

Thermodynamic modelling of aqueous metal sulfate solutions

Petri Kobylin

Thermodynamic modelling of aqueous metal sulfate solutions

Petri Kobylin

A doctoral dissertation completed for the degree of Doctor of Science in Technology to be defended, with the permission of the Aalto University School of Chemical Technology, at a public examination held at the lecture hall V1 of the school on 19 April 2013 at 12.

Aalto University
School of Chemical Technology
Department of Materials Science and Engineering
Metallurgical thermodynamics and modelling

Supervising professor

Professor Pekka Taskinen

Thesis advisor

Professor Pekka Taskinen

Preliminary examiners

Professor Krzysztof Fitzner, AGH University of Science and
Technology, Poland

Doctor Andy Watson, University of Leeds, UK

Opponent

Doctor Erich Königsberger, Murdoch University, Australia

Aalto University publication series

DOCTORAL DISSERTATIONS 41/2013

© Petri Kobylin

ISBN 978-952-60-5055-3 (printed)

ISBN 978-952-60-5056-0 (pdf)

ISSN-L 1799-4934

ISSN 1799-4934 (printed)

ISSN 1799-4942 (pdf)

<http://urn.fi/URN:ISBN:978-952-60-5056-0>

Unigrafia Oy

Helsinki 2013

Finland



Author

Petri Kobylin

Name of the doctoral dissertation

Thermodynamic modelling of aqueous metal sulfate solutions

Publisher School of Chemical Technology

Unit Department of Materials Science and Engineering

Series Aalto University publication series DOCTORAL DISSERTATIONS 41/2013

Field of research Chemical thermodynamics

Manuscript submitted 10 December 2012

Date of the defence 19 April 2013

Permission to publish granted (date) 12 February 2013

Language English

Monograph

Article dissertation (summary + original articles)

Abstract

Acid mine drainage has long been a significant environmental problem in coal and metal sulfide mining. The requirement to recycle and reuse materials has increased significantly, especially in the EU. Dumping and land-filling a neutralised deposit is not an option any more. Thus, efficient techniques for the recycling and reuse of sulfuric acid and/or metal sulfates from the side streams are needed.

When developing alternative solutions, a better understanding of the thermodynamic behaviour of the $\text{MeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ ($\text{Me} = \text{Mn, Ni, Fe}$) system is needed. In the present study a thermodynamic model of the $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{NiSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$, and $\text{MnSO}_4\text{-H}_2\text{O}$ systems has been developed, in order to yield a thermodynamically consistent set of values for the solubility of metal sulfate over a wide range of temperatures and concentrations. The Pitzer mean activity coefficient model has been used in the assessment to take into account the non-ideal behaviour of the aqueous solution. The thermodynamic properties of metal sulfate hydrates were also refined. These metal sulfate solutions have previously been modelled in the literature. Those models have been reviewed critically in this work.

The current model presents the experimental data of metal sulfate water systems over temperature intervals of $-2\text{-}220\text{ }^\circ\text{C}$ (FeSO_4), $-3\text{-}220\text{ }^\circ\text{C}$ (NiSO_4), and $-11\text{-}175\text{ }^\circ\text{C}$ (MnSO_4) and in concentrations from pure water to the solubility limit of metal sulfate hydrates. The model in this work presents solubilities, mean activity coefficients, activities of water, enthalpy, and heat capacity of solution and hydrate dissociation pressure, with good accuracy and consistently, but the model has limitations at temperatures higher than $100\text{ }^\circ\text{C}$ as a result of the lack of experimental data.

The experimental data that are available for the $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$, and $\text{NiSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ systems are also presented with a good accuracy and consistently up to $100\text{ }^\circ\text{C}$ and sulfuric acid concentrations up to 10 mol/kg . The model also predicts well the solubility measurements available in dilute sulfuric acid solutions at $160\text{-}250\text{ }^\circ\text{C}$.

Keywords Modelling, Pitzer model, metal sulfate, activity, CALPHAD method

ISBN (printed) 978-952-60-5055-3

ISBN (pdf) 978-952-60-5056-0

ISSN-L 1799-4934

ISSN (printed) 1799-4934

ISSN (pdf) 1799-4942

Location of publisher Espoo

Location of printing Helsinki

Year 2013

Pages 117

urn <http://urn.fi/URN:ISBN:978-952-60-5056-0>

Tekijä

Petri Kobylin

Väitöskirjan nimi

Metallisulfaattipitoisten vesiliuosten termodynaaminen mallinnus

Julkaisija Kemian tekniikan korkeakoulu**Yksikkö** Materiaalitekniikan laitos**Sarja** Aalto University publication series DOCTORAL DISSERTATIONS 41/2013**Tutkimusala** Kemiallinen termodynamiikka**Käsitteilyajankohdan pvm** 10.12.2012**Väitöspäivä** 19.04.2013**Julkaisuluvan myöntämispäivä** 12.02.2013**Kieli** Englanti **Monografia** **Yhdistelmäväitöskirja (yhteenveto-osa + erillisartikkelit)****Tiivistelmä**

Hiili- ja metallisulfidikaivosten happamat suotovedet ovat pitkään olleet merkittävä ympäristöongelma. Kierrätyksen ja materiaalien uudellenkäytön vaatimukset ovat kasvaneet huomattavasti erityisesti EU:ssa. Neutraloidun maa-aineksen vieminen täyttömaaksi ei ole enää mahdollista. Tarvitaan siis tehokkaita menetelmiä rikkihapon ja metallisulfaattien kierrättämiseksi ja uudelleen käyttämiseksi sivuvirroista.

Kehitettäessä vaihtoehtoisia ratkaisuja tarvitaan parempaa ymmärrystä $\text{MeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ (Me = Mn, Ni, Fe) systeemien termodynaamisesta käyttäytymisestä. Tässä työssä on kehitetty $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{NiSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ ja $\text{MnSO}_4\text{-H}_2\text{O}$ systeemien termodynaamisesti konsistentti tietokanta, jolla voi mm. laskea metallisulfaattien liukoisuuksia laajalla lämpötila- ja konsentraatioalueella. Vesiliuosten epäideaalisuus on huomioitu mallissa Pitzerin keskiaktiivisuuskertoimilla. Kidevedellisten metallisulfaattisuolojen termodynaamiset arvot uudelleenarvioitiin tässä työssä. Yllä olevien systeemien aikaisempia mallinnuksia tarkasteltiin myös kriittisesti tässä työssä.

Nykyinen malli esittää metallisulfaatti-vesi systeemien kokeelliset havaintotulokset lämpötilaväleillä $-2\text{-}220\text{ °C}$ (FeSO_4), $-3\text{-}220\text{ °C}$ (NiSO_4) ja $-11\text{-}175\text{ °C}$ (MnSO_4) sekä konsentraatioalueella puhtaasta vedestä kiteisen metallisulfaatin saostumisrajalle. Mallilla voi laskea liukoisuudet, keskiaktiivisuuskertoimet, veden aktiivisuuden, liuksen entalpijan ja lämpökapasiteetin sekä hydraattien dissosioitumispaineet tarkasti, mutta mallilla on rajoituksensa yli 100 °C lämpötiloissa kokeellisen tiedon niukkuudesta johtuen.

Malli esittää myös saatavilla olevat $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ ja $\text{NiSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ systeemien kokeelliset liukoisuusarvot tarkasti 100 °C ja rikkihappopitoisuuteen 10 mol/kg asti. Malli ennustaa myös hyvin liukoisuusmittauksia laimeissa rikkihappopitoisuuksissa ja korkeissa $160\text{-}250\text{ °C}$ lämpötiloissa.

Avainsanat Mallinnus, Pitzerin yhtälö, metallisulfaatti, aktiivisuus, CALPHAD menetelmä**ISBN (painettu)** 978-952-60-5055-3**ISBN (pdf)** 978-952-60-5056-0**ISSN-L** 1799-4934**ISSN (painettu)** 1799-4934**ISSN (pdf)** 1799-4942**Julkaisupaikka** Espoo**Painopaikka** Helsinki**Vuosi** 2013**Sivumäärä** 117**urn** <http://urn.fi/URN:ISBN:978-952-60-5056-0>

Preface

This work was carried out in the Metallurgical Thermodynamics and Modelling Research Group at Aalto University between 1.1.2009 and 31.12.2012.

Special thanks to Professor Pekka Taskinen for supervising this work. I would also like to thank Lic.Sci. (Tech.) Hannu Sippola, who helped with the modelling and optimisation problems. I would also like to thank the personnel in our research group for providing an excellent environment for research. I would also like to thank Emeritus Professor Simo Liukkonen.

The financial support from the Outokumpu Foundation and Finnish Metals Producers' Foundation and the Research Foundation of Helsinki University of Technology is gratefully acknowledged.

I am grateful to my parents and friends for their support. Finally, and most importantly, I would like to thank my wife, Arja, and children, Kerttu and Martti, for their patience and support for this project.

Espoo, January 21, 2013

Petri Kobylin

List of Publications

This thesis consists of an overview and of the following publications, which are referred to in the text by their Roman numerals.

- I. Petri Kobylin, Thermodynamics of Concentrated Aqueous Solution of NiSO₄, Proceedings of the European Metallurgical Conference 2011 (EMC), Volume 3, ISBN 978-3-940276-38-4. (pp. 957-974).
- II. P.M. Kobylin, H. Sippola, P.A. Taskinen, Thermodynamic modelling of aqueous Fe(II) sulfate solutions, CALPHAD 35 (2011) 499–511.
- III. P.M. Kobylin, P.A. Taskinen, Thermodynamic modelling of aqueous Mn(II) sulfate solutions, CALPHAD 38 (2012) 146–154.
- IV. P.M. Kobylin, H. Sippola, P.A. Taskinen, Thermodynamic model for acidic Fe(II) sulphate from solubility data, CALPHAD 38 (2012) 185-193.
- V. P.M. Kobylin, H. Sippola, P.A. Taskinen, Thermodynamic model for acidic Ni(II) sulfate from solubility data, CALPHAD 40 (2013) 41-47.

Author's Contribution

Publication I: “Thermodynamics of Concentrated Aqueous Solution of NiSO₄”

In this conference paper a thermodynamic model – based on the minimisation of the Gibbs energy – of a binary NiSO₄-H₂O system at -3–220 °C was presented. The author performed the literature survey, critical review of the previous models, and assessment of this binary system using experimental data from the literature (solubilities, including freezing point depression data, activities of water, and enthalpy and heat capacity of solution and hydrate dissociation pressure) and the Pitzer mean activity coefficient model. The thermodynamic properties ($\Delta_f H^\circ_{298.15}$ and $S^\circ_{298.15}$) of nickel sulfate hydrates and the Pitzer parameters were refined. The main contribution of the author was the creation of a thermodynamically consistent model that extended previous models to higher temperatures.

Publication II: “Thermodynamic modelling of aqueous Fe(II) sulfate solutions”

In this paper a thermodynamic model of a binary FeSO₄-H₂O system at -2–220 °C was presented. The author performed the literature survey, critical review of the previous models, and assessment of this binary system using experimental data from the literature (solubilities, including freezing point depression, eutectic and peritectic data, activities of water, and enthalpy and heat capacity of solution and hydrate dissociation pressure) and the Pitzer mean activity coefficient model. The thermodynamic properties ($\Delta_f H^\circ_{298.15}$ and $S^\circ_{298.15}$) of ferrous sulfate hydrates and the Pitzer parameters of this binary system were refined. The main contribution of the author was the creation of a thermodynamically consistent model that extended previous models to higher temperatures.

Publication III: “Thermodynamic modelling of aqueous Mn(II) sulfate solutions”

In this paper the thermodynamic properties of a binary MnSO₄-H₂O system at -11–175 °C were presented. The author performed the literature survey, critical review of the previous models, and assessment of this binary system using experimental data from the literature (solubilities, including freezing point depression and eutectic data, mean activity coefficients, activities of water, and enthalpy and heat capacity of solution) and the Pitzer mean activity coefficient model. The thermodynamic properties ($\Delta_f H^\circ_{298.15}$ and $S^\circ_{298.15}$) of manganese sulfate hydrates and the Pitzer parameters of this binary system were refined. The main contribution of the author was the creation of a thermodynamically consistent model that extended previous models to higher temperatures.

Publication IV: “Thermodynamic model for acidic Fe(II) sulphate from solubility data”

In this paper the thermodynamic properties of a ternary $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ system at 0-100 °C were presented. The author performed the literature survey, critical review of the previous models, and assessment of this ternary system using experimental solubility data from the literature and the Pitzer mean activity coefficient model. The main contribution of the author was the creation of a thermodynamically consistent model that also predicts well the solubility measurements available in dilute sulfuric acid solutions at 160-220 °C.

Publication V: “Thermodynamic model for acidic Ni(II) sulfate from solubility data”

In this paper the thermodynamic properties of a ternary $\text{NiSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ system at 0-90 °C were presented. The author performed the literature survey, critical review of the previous models, and assessment of this ternary system using experimental solubility data from the literature and the Pitzer mean activity coefficient model. The main contribution of the author was the creation of a thermodynamically consistent model that also predicts well water activity data at 25 °C and the solubility measurements available in dilute sulfuric acid solutions at 200-250 °C.

List of symbols and abbreviations

$A-D$	Constants of heat capacity function
A_G-F_G	Constants of Gibbs energy function
$A_{Pitzer}-F_{Pitzer}$	Constants of Pitzer equation parameters
A_L	temperature dependent Debye-Hückel constant (enthalpy)
A_J	temperature dependent Debye-Hückel constant (heat capacity)
A^ϕ	temperature dependent Debye-Hückel constant
a_1-a_2	<i>HKF</i> model ionic specific parameters
a_i	activity of component i
a_w	activity of water
aq	aqueous solution
B_{ca}	interaction parameter for cation (c) and anion (a)
B^ϕ	Pitzer parameter
b	constant (= 1.2) in Pitzer equation
c_1-c_2	<i>HKF</i> model ionic specific parameters
C_{ca}	interaction parameter for cation (c) and anion (a)
C_i	calculated value of property i
C_{ca}^ϕ	concentration dependent Pitzer parameter
$C^{\phi L}$	electrolyte specific Pitzer parameter (enthalpy)
$C^{\phi J}$	electrolyte specific Pitzer parameter (heat capacity)
$C_{ca}^{(o)}$	electrolyte specific Pitzer parameter
$C_{ca}^{(i)}$	electrolyte specific Pitzer parameter
c_p	heat capacity / $J \cdot K^{-1} \cdot mol^{-1}$
c_{p2}	heat capacity of solution / $J \cdot K^{-1} \cdot mol^{-1}$
c_{pw}^o	heat capacity of water / $J \cdot K^{-1} \cdot mol^{-1}$
c_{p2}^o	heat capacity of solution at infinite dilution / $J \cdot K^{-1} \cdot mol^{-1}$
${}^\phi c_p$	apparent heat capacity of solution / $J \cdot K^{-1} \cdot mol^{-1}$
E_i	experimental value of property i
$f(I)$	function of ionic strength and temperature
G_i	conventional Gibbs free energy of component i / $J \cdot mol^{-1}$
G^E	excess Gibbs energy / $J \cdot mol^{-1}$
$G^{E,m}$	excess Gibbs energy (molality) / $J \cdot mol^{-1}$
G_i^o	conventional Gibbs energy component i ($G_i^o = \Delta_f H^o - TS^o \neq \Delta_f G^o$)
$\Delta_f H_{298.15}^o$	molar standard enthalpy of formation (25 °C, 1 bar) / $J \cdot mol^{-1}$
ΔH_{dil}	enthalpy of dilution / $J \cdot mol^{-1}$
$\Delta H_s(T)$	enthalpy of solution / $J \cdot mol^{-1}$
$\Delta H_s^o(T)$	enthalpy of solution at infinite dilution / $J \cdot mol^{-1}$
I	ionic strength of solution
K_{sp}	equilibrium constant of solubility reaction
K_2	equilibrium constant of $HSO_4^- = SO_4^{2-} + H^+$
${}^\phi L$	apparent enthalpy of solution / $J \cdot mol^{-1}$
M	cation
M_w	molar mass of water / 18.01528 $g \cdot mol^{-1}$
m_i	molality of species in solution / $mol \cdot kg^{-1}$
$m_{g,sol}$	mass of solution / g
N	electrically neutral species
n_i, n_j, n_k	amount of species in solution / mol
n_w	amount of water / mol
n	number of water molecules in crystalline solid phase; number of properties (data items) to be reproduced
P	pressure / bar
P_r	reference pressure / bar
R	gas constant / 8.31451 $J \cdot K^{-1} \cdot mol^{-1}$
$S_{298.15}^o$	molar standard entropy (25 °C, 1 bar) / $J \cdot K^{-1} \cdot mol^{-1}$
T	temperature / K

t	temperature / °C
U_i	the uncertainty associated with value E_i
W_i	the weight assigned to property (data item) i
w_w	number of kilograms of water
X	anion; Born function dependent of the dielectric constant of water
Y	Born function dependent of the dielectric constant of water
y	stoichiometric number of $H_2O(g)$ in gas dissociation reactions
z_-	charge of an anion
z_+	charge of a cation
α	the degree of dissociation of HSO_4^- ; solid phase
α_1	electrolyte dependent constant in Pitzer model
α_2	electrolyte dependent constant in Pitzer model
$\beta^{(0)}$	electrolyte specific Pitzer parameter
$\beta^{(1)}$	electrolyte specific Pitzer parameter
$\beta^{(2)}$	electrolyte specific Pitzer parameter
$\beta^{(0)L}$	electrolyte specific Pitzer parameter (enthalpy)
$\beta^{(1)L}$	electrolyte specific Pitzer parameter (enthalpy)
$\beta^{(2)L}$	electrolyte specific Pitzer parameter (enthalpy)
$\beta^{(0)J}$	electrolyte specific Pitzer parameter (heat capacity)
$\beta^{(1)J}$	electrolyte specific Pitzer parameter (heat capacity)
$\beta^{(2)J}$	electrolyte specific Pitzer parameter (heat capacity)
γ_i	activity coefficient of compound i in solution
γ_{\pm}	mean activity coefficient
ε	dielectric constant
θ	solvent specific parameter 228 K
θ_{ij}	temperature dependent ion-ion parameter
${}^E\theta_{ij}(I)$	parameter for long range interactions depending on I only
λ_{ij}	second virial coefficient
λ_{na}	interaction between electrically neutral species and anion
λ_{nc}	interaction between electrically neutral species and cation
μ_i	chemical potential of a component i / $J \cdot mol^{-1}$
μ_i°	standard state chemical potential of component i / $J \cdot mol^{-1}$
μ_{ijk}	third virial coefficient
μ_w	chemical potential of water / $J \cdot mol^{-1}$
μ_w°	standard state chemical potential of water / $J \cdot mol^{-1}$
ν	sum of stoichiometric coefficients of ions $\nu_+ + \nu_-$
ν_i	stoichiometric coefficient of ion i
ν_-	stoichiometric coefficient of an anion
ν_+	stoichiometric coefficient of a cation
ν_{\pm}	mean stoichiometric coefficient of ions
ϕ	osmotic coefficient of compound i
$\Phi_{aa'}$	interaction parameter between anions (a and a')
$\Phi_{cc'}$	interaction parameter between cations (c and c')
Φ^ϕ	virial coefficient
ψ	solvent specific parameter 2600 bar
$\psi_{aa'c}$	interactions between three ions
$\psi_{cc'a}$	interactions between three ions
ω	Born coefficient of ion; constant (= 2.5) in Pitzer equation

Superscripts

$^\circ$	standard state
E	excess
E,m	excess (molality)
'	partial derivative relative to ionic strength

Subscripts

<i>a</i>	anion
<i>c</i>	cation
<i>f</i>	formation
<i>i, j, k</i>	species
<i>M</i>	cation
<i>n</i>	neutral species
<i>r</i>	reaction
<i>X</i>	anion
\pm	mean

Abbreviations

<i>CALPHAD</i>	CALculation of PHase Diagram
<i>EMF</i>	Electromotive force
<i>HKF</i>	Helgeson-Kirkham-Flowers model
<i>Me</i>	metal (Fe, Ni, Mn)
<i>MSE</i>	Mixed Solvent Electrolyte
<i>MTAQ/nplaq</i>	National Physical Laboratory aqueous database in <i>MTDATA</i>
<i>MTDATA</i> [®]	Phase diagram software
<i>NRTL</i>	Non-Random Two-Liquid model
<i>UNIQUAC</i>	UNIversal QUAsiChemical model

Table of Contents

Preface.....	i
List of Publications.....	ii
Author's Contribution.....	iii
List of symbols and abbreviations.....	v
Table of Contents	ix
1. Introduction	1
1.1 Background	1
1.2 Research problem	1
1.3 Method.....	2
1.4 Experimental data.....	2
1.5 Previous models	2
1.5.1 FeSO ₄ -H ₂ SO ₄ -H ₂ O system	2
1.5.2 NiSO ₄ -H ₂ SO ₄ -H ₂ O system	3
1.5.3 MnSO ₄ -H ₂ O system.....	4
1.6 Thermodynamic data.....	4
2. Theory.....	5
2.1 Aqueous solutions.....	5
2.2 General thermodynamic equations	6
2.2.1 Solubility and dissociation reactions	7
2.2.2 Heat capacity of ions	8
3. Pitzer model	9
3.1 Concentration dependence of second and third virial coefficients	11
3.2 First derivative enthalpy.....	13
3.3 Second derivative heat capacity	14
4. Assessment	15
5. Results and discussion	17
5.1 Unary data	17
5.2 Binary systems	19
5.3 Ternary systems	21
6. Conclusions	26
7. References	28

1. Introduction

1.1 Background

This work consists of applications of chemical thermodynamics in systems that involve aqueous electrolyte mixtures. The results of this research are important in hydrometallurgical processes such as nickel refining, the surface finishing of metals by electroplating, manganese ore leaching, and the pickling of stainless steels, in order to improve and develop the system and gain a better understanding of phenomena in the aqueous process solutions, which typically operate at temperatures between 50 and 300 °C.

Acidic metal sulfate solutions are generated on a large scale in the hydro- and pyrometallurgical industries. They are also produced in the steel industry and titanium dioxide production. Acid mine drainage has long been a significant environmental problem in coal and metal sulfide mining. The demand for the recycling and reuse of materials has increased significantly, especially in the EU. The dumping and land-filling of a neutralised deposit are not an option any more. Thus, efficient techniques for the recycling and reuse of sulfuric acid and/or metal sulfates from the side streams are needed.

When alternative solutions are being developed, a better understanding of the thermodynamic behaviour of $\text{MeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ ($Me = \text{Mn, Ni, Fe}$) systems is needed. The principles of chemical thermodynamics utilised in this work can be used to develop greener processes with safer chemicals. Consistent thermodynamic models like the one assessed in this work are generic and not specific to any process. These models can be used, for example, in waste water treatment, as well as the development of chemical processes in the extraction of minerals.

1.2 Research problem

The aim of this thesis was to create a generic and internally consistent thermodynamic model for acidic aqueous ferrous, nickel, and manganese sulfate solutions over a wide range of temperatures and concentrations that can be used in various applications from e.g. the design of hydrometallurgical processes to environmental systems. In order to ensure the internal consistency of the model, the *CALPHAD* (CALculation of PHase Diagrams) method [1] was used. In short, that means that the model was built starting

from the unary data; then the binary systems were carefully modelled and after that ternary systems and so on.

1.3 Method

The thermodynamic model was obtained using the thermodynamic equilibrium calculation program *MTDATA*[®] (www.mtdata-software.com), which uses a global Gibbs energy minimisation routine and includes the Pitzer activity coefficient model [2, 3] for the excess Gibbs energy of the aqueous solutions. This program also includes an assessment module for thermodynamic optimisation, which was used to optimise the Pitzer parameters from the experimental observations.

1.4 Experimental data

Experimental data, including solubilities, eutectic and peritectic points, water activities, mean activity coefficients, osmotic coefficients, *EMF* measurements, vapour pressures, decomposition pressures, freezing point depression temperatures, and enthalpies and heat capacities of solutions from the literature were reviewed and critically evaluated.

1.5 Previous models

The metal sulfate solutions presented in this thesis have previously been modelled in the literature using both the Pitzer model and other solutions models, such as *NRTL* [4], *UNIQUAC* [5] and *MSE* [6]. However, many of these are limited to narrow ranges of either temperatures or concentrations. In this work all the previous model results were reviewed critically and compared to the results of this work and experimental data from the literature.

1.5.1 $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ system

In this work, only ferrous (+2 oxidation state) iron was considered. In aqueous sulfuric acid solutions, ferrous sulfate forms hydrates with 1, 4, 5, 6, and 7 molecules of crystalline water [7]. This chapter summarises the results of the other models. More details of the other models can be found in Publications II and IV.

Reardon and Beckie [8] assessed the $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ system using the Pitzer model. For the $\text{FeSO}_4\text{-H}_2\text{O}$ system they used mean activity coefficients and the heat capacity and enthalpy of solution data to optimise the temperature-dependent Pitzer parameters. The solubility data of FeSO_4 in water were used to generate the temperature-dependent equations for the solubility products (K_{sp}) for $\text{FeSO}_4\cdot 7\text{H}_2\text{O}(\text{s})$ and $\text{FeSO}_4\cdot \text{H}_2\text{O}(\text{s})$, which were then used with the ternary solubility data to generate Pitzer parameters for the $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ system. The Pitzer model of Reardon and Beckie is valid over a temperature range from 10 to 90 °C of the binary $\text{FeSO}_4\text{-H}_2\text{O}$ system and from 10 to 60 °C of the ternary system and up to 6 molal sulfuric acid using the second dissociation constant K_2 from Pitzer et al. [9]. However, the enthalpy of

solution values (ΔH_s) at infinite dilution of Reardon and Beckie are not internally consistent. ΔH_s calculated at 20 °C from the Pitzer parameters gives the value of 16.1 kJ/mol, whereas the derivation of K_{sp} gives a value of about 21.2 kJ/mol [10].

Sippola [10] assessed this ternary system with the Pitzer model using only solubility data. Instead of using solubility products he used the $\Delta_f H^\circ_{298.15}$, $S^\circ_{298.15}$ and $c_p(T)$ data and a simplified *HKF* model [11] for ions. The heat capacity data for $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{s})$ were taken from Lyon and Giauque [12], at 260.8-307.67 K. Sippola fitted and estimated $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}(\text{s})$ and $\text{FeSO}_4 \cdot \text{H}_2\text{O}(\text{s})$ heat capacity data from the literature values of $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}(\text{s})$ and $\text{MgSO}_4 \cdot \text{H}_2\text{O}(\text{s})$. Sippola was able to model the solubility of FeSO_4 in water and up to 6 molal sulfuric acid, using the second dissociation constant K_2 from Matsushima and Okuwaki [13], over a temperature range of 0-100°C.

Kobylin [14] and Kobylin et al. [15] assessed the H_2O - FeSO_4 - H_2SO_4 system at 0-100 °C, using the Pitzer model but excluding unsymmetrical mixing terms. Kobylin et al. followed the same procedure as in Sippola [10], using solubility data only in the parameter optimisation.

1.5.2 NiSO_4 - H_2SO_4 - H_2O system

In aqueous sulfuric acid solutions, nickel (+2 oxidation state) sulfate forms hydrates with 1, 2, 4, 5, 6 (α and β), and 7 molecules of crystalline water [16, 17]. This chapter summarises the results of the other models. More details of the other models can be found in Publications I and V.

Reardon [18] assessed the NiSO_4 - H_2SO_4 - H_2O system using the Pitzer model. For the NiSO_4 - H_2O system he used mean activity coefficients and heat capacity and enthalpy of solution data to optimise the temperature-dependent Pitzer parameters. The solubility data of NiSO_4 in water were used to generate the temperature-dependent equations for the solubility products (K_{sp}) for $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}(\text{s})$, α - $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}(\text{s})$, and β - $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}(\text{s})$, which were used with the ternary solubility data to generate Pitzer parameters for the NiSO_4 - H_2SO_4 - H_2O system. The Pitzer model of Reardon is valid over a temperature range from 0 to 100 °C for the binary NiSO_4 - H_2O system and from 0 to 70 °C for the ternary system and up to 6 molal sulfuric acid, using the second dissociation constant K_2 from Pitzer et al. [9]. The Pitzer model of Reardon lacks the monohydrate $\text{NiSO}_4 \cdot \text{H}_2\text{O}(\text{s})$ phase and that is why it cannot be used at higher temperatures of nickel refining [19], where $\text{NiSO}_4 \cdot \text{H}_2\text{O}(\text{s})$ is the only stable solid phase. This model also exhibits a poor extrapolating behaviour of higher sulfuric acid concentrations.

Kolhinen et al. [20, 21] modelled the NiSO_4 - H_2O system using only solubility data from 0 to 200 °C using $\Delta_f H^\circ_{298.15}$, $S^\circ_{298.15}$, and $c_p(T)$ data and a simplified *HKF* model for ions. The Pitzer model of Kolhinen et al. only seems to work at 0-100 °C. The model does not follow the experimental solubility data from the literature at temperatures above 100 °C where $\text{NiSO}_4 \cdot \text{H}_2\text{O}(\text{s})$ is the stable phase. Kolhinen et al. did not include H_2SO_4 in their assessment.

1.5.3 MnSO₄-H₂O system

Manganese has oxidation states of +2, +3, +4, +6, and +7 but in this work only the most stable +2 state was considered [22]. In aqueous solutions, manganese sulfate forms hydrates with 1, 2, 4, 5, and 7 molecules of crystalline water [23, 24]. This chapter summarises the results of other models. More details of the other models can be found in Publication III.

Przepiera [25] modelled this system as part of his MnSO₄-H₂SO₄-H₂O assessment from 0 to 100 °C using the Pitzer model. Unfortunately, the paper of Przepiera [14] does not give thermodynamic data for the species included in the system and that is why it is not possible to recalculate his results.

Azimi et al. [26, 27] modelled the system using the Mixed Solvent Electrolyte (MSE) model from 0 to 170 °C with the following experimental data from the literature: solubility of MnSO₄, activity of water, mean activity coefficient, and heat capacity of solution data.

Iliuta et al. [28] modelled the system using the extended UNIversal QUAsiChemical (UNIQUAC) model at -11.4 to 100 °C using solubility and osmotic coefficient data.

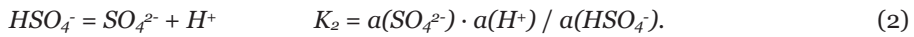
1.6 Thermodynamic data

The thermodynamic data (enthalpy, entropy, and heat capacity) of liquid water were first taken from the *MTDATA*[®] *MTAQ/nplaq* database (resource.npl.co.uk/mtdata/aqueous.htm), but later it was found that the heat capacity data for water were not valid below 25 °C. Since freezing point depression data were used it was necessary to re-evaluate the c_p function of water in this thesis (Publications I and II). The thermodynamic data of the solids (MeSO₄·*n*H₂O(s), *Me* = Fe, Ni, Mn and *n* = number of crystalline water molecules) are not well known; that is why it was decided to optimise the $\Delta_f H^\circ_{298.15}$ and $S^\circ_{298.15}$ values for the solids in this work with the Pitzer parameters.

2. Theory

2.1 Aqueous solutions

Aqueous solutions consist of a solvent composed of water (H₂O) and an electrolyte that in binary systems is MeSO₄ dissolved in the electrolyte solution as the ions Me²⁺ + SO₄²⁻. If the system is in saturation there is salt present with crystalline water MeSO₄·nH₂O(s), where $n = 1-7$, depending on the temperature and metal sulfate. In ternary systems the third component in this work is H₂SO₄, which dissolves in water in two steps:



The K_2 value used in this thesis for reaction (2) is from Matsushima and Okuwaki [13].

$$\log_{10} K_2(T, K) = 577.214 - 246.01 \log_{10} T - \frac{12717}{T} + 0.283133T - 1.37566 \cdot 10^{-4} T^2 \quad (3)$$

The following equations [29] are needed to describe the properties of aqueous solutions. The Gibbs energy of the solvent, the standard state of which is pure water at the temperature and pressure of the solution is

$$G_w = G_w^\circ + RT \ln(a_w). \quad (4)$$

The Gibbs energy of the solute is

$$G_i = G_i^\circ + RT \ln(m_i) + RT \ln(\gamma_i), \quad (5)$$

where the concentration unit m_i is the molality that is used throughout this thesis (moles of solute per kg of water) and γ_i is the activity coefficient of the solute. The hypothetical standard state for the solute is 1 molal ideally diluted solution at the temperature and pressure of the solution.

The osmotic coefficient (ϕ) is calculated from the activity of the water

$$\phi = - \left(\frac{1000}{M_w \sum m_i} \right) \ln(a_w), \quad (6)$$

where M_w is the molecular weight of water (18.01528 g/mol). The dissociation of electrolytes to ions in aqueous solutions is



and the Gibbs energy of the electrolyte is equal to the sum of the Gibbs energies of the ions

$$G(M_{v_+} X_{v_-}) = v_+ G(M^{z_+}) + v_- G(X^{z_-}). \quad (8)$$

For any electrolyte, also in the case of incomplete dissociation,

$$G^\circ(M_{v_+} X_{v_-}) = v_+ G^\circ(M^{z_+}) + v_- G^\circ(X^{z_-}) \quad (9)$$

using Equations (5), (8), and (9) we get

$$m_{MX} \gamma_{MX} = (m_M \gamma_M)^{v_+} (m_X \gamma_X)^{v_-}. \quad (10)$$

In the case of complete dissociation the molalities of the ions are

$$m_M = v_+ m_{MX} \quad (11)$$

$$m_X = v_- m_{MX}. \quad (12)$$

Equations (10) and (5) are usually described with the mean activity coefficient (γ_\pm) so we get Equations (13) and (17), respectively.

$$m_{MX} \gamma_{MX} = (v_\pm m_{MX})^v (\gamma_\pm)^v \quad (13)$$

$$v = v_+ + v_- \quad (14)$$

$$v_\pm^v = (v_+)^{v_+} (v_-)^{v_-} \quad (15)$$

$$\gamma_\pm^v = (\gamma_M)^{v_+} (\gamma_X)^{v_-} \quad (16)$$

$$G_i = G_i^\circ + vRT \ln(v_\pm m_i \gamma_\pm) \quad (17)$$

2.2 General thermodynamic equations

The total Gibbs energy of a system is constructed by writing the Gibbs energies for each species; see Equations (4) and (5). Thus we get

$$G_{tot} = \sum n_i G_i = \sum n_i (G_i^\circ + RT \ln(a_i)). \quad (18)$$

The G_i° term in Equation (18) is derived through the relation:

$$G_i^\circ(T) = \Delta_f H_i^\circ(T) - TS_i^\circ(T). \quad (19)$$

The temperature dependencies of c_p and G are

$$c_p(T) = A + B\left(\frac{T}{K}\right) + C\left(\frac{T}{K}\right)^2 + D\left(\frac{T}{K}\right)^{-2} \quad (20)$$

$$G_i^\circ(T) = A_G + B_G\left(\frac{T}{K}\right) + C_G\left(\frac{T}{K}\right)\ln\left(\frac{T}{K}\right) + D_G\left(\frac{T}{K}\right)^2 + E_G\left(\frac{T}{K}\right)^3 + F_G\left(\frac{T}{K}\right)^{-1}, \quad (21)$$

where A - D and A_G - F_G are constants. From the basic thermodynamic equations for enthalpy and entropy and Equation (19) we can derive the relations between those constants as.

$$\Delta_f H_{298.15}^\circ = A_G - C_G 298.15 - D_G 298.15^2 - 2E_G 298.15^3 + 2F_G 298.15^{-1} \quad (22)$$

$$S_{298.15}^\circ = -B_G - C_G(\ln 298.15 + 1) - 2D_G 298.15 - 3E_G 298.15^2 + F_G 298.15^{-2} \quad (23)$$

$$c_p(T/K) = -C_G - 2D_G T - 6E_G T^2 - 2F_G T^{-2} \quad (24)$$

$$A = -C_G$$

$$B = -2D_G$$

$$C = -6E_G$$

$$D = -2F_G$$

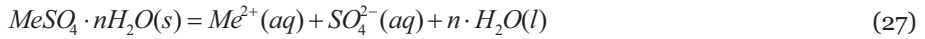
(25)

The general temperature dependency for the Pitzer equation parameter (p), which is needed to calculate the activity (a_i) of Equation (18), is, in this work

$$p = A_{Pitz} + B_{Pitz}\left(\frac{T}{K}\right) + C_{Pitz}\left(\frac{T}{K}\right)\ln\left(\frac{T}{K}\right) + D_{Pitz}\left(\frac{T}{K}\right)^2 + E_{Pitz}\left(\frac{T}{K}\right)^3 + F_{Pitz}\left(\frac{T}{K}\right)^{-1}. \quad (26)$$

2.2.1 Solubility and dissociation reactions

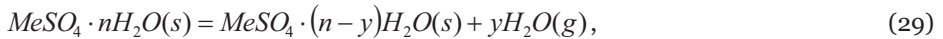
The solubility products of the solid phases in aqueous solutions are expressed by the following equations (27)-(28)



$$K_{SP_n} = \frac{a_{Me^{2+}(aq)} \cdot a_{SO_4^{2-}(aq)} \cdot a_w^n}{a_{MeSO_4 \cdot nH_2O(s)}} = \gamma_{\pm}^2 \cdot m^2 \cdot a_w^n, \quad (28)$$

where $n = 1, 4, 5, 6, 7$; $Me = Fe, Ni, Mn$ and a_w = the activity of water.

The dissociation pressure of the gas-solid reaction for hydrates is



where y is the stoichiometric number of $\text{H}_2\text{O}(\text{g})$ in gas dissociation reactions.

2.2.2 Heat capacity of ions

The heat capacities of the ions were estimated using a simplified Helgeson-Kirkham-Flowers (HKF) model [10]. According to the HKF model [11], the heat capacity of an ion can be calculated with Equation (30)

$$c_p^o = c_1 + \frac{c_2}{(T-\theta)^2} - \left(\frac{2T}{(T-\theta)^3} \right) \left(a_3(P-P_r) + a_4 \ln \left(\frac{\psi-P}{\psi-P_r} \right) \right) + \omega TX + 2TY \left(\frac{\partial \omega}{\partial T} \right)_P - T \left(\frac{1}{\varepsilon} - 1 \right) \left(\frac{\partial^2 \omega}{\partial T^2} \right)_P \quad (30)$$

where T = temperature in Kelvins; P = pressure in bar; P_r = reference pressure in bar; c_1 , c_2 , a_3 , a_4 = ionic specific parameters; ω = Born coefficient of ion; ε = dielectric constant; θ = solvent specific parameter 228 K; ψ = solvent specific parameter 2600 bar.

X and Y are Born functions depending on the dielectric constant of water

$$Y = - \left(\frac{\partial(1/\varepsilon)}{\partial T} \right)_P \quad (31)$$

$$X = \left(\frac{\partial Y}{\partial T} \right)_P. \quad (32)$$

The Born coefficient for an ion is essentially constant below 170 °C [11]. Thus, at the reference pressure, i.e., neglecting pressure effects, Equation (30) simplifies to [10]:

$$c_p^o = c_1 + \frac{c_2}{(T-\theta)^2} + \omega TX, \quad T < 170^\circ\text{C}. \quad (33)$$

3. Pitzer model

The Pitzer model is one of the most commonly used activity coefficient models for aqueous solutions. The original approach assumes that the aqueous solution consists only of ions, and no ion complexes are formed. The model was also validated and its ability to extrapolate to other conditions than those used in the parameter optimisations was tested in this work.

In 1973 Pitzer introduced an interaction model for the excess Gibbs energy of an aqueous solution, which is based on virial coefficients [2, 3]:

$$\frac{G^E}{RT} = n_w f(I) + \frac{1}{n_w} \sum_i \sum_j \lambda_{ij} n_i n_j + \frac{1}{n_w^2} \sum_i \sum_j \sum_k \mu_{ijk} n_i n_j n_k, \quad (34)$$

where n_w is the amount of water in moles, λ_{ij} and μ_{ijk} are the second and third virial coefficients, and n_i , n_j , and n_k are the amounts of species in solution.

$f(I)$ is a function of ionic strength, temperature, and solvent properties and describes the long-range electrostatic forces. Pitzer assumed that the λ and μ coefficients are symmetrical, i.e., $\lambda_{ij} = \lambda_{ji}$ and ignored all short-range interactions between three cations or three anions.

By combining virial coefficients and changing moles to molalities we get:

$$\begin{aligned} \frac{G^{E,m}}{n_w RT} = & f(I) + 2 \sum_c \sum_a m_c m_a \left[B_{ca} + \left(\sum_c m_c z_c \right) C_{ca} \right] \\ & + \sum_c \sum_{c'} m_c m_{c'} \left[2\Phi_{cc'} + \sum_a m_a \psi_{cc'a} \right] + \sum_a \sum_{a'} m_a m_{a'} \left[2\Phi_{aa'} + \sum_c m_c \psi_{aa'c} \right] \\ & + 2 \sum_n \sum_c m_n m_c \lambda_{nc} + 2 \sum_n \sum_a m_n m_a \lambda_{na} \end{aligned} \quad (35)$$

where the sums are over the various cations c, c' , anions a, a' and neutral n species. B_{ca} , C_{ca} , $\Phi_{cc'}$, $\Phi_{aa'}$, $\psi_{cc'a}$, and $\psi_{aa'c}$ are interaction parameters between cations and anions and λ_{nc} and λ_{na} are parameters for interactions between an electrically neutral species and a cation or an anion, respectively. Following the notation of Sippola [29] – note the corrections made to Equations (43) and (44) of this thesis – the osmotic and activity coefficients of species can be derived from Equation (35), assuming that λ and ψ

are independent of concentration and C_{ca}^ϕ is concentration-dependent.

$$\begin{aligned}
 (\phi - 1) = & - \left(\frac{1}{RT \sum_i m_i} \right) \left(\frac{\partial G^{E,m}}{\partial w_w} \right)_{T,p,n_i} = \left(\frac{2}{\sum_i m_i} \right) \left(If^\phi(I) + \sum_c \sum_a m_c m_a [B_{ca}^\phi + ZC^\phi] \right. \\
 & + \sum_c \sum_{<c'} m_c m_{c'} \left[\Phi_{cc'}^\phi + \sum_a m_a \psi_{cc'a} \right] + \sum_a \sum_{<a'} m_a m_{a'} \left[\Phi_{aa'}^\phi + \sum_c m_c \psi_{aa'c} \right] \\
 & \left. + \sum_n \sum_c m_n m_c \lambda_{nc} + \sum_n \sum_a m_n m_a \lambda_{na} \right) \quad (36)
 \end{aligned}$$

where Z and the parameters with osmotic coefficients are

$$Z = \sum_i m_i |z_i| \quad (37)$$

$$f^\phi(I) = \frac{1}{2} \left[f' - \frac{f(I)}{I} \right], \quad f' = \left(\frac{\partial f}{\partial I} \right) \quad (38)$$

$$B_{ca}^\phi = B_{ca} + IB', \quad B' = \left(\frac{\partial B_{ca}}{\partial I} \right) \quad (39)$$

$$C_{ca}^\phi = C_{ca} + \frac{IC'}{2}, \quad C' = \left(\frac{\partial C_{ca}}{\partial I} \right) \quad (40)$$

$$\Phi_{cc'}^\phi = \Phi_{cc'} + I\Phi', \quad \Phi' = \left(\frac{\partial \Phi_{cc'}}{\partial I} \right) \quad (41)$$

$$\Phi_{aa'}^\phi = \Phi_{aa'} + I\Phi', \quad \Phi' = \left(\frac{\partial \Phi_{aa'}}{\partial I} \right). \quad (42)$$

The activity coefficient of a cation M is.

$$\begin{aligned}
 \ln \gamma_M = & \frac{1}{RT} \left(\frac{\partial G^{E,m}}{\partial n_M} \right)_{T,p,n_w,n_j,i \neq M} = z_M^2 f^\gamma(I) + \sum_a m_a [2B_{Ma} + ZC_{Ma}] \\
 & + z_M \sum_c \sum_a m_c m_a C_{ca} + z_M^2 \sum_c \sum_a m_c m_a \left[B'_{ca} + \frac{1}{2} ZC'_{ca} \right] \\
 & + \sum_c m_c \left[2\Phi_{Mc} + \sum_a m_a \psi_{Mca} \right] + z_M^2 \sum_c \sum_{<c'} m_c m_{c'} \Phi'_{cc'} \\
 & + z_M^2 \sum_a \sum_{<a'} m_a m_{a'} \Phi'_{aa'} + \sum_a \sum_{<a'} m_a m_{a'} \psi_{Maa'} + 2 \sum_n m_n \lambda_{nM}
 \end{aligned} \quad (43)$$

The activity coefficient of an anion X is.

$$\begin{aligned}
\ln \gamma_X &= \frac{1}{RT} \left(\frac{\partial G^{E,m}}{\partial n_X} \right)_{T,p,n_w,n_i,i \neq X} = z_X^2 f^\gamma(I) + \sum_c m_c [2B_{cX} + ZC_{cX}] \\
&+ |z_X| \left[\sum_c \sum_a m_c m_a C_{ca} + z_X^2 \sum_c \sum_a m_c m_a \left[B'_{ca} + \frac{1}{2} ZC'_{ca} \right] \right. \\
&+ \sum_a m_a \left[2\Phi_{Xa} + \sum_c m_c \psi_{Xac} \right] + z_X^2 \sum_c \sum_{c'} m_c m_{c'} \Phi'_{cc'} \\
&+ z_X^2 \sum_a \sum_{a'} m_a m_{a'} \Phi'_{aa'} + \sum_c \sum_{c'} m_c m_{c'} \psi_{cc'X} + 2 \sum_n m_n \lambda_{nX}
\end{aligned} \tag{44}$$

The activity coefficient of a neutral species N is

$$\ln \gamma_N = \frac{1}{RT} \left(\frac{\partial G^{E,m}}{\partial n_N} \right)_{T,p,n_w,n_i,i \neq N} = 2 \sum_c m_c \lambda_{Nc} + 2 \sum_a m_a \lambda_{Na} . \tag{45}$$

3.1 Concentration dependence of second and third virial coefficients

This chapter follows the paper by Sippola [29] – note the corrections made to Equations (50), (51), (57), (58) and (59a) of this thesis. Pitzer [2] tried different Debye-Hückel functions and chose the best, which was

$$f^\phi(I) = \frac{-A_\phi \sqrt{I}}{1 + b\sqrt{I}}, \tag{46}$$

where A_ϕ is the temperature- and solvent-dependent Debye-Hückel constant and b is a constant with the value 1.2. Solving f and f' from Equation (38) yields

$$f = -A_\phi \frac{4I}{b} \ln(1 + b\sqrt{I}) \tag{47}$$

$$f' = -A_\phi \left(\frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{b} \ln(1 + b\sqrt{I}) \right). \tag{48}$$

Pitzer used the following concentration dependency for the parameter B_{ca}^ϕ

$$B_{ca}^\phi = \beta^{(0)} + \beta^{(1)} \exp(-\alpha_1 \sqrt{I}) + \beta^{(2)} \exp(-\alpha_2 \sqrt{I}). \tag{49}$$

$\beta^{(0)}$, $\beta^{(1)}$, and $\beta^{(2)}$ are electrolyte-specific Pitzer parameters and α_1 and α_2 are electrolyte-dependent constants. Combining Equations (39) and (49) we get:

$$B_{ca} = \beta^{(0)} + \beta^{(1)} g(\alpha_1 \sqrt{I}) + \beta^{(2)} g(\alpha_2 \sqrt{I}) \tag{50}$$

$$B'_{ca} = \beta^{(1)} g'(\alpha_1 \sqrt{I}) + \beta^{(2)} g'(\alpha_2 \sqrt{I}), \tag{51}$$

where the $g(x)$ and $g'(x)$ functions are

$$g(x) = \frac{2(1 - (1+x)e^{-x})}{x^2} \quad (52a)$$

$$g'(x) = \frac{-2(1 - (1+x + \frac{x^2}{2})e^{-x})}{x^2} = e^{-x} - g(x). \quad (52b)$$

Pitzer [30] compared the calculated and experimental data and ended up with the following values for the electrolyte-dependent constants α_1 and α_2 listed in Table 1.

Table 1. Internal parameters ($b = 1.2$) of the original Pitzer model.

Electrolyte type	α_1	α_2
1-1, 1-2, 1-3, 1-4	2.0	-
2-2	1.4	12
2-3 and higher valence	2.0	50

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

$$\Phi_{ij} = \theta_{ij} + {}^E\theta_{ij}(I), \quad (53)$$

where θ_{ij} and ${}^E\theta_{ij}$ are the Pitzer parameters for the short- and long-range interactions between two ions with the same sign, respectively [31]. Using Equations (41) or (42) we get

$$\Phi_{ij}^\phi = \theta_{ij} + {}^E\theta_{ij}(I) + I {}^E\theta'_{ij}(I) \quad (54)$$

$$\Phi'_{ij} = {}^E\theta'_{ij}(I). \quad (55)$$

${}^E\theta_{ij}$ terms are zero for ions with an equal charge and for ions that are unequal but have same charge these terms can be calculated numerically. Pitzer tested experimental data for 15 different ternary systems and concluded that the ${}^E\theta_{ij}$ terms can be omitted [31].

Later, Harvie et al. [32, 33] included ${}^E\theta_{ij}$ terms in their modification of the Pitzer model, which was shown to improve the fit in multicomponent brine systems. ${}^E\theta_{ij}$ terms can be included in the Pitzer model either by direct numerical integration or by the Pitzer derived analytical approximation method [31].

In the original work Pitzer assumed that the C_{ca} , $\psi_{cc'a}$, and $\psi_{aa'c}$ parameters are independent of the concentration. However, Archer [34] introduced the following concentration dependency of C_{ca}^ϕ

$$C_{ca}^\phi = C_{ca}^{(0)} + C_{ca}^{(1)} \exp(-\omega\sqrt{I}), \quad (56)$$

where $C_{ca}^{(0)}$ and $C_{ca}^{(1)}$ are electrolyte-dependent parameters and ω is usually constant (= 2.5) for all electrolytes. From Equation (40) we get:

$$C_{ca} = C_{ca}^{(0)} + 4C_{ca}^{(1)}h(\omega\sqrt{I}) \quad (57)$$

$$C_{ca} = \frac{4C_{ca}^{(1)}h'(\omega\sqrt{I})}{I}, \quad (58)$$

where the $h(x)$ and $h'(x)$ functions are

$$h(x) = \frac{\left\{6 - \left[6 + x(6 + 3x + x^2)\right]e^{-x}\right\}}{x^4} \quad (59a)$$

$$h'(x) = \frac{e^{-x}}{2} - 2h(x). \quad (59b)$$

It should be noticed that the concentration-dependent C_{ca}^ϕ parameter in Equations (40) and (56) has a different interpretation than in the original Pitzer model [2] but it reduces to C^ϕ if the parameter $C_{ca}^{(2)}$ is set to zero.

3.2 First derivative enthalpy

The temperature derivative of the excess Gibbs energy is called the apparent molal enthalpy of the solution (${}^\phi L$). The relationship between ${}^\phi L$ and the measured enthalpy of the solution $\Delta H_s(T)$ is calculated using Equation (61). The Pitzer model equation for ${}^\phi L$ is in Equation (62)

$${}^\phi L = -T^2 \left(\frac{\partial \left(\frac{G^{E,m}}{T} \right)}{\partial T} \right)_{P,m} \quad (60)$$

$$\Delta H_s(T) = \Delta H_s^\circ(T) + {}^\phi L \quad (61)$$

$${}^\phi L = \nu |z_M z_X| A_L \frac{\ln \left(1 + bI^{\frac{1}{2}} \right)}{2b} - 2\nu_M \nu_X RT^2 m \times \left[\beta^{(0)L} + g \left(\alpha_1 I^{\frac{1}{2}} \right) \beta^{(1)L} + g \left(\alpha_2 I^{\frac{1}{2}} \right) \beta^{(2)L} + \frac{m \nu_M z_M}{2 |z_M z_X|^{\frac{1}{2}}} C^{\phi L} \right] \quad (62)$$

where the symbol A_L refer to

$$\frac{A_L}{RT} = 4T \left(\frac{\partial A_\phi}{\partial T} \right)_P \quad (63)$$

and the Pitzer parameters are temperature derivatives of the activity coefficient parameters

$$\beta^{(i)L} = \left(\frac{\partial \beta^{(i)}}{\partial T} \right)_p, \quad i = 0, 1, 2 \quad (64)$$

$$C^{\phi L} = \left(\frac{\partial C^{\phi}}{\partial T} \right)_p. \quad (65)$$

3.3 Second derivative heat capacity

The apparent molal heat capacity (${}^{\phi}c_p$) is a temperature derivative of ${}^{\phi}L$ according to Equation (66), where c_{p2}° is the heat capacity of a solution at infinite dilution. The relationship between the apparent molal heat capacity (${}^{\phi}c_p$) of the solution and the measured heat capacity of the solution c_{p2} is calculated using Equation (67), where c_{pw}° is the heat capacity of the pure solvent i.e. water. The Pitzer model equation for ${}^{\phi}c_p$ is in Equation (68)

$${}^{\phi}c_p - c_{p2}^{\circ} = \left(\frac{\partial {}^{\phi}L}{\partial T} \right)_{p,m} \quad (66)$$

$${}^{\phi}c_p = \frac{m_{g,sol}c_{p2} - n_w c_{pw}^{\circ}}{n_2} \quad (67)$$

$$\begin{aligned} {}^{\phi}c_p = c_{p2}^{\circ} + \nu |z_M z_X| A_J \frac{\ln \left(1 + bI^{\frac{1}{2}} \right)}{2b} - 2\nu_M \nu_X RT^2 m \\ \times \left[\beta^{(0)J} + g \left(\alpha_1 I^{\frac{1}{2}} \right) \beta^{(1)J} + g \left(\alpha_2 I^{\frac{1}{2}} \right) \beta^{(2)J} + \frac{m \nu_M z_M}{2 |z_M z_X|^{\frac{1}{2}}} C^{\phi J} \right] \end{aligned} \quad (68)$$

where the symbol A_J refer to

$$A_J = \left(\frac{\partial A_L}{\partial T} \right)_p \quad (69)$$

and the Pitzer parameters are the second temperature derivatives of the activity coefficient parameters

$$\beta^{(i)J} = \left(\frac{\partial^2 \beta^{(i)}}{\partial T^2} \right)_p + \frac{2}{T} \left(\frac{\partial \beta^{(i)}}{\partial T} \right)_p, \quad i = 0, 1, 2 \quad (70)$$

$$C^{\phi J} = \frac{\partial^2 C^{\phi}}{\partial T^2} + \frac{2}{T} \left(\frac{\partial C^{\phi}}{\partial T} \right). \quad (71)$$

The values of the Debye-Hückel parameters used in this work are $A_{\phi} = 0.39147$, $A_L = 1985.287$, and $A_J = 32.64$ at 25 °C.

4. Assessment

Evaluation of the thermodynamic properties of the aqueous phase, as well as the condensed metal sulfate hydrates, was carried out using the *MTDATA*[®] assessment module, version 4.81, and *MTDATA* Studio 5.03, using Harvie's modification of the Pitzer equation [32, 33]. The assessment module minimises the weighted sum of squares of errors between the measured and fitted values, according to Equation (72). Thus, the objective function (OF) to be minimised in the parameter optimisation can be written as

$$OF = \sum_{i=1}^n W_i \left(\frac{C_i - E_i}{U_i} \right)^2, \quad (72)$$

where n is the number of properties (data items) to be reproduced, C_i and E_i are the calculated and experimental values of the property i , U_i is the uncertainty associated with the value E_i , and W_i is the weight assigned to the property i ; in this work $W_i = 1$ or 0.

Figure 1 shows schematically the work flow of this assessment procedure. First, the experimental data are collected from the literature and then they are critically evaluated. After that the standard thermodynamic data of each species are collected in a database as $\Delta_f H^\circ_{298.15}$, $S^\circ_{298.15}$, and $c_p(T)$ or $G(T)$; see Equations (19)-(25). An excess Gibbs energy model is also needed, which is the Pitzer model in this work. Finally, the objective function is minimised when optimising the Pitzer parameters and possibly the thermodynamic properties of unknown or not-so-well-known species. If that is done successfully, the result is an internally consistent thermodynamic database.

The most important part is the critical evaluation of the experimental data. It is also important to keep the number of optimised parameters low enough. The objective function is sensitive to the given experimental errors or weights of each data point. In this thesis the weight of each point is 1 with the exception of rejected values, where 0 was used. An important part after optimisation is the validation of the model using data that were not included in the optimisation.

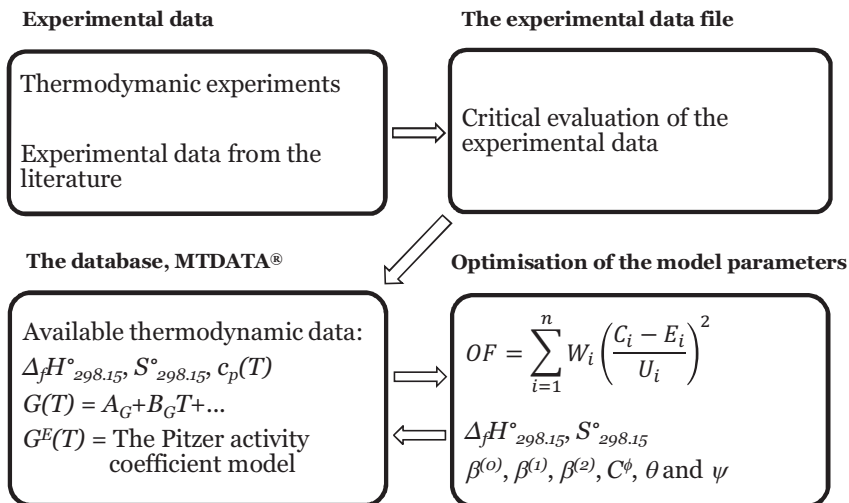


Figure 1. The assessment procedure.

5. Results and discussion

As the *CALPHAD* method [1] was used in order to build an internally consistent thermodynamic model, the results are divided into unary, binary, and ternary chapters. Metal sulfate systems have also been compared in this thesis, showing the results from Publications I-V in a somewhat different way.

5.1 Unary data

It was found out that the heat capacity data of H₂O at a temperature lower than room temperature were not accurate in the *MTDATA*[®] *MTAQ/nplaq* (resource.npl.co.uk/mtdata/aqueous.htm) database. So a recalculation of the properties of H₂O was needed. The data for ions were taken from a simplified Helgeson-Kirkham-Flowers (*HKF*) model from Sippola [10]. Since no proper data for solid phases which include crystalline waters were available, (*CODATA* [35] does not include these values), the enthalpy of the formation and entropy of species were optimised in this work with Pitzer model parameters using c_p data from DeKock [36] for the solids. The results are shown in Tables 2 and 3 with reference to Publications I-III (P_I, P_{II}, or P_{III}), together with the other data used, which were taken from the literature.

Table 2. Heat capacity of species.

T_{max}, K	A	B	$C \cdot 10^{-3}$	$D \cdot 10^5$		
550	106.688	0.8655	0	0	NiSO ₄ ·7H ₂ O(s)	[37]
550	69.435	0.867	0	0	α-NiSO ₄ ·6H ₂ O(s)	[37]
550	147.458	0.6283	0	0	β-NiSO ₄ ·6H ₂ O(s)	[36]
550	24.200	0.3763	0	0	NiSO ₄ ·H ₂ O(s)	[36]
398	379.822	0.3619	0	-82.245	FeSO ₄ ·7H ₂ O(s)	[10]
398	76.078	0.6435	0	0	FeSO ₄ ·4H ₂ O(s)	[10]
398	55.293	0.2798	0	0	FeSO ₄ ·H ₂ O(s)	[10]
550	81.372	1.0041	0	0	MnSO ₄ ·7H ₂ O(s)	[36]
550	101.823	0.7531	0	0	MnSO ₄ ·5H ₂ O(s)	[36]
550	25.784	0.3766	0	0	MnSO ₄ ·H ₂ O(s)	[36]
323.15	16343.10	-66.3614	75.6890	-2964.29	Ni ²⁺ (aq)	[38]
403.15	-586.04	3.6087	-5.7300	-18.4188		
448.15	2790.51	-5.0510	0	-1345.28		
328.15	14279.40	-57.8948	65.9339	-2588.70	Fe ²⁺ (aq)	[10]
413.15	-1363.44	6.4203	-8.5393	165.15		
448.15	3170.88	-5.6005	0	-1585.87		
323.15	13234.90	-53.9590	61.8370	-2365.61	Mn ²⁺ (aq)	[11]
398.15	-414.06	2.8850	-4.8000	-27.90		
448.15	2737.52	-4.9020	0	-1314.44		
328.15	46200.60	-186.8004	211.9290	-8546.29	SO ₄ ²⁻ (aq)	[10]
403.15	1080.77	-0.7188	-3.9917	-676.58		
448.15	5857.78	-10.7722	0	-2907.89		
343.15	21245.30	-84.1929	93.5145	-4083.14	OH ⁻ (aq)	[10]
448.15	-5250.28	20.4720	-23.0421	985.66		
328.15	48246.05	-197.6415	227.7310	-8546.29	HSO ₄ ⁻ (aq)	[10]
403.15	3126.22	-11.5599	11.8103	-676.58		
448.15	7903.23	-21.6133	15.8020	-2907.89		
273.15	2.113	0.1305	0	0	H ₂ O(s)	[Pi]
298.15	134.400	-0.3859	0.6294	0	H ₂ O(l)	[Pi]
373.15	89.810	-0.0943	0.1530	0		
500	311.953	-0.8588	0.8951	-55.991		
1100	28.409	0.0125	0.0004	1.283	H ₂ O(g) ^a	[Pi]

^aMTDATA[®] MTAQ/nplaq 1.0 database.

Table 3. Standard enthalpy and entropy of species.

$\Delta_f H^\circ_{298.15}$, kJ/mol	$S^\circ_{298.15}$, J/molK		
-2976.61	379.16	NiSO ₄ ·7H ₂ O(s)	[P _I]
-2683.73	331.96	α-NiSO ₄ ·6H ₂ O(s)	[P _I]
-2676.56	353.85	β-NiSO ₄ ·6H ₂ O(s)	[P _I]
-1193.71	140.4	NiSO ₄ ·H ₂ O(s)	[P _I]
-3017.51	395.30	FeSO ₄ ·7H ₂ O(s)	[P _{II}]
-2131.06	270.60 ^a	FeSO ₄ ·4H ₂ O(s)	[P _{II}]
-1245.65	141.66	FeSO ₄ ·H ₂ O(s)	[P _{II}]
-3135.92	449.18	MnSO ₄ ·7H ₂ O(s)	[P _{III}]
-2551.23	352.48	MnSO ₄ ·5H ₂ O(s)	[P _{III}]
-1375.75	175.02	MnSO ₄ ·H ₂ O(s)	[P _{III}]
0.0	0.00	H ⁺ (aq)	By definition
-53974	-128.87	Ni ²⁺	[11, 38]
-92260.0	-105.90	Fe ²⁺ (aq)	[10, 11]
-220597.2	-73.64	Mn ²⁺ (aq)	[11]
-909340.0	18.50	SO ₄ ²⁻ (aq)	[35]
-230015.0	-10.90	OH ⁻ (aq)	[35]
-885200.0	137.50	HSO ₄ ⁻ (aq)	[10]
-292.74	44.78	H ₂ O(s)	[39]
-285.83	69.95	H ₂ O(aq)	[35]
-241.83	188.73	H ₂ O(g)	[35]

^aSippola [10] entropy value was used.

5.2 Binary systems

NiSO₄-H₂O, FeSO₄-H₂O and MnSO₄-H₂O systems were modelled in Publications I-III, respectively. The H₂SO₄-H₂O data from Sippola [29] were used to build ternary systems in this work. The primary data used in the parameter optimisation in this work were taken from the solubility and water activity measurements, which represent the primary water vapour pressure data without any assumptions. The data for the enthalpy and heat capacity of solution were also reproduced well. Figures 2-4 (below) summarise some of the results. Since plotting the activity of water as a function of MeSO₄ would not show the difference between the metals in Figure 2, the osmotic coefficient of each binary is shown instead at 25 °C. It can be seen from the figure that the minimum value of the osmotic coefficient for FeSO₄ is about 0.4 mol/kg, while for NiSO₄ and MnSO₄ it is close to 0.9 mol/kg. Figure 3 shows the enthalpy of dilution ($\Delta H_{dil} = \Delta H_s(m) - \Delta H_s(1.11)$) to a reference solution of 1 mol of MeSO₄ per 50 moles of H₂O (1.11 mol/kg) at 25 °C. In that way it is possible to compare the enthalpy of dilution of the different binaries, which is not possible from the figures in Publications I-III because of the different ordinate values. Figure 4 shows the solubility of each metal sulfate in water. The freezing point depression is also shown in the figure. The eutectic temperatures according to the model are -11.4 °C (MnSO₄), -3.18 °C (NiSO₄), and -1.96 °C (FeSO₄). There is an interesting area close to the peritectic temperature (56.5 °C) of FeSO₄ where all the sulfates seem to have roughly the same solubility (3.6 mol/kg) in water, as shown in Figure 4.

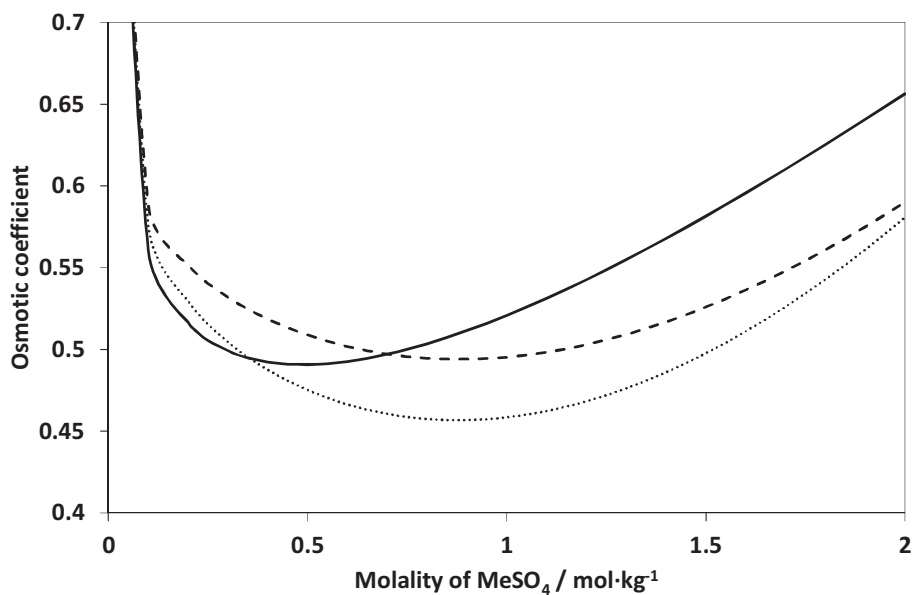


Figure 2. Osmotic coefficient at 25 °C. —FeSO₄-H₂O, - - -MnSO₄-H₂O and ···NiSO₄-H₂O according to this assessment.

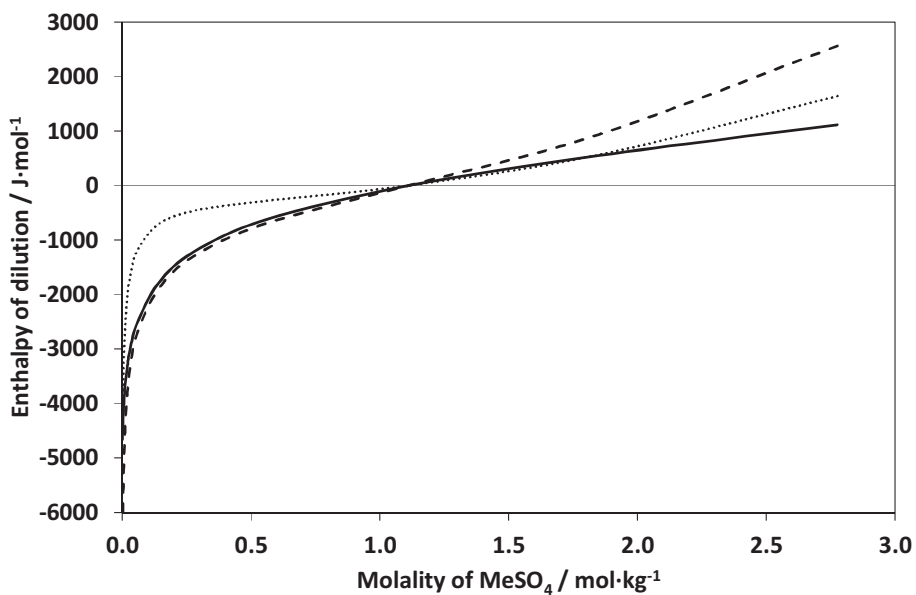


Figure 3. The calculated enthalpy of dilution ($H_s(m)-H_s(1.11)$); the reference solution is thus 1 mol of MeSO₄ per 50 moles H₂O) at 25 °C. —FeSO₄-H₂O, - - -MnSO₄-H₂O and ···NiSO₄-H₂O according to this work.

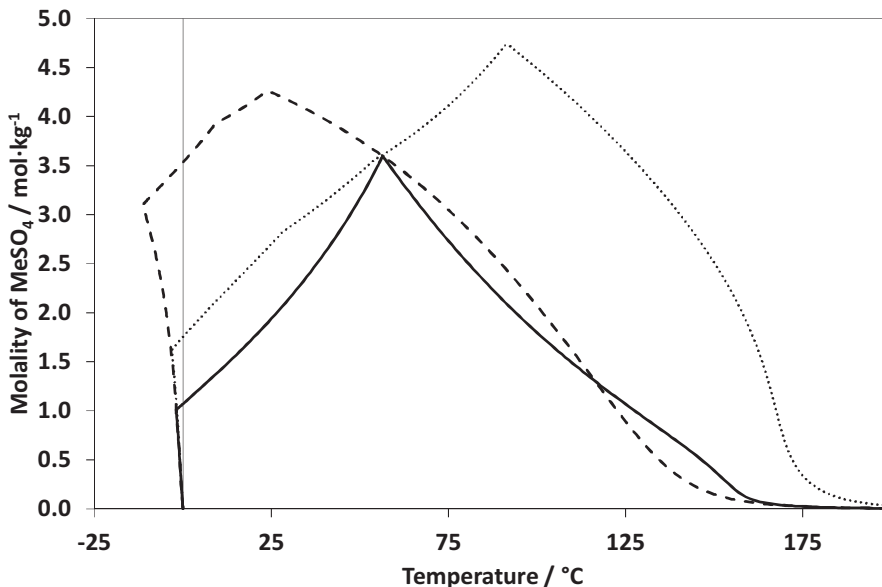


Figure 4. The assessed solubilities of metal sulfate systems. — $\text{FeSO}_4\text{-H}_2\text{O}$, --- $\text{MnSO}_4\text{-H}_2\text{O}$ and $\cdots\text{NiSO}_4\text{-H}_2\text{O}$ obtained in this work.

5.3 Ternary systems

The $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ (Publication IV) and $\text{NiSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ (Publication V) ternaries were modelled using solubility data at 0-100 °C and 0-90 °C, respectively. The model was also validated using the solubility measurements available for dilute sulfuric acid solutions at 160-220 °C and 200-250 °C, respectively. Figures 5-6 show the solubilities of FeSO_4 and NiSO_4 in sulfuric acid at 25 °C. Also shown are stable solid phases and experimental data from the literature. A comparison of the solubility of iron and nickel in sulfuric acid is presented in Figure 7. As can be seen, there are areas where one sulfate is fully dissolved (a homogeneous aqueous solution), while the other sulfate also forms a solid phase. Note that if we add all the components to one solution (the $\text{NiSO}_4\text{-FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ system) there will be new interactions between the ions and the solution may behave in a different way from that shown in Figure 7. Similar comparisons can easily be calculated at other temperatures using this model. The Pitzer parameters evaluated in this work are shown in Table 4.

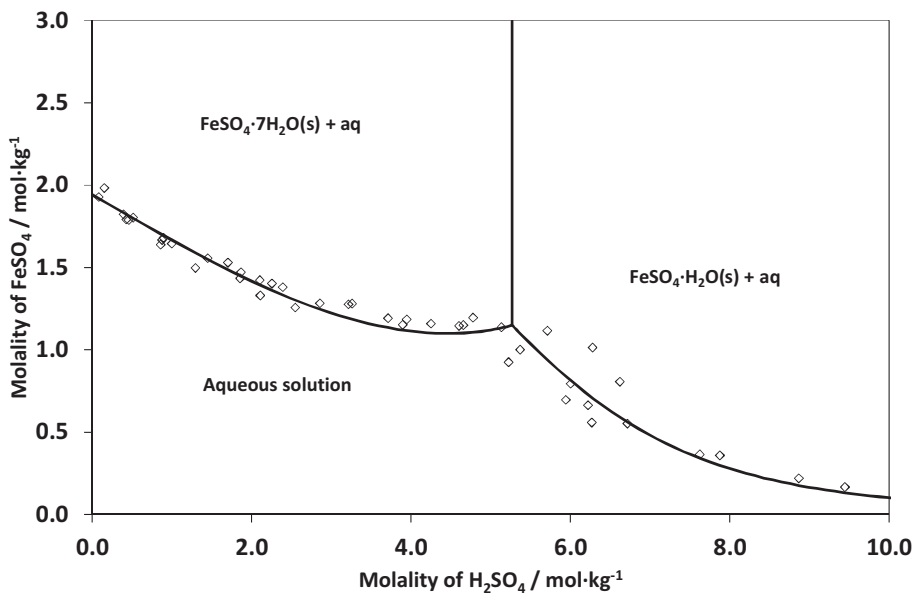


Figure 5. Solubility of ferrous sulfate in sulfuric acid at 298.15 K. The experimental data are from Cameron [40], Bullough et al. [41], and Belopol'skii and Urusov [42].

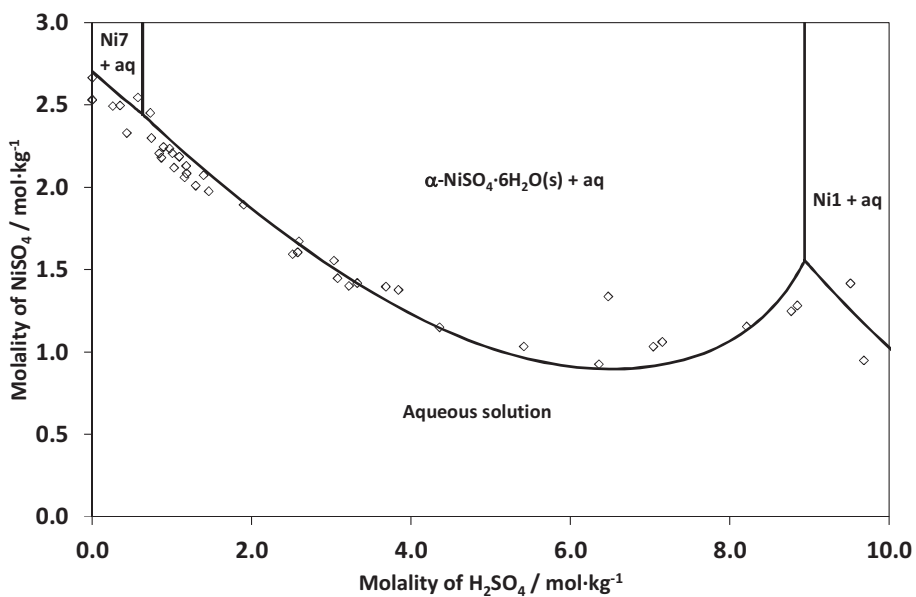


Figure 6. Solubility of NiSO_4 in sulfuric acid at 298.15 K. The experimental data are from Addlestone [43], Shkodina et al. [44], and Rohmer [45]. $\text{Ni7} = \text{NiSO}_4 \cdot 7\text{H}_2\text{O}(\text{s})$ and $\text{Ni1} = \text{NiSO}_4 \cdot \text{H}_2\text{O}(\text{s})$.

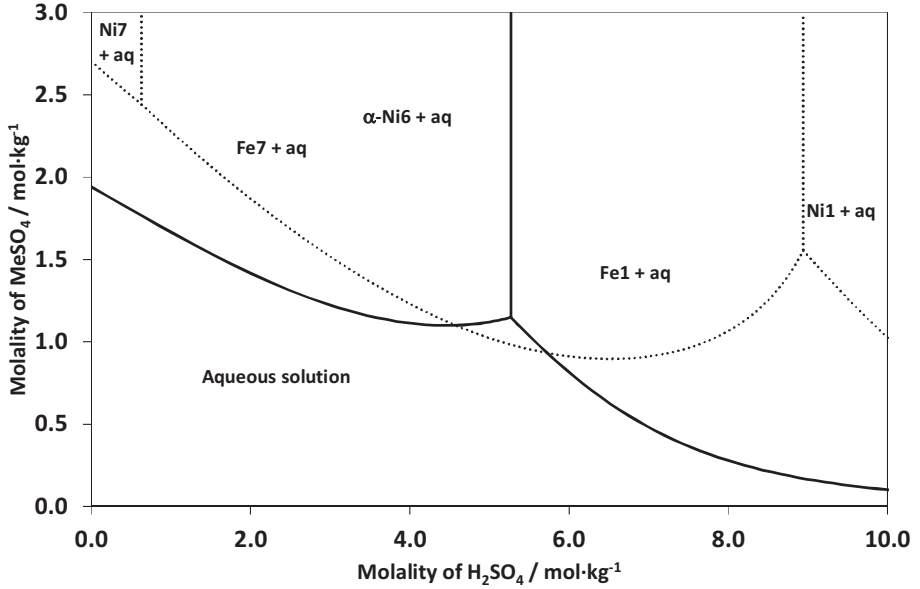


Figure 7. A comparison of the solubilities of the $-\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ and $\cdot\cdot\text{NiSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ system at 298.15 K. $\text{Fe7} = \text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{s})$, $\text{Fe1} = \text{FeSO}_4 \cdot \text{H}_2\text{O}(\text{s})$, $\text{Ni7} = \text{NiSO}_4 \cdot 7\text{H}_2\text{O}(\text{s})$, $\alpha\text{-Ni6} = \alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}(\text{s})$ and $\text{Ni1} = \text{NiSO}_4 \cdot \text{H}_2\text{O}(\text{s})$.

Table 4. Assessed Pitzer parameters used in this work. The Pitzer parameters C_{Pitz} and E_{Pitz} were found unnecessary; see Equation (26).

	A_{Pitz}	B_{Pitz}	$D_{\text{Pitz}} \cdot 10^{-4}$	F_{Pitz}	$p(25^\circ\text{C})$
$\beta^{(0)}_{\text{Ni-SO}_4}$	0.40892			-75.73582	0.15490
$\beta^{(1)}_{\text{Ni-SO}_4}$	7.02089			-1192.39972	3.02156
$\beta^{(2)}_{\text{Ni-SO}_4}$	595.45536	-1.23307		-79106.27192	-37.50820
$C^{\phi}_{\text{Ni-SO}_4}$	-0.09686			41.08029	0.04092
$\beta^{(0)}_{\text{Ni-HSO}_4}$	0.28304				0.28304
$\beta^{(1)}_{\text{Ni-HSO}_4}$	-1.79329			2565.11390	6.81015
$C^{\phi}_{\text{Ni-HSO}_4}$	0.01270				0.01270
$\beta^{(0)}_{\text{Fe-SO}_4}$	5.19343	-0.01609	0.18349	-508.26086	0.32107
$\beta^{(1)}_{\text{Fe-SO}_4}$	15.85143	0.00845	-0.60442	-3205.27313	2.24836
$\beta^{(2)}_{\text{Fe-SO}_4}$	-16.21420				-16.21420
$C^{\phi}_{\text{Fe-SO}_4}$	-0.05882			12.80119	-0.01588
$\beta^{(0)}_{\text{Fe-HSO}_4}$	0.75865			-96.89215	0.43367
$\beta^{(1)}_{\text{Fe-HSO}_4}$	-14.45279			5787.61444	4.95897
$C^{\phi}_{\text{Fe-HSO}_4}$				-3.20972	-0.01077
$\beta^{(0)}_{\text{Mn-SO}_4}$	0.52459			-97.41705	0.19785
$\beta^{(1)}_{\text{Mn-SO}_4}$	92.13163	-0.23483	1.99205	-10896.79701	3.27560
$\beta^{(2)}_{\text{Mn-SO}_4}$	-182.79334			33186.70657	-71.48458
$C^{\phi}_{\text{Mn-SO}_4}$	-0.18843			61.95017	0.01935
$\psi_{\text{Fe-HSO}_4\text{-SO}_4}$	-0.25247			71.40747	-0.01297
$\beta^{(0)}_{\text{H-SO}_4}$	-0.04083			20.48760	0.02789
$C^{\phi}_{\text{H-SO}_4}$	0.18522			-42.79400	0.04169
$\beta^{(0)}_{\text{H-HSO}_4}$	0.02808			54.14100	0.20967
$\beta^{(1)}_{\text{H-HSO}_4}$	-0.00516			147.75900	0.49043

There are still missing ternaries in this aqueous solution database, including $\text{MnSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{NiSO}_4\text{-FeSO}_4\text{-H}_2\text{O}$, $\text{NiSO}_4\text{-MnSO}_4\text{-H}_2\text{O}$, and $\text{FeSO}_4\text{-MnSO}_4\text{-H}_2\text{O}$ systems; those should be modelled in the future. Figures 8-10 show how this model estimates selected metal sulfate water ternaries. In Figure 8 it can be seen that there is need for an interaction parameter ($\theta_{\text{Fe-Ni}}$) between Fe^{2+} and Ni^{2+} ions at 25 °C. It was found that with $\theta_{\text{Fe-Ni}} = 0.1137$ the experimental measurements of Oikova and Panaiotov [46] are well represented.

Figure 9 shows that there seems to be no need for an interaction parameter ($\theta_{\text{Mn-Ni}}$) between Mn^{2+} and Ni^{2+} at 75 °C since this model calculates well the experimental points of Shevchuk et al. [47]. Figure 10 shows the experimental values of Soroka et al. [48] at 100.6 °C. This is the temperature where the experimental measurements deviate a lot for both $\text{FeSO}_4\text{-H}_2\text{O}$ and $\text{MnSO}_4\text{-H}_2\text{O}$; see the $\text{MnSO}_4 = 0$ and $\text{FeSO}_4 = 0$ values in Figure 10. Since these were the only data found for the $\text{MnSO}_4\text{-FeSO}_4\text{-H}_2\text{O}$ ternary system it is difficult to say whether the model or the experiments are more reliable. What is evident is that data of this kind cannot be modelled using only the $\theta_{\text{Mn-Fe}}$ parameter. This kind of validation of the model shows its quality further.

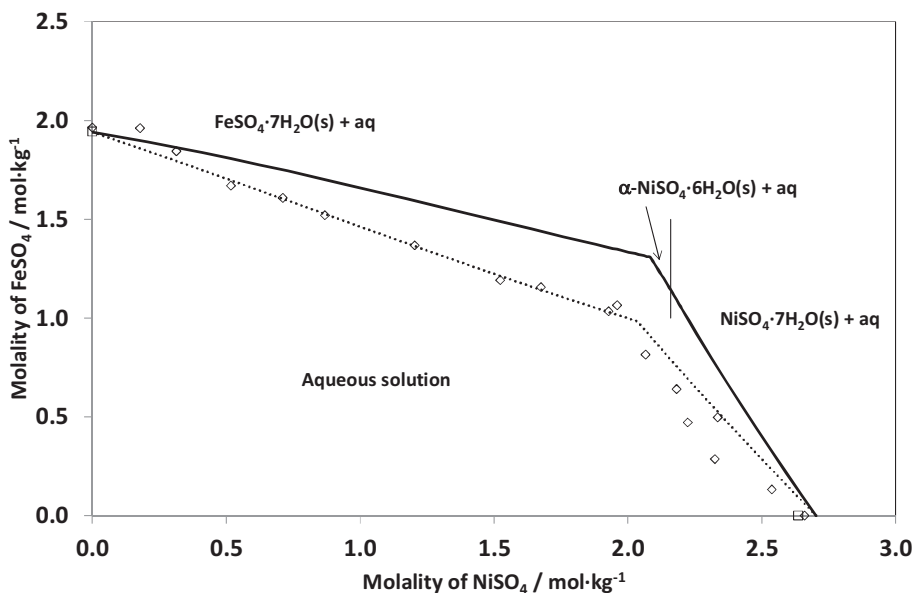


Figure 8. Validation of the model: solubility of the $\text{NiSO}_4\text{-FeSO}_4\text{-H}_2\text{O}$ system at 298.15 K with experimental data by (\diamond) Oikova and Panaiotov [46], (\square) Linke and Seidell [49, 50] and model calculations \cdots with and $-$ without the $\theta_{\text{Fe-Ni}}$ Pitzer parameter; also shown is the transformation line where the crystalline phase of nickel sulfate hydrate will change according to the model.

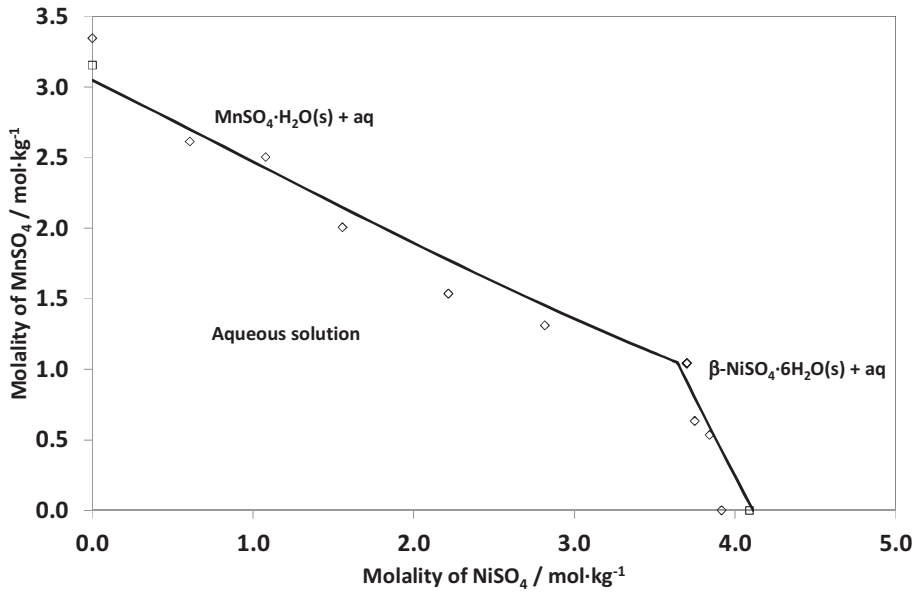


Figure 9. Validation of the model: solubility of the $\text{NiSO}_4\text{-MnSO}_4\text{-H}_2\text{O}$ system at 348.15 K with experimental data by (\diamond) Shevchuk et al. [47], (\square) Krepelka and Rejha [51], Linke and Seidell [50] and — model calculations, without the Pitzer parameter $\theta_{\text{Mn-Ni}}$.

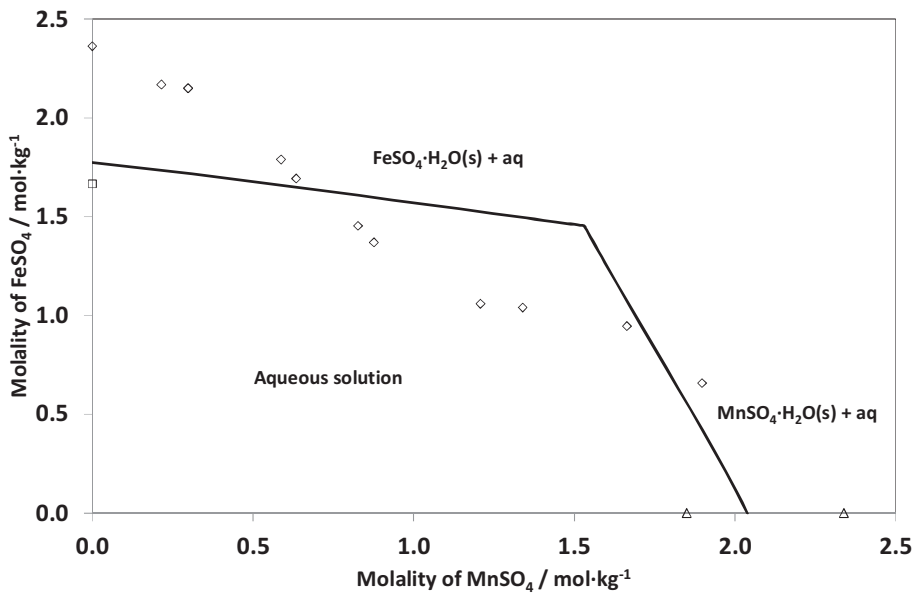


Figure 10. Validation of the model: solubility of the $\text{FeSO}_4\text{-MnSO}_4\text{-H}_2\text{O}$ system at 373.75 K with experimental data by (\diamond) Soroka et al. [48], (\square) Bullough et al. [41], (Δ) Eddy et al. [52], and Krepelka and Rejha [51] and — model calculations.

6. Conclusions

In this thesis the thermodynamics of $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{NiSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$, and $\text{MnSO}_4\text{-H}_2\text{O}$ systems were carefully assessed from the available experimental data (solubilities, eutectic and peritectic points, water activities, mean activity coefficients, osmotic coefficients, EMF data, vapour pressures, decomposition pressures, freezing point depression temperatures, and enthalpies and heat capacities of solution), published in the literature from 1855 to today. Previous thermodynamic models were also critically reviewed.

The current model presents the experimental data available on binary $\text{MeSO}_4\text{-H}_2\text{O}$ systems with a good accuracy and consistently over temperature intervals of $-2\text{--}220\text{ }^\circ\text{C}$ (FeSO_4), $-3\text{--}220\text{ }^\circ\text{C}$ (NiSO_4), and $-11\text{--}175\text{ }^\circ\text{C}$ (MnSO_4) and in concentrations from pure water to the solubility limit of metal sulfate hydrates, but the model has limitations at temperatures higher than $100\text{ }^\circ\text{C}$ as a result of the lack of experimental data. The experimental data available for $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ and $\text{NiSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ systems are presented with a good accuracy and consistently up to 100 and $90\text{ }^\circ\text{C}$, respectively and sulfuric acid concentrations up to 10 mol/kg . The model also predicts well the solubility measurements available in dilute sulfuric acid solutions at $160\text{--}250\text{ }^\circ\text{C}$.

The thermodynamic database created in this thesis still lacks proper assessments of the $\text{FeSO}_4\text{-NiSO}_4\text{-H}_2\text{O}$, $\text{FeSO}_4\text{-MnSO}_4\text{-H}_2\text{O}$, $\text{MnSO}_4\text{-NiSO}_4\text{-H}_2\text{O}$, and $\text{MnSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ ternary systems. The method used in this thesis can be used for other metal sulfates and other anions in order to further expand this aqueous database. It is suggested that the next system to be added to the database should be ferric iron $\text{Fe}_2(\text{SO}_4)_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$. Interactions in four-component systems should also be checked. It is assumed that only a small adjustment will be needed in four-component systems if the binary and ternary systems have been well modelled.

In the modelling of this database the need for experimental work arose. Because of the lack of experimental data, the heat capacity of crystalline $\text{MeSO}_4\cdot n\text{H}_2\text{O(s)}$ should be measured over a wide temperature range, preferably from $0\text{--}500\text{ K}$. More solubility measurements of MeSO_4 in sulfuric acid solutions at higher temperatures, above $90\text{ }^\circ\text{C}$, are also needed to ensure the correct solubilities.

There is also a need to make water activity and vapour pressure measurements at moderate to high temperatures to improve the current model in the area of industrial processes. Since the thermodynamic properties of the crystalline phases evaluated in Publications I, II, and III are related to the chosen values of metal ions, it would be more convenient to use $\Delta_f H^\circ_{298.15}$, $S^\circ_{298.15}$, and c_p values of Fe^{2+} , Ni^{2+} , and Mn^{2+} ions that are well evaluated and generally accepted.

This database for aqueous solutions can be updated in the future if new and more reliable measurements are found. Those new experiments can easily be added to the experimental files of MTDATA[®] and the new parameters of the model will be optimised quickly to improve the model further.

7. References

- [1] P.J. Spencer, A brief history of CALPHAD, CALPHAD 32 (2008) 1-8.
- [2] K.S. Pitzer, Thermodynamics of electrolytes. I. Theoretical basis and general equations, J. Phys. Chem. 77 (1973) 268-277.
- [3] K.S. Pitzer, G. Mayorga, Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent, J. Phys. Chem. 77 (1973) 2300-2308.
- [4] H. Renon, J.M. Prausnitz, Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures, AIChE J. 14 (1968) 135-144.
- [5] D.S. Abrams, J.M. Prausnitz, Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems, AIChE J. 21 (1975) 116-128.
- [6] P. Wang, A. Anderko, R.D. Young, A speciation-based model for mixed-solvent electrolyte systems, Fluid Phase Equilibria 203 (2002) 141-176.
- [7] B.S. Hemingway, R.R. Seal, I.M. Chou, Thermodynamic data for modeling acid mine drainage problems: compilation and estimation of data selected soluble iron-sulfate minerals, Open-File Report 02-161, <http://pubs.usgs.gov/of/2002/of02-161/OF02-161.htm> (12.11.2012), 2002.
- [8] E.J. Reardon, R.D. Beckie, Modelling chemical equilibria of acid mine-drainage: The $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ system, Geochim. Cosmochim. Acta 51 (1987) 2355-2368.
- [9] K.S. Pitzer, R.N. Roy, L.F. Silvester, Thermodynamics of electrolytes. 7. Sulfuric acid, J. Am. Chem. Soc. 99 (1977) 4930-4936.
- [10] H. Sippola, Solubility of ferrous sulphate in sulphuric acid—a thermodynamic model, Licentiate's Thesis (in Finnish), Helsinki University of Technology, 1992.
- [11] E.L. Shock, H.C. Helgeson, Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation of state predictions to 5 kb and 1000°C, Geochim. Cosmochim. Acta 52 (1988) 2009-2036.
- [12] D.N. Lyon, W.F. Giaque, Magnetism and the Third Law of Thermodynamics. Magnetic Properties of Ferrous Sulfate Heptahydrate from 1 to 20 °K. Heat Capacity from 1 to 310 °K, J. Am. Chem. Soc. 71 (1949) 1647-1657.
- [13] Y. Matsushima, A. Okuwaki, The second dissociation constant of sulfuric acid at elevated temperatures from potentiometric measurements, Bull. Chem. Soc. Jpn. 61 (1988) 3344-3346.

- [14] P. Kobylin, Thermodynamic modelling of aqueous solutions for stainless steel pickling processes, Licentiate's Thesis, Helsinki University of Technology, 2002.
- [15] P. Kobylin, T. Kaskiala, J. Salminen, Modeling of $\text{H}_2\text{SO}_4\text{-FeSO}_4\text{-H}_2\text{O}$ and $\text{H}_2\text{SO}_4\text{-Fe}_2(\text{SO}_4)_3\text{-H}_2\text{O}$ Systems for Metallurgical Applications, *Ind. Eng. Chem. Res.* 46 (2007) 2601-2608.
- [16] I. Chou, R.R. Seal II., Acquisition and evaluation of thermodynamic data for morenosite-retgersite equilibria at 0.1 MPa, *Am. Mineral.* 88 (2003) 1943-1948.
- [17] T.E. Graedel, C. Leygraf, Corrosion mechanisms for nickel exposed to the atmosphere, *J. Electrochem. Soc.* 147 (2000) 1010-1014.
- [18] E.J. Reardon, Ion interaction model applied to equilibria in the nickel(II) sulfate-sulfuric acid-water system, *J. Phys. Chem.* 93 (1989) 4630-4636.
- [19] S. Fugleberg, S.-. Hultholm, L. Rosenback, T. Holohan, Development of the Hartley Platinum leaching process, *Hydrometallurgy* 39 (1995) 1-10.
- [20] T. Kolhinen, Liukoisuustasapainot systeemissä $\text{NiSO}_4 - \text{NH}_3 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$, Master's thesis, Helsinki University of Technology, Department of Materials Science and Engineering, 1997.
- [21] T. Kolhinen, H. Jalkanen, Thermodynamic modeling of ammoniacal nickel sulfate solutions, *Scand. J. Metall.* 34 (2005) 334-339.
- [22] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, 2nd ed., Butterworth-Heinemann, Oxford, 1997.
- [23] F.G. Cottrell, On the Solubility of Manganous Sulphate, *J. Phys. Chem.* 4 (1899) 637-656.
- [24] R. Rohmer, Dehydration of manganous sulfate heptahydrate by the aqueous method, *C. R. Hebd. Seances Acad. Sci.* 209 (1939) 315-317.
- [25] A. Przepiera, Solubility equilibria of salts in electrolyte solutions $\text{MeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ Systems, Report (in Polish) 551/35, Prace Naukowe Politechniki Szczecinskiej, Institut Inzynierii Chemicznej I Chemii Fizycznej, 1999.
- [26] G. Azimi, V.G. Papangelakis, J.E. Dutrizac, Modelling of calcium sulphate solubility in concentrated multi-component sulphate solutions, *Fluid Phase Equilib.* 260 (2007) 300-315.
- [27] G. Azimi, Evaluating the Potential of Scaling due to Calcium Compounds in Hydrometallurgical Processes, Dissertation, University of Toronto, Canada, 2010.
- [28] M.C. Iliuta, K. Thomsen, P. Rasmussen, Modeling of heavy metal salt solubility using the extended UNIQUAC model, *AIChE J.* 48 (2002) 2664-2689.
- [29] H. Sippola, Critical evaluation of the 2nd dissociation constants for aqueous sulfuric acid, *Thermochim. Acta* 532 (2012) 65-77.
- [30] K.S. Pitzer, L.F. Silvester, Thermodynamics of electrolytes. 11. Properties of 3:2, 4:2 and other high-valence types, *J. Phys. Chem.* 82 (1978) 1239-1242.

- [31] K.S. Pitzer, Thermodynamics of electrolytes. V. effects of higher-order electrostatic terms, *J. Solution Chem.* 4 (1975) 249-265.
- [32] C.E. Harvie, J.H. Weare, The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-Cl-SO₄-H₂O system from zero to high concentration at 25° C, *Geochim. Cosmochim. Acta* 44 (1980) 981-997.
- [33] C.E. Harvie, N. Møller, J.H. Weare, The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O system to high ionic strengths at 25°C, *Geochim. Cosmochim. Acta* 48 (1984) 723-751.
- [34] D.G. Archer, Thermodynamic properties of the NaCl + H₂O system II. Thermodynamic properties of NaCl(aq), NaCl·H₂O(cr), and phase equilibria, *J. Phys. Chem. Ref. Data* 21 (1992) 793-829.
- [35] J.D. Cox, D.D. Wagman, V.A. Medvedev, CODATA key values for thermodynamics, Hemisphere Pub. Corp., New York, 1989.
- [36] C.W. DeKock, Thermodynamic properties of selected transition metal sulfates and their hydrates, Report IC 8910, U.S. Department of the Interior, Bureau of Mines, 1982.
- [37] J.W. Stout, R.C. Archibald, G.E. Brodale, W.F. Giauque, Heat and entropy of hydration of α-NiSO₄·6H₂O to NiSO₄·7H₂O. Their low-temperature heat capacities, *J. Chem. Phys.* 44 (1966) 405-409.
- [38] M. Hämäläinen, H. Rannikko, H. Sippola, Thermodynamic modelling of aqueous solutions, Report (in Finnish) TKK-V-C108, Department of Materials Science and Engineering, 1991.
- [39] V.P. Glushko, L.V. Gurvich, G.A. Bergman, I.V. Veyts, V.A. Medvedev, G.A. Kchachkurosov, et al., Thermodynamic Properties of Individual Substances, vol 1, part 2, Nauka, Moscow, 1978 (in Russian), p. 310.
- [40] F.K. Cameron, The Solubility of Ferrous Sulphate, *J. Phys. Chem.* 34 (1929) 692-710.
- [41] W. Bullough, T.A. Canning, M.I. Strawbridge, The solubility of ferrous sulphate in aqueous solutions of sulphuric acid, *J. Appl. Chem.* 2 (1952) 703-707.
- [42] A.P. Belopol'skii, V.V. Urusov, System ferrous sulfate-sulfuric acid-water. II. Solubilities and densities of solutions at temperatures from -20 °C to +25 °C, *Zh. Prikl. Khim.* 21 (1948) 781-793.
- [43] J.A. Addlestone, The system nickel sulfate-sulfuric acid-water at 25 °C and 0 °C, *J. Phys. Chem.* 42 (1938) 437-440.
- [44] T.V. Shkodina, M.I. Bakeev, A.A. Zharmenov, O.D. Kemalov, Nickel(2+) sulfate-sulfuric acid-water system at 25, 50 and 75 °C, *Russ. J. Inorg. Chem.* 36 (1991) 138-140.
- [45] R. Rohmer, Contributions to the study of nickel sulfate and of cobalt sulfate, *Ann. Chim.* 11 (1939) 611-725.
- [46] T. Oikova, P. Panaiotov, Thermodynamic study of the nickel(II) sulfate-iron(II) sulfate-water system at 25 °C, *God. Vissh. Khim. -Tekhnol. Inst.* 13 (1979) 171-178.

- [47] V.G. Shevchuk, V.A. Storozhenko, G.V. Petrov, Solubility in the system $\text{MnSO}_4\text{-NiSO}_4\text{-H}_2\text{O}$ at 75 °C, *Russ. J. Inorg. Chem.* 38 (1993) 507-508.
- [48] P.I. Soroka, T.E. Girich, M.L. Simich, Solubility-in the ferrous sulfate-manganese sulfate-water system at boiling temperatures of saturated solutions, *Russ. J. Inorg. Chem.* 31 (1986) 922-923.
- [49] W.F. Linke , A. Seidell , Solubilities, inorganic and metal organic compounds - a compilation of solubility data from the periodical literature, vol 1, 4th ed., D. Van Nostrand Company, Princeton, New Jersey, 1958.
- [50] W.F. Linke, A. Seidell, Solubilities, inorganic and metal organic compounds - a compilation of solubility data from the periodical literature, vol 2, 4th ed., D. Van Nostrand Company, Princeton, New Jersey, 1965.
- [51] J.H. Krepelka, B. Rejha, Solubility of the hydrates of manganous sulfate, *Collect. Czech. Chem. Commun.* 5 (1933) 67-75.
- [52] R.D. Eddy, P.E. Machemer, A.W.C. Menzies, Retroflex Aqueous Solubility Curves, and the Respective Solubilities of the Monohydrate and Monodeuterate of Manganous Sulfate in Ordinary and in Deuterium Water, *J. Phys. Chem.* 45 (1941) 908-915.

Acid mine drainage has long been a significant environmental problem in coal and metal sulfide mining. The demand for the recycling and reuse of materials has increased significantly. When alternative solutions are being developed, a better understanding of the thermodynamic behaviour of aqueous systems is needed.

In the present study a thermodynamic model of the $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{NiSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$, and $\text{MnSO}_4\text{-H}_2\text{O}$ systems has been developed, in order to yield a thermodynamically consistent set of values for the solubility of metal sulfate over a wide range of temperatures and concentrations. The Pitzer mean activity coefficient model has been used in the assessment to take into account the non-ideal behaviour of the aqueous solution. These metal sulfate solutions have previously been modelled in the literature. Those models have been reviewed critically in this work.



ISBN 978-952-60-5055-3
ISBN 978-952-60-5056-0 (pdf)
ISSN-L 1799-4934
ISSN 1799-4934
ISSN 1799-4942 (pdf)

Aalto University
School of Chemical Technology
Department of Materials Science and Engineering
www.aalto.fi

**BUSINESS +
ECONOMY**

**ART +
DESIGN +
ARCHITECTURE**

**SCIENCE +
TECHNOLOGY**

CROSSOVER

**DOCTORAL
DISSERTATIONS**