubility data in aqueous sulfuric acid in the temperature range from 25 to 350 °C. Their model is, according to the authors, valid up to 200 °C. Unsymmetrical mixing terms are excluded in the Pitzer model but Archer's extension⁴⁹ is included. They also demonstrated that extrapolating the K_2 equation used by Clegg and Brimblecombe³⁹ beyond its experimental limits indicates that the dissociation reaction will change from exothermic to endothermic at around 233 K and the standard Gibbs energy change will reach a minimum at about 220 K^{59, 60}.

In 2010, when modelling the $\text{H}^+\text{-NH}_4^+\text{-Na}^+\text{-SO}_4^{2-}\text{-NO}_3^-\text{-Cl}^-\text{-H}_2\text{O}$ system Friese and Ebel⁶¹ refitted the $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ model of Clegg and Brimblecombe³⁹ and extended the experimental data used in assessment by including the degree of dissociation of bisulfate ion by Knopf et al.⁵⁵ and Lund Myhre et al.⁶², more recent isopiestic determinations at 25 °C by Rard⁶³, enthalpy of dilution data at 10, 20 and 40 °C by Rütten et al.⁶⁴ and heat capacity data at 40 °C by Socolik⁶⁵. The number of interaction parameters used were increased up to 11 with an overwhelming 66 fitted terms.

A summary of Pitzer interaction models for aqueous sulfuric acid is presented in table 1.

Table 1. Pitzer interaction models for aqueous sulfuric acid.¹¹

Author(s)	Year	Modifications ^a	Temperature range °C	Number of parameters	Total number of terms	Equation for K_2
Pitzer et al. ⁴³	1977		5 to 55	4	8	Pitzer ⁴³
Reardon and Beckie ⁴⁴	1987	U	5 to 55	4	9	Pitzer ⁴³
Sippola ³⁶	1992	U	5 to 55	4	8	Okuwaki ⁵⁴
Holmes and Mesmer ⁴⁷	1992		25 to 200	5	17	Dickson ⁴⁵
Clegg et al. ²	1994	UA	0 to 55	9	32	Dickson ^{45 b}
Clegg and Brimblecombe ³⁹	1995	M	-70 to 55	10	40	Dickson ^{45 b}
Knopf et al. ⁵⁵	2003	A	-90 to 200	10	34	Knopf ⁵⁵
Christov and Møller ²⁴	2004	U	0 to 200	5	20	Dickson ⁴⁵
Friese and Ebel ⁶¹	2010	M	-70 to 55	11	66	Dickson ^{45 b}

^a U=unsymmetrical mixing terms; A=Archer extension; M=mole fraction scale.

^b Modified to yield 0.01050 at 25 °C.

2.2 Local composition models

Most of the local composition models for $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ system are focused on vapour–liquid equilibrium and the speciation of sulfuric acid. Electrochemical cell measurements are generally omitted in model parameter estimation.

In 1991, Liu and Gren⁶⁶ tested the Liu–Harvey–Prausnitz⁶⁷ model at 25 °C for 55 aqueous solutions including sulfuric acid. For long range forces the model has its own version of the Debye–Hückel equation which includes terms from the Wilson equation used to describe short range forces. Sulfuric acid is assumed to dissociate completely which restricts the concentration range from 1 to 76 m sulfuric acid solution. Furthermore, the interaction parameter between H_2O and SO_4^{2-} has an ad hoc value for sulfuric acid solutions whereas all other sulfate systems have a common value for this interaction.

In 1998 Bosen and Engels⁶⁸ modelled aqueous sulfuric acid solutions up to 80 mol % (96 w%) in the temperature range from 0 to 240 °C with the NRTL equation⁶⁹ which does not include any term for long range forces between ions, that is, the Debye–Hückel term is missing. They assumed complete dissociation of sulfuric acid; thus the bisulfate ion was excluded in their model. The gas phase was assumed to be ideal. They were able to present the vapour pressure data of Collins⁷⁰, Burt⁷¹ and Tarasenkova⁷² with mean relative deviations of 2.6, 3.2 and 3.2 %, respectively. The maximum deviations were 11.6, 12.9 and 9.7 %, respectively. A comparison with the osmotic coefficient data of Robinson and Stokes⁷³, not included in the assessment, yields values of 4.7 % and 38.7 % for the mean relative and maximum deviations, respectively.

Messnaoui and Bounahmidi⁷⁴ used the electrolyte NRTL (eNRTL) by Chen et al.^{75, 76} to model the $\text{CaSO}_4\text{-H}_3\text{PO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ quaternary. The electrolyte NRTL includes the mole fraction based Debye–Hückel term by Pitzer for long range interactions and as the name indicates the NRTL model for short-range forces. There is also a Born term included for the mixed solvents. Messnaoui and Bounahmidi used osmotic coefficient data at 25 °C up to 7 m solution from various sources when including the $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ subsystem in their model. Osmotic data at 50 °C and 75 °C from Zeleznik⁷⁷ were also used in the assessment. The mean square errors for osmotic and stoichiometric mean activity coefficients were 0.032 and 0.079, respectively. Their model performs less accurately than model by Pitzer et al.⁴³ which can be seen in figures 2 and 3 in their paper. The need to improve the model is clearly stated by the authors. However, their model presents more accurately the bisulfate and sulfate concentration estimated from apparent volume⁷⁸ and Raman spectroscopy⁷⁹ measurements. The equation for the second dissociation constant for H_2SO_4 was obtained using thermodynamic values from the Helgeson–Kirkham–Flowers model⁸⁰. Please note that in their article the headers of table 1 for the $\Delta H_{f,298}$ and $\Delta G_{f,298}$ columns are interchanged.

In 2010 Bollas et al.⁸¹ found that the electrolyte NRTL⁷⁶ and the generalized electrolyte NRTL⁸² models are thermodynamically inconsistent since the cationic and anionic mole fraction are assumed constant when activity

coefficients are derived from the excess Gibbs energy equation. They refined the model and tested it by modelling the $\text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ system at 25 °C up to 50 m solution. Hydration as well as undissociated sulfuric acid were also included in their model. They used smoothed stoichiometric osmotic and activity coefficients from Zeleznik⁷⁷, Rard et al.⁸³, Staples⁸⁴ and Vermeulen et al.⁸⁵ in their assessment as well as the averaged values for the degree of HSO_4^- dissociation and undissociated concentration of H_2SO_4 derived from various spectroscopic data. They used a value of 0.0105 for the second dissociation constant of H_2SO_4 at 25 °C from Clegg and Brimblecombe³⁹, based on Pitzer et al.⁴³. Bollas et al.⁸¹ compared, using constant average hydration number, the original electrolyte NRTL model and the refined one with data up to 20 m solution and found out that the original electrolyte NRTL model did not satisfactorily predict together the osmotic coefficient and degree of dissociation of bisulfate. The Average Absolute Relative Deviation (AARD) for stoichiometric osmotic coefficient and degree of dissociation were 1.02 % and 14.83 % for original electrolyte NRTL model and 0.65 % and 1.82 % for the refined model, respectively. They also found that by using the hydration equilibrium reaction instead of a constant hydration number they could extend the model and retain about the same accuracy up to 50 m solution with good extrapolating capability up to 65 m solution. More concentrated solutions would need sulfur trioxide included in the model description since after that concentration the partial pressure of SO_3 becomes important. The total number of fitted terms in excess parameters was 11.

Simonin et al.⁸⁶ introduced in 2006 a MSA–NRTL⁸⁷ based model for aqueous solutions which describes long range forces by a restricted primitive MSA expression⁸⁸ and short range forces by the NRTL equation. Moreover, they included hydration and ion association in their version of the MSA–NRTL model. They tested their model with several strong electrolytes as well as sulfuric and nitric acid at 25 °C. The experimental data used for sulfuric acid was stoichiometric osmotic and activity coefficients by Rard et al.⁸³ in the concentration range from 0.1 to 6.0 mol/kg. For the second dissociation constant K_2 they first used the value of 0.0105 from Pitzer et al.⁴³. Second they released it and finally included also Raman data^{60, 62, 79} in the assessment. The obtained values for K_2 at 25°C were 0.0103 and 0.0117, respectively. The AARD for stoichiometric osmotic coefficients were 0.16 %, 0.13 % and 0.36 %, respectively, and for stoichiometric activity coefficients 0.09 %, 0.08 % and 0.28 %. As the authors state there are some difficulties in simultaneously representing both osmotic and activity coefficients with Raman spectroscopy data. They also noticed that the thermodynamic values are very sensitive to the values of K_2 and of the hydration numbers at low salt concentrations.

Previously, in 2004, Simonin et al.⁸⁹ used binding MSA (BIMSA) to model aqueous sulfuric acid at 25 °C. They used the osmotic coefficient data of Rard et al.⁸³ as experimental data and were able to fit the stoichiometric osmotic coefficient in concentration range from 0 to 27 mol/kg with an AARD of 0.81 %. However, there is a systematic deviation in the dilute region yielding up to 1.4 % AARD in the concentration range from 0.1 to 1 mol/kg.

Campos et al.⁹⁰ used a revised version of the extended UNIQUAC⁹¹ to model the vapour–liquid–equilibria (VLE) of the H₂O–H₂SO₄ system valid in the temperature range from 0 to 150°C. Their model included undissociated sulfuric acid, bisulfate and sulfate ions in aqueous phase as well as sulfuric acid, sulfur trioxide, and sulfuric acid hydrate in a gas phase which was assumed ideal. The second dissociation constants K_2 was taken from NBS tables⁹² assuming that the Gibbs energy change in the dissociation reaction is constant. This yields to the following formula: $\ln K_2 = a/T$. The experimental data used in the fit was total pressure data from Perry's Chemical Handbook⁹³ and dew point data for concentrated sulfuric acid from 65 to 80 w%⁹⁴. The average relative deviations between assessed and experimental pressure obtained were 11.5 % and 7.8 %, respectively. However, the number of data points included in the assessment indicates that data in the temperature range from 150 to 200°C was included in the assessment, too. They also noticed that the deviations in total pressure are higher in dilute regions. This indicates that the presentation of sulfuric acid in dilute regions where bisulfate is more dissociated is inadequate, maybe due to missing Debye–Hückel term in the model and the simple temperature dependency used for the dissociation constant of bisulfate ion (K_2).

Wang et al.⁹⁵⁻⁹⁸ created a UNIQUAC based model for mixed–solvent electrolyte systems which describes long–range and new middle range interactions with a Pitzer-like equation. For short range interactions UNIQUAC is applied. The Helgeson–Kirkham–Flowers (HKF–model) is used for thermodynamic properties for ions. They have modelled several different systems using vapour–liquid–equilibria (VLE), solid–liquid–equilibria (SLE), activity coefficient, heat of mixing and dilution, heat capacity and density data to fit the model parameters. Most diagrams shown are on logarithm scale. Numerical values to describe the quality of the assessments such as standard deviations or residual plots are not given which makes it difficult to realise the true capabilities of the model. However, Lin et al.⁶⁶ and Thomsen et al.⁹⁹ evaluated the capabilities of the model developed by Wang et al.^{97,100}, electrolyte NRTL model by Chen et al.^{75, 76, 82} and Extended UNIQUAC model by Thomsen³⁷ for strong electrolyte solutions and concluded that all these models are able to calculate vapour–liquid equilibrium reasonably well. There are some difficulties in calculating solid–liquid equilibria for multicomponent systems especially in indentifying the solid phase. Unfortunately, no acidic sulfate system is included in the comparison. A summary of local composition models for aqueous sulfuric acid is presented in table 2.

Table 2. Local composition models for aqueous sulfuric acid.¹¹

Author(s)	Year	Model	Temperature °C	Concentration (mol/kg) ^b	Number of excess parameters (terms within)
Liu and Gren ^{66, a}	1991	Liu-Harvey- Prausnitz	25	1 to 76	2
Rosen and Engels ^{68, a}	1998	NRTL	0 to 240	w = 0 to 0.96	10 (17)
Messnaoui and Bounahmidi ⁷⁴	2006	eNRTL	25 to 75	1 to 7	4(6)
Bollas et al. ⁸¹	2010	eNRTL (redefined)	25	0 to 50/65	10
Simonin et al. ⁸⁶	2006	MSA-NRTL	25	0.1 to 6.0	6
Simonin et al. ^{89, c}	2004	MSA (BIMSA)	25	0.1 to 27	6
Campos et al. ⁹⁰	2006	UNIQUAC	0 to 150	w = 0 to 1	7(15)

^a Complete dissociation of sulfuric acid is assumed. ^b or weight fraction w.

^c Bisulfate ion is considered via equilibrium only. No ion specific parameters used.

2.3 Other models

In 1998, Grenthe et al.¹⁰¹ studied the thermodynamics of sulfuric acid in NaClO₄ media at 25°C using potentiometric data only. They modelled the system with Brønsted–Guggenheim–Scatchard (SIT) and Pitzer models and with the latter varied the number of Pitzer parameters used. The second dissociation constant was included in the assessment. They obtained a value of 0.0103 for K₂ with the SIT model and values between 0.0059 and 0.0091 with the Pitzer model depending on the set of parameters used.

Recently, Fraenkel^{102, 103} has argued that aqueous sulfuric acid should be modelled as a 1–3 electrolyte solution. He based his statement on the idea that the mean activity coefficient of aqueous sulfuric acid cannot be modelled as completely dissociated 1–2 or 1–1 electrolytes in low concentrations where Debye–Hückel limiting law is known to be valid. However, sulfuric acid can be modelled as 1–3 electrolyte (H₄SO₅) decomposing completely to an anion (HSO₅⁻) and three hydrogen ions (H⁺).

Fraenkel uses his own extension to the Debye–Hückel equation to calculate the mean activity coefficient assuming that sulfuric acid dissociates completely; thus, no value for the second dissociation constant is needed. This assumption contradicts the recent results by other authors (Tables 1 and 2). The experimental data is taken from Harned and Hamer¹⁰⁴. Fraenkel is aware that this data is considered less accurately so he adjusts it. As a result the values of mean activity coefficients are lowered in the dilute concentration about 5% to yield values from above to below the currently best considered values. Using this modified data he models the sulfuric acid – water system as strong 1–3 electrolyte up to 6 m solution.

3. Theory

3.1 Chemical potential in aqueous solutions

In aqueous solutions the chemical potential of the solvent, that is water, is defined as[†]

$$\mu_w = \mu_w^o + RT \ln(a_w) \quad (2)$$

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

$$\mu_i = \mu_i^o + RT \ln(a_i) = \mu_i^o + RT \ln(m_i / m^o) + RT \ln(\gamma_i) \quad (3)$$

where m_i is the molality, γ_i is the activity coefficient of the solute and m^o is 1 mol/kg to keep the equation dimensionally correct. In further equations molalities are implicitly divided by m^o .

Since concentration is expressed in molalities the standard state is hypothetical, ideally dilute solution of unit molality at the temperature and pressure of the solution.[‡]

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

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

where M_w is the molecular weight of water in g/mol.

Electrolytes dissociate in aqueous solutions

$$M_{v_+} X_{v_-} = v_+ M^{z_+} + v_- X^{z_-} \quad (5)$$

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

$$\mu(M_{v_+} X_{v_-}) \equiv v_+ \mu(M^{z_+}) + v_- \mu(X^{z_-}) \quad (6)$$

This applies also in the case of incomplete dissociation of the electrolyte. Thus, from equations 3 and 6 follows for any electrolyte:

[†] In NBS Tables⁹² the term "hypothetical ideal solution at unit molality" is used. I prefer to use ideally dilute solution instead of ideal solution since it will emphasise the difference between ideally dilute (Henrian) and ideal (Raoultian) solutions.

$$\mu^{\circ}(M_{v_+}X_{v_-}) = v_+\mu^{\circ}(M^{z+}) + v_-\mu^{\circ}(X^{z-}) \quad (7)$$

and

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

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

$$m_M = v_+m_{MX} \quad (9)$$

$$m_X = v_-m_{MX} \quad (10)$$

Thus, from equation (8) the following applies for a completely dissociated electrolyte

$$m_{MX}\gamma_{MX} = (v_{\pm}m_{MX})^v(\gamma_{\pm})^v \quad (11)$$

$$v = v_+ + v_- \quad (12)$$

$$v_{\pm}^v \equiv (v_+)^{v_+}(v_-)^{v_-} \quad (13)$$

$$\gamma_{\pm}^v \equiv (\gamma_M)^{v_+}(\gamma_X)^{v_-} \quad (14)$$

where the term γ_{\pm} is generally called the mean activity coefficient of the electrolyte.

Inserting equation (11) in to equation (3) we get equation 15 for the chemical potential of a completely dissociated electrolyte:

$$\mu_{MX} = \mu_{MX}^{\circ} + vRT \ln(v_{\pm}m_{MX}\gamma_{\pm}) \quad (15)$$

Applying equation 3 for sulfuric acid we obtain^{IV}:

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

where m is the molality of sulfuric acid and

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

Assuming complete dissociation equations (8–10, 15, 16) yield the following expressions for the activity and stoichiometric activity coefficient of sulfuric acid:

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

and furthermore

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

On the other hand, if the incomplete dissociation of sulfuric acid in equation (1) is considered, the following relationship for the activity of sulfuric acid is obtained:

$$a_{H_2SO_4} = m \gamma_{H_2SO_4} = (m_H\gamma_H)^2(m_{SO_4}\gamma_{SO_4}) = K_2m_H\gamma_H m_{HSO_4}\gamma_{HSO_4} \quad (20)$$

and furthermore

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

where α is degree of dissociation of the bisulfate ion.

3.2 Apparent molal properties

An apparent molar property (${}^\phi Y_2$) is defined as

$${}^\phi Y_{MX} = (Y_{sol} - n_w Y_w^*) / n_{MX} \quad (22)$$

where

Y_{sol} = property of the solution

Y^* = property of pure solvent (water)

n_w = amount of solvent (water)

n_{MX} = amount of solute (electrolyte)

which expresses properties of the solution compared to the same amount of pure solvent.

For apparent molar enthalpy ${}^\phi H$ we obtain

$${}^\phi H_{MX} = (H_{sol} - n_w H_w^*) / n_{MX} \quad (23)$$

The enthalpy of the solution (H_{sol}) can be divided to an ideal (H^{id}) and excess part (H^E) so equation 23 yields

$${}^\phi H_{MX} = (H^E + H_{sol}^{id} - n_w H_w^*) / n_{MX} \quad (24)$$

and furthermore

$${}^\phi H_{MX} = (H^E + n_{MX} H_{MX}^0 + n_w H_w^0 - n_w H_w^*) / n_{MX} \quad (25)$$

Since the standard state of the solvent is pure water:

$${}^\phi H_{MX} = H^E / n_{MX} + H_{MX}^0 \quad (26)$$

Thus, the apparent molar enthalpy in aqueous solution is related to the standard state of the electrolyte.

After changing to the molality scale we obtain for relative apparent molal enthalpy ${}^\phi L_{MX}$

$${}^\phi L_{MX} = {}^\phi H_{MX} - H_{MX}^0 = H^E / m_{MX} \quad (27)$$

The excess enthalpy of the solution can be obtained using the Gibbs–Helmholz equation from the excess Gibbs energy (G^E).

$$H^E = -T^2 \left[\partial (G^E / T) / \partial T \right]_{T,P,m} \quad (28)$$

3.3 Pitzer equation

Pitzer⁵⁻¹⁰ introduced an interaction model for the 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 the gas constant (R), absolute temperature (T) and mass of solvent (w_w) is:

$$\begin{aligned}
 \frac{G^{E,m}}{w_w RT} &= f(I) + 2 \sum_c \sum_a m_c m_a \left[B_{ca} + \left(\sum_c m_c z_c \right) C_{ca} \right] \\
 &+ \sum_c \sum_{c'} m_c m_{c'} \left[2\Phi_{cc'} + \sum_a m_a \psi_{cc'a} \right] \\
 &+ \sum_a \sum_{a'} m_a m_{a'} \left[2\Phi_{aa'} + \sum_c m_c \psi_{aa'c} \right] \\
 &+ 2 \sum_n \sum_c m_n m_c \lambda_{nc} + 2 \sum_n \sum_a m_n m_a \lambda_{na}
 \end{aligned} \tag{29}$$

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

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

$$I = 1/2 \sum_i m_i z_i^2 \tag{30}$$

Assuming C , λ and ψ to be independent of concentration, the equations for activity and osmotic coefficients for cation M, anion X and neutral species N are obtained with appropriate differentiation from equation (29) and summarized in equations (31) – (38)

$$\begin{aligned}
 \ln \gamma_M &= \left(\frac{\partial G^{E,m} / RT}{\partial n_M} \right)_{T,p,n_w,n_i, i \neq M} \\
 &= z_M^2 (f'(I)/2) \\
 &+ \sum_a m_a [2B_{Ma} + ZC_{Ma}] + z_M \sum_c \sum_a m_c m_a C_{ca} + z_M^2 \sum_c \sum_a m_c m_a B'_{ca} \\
 &+ \sum_c m_c \left[2\Phi_{Mc} + \sum_a m_a \psi_{Mca} \right] + z_M^2 \sum_c \sum_{c'} m_c m_{c'} \Phi'_{cc'} + z_M^2 \sum_a \sum_{a'} m_a m_{a'} \Phi'_{aa'} \\
 &+ \sum_a \sum_{a'} m_a m_{a'} \psi_{Maa'} + 2 \sum_n m_n \lambda_{nM}
 \end{aligned} \tag{31}$$

where the apostrophe (') indicates a derivation by ion strength and Z is defined as $Z = \sum_i m_i |z_i|$.

For anion and neutral solute we get:

$$\begin{aligned}
\ln \gamma_X &= \left(\frac{\partial G^{E,m} / RT}{\partial n_X} \right)_{T,p,w_w,n_i,i \neq X} \\
&= z_X^2 (f'(I) / 2) \\
&+ \sum_c m_c [2B_{cX} + ZC_{cX}] + |z_X| \left[\sum_c \sum_a m_c m_a C_{ca} + z_X^2 \sum_c \sum_a m_c m_a B'_{ca} \right] \\
&+ \sum_a m_a \left[2\Phi_{Xa} + \sum_c m_c \psi_{Xac} \right] + z_X^2 \sum_c \sum_{c'} m_c m_{c'} \Phi'_{cc'} + z_X^2 \sum_a \sum_{a'} m_a m_{a'} \Phi'_{aa'} \\
&+ \sum_{c < c'} m_c m_{c'} \psi_{cc'X} + 2 \sum_n m_n \lambda_{nX} \\
\ln \gamma_N &= \left(\frac{\partial G^{E,m} / RT}{\partial n_N} \right)_{T,p,w_w,n_i,i \neq N} = 2 \sum_c m_c \lambda_{Nc} + 2 \sum_a m_a \lambda_{Na}
\end{aligned} \tag{32}$$

and for osmotic coefficient

$$\begin{aligned}
(\phi - 1) &= - \left(\frac{1}{\sum_i m_i} \right) \left(\frac{\partial G^{E,m} / RT}{\partial w_w} \right)_{T,p,n_i} \\
&= \left(\frac{2}{\sum_i m_i} \right) \left\{ \begin{aligned} &I f^\phi(I) + \sum_c \sum_a m_c m_a [B_{ca}^\phi + ZC_{ca}] \\ &+ \sum_c \sum_{c'} \left(m_c m_{c'} \left[\Phi_{cc'}^\phi + \sum_a m_a \psi_{cc'a} \right] \right) \\ &+ \sum_a \sum_{a'} \left(m_a m_{a'} \left[\Phi_{aa'}^\phi + \sum_c m_c \psi_{aa'c} \right] \right) \\ &+ \sum_n \sum_c m_n m_c \lambda_{nc} + \sum_n \sum_a m_n m_a \lambda_{na} \end{aligned} \right\}
\end{aligned} \tag{34}$$

where

$$f^\phi(I) = \frac{1}{2} [f' - f(I) / I] \tag{35}$$

$$B_{ca}^\phi = B_{ca} + IB' \tag{36}$$

$$\Phi_{cc'}^\phi = \Phi_{cc'} + I\Phi'_{cc'} \tag{37}$$

$$\Phi_{aa'}^\phi = \Phi_{aa'} + I\Phi'_{aa'} \tag{38}$$

Pitzer⁵ considered three different forms for Debye–Hückel functions $f^\phi(I)$ and concluded that the following one is superior

$$f^\phi = -A_\phi \left[\frac{\sqrt{I}}{(1 + b\sqrt{I})} \right] \tag{39}$$

where b is a constant, 1.2, independent of electrolyte type.

Solving f from equation 35 yields

$$f = -A_\phi \frac{4I}{b} \ln(1 + b\sqrt{I}) \quad (40)$$

and

$$f'/2 \equiv f^\gamma = -A_\phi \left(\frac{\sqrt{I}}{(1 + b\sqrt{I})} + \frac{2}{b} \ln(1 + b\sqrt{I}) \right) \quad (41)$$

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

$$B_{ca}^\phi = \beta^{(0)} + \beta^{(1)} \exp(-\alpha_1 \sqrt{I}) + \beta^{(2)} \exp(-\alpha_2 \sqrt{I}) \quad (42)$$

where α_1 and α_2 are constants, dependent on electrolyte type and β 's are electrolyte specific Pitzer parameters. Thus, from equation (36) follows

$$B_{ca} = \beta^{(0)} + \beta^{(1)} g(\alpha_1 \sqrt{I}) + \beta^{(2)} g(\alpha_2 \sqrt{I}) \quad (43)$$

$$B_{ca}' = \beta^{(1)} g'(\alpha_1 \sqrt{I}) + \beta^{(2)} g'(\alpha_2 \sqrt{I}) \quad (44)$$

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 3^{5,7,9}.

Table 3. Numerical constants in the original Pitzer ion interaction model

Electrolyte type ($v_+ - v_- $)	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 theory¹⁰⁵ Pitzer concluded that the concentration dependency for the interaction parameter for like sign ions is:

$$\Phi_{ij} = \theta_{ij} + {}^E\theta_{ij}(I) \quad (45)$$

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 only⁸. So from equation (37) follows

$$\Phi_{ij}^\phi = \theta_{ij} + {}^E\theta_{ij}(I) + I {}^E\theta_{ij}'(I) \quad (46)$$

$$\Phi_{ij}' = {}^E\theta_{ij}'(I) \quad (47)$$

According to Friedman's mixed electrolyte theory¹⁰⁶ for ions with the same charge ${}^E\theta_{ij}$ terms are zero. For unequally charged but like signs ions these terms can be calculated from a 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.⁸

When modelling brine systems, Harvie and Weare¹⁹ discovered that including ${}^E\theta_{ij}$ terms improves the model significantly, so they included these parameters in their model and calculated the integral 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} the 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:

$$\begin{aligned} (\phi - 1) &= - \left(\frac{1}{\sum_i m_i} \right) \left(\frac{\partial G^{E,m} / RT}{\partial w_w} \right)_{T,p,n_i} \\ &= \left\{ |z_+ z_-| f^\phi(I) + m \left(\frac{2\nu_M \nu_X}{\nu} \right) B_{MX}^\phi + m^2 \left(\frac{2(\nu_M \nu_X)^{3/2}}{\nu} \right) C^\phi \right\} \end{aligned} \quad (48)$$

where $\nu = \nu_M + \nu_X$

More detailed description of the Pitzer model can be found elsewhere^{5, 14, 20, 107}

3.4 NPL Pitzer equation

Recently, a modified Pitzer equation for concentrated aqueous solutions was developed at the National Physical Laboratory (UK)¹⁰⁸. The NPL Pitzer equation is obtained by replacing the modified molality and ion strength defined as^{III}

$$m'_i = \frac{n_i}{\left(n_w + \sum_j n_j \right) M_w} \quad (49)$$

and

$$I' = \frac{1}{2} \sum_i \frac{n_i z_i^2}{\left(n_w + \sum_j n_j \right) M_w} \quad (50)$$

with their counterparts in equations 31–48. The modified molalities will converge to molalities in dilute solutions. Thus, the model coincides with the original Pitzer model at infinite dilution.^{III}

3.5 The second dissociation constant

There has been a lot of debate regarding the correct value of the second dissociation constant for sulfuric acid K_2 ¹⁰⁹. In 1934 Hamer¹¹⁰ estimated a value 0.0120 for K_2 at 25°C which was based on his electrochemical measurements with the cell $H_2|NaHSO_4(m_1),Na_2SO_4(m_2)|AgCl|Ag$.

In 1952 Davies et al.¹¹¹ recalculated Hamer's data including the $NaSO_4^-$ ion pair in the analysis and obtained a value of 0.0103 for K_2 which was also supported by their own electrochemical measurements with the cell $H_2|NaCl(m_1),H_2SO_4(m_2)|AgCl|Ag$.

In 1976, Pitzer¹¹² modelled the behaviour of dilute aqueous sulfuric acid solutions with the experimental data¹¹³ for the cell $Pt,H_2|H_2SO_4|PbSO_4,Pb$ (cell A). He used the following Debye–Hückel extension for the activity coefficients similar to the one used in Pitzer equation.

$$\ln \chi_i = -A_\phi z_i^2 \left(\frac{\sqrt{I}}{(1+b\sqrt{I})} + \frac{2}{b} \ln(1+b\sqrt{I}) \right) \quad (51)$$

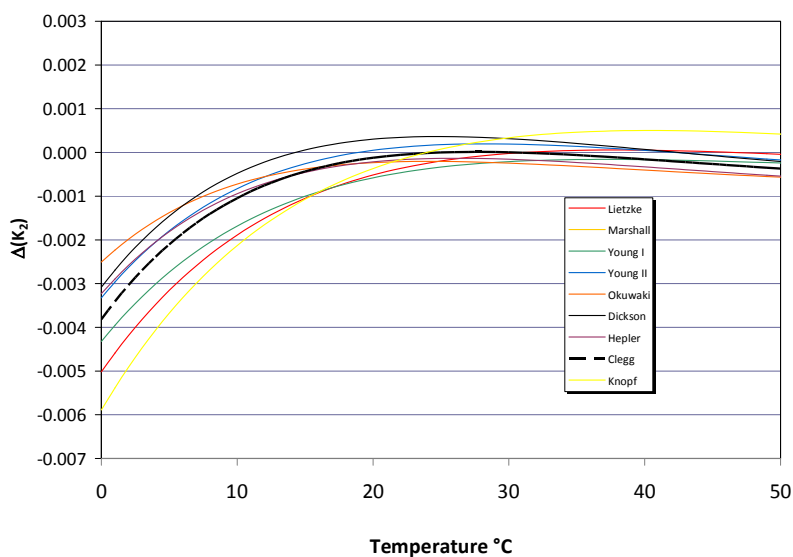
Pitzer varied the value of b from 0.8 to 3.0 and iterated the values of K_2 for the sulfuric acid and the standard potential (E°) for the cell. The best fit was obtained with the value of 2.0, yielding a value of 0.0122 for K_2 but the minimum was very broad so the best value for b cannot, according to Pitzer, be determined. He also found that the value of b does not significantly affect 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 cannot be solved from the electrochemical data used. He continued the analysis with b equal to 1.2, yielding values of 0.0136 for K_2 and about -6 kcal/mol for the enthalpy change (ΔH°) for the second dissociation reaction at 25 °C. The value of ΔH° was recalculated from his data as -25.6 kJ/mol. Pitzer estimated that E° is (-351.3 ± 0.3) mV.^{IV}

In 1977 Pitzer et al.⁴³ modelled the aqueous sulfuric acid system and obtained two equally good models yielding K_2 values of 0.0103 and 0.0120. They preferred the lower value.

Several experimental techniques including electrochemical, conductivity, enthalpy and solubility measurements have been applied to predict the value of K_2 as well as other related thermodynamic properties (Table 4). The differences between these equations as a function of temperature is shown in figure 2 where the equation by Pitzer et al.⁴³ is used as a reference.

Table 4. Thermodynamic properties of the second dissociation reaction of sulfuric acid. ^{IV}

Authors	Year	Temperature range °C	ΔH_{298}° J/mol	ΔS_{298}° J/K mol	$\Delta C_{p,298}^{\circ}$ J/K mol	$K_{2,298}$
Lietzke et al. ¹¹⁴	1961	25 to 225	-20 546	-106.95	-209	0.01030
Marshall and Jones ⁵⁸	1966	25 to 350	-16 128	-92.15	-239	0.01029
Pitzer et al. ⁴³	1977	5 to 55	-23 490	-116.67	0	0.01050
Young et al. ¹¹⁵	1978	5 to 55	-21 693	-110.91	-192	0.01017
Young et al. ¹¹⁵	1978	5 to 55	-22 238	-112.33	-238	0.01068
Matsushima and Okuwaki ⁵⁴	1988	25 to 200	-24 140	-119.01	-218	0.01030
Dickson et al. ⁴⁵	1988	50 to 250	-22 756	-113.92	-275	0.01086
Hovie and Hepler ⁴⁶	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. ⁵⁵	2003	-93 to 200	-18 555	-100.06	-206	0.01058

**Figure 2.** The deviations of K_2 equations ^{2, 45, 46, 54, 55, 58, 115} from the K_2 value estimated by Pitzer et al. ⁴³.

4. Thermodynamic modelling

4.1 Experimental data

All experimental data was taken from literature. After critical evaluation of the experimental data considered the most accurate was chosen and their experimental accuracy estimated as explained in Publications I–IV. The used experimental data is shown in table 5. The most of the selected data has been used previously in thermodynamic modelling of sulfuric acid^{2, 39, 43}.

Conductance measurements^{116,117} were not included in the assessment, since that would require at least either predefined values for limiting conductivities for hydrogen, sulfate and bisulfate ions or including them as fitted parameters in the model. Moreover, since sulfuric acid does not dissociate completely, the degree of dissociation of bisulfate ion is also needed to describe the concentration dependency of conductivity of aqueous sulfuric acid which would complicate the assessment procedure remarkably^{116,118}.

Table 5. Experimental data included and excluded in the evaluation^{I–IV}.

Data	Measurements	Temperature (°C)	m H ₂ SO ₄ (mol/kg)	Excluded molalities (mol/kg)	Estimated experimental accuracy
Cell A ¹¹³	Pt,H ₂ H ₂ SO ₄ PbSO ₄ ,Pb,Hg	0–50	0.001–0.02	All data <0.005	1.0 mV
Cell B ¹¹⁹	Pt,H ₂ H ₂ SO ₄ Hg ₂ SO ₄ ,Hg	5–55	0.1003–7.972	5.767 (5 °C)	1.0 mV
Cell C ¹²⁰	Pt,H ₂ H ₂ SO ₄ PbO ₂ ,PbSO ₄ ,Pt	5–55	0.1–7.199		0.5 mV
Isopiestic data ³³	Critical evaluation	25	0.1–27.0	0.1 (25 °C)	Δφ = 0.005
Isopiestic data ⁴⁷	Isopiestic measurements at ≈110, ≈140 and ≈170 C	110–170	0.5–5.6		Δa _w = 1 %
Vapour pressure data ⁷⁰	Vapour pressure data	25–130	w = 0.1–0.7		Δa _w = 2 %
Heat of solution ³⁹	Relative apparent heat of solution	25	0.1–9.0	All data >6.0	ΔL ^φ = 10%

For cell A all data below 0.005 mol/kg was measured using a bright platinum electrode instead of a platinum black one due to experimental difficulties¹¹³ and was thus excluded. Pitzer et al.⁴³ have also considered data for the cell A below 0.005 mol/kg as unreliable. International volts were changed to absolute volts following Clegg et al.²

For cell B the measurement of 5.767 mol/kg at 5 °C differs clearly from the other measurements and was excluded from the fit. This measurement is

among seven other measurements excluded by Clegg et al.² in their assessment. No apparent reason to exclude a priori the other six measurements was found. All data within the selected concentration range 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 PbSO₄ must be taken into consideration only for sulfuric acid concentrations below 0.04 mol/kg. For cell A, the lead sulfate concentrations approximated by Shrawder and Cowperweite¹¹³ were assumed to be present. To include the effect of lead sulfate solubility the Pitzer parameters for PbSO₄ determined by Paige et al.¹²¹ were included in the model for this cell. A similar treatment is not necessary for cells B and C due to a greater sulfuric acid concentration².

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^{36, 43}. Experimental accuracy is an estimation of a range within which the true value of the measured quantity lies.^{122, 123} 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 complete dissociation.⁴³

$$E = E^0 - (RT/2F)\ln(a_{H_2SO_4}) = E^0 - (RT/2F)\ln(4m^3\gamma_{\pm}^3) \quad (52)$$

In addition for cell C the activity of water is needed

$$E = E^0 + (RT/2F)\ln(a_{H_2SO_4}/a_w^2) = E^0 + (RT/2F)\ln(4m^3\gamma_{\pm}^3/a_w^2) \quad (53)$$

The standard potential (E^0) for cells A to C was expressed as a function of temperature:

$$\Delta_r G^0 = -zFE^0 = A_E + B_ET + C_ET \ln(T) \quad (54)$$

where $A_E - C_E$ are cell specific parameters.

From the isopiestic data of Rard et al.⁸³ at 25°C the lowest value of 0.1 mol/kg concentration was excluded since it deviates as much as the announced accuracy⁸³ 0.5 % from the corrected values of Rard⁴⁸ published in 1983. The stoichiometric osmotic coefficients are estimated to be correct within ± 0.005 which is also in line with previously modelled values, as can be seen in figure 3.

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, that is, 0.005 for each data point.

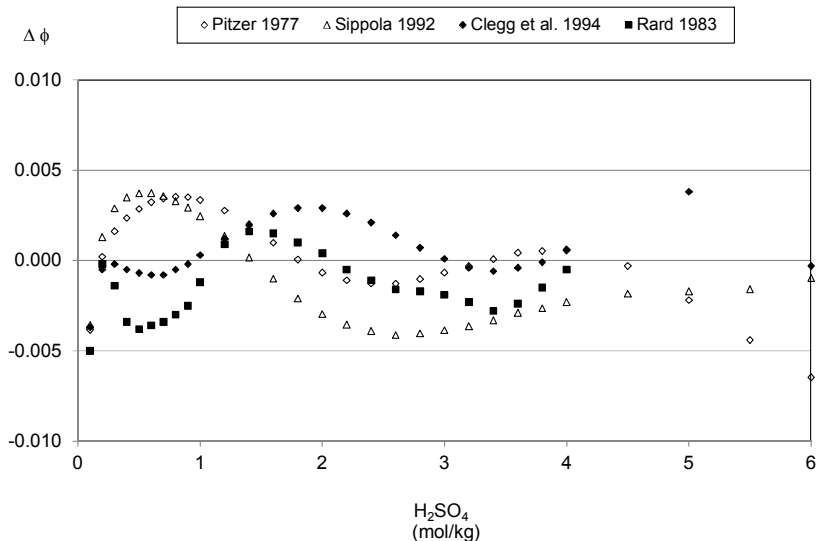


Figure 3. Deviation of the calculated^{2, 36, 43, 48} values of the stoichiometric osmotic coefficient for aqueous sulfuric acid compared to the critically evaluated data of Rard et al.⁸³ at 25 °C. Filled markers indicate values listed in the corresponding reference. Unfilled markers indicate the values calculated from the parameters given in each source.^{IV}

Isopiestic data from Holmes and Mesmer⁴⁷ at temperatures of 383.46, 413.19 and 443.42 K were all included in the assessment whilst data at 473.21 K was reserved for testing the model's extrapolation 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 %.

Vapour pressure data by Vermeulen⁹³, Tarasenkov⁷² and Collins⁷⁰, were critically evaluated^I against Holmes and Mesmer's isopiestic data⁴⁷ and Collins⁷⁰ data was found the most reliable in line with the results of Bosen and Engels⁶⁸. The reported saturated vapour pressures for pure water agree to within 0.2 % with the recent IAPWS 95 equation by Wagner and Pruss¹²⁴ with an obtained standard deviation of 0.04 %. Instead of the actual experimental data, the relative pressures published in table 2 in Collins article⁷⁰ were used in the temperature range of the measurements, thus excluding values at 20 °C and all values above 130 °C.

In precise modelling of aqueous sulfuric acid the non-ideality of the gas phase cannot be ignored at temperatures over 50 °C^{II}. The vapour over sulfuric acid consists practically of water within the concentration and temperature range 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:

$$a_w = (\phi_w / \phi_w^*) (p_w / p_w^*) \quad (55)$$

where ϕ is the fugacity coefficient of water in gas phase, p is pressure and the asterisk refers to pure water.

Fugacity coefficients were estimated using the second virial coefficient

$$\ln\phi = BP/RT \quad (56)$$

The second virial coefficients (B) were obtained from the Wagner–Pruss equation¹²⁴ using Fluidcal software¹²⁵. The relative pressures were taken from table 2 in the article by Collins⁷⁰. The accuracy of water activity calculated from data provided by Collins⁷⁰ was estimated to be 2 %.

The relative apparent heat of solution data from the model of Clegg and Brimblecombe³⁹ was considered to be accurate within 10%. This data was chosen to present enthalpy experimental data since it agrees quite well with experimental data by Wu and Young¹²⁶ at 25 °C. Since this data was used only with the Pitzer model, all data above the 6.0 mol/kg were excluded. A similar procedure was also used for the other data (Table 6).

Table 6. Experimental data excluded when using the Pitzer model.

Data	Measurements	Temperature range (°C)	m H ₂ SO ₄ (mol/kg)
Cell B ¹¹⁹	Pt,H ₂ H ₂ SO ₄ Hg ₂ SO ₄ ,Hg	5 to 55	7.972
Cell C ¹²⁰	Pt,H ₂ H ₂ SO ₄ PbO ₂ ,PbSO ₄ ,Pt	5 to 55	7.199
Isopiestic data ⁸³	Critical evaluation	25	m > 6.0
Vapour pressure data ⁷⁰	Vapour pressure data	25 to 130	w > 0.35

To obtain the effect of used experimental data on results, the experimental data were organized in different data sets shown in table 7.

Table 7. Experimental data sets

Data set	Cell data ^{113,119,120} 0 to 55 °C	Isopiestic data ⁸³ 25°C	Apparent heat of solution data ³⁹ 25 °C	Isopiestic data ⁴⁷ 110 to 170 °C	Vapour pressure data ⁷⁰ 25 to 130 °C
1	x	x			
1b	x	x		x	x
2	x	x	x		
3	x	x	x	x	
4	x	x	x	x	x

4.2 Parameter sets

The parameter sets tested are listed in table 8.

Table 8. Tested parameter sets.^{IV}

Parameter set	H^+ / SO_4^{2-}			H^+ / HSO_4^-			SO_4^{2-} / HSO_4^- θ
	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ	
A	x		x	x	x		
B			x	x	x	x	
C	x		x	x	x	x	
D	x		x	x	x		x
E	x	x	x	x	x		
F	x	x	x	x		x	
G	x	x	x		x	x	
H	x	x		x	x	x	
J		x	x	x	x	x	
K			x	x	x	x	x
L		x	x	x	x		x
M	x		x	x	x	x	x
N	x	x	x	x	x		x
O			x	x	x		x

By default the temperature dependence of the parameters is a $+b/T$ but also temperature dependencies b/T and $a + b/T + cT$ were tested during the research process.

4.3 K₂ equations

Thermodynamic models for aqueous sulfuric acid are generally based on a priori chosen equations for the second dissociation constant K₂. For analysis for the effect of the K₂ equation in modelling aqueous sulfuric acid, the six different K₂-equations listed in table 9 were tested.

Table 9. Tested equations for the second dissociation constant K₂. Original log terms have been transferred to the ln scale by multiplying with ln(10).¹

Equation	$\ln(K_2) = A + B(T/K) + C(T/K) \ln(T/K) + D(T/K)^2 + E/(T/K)$				
	A	B	C	D	E
Pitzer ⁴³	-14.0321	---	---	---	2825.2
Okuwaki ⁵⁴	1329.084	0.6519378	-246.01	-0.000316757	-29282
Dickson ⁴⁵	1295.687	0.5704742	-236.05043	-0.000257206	-30563.94
Hepler ⁴⁶	199.0185	---	-31.8123	---	-6658.95
Clegg ²	1295.653	0.5704742	-236.05043	-0.000257206	-30563.94
Knopf ⁵⁵	-49.7086	-0.059835	10.95231	---	178.1142

4.4 Thermodynamic software

MTDATA^{®,11,12} version 4.81 was used for parameter fitting^{1-IV}. MTDATA is a general tool for calculating thermodynamic equilibria and other thermodynamic properties for solutions or pure substances. It uses the Gibbs energy minimization technique to solve thermodynamic equilibria 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

$$OF = \sum_{i=1}^N w_i \left[\frac{C_i - E_i}{U_i} \right]^2 \quad (57)$$

where

w_i = weight of the experimental value

C_i = calculated value

E_i = experimental value

U_i = uncertainty

All weights for the included experimental data were set to 1.

The Pitzer model in MTDATA includes unsymmetrical mixing terms. These terms are calculated with Chebyshev expansions introduced by Harvie and Weare¹⁹. However during the research process it was found that MTDATA version 4.81 included these terms only if the corresponding θ parameter was included in the specific input file. Thus, zero value for this parameter was used when fitting parameter sets A–C and E–J (Table 8). On the other hand, this feature made it possible to fit the parameters also without unsymmetrical mixing terms and this feature was exploited by fitting the parameters with three different K_2 equations without unsymmetrical mixing terms for comparison.¹

5. Results

The purpose of this thesis was to create a thermodynamic description for aqueous sulfuric acid with a reasonable number of parameters. In Publication I six different equations for the second dissociation constant (K_2) were tested with four different Pitzer parameter sets over the temperature range from 0 to 55°C. The search for the correct dissociation constant equation was continued in Publication II where four different K_2 equations were tested with 14 different parameters sets. The temperature range for the experimental data was extended to 0–170 °C.

The four significant Pitzer parameters were identified but the predicted activity and osmotic coefficients with four different K_2 equations were the same within estimated experimental accuracy. To solve this enigma, the K_2 equation was included in the assessment as a variable in Publication IV. The NPL Pitzer equation was tested in Publication III. The results presented here are a summary of obtained results not a sequential presentation of each publication.

5.1 Pitzer parameters

First the Pitzer parameter sets from A to D with temperature dependency $a+b/T$ were fitted with six different K_2 -equations using dataset 1 as experimental data (Table 7). Parameter set B underperforms when compared to other sets (Table 10).

Table 10. Value of the objective function for parameters set A to D with experimental data set 1.¹

Equation for K_2	Parameter set			
	A	B	C	D
Pitzer ⁴³	0.078	0.119	0.075	0.068
Okuwaki ⁵⁴	0.071	0.116	0.070	0.070
Dickson ⁴⁵	0.068	0.106	0.068	0.068
Hepler ⁴⁶	0.072	0.104	0.071	0.072
Clegg ²	0.073	0.111	0.071	0.073
Knopf ⁵⁵	0.088	0.114	0.084	0.084

There were little differences in fitted values for Pitzer parameter sets A, C and D. The K_2 -equation used does have any significant effect on that, as can be seen in table 11.¹

Table 11. The maximum difference between the fitted values of the parameter sets A, C and D for each K_2 equation.¹

Equation for K_2	Cell A mV	Cell B mV	Cell C mV	Stoichiometric osmotic coefficient	Activity of water
Pitzer ⁴³	0.005	0.20	0.25	0.0001	0.00020
Okuwaki ⁵⁴	0.016	0.05	0.06	<0.0001	0.00014
Dickson ⁴⁵	0.015	0.11	0.12	<0.0001	0.00020
Hepler ⁴⁶	0.010	0.12	0.17	<0.0001	0.00019
Clegg ²	0.015	0.09	0.15	<0.0001	0.00018
Knopf ⁵⁵	0.012	0.12	0.18	<0.0001	0.00017
Exp. accuracy	0.500	1.00	0.50	0.005	

The differences in fitted values between parameter sets A, C and D are well beyond the estimated experimental accuracy so there is no justification to prefer a five parameter set C or D instead of parameter set A. The parameter set A can represent the experimental data equally well as the five parameter sets C and D.¹

After extending the experimental data with vapour pressure data up to 130°C, and osmotic coefficient data from ≈110°C to ≈170°C (dataset 1b) and studied Pitzer parameter sets from A to O, it was found that the most crucial Pitzer parameters are C^{\ominus} for H^+ and SO_4^{2-} interaction and $\beta^{(0)}$ and $\beta^{(1)}$ for H^+ and HSO_4^- interaction. Omitting any of these parameters from the used parameter set will have drastic effect on the quality of the fit. The relationship

between Pitzer parameter sets based on these three most significant parameters are shown in figure 4.

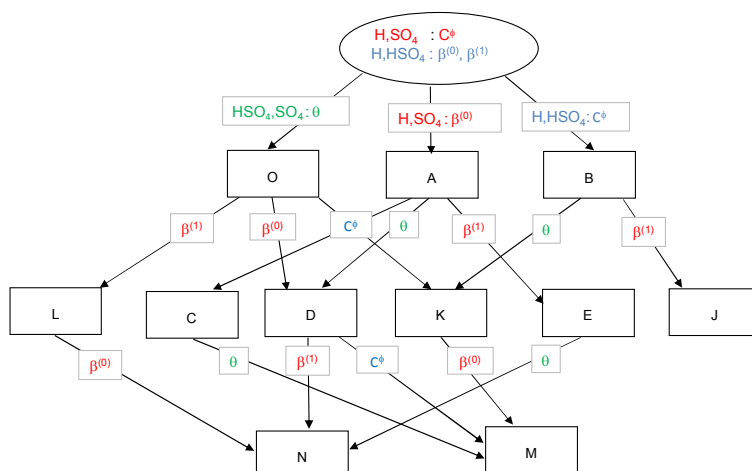


Figure 4. Network of relationships between Pitzer parameter sets.

The obtained values for the objective function using dataset 1b are listed in table 12. The best four parameter set is A. Only two five parameter sets, E and L, have lower or equal objective function values than the best four parameter set Knopf A for each K_2 equation studied. ¹¹

Table 12. Values of objective functions using dataset 1b for different K_2 -equations and parameter sets. ¹¹ Number of parameters are in parenthesis.¹¹

Set	Dickson	Hepler	Knopf	Okuwaki
A(4)	0.056	0.060	0.049	0.058
B(4)	0.074	0.072	0.059	0.077
C(5)	0.055	0.053	0.049	0.054
D(5)	0.055	0.058	0.049	0.058
E(5)	0.045	0.046	0.049	0.049
J(5)	0.063	0.065	0.058	0.061
K(5)	0.073	0.070	0.059	0.073
L(5)	0.048	0.049	0.049	0.050
M(6)	0.037	0.043	0.040	0.044
N(6)	0.042	0.041	0.040	0.040
O(4)	0.100	0.090	0.063	0.101

Chosen parameter set has little effect on the value of objective function for the Knopf equation for K_2 . Moreover, the predicted values by parameter sets A, E and L are very close together for each studied K_2 -equation. This can be seen in table 13 where the standard and maximum deviations between parameter sets A, E and L are displayed for each K_2 equation studied. They are well below the assumed experimental accuracy. Thus, increasing the number of parameters from four to five does not improve the fit. Increasing the number of parameters by 50 % from 4 to six (set N) does not improve the situation

noticeably (Table 14). Thus, increasing the number of parameters beyond four cannot be justified. ¹¹

Table 13. Standard and maximum deviations in predicted values between parameter sets A, E and L for each K_2 equations. ¹¹

	Standard deviation				Maximum deviation			
	Dickson	Hepler	Knopf	Okuwaki	Dickson	Hepler	Knopf	Okuwaki
Cell A (mV)	0.04	0.04	0.03	0.05	-0.10	-0.10	-0.08	-0.08
Cell B (mV)	0.09	0.11	0.06	0.07	-0.22	-0.34	-0.21	-0.21
Cell C (mV)	0.10	0.13	0.07	0.10	-0.23	-0.34	-0.24	-0.31
$\phi_{25^\circ\text{C}}$	0.0004	0.0007	0.0004	0.0007	-0.0009	-0.0013	-0.0009	-0.0011
$\phi_{110^\circ\text{C}}$	0.004	0.005	0.002	0.003	-0.005	-0.007	-0.003	-0.004
$\phi_{140^\circ\text{C}}$	0.005	0.006	0.002	0.004	-0.006	-0.008	-0.003	-0.005
$\phi_{170^\circ\text{C}}$	0.007	0.008	0.003	0.006	-0.011	-0.010	-0.004	-0.012
$\phi_{W=0.1}$	0.004	0.005	0.001	0.002	-0.005	-0.007	-0.002	-0.002
$\phi_{W=0.2}$	0.002	0.003	0.002	0.003	-0.004	-0.005	-0.003	-0.005
$\phi_{W=0.25}$	0.002	0.003	0.002	0.002	-0.003	-0.004	-0.002	-0.003
$\phi_{W=0.3}$	0.002	0.003	0.001	0.004	-0.003	-0.004	-0.001	-0.005
$\phi_{W=0.35}$	0.003	0.003	0.001	0.003	-0.007	-0.005	-0.003	-0.005

Table 14. Standard deviations for parameter sets A and N for each K_2 equations.

	Parameter set A				Parameter set N			
	Dickson	Hepler	Knopf	Okuwaki	Dickson	Hepler	Knopf	Okuwaki
Cell A (mV)	0.20	0.22	0.27	0.21	0.17	0.19	0.24	0.19
Cell B (mV)	0.28	0.27	0.28	0.28	0.27	0.27	0.27	0.27
Cell C (mV)	0.16	0.17	0.15	0.17	0.14	0.13	0.14	0.14
$\phi_{25^\circ\text{C}}$	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
$\phi_{110^\circ\text{C}}$	0.008	0.009	0.006	0.006	0.007	0.007	0.005	0.007
$\phi_{140^\circ\text{C}}$	0.014	0.015	0.007	0.011	0.011	0.013	0.007	0.013
$\phi_{170^\circ\text{C}}$	0.020	0.020	0.012	0.017	0.014	0.016	0.009	0.015
$\phi_{W=0.1}$	0.018	0.017	0.024	0.020	0.023	0.022	0.026	0.025
$\phi_{W=0.2}$	0.030	0.029	0.031	0.029	0.030	0.030	0.030	0.028
$\phi_{W=0.25}$	0.013	0.013	0.013	0.013	0.012	0.012	0.011	0.009
$\phi_{W=0.3}$	0.019	0.019	0.018	0.018	0.017	0.016	0.015	0.015
$\phi_{W=0.35}$	0.019	0.021	0.021	0.022	0.020	0.019	0.019	0.020

5.2 NPL–Pitzer parameters

The NPL–Pitzer parameter sets A–J were first studied with four K_2 -equations: Dickson, Hepler, Knopf and Okuwaki using dataset 1. The temperature dependency of parameter sets was $a + b/T$.^{III}

The concentration of sulfuric acid was first limited up to 10 mol/kg. The parameter sets B–E and J performed best with objective function values of 0.14 or better which are noticeably better than the next best value 0.46 by set F. However, set B fails to present cell B within assumed experimental accuracy in one experimental point and set E fails with one experimental point with cell C. The maximum differences in fitted values with the three best parameter sets C, D and J are well below the assumed experimental accuracies.^{III}

In the next step parameter sets K–O were added and the concentration range was extended to 15 mol/kg. Parameter set B is not able to model aqueous sulfuric acid up 15 m solution at all. For the remaining parameter sets the obtained values of objective function are shown in table 15.^{III}

Table 15. The values of objective functions for each case studied. The dataset 1 was used as experimental data.^{III} Number of parameters are in parenthesis.

Set / K_2	Dickson	Hovey	Knopf	Okuwaki
C(5)	0.29	0.30	0.31	0.32
D(5)	0.11	0.11	0.11	0.11
E(5)	0.34	0.35	0.32	0.33
J(5)	0.22	0.23	0.23	0.22
K(5)	0.12	0.12	0.12	0.12
L(5)	0.18	0.18	0.18	0.19
M(6)	0.11	0.11	0.11	0.11
N(6)	0.11	0.11	0.11	0.11
O(4)	0.19	0.18	0.19	0.18

As can be seen from table 15 the only five parameter sets that succeed better than four parameter set O are sets D and K which both share the same four parameters which set O consist of but not parameter set L which also shares these four parameters. Parameter set O can describe the sulfuric acid – water system better than any five parameter set missing any of these four essential parameters. On the other hand the parameter set O is not capable of predicting cell B and osmotic coefficient data within assumed experimental accuracy.^{III}

The essential NPL Pitzer parameters are (parameter set O)^{III}

- C^ϕ describing the interaction between H^+ and SO_4^{2-} ions
- $\beta^{(0)}$ and $\beta^{(1)}$ describing the interaction between H^+ and HSO_4^- ions and
- θ describing the interaction between SO_4^{2-} and HSO_4^- ions

Parameter sets D and K, including these parameters and enhanced by $\beta^{(0)}$ (H^+ / SO_4^{2-} -interaction) and C^ϕ (H^+ / HSO_4^- -interaction), respectively, can fit the experimental data better than parameter set O.^{III}

However, adding interaction parameter $\beta^{(1)}$ for H^+ / SO_4^{2-} –interaction does not improve the fit (parameter set L). Moreover, nothing is gained if the number of parameters is increased from five to six (sets M and N).^{III}

The differences between fitted values between parameter sets D and K are well beyond assumed experimental accuracy (Table 16). Also the differences between K_2 -equations are insignificant. Thus, parameter sets D and K predict the experimental data equally well but the latter one has better ability to extrapolate the stoichiometric osmotic coefficients up to 27 mol/kg solution at 25°C (Figure 5).

Table 16. Maximum differences in fitted values by parameter set D and K.^{III}

	K ₂ equation				Experimental Accuracy
	Dickson	Hovey	Knopf	Okuwaki	
Cell A, mV	0.03	0.03	0.05	0.04	1.0 mV
Cell B, mV	0.18	0.20	0.22	0.22	1.0 mV
Cell C, mV	0.19	0.21	0.17	0.24	0.5 mV
ϕ_{stoich}	0.001	0.002	0.001	0.002	0.005

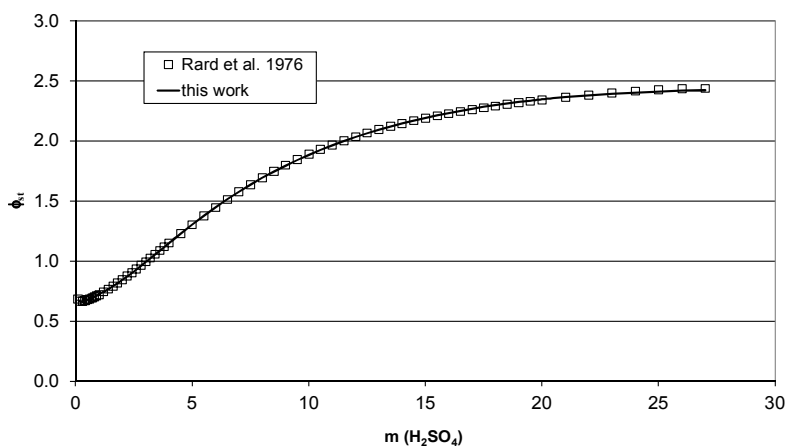


Figure 5. Predicted osmotic stoichiometric coefficient with Dickson K_2 equation and parameter set K compared to the values of critical compilation by Rard et al.⁸³ Values over 15 mol/kg are extrapolated.

5.3 K₂-equation

As far as Gibbs energy related data is considered the predicted values are practically independent of the equation chosen for K₂. However, when considering the differences in standard enthalpy and heat capacity change between the K₂ equations tested (Table 4), it can be expected that the obtained values for enthalpy related properties, such as relative apparent molal enthalpy, differ from each other. In fact this effect can be seen in figure 6.^{II}

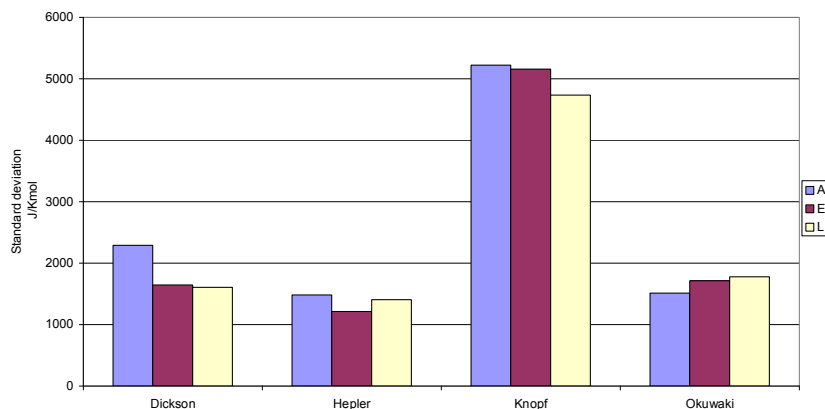


Figure 6. Standard deviation of relative apparent molal enthalpy for parameter sets A, E and L with the Pitzer model for K₂-equations^{45,46,54,55} when compared to the model of Clegg and Brimblecombe³⁹. The dataset used in the fit was 1b and the temperature dependency of each parameter was a + b/T.^{II}

Thus, if including enthalpy related data in the assessment, the equation for K₂ should be included in the assessment, too. To obtain the best equation for the second dissociation constant for sulfuric acid the following equation for K₂ was included in assessment:^{IV}

$$\Delta_r G^0 = -RT \ln(K_2) = A_K + B_K * T + C_K * T * \ln(T/K) \quad (58)$$

where A_K (J/mol), B_K (J/K mol) and C_K (J/K mol) are fitted parameters. The relationship between these parameters and thermodynamic properties for the dissociation reaction of bisulfate ion at 25 °C are:^{IV}

$$\Delta_r H^0 = A_K + C_K * 298.15 \text{ K} \quad (59)$$

$$\Delta_r S^0 = -(B_K + C_K(1 + \ln(298.15))) \quad (60)$$

$$\Delta_r C_p = -C_K \quad (61)$$

Also the effects of the temperature range/dataset used and the temperature dependency of the fitted β⁽⁰⁾-parameters were tested as suggested by results obtained with the NPL Pitzer model¹²⁷.

During the assessment it was found that results are extremely sensitive to the initial values of the parameters A_K–C_K for the second dissociation constant

K_2 (eq. 58). Assuming that the heat capacity change in the dissociation reaction is in the range from -200 to -300 J/K mol, the initial value of C_K was varied from 200 to 300 with step one J/K mol.^{IV}

As a result ten assessments were made each including 100 fits using different initial values for the parameter C_K in the range of 200 to 300 J/K mol. The assessments made are summarized in table 17.^{IV}

Table 17. List of assessments^{IV}

Assessment	Experimental data set	All parameters a + b/T	$\beta^{(0)}$ H ⁺ /SO ₄ ²⁻ b/T	$\beta^{(0)}$ H ⁺ /HSO ₄ ⁻ a + b/T + cT
1	Set 1 (E _{0.55} a _{w,25})	x		
2	Set 2 (E _{0.55} a _{w,25} , ϕ_{L25})	x		
3	Set 3 (E _{0.55} a _{w,25} , ϕ_{L298} , a ₁₁₀₋₁₇₀)	x		
4	Set 4 (E _{0.55} a _{w,25} , ϕ_{L25} , 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} , ϕ_{L25})		x	
7	Set 3 (E _{0.55} a _{w,25} , ϕ_{L298} , a ₁₁₀₋₁₇₀)		x	
8	Set 4 (E _{0.55} a _{w,25} , ϕ_{L25} , a ₁₁₀₋₁₇₀ , p ₂₅₋₁₃₀)			x
9	Set 2 (E _{0.55} a _{w,25} , ϕ_{L25})		x	x
10	Set 4 (E _{0.55} a _{w,25} , ϕ_{L25} , a ₁₁₀₋₁₇₀ , p ₂₅₋₁₃₀)		x	x

Assessment 1 revealed that several K_2 -equations can describe experimental data set 1 almost equally well. It was also found that the thermodynamic properties ΔG° , ΔH° and ΔS° of the electrochemical cell reactions at 25°C are linearly correlated with the same property for the 2nd dissociation reaction of sulfuric acid.^{IV}

The obtained linear parameters and their correlations are listed in table 18.

Table 18. Linear correlation ($Y = a + bX$) parameters between the thermodynamic properties of the dissociation reaction of bisulfate and cell reactions from assessment 1.^{IV}

Estimated property (Y)	Property of the 2nd dissociation reaction of sulfuric acid (X)	a (kJ/mol)	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 (J/K mol)	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

The reason for this linear relationship can be understood if we apply equation (21) instead of (18) for the equations describing electrochemical cell potentials (eqs. 45–46), yielding for cells A and B^{IV}

$$\begin{aligned} E &= E^0 - (RT/2F)\ln(a_{H_2SO_4}) \\ &= E^0 - (RT/2F)\ln(K_2) - (RT/2F)\ln\left(m^2(1-\alpha^2)\gamma_H\gamma_{HSO_4}\right) \end{aligned} \quad (62)$$

and for cell C

$$\begin{aligned} E &= E^0 + (RT/2F)\ln(a_{H_2SO_4}/a_w^2) \\ &= E^0 + (RT/2F)\ln(K_2) + (RT/2F)\ln\left(\frac{m^2(1-\alpha^2)\gamma_H\gamma_{HSO_4}}{a_w^2}\right) \end{aligned} \quad (63)$$

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

The linear relationships between enthalpy and entropy changes disappear when more experimental Gibbs energy related data at higher temperatures or enthalpy data at 25°C are included in the assessment but it persists for Gibbs energy changes. The best objective values for each assessment are shown in table 19.^{IV}

Table 19. The best values of the objective function for each studied assessment.^{IV}

Assessment	Data set	All parameters a + b/T	$\beta^{(0)}$ H ⁺ /SO ₄ ²⁻ b/T	$\beta^{(0)}$ H ⁺ /HSO ₄ ⁻ a + b/T + cT	Objective function Best value
1	Data set 1	x			0.053
5	(E ₀₋₅₅ , a _{w,25})		x		0.054
2	Data set 2	x			0.049
6	(E ₀₋₅₅ , a _{w,25} , ϕ L ₂₅)		x		0.049
9			x	x	0.052
3	Data set 3	x			0.056
7	(E ₀₋₅₅ , a _{w,25} , ϕ L ₂₅ , a ₁₁₀₋₁₇₀)		x		0.070
4	Data set 4	x			0.052
8	(E ₀₋₅₅ , a _{w,25} , ϕ L ₂₅ , a ₁₁₀₋₁₇₀ , p ₂₅₋₁₃₀)			x	0.037
10			x	x	0.037

The following conclusions can be made from table 19:^{IV}

1. The temperature dependency of the $\beta^{(0)}$ H⁺/SO₄²⁻ parameter can be reduced to b/T in the temperature range from 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).
2. Adding cT-term to the temperature dependency of the $\beta^{(0)}$ H⁺/HSO₄⁻ parameter will improve the assessment at higher temperatures (Assessment 4 and 8) but it is not required in the temperature range from 5 to 55°C (Assessment 2 and 9). At higher temperatures this addition succeeds in reducing the temperature dependency of the $\beta^{(0)}$ H⁺/SO₄²⁻ parameter back to b/T (Assessment 8 and 10).

3. The best assessment to describe the thermodynamic properties over the temperature range from 0 to 55 °C is assessment 6 since it includes only 7 terms to describe the temperature dependency of the four Pitzer parameters used.
4. Extending the model to higher temperatures the following combination of temperature dependencies will improve the assessment (Data set 4):
 - Interaction $\text{H}^+/\text{SO}_4^{2-}$: $\beta^{(0)}$ as b/T and C^ϕ as $a + b/T$
 - Interaction $\text{H}^+/\text{HSO}_4^-$: $\beta^{(0)}$ as $a + b/T + cT$ and $\beta^{(1)}$ as $a + b/T$

5.4 Thermodynamic properties of sulfuric acid and electrochemical cells at 25°C

Thermodynamic properties of the 2nd dissociation reaction of sulfuric acid as well as the electrochemical cells at 25 °C are derived from the assessment 6 with dataset 2 covering the temperature range from 0 to 55 °C. The data in this data set also distribute evenly around 25°C so no distortion due to biased temperature range is expected.^{IV}

The obtained thermodynamic values are average values of 78 fits with OF values from 0.049 to 0.055, and the fitted heat capacity change in the 2nd dissociation reaction varies from 202 to 303 J/K mol. 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 20.

Values calculated from CODATA and NBS thermodynamic tables^{128, 129} and from the recent article of Clegg et al.² are also included in the table as well as the average values of 75 fits obtained for assessment 10 with data set 4, covering the temperature range from 0 to 170 °C.

Except for the enthalpy and entropy change for the 2nd dissociation reaction for sulfuric acid, the obtained values are in excellent agreement with the literature values. Extending the experimental data up to 170° C does change the situation.

When modelling aqueous sulfuric acid Pitzer et al.⁴³ obtained two different sets of Pitzer parameters and K_2 -equations describing the behaviour of aqueous sulfuric acid equally well. The corresponding values for K_2 at 25°C were 0.0105 and 0.0120, respectively.

The standard potentials at 25°C for the cells (A–C) and the thermodynamic properties for sulfuric acid at 25°C obtained by Pitzer et al.⁴³ are compared to the values obtained in this work in table 21. The values of the alternate set by Pitzer et al.⁴³ coincide with this work.

Table 20. Obtained thermodynamic properties for sulfuric acid and cells A–C at 298.15 K. ^{IV}

Property	Assessment 6 ^{IV} 0–55°C	Clegg et al. ²	CODATA Key values ¹²⁸	NBS Tables ⁹²	Assessment 10 ^{IV} 0–170°C
H₂SO₄					
$\Delta_r G^\circ_{298}$ (kJ/mol)	11.00 ± 0.27	11.30	11.31	11.37	(10.94)
$\Delta_r H^\circ_{298}$ (kJ/mol)	-25.11 ± 0.80	-22.76	-22.44	-21.93	(-25.78)
$\Delta_r S^\circ_{298}$ (J/K mol)	-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)
$\Delta_r G^\circ_{298}$ (kJ/mol)	67.92 ± 0.10	68.08	67.90	67.48	(67.89)
$\Delta_r H^\circ_{298}$ (kJ/mol)	9.68 ± 0.26	9.74	10.66	10.70	(9.44)
$\Delta_r S^\circ_{298}$ (J/K mol)	-195.35 ± 1.09	-195.66	-191.99	-190.45	(-196.04)
$\Delta_r C_p^\circ_{298}$ (J/K mol)	-359 ± 30	-348.57		-398.6	(-368)
Cell B					
E° (mV)	613.4 ± 0.7	612.36	612.7	615.0	(613.6)
$\Delta_r G^\circ_{298}$ (kJ/mol)	-118.37 ± 0.14	-118.17	-118.22	-118.68	(-118.41)
$\Delta_r H^\circ_{298}$ (kJ/mol)	-166.61 ± 0.18	-166.75	-166.25	-166.15	(-166.68)
$\Delta_r S^\circ_{298}$ (J/K mol)	-161.80 ± 0.74	-162.94	-161.08	-159.20	(-161.88)
$\Delta_r C_p^\circ_{298}$ (J/K mol)	-395 ± 41	-363.71		-397.7	(-404)
Cell C^b					
E° (mV)	1689.5 ± 0.7	1691.0	1689.1	1686.8	(1689.3)
$\Delta_r G^\circ_{298}$ (kJ/mol)	-326.02 ± 0.14	-326.32	-325.95	-325.50	(-325.98)
$\Delta_r H^\circ_{298}$ (kJ/mol)	-306.03 ± 0.15	-305.92	-304.89	-304.93	(-306.01)
$\Delta_r S^\circ_{298}$ (J/K mol)	67.04 ± 0.52	68.42	70.62	69.01	(66.99)
$\Delta_r C_p^\circ_{298}$ (J/K mol)	433 ± 48	424.69		449.3	(446)

^{a)} Thermodynamic values for reaction $\text{Pb(s)} = \text{Pb(Hg)}$ are taken from Bates et al.¹³⁰

^{b)} Thermodynamic values for PbO_2 are from NBS tables ⁹².

Table 21. Thermodynamic properties for sulfuric acid and cells A–C at 298.15 K ^{IV}

Property	Pitzer et al. ⁴³ adopted set	Sippola ^{IV}	Pitzer et al. ⁴³ alternate set
$K_{2,298}$	0.0105	0.0119	0.0120
$\Delta_r G^\circ_{298}$ (kJ/mol)	11.295	11.00 ± 0.27	10.96 ^a
$\Delta_r H^\circ_{298}$ (kJ/mol)	-23.49	-25.11 ± 0.80	(-25.6) ^b
$\Delta_r S^\circ_{298}$ (J/K mol)	-116.67	-121.12 ± 1.87	(-122.6) ^c
$E^\circ(\text{A})$ (mV)	-352.8	-352.0 ± 0.5	-351.75
$E^\circ(\text{B})$ (mV)	612.42	613.4 ± 0.7	613.54
$E^\circ(\text{C})$ (mV)	1690.38	1689.5 ± 0.7	1689.27

^{a)} calculated from K_2 ^{b)} calculated from Pitzer¹¹² ^{c)} calculated as $\Delta S_{298} = (\Delta H_{298} - \Delta G_{298})/T$

5.5 Thermodynamic model for aqueous sulfuric acid

Thirteen different fits in assessment 10 (Dataset 4, 0 to 170 °C) qualify for the thermodynamic values listed in table 20 with $\Delta C_{p,298}^{\circ}$ varying from -220 to -289 J/K mol. The closest fit and thus the best one is a fit with a $\Delta C_{p,298}^{\circ}$ value near -276 J/K mol, later referred as Sippola model. The equation of K_2 for this fit is ^{IV}

$$\begin{aligned} \Delta_r G^{\circ} &= -RT \ln (K_2) & (64) \\ &= 57092.9(\text{J/mol}) - 1724.98(\text{J/K mol}) * T + 275.667(\text{J/K mol}) * T * \ln(T/\text{K}) \end{aligned}$$

Obtained Pitzer parameters for the Sippola model are listed in table 22.

Table 22. Pitzer parameters for the Sippola model. ^{IV}

Pitzer parameter	Interaction	A	b / (T/K)	c (T/K)
$\beta^{(0)}$	$\text{H}^+/\text{SO}_4^{2-}$		12.04250	
C^{ϕ}	$\text{H}^+/\text{SO}_4^{2-}$	0.137684	-30.395	
$\beta^{(0)}$	$\text{H}^+/\text{HSO}_4^-$	0.24106	22.0454	$-3.5118 * 10^{-4}$
$\beta^{(1)}$	H^+/HSO_4	0.333982	39.296	

The obtained thermodynamic properties for the second dissociation reaction of sulfuric acid as well as for electrochemical cells A–C by the Sippola model are compared to the thermodynamic properties in table 23.

Table 23. Thermodynamic properties for the second dissociation reaction of sulfuric acid and electrochemical cells A–C at 25°C obtained by the Sippola model. ^{IV}

Property	Sippola model ^{IV}	Thermodynamic properties ^{IV}
$K_{2,298}$	0.0115	0.0119
$\Delta_r G_{298}^{\circ}$ (kJ/mol)	11.08	11.00 ± 0.27
$\Delta_r H_{298}^{\circ}$ (kJ/mol)	-25.10	-25.11 ± 0.80
$\Delta_r S_{298}^{\circ}$ (J/K mol)	-121.33	-121.12 ± 1.87
$\Delta_r C_{p,298}^{\circ}$ (J/K mol)	-275.67	
$E^{\circ}(\text{A})$ (mV)	-352.24	-352.0 ± 0.5
$E^{\circ}(\text{B})$ (mV)	613.08	613.4 ± 0.7
$E^{\circ}(\text{C})$ (mV)	1689.84	1689.5 ± 0.7

The main differences between the Sippola K_2 equation and other K_2 equations are that it has much lower standard deviations for cell A and for the apparent molal enthalpy at 25°C (Table 24). The data for cell A are from dilute solutions where the relative concentration of SO_4^{2-} is highest. Moreover, the ability to predict the apparent molal enthalpy correctly decrease in the same order (Sippola, Okuwaki, Hepler, Dickson and Knopf) as the enthalpy of the 2nd dissociation reaction increases (-25.11 , -23.50 , -22.76 , -18.56) kJ/mol, respectively. Both these facts support the obtained result that the value of K_2 should be higher and the dissociation reaction more exothermic than currently presumed.

Table 24. Obtained standard deviations with different K_2 -equations. The data used in the assessment were from dataset 4. Parameters and their temperature dependencies were the same in each case (see Table 22).

K_2	Sippola ^{IV}	Dickson	Hepler	Knopf	Okuwaki
Cell A (mV)	0.12	0.18	0.21	0.25	0.20
Cell B (mV)	0.27	0.30	0.27	0.38	0.26
Cell C (mV)	0.14	0.15	0.14	0.21	0.14
$\phi_{25\text{ }^\circ\text{C}}$	0.0006	0.0010	0.0010	0.0015	0.0009
$\phi_{110\text{ }^\circ\text{C}}$	0.005	0.012	0.009	0.025	0.007
$\phi_{140\text{ }^\circ\text{C}}$	0.004	0.016	0.011	0.035	0.008
$\phi_{170\text{ }^\circ\text{C}}$	0.006	0.016	0.012	0.035	0.009
$\phi_{w=0.1}$	0.027	0.036	0.032	0.050	0.030
$\phi_{w=0.2}$	0.031	0.035	0.033	0.042	0.032
$\phi_{w=0.25}$	0.013	0.014	0.013	0.017	0.013
$\phi_{w=0.3}$	0.017	0.016	0.016	0.015	0.015
$\phi_{w=0.35}$	0.018	0.017	0.017	0.016	0.017
${}^{\circ}\text{L}_{25}(\text{J/mol})$	291	1005	617	2813	419
OF (dataset 4)	0.039	0.062	0.052	0.178	0.046

5.6 Stoichiometric activity coefficient of aqueous sulfuric acid

The standard and the maximum deviations of stoichiometric activity coefficients at 25°C by the Sippola model 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 the standard deviations of 0.003 and 0.002, respectively. The mean absolute percentage (maximum) errors at 0, 25 and 50 °C are 0.96 % (2.22 %), 1.67 % (2.06 %) and 1.23 % (1.96%), respectively.^{IV}

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 Clegg et al.² (Table 25)^{IV}. Also the agreement with critical evaluation by Rard et al.⁸³ is good (Figure 7).

Table 25. The stoichiometric activity coefficients for sulfuric acid at dilute solutions. The predicted values by the Sippola model below 0.005 are extrapolated.^{IV}

H ₂ SO ₄ mol/kg	0°C		25°C		50°C	
	Sippola ^{IV}	Clegg et al. ²	Sippola ^{IV}	Clegg et al. ²	Sippola ^{IV}	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

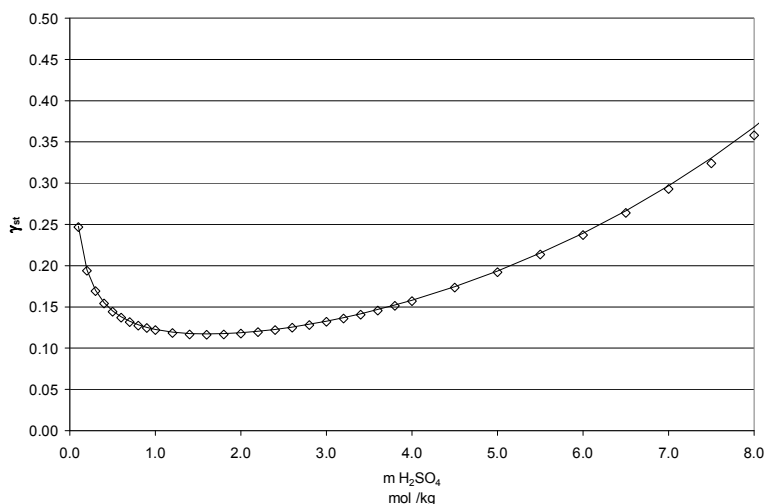


Figure 7. Stoichiometric activity coefficient (line) by Sippola model^{IV} at 25 °C compared to data by Rard et al.⁸³(diamonds). Values over 6 mol/kg are extrapolated.

5.7 Stoichiometric osmotic coefficient of aqueous sulfuric acid

The standard deviation of the values predicted using the Sippola model compared to critically evaluated stoichiometric osmotic coefficient data at 25 °C by Rard et al.⁸³ covering concentrations from 0.2 up to 6 m solution is only 0.0006 (Table 24). The maximum deviation is 0.0011. The predicted value for 0.1 m solution is 0.004 lower than reported by Rard et al.⁸³, which is in excellent agreement with the correction of Rard⁴⁸, that is, -0.005 .^{IV}

The standard deviations with Holmes and Mesmer data at $\approx 110^\circ\text{C}$, $\approx 140^\circ\text{C}$ and $\approx 170^\circ\text{C}$ are 0.005, 0.004 and 0.006, respectively (Table 24) and the maximum deviations are -0.008 , -0.007 and 0.016, respectively. Extrapolated values at $\approx 200^\circ\text{C}$ are 0.009 higher on average than measured (Figure 8).^{IV}

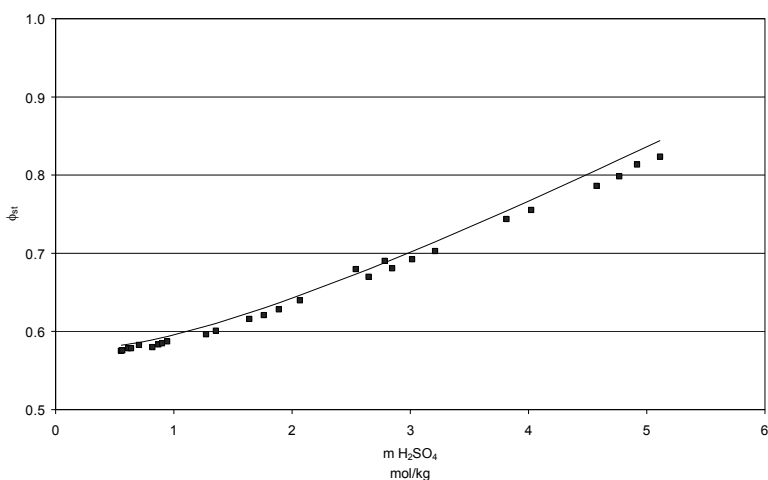


Figure 8. Extrapolated stoichiometric osmotic coefficient (line) by the Sippola model at 473.21 K ($\approx 200^\circ\text{C}$) compared to experimental data by Holmes and Mesmer⁴⁷.^{IV}

The standard (maximum) deviations for predicted stoichiometric osmotic coefficient with the Sippola model at 0, 25 and 50 °C, compared to the values obtained by the model of Clegg et al.² are 0.006 (0.010), 0.002 (0.004) and 0.003 (0.005), respectively. When compared to the model of Clegg and Brimblecombe³⁹ the corresponding values up to 6 m solutions are 0.003 (0.006), 0.002 (0.004) and 0.003 (0.005), respectively. Standard deviations between the models of Clegg et al.² and Clegg and Brimblecombe³⁹ are 0.005, 0.003 and 0.002, respectively.^{IV}

Extrapolated values for the stoichiometric osmotic coefficient at -20°C agree in 0.06 up to 8 m solution with the values calculated by the model of Clegg and Brimblecombe³⁹ (Figure 9).

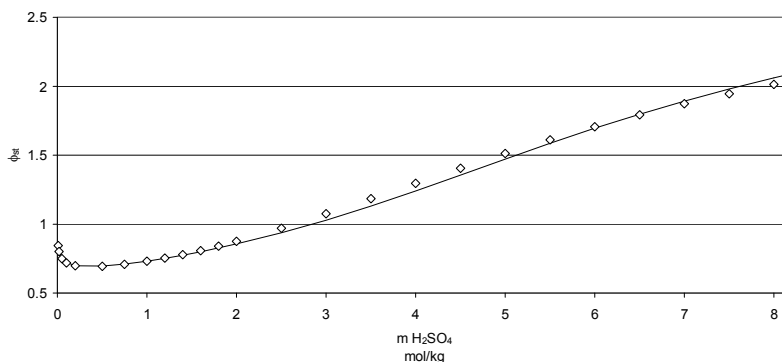


Figure 9. Extrapolated stoichiometric osmotic coefficient (line) by the Sippola model at -20°C compared to the model of Clegg and Brimblecombe³⁹ (diamonds). Calculated values over 6 mol/kg are extrapolated. ^{IV}

5.8 Relative apparent molal enthalpy

The standard (maximum) deviation for relative apparent molal enthalpy for the Sippola model at 25°C compared to the values of Clegg and Brimblecombe³⁹ is $291 (-578) \text{ J/mol}$ ^{IV}. When compared to the original data¹²⁶ used by Clegg and Brimblecombe in the same concentration range from 0.1 to 6 mol/kg, the corresponding value is $286 (-502) \text{ J/mol}$. Thus, the Sippola model predicts the original experimental data at 25°C by Wu and Young¹²⁶ more precisely than the model by Clegg and Brimblecombe³⁹ including them in the assessment.

Even though the enthalpy data were included only at 25°C , the Sippola model can extrapolate the relative apparent molal enthalpy surprisingly well when considering that the enthalpy data used in the assessment were limited to a concentration range from 0.1 to 6.0 mol/kg (Figure 10). However, there is a significant inconsistency with the models at -20°C .

The extrapolation ability of the Sippola model to dilute concentrations is also good (Figure 11).

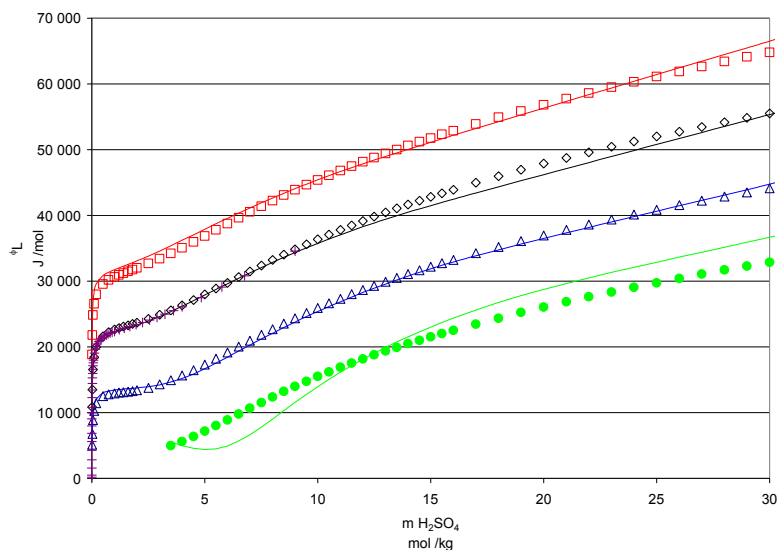


Figure 10. Predicted relative apparent molal enthalpy (line) by Sippola model at -20°C (green), 0°C (blue), 25°C (black) and 50°C (red) compared to the model of Clegg and Brimblecombe³⁹ (symbols). The experimental data at 25°C by Wu and Young¹²⁶ is also displayed (crosshairs). Calculated values above 6 m solutions and outside 25°C are extrapolated.

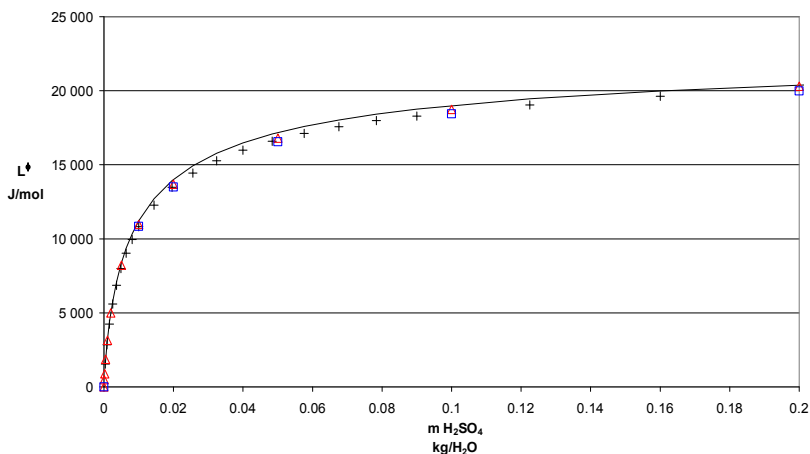


Figure 11. Relative apparent molal enthalpy predicted by the Sippola model (line) at 25°C compared to experimental data by Wu and Young¹²⁶ (crosshair) and models of Clegg et al.² (triangle) and Clegg and Brimblecombe³⁹ (square). Predicted values below 0.1 are extrapolated.^{IV}

5.9 Electrochemical cells

The quality of the Sippola model was tested by calculating the standard cell potential for the cell $\text{Hg}_2\text{SO}_4, \text{Hg} | \text{H}_2\text{SO}_4 | \text{PbO}_2, \text{PbSO}_4$ (cell D) at 25°C , which was not included in the assessment. The standard potential of this cell was calculated using the corresponding values of the cells B and C obtained by the Sippola model (Table 24) which yields a value of 1076.76 mV. This cell was included in the assessment made by Clegg et al.² and they obtained the value 1077.5 mV.^{IV}

The calculated electrochemical potentials by Sippola model agree within 1 mV with the experimental data except for two points which were considered unreliable by Clegg et al.² (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.^{IV}

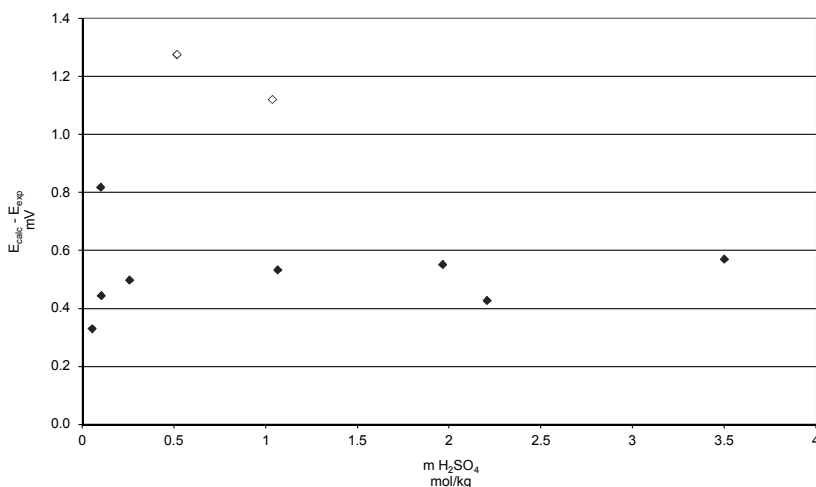


Figure 12. Deviations between the predicted and measured values for the electrochemical cell $\text{Hg}_2\text{SO}_4, \text{Hg} | \text{H}_2\text{SO}_4 | \text{PbO}_2, \text{PbSO}_4$ by the Sippola model at 25°C . International volts are assumed for the experimental data and are converted to absolute volts by multiplying by 1.00033. Neither the experimental data nor the standard electrochemical potential used (1 076.76) mV for this cell were included in the assessment. Unfilled squares indicate experiments considered unreliable.^{IV}

The standard potential for the cell $\text{Hg}_2\text{SO}_4, \text{Hg} | \text{H}_2\text{SO}_4 | \text{PbO}_2, \text{PbSO}_4$ can be evaluated to be $(1076.76 - 0.52)$ mV yielding 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 20). 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.^{IV}

5.10 The capabilities of NPL Pitzer equation

The NPL Pitzer equation is capable of predicting the stoichiometric osmotic coefficient at 25°C up to 27 m solution (Figure 5). The NPL Pitzer equation was further tested by comparing the predicted stoichiometric osmotic coefficients at 0, 25 and 50°C to the values obtained by the more complicated mole fraction based model of Clegg and Brimblecombe³⁹ for sulfuric acid up to 40 m solution. The Dickson et al.⁴⁵ equation for K_2 and parameter set K were used in the calculation. The parameters were fitted using dataset 1 (Table 7) and temperature dependency of the parameters was $a+b/T$. The agreement is excellent considering that all the calculated values above 15 mol/kg (25°C) and 8 mol/kg (0, 50°C) are extrapolated ones (Figure 13).^{III}

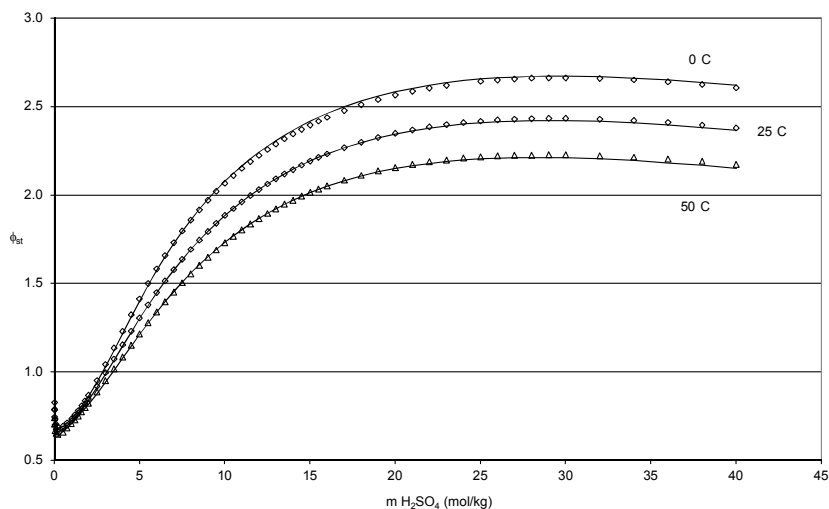


Figure 13. Stoichiometric osmotic coefficient data at 0, 25 and 50 °C predicted by NPL Pitzer model with parameter set K (solid line) and compared to values determined from the model by Clegg and Brimblecombe³⁹ (symbols). All predicted values above 15 mol/kg (25°C) and 8 mol/kg (0, 50°C) are extrapolated (solid line).^{III}

The extrapolation capacity of the NPL Pitzer model at different temperatures was tested by comparing the extrapolated and measured⁴⁷ stoichiometric osmotic coefficients at temperatures 383.46, 413.95, 443.42 and 373.21 K, respectively. Among the tested K_2 equations (Dickson, Hepler, Knopf and Okuwaki) the Okuwaki K_2 equation achieved the lowest standard (maximum) deviations: 0.007 (0.010), 0.0010 (0.016), 0.012(0.029) and 0.023 (0.051), respectively. Extrapolated values are shown in figure 14.^{III}

Recently, Sippola et al.¹³¹ tested the capabilities of the NPL Pitzer equation by modelling the solubility of iron sulfate in aqueous sulfuric acid. They found out that the $H_2SO_4-H_2O$ system can be modelled by NPL Pitzer up to 170°C using parameter set K. The temperature dependency of the NPL Pitzer parameters was $a + b/T$.

The fitted values for the solubility of iron sulfate in aqueous sulfuric acid (Figure 15) are in good agreements with experimental data¹³². Thus, the NPL Pitzer equation is found to be able to fit the solubility of iron sulfate from 0 to 100°C up to 50 m solution.

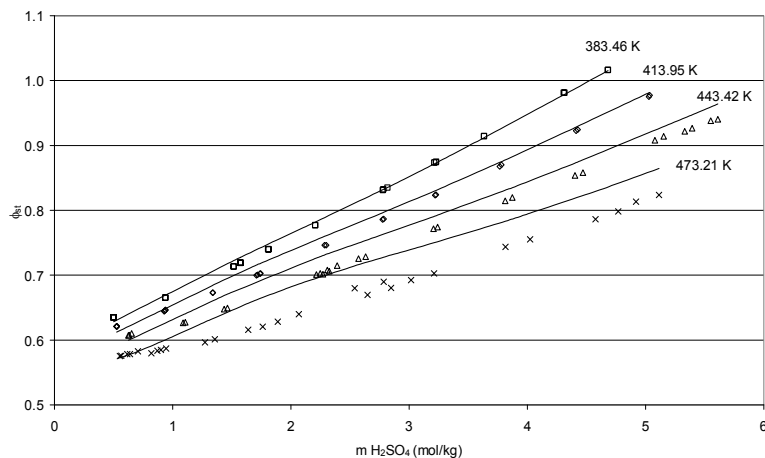


Figure 14. The experimental⁴⁷ and extrapolated stoichiometric osmotic coefficient by the NPL Pitzer model at around 110, 140, 170 and 200 °C. The extrapolated values were calculated using Okuwaki K_2 equation and parameter set K. ^{III}

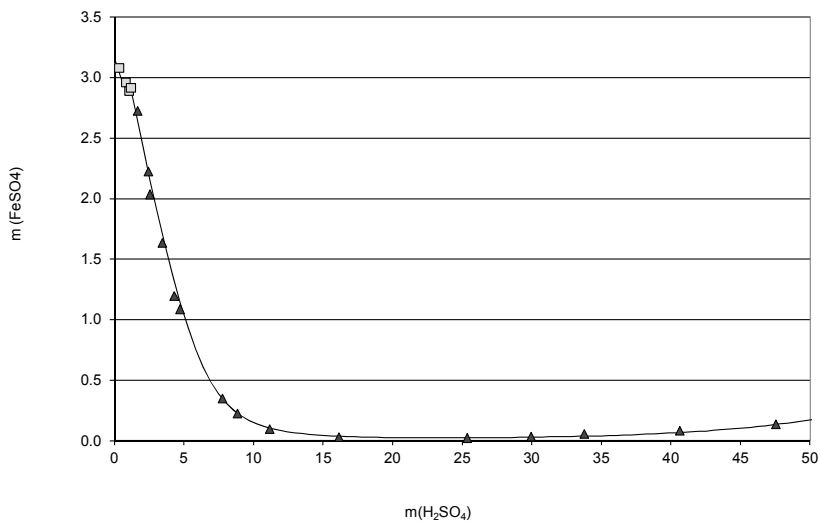


Figure 15. The predicted solubility of iron sulfate in aqueous sulfuric acid with the NPL Pitzer model (solid line) compared to experimental data¹³² at 50°C up to 50 mol/kg. Squares present heptahydrate and triangles monohydrate. The solubility data were included in the assessment.¹³¹

6. Conclusions

6.1 Pitzer and NPL Pitzer parameters

The most crucial Pitzer parameters in temperature range from 0 to 170 °C are

1. C^ϕ for H^+ and SO_4^{2-} interaction
2. $\beta^{(0)}$ and $\beta^{(1)}$ for H^+ and HSO_4^- -interaction.

Omitting any of these parameters from the selected parameter set will have drastic effects on the quality of the fit.

Only four Pitzer parameters, the above mentioned three parameters extended by $\beta^{(0)}$ for H^+/SO_4^{2-} interaction with simple temperature dependency can describe the thermodynamic properties of sulfuric acid up to 6 m solution.

The four essential NPL Pitzer parameters in temperature range from 0 to 170 °C are:

- C^ϕ describing the interaction between H^+ and SO_4^{2-} ions
- $\beta^{(0)}$ and $\beta^{(1)}$ describing the interaction between H^+ and HSO_4^- ions and
- θ describing the interaction between SO_4^{2-} and HSO_4^- ions

These parameters can describe the sulfuric acid – water system better than any five parameter set missing any of these four essential parameters. Adding parameter $\beta^{(0)}$ for H^+ / SO_4^{2-} -interaction (set D) or C^ϕ for H^+ / HSO_4^- -interaction (set K) will improve the fit. The differences in predicted values between parameter sets D and K are well within assumed experimental accuracy but the latter has better extrapolating capabilities.

No more than four parameters with Pitzer model and five with NPL Pitzer model can be justified.

6.2 The second dissociation constant K_2

Sulfuric acid does not dissociate completely in aqueous media to H^+ and SO_4^{2-} ions but an intermediate species, bisulfate, HSO_4^- is formed. (Equation 1). The equilibrium is on the left, on the bisulfate side. Thus, in more concentrated solutions the major species are H^+ and HSO_4^- . The incomplete dissociation cannot be neglected in proper thermodynamic modelling of aqueous sulfuric acid.

However, including the equilibrium between these three species creates an internal redundancy in the thermodynamic description. So, several second dissociation constants K_2 are capable of modelling aqueous sulfuric acid equally well and still lead to the same stoichiometric activity and osmotic coefficients within the limits of experimental accuracy^{IV}.

Moreover, a linear relationship between the thermodynamic properties of the dissociation reaction at 25°C and those for the cell reactions of the electrochemical cells A–C (Table 5) are formed when dataset 1 consisting only of Gibbs energy related data from 0 to 55 °C is used as experimental data. Extending the temperature range of experimental data up to 170°C breaks this linear dependency for enthalpy and entropy but not for Gibbs energy.

Even though different K_2 -equations yield the same values for Gibbs energy related properties, they differ from each other in enthalpy related properties such as relative apparent molal enthalpy. Since the degree of dissociation and the enthalpy of the bisulfate dissociation reaction have a significant effect on enthalpy related properties, the equation describing K_2 cannot be decided a priori but it has to be assessed simultaneously with the other model parameters. Otherwise, the preset values for K_2 will bias the assessment and contribute either additional excess parameters or complicate the temperature dependency of the used parameters. Thus, the equation for K_2 can be fitted if enthalpy related data is included as experimental data in the assessment.

Applying this approach yielded thermodynamically consistent values for electrochemical cells A to C, the 2nd dissociation reaction of sulfuric acid as well a thermodynamic model for aqueous sulfuric acid with excellent extrapolating capabilities. ^{IV} Thermodynamic properties of aqueous sulfuric acid as well as the electrochemical cells at 25°C were extracted from dataset 2 in assessment 6 (Table 17) including electrochemical cell data, critical evaluated osmotic coefficient data and relative apparent molal enthalpy data (Table 20). The data are distributed evenly around 25°C from 0 to 55°C, so any distortion due to biased temperature range is not expected.

The thermodynamic values (Table 20) are average values of 78 fits. The error estimate is either three times the standard deviation or half of the difference between maximum and minimum values. The smaller value is selected.

The best model entitled as the Sippola model from assessment 10 covering a temperature range from 0 to 170 °C and fulfilling these new thermodynamic values most accurately was selected.

The obtained K_2 -equation for the Sippola model is

$$\begin{aligned}
 -RT \ln (K_2) = & 57092.9(\text{J/mol}) - 1724.98(\text{J/K mol})*T \\
 & + 275.667(\text{J/K mol})*T*\ln(T/\text{K})
 \end{aligned}
 \tag{64}$$

and the Pitzer parameters are listed in table 22.

The Sippola model predicts the thermodynamic properties of sulfuric acid up to 6 m solution equally well with only four Pitzer parameters as the more complicated models by Clegg et al.² with 9 parameters and Clegg and Brimblecombe³⁹ with 10 parameters^{IV}. The total numbers of terms in excess parameters are 8, 32 and 40, respectively. It also has excellent extrapolating capabilities for concentration (Table 25), temperature (Figures 8,9,10) and independent experimental electrochemical data (Figure 12). The obtained results validate not only the Sippola model but also the thermodynamic values obtained for sulfuric acid and electrochemical cells.

The average value of 78 fits for K_2 at 25°C obtained from assessment 6 is 0.0119 and the value in the Sippola model is 0.0115. Both values are higher than generally accepted values which lie from 0.01030 to 0.01086 (Table 4). On the other hand they agree quite well with the alternative value of 0.0120 obtained by Pitzer et al.⁴³ (Table 21) and value of 0.0117 obtained by Simonin et al.⁶ when Raman data were included in the fit. The first value is obtained using Pitzer model and the latter by MSA–NRTL model so these values are not model specific.

All this indicates that the correct value for the second dissociation constant K_2 at 25°C lies higher than is currently estimated (Table 4). The reassessed value is 0.0119.

6.3 Thermodynamic properties

Thermodynamic properties obtained are in excellent agreement with thermodynamic values in the literature except for the thermodynamic values of sulfuric acid which deviate somewhat from the values currently considered best (Table 20). However, as demonstrated in this thesis, the thermodynamic model based on these new values is not only capable of predicting the used experimental data equally well as more complicated models but it has also excellent extrapolating capabilities even regarding the electrochemical properties of an independent electrochemical cell. Moreover, the thermodynamic properties obtained for sulfuric acid as well as electrochemical cells are in excellent agreement with the alternate set by Pitzer et al.⁴³ (Table 21).

The calculated standard potential at 25°C using the electrochemical potentials redefined in this work (Table 20) for the cell $\text{Hg}_2\text{SO}_4, \text{Hg} | \text{H}_2\text{SO}_4 | \text{PbO}_2, \text{PbSO}_4$ (cell D) is 1076.1 mV which is less than 0.2 mV lower than the value obtained by the Sippola model.^{IV} The 1.0 mV discrepancy between standard cell potentials for these cells found earlier² vanishes and internally consistent values for the cells B, C and D are established.

Hovey and Hepler⁴⁶ measured the heat capacity of the bisulfate ion and concluded that its value at 25°C is (-17.8 ± 0.8) J/K mol. Combining this with the heat capacity of sulfate ion from NBS tables (-293) J/K mol yields a value of -275 J/K mol for the heat capacity change in the 2nd dissociation reaction. This is in excellent agreement with the value of -275.67 derived from the Sippola K₂-equation (Table 23). The heat capacity of the hydrogen ion is zero by convention.

6.4 NPL Pitzer model

The NPL Pitzer equation is capable of predicting the stoichiometric osmotic coefficient by Rard et al.⁴⁷ at 25°C up to 27 m solution (Figure 5). The values after 15 mol/kg are extrapolated. It can also reproduce the osmotic coefficients calculated by the more complicated model of Clegg and Brimblecombe³⁹ at 0, 25 and 50°C up to 40 m (80 w%) solution even though all values above 15 mol/kg at 25 °C and above 8 mol/kg at 0 and 50°C are extrapolated (Figure 13).

It can also be safely used to estimate osmotic coefficient at higher temperatures albeit the experimental data was limited to 50°C (Figure 14) as well as modelling solubilities in ternary systems (Figure 15) .

Thus, NPL Pitzer equation is shown to extend the capabilities of Pitzer equation to well beyond the six m solution up to more concentrated solutions. However, its ability to model enthalpy related data remains unclear.

7. Discussion

Aqueous sulfuric acid is an important chemical not only for the industry but also with respect to the environment. A need for a simple thermodynamic model is obvious. The thermodynamic model developed here is not only simple but it also has good extrapolating capabilities. Thus, a cornerstone of further thermodynamic description of acidic sulfate systems is laid. The usability of this new model should be tested in the modelling of existing and new ternary or higher order aqueous sulfuric acid systems.

A key factor in modelling aqueous sulfuric acid is using the correct value for the second dissociation constant K_2 . The equilibrium between sulfate and bisulfate ions creates an internal redundancy in the thermodynamic description and thus, the equation of K_2 must be included in the assessment of aqueous sulfuric acid. Using predefined equations for K_2 entails a predefined value not only for the Gibbs energy change in the 2nd dissociation reaction but also for the enthalpy change which is a substantial factor in modelling the enthalpy of the solutions. This can explain the extensive number of parameters and terms used in existing models for aqueous sulfuric acid when the description for enthalpy of solution is included in the assessment.

As can be seen from figure 16 the current versions of K_2 -equations are in agreement at ambient and higher temperatures but the extrapolated values in lower temperatures differ significantly from each other.

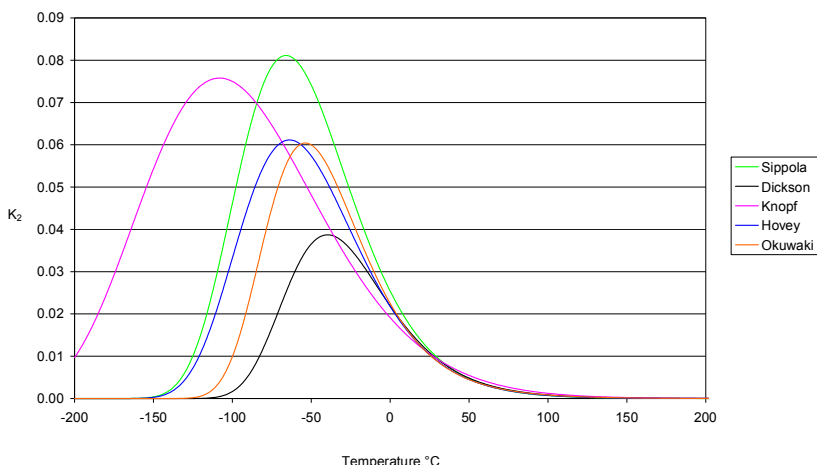


Figure 16. K_2 equations as a function of temperature.

Since the speciation of aqueous sulfuric acid in subzero temperatures¹³³ is important in modelling the behaviour of the atmosphere and thus, in modelling climate change, the used K_2 equation should be critically evaluated against empirical data such as the vapour pressure data for aqueous sulfuric acid measured by Massucci et al.¹³⁴

The thermodynamic properties obtained are in excellent agreement with thermodynamic values in the literature except the thermodynamic values for sulfuric acid. However, these values yield thermodynamically consistent standard electrochemical potentials at 25°C for the cells B – D:

$$\text{Cell B: Pt, H}_2 \mid \text{H}_2\text{SO}_4 \mid \text{Hg}_2\text{SO}_4, \text{Hg}, \quad E^\circ = 613.4 \pm 0.7 \text{ mV}$$

$$\text{Cell C: Pt, H}_2 \mid \text{H}_2\text{SO}_4 \mid \text{PbO}_2, \text{PbSO}_4, \text{Pt}, \quad E^\circ = 1689.5 \pm 0.7 \text{ mV}$$

$$\text{Cell D: Hg}_2\text{SO}_4, \text{Hg} \mid \text{H}_2\text{SO}_4 \mid \text{PbO}_2, \text{PbSO}_4 \quad E^\circ = 1076.1 \pm 1.0 \text{ mV}$$

where the standard electrochemical potential of the cell D is calculated by subtracting the standard electrochemical potential of cell B from that of cell C. The uncertainty of E° for cell D is estimated as a square root of the sum of squares of uncertainties.

Corresponding values for Gibbs energy, enthalpy and entropy changes for the cell reaction in cell D calculated from table 20 are displayed in table 26.

Table 26. Calculated thermodynamic properties for the cell reaction in cell D at 298.15 K.

Property	Sippola	CODATA ¹²⁸	NBS Tables ⁹²
$\Delta_r G^\circ_{298}$ (kJ/mol)	-207.65	-207.73	-206.82
$\Delta_r H^\circ_{298}$ (kJ/mol)	-139.42	-138.64	-138.78
$\Delta_r S^\circ_{298}$ (J/K mol)	228.84	231.7	228.21

These values could be tested if the electrochemical potential of cell the D were measured as a function of temperature.

The NPL Pitzer is capable of predicting activity and osmotic coefficient using only five parameters within eight terms equally well as the more complicated model of Clegg and Brimblecombe³⁹ using ten parameters within 40 terms. Even though the temperature range for NPL Pitzer model is only 0 to 55°C compared to -70 to 55°C and the enthalpy data is not predicted, the difference in the number of fitted terms is remarkable. Moreover, the NPL Pitzer model is capable of extrapolating experimental osmotic data up to $\approx 170^\circ\text{C}$ with standard and maximum deviations of 0.012 and 0.029, respectively.

The ability of NPL Pitzer equation should be tested further including more data in the assessment including electrochemical, osmotic coefficient, vapour pressure, and enthalpy data. Following Popper¹³⁵ some data should be reserved for critical evaluation of the obtained model. Moreover, the effect of the K_2 equation used as well as the analysis of thermodynamic consistency of the NPL Pitzer model itself should also be performed.

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Aqueous sulfuric acid is an important chemical not only for the industry but also to the environment. A need for a simple thermodynamic model is obvious.

The thermodynamic properties of aqueous sulfuric acid were modelled with the Pitzer equation. Both the second dissociation constant K_2 for sulfuric acid and Pitzer parameters were fitted simultaneously. After variation of the experimental data used and the temperature dependency of the Pitzer parameters, it was found that only four parameters with eight terms can describe the thermodynamic properties of aqueous sulfuric acid over a temperature range of 0-170°C.

The thermodynamic properties obtained are in good agreement with literature values as well as with other Pitzer based thermodynamic models for aqueous sulfuric acid.

The recent version of Pitzer equation, NPL Pitzer, was also tested. It was found to accurately predict activity and osmotic



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