Nagra / PSI Chemical Thermodynamic Data Base 01/01

Wolfgang Hummel
Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

Urs Berner
Paul Scherrer Institut, Switzerland

Enzo Curti
Paul Scherrer Institut, Switzerland

F. J. Pearson
Ground-Water Geochemistry
411 East Front St., New Bern, NC, USA

Tres Thoenen
Paul Scherrer Institut, Switzerland

UNIVERSAL PUBLISHERS/uPublish.com
Parkland, Florida

Nagra/PSI Chemical Thermodynamic Data Base 01/01

Universal Publishers/uPUBLISH.com
USA • 2002

ISBN: 1-58112-620-4

www.uPUBLISH.com/books/hummel.htm

The cover shows quartz crystals in a big vein in Grimsel granodiorite (Swiss Alps). Photograph: Comet Photoshopping GmbH, Zürich. The periodic table of the elements indicates the database contents, i.e. elements commonly found as major solutes in natural waters (green), and actinides and fission products (red).

ABSTRACT

The Nagra/PSI Chemical Thermodynamic Data Base has been updated from version 05/92 to 01/01 to support an ongoing safety assessment of a planned Swiss repository for high-level radioactive waste. Database version 05/92 distinguished between "core data" and "supplemental data". Core data are for elements commonly found as major solutes in natural waters. These data are well established and have not been changed to any significant degree in this update. Supplemental data comprise actinides and fission products, Mn, Fe, Si and Al. Our update from version 05/92 to 01/01 involved major revisions for most of the supplemental data. Altogether, more than 70% of our database contents have been updated.

Data for U, Np, Pu, Am and Tc recommended by the internationally recognised NEA TDB project were considered in our update. Our reasons for not accepting several NEA recommendations are documented in detail. Thermodynamic data for Th, Sn, Eu, Pd, Al, and solubility and metal complexation of sulphides and silicates were extensively reviewed. Data for Zr, Ni and Se were examined less rigorously as these elements are currently being reviewed in phase II of the NEA TDB project.

Our experiences from this two year team effort can be summarised as follows. (1) Detailed in-house reviews and critical appraisal of NEA recommendations greatly improved the chemical consistency and quality of the selected data, as shown e.g. by comparison of complexation constants for M(III) and M(IV) oxidation states of actinides and fission products. (2) On the other hand, we could discern major gaps in the data, especially missing carbonate complexes. (3) In some systems, e.g. ThO_2 – H_2O and UO_2 – H_2O, experimental data could not be described by a unique set of thermodynamic constants. There, a pragmatic approach based on solubility data was chosen to provide data for application to performance assessment.

ZUSAMMENFASSUNG

Die Nagra/PSI Datenbank für chemische Thermodynamik wurde im Rahmen einer Sicherheitsanalyse für ein geplantes Schweizer Endlager für hochaktive Abfälle von Version 05/92 auf Version 01/01 aktualisiert. Die Datenbankversion 05/92 unterschied zwischen "Kerndaten" (core data) und "Ergänzungsdaten" (supplemental data). Kerndaten betreffen Elemente die normalerweise die Hauptbestandteile der gelösten Inhaltsstoffe natürlicher Wässer bilden. Diese Daten sind gut fundiert und wurden bei diesem Update nicht wesentlich geändert. Ergänzungsdaten umfassen Aktiniden und Spaltprodukte, Mn, Fe, Si und Al. Unser Update von Version 05/92 zu Version 01/01 bedingte eine wesentliche Überarbeitung der meisten dieser Ergänzungsdaten. Insgesamt wurden mehr als 70% der Werte in unserer Datenbank aktualisiert.

Daten für U, Np, Pu, Am und Tc, die im Rahmen des international anerkannten NEA TDB Projekts empfohlen wurden, sind in unserem Update berücksichtigt. Unsere Gründe dafür, dass wir nicht alle NEA Empfehlungen übernommen haben, sind ausführlich dokumentiert. Thermodynamische Daten für Th, Sn, Eu, Pd und Al, sowie Daten zur Löslichkeit und Metallkomplexierung von Sulfiden und Silikaten wurden detailliert von uns begutachtet. Daten für Zr, Ni und Se haben wir weniger rigoros überprüft, da diese Elemente zur Zeit im Rahmen der Phase II des NEA TDB Projekts begutachtet werden.

Die Erfahrungen aus dieser zweijährigen intensiven Arbeit unserer Gruppe können wie folgt zusammengefasst werden. (1) Ausführliche eigene Begutachtungen und die kritische Bewertung der NEA Empfehlungen haben die chemische Konsistenz und die Qualität der ausgewählten Daten deutlich verbessert. Dies wird z.B. mit einem Vergleich der Komplexbildungskonstanten für die Oxidationszustände M(III) und M(IV) von Aktiniden und Spaltprodukten aufgezeigt. (2) Andererseits konnten wir bedeutende Lücken in den Daten identifizieren. Besonders erwähnt seien hier fehlende Carbonat Komplexe. (3) In einigen Systemen, z.B. $ThO_2 - H_2O$ und $UO_2 - H_2O$, konnten die experimentellen Daten nicht mit einem einzigen widerspruchsfreien Satz thermodynamischer Konstanten beschrieben werden. Um dennoch Datensätze für die Sicherheitsanalyse bereitstellen zu können, wurde in diesen Fällen ein pragmatischer, auf Löslichkeitsdaten basierender Weg gewählt.

RÉSUMÉ

La banque de données chimiques et thermodynamiques de Cisra/PSI a été mise à jour dans le but d'appuyer l'analyse de sécurité en cours pour le dépôt planifié en Suisse de déchets hautement radioactifs. La version 05/92 de cette banque de données distinguait entre "données essentielles" et "données complémentaires". Les données essentielles correspondent aux éléments que l'on trouve communément en concentration élevée dans les eaux naturelles. Ces données sont bien établies et n'ont pas été modifiées de manière significative dans cette mise à jour. Les données complémentaires incluent les actinides et les produits de fission, Mn, Fe, Si et Al. Notre mise à jour de la version 05/92 à 01/01 implique des révisions majeures pour la plupart des données complémentaires. Au total, plus de 70 % de notre banque de données a été revue.

Dans la mise à jour, les données pour U, Np, Pu, Am et Tc recommandées par le projet NEA-TDB, reconnu au niveau international, ont été considérées. Les raisons qui nous amènent à ne pas accepter la totalité des recommandations de NEA ont été documentées en détail. Les données thermodynamiques pour Th, Sn, Eu, Pd, Al, ainsi que la solubilité et la complexation des sulphides et silicates avec les métaux ont été extensivement révisées. Les données pour Zr, Ni et Se ont été examinées avec moins de rigueur, en considérant que ces éléments sont actuellement en révision dans le cadre de la phase II du projet NEA-TDB.

Les enseignements tirés de cet effort de deux ans effectué par notre équipe, peuvent être résumés de la façon suivante. (1) Les révisions accomplies, ainsi que l'évaluation critique des recommandations de NEA, ont amélioré la consistance chimique et la qualité des données sélectionnées. La preuve en est apportée par la comparaison entre elles des constantes de complexation pour les états d'oxydation M(III) et M(IV) des actinides et des produits de fission. (2) D'autre part, nous avons pu discerner des lacunes majeures dans les données, en particulier l'absence de nombreux complexes du carbonate. (3) Pour certains systèmes, par exemple ThO_2 - H_2O et UO_2 - H_2O, l'ensemble des données expérimentales n'a pas pu être décrite par une série unique de constantes thermodynamiques. Dans ce cas, une approche pragmatique basée sur les données de solubilité a été choisie.

PREFACE AND ACKNOWLEDGEMENTS

My first proposal of a database update in 1997 and the support of this proposal by Dr. Bernhard Schwyn (Nagra) initialised the work documented in this report. At that time the modest project plan for a database update envisaged relying mainly on NEA's TDB reviews and to summarise the various bits and pieces of TDB work done at PSI.

Shortly after the project actually commenced in 1999 it turned into a fascinating team effort lasting for two years and resulting in a detailed review and update of more than 70% of our database contents. I want to thank my colleagues at PSI/LES, Drs. Urs Berner, Enzo Curti and Tres Thoenen, and the "founding father" of the original Nagra TDB, Dr. F.J. Pearson, for joining me in the seemingly never-ending task of reviewing a huge pile of literature, and reading, commenting on, and thus significantly improving each others' manuscripts.

The project of updating our database management program, PMATCHC, turned into an equally fascinating multi-national effort involving the designer F.J. Pearson, New Bern, USA, the programmer Svetlana Dmytriyeva, Kiev, Ukraine, the "interface" between designer and programmer Dmitrii A. Kulik, the principal user Tres Thoenen, and myself as the co-ordinator.

Comments and discussions that helped clarifying and improving the most opaque parts of drafts of this report have been provided by Prof. Ingmar Grenthe, KTH Stockholm, Sweden, by Dr. Volker Neck and Prof. J.I. Kim, FZK/INE Karlsruhe, Germany, and by Prof. Th. Fanghänel, FZR/IfR Dresden, Germany.

The entire manuscript of this report has undergone a peer review by an independent reviewer, according to Nagra's QA procedures. The peer review comment records may by obtained on request from Nagra. The peer reviewer is Prof. Ingmar Grenthe, Royal Institute of Technology (KTH), Stockholm, Sweden. His contributions are gratefully acknowledged.

I would like to thank Dr. Paul Wersin (Nagra) for his continuous support of our project, for patiently reminding us of our promised deadlines, for reviewing the entire report, and last but not least, for handling some non-trivial financial aspects of this project.

I appreciate the tireless efforts of Beatrice Gschwend merging "almost compatible" text files from different computer systems, solving numerous technical problems, and doing the layout work of the entire report.

Partial financial support by Nagra is gratefully acknowledged.

Paul Scherrer Institut, February 2002 Wolfgang Hummel

TABLE OF CONTENTS

Abstract I
Zusammenfassung II
Résumé III
Preface and acknowledgements IV
Table of contents V
List of tables XIII
List of figures XVII

1 Introduction 1

2 Database contents 7

2.1 Thermodynamic quantities and equilibrium constants 7

2.2 Medium effects 9
2.2.1 The Debye-Hückel limiting law 10
2.2.2 The extended Debye-Hückel equation 10
2.2.3 Expanded extended Debye-Hückel equations 11
2.2.4 The SIT equation 12
2.2.5 Activity coefficients of neutral species 16

2.3 Temperature effects 17
2.3.1 Temperature dependence of equilibrium constants 17
2.3.2 Constant heat capacity of reaction 19
2.3.3 Constant enthalpy of reaction 19
2.3.4 Temperature dependence and medium effects 20

2.4 Redox 21
2.4.1 Some useful relations 21
2.4.2 SIT for redox reactions 22

2.5 Database structure 25

2.6 Sources of thermodynamic data 30
2.6.1 Sources of core data 30
2.6.2 Sources of supplemental data 31

2.7 References 32

3 Summary of data evaluation 35

3.1 Chemical consistency of selected thermodynamic data 35
3.1.1 A first look at groups of metals and ligands 36
3.1.2 Chemical patterns based on periodic properties of the elements 41
3.1.3 Empirical correlations based on charge/size relations 45

3.2 Conflicting data 49

3.3 Uncertain data 53

3.4 Missing data 55

3.5 Future data needs 56

3.6 References 57

4 Core data 61

4.1 General criteria 61
4.1.1 Elements and master species 61
4.1.2 Solute species, minerals and gases 65

4.2 Oxygen, hydrogen, the electron and water 66
4.2.1 Master species: H^+, e^- or $O_2(g)$, H_2O, $O_2(aq)$, and $H_2(aq)$ 66
4.2.2 Oxide and hydroxide solute species, minerals, and gases 67

4.3 Halides: fluorine, chlorine, bromine and iodine ... 67
4.3.1 Master species: F^-, Cl^-, Br^- and I^- ... 67
4.3.2 Halide solute species ... 67

4.4 Sulphur ... 68
4.4.1 Master species: SO_4^{2-} and HS^- ... 68
4.4.2 Sulphate solute species and minerals ... 68
4.4.3 Reduced sulphur solute species and minerals ... 69

4.5 Nitrogen ... 69
4.5.1 Master species: NO_3^-, $N_2(aq)$, and NH_4^+ ... 69
4.5.2 Nitrogen solute species and gases ... 70

4.6 Phosphate, borate and arsenic ... 70
4.6.1 Master species: HPO_4^{2-}, $HAsO_4^{2-}$, and $B(OH)_3(aq)$ ... 70
4.6.2 Phosphate and borate solute species ... 71
4.6.3 Arsenate solute species and mineral ... 71

4.7 Carbon ... 72
4.7.1 Master species: HCO_3^- and $CH_4(aq)$ ... 72
4.7.2 Carbonate solute species, minerals, and gases ... 73
4.7.3 Reduced carbon species, minerals, and gases ... 73

4.8 References ... 74

5 Supplemental data ... 77

5.1. Aluminium ... 77
5.1.1 The system $Al - H_2O$ ... 77
5.1.1.1 Introduction ... 77
5.1.1.2 Sources and review of data ... 78
5.1.1.2.1 Data treatment ... 79
5.1.1.2.2 Review and selection of reaction data ... 81
5.1.1.2.3 Standard thermodynamic properties of aqueous species and gibbsite ... 88
5.1.1.3 Summary of the system $Al - H_2O$ ... 93
5.1.1.3.1 Elemental aluminium ... 93
5.1.1.3.2 Simple aluminium aqua ion ... 93
5.1.1.3.3 Aluminium oxygen and hydrogen compounds ... 93
5.1.2 Aluminium halogen compounds and complexes ... 95
5.1.2.1 Aqueous halogen complexes ... 95
5.1.2.2 Aluminium halide compounds ... 100
5.1.3 Aluminium chalcogen compounds and complexes ... 101
5.1.3.1 Aqueous aluminium sulphates ... 101
5.1.3.2 Aluminium sulphate compounds ... 102
5.1.4 Group 15 compounds and complexes ... 102
5.1.4.1 Aluminium nitrogen compounds and complexes ... 102
5.1.4.2 Phosphorous compounds and complexes ... 103
5.1.5 Group 14 compounds and complexes ... 103
5.1.5.1 Aluminium carbonate compounds and complexes ... 103
5.1.5.2 Aluminium silicate compounds and complexes ... 103
5.1.6 References ... 105

5.2 Americium ... 120
5.2.1 Elemental americium ... 120
5.2.2 Simple americium aqua ions ... 120
5.2.3 Oxygen and hydrogen compounds ... 121
5.2.3.1 Aqueous americium hydroxide complexes ... 121
5.2.3.2 Solid americium oxides and hydroxides ... 122
5.2.3.3 Americium hydrides ... 124
5.2.4 Halogen compounds and complexes ... 123
5.2.4.1 Aqueous halogen complex ... 123
5.2.4.2 Americium halide compounds ... 124
5.2.5 Chalcogen compounds and complexes ... 125

5.2.5.1 Americium chalcogenides 125
5.2.5.2 Aqueous americium sulphates 125
5.2.6 Group 15 compounds and complexes 126
5.2.6.1 Nitrogen compounds and complexes 126
5.2.6.2 Phosphorous compounds and complexes 126
5.2.6.3 Arsenic, antimony and bismuth compounds 128
5.2.7 Group 14 compounds and complexes 128
5.2.7.1 Carbon compounds and complexes 128
5.2.7.1.1 Americium carbides 128
5.2.7.1.2 Americium carbonate compounds and complexes 128
5.2.7.1.3 Americium cyanide complexes 130
5.2.7.1.4 Americium thiocyanate complexes 130
5.2.7.2 Silicon compounds and complexes 131
5.2.8 References 134

5.3 Calcium 135
5.3.1 References 135

5.4 Europium 136
5.4.1 Elemental europium 136
5.4.2 Free europium aqua ions 136
5.4.3 Oxygen and hydrogen compounds 140
5.4.3.1 Aqueous Eu(III) hydroxide complexes 140
5.4.3.2 Solid Eu(III) oxides and hydroxides 148
5.4.4 Europium(III) carbonate complexes and solids 151
5.4.4.1 Aqueous europium(III) carbonate complexes 151
5.4.4.2 Solid europium(III) carbonate compounds 153
5.4.5 Europium(III)sulphate complexes and solids 155
5.4.5.1 Europium(III) aqueous sulphate complexes 156
5.4.5.2 Europium(III) sulphate solids 158
5.4.6 Europium(III) phosphate complexes and solids 158
5.4.6.1 Eu(III) aqueous phosphate complexes 158
5.4.6.2 $EuPO_4 \cdot nH_2O$ and other phosphate solids 159
5.4.7. Halogenide complexes and compounds 159
5.4.7.1 Eu(III) fluoride aqueous complexes 159
5.4.7.2 Eu(III) fluoride solids 160
5.4.7.3 Eu(III) chloride complexes 160
5.4.7.4 Eu(III) chloride solids 161
5.4.8 Eu(III) nitrate aqueous complexes and solid compounds 161
5.4.9 Acknowledgements 164
5.4.10 References 164

5.5 Iodine 172
5.5.1 References 172

5.6 Iron 173
5.6.1 Hematite 175
5.6.2 Magnetite 176
5.6.3 Pyrite 178
5.6.4 Pyrrhotite 178
5.6.5 Troilite 179
5.6.6 Fe(III) carbonate complexes 180
5.6.7 References 181

5.7 Magnesium 183
5.7.1 Magnesite 183
5.7.2 References 187

5.8 Manganese 188
5.8.1 References 188

5.9 Molybdenum 189
5.9.1 References 189

5.10 Neptunium ... 190
5.10.1 Elemental neptunium ... 190
5.10.2 Neptunium aqua ions ... 190
5.10.2.1 NpO_3^+ ... 191
5.10.2.2 NpO_2^{2+} ... 192
5.10.2.3 NpO_2^+ ... 193
5.10.2.4 Np^{4+} ... 195
5.10.2.5 Np^{3+} ... 195
5.10.3 Neptunium oxygen and hydrogen compounds and complexes ... 197
5.10.3.1 Aqueous neptunium hydroxide complexes ... 197
5.10.3.2 Solid neptunium oxides and hydroxides ... 200
5.10.4 Halogen compounds and complexes ... 204
5.10.4.1 Neptunium halide compounds ... 204
5.10.4.2 Aqueous neptunium fluoride complexes ... 204
5.10.4.3 Aqueous neptunium chloride complexes ... 206
5.10.4.4 Aqueous neptunium bromide complexes ... 207
5.10.4.5 Aqueous neptunium iodide complexes ... 207
5.10.5 Chalcogen compounds and complexes (sulphates) ... 207
5.10.6 Group 15 compounds and complexes ... 209
5.10.6.1 Nitrogen compounds and complexes ... 209
5.10.6.2 Phosphorous compounds and complexes ... 210
5.10.7 Group 14 compounds and complexes ... 211
5.10.7.1 Neptunium carbides ... 211
5.10.7.2 Neptunium carbonates ... 212
5.10.7.3 Neptunium cyanide complexes ... 219
5.10.7.4 Neptunium thiocyanate complexes ... 219
5.10.8 Neptunium group 2 (alkaline-earth) and group 1 (alkali) compounds ... 220
5.10.9 References ... 220

5.11 Nickel ... 226
5.11.1 Elemental nickel ... 226
5.11.2 Simple nickel aqua ion ... 226
5.11.3 (Hydr)oxide compounds and complexes ... 226
5.11.3.1 Aqueous nickel hydroxide complexes ... 226
5.11.3.2 Thermodynamics of $Ni(OH)_2$(cr) and NiO(cr) ... 228
5.11.3.3 Thermodynamics of $NiFe_2O_4$(s) ... 228
5.11.4 Halogen compounds and complexes ... 229
5.11.5 Chalcogen compounds and complexes ... 229
5.11.5.1 Nickel sulphides ... 229
5.11.5.2 Nickel sulphates ... 229
5.11.6 Group 15 compounds and complexes ... 229
5.11.6.1 Nitrogen compounds and complexes ... 229
5.11.6.2 Phosphorous compounds and complexes ... 230
5.11.7 Group 14 compounds and complexes ... 230
5.11.7.1 Nickel carbonates ... 230
5.11.7.2 Nickel silicates ... 231
5.11.8 References ... 235

5.12 Niobium ... 236
5.12.1 References ... 236

5.13 Organics ... 237
5.13.1 Reference ... 237

5.14 Palladium ... 238
5.14.1 Elemental palladium ... 238
5.14.2 Simple palladium aqua ion ... 238
5.14.3 (Hydr)oxide compounds and complexes ... 242
5.14.3.1 Aqueous palladium hydroxide complexes ... 242
5.14.3.2 Solid palladium(II)-oxide/hydroxide ... 243
5.14.4 Halogen compounds and complexes ... 246

5.14.5 Chalcogen compounds and complexes 248
5.14.5.1 Palladium sulphides 248
5.14.5.2 Palladium sulphates 249
5.14.6 Group 15 compounds and complexes 249
5.14.6.1 Nitrogen compounds and complexes 249
5.14.6.2 Phosphorous compounds and complexes 250
5.14.7 Group 14 compounds and complexes 250
5.14.7.1 Palladium carbonates 250
5.14.8 References 253

5.15 Plutonium 256
5.15.1 Elemental plutonium 256
5.15.2 Plutonium aqua ions 256
5.15.2.1 PuO_2^{2+} 257
5.15.2.2 PuO_2^{+} 259
5.15.2.3 Pu^{4+} 260
5.15.2.4 Pu^{3+} 264
5.15.3 Plutonium oxygen and hydrogen compounds and complexes 266
5.15.4 Solid and gaseous plutonium halogen compounds 272
5.15.5 Aqueous plutonium fluoride complexes 273
5.15.6 Aqueous plutonium chloride complexes 275
5.15.7 Aqueous hypochloride complexes 276
5.15.8 Aqueous plutonium bromide complexes 276
5.15.9 Aqueous plutonium iodide complexes 276
5.15.10 Aqueous plutonium sulphate complexes 276
5.15.11 Solid plutonium arsenic, antimony, and bismuth compounds 280
5.15.12 Plutonium nitrogen compounds and complexes 280
5.15.13 Plutonium phosphorous compounds and complexes 281
5.15.14 Plutonium carbides 282
5.15.15 Aqueous plutonium carbonate complexes 282
5.15.15.1 Pu(VI) carbonate complexes 283
5.15.15.2 Pu(V) carbonate complexes 287
5.15.15.3 Pu(IV) carbonate complexes 289
5.15.15.4 Pu(III) carbonate complexes 290
5.15.16 Solid plutonium carbonates 291
5.15.17 Plutonium thiocyanate complexes 291
5.15.18 Plutonium silicides 291
5.15.19 Plutonium alkaline-earth compounds 291
5.15.20 References 297

5.16 Radium 299
5.16.1 References 301

5.17 Selenium 303
5.17.1 Elemental selenium 303
5.17.2 Redox 304
5.17.3 Selenide species 306
5.17.4 Selenite species 306
5.17.5 Selenate species 307
5.17.6 References 309

5.18 Silica and silicates 311
5.18.1 Elemental silicon 311
5.18.2 Silica (quartz) 311
5.18.3 Silica compounds and aqueous species 311
5.18.3.1 Silica compounds 311
5.18.3.2 Aqueous silica species 313
5.18.4 Metal silicate compounds and complexes 315
5.18.4.1 Calcium and magnesium 315
5.18.4.2 Aluminium 316
5.18.4.3 Iron 317

5.18.4.4 Europium ... 317
5.18.4.5 Americium ... 319
5.18.4.6 Uranium ... 319
5.18.4.7 Plutonium ... 321
5.18.5 References ... 323

5.19 Sulphides ... 325
5.19.1 Aqueous sulphide species ... 326
5.19.1.1 $H_2S(g)$ and $H_2S(aq)$ ... 326
5.19.1.2 HS^- ... 329
5.19.1.3 S^{2-} ... 332
5.19.2 Redox reactions ... 332
5.19.3 Actinides ... 333
5.19.3.1 Thorium ... 334
5.19.3.2 Uranium ... 335
5.19.3.3 Neptunium ... 336
5.19.3.4 Plutonium ... 337
5.19.3.5 Americium ... 338
5.19.4 Technetium ... 339
5.19.5 Zirconium ... 341
5.19.6 Tin ... 341
5.19.7 Radium ... 344
5.19.8 Nickel ... 344
5.19.9 Palladium ... 352
5.19.10 Europium ... 353
5.19.11 Appendix: SIT in seawater ... 354
5.19.12 References ... 360

5.20 Technetium ... 363
5.20.1 Elemental technetium ... 363
5.20.2 Simple aqueous technetium ions of each oxidation state ... 363
5.20.2.1 TcO_4^- ... 363
5.20.2.2 TcO_4^{2-} ... 364
5.20.2.3 Tc(V) ... 364
5.20.2.4 Tc(IV) ... 364
5.20.2.5 Tc^{3+} ... 364
5.20.2.6 Tc^{2+} ... 365
5.20.3 Oxide and hydrogen compounds and complexes ... 365
5.20.3.1 Aqueous species formed by hydrolysis and protonation reactions ... 365
5.20.3.2 Solid technetium solids and their hydrates ... 366
5.20.3.3 Gaseous technetium oxides ... 367
5.20.3.4 Technetium hydrides ... 367
5.20.4 Halogen compounds and complexes ... 368
5.20.5 Chalcogen compounds and complexes ... 368
5.20.5.1 Technetium sulphides ... 368
5.20.5.2 Technetium sulphates ... 368
5.20.6 Group 15 compounds and complexes ... 369
5.20.6.1 Nitrogen compounds and complexes ... 369
5.20.6.2 Phosphorous compounds and complexes ... 369
5.20.7 Group 14 compounds and complexes ... 369
5.20.7.1 Carbon compounds and complexes ... 369
5.20.7.1.1 Technetium carbides ... 369
5.20.7.1.2 Technetium carbonates ... 369
5.20.7.1.3 Technetium cyanides and oxycyanides ... 370
5.20.7.2 Silicon compounds and complexes ... 370
5.20.8 Pertechnetates and mixed oxides ... 370
5.20.9 References ... 373

5.21 Thorium ... 375
5.21.1 Basic values ... 375
5.21.2 Hydrolysis ... 376

5.21.3 Carbonate complexes ... 383
5.21.4 Complexes and solids with other ligands ... 385
5.21.5 Phosphate complexes ... 386
5.21.6 Fluoride complexes ... 387
5.21.7 Sulphate complexes ... 388
5.21.8 References ... 398

5.22 Tin ... 403
5.22.1 Basic values ... 403
5.22.2 Redox ... 404
5.22.3 Tin(IV) hydrolysis ... 406
5.22.4 Tin(IV) oxides / hydroxides ... 408
5.22.5 Other tin(IV) complexes / compounds ... 411
5.22.6 Tin(II) hydrolysis ... 414
5.22.7 Tin(II) oxides / hydroxides ... 416
5.22.8 Tin(II) chlorides ... 417
5.22.9 SnOHCl(s) ... 418
5.22.10 Tin(II) fluorides ... 419
5.22.11 Tin(II) carbonates ... 420
5.22.12 Tin(II) nitrates ... 422
5.22.13 Tin(II) sulphates ... 422
5.22.14 Tin(II) phosphates ... 424
5.22.15 References ... 428

5.23 Uranium ... 443
5.23.1 Elemental uranium ... 443
5.23.2 Simple uranium aqua ions ... 443
5.23.3 Oxygen and hydrogen compounds ... 445
5.23.3.1 Aqueous uranium hydroxide complexes ... 445
5.23.3.1.1 U(VI) hydroxide complexes ... 445
5.23.3.1.2 U(V) hydroxide complexes ... 448
5.23.3.1.3 U(IV) hydroxide complexes ... 448
5.23.3.2 Solid uranium oxides and hydroxides ... 455
5.23.3.2.1 U(VI) oxides and hydroxides ... 455
5.23.3.2.2 U(IV) oxides ... 457
5.23.3.2.3 Mixed valence oxides ... 458
5.23.3.3 Uranium hydrides ... 459
5.23.4 Halogen compounds and complexes ... 460
5.23.5 Chalcogen compounds and complexes ... 464
5.23.5.1 Sulphur compounds and complexes ... 464
5.23.5.1.1 Uranium sulphides ... 464
5.23.5.1.2 Uranium sulphites ... 464
5.23.5.1.3 Uranium sulphates ... 464
5.23.5.1.4 Uranium thiosulphates ... 466
5.23.5.2 Selenium compounds and complexes ... 467
5.23.5.3 Tellurium compounds ... 467
5.23.6 Group 15 compounds and complexes ... 467
5.23.6.1 Nitrogen compounds and complexes ... 467
5.23.6.2 Phosphorous compounds and complexes ... 468
5.23.6.3 Arsenic compounds ... 472
5.23.6.4 Antimony compounds ... 472
5.23.7 Group 14 compounds and complexes ... 472
5.23.7.1 Carbon compounds and complexes ... 472
5.23.7.1.1 Uranium carbides ... 472
5.23.7.1.2 Uranium carbonates ... 472
5.23.7.1.3 Uranium thiocyanate complexes ... 477
5.23.7.2 Silicon compounds and complexes ... 477
5.23.8 Alkali and alkaline-earth compounds ... 480
5.23.9 Uranium compounds and uranium minerals ... 480
5.23.10 References ... 489

5.24 Zirconium ... 491
5.24.1 Introduction ... 491
5.24.2 Elemental zirconium ... 492
5.24.3 Free zirconium aqua ions ... 492
5.24.4 Oxygen and hydrogen compounds ... 494
5.24.4.1 Preliminary remarks ... 494
5.24.4.2 Analysis of hydrolysis data ... 495
5.24.4.3 Aqueous hydroxide complexes and solid oxy-hydroxides: data selection ... 497
5.24.5 Halogen compounds and complexes ... 499
5.24.5.1 Fluoride complexes and solids ... 499
5.24.5.2 Zr chloride complexes and solids ... 505
5.24.6 Sulphate compounds and complexes ... 509
5.24.7 Zr carbonate compounds and complexes ... 513
5.24.8 Zr nitrate compounds and complexes ... 515
5.24.9 Zr phosphate compounds and complexes ... 515
5.24.10 Final remarks ... 516
5.24.11 References ... 518

Appendix A: Calculation of thermodynamic properties ... 527

A.1 Introduction ... 527
A.2 Thermodynamic quantities and equilibrium constants ... 527
A.2.1 Constants and units ... 528
A.2.2 Reactions, elements, solute species, minerals and gases ... 528
A.3 Thermodynamic equations ... 530
A.4 PMATCHC calculation scheme ... 532
A.5 Implicit assumptions ... 533
A.6 References ... 540

Appendix B: Tables of recommended thermodynamic properties ... 541

B.1 Reaction properties ... 543
B.2 Properties of formation from the elements and absolute properties ... 551
B.4 Parameters of temperature dependent equilibrium constants ... 560
B.4 Heat capacities and parameters for temperature dependent heat capacity equations ... 563

LIST OF TABLES

2.2.1 Summary of ε(i,k), Δε(reaction) and estimates based on chemical analogy evaluated in this review. 14

2.4.1 Comparison of ΔZ^2 and Δε for Case 1 (oxidation and reduction spatially separated in two electrochemical cells) and Case 2 (oxidation and reduction spatially not separated). 25

2.5.1 Primary master species 27

2.5.2 Secondary master species 27

2.5.3 Example of a database structure for the chemical system H–C–O–Ca–U. 28

2.5.4 Formation reactions of secondary redox master species 29

3.1.1 M(IV) compounds and complexes. 37

3.1.2 M(III) compounds and complexes. 38

3.1.3 M(VI)-dioxo complexes and solids. 39

3.1.4 Actinide redox couples 40

3.1.5 Compilation of formation constants ($\log_{10}\beta_1°$) for monodentate mononuclear complexes included in the updated database. 44

4.1 Thermodynamic data for the elements 62

4.2 Comparison of auxiliary data differing in NTB 91-18 from NEA 63

4.3 Variation of gas solubilities with temperature. 65

5.1.1 Summary of data examined for reactions forming Al^{3+} aqueous species and gibbsite solubility. 109

5.1.2 Thermodynamic properties of formation of elements from several sources used in calculations of properties of formation of gibbsite and aqueous species 110

5.1.3 Thermodynamic properties of formation of water from several sources used in calculations of properties of formation of gibbsite and aqueous species 111

5.1.4 Thermodynamic properties of formation of OH^- from various sources. 112

5.1.5 Thermodynamic properties of formation of gibbsite from various sources. 113

5.1.6 Thermodynamic properties of formation of Al^{3+} from various sources. 114

5.1.7 Thermodynamic properties of formation of $Al(OH)_4^-$ from various sources. 115

5.1.8 Thermodynamic properties of formation of $AlOH^{2+}$ from various sources. 116

5.1.9 Thermodynamic properties of formation of $Al(OH)_2^+$ from various sources. 117

5.1.10 Thermodynamic properties of formation of $Al(OH)_3$ from various sources 118

5.1.11 Comparison of thermodynamic properties of formation of gibbsite as consistency check on species properties chosen. 119

5.1.12 Experimental $\log K_n$ data compiled for the equilibria $AlF_{n-1}^{(4-n)} + F^- \Leftrightarrow AlF_n^{(3-n)}$. 96

5.1.13 Selected aluminium data 104

5.2.1 Selected americium data 132

5.4.1 Conditional constants and auxiliary information used to determine $\log_{10}{}^*\beta_1°$ for $Eu(OH)_2^+$ 142

5.4.2 Comparison of thermodynamic formation constants for $EuOH^{2+}$ 144

5.4.3 Extrapolation of Eu hydrolysis constants with the electrostatic model of NECK & KIM (2000) 146
5.4.4 Selection of Eu(III) thermodynamic data and comparison with the data selected for Am(III) 163
5.4.A1 Experimental data and calculated quantities for SIT regression, referring to Figures 5.4.1, 5.4.2 and 5.4.3 169
5.4.A2 Experimental data and calculated quantities for SIT regression, referring to Figures 5.4.5 and 5.4.6 170
5.4.A3 Experimental data and calculated quantities for SIT regression, referring to Figures 5.4.7 and 5.4.8 170
5.4.A4 Experimental data and calculated quantities for SIT regression, referring to Figures 5.4.9 and 5.4.10 171
5.7.1 Thermodynamic data at 298.15 K and 1 bar as used by KÖNIGSBERGER et al. (1999) 184
5.7.2 Selected thermodynamic data for the "clandestine" solid phases at 298.15 K and 1 bar 186
5.10.1 Selected neptunium data 221
5.11.1 Selected nickel data 232
5.14.1 Experimental data compiled for the redox pair Pd^{2+}/Pd(s), according to the equilibrium $Pd^{2+} + 2e^- \Leftrightarrow$ Pd(s) 240
5.14.2 Selected palladium data 251
5.15.1 Pu(VI) carbonate complexation constants 286
5.15.2 Compilation of selected actinide(IV) carbonate complexation constants 290
5.15.3 Selected plutonium data 292
3.16.1 Selected radium data at 25°C and 1 bar. All from LANGMUIR & RIESE (1985) 301
3.17.1 Compilation of selenium data 308
5.18.1 Selected silica and silicate data 322
5.19.1 Overview of the data update for sulfides 325
5.19.2 Thermodynamic data for thorium sulfide solids at 298.15 K as selected by GRØNVOLD et al. (1984) 333
5.19.3 Thermodynamic data for uranium sulfide solids at 298.15 K as selected by GRENTHE et al. (1992) 336
5.19.4 Thermodynamic data for neptunium sulfide solids at 298.15 K as selected by GRØNVOLD et al. (1984) 337
5.19.5 Thermodynamic data for plutonium sulfide solids at 298.15 K as selected by GRØNVOLD et al. (1984) 338
5.19.6 Thermodynamic data for americium sulfide and oxysulfide solids at 298.15 K as reported by SILVA et al. (1995) 339
5.19.7 Thermodynamic data for technetium sulfide solids at 298.15 K and 1 bar as listed in NTB 91-18 340
5.19.8 Thermodynamic data for tin sulfide solids at 298.15 K and 1 bar as listed in NTB 91-18 342
5.19.9 Thermodynamic data for nickel sulfide solids at 298.15 K and 1 bar as listed in NTB 91-18 346
5.19.10 Thermodynamic data at 298.15 K and 1 bar compiled by MILLS (1974) 347
5.19.11 Values for conditional stability constants of $NiHS^+$ used for extrapolation of the stability constants to $I = 0$ 348

5.19.12 Values for conditional stability constants of $Ni(HS)_2(aq)$ used for extrapolation of the stability constants to $I = 0$ ... 349
5.19.13 Thermodynamic data for palladium sulfide solids at 298.15 K and 1 bar as listed in NTB 91-18 ... 354
5.19.14 Various compositional parameters of seawater as calculated from the salinities at which the nickel bisulfide complexation experiments reported in Tables 5.19.11 and 5.19.12 were performed ... 355
5.19.15 Selected thermodynamic data for sulfide solids and species at 298.15 K and 1 bar ... 358
5.20.1 Selected technetium data ... 371
5.21.1 Compilation of selected Th(IV) data ... 392
5.21.2 Compilation of Th(IV) hydrolysis and carbonate data ... 395
5.22.1 Compilation of selected tin data ... 425
5.22.2 Experimental $\log_{10}K$ values for the reaction $Sn^{2+} + 2e^- \Leftrightarrow Sn(cr)$. ... 404
5.22.3 Experimental $\log_{10}K$ values for the reaction $Sn(OH)_4(aq) + H_2O(l) \Leftrightarrow Sn(OH)_5^- + H^+$. ... 406
5.22.4 Experimental $\log_{10}K$ values for the reaction $Sn(OH)_4(aq) + 2\ H_2O(l) \Leftrightarrow Sn(OH)_6^{2-} + 2\ H^+$. ... 407
5.22.5 Excerpt of solubility measurements as taken form AMAYA et al. (1997) ... 410
5.22.6 Experimental $\log_{10}K$ values for $SnO_2(precip) + 2\ H_2O(l) \Leftrightarrow Sn(OH)_4(aq)$ ... 410
5.22.7 Experimental $\log_{10}K$ values for $CaSn(OH)_6(s) \Leftrightarrow Sn(OH)_6^{2-} + Ca^{2+}$. ... 412
5.22.8 Experimental formation constants for tin(IV) complexes ... 413
5.22.9 Experimental $\log_{10}K$ values for hydrolysis reactions of Sn(II) ... 414
5.22.10 Experimental $\log_{10}K$ values for the solubility of Sn(II) oxides/hydroxides ... 416
5.22.11 Experimental $\log_{10}K$ values for Sn(II) chloride complex formation ... 418
5.22.12 $\text{Log}_{10}K$ values for Sn(II) fluoride complex formation ... 421
5.22.13 Experimental $\log_{10}K$ values for Sn(II) nitrate complex formation ... 423
5.23.1 Selected uranium data ... 482
5.24.1 Compilation of hydrolysis constants for Zr ... 499
5.24.2 Conditional formation constants of Zr fluoride complexes considered for SIT extrapolation ... 500
5.24.3 Formation constants of Zr fluoride complexes, extrapolated to zero ionic strength using SIT ... 503
5.24.4 Interaction coefficients ε(i,k) for Zr^{4+} and fluoride complexes with perchlorate ... 505
5.24.5 Data considered for the extrapolation of the formation constants for Zr chloride complexes at zero ionic strength ... 506
5.24.6 Formation constant and SIT parameters of the Zr monochloride complex ... 507
5.24.7 Data considered for the extrapolation of the formation constants for Zr sulphate complexes at zero ionic strength ... 511
5.24.8 Selection of thermodynamic data for Zr(IV) ... 517
5.24.A1 Experimental data and calculated quantities for SIT regressions, referring to Figure 5.24.2a ... 522
5.24.A2 Experimental data and calculated quantities for SIT regressions, referring to Figure 5.24.2b ... 523
5.24.A3 Experimental data and calculated quantities for SIT regressions, referring to Figure 5.24.3 ... 524

5.24.A4 Experimental data and calculated quantities for SIT regressions, referring to Figure 5.24.4 525
A1 Summary of PMATCH calculation cases 534
A2 List of aqueous species, solids and gases from the Nagra/PSI TDB 01/01 which are affected by the shortcomings of the present version of PMATCHC. 539
B1 Reaction properties 543
B2 Properties of formation from the elements and absolute properties 551
B3 Parameters of temperature dependent equilibrium constants 560
B4 Heat capacities and parameters for temperature dependent heat capacity equations 563

LIST OF FIGURES

1.1 Sketch of the iterative procedure to derive reliable solubility limits and sorption values for performance assessment (PA) by developing problem specific TDB extensions. 4

3.1.1 Correlation between ionic index (z^2/r, square of formal charge divided by ionic radius, after NIBOER & RICHARDSON, 1980) and $\log_{10}\beta_1°$ for the monofluoride complexes of hard cations and Ni(II). 45

3.1.2 Correlation between ionic index (z^2/r, square of formal charge divided by ionic radius, after NIBOER & RICHARDSON, 1980) and $\log_{10}{}^{*}\beta_1°$ for the monohydroxo complexes of hard cations and Ni(II). 46

3.1.3 Correlation between ionic index (z^2/r, square of formal charge divided by ionic radius, after NIBOER & RICHARDSON, 1980) and $\log_{10}\beta_1°$ for the monosulphate complexes of hard cations and Ni(II). 47

3.1.4 Solubility products of the crystalline hydroxides of trivalent hard cations included in the database ($M(OH)_3(cr) + 3\ H^+ \Leftrightarrow M^{3+} + 3\ H_2O$). 48

3.1.5 Solubility products of amorphous hydrous oxides of tetravalent hard cations included in the database ($MO_2(am) + 2\ H_2O \Leftrightarrow M(OH)_4(aq)$). 49

3.2.1 The concentration of dissolved Th(IV) as a function of pH determined for crystalline $ThO_2(cr)$ and amorphous $ThO_2(am)$. The solubility data are taken from MOON (1989). 50

3.2.2 Solubility data of the system Th(IV) - H_2O. 51

3.2.3 Solubility data of the system U(IV) - H_2O. 52

5.1.1 Concentrations of Al^{3+} hydrolysis products and total Al at pH values from 3 to 11 at gibbsite ($Al(OH)_3$) saturation in solution of zero ionic strength. 77

5.1.2 Comparison of total Al^{+3} concentrations at pH values from 3 to 11 at gibbsite saturation in solution of zero ionic strength. 84

5.1.3 Comparison of logK(T) values for association of $Al(OH)_4^-$ (= AlO_2^-) at temperatures from 5 to 95°C. 86

5.1.4 Comparison of logK(T) values for association of $AlOH^{2+}$ at temperatures from 5 to 95°C. 87

5.1.5 Extrapolation to zero ionic strength of experimental data for the formation of $AlF_n^{(3-n)}$ using SIT. 99

5.1.6 Predominance diagram of the system Al–F–H_2O at zero ionic strength, at constant Na concentration of 0.1M and total Al concentration of 10^{-5}M. 100

5.4.1 Determination of $\log_{10}\beta_1°$ and $\Delta\varepsilon$ for $Eu(OH)^{2+}$ based on the SIT equation in NaCl solutions 143

5.4.2 Determination of $\log_{10}\beta_1°$ and $\Delta\varepsilon$ for $Eu(OH)^{2+}$ based on the SIT equation in $NaClO_4$ solutions 143

5.4.3 SIT plot for Am(III) and Cm(III) first hydrolysis constants 144

5.4.4 Solubility of $Eu(OH)_3(cr)$ in carbonate free 0.1 M $NaClO_4$, computed from the constants selected for the database update, and comparison with the data of BERNKOPF (1984). 149

5.4.5 Determination of $\log_{10}\beta_1°$ and $\Delta\varepsilon$ for $Eu(CO_3)^+$ based on the SIT formalism 152

5.4.6 Determination of $\log_{10}\beta_2°$ and $\Delta\varepsilon$ for $Eu(CO_3)_2^-$ based on the SIT formalism 153

5.4.7 Determination of $\log_{10}\beta_1°$ and $\Delta\varepsilon$ for $Eu(SO_4)^+$ based on the SIT formalism 157

5.4.8 Determination of $\log_{10}\beta_2°$ and $\Delta\varepsilon$ for $Eu(SO_4)_2^-$ based on the SIT formalism 157

5.4.9 Determination of $\log_{10}\beta_1°$ and $\Delta\varepsilon$ for $EuCl^{2+}$ based on the SIT formalism 162

5.4.10 Determination of $\log_{10}\beta_2°$ and $\Delta\varepsilon$ for $EuCl_2^+$ based on the SIT formalism 162
5.10.1 Schematic representation of the selection and derivation process of thermodynamic quantities by LEMIRE et al. (2001) for Np^{3+}, Np^{4+}, NpO_2^+ and NpO_2^{2+}. 191
5.14.1 Plot of $\log_{10}K + 4D$ versus I_m for the reaction $Pd^{2+} + 2e^- \Leftrightarrow Pd(s)$ at 25°C 241
5.14.2 Plot of $\log_{10}K$ versus reciprocal temperature for the reaction $Pd^{2+} + 2e^- \Leftrightarrow Pd(s)$ 242
5.14.3 Synopsis of all experimental solubility data of $Pd(OH)_2(am)$ in $NaClO_4$ of VAN MIDDLESWORTH and WOOD (1999), and of WOOD (1991) in dilute solutions. 246
5.14.4 Plot of $\log_{10}K - 2D$ versus I_m for the reaction $PdCl_3^- + Cl^- \Leftrightarrow PdCl_4^{2-}$ at 25°C. 247
5.15.1 Schematic representation of the derivation and selection process of thermodynamic data for PuO_2^{2+} 258
5.15.2 Schematic representation of the derivation and selection process of thermodynamic data for PuO_2^+ 261
5.15.3 Schematic representation of the derivation and selection process of thermodynamic data for Pu^{4+} 262
5.15.4 Schematic representation of the derivation and selection process of thermodynamic data for Pu^{3+} 265
5.18.1 Temperature dependence of total dissolved silica in Swiss groundwaters. 313
5.18.2 Histogram of quartz saturation indices calculated for 284 Swiss groundwater analyses. 314
5.18.3 Contour plot showing the concentration of dissolved silicate needed in order to complex 50% Eu(III) 318
5.18.4 Contour plot showing the concentration of dissolved silicate needed in order to complex 50% U(VI) 320
5.19.1 Experimental data by GAMSJÄGER & SCHINDLER (1969) and BARRET et al. (1988) for the reaction $H_2S(g) \Leftrightarrow H_2S(aq)$ in NaCl solutions at 25°C 328
5.19.2 Experimental data by ALMGREN et al. (1976) and HERSHEY et al. (1988) for the reaction $H_2S(aq) \Leftrightarrow H^+ + HS^-$ in NaCl solutions at 25°C 330
5.19.3 Values of the second dissociation constant of $H_2S(aq)$ as a function of the year of determination 331
5.19.4 Weighted linear regressions for the extrapolation of conditional stability constants in seawater to I=0 for $NiHS^+$ and $Ni(HS)_2(aq)$ 351
5.21.1 Solubility of thorium dioxide as a function of pH from different authors 377
5.21.2 Evaluation of $\Delta\varepsilon$ for the reaction $Th^{4+} + 4\ H_2O \Leftrightarrow Th(OH)_4(aq) + 4\ H^+$ 380
5.21.3 Evaluation of $\Delta\varepsilon$ for the reaction $Th^{4+} + H_2O \Leftrightarrow Th(OH)^{3+} + H^+$ 382
5.22.1 Solubility of $SnO_2(am)$ 408
5.22.2 SIT regression for the reaction $Sn^{2+} + 2e^- \Leftrightarrow Sn(cr)$ 432
5.22.3 Experimental data according to VASIL'EV et al. (1979) 433
5.22.4 SIT regression for the reaction $Sn^{4+} + 2e^- \Leftrightarrow Sn^{2+}$ 434
5.22.5 SIT regression for the reaction $CaSn(OH)_6(precip) \Leftrightarrow Sn(OH)_6^{2-} + Ca^{2+}$. 435
5.22.6 SIT regression for the reaction $Sn^{2+} + H_2O(l) \Leftrightarrow SnOH^+ + H^+$ 436
5.22.7 SIT regression for the reaction $Sn^{2+} + 2\ H_2O(l) \Leftrightarrow Sn(OH)_2(aq) + 2\ H^+$ 437
5.22.8 SIT regression for the reaction $Sn^{2+} + 3\ H_2O(l) \Leftrightarrow Sn(OH)_3^- + 3\ H^+$ 438
5.22.9 SIT regression for the reaction $Sn^{2+} + Cl^- \Leftrightarrow SnCl^+$ 439
5.22.10 SIT regression for the reaction $Sn^{2+} + 2\ Cl^- \Leftrightarrow SnCl_2(aq)$ 440

5.22.11 SIT regression for the reaction $Sn^{2+} + 3\ Cl^- \Leftrightarrow SnCl_3^-$ 441
5.22.12 SIT regression for the reaction $Sn^{2+} + F^- \Leftrightarrow SnF^+$ 442
5.23.1 Solubility data of the system UO_2 - H_2O. The lines have been calculated using thermodynamic constants recommended by GRENTHE et al. (1992). 450
5.23.2 Solubility data of the system UO_2 - H_2O. The thick solid line is calculated using thermodynamic constants estimated in this review. Dotted lines represent the estimated uncertainty. 452
5.23.3 Solubility and predominance diagram of the U(VI)/U(IV) hydroxide system at 25°C in the range 4 < pH < 10, as a function of the redox potential. 459
5.23.4 Venn diagram representing the set of uranium solids in GRENTHE et al. (1992), the set of uranium minerals "officially" recognised (MINERAL DATABASE 1997) and the set of uranium minerals for which thermodynamic data have been selected 481
5.24.1 Solubility data for Zr oxides and hydrous oxides compared with predictions based on the hydrolysis constants selected by BAES & MESMER (1986) 497
5.24.2a SIT plots for the determination of zero ionic strength constants for ZrF^{3+}, ZrF_2^{2+} and ZrF_3^+ 501
5.24.2b SIT plots for the determination of zero ionic strength constants for $ZrF_4(aq)$, ZrF_5^- and ZrF_6^{2-} 502
5.24.3 SIT plots for the determination of zero ionic strength constants for $ZrCl^{3+}$, $ZrCl_2^{2+}$ and $ZrCl_3^+$ 508
5.24.4 SIT plot for the determination of the zero ionic strength constant for formation of $Zr(SO_4)^{2+}$ 512
5.24.5 Solubility of monoclinic zirconia and an unaged Zr oxy-hydroxide precipitate as a function of total carbonate concentration: comparison of experimental data with computed solubility curves 514

1 INTRODUCTION

The safety of radioactive waste disposal is one of the most debated topics in the field of environmental hazards. From a scientific point of view, to be convincing, evaluations of any waste disposal project must be based on sound theories and methods. One of these sound and well-established scientific theories is chemical equilibrium thermodynamics. Heavy metals (i.e. most radionuclides) will not dissolve without limits in the pore fluids of an underground repository due to the precipitation of sparingly soluble solids. Chemical equilibrium thermodynamics allows estimation of the maximum concentration of a given radionuclide in a specified pore fluid. This concept of solubility limits on radionuclide concentrations constitutes one of the pillars of safety of most radioactive waste disposal concepts (HADERMANN 1997).

Thermodynamic constants in PA are used for more than assessing radionuclide solubility limits (BERNER 1995, 1999). They are also used in modelling reference pore waters (PEARSON & SCHOLTIS 1993, CURTI 1993), and they are needed in deriving case-specific sorption coefficients (BRADBURY & BAEYENS 1997). It is important to use the same database throughout this model chain in order to guarantee internally consistent results: The definition of the pore water of a host rock, e.g. the pore water of a clay formation or crystalline rock, is a prerequisite for deriving consistent pore water compositions of cementitious waste and of the backfill of the underground caverns, e.g. bentonite. This bentonite pore water in turn is needed to calculate elemental solubility limits for all radionuclides within the repository. Likewise, cement, backfill and host rock pore water compositions are needed to adjust radionuclide sorption coefficients to these site specific conditions.

The original Nagra Thermochemical Data Base (TDB), issued in 1992, was based on data reviews and experimental studies published through 1990 (PEARSON & BERNER 1991, PEARSON et al. 1992). It was developed to support the performance assessment of a planned Swiss repository for high-level waste in crystalline rock (NAGRA 1994). The Nagra/PSI Chemical Thermodynamic Data Base has now been updated to support the ongoing performance assessment of an alternative repository concept for high-level waste in a clay formation.

Our update work was guided by the following questions which have to be answered when using thermodynamic data in performance assessment:

- Are the thermodynamic data sufficiently accurate ?
- Does the thermodynamic database contain the information necessary to describe the safety relevant processes in sufficient detail?
- Is equilibrium thermodynamics applicable for the system to be modelled?