



## CHEMICAL THERMODYNAMICS OF NICKEL

Includes CD-ROM







### CHEMICAL THERMODYNAMICS OF NICKEL

### CHEMICAL THERMODYNAMICS

 Vol. 1. Chemical Thermodynamics of Uranium (H. Wanner and I. Forest, eds.) Vol. 2. Chemical Thermodynamics of Americium (R.J. Silva et al.)
Vol. 3. Chemical Thermodynamics of Technetium (M.C.A. Sandino and E. Östhols, eds.) Vol. 4. Chemical Thermodynamics of Neptunium and Plutonium (OECD Nuclear Energy Agency, ed.)
Vol. 5. Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium (OECD Nuclear Energy Agency, ed.)

Vol. 6. Chemical Thermodynamics of Nickel (OECD Nuclear Energy Agency, ed.)

**CHEMICAL THERMODYNAMICS 6** 

## Chemical Thermodynamics of Nickel

Heinz GAMSJÄGER (Chairman) Lehrstuhl für Physikalische Chemie Montanuniversität Leoben Leoben (Austria)

Jerzy BUGAJSKI Lehrstuhl für Physikalische Chemie Montanuniversität Leoben Leoben (Austria) Tamás GAJDA Department of Inorganic and Analytical Chemistry University of Szeged Szeged (Hungary)

Robert J. LEMIRE Deep River ON KOJ 1P0 (Canada) Wolfgang PREIS Lehrstuhl für Physikalische Chemie Montanuniversität Leoben Leoben (Austria)

Edited by Federico J. MOMPEAN (Series Editor and Project Co-ordinator) Myriam ILLEMASSÈNE (Volume Editor) and Jane PERRONE OECD Nuclear Energy Agency, Data Bank Issy-les-Moulineaux (France)



ELSEVIER AMSTERDAM • BOSTON • HEIDELBERG • LONDON • NEW YORK • OXFORD PARIS • SAN DIEGO • SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO

2005

Published by ELSEVIER B.V. Radarweg 29 P.O. Box 211, 1000 AE Amsterdam, The Netherlands

ISBN: 0-444-51802-9 ISBN: 0-444-51903-3 (CD-ROM)

Copyright © Organisation for Economic Co-Operation and Development, 2005. All rights reserved. No part of this publication may be reproduced, stored in a retrieval, system or transmitted in any form or by any means, electronic, electrostatic, magnetic tape, mechanical, photocopying, recording or otherwise, without permission in writing from the copyright holders. Queries concerning permission or translation rights should be addressed to: Head of Publications Service, OECD, 2 ne Andre Pascal, 75775 Paris Cedex 16, France

Special regulations for readers in the U.S.A. - This publication has been registered with the Copyright Clearance Center Inc. (CCC), Salem, Massachusetts. Information can be obtained from the CCC about conditions under which photocopies of parts of this publication may be made in the U.S.A. All other copyright questions, including photocopying outside of the U.S.A., should be referred to the OECD.

No responsibility is assumed by the Publisher or by the OECD for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein.

The opinions expressed and arguments employed in this publication are the sole responsibility of the authors and do not necessarily reflect those of the OECD or of the governments of its member countries. Les idées exprimées et les arguments avancés dans cette publication sont ceux des auteurs et ne reflètent pas nécessairement ceux de l'OCDE ou des gouvernments de ses pays membres.

This volume has been reproduced by the publisher from the formatted pages prepared by the editors.

The paper used in this publication meets the requirements of ANSI/NISO Z39.48-1992 (Permanence of Paper).

Printed in The Netherlands

## Preface

This volume is the sixth of the series "Chemical Thermodynamics" edited by the OECD Nuclear Energy Agency (NEA). It is a critical review of the Thermodynamic Data Base of nickel and its compounds initiated by the Management Board of the NEA Thermochemical Database Project Phase II (NEA TDB II).

The TDB Ni review team first met at the University of Leoben, Austria in January 1999. Three subsequent plenary meetings were held at NEA Headquarters at Issy-les-Moulineaux (France) in January 2001, October 2001 and in November 2002, two were held at Leoben in May 2002 and in November 2003. Smaller working subgroups met at Luleå, Sweden in October 1999 and in April 2001. The Executive Group of the Management Board provided scientific assistance in the implementation of the NEA TDB Project Guidelines. Hans Wanner participated in meetings of the Review Team as the designated member of the Executive Group. At the NEA Data Bank the responsibility for the overall co-ordination of the Project was placed with Eric Östhols (from its initiation in 1999 to February 2000), with Stina Lundberg (from March 2000 to September 2000) and with Federico Mompean (since September 2000). Federico Mompean was in charge of the preparation of the successive drafts, updating the NEA thermodynamic database and editing the book to its present final form, with assistance of Myriam Illemassène, Jane Perrone, Katy Ben Said and Cristina Domènech-Ortí.

Originally Willis Forsling, Lars Gunneriusson (Luleå University of Technology, Sweden), Jerzy Bugajski, Heinz Gamsjäger, and Wolfgang Preis (University of Leoben, Austria) participated in the nickel project. In October 2001 Robert Lemire joined the Review Team. As member, chairman and peer reviewer of previous NEA TDB projects he contributed invaluable expertise to seeing the Ni review through to completion. In August 2002 time constraints and the pressure of other commitments forced Willis Forsling and Lars.Gunneriusson to resign from the Review Team and Tamás Gajda, University of Szeged, Hungary, joined as a new member.

Although almost all of the members of the final review team contributed text and comments to several chapters, primary responsibility for the different chapters was divided as follows. Jerzy Bugajski prepared the sections on elemental nickel, silicon compounds and complexes, germanium compounds and complexes and, with the chairman, the section on boron compounds and complexes. Tamás Gajda drafted the sections for halide and pseudohalide complexes, the section for hydroxo complexes, and the sections on nitrato and thiocyanato complexes. Robert Lemire prepared Chapter VI, Discussion of auxiliary data selection, the sections on halates, sulphates, phosphorus compounds and complexes, arsenic compounds and complexes and, with the chairman, the section on solid halides (he also extensively reviewed several of the other sections, and revised the English throughout the text). Wolfgang Preis prepared the sections on the oxide, the sulphides and the hydrogensulphido complexes and, with the chairman, the section on Ni(III,IV) hydroxides (for the Leoben group he also implemented a data base for ionic strength corrections and calculations ensuring internal consistency of the selected values). The chairman drafted the sections on aqua ions, hydroxides and carbonates.

The initial contributions from Willis Forsling and Lars Gunneriusson on halide and pseudohalide complexes and (together with Wolfgang Preis) on hydroxo complexes are gratefully acknowledged as they constituted the starting point for subsequent discussions within the Review Team.

While there is no need to repeat the general purpose of this review a side effect deserves mentioning. The selection of key values, e.g., for Ni<sup>2+</sup>(aq), revealed gaps in our knowledge which may stimulate rewarding projects on the experimental thermodynamics of nickel compounds.

Leoben, Austria, October 2004

Heinz Gamsjäger, Chairman

## Acknowledgements

For the preparation of this book, the authors have received financial support from the NEA TDB Phase II Project. The following organisations take part in the Project:

ANSTO, Australia ONDRAF/NIRAS, Belgium RAWRA, Czech Republic POSIVA, Finland ANDRA, France IPSN (now IRSN), France FZK, Germany JNC, Japan ENRESA, Spain SKB, Sweden SKI, Sweden HSK, Switzerland NAGRA, Switzerland PSI, Switzerland BNFL, UK NIREX, UK DoE, USA

Jerzy Bugajski, Heinz Gamsjäger and Wolfgang Preis would like to express their gratitude to the Institut für Physikalische Chemie of the Montanuniversität Leoben for having provided the infrastructure necessary for their contributions to this project.

Tamás Gajda gratefully acknowledges the technical support of the Department of Inorganic and Analytical Chemistry, University of Szeged.

Robert Lemire wishes to thank Atomic Energy of Canada Limited (AECL) for allowing him to participate in this project, and for allowing him to use the library and other AECL facilities at the Chalk River Laboratories.

The authors also thank Werner Sitte for his help with and comments on the section of silicon compounds and complexes. Heinz Gamsjäger thanks the library staff at the University of Leoben and the Austrian Central Library for Physics for their literature searches and assistance in obtaining copies of many references, he also appreciates the help of Malcolm Rand, Alan Dinsdale, Heiko Kleykamp and Herbert Ipser for their

advice concerning papers difficult to come by.

The unceasing efforts of Federico Mompean, coordinator for the TDB project during the time the main part of the draft of this book was assembled, edited for peer review and finally prepared for the press, is greatly appreciated. His work built on the earlier efforts of Erik Östhols and Stina Lundberg. The authors are indebted to Myriam Illemassène, Jane Perrone and Katy Ben Said who, with admirable alertness and scientific competence, transformed contributions of five authors, prepared in many different formats, into a consistent text with correctly numbered tables and figures. At the NEA Data Bank, Pierre Nagel and Eric Lacroix have provided excellent software and advice, which have eased the editorial and database work. Cynthia Picot, Solange Quarmeau and Amanda Costa from NEA Publications have provided considerable help in editing the present series. Their contributions and the support of many NEA staff members are highly appreciated.

The entire manuscript of this book has undergone a peer review by an independent international group of reviewers, according to the procedures in the TDB-6 Guideline, available from the NEA. The peer reviewers have seen and approved the modifications made by the authors in response to their comments. The peer review comment records may be obtained on request from the OECD Nuclear Energy Agency. The peer reviewers were:

Dr. Donald A. Palmer, Batelle, Oak Ridge National Laboratory, USA

and

Prof. Wolfgang Voigt, University of Freiberg, Germany.

Their contributions are gratefully acknowledged.

# Note from the Chairman of the NEA TDB Project Phase II

The need to make available a comprehensive, internationally recognised and qualityassured chemical thermodynamic database that meets the modelling requirements for the safety assessment of radioactive waste disposal systems prompted the Radioactive Waste Management Committee (RWMC) of the OECD Nuclear Energy Agency (NEA) to launch in 1984 the Thermochemical Database Project (NEA TDB) and to foster its continuation as a semi-autonomous project known as NEA TDB Phase II in 1998.

The RWMC assigned a high priority to the critical review of relevant chemical thermodynamic data of inorganic species and compounds of the actinides uranium, neptunium, plutonium and americium, as well as the fission product technetium. The first four books in this series on the chemical thermodynamics of uranium, americium, neptunium and plutonium, and technetium originated from this initiative.

The organisation of Phase II of the TDB Project reflects the interest in many OECD/NEA member countries for a timely compilation of the thermochemical data that would meet the specific requirements of their developing national waste disposal programmes.

The NEA TDB Phase II Review Teams, comprising internationally recognised experts in the field of chemical thermodynamics, exercise their scientific judgement in an independent way during the preparation of the review reports. The work of these Review Teams has also been subjected to further independent peer review.

Phase II of the TDB Project consisted of: (i) updating the existing, CODATAcompatible database for inorganic species and compounds of uranium, neptunium, plutonium, americium and technetium, (ii) extending it to include selected data on inorganic species and compounds of nickel, selenium and zirconium, (iii) and further adding data on organic complexes of citrate, oxalate, EDTA and iso-saccharinic acid (ISA) with uranium, neptunium, plutonium, americium, technetium, nickel, selenium, zirconium and some other competing cations.

The NEA TDB Phase II objectives were formulated by the 17 participating organisations coming from the fields of radioactive waste management and nuclear regulation. The TDB Management Board is assisted for technical matters by an Executive Group of experts in chemical thermodynamics. In this second phase of the Project, the NEA acts as coordinator, ensuring the application of the Project Guidelines and liaising with the Review Teams.

The present volume is the second one published within the scope of NEA TDB Phase II and contains a database for inorganic species and compounds of nickel. We trust that the efforts of the reviewers, the peer reviewers and the NEA Data Bank staff merit the same high recognition from the broader scientific community as received for previous volumes of this series.

Mehdi Askarieh United Kingdom Nirex limited Chairman of TDB Project Phase II Management Board On behalf of the NEA TDB Project Phase II Participating Organisations:

ANSTO, Australia ONDRAF/NIRAS, Belgium RAWRA, Czech Republic POSIVA, Finland ANDRA, France IPSN (now IRSN), France FZK, Germany JNC, Japan ENRESA, Spain SKB, Sweden SKI, Sweden HSK, Switzerland PSI, Switzerland BNFL, UK Nirex, UK DoE, USA

### **Editor's note**

This is the sixth volume of a series of expert reviews of the chemical thermodynamics of key chemical elements in nuclear technology and waste management. This volume is devoted to the inorganic species and compounds of nickel. The tables contained in Chapters III and IV list the currently selected thermodynamic values within the NEA TDB Project. The database system developed at the NEA Data Bank, see Section II.6, assures consistency among all the selected and auxiliary data sets.

The recommended thermodynamic data are the result of a critical assessment of published information.. The values in the auxiliary data set, see Tables IV-1 and IV-2 have been adopted from CODATA key values or have been critically reviewed in this or earlier volumes of the series.

#### How to contact the NEA TDB Project

Information on the NEA and the TDB Project, on-line access to selected data and computer programs, as well as many documents in electronic format are available at

www.nea.fr.

To contact the TDB project coordinator and the authors of the review reports, send comments on the TDB reviews, or to request further information, please send e-mail to tdb@nea.fr. If this is not possible, write to:

TDB project coordinator OECD Nuclear Energy Agency, Data Bank Le Seine-St. Germain 12, boulevard des Îles F-92130 Issy-les-Moulineaux FRANCE

The NEA Data Bank provides a number of services that may be useful to the reader of this book.

- The recommended data can be obtained via internet directly from the NEA Data Bank.
- The NEA Data Bank maintains a library of computer programs in various areas. This includes geochemical codes such as PHREEQE, EQ3/6, MINEQL, MINTEQ and PHRQPITZ, in which chemical thermodynamic data like those presented in this book are required as the basic input data. These computer codes can be obtained on request from the NEA Data Bank.

## Contents

Pref	ace		v
Ack	nowle	edgement	vii
Note	e fron	n the chairman of the NEA TDB Project Phase II	ix
Edit	Editor's note		xi
Par	•t I	Introductory material	1
I IN	TRO	DUCTION	3
I.1	Ba	skground	3
I.2	Fo	cus of the review	5
I.3	Re	view procedure and results	6
II ST	ΓΑΝΙ	DARDS, CONVENTIONS, AND CONTENTS OF THE TABLES	11
II.1	Syı	nbols, terminology and nomenclature	11
II.	1.1	Abbreviations	11
II.	1.2	Symbols and terminology	13
II.	1.3	Chemical formulae and nomenclature	15
II.	1.4	Phase designators	15
II.	1.5	Processes	17
II.	1.6	Equilibrium constants	18
I	I.1.6.	l Protonation of a ligand	18
I	I.1.6.	2 Formation of metal ion complexes	19
Ľ	I.1.6.	3 Solubility constants	20
I	I.1.6.	4 Equilibria involving the addition of a gaseous ligand	21
I	I.1.6.	5 Redox equilibria	22
11. 	1.7	pH	25
II.	1.8	Order of formulae	27
11.	1.9	Reference codes	
11.2	Un	its and conversion factors	28
11.3	Sta	ndard and reference conditions	31
II.	3.1	Standard state	31
II.	3.2	Standard state pressure	32
II.	3.3	Reference temperature	35

II.4 Fundamental physical constants	35
II.5 Uncertainty estimates	
II.6 The NEA-TDB system	
II.7 Presentation of the selected data	
Part II Tables of selected data	41
III SELECTED NICKEL DATA	43
IV SELECTED AUXILIARY DATA	53
Part III Discussion of data selection	73
V DISCUSSION OF DATA SELECTION FOR NICKEL	75
V.1 Elemental nickel	
V.1.1 Nickel gas	75
V.1.2 Nickel crystal	76
V.1.3 Nickel liquid	78
V.2 Simple nickel aqua ions	79
V.2.1 Ni <sup>2+</sup>	79
V.2.1.1 Gibbs energy of formation of Ni <sup>2+</sup>	80
V.2.1.1.1 Temperature coefficient of the standard electrode potential	
Ni <sup>2+</sup> Ni	82
V.2.1.2 Enthalpy of formation of Ni <sup>2+</sup>	82
V.2.1.3 Partial molar entropy of Ni <sup>2+</sup>	84
V.2.1.3.1 NiSO <sub>4</sub> ·7H <sub>2</sub> O(cr) cycle	84
V.2.1.3.2 NiCl <sub>2</sub> ·6H <sub>2</sub> O(cr) cycle	85
V.2.1.3.3 Entropy of Ni <sup>2+</sup> from its $\Delta_f G_m^o$ and $\Delta_f H_m^o$	86
V.2.1.4 Heat capacity of Ni <sup>2+</sup>	86
V.2.2 Other oxidation states	88
V.2.2.1 Ni <sup>3+</sup>	88
V.3 Oxygen and hydrogen compounds and complexes	90
V.3.1 Aqueous nickel(II) hydroxo complexes	90
V.3.1.1 Hydroxo complexes in acidic or neutral solutions	90
V.3.1.2 Hydroxo complexes in alkaline solutions	99
V.3.2 Solid nickel oxides and hydroxides	102
V.3.2.1 Ni(II) oxide	102
V.3.2.1.1 Solubility measurements	107
V.3.2.2 Ni(II) hydroxides, Ni(OH) <sub>2</sub> (cr)	108
V.3.2.2.1 Crystallography and mineralogy of nickel hydroxide	108

#### CONTENTS

V.3.2.2.1.1 $\beta$ -Ni(OH) <sub>2</sub>	108
V.3.2.2.1.2 α-Ni(OH) <sub>2</sub>	109
V.3.2.2.2 Heat capacity and entropy of Ni(OH) <sub>2</sub> (cr)	109
V.3.2.2.3 Thermodynamic analysis of solubility data of Ni(OH) <sub>2</sub> (s)	111
V.3.2.3 Ni(III, IV) hydroxides	115
V.3.2.3.1 β-NiOOH	116
V.3.2.3.2 γ-NiOOH	118
V.4 Group 17 (halogen) compounds and complexes	119
V.4.1 Nickel halide compounds	119
V.4.1.1 Solid nickel fluoride, NiF <sub>2</sub> (cr)	119
V.4.1.1.1 Enthalpy of formation of NiF <sub>2</sub> (cr)	120
V.4.1.2 Solid nickel chloride, NiCl <sub>2</sub> (cr)	122
V.4.1.2.1 Low-temperature heat capacity and entropy of NiCl <sub>2</sub> (cr)	122
V.4.1.2.2 The high-temperature heat capacity of NiCl <sub>2</sub> (cr)	124
V.4.1.2.3 Enthalpy of formation of NiCl <sub>2</sub> (cr)	124
V.4.1.2.4 Gibbs energy of formation of NiCl <sub>2</sub> (cr)	127
V.4.1.3 Hydrated NiCl <sub>2</sub> solids	128
V.4.1.3.1 Gibbs energy of formation of NiCl <sub>2</sub> ·6H <sub>2</sub> O	128
V.4.1.3.2 Enthalpy of formation of $NiCl_2 \cdot 6H_2O$	128
V.4.1.3.3 The entropy and heat capacity of $NiCl_2 \cdot 6H_2O(cr)$	129
V.4.1.3.4 Gibbs energy and enthalpy of formation of nickel chloride	
tetrahydrate	130
V.4.1.3.5 The entropy and heat capacity of nickel chloride dihydrate	131
V.4.1.3.6 Gibbs energy and enthalpy of formation of nickel chloride	
dihydrate	131
V.4.1.4 Solid nickel bromide, NiBr <sub>2</sub> (cr)	132
V.4.1.4.1 Low-temperature heat capacity and entropy of $NiBr_2(cr)$	132
V.4.1.4.2 The high-temperature heat capacity of $NiBr_2(cr)$	134
V.4.1.4.3 Enthalpy of formation of NiBr <sub>2</sub> (cr)	134
V.4.1.5 Hydrated solid, $NiBr_2 \cdot xH_2O$	135
V.4.1.6 Solid nickel iodide, Nil <sub>2</sub> (cr)	136
V.4.1.6.1 Entropy of $NiI_2(cr)$	136
V.4.1.6.2 Heat capacity of $NiI_2(cr)$	136
V.4.1.6.3 Enthalpy of formation of $NiI_2(cr)$	137
V.4.1.7 Solid nickel iodate compounds	137
V.4.2 Aqueous nickel halide complexes	140
V.4.2.1 Introduction	140
V.4.2.2 Solution structural studies	141
V.4.2.3 Aqueous Ni(II) - fluoro complexes	142
V.4.2.4 Aqueous Ni(II) - chloro complexes	146
V.4.2.5 Aqueous Ni(II) – bromo complexes	153
V.4.2.5.1 Determination of the $Ni^{2+} - Br^-$ ion interaction coefficient	156

V.4.2.6 Aqueous Ni(II) – iodine complexes	157
V.4.2.6.1 Aqueous Ni(II) – iodo complexes	157
V.4.3 Determination of the $Ni^{2+} - ClO_4^-$ ion interaction coefficient	158
V.5 Group 16 (chalcogen) compounds and complexes	161
V.5.1 Sulphur compounds and complexes	161
V.5.1.1 Nickel sulphides	161
V.5.1.1.1 Solid nickel sulphides	161
V.5.1.1.1.1 Crystallography and mineralogy of nickel sulphides	161
V.5.1.1.1.1.1 Heazlewoodite, $Ni_3S_2(cr)$	161
V.5.1.1.1.1.2 $\alpha$ -Ni <sub>7</sub> S <sub>6</sub>	161
V.5.1.1.1.1.3 Pentlandite, (Fe, Ni) <sub>9</sub> S <sub>8</sub> (cr)	161
V.5.1.1.1.1.4 Godlevskite, Ni <sub>9</sub> S <sub>8</sub> (cr)	162
V.5.1.1.1.1.5 Millerite, β-NiS	162
V.5.1.1.1.1.6 Polydymite, $Ni_3S_4(cr)$	162
V.5.1.1.1.1.7 Vaesite, NiS <sub>2</sub> (cr)	163
V.5.1.1.1.2 Ni – S phase diagram	163
V.5.1.1.1.2.1 Ni – S melt	166
V.5.1.1.1.2.2 $\beta_1$ -Ni <sub>3</sub> S <sub>2</sub> and $\beta_2$ -Ni <sub>4</sub> S <sub>3</sub>	167
V.5.1.1.1.2.3 $Ni_3S_2(cr)$ (heazlewoodite)	167
V.5.1.1.1.2.4 $Ni_7S_6(cr)$ and $Ni_9S_8(cr)$	168
V.5.1.1.1.2.5 NiS( $\alpha$ ) and NiS( $\beta$ )	170
V.5.1.1.1.2.6 $NiS_2(cr)$ , vaesite	173
V.5.1.1.1.2.7 $Ni_3S_4(cr)$ , polydymite	174
V.5.1.1.1.2.8 $Ni_{4.5}Fe_{4.5}S_8(cr)$ , pentlandite	174
V.5.1.1.1.3 Discussion of selected thermodynamic properties of nickel	
sulphides	174
V.5.1.1.2 Solubility of NiS(s) and aqueous nickel hydrogen sulphido	
species	177
V.5.1.2 Nickel sulphates	181
V.5.1.2.1 Aqueous nickel (II) sulphato complexes	181
V.5.1.2.1.1 Enthalpy of formation of NiSO <sub>4</sub> (aq)	
V.5.1.2.1.2 Heat capacity values	190
V.5.1.2.2 Solid nickel sulphates	
V.5.1.2.2.1 N1SO <sub>4</sub> ·7H <sub>2</sub> O(cr)	
V.5.1.2.2.1.1 $\alpha$ -NiSO <sub>4</sub> ·6H <sub>2</sub> O	
V.5.1.2.2.1.2 Other hydrated nickel sulphate solids	
V.5.1.2.2.1.3 NISO <sub>4</sub> (cr)	
V.5.2 Selenium compounds and complexes	
V.5.3 Tellurium compounds and complexes	
V.5.3.1 Nickel tellurides	
V.5.3.1.1 NiTe <sub>0.775</sub> ( $\gamma_1$ )	
V.5.3.1.2 N1Te <sub>0.85</sub> ( $\gamma_2$ )	195

V.6	Group 15	compounds and complexes	196
V	.6.1 Nitrog	gen compounds and complexes	196
	V.6.1.1 So	olid nickel nitrates	196
	V.6.1.1.1	Ni(NO <sub>3</sub> ) <sub>2</sub> ·9H <sub>2</sub> O(cr)	196
	V.6.1.1.2	$Ni(NO_3)_2 \cdot 6H_2O(cr)$	196
	V.6.1.1.3	Ni(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O(cr), Ni(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O(cr), Ni(NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O(cr)	198
	V.6.1.1.4	Ni(NO <sub>3</sub> ) <sub>2</sub> (anhydrous)	200
	V.6.1.2 A	queous Ni(II)-nitrato complexes	200
	V.6.1.2.1	Determination of the $Ni^{2+} - NO_3^-$ ion interaction coefficient	203
V	.6.2 Phosp	phorus compounds and complexes	204
٦	V.6.2.1 So	olid nickel phosphorus compounds	204
	V.6.2.1.1	Nickel phosphides	204
	V.6.2.1.2	Nickel phosphates	204
1	V.6.2.2 A	queous nickel phosphorus species	205
	V.6.2.2.1	Simple nickel phosphato complexes	205
	V.6.2.2.2	Aqueous nickel diphosphato complexes	207
V	.6.3 Arser	nic compounds	210
1	V.6.3.1 N	ickel arsenides	210
	V.6.3.1.1	NiAs(cr)	210
	V.6.3.1.2	Ni <sub>11</sub> As <sub>8</sub> (cr)	211
	V.6.3.1.3	Ni <sub>5</sub> As <sub>2</sub> (cr)	212
	V.6.3.1.4	NiAs <sub>2</sub> (cr)	212
	V.6.3.2 N	ickel arsenates	212
	V.6.3.2.1	Solid nickel arsenates	212
	V.6.3.2.2	Aqueous nickel arsenato complexes	213
	V.6.3.3 N	ickel arsenites	214
	V.6.3.3.1	Solid nickel arsenites	214
<b>V.7</b>	Group 14	compounds and complexes	214
V	.7.1 Carbo	on compounds and complexes	214
•	V.7.1.1 N	ickel carbonates	214
	V.7.1.1.1	Solid nickel carbonates	214
	V.7.1.1.1	.1 NiCO <sub>3</sub> (cr)	214
	V.7.1.1	1.1.1 Crystallography and mineralogy of nickel carbonate	214
	V.7.1.1.	1.1.2 Heat capacity and entropy of NiCO <sub>3</sub> (cr)	216
	V.7.1.1.	1.1.3 Thermodynamic analysis of solubility data on gaspéite	217
	V.7.1.1.1	.2 NiCO <sub>3</sub> ·5.5H <sub>2</sub> O(cr)	218
	V.7.1.1.	1.2.1 Crystallography and mineralogy of nickel carbonate	
		hydrate	218
	V.7.1.1	1.2.2 Heat capacity and entropy of NiCO <sub>3</sub> ·5.5H <sub>2</sub> O(cr)	219
	V.7.1.1	1.2.3 Thermodynamic analysis of solubility data on hellyerite	e219
	V.7.1.1.2	Aqueous nickel carbonato complexes	223

CONTENTS

V.7.1.2 Nickel cyanides	226
V.7.1.2.1 Aqueous Ni(II) cyano complexes	226
V.7.1.2.1.1 Complexes in neutral and alkaline solution	226
V.7.1.2.1.2 Protonated complexes	231
V.7.1.3 Nickel thiocyanates	231
V.7.1.3.1 Aqueous nickel thiocyanato complexes	231
V.7.2 Silicon compounds and complexes	238
V.7.2.1 Solid nickel silicates	238
V.7.2.1.1 Nickel orthosilicate $Ni_2SiO_4(cr)$	238
V.7.2.1.1.1 Crystal structure and phase transitions	238
V.7.2.1.1.2 Crystallography and mineralogy of nickel orthosilicate	239
V.7.2.1.1.3 Heat capacity and standard entropy	239
V.7.2.1.1.4 Enthalpy of formation	241
V.7.2.1.1.5 Gibbs energy of formation	243
V.7.3 Germanium compounds and complexes	245
V.7.3.1 Solid nickel germanates	245
V.7.3.1.1 Nickel orthogermanate Ni <sub>2</sub> GeO <sub>4</sub> (cr)	245
V.7.3.1.1.1 Crystal structure of nickel orthogermanate	245
V.7.3.1.1.2 Enthalpy of formation from NiO(cr) and GeO <sub>2</sub> (cr)	245
V.8 Group 13 compounds and complexes	245
V.8.1 Boron compounds and complexes	245
V.8.1.1 Solid nickel borates	245
V.8.1.1.1 Crystal structure	245
V.8.1.1.2 Thermodynamic data for NiO·2B <sub>2</sub> O <sub>3</sub> (s)	246
V.8.1.1.3 Solubility of Ni(BO <sub>2</sub> ) <sub>2</sub> ·4H <sub>2</sub> O(s)	246
V.8.1.2 Aqueous nickel borato complexes	247
VI DISCUSSION OF AUXILIARY DATA SELECTION	
	240
VI.1 Group 15 auxiliary species	
VI.I.I Additional consistent auxiliary data for As compounds	249
VI.2 Other auxiliary species	249
VI.2.1 Auxiliary data for KCl(cr), KBr(cr) and KI(cr)	249
Part IV Appendices	251
A Discussion of selected references	253
B Ionic strength corrections	443
B.1 The specific ion interaction equations	
R 1 1 Background	лл <b>5</b>
D.1.1 Daykervulla	

CONTENTS

B.1.2 Ionic strength corrections at temperatures other that	n 298.15 K451
B.1.3 Estimation of ion interaction coefficients	
B.1.3.1 Estimation from mean activity coefficient data	
B.1.3.2 Estimations based on experimental values of ec	uilibrium constants
at different ionic strengths	
B.1.4 On the magnitude of ion interaction coefficients	457
B.2 Ion interaction coefficients versus equilibrium const	ants for ion pairs458
B.3 Tables of ion interaction coefficients	458
C Assigned uncertainties	
C.1 The general problem	471
C.2 Uncertainty estimates in the selected thermodynami	c data473
C.3 One source datum	
C.4 Two or more independent source data	
C.4.1 Discrepancies	
C.5 Several data at different ionic strengths	479
C.5.1 Discrepancies or insufficient number of data points	s481
C.6 Procedures for data handling	
C.6.1 Correction to zero ionic strength	
C.6.2 Propagation of errors	
C.6.3 Rounding	486
C.6.4 Significant digits	
Bibliography	
List of authors	

This page intentionally left blank

## **List of Figures**

Figure II-1:	Standard order of arrangement of the elements and compounds
	based on the periodic classification of the elements
Figure V-1:	The standard molar heat capacity of nickel as a function
	of temperature
Figure V-2:	Standard electrode potential of Ni   NiSO <sub>4</sub>   Hg <sub>2</sub> SO <sub>4</sub>   Hg at 25°C 81
Figure V-3:	Estimation of the $Ni^{3+}$   $Ni^{2+}$ standard electrode potential
Figure V-4:	Extrapolation to $I_m = 0$ of the experimental data
	for Reaction (V.23) in NaClO <sub>4</sub> media. $\dots$ 96
Figure V-5:	SIT analysis of the experimental data for Reaction (V.23)
	in chloride media, including $\log_{10} {}^*\beta_{1,1}^{\circ}((V.23), 298.15 \text{ K})$
	obtained in NaClO <sub>4</sub>
Figure V-6:	Extrapolation to $I_m = 0$ of the experimental data
	for Reaction (V.25) in perchlorate media
Figure V-7:	Solubility of Ni(OH) <sub>2</sub> (s) in alkaline solutions at 298.15 K 100
Figure V-8:	Experimental results of heat capacity measurements
	on nickel oxide from 3.2 to 1809.7 K 104
Figure V-9:	Comparison between the temperature dependence of the Gibbs
	energy of formation for NiO obtained from electrochemical
	as well as chemical reduction/oxidation equilibrium measurements
	and the prediction based on the present
	selection of thermodynamic properties for NiO 106
Figure V-10:	The heat capacity of $Ni(OH)_2(cr)$ as a function of temperature 110
Figure V-11:	Solubility constant of $Ni(OH)_2$ as a function of temperature 114
Figure V-12:	$\beta$ -Ni(OH) <sub>2</sub>   $\beta$ -NiOOH system. Variation of reversible potential
	with the oxidation state of Ni at 298.15 K and $I=0$
Figure V-13:	$\alpha$ -Ni(OH) <sub>2</sub>   $\gamma$ -NiOOH system. Variation of reversible potential
	with the oxidation state of Ni at 298.15 K and $I=0$
Figure V-14:	Molar heat capacity of anhydrous NiCl <sub>2</sub> between 2 and 30 K 123
Figure V-15:	Heat capacity of anhydrous NiCl <sub>2</sub> (cr) 123
Figure V-16:	$\Delta_r G_m^{\circ}$ –function of Reaction (V.59) 125
Figure V-17:	Third-law analysis of data for Reaction (V.59)
Figure V-18:	Gibbs energy of formation of NiCl <sub>2</sub> (cr) versus temperature 127
Figure V-19:	Values from the heat capacity studies of Stuve et al. [78STU/FER]
	and White and Staveley [82WHI/STA] 133
Figure V-20:	Extrapolation to $I_m = 0$ of the experimental data
	for Reaction (V.70) in NaClO <sub>4</sub> media
Figure V-21:	Extrapolation to $I_m = 0$ of the experimental enthalpies
	for Reaction (V.70) in NaClO <sub>4</sub> media

LIST OF FIGURES

Figure V-22:	Extrapolation to $I=0$ of the $\log_{10}\beta_1$ values reported
	in [75LIB/IIA] for Reaction (V.71) in Ni(II) perchlorate solution 149
Figure V-23:	Extrapolation to $I=0$ of the accepted experimental data
	for Reaction (V.71) in NaClO <sub>4</sub> media
Figure V-24:	Extrapolation to $I=0$ of the $\log_{10}\beta_1$ values reported
	in [78LIB/KOW] for Reaction (V.73) in Ni(II) perchlorate media 155
Figure V-25:	Plot of $\log_{10} \gamma_{\pm}$ versus molality of aqueous NiBr <sub>2</sub> solutions
	at 298.15 K
Figure V-26:	Plot of osmotic coefficient versus molality of aqueous NiBr <sub>2</sub>
	solutions at 298.15 K
Figure V-27:	Osmotic coefficient plotted as a function of molality
	of aqueous Ni(ClO <sub>4</sub> ) <sub>2</sub> solutions at 298.15 K $\dots$ 160
Figure V-28:	Plot of $\log_{10} \gamma_{\pm}$ versus molality of aqueous Ni(ClO <sub>4</sub> ) <sub>2</sub>
	solutions at 298.15 K 160
Figure V-29:	Phase diagram for the binary system $Ni - S$ with T plotted versus
	mole fraction of sulphur 164
Figure V-30:	Section of the calculated phase diagram for
	the composition range $0.30 < x_S < 0.55$
Figure V-31:	Gibbs energy of reaction for (V.79) plotted versus temperature 168
Figure V-32:	Partial pressure of sulphur for various phase equilibria
	in the binary system Ni – S plotted against temperature
Figure V-33:	Gibbs energy function for the stoichiometric composition
	of NiAs-type Ni(II) sulphide, $\alpha$ -NiS, plotted versus temperature 173
Figure V-34:	Plot of equilibrium partial pressure of sulphur versus temperature 176
Figure V-35:	Distribution of nickel sulphide complexes as a function of total
	molality of nickel (II) in aqueous solutions saturated with $H_2S$ ,
	$T = 298.15 \text{ K}, I = 1.00 \text{ mol} \text{ kg}^{-1} \text{ NaCl} \dots 179$
Figure V-36:	Solubility of Ni(II) sulphides in aqueous solutions saturated
U	with $H_2S$ as a function of initial concentration
	of hydrochloric acid at 298.15 K 181
Figure V-37:	The variation of molar conductances of aqueous nickel sulphate
C	solutions with concentration at 25°C
Figure V-38:	Values of $\log_{10} K_1^\circ$ for nickel sulphate association at different
U	temperatures
Figure V-39:	Measured water vapour pressures over hydrated
e	$Ni(NO_3)_2 \cdot 6H_2O(cr)$ [37SAN], [72AUF/CAR]
	and Ni(NO <sub>2</sub> ) $_{2}$ ·4H <sub>2</sub> O(cr) [72AUF/CAR2]
Figure V-40:	Extrapolation to $I=0$ of the constants for Reaction (V.96)
C III	in lithium perchlorate media based on the data in [73FED/SHM] 202
Figure V-41:	Plot of $\log_{10} \gamma_{+}$ versus molality of aqueous Ni(NO <sub>2</sub> ) <sub>2</sub> solutions
	at 298.15 K

xxii

Figure V-42:	Osmotic coefficient plotted as a function of molality
	of aqueous Ni(NO <sub>3</sub> ) <sub>2</sub> solutions at 298.15 K 204
Figure V-43:	Temperature dependence of hellyerite solubility
Figure V-44:	Ionic strength dependence of hellyerite solubility
Figure V-45:	Thermodynamic analysis of hellyerite solubility
Figure V-46:	Three-dimensional predominance diagram for the system
	$Ni^{2+}-CO_2-H_2O223$
Figure V-47:	Calculated solubility of NiCO <sub>3</sub> (cr) in dilute sodium carbonate
	solutions under atmospheric conditions 225
Figure V-48:	Extrapolation to $I=0$ of experimental formation constants
	of Ni(CN) $_{4}^{2-}$ (V.113) determined in NaClO <sub>4</sub> medium
	(insert shows the corresponding plot of data reported
	for KClO <sub>4</sub> medium). $229$
Figure V-49:	Extrapolation to $I=0$ of experimental equilibrium constants
	for Reaction (V.114) determined in NaClO <sub>4</sub> medium 229
Figure V-50:	Extrapolation to $I_m = 0$ of the accepted formation constants
	reported for the formation of NiSCN <sup>+</sup> in perchlorate media 235
Figure V-51:	Extrapolation to $I_m = 0$ of the accepted formation constants reported
	for the formation of $Ni(SCN)_2(aq)$ in perchlorate media 236
Figure V-52:	Extrapolation to $I_m = 0$ of the accepted formation constants reported
	for the formation of Ni(SCN) $_{3}^{-}$ in perchlorate media
Figure V-53:	The standard molar heat capacity of Ni <sub>2</sub> SiO <sub>4</sub> -olivine as a function
	of temperature
Figure V-54:	Standard Gibbs energy of Reaction (V.121) as a function
	of temperature
Figure A-1:	Solubility of precipitated nickel carbonate
Figure A-2:	High temperature enthalpy of anhydrous NiCl <sub>2</sub> 274
Figure A-3:	Plot of $E$ (vs. SHE) versus $\log_{10}([NiSO_4]/m)$ 276
Figure A-4:	Extrapolation to $I_{\rm m}=0$ (using the SIT) of the formation constants
	for the species NiSCN <sup>+</sup> as reported in [58YAT/KOR]
Figure A-5:	Extrapolation of activity coefficients to saturated solution at 25 °C 295
Figure A-6:	Extrapolation of osmotic coefficients to saturated solution at 25 °C 295
Figure A-7:	Plot of $\log_{10} \beta_1$ (A.17) reported in [61LIS/WIL] vs. 1/T 298
Figure A-8:	$\log_{10} \beta_1 - I_m$ plot obtained from the potentiometric data (t=35 °C)
	reported for the $Ni^{2+}$ – SCN <sup>-</sup> system in [61MOH/DAS]
Figure A-9:	Solubility product of Ni(BO <sub>2</sub> ) <sub>2</sub> ·4H <sub>2</sub> O(s) at 22 °C from data
	reported in [61SHC]
Figure A-10:	Nickel and cobalt borate complexes from data in [61SHC]
Figure A-11:	Temperature dependence of $\log_{10} \ \hat{\beta}_{1,1}$ values derived from
	[63BOL/JAU]
Figure A-12:	Temperature dependence of $\log_{10} \beta_{4,4}$ values derived from
	[63BOL/JAU]

LIST OF FIGURES

Figure A-13:	Extrapolation to $I = 0$ of the equilibrium constants
	$\log_{10} {}^*\beta_{1,1}$ (A.23) reported in [64PER] at 20°C, using the SIT 313
Figure A-14:	Plot of $\ln^*\beta_{11}^\circ$ (A.23) recalculated from [64PER] vs. 1/T
Figure A-15:	Temperature dependence of the association constant
-	for the reaction $Ni(CN)_4^2 + CN^- \rightleftharpoons Ni(CN)_5^3$ reported
	in [60MCC/JON]
Figure A-16:	Molar enthalpy of solution of NiSO <sub>4</sub> ·6H <sub>2</sub> O(cr) at 25°C
Figure A-17:	Temperature dependence of $\log_{10} \beta_1$ values of NiSCN <sup>+</sup>
	complex reported in [68MAL/TUR]
Figure A-18:	Heats of reaction determined from the calorimetric data
	of [69IZA/EAT] by using the 298.15 K values of $\log_{10}K_1$
	from [73KAT]
Figure A-19:	Extrapolation to $I=0$ of the formation constant of NiCl <sup>+</sup> using
	Equation (A.40) and the experimental data published
	in [70HAL/VAN]
Figure A-20:	Temperature dependence of $\log_{10} \beta_1$ and $\log_{10} \beta_2$ values
	for the Ni(II) – (SCN) <sup>-</sup> system ( $I=0.2$ M) as reported
	in [71TUR/MAL]
Figure A-21:	Heats of dilution of hydrated nickel nitrate salts based
	on the experimental heats of solution and an assumed heat
	of dilution to infinite dilution of 520 J·mol <sup>-1</sup> for a solution with
	a solvent:salt ratio of 8000:1
Figure A-22:	Experimental [73FED/SHM] and calculated solubility of nickel(II)
	in the aqueous phase with increasing nitrate concentrations
Figure A-23:	Experimental [73FED/SHM] and calculated values of the solubility
	of Ni(IO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O in aqueous LiClO <sub>4</sub> solutions
Figure A-24:	Variation of formation constants from Perlmutter-Hayman
	and Secco [73PER/SEC] with ionic strength
Figure A-25:	Temperature dependence of $\log_{10} K_2$ for the reaction
	$Ni(CN)_4^{2-} + H^+ \rightleftharpoons Ni(HCN)(CN)_3$ at different ionic
	strengths using NaCl
Figure A-26:	Extrapolation to $I=0$ of experimental equilibrium constants
	for the reaction Ni(HCN)(CN) $_3^-$ + H <sup>+</sup> $\rightleftharpoons$ Ni(HCN) $_2$ (CN) $_2$ (aq)
	at different temperatures
Figure A-27:	$\Delta_r H_m^{\circ}(298 \text{ K})$ of reaction of $B_2O_3$ (cr) with MO or $M_2O$
Figure A-28:	Heat capacity of NiS <sub>2</sub> plotted versus temperature
Figure A-29:	SIT-plot of recalculated data from [80MIL/BUG], [65BUR/LIL2]
	and [71OHT/BIE], and the selected $\log_{10} {}^*\beta_{4,4}^{\circ}$ ((A.70), 298.15 K) 391
Figure A-30:	Solubility of NiO in acidic solutions as a function of initial
	molality of HCl 394
Figure A-31:	Solubility of NiO in basic solutions as a function of initial
	molality of NaOH 395

xxiv

Values of $C_{p,m}$ (NiBr <sub>2</sub> , cr) as a function of temperature as reported
by White and Staveley [82WHI/STA] 400
Plot of logarithm of the oxygen partial pressure versus temperature
for the phase equilibria $\alpha$ -NiS / $\beta_2$ -Ni <sub>4</sub> S <sub>3</sub> and $\beta_2$ -Ni <sub>4</sub> S <sub>3</sub> / NiO,
respectively, at $p_{SO_2} = 1$ atm
Logarithm of the oxygen partial pressure plotted as a function
of temperature for the equilibrium $NiS(\alpha) / NiO$ at $p(SO_2) = 1$ atm 408
Plot of logarithm of the oxygen partial pressure versus temperature
for the phase equilibria NiS( $\alpha$ ) / $\beta_2$ -Ni <sub>4</sub> S <sub>3</sub> and $\beta_2$ -Ni <sub>4</sub> S <sub>3</sub> / NiO,
respectively, at $p_{SO_2} = 1$ atm
Heat capacity data for $Ni_3S_2$ as a function of temperature
Heat capacity of "Ni <sub>7</sub> S <sub>6</sub> " consisting of a mixture of $Ni_3S_2$
and $Ni_9S_8$ as a function of temperature
Heat capacity of NiS as a function of temperature 429
Logarithm of stability constants of nickel bisulphide complexes
in seawater (NaCl solutions) plus the Debye-Hückel term for ionic
strength correction plotted as a function
of ionic strength, <i>T</i> = 298.15 K 432
Solubility of theophrastite as determined by the pH
variation method
Ionic strength dependence of theophrastite solubility 440
Plot of $\log_{10} \beta_{1,m} + 4D$ versus $I_{\rm m}$ for reaction (B.12),
at 25°C and 1 bar 455

This page intentionally left blank

## List of Tables

Table II-1:	Abbreviations for experimental methods 11			
Table II-2:	Symbols and terminology			
Table II-3:	Abbreviations used as subscripts of $\Delta$ to denote the type			
	of chemical process			
Table II-4:	Unit conversion factors			
Table II-5:	Factors $\rho$ for the conversion of molarity, $c_{\rm B}$ , to molality, $m_{\rm B}$ ,			
	of a substance B, in various media at 298.15 K			
Table II-6:	Reference states for some elements at the reference temperature			
	of 298.15 K and standard pressure of 0.1 MPa 31			
Table II-7:	Fundamental physical constants 36			
Table III-1:	Selected thermodynamic data for nickel compounds and complexes 44			
Table III-2:	Selected thermodynamic data for reaction involving			
	nickel compounds and complexes			
Table III-3:	Selected temperature coefficients for heat capacities of nickel 52			
Table IV-1:	Selected thermodynamic data for auxiliary compounds			
	and complexes			
Table IV-2:	Selected thermodynamic data for reactions involving auxiliary			
	compounds and complexes 68			
Table V-1:	The temperature coefficients of the heat capacity function			
	for Ni(cr)			
Table V-2:	Enthalpy of Reaction (V.3)			
Table V-3:	Partial molar heat capacity values for Ni(II) salts in aqueous			
	solution at 298.15 K			
Table V-4:	Experimental equilibrium data (logarithmic values)			
	for the hydrolysis of Ni(II) in acidic or neutral solutions			
Table V-5:	Smoothed $C_{p,m}^{\circ}$ data and calculated values for the entropy of NiO 103			
Table V-6:	Literature data for $\log_{10} {}^*K_{s,0}^{\circ}$ (Ni(OH) <sub>2</sub> ) 113			
Table V-7:	Thermodynamic properties of Ni(OH)2(cr) 115			
Table V-8:	Experimental stability constants (logarithmic values)			
	of the species NiF <sup>+</sup> 142			
Table V-9:	Experimental enthalpy values for the Reaction (V.70) 144			
Table V-10:	Experimental formation constants for the NiCl <sup>+</sup> species 147			
Table V-11:	Experimental equilibrium constants for the Reaction (V.72) 152			
Table V-12:	Reaction enthalpies reported for Reaction (V.71)			
Table V-13:	Experimental formation constants of the NiBr <sup>+</sup> complex 154			
Table V-14:	Reaction enthalpies reported for Reaction (V.73) 156			
Table V-15:	Gibbs energy functions for the binary system Ni - S relative			
	to metallic nickel, Ni(s), and gaseous sulphur, S <sub>2</sub> (g)			

xxviii

#### LIST OF TABLES

Table V-16:	Temperatures and enthalpies of transition for $\beta$ -NiS $\rightleftharpoons \alpha$ -NiS 172		
Table V-17:	Temperatures for invariant three-phase equilibria		
	in the binary system Ni - S 175		
Table V-18:	Heat capacity functions of nickel sulphides		
Table V-19:	Standard enthalpy of formation of nickel sulphides at 298.15 K 177		
Table V-20:	Standard entropy of nickel sulphides at 298.15 K 177		
Table V-21:	Heat capacity of nickel sulphides at 298.15 K		
Table V-22:	Recalculated stability constants and SIT parameters		
	for nickel sulphide complexes at $T=298.15$ K and $I=0$		
Table V-23:	Solubility constants for Ni(II) sulphide at $T=298.15$ K and $I=0180$		
Table V-24:	Experimental values for the association constants		
	and other thermodynamic quantities for nickel sulphate		
Table V-25:	Results of reanalysis of NiSO <sub>4</sub> (aq) conductance data using a form		
	of the Lee-Wheaton equation that is compatible		
	with the SIT procedure		
Table V-26:	Experimental values for the first association constant		
	of nickel sulphate determined in the presence		
	of supporting electrolytes 187		
Table V-27:	Formation constants of the NiNO <sup>+</sup> <sub>3</sub> complex (ion pair)		
Table V-28:	Experimental values for the association constants		
	and other thermodynamic quantities		
	for nickel phosphate complexes		
Table V-29:	Experimental values for the association constants and		
	other thermodynamic quantities for nickel		
	pyrophosphate complexes		
Table V-30:	Experimental equilibrium data for the Ni(II) cyanide system 228		
Table V-31:	Experimental enthalpy values for the		
	Reaction (V.113) and (V.114)		
Table V-32:	Experimental equilibrium data for the Ni(II) - thiocyanate system 233		
Table V-33:	Experimental reaction enthalpy values for the formation		
	of Ni(II)-thiocyanate complexes 237		
Table VI-1:	Enthalpy of formation values for KCl(cr), KBr(cr),		
	and KI(cr) at 298.15 K 250		
Table A-1:	Equilibrium constants of Reaction (A.3) [21BER/CRU], [24CRU] 258		
Table A-2:	Equilibrium constants of $NiCl_2(cr) + H_2(g) \rightleftharpoons Ni(cr) + 2 HCl(g) \dots 260$		
Table A-3:	Electrode potential of the cell: Ni NiSO <sub>4</sub> (m) Hg <sub>2</sub> SO <sub>4</sub>  Hg 262		
Table A-4:	Standard electrode potential of Ni <sup>2+</sup>  Ni at 25 °C 276		
Table A-5:	Equilibrium constants of Reaction (A.9) 278		
Table A-6:	Equilibrium constants of Reaction (A.9) [53SAN] 279		
Table A-7:	Enthalpy of formation values calculated from		
	equilibrium gas compositions 282		
Table A-8:	Equilibrium constants of Reaction (A.10) [54SHC/TOL]		

Table A O.	Entholmy of colution of NiCl (or) in U O(1) at 209 15 K [59MUU ] 200			
Table A-9:	Enthalpy of solution of NiCl <sub>2</sub> (cr) in $H_2O(1)$ at 298.15 K [58MOL] 289			
Table A-10:	$\log_{10} p_1$ versus $I_m$			
Table A-11:	Recalculated constants 500			
Table A-12:	Comparison between experimental data [63LIN/LAF]			
	and calculated values of $\log_{10}[p(H_2S/p(H_2))]$ for the coexistence			
	of $N_{13+x}S_2$ with metallic nickel			
Table A-13:	Reported and recalculated $\log_{10} \beta_{1,1}^{\circ}$			
Table A-14:	Dataset			
Table A-15:	Experimental results for the enthalpy of formation for various			
	nickel sulphides determined by calorimetric measurements 345			
Table A-16:	Gibbs energy functions for various nickel sulphides			
Table A-17:	Auxiliary data used in the recalculation of NaBr heat of formation			
	values with the data from [78STU/FER]			
Table A-18:	Corrected formation constants 390			
Table A-19: Stability constants for the complexes NiOH <sup>+</sup> , Ni(OH) <sub>2</sub>				
	and Ni(OH) <sub>3</sub>			
Table A-20:	Stability constants $\log_{10} {}^*\beta_{3,1}^\circ$ for Ni(OH) <sub>3</sub> , $I=0$			
Table A-21:	Enthalpies and entropies of reaction from Skeaff et al 404			
Table A-22:	Enthalpies of formation for solid nickel sulphides at 298.15 K 406			
Table A-23:	Enthalpy of solution of NiCl <sub>2</sub> in H <sub>2</sub> O at 298.15 K [90EFI/FUR] 417			
Table A-24:	$\Delta_{\rm f} H_{\rm m}^{\circ}$ (NiCO <sub>3</sub> , 298.15 K) from decomposition data [91TAR/FAZ] 422			
Table A-25:	Enthalpy of solution of NiCl <sub>2</sub> in H <sub>2</sub> O at 298.15 K [95MAN/KOR] 430			
Table A-26:	Recommended formation constants $({}^*\beta_{n,m}^{\circ})$ and reaction enthalpies			
	for the hydroxo complexes formed in the acidic region,			
	at 298.15 K, $mNi^{2+} + nH_2O(1) \rightleftharpoons Ni_m(OH)_n^{2m-n} + nH^+$			
Table A-27:	Recommended equilibrium constants $({}^{*}K_{s,n,m}^{\circ})$ and reaction			
	enthalpies for the hydroxo complexes formed in the alkaline			
	region, at 298.15 K, $mNi(OH)_2(cr) + nOH \rightleftharpoons Ni_m(OH)_{2m+n}^n \dots 435$			
Table A-28:	Recommended ion interaction coefficients $\varepsilon(i, k)$			
Table A-29:	Standard thermodynamic functions of the aqueous species			
Table B-1: Water activities $a_{\rm H,o}$ at 2968.15 K for the most common ionic				
	media at various concentrations applying Pitzer's ion interaction			
	approach and the interaction parameters given in [91PIT]			
Table B-2:	Debye–Hückel constants as a function of temperature			
	at a pressure of 1 bar below 100°C and at the steam			
	saturated pressure for $t \ge 100^{\circ}$ C			
Table B-3:	The preparation of the experimental equilibrium constants			
1 1010 10 01	for the extrapolation to $I=0$ with the specific ion interaction			
	method at 25°C and 1 bar according to reaction (B 12) 454			
Table B-4.	Ion interaction coefficients $s(i, k)$ (kg-mol <sup>-1</sup> ) for eations			
Table D-4.	<i>i</i> with $k = Cl^{-}$ ClO <sub>2</sub> and NO <sub>2</sub> taken from			
	Ciavatta [80CIA] [88CIA] unless indicated otherwise 460			
	Ciavana [overa], [overa] unless indicated outerwise			

LIST O	F TA	BLES
--------	------	------

Table B-5:	Ion interaction coefficients $\varepsilon(j, k)$ (kg·mol <sup>-1</sup> ) for cations j with
	k = Li, Na and K, taken from Ciavatta [80CIA], [88CIA] unless
	indicated otherwise
Table B-6:	Ion interaction coefficients $\varepsilon(1, j, k)$ and $\varepsilon(2, j, k)$ for cations
	<i>j</i> with $k = CI^-$ , $CIO_4^-$ and $NO_3^-$ (first part), and for anions
	j with $k = \text{Li}^+$ , Na <sup>+</sup> and K <sup>+</sup> (second part), according
	to the relationship $\varepsilon = \varepsilon_1 + \varepsilon_2 \log_{10} I_{\rm m}$ . The data are taken
	from Ciavatta [80CIA], [88CIA]
Table B-7:	SIT interaction coefficient $\varepsilon(j, k)$ kg·mol <sup>-1</sup> for neutral species,
	j, with k, electroneutral combination of ions
Table C-1:	Details of the calculation of equilibrium constant corrected to $I=0$ ,
	using (C.19)

## Part I

## **Introductory material**

This page intentionally left blank