nagra

National Cooperative for the
Disposal of Radioactive Waste

TECHNICAL REPORT 02-16

**Nagra / PSI
Chemical Thermodynamic
Data Base 01/01**

July 2002

W. Hummel, U. Berner, E. Curti,
F.J. Pearson, T. Thoenen

TECHNICAL REPORT 02-16

**Nagra / PSI
Chemical Thermodynamic
Data Base 01/01**

July 2002

W. Hummel[1], U. Berner[1], E. Curti[1],
F.J. Pearson[2], T. Thoenen[1]

[1] Paul Scherrer Institut, CH-5232 Villigen PSI

[2] Ground-Water Geochemistry, 411 East Front St., New Bern,
NC 28560-4916, USA

PREFACE

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.

FOREWORD AND ACKNOWLEDGEMENTS

Paul Scherrer Institut, February 2002 Wolfgang Hummel

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

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?

Accuracy and precision of data. Quantitative estimates of radionuclide speciation and solubility need reliable thermodynamic equilibrium constants. These constants cannot yet be calculated ab initio, so they must be derived from experimental studies of appropriate chemical systems. The increasing demand for reliable speciation and solubility data within the scope of radioactive waste disposal projects has triggered many experimental studies over the last three decades. The results of these studies have been reviewed by international expert groups with the aim of recommending reliable thermodynamic equilibrium constants. The most ambitious international project in this field is the TDB project of OECD's Nuclear Energy Agency (GRENTHE et al. 1992, SILVA et al. 1995, RARD et al. 1999, LEMIRE et al. 2001, see also http://www.nea.fr/). It has been recognised in this project that the documentation of the *precision* of the thermodynamic data in experimental studies is often good. However, the data might be affected by systematic errors and hence, the *accuracy* of these data is often lower than the estimated precision. Differences in the chemical speciation models used in various investigations can be the source of significant systematic errors in the thermodynamic equilibrium constants selected. It is very difficult to give a reliable estimate of this error. In our review work we followed the practice of the NEA TDB project and tried to estimate the accuracy of the recommended thermodynamic quantities. We believe that we achieved this goal, but with varying degrees of success. However, also following the practice of the NEA TDB project, we provide the user of our database with full documentation of our data selection procedures for each recommended quantity. In any case of doubt the user can scrutinise the appropriate documentation to criticise and improve our data selection procedure.

Completeness of the database. There is a long-standing debate about the contents and goals of thermodynamic databases. In a nutshell this debate can be summarised by two extreme viewpoints:

An ideal "puristic" TDB would contain solely "generally accepted" and "well established" quantities based on carefully evaluated sound experimental data. The NEA TDB project aims at such a puristic database. However, due to the uneven distribution of chemical knowledge a puristic TDB will always remain incomplete. It cannot be used for performing predictive work in complex environments without additional expert knowledge.

An ideal "ready-for-application" TDB would contain all the information necessary to describe the chemical system under study in sufficient detail. Performance assessors of planned repositories for radioactive waste would like to have "ready-for-application" databases. However, completeness of a "ready-for-application" TDB cannot be reached "in general" but only for a given application. A certain amount of "site-specific" chemical information is always required to identify gaps in the description of the safety relevant processes, and expert judgement is needed to fill these gaps, e.g.

by applying the methods discussed in GRENTHE et al. (1997). Failure to identify such gaps and to estimate their consequences may result in serious mistakes in performing predictive work.

In the course of the update process of the Nagra/PSI TDB 01/01 we decided to go beyond the puristic TDB ("generally accepted" and "well established" data in Fig. 1.1). We identified important cases of insufficient chemical knowledge leading to gaps in the puristic TDB. The first case reveals insufficient process understanding: A growing number of experimental data for specific systems cannot be interpreted by a unique set of thermodynamic constants ("ill-defined systems" in Fig. 1.1). For these systems we chose a pragmatic approach suited for performance assessment of radioactive waste repositories by including parameters in our TDB that are not thermodynamic constants in a strict sense, but that reproduced relevant experimental observations (see Chapter 3.2). The second case concerns insufficient experimental data: Important thermodynamic equilibrium constants are either uncertain or completely missing. We decided to include some of these uncertain data in our TDB (see Chapter 3.3) and we also included a few estimated data, e.g. radium data (see Chapter 5.16). In spite of these additions, for practical use it may be necessary to complete our database with problem-specific TDB extensions. The iterative procedure leading to estimates of important missing data is outlined in Fig. 1.1. Hints for the user on estimation procedures can be found throughout Chapter 5, e.g. the recommendation to use Am data as estimates for other trivalent actinides. The non-trivial case of estimating ternary hydroxide carbonate complexes for tetravalent actinides is discussed in detail in HUMMEL & BERNER (2002). These problem-specific TDB extensions are not part of this TDB report. They belong with the documentation of the specific applications for which they were derived (Fig. 1.1).

Equilibrium and non-equilibrium systems. The distinction between equilibrium and non-equilibrium systems, especially in the case of redox reactions, is highly case specific. For most potential redox reactions involving nitrogen, sulphur, or radionuclides in different oxidation states, the question of whether equilibrium thermodynamics is applicable for the entire system to be modelled calls for system specific or "extra-thermodynamic" information. This means qualitative kinetic information answering the question "Will a thermodynamically feasible redox reaction actually happen in a specific environment within a given time scale?". We included many redox equilibrium constants in our TDB but we cannot guarantee that any of them represents chemical equilibrium in a specific application. In PA modelling it has to be decided for every redox sensitive radionuclide whether a particular thermodynamic equilibrium applies or whether a fixed oxidation state has to be assumed. This issue continues to be debated in workshops and conferences, and it has been proposed that an international long-term experimental program should explore the kinetic constraints of redox processes for every key radionuclide. Some of these experiments should be set up as "integrated" experiments comprising iron corrosion products, bentonite backfill and radionuclides.
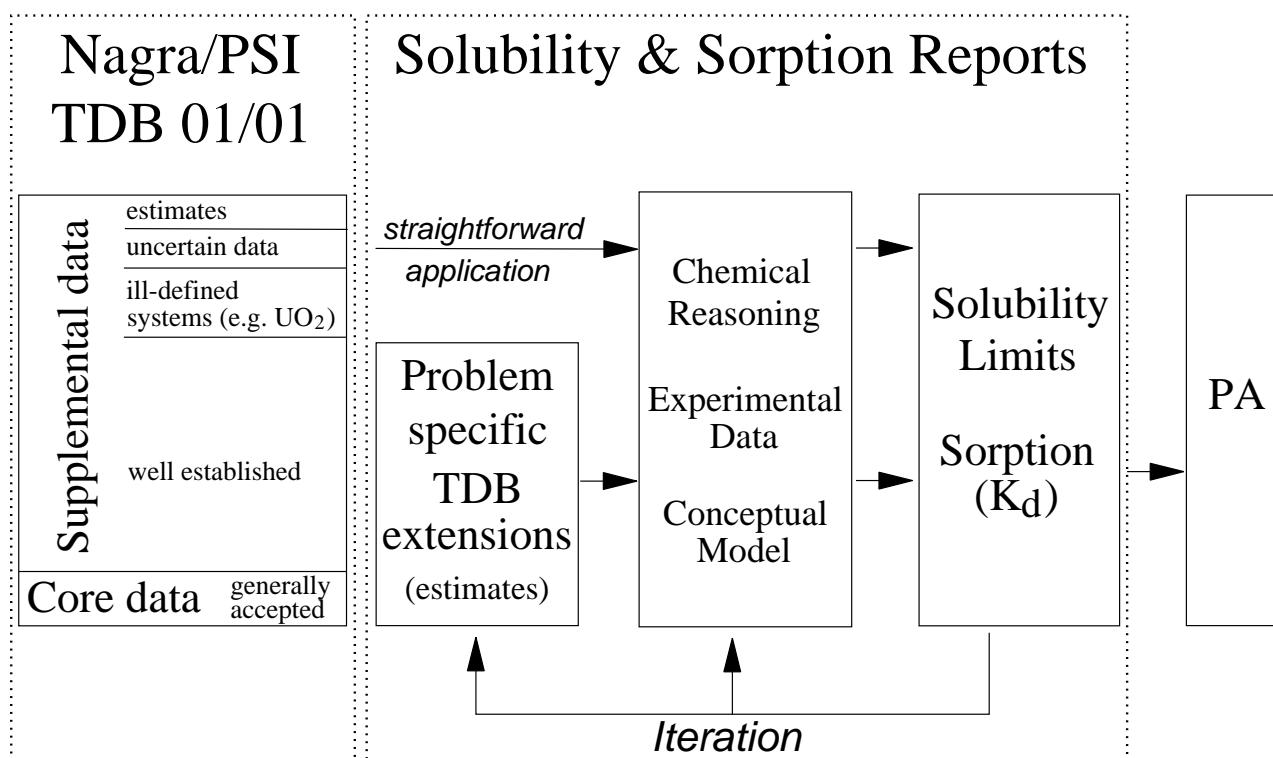
Fig. 1.1:   Sketch of the iterative procedure to derive reliable solubility limits and sorption values for performance assessment (PA) by developing problem specific TDB extensions. A worked example of this procedure can be found in HUMMEL & BERNER (2002).

The Nagra TDB version 05/92 distinguished two types of data, "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.

Data for U, Np, Pu, Am and Tc recommended by the NEA TDB project were considered in our update, and in most cases we followed the NEA recommendations. 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.

This report is the result of a two year team effort of all co-authors. Although all individual reviews have been read and commented on by the other co-authors as part of our in-house quality assurance

procedures, slightly different styles of writing and nuances in review philosophy can be recognised by comparing different chapters of this report. We intentionally did not try to erase these traces of individual preferences.

It should be mentioned that unlike most other database updates, our update includes fewer compounds and complexes than the original version. This is the result of our efforts to discharge ballast, i.e. to remove data for highly soluble salts, and hypothetical, questionable or completely irrelevant compounds and complexes. In addition, data of questionable quality have been removed.

Finally, it is appropriate to comment on the name of our TDB. The first version was called the Nagra Thermochemical Data Base as a short-hand way of writing "Chemical Thermodynamic Data Base". We decided to choose now the longer name in order to avoid ambiguities concerning the term "thermochemical". The official name "Nagra/PSI Chemical Thermodynamic Data Base" is abbreviated in this document to "Nagra/PSI TDB". The slight change from "Nagra TDB" to "Nagra/PSI TDB" symbolises the shift in responsibility for the TDB contents. The different versions of our database are labelled by the date of their official issue. Hence, the original version, finished in May 1992, is named "Nagra TDB 05/92", the current version, finished January 2001, is named "Nagra/PSI TDB 01/01" and future official versions will accordingly be named "Nagra/PSI TDB *month/year*". The most recent information can be found on our home page (http://www.psi.ch/les).

REFERENCES

BERNER, U. (1995): Kristallin-I Estimates of Solubility Limits for Safety Relevant Radionuclides. PSI Report Nr. 95-07, Paul Scherrer Institut, Villigen, Switzerland; Nagra Technical Report NTB 94-08, Nagra, Wettingen, Switzerland, 58p.

BERNER, U. (1999): Concentration Limits in the Cement Based Swiss Repository for Long-lived, Intermediate-level Radioactive Wastes (LMA). PSI Report Nr. 99-10, Paul Scherrer Institut, Villigen, Switzerland, 59p.

BRADBURY, M.H., BAEYENS, B. (1997): Far-Field Sorption Data Bases for Performance Assessment of a L/ILW Repository in an Undisturbed Palfris Marl Host Rock. PSI Report Nr. 97-15, Paul Scherrer Institut, Villigen, Switzerland; Nagra Technical Report NTB 96-05, Nagra, Wettingen, Switzerland, 137p.

CURTI, E. (1993): Modelling Bentonite Pore Waters for the Swiss High-level Radioactive Waste Repository. PSI Report Nr. 93-05, Paul Scherrer Institut, Villigen, Switzerland; Nagra Technical Report NTB 93-45, Nagra, Wettingen, Switzerland, 85p.

GRENTHE, I., FUGER, J., KONINGS, R.J.M., LEMIRE, R.J., MULLER, A.B., NGUYEN-TRUNG, C., WANNER, H. (1992): Chemical Thermodynamics of Uranium. Elsevier, Amsterdam, 715p.

GRENTHE, I., HUMMEL, W., PUIGDOMÈNECH, I. (1997): Chemical Background for the Modelling of Reactions in Aqueous Systems. In: GRENTHE, I., PUIGDOMÈNECH, I. (eds.): Modelling in Aquatic Chemistry, OECD Nuclear Energy Agency, Paris, pp.69-129.

HADERMANN, J. (1997): The Pillars of Safety. In: GRENTHE, I., PUIGDOMÈNECH, I. (eds.): Modelling in Aquatic Chemistry, OECD Nuclear Energy Agency, Paris, pp.577-591.

HUMMEL, W., BERNER, U. (2002): Solubility of actinides in a planned underground repository: Application of chemical thermodynamics for estimation of limiting values. Applied Geochemistry (submitted).

LEMIRE, R.J., FUGER, J., NITSCHE, H., POTTER, P., RAND, M.H., RYDBERG, J., SPAHIU, K., SULLIVAN, J.C., ULLMAN, W.J., VITORGE, P., WANNER, H. (2001): Chemical Thermodynamics of Neptunium & Plutonium. Elsevier, Amsterdam, 845p.

NAGRA (1994): Kristallin-I Safety Assessment Report. Nagra Technical Report NTB 93-22, Nagra, Wettingen, Switzerland, 438p.

PEARSON, F.J., BERNER, U. (1991): Nagra Thermochemical Data Base I. Core Data. Nagra Technical Report NTB 91-17, Nagra, Wettingen, Switzerland, 70p.

PEARSON, F.J., BERNER, U., HUMMEL, W. (1992): Nagra Thermochemical Data Base II. Supplemental Data 05/92. Nagra Technical Report NTB 91-18, Nagra, Wettingen, Switzerland, 284p.

PEARSON, F.J., SCHOLTIS, A. (1993): Chemistry of Reference Waters of the Crystalline Basement of Northern Switzerland for Safety Assessment Studies. Nagra Technical Report NTB 93-07, Nagra, Wettingen, Switzerland, 284p.

RARD, J.A., RAND, M.H., ANDEREGG, G., WANNER, H. (1999): Chemical Thermodynamics of Technetium. Elsevier, Amsterdam, 544p.

SILVA, R.J., BIDOGLIO, G., RAND, M.H., ROBOUCH, P.B., WANNER, H., PUIGDOMÈNECH, I. (1995): Chemical Thermodynamics of Americium. Elsevier, Amsterdam, 374p.

2   DATA BASE CONTENTS

Several computer programs modelling the thermodynamic behaviour of solutions are used to study water-rock interactions in Nagra and PSI projects. These include PHREEQC (PARKHURST & APPELO 1999), MINEQL (WESTALL et al. 1976), and its PSI modification MINSORB, and GEMS, the PSI version of SELEKTOR codes (KARPOV et al. 1997). These programs, and others such as EQ3/6 (WOLERY et al. 1990) and The Geochemist's Workbench (BETHKE 1994, 1996) that are widely used in other nuclear waste programs, require descriptions of the reactions to be modelled and either equilibrium constants (K) or Gibbs free energies ($\Delta_f G$) of their compounds at the temperature of interest. Themochemical data bases for these programs include reaction stoichiometry, $\log K$ or $\Delta_f G$ values for a standard temperature (25°C), and data to calculate equilibrium constants or Gibbs free energies at other temperatures.

Log$K$ values may be determined experimentally or calculated from more basic thermodynamic properties of the constituents of the reactions. Data sets may also include different forms of the reactions for the formation of a given mineral or aqueous species. Thus, log$K$ values frequently cannot be compared directly among several data bases. The Nagra/PSI TDB includes values for the thermodynamic properties of the aqueous species, minerals, and gases it contains, as well as log$K$ values for the reactions among them.

Extensive calculations are needed to maintain consistency among the thermodynamic properties of chemical entities and the characteristics of reactions among them. To speed up the calculations and assure consistency among its contents, the Nagra/PSI data base has been developed and maintained using the thermochemical data base management program, PMATCHC (see Appendix A). Many of the equations described below relating various thermodynamic properties to the values of reaction equilibrium constants are implemented in that program.

This section reviews the basic thermodynamic data types and equations by which they are related, in order to clarify the connections among the various quantities given in the data base. It also includes a description of the activity coefficient expressions used in several geochemical codes and in our reviews to extrapolate data to zero ionic strength, and concludes with a description of the structure and data sources of the Nagra/PSI TDB.

2.1   Thermodynamic quantities and equilibrium constants

Selected thermodynamic data for reactions refer to the reference temperature T° of 298.15 K (25°C) and to the standard state, i.e. a pressure of 0.1 MPa (1 bar) and, for aqueous species, infinite dilution ($I = 0$). The reaction parameters include

$\log_{10}K°$ the equilibrium constant of the reaction, logarithmic

$\Delta_r G_m°$ the molar Gibbs free energy of reaction $(kJ \cdot mol^{-1})$

$\Delta_r H_m°$ the molar enthalpy of reaction $(kJ \cdot mol^{-1})$

$\Delta_r S_m°$ the molar entropy of reaction $(J \cdot K^{-1} \cdot mol^{-1})$

$\Delta_r C_{p,m}°$ the molar heat capacity of reaction $(J \cdot K^{-1} \cdot mol^{-1})$

The equilibrium constant, $K°$, is related to $\Delta_r G_m°$ according to the following relation,

$$\Delta_r G_m° = -R \cdot T° \cdot \ln(10) \cdot \log_{10}K°$$

and the molar quantities $\Delta_r G_m°$, $\Delta_r H_m°$ and $\Delta_r S_m°$ are related according to the Gibbs-Helmholtz equation:

$$\Delta_r G_m° = \Delta_r H_m° - T° \cdot \Delta_r S_m°$$

Thermodynamics of individual entities are tabulated using standard state properties of formation from the elements in their reference state,

$\Delta_f G_m°$ the standard molar Gibbs free energy of formation $(kJ \cdot mol^{-1})$

$\Delta_f H_m°$ the standard molar enthalpy of formation $(kJ \cdot mol^{-1})$

$\Delta_f S_m°$ the standard molar entropy of formation $(J \cdot K^{-1} \cdot mol^{-1})$

$\Delta_f C_{p,m}°$ the standard molar heat capacity of formation $(J \cdot K^{-1} \cdot mol^{-1})$

or the absolute quantities,

$S_m°$ the standard molar entropy $(J \cdot K^{-1} \cdot mol^{-1})$

$C_{p,m}°$ the standard molar heat capacity $(J \cdot K^{-1} \cdot mol^{-1})$

The properties of a reaction are calculated from the standard state properties of its reactants and products as follows:

$$\Delta_r X_m° = \Sigma \Delta_f X_m°(products) - \Sigma \Delta_f X_m°(reactants)$$

where X represents the thermodynamic property.

The standard molar quantities $\Delta_f G_m°$, $\Delta_f H_m°$ and $\Delta_f S_m°$ are related according to the Gibbs-Helmholtz equation:

$$\Delta_f G_m° = \Delta_f H_m° - T° \cdot \Delta_f S_m°$$

For neutral species

$$\Delta_f S_m° = S_m° - \Sigma S_m°(\text{elements})$$

$$\Delta_f C_{p,m}° = C_{p,m}° - \Sigma C_{p,m}°(\text{elements})$$

and for charged species

$$\Delta_f S_m° = S_m° - \Sigma S_m°(\text{elements}) + (n/2) S_m°(H_2(g))$$

$$\Delta_f C_{p,m}° = C_{p,m}° - \Sigma C_{p,m}°(\text{elements}) + (n/2) C_{p,m}°(H_2(g))$$

in which n is the charge (WAGMAN et al. 1982, p. 2-22).

Some gas data are given at 1 atm (0.101325 MPa) in their original sources. The entropy values of gases are sensitive to pressure and were converted from 1 atm to 1 bar using equations given by WAGMAN et al. (1982, p. 2-23):

$$S_m°(\text{bar}) - S_m°(\text{atm}) = R \cdot \ln(1.01325/1.0) = 0.1094 \; J \cdot K^{-1} \cdot mol^{-1}$$

2.2 Medium effects

The selected thermodynamic data in our data base refer to standard state conditions, i.e. infinite dilution ($I = 0$) for aqueous species. Equilibrium constants studied in the laboratory are usually determined in an ionic medium. However, there is no "standard" ionic medium, or ionic strength, preferred in experimental determinations of equilibrium constants. The most "popular" media are $NaClO_4$ and KNO_3 at high concentrations. Both are of no relevance for environmental modelling. Hence, all experimental data have to be extrapolated to zero ionic strength as part of the data review procedure. Users of thermodynamic data given for standard state conditions must recalculate these data to the conditions present in the system under study. Ideally, the same method should be used for extrapolation of experimental data to $I = 0$ and subsequent recalculation to environmental conditions, but usually this is not the case. This section describes the equations used for data extrapolation and the different expressions presently implemented in geochemical programs supporting Nagra and PSI work.

Ionic solutions depart strongly from ideality, and this non-ideality is accounted for by the introduction of an activity coefficient γ_i relating concentration m_i of species i with its "thermodynamic concentration" or activity a_i

$$a_i = m_i \cdot \gamma_i$$

There exists a number of alternative semi-empirical methods for the estimation of activity coefficients. All these electrolyte models are based on microscopic physico-chemical descriptions

of the interactions between dissolved ions, and sometimes the interactions between ions and solvent. However, a self-consistent theory of ionic solutions is still awaited. Until such a theory is available we have to rely on provisional models. The ones described in this section are all based on the Debye-Hückel theory and extensions thereof. For a more detailed discussion see GRENTHE et al. (1997).

2.2.1 The Debye-Hückel limiting law

The classical Debye-Hückel limiting law takes into account only long-range electrostatic interactions between ions of opposite charge treated as mathematical point charges. The Debye-Hückel limiting law is

$$\log_{10} \gamma_i = -A \cdot z_i^2 \cdot \sqrt{I_m}$$

where A is a constant with a value of 0.510 $kg^{1/2} \cdot mol^{-1/2}$ at 298.15K and 0.1MPa, z_i is the ionic charge of species i, and I_m the ionic strength of the particular electrolyte

$$I_m = \frac{1}{2} \Sigma \, m_i \cdot z_i^2$$

The range of validity of the limiting law varies with the electrolyte, typically up to $I_m = 0.01$ mol $\cdot$ kg^{-1} for 1:1 electrolytes, and 0.001 for 3:1 electrolytes. Various empirical attempts to "extend" the range of application of the Debye-Hückel limiting law have been made. Some of them are discussed in the following sections. The limiting law itself is not used in any of the geochemical programs.

2.2.2 The extended Debye-Hückel equation

The introduction of an ion-specific "effective" diameter of the hydrated ion results in the extended Debye-Hückel equation

$$\log_{10} \gamma_i = -A \cdot z_i^2 \cdot \sqrt{I_m} \, / \, (\, 1 + B \cdot \mathring{a}_i \cdot \sqrt{I_m} \,)$$

where B is a constant with a value of $0.328 \cdot 10^{10}$ $kg^{1/2} \cdot mol^{-1/2} \cdot m^{-1}$ at 298.15K and 0.1MPa. The parameter $\mathring{a}_i$ is know as the ion-size parameter or effective diameter of ion i. Values of this parameter for a number of ions were given by KIELLAND (1937) and are repeated in all later publications. These values are adopted for the Nagra/PSI TDB for use with the extended Debye-Hückel equation which is implemented in PHREEQC.

2.2.3   Expanded extended Debye-Hückel equations

The extended Debye-Hückel equation is precise only in dilute solutions, typically to ionic strength of about 0.03, so several expanded versions have been developed and are used in MINEQL, PHREEQC and EQ3/6 to accommodate more concentrated solutions. These are of the form:

$$\log_{10} \gamma_i = -A \cdot z_i^2 \cdot \sqrt{I_m} / (1 + B \cdot a_i \cdot \sqrt{I_m}) + b_i \cdot I_m$$

The parameters in this equation are the same as in the extended Debye-Hückel equation, except for a_i and b_i. Values of a_i and b_i are determined for each ion by fitting the equation to measured activities of pure salt solutions. In PHREEQC this equation is referred to as the WATEQ Debye-Hückel equation, and PARKHURST (1990) has fit this equation to a number of salt solutions. His values are adopted in the Nagra/PSI TDB. Note that no carbonate or bicarbonate solutions have been included in the fits of PARKHURST (1990) and thus, no a_i and b_i parameters for carbonate or bicarbonate are available.

In EQ3/6 the B-dot equation of HELGESON (1969) is used (WOLERY et al. 1990):

$$\log_{10} \gamma_i = -A \cdot z_i^2 \cdot \sqrt{I_m} / (1 + B \cdot å_i \cdot \sqrt{I_m}) + Bdot \cdot I_m$$

In this equation $å_i$ is the ion-size parameter of the extended Debye-Hückel equation, and Bdot is a function only of temperature and equals 0.041 at 25°C, 0.0435 at 50°C, and 0.046 at 100°C (HELGESON 1969, Table 2). EQ3/6 uses the KIELLAND (1937) values of $å_i$, and calculates Bdot values as a function of temperature.

The Davies equation is also widely used to calculate activity coefficients. This equation is written as:

$$\log_{10} \gamma_i = -A \cdot z_i^2 \cdot \sqrt{I_m} / (1 + \sqrt{I_m}) + A \cdot z_i^2 \cdot C_D \cdot I_m$$

Originally, DAVIES (1938) proposed a value of 0.2 for his constant C_D, but later changed this value to 0.3 based on an inspection of additional electrolyte data published since his original publication (DAVIES 1962, p.39-42). The term $B \cdot å_i = 1$ is assumed to be a constant. The only ion-specific parameter in this equation is the charge of the ion, so the equation is often used for uncommon ions for which neither the ion-size parameter, $å_i$, nor the WATEQ parameters a_i and b_i are available. This option is implemented in PHREEQC with $C_D = 0.3$. The Davies equation is generally used to calculate activity coefficients in MINEQL, with $C_D = 0.2$ implemented in the original code. This has been changed to $C_D = 0.3$ in the PSI version of MINEQL used nowadays for Nagra and PSI projects.

2.2.4 The SIT equation

The Debye-Hückel term, which is the dominant term in the expression for the activity coefficients in dilute solutions, accounts for electrostatic, long-range interactions. At higher concentrations short-range, non-electrostatic interactions have to be taken into account as well. This is usually done by adding terms to the Debye-Hückel expression as described in the preceding section. An approach extending to much higher concentrations is the Specific ion Interaction Theory (SIT)

$$\log_{10} \gamma_i = -A \cdot z_i^2 \cdot \sqrt{I_m} / (1 + 1.5 \cdot \sqrt{I_m}) + \Sigma\, \varepsilon(i,k) \cdot m_k$$

where the term $B \cdot \mathring{a}_i = 1.5 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ is assumed to be a constant, and $\varepsilon(i,k)$ is an aqueous species interaction coefficient which describes the specific short-range interactions between aqueous species i and k. The sum extends over all species in solution. In the case of a laboratory system with high concentration of an ionic medium (1:1 salt NX), the SIT equation simplifies to

$$\log_{10} \gamma_M = -A \cdot z_i^2 \cdot \sqrt{I_m} / (1 + 1.5 \cdot \sqrt{I_m}) + \varepsilon(M,X) \cdot I_m$$

for a cation M, and likewise for an anion Y using the interaction coefficient $\varepsilon(Y,N)$. For a detailed discussion of the SIT equation and its relation to the Pitzer formalism see GRENTHE et al. (1997).

The SIT equation has been used in the present update for extrapolating laboratory data to zero ionic strength. The required $\varepsilon(i,k)$ coefficients were taken from RARD et al. (1999) and GRENTHE et al. (1997), or were derived from $\log_{10}K$ data at varying ionic strength whenever possible. For convenience, a summary of $\varepsilon(i,k)$, $\Delta\varepsilon$(reaction) and estimates based on chemical analogies used in this review are compiled in Table 2.2.1. However, note that the SIT equation is presently not implemented in any geochemical program used for Nagra and PSI work.

Besides the technical questions of implementing SIT into existing geochemical programs the consequences for a consistent TDB have to be addressed in a forthcoming update: The various extended Debye-Hückel equations discussed in 2.2.2 and 2.2.3 assign a unique activity coefficient to a given ion at a given ionic strength irrespective of the electrolyte solution. For example, $\gamma_{HCO_3^-}$ is the same in NaCl and KCl at the same ionic strength. In order to account for differences of $a_{HCO_3^-}$ in NaCl and KCl at the same ionic strength the concept of ion pairing is introduced where deviations are assumed to be due to weak complex formation reactions, e.g. of the type
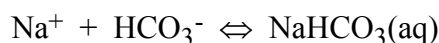
$$Na^+ + HCO_3^- \Leftrightarrow NaHCO_3(aq)$$

which are described by equilibrium constants. In contrast to these ion association models, ion interaction models like SIT account for individual characteristics of electrolytes by different interaction coefficients $\varepsilon(i,k)$, i.e. $\varepsilon(HCO_3^-, Na^+) \neq \varepsilon(HCO_3^-, K^+)$, and a complex like NaHCO3(aq)

must not be included in a consistent speciation model when using the SIT concept. As a consequence, the number of weak complexes to be included in a TDB depends on the model used to calculate activity coefficients. An internally consistent TDB for use with the WATEQ Debye-Hückel equation is different from an internally consistent TDB for use with the SIT equation. However, no unambiguous procedure exists for discriminating weak complexes versus strong ion interactions; see for example the discussion of UO_2Cl_2(aq) versus $\varepsilon(UO_2^{2+}, Cl^-)$ in GRENTHE et al. (1992, p. 192-195).

Table 2.2.1: Summary of $\varepsilon(i,k)$, $\Delta\varepsilon$(reaction) and estimates based on chemical analogy evaluated in this review. See Chapter 5 for more details.

$\varepsilon(i,k)$ estimate	medium	source of estimate		value
$\varepsilon(EuF^{2+},ClO_4^-)$		$\approx \varepsilon(AmF^{2+},ClO_4^-)$	$\approx \varepsilon(EuF_2^+,ClO_4^-)$	$\approx\ 0.39\pm0.04$
$\varepsilon(HSO_4^-,H^+)$	$(Na^+ClO_4^-)$	$\approx \varepsilon(HSO_4^-,Na^+)$		$=\ 0.01\pm0.02$
$\varepsilon(SO_4^{2-},H^+)$	$(Na^+ClO_4^-)$	$\approx \varepsilon(SO_4^{2-},Na^+)$		$=-0.12\pm0.06$
$\varepsilon(SnOHCl(aq),Na^++ClO_4^-)$		$\approx \varepsilon(SnCl_2(aq),Na^++ClO_4^-)$		
$\varepsilon(SnCl_2(aq),\underline{Na}^++ClO_4^-)$		$\approx \varepsilon(SnCl_2(aq),\underline{H}^++ClO_4^-)$		

$\Delta\varepsilon$(reaction)	medium	$\varepsilon(i,k)$ of reaction			value
$\Delta\varepsilon(Al^{3+}+F^-\leftrightarrow AlF^{2+})$	$(NH_4^+NO_3^-)$	$= \varepsilon(AlF^{2+},NO_3^-)$	$- \varepsilon(F^-,NH_4^+)$	$- \varepsilon(Al^{3+},NO_3^-)$	$=-0.23\pm0.21$
$\Delta\varepsilon(AlF^{2+}+F^-\leftrightarrow AlF_2^+)$	$(NH_4^+NO_3^-)$	$= \varepsilon(AlF_2^+,NO_3^-)$	$- \varepsilon(F^-,NH_4^+)$	$- \varepsilon(AlF^{2+},NO_3^-)$	$=-0.04\pm0.17$
$\Delta\varepsilon(AlF_2^++F^-\leftrightarrow AlF_3(aq))$	$(NH_4^+NO_3^-)$	$= (AlF_3(aq),NH_4^++NO_3^-)$	$- \varepsilon(F^-,NH_4^+)$	$- \varepsilon(AlF_2^+,NO_3^-)$	$=-0.09\pm0.22$
$\Delta\varepsilon(AlF_3(aq)+F^-\leftrightarrow AlF_4^-)$	$(NH_4^+NO_3^-)$	$= \varepsilon(AlF_4^-,NH_4^+)$	$- \varepsilon(F^-,NH_4^+)$	$- (AlF_3(aq),NH_4^++NO_3^-)$	$=-0.19\pm0.25$
$\Delta\varepsilon(Eu^{3+}+H_2O\leftrightarrow EuOH^{2+}+H^+)$	(Na^+Cl^-)	$= \varepsilon(EuOH^{2+},Cl^-)$	$+ \varepsilon(H^+,Cl^-)$	$- \varepsilon(Eu^{3+},Cl^-)$	$=-0.45\pm0.36$
$\Delta\varepsilon(Eu^{3+}+H_2O\leftrightarrow EuOH^{2+}+H^+)$	$(Na^+ClO_4^-)$	$= \varepsilon(EuOH^{2+},ClO_4^-)$	$+ \varepsilon(H^+,ClO_4^-)$	$- \varepsilon(Eu^{3+},ClO_4^-)$	$=-0.36\pm0.01$
$\Delta\varepsilon(Am^{3+}+H_2O\leftrightarrow AmOH^{2+}+H^+)$	$(Na^+ClO_4^-)$	$= \varepsilon(AmOH^{2+},ClO_4^-)$	$+ \varepsilon(H^+,ClO_4^-)$	$- \varepsilon(Am^{3+},ClO_4^-)$	$=-0.7\pm0.4$
$\Delta\varepsilon(Cm^{3+}+H_2O\leftrightarrow CmOH^{2+}+H^+)$	$(Na^+ClO_4^-)$	$= \varepsilon(CmOH^{2+},ClO_4^-)$	$+ \varepsilon(H^+,ClO_4^-)$	$- \varepsilon(Cm^{3+},ClO_4^-)$	$=-0.7\pm0.4$
$\Delta\varepsilon(Eu^{3+}+CO_3^{2-}\leftrightarrow EuCO_3^+)$	$(Na^+ClO_4^-)$	$= \varepsilon(EuCO_3^+,ClO_4^-)$	$- \varepsilon(CO_3^{2-},Na^+)$	$- \varepsilon(Eu^{3+},ClO_4^-)$	$=-0.24\pm0.18$
$\Delta\varepsilon(Eu^{3+}+2CO_3^{2-}\leftrightarrow Eu(CO_3)_2^-)$	$(Na^+ClO_4^-)$	$= \varepsilon(Eu(CO_3)_2^-,Na^+)$	$- 2\varepsilon(CO_3^{2-},Na^+)$	$- \varepsilon(Eu^{3+},ClO_4^-)$	$=-1.48\pm0.31$
$\Delta\varepsilon(Eu^{3+}+SO_4^{2-}\leftrightarrow EuSO_4^+)$	$(Na^+ClO_4^-)$	$= \varepsilon(EuSO_4^+,ClO_4^-)$	$- \varepsilon(SO_4^{2-},Na^+)$	$- \varepsilon(Eu^{3+},ClO_4^-)$	$=-0.11\pm0.06$
$\Delta\varepsilon(Eu^{3+}+2SO_4^{2-}\leftrightarrow Eu(SO_4)_2^-)$	$(Na^+ClO_4^-)$	$= \varepsilon(Eu(SO_4)_2^-,Na^+)$	$- 2\varepsilon(SO_4^{2-},Na^+)$	$- \varepsilon(Eu^{3+},ClO_4^-)$	$=-0.04\pm0.16$
$\Delta\varepsilon(Eu^{3+}+Cl^-\leftrightarrow EuCl^{2+})$	$(Na^+ClO_4^-)$	$= \varepsilon(EuCl^{2+},ClO_4^-)$	$- \varepsilon(Cl^-,Na^+)$	$- \varepsilon(Eu^{3+},ClO_4^-)$	$=-0.16\pm0.05$
$\Delta\varepsilon(Eu^{3+}+2Cl^-\leftrightarrow EuCl_2^+)$	$(Na^+ClO_4^-)$	$= \varepsilon(EuCl_2^+,ClO_4^-)$	$- 2\varepsilon(Cl^-,Na^+)$	$- \varepsilon(Eu^{3+},ClO_4^-)$	$=-0.15\pm0.12$
$\Delta\varepsilon(H_2S(g)\leftrightarrow H_2S(aq))$	(Na^+Cl^-)	$= \varepsilon(H_2S(aq),Na^++Cl^-)$			$=\ 0.055\pm0.004$
$\Delta\varepsilon(H_2S(aq)\leftrightarrow HS^-+H^+)$	(Na^+Cl^-)	$= \varepsilon(H_2S(aq),Na^++Cl^-)$	$- \varepsilon(HS^-,Na^+)$	$- \varepsilon(Cl^-,H^+)$	$=-0.142\pm0.009$

Table 2.2.1:   continued

$\Delta\varepsilon$(reaction)	medium	ε(i,k) of reaction				value
$\Delta\varepsilon(Ni^{2+}+HS^-\leftrightarrow NiHS^+)$	(seawater)					$= -1.2\pm0.4$
$\Delta\varepsilon(Ni^{2+}+2HS^-\leftrightarrow Ni(HS)_2(aq))$	(seawater)					$= -1.3\pm0.3$
$\Delta\varepsilon(Pd(cr)\leftrightarrow Pd^{2+}+2e^-)$	$(H^+ClO_4^-)$	$= \varepsilon(Pd^{2+},ClO_4^-)$				$= 0.8\pm0.2$
$\Delta\varepsilon(PdCl_3^-+Cl^-\leftrightarrow PdCl_4^{2-})$	$(H^+ClO_4^-)$	$= \varepsilon(PdCl_4^{2-},H^+)$	$- \varepsilon(PdCl_3^-,H^+)$	$- \varepsilon(Cl^-,H^+)$		$= -0.13\pm0.02$
$\Delta\varepsilon(Sn(cr)\leftrightarrow Sn^{2+}+2e^-)$	$(H^+ClO_4^-)$	$= \varepsilon(Sn^{2+},ClO_4^-)$				$= 0.32\pm0.13$
$\Delta\varepsilon(Sn^{4+}+2e^-\leftrightarrow Sn^{2+})$	$(H^+ClO_4^-)$	$= \varepsilon(Sn^{2+},ClO_4^-)$	$- \varepsilon(Sn^{4+},ClO_4^-)$			$= 0.00\pm0.00$
$\Delta\varepsilon(CaSn(OH)_6(s)\leftrightarrow Ca^{2+}+Sn(OH)_6^{2-})$	$(Na^+ClO_4^-)$	$= \varepsilon(Ca^{2+},ClO_4^-)$		$+ \varepsilon(Sn(OH)_6^{2-},Na^+)$		$= 0.42\pm0.10$
$\Delta\varepsilon(Sn^{2+}+H_2O\leftrightarrow SnOH^++H^+)$	$(Na^+NO_3^-)$	$= \varepsilon(SnOH^+,NO_3^-)$	$+ \varepsilon(H^+,NO_3^-)$	$- \varepsilon(Sn^{2+},NO_3^-)$		$= -0.17$
$\Delta\varepsilon(Sn^{2+}+2H_2O\leftrightarrow Sn(OH)_2(aq)+2H^+)$	$(Na^+NO_3^-)$	$= \varepsilon(Sn(OH)_2(aq),Na^++NO_3^-)$	$+ 2\varepsilon(H^+,NO_3^-)$	$- \varepsilon(Sn^{2+},NO_3^-)$		$= -0.31$
$\Delta\varepsilon(Sn^{2+}+3H_2O\leftrightarrow Sn(OH)_3^-+3H^+)$	$(Na^+NO_3^-)$	$= \varepsilon(Sn(OH)_3^-,Na^+)$	$+ 3\varepsilon(H^+,NO_3^-)$	$- \varepsilon(Sn^{2+},NO_3^-)$		$= 0.09$
$\Delta\varepsilon(Sn^{2+}+Cl^-\leftrightarrow SnCl^+)$	$(Na^+ClO_4^-)$	$= \varepsilon(SnCl^+,ClO_4^-)$	$- \varepsilon(Cl^-,Na^+)$	$- \varepsilon(Sn^{2+},ClO_4^-)$		$= -0.143\pm0.030$
$\Delta\varepsilon(Sn^{2+}+2Cl^-\leftrightarrow SnCl_2(aq))$	$(Na^+ClO_4^-)$	$= \varepsilon(SnCl_2(aq),Na^++ClO_4^-)$	$- 2\varepsilon(Cl^-,Na^+)$	$- \varepsilon(Sn^{2+},ClO_4^-)$		$= -0.28\pm0.06$
$\Delta\varepsilon(Sn^{2+}+3Cl^-\leftrightarrow SnCl_3^-)$	$(Na^+ClO_4^-)$	$= \varepsilon(SnCl_3^-,Na^+)$	$- 3\varepsilon(Cl^-,Na^+)$	$- \varepsilon(Sn^{2+},ClO_4^-)$		$= -0.31\pm0.09$
$\Delta\varepsilon(Sn^{2+}+F^-\leftrightarrow SnF^+)$	$(Na^+ClO_4^-)$	$= \varepsilon(SnF^+,ClO_4^-)$	$- \varepsilon(F^-,Na^+)$	$- \varepsilon(Sn^{2+},ClO_4^-)$		$= -0.02\pm0.24$
$\Delta\varepsilon(Th^{4+}+H_2O\leftrightarrow ThOH^{3+}+H^+)$	$(Na^+ClO_4^-)$	$= \varepsilon(ThOH^{3+},ClO_4^-)$	$+ \varepsilon(H^+,ClO_4^-)$	$- \varepsilon(Th^{4+},ClO_4^-)$		≈ 0.1
$\Delta\varepsilon(Th^{4+}+4H_2O\leftrightarrow Th(OH)_4(aq)+4H^+)$	$(Na^+ClO_4^-)$	$= \varepsilon(Th(OH)_4(aq),Na^++ClO_4^-)$	$+ 4\varepsilon(H^+,ClO_4^-)$	$- \varepsilon(Th^{4+},ClO_4^-)$		$= -1.49\pm0.17$
$\Delta\varepsilon(Zr^{4+}+Cl^-\leftrightarrow ZrCl^{3+})$	$(H^+ClO_4^-)$	$= \varepsilon(ZrCl^{3+},ClO_4^-)$	$- \varepsilon(Cl^-,H^+)$	$- \varepsilon(Zr^{4+},ClO_4^-)$		$= -0.15\pm0.06$
$\Delta\varepsilon(Zr^{4+}+HSO_4^-\leftrightarrow ZrSO_4^{2+}+H^+)$	$(H^+ClO_4^-)$	$= \varepsilon(ZrSO_4^{2+},ClO_4^-)$	$+ \varepsilon(H^+,ClO_4^-)$	$- \varepsilon(HSO_4^-,H^+)$	$- \varepsilon(Zr^{4+},ClO_4^-)$	$= -0.19\pm0.02$
$\Delta\varepsilon(Zr^{4+}+HF\leftrightarrow ZrF^{3+}+H^+)$	(ClO_4^-)	$= \varepsilon(ZrF^{3+},ClO_4^-)$	$+ \varepsilon(H^+,ClO_4^-)$	$- \varepsilon(Zr^{4+},ClO_4^-)$	$- \varepsilon(HF(aq),H^++ClO_4^-)$	$= -0.10\pm0.01$
$\Delta\varepsilon(ZrF^{3+}+HF\leftrightarrow ZrF_2^{2+}+H^+)$	(ClO_4^-)	$= \varepsilon(ZrF_2^{2+},ClO_4^-)$	$+ \varepsilon(H^+,ClO_4^-)$	$- \varepsilon(ZrF^{3+},ClO_4^-)$	$- \varepsilon(HF(aq),H^++ClO_4^-)$	$= -0.06\pm0.01$
$\Delta\varepsilon(ZrF_2^{2+}+HF\leftrightarrow ZrF_3^++H^+)$	(ClO_4^-)	$= \varepsilon(ZrF_3^+,ClO_4^-)$	$+ \varepsilon(H^+,ClO_4^-)$	$- \varepsilon(ZrF_2^{2+},ClO_4^-)$	$- \varepsilon(HF(aq),H^++ClO_4^-)$	$= -0.10\pm0.01$
$\Delta\varepsilon(ZrF_3^++HF\leftrightarrow ZrF_4(aq)+H^+)$	(ClO_4^-)	$= \varepsilon(ZrF_4(aq),H^++ClO_4^-)$	$+ \varepsilon(H^+,ClO_4^-)$	$- \varepsilon(ZrF_3^+,ClO_4^-)$	$- \varepsilon(HF(aq),H^++ClO_4^-)$	$= -0.01\pm0.12$
$\Delta\varepsilon(ZrF_4(aq)+HF\leftrightarrow ZrF_5^-+H^+)$	(ClO_4^-)	$= \varepsilon(ZrF_5^-,H^+)$	$+ \varepsilon(H^+,ClO_4^-)$	$- \varepsilon(ZrF_4(aq),H^++ClO_4^-)$	$- \varepsilon(HF(aq),H^++ClO_4^-)$	$= 0.07\pm0.08$
$\Delta\varepsilon(ZrF_5^-+HF\leftrightarrow ZrF_6^{2-}+H^+)$	(ClO_4^-)	$= \varepsilon(ZrF_6^{2-},H^+)$	$+ \varepsilon(H^+,ClO_4^-)$	$- \varepsilon(ZrF_5^-,H^+)$	$- \varepsilon(HF(aq),H^++ClO_4^-)$	$= 0.25\pm0.10$

2.2.5 Activity coefficients of neutral species

A number of conventions are used to describe the activity coefficients of dissolved neutral species. In the case of the Debye-Hückel limiting law (2.2.1), the extended Debye-Hückel equation (2.2.2) and the Davies equation (2.2.3) activity coefficients for neutral species are equal to one, as there are no charge independent terms in these equations. In the case of the WATEQ Debye-Hückel equation and the B-dot equation (2.2.3) a term proportional to the ionic strength remains for neutral species.

In PHREEQC the equation

$$\log_{10} \gamma_i = 0.1 \cdot I_m$$

is used as default expression for all neutral species at all temperatures. Note that in all MINEQL-type codes

$$\log_{10} \gamma_i = 0$$

is used. This may lead to (small) differences comparing otherwise identical speciation calculations done with PHREEQC and MINEQL.

In EQ3/6, following HELGESON (1969), the activity coefficients for all neutral species are taken as equal to those of dissolved CO_2. These are calculated using the expression:

$$\log_{10} \gamma_i = c_1 \cdot T + c_2 \cdot T^2 + c_3 \cdot T^3 + c_4 \cdot T^4$$

It is also an option in EQ3/6 to calculate neutral species activity coefficients using the B-dot equation.

In the SIT equation the ion interaction coefficients $\varepsilon(i,k)$ unequivocally are assumed to be zero for ions of the same charge sign. However, the case of neutral species is less clear. For uncharged solutes the SIT equation is reduced to one term, and there is no problem with including possible interactions between uncharged and ionic species in the SIT model (GRENTHE et al. 1997). For the sake of simplicity, the guidelines for NEA reviews (GRENTHE et al. 1992) assumed that the interaction coefficients for uncharged species were zero. We generally followed these guidelines, but at least in the cases of $CO_2(aq)$ (GRENTHE et al. 1997), $H_2S(aq)$ (5.19) and $UO_2CO_3(aq)$ (5.23) it can be shown that $\varepsilon(i,k)$ is not zero. In all cases extrapolations with $\varepsilon(i,k) = 0$ and $\varepsilon(i,k) \neq 0$ lead to slightly different $\log_{10} K°$ values. Furthermore, deriving a consistent set of $\varepsilon(i,k)$ for carbonates and sulphides from reaction data depends on this decision. At present, the question "to zero or not to zero" remains open.

2.3   Temperature effects

The present update focused on equilibrium data at 25°C. Temperature information is included when available but no attempt has been made to estimate missing data.

Some of the core species and minerals are accompanied by data that permit $\log_{10}K$ values to be calculated quite precisely to temperatures approaching 100°C. Most of the remaining core and about one third of the selected supplemental data are associated with $\Delta_r H_m°$ values, the molar enthalpy of reaction. However, thermodynamic data selected for most entities in our data base do not inlude any temperature information; they are valid only at 25°C. Hence, it is important to be cautious using any of the supplemental data and much of the core data at temperatures too far removed from 25°C.

This section discusses interrelations of temperature parameters and describes some approximations for modelling temperature effects.

2.3.1   Temperature dependence of equilibrium constants

The following equation is used in PHREEQC and has been adopted as the equation relating $\log_{10}K°$ values to temperature in the Nagra/PSI TDB.

$$\log_{10}K°(T) \ = \ A \ + \ B \cdot T \ + \ C/T \ + \ D \cdot \log_{10}(T) \ + \ E/T^2$$

In this equation, $\log_{10}K°(T)$ is the base 10 logarithm of the equilibrium constant K at the temperature T (K) at ionic strength zero and A, B, C, D and E are constants. The form of this equation results from choosing the equation of MAIER & KELLEY (1932) to express the variation of the heat capacity at constant pressure, $C_{p,m}°$, with absolute temperature, T. The Maier-Kelley equation is written:

$$C_{p,m}°(T) \ = \ a \ + \ b \cdot T \ - \ c/T^2$$

The equation for $\Delta_r C_{p,m}°(T)$ is:

$$\Delta_r C_{p,m}°(T) \ = \ \Delta_r a \ + \ \Delta_r b \cdot T \ - \ \Delta_r c/T^2$$

The following equations show the relations between the temperature dependent equilibrium constant, $\log_{10}K°(T)$, and such other thermodynamic properties of reaction as $\Delta_r G_m°$, $\Delta_r H_m°$, $\Delta_r S_m°$, $\Delta_r C_{p,m}°$ and $\Delta_r a$, $\Delta_r b$ and $\Delta_r c$ of the heat capacity equation.

$$\Delta_r G_m°(T) \ = \ - R \cdot T \cdot \ln(10) \cdot \log_{10}K°(T)$$

$$\Delta_r G_m°(T) = -R \cdot \ln(10) \cdot (A \cdot T + B \cdot T^2 + C + D \cdot T \cdot \log_{10}(T) + E / T)$$

$$\Delta_r H_m°(T) = R \cdot T^2 \cdot \ln(10) \cdot (\partial \log_{10} K°(T) / \partial T)$$

$$\Delta_r H_m°(T) = R \cdot \ln(10) \cdot (B \cdot T^2 - C + D \cdot T / \ln(10) - 2 \cdot E / T)$$

$$\Delta_r S_m°(T) = -\partial \Delta_r G_m°(T) / \partial T$$

$$\Delta_r S_m°(T) = R \cdot \ln(10) \cdot (A + 2 \cdot B \cdot T + D / \ln(10) \cdot (1 + \ln(T)) - E / T^2)$$

$$\Delta_r C_{p,m}°(T) = \partial \Delta_r H_m°(T) / \partial T$$

$$\Delta_r C_{p,m}°(T) = R \cdot \ln(10) \cdot (2 \cdot B \cdot T + D / \ln(10) + 2 \cdot E / T^2)$$

$$\Delta_r a = R \cdot D$$

$$\Delta_r b = 2 \cdot R \cdot \ln(10) \cdot B$$

$$\Delta_r c = -2 \cdot R \cdot \ln(10) \cdot E$$

If sufficient experimental data are available to define all five coefficients A through E, the values of the Gibbs energy, enthalpy, entropy, heat capacity, and all three coefficients a through c of the heat capacity expression, can be found using the above equations.

It is also necessary to be able to calculate values of the coefficients A through E of the $\log_{10} K°(T)$ equation from thermodynamic properties of a reaction. If the coefficients $\Delta_r a$, $\Delta_r b$ and $\Delta_r c$ of the heat capacity equation are available, the coefficients B, D and E are calculated according to:

$$E = -\Delta_r c / (2 \cdot R \cdot \ln(10))$$

$$D = \Delta_r a / R$$

$$B = \Delta_r b / (2 \cdot R \cdot \ln(10))$$

The coefficient C is calculated using $\Delta_r H_m°$ at the reference temperature T°:

$$C = B \cdot T°^2 + D \cdot T° / \ln(10) - 2 \cdot E / T° - \Delta_r H_m°(T°) / (R \cdot \ln(10))$$

$$C = (\Delta_r b / 2 \cdot T°^2 + \Delta_r a \cdot T° + \Delta_r c / T° - \Delta_r H_m°(T°)) / (R \cdot \ln(10))$$

A is calculated from $\Delta_r S_m°$ at the reference temperature T°:

$$A = \Delta_r S_m°(T°) / (R \cdot \ln(10)) - 2 \cdot B \cdot T° - D / \ln(10) \cdot (1 + \ln(T°)) + E / T°^2$$

$$A = (\Delta_r S_m°(T°) - \Delta_r b \cdot T°^2 - \Delta_r a \cdot (1 + \ln(T°)) - \Delta_r c / (2 \cdot T°^2)) / (R \cdot \ln(10))$$

2.3.2   Constant heat capacity of reaction

If $\Delta_r C_{p,m}°$ is known only at the reference temperature T°, it is often assumed to be constant with temperature. In this case, $\Delta_r C_{p,m}° = \Delta_r a$ and $\Delta_r b = \Delta_r c = 0$, so that B = E = 0, and the expression for $\log_{10} K°(T)$ has the form:

$$\log_{10} K°(T) = A + C / T + D \cdot \log_{10}(T)$$

This equation is called the three-term approximation of temperature dependence. From the equations of section 2.3.1 it follows that:

$$D = \Delta_r C_{p,m}° / R$$

$$C = (\Delta_r C_{p,m}° \cdot T° - \Delta_r H_m°(T°)) / (R \cdot \ln(10))$$

$$A = (\Delta_r S_m°(T°) - \Delta_r C_{p,m}° \cdot (1 + \ln(T°)) / (R \cdot \ln(10))$$

Considering the above expressions for the coefficients A and C, and the relation

$$\Delta_r H_m°(T°) - T° \cdot \Delta_r S_m°(T°) = -R \cdot T° \cdot \ln(10) \cdot \log_{10} K°(T°)$$

the expression for $\log_{10} K°(T)$ becomes:

$$\log_{10} K°(T) = \log_{10} K°(T°) + \Delta_r H_m°(T°) / (R \cdot \ln(10)) \cdot (1 / T° - 1 / T) + \Delta_r C_{p,m}°$$
$$/ (R \cdot \ln(10)) \cdot (T° / T - 1 + \ln(T/ T°))$$

This equation is implemented in MINEQL. If $\Delta_r C_{p,m}°$ is not know MINEQL assumes $\Delta_r C_{p,m}° = 0$ and the equation simplifies to the integrated van't Hoff equation, as described in the following section.

2.3.3   Constant enthalpy of reaction

For most reactions, $\Delta_r C_{p,m}°$ is not known and it must be assumed that $\Delta_r H_m°$ is constant with temperature. In this case, B = D = E = 0, and the expression for $\log_{10} K°(T)$ has the form:

$$\log_{10} K°(T) = A + C / T$$

This equation is called the two-term approximation of temperature dependence. From the equations of section 2.3.2 it follows that:

$$C = - \Delta_r H_m°(T°) / (R \cdot \ln(10))$$

$$A = \Delta_r S_m°(T°) / (R \cdot \ln(10))$$

$$\log_{10} K°(T) = \log_{10} K°(T°) + \Delta_r H_m°(T°) / (R \cdot \ln(10)) \cdot (1 / T° - 1 / T)$$

This is the integrated van't Hoff equation as used in MINEQL, PHREEQC and other geochemical programs.

2.3.4 Temperature dependence and medium effects

The temperature coefficients discussed above refer to standard state conditions, i.e. infinite dilution for aqueous species. However, in any real system medium effects have to be considered as discussed in section 2.2.

The temperature dependence of the Debye-Hückel A and B parameters is known and tabulated, e.g. in SILVA et al. (1995, Table B.1). The temperature dependence of Helgeson's Bdot parameter is also known and tabulated, e.g. in HELGESON (1969, Table 2). The ion-size parameter $å_i$ is found to be fairly independent of temperature, at least at temperatures below 175°C (SILVA et al. 1995, p. 317). The temperature dependence of the WATEQ Debye-Hückel parameters a_i and b_i to our knowledge has not been explored, but we expect very small effects, similar to $å_i$ and Bdot.

Hence, in fairly diluted systems, i.e. $I_m < 0.1$, activity coefficients calculated with the various types of extended Debye-Hückel equations (see 2.2.2 and 2.2.3) probably are sufficient to account for temperature effects in non-standard state conditions. For more concentrated solutions the SIT equation (see 2.2.4) would be the suitable method to estimate activity coefficients. However, we then enter the realm of temperature dependent interaction parameters $\varepsilon(i,k)$. A first step in this largely unexplored field is documented in GRENTHE et al. (1997, p. 397-424). More work has still to be done until a pragmatic and consistent treatment of temperature <u>and</u> medium effects in more concentrated solutions can be implemented in our TDB.

2.4   Redox

2.4.1   Some useful relations

Two conventions are commonly used to describe the redox state of solutions and to make calculations involving redox reactions.

The first of these, which is used in PHREEQC (PARKHURST & APPELO 1999) and MINEQL (WESTALL et al. 1976), writes redox reactions in terms of the electron, e⁻, and describes solutions using the electron activity, a_{e^-}, as pe

$$pe = -\log_{10} a_{e^-}$$

or as Eh

$$Eh = pe\left(\frac{RT\ln(10)}{F}\right)$$

where the Faraday constant $F = 96485.309 \text{ J} \cdot \text{V}^{-1} \cdot \text{mol}^{-1}$ and the molar gas constant $R = 8.314510 \text{ J} \cdot \text{K} \cdot \text{mol}^{-1}$. Thus,

$$Eh[V] = pe\ T[K]\ 1.984 \cdot 10^{-4}$$

At 25°C,

$$Eh[V] = pe\ 5.916 \cdot 10^{-2}$$

The second convention, which is used in EQ3/6 (WOLERY 1992), writes redox reactions using $O_2(g)$ and describes the redox state of solutions using oxygen fugacity, $f_{O_2(g)}$.

The reactions given with the Nagra/PSI TDB are written using the electron. These reactions can be rewritten in terms of oxygen fugacity by adding the half-cell reaction

$$O_2(g) + 4H^+ + 4e^- \Leftrightarrow 2H_2O(l) \tag{2.4.1}$$

to eliminate electrons. The corresponding Nernst equation

$$Eh = E° - \frac{RT}{4F}\ln(10)\log_{10}\left(\frac{\left(a_{H_2O(l)}\right)^2}{f_{O_2(g)}\left(a_{H^+}\right)^4}\right) \tag{2.4.2}$$

can be used to establish a relation between Eh, pH, and the oxygen fugacity. At 25˚C, the standard Gibbs free energy for reaction (2.4.1) can be calculated from

$\Delta_f G_m°(H_2O, l, 298.15K) = -237.14$ kJ · mol^{-1}

$$\Delta_r G_m°(2.4.1, 298.15K) = - 474.28 \text{ kJ} \cdot \text{mol}^{-1} \tag{2.4.3}$$

From equation (2.4.3) and

$$\Delta_r G_m°(2.4.1, 298.15K) = -4 \, F \, E°$$

follows that $E° = 1.23$ V. Equation (2.4.2) can then be expressed as

$$Eh = 1.23 + 0.0148 \log_{10} f_{O_2(g)} - 0.0592 \text{pH} - 0.0296 \log_{10} a_{H_2O(l)}$$

2.4.2 SIT for redox reactions

SIT can be used to establish a relationship between the redox potential of a redox couple in a medium of ionic strength I_m and the corresponding quantity at $I = 0$. The redox couple UO_2^{2+}/U^{4+} in a chloride ionic medium shall serve as an example.

It is important to note at the outset that two different cases need to be distinguished:

- **Case 1**: The redox potential of the redox couple in a medium of ionic strength I_m is measured with respect to the standard hydrogen electrode, SHE, in an electrochemical cell setup with the following configuration:

    $Pt(s) \mid H_2(g, f_{H_2(g)} = 1)$, $_{LC}H^+(aq, {}_{LC}a_{H^+} = 1) \mid\mid$

    $$UO_2^{2+}(aq, a_{UO_2^{2+}}), U^{4+}(aq, a_{U^{4+}}), {}_{RC}H^+(aq, {}_{RC}a_{H^+}) \mid Pt(s)$$
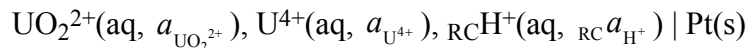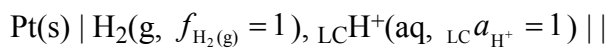
    (LC and RC are used to label H^+ in the left and right half-cell, resp., which are at different activities). In this setup, the reaction in the right half-cell

    $$UO_2^{2+} + 4 \, {}_{RC}H^+ + 2e^- \Leftrightarrow U^{4+} + 2H_2O(l) \tag{2.4.4}$$
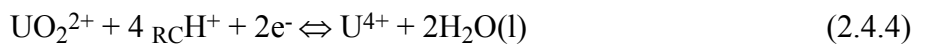
    takes place at ionic strength I_m, and is spatially separated from the left half-cell where the SHE reaction

    $$_{LC}H^+ + e^- \Leftrightarrow 0.5 \, H_2(g) \tag{2.4.5}$$

    takes place at standard conditions (${}_{LC}a_{H^+} = 1$ and $f_{H_2(g)} = 1$). Reactions (2.4.4) and (2.4.5) can be combined, resulting in

$$UO_2{}^{2+} + H_2(g) + 4\,_{RC}H^+ \Leftrightarrow U^{4+} + 2H_2O(l) + 2\,_{LC}H^+ \tag{2.4.6}$$
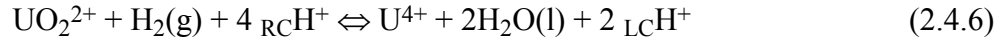
Since $_{LC}a_{H^+} = 1$ and $f_{H_2(g)} = 1$, the equilibrium constant for this reaction

$$\log_{10}K°(2.4.6) = \log_{10} \frac{a_{U^{4+}}\left(a_{H_2O(l)}\right)^2\left(a_{_{LC}H^+}\right)^2}{a_{UO_2{}^{2+}}\left(a_{_{RC}H^+}\right)^4 f_{H_2(g)}}$$

can be simplified to

$$\log_{10}K°(2.4.6) = \log_{10} \frac{a_{U^{4+}}\left(a_{H_2O(l)}\right)^2}{a_{UO_2{}^{2+}}\left(a_{_{RC}H^+}\right)^4}$$

Note that this equilibrium constant contains no terms from the SHE and is equivalent to the equilibrium constant for the half-cell reaction (2.4.4), if the electron activity is neglected. The equilibrium constant for reaction (2.4.6) can be expressed in terms of activity coefficients and the conditional stability constant $\log_{10}K(2.4.6)$

$$\log_{10}K(2.4.6) = \log_{10} \frac{m_{U^{4+}}}{m_{UO_2{}^{2+}}\left(m_{_{RC}H^+}\right)^4}$$

as

$$\log_{10}K°(2.4.6) = \log_{10}K(2.4.6) + \log_{10}\gamma_{U^{4+}} - \log_{10}\gamma_{UO_2{}^{2+}} - 4\log_{10}\gamma_{_{RC}H^+} + 2\log_{10}a_{H_2O(l)}$$

Based on the SIT formalism, these activity coefficients are (for a chloride ionic medium)

$$\log_{10}\gamma_{U^{4+}} = -16D + \varepsilon(U^{4+},Cl^-)m_{Cl^-} \tag{2.4.7}$$

$$\log_{10}\gamma_{UO_2{}^{2+}} = -4D + \varepsilon(UO_2{}^{2+},Cl^-)m_{Cl^-} \tag{2.4.8}$$

$$\log_{10}\gamma_{H^+} = -D + \varepsilon(H^+,Cl^-)m_{Cl^-} \tag{2.4.9}$$

where

$$D = \frac{A\sqrt{I_m}}{1+1.5\sqrt{I_m}}$$

and $A = 0.5100$ mol$^{-1/2}$ · kg$^{1/2}$ at 25°C and 1 atm.

Thus,

$$\log_{10} K°(2.4.6) = \log_{10} K(2.4.6) - 8D + \left(\varepsilon(U^{4+},Cl^-) - \varepsilon(UO_2^{2+},Cl^-) - 4\varepsilon(H^+,Cl^-)\right) m_{Cl^-} + 2\log_{10} a_{H_2O(l)}$$

or

$$\log_{10} K°(2.4.6) = \log_{10} K(2.4.6) - \Delta Z^2 D + m_{Cl^-} \Delta\varepsilon + 2\log_{10} a_{H_2O(l)}$$

where

$$\Delta Z^2 = \left(Z_{U^{4+}}\right)^2 - \left(Z_{UO_2^{2+}}\right)^2 - 4\left(Z_{RC\,H^+}\right)^2 = 8$$

and

$$\Delta\varepsilon(2.4.6) = \varepsilon(U^{4+},Cl^-) - \varepsilon(UO_2^{2+},Cl^-) - 4\varepsilon(H^+,Cl^-)$$

- **Case 2**: Both half-cell reactions are spatially not separated and take place at I_m. In that case, $_{LC}H^+$ and $_{RC}H^+$ are both at the same activity and cannot be distinguished. Therefore, the labels LC and RC can be dropped and the combination of the half-cell reactions (2.4.4) and (2.4.5) results in

$$UO_2^{2+} + H_2(g) + 2\,H^+ \Leftrightarrow U^{4+} + 2H_2O(l) \tag{2.4.10}$$
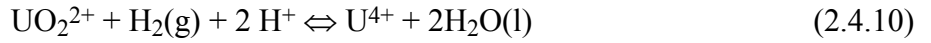
The corresponding equilibrium constant is

$$\log_{10}K°(2.4.10) = \log_{10} \frac{a_{U^{4+}}\left(a_{H_2O(l)}\right)^2}{a_{UO_2^{2+}}\left(a_{H^+}\right)^2 f_{H_2(g)}}$$

Noting that at reasonably low partial pressure of $H_2(g)$ $f_{H_2(g)} \approx p_{H_2(g)}$, the equilibrium constant for reaction (2.4.10) can be expressed in terms of activity coefficients and the conditional stability constant $\log_{10}K(2.4.10)$

$$\log_{10}K(2.4.10) = \log_{10} \frac{m_{U^{4+}}}{m_{UO_2^{2+}}\left(m_{H^+}\right)^2 p_{H_2(g)}}$$

as

$$\log_{10}K°(2.4.10) = \log_{10}K(2.4.10) + \log_{10}\gamma_{U^{4+}} - \log_{10}\gamma_{UO_2^{2+}} - 2\log_{10}\gamma_{H^+} + 2\log_{10} a_{H_2O(l)}$$

Hence, with equations (2.4.7-2.4.9)

$$\log_{10} K°(2.4.10) = \log_{10} K(2.4.10) - 10D + \left(\varepsilon(U^{4+},Cl^-) - \varepsilon(UO_2^{2+},Cl^-) - 2\varepsilon(H^+,Cl^-)\right) m_{Cl^-}$$
$$+ 2\log_{10} a_{H_2O(l)}$$

or

$$\log_{10} K°(2.4.10) = \log_{10} K(2.4.10) - \Delta Z^2 D + m_{Cl^-}\Delta\varepsilon + 2\log_{10} a_{H_2O(l)}$$

where

$$\Delta Z^2 = \left(Z_{U^{4+}}\right)^2 - \left(Z_{UO_2^{2+}}\right)^2 - 2\left(Z_{H^+}\right)^2 = 10$$

and

$$\Delta\varepsilon(2.4.10) = \varepsilon(U^{4+},Cl^-) - \varepsilon(UO_2^{2+},Cl^-) - 2\varepsilon(H^+,Cl^-)$$

Note that GRENTHE et al. (1997) on p. 343-344 claimed erroneously that the last three equations apply to the situation described above as Case 1.

Table 2.4.1 compares ΔZ^2 and $\Delta\varepsilon$ for Case 1 and Case 2.

Table 2.4.1:   Comparison of ΔZ^2 and $\Delta\varepsilon$ for Case 1 (oxidation and reduction spatially separated in two electrochemical cells) and Case 2 (oxidation and reduction spatially not separated).

	Case 1	**Case 2**
ΔZ^2	$\left(Z_{U^{4+}}\right)^2 - \left(Z_{UO_2^{2+}}\right)^2 - 4\left(Z_{RC\,H^+}\right)^2 = 8$	$\left(Z_{U^{4+}}\right)^2 - \left(Z_{UO_2^{2+}}\right)^2 - 2\left(Z_{H^+}\right)^2 = 10$
$\Delta\varepsilon$	$\varepsilon(U^{4+},Cl^-) - \varepsilon(UO_2^{2+},Cl^-) - 4\varepsilon(H^+,Cl^-)$	$\varepsilon(U^{4+},Cl^-) - \varepsilon(UO_2^{2+},Cl^-) - 2\varepsilon(H^+,Cl^-)$

2.5   Database Structure

The database includes information on elements, aqueous species (comprising primary master species, secondary master species, and product species), minerals and other solids, and gases.

Elements were not included in the previous Nagra TDB, but have been added for two reasons. First, they are required for future use of the database with the Gibbs free energy minimization code SELEKTOR (KARPOV et al. 1997), now called GEMS. Second, their properties are used in PMATCHC (see Appendix A) to calculate gram formula weights, and entropies and heat capacities of formation of other entities in the database. Data considered for elements are atomic mass, absolute molar entropy, and absolute isobaric molar heat capacity (see Table 4.1).

The **master species** are the building blocks of the formation reactions for product species, minerals and other solids, and gases. There are two types of master species: Primary master species (see Table 2.5.1) and secondary master species (see Table 2.5.2). In addition to the electron, there is at

least one primary master species for each element contained in the database. As discussed below, it is convenient to define secondary master species. The formation reactions of secondary master species are written entirely in terms of primary master species. Hence, the formation reactions for product species, minerals and other solids, and gases in the database are all given in terms of primary and secondary master species. The ensuing structure of the database is illustrated by a small subsystem (H-C-O-Ca-U) in Table 2.5.3.

Data for **primary master species** include their thermodynamic properties of formation from the elements, absolute entropies and heat capacities, as well as their charge and parameters for the Debye-Hückel and WATEQ Debye-Hückel equations for activity coefficients. Data for **secondary master species** include the stoichiometry and thermodynamic properties of their formation from primary master species, their thermodynamic properties of formation from the elements, absolute entropies and heat capacities, as well as their charge and parameters for the Debye-Hückel and WATEQ Debye-Hückel equations.

Product species are formed in solution by reaction among master species. The database includes the stoichiometry of these reactions and their thermodynamic properties, the thermodynamic properties of the formation of the product species from the elements, absolute entropies and heat capacities, as well as their charge and parameters for the Debye-Hückel and WATEQ Debye-Hückel equations.

Minerals and other **solids**, and **gases** are also formulated in terms of master species. The database includes the same information for them as for product species, except that no charge and activity coefficient parameters are required.

There are several considerations in the choice of master species. First, there must be at least one master species for each element to be included in the database. Second, if the element of interest can undergo redox changes, it is to be decided whether the modeled redox reactions are considered to be always at equilibrium (redox coupled with respect to the element) or not (redox decoupled with respect to the element).

Table 2.5.1:   Primary master species.

Al^{3+}	Eu^{3+}	I^-	Ni^{2+}	$Sn(OH)_4(aq)$
Am^{3+}	F^-	K^+	NO_3^-	Sn^{2+}
Ba^{2+}	Fe^{2+}	Li^+	NpO_2^{2+}	SO_4^{2-}
Br^-	H^+	Mg^{2+}	Pd^{2+}	Sr^{2+}
Ca^{2+}	$H_2O(l)$	Mn^{2+}	PuO_2^{2+}	TcO_4^-
Cl^-	$HAsO_4^{2-}$	MoO_4^{2-}	Ra^{2+}	Th^{4+}
Cs^+	HCO_3^-	Na^+	SeO_3^{2-}	UO_2^{2+}
e^-	HPO_4^{2-}	NbO_3^-	$Si(OH)_4(aq)$	Zr^{4+}

Table 2.5.2:   Secondary master species.

$Al(OH)_4^-$	$H_2(aq)$	$N_2(aq)$	OH^-	$SiO_2(OH)_2^{2-}$
$As(OH)_3(aq)$	$H_2PO_4^-$	$NH_3(aq)$	PO_4^{3-}	SO_3^{2-}
$CH_4(aq)$	$H_2Se(aq)$	NH_4^+	Pu^{3+}	$TcO(OH)_2(aq)$
$CO_2(aq)$	$H_3PO_4(aq)$	Np^{3+}	Pu^{4+}	U^{4+}
CO_3^{2-}	HS^-	Np^{4+}	PuO_2^+	UO_2^+
Eu^{2+}	$HSeO_4^-$	NpO_2^+	$S_2O_3^{2-}$	
Fe^{3+}	$I_2(aq)$	$O_2(aq)$	$SiO(OH)_3^-$	

Table 2.5.3: Example of a database structure for the chemical system H-C-O-Ca-U. Primary master species are set in **boldface**, and secondary master species in ***boldface italics***.

Elements		H	C	O	Ca	U
Primary master species		H^+	HCO_3^-	$H_2O(l)$	Ca^{2+}	UO_2^{2+}
Secondary master species	CO_3^{2-}			$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+$		
	UO_2^+			$UO_2^{2+} + e^- \Leftrightarrow UO_2^+$		
Product species	$UO_2CO_3(aq)$			$UO_2^{2+} + CO_3^{2-} \Leftrightarrow UO_2CO_3(aq)$		
	$UO_2(CO_3)_2^{2-}$			$UO_2^{2+} + 2CO_3^{2-} \Leftrightarrow UO_2(CO_3)_2^{2-}$		
	$UO_2(CO_3)_3^{5-}$			$UO_2^+ + 3CO_3^{2-} \Leftrightarrow UO_2(CO_3)_3^{5-}$		
Minerals and solids	$UO_2CO_3(cr)$			$UO_2^{2+} + CO_3^{2-} \Leftrightarrow UO_2CO_3(cr)$		
	$CaCO_3(cr)$			$Ca^{2+} + HCO_3^- \Leftrightarrow CaCO_3(cr) + H^+$		
Gases	$CO_2(g)$			$HCO_3^- + H^+ \Leftrightarrow CO_2(g) + H_2O(l)$		

If an element is considered **redox coupled**, only a single master species is chosen. Other redox states of the element are written as secondary master species, and their concentrations are calculated based on the redox potential of the solution.

If an element is considered **redox decoupled**, a primary master species must be chosen for each redox state of the element. In this case, a redox potential for the solution can be calculated if measured concentrations of elements in different redox states are available.

With the exception of Sn, all redox elements in this database are considered to be redox coupled. Therefore, for each redox element (e.g. Pu) there is one primary master species (PuO_2^{2+}) and several secondary master species (PuO_2^+, Pu^{4+}, and Pu^{3+}). The formation reactions of all secondary redox master species in the database are listed in Table 2.5.4. Note that it is conventional (IUPAC) to write redox reactions with the electron on the left-hand side - so that the reaction is from oxidized to reduced state. Table 2.5.4 has some equilibria with the electron on the right-hand side. The reason for this is that some primary master species are the oxidized and some the reduced members of the redox couples written, and the reactions in the database have to be written so the secondary master species are products of reactions among master species.

Due to a lack of data linking Sn(II) to Sn(IV) (see Section 5.22), Sn has to be considered redox decoupled and there are two master species for Sn in this database, Sn^{2+} and $Sn(OH)_4(aq)$.

Table 2.5.4:   Formation reactions of secondary redox master species.

H(I)/H(0)	$2H^+ + 2e^- \Leftrightarrow H_2(aq)$
O(-II)/O(0)	$2H_2O(l) \Leftrightarrow O_2(aq) + 4H^+ + 4e^-$
C(IV)/C(-IV)	$HCO_3^- + 9H^+ + 8e^- \Leftrightarrow CH_4(aq) + 3H_2O(l)$
N(V)/N(-III)	$NO_3^- + 10H^+ + 8e^- \Leftrightarrow NH_4^+ + 3H_2O(l)$
N(V)/N(0)	$2NO_3^- + 12H^+ + 10e^- \Leftrightarrow N_2(aq) + 6H_2O(l)$
S(VI)/(-II)	$SO_4^{2-} + 9H^+ + 8e^- \Leftrightarrow HS^- + 4H_2O(l)$
S(VI)/(II)	$2SO_4^{2-} + 10H^+ + 8e^- \Leftrightarrow S_2O_3^{2-} + 5H_2O(l)$
S(VI)/S(IV)	$SO_4^{2-} + 2H^+ + 2e^- \Leftrightarrow SO_3^{2-} + H_2O(l)$
I(-I)/I(0)	$2I^- \Leftrightarrow I_2(aq) + 2e^-$
As(V)/As(III)	$HAsO_4^{2-} + 4H^+ + 2e^- \Leftrightarrow As(OH)_3(aq) + H_2O(l)$
Se(IV)/Se(-II)	$SeO_3^{2-} + 8H^+ + 6e^- \Leftrightarrow H_2Se(aq) + 3H_2O(l)$
Se(IV)/Se(VI)	$SeO_3^{2-} + H_2O(l) \Leftrightarrow HSeO_4^- + H^+ + 2e^-$
Fe(II)/Fe(III)	$Fe^{2+} \Leftrightarrow Fe^{3+} + e^-$
Tc(VII)/Tc(IV)	$TcO_4^- + 4H^+ + 3e^- \Leftrightarrow TcO(OH)_2(aq) + H_2O(l)$
Eu(III)/Eu(II)	$Eu^{3+} + e^- \Leftrightarrow Eu^{2+}$
Np(VI)/Np(III)	$NpO_2^{2+} + 4H^+ + 3e^- \Leftrightarrow Np^{3+} + 2H_2O(l)$
Np(VI)/Np(IV)	$NpO_2^{2+} + 4H^+ + 2e^- \Leftrightarrow Np^{4+} + 2H_2O(l)$
Np(VI)/Np(V)	$NpO_2^{2+} + e^- \Leftrightarrow NpO_2^+$
Pu(VI)/Pu(III)	$PuO_2^{2+} + 4H^+ + 3e^- \Leftrightarrow Pu^{3+} + 2H_2O(l)$
Pu(VI)/Pu(IV)	$PuO_2^{2+} + 4H^+ + 2e^- \Leftrightarrow Pu^{4+} + 2H_2O(l)$
Pu(VI)/Pu(V)	$PuO_2^{2+} + e^- \Leftrightarrow PuO_2^+$
U(VI)/U(IV)	$UO_2^{2+} + 4H^+ + 2e^- \Leftrightarrow U^{4+} + 2H_2O(l)$
U(VI)/U(V)	$UO_2^{2+} + e^- \Leftrightarrow UO_2^+$

In several instances, secondary master species were chosen for convenience in formulating product species, minerals and other solids, or gases. In the case of carbonate, e.g., formation reactions can be formulated in terms of the primary master species HCO_3^-, or in terms of the secondary master species CO_3^{2-}.

2.6 Sources of thermodynamic data

The Nagra TDB 05/92 distinguished two types of data, "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. For TDB 05/92 the supplemental data were selected in groups from one of several existing data sets of varying quality. Our update from version 05/92 to 01/01 focused on major revisions of most of these supplemental data. Hence, to a certain extent the term "supplemental data" now is misleading as the quality of the data has tremendously improved. For historical reasons we decided to retain the original terms "core" and "supplemental" for this update. Development of a more appropriate concept reflecting the quality of the data base contents is the subject of a forthcoming update.

2.6.1 Sources of core data

Several compilations of the thermochemical properties of formation of elements, aqueous species, gases, and solids were used. These include the CODATA tables (GARVIN et al. 1987, COX et al. 1989), the auxiliary data selected as part of the NEA TDB project (GRENTHE et al. 1992) and tables issued by the US National Institute of Science and Technology (NIST, formerly National Bureau of Standards, NBS) (WAGMAN et al. 1982).

The CODATA tables include only few entities, but contain very carefully selected, internally consistent data. Thus, when thermochemical properties are required for the core data, CODATA values were chosen when available. The NEA TDB compilation also uses CODATA values whenever possible, so values for the same entity in the two data bases are always identical. The NIST tables are more complete than the CODATA or NEA compilations, but are older. Thermochemical properties were taken from the NIST tables only if they were not available in the other two compilations.

For the most part, these compilations were used as the sources of the thermochemical properties of the elements and of the master species. Properties of the product species, minerals, and gases were derived from reactions and their equilibrium constants selected from NORDSTROM et al. (1990).

NORDSTROM et al. (1990) is a compilation of data on relatively few elements, with their important aqueous species and minerals. It was assembled by Nordstrom and a large group of his colleagues, and represents what the authors consider to be the best set of thermodynamic data which is available for the elements it includes.

Data were also taken from selected publications on individual elements. The publications are discussed in the sections on data selection in Chapter 4.

2.6.2   Sources of supplemental data

For the original Nagra TDB 05/92 the supplemental data were selected in groups from one of several existing data sets. Data for silica, iron and manganese were taken from the compilation of critically evaluated data of NORDSTROM et al. (1990). Data for uranium were taken from a draft version of the later published NEA uranium review (GRENTHE et al. 1992). Data on palladium, nickel and selenium were taken from a data set compiled from a variety of sources (BAEYENS & MCKINLEY 1989). These data were apparently not critically evaluated with as much care as the Nordstrom and NEA data. Data for the remaining elements were taken from compilations of unknown reliability.

For our update to Nagra/PSI TDB 01/01 we decided to rely on NEA critically reviewed and recommended data whenever possible. NEA reviews were considered in our update for U (GRENTHE et al. 1992), Np & Pu (LEMIRE et al. 2001), Am (SILVA et al. 1995) and Tc (RARD et al. 1999). Our reasons for not accepting all NEA recommendations are documented in detail in Chapter 5.

Thermodynamic data were selected for Th, Sn, Eu, Pd, Al, and solubility and metal complexation of sulphides and silicates based on extensive reviews of original publications. 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. All our reviews are documented in detail in Chapter 5.

Data for manganese and iron were taken from the compilation of NORDSTROM et al. (1990). In the case of iron and magnesium, a few selected papers have been examined concerning aqueous species and minerals not included in Nordstrom's compilation. These additional papers are briefly discussed in Chapter 5.

Data for iodine, molybdenum and niobium were taken from TDB 05/92 without further examination.

2.7 References

BAEYENS, B., MCKINLEY, I.G. (1989): A PHREEQE Data Base for Pd, Ni, and Se. Nagra Technical Report 88-28, Nagra, Wettingen, Switzerland, 59p.

BETHKE, C.M. (1994): The Geochemist's Workbench™ Version 2.0. A User's Guide to Rxn, Act2, Tact, React, and Gtplot. Urbana-Champaign, IL, Hydrogeology Program, University of Illinois, 213p.

BETHKE, C.M. (1996): Geochemical Reaction Modeling. Concepts and Applications. New York, Oxford University Press, 397p.

COX, J.D., WAGMAN, D.D., MEDVEDEV, V.A. (1989): CODATA Key Values for Thermodynamics. New York, Hemisphere, 271p.

DAVIES, C.W. (1938): Journal of the Chemical Society, 2093.

DAVIES, C.W. (1962): Ion Association. London, Butterworths, 189p.

GARVIN, D., PARKER, V.B., WHITE, H.J., JR. (1987): CODATA Thermodynamic Tables: Selctions for Some Compounds of Calcium and Related Mixtures: A Prototype Set of Tables. Washington, D.C., Hemisphere Publishing, 356p.

GRENTHE, I., FUGER, J., KONINGS, R.J.M., LEMIRE, R.J., MULLER, A.B., NGUYEN-TRUNG, C., WANNER, H. (1992): Chemical Thermodynamics of Uranium. Elsevier, Amsterdam, 715p.

GRENTHE, I., PLYASUNOV, A.V., SPAHIU, K. (1997): Estimation of Medium Effects on Thermodynamic Data. In: GRENTHE, I., PUIGDOMÈNECH, I. (eds.): Modelling in Aquatic Chemistry. OECD Nuclear Energy Agency, Paris, pp.325-426.

HELGESON, H.C. (1969): Thermodynamics of hydrothermal systems at elevated temperatures and pressures. American Journal of Science, 267, 729-804.

KARPOV, I.K., CHUDNENKO, K.V., KULIK, D.A. (1997): Modeling chemical mass transfer in geochemical processes: Thermodynamic relations, conditions of equilibria, and numerical algorithms. American Journal of Sience, 297, 767-806.

KIELLAND, J. (1937): Individual activity coefficients of ions in aqueous solutions. Journal of the American Chemical Society, 59, 1675-1678.

LEMIRE, R.J., FUGER, J., NITSCHE, H., POTTER, P., RAND, M.H., RYDBERG, J., SPAHIU, K., SULLIVAN, J.C., ULLMAN, W.J., VITORGE, P., WANNER, H. (2001): Chemical Thermodynamics of Neptunium & Plutonium. Elsevier, Amsterdam, 845p.

MAIER, C.G., KELLEY, K.K. (1932): An equation for the representation of high-temperature heat content data. Journal of the American Chemical Society, 54, 3243-3246.

NORDSTROM, D.K., PLUMMER, L.N., LANGMUIR, D., BUSENBERG, E., MAY, H.M., JONES, B.F., PARKHURST, D.L. (1990): Revised Chemical Equilibrium Data for Major Water-Mineral Reactions and Their Limitations. In: MELCHIOR, D. C., and BASSETT, R. L. (eds.): Chemical Modeling of Aqueous Systems II. Washington, D.C., American Chemical Society, ACS Symposium Series 416, p. 398-413.

PARKHURST, D.L. (1990): Ion-association models and mean activity coefficients of various salts. In: MELCHIOR, D. C., and BASSETT, R. L. (eds.): Chemical Modeling of Aqueous Systems II. Washington, D.C., American Chemical Society, ACS Symposium Series 416, p. 30-43.

PARKHURST, D.L., APPELO, C.A.J. (1999): User's Guide to PHREEQC (Version 2) - A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. Denver, CO, U. S. Geological Survey, Water-Resources Investigations Report 99-4259, 312p.

RARD, J.A., RAND, M.H., ANDEREGG, G., WANNER, H. (1999): Chemical Thermodynamics of Technetium. Elsevier, Amsterdam, 544p.

SILVA, R.J., BIDOGLIO, G., RAND, M.H., ROBOUCH, P.B., WANNER, H., PUIGDOMÈNECH, I. (1995): Chemical Thermodynamics of Americium. Elsevier, Amsterdam, 374p.

WAGMAN, D.D., EVANS, W.H., PARKER, V.B., SCHUMM, R.H., HALOW, I., BAILEY, S.M., CHURNEY, K.L., NUTTALL, R.L. (1982): The NBS tables of chemical thermodynamic properties: Selected values for inorganic and C1 and C2 organic substances in SI units. Journal of Physical and Chemical Reference Data, 11, Supplement No. 2, 1-392.

WESTALL, J.C., ZACHARY, J.L., MOREL, F.M.M. (1976): MINEQL a computer program for the calculation of chemical equilibrium composition of aqueous systems. MIT, Department of Civil Engineering, Technical Note No. 18, 91p.

WOLERY, T.J., JACKSON, K.J., BOURCIER, W.L., BRUTTON, C.J., VIANI, B.E., KNAUSS, K.G., DELANY, J.M. (1990): Current status of the EQ3/6 software package for geochemical modelling. In: MELCHIOR, D. C., and BASSETT, R. L. (eds.): Chemical Modeling of Aqueous Systems II. Washington, D.C., American Chemical Society, ACS Symposium Series 416, p. 104-116.

WOLERY, T.J. (1992): EQ3/6, a software package for geochemical modeling of aqueous systems. UCRL-MA-110662-PT I-IV, Lawrence Livermore National Laboratory, Livermore, CA.

3   SUMMARY OF DATA EVALUATION

The Nagra/PSI TDB has been updated to support performance assessments of the planned Swiss repositories for radioactive waste. In this update we focused our review work on compounds and complexes determining the solubility and sorption of radionuclides.

Hydroxides and carbonates are the major compounds and complexes formed in pore waters contacting the repository host rock, the backfill materials and cementitious waste forms. For most radionuclides knowledge of their hydrolysis behaviour and the formation properties of their sparingly soluble (hydr)oxide solids are essential to the understanding of aqueous systems. In general, groundwaters and near-field pore waters have fairly high carbonate concentrations and thus, strong radionuclide – carbonate complexes and the formation of (hydroxo)carbonate solids may outweigh the strong hydrolysis effect. Some radionuclides also form strong complexes with fluoride, sulphide, phosphate and silicate. Although the concentration of these ligands in natural waters usually is rather low, strong complex formation may result in significant influence on solubility and sorption for some radionuclides. The opposite is true for sulphate. Radionuclide complexes with sulphate are generally weaker than carbonate complexes but due to appreciable amounts of sulphate in pore waters the net effect of sulphate complexation may become important in specific cases.

As a consequence, this review focused on evaluating thermodynamic constants, first for hydroxides and carbonates, and second, for fluorides, sulphates, sulphides, phosphates and silicates.

Our experiences from this two year team effort are summarised in the following sections. (1) Detailed in-house reviews and critical appraisal of NEA recommendations greatly improved the chemical consistency and quality of the selected data, as shown by comparison of complexation constants for M(III) (Eu, Am, Pu) and M(IV) (Sn, Zr, Th, U, Np, Pu) oxidation states of actinides and fission products. (2) In some systems, e.g. $ThO_2 – H_2O$ and $UO_2 – H_2O$, we encountered conflicting data, i.e. the experimental data could not be described by a unique set of thermodynamic constants. In these cases, a pragmatic approach based on solubility data was chosen for application to performance assessment. (3) In some cases we included uncertain data as guidelines for modellers. (4) We could discern major gaps in the data, especially missing carbonate complexes. (5) Finally, future data needs were identified.

3.1   Chemical consistency of selected thermodynamic data

The magnitudes of equilibrium constants of aqueous complexes and solids are expected to reveal characteristic patterns when different groups of metals and ligands are compared. Some overall

patterns can be deduced from the position of the element in the periodic table of the elements (i.e. principal element groups, Irving-Williams series of transition metals, lanthanide systematics). Many empirical and semi-empirical correlations have been discussed in the literature relating aqueous complex and solid formation constants to various parameters, e.g. ionisation potentials, electronegativity, charge/radius ratios, protonation constants. They are important for qualitative appraisal of new data and may be used to estimate constants that are unknown or experimentally difficult to access. For a comprehensive overview of fundamental chemical concepts and estimation methods see GRENTHE et al. (1997); specific applications of such methods for data estimation can be found in BROWN & WANNER (1987) and NECK & KIM (2000).

We did not use such correlations in our present update to estimate formation constants in any systematic way. The selection of updated constants is almost exclusively based on experimental findings. Therefore, chemical patterns and correlations revealed in our selected data may serve as an independent measure of the chemical consistency of the database.

3.1.1   A first look at groups of metals and ligands

Comparing equilibrium constants of cations of the same charge and comparable ionic radii is the obvious first step in exploring the overall chemical consistency of a database. Such metals are expected to form complexes and solids with similar stoichiometry and equilibrium constants.

Complex formation constants of tetravalent actinides, Zr^{4+} and Sn^{4+} are summarised in Table 3.1.1. The $\log_{10}K$ patterns in Table 3.1.1 reveal that our data selected for tetravalent metals form a chemically meaningful ensemble and none of the formation constants seems to be grossly wrong. Note the well known phenomenon that the data for Th(IV) deviate considerably from the other M(IV) actinide ions. For fluoride and hydroxide complexes this can be rationalised in terms of ionic radii (see section 3.1.3 and Figs. 3.1.1 and 3.1.2). Lack of experimental data and experimental data rejected in our review due to insufficient quality resulted in some gaps in Table 3.1.1. However, considering the good overall consistency of these data, Table 3.1.1 can be used to estimate limiting values of missing constants for specific applications. Especially, the mixed hydroxide carbonate complexes of U^{4+}, Np^{4+} and Pu^{4+} are of particular interest in modelling exercises as they may be the dominant species in carbonate rich groundwaters, but practically no experimental data are available to derive reliable constants. For application in the ongoing Nagra performance assessment we estimated limiting values (HUMMEL & BERNER 2002) but these numbers are not included in the Nagra/PSI TDB 01/01.

Table 3.1.1: M(IV) compounds and complexes. For clarity, rounded values without uncertainty ranges are presented here. Complete data are provided in sections 5.10, 5.15 and 5.21 to 5.24.

M^{4+} complexes and solids	$\log_{10}\beta°$					
	Th^{4+}	U^{4+}	Np^{4+}	Pu^{4+}	Zr^{4+}	Sn^{4+}
$MO_2(cr) + 2\ H_2O \Leftrightarrow M(OH)_4(aq)$					−11.6	−8.0
$MO_2(am) + 2\ H_2O \Leftrightarrow M(OH)_4(aq)$	−8.5	−9	−8.3	−10.4		−7.3
$M^{4+} + H_2O \Leftrightarrow MOH^{3+} + H^+$	−2.4	−0.5	−0.3	−0.8	0.3	
$M^{4+} + 4\ H_2O \Leftrightarrow M(OH)_4(aq)+ 4\ H^+$	−18.4	−9	−9.8	−8.4	−9.7	
$M(OH)_4(aq) + H_2O \Leftrightarrow M(OH)_5^- + H^+$					−6.3	−8.0
$M^{4+} + 4\ CO_3^{2-} \Leftrightarrow M(CO_3)_4^{4-}$		35.2	36.7	35.9		
$M^{4+} + 5\ CO_3^{2-} \Leftrightarrow M(CO_3)_5^{6-}$	29.8	34.1	35.6	34.5		
$M^{4+} + CO_3^{2-} + 3\ H_2O \Leftrightarrow$ $M(CO_3)(OH)_3^- + 3\ H^+$	−3.1					
$M^{4+} + SO_4^{2-} \Leftrightarrow MSO_4^{2+}$	7.6	6.6	6.9	6.9	7.0	
$M^{4+} + 2\ SO_4^{2-} \Leftrightarrow M(SO_4)_2(aq)$	11.6	10.5	11.1	11.1		
$M^{4+} + HPO_4^{2-} \Leftrightarrow MHPO_4^{2+}$	13					
$M^{4+} + F^- \Leftrightarrow MF^{3+}$	8.0	9.3	9.0	8.8	10.2	
$M^{4+} + 2\ F^- \Leftrightarrow MF_2^{2+}$	14.2	16.2	15.7	15.7	18.5	
$M^{4+} + 3\ F^- \Leftrightarrow MF_3^{+}$	18.9	21.6			24.7	
$M^{4+} + 4\ F^- \Leftrightarrow MF_4(aq)$	22.3	25.6			30.1	
$M^{4+} + Cl^- \Leftrightarrow MCl^{3+}$		1.7	1.5	1.8	1.5	

As expected from a chemical point of view, the equilibrium constant for Am^{3+} and Eu^{3+} are very similar (Table 3.1.2). Data for Np^{3+} and Pu^{3+} are almost absent and appraisal of chemical consistency is hardly possible although the few formation constants for Pu^{3+} fit well with the patterns derived from the Am^{3+} and Eu^{3+} data.

Table 3.1.2: M(III) compounds and complexes. For clarity, rounded values without uncertainty ranges are presented here. Complete data are provided in sections 5.2, 5.4, 5.10 and 5.15.

M^{3+} complexes and solids	$\log_{10}\beta°$			
	Np^{3+}	Pu^{3+}	Am^{3+}	Eu^{3+}
M(OH)$_3$(cr) + 3 H$^+$ $\Leftrightarrow$ M^{3+} + 3 H$_2$O		15.8	15.2	14.9
M(OH)$_3$(am) + 3 H$^+$ $\Leftrightarrow$ M^{3+} + 3 H$_2$O			17.0	17.6
M$_2$(CO$_3$)$_3$(cr) $\Leftrightarrow$ 2 M^{3+} + 3 CO$_3^{2-}$			−33.4	−35.0
M(OH)CO$_3$(cr) $\Leftrightarrow$ M^{3+} + OH$^-$ + CO$_3^{2-}$			−21.2	−21.7
M^{3+} + H$_2$O $\Leftrightarrow$ MOH^{2+} + H$^+$	−6.8	−6.9	−7.3	−7.6
M^{3+} + 2 H$_2$O $\Leftrightarrow$ M(OH)$_2^+$ + 2 H$^+$			−15.2	−15.1
M^{3+} + 3 H$_2$O $\Leftrightarrow$ M(OH)$_3$(aq) + 3 H$^+$			−25.7	−23.7
M^{3+} + 4 H$_2$O $\Leftrightarrow$ M(OH)$_4^-$ + 4 H$^+$				−36.2
M^{3+} + CO$_3^{2-}$ $\Leftrightarrow$ MCO$_3^+$			7.8	8.1
M^{3+} + 2 CO$_3^{2-}$ $\Leftrightarrow$ M(CO$_3$)$_2^-$			12.3	12.1
M^{3+} + 3 CO$_3^{2-}$ $\Leftrightarrow$ M(CO$_3$)$_3^{3-}$			15.2	
M^{3+} + SO$_4^{2-}$ $\Leftrightarrow$ MSO$_4^+$		3.9	3.9	4.0
M^{3+} + 2 SO$_4^{2-}$ $\Leftrightarrow$ M(SO$_4$)$_2^-$		5.7	5.4	5.7
M^{3+} + HPO$_4^{2-}$ $\Leftrightarrow$ MHPO$_4^+$			3.0	
M^{3+} + F$^-$ $\Leftrightarrow$ MF^{2+}			3.4	3.8
M^{3+} + 2 F$^-$ $\Leftrightarrow$ MF$_2^+$			5.8	6.5
M^{3+} + Cl$^-$ $\Leftrightarrow$ MCl^{2+}		1.2	1.1	1.1
M^{3+} + 2 Cl$^-$ $\Leftrightarrow$ MCl$_2^+$				1.5
M^{3+} + SiO(OH)$_3^-$ $\Leftrightarrow$ MSiO(OH)$_3^{2+}$			8.1	7.9

A similar picture of chemical consistency is observed comparing the hexavalent dioxo cations of U, Np and Pu (Table 3.1.3). The most complete speciation scheme is available for UO_2^{2+}. The overall consistent pattern of all available data can be used to estimate limiting values of missing constants for specific applications.

Table 3.1.3: M(VI)-dioxo complexes and solids. For clarity, rounded values without uncertainty ranges are presented here. Complete data are provided in sections 5.10, 5.15 and 5.23.

MO_2^{2+} complexes and solids	$log_{10}\beta°$		
	UO_2^{2+}	NpO_2^{2+}	PuO_2^{2+}
$MO_2^{2+} + 2\ H_2O \Leftrightarrow MO_2(OH)_2(s) + 2\ H^+$	–6.0	–5.5	–5.5
$MO_2^{2+} + CO_3^{2-} \Leftrightarrow MO_2CO_3(s)$	14.5	14.6	14.2
$MO_2^{2+} + H_2O \Leftrightarrow MO_2OH^+ + H^+$	–5.2	–5.1	–5.5
$MO_2^{2+} + 2\ H_2O \Leftrightarrow MO_2(OH)_2(aq) + 2\ H^+$	–12		–13
$MO_2^{2+} + 3\ H_2O \Leftrightarrow MO_2(OH)_3^- + 3\ H^+$	–19.2	–19	
$MO_2^{2+} + 4\ H_2O \Leftrightarrow MO_2(OH)_4^{2-} + 4\ H^+$	–33	–33	
$2\ MO_2^{2+} + H_2O \Leftrightarrow (MO_2)_2OH^{3+} + H^+$	–2.7		
$2\ MO_2^{2+} + 2\ H_2O \Leftrightarrow (MO_2)_2(OH)_2^{2+} + 2\ H^+$	–5.6	–6.3	–7.5
$3\ MO_2^{2+} + 4\ H_2O \Leftrightarrow (MO_2)_3(OH)_4^{2+} + 4\ H^+$	–11.9		
$3\ MO_2^{2+} + 5\ H_2O \Leftrightarrow (MO_2)_3(OH)_5^+ + 5\ H^+$	–15.6	–17.1	
$3\ MO_2^{2+} + 7\ H_2O \Leftrightarrow (MO_2)_3(OH)_7^- + 7\ H^+$	–31		
$4\ MO_2^{2+} + 7\ H_2O \Leftrightarrow (MO_2)_4(OH)_7^+ + 7\ H^+$	–21.9		
$MO_2^{2+} + CO_3^{2-} \Leftrightarrow MO_2CO_3(aq)$	9.7	9.3	9.3
$MO_2^{2+} + 2\ CO_3^{2-} \Leftrightarrow MO_2(CO_3)_2^{2-}$	16.9	16.5	14.6
$MO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow MO_2(CO_3)_3^{4-}$	21.6	19.4	17.7
$3\ MO_2^{2+} + 6\ CO_3^{2-} \Leftrightarrow (MO_2)_3(CO_3)_6^{6-}$	54	49.8	
$2\ MO_2^{2+} + CO_3^{2-} + 3\ H_2O \Leftrightarrow$ $(MO_2)_2(OH)_3CO_3^- + 3\ H^+$	–0.9	–2.9	
$3\ MO_2^{2+} + CO_3^{2-} + 3\ H_2O \Leftrightarrow$ $(MO_2)_3(OH)_3CO_3^+ + 3\ H^+$	0.7		
$MO_2^{2+} + SO_4^{2-} \Leftrightarrow MO_2SO_4(aq)$	3.2	3.3	3.4
$MO_2^{2+} + 2\ SO_4^{2-} \Leftrightarrow MO_2(SO_4)_2^{2-}$	4.1	4.7	4.4
$MO_2^{2+} + Cl^- \Leftrightarrow MO_2Cl^+$	0.2	0.4	0.7
$MO_2^{2+} + 2\ Cl^- \Leftrightarrow MO_2(Cl)_2(aq)$	–1.1		–0.6
$MO_2^{2+} + F^- \Leftrightarrow MO_2F^+$	5.1	4.6	4.6
$MO_2^{2+} + 2\ F^- \Leftrightarrow MO_2F_2(aq)$	8.6	7.6	7.3

$MO_2^{2+} + 3\ F^- \Leftrightarrow MO_2F_3^-$	10.9	
$MO_2^{2+} + 4\ F^- \Leftrightarrow MO_2F_4^{2-}$	11.7	
$MO_2^{2+} + NO_3^- \Leftrightarrow MO_2NO_3^+$	0.3	
$MO_2^{2+} + PO_4^{3-} \Leftrightarrow MO_2PO_4^-$	13.2	
$MO_2^{2+} + HPO_4^{2-} \Leftrightarrow MO_2HPO_4(aq)$	7.2	6.2
$MO_2^{2+} + H_2PO_4^- \Leftrightarrow MO_2H_2PO_4^+$	3.2	3.3
$MO_2^{2+} + H_3PO_4(aq) \Leftrightarrow MO_2H_3PO_4^{2+}$	0.8	
$MO_2^{2+} + 2\ H_2PO_4^- \Leftrightarrow MO_2(H_2PO_4)_2(aq)$	4.9	
$MO_2^{2+} + 2\ H_3PO_4(aq) \Leftrightarrow MO_2H(H_2PO_4)_2^+ + H^+$	1.7	
$MO_2^{2+} + 2\ HPO_4^{2-} \Leftrightarrow MO_2(HPO_4)_2^{2-}$		9.5

Data for the pentavalent dioxo cations are available only for complexes of NpO_2^+.

Unfortunately, the reduction potentials for U, Np and Pu, summarised in Table 3.1.4, reveal that the impressive chemical consistency observed for actinide ions of the same oxidation state does not apply to the different redox states of these ions. The predominance fields of different redox states vary strongly with the atomic number.

Table 3.1.4: Actinide redox couples.

	$log_{10}K°$		
	U	Np	Pu
$MO_2^{2+} + e^- \Leftrightarrow MO_2^+$	1.484	19.59	15.82
$MO_2^+ + 4\ H^+ + e^- \Leftrightarrow M^{4+} + 2\ H_2O$	7.554	10.21	26.46
$M^{4+} + e^- \Leftrightarrow M^{3+}$		3.70	17.69

Table 2.2.1 in Chapter 2 gives a summary of SIT interaction coefficients derived and used in this review. This collection is far from sufficient to derive a chemically consistent set of interaction coefficients. However, it is important to keep in mind that the accuracy of the whole database and particularly its application to geochemical systems is strongly related to the quality of such auxiliary parameters. Ionic strength correction models and associated problems were not the main focus in the present update but will be an inevitable part of forthcoming database work. Therefore, the principles of chemical consistency need to be extended to the auxiliary data accompanying the database.

3.1.2 Chemical patterns based on periodic properties of the elements

The internal geochemical consistency of the selected thermodynamic constants can further be tested with the help of well-known empirical rules related to periodic properties of the elements. One of the most popular and useful schemes for the semi-quantitative prediction of stability constants is that of classifying cations and ligands into "hard" and "soft" (or 'A' and 'B') groups (SCHWARZENBACH 1961; PEARSON, 1963; STUMM & MORGAN 1996; Fig. III.7 in GRENTHE et al. 1997). This classification scheme is related to the following rules:

Rule 1: The stability of metal complexes and solid compounds with ionic bonding character ("hard" or 'A' metals) increases with decreasing cation radius and increasing charge.

Rule 2: Complexes of "hard" metals become progressively stronger and the solids less soluble for the following orders of donor atoms (PEARSON 1963):

$$\text{group VII : I} < \text{Br} < \text{Cl} \ll \text{F}$$
$$\text{group VI : Te} < \text{Se} < \text{S} \ll \text{O}$$
$$\text{group V   : Bi} < \text{Sb} < \text{As} < \text{P} \ll \text{N}$$

The stability of "soft" metal complexes and solids follows essentially a reversed order.

Many of the updated elements (Ni^{2+}, Al^{3+}, Am^{3+}, Eu^{3+}, Pu^{3+}, Np^{3+}, Th^{4+}, Pu^{4+}, Np^{4+}, U^{4+}, Zr^{4+}) belong to the "hard" and "borderline" cations for which rule 1 applies. However, this rule cannot be used for the two metals with "soft" character included in our update (Sn^{2+}, Pd^{2+}). For homovalent cation series, rule 1 predicts that the stability constants of homologous complexes should increase with decreasing ionic radius, while the solubility products of solids with the same stoichiometry and crystal structure should decrease.

Rule 2 is not very useful in this form since it does not account for the oxidation state of the ligand atoms, nor for the complexation with important oxo-anions like carbonate and phosphate. In addition, only stability sequences among ligands belonging to the same group of the periodic table should be compared. No information is given on the relative stability of, say, fluoride and hydroxo complexes.

Rule 3: SCHWARZENBACH (1961) suggested using the well-established series of acid dissociation constants as an additional guide to predict the sequence of complex stability for a given metal. The $pK_a°$ values of these acids may be regarded as formation constants of the proton (a hard cation) with the anions (ligands) of these acids according to

$$H^+ + B^{z-} \Leftrightarrow HB^{1-z} \qquad\qquad \log_{10}\beta_1° = pK_a°$$

From the sequence of increasing $\log_{10}\beta_1°$ values of the "proton complex", i.e.

$$Cl^- < NO_3^- < SO_4^{2-} < H_2PO_4^- < F^- < HCO_3^- < HPO_4^{2-} < SiO(OH)_3^- < CO_3^{2-} < PO_4^{3-} < OH^-.[1]$$

the sequence of stability constants for complexes of other hard cations can be predicted by analogy.

The validity of rule 3 is corroborated by the good correlations found in the case of Fe(III) complexes and dissociation constants of substituted phenols and salicylic acids (see Fig. III.26 in GRENTHE et al. 1997)

In Table 3.1.5 the $\log_{10}K$ values of the constants included in the database for mononuclear single ligand complexes are listed in a matrix structure for all metals with hard or borderline character, excluding those forming oxo-cations[2]. The purpose of this table is to give a compact "panoramic view" of the selected thermodynamic data. The cations are listed in order of increasing ionic charge and decreasing ionic radius (from left to right) and the ligands in order of increasing softness (from top to bottom). Therefore, constants for hard metals are expected to increase from left to right along rows and to decrease from top to bottom along columns. Whenever a significant anomaly in the expected order appears, the number is highlighted. The table therefore gives a quick overview of the internal consistency of the selected thermodynamic data and allows identification of major anomalies.

In general, the constants follow the predicted trend and increase along rows. Note also that the constants for metal silicate complexes fit very well in the relative order of ligand stability, although they have been classified as "uncertain data" (see Section 3.3) because of ambiguities concerning the stoichiometry of the complexes. Mg, Al and Mn do not follow the general trend. The stability constants of Mg and Al are well established and thus, their behaviour may indicate the limitation of our simple rule when comparing 'A' metals (Mg, Al) and d-transition metals (Fe). The data for Mn need to be thoroughly reviewed before any conclusions can be drawn.

More systematic anomalies, i.e. disagreement with rule 3, appear along columns:

---

[1] Note that pK^0_{H2O} is not equal to pK^0_w because of the peculiar definition of water activity (based on the requirement that the standard state for the solvent is the pure solvent at temperature and pressure of interest). Hence: $pK^0_{H2O} = pK^0_w + \log_{10}$ (55.56 mol / kg H_2O) = 15.74. This means that OH^- is by far the strongest base for the proton, since the next-largest value is $pK^0_{PO4-3} = 12.4$.

[2] Oxo-cations have been excluded because it is not possible to assign a precise ionic radius to them. Therefore, they cannot be inserted unambiguously in Table 3.1.5.

- Monocarbonato complexes are more stable than monohydroxo complexes (by about 2 $\log_{10}$ units). This indicates the preferred formation of bidentate carbonate complexes. The increase in stability due to this chelate effect is not considered by rule 3.

- The monosulphato complexes of alkalis, earth-alkalis and transition metals are more stable than the corresponding monofluoride complexes (by about 1-2 $\log_{10}$ units). The order reverts to normal for tetravalent actinides. The reason for this behaviour is unclear.

Table 3.1.5: Compilation of formation constants ($\log_{10}\beta_1°$) for monodentate mononuclear complexes included in the updated database. The constants are arranged in order of increasing hardness along rows (from left to right) and increasing ligand softness along columns (top to bottom). Constants which do not follow the expected relative order of metal hardness are highlighted in bold face. Values not following the expected order of ligand softness are shown in italics. Only anomalies of more than 0.5 $\log_{10}$ units are highlighted. The ionic radii are for 6-fold coordination and were taken from SHANNON (1976). For Mn(II), Fe(II) and Fe(III) the radii for high-spin complexes were selected.

metals →	K^+	Na^+	Li^+	Ra^{2+}	Ba^{2+}	Sr^{2+}	Ca^{2+}	Mn^{2+}	Fe^{2+}	Mg^{2+}	Ni^{2+}	Np^{3+}	Pu^{3+}	Am^{3+}	Eu^{3+}	Fe^{3+}	Al^{3+}	Th^{4+}	U^{4+}	Np^{4+}	Pu^{4+}	Zr^{4+}
r [Å]	1.38	1.02	0.76	1.48	1.35	1.18	1.00	0.83	0.78	0.72	0.69	1.01	1.00	0.975	0.947	0.645	0.535	0.94	0.89	0.87	0.86	0.72
ligands:																						
OH^-	-0.5	-0.2	0.4	0.5	0.5	0.7	1.2	3.4	4.5	**2.6**	4.5	7.2	7.1	6.7	6.4	11.8	**9.1**	11.6	13.5	13.7	13.2	14.3
PO_4^{3-}	-	-	-	-	-	-	-	-	-	-	*8.4*	-	-	-	-	-	-	-	-	-	-	-
CO_3^{2-}	-	*1.3*	-	2.5	2.7	2.8	3.2	***4.9***	4.4	***3.0***	4.0	-	-	7.8	8.1	-	-	-	-	-	-	-
$SiO(OH)_3^-$	-	-	-	-	-	-	1.2	-	-	1.5	-	-	-	*8.1*	*7.9*	9.7	**7.4**	-	-	-	-	-
HPO_4^{2-}	-	-0.2	-	-	-	-	-	-	-	-	2.9	-	-	3.0	-	-	-	*13*	-	-	-	-
HCO_3^-	-	-0.3	-	-	1.0	1.29	1.1	**2.0**	**2.0**	1.1	1	-	-	-	-	-	-	-	-	-	-	-
F^-	-	-0.2	-	-	-	-	0.9	0.8	1.0	**1.8**	1.3	-	-	3.4	3.8	6.2	7.1	8.0	9.3	9.0	8.8	10.2
$H_2PO_4^-$	-	-	-	-	-	-	-	-	-	-	1.5	-	-	-	-	-	-	-	-	-	-	-
SO_4^{2-}	*0.9*	*0.7*	0.6	*2.8*	2.7	2.3	2.3	2.3	2.3	2.4	2.3	-	3.9	3.9	4.0	4.0	3.9	**7.6**	6.6	6.9	6.9	7.0
NO_3^-	-	-	-	-	-	-	-	-	-	-	0.4	-	-	1.3	-	-	-	-	1.5	1.9	2.0	-
Cl^-	-	-	-	-0.1	-	-	-	**0.6**	0.1	-	0.4	-	1.2	1.1	1.1	1.5	-	-	1.7	1.5	1.8	1.5

3.1.3   Empirical correlations based on charge/size relations

As a final step, correlations are used to test the consistency of the database. In addition to the elements reviewed in this update, some elements are included which have not been reviewed in the present report, but have been inherited from the previous version (e.g. Ca, Na).

A convenient way to compare all the hard cations included in the database is plotting their equilibrium constants against the ionic index (z^2/r, after NIEBOER & RICHARDSON 1980). The ionic index allows us to consider the change in stability due to both ionic radius and ionic charge simultaneously. Therefore, metals of different valence (+I, +II, +III and +IV) can be included in a single plot. Plots have been prepared for the first hydrolysis constants and formation constants of monofluoride and monosulphate complexes. For all other constants, the data are too sparse to allow a correlation across the whole range of metals.
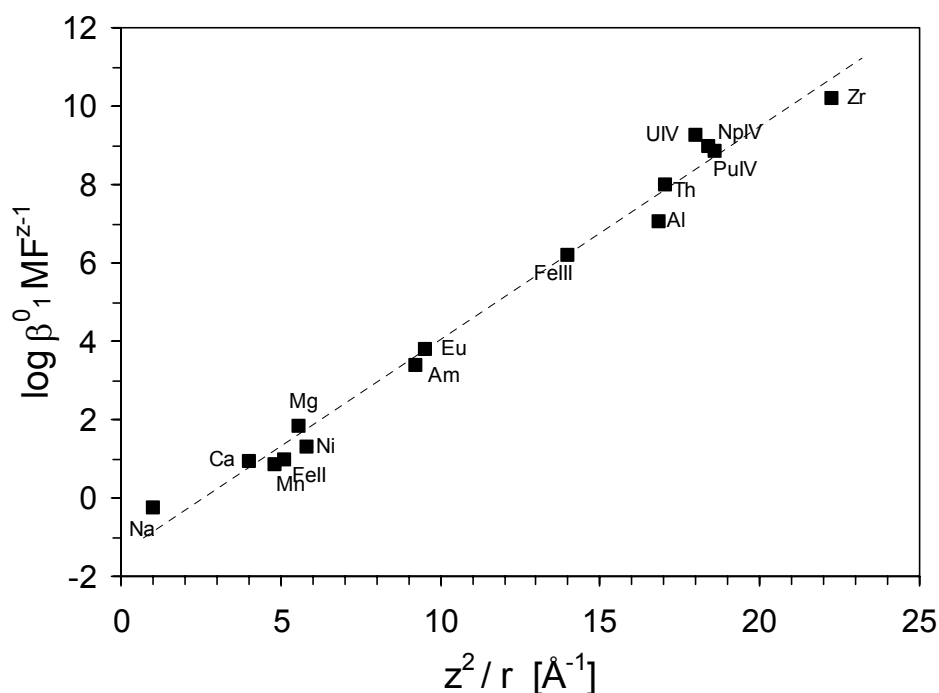
Fig. 3.1.1:   Correlation between ionic index (z^2/r, square of formal charge divided by ionic radius, after NIBOER & RICHARDSON 1980) and $\log_{10}\beta_1°$ for the monofluoride complexes of hard cations and Ni(II).

The plot of formation constants of monofluoride complexes versus the ionic index reveals an excellent correlation (Fig. 3.1.1) indicating an overall consistency of the selected fluoride constants.
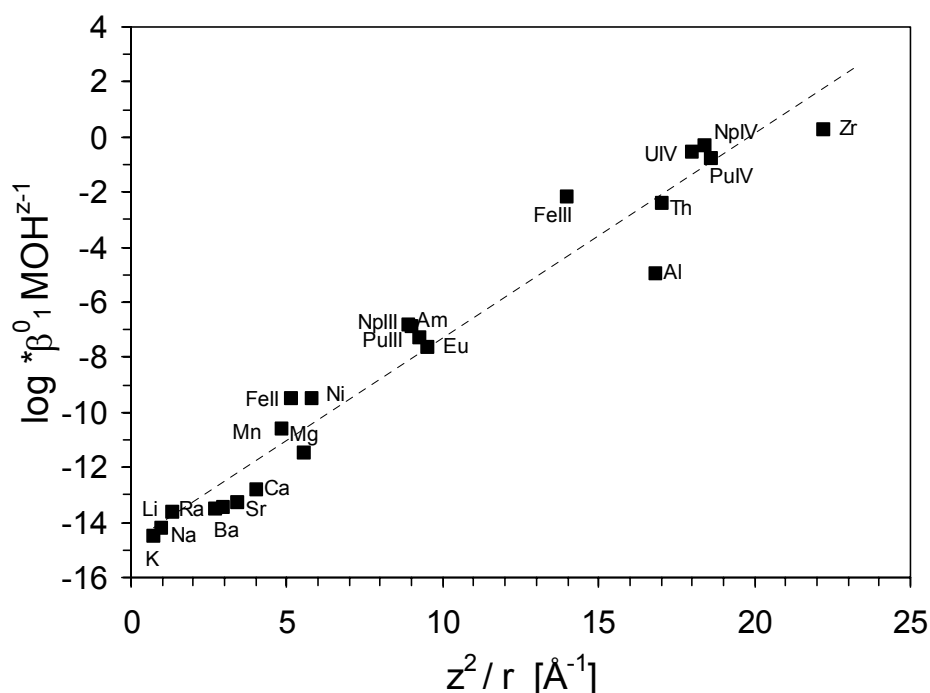
Fig. 3.1.2: Correlation between ionic index (z^2/r, square of formal charge divided by ionic radius, after NIBOER & RICHARDSON 1980) and $\log_{10}{}^*\beta_1°$ for the monohydroxo complexes of hard cations and Ni(II).

Fig. 3.1.2 shows a reasonably well-defined linear trend for the monohydroxo complexes, from which only the constants of $AlOH^{2+}$ and $FeOH^{2+}$ are found to deviate considerably. The Al and Fe(III) constants are well-determined, so that it is not possible to ascribe these anomalies to poor data quality. Rather, they reflect a particular chemical behaviour that cannot be rationalised in terms of these simple empirical rules. On the other hand, the updated constants for trivalent and tetravalent lanthanides/actinides, which would show ambiguous relations with respect to the hard-soft classification rules when treated as isolated groups, fit reasonably well in the general trend defined by all the metals.
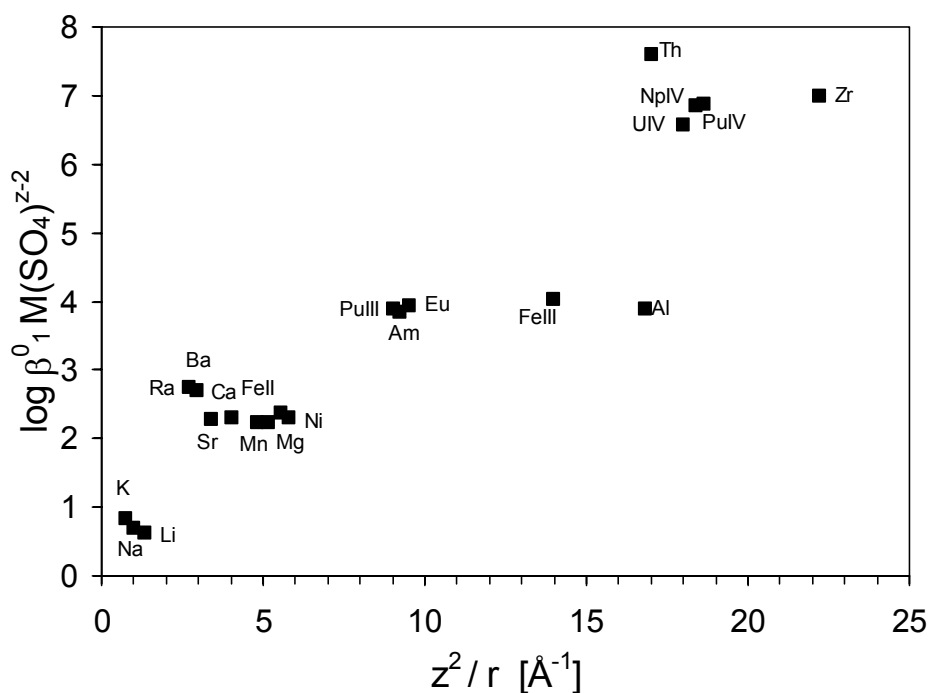
Fig. 3.1.3:　　Correlation between ionic index (z^2/r, square of formal charge divided by ionic radius, after NIBOER & RICHARDSON 1980) and $\log_{10}\beta_1°$ for the monosulphate complexes of hard cations and Ni(II).

Finally, although the monosulphate complexes also follow the overall linear trend found for the two former types of constants (Fig. 3.1.3) the formation constants of monosulphate species of a given charge seem to be nearly independent of the ionic radius. The missing dependence on ionic radius is particularly evident in the case of trivalent cations. It is not clear whether this is an artefact due to experimental problems or a specific chemical behaviour of sulphate.

In spite of their empirical nature, the correlations shown in Figs. 3.1.1 to 3.1.3 indicate a good overall chemical consistency of our database (of course limited to the three types of constants considered). This increases our confidence in the selected data.
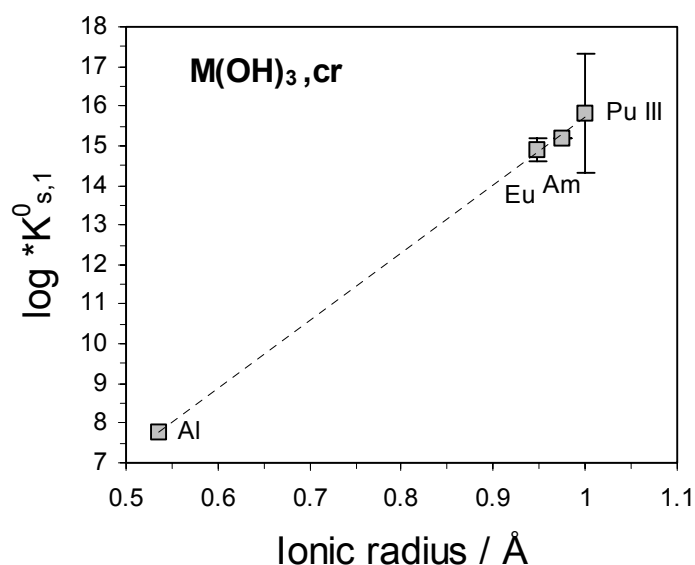
Fig. 3.1.4:   Solubility products of the crystalline hydroxides of trivalent hard cations included in the database ($M(OH)_3(cr) + 3\,H^+ \Leftrightarrow M^{3+} + 3\,H_2O$).

Similar correlations based on ionic radii can be set up for solid phases, although additional difficulties arise from the fact that such phases should be strictly isomorphous (i.e. they should have identical or at least analogous stoichiometry) to allow comparison. A plot for the crystallographically well-defined hydroxides of the trivalent metals Al, Eu, Am and Pu(III) reveals a good agreement with the expectation that their solubilities should increase with increasing ionic radius (Fig. 3.1.4).

In the case of amorphous (hydrous) oxides of tetravalent cations it is difficult to identify significant trends (Fig. 3.1.5). Amorphous SnO_2 seems to be more soluble than the corresponding oxides of tetravalent actinides, in contradiction to the expectation of decreasing solubility with decreasing ionic radius. However, large uncertainties are associated with the solubility constants of these ill-defined solids, and the identity of the solid phase responsible for the measured solubility is highly controversial as discussed in the next section.
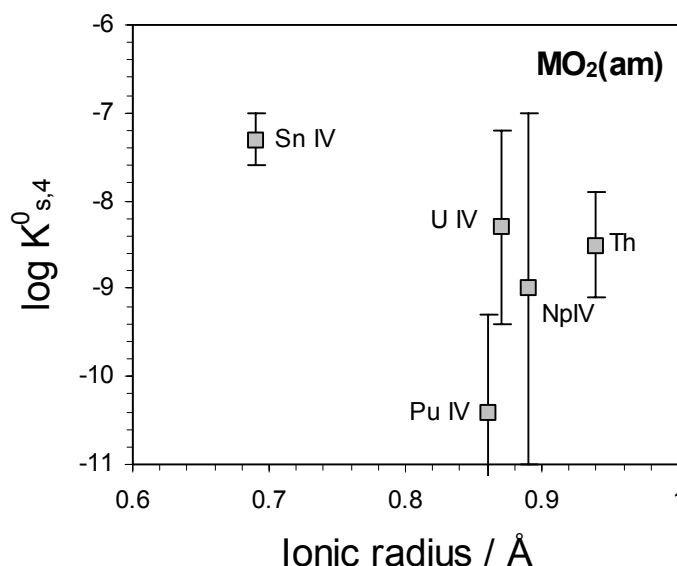
Fig. 3.1.5: Solubility products of amorphous hydrous oxides of tetravalent hard cations included in the database ($MO_2(am) + 2\,H_2O \Leftrightarrow M(OH)_4(aq)$).

3.2 Conflicting data

Parameters describing a particular thermodynamic equilibrium system are derived from experimental quantities obtained by a wide range of methods, e.g. calorimetry, potentiometry, solubility studies. For well studied systems critical examination reveals high quality experimental data that lead to a unique set of thermodynamic constants. The particular equilibrium system then is internally consistent. However, in the course of our reviews we encountered some cases of conflicting experimental data that resisted any attempt to merge them into a unique set of parameters. In the following the conflicting data and our pragmatic solutions are summarised.

In the system Th(IV) – H_2O a set of thermodynamic quantities can be derived from experimental data: (1) The hydrolysis constants $\log_{10}\beta_1°$ and $\log_{10}\beta_4°$ of $ThOH^{3+}$ and $Th(OH)_4(aq)$, respectively, have been determined potentiometrically by several authors over a wide range of ionic strength (see 5.21.2). (2) The thermodynamic properties of $ThO_2(cr)$ have been determined by calorimetry and thus, a solubility product $\log_{10}{}^*K_{s,0}°(cr)$ for $ThO_2(cr) + 4H^+ \Leftrightarrow Th^{4+} + 2H_2O$ can be derived from the available themochemical data (RAI et al. 2000). (3) Several solubility studies of $ThO_2(s)$ have been reported. However, these solubility studies reveal a very peculiar behaviour of $ThO_2(s)$ and these data cannot be made consistent with the other two data sets (see 5.21.2).

The behaviour of $ThO_2(s)$ is visualised most clearly using the data set of MOON (1989) (Fig. 3.2.1): At pH < 5 the solubility measured at a certain pH for crystalline $ThO_2(cr)$ differs by orders of

magnitude from the solubility of amorphous ThO_2(am) measured at the same pH. At pH > 6 both sets of experimental data converge and the solubility of ThO_2(s) becomes independent of pH (Fig. 3.2.1).
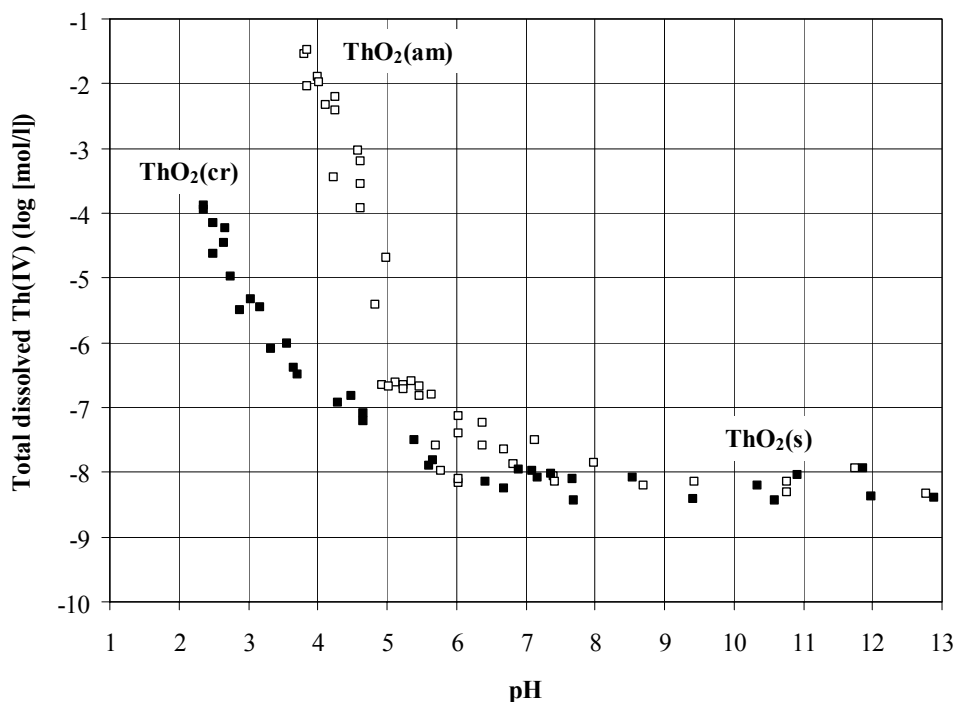
Fig. 3.2.1:   The concentration of dissolved Th(IV) as a function of pH determined for crystalline ThO_2(cr) and amorphous ThO_2(am). The solubility data are taken from MOON (1989).

This behaviour is not an artefact of the methods used by MOON (1989). A synopsis of several solubility studies (BAES et al. 1965, BUNDSCHUH et al. 2000, FELMY et al. 1991, RAI et al. 2000) corroborates his findings (Fig. 3.2.2).

Solubility data for ThO_2(cr) agree fairly well with the solubility predicted by calorimetric data in the range pH < 3. On the other hand, solubility data of amorphous ThO_2(am) indicate a solubility product more than 10 orders of magnitude higher than ThO_2(cr) (Fig. 3.2.2). In both cases, combining the solubility products $\log_{10}{}^{*}K_{s,0}°$(cr) and $\log_{10}{}^{*}K_{s,0}°$(am) with the independently determined hydrolysis constant $\log_{10}\beta_4°$ of Th(OH)$_4$(aq) results in predicted Th concentrations far away from any measured values in neutral and alkaline solutions. In the case of crystalline ThO_2(cr) the concentration of dissolved Th(IV) should fall below any detection limit to [Th] < 10^{-16} M, whereas for equilibrium with amorphous ThO_2(am) concentrations of [Th] > 10^{-7} M are predicted (see question marks in Fig. 3.2.2).
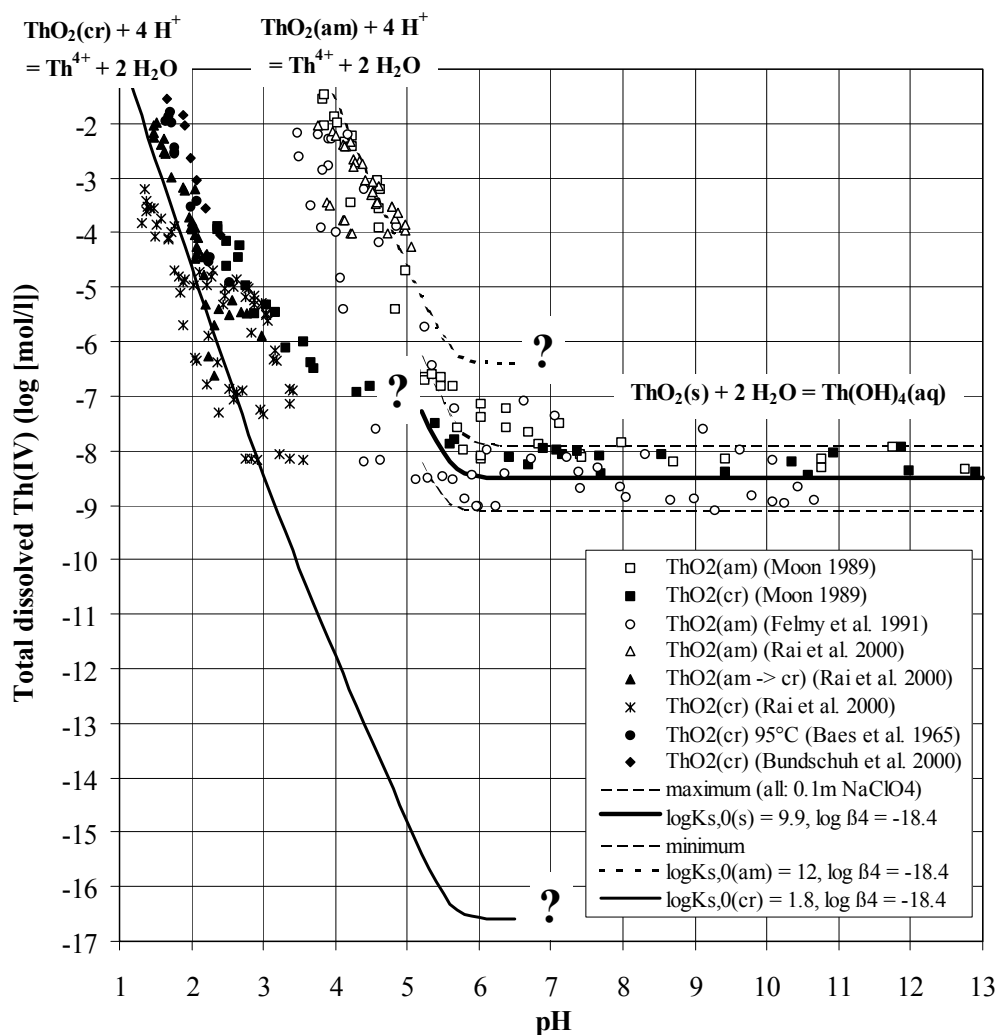
Fig. 3.2.2: Solubility data of the system Th(IV) - H_2O. The thick solid line is calculated using thermodynamic constants selected in this review. Dashed lines represent the estimated uncertainty. The dotted line is calculated using $\log_{10}{}^*K_{s,0}°(am) = 12$ derived from $ThO_2(am)$ data of MOON (1989) and RAI et al. (2000). The thin solid line is calculated using $\log_{10}{}^*K_{s,0}°(cr) = 1.8$ derived from $\Delta_fG_m°$ of $ThO_2(cr)$ (RAI et al. 2000).

All measured solubility data for $ThO_2(s)$ at pH > 6 have been found in the range 10^{-7} M > [Th] > 10^{-9} M. A mean value of $10^{-8.5}$ M represents $^*K_{s,4}°(s)$ for $ThO_2(s) + 2H_2O \Leftrightarrow Th(OH)_4(aq)$. If we combine this constant with the hydrolysis constant $\log_{10}\beta_4°$ of $Th(OH)_4(aq)$ a solubility product for $ThO_2(s)$ is calculated in between the values for $ThO_2(am)$ and $ThO_2(cr)$ (Fig. 3.2.2). This set of parameters now describes the measured solubilities at pH > 6 but cannot account for the solubility variation of more than 10 orders of magnitude at lower pH (see question mark in Fig. 3.2.2).
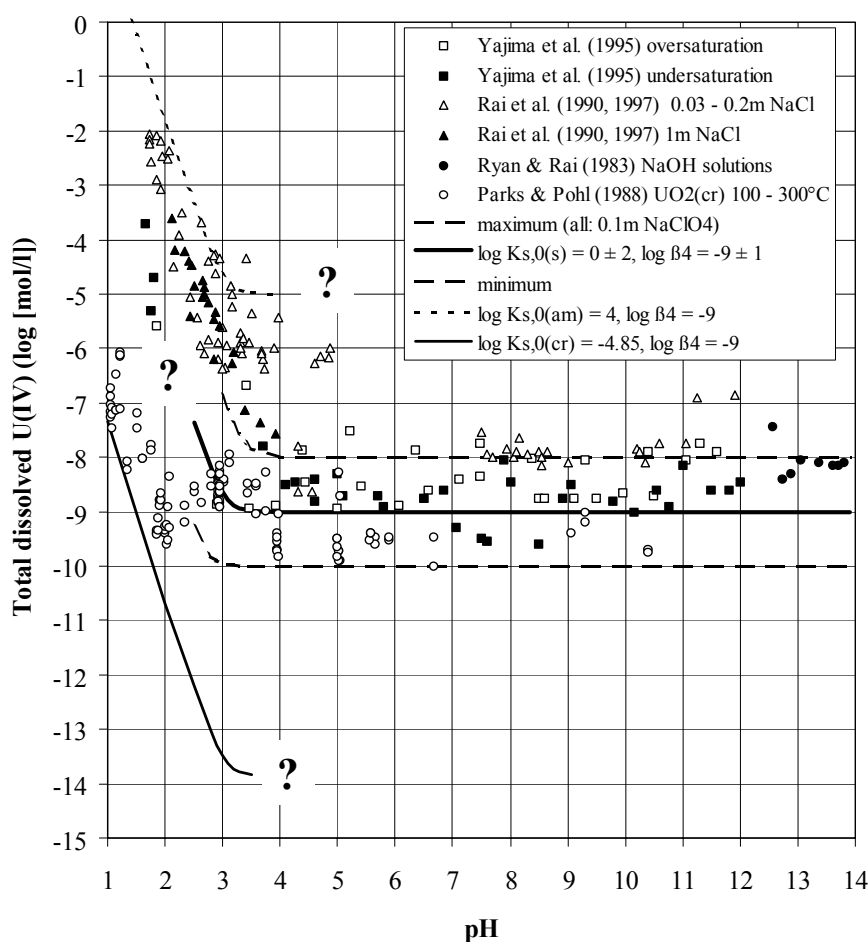
Fig. 3.2.3: Solubility data of the system U(IV) - H_2O. The thick solid line is calculated using thermodynamic constants estimated in this review. Dashed lines represent the estimated uncertainty. The dotted line is calculated using $\log_{10}{}^{*}K_{s,0}°(am) = 4$ given by RAI et al. (1990). The thin solid line is calculated using $\log_{10}{}^{*}K_{s,0}°(cr) = -4.85$ derived from $\Delta_f G_m°$ of $UO_2(cr)$ (GRENTHE et al. 1992).

The same behaviour is found in the system U(IV) – H_2O (Fig. 3.2.3). At pH < 3 the solubility measured for freshly precipitated $UO_2(am)$ and the solubility of $UO_2(cr)$ derived from calorimetric data differ by 9 orders of magnitude. All measured solubility data for $UO_2(s)$ at pH > 5 have been found in the range 10^{-7} M > [U(IV)] > 10^{-10} M. A mean value of 10^{-9} M represents $^{*}K_{s,4}°(s)$ for $UO_2(s) + 2H_2O \Leftrightarrow U(OH)_4(aq)$.

This behaviour is not restricted to Th(IV) and U(IV). Similar patterns have been found for all tetravalent actinides, An(IV). For a more detailed discussion and comparison of An(IV) solubility and hydrolysis see NECK & KIM (2001). These authors conclude from the solubility data measured for $ThO_2(cr)$ and $UO_2(cr)$ that the crystalline dioxide is the solubility limiting solid only at very low pH, where An^{4+} is the predominant aqueous species. They postulate that the bulk crystalline dioxide must be covered with an amorphous surface layer as soon as the An^{4+} ion undergoes

hydrolysis reactions, and the dissolution of $AnO_2(cr)$ seems to become quasi-irreversible. NECK & KIM (2001) conclude that further investigations are needed to verify this hypothesis and to ascertain the chemical form of the solubility limiting solid in natural systems.

Despite this promising qualitative model, we have to conclude that at present the systems ThO_2 – H_2O and UO_2 – H_2O are NOT understood in terms of quantitative equilibrium thermodynamics. The experimental data sets cannot be described by a consistent quantitative model without ad hoc assumptions.

As a pragmatic solution of this dilemma, we decided to rely on measured solubilities of Th(IV) and U(IV) in neutral and alkaline solutions. Hence, the thermodynamic constants selected for our database update do not refer to well defined thorianite, $ThO_2(cr)$, and uraninite, $UO_2(cr)$, used in calorimetric measurements but to the still poorly defined solids $ThO_2(s)$ and $UO_2(s)$ encountered in solubility studies. Furthermore, we considered independently determined hydrolysis constants in the case of Th, and adjusted the missing hydrolysis constant of $U(OH)_4(aq)$ in such a way that it is compatible with all experimental solubility measurements in the system $UO_2(s)$ – H_2O – CO_2 above pH 4. Consequently, the thermodynamic constants selected in this review cannot be used to represent the widely varying solubilities of ThO_2 and UO_2 at low pH.

3.3   Uncertain data

All thermodynamic constants in this database are uncertain to a varying degree. We estimated this degree of uncertainty wherever possible, and as a consequence, most selected constants are associated with a ± sign. However, simply comparing and ranking the selected values according to their ± uncertainty numbers does not tell the complete story. At least two additional classes of "especially uncertain" data have been identified: limiting values and "placeholders".

(1) Some of the selected stability constants are given as limiting values only or as approximate values without uncertainty estimates:

$\log_{10}\beta°$	Reaction
< 6	$Ni^{2+} + 2\,CO_3^{2-} \Leftrightarrow Ni(CO_3)_2^{2-}$
≈ 1	$Ni^{2+} + HCO_3^- \Leftrightarrow NiHCO_3^+$
< -7.0	$Pd^{2+} + 2\,Cl^- + 2\,H_2O(l) \Leftrightarrow PdCl_2(OH)_2^{2-} + 2\,H^+$
< 4	$TcO(OH)_2(aq) + 2\,H^+ \Leftrightarrow TcO^{2+} + 2\,H_2O(l)$
≤ -19	$NpO_2^{2+} + 3\,H_2O(l) \Leftrightarrow NpO_2(OH)_3^- + 3\,H^+$
≤ -33	$NpO_2^{2+} + 4\,H_2O(l) \Leftrightarrow NpO_2(OH)_4^{2-} + 4\,H^+$
≤ -9.73	$PuO_2^+ + H_2O(l) \Leftrightarrow PuO_2OH(aq) + H^+$

Because approximate data of this kind cannot be handled by conventional speciation programs, we were forced to treat these equilibrium constants as exact for the electronic version of the database, and the $\approx$, $<$, and $\leq$ signs had to be dropped. Therefore, should any species defined by one of these formation equations be of importance in the result of a speciation calculation, the approximate nature of this result should be always kept in mind.

(2) Some stability constants have been included in our database as "placeholders":

The Se(0)/Se(-II) redox equilibrium included in our database by no means has the character of a well-established entity. Its value should be regarded as a rough estimate of the behaviour of a poorly known chemical reaction. On the other hand, it is of primary importance in the field of radioactive waste management. Excluding this equilibrium from the database would probably cause more erroneous results than including a rough estimate (see 5.17.2 for a detailed discussion).

The stability constant for $ThHPO_4^{2+}$, $\log_{10}K^{\circ} = 13 \pm 1$, is not recommended as our best estimate for Th phosphate complex formation. We included this value as a placeholder for missing Th phosphate complexes. It should serve as a guard in speciation calculations of Th phosphate systems, warning modellers about the possible importance of phosphate complex formation (see 5.21.5 for a detailed discussion).

Aqueous metal silicate complexes are an entire class of "placeholders" (see 5.18.4). There is ample evidence of strong complex formation but the stoichiometry of the complexes is not yet established. Several speciation schemes have been proposed to interpret experimental data, e.g. 1:2 complexes, chelates, or mixed hydroxide – silicate complexes. Despite these ambiguities we decided to include several metal silicate complexes in our database as guidelines for modellers. If some of these complexes are found to be of crucial importance in some systems, additional experimental studies would be called for.

At present none of the conventional geochemical programs actually considers uncertainties of thermodynamic parameters. We have to deal with the sobering fact that application in routine modelling exercises degrades all efforts no matter how zealous to estimate uncertainties to "NUMBER ± decoration". However, work is in progress to explore in a consistent and systematic manner the uncertainty space of thermodynamic equilibrium calculations. We expect that this ongoing research project will have a strong impact on the art of geochemical modelling. With that prospect in mind our efforts to estimate uncertainties can be considered as an investment in future developments of geochemical modelling.

3.4   Missing data

In theory a thermodynamic database should be complete in terms of all possible compounds and complexes. In practice this goal can only be approximated to a certain degree. It is a delicate balance between including high quality data only and filling gaps with estimated values and "placeholders" as discussed above. The guideline to keep this balance is the question: "Is the missing entity of importance for the envisioned application of our database?"

In the case of Th(IV) and U(IV) hydrolysis we selected values for $ThOH^{3+}$, $Th(OH)_4(aq)$, and UOH^{3+} derived from potentiometric studies, and in addition an estimated value for $U(OH)_4(aq)$. This estimate is of crucial importance for modelling the system $UO_2(s) - H_2O - CO_2$ above pH 4. However, we decided not to include estimated values for the complexes $Th(OH)_2^{2+}$, $Th(OH)_3^+$, $U(OH)_2^{2+}$, and $U(OH)_3^+$ just for the sake of completeness. These complexes would "smooth" the Th(IV) and U(IV) solubility curves at low pH, outside the range of applicability of our selected parameter set (see Figs. 3.2.2 and 3.2.3 and the detailed discussion in NECK & KIM 2001).

However, a few cases of serious data gaps have been identified:

(1)   In the case of tin no meaningful value for the Sn(IV)/Sn(II) redox equilibrium could be derived from experimental data, and no estimate was possible. As a consequence, the tin system is redox de-coupled in our database. This means that two primary master species were selected, one for Sn(II) and one for Sn(IV), and it is not possible to model the behaviour of tin as a function of the redox potential with our database (see 5.22.2 for a detailed discussion).

(2)   Solubility studies indicate the formation of strong Zr carbonate complexes. This is not a surprise considering other metals in the tetravalent oxidation state (Table 3.1.1). However, the experimental data are not sufficient to elucidate the stoichiometry of the limiting carbonate complex, i.e. to discern between a tetra- and a penta-carbonate complex. This prevents the derivation of any meaningful stability constant and no value can be recommended.

(3)   In the case of ferric iron solubility studies also indicate the formation of strong Fe(III) carbonate complexes. A detailed review of the experimental data revealed an unresolved ambiguity concerning the nature of the solubility limiting solid phase (HUMMEL 2000). This ambiguity results in uncertainties of several orders of magnitude of Fe(III) carbonate equilibrium constants, and although the experimental data suggest that Fe(III) carbonate complexes predominate in some carbonate rich groundwaters, no equilibrium constants can be recommended. However, for exploring the possible effects of Fe(III) carbonate complexation in modelling exercises estimates for an equilibrium constant are suggested, though not included in the database (see 5.6.6).

3.5   Future data needs

The most obvious future data needs concern the missing, uncertain, and conflicting data as identified above.

Additional experimental studies are needed in the case of Fe(III) and Zr(IV) carbonate complexation, and in the case of the Sn(IV)/Sn(II) and the Se(0)/Se(-II) redox couples. The molecular structure of metal silicate complexes needs clarification to remove the ambiguity in the speciation schemes of these complexes.

A rather challenging topic of future research concerns the proposed phase transition of tetravalent actinides from $AnO_2(cr)$ to a solid with an amorphous surface layer as soon as the An^{4+} ion undergoes hydrolysis reactions. The consequences of such a reaction for thermodynamic equilibria, solubility and sorption of actinides are largely unexplored.

Ternary species must be considered in models of environmental systems. However, there is no chance to explore experimentally the huge number of possibly forming ternary species. For any specific system the modellers first have to estimate which ternary species might be important and only then experimental studies should be started. As an example, we showed that mixed hydroxide carbonate complexes of U^{4+}, Np^{4+} and Pu^{4+} are of particular interest in carbonate rich ground waters (HUMMEL & BERNER 2002). Further experimental studies are needed to determine their stability constants.

Additional review work in forthcoming updates of our database should consider iron compounds and complexes. The iron system is thought to be of crucial importance in elucidating the redox behaviour of radioactive waste repositories. Preliminary applications indicate that the lack of data in the iron system is a source of major uncertainties associated with the definition of a redox potential. Hence, it is of little value to develop sophisticated redox models for radionuclides as long as the dominant redox processes in a repository are still poorly known.

Another field with a large potential for improvements concerns alumosilicate minerals which are of great importance in determining the chemistry of water in many rock types. In clayish backfill materials alumosilicates are responsible for the retention (sorption, incorporation) of trace elements and participate in determining the redox potential (incorporation of Fe(II)/Fe(III)). Related compound classes (i.e. calcium silicates and calcium aluminates) form the chemical backbone of cementitious material. The thermodynamic properties of these substances are still largely unexplored.

Ongoing research explores the behaviour of solid solutions. The ultimate goal of these projects involving experimental and modelling studies is the development of simple yet sufficiently accurate thermodynamic models of these systems. A future extension of our database should include these model parameters necessary for a consistent description of important solid solution systems.

Although this update emphasised compounds and complexes determining the solubility and sorption of radionuclides for performance assessment calculations, the database itself will be used for a much wider range of PSI, Nagra and Nagra contractor programs. These include laboratory and field geochemical studies of host rock and groundwaters for site characterisation and safety analysis support. Such studies require a much broader set of minerals than included in this version. It is recommended that an early extension of the database should focus on primary and secondary minerals important in the interpretation of samples of natural material.

3.6   References

BAES, C.F., JR., MEYER, N.J., ROBERTS, C.E. (1965): The Hydrolysis of Thorium(IV) at 0 and 95°. Inorg. Chem., 4, 518.

BROWN, P.L., WANNER, H., (1987): Predicted Formation Constants Using the Unified Theory of Metal Ion Complexation. OECD Nuclear Energy Agency, Paris.

BUNDSCHUH, T., KNOPP, R., MÜLLER, R., KIM, J.I., NECK, V., FANGHÄNEL, TH. (2000): Application of LIBD to the determination of the solubility product of thorium(IV)-colloids. Radiochim. Acta, 88, 625.

FELMY, A.R., RAI, D., MASON, M.J. (1991): The Solubility of Hydrous Thorium(IV) Oxide in Chloride Media: Development of an Aqueous Ion-Interaction Model. Radiochim. Acta, 55, 177-185.

GRENTHE, I., FUGER, J., KONINGS, R.J.M., LEMIRE, R.J., MULLER, A.B., NGUYEN-TRUNG, C., WANNER, H. (1992): Chemical Thermodynamics of Uranium. Elsevier, Amsterdam, 715p.

GRENTHE, I., HUMMEL, W., PUIGDOMÈNECH, I. (1997): Chemical Background for the Modelling of Reactions in Aqueous Systems. In: GRENTHE, I., PUIGDOMÈNECH, I. (eds.): Modelling in Aquatic Chemistry. OECD Nuclear Energy Agency, Paris, pp.69-130.

HUMMEL, W. (2000): Comment on "On the influence of carbonate in mineral dissolution: 1. The thermodynamics and kinetics of hematite dissolution in bicarbonate solutions at T = 25°C" by J. Bruno, W. Stumm, P. Wersin, and F. Brandberg. Geochim. Cosmochim. Acta, 64, 2167-2171.

HUMMEL, W., BERNER, U. (2002): Solubility of actinides in a planned underground repository: Application of chemical thermodynamics for estimation of limiting values. Applied Geochemistry (submitted).

MOON, H. C. (1989): Equilibrium Ultrafiltration of Hydrolyzed Thorium(IV) Solutions. Bull. Korean Chem. Soc., 10, 270-272.

NECK, V., KIM, J.I. (2000): An electrostatic approach for the prediction of actinide complexation constants with inorganic ligands – application to carbonate complexes. Radiochim. Acta, 88, 815-822.

NECK, V., KIM, J.I. (2001): Solubility and hydrolysis of tetravalent actinides. Radiochim. Acta, 89, 1-16.

NIEBOER, E., RICHARDSON, D.H.S. (1980): The Replacement of the Nondescript Term 'Heavy Metal' by a Biologically and Chemically Significant Classification of Metal Ions. Environmental Pollution (Series B), 1, 3-26.

PARKS, G.A., POHL, D.C. (1988): Hydrothermal solubility of uraninite. Geochim. Cosmochim. Acta, 52, 863-875.

PEARSON, R.G. (1963): Hard and Soft Acids and Bases. J. Am. Chem. Soc., 85, 3533-3539.

RAI, D., FELMY, A.R., RYAN, J.L. (1990): Uranium(IV) hydrolysis constants and solubility product of $UO_2 \cdot xH_2O$(am). Inorg. Chem., 29, 7852-7865.

RAI, D., FELMY, A.R., STERNER, S.M., MOORE, D.A., MASON, M.J., NOVAK, C.F. (1997): The solubility of Th(IV) and U(IV) hydrous oxides in concentrated NaCl and $MgCl_2$ solutions. Radiochim. Acta, 79, 239-247.

RAI, D., MOORE, D.A., OAKES, C.S., YUI, M. (2000): Thermodynamic model for the solubility of thorium dioxide in the $Na^+ - Cl^- - OH^- - H_2O$ system at 23°C and 90°C. Radiochim. Acta, 88, 297-306.

RYAN, J.L., RAI, D. (1983): The solubility of uranium(IV) hydrous oxide in sodium hydroxide solutions under reducing conditions. Polyhedron, 2, 947-952.

SCHWARZENBACH, G. (1961): The General, Selective, and Specific Formation of Complexes by Metallic Cations. In: EMELÉUS, H.J., SHARPE, A.G. (eds.): Advances in Inorganic Chemistry and Radiochemistry. Academic Press, New York. Vol. 3, pp.257-285.

SHANNON, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Cryst. A32, 751-767.

STUMM, W., MORGAN, J.J. (1996): Aquatic Chemistry. Wiley & Sons, New York, pp.281-288.

YAJIMA, T., KAWAMURA, Y., UETA, S. (1995): Uranium(IV) solubility and hydrolysis constants under reduced conditions. Mat. Res. Soc. Symp. Proc., 353, 1137-1142.

4   CORE DATA

4.1   General criteria

The elements chosen for inclusion in the core data make up the majority of the solids dissolved in most natural waters, or are important complexing ligands. A few additional elements of well-known chemical behaviour are also included.

4.1.1   Elements and master species

Thermochemical data ($S_m°$ and $C_{p,m}°$) have been selected for all elements included in our data base, although most of the entropy and heat capacity values are at present not used in geochemical programs for Nagra and PSI projects. However, a complete data set for elements is required for Gibbs energy minimisation codes like SELEKTOR, and the Nagra/PSI TDB 01/01 is prepared for future use with this type of programs. Table 4.1 gives the thermochemical properties of elements in both the core and the supplemental data set.

Each element in the data base requires at least one primary master species, and a number of secondary master species have been defined for convenience in expressing chemical equilibria. For a detailed description of master species and the general data base structure see Section 2.5.

The sources of the data chosen for master species are principally the CODATA (GARVIN et al. 1987, COX et al. 1989), NEA (RARD et al. 1999) and NIST (WAGMAN et al. 1982) compilations. Generally, CODATA values were used when available. The NEA also uses CODATA values when available, but includes data on species not in the CODATA compilation as well. Table 4.2 summarises minor differences between the Nagra TDB 05/92 and the updated Nagra/PSI TDB 01/01.

Properties of formation of the ions Sr^{2+} and Ba^{2+} are not given by CODATA, and the values in the NIST tables have been superseded. The data of BUSENBERG et al. (1984) for Sr^{2+} and BUSENBERG & PLUMMER (1986) for Ba^{2+} are used.

Table 4.1: Thermodynamic data for the elements. Changes with respect to NTB 91-17 (PEARSON & BERNER 1991) are set in boldface type. CODATA: COX et al. (1989); NEA: RARD et al. (1999); NIST: WAGMAN et al. (1982). S_m° and $C_{p,m}^\circ$: J·mol^{-1}·K^{-1}.

Stable Phase at 25°C	Atomic Weight	Atomic Number	NTB 91-17 S_m°	UPDATE S_m°	Source for Update	NTB 91-17 $C_{p,m}^\circ$	UPDATE $C_{p,m}^\circ$	Source for Update
H_2(g)	1.008	1	130.680	130.680	NEA(CODATA)	28.836	28.836	NEA(CODATA)
O_2(g)	15.999	8	205.152	205.152	NEA(CODATA)	29.378	29.378	NEA(CODATA)
Al(cr)	26.982	13	-	**28.3**	this work	-	**24.2**	this work
Am(cr)	243	95	-	**55.4**	NEA	-	-	-
As(cr)	74.922	33	35.1	35.1	NEA	24.62	**24.64**	NEA
B(cr)	10.812	5	5.90	5.90	NEA(CODATA)	11.09	**11.087**	NEA(CODATA)
Ba(cr)	137.328	56	62.42	62.42	NEA	-	-	-
Br_2(l)	79.904	35	152.21	152.21	NEA(CODATA)	75.69	75.69	NIST
C(cr)	12.011	6	5.74	5.74	NEA(CODATA)	8.517	8.517	NEA(CODATA)
Ca(cr)	40.078	20	41.588	**41.590**	NEA(CODATA)	25.929	25.929	NEA(CODATA)
Cl_2(g)	35.453	17	223.081	223.081	NEA(CODATA)	33.91	**33.949**	NEA(CODATA)
Cs(cr)	132.905	55	-	**85.230**	NEA(CODATA)	-	**32.210**	NEA(CODATA)
Eu(cr)	151.966	63	-	**77.78**	this work	-	-	-
F_2(g)	18.998	9	202.791	202.791	NEA(CODATA)	31.30	**31.304**	NEA(CODATA)
Fe(cr)	55.845	26	-	**27.28**	NIST	-	**25.10**	NIST
I_2(cr)	126.904	53	116.14	116.14	NEA(CODATA)	54.438	54.438	NIST
K(cr)	39.098	19	64.68	64.68	NEA(CODATA)	29.6	29.6	NEA(CODATA)
Li(cr)	6.941	3	29.12	29.12	NEA(CODATA)	24.86	24.86	NEA(CODATA)
Mg(cr)	24.305	12	32.67	32.67	NEA(CODATA)	24.87	**24.869**	NEA(CODATA)
Mn(cr)	54.938	25	-	**32.01**	NIST	-	**26.32**	NIST
Mo(cr)	95.941	42	-	**28.66**	NIST	-	**24.06**	NIST
N_2(g)	14.007	7	191.609	191.609	NEA(CODATA)	29.124	29.124	NEA(CODATA)
Na(cr)	22.99	11	51.3	51.3	NEA(CODATA)	28.23	28.23	NEA(CODATA)
Nb(cr)	92.906	41	-	**36.40**	NIST	-	**24.60**	NIST
Ni(cr)	58.693	28	-	**29.87**	this work	-	-	-
Np(cr)	237	93	-	**50.46**	NEA	-	**29.62**	NEA
P(cr)	30.974	15	41.09	41.09	NEA(CODATA)	23.84	**23.824**	NEA(CODATA)
Pd(cr)	106.421	46	-	**37.82**	this work	-	**25.36**	this work
Pu(cr)	242	94	-	**54.46**	NEA	-	**31.49**	NEA
Ra(cr)	226	88	-	**71**	this work	-	-	-
S(cr)	32.067	16	32.054	32.054	NEA(CODATA)	22.64	**22.750**	NEA(CODATA)
Se(cr)	78.963	34	-	**42.27**	this work	-	**25.03**	this work
Si(cr)	28.086	14	-	**18.81**	this work	-	**19.789**	this work
Sn(cr)	118.711	50	-	**51.18**	this work	-	-	-
Sr(cr)	87.621	38	55.7	55.7	NEA	-	-	-
Tc(cr)	98	43	-	**32.5**	NEA	-	**24.9**	NEA
Th(cr)	232.038	90	-	**51.8**	this work	-	-	-
U(cr)	238.029	92	-	**50.2**	NEA	-	**27.66**	NEA
Zr(cr)	91.224	40	-	**39.0**	this work	-	-	-

Table 4.2: Comparison of auxiliary data differing in NTB 91-17 (PEARSON & BERNER 1991) and NTB 91-18 (PEARSON et al. 1992) from NEA (RARD et al. 1999). Primary data adopted for the database update are set in boldface type. Wherever $\log_{10}K°$ and $\Delta_rH_m°$ are specified, they were preferred over the derived quantities $\Delta_fG_m°$ and $\Delta_fH_m°$, and the latter are given for comparison only. The symbol $\log_{10}K(T)$ indicates that parameters are given in NTB 91-18 for an analytical expression for the temperature dependence of the corresponding equilibrium constant. $C_{p,m}°$ and $S_m°$ in J·mol^{-1}·K^{-1}; $\Delta_fG_m°$, $\Delta_fH_m°$ and $\Delta_rH_m°$ in kJ·mol^{-1}.

	NTB 91-17 $C_{p,m}°$	NEA $C_{p,m}°$	NTB 91-17 $S_m°$	NEA $S_m°$	NTB 91-18 $\Delta_fG_m°$	NEA $\Delta_fG_m°$	NTB 91-18 $\Delta_fH_m°$	NEA $\Delta_fH_m°$	NTB 91-18 $\log_{10}K°$	NEA $\log_{10}K°$	NTB 91-18 $\Delta_rH_m°$	NEA $\Delta_rH_m°$
Primary Master Species												
B(OH)$_3$(aq)			**162.4**	162.4 ± 0.6	-969.3	**-969.268** ± 0.82	**-1072.8**	-1072.8 ± 0.8				
Ba^{2+}			**8.4**	8.4 ± 2.0	-555.36	**-557.656** ± 2.582	-532.5	**-534.8** ± 2.5				
Br$^-$	-141.8		**82.55**	82.55 ± 0.20	**-103.85**	-103.850 ± 0.167	**-121.41**	-121.41 ± 0.15				
Ca^{2+}	-281.38		**-56.2**	-56.2 ± 1.0	-552.807	**-552.806** ± 1.050	-543	**-543** ± 1				
Cl$^-$	-136.4		**56.6**	56.6 ± 0.2	-131.22	**-131.217** ± 0.117	**-167.08**	-167.08 ± 0.10				
Cs$^+$				132.1 ± 0.5		**-291.456** ± 0.535		**-258.0** ± 0.5				
F$^-$	-106.7		**-13.8**	-13.8 ± 0.8	-282.52	**-281.523** ± 0.692	**-335.35**	-335.35 ± 0.65				
H$_2$O(l)	**75.351**	75.351 ± 0.080	**69.95**	69.95 ± 0.03	**-237.14**	-237.140 ± 0.041	**-285.83**	-285.83 ± 0.04				
HAsO$_4^{2-}$			**-1.7**	-1.7 ± 0.6	-714.6	**-714.592** ± 4.008	**-906.34**	-906.34 ± 4.00				
HCO$_3^-$			**98.4**	98.4 ± 0.5	**-586.875**	-586.845 ± 0.251	**-690.215**	-689.93 ± 0.20				
HPO$_4^{2-}$			**-33.5**	-33.5 ± 1.5	-1095.99	**-1095.985** ± 1.567	**-1299**	-1299.0 ± 1.5				
I$^-$			**106.45**	106.45 ± 0.30	-51.72	**-51.724** ± 0.112	**-56.78**	-56.78 ± 0.05				
K$^+$			**101.2**	101.2 ± 0.2	**-282.51**	-282.510 ± 0.116	**-252.14**	-252.14 ± 0.08				
Li$^+$			**12.24**	12.24 ± 0.15	-292.92	**-292.918** ± 0.109	**-278.47**	-278.47 ± 0.08				
Mg^{2+}			**-137**	-137 ± 4	-455.4	**-455.375** ± 1.335	**-467**	-467.0 ± 0.6				
Na$^+$			**58.45**	58.45 ± 0.15	-261.95	**-261.953** ± 0.096	**-240.34**	-240.34 ± 0.06				
NO$_3^-$	-86.6		**146.7**	146.7 ± 0.4	-110.79	**-110.794** ± 0.417	**-206.85**	-206.85 ± 0.40				
SO$_4^{2-}$	-293		**18.5**	18.5 ± 0.4	-744.00	**-744.004** ± 0.418	**-909.34**	-909.34 ± 0.40				
Sr^{2+}			**-31.5**	-31.5 ± 2.0	-563.83	**-563.864** ± 0.781	-550.9	**-550.90** ± 0.50				

	NTB 91-17 $C_{p,m}°$	NEA $C_{p,m}°$	NTB 91-17 $S_m°$	NEA $S_m°$	NTB 91-18 $\Delta_f G_m°$	NEA $\Delta_f G_m°$	NTB 91-18 $\Delta_f H_m°$	NEA $\Delta_f H_m°$	NTB 91-18 $\log_{10}K°$	NEA $\log_{10}K°$	NTB 91-18 $\Delta_r H_m°$	NEA $\Delta_r H_m°$
Secondary Master Species												
As(OH)$_3$(aq)			**195**	**195** ± 1	-639.8	-639.681 ± 4.015	-742.2	-742.2 ± 4.0	**$\log_{10}K°(T)$**		**$\log_{10}K°(T)$**	
CO$_2$(aq)			**119.36**	**119.36** ± 0.60	-385.991	-385.97 ± 0.27	-413.494	-413.26 ± 0.20	**$\log_{10}K°(T)$**		**$\log_{10}K°(T)$**	
CO$_3$$^{2-}$			**-50**	**-50** ± 1	-527.919	-527.90 ± 0.39	-675.314	-675.23 ± 0.25	**$\log_{10}K°(T)$**		**$\log_{10}K°(T)$**	
H$_2$PO$_4$$^-$			**92.5**	**92.5** ± 1.5	-1137.144	-1137.152 ± 1.567	-1302.6	-1302.6 ± 1.5	7.21	**7.212** ± 0.013	**-3.6**	**-3.6** ± 1.0
H$_3$PO$_4$(aq)			161.91	**161.912** ± 2.575	-1149.359	-1149.367 ± 1.576	-1294.1	-1294.120 ± 1.616	9.35	**9.352** ± 0.033	4.9	**4.88** ± 1.17
NH$_3$(aq)			**109.04**	**109.040** ± 0.913	-26.659	-26.673 ± 0.305	-81.148	-81.170 ± 0.326	-9.24	**-9.237** ± 0.022	52.112	**52.09** ± 0.21
NH$_4$$^+$	79.9		**111.17**	**111.170** ± 0.400	-79.4	**-79.398** ± 0.278	**-133.26**	**-133.26** ± 0.25				
OH$^-$	-148.5		**-10.9**	**-10.9** ± 0.2	-157.232	-157.220 ± 0.072	-229.926	-230.015 ± 0.04	**$\log_{10}K°(T)$**		**$\log_{10}K°(T)$**	
PO$_4$$^{3-}$			**-220.97**	**-220.970** ± 12.846	-1025.497	-1025.491 ± 1.576	-1284.4	-1284.400 ± 4.085	**-12.35**	**-12.35** ± 0.03	**14.6**	**14.6** ± 3.8
S$_2$O$_3$$^{2-}$					-519.29	**-519.291** ± 11.345	**-648.5**					
SO$_3$$^{2-}$					-487.47	**-487.472** ± 4.020	**-635.5**					
Product Species												
AsO$_4$$^{3-}$			**-162.8**	**-162.8** ± 0.6	-648.41	**-648.360** ± 4.008	**-888.14**	**-888.14** ± 4.00				
H$_2$AsO$_4$$^-$			**117**	**117** ± 1	-753.17	**-753.203** ± 4.015	**-909.56**	**-909.56** ± 4.00				
H$_3$AsO$_4$(aq)			**184**	**184** ± 1	-766	**-766.119** ± 4.015	**-902.5**	**-902.5** ± 4.0				
HF(aq)			**88**	**88.000** ± 3.362	-299.648	**-299.675** ± 0.702	-322.044	-323.150 ± 0.716	**$\log_{10}K°(T)$**		**$\log_{10}K°(T)$**	
HF$_2$$^-$			92.68	**92.683** ± 8.469	-583.7	**-583.709** ± 1.200	**-655.5**	**-655.500** ± 2.221				
HSO$_3$$^-$					-528.68	**-528.684** ± 4.046	**-514.55**					
HSO$_4$$^-$	-84		**131.7**	**131.7** ± 3.0	-755.346	-755. 315 ± 1.342	-893.212	-886.9 ± 1.0	**$\log_{10}K°(T)$**		**$\log_{10}K°(T)$**	
Gases												
CO$_2$(g)	37.13	**37.135** ± 0.002	213.78	**213.785** ± 0.010	-394.37	-394.373 ± 0.133	-393.51	-393.51 ± 0.13	**$\log_{10}K°(T)$**		**$\log_{10}K°(T)$**	
H$_2$(g)	**28.836**	**28.836** ± 0.002	130.68	**130.680** ± 0.003	0	0	0	0	**$\log_{10}K°(T)$**		**$\log_{10}K°(T)$**	
N$_2$(g)	**29.124**	**29.124** ± 0.001	191.609	**191.609** ± 0.004	0	0	0	0	**$\log_{10}K°(T)$**		**$\log_{10}K°(T)$**	
O$_2$(g)	**29.378**	**29.378** ± 0.003	205.152	**205.152** ± 0.005	0	0	0	0	**$\log_{10}K°(T)$**		**$\log_{10}K°(T)$**	

Several dissolved gases, $O_2(aq)$, $H_2(aq)$, $N_2(aq)$ and $CH_4(aq)$, are included among the primary master species. No CODATA thermodynamic properties are available for these dissolved gases, and only limited data appear in the NIST compilation. However, there are excellent and complete CODATA values for $O_2(g)$, $H_2(g)$ and $N_2(g)$, and NIST data on $CH_4(g)$, and gas solubilities are well known. The solubilities used here are based on equations given by WHITFIELD (1979, Appendix Table 8), which are valid for a temperature range from 0 to between 65 and 75°C. These solubilities are given in Table 4.3. They were used with the relationships given in Section 2.3.1 and CODATA and NIST values for the thermodynamic properties of the gases to calculate the properties of the aqueous primary master species $O_2(aq)$, $H_2(aq)$, $N_2(aq)$ and $CH_4(aq)$.

Table 4.3:   Variation of gas solubilities with temperature. Except as noted, coefficients were derived from those given by WHITFIELD (1979, Appendix Table 8) and are valid from 0 to 65-70°C. The equilibrium constant for the reaction $X(g) \Leftrightarrow X(aq)$ is defined as $\log_{10}K_H°(T) = A + B \cdot T + C / T + D \cdot \log(T) + E / T^2$ where T is in Kelvin.

Gas	Solubility at 25°C [mol/kg]	$\log_{10}K_H°$ at 25°C	A	C	D	B	E
O_2	$1.28 \cdot 10^{-3}$	-2.894	-60.9665	3376.71	18.3976	0.00410133	
H_2	$7.84 \cdot 10^{-4}$	-3.106	-76.4529	3037.28	26.3123	-0.00653321	
N_2	$6.51 \cdot 10^{-4}$	-3.186	-69.9069	3662.36	21.5583	0.00366386	
CH_4	$1.39 \cdot 10^{-3}$	-2.856	-78.0660	3957.20	25.0383	-0.0000622937	
H_2S	$1.03 \cdot 10^{-1}$	-0.988	-63.1992	3572.77	20.2310	0.000562005	
CO_2	$3.39 \cdot 10^{-2}$	-1.470	-67.6795	3796.46	21.6693	-0.000478856	
CO_2*	$3.40 \cdot 10^{-2}$	-1.468	108.3865	-6919.53	-40.4515	0.0198508	669365

Coefficients for CO_2* from PLUMMER & BUSENBERG (1982), valid from 0 to 250°C.

4.1.2   Solute species, minerals and gases

The remainder of this chapter discusses, in addition to the master species, the solute species, minerals and gases in the core data set, including reasons for their selection and for the choice of data for them. The discussion begins with the fundamental master species H_2O, H^+ and e^- and the elements H_2 and O_2. Species associated in solution (ion pairs and complexes), minerals and gases are grouped by anion.

4.2   Oxygen, hydrogen, the electron and water

Water and species representing its component elements hydrogen and oxygen are fundamental to modelling aqueous solutions.

4.2.1   Master species: H^+, e^- or $O_2(g)$, H_2O, $O_2(aq)$, and $H_2(aq)$

The master species for hydrogen is H^+. By convention, all its thermodynamic properties are zero.

The master species associated with redox reactions could be either the electron, e^-, or oxygen gas, $O_2(g)$. For the core data set, the electron has been chosen. Like H^+, all its thermodynamic properties are zero by convention.

In Section 2.4.1 it was discussed that the reaction

$$2\,H_2O \Leftrightarrow O_2(g) + 4\,H^+ + 4\,e^-$$

can be used to convert between redox reactions written in terms of the electron and those written using $O_2(g)$. The properties of this reaction are:

$$\log K^\circ = -83.092$$

$$\Delta_r G_m^\circ = 474.28 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m^\circ = 571.66 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r C_{p,m}^\circ = -63.65 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

From these values and the equations of Section 2.3.1, the equation for the equilibrium constant of the conversion reaction is:

$$\log_{10} K^\circ = 39.32895 - 30851.71\,/\,T - 7.655715 \cdot \log_{10}(T)$$
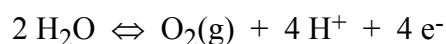
If it is intended to model only very dilute solutions, one can assume that the activity of water, a_{H_2O}, equals one, and water can be left out of the model equations solved. This procedure is followed in the MINEQL code. Other geochemical programs explicitly model the activity of water, so it is included as primary master species in the core data set.

$O_2(aq)$ and $H_2(aq)$ are useful when interpreting dissolved gas analyses, and they are included in the core data set as secondary master species. Their thermodynamic properties of formation were

calculated from CODATA values for $O_2(g)$ and $H_2(g)$ and the gas solubilities in Table 4.3, as described in Section 4.1.1.

4.2.2 Oxide and hydroxide solute species, minerals, and gases

The aqueous species include the OH^- ion, and the OH^- ion pairs with the alkali and alkaline earth metals, i.e. $LiOH(aq)$, $NaOH(aq)$, $KOH(aq)$, $MgOH^+$, $CaOH^+$, $SrOH^+$ and $BaOH^+$. The hydroxide minerals portlandite, $Ca(OH)_2(cr)$, and brucite, $Mg(OH)_2(cr)$ are also included in the core data set.

The thermodynamic data on the reactions forming these species and minerals were taken from the compilation of NORDSTROM et al. (1990). Properties of formation of OH^-, $CaOH^+$, and portlandite, $Ca(OH)_2(cr)$, are included in the CODATA compilations. The CODATA values agree well with values calculated from the reaction data chosen.

The core data set also includes reactions by which one can calculate the oxidation potential for $H^+/H_2(aq)$ and $O_2(aq)/H_2O$, via the definition of $O_2(aq)$ and $H_2(aq)$ as secondary master species, and the partial pressures of $O_2(g)$ and $H_2(g)$ from the dissolved concentrations of $O_2(aq)$, and $H_2(aq)$. The latter reactions can also be used to set concentrations of $O_2(aq)$ and $H_2(aq)$ from defined partial pressures of $O_2(g)$ and $H_2(g)$.

4.3 Halides: fluorine, chlorine, bromine and iodine

4.3.1 Master species: F^-, Cl^-, Br^- and I^-

Species with charges minus one dominate the aqueous solutions of all halide elements, and were chosen as the primary master species. The reference states for fluorine and chlorine are the gases $F_2(g)$ and $Cl_2(g)$, for bromine, the liquid $Br_2(l)$, and for iodine, the solid $I_2(cr)$. CODATA values of $\Delta_f H_m°$ and $S_m°$ are available for all four aqueous ions and elements (see Tables 4.1 and 4.2). The $C_{p,m}°$ values given for F^-, Cl^- and Br^- are from the NIST tables. The NIST values of $S_m°$ for these species agrees with the CODATA values within 0.1 $J·mol^{-1}·K^{-1}$.

4.3.2 Halide solute species

The only hydrolysis products of halide ions which are of sufficient strength to be included in this data base are $HF(aq)$ and HF_2^-. The thermodynamic data for these species are taken from the NEA compilation. The remaining species are $NaF(aq)$, CaF^+ and MgF^+, the data for which are from NORDSTROM et al. (1990). These authors also include data on $HF(aq)$ and HF_2^-. The NEA values

for HF(aq) agree with those calculated from the data of NORDSTROM et al. (1990), but the values for HF_2^- differ by the equivalent of 0.12 in $\log_{10}K°$.

The mineral fluorite, $CaF_2(cr)$, is common in aqueous systems, and may influence ground-water chemistry. In spite of the ubiquity and simple chemistry of this mineral, values for its thermodynamic properties differ widely. Values given by CODATA, NORDSTROM et al. (1990, Table I) and other data bases differ by as much as 0.55 in $\log_{10}K°$. Fluorite is not included in the core data (see Section 5.3).

4.4 Sulphur

Redox processes are important in the sulphur system. Sulphate, S(VI), is stable under oxidising conditions and sulphide, S(-II), under reducing conditions. Under intermediate conditions, elemental sulphur, S(cr), has a small range of stability, and it is included as a mineral in the core data set. Various other species including sulphites, SO_3^{2-}, S(IV), and thiosulphates, $S_2O_3^{2-}$, S(II), may occur metastably. These species are not included in the core data set, but their properties are given in the NIST compilation and they are among the NEA auxiliary species. The species SO_3^{2-}, HSO_3^-, and $S_2O_3^{2-}$ are added to the supplemental data set. However, no metal complexation data involving these species are currently included in this data base.

4.4.1 Master species: SO_4^{2-} and HS^-

SO_4^{2-} is the dominant S(VI) species and is the primary master species for sulphur. The enthalpy and entropy of this species and the Gibbs energy derived from them are CODATA values. Entropy differences between CODATA and NIST compilations are 0.2 and 1.5 $J \cdot mol^{-1} \cdot K^{-1}$, respectively, for S(cr) and SO_4^{2-}. Thus, the $C_{p,m}°$ value shown in Table 4.2, which is based on the NIST $C_{p,m}°$ value, should be used with caution.

$H_2S(aq)$ is the dominant S(-II) species below pH 7 and HS^- at higher pH values. HS^- is defined as secondary master species, and $H_2S(aq)$ is included as a product species. Enthalpy and entropy data for both species are CODATA values. None of the compilations include $C_{p,m}°$ values for any aqueous S(-II) species. However, CODATA gives a full set of values for $H_2S(g)$ and from these and the gas solubilities in Table 4.3, data on $H_2S(aq)$ could be calculated.

4.4.2 Sulphate solute species and minerals

The only SO_4^{2-} hydrolysis species included in the core data is HSO_4^- which prevails below pH 2. The remaining aqueous species are $LiSO_4^-$, $NaSO_4^-$, KSO_4^-, $MgSO_4(aq)$, $CaSO_4(aq)$, $SrSO_4(aq)$

and $BaSO_4(aq)$. The data on these reactions are from NORDSTROM et al. (1990). CODATA properties for HSO_4^- and $CaSO_4(aq)$ are also available. There is good agreement between CODATA $\Delta_f G_m°$ values and those calculated from the reaction data, but the $\Delta_f H_m°$ values agree less well.

The core data set also includes the alkaline earth sulphate minerals gypsum $CaSO_4 \cdot 2H_2O(cr)$, anhydrite $CaSO_4(cr)$, celestite $SrSO_4(cr)$ and barite $BaSO_4(cr)$. The thermodynamic data on the reactions forming these minerals were taken from the compilation of NORDSTROM et al. (1990). The CODATA compilation includes data on the minerals gypsum and anhydrite. Again, there is good agreement between the CODATA and calculated $\Delta_f G_m°$ values, but less agreement in the pairs of $\Delta_f H_m°$ values.

4.4.3   Reduced sulphur solute species and minerals

Sulphide, S(-II), hydrolysis products are $H_2S(aq)$, HS^- and S^{2-}. HS^- is the secondary master species, and $H_2S(aq)$ and S^{2-} are included as a product species. However, S^{2-} is not included in the core data set.

Experimental data for the sulphide hydrolysis reactions, as well as the solubility of $H_2S(g)$, have been reviewed in this update. For a detailed discussion see Section 5.19.1. The selected thermodynamic data are given in Table 5.19.15.

The core data set also includes elemental sulphur, S(rhomb), as a mineral.

4.5   Nitrogen

Redox processes are as important to the chemistry of nitrogen as they are to sulphur chemistry. The dominant oxidation states in natural waters are N(V), nitrate, N(-III), ammonia and amines, and N(0), nitrogen gas. N(III), nitrite, is an important consideration in water supply problems, but is not included in this data set because it is never the dominant nitrogen species.

4.5.1   Master species: NO_3^-, $N_2(aq)$, and NH_4^+

NO_3^-, nitrate, is the dominant N(V) species at all pH values and is the primary master species for nitrogen in the core data set. Dissolved nitrogen is the dominant N(0) species at all pH values with $N_2(aq)$ as secondary master species. $N_2(g)$ is included in the data set as a gas. NH_4^+ is the major N(-III) species below pH 9 and is included in the core data set as secondary master species.

Enthalpy and entropy values for NO_3^- and NH_4^+ are from CODATA. CODATA and NIST entropy values for NO_3^- and NH_4^+ differ by 0.3 and 2 J · mol^{-1} · K^{-1}, respectively. Thus, the $\Delta_f C_{p,m}°$ values, which are based on NIST $C_{p,m}°$ values, should be used with caution. The properties for $N_2(aq)$ were derived from CODATA values for $N_2(g)$ and the solubility of that gas, as described in Section 4.1.1.

4.5.2 Nitrogen solute species and gases

The only aqueous species included is $NH_3(aq)$, which is the dominant N(-III) species at pH values greater than 9. For convenience in formulating metal – amine equilibria, $NH_3(aq)$ is also defined as secondary master species.

$N_2(g)$ is included in the core data set, as are reactions for calculating redox potentials corresponding to analysed concentrations of nitrogen in various redox states. The couples $N_2(aq)/NO_3^-$ and NO_3^-/NH_4^+ are included by defining $N_2(aq)$ and NH_4^+ as secondary master species, respectively.

4.6 Phosphate, borate and arsenic

Phosphorus occurs in the P(V) state as phosphate (PO_4^{3-}) under conditions found in natural waters, and boron in the B(III) state as borate ($B(OH)_3(aq)$). Arsenic can be present both in the As(V) state as arsenate (AsO_4^{3-}), and in the As(III) state as arsenite ($As(OH)_3(aq)$). The solution chemistry of As(V) species closely resembles that of P(V) species, and the chemistry of As(III) species resembles that of B(III) species, so it is convenient to discuss the three elements together. The As(0) state occurs as native arsenic.

4.6.1 Master species: HPO_4^{2-}, $HAsO_4^{2-}$, and $B(OH)_3(aq)$

Each of the four hydrolysis products of phosphate (PO_4^{3-}) dominates within some pH range between 0 and 14. HPO_4^{2-}, which dominates between pH 7 and 12, is the primary master species for phosphorus. The other species, $H_3PO_4(aq)$, $H_2PO_4^-$, and PO_4^{3-} are included in the core data set as secondary master species.

Enthalpy and entropy data for the species HPO_4^{2-} and $H_2PO_4^-$ are CODATA values. The NEA auxiliary data include values for the other species $H_3PO_4(aq)$ and PO_4^{3-}. The NIST compilation includes no heat capacity data for phosphate species.

The master species for boron is boric acid, $B(OH)_3(aq)$, which prevails under neutral and acidic conditions. The properties of this species are from CODATA.

Arsenic occurs in three oxidation states in natural aqueous solutions. The most oxidised form, As(V), arsenate, AsO_4^{3-}, is analogous to phosphate and hydrolyses to arsenic acid. All four arsenate hydrolysis species are dominant at some range between pH 0 and 14. $HAsO_4^{2-}$ dominates between pH 7 and 11, and is the primary master species of arsenic. The other three species are include in the core data set as product species.

According to BAES & MESMER (1976, Section 16.1), As(III) is analogous to boron, and the species actually present are $As(OH)_3(aq)$ at pH values below 9 and $As(OH)_4^-$ at higher pH. $As(OH)_3(aq)$ is chosen as secondary master species. Its thermodynamic properties of formation are those of $H_3AsO_3(aq)$ as given in the NIST compilation.

As(cr) is stable under certain redox conditions at all pH values. It is included as a mineral.

4.6.2 Phosphate and borate solute species

BAES & MESMER (1976, Section 6.1) discuss borate hydrolysis. At dissolved boron concentrations below 0.05m, the only important aqueous species are $B(OH)_3(aq)$ and $B(OH)_4^-$. $B(OH)_3(aq)$ dominates at pH values below 9 and is the master species, while $B(OH)_4^-$ is included as product species. The $\log_{10}K°$ of formation of the species is taken as the mean of expression 1 and 2 given by BAES & MESMER (1976, Table 6.2). The NIST compilation also includes $\Delta_f G_m°$ and $\Delta_f H_m°$ data for $B(OH)_4^-$ (= BO_2^- + 2 H_2O). The NIST and calculated $\Delta_f G_m°$ values agree within the equivalent of 0.1 $\log_{10}K$ units.

Phosphoric acid, $H_3PO_4(aq)$, and all three of its hydrolysis products $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} are included in the core data set. HPO_4^{2-} is the primary master species. The $\log_{10}K°$ and $\Delta_r H_m°$ values for the reactions by which the other (secondary master) species are formed are those adopted by the NEA (see Table 4.2).

4.6.3 Arsenate solute species and mineral

The behaviour of As(V), arsenate, is analogous to that of phosphate. Thus, the core data include arsenic acid, $H_3AsO_4(aq)$, and its three hydrolysis products $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}. The NIST values for $\Delta_f G_m°$ and $\Delta_f H_m°$ of the species are used. These values are also accepted by NEA. The $\log_{10}K°$ values for the reactions among these species calculated from the NIST data agree within 0.2 units with those given by BAES & MESMER (1976, Table 16.1).

Arsenic(III) is similar to borate in that its dissolved species at low concentrations are $As(OH)_3(aq)$ and $As(OH)_4^-$. Both species are included in the core data set with $As(OH)_3(aq)$ as the (secondary)

master species, and data taken from the NIST compilation. The values used for $As(OH)_4^-$ equal those for $AsO_2^- + 2\ H_2O$. The $\log_{10}K°$ and $\Delta_r H_m°$ values for the hydrolysis of $As(OH)_3(aq)$ to $As(OH)_4^-$ agree with those given by BAES & MESMER (1976, Section 16.1) within 0.06 units and $0.2\ kJ \cdot mol^{-1}$, respectively.

Native arsenic, As(cr), is included as a mineral. Its properties of formation equal zero by convention.

4.7 Carbon

Redox processes are important in the carbon system. C(IV) is stable under oxidising conditions and occurs as $CO_2(g)$, or as carbonate, CO_3^{2-}, minerals, and aqueous species. The most reduced form of carbon is C(-IV), represented by methane, $CH_4(g)$. C(0) is also common and is represented by carbohydrates, CH_2O, and elemental carbon, as graphite or diamond. Petroleum hydrocarbons and organic molecules may include carbon in almost any formal oxidation state between (IV) and (-IV). The core data set includes only carbonate species, graphite, and methane.

4.7.1 Master species: HCO_3^- and $CH_4(aq)$

C(IV) occurs as gaseous $CO_2(g)$, or as carbonate, CO_3^{2-}, or one of its hydrolysis products. HCO_3^- is the dominant aqueous species at pH values between 6 and 10, and is chosen as the primary master species of carbon. The other carbonate hydrolysis products, CO_3^{2-} and $CO_2(aq)$ (= $H_2CO_3(aq) - H_2O$), are included as secondary master species. $CO_2(g)$ is also included as a gas.

CODATA recommends a more complete and precise set of thermodynamic properties for $CO_2(g)$ than it does for HCO_3^-, the primary master species chosen for carbonate. To maintain the high precision of the CODATA $CO_2(g)$ data in the core data set, values for the properties of formation of HCO_3^- were calculated from the CODATA $CO_2(g)$ values and the equations representing equilibria among dissolved carbonate species given by PLUMMER & BUSENBERG (1982) and used for the core data, as described in the following section.

Under reducing conditions C(-IV) is important. $CH_4(aq)$ is the secondary master species and gaseous $CH_4(g)$ is also included. Thermodynamic properties for these species are given by the NIST compilation. For $CH_4(g)$, the CODATA and NIST $\Delta_f H_m°$ values are identical, and the $S_m°$ values differ only by $0.04\ J \cdot mol^{-1} \cdot K^{-1}$.

Elemental carbon, C(cr), graphite, is included as a mineral. The absolute entropy of this substance is the same in both the CODATA and NIST compilation.

4.7.2   Carbonate solute species, minerals, and gases

PLUMMER & BUSENBERG (1982) critically evaluated experimental data on the system $CaCO_3$ – H_2O between 0 and 90ºC. The equations they developed describing equilibrium among the carbonate species $CO_2(g)$, $CO_2(aq)$, HCO_3^-, CO_3^{2-}, $CaHCO_3^+$, $CaCO_3(aq)$ and the solubility of $CaCO_3$ minerals calcite and aragonite are widely used (e.g. NORDSTROM et al. 1990), and are adopted for the core data set. BUSENBERG et al. (1984) and BUSENBERG & PLUMMER (1986) describe their subsequent work on carbonate solution and minerals including Sr^{2+} and Ba^{2+}. The data for the solution species $SrHCO_3^+$, $SrCO_3(aq)$, $BaHCO_3^+$, $BaCO_3(aq)$, and the minerals strontianite, $SrCO_3(cr)$, and witherite, $BaCO_3(cr)$, from these sources are also adopted for the core data set.

NORDSTROM et al. (1990) include the data just described in their compilation and also include $\log_{10}K°$ data and $\Delta_r H_m°$ values for the additional solution species $MgHCO_3^+$, $MgCO_3(aq)$, $NaHCO_3(aq)$, and $NaCO_3^-$, and the mineral dolomite, $CaMg(CO_3)_2$(ordered) and $CaMg(CO_3)_2$(disordered). These data are also included in the core data set.

Data for the Ca-, Sr- and Ba-carbonate species and minerals, as well as for the Mg-carbonate species, are given as equations for $\log_{10}K°(T)$ and are valid between 0 to 10 and 80 to 90°C.

From these values the thermodynamic constants of formation of the carbonate species and minerals were calculated and compared with data included in the CODATA compilation and the original values in the articles of Plummer and colleagues. In all but a few cases, the core data are within the uncertainties assigned to the critically evaluated values. The exceptions are the $BaHCO_3^+$ and $BaCO_3(aq)$ values which disagree by such large amounts as to suggest an error in their calculation in the original BUSENBERG & PLUMMER (1986) article. There is also an unexplained difference of about 6 kJ/mol for the $\Delta_f H_m°$ of $CaHCO_3^+$ given in the CODATA compilation.

4.7.3   Reduced carbon solute species, minerals and gases

The reduced carbon entities included in the data base are C(-IV) as dissolved and gaseous methane, $CH_4(aq)$ and $CH_4(g)$, and C(cr) as the mineral graphite.

Graphite is the standard state for elemental carbon, so its properties of formation are zero by convention.

The thermodynamic properties of formation of $CH_4(g)$ are those given in the NIST compilation. The properties of the secondary master species, $CH_4(aq)$, are derived from those of the gas and the solubility data of Table 4.3, as described in Section 4.1.1.

4.8 References

BAES, C.F., Jr, MESMER, R.E. (1976): The Hydrolysis of Cations. New York, John Wiley & Sons, 489p.

BUSENBERG, E., PLUMMER, L.N. (1986): The solubility of $BaCO_3$(cr) (witherite) in CO_2–H_2O solutions between 0 and 90°C, evaluation of the association constants of $BaHCO_3^+$(aq) and $BaCO_3°$(aq) between 5 and 80°C, and a preliminary evaluation of the thermodynamic properties of Ba^{2+}(aq). Geochimica et Cosmochimica Acta, 50, 2225-2233.

BUSENBERG, E., PLUMMER, L.N., Parker, V.B. (1984): The solubility of strontianite ($SrCO_3$) in CO_2–H_2O solutions between 2 and 91°C, the association constants of $SrHCO_3^+$(aq) and $SrCO_3°$(aq) between 5 and 80°C, and an evaluation of the thermodynamic properties of Sr^{2+}(aq) and $SrCO_3$(cr) at 25°C and 1 atm total pressure. Geochimica et Cosmochimica Acta, 48, 2021-2035.

COX, J.D., WAGMAN, D.D., MEDVEDEV, V.A. (1989): CODATA Key Values for Thermodynamics. New York, Hemisphere, 271p.

GARVIN, D., PARKER, V.B., WHITE, H.J., JR. (1987): CODATA Thermodynamic Tables: Selctions for Some Compounds of Calcium and Related Mixtures: A Prototype Set of Tables. Washington, D.C., Hemisphere Publishing, 356p.

NORDSTROM, D.K., PLUMMER, L.N., LANGMUIR, D., BUSENBERG, E., MAY, H.M., JONES, B.F., PARKHURST, D.L. (1990): Revised Chemical Equilibrium Data for Major Water-Mineral Reactions and Their Limitations. In: MELCHIOR, D. C., BASSETT, R. L. (eds.): Chemical Modeling of Aqueous Systems II. Washington, D.C., American Chemical Society, ACS Symposium Series 416, p. 398-413.

PEARSON, F.J., BERNER, U. (1991): Nagra Thermochemical Data Base I. Core Data. Nagra Technical Report NTB 91-17, Nagra, Wettingen, Switzerland, 70p.

PEARSON, F.J., BERNER, U., HUMMEL, W. (1992): Nagra Thermochemical Data Base II. Supplemental Data 05/92. Nagra Technical Report NTB 91-18, Nagra, Wettingen, Switzerland, 284p.

PLUMMER, L.N., BUSENBERG, E. (1982): The solubilities of calcite, aragonite and vaterite in CO_2–H_2O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system $CaCO_3$–CO_2–H_2O. Geochimica et Cosmochimica Acta, 46, 1011-1050.

RARD, J.A., RAND, M.H., ANDEREGG, G., WANNER, H. (1999): Chemical Thermodynamics of Technetium. Elsevier, Amsterdam, 544p.

WAGMAN, D.D., EVANS, W.H., PARKER, V.B., SCHUMM, R.H., HALOW, I., BAILEY, S.M., CHURNEY, K.L., NUTTALL, R.L. (1982): The NBS tables of chemical thermodynamic properties: Selected values for inorganic and C_1 and C_2 organic substances in SI units. Journal of Physical and Chemical Reference Data, 11, Supplement No. 2, 1-392.

WHITFIELD, M. (1979): Activity coefficients in natural waters. In: PYTKOWICZ, R. (ed.): Activity Coefficients in Electrolyte Solutions, Volume II. Boca Raton, Florida, CRC Press, p.153-299.

5   SUPPLEMENTAL DATA

5.1   Aluminium

5.1.1   The system Al – H$_2$O

5.1.1.1   Introduction

Aluminium occurs naturally as Al^{3+}. In aqueous solution it hydrolyses to form a series of species of the form Al(OH)$_n^{3-n}$ with n ranging from 0 to 4.[1] The solubility of aluminium oxides and hydroxides is minimal at near-neutral pH values and becomes higher with both increasing and decreasing pH. This indicates that the most stable aqueous species are Al^{3+} and its hydrolysis products with n = 1 and 4. Figure 5.1.1 illustrates the contribution of the various aluminium hydrolysis products to the solubility of the mineral gibbsite.
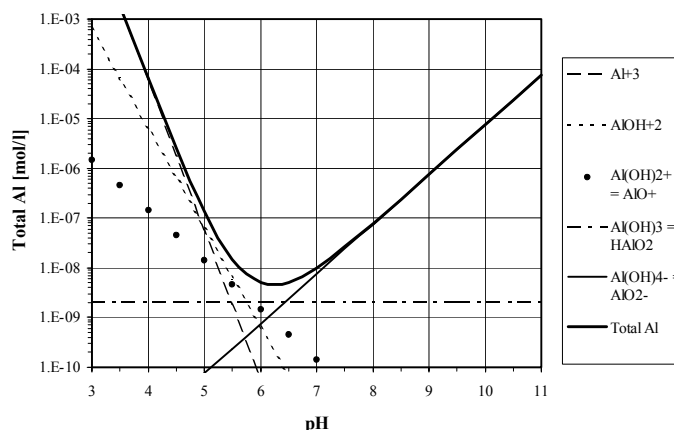
Fig. 5.1.1:   Concentrations of Al^{3+} hydrolysis products and total Al at pH values from 3 to 11 at gibbsite (Al(OH)$_3$) saturation in solution of zero ionic strength. Data from POKROVSKII & HELGESON (1995).

Values of the stability constants of aluminium hydrolysis products are derived from measurements of the solubilities of aluminium solids at various pH values. From such measurements over a range

---

[1] Al^{3+} hydrolysis products are sometimes written in less hydrated forms as AlO$^+$, HAlO$_2$(aq), and AlO$_2^-$ (See Table 5.1.1). The logK values of reactions written with these forms of the species are the same as those written with the fully hydrated forms, *e. g.*,

$$logK\ (Al^{3+} + 2\ H_2O \Leftrightarrow AlO_2^- + 4H^+) = logK\ (Al^{3+} + 4\ H_2O \Leftrightarrow Al(OH)_4^- + 4H^+).$$
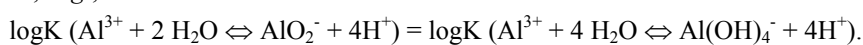
The standard thermodynamic properties of such reactions as

$$AlO_2^- + 2H_2O \Leftrightarrow Al(OH)_4^-$$
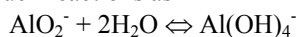
are taken as zero by convention (WAGMAN et al. 1982). The differences in the thermodynamic properties of two forms of the same species correspond to the differences in their water contents. That is:

$$\Delta_f G^0\ Al(OH)_4^- = \Delta_f G^0\ AlO_2^- + 2\ \Delta_f G^0\ H_2O,\ etc.$$

of temperatures, values for the thermodynamic properties ($\Delta_r G^0$, $\Delta_r H^0$, $\Delta_r S^0$ and $\Delta_r Cp^0$) of the hydrolysis reactions can be determined. If the solid used in the dissolution experiment is well characterised and has known thermodynamic properties of formation, the thermodynamic properties of the hydrolysis products can also be determined.

The stability constants for aluminium hydrolysis products and for the solid aluminium hydroxide solubilities that were included in the Nagra TDB 05/92 (PEARSON & BERNER 1991, PEARSON et al. 1992) were taken from a compilation of data by NORDSTROM et al. (1990) for use in geochemical modelling. These values were taken, in turn, from a review of aqueous aluminium data by NORDSTROM & MAY (1989).

Since 1990, a number of new experimental studies on aluminium hydroxide solubility and aluminium speciation have been published, as well as several exhaustive reviews of aluminium chemistry in aqueous solution. From these it appears that the data in the Nagra database should be revised. The Al data to be included in the Nagra/PSI TDB 01/01 are given in Table 5.1.13. The remainder of this chapter provides the rationale for their selection.

5.1.1.2 Sources and review of data

POKROVSKII & HELGESON (1995) and SHOCK et al. (1997) have performed exhaustive reviews of the chemistry of aluminium in aqueous solutions over wide ranges of temperature and pressure. They also provide extensive lists of references to sources of aluminium speciation and solubility data, so such a list need not be presented here. Both reviews conclude that the experimental data on the reaction:

Equation 1 $$Al(OH)_3(cr) + OH^- \Leftrightarrow Al(OH)_4^-$$

obtained at Oak Ridge National Laboratory (ORNL) (WESOLOWSKI 1992) are particularly reliable. From the standard thermodynamic properties of this reaction and selected data on the properties of formation of OH$^-$ and the solid used in the experiment, both calculate values for the properties of formation of Al(OH)$_4^-$.

POKROVSKII & HELGESON (1995) also accept ORNL data (PALMER & WESOLOWSKI 1992, 1993), together with similar results from other studies, for the reaction:
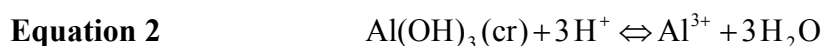
Equation 2 $$Al(OH)_3(cr) + 3H^+ \Leftrightarrow Al^{3+} + 3H_2O$$

From the standard thermodynamic properties of this reaction and selected data on the properties of formation of H_2O, H^+, and the solid used in the experiment, they calculate values for the properties of formation of Al^{3+}.

SHOCK et al. (1997), on the other hand, determined the properties of formation of Al^{3+} from data of COUTURIER et al. (1984) for the reaction:

Equation 3 $Al^{3+} + 2\,H_2O \Leftrightarrow AlO_2^- + 4\,H^+$

and the properties of AlO_2^- ($Al(OH)_4^-$) from the high pH data from the ORNL group.

For the reasons put forward in the remainder of this chaper, the reaction properties of the aluminium hydroxide aqueous species extracted by POKROVSKII & HELGESON (1995) from the data of the ORNL group and other authors have been chosen as the aluminium hydrolysis reaction data included in the Nagra/PSI TDB 01/01.

These reaction data and selected standard thermodynamic data for gibbsite ($Al(OH)_3(cr)$), H_2O, $Al(cr)$, $H_2(g)$, and $O_2(g)$, were then used to develop a consistent set of standard thermodynamic properties for Al^{3+} and its hydrolysis products. These data are also included in the Nagra/PSI TDB 01/01 (Table 5.1.13).

5.1.1.2.1   Data treatment

Thermodynamic data may be presented as standard properties of formation ($\Delta_f G^0$, $\Delta_f H^0$, S^0, Cp^0) of entities of interest, or as standard properties ($\Delta_r G^0$, $\Delta_r H^0$, $\Delta_r S^0$, $\Delta_r Cp^0$) or equilibrium constants (logK) of reactions among them. Solution experimental data such as solubilities generally lead directly to properties of reactions, while data on solids, derived from such experimental techniques as calorimetry and from structural considerations, lead to properties of formation.

For the modelling tasks to which the Nagra/PSI TDB 01/01 will be applied, properties of formation are required for GEM (Gibbs energy minimisation) modelling, with SELEKTOR codes (KARPOV et al. 1997), for example, while equilibrium constants of reactions are used for LMA (law of mass action) modelling with PHREEQC and MINEQL-PSI. Thus, data of both types must be present in the database, and, to assure comparability of modelling results with all codes, the data must be interchangeable and internally consistent.

The internal consistency of the Nagra TDB 05/92 was assured by maintaining all data in the thermodynamic database management program PMATCH (PEARSON & AVIS 1989, PEARSON et al. 1993). To accommodate the additional types of data included in the Nagra/PSI TDB 01/01, and to

improve the ease of use of the program while still maintaining strict internal consistency, a revised database management program, PMATCHC, was developed. The full documentation for this program is given in Appendix A.

The thermodynamic database management program describes the temperature dependence of logK by equation 4:

Equation 4 $$\log K(T) = A + B{\cdot}T + \frac{C}{T} + D{\cdot}\log(T) + \frac{E}{T^2}$$

This expression is also used in PHREEQC (PARKHURST 1995, PARKHURST & APPELO 1999), one of the principal Nagra and PSI geochemical modelling programs, and is commonly used to express experimental data. Its coefficients, A through E, are related to the conventional properties of a reaction, $\Delta_r G^0$, $\Delta_r H^0$, $\Delta_r Cpa^0$, $\Delta_r Cpb^0$ and $\Delta_r Cpc^0$ by simple, algebraic expressions given in many textbooks of geochemical thermodynamics and in the PMATCHC documentation. $\Delta_r Cpa^0$, $\Delta_r Cpb^0$ and $\Delta_r Cpc^0$ in this list are the coefficients a, b and c of the Maier-Kelley expression for heat capacity:

Equation 5 $$Cp = a + b{\cdot}T - \frac{c}{T^2}$$

The values of logK(T) at I = 0 derived by the ORNL group from their own experimental data are also expressed using Equation 4.

The experimental data reviewed by POKROVSKII & HELGESON (1995) and by SHOCK et al. (1997) were used to develop parameters for the revised Helgeson-Kirkham-Flowers (HKF) equation of state for aqueous aluminium species. Neither PMATCH nor PMATCHC is able to calculate reaction properties from the HKF parameters for their constituents, so in order to compare the conclusions of POKROVSKII & HELGESON (1995) and SHOCK et al. (1997) with the results of the ORNL experimental studies and the aluminium data of the Nagra TDB 05/92, it was necessary to make external calculations of reaction properties. This could most simply done by using the SUPCRT92 package of programs (JOHNSON et al. 1992), which are designed to evaluate reaction properties from HKF data on their aqueous constituents.

Among the additions to PMATCHC in its upgrade from PMATCH, were fields for the parameters of the revised Helgeson-Kirkham-Flowers (HKF) equation of state, for the properties of formation of elements, and for the absolute properties (S^0 and Cp^0) of elements and other entities in the database. Programs of the SUPCRT92 package have strict input formatting requirements. To meet these, HKF data from POKROVSKII & HELGESON (1995) were entered in PMATCHC, which was used to write a file that, with minimal hand modifications, could be used as input to the SUPCRT92 package.

The HKF data of SHOCK et al. (1997), together with standard state thermodynamic properties and Maier-Kelley coefficients for minerals and gases formatted for input to the SUPCRT92 package are given in the file *slop98.dat*, which can be down-loaded from *http://zonvark.wustl.edu/geopig/index.html*. SUPCRT92 calculations for the SHOCK et al. (1997) data set were made using this file.

SUPCRT92 calculates the properties of specified reactions at defined temperatures and pressures from HKF data for the aqueous constituents of the reactions. Its output includes tables of reactions properties (logK, $\Delta_r G$, $\Delta_r H$, $\Delta_r S$, $\Delta_r V$, and $\Delta_r Cp$) at the specified temperatures and pressures. The HKF parameter set includes $\Delta_f G^0$, $\Delta_f H^0$ and S^0 for each entity. From these and the properties of the elements, PMATCHC can calculate $\Delta_r G$ and $\Delta_r H$ directly. If only the reaction properties at 25°C, the reference temperature, are desired or properties at other temperatures close enough to 25°C that the van't Hoff equation ($\Delta_r Cp = 0$) is adequate to represent the change of logK with temperature, PMATCHC alone suffices. If a more precise representation of the temperature dependence of the equilibrium constant is needed, $\Delta_r Cp$ data from the SUPCRT92 output can be used. For the data evaluation described here it was found sufficient to consider $\Delta_r Cp$ a constant. However, it would also be possible to fit an equation like the Maier-Kelley equation to the $\Delta_r Cp$ values at various temperatures calculated by SUPCRT92.

5.1.1.2.2   Review and selection of reaction data

The data examined included values derived directly from experimental data by the ORNL group, and data sets extracted from syntheses of the literature by POKROVSKII & HELGESON (1995) and by SHOCK et al. (1997). The data of NORDSTROM et al. (1990), adopted in the Nagra TDB 05/92, were included for comparison. The reactions examined and data for each are given in Table 5.1.1.

In Table 5.1.1, the aluminium aqueous species reactions of interest are numbered 1 through 4. They are included in the Nagra/PSI TDB 01/01 in their conventional form:

Equation 6 $Al^{3+} + n\,H_2O = Al(OH)_n^{3-n} + nH^+$
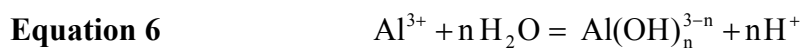
Note that POKROVSKII & HELGESON (1995) and SHOCK et al. (1997) write the species $Al(OH)_3(aq)$ and $Al(OH)_4^{2-}$ with fewer waters, as $HAlO_2^0$ and AlO_2^-, respectively. In addition, SHOCK et al. (1997) write $Al(OH)_2^+$ as AlO^+. The reaction constants and reaction properties are the same for both forms of these species but the properties of formation of the two forms differ by the amounts of water each includes. Table 5.1.1 includes only reaction properties so the data sets can be compared directly.

Reaction 5, for the dissociation of water, is included as a necessary auxiliary reaction.

Reactions 6 and 7 describe the dissolution of gibbsite and represent the experiments actually performed by the ORNL group. The pH values in these experiments were determined by adding HCl or NaOH (or KOH). In addition to increasing the ionic strength of the experimental solutions, the presence of NaOH and HCl made possible the formation of ion pairs such as $NaAl(OH)_4(aq)$, $NaOH(aq)$, $NaCl(aq)$ or $AlCl_n^{3-n}$. The first two are mentioned below. Careful work by the ORNL group found no signs of Al-Cl association at ionic strengths to 5 molal.

In reducing their own data, the ORNL group used Pitzer's equations for total activity coefficients to account both for the effects of changing ionic strengths and for the ion interactions that would lead to the formation of such ion pairs. POKROVSKII & HELGESON (1995), on the other hand, in their reduction of the ORNL and other experimental data, explicitly considered the formation of these ion pairs. They also concluded that $AlCl_n^{3-n}$ ion pairs are of such low stability that they need not be considered, but found that it is necessary to include $NaAlO_2(aq)$, (=$NaAl(OH)_4(aq)$), $NaOH(aq)$ and $NaCl(aq)$ in their model. Data for the first two of these species are included as reactions 8 and 9 in Table 5.1.1.

In our update, ion pairs like $NaOH(aq)$ or $NaHCO_3(aq)$ have been adopted from the Nagra/PSI TDB 05/92 without change. However, our present data evaluation did not aim at providing a data set for saline systems. Only in such systems the question "strong ion interactions and/or weak ion pairs?" becomes important. This topic will be consistently addressed in a future update. Hence, the ion pairs $NaAl(OH)_4(aq)$ and $NaCl(aq)$ are not included in the Nagra/PSI TDB 01/01.

Table 5.1.1 includes values of the coefficients A through E of Equation 4 and the values of logK(25) calculated from them, as well as the thermodynamic properties of the reactions at 25°C. Bold numbers represent the values actually entered into the table. The remaining numbers were calculated. For the NORDSTROM et al. (1990) and ORNL (WESOLOWSKI, 1992; PALMER & WESOLOWSKI, 1992 and 1993) data for the aluminium reactions and the NORDSTROM et al. (1990) data for the dissociation of water, the data entered are logK(T) coefficients. For the POKROVSKII & HELGESON (1995) and SHOCK et al. (1997) data, and the data for the dissociation of water used in SUPCRT92, values for $\Delta_r G^0$, $\Delta_r H^0$, $\Delta_r S^0$, and $\Delta_r Cp^0$ were entered. These were taken from the SUPCRT92 calculations for the several reactions using data of POKROVSKII & HELGESON (1995) or SHOCK et al. (1997) for the constituent components as described above. The column of values for $\Delta_r S^0$, calculated as $(\Delta_r H^0 - \Delta_r G^0)/T$ are also given in the table. These should be identical to the $\Delta_r S^0$ values taken from the SUPCRT92 output but, curiously, they are not. The reason for this has not been sought. Presumably it lurks within the SUPCRT92 program itself or in the HKF formalism

it embodies. To maintain the consistency in the data that follow, the value of $\Delta_r S^0$ calculated from the entered values of $\Delta_r G^0$ and $\Delta_r H^0$ was used.

When reaction property data were entered, values of the logK(T) coefficients A, C, and D, were calculated from them using equations given in the PMATCHC documentation (Appendix A). Coefficients B and E were zero because values for b and c coefficients of the Maier-Kelley equation were not available requiring that $\Delta_r Cp^0$ value be considered invariant with temperature. From the logK(T) coefficients, values of logK(25°C) were then calculated. These were identical to values calculated directly from the value of $\Delta_r G^0$.

When data for the coefficients of the logK(T) expression were entered, values of the reaction properties were calculated from them, again using the equations given in the PMATCHC documentation. Except for H_2O, only data for coefficients A, C, D were available; from which $\Delta_r Cp$ values constant with temperature were calculated. For the $AlOH^{2+}$ reaction, PALMER & WESOLOWSKI (1993) gave only data for A and C, leading to a $\Delta_r Cp^0$ value of zero. Because all five coefficients were entered for H_2O, the values for $\Delta_r Cpb^0$ and $\Delta_r Cpc^0$ could also be calculated, describing the temperature dependence of $\Delta_r Cp^0$. Again, logK(25) values calculated from the logK(T) expression were identical to those calculated directly from the $\Delta_r G^0$ value.

These calculations were carried out in a spreadsheet, the results of which appear as Table 5.1.1. Because they are the results of same calculations as those in PMATCHC, these results can be used to verify the correct operation of parts of the PMATCHC program.

Data for the hydrolysis reactions 1 through 4 are available directly from the NORDSTROM et al. (1990), POKROVSKII & HELGESON (1995) and SHOCK et al. (1997) data sets. ORNL data for reaction 1 are those given by PALMER & WESOLOWSKI (1992). Those for reaction 4 can be calculated as shown in Table 5.1.1 from data for reaction 6 and 7 given by WESOLOWSKI (1992) and PALMER & WESOLOWSKI (1992), respectively, and the dissociation constant for water, reaction 5. There are no ORNL data for reactions 2 and 3. However, these species are relatively weak and contribute little to the total aluminium concentrations, except at pH values around six (see Figure 5.1.1). In the calculations discussed below, data for reactions 2 and 3 from POKROVSKII & HELGESON (1995) were combined with the ORNL data set for reactions 1 and 4 in calculating solubilities.

The data for the several reactions are compared and contrasted from two perspectives. The first examines how well the data reproduce measured gibbsite solubilities at 25°C. The second examines how well logK(T) values calculated from the data sets agree with those measured at a range of temperatures.

5.1.1.2.2.1 25°C data and gibbsite solubility

The first evaluation of the data sets was made by comparing the solubilities of the mineral gibbsite, $Al(OH)_3$, at pH values between 3 and 11, as calculated using the four data sets.

Figure 5.1.2 shows the results. The solubilities refer to a hypothetical solution of zero ionic strength. As the figure shows, the POKROVSKII & HELGESON (1995) reaction properties lead to solubilities virtually identical with those for the reaction properties fit by the ORNL group to their own experimental data. The POKROVSKII & HELGESON (1995) data set thus reproduce, using the HKF equations of state, the data described by the ORNL group using equations of the form of eq. 4.

The SHOCK et al. (1995) data set led to virtually the same solubilities at high pH values but to solubilities lower by a factor of 6 at pH values below about 5. In fitting HKF parameters to experimental data sets, POKROVSKII & HELGESON (1995) relied on measurements of gibbsite solubility at low pH by the ORNL group and other authors who found similar results. SHOCK et al. (1997), on the other hand, used data from COUTURIER et al. (1984) on equilibria between the hydrolysis products themselves. These data led SHOCK et al. (1997) to predict lower solubilities at low pH values than those measured at ORNL and predicted with the data of POKROVSKII & HELGESON (1995). The solubilities calculated using the NORDSTROM et al. (1990) data set are higher than those from the other data sets at all pH values.
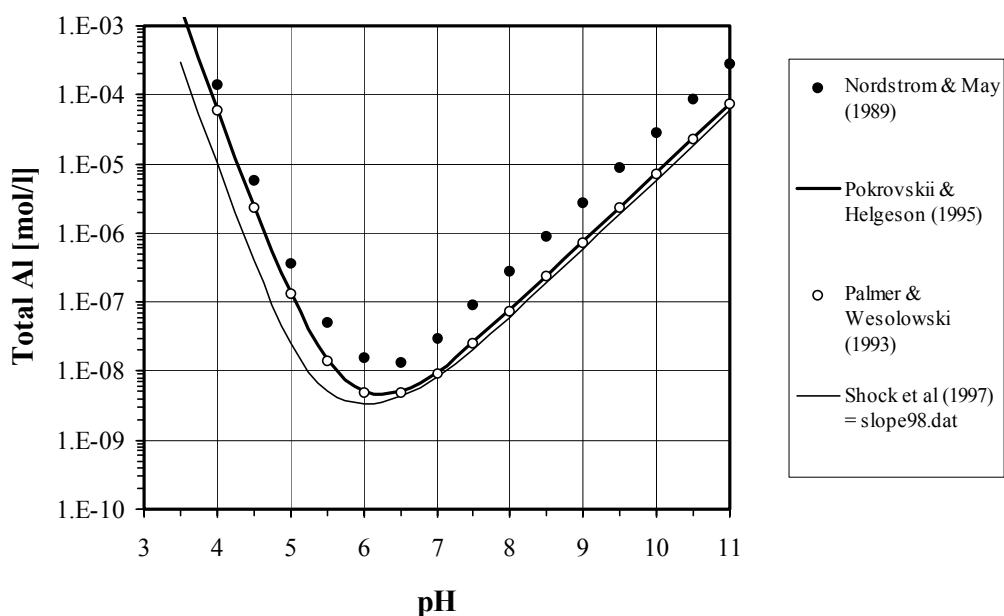
Fig. 5.1.2: Comparison of total Al^{3+} concentrations at pH values from 3 to 11 at gibbsite saturation in solution of zero ionic strength according to data sets of NORDSTROM et al. (1990), POKROVSKII & HELGESON (1995), ORNL (WESOLOWSKI 1992, PALMER & WESOLOWSKI 1992, 1993) and SHOCK et al. (1997) in *slop98.dat*.

In comparing these solubility calculations, it is important to consider the stability constant for gibbsite included in each data set. The solubility used by POKROVSKII & HELGESON (1995) is derived from the ORNL and similar experimental data and so is nearly the same as that recommended by the ORNL group. The value used with the NORDSTROM et al. (1990) aqueous speciation data is that recommended in the same publication, and is the value included in the Nagra TDB 05/92. This value was taken from MAY et al. (1979) and is larger than the value used in any other data set (Table 5.1.1). In their evaluation of previous aqueous aluminium data, POKROVSKII & HELGESON (1995) and the ORNL group emphasise the work of BLOOM & WEAVER (1982), who showed that the techniques used to prepare the solid material used in most of the previously published studies of gibbsite solubility led to a reactive surface area that produced measured solubilities that were too high. In addition, WESOLOWSKI (1992) pointed out that both acetate and bis-tris, used as pH buffers in certain earlier studies, enhanced the solubility of gibbsite, presumably by forming complexes with dissolved aluminium. The study by MAY et al. (1979) is one of those likely to have overestimated gibbsite solubility.

If gibbsite solubility calculations are made using the aluminium speciation data of NORDSTROM et al. (1990) and a gibbsite solubility product of 7.74 (that of the ORNL group) instead of 8.11, the total aluminium concentrations at low pH values are virtually identical with those from the POKROVSKII & HELGESON (1995) and ORNL data. At high pH values, the total aluminium concentrations are above those of POKROVSKII & HELGESON (1995) fit to the ORNL data, but never by more than a factor of 1.6.

The gibbsite solubility product used for the calculations of aluminium solubility with the SHOCK et al. (1997) aluminium speciation data is that in *slop98.dat*. It has the lowest solubility of any of the four data sets. The data are those of HELGESON et al. (1978) which are taken principally from calorimetry rather than from solution chemistry. The solubilities calculated from the SHOCK et al. (1997) data at high pH values are the same as those derived by POKROVSKII & HELGESON (1995) from the ORNL data. This is consistent with the derivation by SHOCK et al. (1997) of AlO_2^- data from the HELGESON et al. (1978) gibbsite properties and the ORNL high pH solubility data. The logK(25) value for the high pH dissolution reaction, reaction 6 in Table 5.1.1, differs from those in POKROVSKII & HELGESON (1995) and WESOLOWSKI (1992) by only 0.1 units while the difference for the low pH dissolution reaction, reaction 5, is 0.8 units. This corresponds to the difference by a factor of six in the low pH results in Figure 5.1.2 and mentioned above.

5.1.1.2.2.2 Temperature dependence

The second step in evaluating the four data sets is to compare the temperature dependence of their logK values. Such comparisons for the two most important hydrolysis products, $Al(OH)_4^-$ and $AlOH^{2+}$, are shown in Figure 5.1.3 and Figure 5.1.4, respectively. In both figures, the lines were calculated with Equation 4 for logK(T) using values of the coefficients A through E, given in Table 5.1.1.
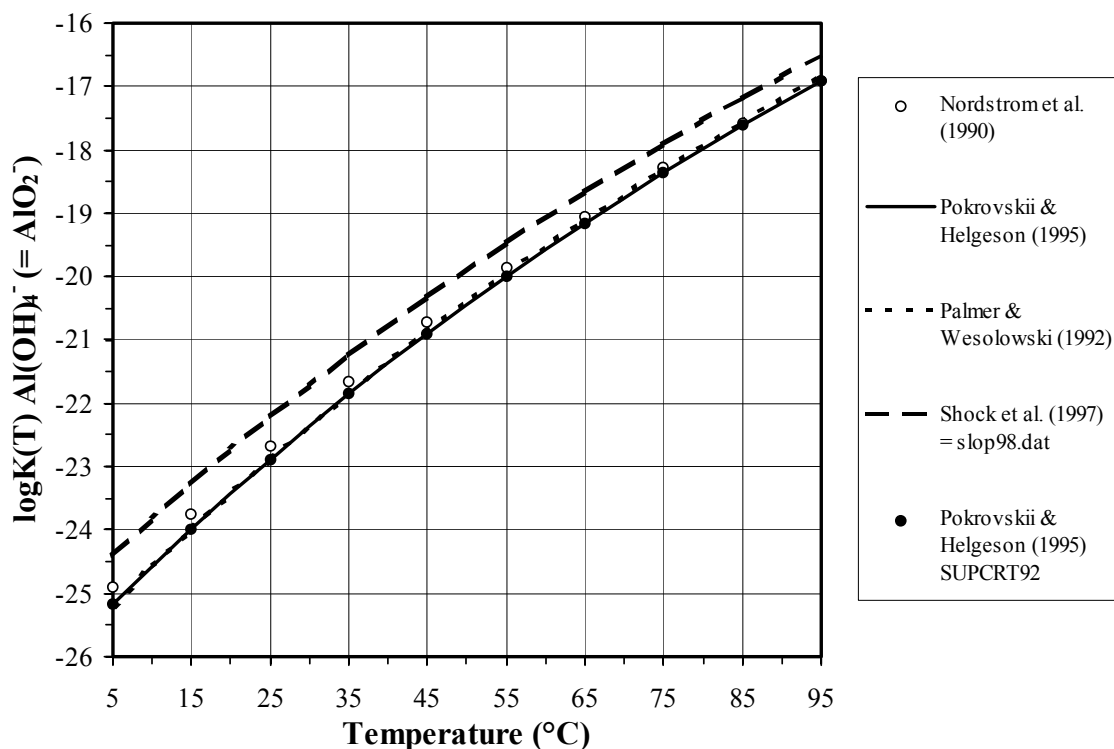
Fig. 5.1.3:   Comparison of logK(T) values for association of $Al(OH)_4^-$ (= AlO_2^-) at temperatures from 5 to 95°C according to data sets of NORDSTROM et al. (1990), POKROVSKII & HELGESON (1995), ORNL (WESOLOWSKI 1992, PALMER & WESOLOWSKI 1992, 1993) and SHOCK et al. (1997) in *slop98.dat*.

In addition to the values calculated from the logK equations, values calculated by SUPCRT92 for the POKROVSKII & HELGESON (1995) data sets are shown as points.

An important observation is that the calculated lines and the SUPCRT92 points are virtually identical. The maximum differences between them are only 0.012 at 95°C for $AlOH^{2+}$ and 0.05 at 5 °C for $Al(OH)_4^-$. As Table 5.1.1 shows, the logK equations developed from the POKROVSKII & HELGESON (1995) HKF parameters have non-zero values only for the A, C, D coefficients. These correspond to reaction properties with constant $\Delta_r Cp$. The SUPCRT92 calculations, on the other hand, are based on the HKF equation of state which has seven parameters to express the effects of

temperature and pressure variations. The fact that the calculated and SUPCRT92 values agree so well indicates that the simple three-term expression adequately represents logK values at temperatures below 100°C.
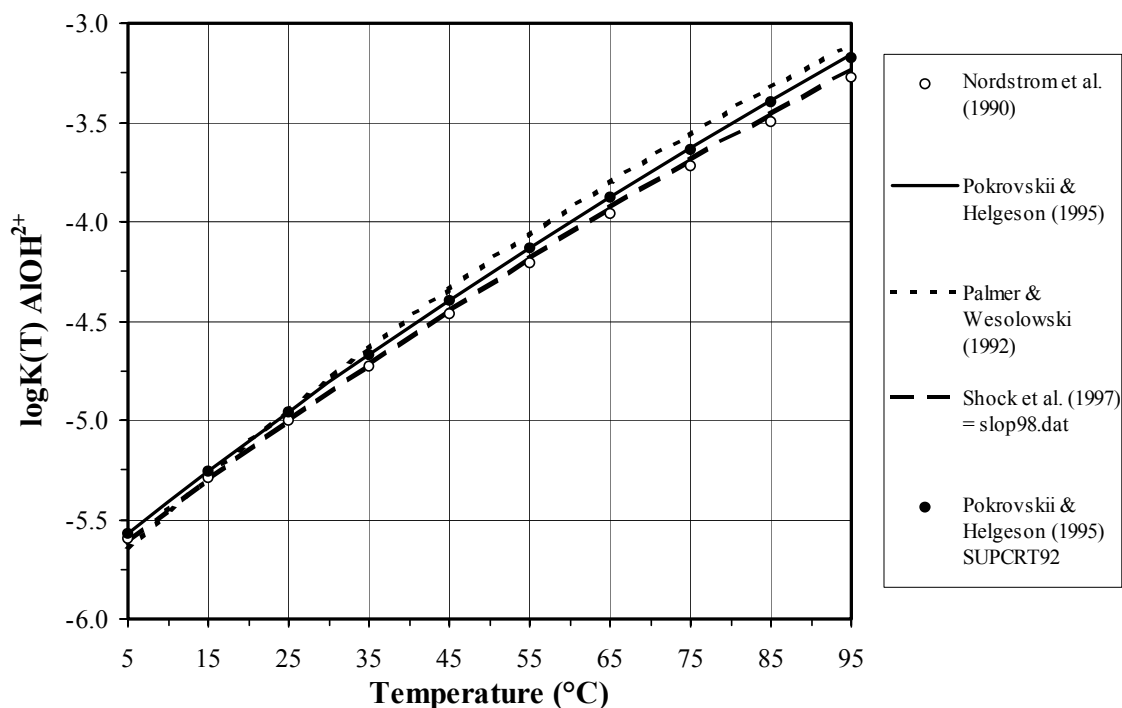
Fig. 5.1.4:   Comparison of logK(T) values for association of AlOH^{2+} at temperatures from 5 to 95°C according to data sets of NORDSTROM et al. (1990), POKROVSKII & HELGESON (1995), ORNL (WESOLOWSKI 1992, PALMER & WESOLOWSKI 1992, 1993) and SHOCK et al. (1997) in *slop98.dat*.

Figure 5.1.3 and Figure 5.1.4 show, there is also good agreement between logK values calculated using equations developed from the POKROVSKII & HELGESON (1995) data and those given by the ORNL group. The maximum differences between them are 0.08 for Al(OH)$_4^-$ at 95°C and 0.08 for AlOH^{2+} at 5°C.

Differences between logK(T) values for Al(OH)$_4^-$ calculated from the NORDSTROM et al. (1990) equation, and values calculated from the ORNL equation, range from −0.07 at 95°C to +0.29 at 5°C. Differences between values from the equations calculated from the data of SHOCK et al. (1997) and values from the ORNL equations range from 0.31 at 95°C to 0.81 at 5°C. The difference at 25°C is 0.67. This is close to the difference of 0.77 between the solubility products of gibbsite associated with each data set. In calculating gibbsite solubility at high pH values, where Al(OH)$_4^-$

prevails, these differences cancel. Thus both the ORNL and SHOCK et al. (1997) data sets give about the same total aluminium contents at gibbsite solubility, as shown in Figure 5.1.2 and discussed above.

As Figure 5.1.4 shows, the differences between the NORDSTROM et al. (1990) equations and the equations describing the data of SHOCK et al. (1997) for logK(T) of $AlOH^{2+}$, range from 0.01 to 0.04 units. However, both give significantly different values from those calculated with the ORNL equation – up to 0.16 units for the NORDSTROM et al. (1990) equation at 95°C .

5.1.1.2.2.3 Data selected

Figure 5.1.3 and Figure 5.1.4 and this discussion, the properties of reaction and the corresponding coefficients for the logK(T) equation based on the data of POKROVSKII & HELGESON (1995) for gibbsite solubility and aluminium hydrolysis are adopted for the Nagra/PSI TDB 01/01. A second possibility would be to adopt the equations of the ORNL group. However, these are available only for $AlOH^{2+}$ and $Al(OH)_4^-$ so equations for the remaining species would have to be adopted from some other data set if solubilities in the pH range from about 5 to 7 are to be successfully calculated. These equations would probably be those based on the POKROVSKII & HELGESON (1995) data. Adopting the equations based on the POKROVSKII & HELGESON (1995) data for all species gives solubilities that are virtually identical with those of the ORNL group at all pH values. Furthermore, it gives logK(T) values for the aluminium hydrolysis products that differ from the ORNL values by less than 0.004 units at 25°C and by less than 0.1 units at 5°C and 95°C .

An additional advantage of the POKROVSKII & HELGESON (1995) data is that they are derived from a set of HKF parameters. This makes them more convenient for use with programs such as SELEKTOR that use this equation of state. However, as discussed in the following section, the standard properties of formation of Al species selected for this database differ from those in POKROVSKII & HELGESON (1995) because the standard properties of the elements and of H_2O used in developing the properties of formation for this database were not necessarily the same as those used by POKROVSKII & HELGESON (1995). Thus, there may be inconsistencies between SELEKTOR calculations based on *slop98.dat* and PHREEQC on MINEQL calculations with this database.

5.1.1.2.3   Standard thermodynamic properties of aqueous species and gibbsite

The preceding discussion addressed the properties of reactions among aqueous aluminium species and gibbsite adopted for the Nagra/PSI TDB 01/01. The properties of formation of these entities are

addressed here. The data discussed and the values adopted are given in Table 5.1.2 through Table 5.1.10.

5.1.1.2.3.1 Elements and H_2O

Table 5.1.2 provides data for the absolute entropies (S^0) and heat capacities (Cp^0) of the elements of interest, O_2, H_2, and Al. Table 5.1.3 gives the Gibbs energy ($\Delta_f G^0$) and enthalpy ($\Delta_f H^0$) of formation and S^0 and Cp^0 data for H_2O, and values for the entropy ($\Delta_f S^0$) and heat capacity ($\Delta_f Cp^0$) of formation calculated from them. The principal sources of such data are CODATA (COX et al. 1989), adopted by the NEA (*e.g.* SILVA et al. 1995) and the U. S. NIST (NBS) (WAGMAN et al. 1982). Coefficients of the Maier-Kelley heat capacity equation for the gases in Table 5.1.2 are those given by KELLEY (1960).

Values in this and similar tables to follow are given both in Joules (J) and calories (cal). The units used in the Nagra/PSI TDB 01/01 are Joules, while the units used in SUPCRT92 (JOHNSON et al. 1992) and databases such as those of POKROVSKII & HELGESON (1995) and SHOCK et al. (1997) intended for use with it are given in calories.

As Table 5.1.2 and Table 5.1.3 show, with the exception of the Cp^0 values for Al(cr) and H_2O, the various sets of data (in kJ or J) differ only in the second decimal place. These differences are larger than the uncertainties assigned by the CODATA group but are within the uncertainties of other data used in developing the properties of the aluminium species. In generating the properties of the aqueous species described below, the CODATA / NEA values were used, as they are, as far as available, for all elements in the Nagra/PSI TDB 01/01. The data for H_2O used by POKROVSKII & HELGESON (1995) and by SHOCK et al. (1997) are those from the equation of state for H_2O embodied in SUPCRT92. They agree with the other data for all properties within the uncertainties assigned by CODATA.

5.1.1.2.3.2 Gibbsite and OH⁻

All the data sets are based ultimately on reaction data, so to develop formation properties requires the definition of the formation properties of one entity in the reaction chain. The entity chosen here is the mineral gibbsite ($Al(OH)_3$), the properties of which, from various sources, are given in Table 5.1.5. Because of its importance in experimental work on gibbsite solubility, properties of formation of OH⁻ must also be available. These are given in Table 5.1.4.

Properties of formation of OH⁻ are given in the CODATA / NEA and NBS compilations of data and are specified by POKROVSKII & HELGESON (1995) and by SHOCK et al. (1997) as well. These data are given in Table 5.1.4. However, for complete internal consistency within the Nagra/PSI TDB

01/01, the OH^- properties it contains must be derived from the properties of H_2, O_2, and H_2O included in the database and the equation describing the reaction among them, the equation of NORDSTROM et al. (1990), shown in Table 5.1.1. The properties of H^+ must also be known. By convention, all H^+ properties of formation equal zero, so they are not included in Table 5.1.2.

The standard properties of gibbsite developed from calorimetric data and recommended by HEMINGWAY & SPOSITO (1989) have been chosen by POKROVSKII & HELGESON (1995) and the ORNL group (PALMER & WESOLOWSKI, 1992). SHOCK et al. (1997) use the formation properties of gibbsite given by HEMINGWAY & ROBIE (1977), which were also selected by HELGESON et al. (1978), and are those in *slop98.dat*.

As Table 5.1.5 shows, the enthalpies of formation in all databases are the same, but the entropies and Gibbs energies of formation used by SHOCK et al. (1997) differ from those in the other two data sets. All heat capacities, except that used by SHOCK et al. (1997), are based on fits to data of HEMINGWAY et al. (1977). These all give virtually the same value at 25°C. The heat capacity data in *slop98.dat*, which were used by SHOCK et al. (1997), are those of HELGESON et al. (1978) which were taken from KELLEY (1960).

For the Nagra/PSI TDB 01/01, the values recommended by HEMINGWAY & SPOSITO (1989) are adopted. The heat capacity coefficients of POKROVSKII & HELGESON (1995) are also adopted. They were fit to the same data set as were the coefficients of HEMINGWAY & SPOSITO (1989) but are in the form of the Maier-Kelley equation and so are usable directly with SUPCRT92 and have the form used in PMATCHC as well.

These properties are the basis of the reaction chain from which the standard properties of formation of Al^{3+}(aq) and its hydrolysis products were developed.

5.1.1.2.3.3 Al^{3+}

The standard properties of Al^{3+}(aq) are given in Table 5.1.6. They were developed from the reaction properties for the dissolution of gibbsite in acid solution (reaction 7, Table 5.1.1) derived by POKROVSKII & HELGESON (1995) from experimental data of PALMER & WESOLOWSKI (1992) and similar experimental data of others. This table and similar tables in this chapter, also include standard properties of formation from other databases.

The enthalpy of formation of Al^{3+}(aq) (-538.424 kJ / mol) is from POKROVSKII & HELGESON (1995) and is the same as the CODATA recommended value. The corresponding value of PALMER & WESOLOWSKI (1992) is more negative because of the use by these authors of non-CODATA

auxiliary data, although within the error assigned by PALMER & WESOLOWSKI (1992), the two values overlap.

The Gibbs energy chosen (-487.740 kJ / mol) is not identical with the value given by POKROVSKII & HELGESON (1995) because of the slightly different values for the properties of H_2O used here and by those authors (Table 5.1.3). The value chosen is 3.77 kJ (0.66 logK units) more negative than the value recommended by CODATA. This is an example of the need to use some non-CODATA standard properties in the Nagra/PSI TDB 01/01 to maintain strict internal consistency with the reaction properties selected.

The S^0 value selected (-337.71 J / mol / K) differs from those in the other data sources shown in Table 5.1.6 because of the different Gibbs energies and enthalpies selected. Table 5.1.6 includes $\Delta_f S^0$ values calculated both from $\Delta S = (\Delta H - \Delta G)/T$ and from the S^0 values included in the respective data sets. It is curious that the two values generated for the SHOCK et al. (1997) database do not agree, because this database is supposed to be internally consistent. The NBS values also do not agree, but this may result from the deliberate choice of data from different sources, as discussed by WAGMAN et al. (1982, p. 2-15).

5.1.1.2.3.4 Al(OH)$_4^-$ (= AlO$_2^-$ + 2 H$_2$O)

The properties of formation of $Al(OH)_4^-$ are given in Table 5.1.7. They were developed from the properties of the Al^{3+}(aq) hydrolysis reaction, reaction 4, Table 5.1.1, based on the data of POKROVSKII & HELGESON (1995), the standard properties of Al^{3+}(aq) given in Table 5.1.6, and the properties of the elements and H_2O in Table 5.1.2 and Table 5.1.3.

Table 5.1.7 also includes standard properties for $Al(OH)_4^-$ from several other databases. The values chosen for the Nagra/PSI TDB 01/01 for the Gibbs energy (-1305.705 kJ / mol) and enthalpy (-1500.822 kJ / mol) agree within a few hundred J with values from all other databases except those from NORDSTROM et al. (1990).

5.1.1.2.3.5 AlOH^{2+}, Al(OH)$_2^+$ (=AlO$^+$ + H$_2$O), and Al(OH)$_3$(aq) (=HAlO$_2$(aq) + H$_2$O)

Data for $AlOH^{2+}$ are given in Table 5.1.8. As before, they are based on the properties of the elements in Table 5.1.2, of H_2O in Table 5.1.3, of Al^{3+}(aq) in Table 5.1.6, and the properties of reaction 1 in Table 5.1.1. The Gibbs energy of formation chosen (-696.58 kJ / mol) agrees with that given by PALMER & WESOLOWSKI (1993) within the uncertainty associated with the latter, but differs from values given in the other data sets. The value chosen for the enthalpy (-774.43 kJ / mol) is between those given by PALMER & WESOLOWSKI (1993) and calculated from the reaction

data of NORDSTROM et al. (1990), but is considerably more negative than that of SHOCK et al. (1997). PALMER & WESOLOWSKI (1993) describe their reaction data with an equation for logK(T) that includes coefficients only for the constant (A) and 1/T (C) terms. That is, their data lead to a $\Delta_r Cp^0$ value of zero. As shown in Table 5.1.8, this leads to a Cp^0 value for $AlOH^{+2}$ of 69.5 J / mol / K. However, based on their reaction data and Cp^0 value for $Al^{+3}(aq)$ (see Table 5.1.6), PALMER & WESOLOWSKI (1993) propose a Cp^0 value of –44 J / mol/ K for this species. Possible reasons for this discrepancy have not been explored.

Properties of formation of $Al(OH)_2^+$ and $Al(OH)_3(aq)$ are given in Table 5.1.9 and Table 5.1.10. As discussed, these are relatively weak complexes and dominate among Al hydrolysis products over only a narrow range of pH values around 6. The properties chosen for $Al(OH)_3(aq)$ are similar to those from the reaction data of NORDSTROM et al. (1990) in the present database, but there are greater differences between the properties of $Al(OH)_2^+$.

5.1.1.2.3.6 Consistency of reaction data and standard properties

The experimental data from which the reaction data and standard property values for Al species are ultimately based include measurements of gibbsite solubility both at high pH (reaction 6, Table 5.1.1) and at low pH (reaction 7, Table 5.1.1). Only data from POKROVSKII & HELGESON (1995) for reaction 7 were actually used in developing the properties of formation chosen for $Al^{3+}(aq)$ and its hydrolysis products including $Al(OH)_4^-$, so the data for reaction 6 can be used to test the overall consistency of the calculation scheme.

This was done using PMATCHC to calculate the standard properties of formation of two gibbsites. One, designated gibbsite_Al^{3+}, is calculated from the standard properties of $Al^{3+}(aq)$ and the properties of the low pH dissolution reaction. This is just the reverse of the calculations shown in Table 5.1.6 in which the properties of $Al^{3+}(aq)$ were found from the accepted standard properties of gibbsite, H_2O and the elements. Thus, it really checks only the calculation of the $Al^{3+}(aq)$ properties.

The second, designated gibbsite_$Al(OH)_4^-$, is calculated from the standard properties of $Al^{3+}(aq)$ and OH^- (Table 5.1.4), and the properties of the high pH dissolution reaction. The data for this reaction were not used in any calculations to this point, so their use here is a check on the consistency of the calculations.

The results are given in Table 5.1.11, in which the standard properties of gibbsites calculated with these two reactions are compared with the accepted gibbsite properties. The values calculated using the low pH reaction are identical with the accepted values, except the value for $\Delta_f Cp^0$, which differs

only by 0.02. The values calculated using the high pH reaction differ by less than 100 J/mol ($<$ 0.02 logK units) for the standard Gibbs energy and enthalpy, by 0.13 J/mol/K in entropy, and by 0.8 J/mol/K in heat capacity. This agreement indicates that the calculation scheme is consistent.

5.1.1.3   Summary of the system Al – H$_2$O

5.1.1.3.1   Elemental aluminium

Aluminium metal and gas are not relevant under environmental conditions. Hence, the gas phase is not included in the data base. The absolute entropy and heat capacity of Al(cr) are included as they are used for the calculation of certain thermodynamic reaction properties. The selected values are taken from CODATA (COX et al. 1989).

$$S_m° \text{ (Al, cr, 298.15 K)} \quad = \quad (28.30 \pm 0.10) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{p,m}° \text{ (Al, cr, 298.15 K)} \quad = \quad (24.20 \pm 0.07) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

5.1.1.3.2   Simple aluminium aqua ion

In aqueous media, aluminium exists exclusively in the +III oxidation state. The selected values for the standard properties of Al^{3+} were derived from reaction properties for the dissolution of gibbsite, Al(OH)$_3$(cr), in acid solution.

$$\Delta_f G_m° \text{ (Al}^{3+}, \text{ aq, 298.15 K)} \quad = \quad \text{-487.740 kJ} \cdot \text{mol}^{-1}$$

$$\Delta_f H_m° \text{ (Al}^{3+}, \text{ aq, 298.15 K)} \quad = \quad \text{-538.424 kJ} \cdot \text{mol}^{-1}$$

$$S_m° \text{ (Al}^{3+}, \text{ aq, 298.15 K)} \quad = \quad \text{-337.71 J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{p,m}° \text{ (Al}^{3+}, \text{ aq, 298.15 K)} \quad = \quad \text{-133.07 J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

5.1.1.3.3   Aluminium oxygen and hydrogen compounds

5.1.1.3.3.1 Aqueous aluminium hydroxide complexes

Thermodynamic data on Al hydrolysis were selected which are consistent with experimental solubility data of gibbsite, Al(OH)$_3$(cr), and the standard properties of Al^{3+}. They refer to the reaction

$$Al^{3+} + n\ H_2O(l) \Leftrightarrow Al(OH)_n^{(3-n)} + n\ H^+$$

$$\log_{10}{}^*\beta_1{}^\circ\ (n = 1,\ 298.15\ \text{K}) \quad = \quad -4.957$$

$$\log_{10}{}^*\beta_2{}^\circ\ (n = 2,\ 298.15\ \text{K}) \quad = -10.594$$

$$\log_{10}{}^*\beta_3{}^\circ\ (n = 3,\ 298.15\ \text{K}) \quad = -16.432$$

$$\log_{10}{}^*\beta_4{}^\circ\ (n = 4,\ 298.15\ \text{K}) \quad = -22.879$$

$$\Delta_r H_m{}^\circ(n = 1,\ 298.15\ \text{K}) \quad = 49.798\ \text{kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m{}^\circ(n = 2,\ 298.15\ \text{K}) \quad = 98.282\ \text{kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m{}^\circ(n = 3,\ 298.15\ \text{K}) \quad = 144.704\ \text{kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m{}^\circ(n = 4,\ 298.15\ \text{K}) \quad = 180.899\ \text{kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r C_{p,m}{}^\circ(n = 1,\ 298.15\ \text{K}) \quad = 127.194\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_r C_{p,m}{}^\circ(n = 2,\ 298.15\ \text{K}) \quad = 134.306\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_r C_{p,m}{}^\circ(n = 3,\ 298.15\ \text{K}) \quad = 155.645\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_r C_{p,m}{}^\circ(n = 4,\ 298.15\ \text{K}) \quad = -57.321\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

5.1.1.3.3.2 Solid aluminium oxides and hydroxides

Al_2O_3(cr): Thermochemical data for corundum, Al_2O_3(cr), are given by COX et al. (1989) as recommended CODATA values

$$\Delta_f H_m{}^\circ\ (Al_2O_3,\ \text{cr},\ 298.15\ \text{K}) = -(1675.7 \pm 1.3)\ \text{kJ} \cdot \text{mol}^{-1}$$

$$S_m{}^\circ\ (Al_2O_3,\ \text{cr},\ 298.15\ \text{K}) = -(50.92 \pm 0.10)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{p,m}{}^\circ\ (Al_2O_3,\ \text{cr},\ 298.15\ \text{K}) = (79.03 \pm 0.20)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Corundum is a high temperature phase formed only in certain igneous and metamorphic rocks. In hydrothermal systems corundum reacts to diaspore (AlOOH) when the temperature decreases. This hydration reaction is hindered at ambient conditions due to very slow reaction kinetics. However, corundum is never formed under groundwater conditions. In summary, we decided not to include corundum in our data base.

$Al(OH)_3$(cr): A number of solubility studies have been reported for gibbsite, $Al(OH)_3$(cr). Scrutinising the available data we selected for the reaction

$$Al(OH)_3(\text{cr}) + 3\ H^+ \Leftrightarrow Al^{3+} + 3\ H_2O(l)$$

$$\log_{10}{}^*K_{s,0}{}^\circ\ (Al(OH)_3,\ \text{cr},\ 298.15\ \text{K}) \quad = \quad 7.756$$

$$\Delta_r H_m{}^\circ(Al(OH)_3,\ \text{cr},\ 298.15\ \text{K}) \quad = \quad -102.784\ \text{kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r C_{p,m}°(Al(OH)_3, cr, 298.15\ K) \qquad = \qquad -1.255\ J \cdot K^{-1} \cdot mol^{-1}$$

$$\Delta_f G_m° \ (Al(OH)_3, cr, 298.15\ K) = \quad -487.740\ kJ \cdot mol^{-1}$$

$$\Delta_f H_m° \ (Al(OH)_3, cr, 298.15\ K) = \quad -538.424\ kJ \cdot mol^{-1}$$

$$S_m° \ (Al(OH)_3, cr, 298.15\ K) \quad = \quad -337.71\ J \cdot K^{-1} \cdot mol^{-1}1$$

$$C_{p,m}° \ (Al(OH)_3, cr, 298.15\ K) \quad = \quad 91.72\ J \cdot K^{-1} \cdot mol^{-1}$$

$C_{p,m}°(Al(OH)_3, cr) = 13.073 + 40.696 \cdot 10^{-3} / T - 2.920 \cdot 10^5 / T^2$, note: $C_{p,m}°$ in $cal \cdot mol^{-1} \cdot K^{-1}$!

5.1.2   Aluminium halogen compounds and complexes

5.1.2.1   Aqueous halogen complexes

Aluminium fluorides: Thermodynamic data on Al fluoride complexation have been reported by BROSSET & ORRING (1943), BAUMANN (1969), AGARWAL & MORENO (1971), KATORINA et al. (1982), YUCHI et al. (1987), and WALKER et al. (1971).

The first study on this topic by BROSSET & ORRING (1943) obtained ñ, the average number of fluoride ions bound per aluminium(III) ion, as a function of fluoride ion concentration, i.e. ñ = f (log[F⁻]), in 0.53M KNO₃ and NH₄NO₃ at 25ºC. In KNO₃ the range of ñ was 0.49 to 3.29; in NH₄NO₃ the range of ñ was 2.23 to 4.65. In the calculation of $\log_{10}K_n$ values BROSSET & ORRING (1943) used six points from the smoothed curve ñ = f (log[F⁻]), ignoring the small systematic differences of data obtained in different media. The stepwise reaction $\log_{10}K_n$ forming $AlF_n^{(3-n)}$ is the dominating equilibrium in the solutions with ñ ≈ n − 0.5 and thus, it is obvious that with a maximum observed value ñ = 4.65, the value of $\log_{10}K_6$ is a very uncertain quantity. KING & GALLAGHER (1959) re-evaluated the experimental data of BROSSET & ORRING (1943) by a more elaborate graphical method, considering that experimental points most appropriate for the evaluation of a particular $\log_{10}K_n$ are those with (n − 0.9) < ñ < (n − 0.1). KING & GALLAGHER (1959) also concluded that the data of BROSSET & ORRING (1943) indicated that different sets of $\log_{10}K_n$ values are appropriate for each of the two media, KNO₃ and NH₄NO₃.

BAUMANN (1969) used a fluoride-sensitive electrode to study the aluminium fluoride complexation in 0.5, 0.3, 0.1 and 0.01M NH₄NO₃ at 25ºC. The range of ñ, the average number of fluoride ions bound per aluminium(III) ion, was 0.5 to 3.8 and thus, the experimental data was not sufficient to define $\log_{10}K_5$ and $\log_{10}K_6$ experimentally. Reasonable values of 1.5 and 0.5, respectively, were chosen to establish the formation curve and to improve the accuracy of the calculated $\log_{10}K_4$.

Table 5.1.12: Experimental $\log K_n$ data compiled for the equilibria $AlF_{n-1}^{(4-n)} + F^- \Leftrightarrow AlF_n^{(3-n)}$. Methods: pot = potentiometry, calc = re-evaluation of BROSSET & ORRING (1943) data, ise = ion selective electrode.

Method	Temp (°C)	Medium (M)	I	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	$\log K_6$	Reference
pot	25	KNO_3	0.53	6.13	5.02	3.85	2.74	1.63	(0.47)	BROSSET & ORRING (1943)
calc	25	KNO_3	0.53	6.16	5.05	3.91	2.71	(1.46)		KING & GALLAGHER (1959)
		NH_4NO_3	0.53			3.57	2.64	1.46	(0.04)	
ise	25	NH_4NO_3	0.5	6.08	4.93	3.69	2.50			BAUMANN (1969)
			0.3	6.29	4.97	3.73	2.50			
			0.1	6.40	5.19	3.91	2.42			
			0.01	6.65	5.44	3.92	2.38			
ise	25	NH_4NO_3	0.5	6.14	5.09	3.93	(3.68)			AGARWAL&MORENO (1971)
			0.2	6.32	5.16	3.85	(3.30)			
			0.1	6.45	5.21	3.79	(3.18)			
			0.05	6.51	5.29	3.76	(3.05)			
	37		0.5	6.29	5.09	3.84	(3.43)			
			0.2	6.39	5.17	3.86	(3.38)			
			0.1	6.49	5.24	3.86	(3.38)			
			0.05	6.71	5.26	3.92	(3.29)			
ise	25	NH_4NO_3	1.0		4.8	3.6	2.6	1.6	0.9	KATORINA et al. (1982)
			0.5		4.98	3.72	2.67			
			0.2	6.40	4.98	3.72	2.67			
ise	25	KNO_3	0.1	6.40	5.24	3.86	(2.7)			YUCHI et al. (1987)
pot	25	$NaClO_4$	1.0	6.09						WALKER et al. (1971)

AGARWAL & MORENO (1971) used the same type of fluoride-sensitive electrode as BAUMANN (1969) to study the aluminium fluoride complexation in 0.5, 0.3, 0.1 and 0.05M KNO_3 at 25 and 37ºC. Formation constants have been calculated by different methods, and the authors reported that best results have been obtained by applying a generalised non-linear least squares fit. However, the values reported for $\log_{10} K_4$ can only be considered as approximate, as the range of experimentally determined values for ñ extends only to about 2.8.

KATORINA et al. (1982) used the fluoride-sensitive electrode to study the aluminium fluoride complexation in 1.0, 0.5, and 0.2M NH_4NO_3 at 25ºC in the pH range 2 − 5. The authors claim that no ionic strength effect has been observed and fitted all experimental data to a common formation curve. This result is somewhat surprising, at least $\log_{10} K_1$, and to a lesser extend $\log_{10} K_2$, are expected to exhibit a measurable dependence on ionic strength. However, a close examination of the numerical data reported by KATORINA et al. (1982) revealed that their results are not in contradiction with our expectations. Measurements in 1.0M NH_4NO_3 cover the range 1.6 < ñ < 5.4, in 0.5M NH_4NO_3 it is 1.0 < ñ < 3.8, and in 0.2M NH_4NO_3 0.7 < ñ < 3.7. Hence, the values of $\log_{10} K_6$ and $\log_{10} K_5$ are experimentally defined only in 1.0M NH_4NO_3 solutions. In the range 1.6 < ñ < 3.7 all data series overlap, and for ñ > 2 we indeed found no variation with ionic strength.

This means that common values of $\log_{10}K_4$ and $\log_{10}K_3$ may represent the experimental data. But towards the "lower end" of the 1.0M data a significant shift commences which may be represented by an increase of $\log_{10}K_2$ by at least 0.1 with respect to the 0.5 and 0.2M data. Finally, the value of $\log_{10}K_1$ is experimentally defined only in 0.2M NH_4NO_3 solutions.

YUCHI et al. (1987) used the fluoride-sensitive electrode to study trivalent metal fluoride complexation in 0.1M KNO_3 at 25ºC. No experimental data for the aluminium fluoride system are reported in this paper (e.g. in Fig. 1 of YUCHI et al. (1987) the caption reads "data for aluminum and yttrium complexes are omitted for clarity"). However, comparing the other data ranges with the reported uncertainties of the respective formation constants, the value reported for $\log_{10}K_4$ can only be considered as approximate.

WALKER et al. (1971) studied the first Al fluoride complexation step by potentiometry in 1.0M $NaClO_4$ at 25°C. They also report an enthalpy of reaction value obtained calorimetrically under the same conditions.

These data, summarised in Table 5.1.12, have been extrapolated to zero ionic strength using SIT. Approximate data, given in parentheses in Table 5.1.12, and values at I < 0.1M have been excluded from the regression analyses. No systematic differences have been found for data referring to KNO_3 or NH_4NO_3 media (Fig. 5.1.5). The $\log_{10}K_1$ value of WALKER et al. (1971) referring to 1.0M $NaClO_4$ has not been included in the regression analysis. Surprisingly, it agrees perfectly with the extrapolated regression line calculated with $\log_{10}K_1$ data in KNO_3 and NH_4NO_3 media (Fig. 5.1.5)

The results are

$$AlF_{n-1}^{(4-n)} + F^- \Leftrightarrow AlF_n^{(3-n)}$$
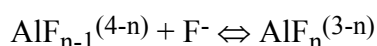
$$\log_{10}K_1° \text{ (n = 1, 298.15 K)} = 7.08 \pm 0.07 \qquad \Delta\varepsilon = -0.23 \pm 0.21$$

$$\log_{10}K_2° \text{ (n = 2, 298.15 K)} = 5.65 \pm 0.08 \qquad \Delta\varepsilon = -0.04 \pm 0.17$$

$$\log_{10}K_3° \text{ (n = 3, 298.15 K)} = 4.05 \pm 0.11 \qquad \Delta\varepsilon = -0.09 \pm 0.22$$

$$\log_{10}K_4° \text{ (n = 4, 298.15 K)} = 2.51 \pm 0.14 \qquad \Delta\varepsilon = -0.19 \pm 0.25$$

$$\log_{10}K_5° \text{ (n = 5, 298.15 K)} = 1.0 \pm 0.2$$

$$\log_{10}K_6° \text{ (n = 6, 298.15 K)} = 0 \pm 0.3$$

Note that the values for $\log_{10}K_5°$ and $\log_{10}K_6°$ are estimates based on two and one data point, respectively, and the observed trend for the other stepwise stability constants (Fig. 5.1.5). Anyhow, AlF_5^{2-} and AlF_6^{3-} are negligible for any natural water (see Fig. 5.1.6).

The fluoride complexation constants evaluated by NORDSTROM & MAY (1996) agree with the values selected in this review within their assigned uncertainties.

Values for the enthalpy of reaction are taken from the careful calorimetric study of LATIMER & JOLLY (1953). They measured $\Delta_r H_m$ values at ionic strengths from 0.06 to 0.2. They did not mention any significant variation with ionic strength and thus, we assumed that their results are also valid at I = 0. Uncertainties are assigned according to the estimates given by LATIMER & JOLLY (1953).

$$\Delta_r H_m°(n = 1, 298.15 \text{ K}) = (1.15 \pm 0.05) \text{ kcal} \cdot \text{mol}^{-1} \rightarrow (4.8 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m°(n = 2, 298.15 \text{ K}) = (0.78 \pm 0.10) \text{ kcal} \cdot \text{mol}^{-1} \rightarrow (3.3 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m°(n = 3, 298.15 \text{ K}) = (0.19 \pm 0.10) \text{ kcal} \cdot \text{mol}^{-1} \rightarrow (0.8 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m°(n = 4, 298.15 \text{ K}) = (0.28 \pm 0.10) \text{ kcal} \cdot \text{mol}^{-1} \rightarrow (1.2 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m°(n = 5, 298.15 \text{ K}) = -(0.75 \pm 0.10) \text{ kcal} \cdot \text{mol}^{-1} \rightarrow -(3.1 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m°(n = 6, 298.15 \text{ K}) = -(1.55 \pm 0.20) \text{ kcal} \cdot \text{mol}^{-1} \rightarrow -(6.5 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$$

The enthalpy data reported by NORDSTROM et al. (1990) and NORDSTROM & MAY (1996) were also taken from LATIMER & JOLLY (1953). Note however, that their first five $\Delta_r H_m°$ values refer to the overall reaction $\log_{10}\beta_n°$ whereas the last one erroneously seems to refer to $\log_{10}K_6°$.

TÓTH et al. (1985) and COUTURIER (1986) report the formation of mixed Al fluoride hydroxide complexes. TÓTH et al. (1985) varied the ionic medium from 0.5M KNO_3 to 0.05M KNO_3/0.45M total fluoride at constant total Al concentration and interpreted the observed pH change (at pH 11) as the formation of $Al(OH)_3F^-$. COUTURIER (1986) reports the formation of the species $AlOHF^+$ and $AlOHF_2(aq)$ in "weakly acidic" solutions and the formation of $Al(OH)_3F^-$ in "weakly basic" solutions (0.1M KNO_3). The stability constants reported by TÓTH et al. (1985) and COUTURIER (1986) for $Al(OH)_3F^-$ differ by more than one order of magnitude. In the present review no attempt has been made to resolve this ambiguity, and the possible importance of these mixed complexes has not been explored.

Aluminium chlorides: Aluminium chloride complexes are expected to be weak and it probably would be difficult to distinguish between complex formation and changes in the activity coefficients of the solutes. Hence, no experimental data on aluminium chloride complexation are available.
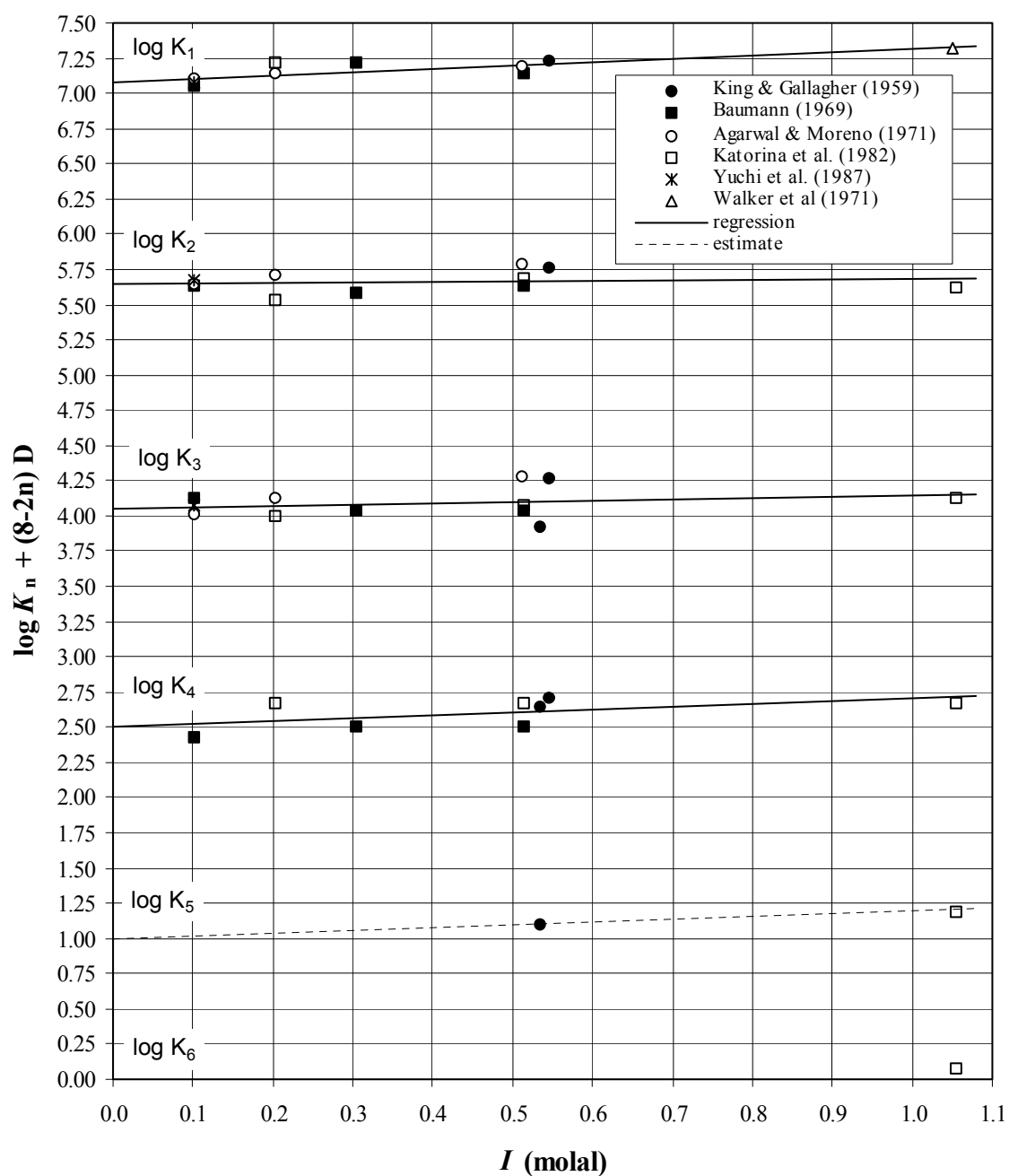
Fig. 5.1.5: Extrapolation to zero ionic strength of experimental data for the formation of $AlF_n^{(3-n)}$ using SIT. The data are taken from Table 5.1.12. Approximate data, given in parentheses in Table 5.1.12, and values at $I < 0.1M$ have been excluded from the regression analyses.

5.1.2.2   Aluminium halide compounds

$AlCl_3(s)$ (hygroscopic), $AlCl_3 \cdot 6H_2O(s)$ (hygroscopic), $AlF_3(s)$ and $AlF_3 \cdot 3H_2O(s)$ are highly soluble (and toxic!) salts. They are of no relevance for environmental modelling.

Thermodynamic data are available for the mineral cryolite (Na_3AlF_6) (NORDSTROM et al. 1990):

$$Na_3AlF_6(s) \Leftrightarrow 3\ Na^+ + Al^{3+} + 6\ F^-$$
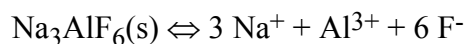
$$\log_{10}K_{s,0}° \text{ (Cryolite, cr, 298.15 K)} = -33.84$$

$$\Delta_r H_m°\text{(Cryolite, cr, 298.15 K)} = 9.09 \text{ kcal} \cdot \text{mol}^{-1} \rightarrow 38.03 \text{ kJ} \cdot \text{mol}^{-1}$$

However, a predominance diagram of the system Al - F - H_2O reveals that cryolite may be of relevance only in extreme water compositions characterised by high fluoride concentrations (Fig. 5.1.6). Following our philosophy of ballast discharge we decided not to include cryolite in the present version of our data base.
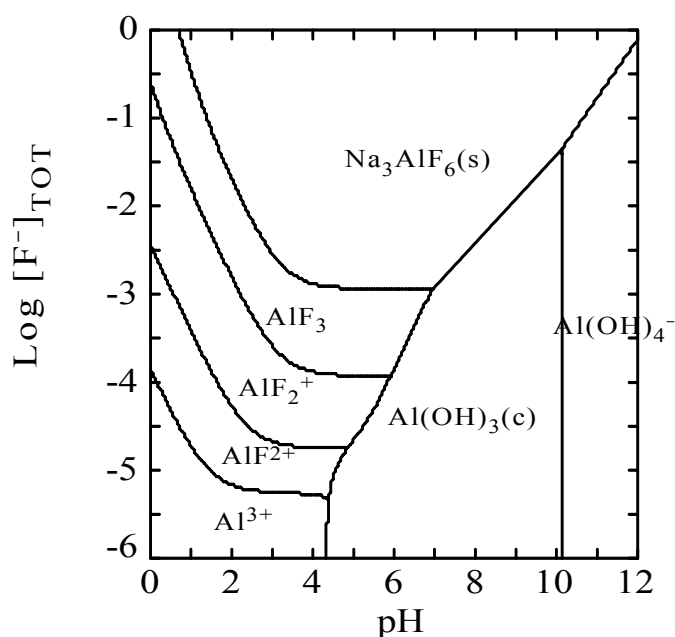
Fig. 5.1.6: Predominance diagram of the system Al – F – H_2O at zero ionic strength, at constant Na concentration of 0.1M and total Al concentration of 10^{-5}M. Data for Al hydrolysis constants and the solubility of gibbsite, $Al(OH)_3(cr)$, as well as aqueous Al fluoride complexes are selected in this review (see Sections 5.1.1.3.3 and 5.1.2.1). The solubility of cryolite, $Na_3AlF_6(s)$ is taken from NORDSTROM et al. (1990).

5.1.3   Aluminium chalcogen compounds and complexes

No data for aluminium sulphides are available. However, Al sulphide complexes are expected to be very weak, if they exist at all; and $Al_2S_3(s)$ is a moisture sensitive substance which decomposes in water! They are of no relevance for environmental modelling.

5.1.3.1   Aqueous aluminium sulphates

Although the complexing of aluminium with sulphate is significantly weaker than with fluoride, it is strong enough to have an effect on potentiometric, conductance and spectroscopic measurements of aluminium sulphate solutions. However, evaluation of published data for aluminium sulphate stability constants revealed largely discrepant values (NORDSTROM & MAY 1996, RIDLEY et al. 1999).

NORDSTROM & MAY (1996) found that published $\log_{10}\beta_1°$ values for the reaction

$$Al^{3+} + n\ SO_4^{2-} \Leftrightarrow Al(SO_4)_n^{(3-2n)}$$
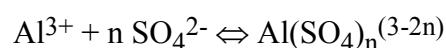
show a bimodal distribution suggesting that the value should be close to either 3.2 or 3.8. They selected the midpoint value, $\log_{10}\beta_1° = 3.5 \pm 0.5$, with an uncertainty that covers the range of "better literature values". RIDLEY et al. (1999) presented a list of literature values for $\log_{10}\beta_1°$ and $\log_{10}\beta_2°$ varying by more than two orders of magnitude, but they did not discuss these discrepancies.

An early attempt to unravel these largely discrepant results within the scope of this review project had to be postponed due to time constraints. We decided to rely in this review on the potentiometric study of RIDLEY et al. (1999). They measured aluminium sulphate complexation in 0.1, 0.2 and 1.0m NaCl media from 50 to 125°C. Their reported experimental results do not show any significant temperature variation for $\log_{10}\beta_1$ data at 50, 75 and 100°C, and for $\log_{10}\beta_2$ data at 50 and 75°C. In all these cases SIT plots of experimental data are compatible with $\Delta\varepsilon \approx 0$ considering the scatter of data points. Hence, unweighted averages of 50, 75 and 100°C $\log_{10}\beta_1+12D$ data, and 50 and 75°C $\log_{10}\beta_2 + 16 D$ data ($D = A\cdot\sqrt{I_m}/(1+1.5\cdot\sqrt{I_m})$) give a reasonable representation of 25°C values at I = 0:

$$\log_{10}\beta_1° (n = 1, 298.15\ K) = 3.9 \pm 0.2$$
$$\log_{10}\beta_2° (n = 2, 298.15\ K) = 5.9 \pm 0.5$$

No enthalpy of reaction values are selected in this review. However, in the temperature range 25 to 75°C constant $\log_{10}\beta_n°$ values are a sufficient approximation to the experimental findings of RIDLEY et al. (1999).

In addition, NORDSTROM et al. (1990) selected $\log_{10}\beta_1° = 0.46$ for the equilibrium $Al^{3+} + HSO_4^- \Leftrightarrow AlHSO_4^{2+}$. The source of this rather weak complex and its compatibility with the experimental findings of RIDLEY et al. (1999) has not been checked in this review. The value is not included in the data base.

5.1.3.2 Aluminium sulphate compounds

$Al_2(SO_4)_3(s)$ and $Al_2(SO_4)_3 \cdot 18H_2O(s)$ are hygroscopic, highly soluble salts. They are of no relevance for environmental modelling.

Thermodynamic data are available for the mineral alunite ($KAl_3(SO_4)_2(OH)_6$) (NORDSTROM et al. 1990):

$$KAl_3(SO_4)_2(OH)_6(s) + 6\,H^+ \Leftrightarrow K^+ + 3\,Al^{3+} + 2\,SO_4^{2-} + 6\,H_2O(l)$$
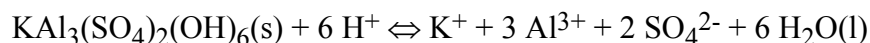
$$\log_{10}{}^*K_{s,0}° \text{ (Alunite, cr, 298.15 K)} = -1.4$$

$$\Delta_r H_m° \text{(Alunite, cr, 298.15 K)} = -50.25 \text{ kcal} \cdot \text{mol}^{-1} \rightarrow -210.25 \text{ kJ} \cdot \text{mol}^{-1}$$

The solubility constant of $KAl_3(SO_4)_2(OH)_6(s)$ reveals that alunite is a highly soluble salt which may be of relevance only in acidic mine waters characterised by high concentrations of sulphuric acid. Following our philosophy of ballast discharge we decided not to include alunite in the present version of our data base.

5.1.4 Group 15 compounds and complexes

5.1.4.1 Aluminium nitrogen compounds and complexes

Aluminium nitrate complexes: Aluminium nitrate complexes are expected to be very weak and it would be difficult to distinguish between complex formation and changes in the activity coefficients of the solutes. Hence, no experimental data on aluminium nitrate complexation are available.

Aluminium nitrate compounds: $Al(NO_3)_3 \cdot 9H_2O(s)$ is a toxic, highly soluble salt used as oxidation agent. It is of no relevance for environmental modelling.

5.1.4.2   Phosphorous compounds and complexes

Aqueous systems involving aluminium – phosphate interactions are notoriously difficult to characterise experimentally and aluminium – phosphate complexes have not often been studied. NORDSTROM & MAY (1996) report two estimated values for the complexes $AlH_2PO_4^{2+}$ and $AlHPO_4^+$. We decided not to include these estimates in the present version of our data base.

More than one hundred rare minerals containing Al and phosphate have been characterised in terms of chemical composition and structural parameters. The chemically simplest one is berlinite, $AlPO_4(s)$. However, no thermodynamic data for any of these compounds are known to us.

5.1.5   Group 14 compounds and complexes

5.1.5.1   Aluminium carbonate compounds and complexes

No values for aluminium – carbonate complexes can be found in thermodynamic data compilations. NORDSTROM & MAY (1996) report that the only experimental study known to them (HEDLUND et al. 1987) can be interpreted by assuming the formation of polymeric aluminium – hydroxide – carbonate (and bicarbonate) species. NORDSTROM & MAY (1996) conclude that the high pCO_2 and the difficulty of interpreting these results indicate that aluminium and carbonate or bicarbonate ions have very weak interactions that can be neglected for most natural waters.

$Al_2(CO_3)_3(s)$ belongs to the class of "non-existing compounds". However, aluminium - carbonate - hydroxide minerals are known ("basic aluminium carbonates" as the chemists call them), for example dawsonite, $NaAl(OH)_2CO_3(s)$. The most important mineral of this type is hydrotalcite, $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O(s)$. Its nickel analogue is takovite, $Ni_6Al_2(OH)_{16}CO_3 \cdot 4H_2O(s)$. Hydrotalcite and takovite are two end-members of a vast group of solid-solutions called "layered double hydroxides" with the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2][(A^{y-})_{x/y}(H_2O)_n]$ where A represents an anion. These solid-solution systems are important in cementitious waste forms and they are explored more generally in studies concerning the immobilisation of hazardous waste. Qualitative results are abundant but no quantitative thermodynamic data have yet been published.

5.1.5.2   Aluminium silicate compounds and complexes

Aqueous aluminium silicate complexes and aluminium silicate minerals are discussed in Chapter 5.18.4.2.

Table 5.1.13: Selected aluminium data.

TDB Version 05/92			TDB Version 01/01					
Name	$\Delta_f G_m°$	$\Delta_f H_m°$	Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$S_m°$	$C_{p,m}°$	Species
	-	-	Al(cr)	0.0	0.0	28.30 ± 0.10	24.20 ± 0.07	Al(cr)
GIBBS_CR	-1156.629	-1300.495	Gibbsite	-1154.89 ± 0.90	-1293.13 ± 0.90	68.44 ± 0.14	91.72*	$Al(OH)_3(cr)$
AL+3	-491.5	-538.4	Al+3	-487.740	-538.424	-337.71	-133.07	Al^{3+}

Name	$\log_{10}\beta°$	$\Delta_r H_m°$	$\Delta_r C_{p,m}°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	$\Delta_r C_{p,m}°$	Reaction
ALOH+2	-5.003	48.079	119.119	AlOH+2	-4.957	49.798	127.194	$Al^{3+} + H_2O(l) \Leftrightarrow AlOH^{2+} + H^+$
ALOH2+	-10.109	112.566	-225.492	Al(OH)2+	-10.594	98.282	134.306	$Al^{3+} + 2\ H_2O(l) \Leftrightarrow Al(OH)_2^+ + 2\ H^+$
ALOH3	-16.940	166.903	-611.908	Al(OH)3	-16.432	144.704	155.645	$Al^{3+} + 3\ H_2O(l) \Leftrightarrow Al(OH)_3(aq) + 3\ H^+$
ALOH4-	-22.665	176.973	-123.592	Al(OH)4-	-22.879	180.899	-57.321	$Al^{3+} + 4\ H_2O(l) \Leftrightarrow Al(OH)_4^- + 4\ H^+$
ALF+2	7.0	4.435	0	AlF+2	7.08 ± 0.07	4.8 ± 0.2		$Al^{3+} + F^- \Leftrightarrow AlF^{2+}$
ALF2+	12.7	8.284	0	AlF2+	12.73 ± 0.11	8.1 ± 0.5		$Al^{3+} + 2\ F^- \Leftrightarrow AlF_2^+$
ALF3	16.8	9.037	0	AlF3	16.78 ± 0.15	8.9 ± 0.7		$Al^{3+} + 3\ F^- \Leftrightarrow AlF_3(aq)$
ALF4-	19.4	9.205	0	AlF4-	19.29 ± 0.20	10.1 ± 0.8		$Al^{3+} + 4\ F^- \Leftrightarrow AlF_4^-$
ALF5-2	20.6	7.699	0	AlF5-2	20.3 ± 0.3	7.0 ± 0.9		$Al^{3+} + 5\ F^- \Leftrightarrow AlF_5^{2-}$
ALF6-3	20.6	-6.987	0	AlF6-3	20.3 ± 0.4	0.5 ± 1.2		$Al^{3+} + 6\ F^- \Leftrightarrow AlF_6^{3-}$
ALSO4+	3.02	8.996	0	AlSO4+	3.9 ± 0.2			$Al^{3+} + SO_4^{2-} \Leftrightarrow AlSO_4^+$
ALSO42-	4.92	11.883	0	Al(SO4)2-	5.9 ± 0.5			$Al^{3+} + 2\ SO_4^{2-} \Leftrightarrow Al(SO_4)_2^-$
ALHSO4+2	0.462	0	0		-	-		$Al^{3+} + HSO_4^- \Leftrightarrow AlHSO_4^{2+}$

Name	$\log_{10}K_{s,0}°$	$\Delta_r H_m°$	Name	$\log_{10}K_{s,0}°$	$\Delta_r H_m°$	$\Delta_r C_{p,m}°$	Reaction
GIBBS_CR	8.11	-95.395	Gibbsite	7.756	-102.784	1.255	$Al(OH)_3(cr) + 3\ H^+ \Leftrightarrow Al^{3+} + 3\ H_2O(l)$
GIBBS_MC	9.35	-102.508		-	-		$Al(OH)_3(micr) + 3\ H^+ \Leftrightarrow Al^{3+} + 3\ H_2O(l)$
AL(OH)3	10.80	-110.876		-	-		$Al(OH)_3(am) + 3\ H^+ \Leftrightarrow Al^{3+} + 3\ H_2O(l)$

*Maier - Kelley coefficients for $C_{p,m}° = a + b/T - c/T^2$: $a = 13.073$, $b = 40.696 \cdot 10^{-3}$, $c = 2.920 \cdot 10^5$, note: $C_{p,m}°$ function in $cal \cdot mol^{-1} \cdot K^{-1}$!

5.1.6   References

AGARWAL, R.P., MORENO, E.C. (1971): Stability constants of aluminium fluoride complexes. Talanta, 18, 873-880.

BAUMANN, E.W. (1969): Determination of stability constants of hydrogen and aluminum fluorides with a fluoride-selective electrode. J. Inorg. Nucl. Chem., 31, 3155-3162.

BLOOM, P.R., WEAVER, R.M. (1982): Effect of the removal of reactive surface material on the solubility of synthetic gibbsites. Clays and Clay Minerals, 30, 281-286.

BROSSET, C., ORRING, J. (1943): Studies on the consecutive formation of aluminium fluoride complexes. Svensk Kemisk Tidskrift, 55, 101-116.

COUTURIER, Y. (1986): Contribution à l'étude des complexes mixtes de l'aluminium(III) avec les ions fluorure et hydroxyde. Bulletin de la Société Chimique de France, 171-177.

COUTURIER, Y., MICHARD, G., SARAZIN, G. (1984): Constantes de formation des complexes hydroxydés de l'aluminium en solution aqueuse de 20 a 70°C. Geochimica et Cosmochimica Acta, 48, 649-659.

COX, J.D., WAGMAN, D.D., MEDVEDEV, V.A. (1989): CODATA Key Values for Thermodynamics. New York, Hemisphere Publishing, 271p.

HEDLUND, R., SJÖBERG, S., ÖHMAN, L.O. (1987): Equilibrium and structural studies of silicon (IV) and aluminium (III) in aqueous solution. 15. A potentiometric study of speciation and equilibria in the Al^{3+}-CO_2(g)-OH system. Acta Chem. Scand. Ser. A 41, 197.

HELGESON, H.C., DELANY, J.M., NESBITT, H.W., BIRD, D.K. (1978): Summary and Critique of the Thermodynamic Properties of Rock-Forming Minerals. American Journal of Science, 278-A, 1-229.

HEMINGWAY, B.S., ROBIE, R.A. (1977): Enthalpies of formation of low albite ($NaAlSi_3O_8$), gibbsite ($Al(OH)_3$) and $NaAlO_2$: revised values for $\Delta H°_{f,298}$ and $\Delta G°_{f,298}$ of some alumino-silicate minerals. U. S. Geological Survey Journal of Research, 5, 413-429.

HEMINGWAY, B.S., ROBIE, R.A., FISHER, J.R., WILSON, W.H. (1977): The heat capacities of gibbsite, $Al(OH)_3$, between 13 and 480 K and magnesite, $MgCO_3$, between 13 and 380 K and their standard entropies at 298.15 K, and the heat capacities of benzoic acid between 12 and 316 K. U. S. Geological Survey Journal of Research, 5, 797-806.

HEMINGWAY, B.S., SPOSITO, G. (1989): Inorganic Aluminum Bearing Solid Phases. In: SPOSITO, G. (ed.): The Environmental Chemistry of Aluminium. CRC Press, Lewis Publishers, Boca Raton, USA, 55-85.

JOHNSON, J.W., OELKERS, E.H., HELGESON, H.C. (1992): SUPCRT92 - A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1-bar to 5000-bar and 0 to 1000-degrees-C. Computers & Geosciences, 18, 899-947.

KARPOV, I.K., CHUDNENKO, K.V., KULIK, D.A. (1997): Modeling chemical mass transfer in geochemical processes: Thermodynamic relations, conditions of equilibria, and numerical algorithms. American Journal of Science, 297, 767-806.

KATORINA, O.V., MASALOVICH, V.M., KOROBITSYN, A. S. (1982): Stability Constants of Aluminium Fluoro-complexes. Russian Journal of Inorganic Chemistry, 27, 1566-1567.

KELLEY, K.K. (1960): High-Temperature Heat-Content, Heat-Capacity, and Entropy Data for the Elements and Inorganic Compounds. Washington, D. C., U. S. Bureau of Mines, Contributions to the Data on Theoretical Metallurgy XIII, 232 p.

KING, E.L., GALLAGHER, P.K. (1959): The thermodynamics of aluminium(III) complex ion reactions. The graphical evaluation of equilibrium quotients from ñ([x]). The Journal of Physical Chemistry, 63, 1073-1076.

LATIMER, W.M., JOLLY, W.L. (1953): Heats and Entropies of Successive Steps in the Formation of AlF_6^{---}. J. Amer. Chem. Soc., 75, 1548-1550.

MAY, H.M., HELMKE, P.A., JACKSON, M.L. (1979): Gibbsite solubility and thermodynamic properties of hydroxy-alumimum ions in aqueous solution at 25°C. Geochimica et Cosmochimica Acta, 43, 861-868.

NORDSTROM, D.K., MAY, H.M. (1989): Aqueous Equilibrium Data for Mononuclear Aluminum Species. In: SPOSITO, G. (ed.): The Environmental Chemistry of Aluminum. CRC Press, Lewis Publishers, Boca Raton, USA, 29-53.

NORDSTROM, D.K., MAY, H.M. (1996): Aqueous Equilibrium Data for Mononuclear Aluminium Species. In: SPOSITO, G. (ed.): The Environmental Chemistry of Aluminium. CRC Press, Lewis Publishers, Boca Raton, USA, 39-80.

NORDSTROM, D.K., PLUMMER, L.N., LANGMUIR, D., BUSENBERG, E., MAY, H.M., JONES, B.F., PARKHURST, D.L. (1990): Revised Chemical Equilibrium Data for Major Water-Mineral Reactions and Their Limitations. In: MELCHIOR, D. C., BASSET, R. L. (eds.): Chemical Modeling of Aqueous Systems II. Washington, D.C., American Chemical Society, ACS Symposium Series 416, 398-413.

PALMER, D.A., WESOLOWSKI, D.J. (1992): Aluminum speciation and equilibria in aqueous solution: II. The solubility of gibbsite in acidic sodium chloride solutions from 30 to 70°C. Geochimica et Cosmochimica Acta, 56, 1093-1111.

PALMER, D.A., WESOLOWSKI, D.J. (1993): Aluminum speciation and equilibria in aqueous solution: III. Potentiometric determination of the first hydrolysis constant of aluminum(III) in sodium chloride solutions to 125°C. Geochimica et Cosmochimica Acta, 57, 2929-2938.

PARKHURST, D.L. (1995): User's Guide to PHREEQC - A Computer Program for Speciation, Reaction-Path, Advective-Transport, and Inverse Geochemical Calculations. Lakewood, CO, U. S. Geological Survey, Water-Resources Investigations Report 95-4227, 143 p.

PARKHURST, D.L., APPELO, C.A.J. (1999): User's Guide to PHREEQC (Version 2) - A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. Denver, CO, U. S. Geological Survey, Water-Resources Investigations Report 99-4259, 312 p.

PEARSON, F.J. JR., AVIS, J.D. (1989): PMATCH: A Program to Manage Thermochemical Data, Version 1.21. Nagra Interner Bericht, Wettingen, Switzerland, 62 p.

PEARSON, F.J. JR., BERNER, U. (1991): Nagra Thermochemical Data Base I. Core Data. Nagra Technical Report NTB 91-17, Wettingen, Switzerland, 70 p.

PEARSON, F.J. JR., BERNER, U., HUMMEL, W. (1992): Nagra Thermochemical Data Base II. Supplemental Data 05/92. Nagra Technical Report NTB 91-18, Wettingen, Switzerland, 284 p.

PEARSON, F.J., AVIS, J.D., NILSSON, K., JENSEN, B.S. (1993): Geochemical databases - Part I: Pmatch: A program to manage thermochemical data - Part II: The experimental validation of geochemical computer models. Final Report EUR 14170 EN, Commission of the European Communities, Luxembourg, 397 p.

POKROVSKII, V.A., HELGESON, H.C. (1995): Thermodynamic properties of aqueous species and the solubilities of minerals at high pressures and temperatures: The system Al_2O_3 - H_2O - NaCl. American Journal of Science, 295, 1255-1342.

RIDLEY, M.K., WESOLOWSKI, D.J., PALMER, D.A., KETTLER, R.M. (1999): Association quotients of aluminum sulphate complexes in NaCl media from 50 to 125°C: Results of a potentiometric and solubility study. Geochimica et Cosmochimica Acta, 63, 459-472.

SHOCK, E.L., SASSANI, D.C., WILLIS, M., SVERJENSKY, D.A. (1997): Inorganic species in geologic fluids: Correlations among standard molal thermodynamic properties of aqueous ions and hydroxide complexes. Geochimica et Cosmochimica Acta, 61, 907-950.

SILVA, R.J., BIDOGLIO, G., RAND, M.H., ROBOUCH, P.B., WANNER, H., PUIGDOMÈNECH, I. (1995): Chemical Thermodynamics of Americium. Elsevier, 374 p.

TÓTH, I., ZÉKÁNY, L., BRÜCHER, E. (1985): Comparative study of hydroxo-fluoro and hydroxo-sulphido mixed ligand complexes of aluminium(III) and gallium(III). Polyhedron, 4, 279-283.

WAGMAN, D.D., EVANS, W.H., PARKER, V.B., SCHUMM, R.H., HALOW, I., BAILEY, S.M., CHURNEY, K.L., NUTTALL, R.L. (1982): The NBS tables of chemical thermodynamic properties: Selected values for inorganic and C_1 and C_2 organic substances in SI units. Journal of Physical and Chemical Reference Data, 11, Supplement No. 2, 1-392.

WALKER, J.B., TWINE, C.R., CHOPPIN, G.R. (1971): Thermodynamic parameters of fluoride complexes of group IIIA ions. J. Inorg. Nucl. Chem., 33, 1813-1817.

WESOLOWSKI, D.J. (1992): Aluminum speciation and equilibria in aqueous solution: I. The solubility of gibbsite in the system Na-K-Cl-OH-Al(OH)$_4$ from 0 to 100°C. Geochimica et Cosmochimica Acta, 56, 1065-1091.

YUCHI, A., HOTTA, H., WADA, H., NAKAGAWA, G. (1987): Mixed Ligand Complexes of Trivalent Metal Ions with an Amine-*N*-polycarboxylate and Fluoride. Bull. Chem. Soc. Japan, 60, 1379-1382.

Table 5.1.1: Summary of data examined for reactions forming Al^{3+} aqueous species and gibbsite solubility. **Bold** numbers represent the values actually entered into the table.

Reaction and Source	logK(Tr)	A	B	C	D	E	DrG	DrH	DrS	(DrH-DrG) / T	DrCp	DrCpa	DrCpb
1) Al+3 + H2O = AlOH+2 + H+													
Nordstrom *et al.* (1990)	-5.003	**-38.253**		**-656.27**	**14.327**		28.557	48.080	65.482	65.482	119.121	119.12144	0
Palmer & Wesolowski (1993) Eq. 7 & Tab. 4	-4.953	**4.76002**		**-2895.92**			28.271	55.442	91.130	91.130	0.000	0	0
Pokrovskii & Helgeson (1995)	-4.957	-40.73041	0	-620.2838	15.29786	0	**28.296**	**49.798**	**72.383**	72.117	**127.194**	127.19	
Shock et al (1997) = slope98.dat	-5.001	-34.51702	0	-889.3228	13.13401	0	**28.543**	**49.585**	**70.291**	70.573	**109.202**	109.20	
2) Al+3 + 2 H2O = Al(OH)2+ + 2 H+	= Al+3 + H2O = AlO+ + 2 H+				**(in Shock et al. 1997)**								
Nordstrom *et al.* (1990)	-10.109	**88.500**	0	**-9391.6**	**-27.121**	0	57.701	112.568	184.026	184.026	-225.497	-225.4968	0
Pokrovskii & Helgeson (1995)	-10.594	-40.36150	0	-3042.0150	16.15333	0	**60.471**	**98.282**	**127.194**	126.818	**134.306**	134.31	
Shock et al (1997) = slope98.dat	-10.342	32.61025	0	-6420.6792	-8.65537	0	**59.032**	**101.466**	**142.256**	142.325	**-71.965**	-71.96	
3) Al+3 +3 H2O = Al(OH)3(aq) + 3 H+	= Al+3 + 2 H2O = HAlO2(aq) + 3 H+				**(in Pokrovskii & Helgeson 1995 and Shock et al. 1997)**								
Nordstrom *et al.* (1990)	-16.940	**226.374**	0	**-18247.8**	**-73.597**	0	96.696	166.906	235.486	235.486	-611.920	-611.92021	0
Pokrovskii & Helgeson (1995)	-16.432	-45.53221	0	-5134.4620	18.71975	0	**93.797**	**144.704**	**171.126**	170.742	**155.645**	155.64	
Shock et al (1997) = slope98.dat	-15.601	91.70758	0	-11463.9412	-27.82801	0	**89.052**	**150.490**	**206.271**	206.064	**-231.375**	-231.38	
4) Al+3 + 4 H2O = Al(OH)4- + 4 H+	= Al+3 + 2 H2O = AlO2- + 4 H+				**(in Pokrovskii & Helgeson 1995 and Shock et al. 1997)**								
Nordstrom *et al.* (1990)	-22.665	**51.578**	0	**-11168.9**	**-14.865**	0	129.373	176.976	159.662	159.662	-123.595	-123.59463	0
ORNL = Reactions (5) - (6) - (7)	-22.877	**-365.20459**	-0.06468122	9992.157	137.6855899	-1119669	130.583	183.734	178.271	178.271	-75.901	1144.783	-2.476615
Pokrovskii & Helgeson (1995)	-22.879	28.86598	0	-10341.7028	-6.89410	0	**130.595**	**180.899**	**169.034**	168.721	**-57.321**	-57.32	
Shock et al (1997) = slope98.dat	-22.203	32.98453	0	-10143.0222	-8.55472	0	**126.738**	**172.979**	**155.226**	155.095	**-71.128**	-71.13	
ORNL = Reactions (5) - (6) - (7) w const DrCp	-22.877	35.86455	0	-10779.1130	-9.12866	0	**130.583**	**183.734**	**178.271**	178.271	**-75.901**	-75.90	0
5) H2O = H+ + OH-													
Nordstrom *et al.* (1990)	-14.000	**-283.9710**	-0.05069842	**13323.00**	**102.24447**	-1119669	79.910	55.905	-80.510	-80.510	-210.947	850.1088	-1.94122
SUPCRT92 (Johnson *et al.* 1992; slop98.dat)	-13.995	69.84765	0	-6212.4515	-25.46288	0	**79.885**	**55.815**	**-80.751**	-80.733	**-211.710**	-211.71	
6) Al(OH)4- = Al(OH)3(cr) + OH-	= AlO2- + 2 H2O = Al(OH)3(cr) + OH-				**(in Pokrovskii & Helgeson 1995 and Shock et al. 1997)**								
Nordstrom *et al.* (1990) = Rean (5) - (4) - (7)	0.556	-3.94259	0	1341.1407	0	0	-3.171	-25.676		-75.480	0.000	0	
Wesolowski (1992) Eq. 12 & Tab. 9	1.143	**96.5506**	0.0139828	-2374.88	-37.02324268		-6.522	-22.516	-53.645	-53.645	-148.201	-307.82872	0.535395
Pokrovskii & Helgeson (1995)	1.132	51.67698	0	-1259.2969	-18.71975	0	**-6.464**	**-22.297**	**-52.718**	-53.102	**-155.645**	-155.64	
Shock et al (1997) = slope98.dat	1.242	48.01496	0	-1099.9359	-17.41138	0	**-7.092**	**-22.104**	**-50.208**	-50.351	**-144.766**	-144.77	
7) Al(OH)3(cr) + 3 H+ = Al+3 + 3 H2O													
Nordstrom *et al.* (1990)	**8.110**	-8.60250	0	4982.8309	0.00000	0	-46.292	**-95.395**		-164.693	0.000		
Palmer & Wesolowski (1992) Eq. 5	7.735	-15.31701		5705.723	1.5821228		-44.151	-105.313	-205.137	-205.137	13.155	13.154516	0
Pokrovskii & Helgeson (1995)	7.756	-10.69018	0	5388.3296	0.15097	0	**-44.271**	**-102.784**	**-196.648**	-196.254	**1.255**	1.26	
Shock et al (1997) = slope98.dat	6.966	-11.15038	0	5030.2880	0.50322	0	-39.765	-95.056	-185.351	-185.449	4.184	4.18	
8) Na+ + Al+3 + 2 H2O- = NaAlO2(aq) +4 H+	= Na+ + Al+3 + 4 H2O- = NaAl(OH)4(aq) +4 H+												
Pokrovskii & Helgeson (1995)	23.626	28.48586	0	8240.7467	-13.13401	0	-134.859	-190.326	-186.188	-186.038	-109.202	-109.20	
9) Na+ + OH- = NaOH(aq)													
Pokrovskii & Helgeson (1995)	-0.800	-86.22125	0	3898.7407	29.23702	0	4.565	-2.163	-22.594	-22.565	243.090	243.09	
Shock et al (1997) = slope98.dat	-0.210	-29.84268	0	1298.6929	10.21534	0	1.197	0.460	-2.929	-2.470	84.935	84.94	

There are disagreements between calculated values in PMATCHC and in this spreadsheet in 5th or lower significant figures.

DrG & DrS values in this spreadsheet are from SUPCRT92 results; PMATCHC calculates DrG & DrH values from properties of species.

Are calculations in SUPCRT92 or PMATCHC incorrect? 　　　　Note that DrS values from SUPCRT92 do not agree with (DrH - DrG)/T, indicating problem may be in SUPCRT92.

Table 5.1.2: Thermodynamic properties of formation of elements from several sources used in calculations of properties of formation of gibbsite and aqueous species discussed in this report.

ELEMENTS					

O2(g)

S0	J / mol K	± J / mol K	cal / mol K	± cal / mol K	
	205.152	**0.005**	**49.033**	**0.001**	**NEA from CODATA (Silva *et al.* 1995); CODATA (Cox *et al.* 1989)**
	205.138		49.029		NBS (Wagman *et al.* 1982)
	205.137		49.029		Shock *et al.* (1997); slop98.dat

Cp0	J / mol K	± J / mol K	cal / mol K	± cal / mol K		a	b*10^3	c*10^-5
	29.378	0.003	7.022	0.001	NEA from CODATA (Silva *et al.* 1995); CODATA (Cox *et al.* 1989)			
	29.355		7.016		NBS (Wagman *et al.* 1982)			
					Shock *et al.* (1997); slop98.dat			
	29.322		7.008			7.16	1.0	-0.4

H2(g)

S0	J / mol K	± J / mol K	cal / mol K	± cal / mol K	
	130.680	**0.003**	**31.233**	**0.001**	**NEA from CODATA (Silva *et al.* 1995); CODATA (Cox *et al.* 1989)**
	130.684		31.234		NBS (Wagman *et al.* 1982)
	130.683		31.234		Shock *et al.* (1997); slop98.dat

Cp0	J / mol K	± J / mol K	cal / mol K	± cal / mol K		a	b*10^3	c*10^-5
	28.836	**0.002**	**6.892**	**0.000**	**NEA from CODATA (Silva *et al.* 1995); CODATA (Cox *et al.* 1989)**			
	28.824		6.889		NBS (Wagman *et al.* 1982)			
					Shock *et al.* (1997); slop98.dat			
	28.818		6.888			6.52	0.78	0.12

Al(cr)

S0	J / mol K	± J / mol K	cal / mol K	± cal / mol K	
	28.30	**0.10**	**6.76**	**0.02**	**NEA from CODATA (Silva *et al.* 1995); CODATA (Cox *et al.* 1989)**
	28.33		6.77		NBS (Wagman *et al.* 1982)

Cp0	J / mol K	± J / mol K	cal / mol K	± cal / mol K	
	24.20	**0.07**	**5.78**	**0.02**	**NEA from CODATA (Silva *et al.* 1995); CODATA (Cox *et al.* 1989)**
	24.35		5.82		NBS (Wagman *et al.* 1982)

Table 5.1.3: Thermodynamic properties of formation of water from several sources used in calculations of properties of formation of gibbsite and aqueous species discussed in this report.

H2O

DfG0	kJ / mol ± kJ / mol	cal / mol ± cal / mol	
	-237.140 ± 0.041	**-56678 ± 10**	**NEA from CODATA (Silva et al. 1995); CODATA (Cox et al. 1989)**
	-237.129	-56675	NBS (Wagman et al. 1982)
	-237.183	-56688	SUPCRT92
DfH0	kJ / mol ± kJ / mol	cal / mol ± cal / mol	
	-285.830 ± 0.040	**-68315 ± 10**	**NEA from CODATA (Silva et al. 1995); CODATA (Cox et al. 1989)**
	-285.830	-68315	NBS (Wagman et al. 1982)
	-285.838	-68317	SUPCRT92
DfS0	J / mol K ± J / mol K	cal / mol K ± cal / mol K	
	-163.303 ± 0.03	**-39.03 ± 0.01**	**NEA from CODATA (Silva et al. 1995); CODATA (Cox et al. 1989)**
	-163.342	-39.04	NBS (Wagman et al. 1982)
	69.923	16.71	SUPCRT92
S0	J / mol K ± J / mol K	cal / mol K ± cal / mol K	
	69.950 ± 0.03	**16.72 ± 0.01**	**NEA from CODATA (Silva et al. 1995); CODATA (Cox et al. 1989)**
	69.910	16.71	NBS (Wagman et al. 1982)
	69.923	16.71	SUPCRT92
DfCp0	J / mol K ± J / mol K	cal / mol K ± cal / mol K	
	31.8495 ± 0.08	**7.61 ± 0.02**	**NEA from CODATA (Silva et al. 1995); CODATA (Cox et al. 1989)**
	72.291	17.28	NBS (Wagman et al. 1982)
	75.312	18.00	SUPCRT92
Cp0	J / mol K ± J / mol K	cal / mol K ± cal / mol K	
	75.351 ± 0.08	**18.01 ± 0.02**	**NEA from CODATA (Silva et al. 1995); CODATA (Cox et al. 1989)**
	72.291	17.28	NBS (Wagman et al. 1982)
	75.312	18.0	SUPCRT92

Table 5.1.4: Thermodynamic properties of formation of OH⁻ from various sources discussed in this report.

OH-

DfG0	kJ / mol	±	kJ / mol	cal / mol	±	cal / mol	
							Nordstrom *et al.* (1990) From H2O = H+ + OH-
	-157.230			**-37579**			**logK = -14.000 DrG = 79.910**
	-157.220	±	0.072	-37576	±	17	NEA from CODATA (Silva *et al.* 1995); CODATA (Cox *et al.* 1989)
	-157.244			-37582			NBS (Wagman *et al.* 1982)
	-157.297			-37595			Pokrovskii & Helgeson (1995); Shock *et al.* (1997); slop98.dat

DfH0	kJ / mol	±	kJ / mol	cal / mol	±	cal / mol	
							Nordstrom *et al.* (1990) From H2O = H+ + OH-
	-229.925			**-54953**			**DrH = 55.905**
	-230.015	±	0.040	-54975	±	10	NEA from CODATA (Silva *et al.* 1995); CODATA (Cox *et al.* 1989)
	-229.994			-54970			NBS (Wagman *et al.* 1982)
	-230.024			-54977			Pokrovskii & Helgeson (1995); Shock *et al.* (1997); slop98.dat

DfS0	J / mol K	±	J / mol K	cal / mol K	±	cal / mol K	
							Nordstrom *et al.* (1990) From H2O = H+ + OH-
	-243.818			**-58.27**			**(DfH0 - DfG0) / Tr**
	-243.813			-58.27			DrS = -80.510

S0	J / mol K	±	J / mol K	cal / mol K	±	cal / mol K	
							Nordstrom *et al.* (1990) From H2O = H+ + OH-
	-10.565			**-2.52**			**DfS0 +S0(elem) - Chg * S0(H2)/2**
	-10.900		0.20	-2.61		0.05	NEA from CODATA (Silva *et al.* 1995); CODATA (Cox *et al.* 1989)
	-10.750			-2.57			NBS (Wagman *et al.* 1982)
	-10.711			-2.56			Pokrovskii & Helgeson (1995); Shock *et al.* (1997); slop98.dat

DfCp0	J / mol K	±	J / mol K	cal / mol K	±	cal / mol K	
							Nordstrom *et al.* (1990) From H2O = H+ + OH-
	-179.098			**-42.8**			**DrCp = -210.947**

Cp0	J / mol K	±	J / mol K	cal / mol K	±	cal / mol K	
							Nordstrom *et al.* (1990) From H2O = H+ + OH-
	-135.596			**-32.4**			**DfCp0 +Cp0(elem) - Chg * Cp0(H2)/2**
	- - - -			- - - -			NEA from CODATA (Silva *et al.* 1995); CODATA (Cox *et al.* 1989)
	-148.500			-35.5			NBS (Wagman *et al.* 1982)
	-136.398			-32.6			SUPCRT92 calculation from HKF data of Shock *et al.* (1997); slop98.dat

Table 5.1.5: Thermodynamic properties of formation of gibbsite from various sources discussed in this report.

GIBBSITE

DfG0	kJ / mol ± kJ / mol	cal / mol ± cal / mol	
	-1154.89 ± 0.90	**-276025 ± 215**	**Hemingway & Sposito (1989) Tab. 7**
	-1154.889 ± 1.213	**-276025 ± 290**	**Robie *et al.* (1979) p. 140**
	-1154.889 ± 1.213	-276025 ± 290	Pokrovskii & Helgeson (1995) Tab. 2
	-1154.9 ± 1.2	-276028 ± 287	Palmer & Wesolowski (1992)
	-1155.49	-276168	Shock *et al.* (1995); Helgeson *et al.* (1978); slop98.dat

DfH0	kJ / mol ± kJ / mol	cal / mol ± cal / mol	
	-1293.13 ± 0.90	**-309065 ± 215**	**Hemingway & Sposito (1989) Tab. 7**
	-1293.128 ± 1.192	**-309065 ± 285**	**Robie *et al.* (1979) p. 140**
	-1293.128 ± 1.192	-309065 ± 285	Pokrovskii & Helgeson (1995) Tab. 2
	-1293.13 ± 1.19	-309065 ± 284	Palmer & Wesolowski (1992)
	-1293.128	-309065	Shock *et al.* (1995); Helgeson *et al.* (1978); slop98.dat

DfS0	J / mol K ± J / mol K	cal / mol K ± cal / mol K	
			Robie *et al.* (1979), Pokrovskii & Helgeson (1995), Hemingway & Sposito (1989)
	-463.7	**-110.8**	**(DfH0 - DfG0) / Tr**
	-463.6	-110.8	S0 - S0(elem) +Chg * S0(H2)/2
			Shock *et al.* (1995); Helgeson *et al.* (1978); slop98.dat
	-461.7	-110.3	(DfH0 - DfG0) / Tr
	-462.0	-110.4	S0 - S0(elem) +Chg * S0(H2)/2

S0	J / mol K ± J / mol K	cal / mol K ± cal / mol K	
	68.440 ± 0.14	**16.36 ± 0.03**	**Hemingway & Sposito (1989) Tab. 7**
	68.440 ± 0.14	**16.36 ± 0.03**	**Robie *et al.* (1979) p. 140**
	68.450 ± 0.13	16.36 ± 0.03	Pokrovskii & Helgeson (1995) Tab. 2
	70.082	16.75	Shock *et al.* (1995); Helgeson *et al.* (1978); slop98.dat

DfCp0	J / mol K ± J / mol K	cal / mol K ± cal / mol K	
	-19.89	**-4.75**	**Hemingway & Sposito (1989) Tab. 7**
	-19.92	-4.76	Robie *et al.* (1979) p. 140

Cp0 and Cp equation coefficients		a	b			c
J / mol K ± J / mol K	cal / mol K ± cal / mol K	(10^3 T)	(10^-4 T^2)	(10^2 /T^0.5)	(10^-5/T^2)	
		Pokrovskii & Helgeson (1995) Tab. 2 Fit to data of Hemingway et al. (1977) in cal / mol-K				
91.72	**21.92**	**13.073**	**40.696**			**-2.920**
		Hemingway & Sposito (1989) Tab. 7 in J / mol-K				
91.73 ± 0.16	21.92 ± 0.04	220.851	60.1252		-26.6764	6.61704
91.70	21.92	Robie *et al.* (1979) p. 140				
		Palmer & Wesolowski (1992) Fit to data of Hemingway *et al.* (1977) in J / mol-K				
91.70	21.92	-24.7390	514.65	-4.163		
		Shock *et al.* (1995); Helgeson *et al.* (1978); slop98.dat in cal / mol-K				
93.08	22.25	8.65	45.60			0.00

Table 5.1.6: Thermodynamic properties of formation of Al^{3+} from various sources discussed in this report.

Al+3(aq)			Chg: 3			From Reaction: Al(OH)3, gibbsite + 3 H+ = Al+3,aq + 3 H2O			
DfG0	**kJ / mol**	**±**	**kJ / mol**	**cal / mol**	**±**	**cal / mol**			
							Pokrovskii & Helgeson (1995)		
	-487.740			**-116573**			logK(25) = 7.756	DrG0 =	-10581
	-487.616			-116543			Pokrovskii & Helgeson (1995) Tab. 3.		
	-487.7 ± 1.5			-116563	±		Palmer & Wesolowski (1992) p. 1099.		
	-483.7			-115609			Shock *et al.* (1997) Tab 4; slop98.dat		
	-485			-115918			NBS (Wagman *et al.* 1982)		
	-491.507	3.338		-117473	798		NEA from CODATA (Grenthe *et al.* 1992); CODATA (Cox *et al.* 1989)		
DfH0	**kJ / mol**	**±**	**kJ / mol**	**cal / mol**	**±**	**cal / mol**			
							Pokrovskii & Helgeson (1995)		
	-538.424			**-128686**			DrH0 = -24565.97		
	-538.4			-128681			Tab. 3 = CODATA		
	-540.9 ± 4.1			-129278	±	980	Palmer & Wesolowski (1992) p. 1099.		
	-530.7			-126834			Shock *et al.* (1997) Tab 4; slop98.dat		
	-531			-126912			NBS (Wagman *et al.* 1982)		
	-538.4	1.5		-128681	359		NEA from CODATA (Grenthe *et al.* 1992); CODATA (Cox *et al.* 1989)		
DfS0	**J / mol K**	**±**	**J / mol K**	**cal / mol K**	**±**	**cal / mol K**			
							Pokrovskii & Helgeson (1995)		
	-169.99			**-40.63**			(DfH0 - DfG0) / Tr		
	-170.37			-40.72			S0 - S0(elem) +Chg * S0(H2)/2		
							Palmer & Wesolowski (1992)		
	-178.4 ± 4.4			-42.65	±	1.04	(DfH0 - DfG0) / Tr		
							Shock *et al.* (1995); slop98.dat		
	-157.52			-37.65			(DfH0 - DfG0) / Tr		
	-157.40			-37.62			S0 - S0(elem) +Chg * S0(H2)/2		
							NBS (Wagman et al.1982)		
	-154.3			-36.87			(DfH0 - DfG0) / Tr		
	-125.7			-30.04			S0 - S0(elem) +Chg * S0(H2)/2		
							NEA from CODATA (Grenthe *et al.* 1992); CODATA (Cox *et al.* 1989)		
	-157.28			-37.59			(DfH0 - DfG0) / Tr		
	-157.304			-37.60			S0 - S0(elem) +Chg * S0(H2)/2		
S0	**J / mol K**	**±**	**J / mol K**	**cal / mol K**	**±**	**cal / mol K**			
	-338.07			-80.80			Pokrovskii & Helgeson (1995) Tab. 3.		
	-337.69			**-80.71**			DfS0 + S0(elem) - Chg*S0(H2)/2		
	-346			-82.7			Palmer & Wesolowski (1992) p. 1099		
	-325			-77.7			Shock *et al.* (1997) Tab 4; slop98.dat		
	-321.7			-76.9			NBS (Wagman *et al.* 1982)		
	-325	10		-77.7	2.4		NEA from CODATA (Grenthe *et al.* 1992); CODATA (Cox *et al.* 1989)		
DfCp0	**J / mol K**	**±**	**J / mol K**	**cal / mol K**	**±**	**cal / mol K**			
							Pokrovskii & Helgeson (1995) Tab. 2.		
	-114.18			**-27.3**			DrCp0 = 1.255		
							Palmer & Wesolowski (1992) p. 1099		
	-102			-24.5			DrCp0 (Tab. 3) = 13 ± 11	kJ / mol-K from solubility data	
	-102			-24.5			DrCp0 (Tab. 2) = 13 ± 9	kJ / mol-K; avg meas. 10 to 55 C	
	-136			-32.5			Shock *et al.* (1997) Tab 4; slop98.dat		
Cp0	**J / mol K**	**±**	**J / mol K**	**cal / mol K**	**±**	**cal / mol K**			
							Pokrovskii & Helgeson (1995) SUPCRT92		
	-133.07			**-31.8**			DfCp0 +Cp0(elem) - Chg * Cp0(H2)/2		
							Palmer & Wesolowski (1992) p. 1099		
	-121			-29.0			DfCp0 +Cp0(elem) - Chg * Cp0(H2)/2		
	-136			-32.5			Shock *et al.* (1997) Tab 4; slop98.dat		

Table 5.1.7: Thermodynamic properties of formation of Al(OH)$_4^-$, from various sources discussed in this report.

Al(OH)4- (= AlO2- + 2 H2O)			Chg: = -1		From reaction: Al+3 + 4 H2O = Al(OH)4- + 4 H+		
DfG0	kJ / mol ± kJ / mol		cal / mol ± cal / mol				
					Pokrovskii & Helgeson (1995)		
	-1305.705		**-312071**		logK(25) = -22.879	DrG0 =	31213
	-1305.726		-312076		Table 3 + 2 H2O		cal / mol
	-1305.6 ± 1.2		-312046 ± 287		Palmer & Wesolowski (1992) p. 1089		
					Nordstrom *et al.* (1990), see Tab. 5.1.1, above		
	-1310.69		-313263		logK(25) = -22.665	DrG0 =	129.373
	-1305.70		-312069		Shock *et al.* (1997) Tab. 4; slop98.dat + 2 H2O		kJ / mol
	-1305.3		-311974		NBS (Wagman *et al.* 1982) AlO2- + 2 H2O		
DfH0	kJ / mol ± kJ / mol		cal / mol ± cal / mol				
					Pokrovskii & Helgeson (1995)		
	-1500.822		**-358705**		DrH0 = 43236	cal / mol	
	-1500.855		-358713		Table 3 + 2 H2O		
	-1500.6 ± 1.5		-358652 ± 359		Palmer & Wesolowski (1992) p. 1089		
					Nordstrom *et al.* (1990), Tab. 5.1.1, above		
	-1504.74		-359642		DrH0 = 176.976	kJ / mol	
	-1501.05		-358759		Shock *et al.* (1997) Tab. 4; slop98.dat + 2 H2O		
	-1502.5		-359106		NBS (Wagman *et al.* 1982)		
DfS0	J / mol K ± J / mol K		cal / mol K ± cal / mol K				
					Pokrovskii & Helgeson (1995)		
	-654.43		**-156.41**		(DfH0 - DfG0) / Tr		
	110.56		26.42		S0 - S0(elem) +Chg * S0(H2)/2		
					Palmer & Wesolowski (1992, Tab 11)		
	-654.0		-156.32		(DfH0 - DfG0) / Tr		
	-625.6 ± 1.0		-149.52 ± 0.24		S0 - S0(elem) +Chg * S0(H2)/2		
					Shock *et al.* (1997)		
	-655.2		-156.60		(DfH0 - DfG0) / Tr		
	109.6		26.20		S0 - S0(elem) +Chg * S0(H2)/2		
					NBS (Wagman et al.1982)		
	-661.4		-158.1		(DfH0 - DfG0) / Tr		
	-634.1		-151.5		S0 - S0(elem) +Chg * S0(H2)/2		
S0	J / mol K ± J / mol K		cal / mol K ± cal / mol K				
	110.6		26.42		**Pokrovskii & Helgeson (1995) Tab. 3 + 2 H2O**		
	-654.43		**-156.41**		**DfS0 + S0(elem) - Chg*S0(H2)/2**		
	111.4 ± 1.0		26.63 ± 0.24		Palmer & Wesolowski (1992) p. 1089		
	109.6		26.20		Shock *et al.* (1997) Tab. 4; slop98.dat + 2 H2O		
	102.9		24.59		NBS (Wagman *et al.* 1982)		
DfCp0	J / mol K ± J / mol K		cal / mol K ± cal / mol K				
					Pokrovskii & Helgeson (1995)		
	-44.1		**-10.54**		DrCp = -13.70	cal / mol-K	
	-69.5		-16.6		SUPCRT92 calc from HKF parameters		
Cp0	J / mol K ± J / mol K		cal / mol K ± cal / mol K				
					Pokrovskii & Helgeson (1995)		
	111.01		**26.53**		**DfCp0 + Cp0(elem) - Chg*Cp0(H2)/2**		
					Palmer & Wesolowski (1993) p. 2934		
	55.2		13.2		Shock *et al.* (1995) Tab. 10; slop98.dat		
	-75.9		-18.1		DrCp0 = -75.901 J / mol-K SeeTab. 5.1.1, above		
	100.8		24.1		Shock *et al.* (1997) Tab. 4; slop98.dat + 2 H2O		

Table 5.1.8: Thermodynamic properties of formation of $AlOH^{2+}$ from various sources discussed in this report.

AlOH+2						Chg: 2	From reaction: Al+3 + H2O = Al(OH)2+ + H+	
DfG0	**kJ / mol**	**±**	**kJ / mol**	**cal / mol**	**±**	**cal / mol**		
							Pokrovskii & Helgeson (1995)	
	-696.58			**-166488**			**logK(25) = -4.957**	**DrG0 = 6763**
	-696.50			-166468			Table 3 + H2O	**cal / mol**
	-697			-166587			Palmer & Wesolowski (1993) p. 2934	
							Nordstrom *et al.* (1990), see Tab. 5.1.1, above	
	-700.1			-167326			logK(25) = -5.003	DrG0 = 28.557
	-692.35			-165475			Shock *et al.* (1995) Tab. 10; slop98.dat	kJ / mol
	-694.1			-165894			NBS (Wagman *et al.* 1982)	
DfH0	**kJ / mol**	**±**	**kJ / mol**	**cal / mol**	**±**	**cal / mol**		
							Pokrovskii & Helgeson (1995)	
	-774.43			**-185094**			**DrH0 = 11902**	**cal / mol**
	-774.44			-185096			Table 3 + 2 H2O	
	-771			-184273			Palmer & Wesolowski (1993) p. 2934	
							Nordstrom *et al.* (1990), see Tab. 5.1.1, above	
	-776.2			-185504			DrH0 = 48.080	kJ / mol
	-766.9			-183300			Shock *et al.* (1995) Tab. 10; slop98.dat	
DfS0	**J / mol K**	**±**	**J / mol K**	**cal / mol K**	**±**	**cal / mol K**		
							Pokrovskii & Helgeson (1995)	
	-261.11			**-62.41**			**(DfH0 - DfG0) / Tr**	
	-195.89			-46.82			S0 - S0(elem) +Chg * S0(H2)/2	
							Palmer & Wesolowski (1993)	
	-248			-59.3			(DfH0 - DfG0) / Tr	
	-222			-53.1			S0 - S0(elem) +Chg * S0(H2)/2	
							Shock *et al.* (1995); slop98.dat	
	-250.1			-59.79			(DfH0 - DfG0) / Tr	
	-184.9			-44.20			S0 - S0(elem) +Chg * S0(H2)/2	
S0	**J / mol K**	**±**	**J / mol K**	**cal / mol K**	**±**	**cal / mol K**		
	-195.9			-46.82			**Pokrovskii & Helgeson (1995) Tab. 3**	
	-261.11			**-62.41**			**DfS0 + S0(elem) - Chg*S0(H2)/2**	
	-185			-44.22			Palmer & Wesolowski (1993) p. 2934	
	-185			-44.2			Shock *et al.* (1995) Tab. 10; slop98.dat	
DfCp0	**J / mol K**	**±**	**J / mol K**	**cal / mol K**	**±**	**cal / mol K**		
							Pokrovskii & Helgeson (1995)	
	44.86			**10.72**			**DrCp = 30.40**	**cal / mol-K**
							Palmer & Wesolowski (1993) Tab 2	
	-82.33			-19.68			**DrCp0 = 0.0**	**J / mol-K**
Cp0	**J / mol K**	**±**	**J / mol K**	**cal / mol K**	**±**	**cal / mol K**		
							Pokrovskii & Helgeson (1995)	
	69.5			**16.6**			**DfCp0 + Cp0(elem) - Chg*Cp0(H2)/2**	
	-44			-10.5			Palmer & Wesolowski (1993) p. 2934	
	-58			-13.8			DfCp0 +Cp0(elem) - Chg * Cp0(H2)/2	
	55			13.2			Shock *et al.* (1995) Tab. 10; slop98.dat	

Table 5.1.9: Thermodynamic properties of formation of $Al(OH)_2^+$ from various sources discussed in this report.

Al(OH)2+ (AlO+ + H2O)						Chg: 1	From reaction: Al+3 +2 H2O = Al(OH)2+ + 2 H+		
DfG0	**kJ / mol**	**±**	**kJ / mol**	**cal / mol**	**±**	**cal / mol**			
							Pokrovskii & Helgeson (1995)		
	-901.55			**-215475**			**logK(25) = -10.594**		**DrG0 = 14453**
	-901.5			-215465			Table 3		**cal / mol**
							Nordstrom *et al.* (1990), see Tab. 5.1.1, above		
	-908.1			-217038			logK(25) = -10.109		DrG0 = 57.701
	-899.0			-214876			Shock *et al.* (1995) Tab. 10; slop98.dat + H2O		kJ / mol
DfH0	**kJ / mol**	**±**	**kJ / mol**	**cal / mol**	**±**	**cal / mol**			
							Pokrovskii & Helgeson (1995)		
	-1011.78			**-241821**			**DrH0 = 23490**		**cal / mol**
	-1011.80			-241825			Table 3		
							Nordstrom *et al.* (1990), see Tab. 5.1.1, above		
	-997.5			-238406			DrH0 = 112.568		kJ / mol
	-1000.88			-239217			Shock *et al.* (1995) Tab. 10; slop98.dat + H2O		
DfS0	**J / mol K**	**±**	**J / mol K**	**cal / mol K**	**±**	**cal / mol K**			
							Pokrovskii & Helgeson (1995)		
	-369.71			**-88.36**			**(DfH0 - DfG0) / Tr**		
	-71.13			-17.00			S0 - S0(elem) +Chg * S0(H2)/2		
							Shock *et al.* (1995); slop98.dat		
	-341.6			-81.64			(DfH0 - DfG0) / Tr		
	-43.0			-10.29			S0 - S0(elem) +Chg * S0(H2)/2		
S0	**J / mol K**	**±**	**J / mol K**	**cal / mol K**	**±**	**cal / mol K**			
	-71.1			-17.00			**Pokrovskii & Helgeson (1995) Tab. 3**		
	-369.71			**-88.36**			**DfS0 + S0(elem) - Chg*S0(H2)/2**		
	-43.0			-10.29			Shock *et al.* (1995) Tab. 10; slop98.dat + H2O		
DfCp	**J / mol K**	**±**	**J / mol K**	**cal / mol K**	**±**	**cal / mol K**			
							Pokrovskii & Helgeson (1995)		
	83.82			**20.03**			**DrCp = 32.10**		**cal / mol**
	0.0						Shock *et al.* (1995) Tab. 10; slop98.dat + H2O		
Cp0	**J / mol K**	**±**	**J / mol K**	**cal / mol K**	**±**	**cal / mol K**			
							Pokrovskii & Helgeson (1995)		
	151.94			**36.31**			**DfCp0 + Cp0(elem) - Chg*Cp0(H2)/2**		
	0.0						Shock *et al.* (1995) Tab. 10; slop98.dat + H2O		

Table 5.1.10: Thermodynamic properties of formation of Al(OH)$_3$ from various sources discussed in this report.

Al(OH)3(aq) (HAlO2 + H2O)			Chg:	0		From reaction: Al+3 + 3 H2O = Al(OH)2+ + 3 H+		

DfG0	kJ / mol	±	kJ / mol	cal / mol	±	cal / mol		
						Pokrovskii & Helgeson (1995)		
	-1105.36			**-264188**		logK(25) = -16.432		**DrG0 = 22418**
	-1105.4			-264188		Table 3 + H2O		**cal / mol**
						Nordstrom *et al.* (1990), see Tab. 5.1.1, above		
	-1106.2			-264396		logK(25) = -16.94		DrG0 = 96.696
	-1106.2			-264388		Shock *et al.* (1997) Tab. 10; slop98.dat + H2O		kJ / mol

DfH0	kJ / mol	±	kJ / mol	cal / mol	±	cal / mol		
						Pokrovskii & Helgeson (1995)		
	-1251.19			**-299041**		**DrH0 = 34585**		**cal / mol**
	-1251.2			-299047		Table 3 + 2 H2O		
						Nordstrom *et al.* (1990), see Tab. 5.1.1, above		
	-1229.0			-293734		DrH0 = 166.906		kJ / mol
	-1237.7			-295817		Shock *et al.* (1997) Tab. 10; slop98.dat + H2O		

DfS0	J / mol K	±	J / mol K	cal / mol K	±	cal / mol K		
						Pokrovskii & Helgeson (1995)		
	-489.10			**-116.90**		**(DfH0 - DfG0) / Tr**		
	42.7			10.21		S0 - S0(elem) +Chg * S0(H2)/2		
						Shock *et al.* (1997); slop98.dat		
	-441.0			-105.41		(DfH0 - DfG0) / Tr		
	90.8			21.71		S0 - S0(elem) +Chg * S0(H2)/2		

S0	J / mol K	±	J / mol K	cal / mol K	±	cal / mol K		
	42.7			10.21		**Pokrovskii & Helgeson (1995) Tab. 3**		
	-489.10			**-116.90**		**DfS0 + S0(elem) - Chg*S0(H2)/2**		
	90.8			21.71		Shock *et al.* (1997) Tab. 10; slop98.dat + H2O		

DfCp	J / mol K	±	J / mol K	cal / mol K	±	cal / mol K		
						Pokrovskii & Helgeson (1995)		
	137.01			**32.75**		**DrCp = 37.2**		**cal / mol**

Cp0	J / mol K	±	J / mol K	cal / mol K	±	cal / mol K		
						Pokrovskii & Helgeson (1995)		
	248.63			**59.42**		**DfCp0 + Cp0(elem) - Chg*Cp0(H2)/2**		
	248.1			59.3		Shock *et al.* (1995) Tab. 10; slop98.dat + H2O		

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

Test of overall internal consistency.
- 1)   Properties Al+3,aq from properties of gibbsite and reaction: Al+3 + 3H2O = gibbsite + 3H+
- 2)   Properties of Al(OH)4- from properties of Al+3,aq and reaction: Al+3 + 4H2O = Al(OH)4- + 4H+

Consistency check:

     Calculate properties of gibbsite_Al+3 from reaction Al+3 + 3 H2O = gibbsite_Al+3 + 3H+

         Should be identical with accepted properties because calculation scheme is just reverse of that used to generate Al+3 properties.

     Calculate properties of gibbsite_Al(OH)4- from reaction Al(OH)4- = gibbsite_Al(OH)4- + OH-

         Difference from accepted properties shows erors generated in calculation scheme.

	DfG0 kJ / mol	DfH0 kJ / mol	DfS0 J / mol-K	DfCp0 J / mol-K	SOURCE:
Gibbsite	-1154.89 ± 0.9	-1293.13 ± 0.9	-463.66 ± 0.14	-19.79 ± 0.16	Hemingway and Sposito (1989) See Table 5.1.5, above.
Gibbsite_Al+3	-1154.889	-1293.13	-463.66	-19.77	Reaction Al+3 + 3 H2O = gibbsite_Al+3 + 3H+
Gibbsite_Al(OH)4-	-1154.937	-1293.215	-463.79	-20.56	Reaction Al(OH)4- = gibbsite_Al(OH)4- + OH-

5.2   Americium

Almost all information on americium is taken from OECD NEA's book "Chemical Thermodynamics of Americium" (SILVA et al. 1995). However, not all recommended values of this NEA review are included in our database since NEA reviews are not restricted to data relevant for radioactive waste management or even environmental modelling in general. We excluded from our database phases and complexes which most probably will never be relevant in environmental systems. In addition to SILVA et al. (1995) new data concerning the first and second hydrolysis constant and silicate complexation of americium are included in our database. The notation of formulae and symbols used in this text follows the NEA recommendations.

5.2.1   Elemental americium

Americium metal, liquid and gas are not relevant under environmental conditions. The absolute entropy of Am(cr) is given in Table 5.2.1 for computational purposes only (i.e. calculation of the entropy of formation of Am^{3+}). Data on americium liquid and gas are not included in the database.

5.2.2   Simple americium aqua ions

In aqueous media, americium exists as the trivalent ion except under strongly oxidising conditions, where the five- and six-valent dioxoamericium ions AmO_2^+ and AmO_2^{2+} are formed. In acid solutions, the former slowly disproportionates to AmO_2^{2+} and Am^{3+}. The free radicals produced from α-particles in water readily reduce these dioxoamericium ions back to Am^{3+}. Tetravalent americium is only stable in the presence of strongly complexing agents such as carbonate or fluoride.

Considering the instability of higher oxidation states of americium aqua ions and the fact that only three carbonate complexes of Am(IV), Am(V) and Am(VI), originating from measurements in 2 M $NaHCO_3/Na_2CO_3$ media, are recommended by SILVA et al. (1995), we decided to restrict our database to Am^{3+}.

There are no solubility or other data from which the Gibbs energies of any of the free americium ions can be related to any of the condensed phase compounds. The Gibbs energies and related properties of the ions therefore depend on estimates of the entropies of the aqua ions, based on comparisons with other actinide and lanthanide ions. We accept the enthalpy value selected by SILVA et al. (1995) (based on experimental data and extrapolated to zero ionic strength)

$$\Delta_f H_m° \ (Am^{3+}, aq, 298.15 \ K) \quad = \quad -(616.7 \pm 1.5) \ kJ \cdot mol^{-1}$$

their estimated entropy value

$$S_m° \ (Am^{3+}, aq, 298.15 \ K) \quad = \quad -(201 \pm 15) \ J \cdot K^{-1} \cdot mol^{-1}$$

and the Gibbs energy of formation calculated from the above values

$$\Delta_f G_m° \text{ (Am}^{3+}\text{, aq, 298.15 K)} \quad = \quad \text{-(598.7} \pm \text{4.8) kJ} \cdot \text{mol}^{-1}$$

5.2.3   Oxygen and hydrogen compounds

5.2.3.1   Aqueous americium hydroxide complexes

Thermodynamic data on Am(III) hydrolysis published until 1991 have been reviewed in detail by SILVA et al. (1995). They refer to the reaction

$$\text{Am}^{3+} + \text{n H}_2\text{O(l)} \Leftrightarrow \text{Am(OH)}_n^{(3-n)} + \text{n H}^+$$
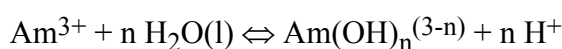
Major difficulties in the experimental determination of equilibrium constants for Am(III) hydrolysis complexes generally come from interfering adsorption and precipitation. Most of the experimental work was carried out in the pH region where the first and the second hydroxo species are present, while only a few data have been reported on the neutral Am(OH)$_3$(aq).

By analogy with neodymium some authors proposed also the existence of Am(OH)$_4^-$. The formation of this negatively charged species would increase the Am(III) solubility in the high pH region. However, a number of experimental studies have shown that such a solubility increase does not occur at pH $\leq$ 13. Thus, there is no experimental evidence for anionic hydrolysis complexes of Am(III).

Although polynuclear hydroxo- or oxo-complexes could conceivably form in the region immediately before precipitation, there is no evidence of their existence.

SILVA et al. (1995) selected the following standard equilibrium constants:

$$\log_{10}{}^*\beta_1° \text{ (n = 1, 298.15 K)} \ = \ \text{-6.4} \pm 0.7$$

$$\log_{10}{}^*\beta_2° \text{ (n = 2, 298.15 K)} \ = \text{-14.1} \pm 0.6$$

$$\log_{10}{}^*\beta_3° \text{ (n = 3, 298.15 K)} \ = \text{-25.7} \pm 0.5$$

The standard Gibbs energies of formation can be calculated from these reaction data. Data on $\Delta_r H_m$ are rather scarce and no recommended values are given by SILVA et al. (1995).

No thermodynamic data can be recommended by SILVA et al. (1995) for any aqueous Am(V) and Am(VI) hydroxide complex.

However, in their re-evaluation of data concerning trivalent actinides NECK et al. (1998) included spectrosocopic studies of Am(III) and Cm(III) hydrolysis published after the deadline (1991) of the review of SILVA et al. (1995). These new studies show that the first and second hydrolysis constant

of Am(III) are weaker by about one order of magnitude than indicated by older solubility and liquid-liquid extraction studies. The third hydrolysis constant is still valid as recommended by SILVA et al. (1995). Hence, NECK et al. (1998) recommended the following equilibrium constants:

$$\log_{10} {}^{*}\beta_1° \text{ (n = 1, 298.15 K)} = -7.3 \pm 0.3$$

$$\log_{10} {}^{*}\beta_2° \text{ (n = 2, 298.15 K)} = -15.2 \pm 0.6$$

$$\log_{10} {}^{*}\beta_3° \text{ (n = 3, 298.15 K)} = -25.7 \pm 0.5$$

We decided to include this set of hydrolysis constants in our database. Note that the revised first and second Am(III) hydrolysis constants agree well with independently evaluated Eu(III) hydrolysis constants (see 5.4).

5.2.3.2   Solid americium oxides and hydroxides

Am_2O_3(cr): There exists a low temperature cubic phase of Am_2O_3(cr) and a high temperature hexagonal phase with a transformation temperature between 973 and 1173 K. Only the enthalpy of formation of the hexagonal high temperature Am_2O_3(cr) has been measured and its entropy has been estimated by SILVA et al. (1995). The high temperature phase of Am_2O_3(cr) is not included in our database.

AmO_2(cr): The enthalpy of formation of AmO_2(cr) has been derived from enthalpy of dissolution measurements and its entropy has been estimated by SILVA et al. (1995). The Gibbs energy of formation of AmO_2(cr) is calculated from these measured and estimated thermochemical data. There are no solubility studies known to us involving AmO_2(cr). Only such studies would allow to assess whether AmO_2(cr) plays any role in aqueous environmental systems and whether the estimated data can actually be used with any confidence in thermodynamic modelling. Thus, AmO_2(cr) is excluded from our database.

Am(OH)$_3$(s): A number of solubility studies have been reported for precipitated Am(OH)$_3$(s). The various studies in the literature cannot describe the dissolution process

$$Am(OH)_3(s) + 3\ H^+ \Leftrightarrow Am^{3+} + 3\ H_2O(l)$$
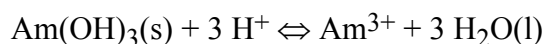
with a unique solubility constant. The difference in $\log_{10} {}^{*}K_{s,0}$ values can be rationalised by assuming variations in particle size and in the nature of the solid hydroxide phase. The distinction between amorphous and crystalline Am(OH)$_3$(s) may be ambiguous. Rather than a continuous network of polynuclear species, the freshly precipitated amorphous body of Am(OH)$_3$(s) can be considered an agglomerate of very small crystals too minute to give diffraction lines but visible by electron microscopy. The ageing processes allow aggregation to larger rods and the appearance of

diffraction patterns. However, the complex ageing behaviour may not end with the most crystalline product. The amorphisation by self-irradiation may prevent this. The rate of this destruction process depends on the specific activity of the Am isotopes. In a study in pure water, the complete degradation required 5 months with ^{241}Am(III). Unlike the fresh amorphous precipitate, the product of degradation did not regenerate crystallinity upon heating. A hydrous oxide phase was suggested to form.

The solubility constants for crystalline and well characterised amorphous americium hydroxide as selected by SILVA et al. (1995) are:

$$\log_{10}{}^*K_{s,0}° \text{ (Am(OH)}_3\text{, cr, 298.15 K)} \quad = \quad 15.2 \pm 0.6$$

$$\log_{10}{}^*K_{s,0}° \text{ (Am(OH)}_3\text{, am, 298.15 K)} \quad = \quad 17.0 \pm 0.6$$

The standard Gibbs energies of formation can be calculated from these reaction data.

No data are selected for **Am(IV), (V) and (VI) hydroxides** by SILVA et al. (1995).

BaAmO$_3$(cr), SrAmO$_3$(cr): The only thermodynamic data for ternary americium oxides are the enthalpies of formation of the perovskite-type compounds BaAmO$_3$(cr) and SrAmO$_3$(cr). BaAmO$_3$(cr) was prepared from BaCO$_3$(cr) and AmO$_2$(s) at temperatures up to 1350 K, and SrAmO$_3$(cr) was formed from the co-precipitated oxalates at 1100 K. Only calorimetric measurements are reported for these solids and hence, these data are not included in our database.

5.2.3.3   Americium hydrides

AmH$_2$(cr) and AmH$_3$(cr) are not relevant under environmental conditions. None of these phases is included in the database.

5.2.4   Halogen compounds and complexes

5.2.4.1   Aqueous halogen complexes

Am(III) fluorides: The number of experimental studies on Am(III) complexation with fluoride ions is relatively limited. SILVA et al. (1995) recommended equilibrium constants for the reactions:

$$\text{Am}^{3+} + n\,\text{F}^- \Leftrightarrow \text{AmF}_n^{(3-n)}$$
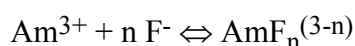
$$\log_{10}\beta_1° \text{ (n = 1, 298.15 K)} \quad = \quad 3.4 \pm 0.4$$

$$\log_{10}\beta_2° \text{ (n = 2, 298.15 K)} \quad = \quad 5.8 \pm 0.2$$

Contrary to selections in earlier reviews, such as an IAEA review or our own former data selection (PEARSON et al. 1992), no values are recommended by SILVA et al. (1995) for the formation of $AmF_3(aq)$ because the only existing data by AZIZ & LYLE (1969) were rejected by the reviewers based on reasons explained in SILVA et al. (1995).

Am(III) chlorides: The existence of the species $AmCl^{2+}$ and $AmCl_2^+$ is well established. Anion exchange measurements in very highly concentrated media indicated the presence of negatively charged species, probably $AmCl_4^-$. However, because of the extensive change in ionic strength in most experimental studies, it is difficult to distinguish unambiguously between complexation effects and activity effects. Hence, SILVA et al. (1995) recommended only one equilibrium constant[2]:

$$Am^{3+} + n\ Cl^- \Leftrightarrow AmCl_n^{(3-n)}$$

$$\log_{10}\beta_1° \text{ (n = 1, 298.15 K)} = 1.05 \pm 0.06$$
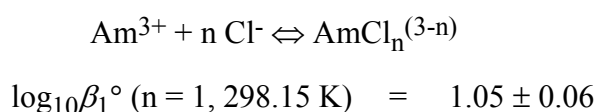
No values for $\log_{10}\beta_2°$ are selected.

Am(III) perchlorates: No clear distinction can be made between very weak complexation effects and large variations of activity coefficients. Therefore, SILVA et al. (1995) did not recommend equilibrium constants for any of the americium perchlorates.

Am(III) bromides and iodides: Only a few studies addressed complex formation of Am(III) with bromide and iodide ions. It is difficult to distinguish between complexation and activity effects in very highly concentrated media as applied in these studies. Thus, no values are selected.

No thermodynamic data are available on the formation of **Am(IV), (V) or (VI) halide** complexes.

5.2.4.2 Americium halide compounds

There are rather few experimental studies from which accurate thermodynamic data for americium halides can be derived:

1. The enthalpy of dissolution of $AmCl_3(cr)$ in the gas phase.

2. The vapour pressure of $AmF_3(cr)$.

3. The equilibrium constant for the solid - gas reaction $AmOCl(cr) + 2\ HCl(g) \Leftrightarrow AmCl_3(cr) + H_2O(g)$ studied from 682 to 880 K.

---

[2] The equilibrium constant for the Am(III) chloride complex is probably too high as judged by the corresponding data for Cm(III) determined by spectroscopy: $\log_{10}\beta_1° = 0.24 \pm 0.03$ (NECK et al. 1998).

4. The equilibrium constant for the solid - gas reaction $AmOBr(cr) + 2\ HBr(g) \Leftrightarrow AmBr_3(cr) + H_2O(g)$ studied from 719 to 890 K.

Therefore, in almost all cases the enthalpy of formation and the standard entropy of americium halides have been estimated.

In the case of $AmF_3(cr)$, a solubility product is derived from these estimated values and compared with experimental data. The americium solubilities calculated with this solubility product were found to be orders of magnitude higher than the americium concentration reported for fluoride solutions having $[ClO_4^-] \approx 0.1$ M. However, it is not certain that these solutions were indeed in equilibrium with crystalline americium trifluoride rather than amorphous (or even hydrated) trifluoride. Hence, the selection made by SILVA et al. (1995) cannot be confirmed with solubility data.

Considering this, we decided that the estimated Gibbs free energies, enthalpies and entropies of $AmF_3(cr)$, $AmF_4(cr)$, $AmCl_3(cr)$, $AmOCl(cr)$, $AmBr_3(cr)$, $AmOBr(cr)$ and $AmI_3(cr)$ will not be included in our database.

5.2.5   Chalcogen compounds and complexes

5.2.5.1   Americium chalcogenides

There are no experimental studies involving the thermodynamic properties for americium chalcogenides. SILVA et al. (1995) summarised the preparative and structural data for these phases, and included a few estimated values for the entropies of the monochalcogenides.

Hence, no data for americium sulphides, sulphates, selenides or tellurides are included in our database.

5.2.5.2   Aqueous americium sulphates

There are a few reliable quantitative studies available in the literature on the Am(III) sulphate system, and all of them refer to solutions of low pH ($\leq$ 3.6). SILVA et al. (1995) recommended equilibrium constants for the reactions[3]:

---

[3]   The equilibrium constants for the Am(III) sulphate complexes are probably too high as judged by the corresponding data for Cm(III) determined by spectroscopy: $\log_{10}\beta_1° = 3.3 \pm 0.1$ and $\log_{10}\beta_2° = 3.7 \pm 0.2$ (NECK et al. 1998).

$$Am^{3+} + n\ SO_4^{2-} \Leftrightarrow Am(SO_4)_n^{(3-2n)}$$
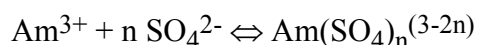
$$log_{10}\beta_1° \ (n = 1, 298.15\ K) \quad = \quad 3.85 \pm 0.03$$

$$log_{10}\beta_2° \ (n = 2, 298.15\ K) \quad = \quad 5.4 \pm 0.7$$

There is no evidence of americium hydrogen-sulphate complex formation.

5.2.6   Group 15 compounds and complexes

5.2.6.1   Nitrogen compounds and complexes

There are no experimental studies on the thermodynamic properties of solid americium nitrides, nitrites or nitrates.

Am(III) azide complexes: SILVA et al. (1995) selected from experimental studies on the complex formation between Am(III) and azide ions a stability constant for the AmN_3^{2+} complex. However, azide complexes are not relevant under environmental conditions and are not included in the database.

Am(III) nitrite complexes: SILVA et al. (1995) selected from an experimental study on the complex formation between Am(III) and nitrite ions a stability constant for the $AmNO_2^{2+}$ complex. However, nitrite complexes are not thought to be of relevance and are not included in our database.

Am(III) nitrate complexes: The Am(III) nitrate system has been investigated in a number of solvent extraction studies. The experimental measurements were interpreted assuming the formation of $AmNO_3^{2+}$ and $Am(NO_3)_2^+$. The corresponding stability constants indicate that the nitrate complexes are weak. It is therefore difficult to distinguish between complex formation and changes in the activity coefficients of the solutes caused by the large changes in solute concentration. Hence, SILVA et al. (1995) relied only on the data obtained for the $AmNO_3^{2+}$ species according to

$$Am^{3+} + NO_3^- \Leftrightarrow AmNO_3^{2+}$$
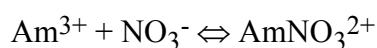
$$log_{10}\beta_1° \ (298.15\ K) \quad = \quad 1.33 \pm 0.20$$

and considered that there is no clear evidence of the existence of higher complexes.

5.2.6.2   Phosphorous compounds and complexes

Aqueous americium phosphorous complexes: There are few reliable studies available in the literature on americium complexation by phosphate anions, and most of these studies were performed

on solutions of low pH and fairly high concentration of phosphoric acid. Experimental studies of equilibira in the americium phosphoric acid system are complicated by the presence of several competing ligands: $H_3PO_4(aq)$, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}. The mono- and dihydrogen phosphate complexes $AmHPO_4^+$ and $Am(H_2PO_4)_n^{(3-n)}$ (n = 1 to 4) have been suggested to interpret the various experimental data.

Within the scope of the NEA review (SILVA et al. 1995) all the available literature data have been reanalysed. The reviewers concluded that the existence of $AmHPO_4^+$ is not clearly proven in the experimental study proposing this complex and thus, the equilibrium constant for the formation of $AmHPO_4^+$ was disregarded.

For the equilibrium

$$Am^{3+} + H_2PO_4^- \Leftrightarrow AmH_2PO_4^{2+}$$

$$\log_{10}\beta_1° \, (298.15 \text{ K}) \;=\; 3.0 \pm 0.5$$
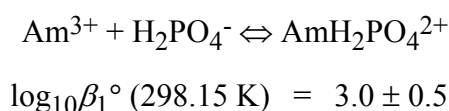
only the first equilibrium constant is recommended by SILVA et al. (1995).

The papers proposing the existence of higher dihydrogen phosphate complexes, $Am(H_2PO_4)_n^{(3-n)}$ (n = 2 to 4), were judged by SILVA et al. (1995) to have used inadequate experimental techniques for a system where several ligands may form various cationic complexes. Hence, these data were disregarded by SILVA et al. (1995).

Likewise, proposed equilibrium constants of phosphate complexes with higher valences of americium have not been recommended by SILVA et al. (1995). The reasons are that either it is not possible to separate ionic strength effects from complex formation in highly concentrated phosphoric acid solutions, or that the experimental data are not adequate to prove the proposed chemical model.

Solid americium phosphorous compounds: The experimental data of a solubility study of [243]Am(III) in phosphate media at pH < 3 were interpreted according to the following reaction:

$$AmPO_4 \cdot x \, H_2O(am) \Leftrightarrow Am^{3+} + PO_4^{3-} + x \, H_2O(l)$$
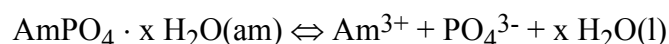
SILVA et al. (1995) selected the solubility constant obtained by this study as recommended value. However, they could not select the corresponding $\Delta_f G_m°$ for $AmPO_4(am, hydr)$ due to the unknown stoichiometry of the solid phase.

We decided not to include this solid phase in our database for the following reasons. The solubility constant has been derived at pH < 3. It is not clear whether the same solid is in equilibrium with

phosphate containing solutions at neutral or alkaline conditions. In addition, since we consider only one dihydrogen phosphate complex, $AmH_2PO_4^{2+}$, in our database, any geochemical model calculation for environmental systems including phosphate at pH > 3 would most probably lead to large errors in dissolved americium concentrations due to the inadequate aqueous speciation model.

5.2.6.3   Arsenic, antimony and bismuth compounds

No thermodynamic data are available for arsenides, arsenates, antimonides and bismuthides of americium.

5.2.7   Group 14 compounds and complexes

5.2.7.1   Carbon compounds and complexes

5.2.7.1.1   Americium carbides

SILVA et al. (1995) selected estimated thermodynamic properties of Am_2C_3(cr). However, carbides are not relevant under environmental conditions and are not included in our database.

5.2.7.1.2   Americium carbonate compounds and complexes

The number of experimentally derived thermodynamic values for solubility products of solids and formation constants of solution species is rather limited. SILVA et al. (1995) concentrated on thermodynamic constants determined from experiments and considered estimates only when they had good chemical justification and when credible data are missing.

Am(III) carbonate complexes: Americium complexation by carbonate has been investigated with a number of different methods. For the reaction

$$Am^{3+} + n\ CO_3^{2-} \Leftrightarrow Am(CO_3)_n^{(3-2n)}$$
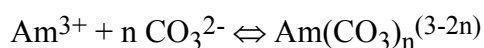
these studies have demonstrated the existence of complexes with n = 1, 2 and 3. There is no experimental evidence on the existence of $Am(CO_3)_4^{5-}$, even at the highest carbonate concentrations. SILVA et al. (1995) recommended the following equilibrium constants

$$\log_{10}\beta_1° \text{ (n = 1, 298.15 K)} \quad = \quad 7.8 \pm 0.3$$

$$\log_{10}\beta_2° \text{ (n = 2, 298.15 K)} \quad = \quad 12.3 \pm 0.4$$

$$\log_{10}\beta_3° \text{ (n = 1, 298.15 K)} \quad = \quad 15.2 \pm 0.6$$

Am(III) bicarbonate complexes: SILVA et al. (1995) concluded that there is no experimental evidence which can prove the existence of americium bicarbonate complexes. Further experimental work is necessary before the reality of these complexes in aqueous solutions is established.

Mixed Am(III) hydroxide-carbonate complexes: All the available experimental data can be re-interpreted with the assumption that only americium carbonate complexes and / or hydrolysis products are formed in aqueous solutions. Further experimental work is needed to confirm or deny the existence of mixed Am(III) hydroxy-carbonate complexes in aqueous solutions.

Higher valences of americium: Measurements in 2 M $NaHCO_3$/Na_2CO_3 media have been interpreted presuming that $Am(IV)(CO_3)_5^{6-}$, $Am(V)O_2(CO_3)_3^{5-}$ and $Am(VI)O_2(CO_3)_3^{4-}$ are the limiting complexes for the IV, V and VI oxidation states, as expected by analogy with U(IV), Np(V) and U(VI) - Pu(VI), respectively. Equilibrium constants for these three complexes are recommended by SILVA et al. (1995). However, as these complexes are the only ones available for higher valences of americium, we preferred to restrict our database to Am^{3+} and thus, values for these three carbonate complexes are not included in our database.

$AmCO_3OH$(s): Americium hydroxy-carbonate is characterised by x-ray diffraction investigations and solubility studies. SILVA et al. (1995) recommended the solubility product for the reaction

$$AmCO_3OH(cr) \Leftrightarrow Am^{3+} + CO_3^{2-} + OH^-$$

$$\log_{10}K_{s,0}° \ (AmCO_3OH, \ cr, \ 298.15 \ K) \quad = \quad -21.2 \pm 1.4$$

From this equilibrium constant and auxiliary data the reaction

$$Am(OH)_3(cr) + CO_2(g) \Leftrightarrow AmCO_3OH(cr) + H_2O(l)$$
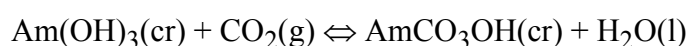
can be calculated as

$$\log_{10}K_p° \ (298.15 \ K) \quad = \quad 4.2 \pm 1.5$$

This results in a large uncertainty of the (fixed) CO_2(g) partial pressure for the equilibrium between the two solids which lies within the range of $2 \cdot 10^{-3}$ bar $> pCO_2 > 2 \cdot 10^{-6}$ bar (3 orders of magnitude as 95% confidence interval !).

$Am_2(CO_3)_3$(s): Americium carbonate is characterised by x-ray diffraction investigations and solubility studies. SILVA et al. (1995) recommended the solubility product for the reaction

$$0.5 \ Am_2(CO_3)_3(cr) \Leftrightarrow Am^{3+} + 1.5 \ CO_3^{2-}$$
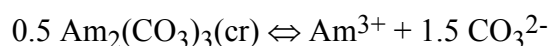
$$\log_{10}K_{s,0}° \ (Am_2(CO_3)_3, \ cr, \ 298.15 \ K) \quad = \quad -16.7 \pm 1.1$$

From this equilibrium constant and auxiliary data the reaction

$$AmCO_3OH(cr) + \tfrac{1}{2}\, CO_2(g) \Leftrightarrow \tfrac{1}{2}\, Am_2(CO_3)_3(cr) + \tfrac{1}{2}\, H_2O(l)$$
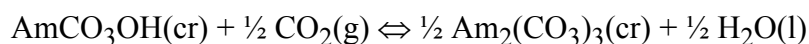
can be calculated as

$$\log_{10} K_p° \,(298.15\ K) \quad = \quad 0.4 \pm 1.8$$

which results in a range of $CO_2(g)$ equilibrium partial pressures for the equilibrium between the two solids of 630 bar $> pCO_2 > 4 \cdot 10^{-5}$ bar (7 orders of magnitude as 95% confidence interval !).

The large uncertainties associated with the phase boundaries between the solids $Am_2(CO_3)_3(cr)$, $AmCO_3OH(cr)$ and $Am(OH)_3(cr)$ pose serious obstacles in geochemical modelling. New experiments aiming at a direct determination of these phase boundaries seem to be necessary. Such direct determinations of phase boundaries are common practice in experimental petrology and can be used as additional information to derive internally consistent sets of thermodynamic constants.

$NaAm(CO_3)_2(s)$ and $Na_3Am(CO_3)_3(s)$: Several publications have appeared with values for the solubility product of $NaAm(CO_3)_2(s)$. These values are based on solubility experiments which have not appeared in the open literature. Thus, due to the lack of experimental details, a value for the solubility product of $NaAm(CO_3)_2(s)$ cannot be recommended by SILVA et al. (1995). No thermodynamic data are available for $Na_3Am(CO_3)_3(s)$.

5.2.7.1.3   Americium cyanide complexes

Qualitative information on the interaction between Am(III) and cyanide ions has been published. More experimental work is needed to confirm the composition and stability of the complexes formed. No value can be recommended for this system.

5.2.7.1.4   Americium thiocyanate complexes

Americium complexation by thiocyanate is quite weak, and its study requires large concentrations of the thiocyanate ligand. Therefore, large background electrolyte concentrations have been used in order to keep activity coefficients nearly constant. Most investigations have been performed by solvent extraction and several mononuclear species have been suggested to interpret the different experimental measurements. Considering all the experimental difficulties, SILVA et al. (1995) recommended only a formation constant for the complex $AmSCN^{2+}$.

However, thiocyanate complexes are presently not included in our database.

5.2.7.2   Silicon compounds and complexes

Americium silicides: Silicides are not relevant under environmental conditions and are not included in our database.

Aqueous americium silicates: Only one paper has recently been published reporting experimental data on Am(III) silicate complexation (WADSAK et al. 2000). The authors interpreted the results of their solvent extraction study, carried out at pH 3.0 – 3.8 in terms of a 1:1 complex according to the equilibrium

$$Am^{3+} + SiO(OH)_3^- \Leftrightarrow AmSiO(OH)_3^{2+}$$
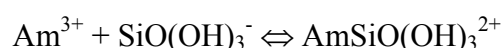
The following constant has been derived for zero ionic strength: $\log \beta_1° = 8.1 \pm 0.2$. Although the stoichiometry of this aqueous species has not been established by other methods, e.g. spectroscopy, the equilibrium constant fits in the overall pattern of aqueous silicate complexes (see section 5.18) and thus, it has been provisionally included in our database.

Solid americium silicate compounds: Structural data have been reported on $AmSiO_4(cr)$. However, tetravalent Am is unlikely to be of importance in natural aquatic systems. Because of the similarity in chemical behaviour between the trivalent actinoids and lanthanoids, one would expect Am(III) to form a variety of compounds with silica as do the rare earths. Unfortunately, no data are available on the solubility constant of any americium silicate compound.

Table 5.2.1: Selected americium data. Numbers in **bold face** are selected in this review. They are at variance from the values recommended by SILVA et al. (1995).

TDB Version 05/92   **TDB Version 01/01**

Name	$\Delta_f G_m°$	$\Delta_f H_m°$	Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$S_m°$	Species
	-	-	Am(cr)	0	0	55.4 ± 2.0	Am(cr)
AM+3	-599.1	-616.7	Am+3	-598.7 ± 4.8	-616.7 ± 1.5	-201.0 ± 15	Am^{3+}

Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Reaction
AMOH+2	-6.5	0	AmOH+2	***-7.3 ± 0.3***		$Am^{3+} + H_2O(l) \Leftrightarrow AmOH^{2+} + H^+$
AMOH2+	-13.8	0	Am(OH)2+	***-15.2 ± 0.8***		$Am^{3+} + 2\ H_2O(l) \Leftrightarrow Am(OH)_2^+ + 2\ H^+$
AMOH3	-25.2	0	Am(OH)3	-25.7 ± 0.5		$Am^{3+} + 3\ H_2O(l) \Leftrightarrow Am(OH)_3(aq) + 3\ H^+$
AMF+2	4.5	0	AmF+2	3.4 ± 0.4		$Am^{3+} + F^- \Leftrightarrow AmF^{2+}$
AMF2+	8.0	0	AmF2+	5.8 ± 0.2		$Am^{3+} + 2\ F^- \Leftrightarrow AmF_2^+$
AMF3	11.2	0	AmF3	-	-	$Am^{3+} + 3\ F^- \Leftrightarrow AmF_3(aq)$
AMCL+2	1.1	0	AmCl+2	1.05 ± 0.06		$Am^{3+} + Cl^- \Leftrightarrow AmCl^{2+}$
AMSO4+	4.0	0	AmSO4+	3.85 ± 0.03		$Am^{3+} + SO_4^{2-} \Leftrightarrow AmSO_4^+$
AMSO42-	5.7	0	Am(SO4)2-	5.4 ± 0.7		$Am^{3+} + 2\ SO_4^{2-} \Leftrightarrow Am(SO_4)_2^-$
	-	-	AmNO3+2	1.33 ± 0.20		$Am^{3+} + NO_3^- \Leftrightarrow AmNO_3^{2+}$
AMH2PO4+	2.649	0	AmH2PO4+2	3.0 ± 0.5		$Am^{3+} + H_2PO_4^- \Leftrightarrow AmH_2PO_4^{2+}$
AMH4PO42	3.698	0		-	-	$Am^{3+} + 2\ H_2PO_4^- \Leftrightarrow Am(H_2PO_4)_2^+$
AMCO3+	8.1	0	AmCO3+	7.8 ± 0.3		$Am^{3+} + CO_3^{2-} \Leftrightarrow AmCO_3^+$
AMCO32-	12.6	0	Am(CO3)2-	12.3 ± 0.4		$Am^{3+} + 2\ CO_3^{2-} \Leftrightarrow Am(CO_3)_2^-$
AMCO33-3	14.2	0	Am(CO3)3-3	15.2 ± 0.6		$Am^{3+} + 3\ CO_3^{2-} \Leftrightarrow Am(CO_3)_3^{3-}$
AMOHCO3	0.7	0		-	-	$Am^{3+} + H_2O(l) + CO_3^{2-} \Leftrightarrow AmOHCO_3(aq) + H^+$
AMOH2CO3	-7.2	0		-	-	$Am^{3+} + 2\ H_2O(l) + CO_3^{2-} \Leftrightarrow Am(OH)_2CO_3^- + 2\ H^+$

Table 5.2.1: continued

Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Reaction
AMOHCO32	4.8	0	-	-	-	$Am^{3+} + H_2O(l) + 2\ CO_3^{2-} \Leftrightarrow AmOH(CO_3)_2^{2-} + H^+$
	-	-	AmSiO(OH)3+2	**8.1 ± 0.2**		$Am^{3+} + SiO(OH)_3^- \Leftrightarrow AmSiO(OH)_3^{2+}$

Name	$\log_{10}K_{s,0}°$	$\Delta_r H_m°$	Name	$\log_{10}K_{s,0}°$	$\Delta_r H_m°$	Reaction
AM(OH)3CR	18.7	0	Am(OH)3(cr)	15.2 ± 0.6		$Am(OH)_3(cr) + 3\ H^+ \Leftrightarrow Am^{3+} + 3\ H_2O(l)$
	-	-	Am(OH)3(am)	17.0 ± 0.6		$Am(OH)_3(am) + 3\ H^+ \Leftrightarrow Am^{3+} + 3\ H_2O(l)$
	-	-	AmCO3OH(cr)	-21.2 ± 1.4		$AmCO_3OH(cr) \Leftrightarrow Am^{3+} + CO_3^{2-} + OH^-$
	-	-	Am(CO3)1.5(cr)	-16.7 ± 1.1		$0.5\ Am_2(CO_3)_3(cr) \Leftrightarrow Am^{3+} + 1.5\ CO_3^{2-}$

5.2.8 References

AZIZ, A., LYLE, S.J. (1969): Equilibrium constants of aqueous fluoro complexes of scandium, yttrium, americium(III) and curium(III) by extraction into di-2-ethylhexyl phosphoric acid. J. Inorg. Nucl. Chem., 31, 3471-3480.

NECK, V., FANGHÄNEL, TH., KIM, J.I. (1998): Aquatische Chemie und thermodynamische Modellierung von trivalenten Actiniden. Wissenschaftliche Berichte FZKA 6110, Forschungszentrum Karlsruhe, Karlsruhe, Germany, 108p.

PEARSON, F.J., BERNER, U., HUMMEL, W. (1992): Nagra Thermochemical Data Base II. Supplemental Data 05/92. Nagra Technical Report NTB 91-18, Nagra, Wettingen, Switzerland, 284p.

SILVA, R.J., BIDOGLIO, G., RAND, M.H., ROBOUCH, P.B., WANNER, H., PUIGDOMÈNECH, I. (1995): Chemical Thermodynamics of Americium. Elsevier, Amsterdam, 374p.

WADSAK, W., HRNECEK, E., IRLWECK, K. (2000): Formation of americium(III) complexes with aqueous silicic acid. Radiochim. Acta, 88, 61-64.

5.3   Calcium

The mineral fluorite, $CaF_2(cr)$, is common in aqueous systems, and may influence ground-water chemistry. In spite of the ubiquity and simple chemistry of this mineral, values for its thermodynamic properties differ widely. Values given by CODATA, NORDSTROM et al. (1990, Table I) and other data bases differ by as much as 0.55 in $\log_{10}K°$. Hence, fluorite is included as supplemental data only, and reaction data for this mineral are taken from NORDSTROM et al. (1990).

The results of potentiometric titrations of $Si(OH)_4(aq)$ in the presence of Ca^{2+} in 1 M $NaClO_4$ up to pH 9 are reported by SANTSCHI & SCHINDLER (1974). The results of this experimental study are not unambiguous in terms of the speciation model. Two limiting situations are discussed by SANTSCHI & SCHINDLER (1974). Based on chemical arguments, the most probable interpretation of the experimental data could be done in terms of two species, $CaSiO(OH)_3^+$ and $CaSiO_2(OH)_2(aq)$. Values for the stability constants of these complexes are extrapolated from 1M $NaClO_4$ to zero ionic strength and included as supplemental data. For a detailed discussion see Section 5.18.4.1.

No other calcium compounds and complexes are included in the supplemental data set.

5.3.1   References

NORDSTROM, D.K., PLUMMER, L.N., LANGMUIR, D., BUSENBERG, E., MAY, H.M., JONES, B.F., PARKHURST, D.L. (1990): Revised Chemical Equilibrium Data for Major Water-Mineral Reactions and Their Limitations. In: MELCHIOR, D. C., BASSETT, R. L. (eds.): Chemical Modeling of Aqueous Systems II. Washington, D.C., American Chemical Society, ACS Symposium Series 416, p. 398-413.

SANTSCHI, P.H., SCHINDLER, P.W. (1974): Complex formation in the ternary systems Ca^{II}–H_4SiO_4–H_2O and Mg^{II}–H_4SiO_4–H_2O. J. Chem. Soc. Dalton Transactions, 181-184.

5.4 Europium

In the framework of the Nagra/PSI TDB update, europium has been selected as a new element to be included in the database. Although it is of limited relevance to repository safety, europium is widely used in laboratory experiments as analogue of trivalent actinides. The correct evaluation of the results from such experiments largely depends on the quality of the equilibrium constants used. In this report thermodynamic data for Eu(III) are evaluated and selected for inclusion in the database. Concerning reactions involving Eu(II), only the Eu^{3+}/Eu^{2+} redox equilibrium and the formation properties of the free europeous ion have been included.

Emphasis is placed on the evaluation of equilibrium constants for Eu(III) hydrolysis and carbonate complexation, as well as on the solubility products of the (hydr)oxides and carbonates, since reactions involving these complexes and solids limit the Eu concentration in most aquatic systems.

The results of our evaluation show that the majority of the selected Eu(III) constants are fairly close to the corresponding values for Am(III), as expected on the basis of the similar chemical properties of these two elements. However, there is some disagreement with the first and second Am(III) hydrolysis constant recommended by SILVA et al. (1995).

In this chapter the thermodynamic data for Eu included in the Nagra/PSI database update are collected and discussed. Symbols and notation used in this text follow the guidelines of GRENTHE & PUIGDOMENECH (1997). All selected data are summarised in Table 5.4.4.

5.4.1 Elemental europium

Elemental europium, either in gaseous, liquid or metallic form, is unstable in natural environments. It is included in the database only for computational purposes, since the absolute molar entropy of metallic Eu (77.8 J K^{-1} mol^{-1}, taken from WAGMAN et al. 1982) is required to derive the entropy of formation of the free aqueous ions.

5.4.2 Free europium aqua ions

The most stable oxidation state of Eu in aqueous solutions is the trivalent, as for the other lanthanides. Europium is however the only rare earth element which can be easily reduced to the divalent state in aqueous solutions. Metallic Mg or Zn can perform this reduction and stable solutions are obtained (COTTON & WILKINSON 1982). The standard potential for the reduction of europic to europeous ion (BARD et al. 1985)

$$Eu^{3+} + e^- \Leftrightarrow Eu^{2+}, \ E^0_{(red)} = -0.35 \text{ V}$$
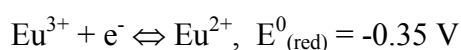
lies slightly above that for reduction of divalent to metallic iron (-0.44 V) and it is thus conceivable that Eu^{2+} may be stable in the repository near-field. The existence of Eu^{2+} in strongly reducing natural environments has been reported and is also the cause of the well-known "Eu anomalies" in crustal rocks (BROOKINS 1989). Unfortunately, thermodynamic data on aqueous Eu(II) complexes and solids are practically non-existent, so that only the free aqueous ion will be included in the database. From the reduction potential reported above we derive:

$$\log_{10}K^0 (Eu^{3+} + e^- \Leftrightarrow Eu^{2+}) = E^0_{(red)} F /(RT \ln10) = -5.92$$

where F is Faraday's constant, R is the gas constant and T the absolute temperature.

Eu^{2+} has a relatively large ionic radius (0.117 nm in octahedral coordination; see SHANNON 1976) practically identical to that of Sr^{2+} (0.118 nm). Considering further the similar chemical properties of lanthanides and alkaline-earth elements, it is reasonable to assume that Eu^{2+} will have a strong affinity to Sr^{2+}. Strontium hydrolysis is very weak and starts at very high pH ($\log_{10}*\beta^0_{1,1}$ = -13.3, see BAES & MESMER 1976). Furthermore, Sr complexation with common inorganic ligands like carbonate, sulphate and chloride is rather weak. Therefore, in most groundwaters the speciation of the europeous ion will be dominated by the free aqueous ion. This implies that it is sufficient to use the above equilibrium when modelling reducing solution in the acidic region. For speciation calculations at higher pH, one is advised to use the complexation data on Sr(II) available in the database as estimates of the corresponding Eu(II) constants.

A scoping calculation indicates that assuming oxidation potentials in the lower range of the values predicted in the near-field of a high-level waste repository leads to significant proportions of reduced europium. For instance, CURTI (1993) predicted a potential of -400 mV (pE = -6.76) for a bentonite pore water in equilibrium with pyrite and magnetite. Under such conditions, $\sim$ 90 % of the total dissolved Eu would be in the divalent state, while only $\sim$10 % would be in the trivalent state.

Thermodynamic properties for the free Eu^{3+} ions have been derived by two methods:

(A)   With the help of standard half-cell potentials for the Eu^0/Eu^{2+} and Eu^{2+}/Eu^{3+} couples (BARD et al. 1985):

$Eu^{3+} + e^-$	$\Leftrightarrow Eu^{2+}$	$E^0_{(red)}$ = -0.35 V	x 1	= -0.35 V eq.
$Eu^{2+} + 2 e-$	$\Leftrightarrow Eu^0$	$E^0_{(red)}$ = -2.80 V	x 2	= -5.60 V eq.
$Eu^{3+} + 3 e-$	$\Leftrightarrow Eu^0$	$E^0_{(red)}$ = -1.983 V		= (-0.35 - 5.60) / 3 V
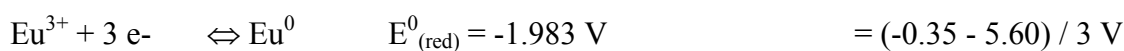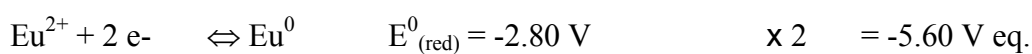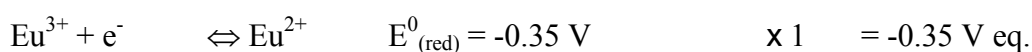
BARD et al. (1985) give $E^0_{(red)}$ = -0.35 ± 0.03 V for the reduction from the trivalent to divalent state, based on a series of e.m.f. measurements, while the potential for the reduction from divalent to metallic europium ($E^0_{(red)}$ = -2.80 V) was calculated from calorimetric data. Thus, the resulting standard reduction potential of -1.983 V for the half-cell $Eu^{3+} + 3e^- = Eu^0$, reported by BARD et al. (1985), is not based on experimental data alone. Using this half-cell potential one obtains:

$$\Delta_f G_m^0 \ (Eu^{3+}, aq, 298.15 \ K) = E^0_{(red)} \ F \ n =$$

$$= -1.983 \ V \ x \ 96.4935 \ kA \ s \ mol^{-1} \ x \ 3 = -574.0 \ kJ \ mol^{-1}.$$

(B) Applying the most recent calorimetric data for $Eu(OH)_3(cr)$ ($\Delta_f H_m^0$ = -1319.1 ± 15 kJ mol^{-1}, see Table 3 in DIAKONOV et al. 1998), $S^0(Eu,cr)$ = 77.8 J K^{-1} mol^{-1} from WAGMAN et al. (1982), CODATA values for $\Delta_f G_m^0(H_2O,l)$, $S^0(O_2,g)$, $S^0(H_2,g)$ (COX et al. 1989); and combining them with the selected solubility constant of crystalline $Eu(OH)_3$ ($\log_{10} {*}K^0_{s,0}$ = 14.9 ± 0.3, see 5.4.3.2).

As a first step, the free energy of formation for the crystalline hydroxide is determined:

$\Delta_f G_m^0 \ _{(Eu(OH)_3, \ cr)} =$

$= \Delta_f H_m^0 \ _{(Eu(OH)_3, \ cr)} - T^0 \ x \ [S^0_{(Eu(OH)_3, \ cr)} - S^0_{(Eu, \ cr)} - (3/2) \ S^0_{(O_2, \ g)} - (3/2) \ S^0_{(H_2, \ g)}] =$

$= -1319.1 ± 15 - 298.15 \ x \ [0.11988 ± 0.005 - 0.0778 - (3/2) \ 0.205152 - (3/2) \ 0.13068] =$

$= -1181.5 ± 15.1 \ kJ \ mol^{-1}$.

This value is then used to compute the free energy of the aqueous ion, based on the equilibrium:

$$Eu(OH)_3 \ (cr) + 3 \ H^+ \Leftrightarrow Eu^{3+} + 3 \ H_2O$$

$\Delta_f G_m^0 \ _{(Eu^{3+}, \ aq, \ 298.15 \ K)} = \Delta_r G_m^0 - 3 \ \Delta_f G_m^0_{(H_2O,l)} + 3 \ \Delta_f G_m^0_{(H^+,aq)} + \Delta_f G_m^0 \ _{(Eu(OH)_3, \ cr)}$

$\Delta_f G_m^0 \ _{(Eu^{3+}, \ aq, \ 298.15 \ K)} = -RT \ ln {*}K^0_{s,0} - 3 \ \Delta_f G_m^0_{(H_2O,l)} + \Delta_f G_m^0 \ _{(Eu(OH)_3, \ cr)} =$

$= -0.0083147 \ x \ 298.15 \ x \ ln10 \ x \ 14.9 ± 0.3 - 3 \ x \ (-237.1) - 1181.5 ± 13.5 = -555.1 ± 13.6 \ kJ \ mol^{-1}$

Note that the two independent free energy values calculated above for the aqueous Eu^{3+} ion agree within their uncertainties, thus increasing the confidence in these numbers. For reasons of internal consistency the latter value (-555.1 ± 13.6 kJ mol^{-1}) has been adopted, since it is directly related to the solubility constant of crystalline Eu hydroxide selected for the database update (see section 5.4.3.2).

However, both values derived above differ significantly from the corresponding NEA recommended free energy of formation for Am^{3+} (-598.7 ± 4.8 kJ mol^{-1}), which is expected to be similar on the base of the chemical analogy of the two elements. This discrepancy may be partly related to a possible error in the $\Delta_f H_m^0{}_{(Eu(OH)_3,cr)}$ value used in our calculation: DIAKONOV et al. (1998) give -1319.1 kJ mol^{-1} for this quantity, while the formation enthalpies of all other lanthanide hydroxides are reported to be in the interval -1395.5 to -1432.5 kJ mol^{-1}. Using the latter formation enthalpy values instead of -1319.1 kJ mol^{-1} in the above calculation would yield considerably lower free energies (~ -632 to -668 kJ mol^{-1}). In order to explain the reliability of the selected $\Delta_f H_m^0$ value, a detailed study of the source literature would be necessary. We prefer for the moment to accept the value of -1319.1 kJ mol^{-1}, with the reminder that it should be checked in a future review.

The following entropy values have been retrieved from two compilations of thermodynamic data:

S_m^0 (Eu , cr, 298.15 K)   =   58.6   J mol^{-1} K^{-1} (LATIMER 1952)

                                =   77.78   J mol^{-1} K^{-1} (WAGMAN et al. 1982)

S_m^0 (Eu^{3+}, aq, 298.15 K) =   -177.0   J mol^{-1} K^{-1} (LATIMER 1952)

                                =   -222.0   J mol^{-1} K^{-1} (WAGMAN et al. 1982)

S_m^0 (Eu^{2+}, aq, 298.15 K) =   -8.0   J mol^{-1} K^{-1} (WAGMAN et al. 1982)

Using the entropies of WAGMAN et al. (1982) and the CODATA value for the molar entropy of hydrogen gas:

$$Eu(cr) + 3H^+ \Leftrightarrow Eu^{3+}(aq) + 1.5\ H_2(g)$$
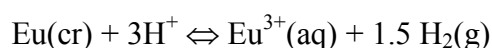
$$\Delta_f S_m^0{}_{(Eu^{3+},\ aq)} = S_m^0{}_{(Eu^{3+},\ aq)} + 1.5\ S_m^0{}_{(H_2,\ g)} - 3\ S_m^0{}_{(H^+,\ aq)} - S_m^0{}_{(Eu,\ cr)}$$

$$\Delta_f S_m^0{}_{(Eu^{3+},\ aq)} = -222 + 1.5 \times 130.68 - 3 \times 0 - 77.78\ =\ -103.76\ JK^{-1}\ mol^{-1}$$

the following formation enthalpy for the aqueous Eu^{3+} ion is obtained:

$$\Delta_f H_m^0{}_{(Eu^{3+},\ aq)} = \Delta_f G_m^0{}_{(Eu^{3+},\ aq)} + T^0\ \Delta_f S_m^0{}_{(Eu^{3+},\ aq)}$$

$$\Delta_f H_m^0{}_{(Eu^{3+},\ aq)} = -555.1 \pm 13.6\ + 298.15 \times (-0.10376) = -586.0\ \pm 13.6\ \ kJ\ mol^{-1}$$

Applying the entropy values of LATIMER (1952) leads to $\Delta_f H_m^0{}_{(Eu^{3+},\ aq)}$ = -572.6 ± 13.6 kJ mol^{-1}. We give however the preference to the values derived using the entropies of WAGMAN et al. (1982),

since this compilation is more recent and complete and the $S_m^0{}_{(Eu, cr)}$ given in Latimer's compilation is only an estimated value.

The free energy of formation of the europeous ion can be now computed with the help of $\Delta_f G_m^0{}_{(Eu^{3+}, aq)}$ = -555.1 kJ mol^{-1} and the standard reduction potential:

$$Eu^{3+} + \frac{1}{2} H_2(g) \Leftrightarrow Eu^{2+} + H^+ \qquad E_0 = -0.35 \pm 0.03 \text{ V}$$
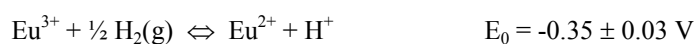
$$\Delta_f G_m^0{}_{(Eu^{2+}, aq)} = \Delta_r G_m^0 + \Delta_f G_m^0{}_{(Eu^{3+}, aq)} = -F E_0 + \Delta_f G_m^0{}_{(Eu^{3+}, aq)}$$

$$\Delta_f G_m^0{}_{(Eu^{2+}, aq)} = -96.4935 \text{ kJ V}^{-1} \text{ mol}^{-1} \times (-0.35 \pm 0.03 \text{ V}) - 555.1 \pm 13.6 \text{ kJ mol}^{-1}$$
$$= -521.3 \pm 13.9 \text{ kJ mol}^{-1}$$

5.4.3 Oxygen and hydrogen compounds

The selection of data for Eu(III) complexes and solids involving oxygen and hydrogen is based on a detailed review of published experimental data. Although several investigations are available, the results are often conflicting and require reinterpretation in the framework of the specific ion interaction (SIT) theory (GRENTHE et al. 1997).

5.4.3.1 Aqueous Eu(III) hydroxide complexes

5.4.3.1.1 First hydrolysis constant

Trivalent lanthanides hydrolyse only slightly below pH 7 while in basic solutions very insoluble hydroxides precipitate. This situation makes it difficult to study the hydrolysis of lanthanides, due to the low concentrations involved and the possible competition with other strong ligands (e.g. carbonate).

Although a variety of mono- and polynuclear hydroxide complexes of lanthanides are known, complexation constants at zero ionic strength can be extrapolated with good confidence only for the first mononuclear species $Ln(OH)^{2+}$. BAES & MESMER (1976) give a complete set of $\log_{10}\beta^0{}_1$ constants for trivalent lanthanides, all lying within 0.9 $\log_{10}$ units. These values are based on studies conducted in 0.5 M and 3 M ClO_4^- and are consistent with independent estimates based on cross correlations with constants for other 1:1 lanthanide complexes. From these data, BAES & MESMER (1976) obtained $\log_{10}*\beta^0{}_1 = -7.8 \pm 0.2$ for $EuOH^{2+}$.

NECK et al. (1998) reviewed the hydrolysis of trivalent actinides, including a few data available for Eu(III) and Nd(III). By inspecting Table 3.4 in the cited work, it becomes evident that in two of

three experimental studies where conditional constants of *both* Am(OH)$^{2+}$ and Eu(OH)$^{2+}$ were determined, the formation constants of these two species are indistinguishable within the given uncertainties. The authors come to the general conclusion that, if a consistent method is applied to derive zero ionic strength constants, no significant differences are found among corresponding constants for Am(III), Cm(III), Eu(III) and Nd(III). They thus propose, based on a Pitzer development, the following unique set of hydrolysis constants for the mentioned trivalent ions:

$$\log_{10}*\beta^0_{1,1} = -7.3 \pm 0.3$$

$$\log_{10}*\beta^0_{1,2} = -15.2 \pm 0.8$$

$$\log_{10}*\beta^0_{1,3} = -25.7 \pm 0.6$$

referring to the general reaction:

$$M^{3+} + n\,H_2O \Leftrightarrow M(OH)_n^{3-n} + n\,H^+ .$$

A problem with this approach is that there is a considerable bias in the data, since the majority of the conditional constants used by NECK et al. (1998) to obtain these values refers to the actinides, not to europium.

For this review, we prefer to evaluate the Eu(III) hydrolysis data alone, including supplemental data not considered in NECK et al. (1998). From these data, the first hydrolysis constant at zero ionic strength was determined by means of the specific ion interaction theory (SIT), as described in GRENTHE et al. (1997). Table 5.4.1 summarises the conditional constants used for the extrapolations, while Figures 5.4.1 and 5.4.2 show the least square regressions[4] through the constants obtained in NaCl and NaClO$_4$ solutions, respectively. The results of our extrapolations are summarised in Table 5.4.2 and compared to the $\log_{10}*\beta^0_1$ values determined by BAES & MESMER (1976) and NECK et al. (1998). Both SIT extrapolations (from NaCl and NaClO$_4$ data) yield values lying close to and within the range of the $\log_{10}*\beta^0_1$ values given in the mentioned references. In view of the very small standard deviation associated to our extrapolation from the NaClO$_4$ data, we decided to select this value for inclusion in the thermodynamic database:

---

[4]   The regressions in this chapter were calculated with unweighted data since it is not possible to assign reliable uncertainties to the conditional constants. Although uncertainties have been assigned to most conditional constants in the source references, these are in most cases of purely statistical nature and the frequently dominating systematic errors have not been determined. In an unweighted regression the standard deviation of $\log_{10}\beta^0$ is determined by the scatter of the data, while in the original SIT method it is determined by the uncertainty of each single data point. Assigning equal uncertainties to all data is mathematically equivalent to performing an unweighted regression, as the standard deviation terms cancel out in the least square regression formulae (see p. 704 in SILVA et al. 1992, and discussion in BEVINGTON 1969 p. 99 ff.).

$$\log_{10}*\beta^0_1 = -7.64 \pm 0.04$$

Although this is about one order of magnitude lower than the currently recommended NEA value for the corresponding Am(III) constant, it is fairly close to the generic constant given by NECK & KIM (2000) for the trivalent actinides ($\log_{10}*\beta^0_{1,1} \sim -7.3$). From the slope of the regression presented in Fig. 5.4.2, we obtain $\Delta\varepsilon = -0.36 \pm 0.01$. For the equivalent Am hydrolysis reaction, using the interaction coefficients tabulated in GRENTHE (1997) one calculates:

$\Delta\varepsilon \qquad = \varepsilon(H^+,ClO_4^-) + \varepsilon(AmOH^{2+}, ClO_4^-) - \varepsilon(Am^{3+}, ClO_4^-)$

$\Delta\varepsilon \qquad = 0.14 \pm 0.02 + 0.39 \pm 0.04 - 0.49 \pm 0.03 = 0.04 \pm 0.05$

Table 5.4.1: Conditional constants and auxiliary information used to determine $\log_{10}*\beta^0_1$ of Eu(OH)$_2^+$. [*] Constant obtained from the relation $\log_{10}*\beta_1 = \log_{10}\beta_1 + \log_{10}K_w$ using the original data given in the source reference ($\log_{10}\beta_1 = 5.84 \pm 0.47$ and $\log_{10}K_w = -13.78$ for 0.1 M NaClO$_4$).

T (^oC)	I (M)	Medium	Method	$\log_{10}*\beta_{1,1}$	Reference
25	0.7	NaCl	Extraction	-7.31 ± 0.20	CACECI & CHOPPIN (1983)
30	2.0	NaCl	pH titration	-8.29 ± 0.02	JIMENEZ-REYES et al. (1999)
30	2.0	NaCl	Extraction	-8.45 ± 0.23	JIMENEZ-REYES et al. (1999)
30	4.0	NaCl	Extraction	-6.33 ± 0.09	JIMENEZ-REYES et al. (1994)
25	5.0	NaClO$_4$	Extraction	-6.34 ± 0.05	SOLACHE-RIOS & CHOPPIN (1990)
25	1.0	NaClO$_4$	pH titration	-8.12 ± 0.02	NAIR et al. (1982)
25	1.0	NaClO$_4$	Extraction	-8.10 ± 0.40	LUNDQVIST (1982)
25	0.05	NaClO$_4$	pH titration	-8.03 ± 0.03	USHERENKO & SKORIK (1972)
25	0.1	NaClO$_4$	Solubility	-7.94 ± 0.47 [*]	BERNKOPF (1984)

$$Eu^{3+} + H_2O = EuOH^{2+} + H^+$$
(NaCl data)

- ◆ Caceci and Choppin (1983)
- ▲ Jimenez-Reyes and Solache-Rios (1994)
- ■ Jimenez-Reyes et al. (1999), extraction
- ▨ Jimenez-Reyes et al. (1999), titration
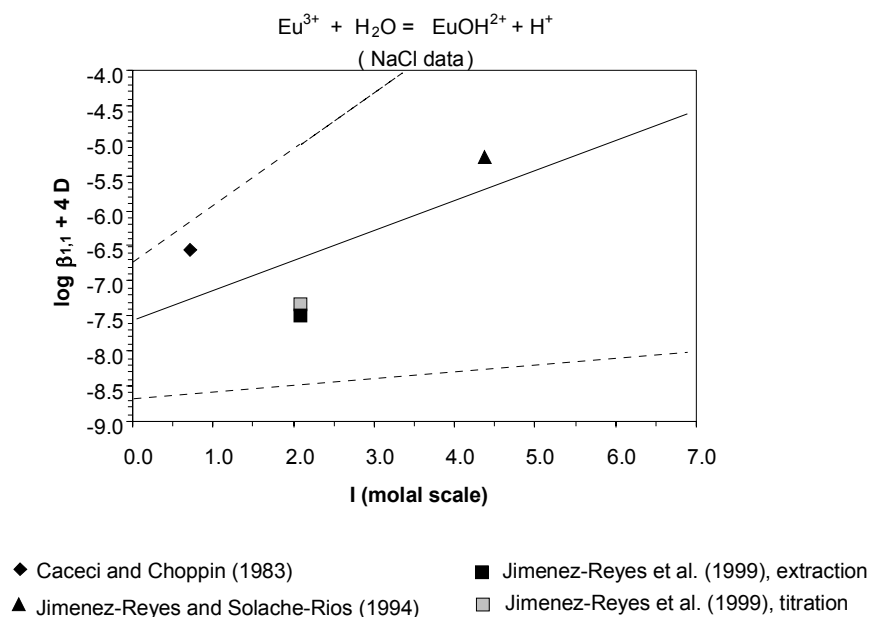
Fig. 5.4.1: Determination of $\log_{10}\beta^0_1$ and $\Delta\varepsilon$ for $Eu(OH)^{2+}$ based on the SIT equation (GRENTHE et al. 1997). The unweighted regression through conditional constants in NaCl solutions yields $\log_{10}*\beta^0_1 = -7.7 \pm 1.0$ and $\Delta\varepsilon = -0.45 \pm 0.36$.

$$Eu^{3+} + H_2O = EuOH^{2+} + H^+$$
(NaClO$_4$ data)

- ○ Bernkopf (1984)
- O Usherenko and Skorik (1972)
- ▲ Lundqvist (1982)
- ▨ Nair et al. (1982)
- ◆ Solache-Rios and Choppin (1990)
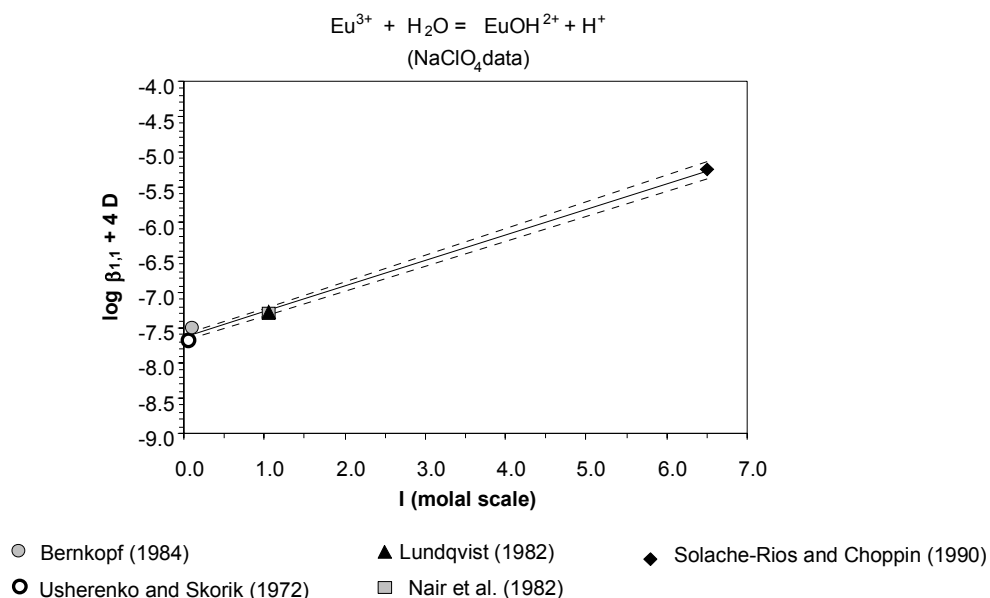
Fig. 5.4.2: Determination of $\log_{10}\beta^0_1$ and $\Delta\varepsilon$ for $Eu(OH)^{2+}$ based on the SIT equation (GRENTHE et al. 1997). The unweighted regression through conditional constants in NaClO$_4$ solutions yields $\log_{10}*\beta^0_1 = -7.64 \pm 0.04$ and $\Delta\varepsilon = -0.36 \pm 0.01$.

Table 5.4.2: Comparison of thermodynamic formation constants for Eu(OH)$^{2+}$.

Method	$\log_{10}{}^*\beta^0_1$ (EuOH^{2+})		Reference
Debye-Hückel	-7.8	± 0.2	BAES & MESMER (1976)
Pitzer	-7.3	± 0.3	NECK et al. (1998)
SIT (NaCl)	-7.7	± 1.0	present work
SIT (NaClO$_4$)	-7.64	± 0.04	present work

An^{3+} + H$_2$O = AnOH^{2+} + H$^+$
(NaClO$_4$ data)

▲ Wimmer (1992) ● Nair et al. (1982)
□ Stadler and Kim (1988) ■ Lundqvist (1982)
◇ Bernkopf (1984)
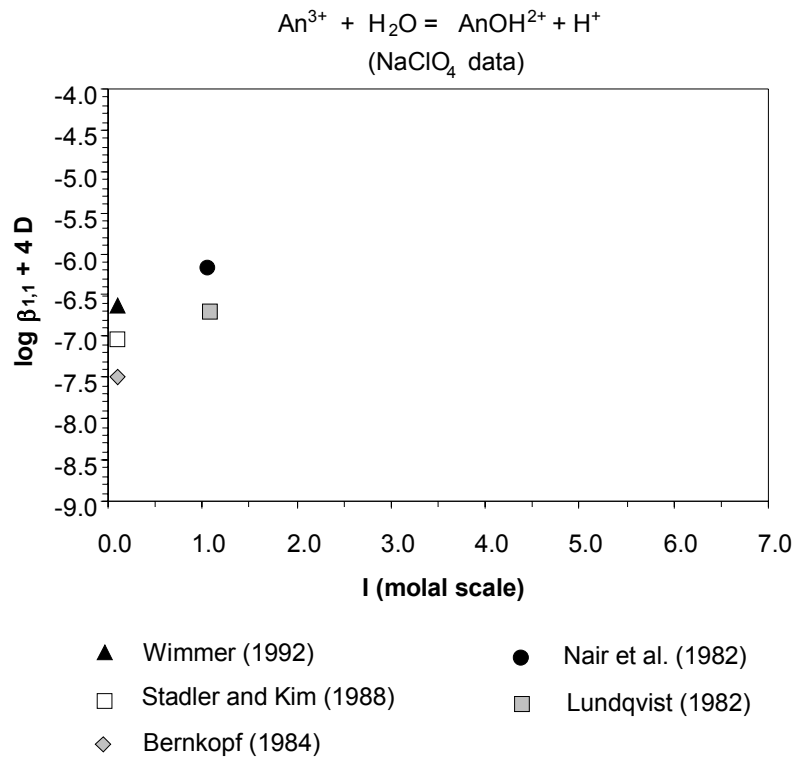
Fig. 5.4.3: SIT plot for Am(III) and Cm(III) first hydrolysis constants based on data compiled in NECK et al. (1998).

There is thus an inconsistency between the tabulated interaction coefficients for Am and the present extrapolation. In order to obtain clarity on this point, we plotted the conditional constants for the

mono-hydroxo complexes of Am and Cm, compiled in NECK et al. (1998) on Fig. 5.4.3. Although not well defined, the linear extrapolation yields $\Delta\varepsilon$ = -0.67 ± 0.39, which also disagrees with the value of 0.04 ± 0.09 calculated from the NEA interaction coefficients. This indicates that one or more of the tabulated interaction coefficients used in the equation above is probably in error. In contrast, the $\Delta\varepsilon$ values extrapolated here for the Am, Cm and Eu first hydrolysis reactions agree, within their uncertainties. If the other interaction coefficients involved are correct, then $\varepsilon(Am^{3+}$, $ClO_4^-)$ and $\varepsilon(Eu^{3+}, ClO_4^-)$ would have to lie between 0.9 and 1.2 in order to produce the observed $\Delta\varepsilon$ values. This would qualitatively agree with new indications for a high $\varepsilon(Th^{4+}, ClO_4^-)$ value of ~2 (see chapter 5.21.2). It is noteworthy that the Am interaction coefficients tabulated in GRENTHE (1997), which have been directly taken over from the NEA review (see p. 322 in SILVA et al. 1995), are estimates based on analogies with trivalent lanthanides. Since interaction coefficients of lanthanides are well established, the errors made in transferring them to Am(III) should not be large.

5.4.3.1.2   Higher hydrolysis constants

Constants for the second, third and even the fourth mononuclear hydroxo complex are occasionally given in the literature, but these values appear to be questionable and have been discarded in the present review. However, since there is no doubt that such complexes are formed and may become dominant at high pH, it is desirable to obtain reliable formation constants for these species from other sources.

A new method for the estimation of unknown complexation constants, based on consideration of ligand-ligand repulsion and complex geometry, has been recently developed by NECK & KIM (2000). The method requires a well established first complexation constant, from which the subsequent formation constants are derived based on electrostatic and stereochemical principles. The basic idea of this model is that the stability of each subsequent constant is lowered by the increasing repulsive interactions among the ligands. A cumulative ligand-ligand repulsion term must thus be calculated from the distances and angles characterising the complex. In order to be operational, the model also requires empirical parameters describing the electrostatic shielding caused by the insertion of the central metal between the ligands, which mitigates the repulsive forces. The shielding parameters must be determined, using a virial expansion, from an independent set of complexation constants for a different, but chemically analogous, central metal.

For the Eu hydrolysis, we are in the fortunate position to have a well-defined first hydrolysis constant and a set of hydrolysis constants for trivalent actinides. We therefore used the optimised set of constants determined by NECK et al. (1998) for $An(OH)^{2+}$, $An(OH)_2^+$, $An(OH)_3^0(aq)$ to fit the

shielding parameters and then use the so-determined parameters to estimate the second, third and fourth hydrolysis constants of europium. The parameters used for the extrapolation and the model results are summarised in Table 5.4.3. A comparison of the extrapolated second and third Eu hydrolysis constants with the corresponding constants for the trivalent actinides proposed by NECK et al. (1998) shows that the Eu hydrolysis is predicted to be considerably weaker than for Am(III) and Cm(III). This is a direct consequence of the fact that the formation constant for $Eu(OH)^{2+}$ has been fixed (based on the well defined SIT correlation presented in Fig. 5.4.2) at ~ 0.3 $\log_{10}$ units below the constant for $An(OH)^{2+}$ proposed by NECK et al. (1998). The electrostatic attraction exerted by Eu^{3+} is thus predicted to be smaller than that of Am^{3+} or Cm^{3+}, which translates in a decreased stability of the higher Eu hydroxo-complexes.

Table 5.4.3: Extrapolation of Eu-hydrolysis constants with the electrostatic model of NECK & KIM (2000). Simple, symmetrical complex geometries have been assumed (linear, trigonal planar and tetrahedral for the dihydroxo- trihydroxo- and tetrahydroxo-complexes, respectively).

Input parameters		
metal-ligand distance for trivalent lanthanides and actinides:	$d_{ML} = 0.245$ nm	NECK & KIM (2000)
Hydrolysis constants used to determine the shielding parameters:	$\log_{10}*\beta^0_1 = -7.3$ $\log_{10}*\beta^0_2 = -15.2$ $\log_{10}*\beta^0_3 = -25.7$	NECK et al. (1998)
First hydrolysis constant for Eu:	$\log_{10}*\beta^0_1 = -7.64$	this work
Results		
shielding parameters:	$C_0 = -60$ / $C_1 = 157$ / $C_{20} = -15$	this work
Extrapolated Eu-hydrolysis constants:	$\log_{10}*\beta^0_2 = -15.9$ $\log_{10}*\beta^0_3 = -26.7$ $\log_{10}*\beta^0_4 = -40.1$	this work

However, the constants extrapolated by means of the electrostatic model are evidently inconsistent with the experimental solubility data. If used to model the $Eu(OH)_3$ (cr) solubilities measured by BERNKOPF (1984), they predict equilibrium concentrations between 10^{-12} M and 10^{-11} M at pH values between 11-12, whereas the experiments indicate $\sim 10^{-9}$ M. One is thus forced to reject the results of the electrostatic model.

We propose therefore to rely on the data of BERNKOPF (1984) to derive zero ionic strength constants for the higher Eu hydroxo complexes, since this is the unique detailed investigation based on the solubility method and applied over a wide pH range.

In order to reduce the conditional constants (K) to zero ionic strength (K^0), we resort to the SIT theory, which is based on the equation (GRENTHE et al. 1997):

$$\log_{10}K^0 = \log_{10}K - D\,\Delta z^2 + m\,\Delta\varepsilon$$

where
$$D = \frac{A\sqrt{I_m}}{1 + 1.5\sqrt{I_m}}.$$

D is a Debye-Hückel term dependent on the ionic strength I_m (molality scale) and the Debye-Hückel limiting slope parameter ($A = 0.5091$ at 25 °C). $\Delta\varepsilon$ and Δz^2 are the stoichiometric sums of the ion-ion interaction parameters and of the squares of the charges over all species involved in the reaction, respectively. The quantity m is the molal electrolyte concentration. From the equation above, using tabulated values of Am species for the interaction parameters[5] (see GRENTHE et al. 1997, Tables X.1 and X.2) one obtains:

Reaction: (in 0.1 M NaClO₄)	$\log_{10}\beta_n$ (BERNKOPF 1984)	$- D$	Δz^2	$+$	m	$\Delta\varepsilon$	$=$	$\log_{10}\beta^0_n$	$\log_{10}{}^*\beta^0_n$ or $\log_{10}{}^*K^0_{s,0}$
$Eu^{3+} + OH^- \Leftrightarrow EuOH^{2+}$	5.84	- 0.109	(-6)	+	0.1	(-0.14)	=	6.5	-7.5 ± 0.5 [6]
$Eu^{3+} + 2\,OH^- \Leftrightarrow Eu(OH)_2{}^+$	11.88	- 0.109	(-10)	+	0.1	(-0.40)	=	12.9	-15.1 ± 0.2
$Eu^{3+} + 3\,OH^- \Leftrightarrow Eu(OH)_3{}^0$	17.08	- 0.109	(-12)	+	0.1	(-0.61)	=	18.3	-23.7 ± 0.1
$Eu^{3+} + 4\,OH^- \Leftrightarrow Eu(OH)_4{}^-$	18.57	- 0.109	(-12)	+	0.1	(-0.65)	=	19.8	-36.2 ± 0.5
$Eu^{3+} + 3\,OH^- \Leftrightarrow Eu(OH)_3(cr)$	25.84	- 0.109	(-12)	+	0.1	(-0.61)	=	27.1	14.9 ± 0.3

The solubility curve of crystalline $Eu(OH)_3$ as a function of the hydroxyl ion concentration, computed with MINEQL/PSI from the hydrolysis and solubility constants tabulated above, is shown on Fig. 5.4.4 together with the experimental data. The small deviations occurring at pH < 7 arise from neglecting two polymeric species assumed by BERNKOPF (1984) in his model. We did not include these two species in the database, because there is not sufficient evidence for their existence.

The data of BERNKOPF (1984) are characterised by a wide region of constant, low solubility (pH 9 to 12) which implies a particularly stable trihydroxo complex and a relatively weak tetrahydroxo

---

5 The NEA interaction coefficients for Am are tolerated here, although they may be in error. This is because the $m_i\,\Delta\varepsilon$ term is of minor importance, as Bernkopf 's experiments were carried out at low ionic strength (0.1 M).

6 Uncertainties as given in BERNKOPF (1984).

species. The increase in total Eu concentration between pH 12 and 13 is minimal and the solubility does not exceed 10^{-8} M. These data agree with the results of experiments carried out in artificial cement pore water at pH = 13.3, in which Eu was found to precipitate at total added concentrations as low as $\sim 10^{-9}$ to 10^{-8} M (TITS et al. 1998).

Nevertheless, Bernkopf's measurements are not unambiguous. The marked differences between his Eu(OH)$_3$ results and Am(OH)$_3$ solubility data from other sources (see e.g. NECK et al. 1998) suggest that the data presented in Fig. 5.4.4 may be affected by experimental inconsistencies. Specifically, the solubilities measured by BERNKOPF (1984) are the lowest of all available studies and the predominance region of the trihydroxo complex is much wider than for Am(OH)$_3$. These anomalous features of the solubility curve shown in Fig. 5.4.4 could also be interpreted assuming interaction with two different solids (Neck, pers. comm.): an amorphous Eu(OH)$_3$ at the begin of the titration (pH=12.8) and a crystalline form towards the end (pH $\sim$ 6.5). A conversion from amorphous to crystalline form appears possible in view of the long duration of the titrations (several days) and is also supported by the similarity of Bernkopf's data with the solubility of amorphous Am(OH)$_3$ in the alkaline region: Combining the appropriate constants in Table 5.4.4 one obtains $\log_{10}K_{s,3}{}^0 = -8.8$ for the reaction Eu(OH)$_3$ (cr) = Eu(OH)$_3$ (aq). This value is very close to $\log_{10}K_{s,3}{}^0 = -8.7$ for Am(OH)$_3$ (am) = Am(OH)$_3$ (aq), resulting from the selected Am data. Note also that the disagreement between the predictions of the electrostatic model and the constants derived from Bernkopf's data would be understandable if the data of Fig. 5.4.4 really represent mixed equilibria.

Nevertheless, since this question cannot be resolved without additional careful measurements, we prefer to rely on the original interpretation (equilibrium with a single crystalline Eu hydroxide). The $\log_{10}*\beta^0{}_n$ values extrapolated from the original $\log_{10}\beta_n$ constants determined by BERNKOPF (1984) are thus included in the present update, with exception of the first hydrolysis constant, for which the slightly lower value $\log_{10}*\beta^0{}_n = -7.64 \pm 0.04$, previously determined by means of the SIT regression illustrated in Fig. 5.4.2, has been selected.

5.4.3.2 Solid Eu(III) oxides and hydroxides

Lanthanides form a variety of hydrous and anhydrous oxides in nature (HENDERSON 1984). These compounds usually have a complex stoichiometry and are formed mostly in high-temperature environments. They are therefore excluded from our database.
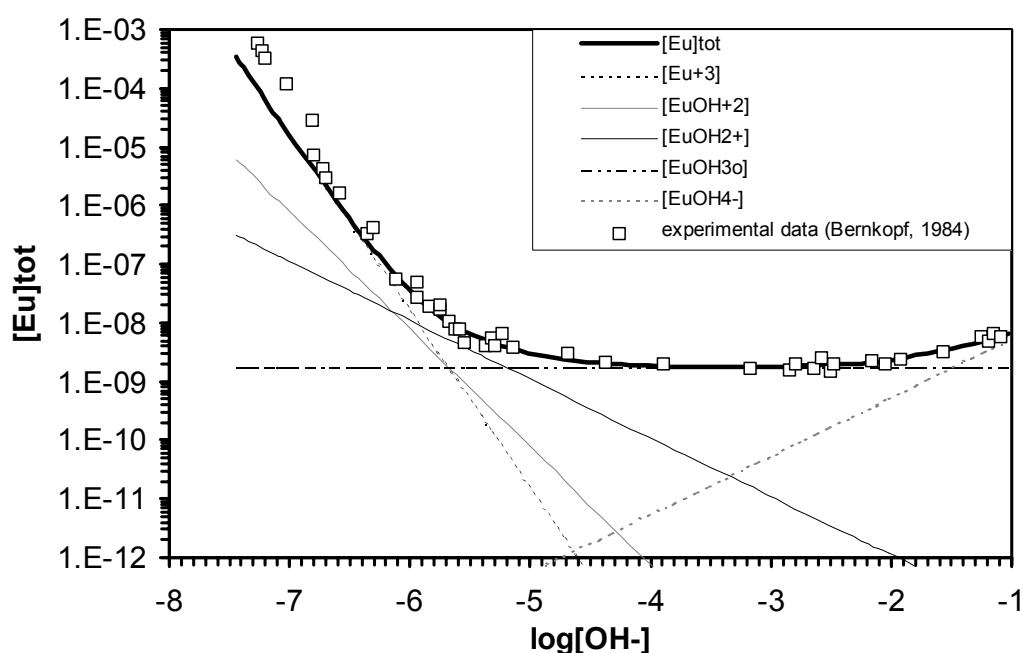
Fig. 5.4.4: Solubility curve of Eu(OH)$_3$ (cr) in carbonate free 0.1 M NaClO$_4$, computed from the constants selected for the database update, compared with the data of BERNKOPF (1984). Note that hydroxyl ion concentrations have not been converted to the pH scale.

Under laboratory conditions, all lanthanides form sparingly soluble hydroxides, which upon ageing are transformed into crystalline, isomorphous compounds with stoichiometry Ln(OH)$_3$. Based on a review by AKSEL'RUD (1963), who studied aged precipitates and was able to correlate the solubility product of several Ln(OH)$_3$ products with the *a* lattice parameter, BAES & MESMER (1976) derived $\log_{10}{}^*K^0_{s,0} = 17.5$ for the reaction:

$$Eu(OH)_3\ (cr) + 3\ H^+ \Leftrightarrow Eu^{3+} + 3\ H_2O\ .$$

However, DIAKONOV et al. (1998) claim that the data of AKSEL'RUD (1963), on which the constant reported above is based[7], are incompatible with more recent solubility measurements. They state: "It is demonstrated in this paper…that data from AKSEL'RUD (1963) for Y-, Nd- and Pr-hydroxides are incompatible with other reliable values." And later: "We believe…that the data set proposed by BAES & MESMER (1976) should be corrected for most of the light REE-hydroxide solids." Indeed,

---

[7] The data used to determine the solubility product of Eu(OH)$_3$ stem from dissolution experiments with Y-, Pr- and Nd hydroxides, not directly from experiments with Eu hydroxide.

the Ln(OH)$_3$ solubility constants of BAES & MESMER (1986) appear to be about 1-2 log$_{10}$ units higher than those determined from other studies performed with well crystallised products.

DIAKONOV et al. (1998) propose the following solubility products: log$_{10}$K$^{0b}_{s10}$ = -26.54 ($\pm$ 0.6)[8] for crystalline and -24.40 $\pm$ 0.84 for amorphous Eu-hydroxides (see Table 5 of the cited reference). These values, based on work performed mainly in Russian laboratories translate, in the notation adopted for this report and after rounding, to:

$$\log_{10}{*}K^0_{s,0}\,(Eu(OH)_3, \text{cr}, 298.15\,K) = 15.5 \pm 0.6$$

$$\log_{10}{*}K^0_{s,0}\,(Eu(OH)_3, \text{am}, 298.15\,K) = 17.6 \pm 0.8.$$

As previously discussed, BERNKOPF (1984) measured the solubility of crystalline Eu(OH)$_3$ in 0.1 M NaClO$_4$ over a wide pH range (6 to 13), obtaining log$_{10}$K$^b_{s10}$ = -25.84 $\pm$ 0.31. Our extrapolation to zero ionic strength using the SIT procedure with ε(Eu^{3+},ClO$_4^-$) = 0.49 and ε(OH$^-$, Na$^+$) = 0.04 yielded log$_{10}$K$^{0b}_{s10}$ = -27.1 $\pm$ 0.3, which translates to log$_{10}$*K$^0_{s,0}$ (Eu(OH)$_3$, cr, 298.15 K) = 14.9 $\pm$ 0.3. This is 0.6 log$_{10}$ units less than the value selected by DIAKONOV et al. (1998). We decided to select Bernkopf's constant for crystalline Eu(OH)$_3$ to keep consistency with the selected hydrolysis constants, while log$_{10}$*K$^0_{s,0}$ (Eu(OH)$_3$, am, 298.15 K) = 17.6 $\pm$ 0.8 was selected to represent the amorphous compound.

The discrepancy to the constant given by DIAKONOV et al. (1998) for the crystalline hydroxide cannot be easily explained in view of the difficulty in retrieving useful raw data from the Russian source references. A consultation of a review published by AKSEL'RUD (1963) revealed that the compound used in his potentiometric titration study was most probably also crystalline Eu-hydroxide (150 days ageing time), but too little details are given on the procedures adopted for the extrapolation to zero ionic strength. One also cannot exclude that transformation processes of the solid phase, similar to those suspected for Bernkopf's experiments, may have occurred. Note however, that both values selected for the present update reasonably agree with the corresponding constants selected for Am-hydroxide in the NEA review (15.2 and 17.0, see SILVA et al. 1995).

Finally, we would like to point out that the solubilities resulting from the selected constants for both crystalline and amorphous Eu hydroxide are about two orders of magnitude higher than for the corresponding Am solids. This effect results from the discrepant formation constants for the tri-hydroxo complexes (log$_{10}\beta^0_3$ = -23.7 for Eu, -25.7 for Am). The higher stability of the Eu tri-

---

[8]   This uncertainty was estimated from the corresponding constants given for Gd and Sm hydroxides.

hydroxo complex derives directly from the choice of Bernkopf's data to represent the solubility of the crystalline compound. The obvious consequence is that, if the suspected phase transformation from amorphous to crystalline form indeed occurred during the mentioned experiments, the formation constant selected for Eu(OH)$_3$(aq) in this update would be incorrect. However, in the absence of unequivocal data, we are presently not in a position to resolve this dilemma.

5.4.4   Europium(III) carbonate complexes and solids

There is quite a large number of experimental studies dealing with the Eu(III)-carbonate aqueous complexes. The selection presented below is mainly based on experimental work and compilations by RAO & CHATT (1991) and LEE & BYRNE (1993a), which rely on solvent extraction methods. In contrast, solubility data for Eu(III) carbonates proved to be scarce and needed to be supported by studies of other lanthanide carbonates.

5.4.4.1   Aqueous europium(III) carbonate complexes

Like other trivalent lanthanides, europium forms strong complexes with carbonate species. Constants for mononuclear complexes with one to four carbonate ligands and for a single-ligand Eu(III)-bicarbonate complex are reported. Yet, only the constants for the monocarbonate and dicarbonate species are well assessed. We will limit therefore our selection to the latter two complexes with the remainder that this list is not exhaustive and does not cover all possible pH and ligand concentration conditions.

Figures 5.4.5 and 5.4.6 show SIT extrapolations of the formation constants for Eu(CO$_3$)$^+$ and Eu(CO$_3$)$_2^-$ to zero ionic strength, computed from conditional constants reported by RAO & CHATT (1991) and LEE & BYRNE (1993a).

The regressions yield:

$$\log_{10}\beta^0_1 = \ 8.1 \pm 0.2$$

$$\log_{10}\beta^0_2 = 12.1 \pm 0.3$$

which are included in the thermodynamic database. The selected $\log_{10}\beta^0_2$ differs by 0.7 $\log_{10}$ units from that recommended by GLAUS et al. (1997) (12.8 $\pm$ 0.1, see p. 148 of the cited reference). However, GLAUS et al. (1997) did not consider the data of RAO & CHATT (1988) and CHATT & RAO (1989), and extrapolations to zero ionic strength were made using SIT coefficients for Am. This resulted in a gentler regression slope ($\Delta\varepsilon$ = -0.28, see below) and higher $\log_{10}\beta^0_2$.

The $\Delta\varepsilon$ values extrapolated from the regressions presented in Figures 5.4.5 and 5.4.6 can be compared with those computed from tabulated ε–values for the corresponding Am reactions (GRENTHE et al. 1997), yielding:

$$\Delta\varepsilon\,(Am^{3+} + CO_3^{2-} = AmCO_3^+) \quad = \varepsilon(AmCO_3^+,ClO_4^-) - \varepsilon(CO_3^{2-},Na^+) - \varepsilon(Am^{3+}, ClO_4^-) =$$

$$= \quad 0.17 \pm 0.04 \quad -(-0.08 \pm 0.03\,) - 0.49 \pm 0.03 \quad =$$

$$= \quad \mathbf{-0.24 \pm 0.06}$$

$$\Delta\varepsilon\,(Eu^{3+} + CO_3^{2-} = EuCO_3^+) \quad = \quad \mathbf{-0.24 \pm 0.18}$$
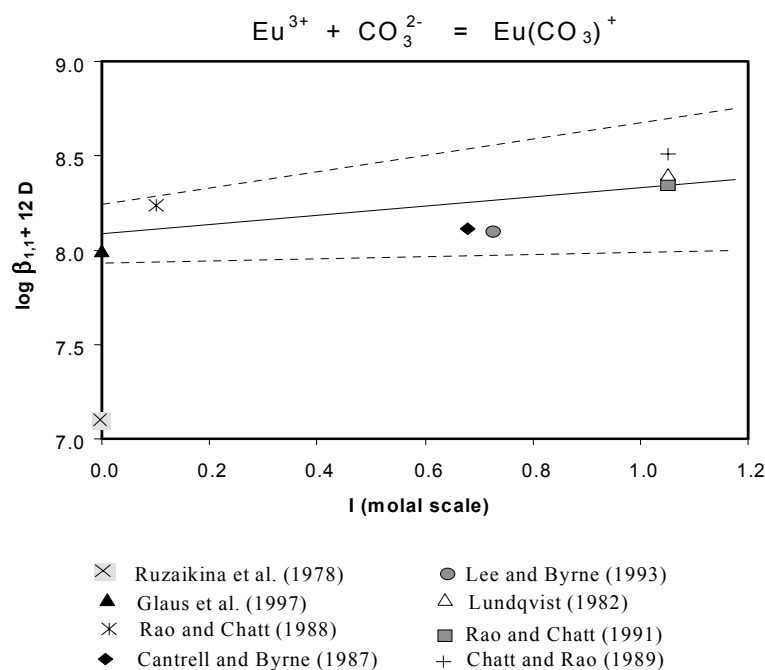
Fig. 5.4.5: Determination of $\log_{10}\beta^0_1$ and $\Delta\varepsilon$ for $Eu(CO_3)^+$ based on the SIT formalism (GRENTHE et al. 1997). The unweighted regression through conditional constants given in the literature yields $\log_{10}\beta^0_1 = 8.1 \pm 0.2$ and $\Delta\varepsilon = -0.24 \pm 0.18$. The zero ionic strength constants of GLAUS et al. (1997) and RUZAIKINA et al. (1978) are given for comparison but were not included in the regression.

and $\Delta\varepsilon\,(Am^{3+} + 2\,CO_3^{2-} = Am(CO_3)_2^-) = \varepsilon(Am(CO_3)_2^-,Na^+) - 2\,\varepsilon(CO_3^{2-},Na^+) - \varepsilon(Am^{3+}, ClO_4^-)$

$$= \quad 0.05 \pm 0.04 \quad - 2\,(-0.08 \pm 0.03\,) - 0.49 \pm 0.03$$

$$= \quad \mathbf{-0.28 \pm 0.08}$$

$$\Delta\varepsilon\,(Eu^{3+} + 2\,CO_3^{2-} = Eu(CO_3)_2^-) \quad = \quad \mathbf{-1.48 \pm 0.31}$$

Thus, for the formation reaction of the monocarbonato complex, there is an excellent agreement between Eu and Am interaction parameters. In the case of the dicarbonato complex the $\Delta\varepsilon$ values

for the Eu and Am reactions differ conspicuously, indicating discrepancies between tabulated ε-values and the experimental data. Presently, we cannot resolve this inconsistency.

RAO & CHATT (1991) report the much lower formation constants determined by RUZAIKINA et al. (1978). We did not attempt - due to the tight deadline of the TDB update - to explain this incongruence and we limit us to quote RAO & CHATT (1991), who state: "The β^0 values of Ruzaikina et al. ... are smaller by one order of magnitude and two and one-half orders of magnitude, than those reported by others. These discrepancies appear to be attributable to the experimental conditions used in the former study."

$$Eu^{3+} + 2\,CO_3^{2-} = Eu(CO_3)_2^-$$

⊠ Ruzaikina et al. (1978)	● Lee and Byrne (1993)
▲ Glaus et al. (1997)	△ Lundqvist (1982)
✳ Rao and Chatt (1988)	■ Rao and Chatt (1991)
◆ Cantrell and Byrne (1987)	+ Chatt and Rao (1989)
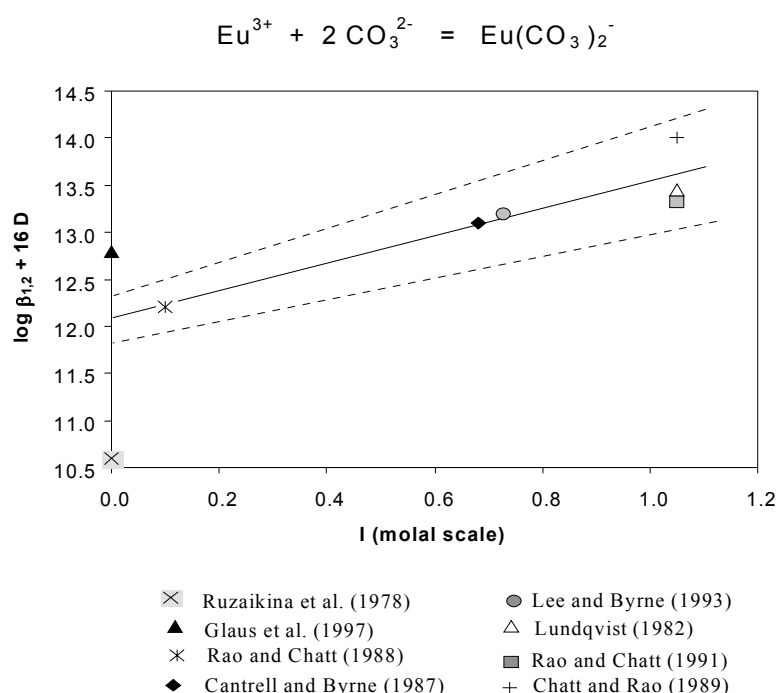
Fig. 5.4.6: Determination of $\log_{10}\beta^0_2$ and $\Delta\varepsilon$ for $Eu(CO_3)_2^-$ based on the SIT formalism (GRENTHE et al. 1997). The unweighted regression through conditional constants given in the literature yields $\log_{10}\beta^0_2 = 12.1 \pm 0.3$ and $\Delta\varepsilon = -1.48 \pm 0.31$. The extrapolations of GLAUS et al. (1997) and RUZAIKINA et al. (1978) are given for comparison but were not considered in the regression.

5.4.4.2   Solid europium(III) carbonate compounds

At low temperature, lanthanides form a variety of carbonate solids, including hydrous and anhydrous simple carbonates, hydroxo-carbonates and bicarbonates (JORDANOV & HAVEZOV 1966). Solubility data are reported for carbonates with stoichiometry $(Eu_2CO_3) \cdot nH_2O$ and for the hydroxo-carbonate $EuOH(CO)_3$ (FIRSCHING & MOHAMMADZADEL 1986; RUNDE et al. 1992). Only data for these two solids will be included in the database.

5.4.4.2.1 $Eu_2(CO_3)_3 \cdot nH_2O$ and $EuOH(CO_3)$

FIRSCHING & MOHAMMADZADEL (1986) measured the solubility of REE carbonates, including the europium compound, in 0.01 M perchloric acid by complexometric titration with EDTA. Speciation calculations based on the analytical data given in the source reference (pH and total Eu concentration) revealed a good internal consistency of the data: Assuming that an amount of Eu carbonate corresponding to the measured metal concentrations is dissolved in a closed system (sealed vessel with negligible gas phase volumes were used in the experiments) resulted in calculated pH's matching the analytical values. These data seem thus appropriate to derive a solubility constant. We calculated $\log_{10}K^0_{s,0}$ = -33.7 ± 0.5 for the equilibrium

$$Eu_2(CO_3)_3 \text{ (cr)} \Leftrightarrow 2\ Eu^{3+} + 3\ CO_3^{2-}$$
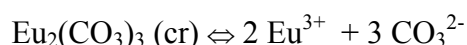
using Davies' equation for the ionic strength correction. Application of the SIT formalism was not necessary in view of the very low ionic strength of the experiments.

This constant deviates considerably from that given in the source reference ($\log_{10}K^0_{s,0}$ = -35.03 ± 0.25). The difference seems to arise from an erroneous equation in the extrapolation procedure (equation 14 in FIRSCHING & MOHAMMADZADEL 1986), which neglects the transformation of the thermodynamic constants for bicarbonate and carbonate ion formation into conditional constants. Note that our recalculation is consistent with that of RUNDE et al. (1992), who give $\log_{10}K^0_{s,0}$ = -33.5.

An intrinsic problem of these data is that the identity of the solid was not verified by X-ray diffraction. Our speciation calculations indicate that assuming dissolution of the basic carbonate $EuOH(CO_3)$ instead of the simple form would result in a difference in pH of only 0.1 units, which is probably within the analytical precision. In contrast, the solids used in the study of RUNDE et al. (1992) were carefully verified using diffractometric and spectroscopic methods. These authors found the hydroxo-carbonate to be the stable phase at atmospheric pCO_2, while the simple form precipitated at or above pCO_2 = 0.01 atm (at slightly acidic pH). Based on these observations we conclude that FIRSCHING & MOHAMMADZADEL (1986) effectively worked with $Eu_2(CO_3)_3 \cdot nH_2O$.

RUNDE et al. (1992) determined the solubility products of both solids in 0.1 M sodium perchlorate and give conditional solubility products of $\log_{10}K_{s,0}$ = -31.78 ± 0.22 for $Eu_2(CO_3)_3 \cdot nH_2O$ and $\log_{10}K_{s,0}$ = -20.18 ± 0.09 for $EuOH(CO_3)$. Both constants have been extrapolated to zero ionic strength with the SIT model, using the interaction coefficients $\varepsilon(Eu^{3+}, ClO_4^-)$ = 0.5 ± 0.03, $\varepsilon(CO_3^{2-}, Na^+)$ = -0.08 ± 0.03 and $\varepsilon(OH^-, Na^+)$ = 0.04 ± 0.01 (GRENTHE et al. 1997):

$$\log_{10}K^0_{s,0}\ (\ Eu_2(CO_3)_3\ )\quad = -35.0 \pm 0.3$$

$$\log_{10}K^0_{s,0} \ (\ Eu \ OH \ (CO_3) \ ) = -21.7 \pm 0.1$$

The $\log_{10}K^0_{s,0} = -35.0 \pm 0.3$ determined for $Eu_2(CO_3)_3 \cdot nH_2O$ deviates from $\log_{10}K^0_{s,0} = -33.7 \pm 0.5$ obtained from the data of FIRSCHING & MOHAMMADZADEL (1986). Applying the constant of RUNDE et al. (1992) to the experimental conditions of Firsching and Mohammadzadel (pH = 4.9, $[Eu]_{total} \cong [Eu^{3+}] = 3.5 \ x \ 10^{-3}$ M) leads to significantly smaller Eu equilibrium concentrations (~7 x 10^{-4} M). This incongruence may be due to differences in the stoichiometry and crystallinity of the solids used in the two investigations, but it cannot be resolved. The constants of RUNDE et al. (1992) must be given more credit by virtue of the careful characterisation of the solids. The SIT extrapolated constants reported above are thus included in the database.

5.4.5   Europium(III) sulphate complexes and solids

Eu(III) sulphate complexes are much weaker than carbonate complexes. Yet, since sulphate concentrations may become important in pore waters associated to repository environments, such complexes may help to control Eu solubility limits and should therefore be included in the database.

Assuming a maximum sulphate concentration of 10^{-2} M (upper limit in cement pore waters) and a pH of 7, we can estimate the minimum value required for any sulphate complexation constant $\beta^0_{1,n}$ in order for the complex $Eu(SO_4)_n^{3-2n}$ to contribute at least 1% to the total Eu concentration, assuming $Eu(OH)_m^{3-m}$ as the dominating hydroxo complex:

$$Eu^{3+} + n \ SO_4^{2-} \Leftrightarrow Eu(SO_4)_n^{3-2n} \qquad\qquad \beta_{1,n}$$

$$- \quad Eu^{3+} + m \ H_2O \Leftrightarrow Eu(OH)_m^{3-m} + m \ H^+ \qquad\qquad {}^*\beta_{1,m}$$

$$Eu(OH)_m^{3-m} + n \ SO_4^{2-} + m \ H^+ \Leftrightarrow Eu(SO_4)_n^{3-2n} + m \ H_2O \qquad K_x = \beta_{1,n}/{}^*\beta_{1,m}$$
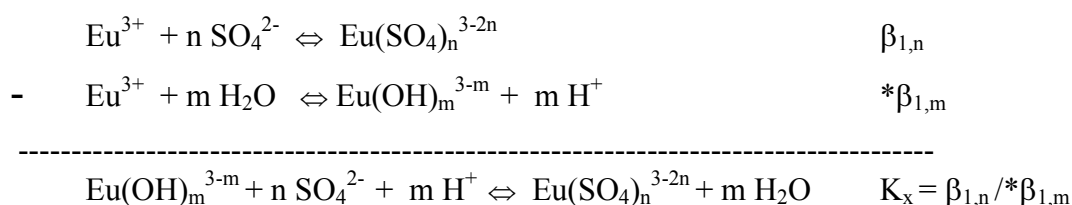
From the combined reactions above and the requirement for 1% contribution of the sulphate complexes one obtains:

$$\frac{[Eu(SO_4)_n^{3-2n}]}{[Eu(OH)_m^{3-m}]} = \frac{\beta_{1,n}[SO_4^{2-}]^n[H^+]^m}{{}^*\beta_{1,m}} \equiv 10^{-2}$$

and the minimum $\log_{10}\beta_n$ which fulfils the specified condition is given by:

$$\log_{10}\beta_{1,n} = \log_{10}{}^*\beta_{1,m} - n \ \log_{10}[SO_4^{2-}] + m \ p[H^+] - 2$$

Inserting the appropriate hydrolysis constant (at $p[H^+] = 7$ the dominating hydroxo species is $EuOH_2^+$, hence $\log_{10}{}^*\beta_{1,m} = \log_{10}{}^*\beta_{1,1} = -7.6$) and the previously specified values for $\log_{10}[SO_4^{2-}]$ and $p[H^+]$ into the equation above, one obtains $\log_{10}\beta_{1,1} = \log_{10}\beta_1 = -0.6$ and $\log_{10}\beta_{1,2} = \log_{10}\beta_2 = 1.4$

as the critical values of the formation constants for the mono- and di-sulphate complexes. Since measured $\log_{10}\beta_1$ and $\log_{10}\beta_2$ constants are orders of magnitude larger, one concludes that sulphate complexes could indeed become dominant (at least at pH < 7) and should therefore be included in the thermodynamic database.

5.4.5.1   Europium(III) aqueous sulphate complexes

There is a number of studies on the complexation of Eu(III) with sulphate ions, mainly relying on solvent extraction and ion exchange experiments, which report formation constants for $Eu(SO_4)^+$ and $Eu(SO_4)_2^-$. A thorough review of these data is not possible at the moment, so we will only select the data based on SIT extrapolations of conditional constants obtained from the experiments in 0.5 to 2 M $NaClO_4$ solutions reported in the "IUPAC stability constants database" (IUPAC 1997). Figures 5.4.7 and 5.4.8 report the data and the linear fits yielding: $\log_{10}\beta^0_1 = 3.95 \pm 0.08$ and $\Delta\varepsilon = -0.11 \pm 0.06$; $\log_{10}\beta^0_2 = 5.71 \pm 0.21$ and $\Delta\varepsilon = -0.04 \pm 0.16$.

One of the source references of the conditional constants used for the regression was examined in some detail (AZIZ et al. 1968). All other constants were taken without any check of the quality of the data. However, an indirect "quality assessment" results from by the standard deviation of the regression and the comparison of the resulting interaction coefficient for the complex with tabulated data. For the monosulphate complex we observe a reasonably good fit and one obtains, taking the interaction coefficients given in GRENTHE et al. (1997):

$\varepsilon_{(EuSO_4^+, ClO_4^-)} = \Delta\varepsilon + \varepsilon_{(Eu^{3+}, ClO_4^-)} + \varepsilon_{(SO_4^-,Na^+)}$

$= -0.11 \pm 0.06 + 0.50 \pm 0.03 - 0.12 \pm 0.06$

$= 0.27 \pm 0.09$

This interaction coefficient is remarkably close to that for the corresponding Am complex, $\varepsilon_{(AmSO_4^+,ClO_4^-)} = 0.22 \pm 0.08$, and has also an acceptable standard deviation. This increases our confidence in the extrapolated constant for $Eu(SO_4)^+$. In contrast, for $Eu(SO_4)_2^-$ the extrapolated interaction parameter is inaccurate and a higher uncertainty must therefore be assigned to the corresponding constant:

$\varepsilon_{(Eu(SO_4)_2^-, Na^+)} = \Delta\varepsilon + \varepsilon_{(Eu^{3+}, ClO_4^-)} + 2\ \varepsilon_{(SO_4^-,Na^+)}$

$= -0.04 \pm .16 + 0.50 \pm .03 - 2 \times 0.12 \pm .06$

$= 0.22 \pm 0.20$

This value is quite large and differs from the analogous NEA coefficient for Am (-0.05± 0.05) but is still within the range of all other tabulated anion-Na^+ ε-coefficients (see GRENTHE et al. 1997).

$$Eu^{3+} + SO_4^{2-} = Eu(SO_4)^+$$

✳ Aziz et al. (1968)   ◆ Sekine (1965)
▲ Antipenko et al. (1973)   ⬤ Carvalho and Choppin (1967)
☐ Bansal et al. (1964)
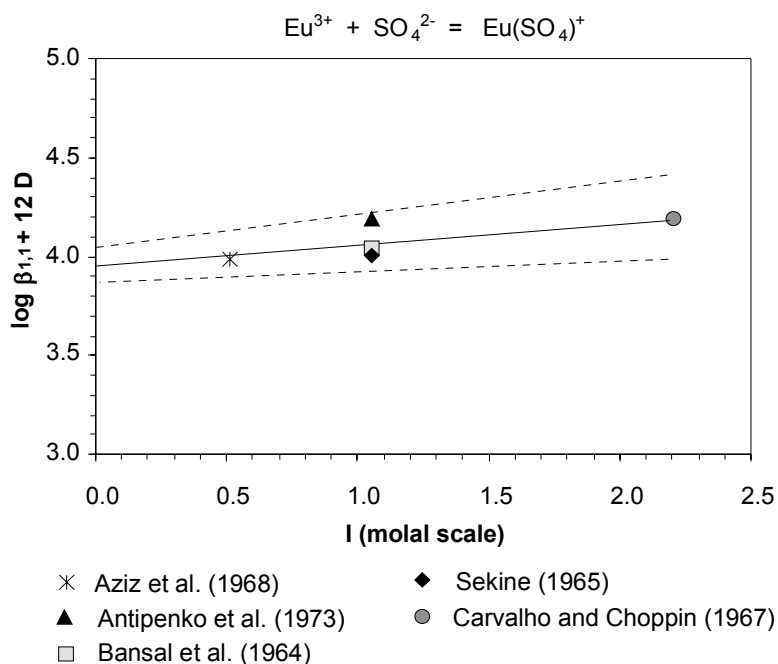
Fig. 5.4.7: Determination of $\log_{10}\beta^0_1$ and $\Delta\varepsilon$ for $Eu(SO_4)^+$ based on the SIT formalism (GRENTHE et al. 1997). The regression through the conditional constants yields $\log_{10}\beta^0_1 = 3.95 \pm 0.08$ and $\Delta\varepsilon = -0.11 \pm 0.06$.

$$Eu^{3+} + 2\,SO_4^{2-} = Eu(SO_4)_2^-$$

✳ Aziz et al. (1968)   ◆ Sekine (1965)
☐ Bansal et al. (1964)   ⬤ Carvalho and Choppin (1967)
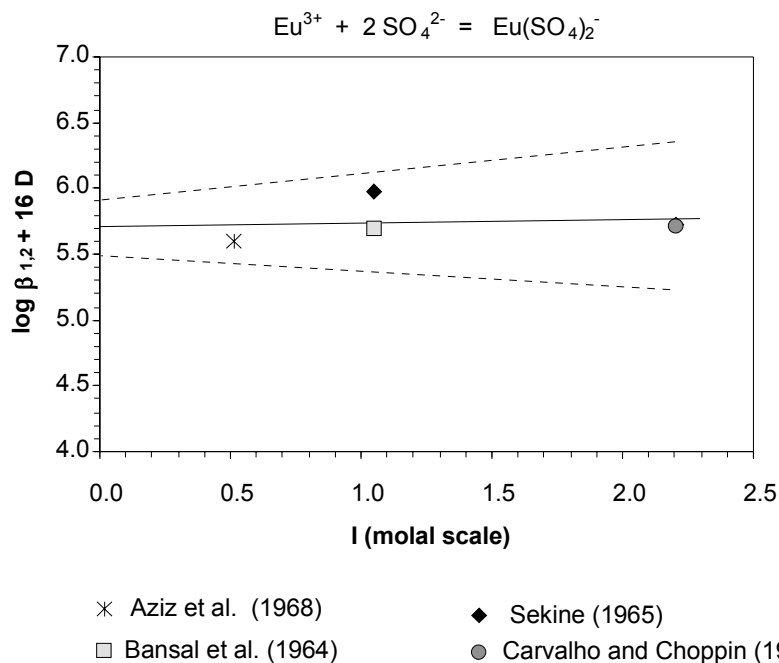
Fig. 5.4.8: Determination of $\log_{10}\beta^0_2$ and $\Delta\varepsilon$ for $Eu(SO_4)_2^-$ based on the SIT formalism (GRENTHE et al. 1997). The regression through the conditional constants yields $\log_{10}\beta^0_2 = 5.71 \pm 0.21$ and $\Delta\varepsilon = -0.04 \pm 0.16$.

Given the consistency and acceptable statistical uncertainty of these results we include the constants defined by the linear regressions of Figures 5.4.7 and 5.4.8 in the database:

$$\log_{10}\beta^0_1\,(EuSO_4^+) = \ 3.95 \pm 0.08$$

$$\log_{10}\beta^0_2\,(Eu(SO_4)_2^-) = 5.7 \pm 0.2$$

Note that these values compare well with those for Am(III) sulphate complexes recommended by the NEA reviewers (SILVA et al. 1995), also included in the present update (see 5.2.5.2): 3.85 ± 0.03 for $\log_{10}\beta^0_1\,(AmSO_4^+)$ and 5.4 ± 0.7 for $\log_{10}\beta^0_2\,(Am(SO_4)_2^-)$.

5.4.5.2 Europium(III) sulphate solids

Lanthanides form in general soluble sulphates (see e.g. REMY 1949, Vol. 2, p. 524), for which no solubility data could be retrieved. Considering also that Eu(III) forms insoluble hydroxides and carbonates, it appears unlikely that sulphates will play any role in limiting the solubility of Eu in natural environments. Thus, solid sulphates are not included in the database.

5.4.6   Europium(III) phosphate complexes and solids

5.4.6.1   Eu(III) aqueous phosphate complexes

We could not find any experimental work dealing with the complexation of Eu(III) with phosphate. However, some data on other lanthanides exist. BYRNE et al. (1991), using distribution methods based on organic solvent extraction, studied the complexation of trivalent Ce and Gd by phosphate ions in 0.68 M sodium perchlorate at pH's varying from 4.5 to 7.0. The results are somewhat surprising: Whereas for Ce(III) a single complex, $CePO_4(aq)$, was sufficient to explain the data, four complexes ($GdPO_4(aq)$, $GdH_2PO_4^{2+}$, $GdHPO_4^+$, $Gd(HPO_4)_2^-$) were required to model the Gd data.

The authors state cryptically: "Since superfluous terms in the complexation models should exhibit large relative uncertainties, the observation that all of the complexation constants are relatively well defined indicates that all of the complexation constants…are required for a complete description of the data". In other words, the justification for selecting four complexes is that assuming them leads to an acceptable fit with similar statistical errors for all complexes. None of these complexes has been directly nor indirectly identified. In our opinion, it is very unlikely that Gd(III) and Ce(III) will have such a different complexation behaviour and this discrepancy appears suspect.

Since a re-interpretation of these results is beyond the scope of the present report, and considering the complexity of the phosphate system (at least three ligand species must be taken into account due

to the stepwise deprotonation of phosphoric acid), we cannot recommend any constant for Eu(III)-phosphate complexes.

5.4.6.2   EuPO$_4 \cdot$ nH$_2$O and other phosphate solids

Various solubility products of lanthanide phosphates have been published (see BYRNE & KIM 1993, and references therein). All are based on experiments conducted at pH < 4. Although these data appear to be consistent, the application of these solubility products to alkaline solutions is problematic, due to the very poor knowledge of complexation reactions with phosphate species. For this reason we do not include Eu phosphate solids in the present update.

5.4.7   Halogenide complexes and compounds

Lanthanides are known to form strong complexes and insoluble solids with fluoride. Therefore thermodynamic data for Eu(III) fluorides are relevant, even if fluoride concentrations in most low-temperature ground waters are small. The interaction with chloride is weaker, but this is compensated by the usually much larger concentrations of this anion in natural waters. Thus data for the Eu(III)-chloride system are also required.

5.4.7.1   Eu(III) - fluoride aqueous complexes

Several studies on the complexation of fluoride with Eu(III) and other trivalent lanthanides have been published. From the large number of studies available, LnF^{2+} and LnF$_2^+$ emerge as the relevant species. We also consider these species for the present update and base our selection on the work of LEE & BYRNE (1993b) which, in addition to experimental results, also includes a detailed review of previously published constants. These authors recommend $\log_{10}\beta^0_1 = 4.13$ and $\log_{10}\beta^0_2 = 6.66$ for EuF^{2+} and EuF$_2^+$, respectively. These constants are based on solvent extraction studies at pH's of 4 to 7.5 in 0.68 M sodium perchlorate and were derived with a Pitzer formalism for the extrapolation to zero ionic strength. The variation of published conditional constants, determined through independent studies conducted in various ionic media (0.5 or 1.0 M), is surprisingly small for both complexes ($\pm 0.2 \log_{10}$ units for the 1:1 complex and $\pm 0.5 \log_{10}$ units for the 1:2 complex).

Taking the mentioned statistical variation of the published values as a measure of uncertainty, we extrapolated the conditional constants determined by LEE & BYRNE (1993b) in 0.68 M NaClO$_4$ to zero ionic strength applying the SIT formalism. Following interaction parameters, taken from GRENTHE et al. (1997), were used: $\varepsilon(F^-,Na^+) = 0.02 \pm _{0.02}$, $\varepsilon(Eu^{3+},ClO_4^-) = 0.50 \pm _{0.03}$ and $\varepsilon(EuF^{2+},ClO_4^-) = \varepsilon(EuF_2^+,ClO_4^-) = \varepsilon(AmF^{2+},ClO_4^-) = 0.39 \pm _{0.04}$, yielding:

$$\log_{10}\beta^0_1 (EuF^{2+}) = 3.8 \pm 0.2$$

$$\log_{10}\beta^0_2 (EuF_2{}^+) = 6.5 \pm 0.5$$

The constants above are ~ 0.2 $\log_{10}$ below the extrapolations given in the source reference. For reasons of internal consistency, we prefer to select these values, since they were derived from the same SIT formalism used throughout this report for the reduction of conditional constants to zero ionic strength.

5.4.7.2   Eu(III) - fluoride solids

The IUPAC database (IUPAC, 1997) reports two solubility products for the simple Eu trifluoride: MENON & JAMES (1989) give $\log_{10}K^0_{s,0}$ (EuF$_3$, cr) = -13.1 while LINGANE (1968) reports a much lower value, $\log_{10}K_{s,0}$ (EuF$_3$, cr) = -16.7 from experiments at a ionic strength of 0.03 M (NaF + NaCl medium at 25ºC). This discrepancy probably reflects differences in the crystallinity of the solids used. The constant determined by LINGANE (1968) stems from precise and slow potentiometric titrations with a fluoride-sensitive electrode. We therefore selected Lingane's constant as starting point for the determination of $\log_{10}K^0_{s,0}$. The SIT extrapolation using ε(Eu^{3+},F$^-$) ~ ε(Eu^{3+},Cl$^-$) = 0.22, ε(Cl$^-$,Na$^+$) = 0.03 and ε(F$^-$,Na$^+$) = 0.02 (GRENTHE et al. 1997) yields:

$$\log_{10}K^0_{s,0} \ (EuF_3, cr) = -17.4 \ \pm 0.5,$$

which is included in the database update. The associated uncertainty was estimated from the statistical variation of $\log_{10}K_{s,0}$ among lanthanide trifluorides. It does not correspond to the standard deviation of $\pm$ 0.05 given in the source reference, which is probably not representative in view of the narrow pH and concentration ranges used in the experiments (pH ~ 4.7, [F]$_{tot}$ ~ 2-6 x 10^{-5} M, [Eu]$_{tot}$ ~ 1 x 10^{-4} to 6 x 10^{-3} M). Note that the value of -17.4 is corroborated by $\log_{10}K^0_{s,0}$ (GdF$_3$,cr) = -17.3 and $\log_{10}K^0_{s,0}$ (SmF$_3$, cr) = -16.0 in the study of MENON & JAMES (1989). The high solubility product determined by MENON & JAMES (1989) for EuF$_3$ is a single anomaly in the series LnF$_3$ crystalline compounds and is therefore discarded.

5.4.7.3   Eu(III) - chloride aqueous complexes

For this update, we selected formation constants from experiments performed in sodium perchlorate at ionic strengths between 1 and 5 M. These data were selected without being reviewed in detail from the IUPAC database (IUPAC 1997) and extrapolated to zero ionic strength with the help of SIT. The regressions (Figures 5.4.9 and 5.4.10) yield the following constants for the monochloride and dichloride complexes:

$$\log_{10}\beta^0_1 \, (\mathrm{EuCl^{2+}}) = 1.1 \pm 0.2$$

$$\log_{10}\beta^0_2 \, (\mathrm{EuCl_2^+}) = 1.5 \pm 0.5$$

In spite of the quite large statistical uncertainties of these extrapolations, the results are consistent with tabulated SIT parameter values. The $\Delta\varepsilon$ resulting from the regression shown in Fig. 5.4.9 coincides with the value calculated using the data tabulated in GRENTHE et al. (1997):

$$\Delta\varepsilon(\text{regression}) = -0.16 \pm 0.05$$

$$\Delta\varepsilon(\text{calculated}) \cong \varepsilon(\mathrm{AmCl^+}, \mathrm{ClO_4^-}) - \varepsilon(\mathrm{Eu^{3+}}, \mathrm{ClO_4^-}) - \varepsilon(\mathrm{Cl^-}, \mathrm{Na^+})$$
$$= \; 0.39 \pm .04 - 0.50 \pm .03 - 0.03 \pm .01$$
$$= -0.14 \pm .08.$$

5.4.7.4 Eu(III) - chloride solids

Lanthanides, including Eu, form very soluble chlorides. Since saturation of this compound will not be reached in groundwaters associated with the repository systems planned in Switzerland, solid Eu(III)-chlorides are not included in the database.

5.4.8 Eu(III) - nitrate aqueous complexes and solid compounds

There is a number of experimental studies on nitrate complexes of Eu(III), which indicate $\mathrm{EuNO_3^+}$ as the only identifiable complex. An attempt to extrapolate the constants reported in the IUPAC database from studies in 0.5 to 4.0 M sodium perchlorate yields $\log_{10}\beta^0_1(\mathrm{EuNO_3^+}) = 2.7 \pm 0.3$. This value is more than one order of magnitude above the value for $\mathrm{AmNO_3^+}$ recommended by the NEA reviewers (1.33 ± 0.20) (see 5.2.5.1) and appears to be too high for a nitrate complex, when compared with the magnitude of the homologous $\mathrm{F^-}$ and $\mathrm{SO_4^{2-}}$ complexes.

Considering further the low nitrate concentrations in natural ground waters, the weakness of Ln(III) nitrate complexes in general and the high solubility of Ln(III) nitrates, it is concluded that thermodynamic data for the Eu(III)-nitrate system are not of critical importance for problems related to safety assessments. Eu(III)-nitrate data are therefore not included in the present update.

$Eu^{3+} + Cl^- = EuCl^{2+}$
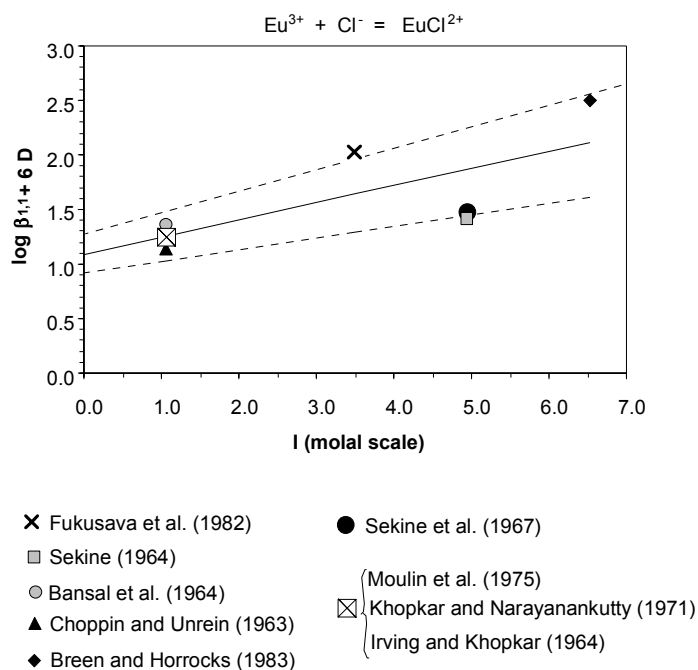
Fig. 5.4.9: Determination of $\log_{10}\beta^0_1$ and $\Delta\varepsilon$ for $EuCl^{2+}$ based on the SIT formalism (GRENTHE et al. 1997). The regression through the selected conditional constants yields $\log_{10}\beta^0_1$ = 1.09 ± 0.17 and $\Delta\varepsilon$ = -0.16 ± 0.05.

$Eu^{3+} + 2 Cl^- = EuCl_2^+$
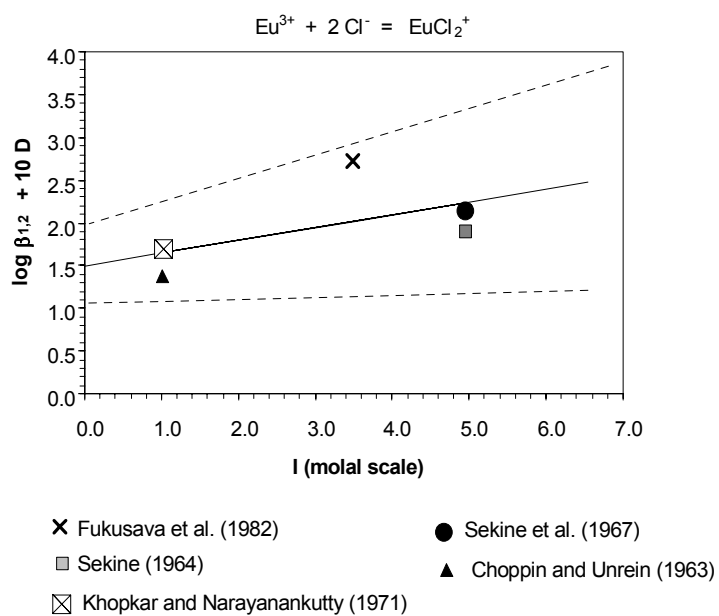
Fig. 5.4.10: Extrapolation of $\log_{10}\beta^0_2$ and $\Delta\varepsilon$ for $EuCl_2^+$ based on the SIT formalism (GRENTHE et al. 1997). The regression through the selected conditional constants yields $\log_{10}\beta^0_2$ = 1.50 ± 0.45 and $\Delta\varepsilon$ = -0.15 ± 0.12.

Table 5.4.4:   Selection of Eu(III) thermodynamic data and comparison with the data selected for Am(III), see Chapter 5.2

Europium

Name	$\Delta_f G_m^o$ [kJ mol^{-1}]	$\Delta_f H_m^o$ [kJ mol^{-1}]	S_m^o [J mol^{-1} K^{-1}]	Species/ Reaction	$\log_{10}K^o$
n.n.	0.0	0.0	77.78	Eu(cr)	
Eu+3	-555.1±13.6	-586.0±13.6	-222.0	Eu^{3+}	
Eu+2	-521.3±13.9	-507.9	-8.0	Eu^{3+} + e$^-$ ⇔ Eu^{2+}	-5.92

Name	$\log_{10}$ $^{(*)}\beta_{1,n}^o$ (Eu)	$\Delta_f H_m^o$ [kJ mol^{-1}]	$\log_{10}$ $^{(*)}\beta_{1,n}^o$ (Am)	Reaction
EuOH+2	-7.64±0.04	-	-7.3±0.3	Eu^{3+} + H$_2$O(l) ⇔ EuOH^{2+} + H$^+$
Eu(OH)2+	-15.1±0.2	-	-15.2±0.8	Eu^{3+} + 2 H$_2$O(l) ⇔ Eu(OH)$_2^+$ + 2 H$^+$
Eu(OH)3	-23.7±0.1	-	-25.7±0.5	Eu^{3+} + 3 H$_2$O(l) ⇔ Eu(OH)$_3$(aq) + 3 H$^+$
Eu(OH)4-	-36.2±0.5	-	-	Eu^{3+} + 4 H$_2$O(l) ⇔ Eu(OH)$_4^-$ + 4 H$^+$
EuCO3+	8.1±0.2	-	7.8±0.3	Eu^{3+} + CO$_3^{2-}$ ⇔ EuCO$_3^+$
Eu(CO3)2-	12.1±0.3	-	12.3±0.4	Eu^{3+} + 2 CO$_3^{2-}$ ⇔ Eu(CO$_3$)$_2^-$
EuSO4+	3.95±0.08	-	3.85±0.03	Eu^{3+} + SO$_4^{2-}$ ⇔ EuSO$_4^+$
Eu(SO4)2-	5.7±0.2	-	5.4±0.7	Eu^{3+} + 2 SO$_4^{2-}$ ⇔ Eu(SO$_4$)$_2^-$
EuF+2	3.8±0.2	-	3.4±0.4	Eu^{3+} + F$^-$ ⇔ EuF^{2+}
EuF2+	6.5±0.5	-	5.8±0.2	Eu^{3+} + 2 F$^-$ ⇔ EuF$_2^+$
EuCl+2	1.1±0.2	-	1.05	Eu^{3+} + Cl$^-$ ⇔ EuCl^{2+}
EuCl2+	1.5±0.5		-	Eu^{3+} + 2 Cl$^-$ ⇔ EuCl$_2^+$

Name	$\log_{10}$ $^{(*)}K_{S,0}^o$ (Eu)	$\Delta_f H_m^o$ [kJ mol^{-1}]	$\log_{10}$ $^{(*)}K_{S,0}^o$ (Am)	Reaction
EU(OH)3(cr)	14.9±0.3	-1319.1	15.2±0.6	Eu(OH)$_3$(cr) + 3 H$^+$ ⇔ Eu^{3+} + 3 H$_2$O(l)
EU(OH)3(am)	17.6±0.8	-	17.0±0.6	Eu(OH)$_3$(am) + 3 H$^+$ ⇔ Eu^{3+} + 3 H$_2$O(l)
EU2(CO3)3(cr)	-35.0±0.3	-	-33.4±2.2	Eu$_2$(CO$_3$)$_3$(cr) ⇔ 2 Eu^{3+} + 3 CO$_3^{2-}$
EUOHCO3(cr)	-21.7±0.1	-	-21.2±1.4	EuOHCO$_3$(cr) ⇔ Eu^{3+} +OH$^-$ +CO$_3^{2-}$
EUF3(cr)	-17.4±0.5	-	-	EuF$_3$(cr) ⇔ Eu^{3+} + 3 F$^-$

5.4.9   Acknowledgements

5.4.10   References

AKSEL'RUD N.V. (1963): Hydroxide chlorides and hydroxides of elements of the scandium subgroup and of the lanthanides. Russ. Chem. Rev. 32(7), 353-366.

ANTIPENKO B., BATAYEV I., PRIVALOVA T. (1973): Relaxation spectroscopy as a method of investigating complex formation reactions in solution. Zhur. Neorg. Khim. 18(3), 318-321.

AZIZ A., LYLE S.J., NAQVI S.J. (1968): Chemical equilibria in Americium and Curium sulphate and oxalate systems and an application of a liquid scintillation counting method. J. Inorg. Nucl. Chem. 30, 1013-1018.

BAES C.F., Jr., MESMER R.E. (1976): The Hydrolysis of Cations. New York, John Wiley & Sons, 489p.

BANSAL B.M., PATIL S.K., SHARMA H.D. (1964): Chloride, nitrate and sulphate complexes of europium(III) and americium(III). J. Inorg. Nucl. Chem. 26, 993.

BARD A.J., PARSONS R., JORDAN J. (1985): Standard potentials in aqueous solutions. Marcel Dekker, Inc.

BERNKOPF M.F. (1984): Hydrolysereaktionen und Karbonatkomplexierung von dreiwertigem Americium im natürlichen aquatischen System. Ph.D. thesis, Institut für Radiochemie, Technische Universität München, Germany, 200 p.

BEVINGTON PH.R. (1969): Data reduction and error analysis for the physical sciences. Mc-Graw-Hill, New York, 336 p.

BREEN P., HORROCKS W. (1983): Europium(III) luminescence excitation spectroscopy. Inner-sphere complexation of europium(III) by chloride, thiocyanate and nitrate ions. Inorg. Chem. 22, 536-540.

BROOKINS D.G. (1989): Aqueous geochemistry of rare earth elements. In: Geochemistry and Mineralogy of rare earth elements. B.R. Lipin & G.A. McKay (eds.): Reviews in Mineralogy, Vol. 21. The Mineralogical Society of America, Washington D.C.

BYRNE R.H., KIM K.H. (1993): Rare earth precipitation and coprecipitation behavior: the limiting role of PO_4^{3-} on dissolved rare earth concentrations in seawater. Geochim. Cosmochim. Acta 57, 519-526.

BYRNE R.H., LEE J.H., BINGLER L.S. (1991): Rare earth element complexation by PO_4^{3-} ions in aqueous solution. Geochim. Cosmochim. Acta 55, 2729-2735.

CACECI M.S., CHOPPIN G.R. (1983): The determination of the first hydrolysis constant of Eu(III) and Am(III). Radiochim. Acta 33, 101-104.

CANTRELL K.J., BYRNE R.H. (1987): Rare earth element complexation by carbonate and oxalate ions. Geochim. Cosmochim. Acta 51, 597-605.

CARVALHO, DE, R.G., CHOPPIN G.R. (1967): Lanthanide and actinide sulphate complexes I-. Determination of stability constants. J. Inorg. Nucl. Chem. 29, 725-735.

CHATT A., RAO R.R. (1989): Complexation of Europium(III) with carbonate ions in groundwater. In: W. Lutze & R.C. Ewing (eds.), Scientific Basis for Nuclear Waste Management XII. Mat. Res. Soc. Symp. Proc. 127, 897-904.

CHOPPIN G., UNREIN P. (1963): J. Inorg. Nucl. Chem. 25, 387.

COTTON F. A., WILKINSON G. (1982): Anorganische Chemie. VCH Verlagsgesellschaft Gmbh, Weinheim, Germany, 1420 p.

COX J. D., WAGMAN D. D., MEDVEDEV V. A. (1989): CODATA key values for thermodynamics. Hemisphere Publishing Corporation, New York, 271 p.

CURTI E. (1993): Modelling bentonite pore waters for the Swiss high-level radioactive waste repository. PSI Report Nr. 93-05, Paul Scherrer Institut, Villigen, Switzerland and Nagra Technical Report NTB 93-45, Nagra, Wettingen, Switzerland.

DIAKONOV I.I., RAGNASDOTTIR K.V., TAGIROV B.R. (1998): Standard thermodynamic properties and heat capacity equations of rare earth hydroxides: II. Ce(III)-, Pr-, Sm-, Eu(III), Gd-, Tb-, Dy-, Ho-, Er-, Tm- Yb- and Y-hydroxides. Comparison of thermochemical and solubility data. Chemical Geology 151, 327-347.

FIRSCHING F.H., MOHAMMADZADEL J. (1986): Solubility products of rare-earth carbonates. J. Chem. Eng. Data 31, 40-42.

FUKUSAWA T., KAWASUJI I., et al. (1982): Investigation on the complex formation of some lanthanoids(III) and actinoids(III) with chloride and bromide. Bull. Chem. Soc. Jpn. 55, 726-729.

GLAUS M.A., HUMMEL W., VAN LOON L.R. (1997): Experimental determination and modelling of trace metal-humate interactions: a pragmatic approach for applications in groundwater. PSI report 97-13, Paul Scherrer Institut.

GRENTHE I., PUIGDOMENECH I. (1997): Symbols, Standards, and Conventions. In: I. Grenthe and I. Puigdomenech (eds.), Modelling in Aquatic Chemistry. pp. 35-68. OECD, Nuclear Energy Agency, Paris.

GRENTHE I., SPAHIU K., PLYASUNOV A. V. (1997): Estimations of medium effects on thermodynamic data. In: I. Grenthe and I. Puigdomenech (eds.), Modelling in Aquatic Chemistry. pp. 325-426. OECD, Nuclear Energy Agency, Paris.

HENDERSON P. (1984): Rare Earth element geochemistry. Developments in Geochemistry 2, Elsevier, Amsterdam, 510 p.

IRVING H.M., KHOPKAR P.K. (1964): The stability of the chloride complexes of europium. J. Inorg. Nucl. Chem. 26, 1561.

IUPAC (1997): Stability Constants Database. Academic Software, Timble, OTLEY, Yorkshire (U.K.).

JIMÉNEZ-REYES M., SOLACHE-RIOS M. (1994): The first hydrolysis constant of Eu(III) in 4M ionic strength at 303 K. Radiochim. Acta 64, 201-203.

JIMÉNEZ-REYES M., SOLACHE-RIOS M., ROJAS-HERNANDEZ A. (1999): Behaviour of Europium(III) and its hydroxo and carbonate complexes in a solvent extraction system with HDBM in 2 M NaCl at 303 K. Radiochim. Acta 87, 125-133.

JORDANOV N., HAVEZOV I. (1966): Löslichkeitsprodukte der normalen Carbonate einiger dreiwertiger seltener Erden ($E_2(CO_3)_3 \cdot nH_2O$). Zeit. anorg. allg. Chemie 347, 101-106.

KHOPKAR P., NARAYANANKUTTY P. (1971): J. Inorg. Nucl. Chem. 33, 495.

LATIMER W.M. (1952): Oxidation potentials. Prentice-Hall, Englewood Cliffs, N.J. (USA), 392 p.

LEE J.H., BYRNE R.H. (1993a): Complexation of trivalent rare earth elements (Ce, Eu, Gd, Tb, Yb) by carbonate ions. Geochimica et Cosmochimica Acta 57, 295-302.

LEE J.H., BYRNE R.H. (1993b): Rare earth element complexation by fluoride ions in aqueous solution. J. Sol. Chem. 22(8), 751-766.

LINGANE J.J. (1968): Further study of the lanthanum fluoride membrane electrode for potentiometric determination and titration of fluoride. Anal.Chem. 40, 935-939.

LUNDQVIST R. (1982): Hydrophilic complexes of the actinides. I. Carbonates of trivalent Americium and Europium. Acta Chem. Scand. A36, 741.

MENON M.P., JAMES J. (1989): Solubilities, solubility products and solution chemistry of lanthanon trifluoride-water systems. J. Chem. Soc., Faraday Trans. I 85(9), 2683-2694.

MOULIN N., HUSSONOIS M., BRILLARD L., et al. (1975): J. Inorg. Nucl. Chem. 37, 2521.

NAIR G.M., CHANDER K., JOSHI J.K. (1982): Hydrolysis constants of Plutonium(III) and Americium(III). Radiochim. Acta 30, 37-40.

NECK V., FANGHÄNEL TH., KIM J.I. (1998): Aquatische Chemie und thermodynamische Modellierung von trivalenten Actiniden. Wissenschaftlicher Bericht FZKA 6110, Forschungszentrum Karlsuhe, Karlsruhe (Germany).

NECK V., KIM J.I. (2000): An electrostatic approach for the prediction of actinide complexation constants with inorganic ligands. Application to carbonate complexes. Radiochim. Acta 88, 815-822.

RAO R.R., CHATT A. (1988): Characterisation of europium(III) carbonate complexes in simulated groundwater by solvent extraction. J. Radioanal. Nucl. Chem. Articles 124, 211.

RAO R.R., CHATT A. (1991): Studies on the stability constants of europium(III) carbonate complexes and application of SIT and ion-pairing models. Radiochim. Acta 54, 181-188.

REMY H. (1949): Lehrbuch der anorganischen Chemie. Akademische Verlagsgesellschaft Geest & Portig K.-G, Leipzig, 5th edition.

RUNDE W., MEINRATH G., KIM J.I. (1992): A study of solid-liquid phase equilibria of trivalent lanthanide and actinide ions in carbonate systems. Radiochi. Acta 58/59, 93-100.

RUZAIKINA L.V., MAROV I.N., RHYABUKHIM V.A., ERMAKOV A.N., FILIMONOVA V.N. (1978): Zh. Anal. Khim. 33, 1082.

SEKINE T. (1964): Complex formation of La(III), Eu(III), Lu(III) and Am(III) with oxalate, sulphate, chloride and thiocyanate ions. J. Inorg. Nucl. Chem. 26, 1463-1465.

SEKINE T. (1965): Solvent extraction study of trivalent actinide and lanthanide complexes in aqueous solutions - II. Sulfate complexes of La(III), Eu(III), Lu(III), and Am(III) in 1 M Na(ClO$_4$). Acta Chem. Scand. 19, 1469-1475.

SEKINE T., SAKAMOTO I., SATO T., TAIRA T. (1967): Complexes of europium(II) with nitrate and chloride ions in 4 M H(ClO$_4$) and Na(ClO$_4$). Bull. Chem. Soc. Jpn. 40, 251-254.

SHANNON R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica A32, 751-767.

SILVA R. J., BIDOGLIO G., RAND M. H., ROBOUCH P. B., WANNER H., PUIGDOMENECH I. (1995): Chemical Thermodynamics of Americium. OECD Nuclear Energy Agency, Elsevier, Amsterdam, 374 p.

SOLACHE-RIOS M., CHOPPIN G.R. (1990): In: VIII Simposio sobre quimica nuclear, radioquimica y quimica de radiaciones. Toluca, Mexico, July 9-13, 1990 (cited in Jimenez-Reyes and Solache-Rios, 1994).

STADLER S., KIM J.I. (1988): Hydrolysis reactions of Am(III) and Am(V). Radiochim. Acta 44/45, 39.

TITS J., BRADBURY M.H., WIELAND E., MANTOVANI M. (1998): The uptake of Cs, Sr, Ni, Eu and Th by CSH phases under high pH cement pore water conditions. Technical Report TM-44-98-01, Paul Scherrer Institut, Villigen, Switzerland.

USHERENKO L.N., SKORIK N.A. (1972): Hydrolysis of rare earth metal, Yttrium, Scandium and Thorium ions in water and water-ethanol mixtures. Russ. J. Inorg. Chem. 17(11), 1533-1535.

WAGMAN D.D., EVANS W.H. et al. (1982): The NBS tables of chemical thermodynamic properties. J. Phys. Chem. Ref. Data 11 (Suppl. No. 2), 390 p.

WIMMER H. (1992): Laser-induzierte optische Spektroskopie zur Speziation von f-Elementen in natürlichen aquatischen Systemen. Ph.D. thesis, Technische Universität München, München, Germany.

Appendix

The following tables (5.4.A1 to 5.4.A4) list (for the purpose of traceability) the detailed numerical values of the SIT extrapolations carried out in the present report.

Table 5.4.A1: Experimental data and calculated quantities for SIT regressions, referring to Figures 5.4.1, 5.4.2 and 5.4.3.

Medium	$T / {}^{\circ}C$	A(T)	I(M)	molality factor	I(m)	D	$\log a_{H2O}$	$\log_{10}{}^*\beta_1$	$\log{}^*\beta_1 - \Delta z^2 A D - n \log_{10} a_{H2O}$	Reference
										Figure 5.4.1
NaCl	25	0.5091	0.7	1.0185	0.71	3.73E-01	-4.99E-03	-7.31	-6.55	CACECI & CHOPPIN (1983)
NaCl	30	0.5135	2.0	1.0434	2.09	4.56E-01	-2.16E-02	-8.29	-7.33	JIMENEZ-REYES et al (1999)
NaCl	30	0.5135	2.0	1.0434	2.09	4.56E-01	-2.16E-02	-8.45	-7.49	JIMENEZ-REYES et al.(1999)
NaCl	30	0.5135	4.0	1.0933	4.37	5.06E-01	-4.99E-02	-6.33	-5.24	JIMENEZ-REYES et al.(1994)
										Figure 5.4.2
NaClO4	25	0.5091	5.0	1.3000	6.5	5.28E-01	-8.27E-03	-6.34	-5.26	SOLACHE-RIOS & CHOPPIN (1990)
NaClO4	25	0.5091	1.0	1.0499	1.05	4.04E-01	-9.10E-03	-8.12	-7.29	NAIR et al.(1982)
NaClO4	25	0.5091	1.0	1.0499	1.05	4.04E-01	-9.10E-03	-8.10	-7.27	LUNDQVIST (1982)
NaClO4	25	0.5091	0.05	1.0050	0.05	1.68E-01	-8.55E-03	-8.03	-7.68	USHERENKO Y SKORIK (1972)
NaClO4	25	0.5091	0.10	1.0073	0.10	2.15E-01	-8.58E-03	-7.94	-7.49	BERNKOPF (1984)
										Figure 5.4.3
NaClO4	25	0.5091			0.10	2.14E-01	-8.58E-03	-7.93	-7.48	BERNKOPF (1984)
NaClO4	25	0.5091			0.10	2.14E-01	-8.58E-03	-7.48	-7.03	STADLER & KIM (1988)
NaClO4	25	0.5091			0.10	2.14E-01	-8.58E-03	-7.1	-6.6	WIMMER (1992)
NaClO4	25	0.5091			1.05	4.04E-01	-9.10E-03	-7.5	-6.7	LUNDQVIST (1982)
NaClO4	25	0.5091			1.05	4.04E-01	-9.10E-03	-7.0	-6.2	NAIR et al. (1982)

Table 5.4.A2: Experimental data and calculated quantities for SIT regressions, referring to Figures 5.4.5 and 5.4.6. All data stem from NaClO$_4$ experiments at 25 ^{o}C.

A(T)	I(M)	molality factor	I(m)	D	log$_{10}$β$_1$	log$_{10}$β$_1$ - Δz^2 A D	log$_{10}$β$_2$	log$_{10}$β$_2$ - Δz^2 A D	Reference
0.5091	0.7	1.0402	0.73	0.37	5.81	8.10	10.14	13.19	LEE & BYRNE (1993A)
0.5091			0.68	0.37	5.86	8.11	10.10	13.10	CANTRELL & BYRNE (1987)
0.5091	0.1	1.0073	0.10	0.22	6.92	8.23	10.42	12.17	RAO & CHATT (1988)
0.5091	1.0	1.0499	1.05	0.40	6.04	8.51	10.16	13.45	CHATT & RAO (1989)
0.5091	1.0	1.0499	1.05	0.40	5.88	8.35	10.03	13.32	RAO & CHATT (1991)
0.5091	1.0	1.0499	1.05	0.40	5.93	8.40	10.72	14.01	LUNDQVIST (1982)

Table 5.4.A3: Experimental data and calculated quantities for SIT regressions, referring to Figures 5.4.7 and 5.4.8. All data stem from NaClO$_4$ experiments at 25 ^{o}C.

A(T)	I(M)	molality factor	I(m)	D	log$_{10}$β$_1$	log$_{10}$β$_1$ - Δz^2 A D	log$_{10}$β$_2$	log$_{10}$β$_2$ - Δz^2 A D	Reference
0.5091	1.0	1.0499	1.05	0.40	1.72	4.19			ANTIPENKO et al. (1973)
0.5091	0.5	1.0256	0.51	0.35	1.88	3.99	2.79	5.60	AZIZ et al. (1968)
0.5091	2.0	1.1037	2.21	0.46	1.38	4.19	1.98	5.73	CARVALHO & CHOPPIN (1967)
0.5091	1.0	1.0499	1.05	0.40	1.54	4.01	2.69	5.98	SEKINE (1965)
0.5091	1.0	1.0499	1.05	0.40	1.57	4.04	2.40	5.69	BANSAL et al. (1964)

Table 5.4.A4: Experimental data and calculated quantities for SIT regressions, referring to Figures 5.4.9 and 5.4.10. All data stem from NaClO$_4$ experiments at 25 ± 5 $^{\circ}$C.

A(T)	I(M)	molality factor	I(m)	D	$\log_{10}\beta_1$	$\log_{10}\beta_1 - \Delta z^2 A\,D$	$\log_{10}\beta_2$	$\log_{10}\beta_2 - \Delta z^2 A\,D$	Reference
0.5091	5.0	1.3076	6.54	0.53	0.89	2.50			BREEN & HORROCKS (1983)
0.5091	3.0	1.1652	3.50	0.49	0.52	2.02	0.22	2.72	FUKUSAWA & KAWASUJI (1982)
0.5091	1.0	1.0499	1.05	0.40	0.07	1.30			MOULIN et al. (1975)
0.5091	1.0	1.0499	1.05	0.40	0.01	1.24	-0.37	1.69	KHOPKAR & NARAYANANKUTTY (1971)
0.5091	4.0	1.2364	4.95	0.51	-0.06	1.51	-0.48	2.13	SEKINE et al. (1967)
0.5091	1.0	1.0499	1.05	0.40	0.13	1.36			BANSAL et al. (1964)
0.5091	1.0	1.0499	1.05	0.40	-0.01	1.22			IRVING & KHOPKAR (1964)
0.5091	4.0	1.2364	4.95	0.51	-0.15	1.42	-0.72	1.89	SEKINE (1964)
0.5091	1.0	1.0499	1.05	0.40	-0.10	1.13	-0.70	1.36	CHOPPIN & UNREIN (1963)

5.5 Iodine

Only three aqueous species of iodine were given by PEARSON et al. (1992), they are all adopted without change.

I^- is the master species with data of formation taken from COX et al. (1989). The equilibrium constants for $I_2(aq)$ and I_3^- were taken from an undocumented PHREEQE database (PHREEQE-PSI 04/91).

In the present database, the formation reaction for I_3^- is written in terms of $I_2(aq)$ instead of I^-, therefore

$$3I^- \Leftrightarrow I_3^- + 2e^- \qquad\qquad (5.5.1)$$

with $\log_{10}\beta^{\circ}$ (5.5.1, 298.15 K) = -18.08 (PEARSON et al. 1992) was replaced by

$$I^- + I_2(aq) \Leftrightarrow I_3^- \qquad\qquad (5.5.2)$$

$$\log_{10}K^{\circ}(5.5.2, 298.15\ K) = 2.87$$

using

$$2I^- \Leftrightarrow I_2(aq) + 2e^- \qquad\qquad (5.5.3)$$

with

$$\log_{10}K^{\circ}(5.5.3, 298.15\ K) = -20.95$$

5.5.1 References

COX, J.D., WAGMAN, D.D. & MEDVEDEV, V.A. (1989): CODATA Key Values for Thermodynamics. Hemisphere Publishing Corp., New York.

PEARSON, F.J., JR., BERNER, U. & HUMMEL, W. (1992): Nagra Thermochemical Data Base II. Supplemental Data 05/92. Nagra Technical Report NTB 91-18, Nagra, Wettingen, Switzerland, 284 pp.

5.6   Iron

All data for iron given by PEARSON et al. (1992) are adopted without change.

The master species for iron is Fe^{2+}, ferrous iron, which is the stable oxidation state in aqueous solutions under reducing conditions, and is relatively soluble. The properties of formation are those given by WAGMAN et al. (1982).

The other iron redox state of importance is Fe^{3+}, ferric iron, which is stable under oxidizing conditions. For the oxidation of Fe^{2+} to Fe^{3+}

$$Fe^{2+} \Leftrightarrow Fe^{3+} + e^-$$ (5.6.1)
$$\log_{10}K°(5.6.1, 298.15K) = -13.02$$

and

$$\Delta_r H_m° (5.6.1, 298.15K) = 40.5 \text{ kJ} \cdot \text{mol}^{-1}$$

(NORDSTROM et al. 1990). Fe^{3+} forms relatively insoluble hydroxide solids and does not occur in measurable quantities in true solution, except under acid conditions. Ferric hydroxides readily form colloids. In oxidizing waters that have not been carefully filtered before analysis, these colloids can give rise to measurable iron concentrations at mid to high pH values.

All data for the complexation of Fe^{2+} and Fe^{3+} with inorganic ligands are taken from NORDSTROM et al. (1990) as well as data for the solid iron phases $FeCO_3$(siderite), $FeSO_4 \cdot 7H_2O$(melanterite), $FeOOH$(goethite), and $Fe(OH)_3$(ferrihydrite). Metallic iron, Fe(cr), is also included. It is unstable in contact with water, but may be useful as a reactant when modeling corrosion and gas generation processes. NORDSTROM et al. (1990) gave two $\log_{10}K°$ values for siderite and ferrihydrite to indicate the range of stability of these minerals with varying cristallinity. They referred to the more soluble minerals as siderite(precipitated) and ferrihydrite(amorphous) and to the less soluble minerals as siderite(crystalline) and ferrihydrite(microcrystalline)[9]. In the present database they are labelled as $FeCO_3$(pr), $Fe(OH)_3$(am), siderite, and $Fe(OH)_3$(mic), respectively.

Note that PEARSON et al. (1992) wrote the formation reactions for aqueous Fe^{3+}-species and the dissociation reactions for Fe^{3+}-solids in terms of Fe^{2+} instead of Fe^{3+}. For the present database, they have been reformulated in terms of Fe^{3+} using $\log_{10}K°(5.6.1, 298.15K)$, and all reactions are therefore written in the form as originally given by NORDSTROM et al. (1990). This concerns the following species and solids:

---

[9]   Note that NORDSTROM et al. (1990) and consequently also PEARSON et al. (1992) confused the $\log_{10}K°$ values of ferrihydrite(amorphous) and ferrihydrite(microcristalline).

$Fe(OH)_2^+$	FeF^{2+}
$Fe(OH)_3(aq)$	FeF_2^+
$Fe(OH)_4^-$	$FeF_3(aq)$
$Fe(SO4)_2^-$	$FeHSO_4^{2+}$
$Fe_2(OH)_2^{4+}$	$FeOH^{2+}$
$Fe_3(OH)_4^{5+}$	$FeSO_4^+$
$FeCl^{2+}$	$Fe(OH)_3(am)$
$FeCl_2^+$	$Fe(OH)_3(mic)$
$FeCl_3(aq)$	$FeOOH(goethite)$

In a late stage of the update of the Nagra/PSI TDB, a Nagra Internal Report (PEARSON 1994, not listed in the references) was found that added data for a set of five iron minerals Fe_2O_3(hematite), Fe_3O_4(magnetite), FeS_2(pyrite), FeS(pyrrhotite), and FeS(troilite) (see Table 5.7.2 at the end of Section 5.7), and for $FeCO_3$(magnesite) (see Section 5.7 and Table 5.7.2) to the Nagra Thermochemical Database (PEARSON et al. 1992). As Nagra Internal Reports are not to be cited, these phases have been leading a clandestine life and have never been officially documented.

The data in PEARSON (1994, not listed in the references) for hematite, magnetite, pyrite, pyrrohite, and troilite all refer to "data0.com.R10S", a datafile distributed with an old version of EQ3/6. This datafile was not available to us and the original references could not be traced back. Therefore, we decided to discard these data for our database update; instead, we provide a set of new data, preferably chosen from solubility experiments. Note that due to time constraints we were not able to make a thorough review of all available experiments and to provide a set of thermochemical data fully consistent with our database. All we could do was a quick evaluation of experiments that appeared to be reasonable at first glance and the quality of the recommended data may not conform to the highest standards. For the iron sulfide minerals our data selection is based on the review by DAVISON (1991).

Owing to the importance of steel corrosion products with respect to the redox state of the repository near-field, it is suggested that iron be the subject of a more extensive review for a future update of the Nagra/PSI TDB.

5.6.1   Hematite

DIAKONOV et al. (1999) measured the solubility of well-crystallized natural and synthetic hematite (Fe_2O_3) in NaOH-NaCl solutions (0.007 - 2.0 m NaOH) at 60, 110, 150, 200, 250 and 300°C at saturated water vapor pressure and under excess oxygen in the pH range from 9.3 to 13.1. Duration of experiments was up to 208 days at 60°C and between 4 and 82 days at higher temperatures. Equilibrium was attained from undersaturation. The reversibility of equilibrium was checked at 60°C with a precipitation experiment that produced the same final iron concentrations as the dissolution experiments. XRD analyses made before and after the experiments confirmed that no changes in the solid phase took place during the experiments. No differences in measured aqueous iron concentrations were observed between experiments with synthetic and natural hematites. For the interpretation of the experimental results, $Fe(OH)_4^-$ was the only iron(III) species considered which is reasonable for the pH-range of these experiments. The dissolution of hematite was therefore described by

$$Fe_2O_3(hematite) + 5H_2O(l) \Leftrightarrow 2Fe(OH)_4^- + 2H^+ \tag{5.6.2}$$

Assuming unit activity for water and hematite, the dissociation constant $K°_{s,14}$(5.6.2) was calculated for each experiment from the measured molalities of Fe and the calculated pH, using activity coefficients of charged species calculated according to the equation proposed by HELGESON et al. (1981) for concentrated NaCl solutions. These dissociation constants were then extrapolated to 25°C by fitting them to the Helgeson-Kirkham-Flowers (HKF) equation of state HELGESON et al. (1981), resulting in

$$\log_{10} K°_{s,14}(5.6.2, 298.15 \text{ K}) = -42.08$$

Reaction (5.6.2) can be expressed in terms of Fe^{3+} by considering

$$Fe^{3+} + 4H_2O(l) \Leftrightarrow Fe(OH)_4^- + 4H^+ \tag{5.6.3}$$
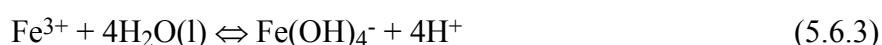
with

$$\log_{10} K°_{14}(5.6.3, 298.15 \text{ K}) = -21.6$$

according to PEARSON et al. (1992).

Subtracting reaction (5.6.3) twice from reaction (5.6.2) leads to

$$Fe_2O_3(hematite) + 6H^+ \Leftrightarrow 2Fe^{3+} + 3H_2O(l) \tag{5.6.4}$$
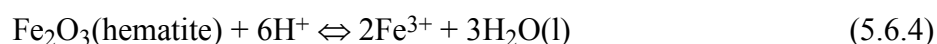
with

$$\log_{10}K^{\circ}_{s,0}(5.6.4, 298.15\ K) = 1.12$$

We recommend this value for the database update.

The solubility constant for hematite given by PEARSON (1994, not listed in the references)

$$\log_{10}K^{\circ}_{s,0}(5.6.5, 298.15\ K) = 26.13$$

applies to the dissolution of hematite involving Fe(II) instead of Fe(III):

$$Fe_2O_3(hematite) + 6H^+ + 2e^- \Leftrightarrow 2Fe^{2+} + 3H_2O(l) \qquad (5.6.5)$$
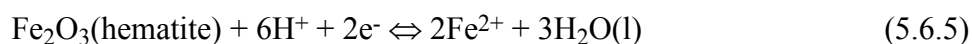
The corresponding value for $\log_{10}K^{\circ}_{s,0}(5.6.4, 298.15\ K)$ can be calculated by considering

$$Fe^{2+} \Leftrightarrow Fe^{3+} + e^- \qquad (5.6.1)$$

for which

$$\log_{10}K^{\circ}(5.6.1, 298.15\ K) = -\ 13.02$$

Therefore

$$\log_{10}K^{\circ}_{s,0}(5.6.4, 298.15\ K) = 0.09$$

which differs by more than one order of magnitude from the selected equilibrium constant.

5.6.2 Magnetite

The solubility of Fe_3O_4(magnetite) was measured by SWEETON & BAES (1970) in dilute aqueous solutions saturated with $H_2(g)$ at temperatures between 50 and 300°C. The measurements were made in an experimental setup that streamed a continuous flow of aqueous solution (ranging in composition from 0.4 mmol·kg^{-1} KOH to 0.1 mmol·kg^{-1} HCl) over a bed of synthetic magnetite. Equilibrium was therefore attained from undersaturation. The extracted solution was then analysed for iron. Chemical and X-ray analyses before and after the experiments revealed no compositional or structural changes in magnetite. For the interpretation of the experimental results Fe^{2+}, $Fe(OH)^+$, $Fe(OH)_2$(aq), and $Fe(OH)_3^-$ were considered as iron species in equilibrium with magnetite according to

$$1/3Fe_3O_4(magnetite) + (2-b)H^+ + 1/3H_2(g) \Leftrightarrow Fe(OH)_b^{(2-b)+} + (4/3-b)H_2O(l) \qquad (5.6.6)$$
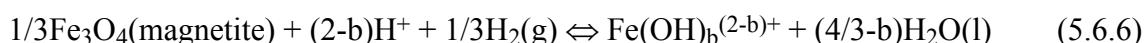
with b = 0 for Fe^{2+}, b = 1 for $Fe(OH)^+$, b = 2 for $Fe(OH)_2$(aq), and b = 3 for $Fe(OH)_3^-$.

Ferric iron was neglected because data from the literature suggested that the proportion of dissolved iron in the ferric state is negligible at pH values below 9 and rather small above. Temperature dependent equilibrium constants of reaction (5.6.6) for each species were then fit to the experimental data. The best fits were obtained by including all four ferrous iron species. Thus, in the case of

$$1/3 Fe_3O_4(\text{magnetite}) + 2H^+ + 1/3 H_2(g) \Leftrightarrow Fe^{2+} + 4/3 H_2O(l) \qquad (5.6.7)$$
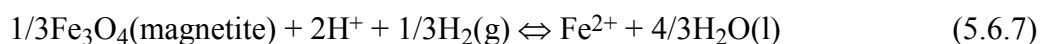
the following expression was found for the equilibrium constant (in units of calories)

$$R \ln K°(5.6.7, T) = \frac{26876}{T} + 9.81(\ln T - 1) - 81.21$$

from which follows (with R = 1.9872 cal $\cdot$ mol^{-1} $\cdot$ K^{-1})

$$\log_{10} K°(5.6.7, 298.15 \text{ K}) = 12.02$$

Reaction (5.6.7) can be tripled and reformulated as

$$Fe_3O_4(\text{magnetite}) + 8H^+ + 2e^- \Leftrightarrow 3Fe^{2+} + 4H_2O(l) \qquad (5.6.8)$$

by adding

$$2H^+ + 2e^- \Leftrightarrow H_2(g) \qquad (5.6.9)$$
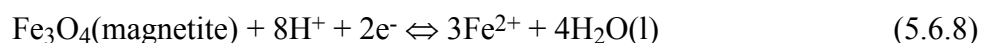
with $\log_{10} K°(5.6.9, 298.15 \text{ K}) = 0$. Therefore

$$\log_{10} K°(5.6.8, 298.15 \text{ K}) = 36.06$$

Finally, from reactions (5.6.6) and (5.6.8) follows

$$Fe_3O_4(\text{magnetite}) + 8H^+ \Leftrightarrow Fe^{2+} + 2Fe^{3+} + 4H_2O(l) \qquad (5.6.10)$$
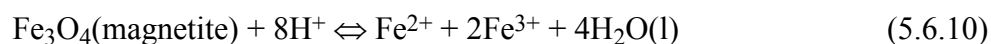
and, using the values for $\log_{10} K°(5.6.6, 298.15 \text{ K})$ and $\log_{10} K°(5.6.8, 298.15 \text{ K})$ reported above,

$$\log_{10} K°(5.6.10, 298.15 \text{ K}) = 10.02$$

This value is recommended for the database update.

The solubility constant for magnetite given by PEARSON (1994, not listed in the references)

$$\log_{10} K°_{s,0}(5.6.8, 298.15 \text{ K}) = 36.494$$

applies to reaction (5.6.8).

The corresponding value for $\log_{10}K°_{s,0}$(5.6.10, 298.15 K) can be calculated by considering reaction (5.6.6) and adding twice the value of $\log_{10}K°$(5.6.6, 298.15 K) to $\log_{10}K°_{s,0}$(5.6.8, 298.15 K). Thus

$$\log_{10}K°_{s,0}(5.6.10, 298.15 \text{ K}) = 10.454$$

5.6.3 Pyrite

The low solubility of FeS_2(pyrite) makes the direct measurement of the solubility product rather difficult. In a review on the solubility of iron sulfides in synthetic and natural waters at ambient temperature DAVISON (1991) rejected the solubility measurements on pyrite by OLSHANSKII & IVANENKO (1958) and TEWARI et al. (1978) (we did not examine these references). According to DAVISON (1991), the data presented by OLSHANSKII & IVANENKO (1958) are suspect because there was no systematic dependence of aqueous iron on pH and it is doubtful whether the measurements were made at equilibrium. Similarly, the aqueous iron concentrations measured by TEWARI et al. (1978) did not vary with pH and were so close to the background iron concentration that there appeared to be no discernible interaction with pyrite. Therefore, DAVISON (1991) concluded that the solubility product of pyrite has to be calculated from free energies of formation. We calculated the Gibbs free energy of reaction for

$$FeS_2(\text{pyrite}) + 2H^+ + 2e^- \Leftrightarrow Fe^{2+} + 2HS^- \tag{5.6.11}$$
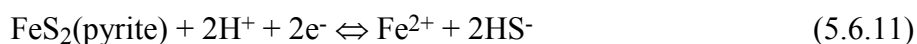
from $\Delta_f G_m°$(pyrite, 298.15 K) = -160.1 kJ·mol^{-1} (ROBIE & HEMINGWAY 1995), $\Delta_f G_m°$(Fe^{2+}, 298.15 K) = -78.9 kJ·mol^{-1} (PEARSON et al. 1992), and $\Delta_f G_m°$(HS$^-$, 298.15 K) = 12.243 kJ·mol^{-1} (see Section 5.19), resulting in $\Delta_r G_m°$(5.6.12, 298.15 K) = 105.7 kJ·mol^{-1} which corresponds to

$$\log_{10}K°_{s,0}(5.6.11, 298.15 \text{ K}) = -18.5$$

In the absence of reliable solubility data, we propose to use this value for the database update.

5.6.4 Pyrrhotite

$Fe_{1-x}S$(pyrrhotite) is a non-stoichiometric iron sulfide mineral with a range of compositions between Fe_7S_8 and FeS. Pyrrhotite appears in two main crystal forms, hexagonal and monoclinic, and has several modifications (CRAIG & SCOTT 1976). In contrast to FeS(am), FeS_{1-x}(mackinawite), Fe_3S_4(greigite), and FeS_2(pyrite), low-temperature hexagonal pyrrhotite is rare in marine sediments (MORSE et al. 1987) — an important environment of sulfide formation at ambient temperatures.

In his analysis of solubility experiments, DAVISON (1991) used the stoichiometric endmember FeS(pyrrhotite), as the departure from stoichiometry is small and often ill-defined. All of the

available solubility data for pyrrhotite were obtained by approaching equilibrium from undersaturation. The early measurements by FOREMAN (1929) (reference not examined) provided inconsistent results. The data by TEWARI et al. (1978) (reference not examined) failed to produce the expected straight line in a plot of $\log_{10}[Fe^{2+}]$ versus pH (TEWARI et al. 1978 themselves were uncertain as to whether equilibrium was established) and the measurements by BERNER (1967) are restricted to a single point. These data alone do not allow a reliable estimate for the solubility of pyrrhotite. HEINDL & GAMSJÄGER (1977) and GAMSJÄGER et al. (1982) made solubility measurements on natural and synthetic monoclinic pyrrhotite and on synthetic hexagonal pyrrhotite in 1 m sodium perchlorate solutions at 50°C. All data give the expected straight lines in the iron vs. pH plots. DAVISON (1991) recalculated the conditional solubility constants to standard conditions by using activity coefficients taken from WHITFIELD (1979). The solubility constants were extrapolated to 25°C by using heats of formation of troilite.

Although the data by HEINDL & GAMSJÄGER (1977) and GAMSJÄGER et al. (1982) in 1 m sodium perchlorate at 50°C appear to be reliable we are not convinced that the extrapolations by DAVISON (1991) to infinite dilution and 25°C are able to withstand closer scrutiny. In the absence of a better alternative for these extrapolations we cannot recommend the data by HEINDL & GAMSJÄGER (1977) and GAMSJÄGER et al. (1982) for the present update. As the original reference for the data on pyrrhotite given by PEARSON (1994, not listed in the references) could not be traced back, the quality of the data cannot be judged and we are forced to exclude pyrrhotite from the database.

5.6.5   Troilite

FeS(troilite) is the polymorph of stoichiometric FeS(cr) that is stable below 140°C. A common constituent of meteorites, troilite is only occasionally found in terrestrial environments, usually together with low-temperature hexagonal pyrrhotite, $Fe_{1-x}S(cr)$ (CRAIG & SCOTT 1976). All of the solubility data for troilite reviewed by DAVISON (1991) were approached from undersaturation. The data by TEWARI & CAMPBELL (1976) (reference not examined) and TEWARI et al. (1978) (reference not examined) for two different samples of natural troilite produce a good straight line in a plot of $\log_{10}[Fe^{2+}]$ versus pH. Using these data, DAVISON (1991) calculated

$$\log_{10}K°(5.6.12, 298.15 \text{ K}) = - (5.31 \pm 0.20)$$

for

$$FeS(troilite) + H^+ \Leftrightarrow Fe^{2+} + HS^- \tag{5.6.12}$$

We recommend this value for the database update but one should be warned that troilite (just like pyrrhotite) may not be the relevant iron sulfide in low-temperature aquatic environments.

5.6.6 Fe(III) carbonate complexes

Within the scope of the update of the Nagra/PSI TDB the investigation of BRUNO et al. (1992) attracted our attention because it is to our present knowledge the only publication exploring the carbonate complexation of ferric iron. The lack of stability constants of Fe(III) carbonate complexes is regarded as a serious deficiency in our database, and therefore, the work of BRUNO et al. (1992) has been carefully reviewed with the aim of including their results in our database.

The findings of BRUNO et al. (1992) unfortunately are disguised by gross computational errors and some inconsistencies in the treatment of their experimental data that, in turn, hide an unresolved ambiguity in their experiments (HUMMEL 2000).

The stability constants of the complexes as reported by BRUNO et al. (1992) are such small numbers that Fe(III) carbonate complexes are predicted to be completely negligible in any aqueous system. A detailed re-examination of the reported experimental data by HUMMEL (2000) revealed that these small number resulted from computational errors of 19 orders of magnitude. However, using the correctly derived constants and assuming solubility equilibrium with hematite lead to the stunning picture of carbonate complexes dominating the entire aqueous chemistry of ferric iron and contradicted experimental evidence of Fe(III) solubility at high pH. The conclusion is that the solubility controlling solid phase in the experiments of BRUNO et al. (1992) was not the initial hematite but most probably some freshly precipitated ferrihydrite (HUMMEL 2000).

BRUNO & DURO (2000) agreed with the general conclusions of HUMMEL (2000) and stated that "all the inconclusive issues of this particular work - identification of the controlling solid phase and the existence and stability of the mixed Fe(III) hydroxo-carbonato complexes - are now part of an ongoing Ph.D. thesis".

In conclusion, at the present stage of knowledge of the Fe(III) carbonate system no equilibrium constants can be recommended for our database. However, for exploring the possible effects of Fe(III) carbonate complexation in modelling exercises the following estimates can be used

$$Fe^{3+} + 2\,CO_3^{2-} \Leftrightarrow Fe(CO_3)_2^{-} \qquad\qquad 20 \leq \log_{10}\beta_2° \leq 22$$
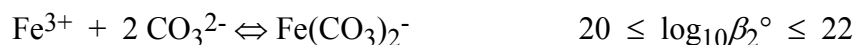
Note that this range of stability has been estimated based on the experimental data of BRUNO et al. (1992) by <u>assuming</u> $Fe(OH)_3(am)$ or $Fe(OH)_3(mic)$, respectively, as the solubility controlling phase. For a detailed discussion see HUMMEL (2000).

5.6.7 References

BERNER, R.A. (1967): Thermodynamic stability of sedimentary iron sulfides. American Journal of Science, 265, 773-785.

BRUNO, J. & DURO L. (2000): Reply to W. Hummel's comment on and correction to "On the influence of carbonate in mineral dissolution: 1. The thermodynamics and kinetics of hematite dissolution in bicarbonate solutions at T = 25°C" by J. Bruno, W. Stumm, P. Wersin, and F. Brandberg. Geochimica et Cosmochimica Acta, 64, 2173-2176.

BRUNO, J., STUMM, W., WERSIN, P. & BRANDBERG F. (1992): On the influence of carbonate in mineral dissolution: 1. The thermodynamics and kinetics of hematite dissolution in bicarbonate solutions at T = 25°C. Geochimica et Cosmochimica Acta, 56, 1139-1147.

CRAIG, J.R. & SCOTT, S.D. (1976): Sulfide phase equilibria. In: RIBBE, P.H. (ed.): Sulfide Mineralogy. Reviews in Mineralogy, 1, Mineralogical Society of America, CS1-CS110.

DAVISON, W. (1991): The solubility of iron sulphides in synthetic and natural waters at ambient temperature. Aquatic Sciences, 53, 309-329.

DIAKONOV, I.I., SCHOTT, J., MARTIN, F., HARRICHOURRY, J.-C. & ESCALIER, J. (1999): Iron(III) solubility and speciation in aqueous solutions. Experimental study and modelling: Part 1. Hematite solubility from 60 to 300°C in NaOH-NaCl solutions and thermodynamic properties of $Fe(OH)_4^-$(aq). Geochimica et Cosmochimica Acta, 63, 2247-2261.

FOREMAN, F. (1929): Hydrothermal experiments on solubility, hydrolysis and oxidation of iron and copper sulphides. Economic Geology, 24, 811-837.

GAMSJÄGER, H., REITERER, F. & HEINDL, R. (1982): Solubility constants and free enthalpies of metal sulphides and carbonates. Berichte der Bunsengesellschaft für Physikalische Chemie, 86, 1046-1049.

HEINDL, R. & GAMSJÄGER, H. (1977): Solubility constants and free enthalpies of metal sulphides, Part 6: A new solubility cell. Monatshefte für Chemie, 108, 1365-1369.

HELGESON, H.C., KIRKHAM, D.H. & FLOWERS, G.C. (1981): Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°C and 5 kbar. American Journal of Science, 281, 1249-1516.

HUMMEL, W. (2000): Comment on "On the influence of carbonate in mineral dissolution: 1. The thermodynamics and kinetics of hematite dissolution in bicarbonate solutions at T = 25°C" by J. Bruno, W. Stumm, P. Wersin, and F. Brandberg. Geochimica et Cosmochimica Acta, 64, 2167-2171.

MORSE, J.W., MILLERO, F.J., CORNWELL, J.C. & RICKARD, D. (1987): The chemistry of the hydrogen sulfide and iron sulfide systems in natural waters. Earth-Science Reviews, 24, 1-42.

NORDSTROM, D.K., PLUMMER, L.N., LANGMUIR, D., MAY, H.M., JONES, B.F. & PARKHURST, D.L. (1990): Revised chemical equilibrium data for major water-mineral reactions and their limitations. In: MELCHIOR, D.C. & BASSETT, R.L. (eds.): Chemical Modeling of Aqueous Systems II. ACS Symposium Series 416, American Chemical Society, Washington D.C., 398-413.

OLSHANSKII, Y.I. & IVANENKO, V.V. (1958): Mechanism of mass transfer in the formation of hydrothermal deposits of sulphides. Tr. Inst. Geol. rudn. Mestorosh., 16, 14-46.

PEARSON, F.J., JR., BERNER, U. & HUMMEL, W. (1992): Nagra Thermochemical Data Base II. Supplemental Data 05/92. Nagra Technical Report NTB 91-18, Nagra, Wettingen, Switzerland, 284 pp.

ROBIE, R.A. & HEMINGWAY, B.S. (1995): Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pascals) pressure and at higher temperatures. United States Geological Survey Bulletin, 2131, 453.

SWEETON, F.H. & BAES, C.F., JR. (1970): The solubility of magnetite and hydrolysis of ferrous ion in aqueous solutions at elevated temperatures. Journal of Chemical Thermodynamics, 2, 479-500.

TEWARI, P.H. & CAMPBELL, A.B. (1976): Dissolution of iron sulphide (troilite) in aqueous sulphuric acid. Journal of Physical Chemistry, 80, 1844-1848.

TEWARI, P.H., WALLACE, G. & CAMPBELL, A.B. (1978): The solubility of iron sulphides and their role in mass transport in Girdler-Sulphide heavy water plants. Report AECL-5960, Atomic Energy Canada Ltd., 34 pp.

WAGMAN, D.D., EVANS, W.H., PARKER, V.B., SCHUMM, R.H., HALOW, I., BAILEY, S.M., CHURNEY, K.L. & NUTTALL, R.L. (1982): The NBS tables of chemical thermodynamic properties: Selected values for inorganic and C_1 and C_2 organic substances in SI units. Journal of Physical and Chemical Reference Data, 11, Supplement No. 2, 1-392.

WHITFIELD, M. (1979): Activity coefficients in natural waters. In: PYTKOWICZ, R.M. (ed.): Activity Coefficients in Electrolyte Solutions. Vol. 2, CRC Press, Boca Raton, Florida.

5.7   Magnesium

All data for magnesium given by PEARSON & BERNER (1991) are adopted without change. In addition, data for magnesite was given in a Nagra Internal Report (PEARSON 1994, not listed in the references, see discussion in Section 5.6). These data referred to the EQ3/6 datafile "SUP-R10 (SUPCRT-91)" (?). Since this datafile was not available to us, the original reference for the data could not be traced back. For this reason, more recent data based on solubility experiments are added to the database.

5.7.1   Magnesite

KÖNIGSBERGER et al. (1999) developed a comprehensive low-temperature model for the geochemical system Na_2CO_3-$MgCO_3$-$CaCO_3$-H_2O based on calorimetrically determined $\Delta_f H_m°$(298.15 K) values, $S_m°$(298.15 K) values and $c_{p,m}°(T)$ functions taken from the literature, as well as on $\mu°$(298.15 K) values of carbonate solids that they derived from solubility measurements. Equilibrium conditions were determined with a Gibbs free energy minimization algorithm. When the resulting thermodynamic quantities are combined with temperature dependent Pitzer parameters taken from the literature, solubilities of carbonate minerals calculated for a wide range of conditions generally agree well with experimental data.

The thermodynamic data determined by KÖNIGSBERGER et al. (1999) for $MgCO_3$(magnesite) were based on the standard heat capacity function and standard entropy determined by HEMINGWAY et al. (1977) (reference not examined) and on the solubility measurements by RIESEN (1969) (reference not examined) on synthetic and natural magnesites at 25 and 50˚C. The 25˚C data for a natural magnesite from Trieben, Austria, resulted in $\Delta_f H_m°$(natural magnesite, 298.15 K) = -(1117.94 ± 0.40) kJ $\cdot$ mol^{-1} while the 25˚C data for a synthetic magnesite resulted in a significantly lower value of $\Delta_f H_m°$(synthetic magnesite, 298.15 K) = - (1114.36 ± 0.40) kJ $\cdot$ mol^{-1}. With the data listed in Table 5.7.1, reaction enthalpies and entropies can be calculated for the equilibrium

$$MgCO_3(magnesite) + H^+ \Leftrightarrow Mg^{2+} + HCO_3^- \qquad (5.7.1)$$
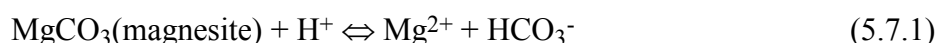
resulting in $\Delta_r H_m°$(5.7.1, 298.15 K) = -38.99 kJ·mol^{-1} for natural and in $\Delta_r H_m°$(5.7.1, 298.15 K) = -42.57 kJ·mol^{-1} for synthetic magnesite. $\Delta_r S_m°$(5.7.1, 298.15 K) = -103.69 J·K^{-1}·mol^{-1} for both solids. From the Gibbs-Helmholtz equation (G = H - TS) then follows that $\Delta_r G_m°$(5.7.1, 298.15 K) = -8.07 kJ·mol^{-1} for natural and $\Delta_r G_m°$(5.7.1, 298.15 K) = -11.65 kJ·mol^{-1} for synthetic magnesite.

Table 5.7.1 Thermodynamic data at 298.15 K and 1 bar as used by KÖNIGSBERGER et al. (1999).

	$\Delta_f H_m^\circ$	S_m°
	(kJ·mol^{-1})	(J·K^{-1}·mol^{-1})
MgCO$_3$(synthetic magnesite)	-1114.36	65.09
MgCO$_3$(natural magnesite)	-1117.94	65.09
H$^+$	0	0
Mg^{2+}	-467.0	-137
HCO3$^-$	-689.93	98.4

These two values correspond to

$$\log_{10}K^\circ(5.7.1, 298.15 \text{ K}) = 1.414$$

for natural and to

$$\log_{10}K^\circ(5.7.1, 298.15 \text{ K}) = 2.041$$

for synthetic magnesite.

As KÖNIGSBERGER et al. (1999) did not comment on this discrepancy and we did not have access to the thesis by RIESEN (1969) we had to rely on our gut feeling to choose between these values and we decided to recommend the latter for our database update, assuming that the composition of the synthetic magnesite was better constrained than that of the natural magnesite. This choice can be rationalized by the following argument: Reaction (5.7.1) can be combined with the equilibrium for

$$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+ \tag{5.7.2}$$

for which

$$\log_{10}K^\circ(5.7.2, 298.15 \text{ K}) = -10.329$$

(NEA, RARD et al. 1999), resulting in

$$MgCO_3(\text{magnesite}) \Leftrightarrow Mg^{2+} + CO_3^{2-} \tag{5.7.3}$$

with the solubility product constants

$$\log_{10}K_{s,0}^\circ(\text{natural magnesite, 298.15 K}) = -8.915$$

$$\log_{10}K_{s,0}^\circ(\text{synthetic magnesite, 298.15 K}) = -8.288$$

Comparison with the solubility product constant for calcite

$$\log_{10}K_{s,0}{}^{\circ}(\text{calcite, 298.15 K}) = -8.48$$

(PEARSON et al. 1992) reveals that natural magnesite is less soluble and synthetic magnesite more soluble than calcite. According to Fajan's rule, magnesite is expected to be more soluble than calcite, since partition coefficents describing the coprecipitation of Mg in calcite are always < 1 (CURTI 1999). Thus, the recommended value for synthetic magnesite is consistent with this empirical geochemical rule, quite in contrast to the rejected value for natural magnesite.

Table 5.7.2: Selected thermodynamic data for the "clandestine" solid phases at 298.15 K and 1 bar. Data from PEARSON (1994, not listed in the references) are given for comparison.
n.c.: not calculated.

PEARSON (1994)			TDB Version 01/01			
Name	$\log_{10}K_{s,0}°$	$\Delta_rH_m°$	Name	$\log_{10}K_{s,0}°$	$\Delta_rH_m°$	Reaction
HEMATITE	26.130	-214.770		n.c.	-	$Fe_2O_3(hematite) + 6H^+ + 2e^- \Leftrightarrow 2Fe^{2+} + 3H_2O(l)$
	0.09	n.c.	hematite	1.12	-	$Fe_2O_3(hematite) + 6H^+ \Leftrightarrow 2Fe^{3+} + 3H_2O(l)$
MAGNETITE	36.494	-301.950		n.c.	-	$Fe_3O_4(magnetite) + 8H^+ + 2e^- \Leftrightarrow 3Fe^{2+} + 4H_2O(l)$
	10.454	n.c.	magnetite	10.02	-	$Fe_3O_4(magnetite) + 8H^+ \Leftrightarrow Fe^{2+} + 2Fe^{3+} + 4H_2O(l)$
PYRITE	-16.222	46.230	pyrite	-18.5	-	$FeS_2(pyrite) + 2H^+ + 2e^- \Leftrightarrow Fe^{2+} + 2HS^-$
PYRRHOTITE	-3.715	-8.370	pyrrhotite	-	-	$FeS(pyrrhotite) + H^+ \Leftrightarrow Fe^{2+} + HS^-$
TROILITE	-3.814	-7.750	troilite	-5.31 ± 0.20	-	$FeS(troilite) + H^+ \Leftrightarrow Fe^{2+} + HS^-$
MAGNESITE	2.294	-45.819	magnesite	2.041	-	$MgCO_3(magnesite) + H^+ \Leftrightarrow Mg^{2+} + HCO_3^-$

5.7.2   References

CURTI, E. (1999): Coprecipitation of radionuclides with calcite: estimation of partition coefficients based on a review of laboratory investigations and geochemical data. Applied Geochemistry, 14, 433-445.

HEMINGWAY, B.S., ROBIE, R.A., FISHER, J.R. & WILSON, W.H. (1977): Heat capacity of gibbsite, Al(OH)$_3$, between 13 and 480 K and magnesite, MgCO$_3$, between 13 and 380 K and their standard entropies at 298.15 K, and the heat capacities of benzoic acid between 12 and 316 K. Journal of Research of the U.S. Geological Survey, 5, 797-806.

KÖNIGSBERGER, E., KÖNIGSBERGER, L.-C. & GAMSJÄGER, H. (1999): Low-temperature thermodynamic model for the system Na$_2$CO$_3$-MgCO$_3$-CaCO$_3$-H$_2$O. Geochimica et Cosmochimica Acta, 63, 3105-3119.

PEARSON, F.J., JR. & BERNER, U. (1991): Nagra Thermochemical Data Base I. Core Data. Nagra Technical Report NTB 91-17, Nagra, Wettingen, Switzerland, 70 pp.

PEARSON, F.J., JR., BERNER, U. & HUMMEL, W. (1992): Nagra Thermochemical Data Base II. Supplemental Data 05/92. Nagra Technical Report NTB 91-18, Nagra, Wettingen, Switzerland, 284 pp.

RARD, J.A., RAND, M.H., ANDEREGG, G. & WANNER, H. (1999): Chemical Thermodynamics of Technetium. Chemical Thermodynamics 3. Elsevier, Amsterdam. 544 pp.

RIESEN, W.F. (1969): Thermodynamische Untersuchungen am quaternären System Ca^{2+}-Mg^{2+}-CO$_2$-H$_2$O. Ph.D. thesis, University of Bern.

5.8 Manganese

All data for manganese are adopted without change from PEARSON et al. (1992).

The master species for manganese is Mn^{2+}, the manganous ion. This species is stable in aqueous solutions under most oxidizing conditions. Its properties of formation are those given by WAGMAN et al. (1982). In the presence of dissolved oxygen, relatively insoluble Mn^{3+} and Mn^{4+} oxide and hydroxide solids form (see below), lowering the dissolved manganese concentration. Mn^{3+} and Mn^{4+} do not occur in measurable quantities in aqueous solutions, however, and are therefore not included in the present database.

Data for complexes of Mn^{2+} with inorganic ligands are taken form NORDSTROM et al. (1990). These include $MnCl^+$, $MnCl_2(aq)$, $MnCl_3^-$, $MnCO_3(aq)$, $MnHCO_3^+$, MnF^+, $MnOH^+$, and $MnSO_4(aq)$.

Data for manganese solids are also taken from NORDSTROM et al. (1990). These include the Mn^{2+} carbonate, $MnCO_3$(rhodochrosite), the Mn^{2+} hydroxide, $Mn(OH)_2$(pyrochroite), the Mn^{3+} and Mn^{4+} hydroxide and oxides $MnOOH$(manganite), Mn_3O_4(hausmannite), and MnO_2(pyrolusite). Note that, following NORDSTROM et al. (1990), there are two values for the solubility constant of rhodochrosite. NORDSTROM et al. 1990 designated the more stable solid as rhodochrosite(crystalline) and the less stable as rhodochrosite(synthetic). In the present database the former is labelled rhodochrosite and the latter rhodochrosite(syn).

5.8.1 References

NORDSTROM, D.K., PLUMMER, L.N., LANGMUIR, D., MAY, H.M., JONES, B.F. & PARKHURST, D.L. (1990): Revised chemical equilibrium data for major water-mineral reactions and their limitations. In: MELCHIOR, D.C. & BASSETT, R.L. (eds.): Chemical Modeling of Aqueous Systems II. ACS Symposium Series 416, American Chemical Society, Washington D.C., 398-413.

PEARSON, F.J., JR., BERNER, U. & HUMMEL, W. (1992): Nagra Thermochemical Data Base II. Supplemental Data 05/92. Nagra Technical Report NTB 91-18, Nagra, Wettingen, Switzerland, 284 pp.

WAGMAN, D.D., EVANS, W.H., PARKER, V.B., SCHUMM, R.H., HALOW, I., BAILEY, S.M., CHURNEY, K.L. & NUTTALL, R.L. (1982): The NBS tables of chemical thermodynamic properties: Selected values for inorganic and C_1 and C_2 organic substances in SI units. Journal of Physical and Chemical Reference Data 11, Supplement No. 2, 1-392.

5.9   Molybdenum

All data for molybdenum are adopted without change from PEARSON et al. (1992).

The master species for molybdenum is MoO_4^{2-}, in which molybdenum is present as Mo(VI). The properties of formation of this species are taken from WAGMAN et al. (1982). No other aqueous molybdenum species is included in the database.

Three molybdenum solid phases are included in the database: Elemental molybdenum, Mo(cr), and the oxides MoO_2(tugarinovite), and MoO_3(molybdite). The properties of the solids are those given by WAGMAN et al. (1982).

5.9.1   References

PEARSON, F.J., JR., BERNER, U. & HUMMEL, W. (1992): Nagra Thermochemical Data Base II. Supplemental Data 05/92. Nagra Technical Report NTB 91-18, Nagra, Wettingen, Switzerland, 284 pp.

WAGMAN, D.D., EVANS, W.H., PARKER, V.B., SCHUMM, R.H., HALOW, I., BAILEY, S.M., CHURNEY, K.L. & NUTTALL, R.L. (1982): The NBS tables of chemical thermodynamic properties: Selected values for inorganic and C_1 and C_2 organic substances in SI units. Journal of Physical and Chemical Reference Data, 11, Supplement No. 2, 1-392.

5.10   Neptunium

All information is taken from OECD NEA's book "Chemical Thermodynamics of Neptunium & Plutonium" (LEMIRE et al. 2001). However, not all recommended values are included in our database since the NEA reviews are not restricted to data relevant for radioactive waste management or even environmental modelling in general. We tried to exclude from our database all phases and complexes which most probably will never be relevant in environmental systems. The notation of formulae and symbols used in this text follows the NEA recommendations.

5.10.1   Elemental neptunium

Neptunium metal, liquid and gas are not relevant under environmental conditions. Hence, the liquid and gas phases are not included in the database. The absolute entropy and heat capacity of Np(VI) are included as they are used for the calculation of certain thermodynamic reaction properties. The selected values are based on low temperature calorimetry of neptunium metal.

$$S_m^\circ \text{ (Np, cr, } \alpha, 298.15 \text{ K)} \quad = \quad (50.46 \pm 0.80) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{p,m}^\circ \text{ (Np, cr, } \alpha, 298.15 \text{ K)} \quad = \quad (29.62 \pm 0.80) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

5.10.2   Neptunium aqua ions

Neptunium exists in aqueous solution in the oxidation states +III, +IV, +V, +VI and +VII. The selected thermodynamic quantities for Np^{3+}, Np^{4+}, NpO_2^+ and NpO_2^{2+} are strongly connected, and there is a minimum amount of redundant information to provide confirmation for these values. The selection process used in LEMIRE et al. (2001) relies strongly on an enthalpy of formation value for Np^{4+} derived from measurements of the enthalpy of dissolution of neptunium metal and subsequent oxidation of the neptunium to the +IV oxidation state. Values for the entropies are all linked to values for the solubility and enthalpy of formation of $NpO_2(NO_3)_2 \cdot 6H_2O(s)$. Potential measurements of the formal redox potentials, their temperature dependence, and calorimetric measurements are used to link and derive the other thermodynamic quantities.

This highly interconnected procedure of data selection and linking cannot be described in any linear sequence without numerous forward and backward references. The detailed discussion in chapter 7 of LEMIRE et al. (2001) therefore is hard to follow. In order to support the reader in unravelling the threads of this Gordian knot, a schematic representation of the NEA data selection and derivation process of thermodynamic quantities for Np^{3+}, Np^{4+}, NpO_2^+ and NpO_2^{2+} is given in Fig. 5.10.1. We hope that referring to this figure while reading the following sections, which are a condensed and slightly rearranged version of chapter 7 of LEMIRE et al. (2001), the reader should be able to digest them without detrimental effects.

$NpO_2(NO_3)_2 \cdot 6H_2O(s) \Leftrightarrow NpO_2^{2+} + 2NO_3^- + 6H_2O(l)$

       solubility   enthalpy of dissolution

          $\Delta_r G_m^\circ$ $\Delta_r H_m^\circ$

                 ↘   ↙

             $\Delta_r S_m^\circ$ $S_m^\circ(NpO_2(NO_3)_2 \cdot 6H_2O(s))$ **estimated**

                ↓   ↙

NpO_2^{2+} $\Delta_f G_m^\circ$ S_m° $\Delta_f H_m^\circ$

          ↑   ↓   ↑

  $NpO_2^{2+} + \frac{1}{2}H_2(g) \Leftrightarrow NpO_2^+ + H^+$

   redox potential   ↙ $\partial E^\circ / \partial T$ **T variation of redox potential**

  $E^\circ \rightarrow \Delta_r G_m^\circ \rightarrow \Delta_r S_m^\circ \leftarrow \Delta_r H_m^\circ \leftarrow$ **average**

                                 ↖ $NpO_2^+ \rightarrow NpO_2^{2+}$ **calorimetry**

                                           H_2O_2

        ↑   ↓   ↑

NpO_2^+ $\Delta_f G_m^\circ$ S_m° $\Delta_f H_m^\circ$

         ↑   ↓   ↑

  $NpO_2^+ + 3H^+ + \frac{1}{2}H_2(g) \Leftrightarrow Np^{4+} + 2H_2O(l)$

   redox potential

  $E^\circ \rightarrow \Delta_r G_m^\circ \rightarrow \Delta_r S_m^\circ \leftarrow \Delta_r H_m^\circ \leftarrow \partial E^\circ / \partial T$ **T variation of redox potential**

        ↑   ↓   ↑

             S_m° $Np(cr,\alpha) + 4H^+ + \frac{1}{4}O_2 \rightarrow Np^{4+} + 1\frac{1}{2}H_2(g) + \frac{1}{2}H_2O(l)$

Np^{4+} $\Delta_f G_m^\circ$ $\leftarrow \Delta_f H_m^\circ \leftarrow$ **enthalpy of dissolution**

            ↖   ↙

           $\Delta_f S_m^\circ$ $\leftarrow$ $S_m^\circ(Np, cr, \alpha) \leftarrow$ **low temperature calorimetry**

        ↓   ↓   ↓

$Np^{4+} + \frac{1}{2}H_2(g) \Leftrightarrow Np^{3+} + H^+$

   redox potential

  $E^\circ \rightarrow \Delta_r G_m^\circ \rightarrow \Delta_r S_m^\circ \leftarrow \Delta_r H_m^\circ \leftarrow \partial E^\circ / \partial T$ **T variation of redox potential (discarded)**

        ↓   ↓   ↑

                         $Np(cr,\alpha) + 3H^+ \rightarrow Np^{3+} + 1\frac{1}{2}H_2(g)$

Np^{3+} $\Delta_f G_m^\circ$ S_m° $\Delta_f H_m^\circ \leftarrow$ **enthalpy of dissolution**

Fig. 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+}. Quantities in **bold face** are based on experimental data and an estimate, all others are calculated therefrom. Arrows indicate the links in the chain of thermodynamic calculations.

5.10.2.1 NpO_3^+

Heptavalent neptunium can be generated in alkaline solutions, but is reduced by water to Np(VI) over a period of hours to weeks at room temperature. Hence, Np(VII) is not included in our database.

5.10.2.2 NpO_2^{2+}

The standard entropy for NpO_2^{2+} is derived from the solubility and the enthalpy of dissolution of the salt $NpO_2(NO_3)_2 \cdot 6H_2O(s)$ in water. From solubility measurements the solubility product

$$NpO_2(NO_3)_2 \cdot 6H_2O(s) \Leftrightarrow NpO_2^{2+} + 2NO_3^- + 6H_2O(l)$$
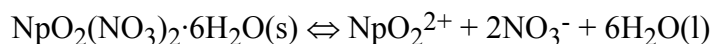
has been determined as $\log_{10}{}^*K_{s,0}° = 2.15 \pm 0.19$ or $\Delta_r G_m° = -12.30 \pm 1.09$ kJ·mol^{-1}. Due to the saturation molality of 2.95 ± 0.26 of this salt, corresponding to a high ionic strength of $I = 8.9$ m, the extrapolation to zero ionic strength is a somewhat uncertain procedure. Note that the solubility product of neptunyl nitrate is of importance for deriving the Gibbs energy of formation of the Np(n) aqua ion. However, this solid is not included in our database because of its high solubility. The enthalpy of solution in water of this salt has also been measured. The result, corrected for hydrolysis, is $\Delta_r H_m° = 18.83 \pm 1.67$ kJ·mol^{-1}. From $\Delta_r G_m°$ and $\Delta_r H_m°$ a value of $\Delta_r S_m° = 104.4 \pm 7.6$ J·K^{-1}·mol^{-1} has been calculated. LEMIRE et al. (2001) accepted an estimate for the standard entropy of the salt $S_m°(NpO_2(NO_3)_2 \cdot 6H_2O(s)) = 516.3 \pm 8.0$ J·K^{-1}·mol^{-1} without any further comment, and using this value, $\Delta_r S_m°$ and CODATA auxiliary values, determined

$$S_m° \ (NpO_2^{2+}, aq, 298.15 \ K) \quad = \quad -(92.4 \pm 10.5) \ J \cdot K^{-1} \cdot mol^{-1}$$

The values for the standard Gibbs energy of formation and enthalpy of formation of NpO_2^{2+} are derived from values of the standard potential of the reaction

$$NpO_2^{2+} + \tfrac{1}{2}H_2(g) \Leftrightarrow NpO_2^+ + H^+$$
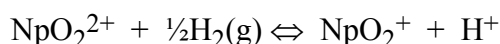
and its temperature variation based on electrochemical measurements and calorimetric data. The formal potential (at 1 M $HClO_4$) selected by LEMIRE et al. (2001) has been extrapolated to zero ionic strength using SIT with $\Delta\varepsilon = -(0.21 \pm 0.03)$ kg · mol^{-1} to obtain the standard potential

$$E° \ (298.15 \ K) \ = \ (1.159 \pm 0.004) \ V$$

This corresponds to $\qquad \log_{10}K° \ (298.15 \ K) \ = \ (19.59 \pm 0.07)$

or $\qquad \Delta_r G_m° \ (298.15 \ K) \ = \ -(111.8 \pm 0.4) \ kJ \cdot mol^{-1}$

From the temperature dependence of this potential at 1 M $HClO_4$ $\Delta_r S_m(1M \ HClO_4) = \partial E°'/\partial T \cdot F = -(26.05 \pm 4.82)$ J·K^{-1}·mol^{-1} is obtained (F is the Faraday constant). Using this value and the accepted $\Delta_r G_m(1M \ HClO_4) = -(109.70 \pm 0.10)$ kJ·mol^{-1}, $\Delta_r H_m(1M \ HClO_4) = -(117.47 \pm 1.44)$ kJ·mol^{-1} is calculated. The enthalpy of transfer to infinite dilution is assumed to be zero and thus, the value of $\Delta_r H_m°$ is the same as $\Delta_r H_m(1M \ HClO_4)$.

A second, independent value of $\Delta_r H_m° = $ -(117.4 ± 0.6) kJ·mol^{-1} is obtained from calorimetric measurements of the oxidation of NpO_2^+ to NpO_2^{2+} by hydrogen peroxide.

The weighted average of these two independent values is

$$\Delta_r H_m°(298.15 \text{ K}) = \text{-}(117.4 \pm 0.6) \text{ kJ} \cdot \text{mol}^{-1}.$$

From $\Delta_r H_m°$ and the selected value of $\Delta_f H_m°$ (NpO_2^+) (see 5.10.2.3) LEMIRE et al. (2001) determined the selected value

$$\Delta_f H_m° (NpO_2^{2+}, \text{aq}, 298.15 \text{ K}) = \text{-}(860.7 \pm 4.7) \text{ kJ} \cdot \text{mol}^{-1}$$

Similarly, using $\Delta_r G_m°$ and the selected value of $\Delta_f G_m°(NpO_2^+)$ (see 5.10.2.3) LEMIRE et al. (2001) determined the selected value

$$\Delta_f G_m° (NpO_2^{2+}, \text{aq}, 298.15 \text{ K}) = \text{-}(795.9 \pm 5.6) \text{ kJ} \cdot \text{mol}^{-1}$$

Taking $\Delta_r G_m°$ and $\Delta_r H_m°$,

$$\Delta_r S_m° = \text{-}(18.9 \pm 2.3) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

is calculated. This value is required in the following section (5.10.2.3).

5.10.2.3 NpO_2^+

The standard entropy for NpO_2^+ is derived from the value of $S_m°$ (NpO_2^{2+}) and $\Delta_r S_m°$ of the standard potential Np(VI) / Np(V) (see 5.10.2.2),

$$S_m° (NpO_2^+, \text{aq}, 298.15 \text{ K}) = \text{-}(45.9 \pm 10.7) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Note, that $S_m°(NpO_2^+)$ is significantly different from earlier estimates. In addition, widely discrepant and non-systematic values for $S_m°$ (MO_2^+(aq), M = U, Np, Pu, Am) of -25, -46, +1, -21 $J \cdot K^{-1} \cdot mol^{-1}$, respectively, were found by LEMIRE et al. (2001) in contrast to previous reviews that relied more heavily on estimates. The differences in the entropy values for these key ions appear to be beyond those easily attributable to specific experimental uncertainties, and need to be confirmed or refuted by further experimental work.

The values for the standard Gibbs energy of formation and enthalpy of formation of NpO_2^+ are derived from the values of the standard potential and its temperature variation based on electrochemical potential measurements.
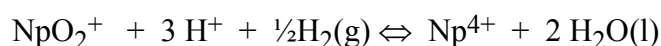
$$NpO_2^+ + 3 H^+ + \tfrac{1}{2}H_2(g) \Leftrightarrow Np^{4+} + 2 H_2O(l)$$

The formal potential (at 1 M $HClO_4$) selected by LEMIRE et al. (2001) has been extrapolated to zero ionic strength using SIT with $\Delta\varepsilon = +(0.17 \pm 0.09)$ kg · mol^{-1} to obtain the standard potential

$$E° \text{ (298.15 K)} = (0.604 \pm 0.007) \text{ V}$$

This corresponds to $\log_{10}K°$ (298.15 K) $= (10.21 \pm 0.12)$

or $\Delta_r G_m°$ (298.15 K) $= -(58.3 \pm 0.7)$ kJ · mol^{-1}

From the temperature dependence of this potential at 1 M $HClO_4$ $\Delta_r S_m$(1M $HClO_4$) = $\partial E°'/\partial T \cdot F$ = -(259.5 ± 5.8) J·K^{-1}·mol^{-1} is obtained (F is the Faraday constant). Using this value and the accepted $\Delta_r G_m$(1M $HClO_4$) = -(71.7 ± 0.1) kJ·mol^{-1}, $\Delta_r H_m$(1M $HClO_4$) = -(149.1 ± 1.7) kJ·mol^{-1} is calculated. The enthalpy of transfer to infinite dilution is assumed to be 0.42 kJ·mol^{-1}. The reasoning for this correction is that it was done to account for the extent of the first hydrolysis reaction of Np^{4+} (see 5.10.2.4) but a similar correction for NpO_2^+ is negligible. Thus, the correction of 0.42 kJ·mol^{-1} can be applied directly to the accepted value of $\Delta_r H_m$(1M $HClO_4$) to determine

$$\Delta_r H_m°(298.15 \text{ K}) = -(149.5 \pm 1.7) \text{ kJ · mol}^{-1}.$$

From $\Delta_r H_m°$ of the above reaction and the selected value of $\Delta_f H_m°$ (Np^{4+}) (see 5.10.2.4) LEMIRE et al. (2001) determined the selected value

$$\Delta_f H_m° \text{ (NpO}_2^+, \text{ aq, 298.15 K)} = -(978.2 \pm 4.6) \text{ kJ · mol}^{-1}$$

Similarly, using $\Delta_r G_m°$ and the selected value of $\Delta_f G_m°$ (Np^{4+}) (see 5.10.2.4) LEMIRE et al. (2001) determined the selected value

$$\Delta_f G_m° \text{ (NpO}_2^+, \text{ aq, 298.15 K)} = -(907.8 \pm 5.6) \text{ kJ · mol}^{-1}$$

Taking $\Delta_r G_m°$ and $\Delta_r H_m°$,

$$\Delta_r S_m° = -(305.9 \pm 6.2) \text{ J · K}^{-1} \text{ · mol}^{-1}$$

is calculated. This value is required in the following section (5.10.2.4).

Based on reported apparent molar heat capacities of NpO_2ClO_4(aq) as a function of temperature LEMIRE et al. (2001) calculated the partial molar heat capacity of NpO_2^+ as

$$C_{p,m}° \text{ (NpO}_2^+, \text{ aq, 298.15 K)} = -(4 \pm 25) \text{ J · K}^{-1} \text{ · mol}^{-1}$$

Note that for our database we combined the above $\log_{10}K° = (10.21 \pm 0.12)$ with the Np(VI) / Np(V) equilibrium of section 5.10.2.2, i.e. $\log_{10}K° = (19.59 \pm 0.07)$, and $\log_{10}K° = 0$ (by definition) for $\frac{1}{2}H_2(g) \Leftrightarrow H^+ + e^-$ in order to obtain

$$NpO_2^{2+} + 4\,H^+ + 2\,e^- \Leftrightarrow Np^{4+} + 2\,H_2O(l)$$
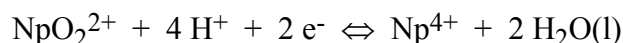
$$\log_{10}K° \,(298.15\,K) \,=\, (29.80 \pm 0.14)$$

5.10.2.4 Np^{4+}

The enthalpy of formation of Np^{4+} was derived from calorimetric measurements of the dissolution of neptunium metal in HCl in the presence of dissolved oxygen according to the reaction:

$$Np(cr,\alpha) + 4\,H^+ + 0.25\,O_2(dissolved) \rightarrow Np^{4+} + 1.5\,H_2(g) + 0.5\,H_2O(l)$$
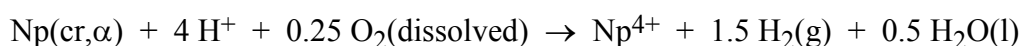
$$\Delta_f H_m° \,(Np^{4+}, aq, 298.15\,K) \quad = \quad -(556.0 \pm 4.2)\,kJ \cdot mol^{-1}$$

To evaluate other thermodynamic data in 1 M $HClO_4$ (see 5.10.2.3 & 5.10.2.5) a correction of 0.42 $kJ \cdot mol^{-1}$ is applied to $\Delta_f H_m°$ in order to account for the first hydrolysis reaction of Np^{4+} in 1 M $HClO_4$, resulting in $\Delta_f H_m(Np^{4+}, 1\,M\,HClO_4, 298.15\,K) = -(555.6 \pm 4.2)\,kJ \cdot mol^{-1}$.

$S_m°(Np^{4+})$ is calculated from the value of $S_m° \,(NpO_2^+)$ and $\Delta_r S_m°$ of the standard potential Np(V) / Np(IV) (see 5.10.2.3), and CODATA auxiliary data to give

$$S_m° \,(Np^{4+}, aq, 298.15\,K) \quad = \quad -(426.4 \pm 12.4)\,J \cdot K^{-1} \cdot mol^{-1}$$

Based on this, CODATA values and $S_m°(Np, cr, \alpha, 298.15\,K) = (50.46 \pm 0.80)\,J \cdot K^{-1} \cdot mol^{-1}$ (see 5.10.1), $\Delta_f S_m°(Np^{4+}) = -(215.5 \pm 12.4)\,J \cdot K^{-1} \cdot mol^{-1}$ is calculated. Then, using the Gibbs-Helmholtz relation and the selected values for $\Delta_f H_m°(Np^{4+})$, the selected standard Gibbs energy of formation of Np^{4+} is calculated as

$$\Delta_f G_m° \,(Np^{4+}, aq, 298.15\,K) \quad = \quad -(491.8 \pm 5.6)\,kJ \cdot mol^{-1}$$

5.10.2.5 Np^{3+}

The enthalpy of formation of Np^{3+} is derived from calorimetric measurements of the dissolution of neptunium metal in HCl according to the reaction:

$$Np(cr,\alpha) + 3\,H^+ \rightarrow Np^{3+} + 1.5\,H_2(g)$$
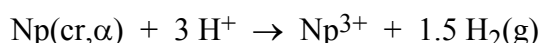
$$\Delta_f H_m° \,(Np^{3+}, aq, 298.15\,K) \quad = \quad -(527.2 \pm 2.1)\,kJ \cdot mol^{-1}$$

The values for the standard Gibbs energy of formation and the standard entropy of Np^{3+} have been derived from potential measurements for the reaction

$$Np^{4+} + \tfrac{1}{2}H_2(g) \Leftrightarrow Np^{3+} + H^+$$
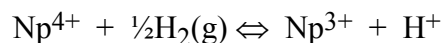
The standard potential selected by LEMIRE et al. (2001) is

$$E° (298.15 \text{ K}) = (0.219 \pm 0.010) \text{ V}$$

This corresponds to $\log_{10}K° (298.15 \text{ K}) = (3.70 \pm 0.17)$

or $\Delta_r G_m° (298.15 \text{ K}) = \text{-}(21.1 \pm 1.0) \text{ kJ} \cdot \text{mol}^{-1}$

From the temperature dependence of this potential at 1M $HClO_4$, $\Delta_r S_m(\text{1M } HClO_4) = \partial E°'/\partial T \cdot F = (131.2 \pm 4.8) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ is obtained (F is the Faraday constant). Using this value and the accepted $\Delta_r G_m(\text{1M } HClO_4) = \text{-}(15.0 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_r H_m(\text{1M } HClO_4) = (24.2 \pm 1.5) \text{ kJ} \cdot \text{mol}^{-1}$ is calculated. Using $\Delta_f H_m(Np^{4+}, \text{1M } HClO_4) = \text{-}(556.6 \pm 4.2) \text{ kJ} \cdot \text{mol}^{-1}$ (see 5.10.2.4), the NEA reviewers calculated from electrochemical data $\Delta_f H_m(Np^{3+}, \text{1M } HClO_4) = \text{-}(531.5 \pm 12.3) \text{ kJ} \cdot \text{mol}^{-1}$, and assumed that $\Delta_f H_m(Np^{3+}) \approx \Delta_f H_m°(Np^{3+})$. This value, -(531.5 ± 12.3) $\text{kJ} \cdot \text{mol}^{-1}$, is somewhat more negative than the value based on calorimetric data, -(527.2 ± 2.1) $\text{kJ} \cdot \text{mol}^{-1}$. LEMIRE et al. (2001) selected the latter one because of its smaller uncertainty and discarded the value derived from electrochemical measurements.

From the selected values for $\Delta_f H_m°$ (Np^{4+}) (see 5.10.2.4) and $\Delta_f H_m°$ (Np^{3+}), $\Delta_r H_m° = (28.8 \pm 4.7)$ $\text{kJ} \cdot \text{mol}^{-1}$ of the redox reaction is calculated. From this value and $\Delta_r G_m°$, $\Delta_r S_m° = (167.5 \pm 16.0)$ $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ is obtained. Hence, with CODATA auxiliary data and the previously selected value for $S_m°$ (Np^{4+}) (see 5.10.2.4)

$$S_m° (Np^{3+}, \text{aq, 298.15 K}) \quad = \quad \text{-}(193.6 \pm 20.3) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

is calculated.

The standard Gibbs energy of formation

$$\Delta_f G_m° (Np^{3+}, \text{aq, 298.15 K}) \quad = \quad \text{-}(512.9 \pm 5.7) \text{ kJ} \cdot \text{mol}^{-1}$$

was obtained using $\Delta_r G_m°$ of the above reaction and $\Delta_f G_m°$ (Np^{4+}) (see 5.10.2.4).

Note that for our database we combined the above $\log_{10}K° = (3.70 \pm 0.17)$ with the Np(VI) / Np(V) equilibrium of section 5.10.2.2, i.e. $\log_{10}K° = (19.59 \pm 0.07)$, the Np(V) / Np(IV) equilibrium of

section 5.10.2.3, i.e. $\log_{10}K° =$ (10.21 ± 0.12), and $\log_{10}K° = 0$ (by definition) for $\frac{1}{2}H_2(g) \Leftrightarrow H^+ +$ e^- in order to obtain

$$NpO_2^{2+} + 4\,H^+ + 3\,e^- \Leftrightarrow Np^{3+} + 2\,H_2O(l)$$
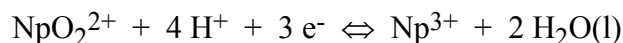
$$\log_{10}K° \ (298.15\ K) = (33.50 \pm 0.23)$$

5.10.3   Neptunium oxygen and hydrogen compounds and complexes

5.10.3.1   Aqueous neptunium hydroxide complexes

5.10.3.1.1 Neptunium(VII) hydroxide complexes

Only limited information on these species appears to be available. No thermodynamic parameters have been estimated by LEMIRE et al. (2001).

5.10.3.1.2 Neptunium(VI) hydroxide complexes

Np(VI) hydrolysis constants refer to the reaction

$$m\,NpO_2^{2+} + n\,H_2O(l) \Leftrightarrow (NpO_2)_m(OH)_n^{(2m-n)} + n\,H^+$$
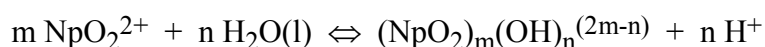
A self-consistent set of values derived from potentiometric measurements has been accepted by LEMIRE et al. (2001)

$$\log_{10}{}^*\beta_1° \ \ (298.15\ K) \quad = \quad -5.1 \pm 0.4$$

$$\log_{10}{}^*\beta_{2,2}° \ (298.15\ K) \quad = \quad -6.27 \pm 0.21$$

$$\log_{10}{}^*\beta_{5,3}° \ (298.15\ K) \quad = \quad -17.12 \pm 0.22.$$

Several groups have reported values for the potential of the Np(VI) / Np(V) couple in highly concentrated hydroxide solutions. If the major Np(VI) species in the alkaline solutions are not polymeric, and if the Np(V) species is assumed to be $NpO_2(OH)_2^-$, the potential of the Np(VI) / Np(V) couple can be rationalised if the Np(VI) species is either $NpO_2(OH)_3^-$ or $NpO_2(OH)_4^{2-}$. Possible hydrolysis constants have been proposed. There does not appear to be a substantive reason for preferring one species in favour of the other. If anionic polymers exist (as they have been found in the uranium system), both proposed constants may be regarded as limiting values.

$$\log_{10}{}^*\beta_3° \ (298.15\ K) \qquad \leq -19$$

$$\log_{10}{}^*\beta_4° \ (298.15\ K) \qquad \leq -33$$

There does not appear to be any reliable data to supply thermodynamic parameters for $NpO_2(OH)_2(aq)$ or for polymeric neutral or anionic Np(VI) hydrolysis species, although such species may well exist. Note that a constant has been selected for the analogous species $PuO_2(OH)_2(aq)$ (LEMIRE et al. 2001).

5.10.3.1.3 Neptunium(V) hydroxide complexes

Several groups have reported values for the formation constants for neptunium(V) hydroxo species. However, there is no consensus as to the value for the formation constant of $NpO_2OH(aq)$. The differences between the results of the long-term studies of the solubility of $NpO_2OH(am)$ and the fairly extensive data from other studies cannot be resolved at this time. LEMIRE et al. (2001) decided to select hydrolysis constants for NpO_2^+ based only on the studies of the solubility of $NpO_2OH(am)$. Because it is an amorphous solid, it is very difficult to characterise. Under oxidising conditions, $NpO_2OH(am)$ may not be the stable neptunium solid in contact with aqueous solutions even though it may be in equilibrium with Np(V) solution species. This suggests that values for the hydrolysis constants of Np(V) must be accepted only with considerable caution.

$$NpO_2^+ + n\,H_2O(l) \Leftrightarrow NpO_2(OH)_n^{(1-n)} + n\,H^+$$

$$\log_{10}{}^*\beta_1° \ (n = 1, 298.15\ K) \quad = \quad -11.3 \pm 0.7$$

$$\log_{10}{}^*\beta_2° \ (n = 2, 298.15\ K) \quad = \quad -23.6 \pm 0.5$$
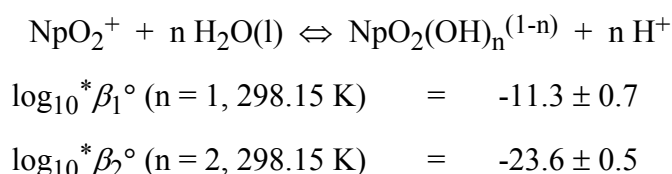
In the absence of experimental data, estimated entropy values have been accepted by LEMIRE et al. (2001):

$$S_m° \ (NpO_2OH, aq, 298.15\ K) \quad = \quad (25 \pm 60)\ J \cdot K^{-1} \cdot mol^{-1}$$

$$S_m° \ (NpO_2(OH)_2^-, aq, 298.15\ K) \quad = \quad (40 \pm 100)\ J \cdot K^{-1} \cdot mol^{-1}$$

5.10.3.1.4 Neptunium(IV) hydroxide complexes

Three quantitative studies of the first hydrolysis step for Np^{4+} have been reported.

$$Np^{4+} + H_2O(l) \Leftrightarrow NpOH^{3+} + H^+$$
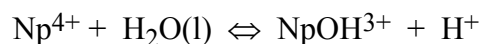
The results are in qualitative agreement but show significant scatter. Therefore, LEMIRE et al. (2001) selected a value based on the unweighted average of the results of these studies after correction to zero ionic strength

$$\log_{10}{}^*\beta_1° \ (298.15\ K) \quad = \quad -0.29 \pm 1.00$$

In acidic solutions, there is certainly evidence of species more extensively hydrolysed than $NpOH^{3+}$, but the structure and charge of these species have not been established.

There is no experimental evidence that $Np(OH)_3^+$ is formed in the Np(IV) - water system, and this species is not credited by LEMIRE et al. (2001).

Several studies reported a limiting, pH independent solubility of "neptunium(IV) hydrous oxide" or "$Np(OH)_4$" in neutral to very basic solutions at room temperature in the presence of reducing agents. This solubility is interpreted in terms of

$$NpO_2(hyd, am) + 2 H_2O(l) \Leftrightarrow Np(OH)_4(aq)$$
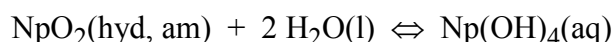
$$\log_{10}K_{s,4}° (298.15 \text{ K}) = -8.3 \pm 0.3$$

and the solubility product as selected by LEMIRE et al. (2001) (see 5.10.3.2.4)

$$NpO_2(hyd, am) + 4 H^+ \Leftrightarrow Np^{4+} + 2 H_2O(l)$$

$$\log_{10}{}^*K_{s,0}° (298.15 \text{ K}) = 1.5 \pm 1.0$$

is considered. Hence, the following value is calculated and recommended by LEMIRE et al. (2001):

$$Np^{4+} + 4 H_2O(l) \Leftrightarrow Np(OH)_4(aq) + 4 H^+$$

$$\log_{10}{}^*\beta_4° = \log_{10}K_{s,4}° - \log_{10}{}^*K_{s,0}° = -9.8 \pm 1.1$$

It is clear from the above mentioned solubility measurements up to very basic solutions that $Np(OH)_5^-$ is not an important hydrolysis species for Np(IV). Thus, no value is proposed for this species by LEMIRE et al. (2001).

5.10.3.1.5 Neptunium(III) hydroxide complexes

The literature appears to contain only one experimental study of the equilibrium

$$Np^{3+} + H_2O(l) \Leftrightarrow NpOH^{2+} + H^+$$
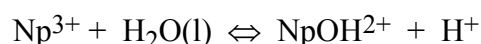
in 0.3 M $NaClO_4$ (see LEMIRE et al. 2001) and the results seem reliable. The value has been extrapolated to zero ionic strength using SIT coefficients from the corresponding Am system, i.e. $\Delta\varepsilon = +(0.04 \pm 0.09) \text{ kg} \cdot \text{mol}^{-1}$. LEMIRE et al. (2001) recommended

$$\log_{10}{}^*\beta_1° (298.15 \text{ K}) \qquad = \qquad -6.8 \pm 0.3$$

5.10.3.2 Solid neptunium oxides and hydroxides

5.10.3.2.1 Neptunium(VII) oxides and hydroxides

No thermodynamic data for Np(VII) oxides and hydroxides are available.

5.10.3.2.2 Neptunium(VI) oxides and hydroxides

NpO_3(cr): No successful attempts to prepare this compound have been reported. It seems that synthesis of this anhydrous oxide from the lower oxides is not feasible at practical oxygen pressures and no thermodynamic data have been selected by LEMIRE et al. (2001).

$NpO_3 \cdot H_2O$(cr): The extensively studied U(VI)-water system has been found to be quite complex. Thus, even with the sparse experimental data available it is evident that different solids can be found in the corresponding Np(VI)-water system. For the purposes of the NEA review (LEMIRE et al. 2001), two different solids with the same apparent stoichiometry have been distinguished as $NpO_3 \cdot H_2O$(cr) and $NpO_2(OH)_2$(cr). Appraising the published solubility studies LEMIRE et al. (2001) accepted a value of

$$\log_{10}{}^*K_{s,0}° \text{ (NpO}_3 \cdot \text{H}_2\text{O, cr, 298.15 K)} \quad = \quad 5.47 \pm 0.40$$

for the reaction

$$\text{NpO}_3 \cdot \text{H}_2\text{O(cr)} + 2\,\text{H}^+ \Leftrightarrow \text{NpO}_2^{2+} + 2\,\text{H}_2\text{O(l)}$$
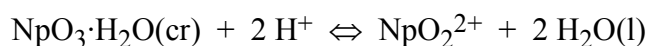
It is likely that one or more of the other solids reported in the Np oxide-hydroxide system (LEMIRE et al. 2001) are similar in stability to this compound. No calorimetric measurements have been carried out for $NpO_3 \cdot H_2O$(cr). However, calorimetric results have been reported for $NpO_2(OH)_2$(cr) leading to an estimate of

$$\Delta_f H_m° \text{ (NpO}_2(\text{OH})_2, \text{ cr, 298.15 K)} \quad = \quad \text{-(1377} \pm 5\text{) kJ} \cdot \text{mol}^{-1}$$

Based on the findings for the corresponding uranium solids, LEMIRE et al. (2001) argue that, regardless of the actual structures of the solids, the value of $\Delta_f G_m°(\text{NpO}_2(\text{OH})_2(\text{cr}))$ can be estimated as identical to that selected for $NpO_3 \cdot H_2O$(cr):

$$\Delta_f G_m° \text{ (NpO}_2(\text{OH})_2,\text{cr, 298.15 K)} \equiv \Delta_f G_m° \text{ (NpO}_3 \cdot \text{H}_2\text{O, cr, 298.15 K)} = \text{-(1239.0} \pm 6.4\text{) kJ} \cdot \text{mol}^{-1}$$

Combining this with the value derived for $\Delta_f H_m°(\text{NpO}_2(\text{OH})_2, \text{ cr, 298.15 K})$ and using $S_m°(\text{Np, cr, }\alpha, 298.15 \text{ K})$ (see 5.10.1) and CODATA values leads to

$$S_m° \text{ (NpO}_2(\text{OH})_2, \text{ cr, 298.15 K)} \quad = \quad (129 \pm 28) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

In addition, a molar heat capacity for this compound has been estimated by LEMIRE et al. (2001).

We decided to include the solubility product of $NpO_3 \cdot H_2O(cr)$ into our database, but to discard the thermochemical data of $NpO_2(OH)_2(cr)$. The reasoning for this decision is as follows. Including data for both solids would mean that we have two solids with exactly the same solubility product at 25°C but enthalpy (and entropy) data solely for $NpO_2(OH)_2(cr)$. Any calculation at temperatures other than 25°C would result in different results for both solids caused by this inconsistency. Including only the values for $NpO_2(OH)_2(cr)$ would mean that we discard a measured solubility product, i.e. that of $NpO_3 \cdot H_2O(cr)$, in favour of an estimate by chemical analogy. Merging the two data sets into one for "hydrated Np(VI) oxide" would blur the differences discussed by LEMIRE et al. (2001). Hence, the question of the temperature dependence of these solubility products is postponed to the next update of our database.

5.10.3.2.3 Neptunium(V) oxides and hydroxides

$Np_2O_5(cr)$: Appraising two experimental studies of the enthalpy of formation for a compound assumed to be $Np_2O_5(cr)$ LEMIRE et al. (2001) selected the value

$$\Delta_f H_m° \text{ (Np}_2\text{O}_5\text{, cr, 298.15 K)} \quad = \quad -(2162.7 \pm 9.5) \text{ kJ} \cdot \text{mol}^{-1}$$

One study reported measurements of the solubility of $Np_2O_5(cr)$ in aqueous solutions as a function of pH. Measurements for pH < 8 can be used to obtain for the reaction

$$\tfrac{1}{2} \text{ Np}_2\text{O}_5\text{(cr)} \ + \ \text{H}^+ \ \Leftrightarrow \ \text{NpO}_2{}^+ \ + \ \tfrac{1}{2} \text{ H}_2\text{O(l)}$$
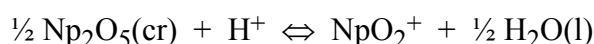
a value of

$$\log_{10}{}^*K_{s,0}° \text{ (Np}_2\text{O}_5\text{, cr, 298.15 K)} \quad = \quad 3.90 \pm 0.02$$

From this value and the selected $\Delta_f H_m°$, $S_m°(\text{Np}_2\text{O}_5\text{, cr, 298.15 K}) = (95 \pm 46)$ J·K^{-1}·mol^{-1} is calculated. LEMIRE et al. (2001) argue that this value is not in agreement with entropy values previously estimated, and that this value is almost certainly too small for well-crystallised bulk $Np_2O_5(cr)$. They accepted a mean value calculated from two previous estimates

$$S_m° \text{ (Np}_2\text{O}_5\text{, cr, 298.15 K)} \quad = \quad (174 \pm 20) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

as a value for "ideal", crystalline $Np_2O_5(cr)$, and hence

$$\Delta_f G_m° \text{ (Np}_2\text{O}_5\text{, cr, 298.15 K)} \quad = \quad -(2031.6 \pm 11.2) \text{ kJ} \cdot \text{mol}^{-1}$$

The heat capacity of $Np_2O_5(cr)$ has been measured from 350 to 750 K by drop calorimetry (LEMIRE et al. 2001). From this data the NEA recommended value is calculated:

$$C_{p,m}° \text{ (Np}_2\text{O}_5\text{, cr, 298.15 K)} \quad = \quad -(128.6 \pm 5.0) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

We decided not to include into our database these thermochemical data of Np_2O_5(cr) consisting of measured $\Delta_f H_m°$ and $C_{p,m}°$ and an estimated $S_m°$ because of their inconsistency with measured solubilities. Note that the resulting $\Delta_f G_m°$(Np_2O_5, cr, 298.15 K) leads to a solubility product

$$\log_{10}{}^*K_{s,0}° \ (Np_2O_5, \ cr, \ 298.15 \ K) \qquad = \qquad 1.9 \pm 1.0$$

which is two orders of magnitude lower than the value derived from solubility measurements on Np_2O_5(cr) (which ultimately have been discarded by LEMIRE et al. (2001) due to entropy arguments, see above). In addition, this value is three orders of magnitude lower than the recommended value for NpO_2OH(am,aged) (see below). Hence, including the recommended Np_2O_5(cr) data into our database would invariably lead to unrealistic low Np(V) concentrations in any model calculation, orders of magnitude lower than any measured value.

$NpO_2(OH)$(am): Experimental values for the solubility of $NpO_2(OH)$(am) as a function of pH are in reasonable agreement up to pH values near 10. Above that pH even trace quantities of dissolved CO_2(g) will react to form carbonato complexes and increase the solubility of the solid, and, in the absence of CO_2, hydrolysis reactions may be important. Hence, at high pH the solubility results would be expected to show more scatter, and this is indeed what has been found (LEMIRE et al. 2001). In view of the scatter in the solubilities, ill-defined ageing effects on the solid and the discrepancies in the reported hydrolysis constants for Np(V) (see 5.10.3.1.3) that preclude selection of solubility products and hydrolysis constants from independent experimental data, it is difficult to select an accurate value for the solubility product of $NpO_2(OH)$(am)

$$NpO_2(OH)(am) \ + \ H^+ \ \Leftrightarrow \ NpO_2^+ \ + \ H_2O(l)$$
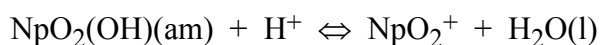
LEMIRE et al. (2001) accepted that the nature of the precipitated solid changes with time and with the medium with which it is brought to equilibrium. For "freshly precipitated" (green) material in a low ionic strength medium

$$\log_{10}{}^*K_{s,0}° \ (NpO_2(OH), \ am, \ "fresh", \ 298.15 \ K) \quad = \quad 5.3 \pm 0.2$$

has been selected. The "aged" (white) solid may be a slightly more ripened form of the hydroxide, or it may be a material with a surface layer of Np_2O_5, or even incorporating alkali metals. A value

$$\log_{10}{}^*K_{s,0}° \ (NpO_2(OH), \ am, \ "aged", \ 298.15 \ K) \quad = \quad 4.7 \pm 0.5$$

has been accepted by LEMIRE et al. (2001) for the "aged" solid, and the uncertainty has been assigned to reflect the uncertainty in the nature of the compound.

The enthalpy of solution of amorphous $NpO_2(OH)$ has been measured by two different groups. As it is not clear how ageing of this compound may influence the measured enthalpy of solution,

LEMIRE et al. (2001) accepted an unweighted average of the results from the two sets of measurements as representative for both, "fresh" and "aged" $NpO_2(OH)$:

$$\Delta_r H_m° \text{ (NpO}_2\text{(OH), am, 298.15 K)} = \text{-(41.1} \pm 3.0) \text{ kJ} \cdot \text{mol}^{-1}$$

In the absence of any experimental data, LEMIRE et al. (2001) recommend an estimated value for the heat capacity of $NpO_2(OH)$(am). However, we prefer not to include this estimate into our database.

5.10.3.2.4 Neptunium(IV) oxides and hydroxides

NpO_2(cr): The enthalpy of formation of NpO_2(cr) has been determined from the heat of combustion of α-Np(cr) as

$$\Delta_f H_m° \text{ (NpO}_2\text{, cr, 298.15 K)} = \text{-(1074.0} \pm 2.5) \text{ kJ} \cdot \text{mol}^{-1}$$

and, derived from low temperature heat capacity measurements, values for the entropy and heat capacity have been recommended by LEMIRE et al. (2001)

$$S_m° \text{ (NpO}_2\text{, cr, 298.15 K)} = \text{(80.3} \pm 0.4) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{p,m}° \text{ (NpO}_2\text{, cr, 298.15 K)} = \text{(66.2} \pm 0.5) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

These thermochemical data result in

$$\Delta_f G_m° \text{ (NpO}_2\text{, cr, 298.15 K)} = \text{-(1021.7} \pm 2.5) \text{ kJ} \cdot \text{mol}^{-1}$$

which in turn can be interpreted as a solubility product of the reaction

$$NpO_2\text{(cr)} + 4\,H^+ \Leftrightarrow Np^{4+} + 2\,H_2O\text{(l)}$$
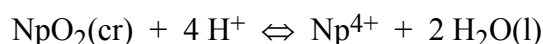
$$\log_{10}{}^*K_{s,0}° \text{ (NpO}_2\text{, cr, 298.15 K)} = \text{-9.8} \pm 0.4$$

This value is more than 10 (!) orders of magnitude lower than the solubility product selected for hydrous Np(IV) oxide (see following section). Similar difficulties have been encountered in the U(IV) - water system comparing the relative stabilities of crystalline UO_2 and "hydrous UO_2" predicted from thermochemical data and solubility studies (see sections 3.2 and 5.23). We decided not to include the thermochemical data of NpO_2(cr) into our database, as any speciation calculation using these data would result in Np concentrations orders of magnitude below any measured value.

NpO_2(hyd,am): Based on a solubility study of $NpO_2 \cdot xH_2O$(am) LEMIRE et al. (2001) recalculated and recommended a solubility product

$$NpO_2\text{(hyd, am)} + 4\,H^+ \Leftrightarrow Np^{4+} + 2\,H_2O\text{(l)}$$
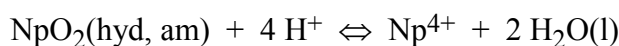
$$\log_{10}{}^{*}K_{s,0}° \text{ (NpO}_2\text{, hyd, am, 298.15 K)} \quad = \quad 1.53 \pm 1.00$$

This "best" value found for ${}^{*}K_{s,0}°$ is greater than the value suggested for the corresponding uranium compound ($\log_{10}{}^{*}K_{s,0}° = 0 \pm 2$) (see 5.23), and the value suggested for the corresponding plutonium solid is smaller ($\log_{10}{}^{*}K_{s,0}° = -2 \pm 1$). These differences are probably more a reflection of uncertainties related to the ill-defined nature of the solids than an indication of large differences in behaviour between the three actinide systems.

5.10.3.2.5 Neptunium(III) oxides and hydroxides

No chemical thermodynamic quantities have been selected by LEMIRE et al. (2001) for $Np_2O_3(s)$. No thermodynamic data for $Np(OH)_3(s)$ have been reported.

5.10.4 Halogen compounds and complexes

5.10.4.1 Neptunium halide compounds

LEMIRE et al. (2001) selected thermochemical data for the following solid halide compounds:

Solid fluorides: $NpF_3(cr)$, $NpF_4(cr)$, $NpF_5(cr)$, $NpF_6(cr)$, $NpO_2F_2(cr)$, $Na_3NpF_8(cr)$

Solid chlorides: $NpCl_3(cr)$, $NpCl_4(cr)$, $NpOCl_2(cr)$, $Cs_2NpCl_6(cr)$, $Cs_3NpO_2Cl_4(cr)$, $Cs_2NpO_2Cl_4(cr)$, $Cs_2NaNpCl_6(cr)$

Solid bromides: $NpBr_3(cr)$, $NpBr_4(cr)$, $NpOBr_2(cr)$, $Cs_2NpBr_6(cr)$

Solid iodide: $NpI_3(cr)$

As the formation of these solids in aqueous environmental systems is doubtful and none of the data were gathered from solubility experiments, they are not included in our database.

LEMIRE et al. (2001) also selected thermochemical data for the following gaseous halides:

Gaseous fluorides: $NpF(g)$, $NpF_2(g)$, $NpF_3(g)$, $NpF_4(g)$, $NpF_6(g)$

Gaseous chlorides: $NpCl_3(g)$, $NpCl_4(g)$

These gases are hardly relevant for aqueous environmental systems and are therefore excluded from our database update.

5.10.4.2 Aqueous neptunium fluoride complexes

5.10.4.2.1 Aqueous Np(III) fluorides

No fluoride complexes of Np^{3+} have been identified.

5.10.4.2.2   Aqueous Np(IV) fluorides

All experiments were carried out in strongly acidic solutions, and thus the relevant equilibrium is

$$Np^{4+} + n\,HF(aq) \Leftrightarrow NpF_n^{(4-n)} + n\,H^+$$
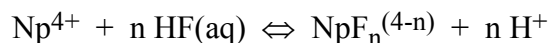
The values for $\log_{10}{}^*\beta_1$ are in good agreement and LEMIRE et al. (2001) could do a simultaneous determination of $\log_{10}{}^*\beta_1° = 5.78 \pm 0.14$ and $\Delta\varepsilon = -(0.12 \pm 0.04)\ kg \cdot mol^{-1}$ by weighted linear regression of the experimental data. The value of $\log_{10}{}^*\beta_2° = 9.34 \pm 0.29$ has been obtained by extrapolating the reported constants to zero ionic strength using $\Delta\varepsilon = -(0.18 \pm 0.15)\ kg \cdot mol^{-1}$ from the corresponding U(IV) fluoride system, and taking the weighted average of the results. Both constants have been converted using the NEA recommended protonation constant of fluoride (LEMIRE et al. 2001) to conform to the equilibrium

$$Np^{4+} + n\,F^- \Leftrightarrow NpF_n^{(4-n)}$$

$$\log_{10}\beta_1°\ (n = 1, 298.15\ K) \quad = \quad 8.96 \pm 0.14$$

$$\log_{10}\beta_2°\ (n = 2, 298.15\ K) \quad = \quad 15.7 \pm 0.3$$
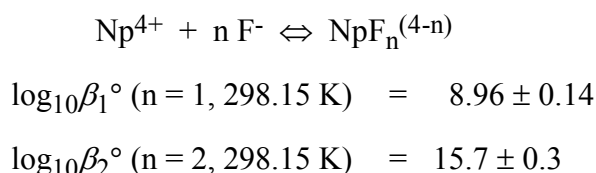
From equilibrium constants measured at 10, 25 and 40°C it is possible to extract an enthalpy of reaction for the 1:1 complex:

$$\Delta_r H_m°\ (n = 1, 298.15\ K) \quad = \quad (1.5 \pm 2.0)\ kJ \cdot mol^{-1}$$

Data for the 1:3 and 1:4 complexes were published by two groups. However, the values differ considerably, even after correction to zero ionic strength using SIT interaction parameters from the corresponding U(IV) fluoride system. Hence, LEMIRE et al. (2001) did not consider it possible to make any selection for the formation constants of NpF_3^+ and $NpF_4(aq)$.

5.10.4.2.3   Aqueous Np(V) fluorides

Fluoride complexation has been studied in near-neutral solutions by several authors using spectrophotometry, solvent extraction and potentiometric techniques. Although the results are not entirely consistent, the disagreement is not serious and LEMIRE et al. (2001) selected a weighted average

$$NpO_2^+ + n\,F^- \Leftrightarrow NpO_2F_n^{(1-n)}$$

$$\log_{10}\beta_1°\ (n = 1, 298.15\ K) \quad = \quad 1.2 \pm 0.3$$
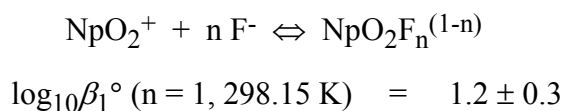
Only one study reported a value for the 1:2 complex, but this value has not been selected by LEMIRE et al. (2001) because this value would be inconsistent with the selected value of $\log_{10}\beta_1°$.

5.10.4.2.4   Aqueous Np(VI) fluorides

The investigation of fluoride complexation of Np(VI) is complicated by the fact that NpO_2^{2+} has oxidising properties, and that reduction to Np(IV) is favoured in acidic medium and in the presence of fluoride ions. Appraising all available data by weighting them according to the reliability of the experimental work, LEMIRE et al. (2001) extrapolated the experimental data using SIT interaction coefficients from the corresponding U(VI) fluoride equilibria and recommended the following weighted averages:

$$NpO_2^{2+} + n\,F^- \Leftrightarrow NpO_2F_n^{(2-n)}$$

$$\log_{10}\beta_1° \text{ (n = 1, 298.15 K)} \quad = \quad 4.57 \pm 0.07$$

$$\log_{10}\beta_2° \text{ (n = 2, 298.15 K)} \quad = \quad 7.60 \pm 0.08$$
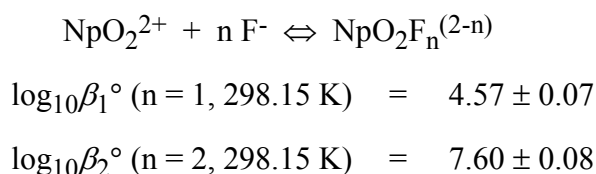
Some authors have reported formation constants for the 1:3 complex, $NpO_2F_3^-$, but the results are conflicting. Additional experimental investigations will be necessary to obtain a consistent picture on the formation of $NpO_2F_3^-$. No value has been selected by LEMIRE et al. (2001).

5.10.4.3   Aqueous neptunium chloride complexes

5.10.4.3.1   Aqueous Np(III) chlorides

There is only one quantitative information on chloride complexation of Np^{3+}. However, due to the very high and varying ionic strength (LiCl) used in this study LEMIRE et al. (2001) could not select any value for zero ionic strength.

5.10.4.3.2   Aqueous Np(IV) chlorides

The selected value for the formation constant of

$$Np^{4+} + Cl^- \Leftrightarrow NpCl^{3+}$$
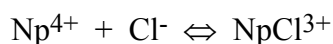
was calculated from a weighted SIT extrapolation of data obtained by three experimental studies with $\Delta\varepsilon = -(0.15 \pm 0.18)\ kg \cdot mol^{-1}$

$$\log_{10}\beta_1° \text{ (298.15 K)} \quad = \quad 1.5 \pm 0.3$$

The 1:2 complex, $NpCl_2^{2+}$, and the 1:3 complex, $NpCl_3^+$, if they exist, are very week. The reported constants might well be artefacts due to medium changes, and LEMIRE et al. (2001) did not select any thermodynamic data for these complexes.

5.10.4.3.3   Aqueous Np(V) chlorides

Some authors have published formation constants for $NpO_2Cl(aq)$ and $NpO_2Cl_2^-$ at ionic strengths from 2 to 5 M. The stability of these complexes is very low and some results can equally well interpreted as ionic strength effects. LEMIRE et al. (2001) concluded that it would be highly speculative to make a selection of thermodynamic data on the basis of the existing data.

5.10.4.3.4   Aqueous Np(VI) chlorides

Experimental data for the Np(VI) chloride system have been reported, but a statistical treatment of these data seems difficult. LEMIRE et al. (2001) therefore adopted the SIT interaction coefficient evaluated for the corresponding Pu(VI) system and increased its uncertainty by 0.05, i.e. $\Delta\varepsilon = -(0.08 \pm 0.13)$ kg $\cdot$ mol^{-1}, to extrapolate the experimental data to zero ionic strength, and selected the weighted average of the resulting values

$$NpO_2^{2+} + Cl^- \Leftrightarrow NpO_2Cl^+$$

$$\log_{10}\beta_1^\circ \ (n = 1, 298.15 \ K) \quad = \quad 0.40 \pm 0.17$$
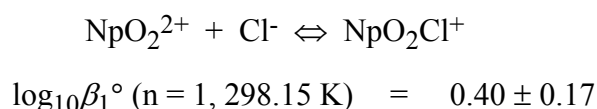
Two publications reported (very small) constants for the formation of the 1:2 complex. The NEA reviewers concluded that these small values are likely due to inter-ionic interactions, rather than to the formation of $NpO_2Cl_2(aq)$, and did not select any value.

5.10.4.4   Aqueous neptunium bromide complexes

No thermodynamic data for aqueous neptunium bromide complexes have been selected by LEMIRE et al. (2001).

5.10.4.5   Aqueous neptunium iodide complexes

LEMIRE et al. (2001) selected equilibrium constants for the generally rather weak complexes NpI^{3+}, $NpO_2IO_3(aq)$ and $NpO_2IO_3^+$. However, iodine complexes of neptunium are not thought to be of relevance for geochemical modelling and are not included in our database.

5.10.5   Chalcogen compounds and complexes

There are no experimental studies available involving the thermodynamic properties for neptunium chalcogenide solids, such as sulphides, sulphites, sulphates, selenides or tellurides.

Likewise, no experimental data are available for aqueous complexes of neptunium sulphides, selenides or tellurides. LEMIRE et al. (2001) discuss reports of aqueous Np(V) sulphite complex formation but they cannot recommend any thermodynamic data.

5.10.5.1   Aqueous Np(VI) sulphates

Appraising four reliable quantitative studies available in the literature on the Np(VI) sulphate system, LEMIRE et al. (2001) recommended equilibrium constants and reaction enthalpies for:

$$NpO_2^{2+} + n\ SO_4^{2-} \Leftrightarrow NpO_2(SO_4)_n^{(2-2n)}$$
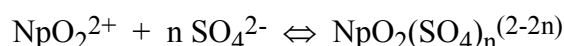
$$\log_{10}\beta_1^\circ\ (n = 1, 298.15\ K)\ =\ 3.28 \pm 0.06$$

$$\log_{10}\beta_2^\circ\ (n = 2, 298.15\ K)\ =\ 4.70 \pm 0.10$$

$$\Delta_r H_m^\circ\ (n = 1, 298.15\ K)\ =\ (16.7 \pm 0.5)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m^\circ\ (n = 2, 298.15\ K)\ =\ (26.0 \pm 1.2)\ kJ \cdot mol^{-1}$$

5.10.5.2   Aqueous Np(V) sulphates

Five experimental studies describing the Np(V) sulphate complexes have been reported. In all cases only one complex was observed:

$$NpO_2^+ + SO_4^{2-} \Leftrightarrow NpO_2SO_4^-$$
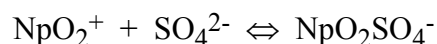
On the basis of the most reliable data at 25°C LEMIRE et al. (2001) recommended

$$\log_{10}\beta_1^\circ\ (298.15\ K)\ =\ 0.44 \pm 0.27$$

The enthalpy of this reaction has been determined from the measured temperature variation at 5, 25 and 40°C

$$\Delta_r H_m^\circ\ (298.15\ K)\ =\ (23.2 \pm 7.2)\ kJ \cdot mol^{-1}$$

5.10.5.3   Aqueous Np(IV) sulphates

There are seven reliable studies describing the Np(IV) sulphate complexes. Because of concern about interference due to hydrolysis, all Np(IV) experiments were performed in strong acid medium. The results are therefore interpreted to describe the reactions

$$Np^{4+} + q\ HSO_4^- \Leftrightarrow Np(SO_4)_q^{(4-2q)} + q\ H^+$$

Using the SIT extrapolation procedure, with $\Delta\varepsilon(q = 1) = -(0.19 \pm 0.06)$ kg $\cdot$ mol^{-1} and $\Delta\varepsilon(q = 2) = -(0.29 \pm 0.11)$ kg $\cdot$ mol^{-1}, the recommended values were found to be

$$\log_{10}\beta_1° \, (q = 1, \, 298.15 \text{ K}) \; = \; 4.87 \pm 0.15$$

$$\log_{10}\beta_2° \, (q = 2, \, 298.15 \text{ K}) \; = \; 7.09 \pm 0.25$$

The enthalpy of this reaction has been determined from the measured temperature variation

$$\Delta_r H_m° \, (q = 1, \, 298.15 \text{ K}) \; = \; (7.38 \pm 8.8) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m° \, (q = 2, \, 298.15 \text{ K}) \; = \; (10.5 \pm 3.6) \text{ kJ} \cdot \text{mol}^{-1}$$

For our database update, these complex formation reactions were rewritten in terms of SO_4^{2-} instead of HSO_4^- using the NEA recommended protonation equilibrium constant (1.98 ± 0.05) and enthalpy (22.44 ± 1.1) kJ $\cdot$ mol^{-1}:

$$Np^{4+} \; + \; n \, SO_4^{2-} \; \Leftrightarrow \; Np(SO_4)_n^{(4-2q)}$$
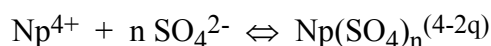
$$\log_{10}\beta_1° \, (n = 1, \, 298.15 \text{ K}) \; = \; 6.85 \pm 0.16$$

$$\log_{10}\beta_2° \, (n = 2, \, 298.15 \text{ K}) \; = \; 11.15 \pm 0.27$$

$$\Delta_r H_m° \, (n = 1, \, 298.15 \text{ K}) \; = \; (29.8 \pm 8.9) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m° \, (n = 2, \, 298.15 \text{ K}) \; = \; (55.4 \pm 3.9) \text{ kJ} \cdot \text{mol}^{-1}$$

5.10.5.4   Aqueous Np(III) sulphates

No experimental evidence for the stability of Np(III) sulphate complexes was found by LEMIRE et al. (2001).

5.10.6   Group 15 compounds and complexes

5.10.6.1   Nitrogen compounds and complexes

Np nitrides: Thermochemical data for NpN(cr) have been selected by LEMIRE et al. (2001). However, this phase is hardly relevant to environmental systems. It is not included in our database.

Np azide complexes: No data have been selected by LEMIRE et al. (2001) for Np azide complexes.

Np nitrite complexes: There is only one publication dealing with Np(V) nitrite complex formation. However, LEMIRE et al. (2001) concluded that in view of the paucity of the available data no selection can be made.

Np nitrate solids: The solubility of $NpO_2(NO_3)_2 \cdot 6H_2O(s)$ in water has been measured. From these measurements, and activities from the corresponding uranium system, $\Delta_r G_m°$ has been calculated. This value has been used in determining the value of $S_m°(NpO_2^{2+}, aq, 298.15\ K)$ (see 5.10.2.2). However, due to its high solubility (saturation molality of 2.95 ± 0.26) this salt is not included in our database. No thermodynamic data have been reported for other Np nitrate solids.

Aqueous Np(III) nitrates: No Np^{3+} nitrate complexes have been identified.

Aqueous Np(IV) nitrates: Complex formation in Np(IV) nitrate systems has been studied by several investigators. However, all inner sphere complexes beyond the first are extremely weak even at moderate nitrate concentrations, and calculations have shown that effects of higher complexes can often be accounted for by considering activity coefficient changes in sequential substitution for large amounts of the medium ions (e.g. perchlorate) by nitrate ions, and assuming only the formation of the first complex up to 2M nitrate. Hence, LEMIRE et al. (2001) selected only an equilibrium constant for the $NpNO_3^{3+}$ species according to

$$Np^{4+} + NO_3^- \Leftrightarrow NpNO_3^{3+}$$

$$\log_{10}\beta_1° \ (298.15\ K) \ = \ 1.90 \pm 0.15$$
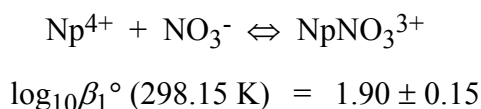
Aqueous Np(V) nitrates: Cation exchange and distribution studies have been used to obtain quantitative data on the stability of Np(V) nitrate complexes. However, the observed experimental effects can be explained solely as changes of activity coefficients. This together with spectrophotometric evidence on the lack of changes in spectra at nitrate concentrations up to 4M confirms the absence of inner sphere Np(V) nitrate complexes.

Aqueous Np(VI) nitrates: There is no direct experimental (e.g. spectroscopic) evidence for inner sphere Np(VI) nitrate complexation reported in the literature. LEMIRE et al. (2001) concluded that Np(VI) nitrate complexes are weak, as it is also the case for the other actinides. This makes it difficult to distinguish between complex formation and changes in the activity coefficients of the species studied. They state "if a β_1 value for the formation of $NpO_2NO_3^+$ is required, the use of the first association constant recommended for the analogous uranium system will probably not cause too large an error".

5.10.6.2 Phosphorous compounds and complexes

Aqueous Np(III) phosphates: There are no experimental data for the Np(III) phosphate system. Estimated constants have been rejected by LEMIRE et al. (2001) because they are based on a study of the Pu(III) phosphate system which also has been rejected by LEMIRE et al. (2001).

Aqueous Np(IV) phosphates: There are no published experimental data for the Np(IV) phosphate system. Estimated constants have been rejected by LEMIRE et al. (2001) because they are based on a study of the Pu(IV) phosphate system which also has been rejected by LEMIRE et al. (2001).

Aqueous Np(V) phosphates: There have been several studies of the aqueous Np(V) phosphate system using spectrophotometric, ion exchange or co-precipitation methods, and the results are in reasonable agreement. The weighted average of three values extrapolated to zero ionic strength has been selected by LEMIRE et al. (2001):

$$NpO_2^+ + HPO_4^{2-} \Leftrightarrow NpO_2HPO_4^-$$

$$\log_{10}\beta_1°\,(298.15\ K)\ =\ 2.95 \pm 0.10$$
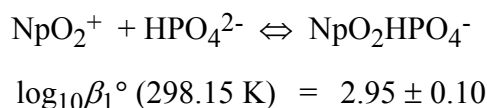
There are conflicting hypotheses as to the stoichiometry of other Np(V) phosphate complexes at high pH. Therefore, none of these constants corresponding to the formation of the species $NpO_2H_2PO_4(aq)$, $NpO_2(H_2PO_4)_2^-$, $NpO_2(HPO_4)_2^{3-}$ and $NpO_2PO_4^{2-}$ have been selected.

Aqueous Np(VI) phosphates: For the Np(VI) phosphate system there is only one study, apparently with some uncertainties as to the stoichiometry of the species and there is not enough information to permit recalculations. The values reported in this work have been selected by LEMIRE et al. (2001) with substantially increased uncertainty limits:

$$NpO_2^{2+} + H_2PO_4^- \Leftrightarrow NpO_2H_2PO_4^+$$

$$\log_{10}\beta_1°\,(298.15\ K)\ =\ 3.32 \pm 0.50$$

$$NpO_2^{2+} + HPO_4^{2-} \Leftrightarrow NpO_2HPO_4(aq)$$

$$\log_{10}\beta_1°\,(298.15\ K)\ =\ 6.2 \pm 0.7$$

$$NpO_2^{2+} + 2\,HPO_4^{2-} \Leftrightarrow NpO_2(HPO_4)_2^{2-}$$

$$\log_{10}\beta_2°\,(298.15\ K)\ =\ 9.5 \pm 1.0$$
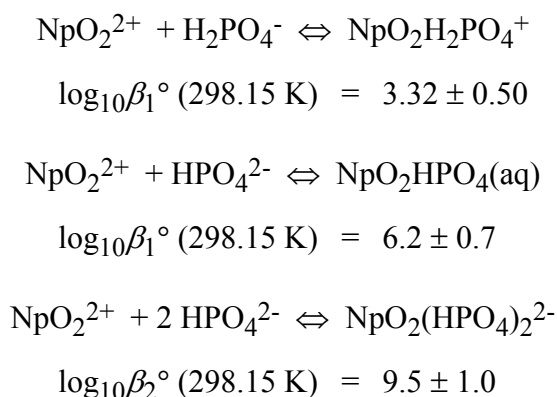
5.10.7   Group 14 compounds and complexes

5.10.7.1   Neptunium carbides

LEMIRE et al. (2001) selected thermochemical data for $NpC_{0.91}(cr)$ and $Np_2C_3(cr)$. However, carbides are not relevant under environmental conditions and are not included in our database.

5.10.7.2 Neptunium carbonates

5.10.7.2.1 Aqueous neptunium carbonates

Neptunium is the most stable actinide element in the +V oxidation state. Hence there are more published works on complexes of Np(V) than on the complexes of the other elements of the actinide(V) series, and the stoichiometries of these actinide(V) species were usually determined from experimental information concerning Np(V). Conversely, Np(IV) and Np(VI) species are expected to be the same as those reasonably well-documented for uranium. There is usually not enough information to determine the stoichiometry and to propose thermodynamic data for all these expected Np(IV) and Np(VI) species. Therefore, the NEA review on neptunium has extensively used the analogy with the uranium system (for SIT coefficients of anions with charge -1 to -3, and for stoichiometry) and prefers proposing values with large uncertainties or even maximum formation constants, rather than proposing no value at all. Values could have been proposed for Np(III) species in the same way, by analogy with values for Am(III) species; but usually Np(III) reduces water under conditions where Np(III) carbonate complexes are expected to form.

5.10.7.2.1.1 Np(VI) carbonate complexes

There is satisfactory experimental information available for only two Np(VI) complexes in aqueous carbonate / bicarbonate media, namely for the limiting complex $NpO_2(CO_3)_3^{4-}$ and the trinuclear species $(NpO_2)_3(CO_3)_6^{6-}$, formed by polymerisation of the limiting complex.

This is a sparse set when compared with the species and thermodynamic data proposed for uranium(VI) carbonate and mixed carbonate-hydroxide complexes, $UO_2CO_3(aq)$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, $(UO_2)_3(CO_3)_6^{6-}$, $(UO_2)_2CO_3(OH)_3^-$, $(UO_2)_3O(OH)_2(HCO_3)^+$, and the solids $UO_2CO_3(s)$, $Na_4UO_2(CO_3)_3(s)$.

Using the complexes $NpO_2(CO_3)_3^{4-}$ and $(NpO_2)_3(CO_3)_6^{6-}$ as a starting point, several other published studies have been interpreted or reinterpreted by LEMIRE et al. (2001) in order to derive solubility products for $K_4UO_2(CO_3)_3(s)$, $(NH_4)_4UO_2(CO_3)_3(s)$ and $NpO_2CO_3(s)$, and formation constants of $NpO_2(CO_3)_2^{2-}$, $NpO_2CO_3(aq)$ and $(NpO_2)_2CO_3(OH)_3^-$.

The Np(VI) carbonate limiting complex: Due to the lack of other reliable data, LEMIRE et al. (2001) only used potential measurements of the redox equilibrium

$$NpO_2(CO_3)_3^{4-} + e^- \Leftrightarrow NpO_2(CO_3)_3^{5-}.$$
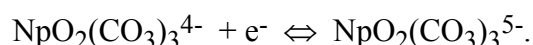
The value selected from linear regression of experimental data is

$$E° \ (298.15 \ \text{K}) \ = \ (0.338 \pm 0.006) \ \text{V}$$

This $E°$ value was combined with the standard potential for the NpO_2^{2+}/NpO_2^+ redox couple (see 5.10.2.2) and the formation constant for the species $NpO_2(CO_3)_3^{5-}$ (see below) to calculate for

$$NpO_2^{2+} \ + \ 3 \ CO_3^{2-} \ \Leftrightarrow \ NpO_2(CO_3)_3^{4-}$$

$$\log_{10}\beta_3° \ (298.15 \ \text{K}) \ = \ 19.37 \pm 0.19$$
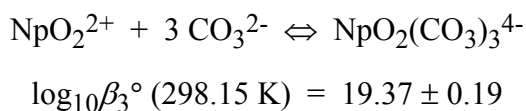
Appraising all available data, the temperature dependence of this reaction is best described by

$$\Delta_r H_m° \ (298.15 \ \text{K}) \ = \ -(41.9 \pm 4.1) \ \text{kJ} \cdot \text{mol}^{-1}$$

Other mononuclear Np(VI) carbonate complexes: There is no reliable published work proposing formation constants for the mononuclear Np(VI) carbonate complexes other than $NpO_2(CO_3)_3^{4-}$. Recently proposed values for the formation constants of $NpO_2CO_3(aq)$ and $NpO_2(CO_3)_2^{2-}$ are based on solubility measurements of $NpO_2CO_3(s)$ in 3 M $NaClO_4$. This work has been accepted by LEMIRE et al. (2001) even though the values were determined from an overly sparse set of solubility measurements. The extrapolation to zero ionic strength has been done using SIT coefficients of the corresponding U(VI) system and resulted in

$$NpO_2^{2+} \ + \ 2 \ CO_3^{2-} \ \Leftrightarrow \ NpO_2(CO_3)_2^{2-}$$

$$\log_{10}\beta_2° \ (298.15 \ \text{K}) \ = \ 16.52 \pm 0.73$$

$$NpO_2^{2+} \ + \ CO_3^{2-} \ \Leftrightarrow \ NpO_2CO_3(aq)$$

$$\log_{10}\beta_1° \ (298.15 \ \text{K}) \ = \ 9.32 \pm 0.61$$
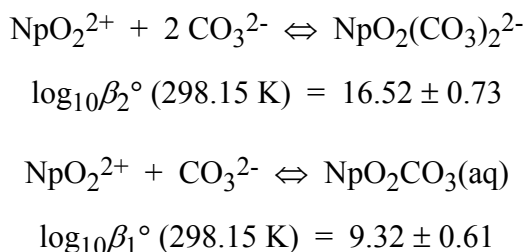
The carbonate trinuclear Np(VI) complex: The polymerisation reaction

$$3 \ NpO_2(CO_3)_3^{4-} \ \Leftrightarrow \ 3 \ CO_3^{2-} \ + (NpO_2)_3(CO_3)_6^{6-}$$

is well established, but there are still only two values (at 1 and 3 M $NaClO_4$) for the extrapolation to zero ionic strength. Analogy with uranium should not be used for ionic strength corrections of this type of equilibrium because complexes with large negative charges (-5 or -6) often have been found to have unusual SIT coefficients, probably due to ion pairing. Rather than not selecting any value for this equilibrium, a value having a large uncertainty is calculated using the only two available data

$$\log_{10}K° \ (298.15 \ \text{K}) \ = \ -8.27 \pm 1.45$$

Using this value and the above selected $\log_{10}\beta_3°$, the equilibrium constant

$$3 \, NpO_2^{2+} \, + \, 6 \, CO_3^{2-} \, \Leftrightarrow \, (NpO_2)_3(CO_3)_6^{6-}$$
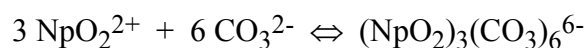
$$\log_{10}\beta_{6,3}° \, (298.15 \, K) \, = \, 49.84 \pm 1.56$$

is selected.

Mixed hydroxide-carbonate complexes of Np(VI): There is evidence from one publication that mixed hydroxide-carbonate complexes can form. LEMIRE et al. (2001) accepted a value at 1M $NaClO_4$ for the reaction

$$2 \, NpO_2(CO_3)_3^{4-} \, + \, 7 \, H^+ \, \Leftrightarrow \, (NpO_2)_2CO_3(OH)_3^- \, + \, 5 \, CO_2(g) \, + \, 7 \, H_2O(l)$$
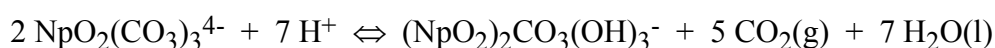
$$\log_{10}K \, (1M \, NaClO_4, \, 298.15 \, K) \, = \, 41.75 \pm 1.46$$

Using data selected in LEMIRE et al. (2001) and SIT coefficients of the corresponding uranium system, this corresponds to

$$2 \, NpO_2^{2+} \, + \, CO_3^{2-} \, + \, 3 \, H_2O(l) \Leftrightarrow (NpO_2)_2CO_3(OH)_3^- \, + \, 3 \, H^+$$
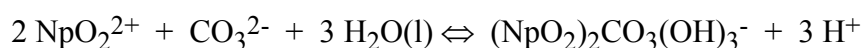
$$\log_{10}K° \, (298.15 \, K) \, = \, -2.87 \pm 1.64$$

Mixed actinide carbonate complexes: A re-evaluation of data discussed earlier in GRENTHE et al. (1992) considering the selected Np constants resulted in

$$2 \, UO_2^{2+} \, + \, NpO_2^{2+} \, + \, 6 \, CO_3^{2-} \, \Leftrightarrow \, (UO_2)_2NpO_2(CO_3)_6^{6-}$$
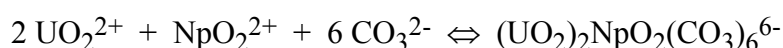
$$\log_{10}K° \, (298.15 \, K) \, = \, 53.59 \pm 2.70$$

5.10.7.2.1.2   Np(V) carbonate complexes

Appraising all available information LEMIRE et al. (2001) concluded that, aside from the mixed hydroxide-carbonate complex(es), formed only in concentrated hydroxide-carbonate media, the Np(V) complexes in carbonic acid / bicarbonate / carbonate aqueous solutions are clearly mononuclear, and contain only carbonate ligands ($NpO_2(CO_3)_n^{(1-2n)}$, n = 1,2,3).

Mononuclear Np(V) carbonate complexes: Three types of experimental measurements, liquid-liquid extraction, spectrophotometry and solubility, have been used by LEMIRE et al. (2001) to derive constants for Np(V) carbonate complexes. After a very detailed discussion, LEMIRE et al. (2001) concluded that, despite the extensive work on these systems, there is still some doubt about the value to be selected for the formation constant of $NpO_2CO_3^-$, and especially the value of the SIT interaction coefficient for this species. These uncertainties then propagate into uncertainties of the cumulative formation constants and SIT coefficients of the other carbonate species.

Appraising different data sets from solubility studies and spectrophotometric determinations, but not considering liquid-liquid extraction data, LEMIRE et al. (2001) selected the results from unweighted linear regressions of the experimental data for the reactions

$$NpO_2^+ + CO_3^{2-} \Leftrightarrow NpO_2CO_3^-$$

$$\log_{10}\beta_1° \text{ (298.15 K)} = 4.96 \pm 0.06$$

$$NpO_2CO_3^- + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_2^{3-}$$

$$\log_{10}K_2° \text{ (298.15 K)} = 1.57 \pm 0.08$$

$$NpO_2(CO_3)_2^{3-} + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-}$$
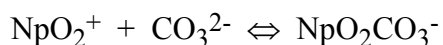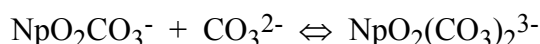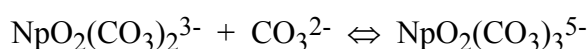
$$\log_{10}K_3° \text{ (298.15 K)} = -1.03 \pm 0.11$$

with $\Delta\varepsilon = -(0.35 \pm 0.14)$, $\Delta\varepsilon = -(0.07 \pm 0.05)$ and $\Delta\varepsilon = -(0.12 \pm 0.06)$ kg · mol^{-1}, respectively. From the selected $\beta_1°$, $K_2°$ and $K_3°$ values the cumulative stability constants are calculated

$$\log_{10}\beta_2° \text{ (298.15 K)} = 6.53 \pm 0.10$$

$$\log_{10}\beta_3° \text{ (298.15 K)} = 5.50 \pm 0.15$$

LEMIRE et al. (2001) concluded that no reliable experimental data are available concerning the temperature dependence of Np(V) carbonate complexation. However, from $\Delta_r H_m°(NpO_2(CO_3)_3^{4-} + e^- \Leftrightarrow NpO_2(CO_3)_3^{5-}) = -88.8 \pm 2.9$ kJ·mol^{-1}, $\Delta_r H_m°(NpO_2^{2+} + 3CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{4-}) = -41.9 \pm 4.1$ kJ·mol^{-1} and $\Delta_r H_m°(NpO_2^{2+} + ½H_2(g) \Leftrightarrow NpO_2^+ + H^+) = -117.4 \pm 0.6$ kJ·mol^{-1}, LEMIRE et al. (2001) calculated the enthalpy for the reaction

$$NpO_2^+ + 3\,CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-}$$
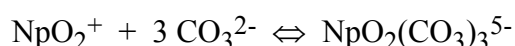
$$\Delta_r H_m° \text{ (298.15 K)} = -(13.3 \pm 5.1) \text{ kJ · mol}^{-1}.$$

Using $\Delta_f H_m°(NpO_2^+) = -(978.2 \pm 4.6)$ kJ·mol^{-1} (see 5.10.2.3) and $\Delta_f H_m°(CO_3^{2-}) = -(675.23 \pm 0.25)$ kJ·mol^{-1}, $\Delta_f H_m°(NpO_2(CO_3)_3^{5-}$, aq, 298.15 K$) = -(3017.12 \pm 6.89)$ kJ·mol^{-1} is calculated (and used in 5.10.7.2.1.3 for further calculations).

Mixed hydroxide-carbonate complexes of Np(V): There is spectrophotometric evidence for the formation of mixed hydroxide-carbonate complexes at high pH, possibly $NpO_2(CO_3)_2OH^{4-}$ and/or $NpO_2CO_3(OH)_2^{3-}$. Scrutinising all the published data LEMIRE et al. (2001) selected for the reaction

$$NpO_2(CO_3)_3^{5-} + OH^- \Leftrightarrow NpO_2(CO_3)_2OH^{4-} + CO_3^{2-}$$

$$\log_{10}K° \text{ (298.15 K)} = 3.20 \pm 1.16.$$

Using $\log_{10}\beta_3°(NpO_2^+ + 3CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-}) = 5.50 \pm 0.15$ selected by LEMIRE et al. (2001), we recalculate this according to the reaction

$$NpO_2^+ + 2\,CO_3^{2-} + H_2O(l) \Leftrightarrow NpO_2(CO_3)_2OH^{4-} + H^+$$

$$\log_{10}{}^*K° \,(298.15\ K) \;=\; -5.30 \pm 1.17.$$
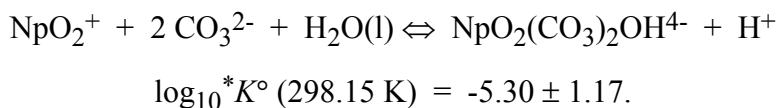
5.10.7.2.1.3   Np(IV) carbonate complexes

The model assumed by LEMIRE et al. (2001), namely that the species $Np(OH)_4(aq)$, $Np(CO_3)_5^{6-}$ and $Np(CO_3)_4^{4-}$ are probably formed in concentrated carbonate / bicarbonate media, seems to be sufficient to explain all published data. There are insufficient data to allow the selection of formation constant values for other complexes, but that does not mean they do not exist.

Sections 12.1.2.1.4.a and 12.1.2.1.4.b in LEMIRE et al. (2001) discussing the data selection for Np(IV) carbonate complexes are the most opaque ones in the entire neptunium book. It needed some fierce attacks of an experienced reader of the NEA TDB books to unravel the threads of thought leading to the NEA recommended values. Essentially, these two sections have to be read backwards, starting at the end of the second section, in order to catch their logic. The whole story boils down to the following three steps:

Data of a very recent Np(IV) solubility study have been reinterpreted by LEMIRE et al. (2001) in terms of the equilibrium

$$NpO_2(hyd,\ am) + 4\,CO_3^{2-} + 2\,H_2O(l) \Leftrightarrow Np(CO_3)_4^{4-} + 4\,OH^-$$

$$\log_{10}K_{s,4}° \,(NpO_2,\ hyd,\ am,\ 298.15\ K) \;=\; -17.79 \pm 0.22.$$
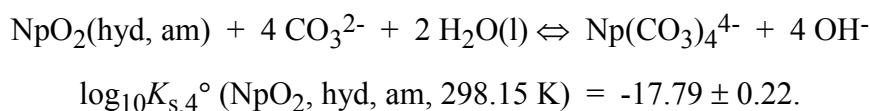
Using the solubility product of $NpO_2(hyd, am)$ as selected in 5.10.3.2.4, $\log_{10}{}^*K_{s,0}° = 1.53 \pm 1.00$, a complex formation constant has been calculated for the reaction

$$Np^{4+} + 4\,CO_3^{2-} \Leftrightarrow Np(CO_3)_4^{4-}$$

$$\log_{10}\beta_4° \,(298.15\ K) \;=\; 36.69 \pm 1.11.$$
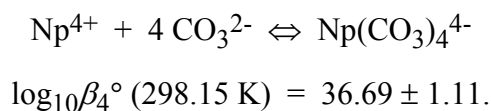
Reanalysis of data from a spectrophotometric study of the dissociation of the limiting Np(IV) carbonate complex resulted in

$$Np(CO_3)_4^{4-} + CO_3^{2-} \Leftrightarrow Np(CO_3)_5^{6-}$$

$$\log_{10}K_5° \,(298.15\ K) \;=\; -1.07 \pm 0.30.$$
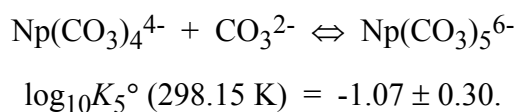
This value has been accepted by LEMIRE et al. (2001) as the best estimate of K_5 at 25°C. Combining the selected values of K_5 and β_4 resulted in

$$Np^{4+} + 5\,CO_3{}^{2-} \Leftrightarrow Np(CO_3)_5{}^{6-}$$

$$\log_{10}\beta_5° (298.15\ K) = 35.62 \pm 1.15.$$
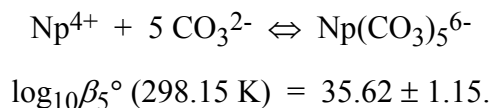
Due to the lack of appropriate experimental studies we cannot propose thermodynamic values for the formation of mixed hydroxide-carbonate complexes of Np(IV). However, scoping calculations (HUMMEL & BERNER 2002) showed that such complexes can be of importance in environmental modelling. Further experimental investigations are needed to close this gap of chemical knowledge.

5.10.7.2.1.4   Np(III) carbonate complexes

Np^{3+} can be prepared and stabilised in non-complexing (acidic) reducing aqueous solutions. Nevertheless, Np(III) complexes that may be formed in carbonate aqueous solutions are probably not stable. As is the case for Am^{3+}, the Np^{3+} cation is expected to be complexed by the carbonate anion in near-neutral or basic aqueous solutions. In such conditions, $Np(OH)_4(aq)$ or other Np(IV) complexes strongly stabilise neptunium in the +4 oxidation state, and Np(III) is usually oxidised to Np(IV) by water. For this reason, there have been no reliable experimental studies that can be used to propose thermodynamic values for the formation of intermediary Np(III) complexes in bicarbonate / carbonate media. Thus, no values for such complexes have been selected by LEMIRE et al. (2001). As a guideline, complexation constants of Am(III) or lanthanide(III) chemical analogues could be used as reasonable approximations.

5.10.7.2.2   Solid neptunium carbonates

5.10.7.2.2.1   Solid Np(VI) carbonates

There have been several publications on Np(VI) solubility in carbonate / bicarbonate aqueous solutions. The available experimental information has been interpreted or reinterpreted by LEMIRE et al. (2001) considering the following equilibria

$$(NH_4)_4NpO_2(CO_3)_3(s) \Leftrightarrow 4\,NH_4{}^+ + NpO_2(CO_3)_3{}^{4-}$$

$$\log_{10}K_{s,3}° (298.15\ K) = -7.44 \pm 0.30$$

$$K_4NpO_2(CO_3)_3(s) \Leftrightarrow 4\,K^+ + NpO_2(CO_3)_3{}^{4-}$$

$$\log_{10}K_{s,3}° (298.15\ K) = -7.03 \pm 0.88$$
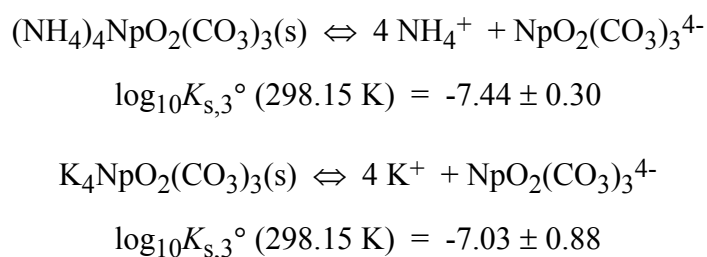
This was done even though the solid phase $K_4NpO_2(CO_3)_3(s)$ was not properly characterised. The corresponding equilibrium constants were extrapolated to zero ionic strength by performing linear SIT regressions resulting in $\varepsilon_{(NpO_2(CO_3)_3^{4-}, NH_4^+)} = -(0.78 \pm 0.30)$ kg · mol^{-1} and in $\varepsilon_{(NpO_2(CO_3)_3^{4-}, K^+)} = -(0.62 \pm 0.42)$ kg · mol^{-1}. Using the previously selected constant $\log_{10}\beta_3°$ $(NpO_2(CO_3)_3^{4-}) = 19.37 \pm 0.19$ values are calculated for

$$(NH_4)_4NpO_2(CO_3)_3(s) \Leftrightarrow 4\,NH_4^+ + NpO_2^{2+} + 3\,CO_3^{2-}$$

$$\log_{10}K_{s,0}° \text{ (298.15 K)} = -26.81 \pm 0.35$$

$$K_4NpO_2(CO_3)_3(s) \Leftrightarrow 4\,K^+ + NpO_2^{2+} + 3\,CO_3^{2-}$$
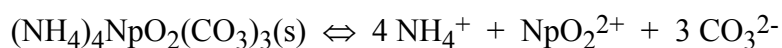
$$\log_{10}K_{s,0}° \text{ (298.15 K)} = -26.40 \pm 0.90$$

Solubility measurements involving the solid $NpO_2CO_3(s)$ have been recalculated by LEMIRE et al. (2001) with fixed β_3 and $\beta_{6,3}$ values (see 5.10.7.2.1.1) and corrected to zero ionic strength

$$NpO_2CO_3(s) \Leftrightarrow NpO_2^{2+} + CO_3^{2-}$$
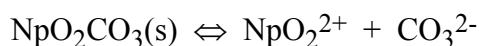
$$\log_{10}K_{s,0}° \text{ (298.15 K)} = -14.60 \pm 0.47$$

The latter three equilibria are included in our database.

5.10.7.2.2.2   Solid Np(V) carbonates

LEMIRE et al. (2001) concluded that in most, if not all, of the published solubility studies the hydrated $NaNpO_2CO_3(s)$ compound ripened gradually near 25°C, and a solid phase dehydration transformation is suspected just above room temperature. It is not clear whether this is a kinetic problem or whether (at least) two solubility products should be selected. LEMIRE et al. (2001) decided to select two solubility products corresponding to the equilibrium

$$NaNpO_2CO_3 \cdot xH_2O(s) \Leftrightarrow Na^+ + NpO_2^+ + CO_3^{2-} + x\,H_2O(l)$$
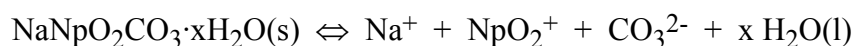
with

$$\log_{10}K_{s,0}° \text{ (x=3.5, 298.15 K)} = -11.16 \pm 0.35$$

for freshly precipitated $NaNpO_2CO_3 \cdot 3.5H_2O(s)$ and

$$\log_{10}K_{s,0}° \text{ (x=0, 298.15 K)} = -11.66 \pm 0.50$$

for the aged or less hydrated compound $NaNpO_2CO_3(s)$ where x is unknown (no H_2O molecule is taken into account when calculating ΔG_m values involving this last solid phase). These selected values are consistent with all published data.

In the case of hydrated $Na_3NpO_2(CO_3)_2(s)$ it is not clear if there is a true solid phase dehydration transformation with increasing temperature between solids otherwise having the same stoichiometry, or whether there might be solid phases with stoichiometries between $NaNpO_2CO_3(s)$ and $Na_3NpO_2(CO_3)_2(s)$. The value selected by LEMIRE et al. (2001) for the equilibrium

$$Na_3NpO_2(CO_3)_2(s) \Leftrightarrow 3\,Na^+ + NpO_2^+ + 2\,CO_3^{2-}$$
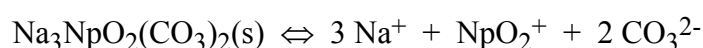
$$\log_{10}K_{s,0}°\,(\,298.15\ K) \ = \ -14.70 \pm 0.66$$

refers to the freshly precipitated compound.

5.10.7.2.2.3   Solid Np(IV) carbonates

Np(IV) solubility in neutral media is $10^{-(8.3\pm0.3)}$ M and was interpreted in terms of the equilibrium

$$NpO_2(hyd,\ am) + 2\,H_2O(l) \Leftrightarrow Np(OH)_4(aq)$$
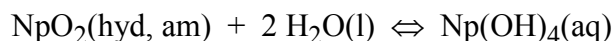
(see 5.10.3.1.4). Hence, under these conditions, no carbonate solid phase containing Np(IV) was formed. In more concentrated alkali metal carbonate media, the solubility increased as a result of $Np(CO_3)_4^{4-}$ and $Np(CO_3)_5^{6-}$ formation. The solubility is undoubtedly determined by some new solid phase or phases, possibly including alkali metal cations and $Np(CO_3)_5^{6-}$ anions. But no thermodynamic data could be estimated for these possible solid phases (LEMIRE et al. 2001).

5.10.7.3   Neptunium cyanide complexes

Formation constants for cyano complexes of Np(V) (measured at I = 5 M) have been reported. However, LEMIRE et al. (2001) conclude that, although there is good evidence for complex formation, the published results cannot be used to derive serviceable values for I = 0, and the stoichiometries of the major complexes need to be confirmed by other experiments.

5.10.7.4   Neptunium thiocyanate complexes

LEMIRE et al. (2001) discussed thiocyanate complexes of Np(IV), namely $NpSCN^{3+}$, $Np(SCN)_2^{2+}$ and $Np(SCN)_3^+$, and selected data for the 1:1 and 1:2 complex. In addition, an equilibrium constant

for $NpO_2SCN(aq)$ is given as a guideline, but it is not recommended by LEMIRE et al. (2001). However, thiocyanate complexes are presently not included in our database.

5.10.8   Neptunium group 2 (alkaline-earth) and group 1 (alkali) compounds

Several ternary oxides of alkaline-earth and alkali metal elements with neptunium have been reported. However, thermodynamic data for these compounds are limited. Enthalpy of formation values, derived from enthalpy of solution measurements in 1 M HCl, have been selected by LEMIRE et al. (2001) for $Sr_3NpO_6(cr)$, $Ba_3NpO_6(cr)$, $Ba_2MgNpO_6(cr)$, $Ba_2CaNpO_6(cr)$, $Ba_2SrNpO_6(cr)$, $Li_2NpO_4(cr)$, α-Na_2NpO_4, β-Na_2NpO_4, β-Na_4NpO_5, $Na_2Np_2O_7(cr)$, $K_2NpO_4(cr)$, $K_2Np_2O_7(cr)$, $Rb_2Np_2O_7(cr)$ and $Cs_2NpO_4(cr)$. There are no solubility products or $\Delta_f G_m°$ values for any of these phases. They are not included in our database.

5.10.9   References

GRENTHE, I., FUGER, J., KONINGS, R.J.M., LEMIRE, R.J., MULLER, A.B., NGUYEN-TRUNG, C., WANNER, H. (1992): Chemical Thermodynamics of Uranium. Elsevier, Amsterdam, 715p.

HUMMEL, W., BERNER, U. (2002): Solubility of actinides in a planned underground repository: Application of chemical thermodynamics for estimation of limiting values. Applied Geochemistry (submitted).

LEMIRE, R.J., FUGER, J., NITSCHE, H., POTTER, P., RAND, M.H., RYDBERG, J., SPAHIU, K., SULLIVAN, J.C., ULLMAN, W.J., VITORGE, P., WANNER, H. (2001): Chemical Thermodynamics of Neptunium & Plutonium. Elsevier, Amsterdam, 845p.

Table 5.10.1: Selected neptunium data. All data included in TDB Version 01/01 are taken from LEMIRE et al. (2001).

TDB Version 05/92   **TDB Version 01/01**

Name	$\Delta_f G_m°$	$\Delta_f H_m°$	Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$S_m°$	$C_{p,m}°$	Species
	-	-	Np(cr)	0.0	0.0	50.46 ± 0.80	29.62 ± 0.80	Np(cr)
NP+3	-517.1	-527.2	Np+3	-512.9 ± 5.7	-527.2 ± 2.1	-193.6 ± 20.3		Np^{3+}
NP+4	-502.9	-556.1	Np+4	-491.8 ± 5.6	-556.0 ± 4.2	-426.4 ± 12.4		Np^{4+}
NPO2+	-915.0	-978.2	NpO2+	-907.8 ± 5.6	-978.2 ± 4.6	-45.9 ± 10.7	-4 ± 25	NpO_2^+
NPO2+2	-795.8	-860.6	NpO2+2	-795.9 ± 5.6	-860.7 ± 4.7	-92.4 ± 10.5		NpO_2^{2+}

Name	Redox	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Reaction
NP+3	III	2.488	28.9				$Np^{4+} + e^- \Leftrightarrow Np^{3+}$
	III	-	-	Np+3	33.50 ± 0.23		$NpO_2^{2+} + 4\ H^+ + 3\ e^- \Leftrightarrow Np^{3+} + 2\ H_2O(l)$
NPOH+2	III	-7.0	0	NpOH+2	-6.8 ± 0.3		$Np^{3+} + H_2O(l) \Leftrightarrow NpOH^{2+} + H^+$
NPOH2+	III	-15.0	0		-	-	$Np^{3+} + 2\ H_2O(l) \Leftrightarrow Np(OH)_2^+ + 2\ H^+$
NPOH3	III	-25.0	0		-	-	$Np^{3+} + 3\ H_2O(l) \Leftrightarrow Np(OH)_3(aq) + 3\ H^+$
NPOH4-	III	-35.0	0		-	-	$Np^{3+} + 4\ H_2O(l) \Leftrightarrow Np(OH)_4^- + 4\ H^+$
NP2OH2+4	III	-14.0	0		-	-	$2\ Np^{3+} + 2\ H_2O(l) \Leftrightarrow Np_2(OH)_2^{4+} + 2\ H^+$
NP3OH5+4	III	-32.0	0		-	-	$3\ Np^{3+} + 5\ H_2O(l) \Leftrightarrow Np_3(OH)_5^{4+} + 5\ H^+$
NPCO3+	III	9.6	0		-	-	$Np^{3+} + CO_3^{2-} \Leftrightarrow NpCO_3^+$
NPCO32-	III	12.9	0		-	-	$Np^{3+} + 2\ CO_3^{2-} \Leftrightarrow Np(CO_3)_2^-$
NPCO33-3	III	16.2	0		-	-	$Np^{3+} + 3\ CO_3^{2-} \Leftrightarrow Np(CO_3)_3^{3-}$

Table 5.10.1: continued

TDB Version 05/92				TDB Version 01/01			
Name	Redox	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Reaction
	IV	-	-	Np+4	29.80 ± 0.14		$NpO_2^{2+} + 4\ H^+ + 2\ e^- \Leftrightarrow Np^{4+} + 2\ H_2O(l)$
NPOH+3	IV	-1.5	0	NpOH+3	-0.29 ± 1.00		$Np^{4+} + H_2O(l) \Leftrightarrow NpOH^{3+} + H^+$
NPOH2+2	IV	-4.0	0		-	-	$Np^{4+} + 2\ H_2O(l) \Leftrightarrow Np(OH)_2^{2+} + 2\ H^+$
NPOH3+	IV	-8.0	0		-	-	$Np^{4+} + 3\ H_2O(l) \Leftrightarrow Np(OH)_3^+ + 3\ H^+$
NPOH4	IV	-13.0	0	Np(OH)4	-9.8 ± 1.1		$Np^{4+} + 4\ H_2O(l) \Leftrightarrow Np(OH)_4(aq) + 4\ H^+$
NPOH5-	IV	-20.0	0		-	-	$Np^{4+} + 5\ H_2O(l) \Leftrightarrow Np(OH)_5^- + 5\ H^+$
NPF+3	IV	8.3	0	NpF+3	8.96 ± 0.14	1.5 ± 2.0	$Np^{4+} + F^- \Leftrightarrow NpF^{3+}$
NPF2+2	IV	14.5	0	NpF2+2	15.7 ± 0.3		$Np^{4+} + 2\ F^- \Leftrightarrow NpF_2^{2+}$
NPF3+	IV	20.3	0		-	-	$Np^{4+} + 3\ F^- \Leftrightarrow NpF_3^+$
NPF4	IV	25.1	0		-	-	$Np^{4+} + 4\ F^- \Leftrightarrow NpF_4(aq)$
NPCL+3	IV	1.2	0	NpCl+3	1.5 ± 0.3		$Np^{4+} + Cl^- \Leftrightarrow NpCl^{3+}$
NPCL2+2	IV	1.9	0		-	-	$Np^{4+} + 2\ Cl^- \Leftrightarrow NpCl_2^{2+}$
NPSO4+2	IV	3.9	0	NpSO4+2	6.85 ± 0.16	29.8 ± 8.9	$Np^{4+} + SO_4^{2-} \Leftrightarrow NpSO_4^{2+}$
NPSO42	IV	5.7	0	Np(SO4)2	11.05 ± 0.27	55.4 ± 3.9	$Np^{4+} + 2\ SO_4^{2-} \Leftrightarrow Np(SO_4)_2(aq)$
NPNO3+3	IV	1.6	0	NpNO3+3	1.90 ± 0.15		$Np^{4+} + NO_3^- \Leftrightarrow NpNO_3^{3+}$
NPNO32+2	IV	2.2	0		-	-	$Np^{4+} + 2\ NO_3^- \Leftrightarrow Np(NO_3)_2^{2+}$
NPOH3CO3	IV	-1.0	0		-	-	$Np^{4+} + CO_3^{2-} + 3\ H_2O(l) \Leftrightarrow Np(OH)_3CO_3^- + 3\ H^+$
	IV	-	-	Np(CO3)4-4	36.69 ± 1.11		$Np^{4+} + 4\ CO_3^{2-} \Leftrightarrow Np(CO_3)_4^{4-}$
	IV	-	-	Np(CO3)5-6	35.62 ± 1.15		$Np^{4+} + 5\ CO_3^{2-} \Leftrightarrow Np(CO_3)_5^{6-}$

Table 5.10.1: continued

TDB Version 05/92				TDB Version 01/01			
Name	Redox	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Reaction
NPO2+	V	-10.894	149.56	-	-	-	$Np^{4+} + 2\,H_2O(l) \Leftrightarrow NpO_2^+ + 4\,H^+ + e^-$
	V	-	-	NpO2+	19.59 ± 0.07		$NpO_2^{2+} + e^- \Leftrightarrow NpO_2^+$
NPO2OH	V	-9.0	0	NpO2(OH)	-11.3 ± 0.7	$S_m° \; 25 \pm 60$	$NpO_2^+ + H_2O(l) \Leftrightarrow NpO_2OH(aq) + H^+$
	V	-	-	NpO2(OH)2-	-23.6 ± 0.5	$S_m° \; 40 \pm 100$	$NpO_2^+ + 2\,H_2O(l) \Leftrightarrow NpO_2(OH)_2^- + 2\,H^+$
	V	-	-	NpO2F	1.2 ± 0.3		$NpO_2^+ + F^- \Leftrightarrow NpO_2F(aq)$
NPO2CL	V	-0.1	0	-	-		$NpO_2^+ + Cl^- \Leftrightarrow NpO_2Cl(aq)$
	V	-	-	NpO2SO4-	0.44 ± 0.27	23.2 ± 7.2	$NpO_2^+ + SO_4^{2-} \Leftrightarrow NpO_2SO_4^-$
NPO2NO3	V	-0.05	0		-	-	$NpO_2^+ + NO_3^- \Leftrightarrow NpO_2NO_3(aq)$
NPO2HPO4	V	3.55	0	NpO2HPO4-	2.95 ± 0.10		$NpO_2^+ + HPO_4^{2-} \Leftrightarrow NpO_2HPO_4^-$
NPO2HCO3	V	12.6	0		-	-	$NpO_2^+ + CO_3^{2-} + H^+ \Leftrightarrow NpO_2HCO_3(aq)$
NPO2H2CO	V	24.6	0		-	-	$NpO_2^+ + 2\,CO_3^{2-} + 2\,H^+ \Leftrightarrow NpO_2(HCO_3)_2^-$
	V	-	-	NpO2CO3-	4.96 ± 0.06		$NpO_2^+ + CO_3^{2-} \Leftrightarrow NpO_2CO_3^-$
	V	-	-	NpO2(CO3)2-3	6.53 ± 0.10		$NpO_2^+ + 2\,CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_2^{3-}$
	V	-	-	NpO2(CO3)3-5	5.50 ± 0.15	-13.3 ± 5.1	$NpO_2^+ + 3\,CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-}$
	V	-	-	NpO2(CO3)2OH-4	-5.30 ± 1.17		$NpO_2^+ + 2\,CO_3^{2-} + H_2O(l) \Leftrightarrow NpO_2(CO_3)_2OH^{4-} + H^+$
NPO2+2	VI	-31.777	267.16		-	-	$Np^{4+} + 2\,H_2O(l) \Leftrightarrow NpO_2^{2+} + 4\,H^+ + 2\,e^-$
NPO2OH+	VI	-5.1	0	NpO2OH+	-5.1 ± 0.4		$NpO_2^{2+} + H_2O(l) \Leftrightarrow NpO_2OH^+ + H^+$
NPO2OH2	VI	-11.5	0		-	-	$NpO_2^{2+} + 2\,H_2O(l) \Leftrightarrow NpO_2(OH)_2(aq) + 2\,H^+$
NPO2OH3-	VI	-20.7	0	NpO2(OH)3-	≤ -19		$NpO_2^{2+} + 3\,H_2O(l) \Leftrightarrow NpO_2(OH)_3^- + 3\,H^+$

Table 5.10.1: continued

TDB Version 05/92				TDB Version 01/01			
Name	Redox	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Reaction
	VI	-	-	NpO2(OH)4-2	≤ -33		$NpO_2^{2+} + 4\,H_2O(l) \Leftrightarrow NpO_2(OH)_4^{2-} + 4\,H^+$
NPO22OH+	VI	-4.0	0		-	-	$2\,NpO_2^{2+} + H_2O(l) \Leftrightarrow (NpO_2)_2OH^{3+} + H^+$
NPO22OH2	VI	-6.4	0	(NpO2)2(OH)2+2	-6.27 ± 0.21		$2\,NpO_2^{2+} + 2\,H_2O(l) \Leftrightarrow (NpO_2)_2(OH)_2^{2+} + 2\,H^+$
NPO23OH5	VI	-17.5	0	(NpO2)3(OH)5+	-17.12 ± 0.22		$3\,NpO_2^{2+} + 5\,H_2O(l) \Leftrightarrow (NpO_2)_3(OH)_5^{+} + 5\,H^+$
NPO2F+	VI	4.5	0	NpO2F+	4.57 ± 0.07		$NpO_2^{2+} + F^- \Leftrightarrow NpO_2F^+$
NPO2F2	VI	7.8	0	NpO2F2	7.60 ± 0.08		$NpO_2^{2+} + 2\,F^- \Leftrightarrow NpO_2F_2(aq)$
NPO2CL+	VI	0.25	0	NpO2Cl+	0.40 ± 0.17		$NpO_2^{2+} + Cl^- \Leftrightarrow NpO_2Cl^+$
NPO2SO4	VI	3.3	0	NpO2SO4	3.28 ± 0.06	16.7 ± 0.5	$NpO_2^{2+} + SO_4^{2-} \Leftrightarrow NpO_2SO_4(aq)$
NPO2SO42	VI	4.7	0	NpO2(SO4)2-2	4.70 ± 0.10	26.0 ± 1.2	$NpO_2^{2+} + 2\,SO_4^{2-} \Leftrightarrow NpO_2(SO_4)_2^{2-}$
NPO2NO3+	VI	-0.25	0		-	-	$NpO_2^{2+} + NO_3^- \Leftrightarrow NpO_2NO_3^+$
				NpO2H2PO4+	3.32 ± 0.50		$NpO_2^{2+} + H_2PO_4^- \Leftrightarrow NpO_2H_2PO_4^+$
				NpO2HPO4	6.2 ± 0.7		$NpO_2^{2+} + HPO_4^{2-} \Leftrightarrow NpO_2HPO_4(aq)$
				NpO2(HPO4)2-2	9.5 ± 1.0		$NpO_2^{2+} + 2\,HPO_4^{2-} \Leftrightarrow NpO_2(HPO_4)_2^{2-}$
NPO2CO3	VI	10.0	0	NpO2CO3	9.32 ± 0.61		$NpO_2^{2+} + CO_3^{2-} \Leftrightarrow NpO_2CO_3(aq)$
NPO2CO32	VI	17.0	0	NpO2(CO3)2-2	16.52 ± 0.73		$NpO_2^{2+} + 2\,CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_2^{2-}$
NPO2CO33	VI	21.0	0	NpO2(CO3)3-4	19.37 ± 0.19	-41.9 ± 4.1	$NpO_2^{2+} + 3\,CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{4-}$
	VI	-	-	(NpO2)3(CO3)6-6	49.84 ± 1.56		$3\,NpO_2^{2+} + 6\,CO_3^{2-} \Leftrightarrow (NpO_2)_3(CO_3)_6^{6-}$
	VI	-	-	(NpO2)2CO3(OH)3-	-2.87 ± 1.64		$2NpO_2^{2+} + CO_3^{2-} + 3H_2O(l) \Leftrightarrow (NpO_2)_2CO_3(OH)_3^- + 3H^+$
	VI	-	-	(UO2)2NpO2(CO3)6-6	53.59 ± 2.70		$2\,UO_2^{2+} + NpO_2^{2+} + 6\,CO_3^{2-} \Leftrightarrow (UO_2)_2NpO_2(CO_3)_6^{6-}$

Table 5.10.1: continued

TDB Version 05/92				TDB Version 01/01			
Name	Redox	$\log_{10}K_{s,0}°$	$\Delta_r H_m°$	Name	$\log_{10}K_{s,0}°$	$\Delta_r H_m°$	Reaction
NP(OH)3CR	III	22.0	0		-	-	$Np(OH)_3(cr) + 3\,H^+ \Leftrightarrow Np^{3+} + 3\,H_2O(l)$
NP(OH)4CR	IV	0.8	0		-	-	$Np(OH)_4(cr) + 4\,H^+ \Leftrightarrow Np^{4+} + 4\,H_2O(l)$
	IV	-	-	NpO2(am)(hyd)	1.5 ± 1.0		$NpO_2(am,hyd) + 4\,H^+ \Leftrightarrow Np^{4+} + 2\,H_2O(l)$
NPO2	IV	-2.7	0		-	-	$NpO_2(cr) + 4\,H^+ \Leftrightarrow Np^{4+} + 2\,H_2O(l)$
	V	-	-	NpO2OH(am)(fr)	5.3 ± 0.2	-41.1 ± 3.0	$NpO_2OH(am,fresh) + H^+ \Leftrightarrow NpO_2^+ + H_2O(l)$
NPO2OHCR	V	4.9	0	NpO2OH(am)(ag)	4.7 ± 0.5	-41.1 ± 3.0	$NpO_2OH(am,aged) + H^+ \Leftrightarrow NpO_2^+ + H_2O(l)$
	V	-	-	NaNpO2CO3:3.5H2O(s)(fr)	-11.16 ± 0.35		$NaNpO_2CO_3 \cdot 3.5H_2O(s,fresh) \Leftrightarrow Na^+ + NpO_2^+$ $+ CO_3^{2-} + 3.5H_2O(l)$
	V	-	-	NaNpO2CO3(s)(ag)	-11.66 ± 0.50		$NaNpO_2CO_3(s,aged) \Leftrightarrow Na^+ + NpO_2^+ + CO_3^{2-}$
	V	-	-	Na3NpO2(CO3)2(s)	-14.70 ± 0.66		$Na_3NpO_2(CO_3)_2(s) \Leftrightarrow 3\,Na^+ + NpO_2^+ + 2\,CO_3^{2-}$
NPO2OH2C	VI	5.3	0	NpO3:H2O(cr)	5.47 ± 0.40		$NpO_3 \cdot H_2O(cr) + 2\,H^+ \Leftrightarrow NpO_2^{2+} + 2\,H_2O(l)$
	VI	-	-	NpO2CO3(s)	-14.60 ± 0.47		$NpO_2CO_3(s) \Leftrightarrow NpO_2^{2+} + CO_3^{2-}$
	VI	-	-	K4NpO2(CO3)3(s)	-26.40 ± 0.90		$K_4NpO_2(CO_3)_3(s) \Leftrightarrow 4\,K^+ + NpO_2^{2+} + 3\,CO_3^{2-}$
	VI	-	-	(NH4)4NpO2(CO3)3(s)	-26.81 ± 0.35		$(NH_4)_4NpO_2(CO_3)_3(s) \Leftrightarrow 4\,NH_4^+ + NpO_2^{2+}$ $+ 3\,CO_3^{2-}$

5.11 Nickel

The thermodynamics of nickel is one of the topics of the ongoing Phase II of the OECD NEA Thermodynamic Data Base (TDB) project. Two review teams are presently evaluating nickel data: The Nickel Review Group takes care of the inorganic compounds and complexes of nickel, whereas the Simple Organics Group reviews nickel complexation with oxalate, citrate and EDTA. These reviews will not be finished and published before 2003.

We decided not to parallel these efforts of international review teams and to postpone a detailed discussion of all nickel data to a future update of our database. Hence, for the current update, only a few selected topics have been evaluated in some detail (i.e. nickel hydrolysis, carbonate and sulphide compounds and complexes, and nickel amine complexation) and the results have been (or will be) published by GRAUER (1999), VAN LOON & HUMMEL (1999), BAEYENS et al. (2001), HUMMEL & CURTI (2001), THOENEN (in prep.). The other nickel data are taken from the previous version of our database (PEARSON et al. 1992) without further discussion.

5.11.1 Elemental nickel

The absolute entropy of nickel metal is taken from CODATA, as reported in PLYASUNOVA et al. (1998).

5.11.2 Simple nickel aqua ion

In aqueous media, nickel exists only in the divalent oxidation state Ni(II). The thermodynamics of the free ion Ni^{2+} has recently been evaluated by PLYASUNOVA et al. (1998) from potentiometric and calorimetric data. Their recommended values are

$$\Delta_f H_m^\circ \ (Ni^{2+}, \text{aq}, 298.15 \text{ K}) \quad = \quad -(54.1 \pm 2.5) \text{ kJ} \cdot \text{mol}^{-1}$$

$$S_m^\circ \ (Ni^{2+}, \text{aq}, 298.15 \text{ K}) \quad = \quad -(130 \pm 3) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Using the selected values of the enthalpy of formation and absolute entropy one obtains:

$$\Delta_f G_m^\circ \ (Ni^{2+}, \text{aq}, 298.15 \text{ K}) \quad = \quad -(45.5 \pm 3.4) \text{ kJ} \cdot \text{mol}^{-1}$$

5.11.3 (Hydr)oxide compounds and complexes

5.11.3.1 Aqueous nickel hydroxide complexes

The aqueous chemistry of Ni^{2+} in general, and its hydrolysis in particular, has been poorly investigated compared to other divalent transition metals (e.g. Mn, Fe, Co). The experimental data that can be used to evaluate the thermodynamics of hydroxo-complexes of Ni^{2+} are relatively

limited. In acidic or near neutral solutions, hydrolysis of Ni^{2+} is weak. For a long time, $NiOH^+$ was considered as the only hydrolysis product of Ni whose stability was well known. In addition, polynuclear species have been recognised to be predominant at relatively high Ni concentrations. After evaluation of all available data (mostly determined by potentiometric titration) until 1993, PLYASUNOVA et al. (1998) recommended the following values:

$$Ni^{2+} + H_2O(l) \Leftrightarrow NiOH^+ + H^+$$

$$\log_{10}{}^*\beta_1° \,(298.15\ K) = \quad -9.50 \pm 0.36$$

$$\Delta_r H_m° \,(298.15\ K) = 50 \pm 21\ kJ \cdot mol^{-1}$$

$$2\ Ni^{2+} + H_2O(l) \Leftrightarrow Ni_2OH^{3+} + H^+$$

$$\log_{10}{}^*\beta_{21}° \,(298.15\ K) = \quad -9.8 \pm 1.2$$

$$\Delta_r H_m° \,(298.15\ K) = 35 \pm 17\ kJ \cdot mol^{-1}$$

$$4\ Ni^{2+} + 4\ H_2O(l) \Leftrightarrow Ni_4(OH)_4^{4+} + 4\ H^+$$

$$\log_{10}{}^*\beta_{44}° \,(298.15\ K) = \quad -27.9 \pm 1.0$$

$$\Delta_r H_m° \,(298.15\ K) = 170 \pm 17\ kJ \cdot mol^{-1}$$
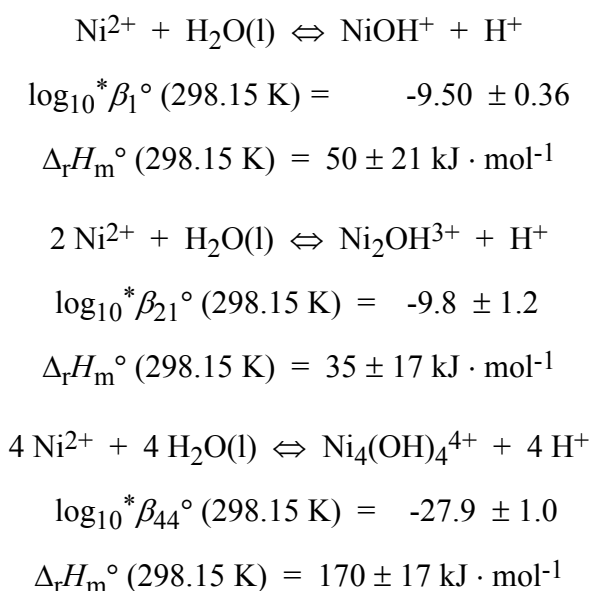
A major part of the quantitative experimental information (i.e. all studies concerning the formation of $Ni(OH)_2(aq)$, $Ni(OH)_3^-$ and $Ni(OH)_4^{2-}$ complexes) has been based on solubility measurements. Considering all available solubility data until 1993, PLYASUNOVA et al. (1998) recommended the following values:

$$Ni(OH)_2(cr) \Leftrightarrow Ni(OH)_2(aq)$$

$$\log_{10}{}^*K_{s,2}° \,(298.15\ K) = -7.52 \pm 0.80$$

$$\Delta_r H_m° \,(298.15\ K) = 7.11 \pm 3.06\ kJ \cdot mol^{-1}$$

$$Ni(OH)_2(cr) + OH^- \Leftrightarrow Ni(OH)_3^-$$

$$\log_{10}{}^*K_{s,3}° \,(298.15\ K) \quad = -5.2 \pm 1.4$$

$$\Delta_r H_m° \,(298.15\ K) = -13.98 \pm 8.24\ kJ \cdot mol^{-1}$$

$$Ni(OH)_2(cr) + 2\ OH^- \Leftrightarrow Ni(OH)_4^{2-}$$

$$\log_{10}{}^*K_{s,4}° \,(298.15\ K) \quad = -6.43 \pm 0.23$$
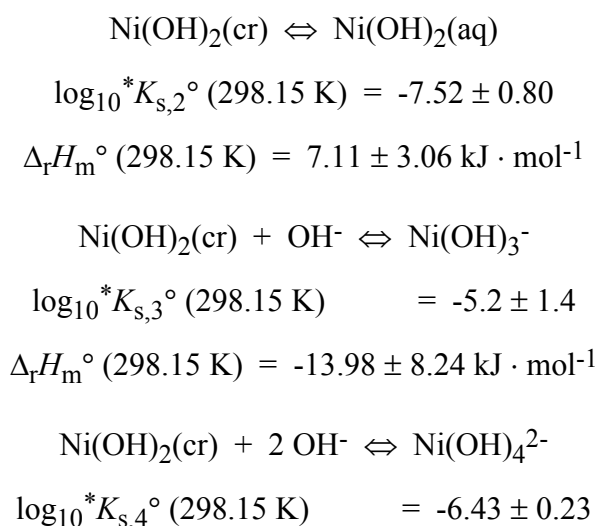
The values of $\log_{10}{}^*\beta_{1x}°$ (x = 2, 3, 4) calculated from $\log_{10}{}^*K_{s,x}°$ (x = 2, 3, 4) now depend on the selected value of the $Ni(OH)_2(cr)$ solubility product, $\log_{10}{}^*K_{s,0}°$, and therefore cannot be modified independently.

5.11.3.2   Thermodynamics of $Ni(OH)_2(cr)$ and $NiO(cr)$

A range of solubility products of $Ni(OH)_2(s)$ has been reported in the literature. PLYASUNOVA et al. (1998) based their evaluation of a recommended value on two constraints. First, the crystalline product $Ni(OH)_2(cr)$ is known to be most stable phase at ambient temperature. The oxide, $NiO(cr)$, is formed by the dehydration of $Ni(OH)_2(cr)$ at temperatures as high as 440 - 558 K. Second, PLYASUNOVA et al. (1998) considered the thermochemical data reported for $NiO(cr)$ as reliable, and thus, the selected $NiO(cr)$ data imposed an upper limit for the solubility product of $Ni(OH)_2(cr)$. Considering these two constraints, PLYASUNOVA et al. (1998) evaluated all literature data for the solubility product of $Ni(OH)_2(cr)$ up to 1993 and recommended the following values:

$$Ni(OH)_2(cr) \Leftrightarrow Ni^{2+} + 2\ OH^-$$

$$\log_{10}{}^*K_{s,0}° \text{ (298.15 K)} \quad = -17.48 \pm 0.54$$

$$S_m° \text{ (}Ni(OH)_2\text{, cr, 298.15 K)} = (73 \pm 10)\ J \cdot K^{-1} \cdot mol^{-1}$$

Recently, a new experimental study of $Ni(OH)_2(cr)$ solubility (MATTIGOD et al. 1997) reported nickel concentrations which are inconsistent with the above selected value. The dissolved nickel concentrations are about two orders of magnitude higher than the previously reported values. At present, we do not see an obvious way to remove this inconsistency (HUMMEL & CURTI 2001), and an in-depth new review of the Ni - H_2O system seems to be necessary. However, this is the task of the NEA Nickel Review Group. As tentative values, until the results of the NEA review are available, we include the data set selected by PLYASUNOVA et al. (1998) in our database.

5.11.3.2   Thermodynamics of $NiFe_2O_4(s)$

Thermochemical data of a nickel spinel, $NiFe_2O_4(s)$, is included in PEARSON et al. (1992). This solid is a hypothetical end-member of the rather complicated spinel solid solution system. The pure nickel end-member $NiFe_2O_4(s)$ is not found in nature, it is a synthetic product and no solubility study of this solid has been reported. Including the thermochemical data of $NiFe_2O_4(s)$ in calculations concerning aqueous environmental systems can result in grossly erroneous results. Therefore, we decided to discard this solid from our database.

5.11.4 Halogen compounds and complexes

All nickel halide solids are highly soluble salts. The anhydrous forms are sold with the label "hygroscopic" on the bottle, implying instantaneous dissolution in water. They are not relevant under environmental conditions and thus, they are not included in our database.

Aqueous nickel fluoride and chloride complexes are rather weak. They are taken without further evaluation from PEARSON et al. (1992).

5.11.5 Chalcogen compounds and complexes

5.11.5.1 Nickel sulphides

A detailed evaluation and discussion of literature data on nickel sulphide compounds and complexes by THOENEN (2002) revealed that no reliable data for nickel sulphide solids are available (see chapter 5.19.8). Consequently, all nickel sulphide solids included in PEARSON et al. (1992) are discarded in the update of our database. However, data concerning aqueous nickel sulphide complexation have been published and the following values are recommended and included in our database (see chapter 5.19.8):

$$Ni^{2+} + HS^- \Leftrightarrow NiHS^+$$

$$\log_{10}\beta_1^\circ \, (298.15 \text{ K}) = 5.8$$

$$Ni^{2+} + 2\,HS^- \Leftrightarrow Ni(HS)_2(aq)$$
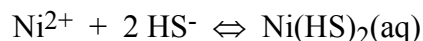
$$\log_{10}\beta_2^\circ \, (298.15 \text{ K}) = 11.6$$

5.11.5.2 Nickel sulphates

Nickel sulphate solids are highly soluble salts. They are not relevant under environmental conditions and thus, they are not included in our database.

Aqueous nickel sulphate complexes are taken without further evaluation from PEARSON et al. (1992).

5.11.6 Group 15 compounds and complexes

5.11.6.1 Nitrogen compounds and complexes

Nickel nitrate solids are highly soluble salts. They are not relevant under environmental conditions and thus, they are not included in our database.

Aqueous nickel nitrate complexes are rather weak. They are taken without further evaluation from PEARSON et al. (1992).

Aqueous nickel amine complexes can be relevant for modelling work concerning the degradation products of anion exchange resins in a repository (VAN LOON & HUMMEL 1999). The stability constants for nickel amine complexes are taken from the seminal work of BJERRUM (1941).

5.11.6.2   Phosphorous compounds and complexes

Some data on nickel phosphate compounds can be found in the literature. For the present update of our database, no evaluation of these data has been done and none of these compounds is included in the database.

Aqueous nickel phosphate complexes are taken without further evaluation from PEARSON et al. (1992).

5.11.7   Group 14 compounds and complexes

5.11.7.1   Nickel carbonates

Nickel forms a number of hydrous carbonates, for which no thermodynamic data have yet been reported. Anhydrous Ni carbonate is found in natural low-temperature environments as the mineral gaspeite, an alteration product of Ni ores. It is always impure. The solubility product of $NiCO_3(cr)$ as reported in most common databases is wrong by several orders of magnitude. The dubious origin of this number and a new evaluation of the solubility product has been discussed in detail by GRAUER (1999). He recommended:

$$NiCO_3(cr) \Leftrightarrow Ni^{2+} + CO_3^{2-}$$

$$\log_{10}K° (298.15\ K) = -11.2 \pm 0.3$$
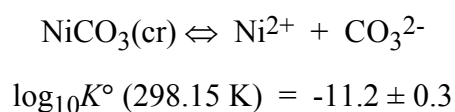
All numbers floating around in the literature for aqueous nickel carbonate complexes are estimates. No experimental study has been published yet. As discussed in detail by HUMMEL & CURTI (2001), the estimates vary by several orders of magnitude and a detailed re-evaluation of the proposed estimation procedures is a rather sobering experience concerning the quality of the estimated numbers. In conclusion, HUMMEL & CURTI (2001) propose wide expectation ranges for aqueous nickel carbonate complexes:

$$Ni^{2+} + CO_3^{2-} \Leftrightarrow NiCO_3(aq) \qquad 4 < \log_{10}K_1° < 5.5$$

$$NiCO_3(aq) + CO_3^{2-} \Leftrightarrow Ni(CO_3)_2^{2-} \qquad \log_{10}K_2° < \log_{10}K_1° - 2$$

$$Ni^{2+} + HCO_3^- \Leftrightarrow NiHCO_3^+ \qquad 1 < \log_{10}K_H° < 2$$
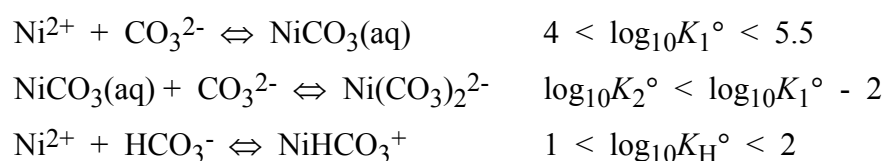
A recent experimental study by BAEYENS et al. (2001) revealed that $\log_{10}K_1°$ is located at the lower end of the expectation range. Exploring the effects of pH variation within two orders of magnitude (7.5 - 9.5), preliminary conclusions can be drawn concerning the stability of $NiHCO_3^+$. An upper limit of $\log_{10}K_H° < 1.5$ is compatible with the experimental findings of BAEYENS et al. (2001), and we can assume that this equilibrium also is located at the lower end of the expectation range, i.e. $\log_{10}K_H° \approx 1$. The experimental observations of BAEYENS et al. (2001) at high carbonate concentrations corroborate the relation derived by HUMMEL & CURTI (2001). However, only a limiting value can presently be proposed: $\log_{10}K_2° < 2$. More work is needed to confirm the results of this first experimental study of nickel carbonate complexation. For the time being we decided to include in our database, as tentative values:

$$\log_{10}K_1° \; (298.15 \; K) \; = \; 4.0 \pm 0.3$$

$$\log_{10}K_2° \; (298.15 \; K) \; < \; 2$$

$$\log_{10}K_H° \; (298.15 \; K) \; \approx \; 1$$

5.11.7.2   Nickel silicates

Some thermochemical data of nickel silicate solids are included in PEARSON et al. (1992). These solids are hypothetical end-members of complicated Ni - Mg - Fe - silicate solid solutions (i.e. the olivine and pyroxene system) which are anyway typical for magmatic systems (T > 800°C). The pure nickel end-members nickel-olivine, $Ni_2SiO_4(s)$, and nickel-pyroxene, $NiSiO_3(s)$, are not found in nature. All these solids are synthetic products and no solubility study of any of these solids has been reported. Including the thermochemical data of these solids in calculations concerning aqueous environmental systems can result in meaningless results. Therefore, we decided to discard these solids from our database.

Table 5.11.1: Selected nickel data.

TDB Version 05/92   **TDB Version 01/01**

Name	$\Delta_f G_m°$	$\Delta_f H_m°$	Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$S_m°$	$C_{p,m}°$	Species
	-	-	Ni(cr)	0.0	0.0	29.87 ± 0.21		Ni(cr)
NI+2	-45.6	-54.0	Ni+2	-45.5 ± 3.4	-54.1 ± 2.5	-130 ± 3		Ni^{2+}

Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	$\Delta_f H_m°$	Reaction
NIOH+	-9.71	51.923	NiOH+	-9.50 ± 0.36	50 ± 21		$Ni^{2+} + H_2O(l) \Leftrightarrow NiOH^+ + H^+$
NIOH2	-20.0	0	Ni(OH)2	-18.0 ± 1.0		-540 ± 13	$Ni^{2+} + 2\,H_2O(l) \Leftrightarrow Ni(OH)_2(aq) + 2\,H^+$
NIOH3-	-30.0	0	Ni(OH)3-	-29.7 ± 1.5		-791 ± 18	$Ni^{2+} + 3\,H_2O(l) \Leftrightarrow Ni(OH)_3^- + 3\,H^+$
NIOH4-	-44.0	0	Ni(OH)4-2	-44.9 ± 0.6			$Ni^{2+} + 4\,H_2O(l) \Leftrightarrow Ni(OH)_4^{2-} + 4\,H^+$
NI2OH3+	-10.7	0	Ni2OH+3	-9.8 ± 1.2	35 ± 17		$2\,Ni^{2+} + H_2O(l) \Leftrightarrow Ni_2OH^{3+-} + H^+$
Ni4(OH)4	-27.74	0	Ni4(OH)4-4	-27.9 ± 1.0	170 ± 17		$4\,Ni^{2+} + 4\,H_2O(l) \Leftrightarrow Ni_4(OH)_4^{4+} + 4\,H^+$
NIF+	1.3	0	NiF+	1.3			$Ni^{2+} + F^- \Leftrightarrow NiF^+$
NICL+	0.40	0	NiCl+	0.4			$Ni^{2+} + Cl^- \Leftrightarrow NiCl^+$
NICL2	0.96	0	NiCl2	0.96			$Ni^{2+} + 2\,Cl^- \Leftrightarrow NiCl_2(aq)$
	-	-	NiHS+	5.8			$Ni^{2+} + HS^- \Leftrightarrow NiHS^+$
	-	-	Ni(HS)2	11.6			$Ni^{2+} + 2\,HS^- \Leftrightarrow Ni(HS)_2(aq)$
NiSO4	2.31	13.975	NiSO4	2.31	13.975		$Ni^{2+} + SO_4^{2-} \Leftrightarrow NiSO_4(aq)$
NISO42	3.2	0	Ni(SO4)2-2	3.2			$Ni^{2+} + 2\,SO_4^{2-} \Leftrightarrow Ni(SO_4)_2^{2-}$

Table 5.11.1: continued

TDB Version 05/92   **TDB Version 01/01**

Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	$\Delta_f H_m°$	Reaction
NINO3+	0.4	0	NiNO3+	0.4			$Ni^{2+} + NO_3^- \Leftrightarrow NiNO_3^+$
NINO32	-0.6	0	Ni(NO3)3	-0.6			$Ni^{2+} + 2\,NO_3^- \Leftrightarrow Ni(NO_3)_2(aq)$
	-	-	NiNH3+2	2.7			$Ni^{2+} + NH_3(aq) \Leftrightarrow NiNH_3^{2+}$
NINH32	5.11	-31.673	Ni(NH3)2+2	4.9			$Ni^{2+} + 2\,NH_3(aq) \Leftrightarrow Ni(NH_3)_2^{2+}$
	-	-	Ni(NH3)3+3	6.5			$Ni^{2+} + 3\,NH_3(aq) \Leftrightarrow Ni(NH_3)_3^{2+}$
	-	-	Ni(NH3)4+2	7.6			$Ni^{2+} + 4\,NH_3(aq) \Leftrightarrow Ni(NH_3)_4^{2+}$
	-	-	Ni(NH3)5+2	8.3			$Ni^{2+} + 5\,NH_3(aq) \Leftrightarrow Ni(NH_3)_5^{2+}$
NINH36	8.88	-93.807	Ni(NH3)6+2	8.2			$Ni^{2+} + 6\,NH_3(aq) \Leftrightarrow Ni(NH_3)_6^{2+}$
NIH2PO4+	1.544	0	NiH2PO4+	1.544			$Ni^{2+} + H_2PO_4^- \Leftrightarrow NiH_2PO_4^+$
NIHPO4	2.934	0	NiHPO4	2.934			$Ni^{2+} + HPO_4^{2-} \Leftrightarrow NiHPO_4(aq)$
NIPO4-	8.374	0	NiPO4-	8.374			$Ni^{2+} + PO_4^{3-} \Leftrightarrow NiPO_4^-$
NIHP2O7-	9.258	0	NiHP2O7-	9.258			$Ni^{2+} + 2\,HPO_4^{2-} + H^+ \Leftrightarrow NiHP_2O_7^- + H_2O(l)$
NIP2O7-2	3.088	9.917	NiP2O7-2	3.088	9.917		$Ni^{2+} + 2\,HPO_4^{2-} \Leftrightarrow NiP_2O_7^{2-} + H_2O(l)$
NICO3	5.78	0	NiCO3	4.0 ± 0.3			$Ni^{2+} + CO_3^{2-} \Leftrightarrow NiCO_3(aq)$
NICO32	10.11	0	Ni(CO3)2-2	< 6			$Ni^{2+} + 2\,CO_3^{2-} \Leftrightarrow Ni(CO_3)_2^{2-}$
NIHCO3+	3.081	0	NiHCO3+	≈ 1			$Ni^{2+} + HCO_3^- \Leftrightarrow NiHCO_3^+$

Table 5.11.1: continued

TDB Version 05/92			TDB Version 01/01			
Name	$\log_{10}K_{s,0}°$	$\Delta_r H_m°$	Name	$\log_{10}K_{s,0}°$	$S_m°$	Reaction
NI(OH)2S	12.73	-22.93	Theophrastite	10.5 ± 0.5	73 ± 10	$Ni(OH)_2(cr) + 2 H^+ \Leftrightarrow Ni^{2+} + 2 H_2O(l)$
NIO	12.45	-23.93		-	-	$NiO(cr) + 2 H^+ \Leftrightarrow Ni^{2+} + H_2O(l)$
NIFE2O4	31.36	-70.4		-	-	$NiFe_2O_4(s) + 8 H^+ + 2 e^- \Leftrightarrow Ni^{2+} + 2 Fe^{2+} + 4 H_2O(l)$
NIF2S	-0.35	-15.7		-	-	$NiF_2(s) \Leftrightarrow Ni^{2+} + 2 F^-$
NIS	-9.221	0.16		-	-	$NiS(s) + H^+ \Leftrightarrow Ni^{2+} + HS^-$
NIS2	-39.851	44.3		-	-	$NiS_2(s) + 2 H^+ + 2 e^- \Leftrightarrow Ni^{2+} + 2 HS^-$
NI3S2	-34.691	34.5		-	-	$Ni_3S_2(s) + 2 H^+ \Leftrightarrow 3 Ni^{2+} + 2 HS^- + 2 e^-$
NI3S4	-102.311	98.0		-	-	$Ni_3S_4(s) + 4 H^+ + 2 e^- \Leftrightarrow 3 Ni^{2+} + 4 HS^-$
NISO47AQ	-2.02	2.92		-	-	$NiSO_4 \cdot 7H_2O(s) \Leftrightarrow Ni^{2+} + SO_4^{2-} + 7 H_2O(l)$
NICO3S	-6.97	-9.1	Ni(CO3)(cr)	-11.2 ± 0.3		$NiCO_3(cr) \Leftrightarrow Ni^{2+} + CO_3^{2-}$
NI2SIO4	19.31	-40.99		-	-	$Ni_2SiO_4(s) + 4 H^+ \Leftrightarrow 2 Ni^{2+} + Si(OH)_4(aq)$
NI2SIO4S	20.71	-42.61		-	-	$Ni_2SiO_4(s) + 4 H^+ \Leftrightarrow 2 Ni^{2+} + Si(OH)_4(aq)$
NISIO3	-2.06	0		-	-	$NiSiO_3(s) + 2 H^+ + H_2O(l) \Leftrightarrow Ni^{2+} + Si(OH)_4(aq)$

5.11.8   References

BAEYENS, B., BRADBURY, M.H., HUMMEL, W. (2001): Determination of aqueous Ni-carbonate and Ni-oxalate complexation constants. In preparation.

BJERRUM, J. (1941): Metal Ammine Formation in Aqueous Solution. P. Haase and Son, Copenhagen, (reprinted 1957), 296 p.

GRAUER, R. (1999): Solubility Products of M(II) - Carbonates. Edited and translated by U. Berner. PSI Bericht Nr. 99-04, Villigen, Switzerland, and Nagra NTB 99-03, Wettingen, Switzerland, 24 p.

HUMMEL, W., CURTI, E. (2001): Nickel aqueous speciation at ambient conditions: A thermodynamic elegy. In preparation.

MATTIGOD, S.V., RAI, D., FELMY, A.R., RAO, L. (1997): Solubility and solubility product of crystalline $Ni(OH)_2$. J. Solution Chem., 26, 391-403.

PEARSON, F.J., BERNER, U., HUMMEL, W. (1992): Nagra Thermochemical Data Base II. Supplemental Data 05/92. Nagra Technical Report NTB 91-18, Nagra, Wettingen, Switzerland, 284 p.

PLYASUNOVA, N.V., ZHANG, Y., MUHAMMED, M. (1998): Critical evaluation of thermodynamics of complex formation of metal ions in aqueous solutions. IV. Hydrolysis and hydroxo-complexes of Ni^{2+} at 298.15 K. Hydrometallurgy, 48, 43-63.

THOENEN, T. (2002): Chemical Thermodynamics of Sulfide in Aqueous Systems. PSI Report, Paul Scherrer Institut, Villigen, Switzerland. In preparation.

VAN LOON, L.R., HUMMEL, W. (1999): The Degradation of Strong Basic Anion Exchange Resins and Mixed Bed Ion Exchange Resins. Effect of Degradation Products on Radionuclide Speciation. Nuclear Technology, 128, 388-401.

5.12 Niobium

All data for niobium aqueous species and minerals in our supplemental data set are based on properties of formation given by WAGMAN et al. (1982). The primary master species for niobium is NbO_3^-, in which niobium is present as Nb(V). The hydrolysis species $Nb(OH)_5(aq)$ and $Nb(OH)_4^+$ are included as product species. Note that all data for NbO_3^-, $Nb(OH)_5(aq)$ and $Nb(OH)_4^+$ apply only to $I = 1$ M.

WAGMAN et al. (1982) include data for a number of niobium solids. Only the oxides $Nb_2O_5(cr)$ of Nb(V), and $NbO_2(cr)$ of Nb(IV) are included here.

Recently, LOTHENBACH et al. (1999, p.275-289) reviewed in detail the thermodynamic data of niobium. They report that solubility measurements of $Nb_2O_5(s)$ indicate the presence of a negatively charged species in the pH range 7 to 10 . The simplest assumption is that $Nb(OH)_6^-$ (= $NbO_3^- + 3 H_2O$) is the predominant species under these conditions. In neutral and acidic solutions the solubility measurements indicate an uncharged species, assumed to be $Nb(OH)_5(aq)$. $Nb(OH)_6^-$, $Nb(OH)_5(aq)$ and $Nb_2O_5(s)$ are the only niobium species and compounds for which LOTHENBACH et al. (1999, Table 3.5) select thermodynamic data. The hydrolysis constant for the $Nb(OH)_5(aq)$ – $Nb(OH)_6^-$ equilibrium agrees fairly well with the constant derived from the data of WAGMAN et al. (1982). However, according to recent measurements, the solubility of $Nb_2O_5(s)$ is more than three orders of magnitude lower than indicated by older publications and adopted by WAGMAN et al. (1982). Also, the solid $NbO_2(s)$ is thermodynamically unstable in the presence of water where the pentoxide, $Nb_2O_5(s)$, is formed under reduction of water (LOTHENBACH et al. 1999).

5.12.1 References

LOTHENBACH, B., OCHS, M., WANNER, H., YUI, M. (1999): Thermodynamic Data for the Speciation and Solubility of Pd, Pb, Sn, Sb, Nb and Bi in Aqueous Solution. LNC TN8400 99-011, Japan Nuclear Cycle Development Institute, Ibaraki, Japan.

WAGMAN, D.D., EVANS, W.H., PARKER, V.B., SCHUMM, R.H., HALOW, I., BAILEY, S.M., CHURNEY, K.L., NUTTALL, R.L. (1982): The NBS tables of chemical thermodynamic properties: Selected values for inorganic and C_1 and C_2 organic substances in SI units. Journal of Physical and Chemical Reference Data, 11, Supplement No. 2, 1-392.

5.13   Organics

Many organic substances yield anions that form aqueous complexes with metallic cations. Such substances may be naturally present in groundwater, or may be in the waste itself. There is an enormous number of organic compounds which are capable of forming complexes in aqueous solutions, and many organic ligands are included in some data bases.

For the original Nagra TDB 05/92 we had adopted a different approach. Rather than trying to assemble data on a large number of organic ligands, HUMMEL (1991) had chosen four compounds that are typical of large classes of complexing ligands. These ligands are two carboxylic acids, oxalic (ox) and citric (cit) acid, and two polyaminepolycarboxylic acids, nitrilotriacetic (nta) and ethylenediaminetetraacetic (edta) acid.

Equilibrium constants for protonation and metal complexation data for ox, cit, nta and edta had been compiled by HUMMEL (1991) from other data bases, and a few data had been estimated using chemical systematics and correlation procedures. All these data were included in the Nagra TDB 05/92.

The same approach is now adopted by NEA in its TDB phase II project. The ligands chosen are oxalic (ox), citric (cit), ethylenediaminetetraacetic (edta), and isosaccharinic (isa) acid. Protonation and metal complexation data for ox, cit, edta and isa are currently reviewed by an international expert team. The results of this study are expected to be published in 2002.

For the Nagra/PSI TDB 01/01 we decided to remove all data referring to organic ligands (HUMMEL 1991) and to wait for the completion of the NEA TDB review. Then the complexation of metals by organic ligands will be reconsidered in a forthcoming update of our Nagra/PSI TDB.

5.13.1   Reference

HUMMEL, W. (1991): Thermodynamic Data Base for Organic Ligands. Internal Report TM-41-91-43, Paul Scherrer Institut, Villigen, Switzerland, 52p.

5.14   Palladium

Thermodynamic data of inorganic compounds and complexes of palladium included in PEARSON et al. (1992) had been taken from the database of BAEYENS & MCKINLEY (1989) without any further evaluation. Meanwhile, a detailed review of thermodynamic data of palladium has been published by LOTHENBACH et al. (1999). We basically follow their argumentation and accept their recommendations with the exception of the redox potential $Pd^{2+}/Pd(s)$, which has been re-evaluated in the present review. Concerning hydrolysis of palladium and solubility of $Pd(OH)_2(am)$ we have included in our evaluation the most recent publications until end of December 2000. In addition, the available information about palladium sulphides and sulphates is briefly discussed.

5.14.1   Elemental palladium

In contrast to most radionuclides in our database, thermodynamic data on elemental palladium are not only included for computational purposes. As a member of the platinum group of elements, palladium occurs in nature mainly in elemental form or as inter-metallic compound. In addition, sulphide (and arsenide) minerals of palladium are known (see section 5.14.5.1). Hence, elemental palladium is an important solid for modelling studies concerning solubility and complexation of palladium.

No CODATA values have been published for palladium. The absolute entropy and heat capacity of palladium metal recommended by different compilations like WAGMAN et al. (1982) or SASSANI & SHOCK (1998) vary less than 0.5 $J \cdot K^{-1} \cdot mol^{-1}$. We did not check if this similarity arises from re-evaluating the same set of experimental data by each compilation. We decided to accept the values evaluated in the most recent review by SASSANI & SHOCK (1998) (note that all data in this publication are given in calories rather than joules, and that no error estimates are given for their thermochemical data):

$$S_m^\circ \text{ (Pd, cr, 298.15 K)} \quad = \quad 37.82 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{p,m}^\circ \text{ (Pd, cr, 298.15 K)} \quad = \quad 25.36 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

5.14.2   Simple palladium aqua ion

In aqueous media, palladium complexes are found only in the divalent oxidation state Pd(II). The thermodynamics of the free ion Pd^{2+} has recently been evaluated by SASSANI and SHOCK (1998). They estimated the absolute entropy of Pd^{2+} and took the Gibbs energy of formation from the standard potential $Pd^{2+}/Pd(s)$ as recommended by IZATT et al. (1967). However, the latter publication has been criticised by LOTHENBACH et al. (1999) who preferred the value measured by TEMPELTON et al. (1943) in concentrated $HClO_4$ and extrapolated this value to zero ionic strength

with estimated SIT coefficients. This procedure leads to a completely different standard potential at $I = 0$ than the value recommended by IZATT et al. (1967). Therefore, we decided to re-evaluate the standard potential of the $Pd^{2+}/Pd(s)$ couple from published data.

Experimental data for the redox potential of the half cell

$$Pd^{2+} + 2\,e^- \Leftrightarrow Pd(s)$$
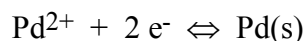
are compiled in Table 5.14.1. Note that the careful and reliable measurements of TEMPELTON et al. (1943) have been carried out in 4 molal $HClO_4$, and not in 4 molar solutions as assumed by LOTHENBACH et al. (1999) (f in TEMPELTON et al. (1943) means "formula weights per kilogram water"). The redox potential given by IZATT et al. (1967) has been measured at low ionic strength and extrapolated by the authors to zero ionic strength using an extended Debye-Hückel expression. No data and no experimental details are reported by IZATT et al. (1967), and we agree with LOTHENBACH et al. (1999) that the $Pd^{2+}/Pd(s)$ redox potential should not be based on this value. However, the same group published additional data about this topic, measured in 3.94 m $HClO_4$ in the temperature range 10 to 40°C. The study by LEVANDA et al. (1968) using the same methods as the other groups, but varying the background electrolyte from 1.06 to 4.87 m $HClO_4$, allows an extrapolation to zero ionic strength by regression analysis. The most "recent" publication known to us is the study of JACKSON & PANTONY (1971) using polarography. The measurements have been carried out in 0.2M $HClO_4$ and the results are given at zero ionic strength (i.e. extrapolated by the authors using a not specified version of the Debye-Hückel formalism). The redox potential reported by JACKSON & PANTONY (1971) is associated with a rather large uncertainty.

Linear regression analysis comprised the data of TEMPELTON et al. (1943), LEVANDA et al. (1968) and IZATT et al. (1970). As the assigned uncertainties to all values are basically the same, an unweighted regression has been preferred. This results in the same constant and slope as a weighted regression with equal weights, but the uncertainties of the regression parameters are based on data scatter and not on the assigned individual uncertainties. The results are

$$\log_{10}K° \,(298.15\ \mathrm{K}) \,=\, 30.8 \pm 0.8$$

$$-\Delta\varepsilon \,=\, \varepsilon(Pd^{2+}, ClO_4^-) \,=\, 0.8 \pm 0.2$$

As can be seen in Fig. 5.14.1, an overall consistent picture emerges although the data of IZATT et al. (1967) and of JACKSON & PANTONY (1971) at zero ionic strength have not been included in the regression analysis. The only splotch disturbing this nice picture is an SIT interaction coefficient twice as high as expected for divalent cations.

Table 5.14.1: Experimental data compiled for the redox pair $Pd^{2+}/Pd(s)$, according to the equilibrium $Pd^{2+} + 2e^- \Leftrightarrow Pd(s)$. Methods: pot = potentiometry, vlt = voltammetry. Uncertainty estimates are based on statements in the papers, they should represent 95% of the statistical uncertainty.

Method	Temp (°C)	Medium	I (molal)	Formal potential E (V)	$\log_{10}K$	Reference
pot	25	$HClO_4$	4.02	0.987 ± 0.007	33.4 ± 0.2	TEMPELTON et al. (1943)
pot	25	$I \rightarrow 0$		0.915 ± 0.010	30.9 ± 0.3	IZATT et al. (1967)
pot	25	$HClO_4$	1.06	0.920 ± 0.006	31.1 ± 0.2	LEVANDA et al. (1968)
			2.22	0.924 ± 0.006	31.2 ± 0.2	
			3.46	0.952 ± 0.006	32.2 ± 0.2	
			4.87	0.996 ± 0.006	33.7 ± 0.2	
pot	10	$HClO_4$	3.94	0.978 ± 0.004	34.8 ± 0.2	IZATT et al. (1970)
	15			0.979 ± 0.010	34.2 ± 0.3	
	20			0.975 ± 0.010	33.5 ± 0.3	
	25			0.979 ± 0.010	33.1 ± 0.3	
	30			0.978 ± 0.006	32.5 ± 0.2	
	35			0.972 ± 0.010	31.8 ± 0.3	
	40			0.960 ± 0.008	30.9 ± 0.3	
vlt	25	$I \rightarrow 0$		0.91 ± 0.06	30.8 ± 2.0	JACKSON & PANTONY (1971)

Taking $\log_{10}K°$ from the regression analysis we obtain

$$\Delta_f G_m° \text{ (Pd}^{2+}\text{, aq, 298.15 K)} \quad = \quad (175.8 \pm 4.6) \text{ kJ} \cdot \text{mol}^{-1}$$

Using the estimated entropy from SASSANI & SHOCK (1998)

$$S_m° \text{ (Pd}^{2+}\text{, aq, 298.15 K)} \quad = \quad -88.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

and the value $S_m°$(Pd, cr, 298.15 K) = 37.82 J·K^{-1}·mol^{-1}, selected from SASSANI & SHOCK(1998) in section 5.14.1, we obtain for the enthalpy of formation:

$$\Delta_f H_m° \text{ (Pd}^{2+}\text{, aq, 298.15 K)} \quad = \quad (177.2 \pm 4.6) \text{ kJ} \cdot \text{mol}^{-1}$$
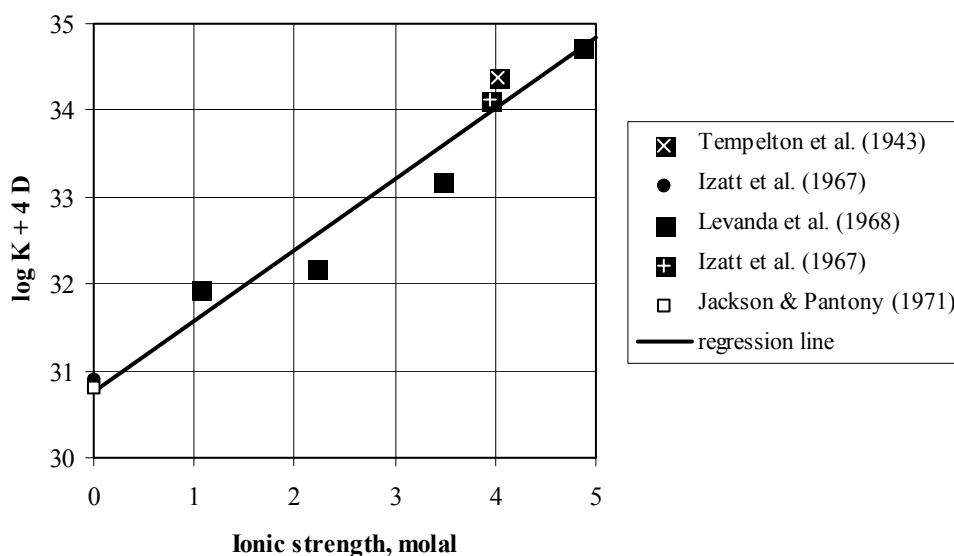
Fig. 5.14.1: Plot of $\log_{10}K + 4D$ versus I_m for the reaction $Pd^{2+} + 2e^- \Leftrightarrow Pd(s)$ at 25°C. Note that this reaction corresponds to the reaction $Pd^{2+} + H_2(g) \Leftrightarrow Pd(s) + 2H^+$ where H^+ represents the cation in the standard hydrogen electrode, as all E(V) data in Table 5.14.1 are given as formal potentials with reference to the standard hydrogen electrode. Hence, H^+ is already in standard conditions and its activity coefficient must not be included in the expression for extrapolation to $I = 0$. The straight line shows the result of an unweighted linear regression using data compiled in Table 5.14.1: $\Delta\varepsilon = -0.8 \pm 0.2$; $\log_{10}K° = 30.8 \pm 0.8$. The values at $I = 0$ have not been included in the regression analysis.

The temperature dependence of the $Pd^{2+}/Pd(s)$ redox potential has been measured by IZATT et al. (1970) in 3.94 m $HClO_4$ in the temperature range 10 to 40°C. Extrapolating $\Delta_f H_m°$ to 3.94m $HClO_4$ can be achieved using the SIT model (see equation (IX.72) on page 412 of GRENTHE et al. (1997)) with an interaction coefficient $\varepsilon_L(Pd^{2+}, ClO_4^-) \approx \varepsilon_L(Mg^{2+}, Cl^-) = -1.2 \cdot 10^{-3}$ kg·K^{-1}·mol^{-1} (note that ε_L is the temperature derivative of the usual SIT ε). This results in $\Delta_r H_m = -\Delta_f H_m = -175.9$ kJ·mol^{-1}. Taking this value and $\log_{10}K$ at 3.94 m $HClO_4$ from our regression analysis, the temperature dependence can be predicted in the temperature range 10 to 40°C by the van't Hoff approximation, i.e. $\Delta_r H_m = $ constant. As can be seen in Fig. 5.14.2, the predictions are compatible with the measurements.
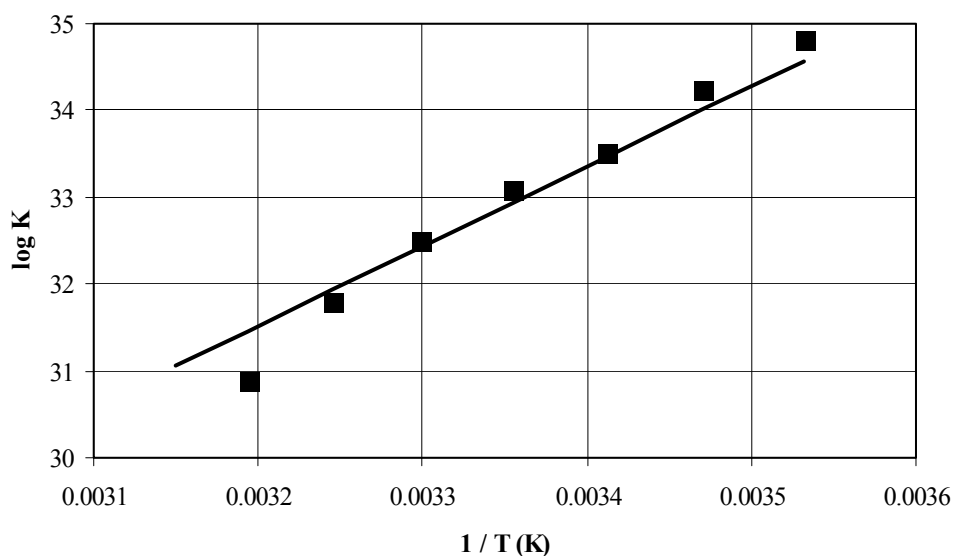
Fig. 5.14.2: Plot of $\log_{10}K$ versus reciprocal temperature for the reaction $Pd^{2+} + 2e^- \Leftrightarrow Pd(s)$. The experimental data in 3.94 m $HClO_4$ have been taken from IZATT et al. (1970) (see Table 5.14.1). The straight line has been calculated using $\Delta_f G_m°$ and $\Delta_f H_m°$ for Pd^{2+} as recommended in this review.

5.14.3 (Hydr)oxide compounds and complexes

5.14.3.1 Aqueous palladium hydroxide complexes

Here we agree with the discussion and conclusions of LOTHENBACH et al. (1999) which reads as follows:

"The Pd^{2+} aqua ion is a fairly strong acid: Non-complexing solutions of Pd^{2+} are stable at pH = 0 but start hydrolysing at pH $\approx$ 0.7 (WANNER 1984). However, the reproducibility of the visible absorption spectra around pH $\approx$ 0.7 and higher is poor, indicating that the reaction may not be a simple, mononuclear hydrolysis reaction leading to $PdOH^+$, $Pd(OH)_2$(aq), etc. In contrast, the hydrolysis of Pd^{2+} most probably involves polynuclearisation and the subsequent formation of colloidal species. Papers reporting hydrolysis constants of Pd^{2+} are thus to be regarded with great care. The published hydrolysis data of IZATT et al. (1967) and NABIVANETS and KALABINA (1970) are unreliable. WOOD (1991) observed an increase of the solubility of Pd metal at pH values above 11, but the solution composition varied strongly. On this basis it is not possible to select any hydrolysis constants for palladium(II)."

The situation is still the same, no reliable potentiometric or spectroscopic study concerning Pd hydrolysis has come to our attention until the final stage of this review (Dec. 2000). However, after

completion and publication of the report by LOTHENBACH et al. (1999), an extensive solubility study of amorphous Pd(OH)$_2$ has been published by VAN MIDDLESWORTH & WOOD (1999). These new experimental solubility data, together with a re-appraisal of older data by WOOD (1991), enabled us to estimate palladium hydrolysis constants relevant for modelling of palladium solubility in groundwater and cement porewater (see following section).

5.14.3.2   Solid palladium(II)-oxide/hydroxide

Here also we agree with the discussion and conclusions of LOTHENBACH et al. (1999) concerning the publications up to the early nineties:

In the presence of oxygen Pd(cr) is oxidised to PdO(cr) at 600°C. In solutions which contain Pd(II), an amorphous, yellow-brown palladium-oxide-hydrate precipitates, PdO·H$_2$O(precip) or Pd(OH)$_2$ (precip) (GLEMSER & PEUSCHEL 1955). In the absence of water, Pd(OH)$_2$(precip) dehydrates to PdO(cr) above 90°C, while in the presence of water above 100°C, a PdO(s) solid with disturbed lattice is produced, indicating the incorporation of H$_2$O in the lattice (GLEMSER & PEUSCHEL 1955).

The standard Gibbs molar energy of formation of PdO(s) has been determined at 700 - 1000 K. These thermochemical data can be extrapolated to 25°C and subsequently interpreted in terms of a solubility product. However, the phase precipitated from aqueous solution is PdO·H$_2$O(precip) or Pd(OH)$_2$(precip) and not PdO(cr). Hence, no thermochemical data for PdO(cr) are included in our database.

Only few experimental determinations of the solubility of Pd(OH)$_2$(precip) in aqueous solutions have been published.

NABIVANETS & KALABINA (1970) measured a constant Pd(II) concentration of $4 \cdot 10^{-6}$ M between pH 3 and 11 in 0.1M perchlorate media, corresponding to log$K$ = -5.4 for the reaction Pd(OH)$_2$(precip) $\Leftrightarrow$ Pd(OH)$_2$(aq). They did not indicate any detection limit and LOTHENBACH et al. (1999) suspect that the measured minimum Pd(II) concentration reflects the detection limit of the analytical method used by NABIVANETS & KALABINA (1970).

WOOD (1991) determined a constant Pd(II) concentration of approximately $9 \cdot 10^{-8}$ M between pH 8 and 11 in diluted solutions. Unfortunately, Wood (1991) was not able to show whether Pd(s), which he used as a starting material, or Pd(OH)$_2$(precip), which he expected based on the Eh measurements, was the solubility limiting phase present. However, it is interesting to note that above pH 12 the Pd(II) concentration curves determined by both, NABIVANETS & KALABINA 1970) and WOOD (1991), agree well.

VAN MIDDLESWORTH & WOOD (1999) measured the solubility of amorphous $Pd(OH)_2(am)$ in $NaClO_4$ over a wide range of parameters ($0 \leq pH \leq 12$, $0.1m \leq [NaClO_4] \leq 1.0m$, $25°C \leq Temp \leq 70°C$). As can be seen in Fig. 5.14.3, a synopsis of all experimental data of VAN MIDDLESWORTH & WOOD (1999) in $NaClO_4$, a quite consistent overall pattern emerges. In the range $3 \leq pH \leq 10$ the measured Pd concentrations are independent of pH, and no significant ionic strength or temperature dependence can be detected. We can safely assume that dissolved Pd does not form polynuclear species at concentrations of $[Pd] \leq 10^{-7}$ M. Hence, the equilibrium is

$$Pd(OH)_2(am) \iff Pd(OH)_2(aq)$$
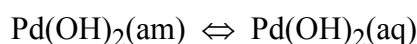
$$\log_{10}{}^*K_{s,2} = -7.3 \pm 0.5$$

Such an equilibrium involving only neutral species is expected to exhibit very small variation with ionic strength and temperature, and thus, $\log_{10}{}^*K_{s,2} \approx \log_{10}{}^*K_{s,2}°$.

At pH < 3 the measured Pd concentration increases with decreasing pH. Again, no dependence on ionic strength and temperature can be detected. At Pd(II) concentrations of less than 10^{-6}M we do not expect that polynuclear Pd species will dominate. Thus, most probably this effect is due to the equilibrium

$$Pd(OH)_2(am) + H^+ \iff PdOH^+ + H_2O(l)$$

or to

$$Pd(OH)_2(am) + 2 H^+ \iff Pd^{2+} + 2 H_2O(l)$$
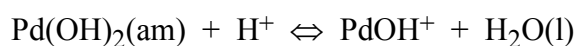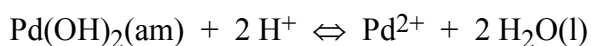
However, the scatter of experimental data does not allow a clear-cut distinction between a region of slope -1, corresponding to the former equilibrium, and a region of slope -2, corresponding to the latter equilibrium.

As a limiting case we assumed that the species $Pd(OH)_2(aq)$ does not predominate at pH < 2, and that $PdOH^+$ might be a minor species in all cases. This limiting case is compatible with

$$\log_{10}{}^*K_{s,0}° = -3.3 \pm 1$$

and, consequently, via the relation $\log_{10}{}^*\beta_2° = \log_{10}{}^*K_{s,2}° - \log_{10}{}^*K_{s,0}°$, we got an estimate of the second hydrolysis constant of Pd(II):

$$Pd^{2+} + 2 H_2O(l) \iff Pd(OH)_2(aq) + 2 H^+$$
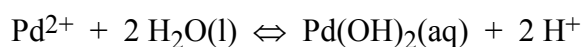
$$\log_{10}{}^*\beta_2° = -4 \pm 1$$

The effect of these estimated constants is shown in Fig. 5.14.3 as solid line (mean values) and dotted lines (minimum and maximum values according to the 95% uncertainty limits).

If we assume a rather strong first hydrolysis constant of $\log_{10}*\beta_1° = -1.5$ the Pd(II) speciation is dominated by $PdOH^+$ in the range $1.5 < pH < 3$. However, its overall effect on the measured Pd solubility is minor and remains well within the estimated uncertainty of our model comprising only $\log_{10}*K_{s,0}°$ and $\log_{10}*K_{s,2}°$ (see Fig. 5.14.3, dashed line). Considering these small effects on solubility, the scatter of experimental data, and the probably large influence of polynuclear species above 10^{-5} M Pd, we did not attempt to fit any $\log_{10}*\beta_1°$ value to the solubility data of VAN MIDDLESWORTH & WOOD (1999).

In the alkaline region above pH 10, the measured Pd(II) concentrations increase with pH. In addition, the scatter of data increases, which may partly be caused by the onset of a temperature effect on the solubility equilibria. We did not explore the temperature effects in this review. However, the data of WOOD (1991), measured at room temperature in dilute solutions, fit nicely with the new data of VAN MIDDLESWORTH & WOOD (1999), see Fig. 5.14.3. This indicates that the solubility limiting phase in the study of WOOD (1991) most probably was $Pd(OH)_2$(am), although the starting material had been Pd metal and Wood could not prove (nor disprove!) the formation of $Pd(OH)_2$(am) during his long term experiments. Thus, the results indicate that during the experiments of WOOD (1991) the Pd metal particles underwent surface oxidation, with the formation of a $Pd(OH)_2$(am) coating. Appraising all solubility data of WOOD (1991) and VAN MIDDLESWORTH & WOOD (1999) in the alkaline region we assumed that the increase of Pd solubility with pH commences somewhere in the region $10.5 < pH < 12.5$. This is compatible with the equilibrium

$$Pd^{2+} + 3\,H_2O(l) \Leftrightarrow Pd(OH)_3^- + 3\,H^+$$

$$\log_{10}*\beta_3° = -15.5 \pm 1$$

The effect of this estimated constant at pH > 10 is shown in Fig. 5.14.3 as solid line (mean values) and dotted lines (minimum and maximum values according to the 95% uncertainty limits).

The existence of the species $Pd(OH)_4^{2-}$ in concentrated NaOH solutions can be inferred from a crystal structure analysis of $Ba[Pd(OH)_4]\cdot H_2O$ (ZAITSEV et al. 1991). Two data points of WOOD (1991) measured at pH 13.7 are compatible with $\log_{10}*\beta_4 = -29$, indicating that $Pd(OH)_4^{2-}$ may dominate at pH > 13.5 (dashed line in Fig. 5.14.3). However, considering the difficulties of determining pH and ionic strength effects in this region, and regarding the scatter of experimental data at pH > 10, we did not attempt to fit any $\log_{10}*\beta_4°$ value to the solubility data of WOOD

(1991). Although by neglecting the tetrahydoxo - species the Pd solubility may be underestimated at pH > 13, the error will be less than one order of magnitude.
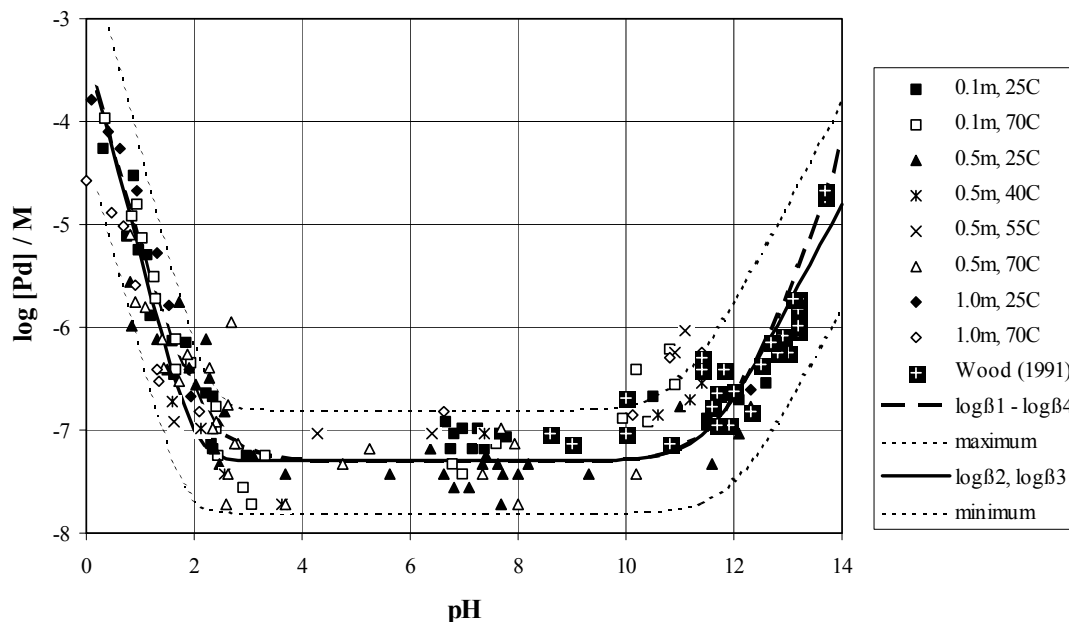
Fig. 5.14.3: Synopsis of all experimental solubility data of Pd(OH)$_2$(am) in NaClO$_4$ VAN MIDDLESWORTH & WOOD (1999), and of WOOD (1991) in dilute solutions. The lines represent different speciation models, see text for a detailed explanation.

5.14.4 Halogen compounds and complexes

Palladium is a typical B-metal ("soft" character). In contrast to the actinides, Pd^{2+} forms weak complexes with fluoride but strong complexes with chloride, bromide and iodide. Hence, no data for palladium fluoride complexes have been reported.

The bromide complexes measured by ELDING (1972) are as reliable as the corresponding chloride complexes (see following section). Also data concerning palladium iodide complexes can be found in the literature. The isotope ^{129}I is of concern in radioactive waste management. However, the total concentration of iodine and bromine in pore waters is so low that iodide and bromide complexes of palladium are not thought to be of relevance for geochemical modelling and thus, they are not included in our database.

Data for palladium chloride complexes are abundant. However, we did not review all of these published data in detail but rather rely on the judgement of LOTHENBACH et al. (1999) that the most reliable study of Pd(II) chloride complexes is the spectrophotometric investigation by ELDING (1972) in 1M HClO$_4$. The extrapolation of these data to zero ionic strength has been done by

LOTHENBACH et al. (1999) using the SIT formalism with $\Delta\varepsilon$ coefficients estimated by chemical analogy. Their results are:

$$Pd^{2+} + Cl^- \Leftrightarrow PdCl^+ \qquad \log_{10}\beta_1° = \; 5.1 \pm 0.2 \qquad \Delta\varepsilon = -0.21$$

$$Pd^{2+} + 2\,Cl^- \Leftrightarrow PdCl_2(aq) \qquad \log_{10}\beta_2° = \; 8.3 \pm 0.2 \qquad \Delta\varepsilon = -0.58$$

$$Pd^{2+} + 3\,Cl^- \Leftrightarrow PdCl_3^- \qquad \log_{10}\beta_3° = 10.9 \pm 0.2 \qquad \Delta\varepsilon = -0.43$$

$$Pd^{2+} + 4\,Cl^- \Leftrightarrow PdCl_4^{2-} \qquad \log_{10}\beta_4° = 11.7 \pm 0.2 \qquad \Delta\varepsilon = -0.56$$
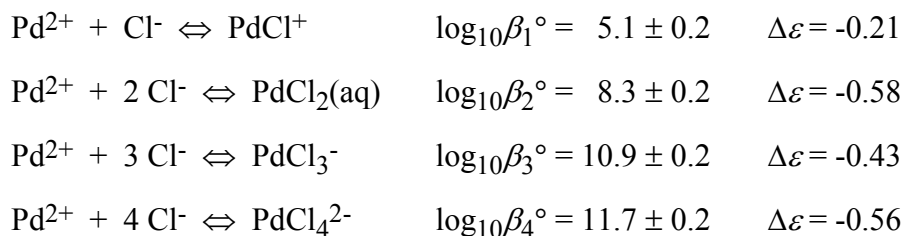
At least one additional check can be made on the validity of the SIT extrapolation procedure. The stepwise stability constant $\log_{10}K_4$ has been investigated by LEVANDA (1968) in 1 - 4M LiClO$_4$. For this constant LOTHENBACH et al. (1999) derive from the data of ELDING (1972):

$$PdCl_3^- + Cl^- \Leftrightarrow PdCl_4^{2-} \qquad \log_{10}K_4° = 0.83 \qquad \Delta\varepsilon = -0.13$$
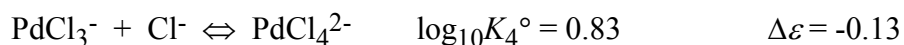
A regression analysis comprising the data of LEVANDA (1968) and ELDING (1972) gives (see Fig. 5.14.4)

$$\log_{10}K_4° = 0.85 \pm 0.05 \qquad \Delta\varepsilon = -0.13 \pm 0.02$$

The excellent agreement of these results adds some confidence in the extrapolation procedure and the recommended values for palladium(II) chloride complexes.
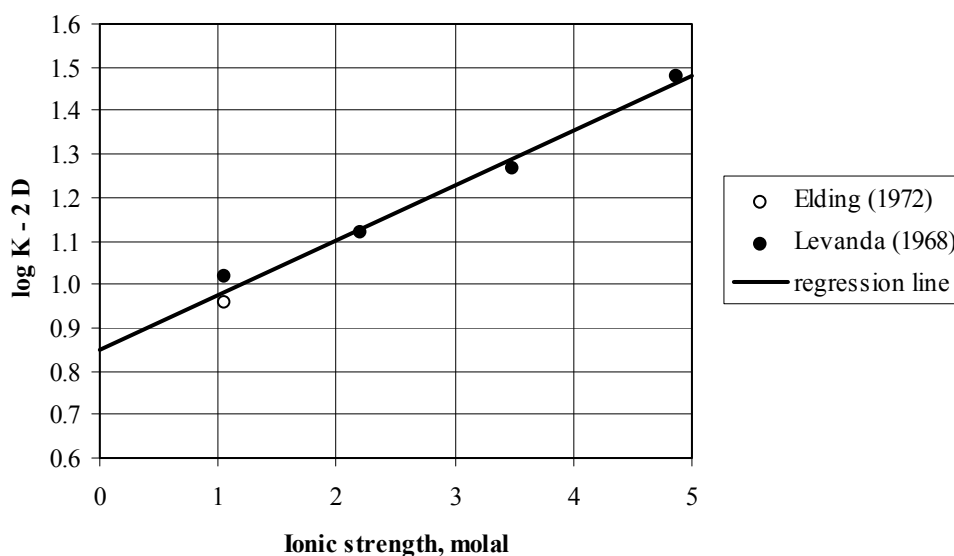
Fig. 5.14.4:   Plot of $\log_{10}K - 2D$ versus I_m for the reaction $PdCl_3^- + Cl^- \Leftrightarrow PdCl_4^{2-}$ at 25°C. The straight line shows the result of the linear regression: $\Delta\varepsilon = -0.13 \pm 0.02$; $\log_{10}K_4° = 0.85 \pm 0.05$.

Several hydrolysis studies of Pd(II) have been carried out in seawater. In seawater hydrolysis of Pd(II) (more correctly: $PdCl_4^{2-}$) starts at pH values between 7 and 8 (KUMP & BYRNE 1989). From the spectroscopic work of KUMP & BYRNE (1989), LOTHENBACH et al. (1999) derived a constant for the formation of $PdCl_3OH^{2-}$, and a limiting constant for the formation of $PdCl_2(OH)_2^{2-}$, both from $PdCl_4^{2-}$:

$$PdCl_4^{2-} + H_2O(l) \Leftrightarrow PdCl_3OH^{2-} + Cl^- + H^+ \qquad \log_{10}{}^*K° = -9.2 \pm 0.3$$

$$PdCl_4^{2-} + 2\,H_2O(l) \Leftrightarrow PdCl_2(OH)_2^{2-} + 2\,Cl^- + H^+ \qquad \log_{10}{}^*K° \leq -18.7$$
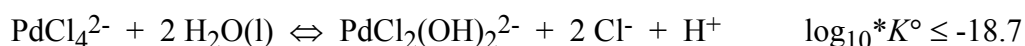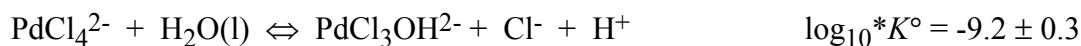
Most recently, BYRNE and YAO (2000) provided a new quantitative assessment of the first equilibrium. Their spectrophotometric measurements in 0.5 M NaCl result in a constant of $\log_{10}{}^*K° = -9.25$ (extrapolated to $I = 0$ by BYRNE & YAO (2000)). This result is in excellent agreement with the value derived by LOTHENBACH et al. (1999) from the KUMP & BYRNE (1989) data.

Note that VAN MIDDLESWORTH & WOOD (1999) did solubility measurements of $Pd(OH)_2$(am) in KCl solutions and concluded from their results that the complex formation of $PdCl_3OH^{2-}$ should be two orders of magnitude stronger than inferred from the work of KUMP & BYRNE (1989). However, BYRNE & YAO (2000) showed that in concentrated chloride solutions the solubility limiting solid is no longer $Pd(OH)_2$(s) but a solid solution $PdCl_x(OH)_{2-x}$(s). In the case of 0.5 M NaCl, BYRNE & YAO (2000) estimated a composition of $PdCl_{0.27}(OH)_{1.73}$(s). Hence, Pd solubility data in chloride solutions cannot be interpreted straightforwardly by assuming $Pd(OH)_2$(s) as the solubility limiting phase.

5.14.5 Chalcogen compounds and complexes

5.14.5.1 Palladium sulphides

For a detailed evaluation and discussion of literature data on sulphide compounds and complexes see THOENEN (2002). The following summary applies for palladium (see chapter 5.19.9):

Vysotskite, PdS(cr), is the only pure Pd-sulphide mineral. PdS_2(s) and Pd_4S(s) have been synthesised at high temperatures. Only a few low temperature solubility studies of PdS(s) have been performed, they are either inconclusive or unreliable. None of the data for Pd-sulphide solids in PEARSON et al. (1992) could be included in the database update.

Although several palladium bisulphide complexes such as $Pd(HS)^+$, $Pd(HS)_2$(aq), $Pd(HS)_3^-$ and $Pd(HS)_4^{2-}$ have been discussed in the literature, there is a lack of trustworthy low temperature data (see THOENEN (2002) for a discussion) and none can be recommended.

5.14.5.2   Palladium sulphates

An aqueous palladium sulphate complex has been reported by J ACKSON & P ANTONY (1971). Their polarographic study of the system Pd(II) sulphate - Pd(cr) in 0.2 M $HClO_4$ has been interpreted in terms of the equilibrium $Pd^{2+} + 2\ SO_4^{2-} \Leftrightarrow Pd(SO_4)_2^{2-}$ with $\log_{10}\beta_2 = 3.16 \pm 0.15$. This value is the source of the number found in P EARSON et al. (1992), extrapolated to zero ionic strength using the Davies equation with a parameter 0.3: $\log_{10}\beta_2° = 4.16$. However, the small uncertainty given in J ACKSON & P ANTONY (1971) is misleading. The authors themselves state that "the result is tentative but no previous value appears to have been reported for the complex". In the same paper J ACKSON & P ANTONY (1971) report a Pd^{2+}/Pd(s) redox potential with a very large uncertainty, although, by chance, the number fits nicely in the overall picture (see Fig. 5.14.1 and Table 5.14.1). In addition, J ACKSON & P ANTONY (1971) studied Pd(II) chloride complexation by the same method as used in their Pd(II) sulphate work and reported stability constants more than two orders (!) of magnitude lower than all other studies, e.g. E LDING (1972).

We conclude that the stability constant reported by J ACKSON & P ANTONY (1971) is very uncertain, to say the least. No other study about aqueous palladium sulphate complexation is known to us. Thus, we decided to remove this number from our database.

5.14.6   Group 15 compounds and complexes

5.14.6.1   Nitrogen compounds and complexes

No thermodynamic data have been reported concerning palladium nitrate compounds and complexes. $Pd(NO_3)_2$(s) is a commercially available soluble salt. Pd(II) nitrate complexes are expected to be rather weak. Hence, palladium nitrate compounds and complexes may not be relevant for the modelling of environmental systems.

Aqueous nickel amine complexes are very stable and they can be relevant for modelling work concerning the degradation products of anion exchange resins in a repository (V AN L OON & H UMMEL 1999). R ASMUSSEN & J ØRGENSEN (1968) determined the consecutive formation constants of all four amino complexes of Pd(II) using visible absorption spectroscopy. This study is reliable and can be recommended (L OTHENBACH et al. 1999). Due to the isocoulombic equilibria, the ionic strength dependence will be very small, and the constants reported by R ASMUSSEN & J ØRGENSEN (1968) for 1M $NaClO_4$ are thus recommended at any ionic strength with an uncertainty of ±0.2 (L OTHENBACH et al. 1999):

$$Pd^{2+} + n\ NH_3(aq) \Leftrightarrow Pd(NH_3)_n^{2+}$$

$$\log_{10}\beta_1° \ (n = 1, 298.15\ K) \ = \ 9.6 \pm 0.2$$
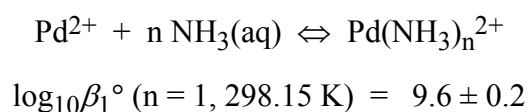
$$\log_{10}\beta_2° \ (n = 2, 298.15 \ K) \ = \ 18.5 \pm 0.2$$

$$\log_{10}\beta_3° \ (n = 3, 298.15 \ K) \ = \ 26.0 \pm 0.2$$

$$\log_{10}\beta_4° \ (n = 4, 298.15 \ K) \ = \ 32.8 \pm 0.2$$

It is very likely that mixed ammonia hydroxo complexes are formed in the Pd(II) - H_2O - NH_3 system. A palladium-ammonia-dihydroxo compound, $Pd(NH_3)_2(OH)_2(s)$, named Palladamin, is known since the middle of the 19th century (MÜLLER 1853, GMELIN 1942). However, no thermodynamic data, neither about solid compounds nor about aqueous complexes have been reported. For a detailed discussion and estimates of maximum stabilities of such mixed complexes see VAN LOON & HUMMEL (1999).

5.14.6.2 Phosphorous compounds and complexes

No thermodynamic data have been reported concerning palladium phosphate compounds and complexes.

5.14.7 Group 14 compounds and complexes

5.14.7.1 Palladium carbonates

No thermodynamic data have been reported concerning palladium carbonate compounds and complexes.

It has been argued by LOTHENBACH et al. (1999) "that carbonate complexes of Pd(II) may simply not form at all because of the enormous competition by hydroxide". On the other hand, mixed palladium carbonate compounds have been reported (GMELIN 1942). For example, the above mentioned Palladamin (see 5.14.6.1) is stable only in a CO_2-free atmosphere. Its solution, as well as the crystalline solid, takes up CO_2 rapidly, forming $Pd(NH_3)_2CO_3(s)$. It is remarkable in this context that to our present knowledge, the formation of pure palladium carbonate compounds has never been observed, neither in nature nor in the laboratory. The formation of mixed complexes with hard anions like carbonate, however, seems to be facilitated when at least two Pd bonds are occupied by ammonia or chloride. The long list of mixed compounds of this type described in GMELIN (1942) corroborates this general observation. The recent work concerning the solid solution $PdCl_x(OH)_{2-x}(s)$ (see section 5.14.4) also points in this direction.

Table 5.14.2 Selected palladium data.

TDB Version 05/92   **TDB Version 01/01**

Name	$\Delta_f G_m°$	$\Delta_f H_m°$	Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$S_m°$	$C_{p,m}°$	Species
	-	-	Pd(cr)	0.0	0.0	37.82	25.36	Pd(cr)
PD+2	176.5	149	Pd+2	175.8 ± 4.6	177.2 ± 4.6	-88.3		Pd^{2+}

Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Reaction
PDOH+	-1.87	0	PdOH+	-	-	$Pd^{2+} + H_2O(l) \Leftrightarrow PdOH^+ + H^+$
PDOH2	-3.80	0	Pd(OH)2	-4 ± 1		$Pd^{2+} + 2\,H_2O(l) \Leftrightarrow Pd(OH)_2(aq) + 2\,H^+$
PDOH3-	-15.94	0	Pd(OH)3-	-15.5 ± 1		$Pd^{2+} + 3\,H_2O(l) \Leftrightarrow Pd(OH)_3^- + 3\,H^+$
PDOH4-	-29.36	0		-	-	$Pd^{2+} + 4\,H_2O(l) \Leftrightarrow Pd(OH)_4^{2-} + 4\,H^+$
PDCL+	3.97	-19.832	PdCl+	5.1 ± 0.2		$Pd^{2+} + Cl^- \Leftrightarrow PdCl^+$
PDCL2	7.51	0	PdCl2	8.3 ± 0.2		$Pd^{2+} + 2\,Cl^- \Leftrightarrow PdCl_2(aq)$
PDCL3-	10.32	0	PdCl3-	10.9 ± 0.2		$Pd^{2+} + 3\,Cl^- \Leftrightarrow PdCl_3^-$
PDCL4-2	12.04	-30.543	PdCL4-2	11.7 ± 0.2		$Pd^{2+} + 4\,Cl^- \Leftrightarrow PdCl_4^{2-}$
	-	-	PdCl3OH-2	2.5 ± 0.3		$Pd^{2+} + 3\,Cl^- + H_2O(l) \Leftrightarrow PdCl_3OH^{2-} + H^+$
	-	-	PdCl2(OH)2-2	< -7.0		$Pd^{2+} + 2\,Cl^- + 2\,H_2O(l) \Leftrightarrow PdCl_2(OH)_2^{2-} + 2\,H^+$
PDBR+	7.22	0		-	-	$Pd^{2+} + Br^- \Leftrightarrow PdBr^+$
PDBR3-	12.06	0		-	-	$Pd^{2+} + 3\,Br^- \Leftrightarrow PdBr_3^-$
PDBR4-2	13.78	-47.698		-	-	$Pd^{2+} + 4\,Br^- \Leftrightarrow PdBr_4^{2-}$
PDI+	10.42	0		-	-	$Pd^{2+} + I^- \Leftrightarrow PdI^+$
PDI4-2	22.64	0		-	-	$Pd^{2+} + 4\,I^- \Leftrightarrow PdI_4^{2-}$
PDSO4-2	4.16	0		-	-	$Pd^{2+} + 2\,SO_4^{2-} \Leftrightarrow Pd(SO_4)_2^{2-}$

Table 5.14.2 continued

TDB Version 05/92			TDB Version 01/01			
Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Reaction
PDNH3+2	9.588	0	Pd(NH3)+2	9.6 ± 0.2		$Pd^{2+} + NH_3(aq) \Leftrightarrow PdNH_3^{2+}$
PDNH32+2	18.476	0	Pd(NH3)2+2	18.5 ± 0.2		$Pd^{2+} + 2\,NH_3(aq) \Leftrightarrow Pd(NH_3)_2^{2+}$
PDNH33+2	25.964	0	Pd(NH3)3+2	26.0 ± 0.2		$Pd^{2+} + 3\,NH_3(aq) \Leftrightarrow Pd(NH_3)_3^{2+}$
PDNH34+2	32.752	0	Pd(NH3)4+2	32.8 ± 0.2		$Pd^{2+} + 4\,NH_3(aq) \Leftrightarrow Pd(NH_3)_4^{2+}$

Name	$\log_{10}K_{s,0}°$	$\Delta_r H_m°$	Name	$\log_{10}K_{s,0}°$	$\Delta_r H_m°$	Reaction
PD.METAL	-30.93	148.95	Pd(cr)	-30.8 ± 0.8	177.2 ± 4.6	$Pd(cr) \Leftrightarrow Pd^{2+} + 2\,e^-$
PD(OH)2S	-1.6	-6.6	Pd(OH)2(s)	-3.3 ± 1		$Pd(OH)_2(cr) + 2\,H^+ \Leftrightarrow Pd^{2+} + 2\,H_2O(l)$
PDO	-4.4	-12.3	-	-		$PdO(cr) + 2\,H^+ \Leftrightarrow Pd^{2+} + H_2O(l)$
PDSS	-46.391	46.2	-	-		$PdS(s) + H^+ \Leftrightarrow Pd^{2+} + HS^-$
PDS2	-69.351	79.0	-	-		$PdS_2(s) + 2\,H^+ + 2\,e^- \Leftrightarrow Pd^{2+} + 2\,HS^-$
PD4S	-138.471	152.6	-	-		$Pd_4S(s) + H^+ \Leftrightarrow 4\,Pd^{2+} + HS^- + 6\,e^-$

5.14.8   References

BAEYENS, B., MCKINLEY, I.G. (1989): A PHREEQE Database for Pd, Ni and Se. PSI Bericht Nr. 34, Paul Scherrer Institut, Villigen, Switzerland.

BYRNE, R.L., YAO, W. (2000): Formation of palladium(II) hydroxychloride complexes and precipitates in sodium chloride solutions and seawater. Geochim. Cosmochim. Acta, 64, 4153-4156.

ELDING, L.I. (1972): Palladium(II) Halide Complexes. I. Stabilities and Spectra of palladium(II) Chloro and Bromo Aqua Complexes. Inorganica Chimica Acta, 6, 647-651.

GLEMSER, O., PEUSCHEL, G. (1955): Beitrag zur Kenntnis des Systems PdO/H_2O. Zeitschrift für anorganische und allgemeine Chemie, 281, 44-53.

GMELIN, L. (1942): Gmelins Handbuch der Anorganischen Chemie, Palladium. Lieferung 2, System-Nummer 65, Verlag Chemie GmbH, Weinheim/ Bergstrasse (Photomechanischer Nachdruck 1968).

GRENTHE, I., PLYASUNOV, A.V., SPAHIU, K. (1997): Estimation of Medium Effects on Thermodynamic Data. In: GRENTHE, I., PUIGDOMÈNECH, I. (eds.): Modelling in Aquatic Chemistry, OECD Nuclear Energy Agency, Paris, pp.325-426.

IZATT, R.M., EATOUGH, D., CHRISTENSEN, J.J. (1967): A Study of Pd^{2+}(aq) Hydrolysis. Hydrolysis Constants and the Standard Potential for the Pd, Pd^{2+} Couple. Journal of the Chemical Society, Section A, 1301-1304.

IZATT, R.M., EATOUGH, D., MORGAN, C.E., CHRISTENSEN, J.J. (1970): Half Cell Potential of the Pd,Pd^{2+} Couple in 3.94-molal Perchloric Acid and the Entropy of Pd^{2+}(aq). Journal of the Chemical Society, Section A, 2514-2515.

JACKSON, E., PANTONY, D.A. (1971): Investigations in platinum metal group electrochemistry: II The Pd(II)-Pd° reduction. Journal of Applied Electrochemistry, 1, 283-291.

KUMP, L.R., BYRNE, R.H. (1989): Palladium Chemistry in Seawater. Environ. Sci. Technol., 23, 663-665.

LEVANDA, O.G. (1968): Influence of Ionic Strength on the Stability Constant of the Tetrachloropalladate(II) Ion in Water. Russian Journal of Inorganic Chemistry, 13, 1707-1708.

LEVANDA, O.G., MOISEEV, I.I., VARGAFTIK, M.N. (1968): Potentiometric investigation of complexing between palladium(II) and chloride ions. Bulletin of the Academy of Sciences of the USSR 2237-2239 (translated from: Izvestiya Akademii Nauk USSR, Seriya Khimicheskaya 2368-2370).

LOTHENBACH, B., OCHS, M., WANNER, H., YUI, M. (1999): Thermodynamic Data for the Speciation and Solubility of Pd, Pb, Sn, Sb, Nb and Bi in Aqueous Solution. LNC TN8400 99-011, Japan Nuclear Cycle Development Institute, Ibaraki, Japan.

MÜLLER, H. (1853): Ueber die Palladamine. Liebigs Annalen der Chemie, 86, 341-368.

NABIVANETS, B.I., KALABINA, L.V. (1970): State of Palladium(II) in Perchlorate Solutions. Russian Journal of Inorganic Chemistry, 15, 818-821.

PEARSON, F.J., BERNER, U., HUMMEL, W. (1992): Nagra Thermochemical Data Base II. Supplemental Data 05/92. Nagra Technical Report NTB 91-18, Nagra, Wettingen, Switzerland, 284 p.

RASMUSSEN, L., JØRGENSEN, C.K. (1968) : Palladium(II) Complexes I. Spectra and Formation Constants of Ammonia and Ethylenediamine Complexes. Acta Chemica Scandinavica, 22, 2313-2323.

SASSANI, D.C., SHOCK, E.L. (1998): Solubility and transport of platinum-group elements in supercritical fluids: Summary and estimates of thermodynamic properties for ruthenium, rhodium, palladium, and platinum solids, aqueous ions, and complexes to 1000°C and 5 kbar. Geochim. Cosmochim. Acta, 62, 2643-2671.

TEMPLETON, D.H., WATT, G.W., GARNER, C.S. (1943): The Formal Electrode Potentials of Palladium in Aqueous Hydrochloric and Perchloric Acid Solutions. Stability of Chloropalladite Ion. Journal of the American Chemical Society, 65, 1608-1612.

THOENEN, T. (2002): Chemical Thermodynamics of Sulfide in Aqueous Systems. PSI Report, Paul Scherrer Institut, Villigen, Switzerland. In preparation.

VAN LOON, L.R., HUMMEL, W. (1999): The Degradation of Strong Basic Anion Exchange Resins and Mixed Bed Ion Exchange Resins. Effect of Degradation Products on Radionuclide Speciation. Nuclear Technol., 128, 388-401.

VAN MIDDLESWORTH, J.M., WOOD, S.A. (1999): The stability of palladium(II) hydroxide and hydroxy-chloride complexes: An experimental solubility study at 25-85°C and 1 bar. Geochim. Cosmochim. Acta, 63, 1751-1765.

WAGMAN, D.D., EVANS, W.H., PARKER, V.B., SCHUMM, R.H., HALOW, I., BAILEY, S.M., CHURNEY, K.L., NUTTALL, R.L. (1982): The NBS tables of chemical thermodynamic properties. J. Phys. Chem. Ref. Data, Vol. 11, Suppl. 2.

WANNER, H. (1984): Bildung und Hydrolyse von Palladium-Komplexen mit Pyridin, 2,2'-Bipyridil and 1,10-Phenantrolin. Ph.D. Dissertation, ETH Nr. 7628, Zürich, Switzerland.

WOOD, S. (1991): Experimental determination of the hydrolysis constants of Pt^{2+} and Pd^{2+} at 25°C from solubility of Pt and Pd in aqueous hydroxide solutions. Geochim. Cosmochim. Acta, 55, 1759-1767.

ZAITSEV, B.E., IVANOV-EMIN, B.N., PETRISHCHEVA, L.P., IL'INETS, A.M., BATURIN, N.A., REGEL, L.L., DOLGANEV, V.P. (1991): Preparation and structure of alkaline-earth metal hydroxopalladates(II). Russian Journal of Inorganic Chemistry, 36, 74-77.

5.15 Plutonium

All information on plutonium reported in this section was taken (in large parts verbatim) from the NEA review of the "Chemical Thermodynamics of Neptunium & Plutonium" by LEMIRE et al. (2001). The data selected for the database update are listed in Table 5.15.3 at the end of this section.

Several data included in our update deviate from the recommendations by LEMIRE et al. (2001) and are marked with boldface type in Table 5.15.3.

5.15.1 Elemental plutonium

Plutonium metal, liquid and gas are not relevant under environmental conditions and are therefore not included in the database. The heat capacity and third-law entropy of Pu(cr, α), however, are included, as they are used for the calculation of certain thermodynamic reaction properties. The selected values are:

$$C_{p,\mathrm{m}}°(\mathrm{Pu, cr, }\alpha\mathrm{, 298.15\ K}) = (31.49 \pm 0.40)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$S_{\mathrm{m}}°(\mathrm{Pu, cr, }\alpha\mathrm{, 298.15\ K}) = (54.46 \pm 0.80)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

5.15.2 Plutonium aqua ions

Plutonium in aqueous solution exists in the oxidation states III, IV, V, VI, and VII. In acidic solutions, the reduction potentials of the Pu^{4+}/Pu^{3+}, PuO_2^+/Pu^{4+}, and PuO_2^{2+}/Pu^{4+} couples lie relatively close to each other and multiple oxidation states can coexist in solution. Therefore, the determination of thermodynamic data for specific redox couples may be hampered by the presence of plutonium in redox states unrelated to those under investigation. In solutions less than 1 M in acid, Pu(IV) undergoes slow disproportionation to Pu(III) and Pu(VI), whereas Pu(V) disproportionates to Pu(III), Pu(IV), and Pu(VI) in acidic solutions. The selected thermodynamic data for Pu^{3+}, Pu^{4+}, PuO_2^+, and PuO_2^{2+} are strongly connected, and there is only a minimum amount of redundancy to provide confirmation for these values.

Pu(VII) is stable only in strongly basic solution, but there are no recommended data for any heptavalent plutonium species, complexes or compounds.

In our database update, PuO_2^{2+} is the primary master species. The secondary master species Pu^{3+}, Pu^{4+}, and PuO_2^+ are related to PuO_2^{2+} by the following redox reactions:

$$PuO_2^{2+} + 4H^+ + 3e^- \Leftrightarrow Pu^{3+} + 2H_2O(l) \qquad (cf.\ \text{Section 5.15.2.1})$$

$$PuO_2^{2+} + 4H^+ + 2e^- \Leftrightarrow Pu^{4+} + 2H_2O(l) \qquad (cf.\ \text{Section 5.15.2.3})$$

$$PuO_2^{2+} + e^- \Leftrightarrow PuO_2^+ \qquad\qquad (cf. \text{ Section 5.15.2.2})$$
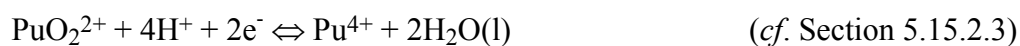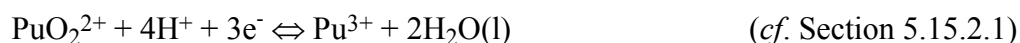
The detailed discussion by LEMIRE et al. (2001) of the data derivation and selection process for PuO_2^{2+}, PuO_2^+, Pu^{4+}, and Pu^{3+} (given in their Chapter 16) is very intricate and hard to follow.

In order to guide the reader through our condensed version of Chapter 16 presented below, schematic representations of the data derivation process for each of the plutonium aqua ions are shown in Figures 5.15.1 to 5.15.4.

5.15.2.1 PuO_2^{2+}

Derivation of $\log_{10}{}^*K°(5.15.1, 298.15\ K)$ and $\Delta_f G_m°(PuO_2^{2+}, 298.15\ K)$

$\Delta_r G_m(5.15.1, 1\ M\ HClO_4, 298.15\ K)$ for the reaction

$$PuO_2^{2+} + 4H^+ + 3e^- \Leftrightarrow Pu^{3+} + 2H_2O(l) \qquad\qquad (5.15.1)$$
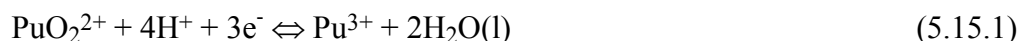
was calculated by combining the Gibbs free energy of reaction for the Pu^{4+} disproportionation equilibrium

$$3Pu^{4+} + 2H_2O(l) \Leftrightarrow PuO_2^{2+} + 2Pu^{3+} + 4H^+ \qquad\qquad (5.15.2)$$

with the Gibbs free energy of reaction corresponding to the Pu^{4+}/Pu^{3+} redox potential of

$$Pu^{4+} + e^- \Leftrightarrow Pu^{3+} \qquad\qquad (5.15.3)$$
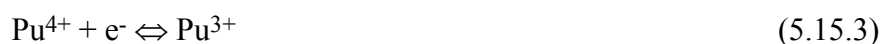
$\Delta_r G_m(5.15.1, 1\ M\ HClO_4, 298.15\ K)$ was then extrapolated to $I = 0$ according to SIT. In the absence of reliable values for the interaction coefficients of Pu^{3+} and PuO_2^{2+} with ClO_4^-, corresponding values of the homologous ions Nd^{3+} and UO_2^{2+} were used. From the resulting $\Delta_r G_m°(5.15.1, 298.15\ K)$ follows

$$\log_{10}{}^*K°(5.15.1, 298.15\ K) = (50.97 \pm 0.15)$$

$\Delta_f G_m°(PuO_2^{2+}, 298.15\ K)$ was calculated from $\Delta_r G_m°(5.15.1, 298.15\ K)$ together with the selected $\Delta_f G_m°(Pu^{3+}, aq, 298.15\ K)$, *cf.* Section 5.15.2.4, and CODATA auxiliary data:

$$\Delta_f G_m°(PuO_2^{2+}, 298.15\ K) = - (762.4 \pm 2.8)\ kJ \cdot mol^{-1}$$

Derivation of $\Delta_f H_m°(PuO_2^{2+}, 298.15\ K)$

$\Delta_f H_m°(PuO_2^{2+}, 298.15\ K)$ was calculated from an average value for $\Delta_r H_m°(298.15\ K)$ for

$$Pu^{3+} + 2H_2O(l) \Leftrightarrow PuO_2^{2+} + H^+ + 3/2H_2(g) \qquad\qquad (5.15.4)$$

(5.15.3)		**3 Pu³⁺**	⇔	**3 Pu⁴⁺**	**+ 3 e⁻**			$E^{•'}$ → ① $\Delta_r G_m$
(5.15.2)		**3 Pu⁴⁺ + 2 H₂O(l)**	⇔	**PuO₂²⁺ + 2 Pu³⁺ + 4 H⁺**				② $\Delta_r G_m$

| (5.15.1) | | **Pu³⁺ + 2 H₂O(l)** | ⇔ | **PuO₂²⁺ + 4 H⁺ + 3 e⁻** | | | ① + ② → $\Delta_r G_m$ ↓ SIT ↓ |

$\Delta_f G_m°$:

| $\Delta_f G_m°(Pu^{3+})$ see Fig. 5.15.4 | $\Delta_f G_m°(H_2O, l)$ CODATA | ③ $\Delta_f G_m°(PuO_2^{2+})$ calculated | 0 | 0 | $\Delta_r G_m°$ |

$\log_{10} {}^*K°$:

$\log_{10} {}^*K°$

| (5.15.4) | | **Pu³⁺ + 2 H₂O(l)** | ⇔ | **PuO₂²⁺ + H⁺ + 1.5 H₂(g)** | | | $\Delta_r H_m$ assumed to be equal to ↓ |

$\Delta_f H_m°$:

| $\Delta_f H_m°(Pu^{3+})$ see Fig. 5.15.4 | $\Delta_f H_m°(H_2O, l)$ CODATA | ④ $\Delta_f H_m°(PuO_2^{2+})$ calculated | 0 | 0 | $\Delta_r H_m°$ |

| (5.15.5) | **Pu(α, cr) + 2 H⁺ + O₂(g)** | ⇔ | **PuO₂²⁺ + H₂(g)** |

$\Delta_r H_m°$:

| 0 | 0 | 0 | ④ $\Delta_f H_m°(PuO_2^{2+})$ from above | 0 | ⑤ $\Delta_r H_m°$ calculated |

$\Delta_r G_m°$:

| 0 | 0 | 0 | ③ $\Delta_f G_m°(PuO_2^{2+})$ from above | 0 | ⑥ $\Delta_r G_m°$ calculated | ⑤ ⑥ ↓ |

$S_m°$:

| $S_m°(Pu, α, cr)$ NEA | 0 | $S_m°(O_2, g)$ CODATA | $S_m°(PuO_2^{2+})$ calculated | $S_m°(H_2, g)$ CODATA | | $\Delta_r S_m°$ |

Fig. 5.15.1: Schematic representation of the derivation and selection process of thermodynamic data for PuO₂²⁺ by LEMIRE et al. (2001).

determined from two independent calorimetric measurements in 0.5 and 1.0 M $HClO_4$ (assuming the heat of transfer to infinite dilution to be negligible) together with the selected $\Delta_f H_m°(298.15\ K)$ for Pu^{3+} (*cf.* Section 5.15.2.4) and CODATA auxiliary data:

$$\Delta_f H_m°(PuO_2^{2+}, 298.15\ K) = - (822.0 \pm 6.6)\ kJ \cdot mol^{-1}$$

Derivation of $S_m°(PuO_2^{2+}, 298.15\ K)$

$\Delta_r S_m°(5.15.5, 298.15\ K)$ for the reaction

$$Pu(cr, \alpha) + 2H^+ + O_2(g) \Leftrightarrow PuO_2^{2+} + H_2(g) \tag{5.15.5}$$
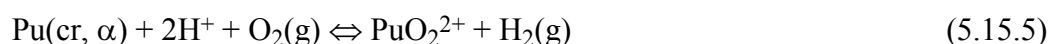
was calculated from the Gibbs-Helmholtz equation (G = H - TS) applied to reaction (5.15.5), using $\Delta_r G_m°(5.15.5, 298.15\ K)$, which is equivalent to the selected value for $\Delta_f G_m°(PuO_2^{2+}, 298.15\ K)$, and $\Delta_r H_m°(5.15.5, 298.15\ K)$, which is equivalent to the selected value for $\Delta_f H_m°(PuO_2^{2+}, 298.15\ K)$.

The standard molar entropy of PuO_2^{2+}

$$S_m°(PuO_2^{2+}, 298.15\ K) = - (71.2 \pm 22.1)\ J \cdot K^{-1} \cdot mol^{-1}$$

was then calculated from $\Delta_r S_m°(5.15.5, 298.15\ K)$ of the reaction using the selected $S_m°(Pu, cr, \alpha, 298.15\ K)$, *cf.* Section 5.15.1, and CODATA auxiliary values.

5.15.2.2 PuO_2^+

Derivation of $\log_{10}K°(5.15.7, 298.15\ K)$ and $\Delta_f G_m°(PuO_2^+, 298.15\ K)$

The standard potential of the reaction

$$PuO_2^{2+} + 1/2H_2(g) \Leftrightarrow PuO_2^+ + H^+ \tag{5.15.6}$$

was derived from formal potentials measured in 1 M $HClO_4$ which were recalculated to standard conditions using SIT. The corresponding equilibrium constant is

$$\log_{10}{}^*K°(5.15.6, 298.15\ K) = (15.82 \pm 0.09)$$

Note that the value of this constant, as well as the values for $\Delta_r G_m°(5.15.3, 298.15\ K)$ and $\Delta_r H_m°(5.15.6, 298.15\ K)$, also apply to the reaction

$$PuO_2^{2+} + e^- \Leftrightarrow PuO_2^+ \tag{5.15.7}$$

because reaction (5.15.7) can be obtained by subtracting

$$1/2H_2(g) \Leftrightarrow H^+ + e^- \tag{5.15.8}$$

from reaction (5.15.6), and because $\Delta_r G_m°$(5.15.8, 298.15 K) and $\Delta_r H_m°$(5.15.8, 298.15 K) are both equal to zero. Thus

$$\log_{10} K°(5.15.7, 298.15 \text{ K}) = (15.82 \pm 0.09)$$

$\Delta_f G_m°$(PuO_2^+, 298.15 K) was calculated from $\Delta_r G_m°$(5.15.6, 298.15 K) corresponding to the selected $\log_{10}{}^* K°$(5.15.6, 298.15 K) and from the selected $\Delta_f G_m°$(PuO_2^{2+}, 298.15 K), *cf.* Section 5.15.2.1

$$\Delta_f G_m°(PuO_2^+, 298.15 \text{ K}) = - (852.6 \pm 2.9) \text{ kJ} \cdot \text{mol}^{-1}$$

Derivation of $\Delta_f H_m°$(PuO_2^+, 298.15 K)

$\Delta_r H_m°$(5.15.6, 298.15 K) was calculated from the temperature change of the formal potential in 1 M HClO$_4$, neglecting the small heat of transfer to infinite dilution. The selected value

$$\Delta_f H_m°(PuO_2^+, 298.15 \text{ K}) = - (910.1 \pm 8.9) \text{ kJ} \cdot \text{mol}^{-1}$$

was then obtained from $\Delta_r H_m°$(5.15.6, 298.15 K) by using the selected value for $\Delta_f H_m°$(PuO_2^{2+}, 298.15 K), *cf.* Section 5.15.2.1.

Derivation of $S_m°$(PuO_2^+, 298.15 K)

$\Delta_r S_m°$(5.15.6, 298.15 K) was obtained from the Gibbs-Helmholtz equation, using $\Delta_r G_m°$(5.15.6, 298.15 K) corresponding to the selected value of $\log_{10} K°$(5.15.6, 298.15 K) and from $\Delta_r H_m°$(5.15.6, 298.15 K).

$S_m°$(PuO_2^+, 298.15 K) was then calculated from $\Delta_r S_m°$(5.15.6, 298.15 K) using the selected value for $S_m°$(PuO_2^{2+}, 298.15 K), *cf.* Section 5.15.2.1, and CODATA auxiliary data

$$S_m°(PuO_2^+, 298.15 \text{ K}) = (1 \pm 30) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

5.15.2.3 Pu^{4+}

Derivation of $\log_{10} K°$(5.15.10, 298.15 K) and $\Delta_f G_m°$(Pu^{4+}, 298.15 K)

The standard potential of the reaction

$$Pu^{4+} + 1/2H_2(g) \Leftrightarrow Pu^{3+} + H^+ \tag{5.15.9}$$

was derived from experimental determinations of the Pu^{4+}/Pu^{3+} potential in 1 M HClO$_4$, $E°'$(5.15.9,1 M HClO$_4$, 298.15 K), that were extrapolated to $I = 0$ using SIT. The selected value

$$\log_{10}{}^* K°(5.15.9, 298.15 \text{ K}) = (17.69 \pm 0.04)$$

| (5.15.7) | PuO_2^{2+} + e^- ⇔ PuO_2^+ | $\log_{10} K°$ |

$\uparrow$
identical to
$\uparrow$
$\log_{10} {}^*K°$
$\uparrow$
$E°$
$\uparrow$
SIT

| (5.15.6) | PuO_2^{2+} + 0.5 $H_2(g)$ ⇔ PuO_2^+ + H^+ | $\boxed{E^{•\prime}}$ | $\boxed{dE^{•\prime}/dT}$ |

SIT
$\downarrow$
$E°$
$\downarrow$
$\log_{10} {}^*K°$
$\downarrow$

$\Delta_r H_m = \Delta_r H_m°$
$\downarrow$

| $\Delta_f G_m°$: | $\Delta_f G_m°(PuO_2^{2+})$ see Fig. 5.15.1 | 0 | $\Delta_f G_m°(PuO_2^+)$ calculated | | ① $\Delta_r G_m°$ |

| $\Delta_f H_m°$: | $\Delta_f H_m°(PuO_2^{2+})$ see Fig. 5.15.1 | 0 | $\Delta_f H_m°(PuO_2^+)$ calculated | 0 | ② $\Delta_r H_m°$ | ① ② $\downarrow$ |

| $S_m°$: | $S_m°(PuO_2^{2+})$ see Fig. 5.15.1 | $S_m°(H_2, g)$ CODATA | $S_m°(PuO_2^+)$ calculated | 0 | $\Delta_r S_m°$ |

Fig. 5.15.2: Schematic representation of the derivation and selection process of thermodynamic data for PuO_2^+ by LEMIRE et al. (2001).

(5.15.10)   **Pu^{4+} + e$^-$ ⇔ Pu^{3+}**   **$\log_{10}K^{\bullet}$**

↑
identical to
↑
$\log_{10}{}^{*}K^{\circ}$
↑
E°
↑
SIT

(5.15.9)   **Pu^{4+} + 0.5 H$_2$(g) ⇔ Pu^{3+} + H$^+$** $\boxed{E^{\bullet\prime}}$ $\boxed{dE^{\bullet\prime}/dT}$

    ① ②

↓   ↓   ↓

① $\Delta_r G_m$(1M HClO$_4$)   ② $\Delta_r S_m$(1M HClO$_4$) $\Delta_r H_m$(1M HClO$_4$)

↓   ↓
SIT
↓

$\Delta_f G_m^{\circ}$:   [$\Delta_f G_m^{\circ}$(Pu^{4+}) calculated]   0 $\Delta_f G_m^{\circ}$(Pu^{3+}) see Fig. 5.15.4   ③ $\Delta_r G_m^{\circ}$ assumed to be equal to

↓

$\Delta_f H_m^{\circ}$:   [$\Delta_f H_m^{\circ}$(Pu^{4+}) calculated]   0 $\Delta_f H_m^{\circ}$(Pu^{3+}) see Fig. 5.15.4   0   ④ $\Delta_r H_m^{\circ}$

③ ④
↓

S_m°:   [S_m°(Pu^{4+}) calculated] S_m°(H$_2$, g) CODATA S_m°(Pu^{3+}) see Fig. 5.15.4   0 $\Delta_r S_m^{\circ}$

Fig. 5.15.3:   Schematic representation of the derivation and selection process of thermodynamic data for Pu^{4+} by LEMIRE et al. (2001).

was then calculated from the standard potential. Analogous to the PuO_2^{2+}/PuO_2^+ couple discussed above, $\log_{10}{}^*K°$(5.15.9, 298.15 K) is identical to $\log_{10}K°$(5.15.10, 298.15 K) for the reaction

$$Pu^{4+} + e^- \Leftrightarrow Pu^{3+} \qquad\qquad\qquad (5.15.10)$$

Therefore

$$\log_{10}K°(5.15.10,\ 298.15\ K) = (17.69 \pm 0.04)$$

$\Delta_r G_m°$(5.15.9, 298.15 K) was obtained from $\log_{10}{}^*K°$(5.15.9, 298.15 K) and used together with the selected value for $\Delta_f G_m°$(Pu^{3+}, 298.15 K), *cf.* Section 5.15.2.4, for the calculation of

$$\Delta_f G_m°(Pu^{4+},\ 298.15\ K) = -(478.0 \pm 2.7)\ kJ\cdot mol^{-1}$$

Pu^{4+} can be expressed in terms of the primary master species PuO_2^{2+} by subtracting reaction (5.15.10) from reaction (5.15.1), resulting in

$$PuO_2^{2+} + 4H^+ + 2e^- \Leftrightarrow Pu^{4+} + 2H_2O(l)$$
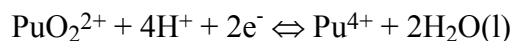
with

$$\log_{10}K°(298.15\ K) = (33.28 \pm 0.15)$$

calculated from $\log_{10}K°$(5.15.10, 298.15 K) = (17.69 ± 0.04) and $\log_{10}K°$(5.15.1, 298.15 K) = (50.97 ± 0.15).

Derivation of $\Delta_f H_m°$(Pu^{4+}, 298.15 K)

$\Delta_r G_m$(5.15.9, 1 M $HClO_4$, 298.15 K) was calculated from $E°'$(5.15.9, 1 M $HClO_4$, 298.15 K) while

$\Delta_r S_m$(5.15.9, 1 M $HClO_4$, 298.15 K) was obtained from measured temperature coefficients of the Pu^{4+}/Pu^{3+} potential.

$\Delta_r G_m$(5.15.9, 1 M $HClO_4$, 298.15 K) and $\Delta_r S_m$(5.15.9, 1 M $HClO_4$, 298.15 K) were then used for the calculation of $\Delta_r H_m$(5.15.9, 1 M $HClO_4$, 298.15 K) which was assumed to be equal to $\Delta_r H_m°$(5.15.9, 298.15 K). Finally,

$$\Delta_f H_m°(Pu^{4+},\ 298.15\ K) = -(539.9 \pm 3.1)\ kJ\cdot mol^{-1}$$

was obtained from $\Delta_r H_m°$(5.15.9, 298.15 K) and the selected $\Delta_f H_m°$(Pu^{3+}, 298.15 K), *cf.* Section 5.15.2.4.

Derivation of $S_m°(Pu^{4+}, 298.15 K)$

The standard entropy of reaction (5.15.9) was derived from $\Delta_r G_m°(5.15.9, 298.15 K)$ and $\Delta_r H_m°(5.15.9, 298.15 K)$ and was used together with $S_m°(Pu^{3+}, 298.15 K)$, *cf.* Section 5.15.2.4, and CODATA auxiliary data for the calculation of

$$S_m°(Pu^{4+}, 298.15 K) = - (414.5 \pm 10.2) \; J \cdot K^{-1} \cdot mol^{-1}$$

5.15.2.4   Pu^{3+}

Derivation of $S_m°(Pu^{3+}, 298.15 K)$

Based on the experimentally determined standard Gibbs free energy and enthalpy of the dissolution reaction

$$PuCl_3 \cdot 6H_2O(cr) \rightarrow Pu^{3+} + 3Cl^- + 6H_2O(l) \tag{5.15.11}$$
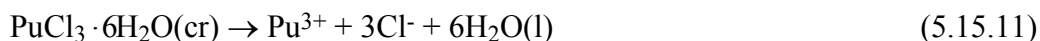
and using the Gibbs-Helmholtz equation, $\Delta_r S_m°(5.15.11, 298.15 K)$ was calculated, from which $S_m°(Pu^{3+}, 298.15 K)$ was obtained using CODATA auxiliary data and the selected estimated (!) value for $S_m°(PuCl_3 \cdot 6H_2O, cr, 298.15 K)$. Thus

$$S_m°(Pu^{3+}, 298.15 K) = - (184.5 \pm 6.2) \; J \cdot K^{-1} \cdot mol^{-1}$$

Note that $PuCl_3 \cdot 6H_2O(cr)$, is not contained in the database update.

Derivation of $\Delta_f H_m°(Pu^{3+}, 298.15 K)$

$\Delta_f H_m°(Pu^{3+}, 298.15 K)$ was derived from calorimetric measurements of the enthalpies of solution of $Pu(cr, \alpha)$ and $PuCl_3(cr)$ in $HCl(aq)$. The selected value is

$$\Delta_f H_m°(Pu^{3+}, aq, 298.15 K) = - (591.8 \pm 2.0) \; kJ \cdot mol^{-1}$$

Derivation of $\Delta_f G_m°(Pu^{3+}, 298.15 K)$

$\Delta_r S_m°(5.15.12, 298.15 K)$ for

$$Pu(cr, \alpha) + 3H^+ \Leftrightarrow Pu^{3+} + 3/2H_2(g) \tag{5.15.12}$$

was calculated from $S_m°(Pu^{3+}, 298.15 K)$ and $S_m°(Pu, cr, \alpha, 298.15 K)$, *cf.* Section 5.15.1. $\Delta_r S_m°(5.15.12, 298.15 K)$ is identical to $\Delta_f S_m°(Pu^{3+}, 298.15 K)$. The latter was used together with the selected value for $\Delta_f H_m°(Pu^{3+}, 298.15 K)$ to calculate

$$\Delta_f G_m°(Pu^{3+}, aq, 298.15 K) = - (579.0 \pm 2.7) \; kJ \cdot mol^{-1}$$

according to the Gibbs-Helmholtz equation.

(5.15.11)	$PuCl_3 \cdot 6H_2O(cr) \Leftrightarrow$	Pu^{3+}	$+$ 3 Cl⁻	$+$ 6 $H_2O(l)$	① $\Delta_r G_m^\bullet$ ② $\Delta_r H_m^\bullet$

① ②
↓

$\Delta_r S_m^\circ$

| S_m°: | $S_m^\circ(PuCl_3 \cdot 6H_2O, cr)$ **estimated** by NEA | ③ $S_m^\circ(Pu^{3+})$ calculated | $S_m^\circ(Cl^-)$ NEA | $S_m^\circ(H_2O, l)$ CODATA | |

(5.15.12)	$Pu(\alpha, cr)$ $+$ 3 H⁺ $\Leftrightarrow$	Pu^{3+}	$+1.5$ $H_2(g)$	

$\Delta_f H_m^\circ$: ④ $\Delta_f H_m^\bullet(Pu^{3+})$

| $\Delta_r S_m^\circ$: | $S_m^\circ(Pu, \alpha, cr)$ NEA | 0 | ③ $S_m^\circ(Pu^{3+})$ from above | $S_m^\circ(H_2, g)$ CODATA | $\Delta_r S_m^\circ$ calculated |

↓
identical to

⑤ $\Delta_f S_m^\circ(Pu^{3+})$ ←   ←   ←   ←

④ ⑤
↓

$\Delta_f G_m^\circ$: $\Delta_f G_m^\bullet(Pu^{3+})$

Fig. 5.15.4:   Schematic representation of the derivation and selection process of thermodynamic data for Pu^{3+} by LEMIRE et al. (2001).

5.15.3   Plutonium oxygen and hydrogen compounds and complexes

5.15.3.1   Pu(VI) hydroxide complexes

From the earliest beginnings of studies on this system in the 1940's, experimental problems have been reported that were caused by the slow kinetics of some of the hydrolysis reactions in neutral and basic solutions. This has been confirmed in later potentiometric and spectrophotometric studies and means that results from most of these studies cannot be used to determine equilibrium constants without some reservations. In addition, radiolysis is caused by the α-decay of plutonium in solution which results in species that promote the reduction of Pu(VI) in perchloric acid solution.

Identity and stability of Pu(VI) hydrolysis species were derived from solubility studies involving $PuO_2(OH)_2 \cdot H_2O(cr)$, *cf.* Section 5.15.3.5, and from spectrophotometric and potentiometric studies.

Debates have continued over the years as to whether the first hydrolysis species is the monomer or the dimer, at Pu(VI) concentrations greater than 10^{-5} mol·kg^{-1}. Much of the spectrophotometric and potentiometric data in the literature can be equally well interpreted in terms of either PuO_2OH^+ or $(PuO_2)_2(OH)_2^{2+}$ and by assuming the other hydrolysis species to be absent. However, some studies also suggest that both species coexist. It appears that the higher polymeric species, i.e. $(PuO_2)_3(OH)_5^+$ and $(PuO_2)_4(OH)_7^+$ deduced from potentiometric studies, are metastable relative to $PuO_2(OH)_2(aq)$, if they exist at all. There is also evidence for the existence of $PuO_2(OH)_4^{2-}$ and $PuO_2(OH)_3^-$, although no hydrolysis constants are known. Note that limiting values for the analogous species $NpO_2(OH)_3^-$ and $NpO_2(OH)_4^{2-}$ have been selected by LEMIRE et al. (2001).

LEMIRE et al. (2001) selected data for three hydrolysis reactions:

$$PuO_2^{2+} + H_2O(l) \Leftrightarrow PuO_2OH^+ + H^+ \qquad (5.15.13)$$

$$2\,PuO_2^{2+} + 2\,H_2O(l) \Leftrightarrow (PuO_2)_2(OH)_2^{2+} + 2\,H^+ \qquad (5.15.14)$$

$$PuO_2^{2+} + 2\,H_2O(l) \Leftrightarrow PuO_2(OH)_2(aq) + 2\,H^+ \qquad (5.15.15)$$
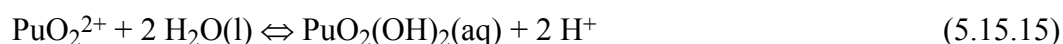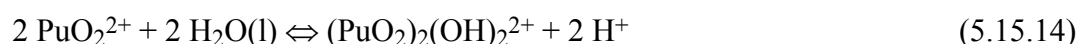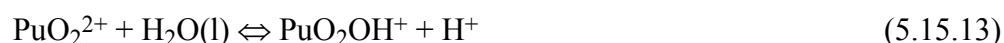
The selected constants are

$$\log_{10}{}^*\beta_1{}^\circ(5.15.13,\ 298.15\ \mathrm{K}) = -\,(5.5 \pm 0.5)$$

$$\Delta_r H_m{}^\circ(5.15.13,\ 298.15\ \mathrm{K}) = (28 \pm 15)\ \mathrm{kJ \cdot mol^{-1}}$$

$\log_{10}{}^*\beta_{2,2}{}^\circ(5.15.14,\ 298.15\ \mathrm{K}) = -\left(7.5\,{}^{+0.5}_{-1.0}\right)$, and $\log_{10}{}^*\beta_{2,1}{}^\circ(5.15.15,\ 298.15\ \mathrm{K}) = -\left(13.2\,{}^{+0.5}_{-1.5}\right)$.

For our database update, we prefer to replace the unsymmetrical by symmetrical uncertainties. Thus

$$\log_{10}{}^*\beta_{2,2}{}^\circ(5.15.14,\ 298.15\ \mathrm{K}) = -\,(7.5 \pm 1.0)$$

$$\log_{10}{}^{*}\beta_{2,1}°(5.15.15, 298.15 \text{ K}) = - (13.2 \pm 1.5)$$

5.15.3.2 Pu(V) hydroxide complexes

There are only a few studies of Pu(V) hydrolysis due to possible problems associated with disproportionation or precipitation in the pH range where hydrolysis is likely to occur. Only limiting values for the hydrolysis constant of

$$\text{PuO}_2^+ + \text{H}_2\text{O(l)} \Leftrightarrow \text{PuO}_2\text{OH(aq)} + \text{H}^+ \qquad\qquad (5.15.16)$$
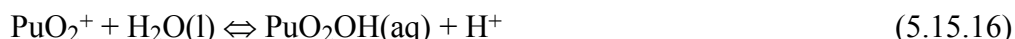
can be gained from experimental data. The selected limiting value for the first hydrolysis constant is

$$\log_{10}{}^{*}\beta_1°(5.15.16, 298.15 \text{ K}) \leq -9.73$$

based on a study using laser induced photoacoustic spectroscopy.

There is experimental evidence that Pu(V) is unlikely to disproportionate in basic solution and that significant concentrations of Pu(V) species can be found in neutral and basic aqueous solutions of plutonium.

5.15.3.3 Pu(IV) hydroxide complexes

There have been quite a number of potentiometric, solubility, extraction, and spectroscopic studies of the first hydrolysis constant of Pu(IV). Experimental observations may be time dependent because of slow oxidation, disproportionation, radiolysis, or polymerization reactions. Therefore, reliable hydrolysis constants can only be determined from studies in which the electrochemical potential was carefully controlled, or in which the equilibrium total of Pu(IV) in solution was measured, or the measurements were carried out rapidly. Spectrophotometric measurements are probably less prone to some of the possible systematic errors originating from slow disproportionation of Pu(IV). Therefore, the selected equilibrium constant for

$$\text{Pu}^{4+} + \text{H}_2\text{O(l)} \Leftrightarrow \text{PuOH}^{3+} + \text{H}^+ \qquad\qquad (5.15.17)$$

was obtained by taking the mean of three independent spectroscopic determinations in perchlorate media extrapolated to $I = 0$ using SIT

$$\log_{10}{}^{*}\beta_1°(5.15.17, 298.15 \text{ K}) = - (0.78 \pm 0.60)$$

The resulting value is the same (within the uncertainties) as those selected for the corresponding reactions involving uranium (GRENTHE et al. 1992), and neptunium (LEMIRE et al. 2001).

The value

$$\Delta_r H_m°(5.15.17, 298.15\ K) = (36 \pm 10)\ kJ \cdot mol^{-1}$$

was calculated from a spectrophotometric study of the temperature dependence of the first hydrolysis constant.

According to LEMIRE et al. (2001), none of the available studies provide good thermodynamic data for higher hydrolysis species of Pu(IV). Equilibrium measurements are difficult to obtain and radiolytic reactions can be important. The studies of Rai and coworkers (*cf.* LEMIRE et al. 2001 for references) established that at near neutral pH similar total plutonium concentrations were found regardless whether the initial solid was "$^{239}Pu(OH)_4(am)$" or $^{239}PuO_2(cr)$. The stable solution plutonium species over this solid (designated by the authors as "less crystalline") tended to be Pu(VI)[1] or Pu(V) species - only approximately 1% of the plutonium was found to be Pu(IV) and Pu(III). Rai concluded that, near neutral pH, measurements of Eh for plutonium solutions were unreliable because the potential in the system was unpoised. Therefore, at best, only a limiting value can be calculated from these studies for the stability of $^{239}Pu(OH)_4(aq)$. Calculations indicate that for an unpoised system with respect to potential, using the selected value for $\Delta_f G_m°(PuO_2, hyd, aged, 298.15\ K) = - (963.7 \pm 6.3)\ kJ \cdot mol^{-1}$ (LEMIRE et al. 2001), the value

$$\Delta_f G_m°(Pu(OH)_4, aq, 298.15\ K) = - (1387)\ kJ \cdot mol^{-1}$$

is compatible with the results of the experimental study.

If this is accepted, the values of $\log_{10}$ of the equilibrium constants for the reactions

$$MO_2(cr) + 2H_2O(l) \Leftrightarrow M(OH)_4(aq)\ \ (M = U, Np, Pu)$$
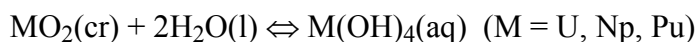
for M = U, Np, and Pu are -9.4, -19.6, and -14.9, respectively. It is surprising that the equilibrium constants for these reactions are in such poor agreement. Thus, LEMIRE et al. (2001) did not recommend any data for Pu(OH)$_4$(aq).

In contrast to LEMIRE et al. (2001) we chose to include Pu(OH)$_4$(aq) in the database update. Ignoring Pu(OH)$_4$(aq) would lead to unrealistically low solubilities for PuO$_2$(s), *cf.* Section 5.15.3.5. Based on experimental data by LIERSE & KIM (1986) ($I = 1$ M, HClO$_4$/NaClO$_4$) and RAI et al. (1999) ($I \le 0.1$ M, KOH), NECK & KIM (2001) determined log[Pu(IV)] = - (10.4 $\pm$ 0.5) in equilibrium with PuO$_2$(hyd, aged) at pH > 7 (experimental data were obtained at pH between 8 and 13). Because Pu(OH)$_4$(aq) is the dominant Pu(IV) species under these conditions, it follows that

---

[1]   Note that LEMIRE et al. (2001) wrote Pu(IV) instead of Pu(VI).

$$\log_{10}K_{s,4}(5.15.18, 298.15 \text{ K}) = -(10.4 \pm 0.5)$$

for the solubility reaction

$$PuO_2(hyd, aged) + 2H_2O(l) \Leftrightarrow Pu(OH)_4(aq) \tag{5.15.18}$$
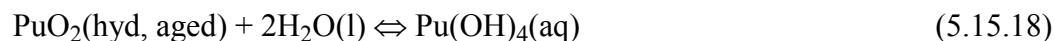
under the assumption that the activity coefficient of $Pu(OH)_4(aq)$ and the activities of $PuO_2(hyd)$ and of $H_2O(l)$ are all unity. As discussed below in Section 5.15.3.5, the solubility product for

$$PuO_2(hyd, aged) + 4H^+ \Leftrightarrow Pu^{4+} + 2H_2O(l) \tag{5.15.19}$$

is

$$\log_{10}{}^*K_{s,0}°(5.15.19, 298.15 \text{ K}) = -(2.0 \pm 1.0)$$

Subtracting reaction (5.15.19) from reaction (5.15.18) results in

$$Pu^{4+} + 4H_2O(l) \Leftrightarrow Pu(OH)_4(aq) + 4H^+ \tag{5.15.20}$$

with

$$\log_{10}{}^*\beta_4°(5.15.20, 298.15 \text{ K}) = -(8.4 \pm 1.1)$$

This value is included in the database update.

5.15.3.4   Pu(III) hydroxide complexes

Pu(III) is unstable in aqueous solution with respect to oxidation by air. The selected hydrolysis constant

$$\log_{10}{}^*\beta_1°(298.15 \text{ K}) = -(6.9 \pm 0.3)$$

for

$$Pu^{3+} + H_2O(l) \Leftrightarrow PuOH^{2+} + H^+$$
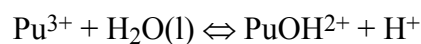
was based on an average value of four potentiometric measurements at $I \le 0.05$ M (NaCl or NaClO$_4$) after corrections for temperature and chloride complexation, and on two values obtained by the radio-tracer solvent extraction method at 0.1 and 0.2 M LiClO$_4$, extrapolated to $I = 0$ with a $\Delta\varepsilon$ estimated by analogy to lanthanide systems. The selected value for $\log_{10}{}^*\beta_1°(298.15 \text{ K})$ is consistent with the value of the first hydrolysis constant of Am(III) selected by SILVA et al. (1995), $-(6.4 \pm 0.2)$. Note that the consistency is even better with the recently revised value for Am(III) of $-(7.3 \pm 0.3)$ (see Section 5.2.3).

5.15.3.5   Solid plutonium oxides and hydroxides

LEMIRE et al. (2001) recommended values of $S_m°$ and $\Delta_f H_m°$ for PuO_2(cr), Pu_2O_3(cr), $PuO_{1.61}$(bcc), and $PuO_{1.52}$(bcc), from which they calculated values for $\Delta_f G_m°$. As there are no solubility studies of these solids, they are not included in the database update.

The solid precipitated from aqueous Pu(VI) by ammonia was characterized as $PuO_2(OH)_2 \cdot H_2O$(cr). There are at least five solubility studies in the literature but all of them neglected a thorough characterization of the solid. The reported solubility constants vary considerably. For the reaction

$$PuO_2(OH)_2 \cdot H_2O(cr) + 2H^+ \Leftrightarrow PuO_2^{2+} + 3H_2O(l)$$
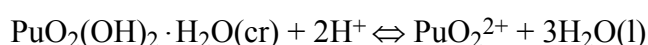
the selected solubility constant is

$$\log_{10} {}^*K_{s,0}°(298.15\ K) = (5.5 \pm 1.0)$$

There are no experimentally determined values for the entropy or enthalpy of formation of $PuO_2(OH)_2$(cr) or its hydrates. The value

$$S_m°(PuO_2(OH)_2 \cdot H_2O,\ cr,\ 298.15\ K) = (190 \pm 40)\ J \cdot K^{-1} \cdot mol^{-1}$$

was selected by analogy with $UO_3 \cdot 2H_2O$(cr) for which $S_m°(298.15\ K)$ was reported to be $(188.54 \pm 38)\ J \cdot K^{-1} \cdot mol^{-1}$. In the absence of any heat capacity determinations, the value

$$C_{p,m}°(PuO_2(OH)_2 \cdot H_2O,\ cr,\ 298.15\ K) = (170 \pm 20)\ J \cdot K^{-1} \cdot mol^{-1}$$

was selected based on a Kopp's rule calculation and by analogy with the experimental value of $(172 \pm 0.34)\ J \cdot K^{-1} \cdot mol^{-1}$ for $C_{p,m}°(UO_3 \cdot H_2O,\ cr,\ 298.15\ K)$. Kopp's rule states that the molar heat capacity of a solid compound is equal to the sum of the atomic heats of its component elements.

Because the values for $S_m°(PuO_2(OH)_2 \cdot H_2O,\ cr)$ and for $C_{p,m}°(PuO_2(OH)_2 \cdot H_2O,\ cr)$ were based on estimates only, they are not included in the database update.

A value of

$$\log_{10} {}^*K_{s,0}°(298.15\ K) = (5.0 \pm 0.5)$$

for the reaction

$$PuO_2OH(am) + H^+ \Leftrightarrow PuO_2^+ + H_2O(l)$$
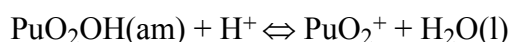
was recommended, based on a solubility product determined from the initial pH of precipitation from a $2.1 \cdot 10^{-3}$ M Pu(V) solution. The selected value

$$S_m°(PuO_2OH, am, 298.15\ K) = (97 \pm 15)\ J \cdot K^{-1} \cdot mol^{-1}$$

was estimated as the sum of $S_m°(PuO_2)$ and the entropy contribution of an OH$^-$ group attached to a singly charged metal ion. The selected value

$$C_{p,m}°(PuO_2OH, am, 298.15\ K) = (86 \pm 20)\ J \cdot K^{-1} \cdot mol^{-1}$$

was estimated from a Kopp's rule calculation.

Because both values for $S_m°(PuO_2OH, am, 298.15\ K)$ and $C_{p,m}°(PuO_2OH, am, 298.15\ K)$ were based on estimates only, they are not included in the database update.

The experimental investigation of the solubility of solids resulting from hydrolysis of Pu(IV) is hampered by a number of effects:

Except in strongly acidic solutions, only a small percentage of the total plutonium in aqueous solution in equilibrium with a Pu(IV) hydrolytic solid is tetravalent. This is due to the disproportionation of Pu(IV) to Pu(III) and Pu(VI).

Radiolysis influences the crystallinity of the investigated solids. When $^{239}PuO_2$(cr) is contacted with water it is slowly converted to (or coated with) a less crystalline form. The hydrated amorphous form of $PuO_2 \cdot xH_2O$(am) is gradually converted to a similar slightly crystalline form, but crystallization does not proceed beyond this stage. When $^{238}PuO_2$(cr) is contacted with water, the solid is converted to the amorphous state.

Moderately acidic Pu(IV) solutions often contain a colloidal plutonium species, probably finely dispersed $PuO_2 \cdot xH_2O$, which can lead to high apparent solubilities.

On the basis of two solubility experiments on well aged hydrated PuO_2, or Pu(OH)$_4$(am), which appear to have coped most successfully with the experimental difficulties, a value of

$$\log_{10}K_{s,0}°(298.15\ K) = - (58 \pm 1)$$

was selected for the reaction

$$PuO_2(hyd, ag) + 2H_2O(l) \Leftrightarrow Pu^{4+} + 4OH^-$$
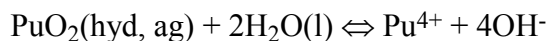
For the database update the solubility of PuO_2(hyd, ag) is written as

$$PuO_2(hyd, ag) + 4H^+ \Leftrightarrow Pu^{4+} + 2H_2O(l) \tag{5.15.19}$$
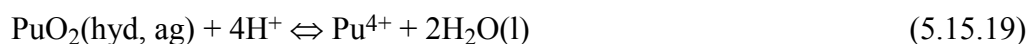
and the solubility product accordingly recalculated to

$$\log_{10}*K_{s,0}°(5.15.19, 298.15\ K) = - (2.0 \pm 1.0)$$

Note that this solubility product only applies to precipitated solids that were aged for several months near room temperature. Freshly precipitated solids may be more soluble.

Experimental studies of the solubility of actinide(III) hydroxides are very rare. The selected value of

$$\log_{10}{}^{*}K_{s,0}{}^{\circ}(298.15 \text{ K}) = (15.8 \pm 1.5)$$

for the reaction

$$\text{Pu(OH)}_3(\text{cr}) + 3\text{H}^{+} \Leftrightarrow \text{Pu}^{3+} + 3\text{H}_2\text{O(l)}$$
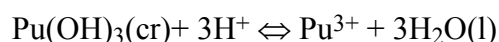
was based on a solubility experiment done in deionized water. This solubility product is consistent with the values selected by SILVA et al. (1995) for Am(OH)$_3$(am), $\log_{10}{}^{*}K_{s,0}{}^{\circ}(298.15 \text{ K}) = (17.0 \pm 0.6)$, and for Am(OH)$_3$(cr), $\log_{10}{}^{*}K_{s,0}{}^{\circ}(298.15 \text{ K}) = (15.2 \pm 0.6)$.

5.15.4 Solid and gaseuos plutonium halogen compounds

LEMIRE et al. (2001) selected thermodynamic data for the following solid halogen compounds:

Solid fluorides: PuF$_3$(cr), PuF$_4$(cr), PuF$_6$(cr), PuOF(cr)

Solid chlorides: PuCl$_3$(cr), PuCl$_3 \cdot$ 6H$_2$O(cr), PuCl$_4$(cr), PuOCl(cr), Cs$_2$NaPuCl$_6$(cr), Cs$_3$PuCl$_6$(cr), CsPu$_2$Cl$_7$(cr), Cs$_2$PuCl$_6$(cr)

Solid bromides: PuBr$_3$(cr), PuOBr(cr), Cs$_2$PuBr$_6$(cr)

Solid iodides: PuI$_3$(cr), PuOI(cr)

As the formation of these solids in aqueous environmental systems is doubtful and none of the data were gathered from solubility experiments, they are not included in the database update.

LEMIRE et al. (2001) also selected thermodynamic data for the following gaseous halogen compounds:

Gaseous fluorides: PuF(g), PuF$_2$(g), PuF$_3$(g), PuF$_4$(g), PuF$_6$(g)

Gaseous chlorides: PuCl$_3$(g), PuCl$_4$(g)

Gaseous bromides: PuBr$_3$(g)

Gaseous iodides: PuI$_3$(g)

These gases are hardly relevant for aqueous environmental systems and are therefore excluded from the database update.

5.15.5 Aqueous plutonium fluoride complexes

Two studies reported data on fluoride complexation of Pu^{3+}, but these were rejected by LEMIRE et al. (2001) and are therefore not included in the database update. Am data can be used as chemical analogues in model calculations.

No fluoride complexes of PuO_2^+ have been identified.

5.15.5.1 Pu(IV) fluoride complexes

Experimentally determined concentration constants have been published for the reaction

$$Pu^{4+} + HF(aq) \Leftrightarrow PuF^{3+} + H^+ \tag{5.15.21}$$

As the considered constants from 6 experimental studies refer only to two different ionic strength values ($I = 1$ M and $I = 2$ M), a linear SIT fit was not thought to be feasible and the constants were extrapolated to $I = 0$ by using $\Delta\varepsilon$ from the corresponding Np(IV) fluoride system. The weighted average of the values for $\log_{10}{}^*\beta_1°(5.15.21, 298.15$ K) were then converted to $\log_{10}\beta_1°(5.15.22, 298.15$ K) for

$$Pu^{4+} + F^- \Leftrightarrow PuF^{3+} \tag{5.15.22}$$

by using the selected protonation constant of fluoride, $\log_{10}{}^*K°(H^+ + F^- \Leftrightarrow HF(aq), 298.15$ K) = (3.18 ± 0.02). The resulting selected value is

$$\log_{10}\beta_1°(5.15.22, 298.15 \text{ K}) = (8.84 \pm 0.10)$$

For the reaction

$$Pu^{4+} + 2HF(aq) \Leftrightarrow PuF_2^{2+} + 2H^+ \tag{5.15.23}$$

concentration constants from 4 experimental studies (at $I = 1$ M and $I = 2$ M) were considered. As above, a linear SIT fit was not thought to be feasible and the constants were extrapolated to $I = 0$ by using a $\Delta\varepsilon$ from the corresponding U(IV) fluoride system. The weighted average of the values for $\log_{10}{}^*\beta_2°(5.15.23, 298.15$ K) were then converted to $\log_{10}\beta_2°(5.15.24, 298.15$ K) for

$$Pu^{4+} + 2F^- \Leftrightarrow PuF_2^{2+} \tag{5.15.24}$$

by using the selected protonation constant of fluoride. The resulting selected value is

$$\log_{10}\beta_2°(5.15.24, 298.15 \text{ K}) = (15.7 \pm 0.2)$$

From equilibrium constants measured at 1, 7.5, 15 and 25°C reported in one study, $\Delta_r H_m°$(5.15.21, 298.15 K) and $\Delta_r H_m°$(5.15.23, 298.15 K) were extracted and combined with the enthalpy of protonation of the fluoride ion, resulting in the following selected values

$$\Delta_r H_m°(5.15.22, 298.15 \text{ K}) = (9.1 \pm 2.2) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m°(5.15.24, 298.15 \text{ K}) = (11 \pm 5) \text{ kJ} \cdot \text{mol}^{-1}$$

Data for the 1:3 and 1:4 complexes were published in one study but were rejected by LEMIRE et al. (2001).

5.15.5.2 Pu(VI) fluoride complexes

As in the case of Np(VI), the investigation of fluoride complexation of Pu(VI) is complicated by the fact that reduction of Pu(VI) to Pu(IV) is favored in acidic media and in the presence of fluoride ions. Constants reported in the literature refer either to

$$PuO_2^{2+} + HF(aq) \Leftrightarrow PuO_2F^+ + H^+ \tag{5.15.25}$$

and

$$PuO_2^{2+} + 2HF(aq) \Leftrightarrow PuO_2F_2(aq) + 2H^+ \tag{5.15.26}$$

or to

$$PuO_2^{2+} + F^- \Leftrightarrow PuO_2F^+ \tag{5.15.27}$$

and

$$PuO_2^{2+} + 2F^- \Leftrightarrow PuO_2F_2(aq) \tag{5.15.28}$$
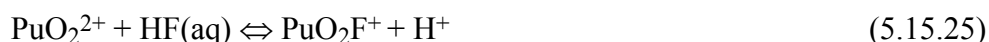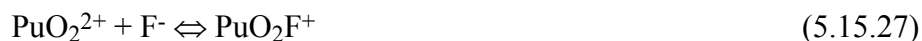
depending on the experimental conditions. Only two experimental studies on the 1:1 complex were deemed reliable, both referring to Reaction (5.15.25), and the constants were corrected to $I = 0$ using $\Delta\varepsilon$ from the corresponding Np(VI) system. The selected value is a weighted average of the two constants with an increased uncertainty in order to reflect the absence of reliable studies in acidic media, in which noticeably lower constants were obtained in the case of Np(VI)

$$\log_{10}\beta_1°(5.15.27, 298.15 \text{ K}) = (4.56 \pm 0.20)$$

There is only one credible study for the 1:2 complex (at 0.1 M and 1 M NaClO$_4$). The constants for Reaction (5.15.28) were corrected to $I = 0$ by using $\Delta\varepsilon$ from the corresponding Np(VI) system, but did not agree well. Agreement could be only reached by assuming a $\Delta\varepsilon$ that is not commonly observed in such systems. As more reliable experiments are not available, the unweighted average

of the two values was selected, with an associated uncertainty range that covers the range of expectancy of the two values.

$$\log_{10}\beta_2°(5.15.28, 298.15 \text{ K}) = (7.25 \pm 0.45)$$

Reported formation constants for the 1:3 complex, $PuO_2F_3^-$, were rejected by LEMIRE et al. (2001).

5.15.6   Aqueous plutonium chloride complexes

There appears to be no experimental identification of any chloride complexes for Pu(V). Therefore, only Pu(III), Pu(IV), and Pu(VI) chloride complexes are considered.

5.15.6.1   Pu(III) chloride complexes

From several experimental studies of 1:1 complexes, only data of a single study were found to be reliable. The concentration constants for the reaction

$$Pu^{3+} + Cl^- \Leftrightarrow PuCl^{2+}$$
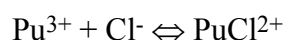
were extrapolated to $I = 0$ by adopting a value for $\Delta\varepsilon$ from the corresponding Am(III) system. The weighted average of the resulting values for $\log_{10}\beta_1°(298.15 \text{ K})$ was selected with an increased uncertainty due to the fact that the value is based on a single study

$$\log_{10}\beta_1°(298.15 \text{ K}) = (1.2 \pm 0.2)$$

5.15.6.2   Pu(IV) chloride complexes

The selected value for the formation constant of

$$Pu^{4+} + Cl^- \Leftrightarrow PuCl^{3+}$$
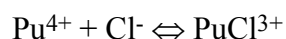
was calculated from an SIT extrapolation of data obtained by five experimental studies in mixed chloride/perchlorate media (I between 1 M and 5 M)

$$\log_{10}\beta_1°(298.15 \text{ K}) = (1.8 \pm 0.3)$$

Data for the 1:2 complex, $PuCl_2^{2+}$, were obtained at high ionic strengths only and could not be extrapolated to $I = 0$. In addition, there are large variations in the published data. Therefore no formation constant was recommended.

Data for the 1:3 and 1:4 complexes, $PuCl_3^+$ and $PuCl_4(aq)$, resp., were also obtained at high ionic strengths only, preventing extrapolation to $I = 0$, and no formation constants could be recommended.

5.15.6.3   Pu(VI) chloride complexes

In a careful and comprehensive spectroscopic study, formation constants for

$$PuO_2^{2+} + Cl^- \Leftrightarrow PuO_2Cl^+$$
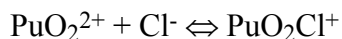
were determined at $I = 2$ M and $I = 3$ M and extrapolated to $I = 0$ by SIT. The resulting constant

$$\log_{10}\beta_1°(298.15 \text{ K}) = (0.70 \pm 0.13)$$

was then used to evaluate the formation constant for

$$PuO_2^{2+} + 2Cl^- \Leftrightarrow PuO_2Cl_2 \text{ (aq)}$$
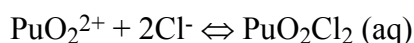
at variable ionic strengths, again using SIT to extrapolate to $I = 0$, with

$$\log_{10}\beta_2°(298.15 \text{ K}) = - (0.6 \pm 0.2)$$

Both formation constants were selected.

5.15.7   Aqueous plutonium hypochlorite complexes

In concentrated aqueous NaCl solutions, plutonium radiation was reported to produce a steady state concentration of hypochlorite ion, ClO^-. The oxidizing character of hypochlorite stabilizes the Pu(VI) oxidation state, but at the same time forms complexes with PuO_2^{2+}. Reported formation constants for $PuO_2(OH)ClO(aq)$ were not selected, because they were based on questionable assumptions.

5.15.8   Aqueous plutonium bromide complexes

The selected data for $PuBr^{3+}$ is not included in the database update because the complex is very weak and bromide is not relevant under environmental conditions.

5.15.9   Aqueous plutonium iodine complexes

The selected data for PuI^{2+} are not included in the database update because the complex is very weak and not relevant under environmental conditions.

5.15.10   Aqueous plutonium sulfate complexes

Data were selected for sulfate complexes of Pu(VI), Pu(IV), and Pu(III). There appears to be no experimental evidence concerning the stability of Pu(V) sulfate complexes which is surprising given the fact that Pu(V) is the dominant oxidized plutonium species in natural waters.

5.15.10.1   Pu(VI) sulfate complexes

There are only two studies concerning the formation of Pu(VI) sulfate complexes. One of the studies reported the concentration constant at I = 2.2 M H(ClO$_4^-$,HSO$_4^-$) of the 1:1 complex according to

$$PuO_2^{2+} + HSO_4^{2-} \Leftrightarrow PuO_2SO_4(aq) + H^+ \qquad (5.15.29)$$

The value was extrapolated to $\log_{10}\beta_1°$(5.15.29, 298.15 K) using a value for $\Delta\varepsilon$ estimated from the analogous uranium sulfate complex. The other study reported concentration constants at I = 0.13 - 0.82 M H(ClO$_4^-$,HSO$_4^-$) for

$$PuO_2^{2+} + SO_4^{2-} \Leftrightarrow PuO_2SO_4(aq) \qquad (5.15.30)$$

The measured values were extrapolated to $\log_{10}\beta_1°$(5.15.30, 298.15 K) by means of an SIT fit. $\log_{10}\beta_1°$(5.15.29, 298.15 K) was then obtained by using the selected auxiliary data for the protonation constant of SO$_4^{2-}$. The same auxiliary data was used to recalculate the average of the two values for $\log_{10}\beta_1°$(5.15.29, 298.15 K) to the selected value

$$\log_{10}\beta_1°(5.15.30, 298.15 \text{ K}) = (3.38 \pm 0.20)$$

The selected formation constant for

$$PuO_2^{2+} + 2SO_4^{2-} \Leftrightarrow PuO_2(SO_4)_2^{2-} \qquad (5.15.31)$$

was obtained from the reported concentration constants at I = 0.13 - 0.82 M (HClO$_4^-$, HSO$_4^-$) which were extrapolated to I = 0 by means of an SIT fit. The selected value is

$$\log_{10}\beta_2°(5.15.31, 298.15 \text{ K}) = (4.4 \pm 0.2)$$

The selected reaction enthalpies were determined in a calorimetric study:

$$\Delta_r H_m°(5.15.30, 298.15 \text{ K}) = (16.1 \pm 0.6) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m°(5.15.31, 298.15 \text{ K}) = (43 \pm 9) \text{ kJ} \cdot \text{mol}^{-1}$$

5.15.10.2   Pu(IV) sulfate complexes

There is a number of independent evaluations concerning the stability of Pu(IV) sulfate complexes. Although there are reports of mixed HSO$_4^-$ - SO$_4^{2-}$ complexes, the best experiments are most consistent with the formation of 1:1 and 1:2 Pu(IV)-SO$_4^{2-}$ complexes:

$$Pu^{4+} + HSO_4^- \Leftrightarrow PuSO_4^{2+} + H^+ \qquad (5.15.32)$$

$$Pu^{4+} + 2HSO_4^- \Leftrightarrow Pu(SO_4)_2(aq) + 2H^+ \qquad (5.15.33)$$
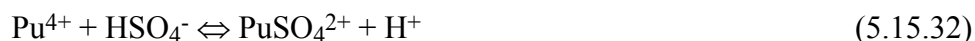
The most reliable value of $\log_{10}^{*}\beta_1^{\circ}$(5.15.32, 298.15 K) at I = 2.2 M $HClO_4$ or $(H,Na)ClO_4$ is the weighted average of several independent experimental determinations. The value at I = 2.2 M was extrapolated to standard conditions by using SIT with a $\Delta\varepsilon$ determined for the analogous U(IV) complex, resulting in the selected value

$$\log_{10}^{*}\beta_1^{\circ}(5.15.32, 298.15 \text{ K}) = (4.91 \pm 0.22)$$

The selected value

$$\log_{10}^{*}\beta_2^{\circ}(5.15.33, 298.15 \text{ K}) = (7.18 \pm 0.32)$$

was determined in a similar fashion. LEMIRE et al. (2001) stress that caution is advised in the use of this value outside of the range of H^+ concentrations in which the experimental values were determined (1 - 2 M).

For the database update, these complex formation reactions were rewritten in terms of SO_4^{2-} instead of HSO_4^-:

$$Pu^{4+} + SO_4^{2-} \Leftrightarrow PuSO_4^{2+} \tag{5.15.34}$$

$$Pu^{4+} + 2SO_4^{2-} \Leftrightarrow Pu(SO_4)_2(aq) \tag{5.15.35}$$

Therefore, $\log_{10}^{*}\beta_1^{\circ}$(5.15.32, 298.15 K) and $\log_{10}^{*}\beta_2^{\circ}$(5.15.33, 298.15 K) were recalculated by adding once or twice the selected protonation constant of SO_4^{2-}, $\log_{10}^{*}\beta_1^{\circ} = (1.98 \pm 0.05)$

$$\log_{10}\beta_1^{\circ}(5.15.34, 298.15 \text{ K}) = (6.89 \pm 0.23)$$

$$\log_{10}\beta_2^{\circ}(5.15.35, 298.15 \text{ K}) = (11.14 \pm 0.34)$$

5.15.10.3   Pu(III) sulfate complexes

There are four experimental studies concerning Pu(III) sulfate complexation. Although Pu(III) bisulfate complexes have been postulated, namely $Pu(HSO_4)_2^+$ and $Pu(SO_4)(HSO_4)(aq)$, the results were interpreted by LEMIRE et al. (2001) to be consistent with the reactions:

$$Pu^{3+} + HSO_4^- \Leftrightarrow PuSO_4^+ + H^+ \tag{5.15.36}$$

$$Pu^{3+} + 2HSO_4^- \Leftrightarrow Pu(SO_4)_2^- + 2H^+ \tag{5.15.37}$$

The selected values for the reaction enthalpies

$$\Delta_r H_m^{\circ}(5.15.36, 298.15 \text{ K}) = - (5.2 \pm 2.0) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m^{\circ}(5.15.37, 298.15 \text{ K}) = - (33 \pm 16) \text{ kJ} \cdot \text{mol}^{-1}$$

were calculated from reported temperature variations of $\log_{10}^{*}\beta_1^{\circ}$(5.15.36) and $\log_{10}^{*}\beta_1^{\circ}$(5.15.37).

LEMIRE et al. (2001) used a rather peculiar procedure to extract $\log_{10}*\beta_1°(5.15.36)$ from the four experimental studies but did not comment on it: The concentration constants from two studies were independently extrapolated to $I = 0$ by performing an SIT fit to the data. The average of the two $\Delta\varepsilon$ values was used to extrapolate the results of the other two studies to $I = 0$. The resulting $\log_{10}*\beta_1°(5.15.36)$ of one of these studies was further extrapolated from 28 to 25°C by using the selected value for $\Delta_r H_m°(5.15.36, 298.15\ K)$. An average of these four formation constants resulted in the selected

$$\log_{10}*\beta_1°(5.15.36, 298.15\ K) = (1.93 \pm 0.61)$$

The selected value for

$$\log_{10}*\beta_2°(5.15.37, 298.15\ K) = (1.74 \pm 0.76)$$

was derived in a similar fashion from the same studies.

For the database update, the complex formation reactions were cast in terms of SO_4^{2-} instead of HSO_4^-:

$$Pu^{3+} + SO_4^{2-} \Leftrightarrow PuSO_4^+ \tag{5.15.38}$$
$$Pu^{3+} + 2SO_4^{2-} \Leftrightarrow Pu(SO_4)_2^- \tag{5.15.39}$$

Therefore, $\log_{10}*\beta_1°(5.15.36, 298.15\ K)$ and $\log_{10}*\beta_2°(5.15.37, 298.15\ K)$ were recalculated by adding once or twice the selected protonation constant of SO_4^{2-}, $\log_{10}*\beta_1° = (1.98 \pm 0.05)$:

$$\log_{10}\beta_1°(5.15.38, 298.15\ K) = (3.9 \pm 0.6)$$
$$\log_{10}\beta_2°(5.15.39, 298.15\ K) = (5.7 \pm 0.8)$$

In a similar fashion, $\Delta_r H_m°(5.15.36, 298.15\ K)$ and $\Delta_r H_m°(5.15.37, 298.15\ K)$ were recalculated by adding once or twice $\Delta_r H_m°(5.15.40, 298.15\ K)$, the enthalpy of protonation (see below), resulting in

$$\Delta_r H_m°(5.15.38, 298.15\ K) = (17.2 \pm 2.3)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m°(5.15.39, 298.15\ K) = (12 \pm 16)\ kJ \cdot mol^{-1}$$

$\Delta_r H_m°(5.15.40, 298.15\ K) = (22.44 \pm 1.08)$ for the protonation of SO_4^{2-}

$$SO_4^{2-} + H^+ \Leftrightarrow HSO_4^- \tag{5.15.40}$$

was calculated from selected auxiliary data:

$$\Delta_f H_m°(SO_4^{2-}, 298.15\ K) = -(909.340 \pm 0.400)\ kJ \cdot mol^{-1}$$

$$\Delta_f H_m°(HSO_4^-, 298.15\ K) = -(886.900 \pm 1.000)\ kJ \cdot mol^{-1}$$

5.15.11 Solid plutonium arsenic, antimony, and bismuth compounds

In addition to plutonium nitrogen compounds and complexes (Section 5.15.12) and to plutonium phosphorous compounds and complexes (Section 5.15.13), LEMIRE et al. (2001) also discuss plutonium arsenic compounds (PuAs, cr), plutonium antimony compounds (PuSb, cr; $PuSb_2$, cr), and plutonium bismuth compounds (PuBi, cr; $PuBi_2$, cr). They selected $\Delta_f G_m°$ values for PuAs(cr), PuSb(cr), PuBi(cr), and $PuBi_2$(cr), all of which are based on estimates or on high-temperature measurements and are therefore not included in the database update.

5.15.12 Plutonium nitrogen compounds and complexes

In addition to plutonium nitrates which are discussed in Section 5.15.12.1, LEMIRE et al. (2001) also mention plutonium nitrides, PuN(cr) and PuN(g), and plutonium azide complexes. Only data for PuN(cr) were selected. As this phase is hardly relevant to environmental systems, no data were included in the database update.

5.15.12.1 Plutonium nitrates

The only plutonium nitrate solids discussed by LEMIRE et al. (2001) are $Pu(NO_3)_4 \cdot 5H_2O(s)$ (no data recommended) and $PuO_2(NO_3)_2 \cdot 6H_2O(s)$. As these highly soluble salts are hardly relevant to environmental systems, no data were included in the database update.

Experimental data for the Pu(III) nitrate complexes, $PuNO_3^{2+}$, $Pu(NO_3)_2^+$, and $Pu(NO_3)_3$(aq) were not considered to be reliable by LEMIRE et al. (2001), nor were data for the Pu(VI) nitrate complexes, $PuO_2NO_3^+$ and $PuO_2(NO_3)_2$(aq). No nitrate complexes of Pu(V) are known. Therefore, only data for Pu(IV) nitrates were selected.

Pu(IV) nitrate complexes are relatively well studied and formation constants have been reported for $Pu(NO_3)^{3+}$, $Pu(NO_3)_2^{2+}$, $Pu(NO_3)_3^+$, and $Pu(NO_3)_4$(aq). However, in many cases it is difficult to separate the weak complex formation of Pu(IV) from changes in activity coefficients which could equally well describe the experimental data. Indeed, in most works, values of formation constants of two or more (as many as four) Pu(IV) nitrate complexes are necessary to fit the experimental data. Furthermore, in most of the cases the overall formation constant for the third or fourth complex is lower than for the second formation constant which is unusual for complexation.

As the 1:1 complex has been spectrophotometrically identified, values of the concentration constants for

$$Pu^{4+} + NO_3^- \Leftrightarrow Pu(NO_3)^{3+}$$
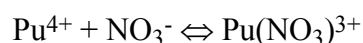
from different studies were used to determine $\log_{10}\beta_1°(298.15\ \text{K})$ by applying an SIT fit to the data, resulting in a selected value of

$$\log_{10}\beta_1°(298.15\ \text{K}) = (1.95 \pm 0.15)$$

There is evidence that anionic complexes form at very high nitrate concentrations in acidic solutions but no thermodynamic data are available.

5.15.13   Plutonium phosphorous compounds and complexes

Besides PuP(cr), which is irrelevant in environmental systems and has therefore not been included in the database update, $PuPO_4$(s, hyd), and $Pu(HPO_4)_2$(am), only aqueous plutonium phosphorous complexes were discussed by LEMIRE et al. (2001).

5.15.13.1   Pu(III) phosphates

There is only one quantitative study of the Pu(III) phosphate system dealing with solubility measurements of $PuPO_4 \cdot xH_2O$(s). The solubility data at pH values < 4 were recalculated by LEMIRE et al. (2001) to obtain the solubility product for the reaction

$$PuPO_4 \cdot xH_2O(s) \Leftrightarrow Pu^{3+} + PO_4^{3-} + xH_2O(l)$$
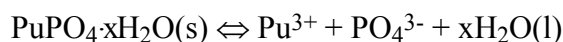
which can also be expressed as

$$PuPO_4(s, hyd) \Leftrightarrow Pu^{3+} + PO_4^{3-}$$
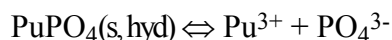
The value $\log_{10}K_{s,0}°$(0.5 M NaClO$_4$, 298.15 K) = - (21.5 ± 0.5) was recalculated to $I = 0$ resulting in

$$\log_{10}K_{s,0}°(298.15\ \text{K}) = - (24.6 \pm 0.8)$$

5.15.13.2   Pu(IV) phosphates

Three studies investigated aqueous Pu(IV) phosphates, based on solubility measurements of gelatinous $Pu(HPO_4)_2 \cdot xH_2O$(s). The solubility product and the concentration constant for the complex with one phosphate group were selected from one study. Recalculation from $I = 2.08$ M (H, Na)NO$_3$ using selected SIT parameters resulted in

$$\log_{10}\beta_1°(298.15\ \text{K}) = (2.4 \pm 0.3)$$

for

$$Pu^{4+} + H_3PO_4(aq) \Leftrightarrow PuH_3PO_4^{4+}$$
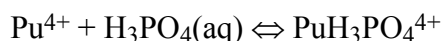
and in

$$\log_{10} K_{s,0}°(298.15 \text{ K}) = - (30.45 \pm 0.51)$$

for

$$Pu(HPO_4)_2 \cdot xH_2O(s) \Leftrightarrow Pu^{4+} + 2HPO_4^{2-} + xH_2O(l)$$

For the database update, this solubility reaction was writtten as

$$Pu(HPO_4)_2(am, hyd) \Leftrightarrow Pu^{4+} + 2HPO_4^{2-}$$
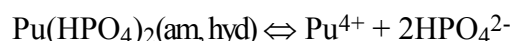
5.15.13.3   Pu(V) phosphates

The only quantitative study on Pu(V) phosphate complexes is a study using the sorption-coprecipitation of Pu(V) on Fe(III) hydroxide to determine the formation constant of $PuO_2HPO_4^-$. The value was not selected since no confirmation from other more conventional experimental methods is available.

5.15.13.4   Pu(VI) phosphates

The Pu(VI) phosphate system has been studied experimentally mainly by solubility measurements. Solubilities of $NH_4PuO_2PO_4(s)$ and $PuO_2HPO_4 \cdot 4H_2O(s)$ were used to derive formation constants for $NH_4PuO_2PO_4(aq)$ and $PuO_2HPO_4(aq)$. These data were rejected due to insufficient characterization of the solids. Reported formation constants for $PuO_2H_2PO_4^+$ obtained by solvent extraction were rejected because details of the experimental study were not available.

5.15.14   Plutonium carbides

LEMIRE et al. (2001) selected thermodynamic data for $PuC_{0.84}(cr)$, $Pu_2C_3(cr)$, $Pu_3C_2(cr)$, and $PuC_2(cr)$. However, carbides are not relevant for environmental systems and are therefore not included in the database update.

5.15.15 Aqueous plutonium carbonate complexes

Experimental problems associated with the derivation of composition and stability of Pu carbonate complexes are manifold: It is difficult to identify and maintain the oxidation state of Pu, sparingly soluble solids may precipitate during an experiment, and complexes are difficult to identify in solutions containing both OH^- and CO_3^{2-}/HCO_3^- ions. As a result of these difficulties, commonly no unique complexation model can be developed to explain experimental results. LEMIRE et al. (2001) were guided by the principle that where more than one model appeared to be compatible

with experimental results, the model with the minimum number of complexes that contain the minimum number of ligands was chosen as most likely. This principle is an application of Ockham's razor, a very stimulating exposition of which is presented by Roald Hoffmann, Barry K. Carpenter, and Vladimir I. Minkin (1997) in the article "Ockham's Razor and Chemistry", HYLE, an International Journal for the Philosophy of Chemistry, 3, 3-28 (http://www.hyle.org/journal/issues/3/hoffman.htm).

5.15.15.1 Pu(VI) carbonate complexes

5.15.15.1.1 Monocarbonato complex

The formation constant of the monocarbonato complex selected by LEMIRE et al. (2001) was based on SULLIVAN & WOODS (1982) and ROBOUCH & VITORGE (1987). The spectrophotometric and calorimetric study by SULLIVAN & WOODS (1982) reported the formation constant of a hydroxy-monocarbonato complex in 0.1 M $NaClO_4$ according to

$$PuO_2(OH)_2(aq) + HCO_3^- \Leftrightarrow PuO_2CO_3OH^- + H_2O(l) \tag{5.15.41}$$
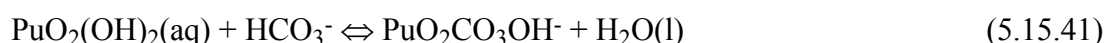
as $\log_{10}\beta_1$(5.15.41, 0.1 M $NaClO_4$, 298.15 K) = (2.67 ± 0.60)

A reanalysis of these results suggested that an equally likely interpretation would involve the formation of a monocarbonato complex (which is more consistent with the analogous U(VI) (GRENTHE et al. 1992), and Np(VI) systems, (LEMIRE et al. 2001):

$$PuO_2(OH)_2(aq) + HCO_3^- \Leftrightarrow PuO_2CO_3(aq) + OH^- + H_2O(l) \tag{5.15.42}$$
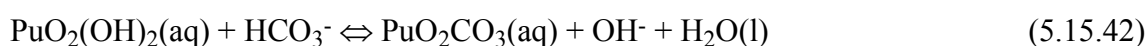
Therefore the reported $\log_{10}\beta_1$(5.15.41, 0.1 M $NaClO_4$, 298.15 K) by SULLIVAN & WOODS (1982) was assumed to refer to reaction (5.15.42) and thus $\log_{10}*\beta_1$(5.15.42, 0.1 M $NaClO_4$, 298.15 K) = (2.67 ± 0.60). The SIT correction is very small, and $\log_{10}*\beta_1°$(5.15.42, 298.15 K) = (2.67 ± 0.60). On the basis of a thermodynamic cycle using the recommended values for the stability of $PuO_2(OH)_2$(aq), *cf.* Section 5.15.3.1, and the auxiliary data for the stability of water and dissociation of bicarbonate, LEMIRE et al. (2001) calculated the equilibrium constant for the reaction

$$PuO_2^{2+} + CO_3^{2-} \Leftrightarrow PuO_2CO_3(aq) \tag{5.15.43}$$

and obtained $\log_{10}\beta_1°$(5.15.43, 298.15 K) = $\left(13.8^{+0.8}_{-1.6}\right)$. The asymmetry in errors is due to the asymmetry in errors assigned to the formation of $PuO_2(OH)_2$(aq), *cf.* Section 5.15.3.1.

ROBOUCH & VITORGE (1987) determined the value of $\log_{10}\beta_1$(5.15.43, 3.5 m $NaClO_4$, 20°C) = (8.6 ± 0.6) from solubilities. This was recalculated to I = 0 by SIT, using the value of ε(UO_2^{2+},

ClO_4^-) = (0.46 ± 0.03) kg· mol^{-1} as an estimate for $\varepsilon(PuO_2^{2+}, ClO_4^-)$, but with errors expanded to ±0.8, resulting in $\log_{10}\beta_1°(5.15.43, 20°C) = (9.3 ± 0.5)$. This result was assumed to apply also to 25°C. Because the discrepancy between the two values for $\log_{10}\beta_1°(5.15.43)$ is large, LEMIRE et al. (2001) selected their unweighted mean as recommended value

$$\log_{10}\beta_1°(5.15.43, 298.15 \text{ K}) = (11.6 ± 3.0)$$

We do not agree with this choice. A discrepancy of more than four orders of magnitude between the two values for $\log_{10}\beta_1°(5.15.43)$ is too large to justify the simple selection of the mean (even if unweighted), and a decision has to be made. We chose to select the value based on ROBOUCH & VITORGE (1987)

$$\log_{10}\beta_1°(5.15.43, 298.15 \text{ K}) = (9.3 ± 0.5)$$

because it is close to the value of 9.6 ± 0.3 determined experimentally by PASHALIDIS et al. (1997). Incidentally, this paper was ignored by LEMIRE et al. (2001). This lower value for $\log_{10}\beta_1°$ (together with the selected values for $\log_{10}\beta_2°$ and $\log_{10}\beta_3°$ discussed below) is also more in line with the succession of the values for $\log_{10}\beta_1°$, $\log_{10}\beta_2°$, and $\log_{10}\beta_3°$ expected from the semi-empirical electrostatic approach by NECK & KIM (2000) for the prediction of actinide complexation constants (*cf.* Table 5.15.1).

No value for $\Delta_r H_m°(5.15.43, 298.15 \text{ K})$ was selected.

5.15.15.1.2 Dicarbonato complex

The association constant for

$$PuO_2^{2+} + 2CO_3^{2-} \Leftrightarrow PuO_2(CO_3)_2^{2-}$$
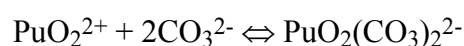
selected by LEMIRE et al. (2001) was based on experimental data by ROBOUCH & VITORGE (1987) and ULLMAN & SCHREINER (1988). ROBOUCH & VITORGE (1987) determined $\log_{10}\beta_2$ from solubility experiments in 3 M $NaClO_4$ at (20 ± 1)°C. LEMIRE et al. (2001) extrapolated the value to $I = 0$ according to SIT, using the selected interaction coefficients for the analogous U(VI) species. They recalculated the resulting $\log_{10}\beta_2$ to 25 °C using the selected value for $\Delta_r H_m°(298.15 \text{ K})$ based on enthalpy titrations by ULLMAN & SCHREINER (1988)

$$\Delta_r H_m°(298.15 \text{ K}) = - (27 ± 4) \text{ kJ} \cdot \text{mol}^{-1}$$

Thus, $\log_{10}\beta_2°(298.15 \text{ K}) = (13.9 ± 1.4)$ was obtained.

ULLMAN & SCHREINER (1988) determined $\log_{10}\beta_2°(298.15 \text{ K}) = (15.1 \pm 1.2)$ using a procedure inconsistent with the procedures adopted by LEMIRE et al. (2001). To account for this, LEMIRE et al. (2001) expanded the uncertainty such that $\log_{10}\beta_2°(298.15 \text{ K}) = (15.1 \pm 2.2)$.

The unweighted average of the two values for $\log_{10}\beta_2°(298.15 \text{ K})$ based on ROBOUCH & VITORGE (1987) and on ULLMAN & SCHREINER (1988) was selected as the stability constant for $PuO_2(CO_3)_2^{2-}$

$$\log_{10}\beta_2°(298.15 \text{ K}) = (14.5 \pm 2.6)$$

We do not agree with this value. It is not reasonable to select the unweighted average of these two values, because they have a much larger overlap of uncertainties (even if the smaller uncertainty for the value based on ULLMAN & SCHREINER 1988 is chosen), than the two values for the tricarbonato complex, whose weighted average was selected (see below). Therefore we selected the weighted average of (13.9 ± 1.4) and (15.1 ± 1.2) for the database update

$$\log_{10}\beta_2°(298.15 \text{ K}) = (14.6 \pm 0.9)$$

5.15.15.1.3 Tricarbonato complex

The stability constant for

$$PuO_2^{2+} + 3CO_3^{2-} \Leftrightarrow PuO_2(CO_3)_3^{4-} \tag{5.15.44}$$

was estimated from solubility experiments in 3 M $NaClO_4$ at 20°C. The measured value was extrapolated to $I = 0$ by SIT using the value of $\varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$ as an estimate for $\varepsilon(PuO_2^{2+}, ClO_4^-)$, but with errors expanded to ± 0.5, and $\varepsilon(PuO_2(CO_3)_3^{4-}, Na^+) = - (0.2 \pm 0.3) \text{ kg} \cdot \text{mol}^{-1}$ (calculated from the mean and the range of the analogous interaction coefficients for $UO_2(CO_3)_3^{4-}$ and $NpO_2(CO_3)_3^{4-}$) and then recalculated to 25 °C using the selected value for $\Delta_r H_m°(5.15.44, 298.15 \text{ K})$ based on enthalpy titrations

$$\Delta_r H_m°(5.15.44, 298.15 \text{ K}) = - (38.6 \pm 2.0) \text{ kJ} \cdot \text{mol}^{-1}$$

The weighted average of the resulting $\log_{10}\beta_3°(298.15 \text{ K})$ and the value determined by another experiment (with increased uncertainties to account for unorthodox calculation procedures) was selected as the stability constant for $PuO_2(CO_3)_3^{4-}$

$$\log_{10}\beta_3°(5.15.44, 298.15 \text{ K}) = (17.7 \pm 0.9)$$

Table 5.15.1:   Pu(VI) carbonate complexation constants.

	PASHALIDIS et al. (1997)	NECK & KIM (2000)	LEMIRE et al. (2001)	this work
$\log_{10}\beta_1°$	9.6 ± 0.3	9.1	11.6 ± 3.0	9.3 ± 0.5
$\log_{10}\beta_2°$	15.0 ± 0.5	15.0	14.5 ± 2.6	14.6 ± 0.9
$\log_{10}\beta_3°$	17.5 ± 0.2	17.9	17.7 ± 0.9	17.7 ± 0.9

5.15.15.1.4 Dicarbonato trimer

In an experimental study, spectrophotometric and potentiometric data were interpreted in terms of the reaction

$$3PuO_2(CO_3)_3{}^{4-} \Leftrightarrow (PuO_2)_3(CO_3)_6{}^{6-} + 3CO_3{}^{2-} \tag{5.15.45}$$

with $\log_{10}K$(5.15.45, I = 3 M NaClO$_4$, 22°C) = - (7.5 ± 0.5). These experiments were performed at high total Pu(VI) concentrations, high ionic strength and near neutral pH, conditions which appear to stabilize this and similar polymeric species. The above value for $\log_{10}K$(5.15.45, I = 3 M NaClO$_4$, 22°C) was accepted for the conditions at which it was measured, but it cannot be reliably extrapolated to the standard state conditions because of the large variations in the estimated interaction coefficients for the analogous U(VI) (GRENTHE et al. 1992), and Np(VI) species, (LEMIRE et al. 2001). Given the apparently limited extent of the stability of this complex at lower ionic strengths, such an extrapolation, even if possible, would require caution.

Together with the enthalpy and $\Delta\varepsilon$ of reaction (5.15.44), $\log_{10}\beta_3°$(5.15.44, 298.15 K) was extrapolated to I = 3 M NaClO$_4$ and 22°C, resulting in $\log_{10}\beta_3$(5.15.44, I = 3 M NaClO$_4$, 22°C) = (19.2 ± 1.4). This was used to calculate the stability of the dicarbonato trimer

$$3PuO_2{}^{2+} + 6CO_3{}^{2-} \Leftrightarrow (PuO_2)_3(CO_3)_6{}^{6-} \tag{5.15.46}$$
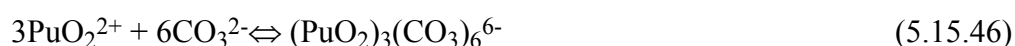
with $\log_{10}\beta_{6,3}$(5.15.46, I = 3 M NaClO$_4$, 22°C) = (50.1 ± 2.5).

Because standard state data at I = 0 are not available, the dicarbonato trimer is not included in the database update.

5.15.15.1.5 Mixed U(VI) Pu(VI) carbonate complexes

GRENTHE et al. (1995) reported

$$\log_{10}K°(5.15.47, 298.15 \text{ K}) = - (8.2 \pm 1.3)$$

for

$$2UO_2(CO_3)_3^{4-} + PuO_2(CO_3)_3^{4-} \Leftrightarrow (UO_2)_2(PuO_2)(CO_3)_6^{6-} + 3CO_3^{2-} \qquad (5.15.47)$$
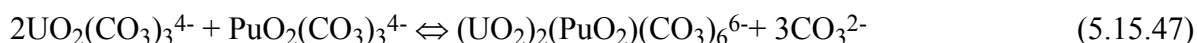
based on an extrapolation of experimental data at $(22 \pm 1)°C$ in 3 M $NaClO_4$, assuming that ε-values are the same if Pu is replaced with U. The value $\log_{10}K°(5.15.47, 298.15 \text{ K}) = - (8.2 \pm 1.3)$ was accepted by LEMIRE et al. (2001).

For the database update we reformulated the formation of $(UO_2)_2(PuO_2)(CO_3)_6^{6-}$ to

$$2UO_2^{2+} + PuO_2^{2+} + 6CO_3^{2-} \Leftrightarrow (UO_2)_2(PuO_2)(CO_3)_6^{6-} \qquad (5.15.48)$$
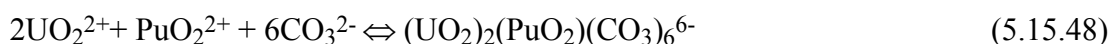
The selected value

$$\log_{10}K°(5.15.48, 298.15 \text{ K}) = (52.7 \pm 1.6)$$

was calculated from $\log_{10}K°(5.15.47, 298.15 \text{ K})$, $\log_{10}\beta_3°(5.15.44, 298.15 \text{ K})$ and from the selected

$$\log_{10}\beta_3°(5.15.49, 298.15 \text{ K}) = (21.60 \pm 0.05)$$

for the reaction

$$UO_2^{2+} + 3CO_3^{2-} \Leftrightarrow UO_2(CO_3)_3^{4-} \qquad (5.15.49)$$

5.15.15.2   Pu(V) carbonate complexes

A stability constant for

$$PuO_2^+ + CO_3^{2-} \Leftrightarrow PuO_2CO_3^- \qquad (5.15.50)$$

was determined by laser photoacoustic spectrometry at $I = 0.5$ M $NaClO_4$ and 23°C. It was extrapolated to $I = 0$ using SIT with the recommended value of ε for the analogous Np(V) carbonate complex as an estimate for $\varepsilon(PuO_2CO_3^-, Na^+)$ (with expanded uncertainty). Assuming that measurements at 23°C are equally valid at 25°C, the selected constant is

$$\log_{10}\beta_1°(5.15.50, 298.15 \text{ K}) = (5.12 \pm 0.14)$$

This value is statistically identical to the value selected for the Np system $\log_{10}\beta_1°(NpO_2CO_3^-, 298.15 \text{ K}) = (4.96 \pm 0.06)$ (LEMIRE et al. 2001).

No analogous species has been reported for the U system (note that UO_2^+ has a very limited stability field).

The stability of the limiting Pu(V) carbonate complex at high carbonate concentrations was determined from measurements of the formal potential of the Pu(VI)/Pu(V) couple at 25°C in 0.3 - 1.5 M Na_2CO_3. On the basis of the reversibility of the couple and of the stoichiometry of the limiting $Pu(VI)O_2(CO_3)_3^{4-}$ complex, the limiting complex was assumed to be $Pu(V)O_2(CO_3)_3^{5-}$ and to be formed by a single electron transfer

$$PuO_2(CO_3)_3^{4-} + e^- \Leftrightarrow PuO_2(CO_3)_3^{5-} \tag{5.15.51}$$

It is possible that the resulting $PuO_2(CO_3)_3^{5-}$ complex could lose a CO_3^{2-} after the reduction of $PuO_2(CO_3)_3^{4-}$, but there is no independent evidence for the stoichiometry of the limiting Pu(V) carbonate complex. In analogy to the Np(V) species (LEMIRE et al. 2001), the tricarbonato stoichiometry of the limiting complex was accepted by LEMIRE et al. (2001). The reported formal potentials of reaction (5.15.51) at 25°C in 0.3 - 1.5 M Na_2CO_3 were extrapolated to $I = 0$ by an SIT fit to the data (the extensive dataset of a single, carefully performed study was considered, because insufficient experimental details were given in the other four studies to evaluate possible effects of non-negligible junction potentials). The resulting standard potential for reaction (5.15.51), $E°(5.15.51, 298.15 \text{ K}) = (186 \pm 10)$ mV was then converted into $\Delta_r G_m°(5.15.51, 298.15 \text{ K}) = - (17.9 \pm 1.0)$ kJ·mol^{-1} and used with the selected $\Delta_r G_m°$ for the reactions

$$PuO_2^{2+} + e^- \Leftrightarrow PuO_2^+ \tag{5.15.4}$$

$$PuO_2^{2+} + 3CO_3^{2-} \Leftrightarrow PuO_2(CO_3)_3^{4-} \tag{5.15.44}$$

$\Delta_r G_m°(5.15.4, 298.15 \text{ K}) = - (90.29 \pm 0.52)$ kJ·mol^{-1} and $\Delta_r G_m°(5.15.44, 298.15 \text{ K}) = - (101 \pm 5)$ kJ·mol^{-1} to calculate $\Delta_r G_m°(5.15.52, 298.1)$ for

$$PuO_2^+ + 3CO_3^{2-} \Leftrightarrow PuO_2(CO_3)_3^{5-} \tag{5.15.52}$$

resulting in $\Delta_r G_m°(5.15.52, 298.1) = - (28.68 \pm 5.25)$ kJ.mol-1 and

$$\log_{10}\beta_3°(5.15.52, 298.15 \text{ K}) = (5.03 \pm 0.92)$$

$\Delta_r S_m°(5.15.51, 298.15 \text{ K})$ was estimated at infinite dilution based on the temperature dependence of the reduction potential at each of the four ionic strengths. $\Delta_r S_m°(5.15.51, 298.15 \text{ K})$ was used together with $\Delta_r G_m°(5.15.51, 298.15 \text{ K})$, the latter of which was obtained from the standard potential of reaction (5.15.51), for the calculation of $\Delta_r H_m°(5.15.51, 298.15 \text{ K})$. Finally,

$$\Delta_r H_m°(5.15.52, 298.15 \text{ K}) = - (19.11 \pm 8.50) \text{ kJ·mol}^{-1}$$

was calculated from $\Delta_r H_m°(5.15.51, 298.15\ K)$ using the selected enthalpy data for reactions (5.15.4) and (5.15.44).

In contrast to the neptunium system where data for $NpO_2(CO_3)_2^{3-}$ was selected, there is no experimental evidence for the existence of $PuO_2(CO_3)_2^{3-}$.

5.15.15.3 Pu(IV) carbonate complexes

Solubility experiments with Pu(IV) solids in basic carbonate and bicarbonate media show that plutonium solubility increases dramatically over that expected in basic, carbonate-free media. This clearly indicates that one or more highly co-ordinated carbonate complexes are formed under such conditions. Spectrophotometric experiments suggest that at least two carbonate complexes are formed and that at most three carbonate complexes are needed to describe the solubility data. There have been some discussions as to whether mixed hydroxide carbonate complexes are important in basic Pu(IV) containing solutions. The best currently available experiments indicate that such species, if found, are not dominant. Experiments that have lead to assuming mixed hydroxide carbonate complexes can in most cases be explained by the independent formation of hydrolysis products and carbonate complexes.

In a conventional spectrophotometric study starting with the limiting complex in concentrated CO_3^{2-} media, CAPDEVILA (1992) and CAPDEVILA et al. (1996) found that their observations could be described by assuming only two carbonate complexes. Consistent with constraints imposed by solubility experiments of other authors, they identified these complexes as $Pu(CO_3)_4^{4-}$ and $Pu(CO_3)_5^{6-}$. CAPDEVILA et al. (1996) reanalyzed the experimental results by CAPDEVILA (1992) in order to determine the stability constant for

$$Pu(CO_3)_4^{4-} + CO_3^{2-} \Leftrightarrow Pu(CO_3)_5^{6-} \tag{5.15.53}$$

at $I = 0$ from experiments performed between $I = 0.2$ to 4.5 m at $(22 \pm 1)°C$. Their value was accepted by LEMIRE et al. (2001) as the best estimate for

$$\log_{10} K_5°(5.15.53, 298.15\ K) = -(1.36 \pm 0.09)$$

CAPDEVILA et al. (1996) assigned a value of

$$\log_{10}\beta_5(5.15.54, I = 3\ M\ NaClO_4, 22°C) = (35.8 \pm 1.3)$$

to the reaction

$$Pu^{4+} + 5CO_3^{2-} \Leftrightarrow Pu(CO_3)_5^{6-} \tag{5.15.54}$$

According to LEMIRE et al. (2001), insufficient independent evidence is available to extrapolate this value to $I = 0$.

For the purposes of the database update we attempted to estimate a value for $\log_{10}\beta_5°(5.15.54)$ using SIT with $\Delta\varepsilon(5.15.54) = - (0.42 \pm 0.54)$ kg·mol^{-1}, calculated from the selected values $\varepsilon(Pu^{4+}, ClO_4^-) = (0.82 \pm 0.06)$ kg· mol^{-1} and $\varepsilon(CO_3^{2-}, Na^+) = - (0.08 \pm 0.03)$ kg· mol^{-1}. The value of $\varepsilon(Pu(CO_3)_5^{6-}, Na^+) = (0.00 \pm 0.52)$ kg·mol^{-1} was assumed to be equal to the value of $\varepsilon(Np(CO_3)_5^{6-}, Na^+)$ reported by LEMIRE et al. (2001) on p. 278. Noting that $\Delta Z^2(5.15.42) = 0$, $\log_{10}\beta_5°(5.15.54)$ can be calculated from

$$\log_{10}\beta_5°(5.15.54) = \log_{10}\beta_5(5.15.54) + \Delta\varepsilon(5.15.54)\ I$$

Neglecting the small temperature difference of 3˚C and expanding the uncertainty from 2.37 to 2.5

$$\log_{10}\beta_5°(5.15.54,\ 298.15\ K) = (34.5 \pm 2.5)$$

which is selected for the database update. For the reaction

$$Pu^{4+} + 4CO_3^{2-} \Leftrightarrow Pu(CO_3)_4^{4-} \tag{5.15.55}$$
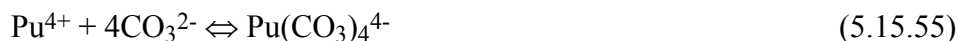
$\log_{10}\beta_4°(5.15.55,\ 298.15\ K)$ can now be calculated from $\log_{10}\beta_5°(5.15.54,\ 298.15\ K)$ and $\log_{10}K_5°(5.15.53,\ 298.15\ K)$. The selected value for the database update is therefore

$$\log_{10}\beta_4°(5.15.55,\ 298.15\ K) = (35.9 \pm 2.5)$$

Table 5.15.2: Compilation of selected actinide(IV) carbonate complexation constants.

Reaction	Const.	Th(IV)	U(IV)	Np(IV)	Pu(IV)
$An^{4+} + 4CO_3^{2-} \Leftrightarrow An(CO_3)_4^{4-}$	$\log_{10}\beta_4°$	-	35.22 ± 1.03	36.69 ± 1.11	35.9 ± 2.5
$An^{4+} + 5CO_3^{2-} \Leftrightarrow An(CO_3)_5^{6-}$	$\log_{10}\beta_5°$	29.8 ± 1.1	34.1 ± 1.0	35.62 ± 1.07	34.5 ± 2.5

5.15.15.4 Pu(III) carbonate complexes

Because Pu(III) oxidizes easily to Pu(IV) in basic aqueous solutions there are no experimental studies with respect to the identity and stability of Pu(III) carbonate complexes. Based on an analogy between trivalent actinides and trivalent lanthanides, stability constants were estimated for $PuCO_3^+$ and $Pu(CO_3)_2^-$. In the absence of an experimental verification of the existence of these species and confirmation of their stabilities, these values were not selected by LEMIRE et al. (2001). Am data can be used as chemical analogues in model calculations.

5.15.16   Solid plutonium carbonates

The only available thermodynamic data for plutonium carbonate solids are for Pu(VI) carbonate.

Additional solids have been reported: $K_4PuO_2(CO_3)_3(s)$, $(NH_4)_4PuO_2(CO_3)_3(s)$, $Ni_2PuO_2(CO_3)_3(s)$, $(NH_4)_2PuO_2(CO_3)_2(s)$, and $HgPuO_2(CO_3)_2 \cdot xH_2O(s)$. For all of these phases, however, thermodynamic and crystallographic data are missing.

The solubility product of $PuO_2CO_3(s)$ was measured in 3 M $NaClO_4$ at 20˚C. Extrapolation to $I = 0$ by SIT using a $\Delta\varepsilon$ value calculated from the selected ε values for PuO_2^{2+} and CO_3^{2-} resulted in $\log_{10}K_{s,0}°(293.15 \text{ K}) = - (14.2 \pm 0.3)$. In the absence of enthalpy data for

$$PuO_2CO_3(s) \Leftrightarrow PuO_2^{2+} + CO_3^{2-}$$
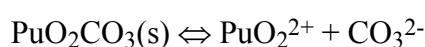
this value was selected as the best estimate for the solubility product at 25˚C. Therefore

$$\log_{10}K_{s,0}°(298.15 \text{ K}) = - (14.2 \pm 0.3)$$

5.15.17   Plutonium thiocyanate complexes

LEMIRE et al. (2001) discussed thiocyanate complexes of Pu(III), namely $PuSCN^{2+}$, $Pu(SCN)_2^+$, and $Pu(SCN)_3(aq)$, and selected data for the 1:1 complex. However, thiocyanate complexes are not included in the Nagra/PSI Thermochemical Database.

5.15.18   Plutonium silicides

A number of plutonium silicides are known: $Pu_5Si_3(s)$, $Pu_3Si_2(s)$, $PuSi(s)$, $Pu_3Si_5(s)$, and $PuSi_2(s)$. There are no solubility products or $\Delta_fG_m°$ values for any of these phases.

5.15.19   Plutonium alkaline-earth compounds

Several ternary oxides of alkaline earths elements with plutonium have been reported, but thermodynamic data are limited and only available for $Sr_3PuO_6(cr)$, $SrPuO_3(cr)$, $Ba_3PuO_6(cr)$, $BaPuO_3(cr)$, $Ba_2MgPuO_6(cr)$, $Ba_2CaPuO_6(cr)$, and $Ba_2SrPuO_6(cr)$. There are no solubility products or $\Delta_fG_m°$ values for any of these phases.

Table 5.15.3: Selected plutonium data. All data from LEMIRE et al. (2001), with the exception of those in ***boldface italics***.

TDB Version 05/92   **TDB Version 01/01**

Name	$\Delta_f G_m°$	$\Delta_f H_m°$	Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$S_m°$	$C_{p,m}°$	Species
-	-	-	Pu	0.0	0.0	54.46 ± 0.80	31.49 ± 0.40	Pu(cr, α)
PU+3	-578.6	-592.0	Pu+3	-579.0 ± 2.7	-591.8 ± 2.0	-184.5 ± 6.2		Pu^{3+}
PU+4	-481.6	-536.4	Pu+4	-478.0 ± 2.7	-539.9 ± 3.1	-414.5 ± 10.2		Pu^{4+}
PUO2+	-849.8	-914.6	PuO2+	-852.6 ± 2.9	-910.1 ± 8.9	1 ± 30		PuO_2^+
PUO2+2	-756.9	-822.2	PuO2+2	-762.4 ± 2.8	-822.0 ± 6.6	-71.2 ± 22.1		PuO_2^{2+}

Name	Redox	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Reaction
-	III	-	-	Pu+3	50.97 ± 0.15	-	$PuO_2^{2+} + 4\ H^+ + 3\ e^- \Leftrightarrow Pu^{3+} + 2\ H_2O(l)$
-	IV	-	-	Pu+4	33.28 ± 0.15	-	$PuO_2^{2+} + 4\ H^+ + 2\ e^- \Leftrightarrow Pu^{4+} + 2\ H_2O(l)$
-	V	-	-	PuO2+	15.82 ± 0.09	-	$PuO_2^{2+} + e^- \Leftrightarrow PuO_2^+$
PU+3	III	16.994	-55.6		-	-	$Pu^{4+} + e^- \Leftrightarrow Pu^{3+}$
PUOH+2	III	-7.0	0	PuOH+2	-6.9 ± 0.3	-	$Pu^{3+} + H_2O(l) \Leftrightarrow PuOH^{2+} + H^+$
PUOH2+	III	-15.0	0	-	-	-	$Pu^{3+} + 2\ H_2O(l) \Leftrightarrow Pu(OH)_2^+ + 2\ H^+$
PUOH3	III	-26.0	0	-	-	-	$Pu^{3+} + 3\ H_2O(l) \Leftrightarrow Pu(OH)_3(aq) + 3\ H^+$
PUOH4-	III	-33.0	0	-	-	-	$Pu^{3+} + 4\ H_2O(l) \Leftrightarrow Pu(OH)_4^- + 4\ H^+$
PUCL+2	III	0.8	0	PuCl+2	1.2 ± 0.2	-	$Pu^{3+} + Cl^- \Leftrightarrow PuCl^{2+}$
PUSO4+	III	3.1	0	PuSO4+	3.9 ± 0.6	17.2 ± 2.3	$Pu^{3+} + SO_4^{2-} \Leftrightarrow PuSO_4^+$
-	III	-	-	Pu(SO4)2-	5.7 ± 0.8	12 ± 16	$Pu^{3+} + 2\ SO_4^{2-} \Leftrightarrow Pu(SO_4)_2^-$
PUH2SO42	III	6.9	0	-	-	-	$Pu^{3+} + 2\ SO_4^{2-} + 2\ H^+ \Leftrightarrow Pu(HSO_4)_2^+$
PU2HPO4+	III	2.45	0	-	-	-	$Pu^{3+} + H_2PO_4^- \Leftrightarrow PuH_2PO_4^{2+}$
PUCO3+	III	9.6	0	-	-	-	$Pu^{3+} + CO_3^{2-} \Leftrightarrow PuCO_3^+$
PUCO32-	III	12.9	0	-	-	-	$Pu^{3+} + 2\ CO_3^{2-} \Leftrightarrow Pu(CO_3)_2^-$
PUCO33-3	III	16.2	0	-	-	-	$Pu^{3+} + 3\ CO_3^{2-} \Leftrightarrow Pu(CO_3)_3^{3-}$

Table 5.15.3: continued

TDB Version 05/92				TDB Version 01/01			
Name	Redox	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Reaction
PUOH+3	IV	-0.7	48.283	PuOH+3	-0.78 ± 0.60	36 ± 10	$Pu^{4+} + H_2O(l) \Leftrightarrow PuOH^{3+} + H^+$
PUOH2+2	IV	-2.3	74.517	-	-	-	$Pu^{4+} + 2\ H_2O(l) \Leftrightarrow Pu(OH)_2^{2+} + 2\ H^+$
PUOH3+	IV	-5.3	96.525	-	-	-	$Pu^{4+} + 3\ H_2O(l) \Leftrightarrow Pu(OH)_3^+ + 3\ H^+$
PUOH4	IV	-9.5	109.244	Pu(OH)4	***-8.4 ± 1.1***	**-**	***Pu⁴⁺ + 4 H₂O(l) ⇔ Pu(OH)₄(aq) + 4 H⁺***
PUOH5-	IV	-15.0	125.855	-	-	-	$Pu^{4+} + 5\ H_2O(l) \Leftrightarrow Pu(OH)_5^- + 5\ H^+$
PUF+3	IV	7.9	24.686	PuF+3	8.84 ± 0.10	9.1 ± 2.2	$Pu^{4+} + F^- \Leftrightarrow PuF^{3+}$
-	IV	-	-	PuF2+2	15.7 ± 0.2	11 ± 5	$Pu^{4+} + 2\ F^- \Leftrightarrow PuF_2^{2+}$
PUCL+3	IV	0.9	17.405	PuCl+3	1.8 ± 0.3	-	$Pu^{4+} + Cl^- \Leftrightarrow PuCl^{3+}$
PUCL2+2	IV	1.9	0	-	-	-	$Pu^{4+} + 2\ Cl^- \Leftrightarrow PuCl_2^{2+}$
PUSO4+2	IV	5.8	12.468	PuSO4+2	6.89 ± 0.23	-	$Pu^{4+} + SO_4^{2-} \Leftrightarrow PuSO_4^{2+}$
PUSO42	IV	10.2	41.338	Pu(SO4)2	11.14 ± 0.34	-	$Pu^{4+} + 2\ SO_4^{2-} \Leftrightarrow Pu(SO_4)_2(aq)$
PUSO43-2	IV	11.5	0	-	-	-	$Pu^{4+} + 3\ SO_4^{2-} \Leftrightarrow Pu(SO_4)_3^{2-}$
PUNO3+3	IV	1.8	0	PuNO3+3	1.95 ± 0.15	-	$Pu^{4+} + NO_3^- \Leftrightarrow PuNO_3^{3+}$
PUHPO4+2	IV	13.549	40.624	-	-	-	$Pu^{4+} + HPO_4^{2-} \Leftrightarrow PuHPO_4^{2+}$
PUH2PO42	IV	24.297	26.648	-	-	-	$Pu^{4+} + 2\ HPO_4^{2-} \Leftrightarrow Pu(HPO_4)_2(aq)$
PUH3PO43	IV	32.946	-5.111	-	-	-	$Pu^{4+} + 3\ HPO_4^{2-} \Leftrightarrow Pu(HPO_4)_3^{2-}$
PUH4PO44	IV	42.995	-74.149	-	-	-	$Pu^{4+} + 4\ HPO_4^{2-} \Leftrightarrow Pu(HPO_4)_4^{4-}$
-	IV	-	-	PuH3PO4+4	2.4 ± 0.3	-	$Pu^{4+} + H_3PO_4(aq) \Leftrightarrow PuH_3PO_4^{4+}$
PUCO3+2	IV	41.0	-186.69	-	-	-	$Pu^{4+} + CO_3^{2-} \Leftrightarrow PuCO_3^{2+}$
-	IV	-	-	Pu(CO3)4-4	***35.9 ± 2.5***	**-**	***Pu⁴⁺ + 4 CO₃²⁻ ⇔ Pu(CO₃)₄⁴⁻***
-	IV	-	-	Pu(CO3)5-6	***34.5 ± 2.5***	**-**	***Pu⁴⁺ + 5 CO₃²⁻ ⇔ Pu(CO₃)₅⁶⁻***
PUOH3CO3	IV	-1.0	0	-	-	-	$Pu^{4+} + CO_3^{2-} + 3\ H_2O(l) \Leftrightarrow$ $Pu(OH)_3CO_3^- + 3H^+$

Table 5.15.3: continued

TDB Version 05/92				TDB Version 01/01			
Name	Redox	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Reaction
PUO2+	V	-18.585	193.460	-	-	-	$Pu^{4+} + 2\ H_2O(l) \Leftrightarrow PuO_2^+ + 4\ H^+ + e^-$
PUO2OH	V	-9.7	0	PuO2OH	$\leq$ -9.73	-	$PuO_2^+ + H_2O(l) \Leftrightarrow PuO_2OH(aq) + H^+$
PUO2CL	V	0.17	0	-	-	-	$PuO_2^+ + Cl^- \Leftrightarrow PuO_2Cl(aq)$
-	V	-	-	PuO2CO3-	5.12 ± 0.14	-	$PuO_2^+ + CO_3^{2-} \Leftrightarrow PuO_2CO_3^-$
-	V	-	-	PuO2(CO3)3-5	5.03 ± 0.92	-19.11 ± 8.50	$PuO_2^+ + 3\ CO_3^{2-} \Leftrightarrow PuO_2(CO_3)_3^{5-}$
PUO2+2	VI	-34.860	285.860	-	-	-	$Pu^{4+} + 2\ H_2O(l) \Leftrightarrow PuO_2^{2+} + 4\ H^+ + 2\ e^-$
PUO2OH+	VI	-5.6	0	PuO2OH+	-5.5 ± 0.5	28 ± 15	$PuO_2^{2+} + H_2O(l) \Leftrightarrow PuO_2OH^+ + H^+$
PUO2OH2	VI	-11.0	0	PuO2(OH)2	$-13.2 \pm \mathit{1.5}$	-	$PuO_2^{2+} + 2\ H_2O(l) \Leftrightarrow$ $PuO_2(OH)_2(aq) + 2\ H^+$
PUO2OH3-	VI	-20.7	0	-	-	-	$PuO_2^{2+} + 3\ H_2O(l) \Leftrightarrow PuO_2(OH)_3^- + 3\ H^+$
PUO22OH+	VI	-4.3	0	-	-	-	$2\ PuO_2^{2+} + H_2O(l) \Leftrightarrow (PuO_2)_2OH^{3+} + H^+$
PUO22OH2	VI	-8.3	0	(PuO2)2(OH)2+2	$-7.5 \pm \mathit{1.0}$	-	$2\ PuO_2^{2+} + 2\ H_2O(l) \Leftrightarrow$ $(PuO_2)_2(OH)_2^{2+} + 2\ H^+$
PUO23OH5	VI	-21.7	0	-	-	-	$3\ PuO_2^{2+} + 5\ H_2O(l) \Leftrightarrow$ $(PuO_2)_3(OH)_5^+ + 5\ H^+$
PUO2F+	VI	5.7	0	PuO2F+	4.56 ± 0.20	-	$PuO_2^{2+} + F^- \Leftrightarrow PuO_2F^+$
PUO2F2	VI	11.0	0	PuO2F2	7.25 ± 0.45	-	$PuO_2^{2+} + 2\ F^- \Leftrightarrow PuO_2F_2(aq)$
PUO2F3-	VI	15.8	0	-	-	-	$PuO_2^{2+} + 3\ F^- \Leftrightarrow PuO_2F_3^-$
PUO2F4-2	VI	18.7	0	-	-	-	$PuO_2^{2+} + 4\ F^- \Leftrightarrow PuO_2F_4^{2-}$
PUO2CL+	VI	0.2	0	PuO2Cl+	0.70 ± 0.13	-	$PuO_2^{2+} + Cl^- \Leftrightarrow PuO_2Cl^+$
PUO2CL2	VI	-0.25	0	PuO2Cl2	-0.6 ± 0.2	-	$PuO_2^{2+} + 2\ Cl^- \Leftrightarrow PuO_2Cl_2(aq)$

Table 5.15.3: continued

TDB Version 05/92				TDB Version 01/01			
Name	Redox	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Reaction
PUO2SO4	VI	3.0	0	PuO2SO4	3.38 ± 0.20	16.1 ± 0.6	$PuO_2^{2+} + SO_4^{2-} \Leftrightarrow PuO_2SO_4(aq)$
-	VI	-	-	PuO2(SO4)2-2	4.4 ± 0.2	43 ± 9	$PuO_2^{2+} + 2\ SO_4^{2-} \Leftrightarrow PuO_2(SO_4)_2^{2-}$
PUO2H2PO	VI	3.95	0	-	-	-	$PuO_2^{2+} + H_2PO_4^- \Leftrightarrow PuO_2H_2PO_4^+$
PUO2CO3	VI	13.2	0	PuO2CO3	*9.3 ± 0.5*		$PuO_2^{2+} + CO_3^{2-} \Leftrightarrow PuO_2CO_3(aq)$
PUO2CO32	VI	14.9	0	PuO2(CO3)2-2	*14.6 ± 0.9*	-27 ± 4	$PuO_2^{2+} + 2\ CO_3^{2-} \Leftrightarrow PuO_2(CO_3)_2^{2-}$
PUO2CO33	VI	20.9	0	PuO2(CO3)3-4	17.7 ± 0.9	-38.6 ± 2.0	$PuO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow PuO_2(CO_3)_3^{4-}$
PUO2OHCO	VI	9.85	0	-	-	-	$PuO_2^{2+} + CO_3^{2-} + H_2O(l) \Leftrightarrow$ $PuO_2(OH)CO_3^- + H^+$
PUO2OH2C	VI	-5.0	0	-	-	-	$PuO_2^{2+} + CO_3^{2-} + 2\ H_2O(l) \Leftrightarrow$ $PuO_2(OH)_2CO_3^{2-} + 2\ H^+$
-	VI	-	-	(UO2)2PuO2(CO3)6-6	52.7 ± 1.6	-	$2\ UO_2^{2+} + PuO_2^{2+} + 6\ CO_3^{2-} \Leftrightarrow$ $(UO_2)_2PuO_2(CO_3)_6^{6-}$

Name	Redox	$\log_{10}K_{s,0}°$	$\Delta_r H_m°$	Name	$\log_{10}K_{s,0}°$		Reaction
PU(OH)3CR	III	22.3	-148.323	Pu(OH)3(cr)	15.8 ± 1.5		$Pu(OH)_3(cr) + 3\ H^+ \Leftrightarrow Pu^{3+} + 3\ H_2O(l)$
PU2O3	III	48.1	-360.326	-	-		$Pu_2O_3(cr) + 6\ H^+ \Leftrightarrow 2\ Pu^{3+} + 3\ H_2O(l)$
PUF3CR	III	-10.0	-46.317	-	-		$PuF_3(cr) \Leftrightarrow Pu^{3+} + 3\ F^-$
PUCL3CR	III	-11.4	0	-	-		$PuCl_3(cr) \Leftrightarrow Pu^{3+} + 3\ Cl^-$
-	III	-	-	PuPO4(s,hyd)	-24.6 ± 0.8		$PuPO_4(s, hyd) \Leftrightarrow Pu^{3+} + PO_4^{3-}$
PU(OH)4CR	IV	1.0	-68.910	-	-		$Pu(OH)_4(cr) + 4\ H^+ \Leftrightarrow Pu^{4+} + 4\ H_2O(l)$
-	IV	-	-	PuO2(hyd,ag)	-2.0 ± 1.0		$PuO_2(hyd, aged) + 4\ H^+ \Leftrightarrow Pu^{4+} + 2\ H_2O(l)$

Table 5.15.3: continued

TDB Version 05/92				**TDB Version 01/01**		
Name	Redox	$\log_{10}K_{s,0}°$	$\Delta_r H_m°$	Name	$\log_{10}K_{s,0}°$	Reaction
PUO2	IV	-7.0	-52.091	-	-	$PuO_2(cr) + 4\ H^+ \Leftrightarrow Pu^{4+} + 2\ H_2O(l)$
PUF4CR	IV	-13.0	-99.998	-	-	$PuF_4(cr) / Pu^{4+} + 4\ F^-$
PUH2P42C	IV	-27.997	-34.472	Pu(HPO4)2(am,hyd)	-30.45 ± 0.51	$Pu(HPO_4)_2(am,\ hyd) \Leftrightarrow Pu^{4+} + 2\ HPO_4^{2-}$
PUO2OHCR	V	5.5	-42.677	PuO2OH(am)	5.0 ± 0.5	$PuO_2OH(am) + H^+ \Leftrightarrow PuO_2^+ + H_2O(l)$
-	VI	-	-	PuO2(OH)2:H2O(cr)	5.5 ± 1.0	$PuO_2(OH)_2 \cdot H_2O(cr) + 2\ H^+ \Leftrightarrow$ $PuO_2^{2+} + 3\ H_2O(l)$
PUO3	VI	3.5	-35.900	-	-	$PuO_3(cr) + 2\ H^+ \Leftrightarrow PuO_2^{2+} + H_2O(l)$
PLHPO4CR	VI	-13.05	-10.583	-	-	$PuO_2HPO_4\ (cr) \Leftrightarrow PuO_2^{2+} + HPO_4^{2-}$
PLCO3CR	VI	-14.0	0	PuO2CO3(s)	-14.2 ± 0.3	$PuO_2CO_3(s) \Leftrightarrow PuO_2^{2+} + CO_3^{2-}$

5.15.20   References

CAPDEVILA, H. (1992): Données thermodynamiques sur l'oxydoréduction du plutonium en milieux acide et carbonate. Ph.D. Thesis , Université de Paris-Sud, Paris.

CAPDEVILA, H., VITORGE, P., GIFFAUT, E. & DELMAU, L. (1996): Spectrophotometric study of the dissociation of the Pu(IV) carbonate limiting complex. Radiochimica Acta, 74, 93-98.

GRENTHE, I., FUGER, J., KONINGS, R.J.M., LEMIRE, R.J., MULLER, A.B., NGUYEN-TRUNG, C. & WANNER, H. (1992): Chemical Thermodynamics of Uranium. Chemical Thermodynamics, Vol. 1, North-Holland, Amsterdam. 715 pp.

GRENTHE, I., PUIGDOMENECH, I., SANDINO, M.C.A. & RAND, M.H. (1995): Corrections to the Uranium NEA-TDB review. In: SILVA, R.J., BIDOGLIO, G., RAND, M.H., ROBOUCH, P.B., WANNER, H. & PUIGDOMENECH, I. (eds.): Chemical Thermodynamics of Americium. Chemical Thermodynamics, Vol. 2, North-Holland, Amsterdam, 347-374.

LEMIRE, R.J., FUGER, J., NITSCHE, H., POTTER, P., RAND, M.H., RYDBERG, J., SPAHIU, K., SULLIVAN, J.C., ULLMAN, W.J., VITORGE, P. & WANNER, H. (2001): Chemical Thermodynamics of Neptunium & Plutonium. Chemical Thermodynamics, Vol. 4, NEA/OECD, Paris. 845 pp.

LIERSE, C. & KIM, J.I. (1986): Chemisches Verhalten von Plutonium in natürlichen aquatischen Systemen: Hydrolyse, Carbonatkomplexierung und Redoxreaktionen. Report RCM 02286, Institut für Radiochemie, Technische Universität München.

NECK, V. & KIM, J.I. (2000): An electrostatic approach for the prediction of actinide complexation constants with inorganic ligands - application to carbonate complexes. Radiochimica Acta, 88, 815-822.

NECK, V. & KIM, J.I. (2001): Solubility and hydrolysis of tetravalent actinides. Radiochimica Acta, 89, 1-16.

PASHALIDIS, I., CZERWINSKI, K.R., FANGHÄNEL, T. & KIM, J.I. (1997): Solid-liquid phase equilibria of Pu(VI) and U(VI) in aqueous carbonate systems. Determination of stability constants. Radiochimica Acta, 76, 55-62.

RAI, D., HESS, N.J., FELMY, A.R., MOORE, D.A., YUI, M. & VITORGE, P. (1999): A thermodynamic model for the solubility of $PuO_2(am)$ in the aqueous K^+-HCO_3^--CO_3^{2-}-OH^--H_2O system. Radiochimica Acta, 86, 89.

ROBOUCH, P. & VITORGE, P. (1987): Solubility of $PuO_2(CO_3)$. Inorganica Chimica Acta, 140, 239-242.

SILVA, R.J., BIDOGLIO, G., RAND, M.H., ROBOUCH, P.B., WANNER, H. & PUIGDOMENECH, I. (1995): Chemical Thermodynamics of Americium. Chemical Thermodynamics, Vol. 2, North-Holland, Amsterdam. 374 pp.

SULLIVAN, J.C. & WOODS, M. (1982): Thermodynamics of plutonium(VI) interaction with bicarbonate. Radiochimica Acta, 31, 45-50.

ULLMAN, W.J. & SCHREINER, F. (1988): Calorimetric determination of the enthalpies of the carbonate complexes of U(VI), Np(VI), and Pu(VI) in aqueous solution at 25°C. Radiochimica Acta, 43, 37-44.

5.16   Radium

The thermodynamic properties of radium included in the Nagra/PSI TDB 01/01 (see Table 5.16.1) are all taken from LANGMUIR & RIESE (1985). Due to a lack of experimental investigations, all data are based on estimates only, with the notable exception of the solubility product for $RaSO_4(cr)$.

Ra(cr) and Ra^{2+}: $S_m°(Ra, cr)$, $\Delta_f G_m°(Ra^{2+})$, $\Delta_f H_m°(Ra^{2+})$, and $S_m°(Ra^{2+})$ are all estimates by WAGMAN et al. (1982).

$RaOH^+$: LANGMUIR & RIESE (1985) plotted the formation constants ($\log_{10}K°$ values) for $CaOH^+$, $SrOH^+$ and $BaOH^+$ by BAES & MESMER (1981) against the effective ionic radii of Ca^{2+}, Sr^{2+}, Ba^{2+} and Ra^{2+} in 8-fold coordination. From the observed trend they estimated the formation constant of

$$Ra^{2+} + OH^- \Leftrightarrow RaOH^+ \tag{5.16.1}$$

to be

$$\log_{10}K°(5.16.1, 298.15\ K) = 0.5$$

The enthalpy of reaction was taken to be

$$\Delta_r H_m°(5.16.1, 298.15\ K) = 1.1\ kcal \cdot mol^{-1}$$

assuming it to be identical with the corresponding value for $BaOH^+$.

$RaCl^+$: LANGMUIR & RIESE (1985) estimated $\log_{10}K°$ for

$$Ra^{2+} + Cl^- \Leftrightarrow RaCl^+ \tag{5.16.2}$$

by using the Fuoss equation (FUOSS 1958), an electrostatic model for calculating formation constants of ion pairs:

$$\log_{10}K°(5.16.2, 298.15\ K) = -0.10$$

The Fuoss equation was also used to estimate $\Delta_r S_m°(5.16.2, 298.15\ K)$ which then lead to

$$\Delta_r H_m°(5.16.2, 298.15\ K) = 0.50\ kcal \cdot mol^{-1}$$

using the Gibbs-Helmholtz equation with $\Delta_r G_m°(5.16.2, 298.15\ K)$ calculated from $\log_{10}K°(5.16.2, 298.15\ K)$.

$RaCO_3(aq)$: LANGMUIR & RIESE (1985) estimated a formation constant for $BaCO_3(aq)$ using the oxalate method (linear relation between $\log_{10}K°$ values of 1:1 carbonate and 1:1 oxalate complexes for various cations) by LANGMUIR (1979). Linear extrapolation of the $\log_{10}K°$ values for $BaCO_3(aq)$ (estimated above) and $SrCO_3(aq)$ (PLUMMER 1983, oral communication) plotted against the effective ionic radii of Sr^{2+}, Ba^{2+} and Ra^{2+} in 8-fold coordination resulted in

$$\log_{10}K°(5.16.3, 298.15 \text{ K}) = 2.5$$

for

$$Ra^{2+} + CO_3^{2-} \Leftrightarrow RaCO_3(aq) \tag{5.16.3}$$

The Fuoss equation was used to estimate $\Delta_r S_m°(5.16.3, 298.15 \text{ K})$ which then lead to

$$\Delta_r H_m°(5.16.3, 298.15 \text{ K}) = 1.07 \text{ kcal} \cdot \text{mol}^{-1}$$

RaSO$_4$(aq): LANGMUIR & RIESE (1985) estimated $\log_{10}K°(5.16.4)$ and $\Delta_r S_m°(5.16.4)$ for the reaction

$$Ra^{2+} + SO_4^{2-} \Leftrightarrow RaSO_4(aq) \tag{5.16.4}$$

by using the Fuoss equation. They obtained

$$\log_{10}K°(5.16.4, 298.15 \text{ K}) = 2.75$$

and calculated $\Delta_r H_m°(5.16.4)$ from $\Delta_r S_m°(5.16.4)$

$$\Delta_r H_m°(5.16.4, 298.15 \text{ K}) = 1.3 \text{ kcal} \cdot \text{mol}^{-1}$$

RaCO$_3$(cr): LANGMUIR & RIESE (1985) plotted the solubility product constants ($\log_{10}K_{s,0}°$ values) for SrCO$_3$(cr), strontianite (BUSENBERG et al. 1984), and BaCO$_3$(cr), witherite (calculated from Gibbs free energy data given by WAGMAN et al. 1982), against the effective ionic radii of Sr^{2+}, Ba^{2+} and Ra^{2+} in 8-fold coordination and obtained an estimate of $\log_{10}K_{s,0}°$ for

$$RaCO_3(cr) \Leftrightarrow Ra^{2+} + CO_3^{2-} \tag{5.16.5}$$

$$\log_{10}K_{s,0}°(5.16.5, 298.15 \text{ K}) = -8.3$$

from an extrapolation of the linear trend.

$S_m°(RaCO_3, cr)$ was estimated and used to calculate

$$\Delta_r H_m°(5.16.5, 298.15 \text{ K}) = 2.8 \text{ kcal} \cdot \text{mol}^{-1}$$

Note that in their Table 2, LANGMUIR & RIESE (1985) gave the wrong sign for this value.

RaSO$_4$(cr): NIKITIN & TOLMATSCHEFF (1933) (reference not examined) measured the solubility of RaSO$_4$(cr) at 20°C in pure water and in Na$_2$SO$_4$ solutions. Their experimental data were used by LANGMUIR & RIESE (1985) to extract the solubility product constant

$$\log_{10}K_{s,0}°(5.16.6, 298.15 \text{ K}) = -10.26$$

for

$$RaSO_4(cr) \Leftrightarrow Ra^{2+} + SO_4^{2-} \tag{5.16.6}$$

The corresponding enthalpy of reaction

$$\Delta_r H_m°(5.16.6, 298.15 \text{ K}) = 9.4 \text{ kcal} \cdot \text{mol}^{-1}$$

was estimated by LANGMUIR & RIESE (1985) through extrapolation of a linear plot of the dissociation enthalpies for $SrSO_4(cr)$, celestine, and $BaSO_4(cr)$, barite, against the effective ionic radii of the cations in 8-fold coordination.

Note that in their Table 2, LANGMUIR & RIESE (1985) gave the wrong sign for this value.

Table 5.16.1: Selected radium data at 25°C and 1 bar. All from LANGMUIR & RIESE (1985). Note that these authors gave a wrong sign for $\Delta_r H_m°(RaCO_3, cr, 298.15 \text{ K})$ and $\Delta_r H_m°(RaSO_4, cr, 298.15 \text{ K})$.

$\Delta_f G_m°$	$\Delta_f H_m°$	$S_m°$	$\log_{10} K°$	$\Delta_r H_m°$	Species, Reaction
0	0	71			Ra(cr)
-561.5	-527.6	54			Ra^{2+}
			0.5	4.6	$Ra^{2+} + OH^- \Leftrightarrow RaOH^+$
			-0.10	2.1	$Ra^{2+} + Cl^- \Leftrightarrow RaCl^+$
			2.5	4.48	$Ra^{2+} + CO_3^{2-} \Leftrightarrow RaCO_3(aq)$
			2.75	5.4	$Ra^{2+} + SO_4^{2-} \Leftrightarrow RaSO_4(aq)$
			-8.3	11.7	$RaCO_3(cr) \Leftrightarrow Ra^{2+} + CO_3^{2-}$
			-10.26	39.3	$RaSO_4(cr) \Leftrightarrow Ra^{2+} + SO_4^{2-}$

5.16.1   References

BAES, C.F.JR, & MESMER, R.E. (1981): The thermodynamics of cation hydrolysis. American Journal of Science, 281, 935-962.

BUSENBERG, E., PLUMMER, L.N. & Parker, V.B. (1984): The solubility of strontianite ($SrCO_3$) in CO_2–H_2O solutions between 2 and 91°C, the association constants of $SrHCO_3^+(aq)$ and $SrCO_3°(aq)$ between 5 and 80°C, and an evaluation of the thermodynamic properties of $Sr^{2+}(aq)$ and $SrCO_3(cr)$ at 25°C and 1 atm total pressure. Geochimica et Cosmochimica Acta, 48, 2021-2035.

FUOSS, R.D. (1958): Ionic association III. The equilibrium between ion pairs and free ions. Journal of the American Chemical Society, 80, 5059-5061.

LANGMUIR, D. (1979): Techniques of estimating thermodynamic properties for some aqueous complexes of geochemical interest. In: JENNE, E.A. (ed.): Chemical Modeling in Aqueous Systems, American Chemical Society Symposium Series, 93, 353-387.

LANGMUIR, D. & RIESE, A.C. (1985): The thermodynamic properties of radium. Geochimica et Cosmochimica Acta, 49, 1593-1601.

NIKITIN, B. & TOLMATSCHEFF, P. (1933): Ein Beitrag zur Gültigkeit des Massenwirkungsgesetzes II. Quantitative Bestimmung der Löslichkeit des Radiumsulfates in Natriumsulfatlösungen und in Wasser. Zeitschrift für Physikalische Chemie, A167, 260-272.

WAGMAN, D.D., EVANS, W.H., PARKER, V.B., SCHUMM, R.H., HALOW, I., BAILEY, S.M., CHURNEY, K.L. & NUTTALL, R.L. (1982): The NBS tables of chemical thermodynamic properties: Selected values for inorganic and C_1 and C_2 organic substances in SI units. Journal of Physical and Chemical Reference Data, 11, Supplement No. 2, 1-392.

5.17   Selenium

The thermodynamics of selenium is one of the topics of the ongoing Phase II of the OECD NEA Thermodynamic Database (TDB) project. Although this review will not be finished before early 2002 (according to a recent NEA TDB progress report), we decided not to parallel the efforts of the selenium review team. However, we recognised that currently available Se data (PEARSON et al. 1992) partly deviate from those already provided in NEA's set of recommended auxiliary data and that very small differences even exist within the NEA review series (RARD et al. 1999, SILVA et al. 1995, GRENTHE et al. 1992).

In order to keep the Nagra/PSI TDB 01/01 as consistent as possible with the NEA recommended values, the present note provides adjustments of corresponding equilibria. Additionally, original literature sources leading to the compiled values, taken from a very recent compilation of Se-data (SÉBY et al. 2001), are provided where appropriate.

The compilation of SÉBY et al. (2001) lists a large number of "solubility products" for metal selenates, -selenites and -selenides. However, selenates and selenites generally have high solubilities and it is questionable, whether such solids will ever be solubility limiting phases in environmental system or not. On the other hand, many metal selenides are reported to have extremely low solubility products (similar to the sulphides; the winner in this list is PtSe with a $\log_{10}K_{so}$ of -81.4 !). These low solubility products are then "compensated" with rather high complex formation constants, in order to describe the measured solute concentrations. We do not think that these data should flow into the update in their present state. Moreover, it will be very instructive to see how the NEA review team will deal with this rather controversial collection of data.

The Nagra TDB 05/92 (PEARSON et al. 1992) includes only 8 aqueous species and elemental Se, but no metal complexes (they had already been dropped during an earlier, not well documented update). The NEA auxiliary data (RARD et al. 1999, SILVA et al. 1995, GRENTHE et al. 1992) recommend 5 equilibria, but unfortunately two important redox equilibria are not included.

5.17.1   Elemental Selenium

Based on GRØNVOLD et al. (1984) the NEA recommends

S_m° **(Se, cr, 298.15 K)** $= 42.27 \pm 0.05$ **J mol^{-1} K^{-1},**

$C_{p,m}^\circ$ **(Se, cr, 298.15 K)** $= 25.03 \pm 0.05$ **J mol^{-1} K^{-1}.**

5.17.2. Redox

For the equilibrium

$$H_2SeO_3(aq) + 4\ I^- + 4\ H^+ \Leftrightarrow Se(cr) + 2\ I_2(cr) + 3\ H_2O(l) \tag{5.17.1}$$
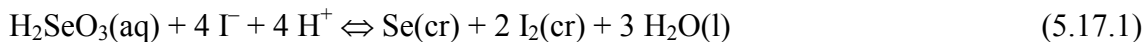
the NEA recommends $\mathbf{log_{10}K_{so}°(5.17.1) = 13.84 \pm 0.10}$, based on an experimental study from SCHOTT et al. (1928). According to SÉBY et al. (2001) at least two independent studies (NEVSKII et al. 1968, OSMAN-ZADE & VAGRAMYAN 1966) seem to confirm this constant. Using $\Delta_f G_m°(I^-, aq, 298.15\ K) = -51.72 \pm 0.11\ kJ\ mol^{-1}$ (taken from COX et al. 1989) GRENTHE et al. (1992) calculate $\Delta_f G_m°(H_2SeO_3, aq, 298.15\ K) = -425.5 \pm 0.6\ kJ\ mol^{-1}$ (note that the value tabulated in a later issue of the NEA series is $-425.527 \pm 0.736\ kJ\ mol^{-1}$; RARD et al. 1999). When re-writing equilibrium (5.17.1) as a half-reaction one obtains

$$H_2SeO_3(aq) + 4\ H^+ + 4\ e^- \Leftrightarrow Se(cr) + 3\ H_2O(l) \tag{5.17.1a}$$
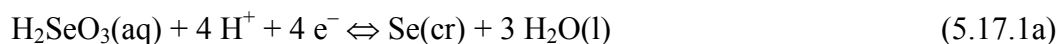
with $\mathbf{log_{10}K°(5.17.1a) = 50.09 \pm 0.13}$.

With the exception of the Se(IV)/Se(0) couple given above, the NEA auxiliary data do not include further redox data. SÉBY et al. (2001) list 3 constants ($E^0(5.17.2) = 1.088\ V$; $1.090\ V$, $1.090\ V$) for the equilibrium

$$HSeO_4^- + 3\ H^+ + 2\ e^- \Leftrightarrow H_2SeO_3(aq) + H_2O(l), \tag{5.17.2}$$
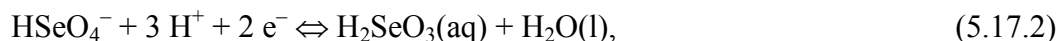
but it seems rather obvious that all three values trace back to the same experimental study by SCHOTT et al. (1928). The other references mentioned in SÉBY et al. (2001) (i.e. LATIMER 1952, VAN MUYLER & POURBAIX 1964, ZHDANOV 1985 and MASSCHELEYN et al. 1991) are not related to experimental work. The value of $E^0(5.17.2) = 1.088\ V$ from SCHOTT et al. (1928) leads to $\mathbf{log_{10}K°(5.17.2) = 36.78}$, and we derive

$$\Delta_f G_m°(HSeO_4^-, aq, 298.15\ K) = -452.7\ kJ\ mol^{-1}.$$

No uncertainty is available for this constant.

Data for the reduction of Se(0) to selenide are unclear. SÉBY et al. (2001) state that "*no direct experimental measurements of the redox standard potential is available in the literature*". It seems that presently available numbers are mainly the result of guesswork based on combining Gibbs free energies. The two different reduction potentials ($E^0(5.17.3) = -0.400\ V$; $-0.115\ V$) provided by SÉBY et al. (2001, Tab. 4) for the equilibrium

$$Se(s) + 2\ H^+ + 2\ e^- \Leftrightarrow H_2Se(aq) \tag{5.17.3}$$

give either $\mathbf{log_{10}K°(5.17.3) = -13.5}$ or $\mathbf{-3.9}$. The huge difference is traced back to the selection of Gibbs free energy of formation of $H_2Se(aq)$. LATIMER (1952) gave $-77\ kJ\ mol^{-1}$, based on old NBS

Tables. However, it seems that the National Bureau of Standards has changed this value to -22.2 kJ mol^{-1}, a number which, in our days, seems to be accepted by several database builders (ZHDANOV 1985, WOODS & GARRELS 1987, MASSCHELEYN et al. 1991). Note that -22.2 kJ mol^{-1} correspond much better to the Gibbs free energy of the chemically similar H$_2$S(aq) (-28 ± 2 kJ mol^{-1}; CODATA) than do Latimer's -77 kJ mol^{-1}.

These findings force us to answer two questions:

    i)   does it make sense to keep selenide in the database?

    ii)   which of the two numbers should be selected?

As mentioned above, we will not replicate the work of NEA's selenium review team. Therefore, we do not perform a scientific study on this subject, but we try to make a reasonable **decision**. Dropping selenide, Se(–II), from the database would probably significantly deteriorate its applicability. To our knowledge, the existence of selenide in subsurface, reducing environments is well established. In the waste management literature, sparingly soluble solids like native Se, ferro-selite (FeSe$_2$) or achavalite (FeSe) are considered to control dissolved selenium (see for example LANGMUIR & APTED 1992), but according to ordinary textbooks (STANTON 1972) selenide is strongly associated with sulfide minerals. Thus, Se(–II)-control by mixed phases or even solid solutions with sulfides would certainly be a meaningful alternative to the rather exotic pure selenide minerals. Since selenium is a high priority element in geological disposal of nuclear waste (one of the reasons to review the thermodynamics of this element), we **decide** to maintain selenide in the database.

As already indicated, the more recent literature seems to give preference to **log$_{10}$K°(5.17.3) = –3.9/** $\Delta_f G_m°$(H$_2$Se, aq, 298.15 K) = -22.2 kJ mol^{-1} (no uncertainties given). SÉBY et al. (2001) recommend the same constant, unfortunately without giving more details. We **decide** to keep this value.

Note that for the reason of convenience the reaction forming H$_2$Se(aq) compiled in Table 5.17.1 is given as the homogeneous equilibrium

$$H_2Se(aq) + 3\ H_2O(l) \Leftrightarrow H_2SeO_3(aq) + 6\ H^+ + 6\ e^-, \qquad (5.17.3a)$$
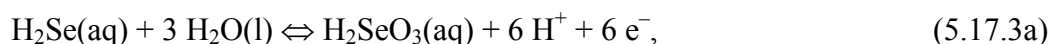
which actually represents a linear combination of the equilibria (5.17.1a) and (5.17.3). It is not clear, whether the experimental data behind the two sets of data describe identical modifications of elemental Se or not, and, thus, whether combining the two equilibria is really allowed or not.

It is clearly stated here that the redox equilibrium (5.17.3a) does by no means have the character of a reviewed entity. It should be regarded as a placeholder for a poorly known chemical behaviour which, on the other hand, is of primary importance in the field of waste

management. Dropping this equilibrium from the database would probably cause more erroneous results in applications than keeping it. It's indispensable to replace this equilibrium with the result expected from the NEA selenium review team.

5.17.3   Selenide species

For the deprotonation of di-hydrogen selenide

$$H_2Se(aq) + \Leftrightarrow HSe^- + H^+ \tag{5.17.4}$$

the NEA auxiliary data recommend **$\log_{10}K°(5.17.4) = -3.8 \pm 0.3$,** based on an average of three constants reviewed and discussed by PERRIN (1982). According to the compilation of SÉBY et al. (2001) no new experimental studies have been performed since Perrin's review in 1982. From equilibrium (5.17.4) and $\Delta_f G_m°(H_2Se, aq, 298.15\ K) = -22.2\ kJ\ mol^{-1}$ we obtain

$$\Delta_f G_m°(HSe^-, aq, 298.15\ K) = -43.9\ kJ\ mol^{-1},$$

with an uncertainty of at least $\pm 1.7\ kJ\ mol^{-1}$.

The Nagra TDB 05/92 includes a formation constant for the free selenide ion Se^{2-}:

$$HSe^- \Leftrightarrow Se^{2-} + H^+ \tag{5.17.5}$$

with $\log_{10}K°(5.17.5) = -14.944$. Comparable to sulfide, selenide is a very strong base and measurable quantities in solution will exist only above pH 13 to 14 (according to the given value). Reported $\log_{10}K°(5.17.5)$ values range from -11 to -15 and SÉBY et al. (2001) recommend to use $\log_{10}K°(5.17.5) = -14 \pm 1$. However, the NEA review team (GRENTHE et al. 1992) did not accept the thermodynamic data for Se^{2-} in their set of auxiliary data. Presently, there is no need to include Se^{2-} in the database since no metal selenide complexes or sparingly soluble solids are included. We follow the recommendation of GRENTHE et al. (1992) and drop the above equilibrium from the database.

5.17.4   Selenite species

There is nothing to add to the evaluation made in GRENTHE et al. (1992, section VI.2.2.3 pp.381/382). SÉBY et al. (2001) give only one new reference dealing with this subject (DASGUPTA & NARA 1990), but the values derived by this most recent paper are well within the uncertainty range already given by GRENTHE et al. (1992).

Based on BAES & MESMER (1976) and PERRIN (1982) the NEA reviewers selected

$$HSeO_3^- \Leftrightarrow SeO_3^{2-} + H^+ \tag{5.17.6}$$

with **log$_{10}$K°(5.17.6) = –8.4 ± 0.1,** and

$$H_2SeO_3 \Leftrightarrow HSeO_3^- + H^+ \qquad (5.17.7)$$

with **log$_{10}$K°(5.17.7) = –2.8 ± 0.2.**

The Gibbs free energies are thus

$$\Delta_f G_m°(HSeO_3^-, aq, 298.15\ K) = -409.5 \pm 1.3\ kJ\ mol^{-1}$$
$$\Delta_f G_m°(SeO_3^{2-}, aq, 298.15\ K) = -361.6 \pm 1.4\ kJ\ mol^{-1}.$$

From ARNEK & BARCZA (1972) the NEA reviewers accepted

$$\Delta_r H_m°(6, 298.15\ K) = -5.02 \pm 0.50\ kJ\ mol^{-1},$$
$$\Delta_r H_m°(7, 298.15\ K) = -7.07 \pm 0.50\ kJ\ mol^{-1}$$

and calculated

$$\Delta_r S_m°(6, 298.15\ K) = -177.7 \pm 2.5\ J\ mol^{-1}$$
$$\Delta_r S_m°(7, 298.15\ K) = -77.3 \pm 4.2\ J\ mol^{-1}.$$

5.17.5   Selenate species

There is nothing to add to the evaluation made in GRENTHE et al. (1992, section VI.2.2.4 pp.382/383), and also SÉBY et al. (2001) do not give any new reference dealing with selenate protonation. The NEA reviewers accepted

$$HSeO_4^- \Leftrightarrow SeO_4^{2-} + H^+ \qquad (5.17.8)$$

with **log$_{10}$K°(5.17.8) = –1.80 ± 0.14,** based on data from NAIR (1964) and GHOS & NAIR (1970).

From GHOS & NAIR (1970) the NEA reviewers further accepted

$$\Delta_r H_m°(8, 298.15\ K) = -23.8 \pm 5.0\ kJ\ mol^{-1}$$

and calculated

$$\Delta_r S_m°(8, 298.15\ K) = -114 \pm 17\ J\ mol^{-1}.$$

Table 5.17.1: Compilation of selenium data.

TDB Version 05/92			TDB Version 01/01					
Name	$\Delta_f G_m°$	$\Delta_f H_m°$	Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$S_m°$	$C_{p,m}°$	Species
SE	0.0	0.0	Se(cr)	**0.0**	**0.0**	**42.27±0.05**	**25.03±0.05**	Se(cr)
SEO3-2	−369.8	−509.2	SeO3−2	**-361.60±1.47**				SeO_3^{2-}
Redox								
Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Reaction		
HSEO4−	−38.31	201.34		**−36.78**		$H_2SeO_3(aq) + H_2O(l) \Leftrightarrow HSeO_4^- + 3\ H^+ + 2\ e^-$		
H2SE	−44.761	341.18		**−46.19**		*) $H_2Se(aq) + 3\ H_2O(l) \Leftrightarrow H_2SeO_3(aq) + 6\ H^+ + 6\ e^-$		
Selenide								
Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Reaction		
HSE−	−3.819	−3.3	HSe−	**−3.8±0.3**		$H_2Se(aq) \Leftrightarrow HSe^- + H^+$		
SE−2	−14.944	48.1				$HSe^- \Leftrightarrow Se^{2-} + H^+$		
Selenite								
Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Reaction		
HSEO3−	−8.4	−5.02		**−8.4±0.1**	**−5.02±0.50**	$HSeO_3^- \Leftrightarrow SeO_3^{2-} + H^+$		
H2SEO3	−2.8	−7.07		**−2.8±0.2**	**−7.07±0.50**	$H_2SeO_3(aq) \Leftrightarrow HSeO_3^- + H^+$		
Selenate								
Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Reaction		
SEO4-2	−1.909	−17.5	SeO4−2	**−1.80±0.14**	**−23.8±5.0**	$HSeO_4^- \Leftrightarrow SeO_4^{2-} + H^+$		
Selenium solids								
Name	$\log_{10}K_{s,0}°$	$\Delta_r H_m°$	Name	$\log_{10}K_{s,0}°$	$\Delta_r H_m°$	Reaction		
SE	−48.65	360.38	Se(cr)	**−50.09±0.13**		$Se(cr) + 3\ H_2O(l) \Leftrightarrow H_2SeO_3(aq) + 4\ H^+ + 4\ e^-$		

*) Note that for convenience reasons this reaction is represented as a linear combination of equilibria (5.17.1a) and (5.17.3)

5.17.6   References

COX J.D., WAGMAN D.D., MEDVEDEV V.A. (1989): CODATA Key Values for Thermodynamics. Hemisphere Publishing Corp., New York, 271p.

GRENTHE I., FUGER J., KONINGS R.J.M., LEMIRE R.J., MULLER A.B., NGUYEN-TRUNG C., WANNER H. (1992): Chemical Thermodynamics Vol. 1: Chemical Thermodynamics of Uranium. OECD/NEA, North-Holland Elsevier, ISBN 0 444 89381 4.

LANGMUIR D., APTED M.J. (1992): Backfill modification using geochemical principles to optimise high level nuclear waste isolation in a geological repository. Mat. Res. Soc. Symp. Proc., 257, 13-24.

PEARSON F.J., BERNER U., HUMMEL W. (1992): Nagra Thermochemical Data Base II. Supplemental Data 05/92. Nagra Technical Report NTB 91-18, Nagra, Wettingen, Switzerland, 284p.

RARD J.A., RAND M.H., ANDEREGG G., WANNER H. (1999): Chemical Thermodynamics Vol. 3: Chemical Thermodynamics of Technetium. OECD/NEA, North-Holland Elsevier, ISBN 0-444-503780-1.

SÉBY F., POTIN-GAUTIER M., GIFFAUT E., BORGE G., DONARD O.F.X. (2001): A critical review of thermodynamic data for Selenium species at 25 °C. Chemical Geology, 171, 173-194.

SILVA R.J., BIDOGLIO G., RAND M.H., ROBUCH P., WANNER H., PUIGDOMENECH I. (1995): Chemical Thermodynamics Vol. 2: Chemical Thermodynamics of Americium. OECD/NEA, North-Holland Elsevier, ISBN 0 444 82281 X.

STANTON R.L. (1972): Ore Petrology. McGraw-Hill, New York, 713p.

Indirectly cited references

ARNEK R., BARCZA L. (1972): Thermochemical studies of hydrolytic reactions: 11. Polyselenite equilibria in various ionic media. Acta Chem. Scand., 26, 213-217.

BAES C.F., JR., MESMER R.E. (1976): The Hydrolysis of Cations. John Wiley, New York, Reprint Edition, R.E.Krieger Publishing (1986).

DASGUPTA P.K., NARA O. (1990): Measurement of acid dissociation constants of weak acids by cation exchange and conductometry. Anal. Chem., 62, 1117-1122.

GHOS R., NAIR V.S.K. (1970): Studies on metal complexes in aqueous solution: III. The biselenate ion and transition metal selenates. J. Inorg. Nucl. Chem., 32, 3041-3051.

GRØNVOLD F., DROWART J., WESTRUM E.F., JR. (1984): The chemical thermodynamics of actinide elements and compounds: Part 4. The actinide chalcogenides (excluding oxides). Vienna: International Atomic Energy Agency, 265p.

LATIMER W.L. (1952): The Oxidation States of the Elements and their Potentials in Aqueous Solutions. 2nd edn., Prentice-Hall, Englewood Cliffs, N.J.

MASSCHELEYN P.H., DELAUME R.D., PATRICK W.H. (1991): Biogeochemical behaviour of selenium in anoxic soils and sediments: an equilibrium thermodynamic approach. J. Environ. Sci. Health, 26, 555-573.

VAN MUYLDER J., POURBAIX M. (1964): Sélénium, Atlas d' Équilibres Électrochimiques à 25 °C. Paris

NAIR V.S.K. (1964): Dissociation of the biselenate ion. J. Inorg. Nucl. Chem., 26, 1911-1917.

NEVSKII O.B., GERASIMOV A.D., D'YACHKOVA N.N. (1968): Reduction potentials of tellurium and selenium in chloride solutions. Elektrokhimiya, 4, 624-629.

OSMAN-ZADE S.D., VAGRAMYAN A.T. (1966): The reversible potential of the selenium electrode in selenic acid solutions. Elektrokhimiya 2, 76-77.

PERRIN D.D. (1982): Ionisation constants for inorganic acids and bases in aqueous solution. 2nd ed., IUPAC Chemical Data Series 29, Oxford Pergamon Press, 180p.

SCHOTT H.F., SWIFT E.H., YOST D.M. (1928): The reduction potential of selenium and the free energy of aqueous selenous acid. J. Am. Chem. Soc., 50, 721-727.

WOODS T.L., GARRELS R.M. (1987): Thermodynamic Values at Low Temperature for Natural Inorganic Materials. An Uncritical Summary. Oxford University Press, New York.

ZHDANOV S.I. (1985): Sulfur, selenium, tellurium and polonium. In: BARD A.J., JORDAN R. (eds.): Standard Potentials in Aqueous Solution. Marcel Dekker, New York p.93-125.

5.18   Silica and silicates

5.18.1   Elemental silicon

Silicon metal and gas are not relevant under environmental conditions. Hence, the gas phase is not included in the data base. The absolute entropy and heat capacity of Si(cr) are included as they are used for the calculation of certain thermodynamic reaction properties. The selected values are taken from CODATA (Cox et al. 1989).

$$S_m° \text{ (Si, cr, 298.15 K)} \quad = \quad (18.810 \pm 0.08) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{p,m}° \text{ (Si, cr, 298.15 K)} \quad = \quad (19.789 \pm 0.030) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

5.18.2   Silica (quartz)

The selected values for SiO_2(cr), quartz, are taken from CODATA (Cox et al. 1989).

$$\Delta_f H_m° \text{ (SiO}_2\text{, cr, 298.15 K)} \quad = \quad -(910.700 \pm 1.0) \text{ kJ} \cdot \text{mol}^{-1}$$

$$S_m° \text{ (SiO}_2\text{, cr, 298.15 K)} \quad = \quad (41.460 \pm 0.20) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{p,m}° \text{ (SiO}_2\text{, cr, 298.15 K)} \quad = \quad (44.602 \pm 0.30) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

and the Gibbs energy of formation calculated from the above values and $S_m°$ (Si, cr, 298.15 K)

$$\Delta_f G_m° \text{ (SiO}_2\text{, cr, 298.15 K)} \quad = \quad -(856.287 \pm 1.0) \text{ kJ} \cdot \text{mol}^{-1}$$

5.18.3   Silica compounds and aqueous species

5.18.3.1   Silica compounds

Dissolution of silica in water in the pH range where $Si(OH)_4$(aq) is the dominant aqueous silica species can be expressed by the reaction

$$SiO_2(s) + 2 H_2O(l) \Leftrightarrow Si(OH)_4(aq)$$
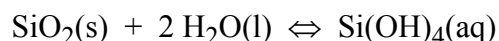
Taking the activity of the solid phase and water to be 1, as well as the activity coefficient of $Si(OH)_4$(aq) leads to

$$\log_{10} K_s = m_{\text{Si(dissolved)}}$$

where m is the measured concentration of dissolved silica in moles/kg H_2O.

New solubility data for quartz have been reported by RIMSTIDT (1997). Note, that the duration of his solubility experiment at 21°C lasted for more than 13 years! GUNNARSSON & ARNORSSON (2000) discussed and simultaneously fitted these new data, their own experiments on amorphous silica, and all published solubility data of quartz and amorphous silica. Their results are:

$$\log_{10}K_s° \text{ (Quartz, cr, 298.15 K)} = -3.746$$

$$\log_{10}K_s° \text{ (Silica, am, 298.15 K)} = -2.713$$

$$\Delta_r H_m°\text{(Quartz, cr, 298.15 K)} = 20.638 \ kJ \cdot mol^{-1}$$

$$\Delta_r H_m°\text{(Silica, am, 298.15 K)} = 14.595 \ kJ \cdot mol^{-1}$$

In the range 0 to 350°C the solubility of quartz and amorphous silica can be precisely described by

$$\log_{10}K_s \text{ (Quartz, cr)} = -34.188 + 197.47 / T - 5.851 \cdot 10^{-6} \ T^2 + 12.245 \log_{10}T$$

$$\log_{10}K_s \text{ (Silica, am)} = -8.476 - 485.24 / T - 2.268 \cdot 10^{-6} \ T^2 + 3.068 \log_{10}T$$

However, in the range 0 to 250°C the solubility of quartz and amorphous silica exhibit a simple van't Hoff behaviour (RIMSTIDT 1997, GUNNARSSON & ARNORSSON 2000). This means that in this temperature range a two-term approximation of temperature dependence is sufficient, i.e. the integrated van't Hoff equation including only $\log_{10}K_s°$ and $\Delta_r H_m°$ (see 2.3.3).

The solubility of amorphous silica has not changed at T < 200°C compared with earlier results. However, the solubility of quartz is significantly higher than given in most previous compilations, e.g. by NORDSTROM et al. (1990). The old quartz solubility constant at 25°C was based on rather dubious data not in accord with most data measured at other temperatures (RIMSTIDT 1997).

Based on the old quartz solubility almost all groundwaters had been calculated to be significantly supersaturated with respect to quartz (Figs. 5.18.1 and 5.18.2). In an attempt to remedy this disturbing situation the solubility of chalcedony has been widely used in speciation calculations. However, the chalcedony data are based on measurements of a few ill-defined samples, as discussed by RIMSTIDT (1997). Using the new quartz solubility in speciation calculations the situation has changed, most groundwaters are now saturated or only slightly supersaturated with respect to quartz (Figs. 5.18.1 and 5.18.2). Hence, the dubious value of chalcedony solubility has been removed from the data base.
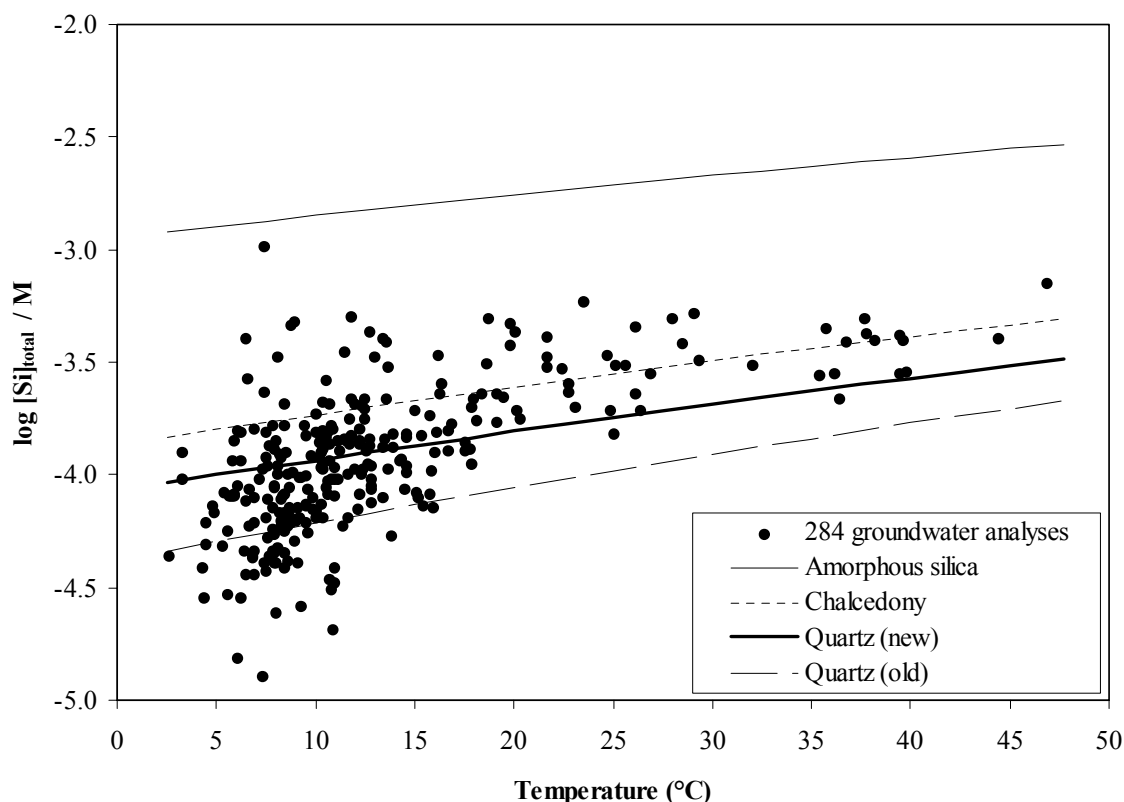
Fig. 5.18.1: Temperature dependence of total dissolved silica in Swiss groundwaters. The solubility of amorphous silica and quartz (new) is calculated with the integrated van't Hoff equation (see 2.3.3) using $\log_{10}K_s°$ and $\Delta_rH_m°$ selected in this review. Note that the four term temperature functions of GUNNARSSON & ARNORSSON (2000) give identical results in this temperature range. The solubility of chalcedony and quartz (old) is calculated with the temperature function given by NORDSTROM et al. (1990).

5.18.3.2 Aqueous silica species

In aqueous media, silicon exists exclusively in the +IV oxidation state. The relevant species in solutions at pH < 9 is $Si(OH)_4(aq)$. The thermodynamic properties of this species are based on CODATA (COX et al. 1989) values for $SiO_2(cr)$, quartz, (see 5.18.2) and the solubility of that mineral (see 5.18.3.1).

In ordinary groundwater the species $Si(OH)_4(aq)$ predominates. In alkaline waters a deprotonated species gains importance and at very high pH a second deprotonation step is observed. The thermodynamic data are taken from NEA auxiliary data (GRENTHE et al. 1992):

$$Si(OH)_4(aq) \Leftrightarrow SiO(OH)_3^- + H^+ \qquad \log_{10}K° = -9.81 \pm 0.02$$

$$SiO(OH)_3^- \Leftrightarrow SiO_2(OH)_2^{2-} + H^+ \qquad \log_{10}K° = -13.33 \pm 0.09$$
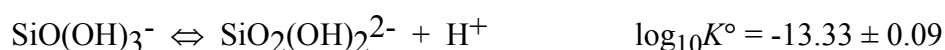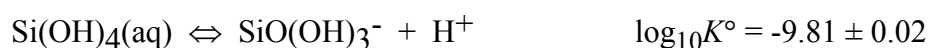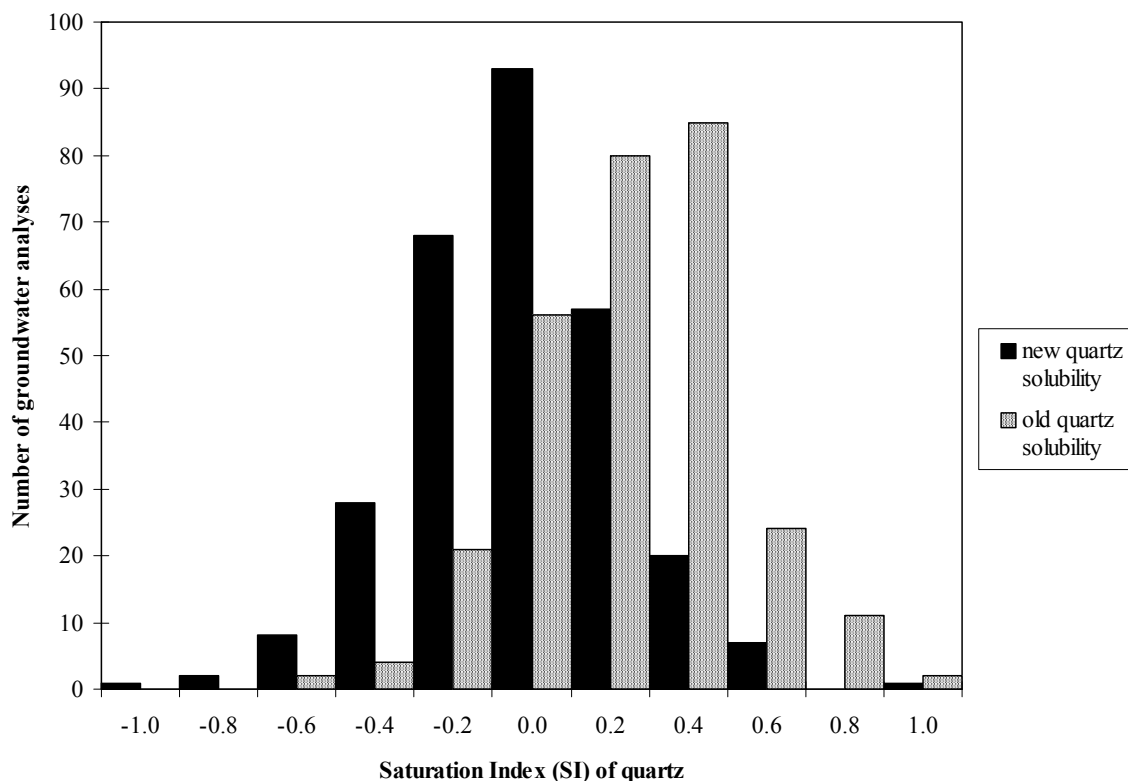
Fig. 5.18.2: Histogram of quartz saturation indices calculated for 284 Swiss groundwater analyses shown in Fig. 5.18.1.

In the pH range above 10 and millimolar and higher concentrations of dissolved silica polymeric silicate species predominate. Stability constants for several polymeric species have been reported and accepted by NEA as auxiliary data. They all originate from SJÖBERG et al. (1985), and they are valid for a limited pH and concentration range, i.e. $11 < pH < 12.2$ and $0.008\ M < [SiO_2(tot)] < 0.048\ M$. At the upper concentration limit even more complicated polymeric species form which cannot be described in any quantitative manner (SJÖBERG et al. 1985).

In an attempt to "expand" this pH and concentration range EIKENBERG (1990) "adapted" some of these polymer stability constants in order to fit measured amorphous silica and quartz solubility data. The results are inconsistent with the experimental findings of SJÖBERG et al. (1985). Considering the limited range of validity of the values reported by SJÖBERG et al. (1985) and the unsatisfactory fitting procedure of EIKENBERG (1990) we decided not to include any polymeric silicate species in the present version of our database. In a future update we will re-evaluate the solubility of quartz and amorphous SiO_2 at high pH on the basis the reliable study of SJÖBERG et al. (1985) and other experimental information.

5.18.4 Metal silicate compounds and complexes

5.18.4.1 Calcium and magnesium

Aqueous Ca and Mg silicates: The results of potentiometric titrations of $Si(OH)_4(aq)$ in the presence of Ca^{2+} and Mg^{2+} in 1 M $NaClO_4$ up to pH 9 are reported by SANTSCHI & SCHINDLER (1974). In order to avoid the formation of polymeric silicate species as well as the precipitation of amorphous silica, the total ligand concentration did not exceed $2.3 \cdot 10^{-3}$ M. In preliminary experiments it was found that the complexes formed are rather weak. Comparatively high concentrations of both, the reacting metal ions and the inert salt were therefore required.

The results of this experimental study are not unambiguous in terms of the speciation model. Two limiting situations are discussed by SANTSCHI & SCHINDLER (1974). Based on chemical arguments, the most probable interpretation of the experimental data could be done in terms of two equilibria:

$$M^{2+} + SiO(OH)_3^- \Leftrightarrow MSiO(OH)_3^+ \qquad \text{(a)}$$

$$M^{2+} + SiO_2(OH)_2^{2-} \Leftrightarrow MSiO_2(OH)_2(aq) \qquad \text{(b)}$$

Values for the stability constants are extrapolated from 1 M $NaClO_4$ to zero ionic strength using the SIT formalism (GRENTHE et al. 1992):

Ca	$\log_{10}K°(eq.a) = 1.2 \pm 0.1$	and	$\log_{10}K°(eq.b) = 4.6 \pm 0.2$
Mg	$\log_{10}K°(eq.a) = 1.5 \pm 0.2$	and	$\log_{10}K°(eq.b) = 5.7 \pm 0.2$

Although the stoichiometry of these complexes and their stability constants have not been explored by other studies we decided to include them in our data base as guidelines for modellers. If these complexes are found to be of crucial importance in some systems, additional experimental studies are recommended.

Solid Ca and Mg silicates: Thermodynamic data for the Mg silicate solids chrysotile, sepiolite, and kerolite have been selected by NORDSTROM et al. (1990). We did not explore the thermodynamics of these sheet silicates and decided not to include them in the data base.

Calcium silicate hydrates (CSH) and calcium aluminium silicate hydrates (CASH) are important solid phases in cementitious systems. However, these phases form solid solutions and their appropriate thermodynamic representation is the subject of ongoing research.

5.18.4.2   Aluminium

Aqueous aluminium silicates: Three papers have been published reporting experimental data on Al silicate complexation: BROWNE & DRISCOLL (1992), FARMER & LUMSDON (1994), and POKROVSKI et al. (1996). For the equilibrium

$$Al^{3+} + SiO(OH)_3^- \Leftrightarrow AlSiO(OH)_3^{2+}$$
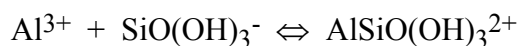
the following constants are derived for zero ionic strength: $\log_{10}K° = 8.7 \pm 0.1$ (BROWNE & DRISCOLL 1992), 7.3 ± 0.1 (FARMER & LUMSDON 1994), and 7.5 ± 0.2 (POKROVSKI et al. 1996). As discussed by FARMER & LUMSDON (1994), the value given by BROWNE & DRISCOLL (1992) seems not to be reliable. However, there is a close agreement of the latter two values and a stability constant of $\log_{10}K° = 7.4 \pm 0.2$ can be derived.

All these studies have been carried out at $3.5 < pH < 5.5$. Recently, a study of aluminium silicate complexation in the alkaline region has been reported by POKROVSKI et al. (1998). The results of this study have been interpreted in terms of the equilibrium

$$Al(OH)_4^- + Si(OH)_4(aq) \Leftrightarrow Al(OH)_3SiO(OH)_3^- + H_2O(l)$$
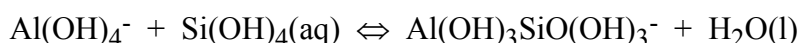
with $\log_{10}K° = 3.64 \pm 0.20$. It is not clear from the extended abstract of POKROVSKI et al. (1998) whether this stoichiometry can be considered as well-established, or for example, a bidentate complex is formed by a rather similar condensation reaction

$$Al(OH)_4^- + Si(OH)_4(aq) \Leftrightarrow Al(OH)_2SiO_2(OH)_2^- + 2 H_2O(l)$$

in analogy to the species $MSiO_2(OH)_2(aq)$ proposed by SANTSCHI & SCHINDLER (1974) for Ca and Mg. According to POKROVSKI (personal communication) molecular modelling work indicates that no bidentate complex is formed.

The complex $AlSiO(OH)_3^{2+}$ seems fairly well established but it is of little importance for groundwater modelling. The complex $Al(OH)_3SiO(OH)_3^-$ and its stability constant still refers to an "extended abstract" of POKROVSKI et al. (1998) and the message "We are currently preparing a full paper on Al-Si complexing for publication in Geochimica et Cosmochimica Acta" (POKROVSKI, personal communication).

We decided to include both complexes in our data base as guidelines for modellers. However, one should be aware of the provisional status of the equilibrium involving the complex $Al(OH)_3SiO(OH)_3^-$.

Solid aluminium silicate compounds: Thermodynamic data are available for the mineral kaolinite $(Al_2Si_2O_5(OH)_4)$ (NORDSTROM et al. 1990):

$$Al_2Si_2O_5(OH)_4(s) + 6 H^+ \Leftrightarrow 2 Al^{3+} + 2 Si(OH)_4(aq) + H_2O(l)$$
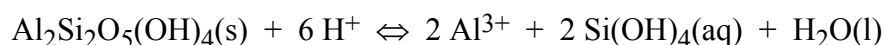
$$\log_{10}{}^{*}K_{s,0}° \text{ (Kaolinite, cr, 298.15 K)} = 7.435$$

$$\Delta_r H_m°\text{(Kaolinite, cr, 298.15 K)} = -35.3 \text{ kcal} \cdot \text{mol}^{-1} \rightarrow -147.7 \text{ kJ} \cdot \text{mol}^{-1}$$

The values for kaolinite are derived from measured solubilities and are included in our data base.

Aluminium silicate minerals are of great importance in determining the chemistry of water in many rock types. A number of characteristics of these minerals makes collection of their thermodynamic data and their modelling very difficult. One characteristic is that many react so slowly at laboratory and normal groundwater temperatures that frequently it is not possible to attain equilibrium in reasonable experimental times. Thus, high temperature data extrapolated to lower temperatures are often used for groundwater modelling. Another characteristic is that such important aluminium silicate minerals as the clays have highly variable chemical compositions which adds uncertainty to their behaviour in solution.

A detailed review of aluminium silicate minerals should be given high priority within the scope of a forthcoming update of our data base.

5.18.4.3   Iron

Four papers have been published reporting experimental data on Fe(III) silicate complexation: WEBER & STUMM (1965), PORTER & WEBER (1971), OLSON & O'MELIA (1973), and REARDON (1979). For the equilibrium

$$Fe^{3+} + SiO(OH)_3^- \Leftrightarrow FeSiO(OH)_3^{2+}$$
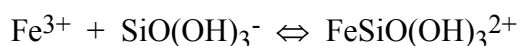
the following constants are derived for zero ionic strength: $\log_{10}K° = 10.0$ (WEBER & STUMM 1965), 9.5 (PORTER & WEBER 1971), 9.6 and 9.8 from spectrophotometric and polarographic data, respectively (OLSON & O'MELIA 1973), and 9.8 from silica solubility data (REARDON 1979). These constants are in close agreement and an unweighted mean is $\log_{10}K° = 9.7 \pm 0.3$.

Note that all these studies have been carried out at pH < 4. No conclusions can be drawn from these investigations whether bidentate Fe(III) complexes with $SiO_2(OH)_2^{2-}$ form at high pH in analogy with Ca and Mg complexation, or whether a complex of the stoichiometry $Fe(OH)_n SiO(OH)_3^{2-n}$ dominates in neutral and alkaline groundwater in analogy with Al.

5.18.4.4   Europium

Only one paper has been published reporting experimental data on Eu(III) silicate complexation (JENSEN & CHOPPIN 1996). The authors interpreted the results of their solvent extraction study, carried out at pH 4, 6 and 9, in terms of 1:1 and 1:2 complexes according to the equilibrium

$$Eu^{3+} + n\ SiO(OH)_3^- \Leftrightarrow Eu(SiO(OH)_3)_n^{3-n}$$
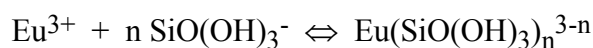
The following constants are derived for zero ionic strength: $\log_{10}\beta_1° = 7.9 \pm 0.2$ and $\log_{10}\beta_2° = 12.8 \pm 0.4$.

Note that at present no independent study of metal silicate complexation corroborates the formation of 1:2 complexes. Even if the stoichiometry of these complexes and the reported stability constants have not been explored by other studies we decided to include them into our data base as guidelines for modellers. The consequences of the new Eu(III) silicate data are shown in Fig. 5.18.3: For most Swiss ground waters $10^{-3.0}$ M to $10^{-3.5}$ M dissolved silicate is needed in order to complex 50% of the dissolved Eu(III). Considering the measured silicate concentrations in these waters (Fig. 5.18.1) we expect that Eu silicate complexes in general will not dominate the Eu speciation. But on the other hand, Eu silicate complexes cannot be neglected as they compete with Eu carbonate and other complexes and may reach 30% or more of the dissolved europium.
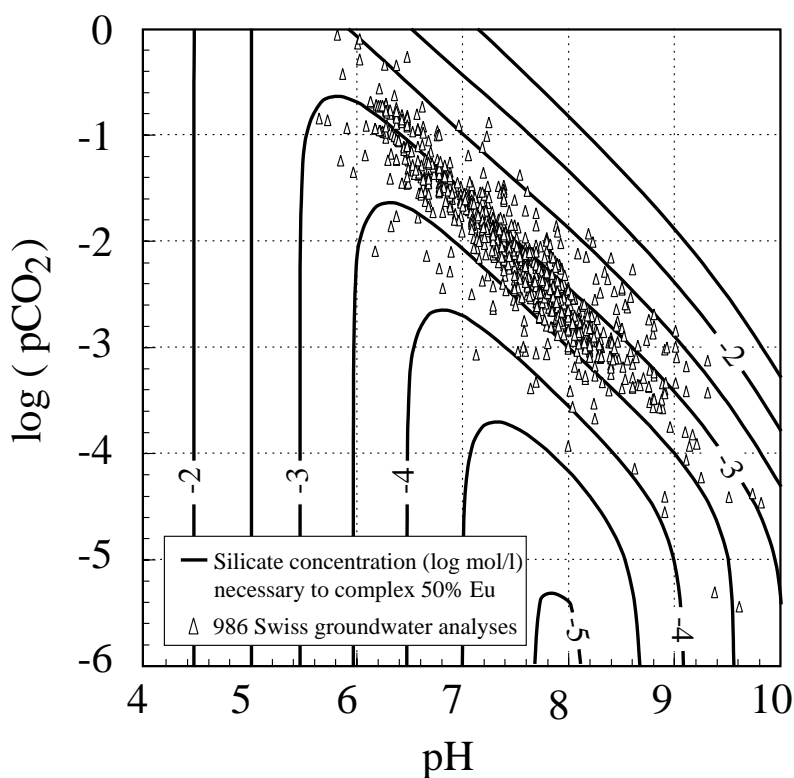
Fig. 5.18.3: Contour plot showing the concentration of dissolved silicate needed in order to complex 50% Eu(III) as a function of pH and CO_2 partial pressure at 25°C and $I = 0.1$ M, $[Eu]_{total} = 10^{-7}$ M and $[Ca]_{total} = 10^{-4}$ M. The precipitation of solids is suppressed.

5.18.4.5   Americium

Only one paper has been published reporting experimental data on Am(III) silicate complexation (WADSAK et al. 2000). The authors interpreted the results of their solvent extraction study, carried out at pH 3.0 – 3.8 in terms of a 1:1 complex according to the equilibrium

$$Am^{3+} + SiO(OH)_3^- \Leftrightarrow AmSiO(OH)_3^{2+}$$
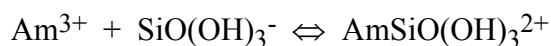
The following constant has been derived for zero ionic strength: $\log_{10}\beta_1^\circ = 8.1 \pm 0.2$.

The reported value agrees with the findings of JENSEN & CHOPPIN (1996) for Eu and it is provisionally included in our data base. WADSAK et al. (2000) limited their study to acidic conditions and thus, no conclusions can be drawn concerning the existence of a 1:2 americium silicate complex in alkaline solutions.

5.18.4.6   Uranium

Four papers and a PhD thesis have been published reporting experimental data on U(VI) silicate complexation: PORTER & WEBER (1971), SATOH & CHOPPIN (1992), MOLL (1997), JENSEN & CHOPPIN (1998), and MOLL et al. (1998). All the experimental data have been interpreted in terms of the same equilibrium:

$$UO_2^{2+} + SiO(OH)_3^- \Leftrightarrow UO_2SiO(OH)_3^+$$
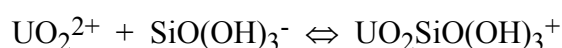
The following constants are derived for zero ionic strength: $\log_{10}K^\circ = 8.0 \pm 0.1$ by interpreting spectrophotometric data (PORTER & WEBER 1971) and $\log_{10}K^\circ = 7.6 \pm 0.1$ from solvent extraction data (SATOH & CHOPPIN 1992). However, the results of SATOH & CHOPPIN (1992) have been criticised by JENSEN & CHOPPIN (1998): The effect of the formation of an aqueous complex of uranyl with the extractant thenoyltrifluoroacetone (TTA) was not considered in the original data analysis. When the formation of $UO_2(TTA)^+$ is included in the data evaluation, a corrected value of $\log_{10}K^\circ = 8.0 \pm 0.2$ results (JENSEN & CHOPPIN 1998). This corrected constant is in good agreement with PORTER & WEBER (1971). However, in both cases possible systematic errors due to the formation of polymeric silicate species may affect the results.

The constant $\log_{10}K^\circ = 7.1 \pm 0.1$ reported by JENSEN & CHOPPIN (1998) is one order of magnitude lower than the former two. This constant has been derived from new solvent extraction measurements, designed to avoid any influence of polymeric species on U(VI) complexation. On the other hand, the results of MOLL (1997) and MOLL et al. (1998) derived from spectroscopic studies are significantly at variance with the results of JENSEN & CHOPPIN (1998): $\log_{10}K^\circ = 9.0 \pm 0.4$ and $\log_{10}K^\circ = 9.5 \pm 0.2$, respectively. Note that in both cases it was necessary to re-evaluate the

stability constants. The extrapolation to zero ionic strength by MOLL (1997) and MOLL et al. (1998) is erroneous, not only in sign but also by neglecting that the pH is given in both studies on the activity scale rather than on the concentration scale. In addition, the experimental values reported in MOLL et al. (1998) have been refitted after discarding one measurement at very low silica concentration. In contrast to the original fit this new calculation clearly indicates a 1:1 complex formation and gives constant values over the entire concentration range.
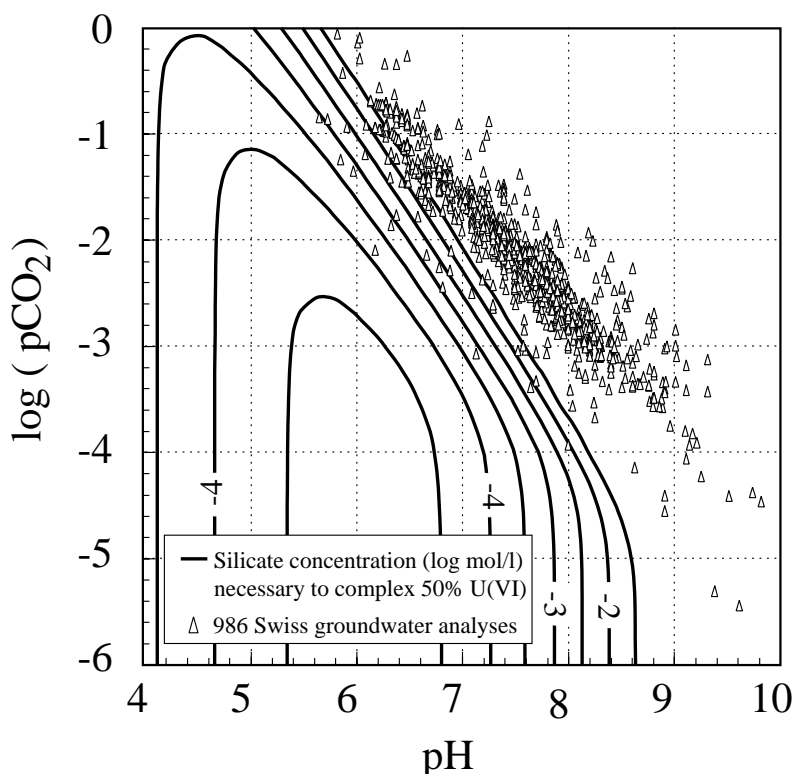
Fig. 5.18.4:   Contour plot showing the concentration of dissolved silicate needed in order to complex 50% U(VI) as a function of pH and CO_2 partial pressure at 25°C and $I = 0.1$ M, $[U(VI)]_{total} = 10^{-7}$ M and $[Ca]_{total} = 10^{-4}$ M. The precipitation of solids is suppressed. For the equilibrium $UO_2^{2+} + SiO(OH)_3^- \Leftrightarrow UO_2SiO(OH)_3^+$ the maximum value reported in the literature ($\log_{10}K° = 9.5$) has been taken.

Unfortunately, the two most recent studies, JENSEN & CHOPPIN (1998) and MOLL et al. (1998), both claiming to report experiments especially designed to minimise the formation of polymeric silicate species, give results disparate by more than two orders of magnitude! As long as this discrepancy is not resolved, no value for U(VI) silicate complexation can be recommended.

Scoping calculations using the maximum value of U(VI) silicate complexation reported in the literature ($\log_{10}K° = 9.5$) reveal that almost all Swiss ground waters are located above any feasible

silicate concentration (Fig. 5.18.4). This effect is due to the strong competition of U(VI) carbonate complexes formed in most of these waters. Hence, we do not expect any influence of silicate complexation in common ground waters. However, the effect of U(VI) silicate complexes in neutral and slightly acidic surface water in equilibrium with atmospheric CO_2 (pCO_2 = $10^{-3.5}$ bar) remains to be explored.

5.18.4.7   Plutonium

No reliable data are available for Pu silicate complexation under groundwater conditions.

Only one paper has been published reporting experimental data on Pu(IV) silicate complexation (PAZUKHIN et al. 1990). The authors report a value for a very weak Pu(IV) - silicate complex derived from spectrophotometric measurements. However, the equilibrium this value refers to and the stoichiometry of the complex are not defined in the paper. The measurements of PAZUKHIN et al. (1990) have been carried out solely at pH 1.4 and the authors presume that probably a $PuSi(OH)_4^{4+}$ complex might have formed. Considering the shortcomings of this paper no value for Pu(IV) silicate complexation can be recommended.

Table 5.18.1: Selected silica and silicate data.

TDB Version 05/92			TDB Version 01/01					
Name	$\Delta_f G_m°$	$\Delta_f H_m°$	Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$S_m°$	$C_{p,m}°$	Species
	-	-	Si(cr)	0.0	0.0	18.810 ± 0.08	19.789 ± 0.030	Si(cr)
	-856.175	-910.360	Quartz	-856.287 ± 1.0	-910.700 ± 1.0	41.460 ± 0.20	44.602 ± 0.30	$SiO_2(cr)$
SI(OH)4	-1307.735	-1456.960	Si(OH)4	-1309.183	-1461.723	178.851	237.370	$Si(OH)_4(aq)$

Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Reaction
SIO(OH)3-	-9.81	25.6	SiO(OH)3-	-9.81 ± 0.02	25.6 ± 2.0	$Si(OH)_4(aq) \Leftrightarrow SiO(OH)_3^- + H^+$
SIO2(OH)2-2	-23.14	75.0	SiO2(OH)2-2	-23.14 ± 0.09	75 ± 15	$Si(OH)_4(aq) \Leftrightarrow SiO_2(OH)_2^{2-} + 2 H^+$
	-	-	CaSi(OH)3+	1.2 ± 0.1		$Ca^{2+} + SiO(OH)_3^- \Leftrightarrow CaSiO(OH)_3^+$
	-	-	CaSiO2(OH)2	4.6 ± 0.2		$Ca^{2+} + SiO_2(OH)_2^{2-} \Leftrightarrow CaSiO_2(OH)_2(aq)$
	-	-	MgSiO(OH)3+	1.5 ± 0.2		$Mg^{2+} + SiO(OH)_3^- \Leftrightarrow MgSiO(OH)_3^+$
	-	-	MgSiO2(OH)2	5.7 ± 0.2		$Mg^{2+} + SiO_2(OH)_2^{2-} \Leftrightarrow MgSiO_2(OH)_2(aq)$
	-	-	AlSiO(OH)3+2	7.4 ± 0.2		$Al^{3+} + SiO(OH)_3^- \Leftrightarrow AlSiO(OH)_3^{2+}$
	-	-	Al(OH)6SiO-	3.6 ± 0.2		$Al(OH)_4^- + Si(OH)_4(aq) \Leftrightarrow Al(OH)_3SiO(OH)_3^- + H_2O(l)$
	-	-	FeSiO(OH)3+2	9.7 ± 0.3		$Fe^{3+} + SiO(OH)_3^- \Leftrightarrow FeSiO(OH)_3^{2+}$
	-	-	EuSiO(OH)3+2	7.9 ± 0.2		$Eu^{3+} + SiO(OH)_3^- \Leftrightarrow EuSiO(OH)_3^{2+}$
	-	-	Eu(SiO(OH)3)2+	12.8 ± 0.4		$Eu^{3+} + 2 SiO(OH)_3^- \Leftrightarrow Eu(SiO(OH)_3)_2^+$
	-	-	AmSiO(OH)3+2	8.1 ± 0.2		$Am^{3+} + SiO(OH)_3^- \Leftrightarrow AmSiO(OH)_3^{2+}$

Name	$\log_{10}K_{s,0}°$	$\Delta_r H_m°$	Name	$\log_{10}K_{s,0}°$	$\Delta_r H_m°$	Reaction
QUARTZ	-3.98	25.06	Quartz	-3.746[1]	20.637	$SiO_2(cr) + 2 H_2O(l) \Leftrightarrow Si(OH)_4(aq)$
CHALCEDONY	-3.551	19.757		-	-	$SiO_2(micr) + 2 H_2O(l) \Leftrightarrow Si(OH)_4(aq)$
SIO2_AM	-2.712	13.995	SiO2(am)	-2.714[2]	14.594	$SiO_2(am) + 2 H_2O(l) \Leftrightarrow Si(OH)_4(aq)$
KAOLINITE	7.435	-147.695	Kaolinite	7.435	-147.7	$Al_2Si_2O_5(OH)_4 + 6H^+ \Leftrightarrow 2 Al^{3+} + 2 Si(OH)_4(aq) + H_2O(l)$

[1] Temperature dependence of $\log_{10}K_{s,0}$ (Quartz, cr) = $-34.188 + 197.47 / T - 5.851 \cdot 10^{-6} T^2 + 12.245 \log_{10}T$

[2] Temperature dependence of $\log_{10}K_{s,0}$ (Silica, am) = $-8.476 - 485.24 / T - 2.268 \cdot 10^{-6} T^2 + 3.068 \log_{10}T$

5.18.5   References

BROWNE, B.A., DRISCOLL, C.T. (1992): Soluble aluminum silicates: stoichiometry, stability, and implications for environmental geochemistry. Science, 256, 1667-1670.

COX, J.D., WAGMAN, D.D., MEDVEDEV, V.A. (1989): CODATA Key Values for Thermodynamics. New York, Hemisphere Publishing, 271p.

EIKENBERG, J. (1990): On the problem of silica solubility at high pH. PSI Bericht Nr. 74, Paul Scherrer Institut, Villigen, Switzerland, 54p.

FARMER, V.C., LUMSDON, D.G. (1994): An assessment of complex formation between aluminium and silicic acid in acidic solutions. Geochim. Cosmochim. Acta, 58, 3331-3334.

GRENTHE, I., FUGER, J., KONINGS, R.J.M., LEMIRE, R.J., MULLER, A.B., NGUYEN-TRUNG, C., WANNER, H. (1992): Chemical Thermodynamics of Uranium. Elsevier, Amsterdam, 715p.

GUNNARSSON, I., ARNORSSON, S. (2000): Amorphous silica solubility and the thermodynamic properties of $H_4SiO_4^o$ in the range of 0º to 350ºC at P_{sat}. Geochim. Cosmochim. Acta, 64, 2295-2307.

JENSEN, M.P., CHOPPIN, G.R. (1996): Complexation of Europium(III) by Aqueous Orthosilicic Acid. Radiochim. Acta, 72, 143-150.

JENSEN, M.P., CHOPPIN, G.R. (1998): Complexation of Uranyl(VI) by Aqueous Orthosilicic Acid. Radiochim. Acta, 82, 83-88.

MOLL, H. (1997): Zur Wechselwirkung von Uran mit Silicat in wäßrigen Systemen. Ph.D. Dissertation, University of Dresden, Germany, 182p.

MOLL, H., GEIPEL, G., BRENDLER, V., BERNHARD, G., NITSCHE, H. (1998): Interaction of uranium(VI) with silicic acid in aqueous solutions studied by time-resolved laser-induced fluorescence spectroscopy (TRLFS). Journal of Alloys and Compounds, 271-273, 765-768.

NORDSTROM, D.K., PLUMMER, L.N., LANGMUIR, D., BUSENBERG, E., MAY, H.M., JONES, B.F., PARKHURST, D.L. (1990): Revised Chemical Equilibrium Data for Major Water-Mineral Reactions and Their Limitations. In: MELCHIOR, D. C., BASSET, R. L. (eds.): Chemical Modeling of Aqueous Systems II. Washington, D.C., American Chemical Society, ACS Symposium Series 416, 398-413.

OLSON, L.L., O'MELIA, C.R. (1973): The interaction of Fe(III) with Si(OH)4. J. Inorg. Nucl. Chem., 35, 1977-1985.

PAZUKHIN, E.M., KRIVOKHATSKII, A.S., KUDRYAVTSEV, E.G. (1990): Possible formation of Pu(IV) complexes with silicic acid. Soviet Radiochemistry, 32, 325-330.

POKROVSKI, G.S., SCHOTT, J., HARRICHOURY, J.-C., SERGEYEV, A. S. (1996): The stability of aluminum silicate complexes in acidic solutions from 25 to 150°C. Geochim. Cosmochim. Acta, 60, 2495-2501.

POKROVSKI, G.S., SCHOTT, J., SALVI, S., GOUT, R., KUBICKI, J.D. (1998): Structure and stability of aluminum-silica complexes in neutral to basic solutions. Experimental study and molecular orbital calculations. Mineralogical Magazine, 62A, 1194-1195.

PORTER, R.A., WEBER, W.J. (1971): The interaction of silicic acid with iron(III) and uranyl ions in dilute aqueous solution. J. Inorg. Nucl. Chem., 33, 2443-2449.

REARDON, E.J. (1979): Complexing of silica by iron(III) in natural waters. Chem. Geol., 25, 339-345.

RIMSTIDT, J.D. (1997): Quartz solubility at low temperatures. Geochim. Cosmochim. Acta, 61, 2553-2558.

SANTSCHI, P.H., SCHINDLER, P.W. (1974): Complex formation in the ternary systems Ca^{II}-H_4SiO_4-H_2O and Mg^{II}-H_4SiO_4-H_2O. J. Chem. Soc. Dalton Transactions, 181-184.

SATOH, I., CHOPPIN, G.R. (1992): Interaction of Uranyl(VI) with Silicic Acid. Radiochim. Acta, 56, 85-87.

SJÖBERG, S., ÖHMAN, L.O., INGRI, N. (1985): Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. 11. Polysilicate Formation in Alkaline Aqueous Solution. A Combined Potentiometric and ^{29}Si NMR Study. Acta Chemica Scandinavica, A39, 93-107.

WADSAK, W., HRNECEK, E., IRLWECK, K. (2000): Formation of americium(III) complexes with aqueous silicic acid. Radiochim. Acta, 88, 61-64.

WEBER, W.J., STUMM, W. (1965): Formation of a silicato-iron(III) complex in dilute aqueous solution. J. Inorg. Nucl. Chem., 27, 237-239.

5.19   Sulfides

The update of the Nagra Thermochemical Database (NTB 91-17, PEARSON & BERNER 1991, and NTB 91-18, PEARSON et al. 1992) was focused on the following elements: Th, U, Np, Pu, Am, Tc, Zr, Sn, Ra, Ni, Pd, and Eu. All of the sulfide data contained in NTB 91-18 and all of the data recommended for the database update are presented in Table 5.19.15. With respect to the elements cited above, no sulfide data from NTB 91-18 have been retained and only data for Sn- and Ni-sulfides are recommended for the database update, see Table 5.19.1.

Table 5.19.1:   Overview of the data update for sulfides

	NTB 91-18	Database Update
Th	no data	no data recommended
U	no data	no data recommended
Np	no data	no data recommended
Pu	no data	no data recommended
Am	no data	no data recommended
Tc	all data from NTB 91-18 deleted	no new data recommended
Zr	no data	no data available
Sn	all data from NTB 91-18 deleted	**new data recommended SnS(pr)**
Ra	no data	no data available
Ni	all data from NTB 91-18 deleted	**new data recommended NiHS$^+$ Ni(HS)$_2$(aq)**
Pd	all data from NTB 91-18 deleted	no new data recommended
Eu	no data	no data available

This section gives a short documentation on the data from NTB 91-18 that have been deleted from the database and on the data that have been included in the update. More details as well as the discussion of data that were not recommended for the update can be found in a broader study in preparation on "The Chemical Thermodynamics of Sulfide in Aqueous Systems" (THOENEN in prep.).

Note that throughout this section estimated data appearing in tables are enclosed by braces { }.

5.19.1 Aqueous sulfide species

For $H_2S(aq)$ only the first dissociation constant can be reliably measured. The sulfide ion is a much stronger base than the hydroxide ion, OH^-, and cannot be found in measurable quantities in aqueous solutions.

The primary master species chosen for sulfur is SO_4^{2-} and is related to the secondary master species HS^- by equation (5.19.13).

5.19.1.1 $H_2S(g)$ and $H_2S(aq)$

The Gibbs free energy of reaction for the dissolution of $H_2S(g)$ in aqueous solution

$$H_2S(g) \Leftrightarrow H_2S(aq) \tag{5.19.1}$$

can be calculated from NEA auxiliary data (RARD et al. 1999), $\Delta_f G_m°(H_2S, g, 298.15\ K) = -(33.443 \pm 0.500)\ kJ \cdot mol^{-1}$ and $\Delta_f G_m°(H_2S, aq, 298.15\ K) = -(27.648 \pm 2.115)\ kJ \cdot mol^{-1}$, which are based on the corresponding CODATA values for $\Delta_f H_m°$ and $S_m°$. Therefore

$$\Delta_r G_m°(5.19.1, 298.15\ K) = (5.795 \pm 2.173)\ kJ \cdot mol^{-1}$$

and

$$\log_{10} K°(5.19.1, 298.15\ K) = -(1.02 \pm 0.38)$$

The solubility of $H_2S(g)$ in NaCl solutions at 25°C was measured by GAMSJÄGER & SCHINDLER (1969) and BARRET et al. (1988), see THOENEN (in prep.) for a discussion. We used these data to determine $\log_{10} K°(5.19.1, 298.15\ K)$ and the ion interaction coefficients of $H_2S(aq)$ according to the specific ion interaction theory (SIT) (GRENTHE et al. 1997): The activity coefficient of $H_2S(aq)$ in an ionic medium (1:1 salt NX) is given by

$$\log_{10} \gamma_{H_2S(aq)} = \varepsilon(H_2S(aq), N^+) m_{N^+} + \varepsilon(H_2S(aq), X^-) m_{X^-} \tag{5.19.2}$$

which is equivalent to

$$\log_{10} \gamma_{H_2S(aq)} = \varepsilon(H_2S(aq), N^+ + X^-) m_{NX}, \tag{5.19.3}$$

with

$$\varepsilon(H_2S(aq), N^+ + X^-) = \varepsilon(H_2S(aq), N^+) + \varepsilon(H_2S(aq), X^-), \tag{5.19.4}$$

and

$$\varepsilon(H_2S(aq),N^+) = \varepsilon(H_2S(aq),X^-),\tag{5.19.5}$$

if $m_{N^+} = m_{X^-} = m_{NX}$.

The equilibrium constant for the solubility of $H_2S(g)$ in aqueous solution is

$$K^\circ(5.19.1) = \frac{\gamma_{H_2S(aq)}m_{H_2S(aq)}}{f_{H_2S(g)}},\tag{5.19.6}$$

and the corresponding conditional stability constant

$$K(5.19.1) = \frac{m_{H_2S(aq)}}{f_{H_2S(g)}}.\tag{5.19.7}$$

From equations (5.19.3), (5.19.6), and (5.19.7) follows that

$$\log_{10}K(5.19.1) = \log_{10}K^\circ(5.19.1) - \varepsilon(H_2S(aq), N^+ + X^-)m_{NX}.\tag{5.19.8}$$

We used this equation to extract $\log_{10}K^\circ$(5.19.1, 298.15 K) and $\varepsilon(H_2S(aq), Na^+ + Cl^-)$ from the experimental data at 25°C by GAMSJÄGER & SCHINDLER (1969) and BARRET et al. (1988), see Fig. 5.19.1, and obtained

$$\log_{10}K^\circ(5.19.1, 298.15\ K) = -(1.02 \pm 0.01)$$

$$\varepsilon(H_2S(aq), Na^+ + Cl^-) = (0.055 \pm 0.004)\ kg \cdot mol^{-1}$$

from an unweighted linear regression (with uncertainties of 2σ determined from the fit), see THOENEN (in prep.) for more details. This value for $\log_{10}K^\circ$(5.19.1, 298.15 K) is identical to the one determined above from NEA auxiliary data, except for the smaller uncertainty.

Equation (5.19.1) can be rewritten in terms of the sulfide master species HS^-

$$H_2S(g) \Leftrightarrow HS^- + H^+\tag{5.19.9}$$

by addition of equations (5.19.1) and (5.19.10), see Section 5.19.1.2,. Therefore, the recommended value

$$\log_{10}{}^*K^\circ(5.19.9, 298.15\ K) = -(8.01 \pm 0.17)$$

was calculated from $\log_{10}K^\circ$(5.19.1, 298.15 K) = $-$ (1.02 $\pm$ 0.01), see above, and from the recommended value for $\log_{10}{}^*K^\circ$(5.19.10, 298.15 K) = $-$ (6.99 $\pm$ 0.17), see Section 5.19.1.2.
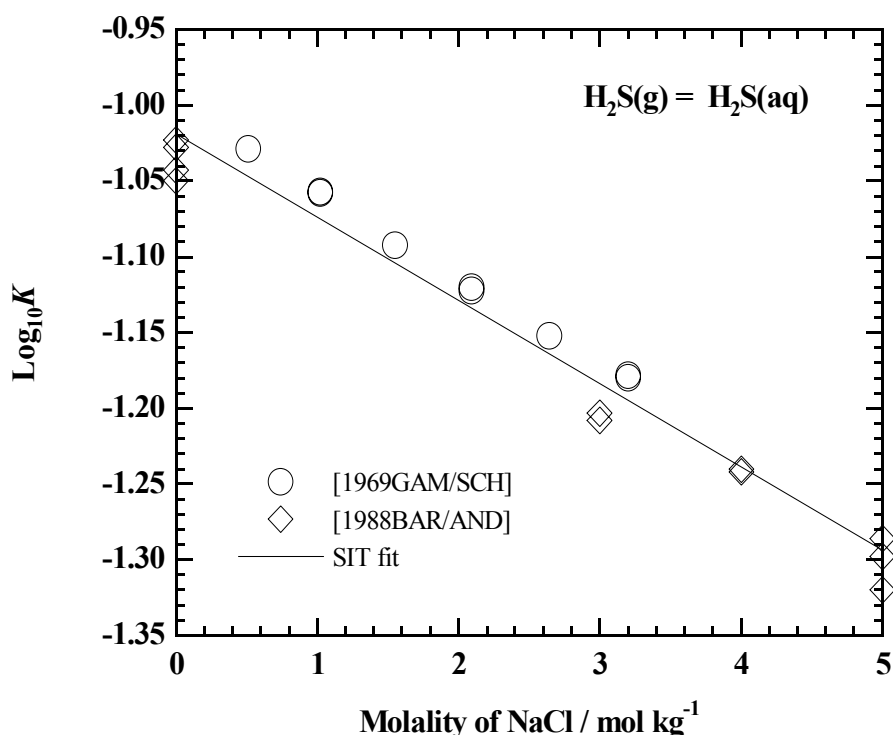
Fig. 5.19.1:   Experimental data by GAMSJÄGER & SCHINDLER (1969) [1969GAM/SCH] and BARRET et al. (1988) [1988BAR/AND] for the reaction $H_2S(g) \Leftrightarrow H_2S(aq)$ in NaCl solutions at 25°C. The straight line represents an unweighted linear regression, resulting in $\log_{10}K°(5.19.1) = -(1.02 \pm 0.01)$ and $\varepsilon(H_2S(aq), Na^+ + Cl^-) = (0.055 \pm 0.004)$ kg·mol^{-1}.

The enthalpy of reaction for the dissolution of $H_2S(g)$ in aqueous solution according to equation (5.19.1) can be calculated from NEA auxiliary data (CODATA values) (RARD et al. 1999), $\Delta_f H_m°(H_2S, g, 298.15 \text{ K}) = -(20.6 \pm 0.5)$ kJ·mol^{-1} and $\Delta_f H_m°(H_2S, aq, 298.15 \text{ K}) = -(38.6 \pm 1.5)$ kJ·mol^{-1}. Therefore,

$$\Delta_r H_m°(5.19.1, 298.15 \text{ K}) = -(18.0 \pm 1.6) \text{ kJ·mol}^{-1}$$

Addition of this to $\Delta_r H_m°(5.19.10, 298.15 \text{ K}) = (22.3 \pm 2.1)$ kJ·mol^{-1}, see Section 5.19.1.2, leads to

$$\Delta_r H_m°(5.19.9, 298.15 \text{ K}) = (4.3 \pm 2.6) \text{ kJ·mol}^{-1}$$

which we recommend for the database update.

5.19.1.2   HS⁻

The NEA auxiliary data (RARD et al. 1999), $\Delta_f H_m°$(HS⁻, aq, 298.15 K) and $S_m°$(HS⁻, aq, 298.15 K) were taken from CODATA, and $\Delta_f G_m°$(HS⁻, aq, 298.15 K) was calculated from these. All are adopted for the database update.

$$\Delta_f H_m°(\text{HS}^-, \text{aq}, 298.15\text{ K}) = -(16.3 \pm 1.5)\text{ kJ}\cdot\text{mol}^{-1}$$

$$S_m°(\text{HS}^-, \text{aq}, 298.15\text{ K}) = (67 \pm 5)\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m°(\text{HS}^-, \text{aq}, 298.15\text{ K}) = (12.243 \pm 2.115)\text{ kJ}\cdot\text{mol}^{-1}$$

Apart from the uncertainties, the former two values are identical to the values from NTB 91-18, while the latter one is only slightly different (NTB 91-18: $\Delta_f G_m°$(HS⁻, aq, 298.15 K) = 12.240 kJ $\cdot$ mol⁻¹).

In the NEA review on the chemical thermodynamics of uranium (GRENTHE et al. 1992), the Gibbs free energy of reaction for

$$\text{H}_2\text{S(aq)} \Leftrightarrow \text{HS}^- + \text{H}^+ \qquad\qquad (5.19.10)$$
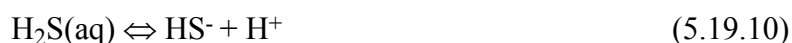
was calculated from the above mentioned NEA auxiliary data, $\Delta_f G_m°$(H₂S, aq, 298.15 K) and $\Delta_f G_m°$(HS⁻, aq, 298.15 K). Therefore

$$\Delta_r G_m°(5.19.10, 298.15\text{ K}) = (39.891 \pm 2.991)\text{ kJ}\cdot\text{mol}^{-1}$$

and

$$\log_{10}{}^*K°(5.19.10, 298.15\text{ K}) = -(6.99 \pm 0.52)$$

GRENTHE et al. (1992) argued that the uncertainty of $\log_{10}{}^*K°$(5.19.10, 298.15 K) is certainly too large. The average of nine reported equilibrium constants is $\log_{10}{}^*K°$(5.19.10, 298.15 K) = - 6.96, and the largest deviation of a single value from the average is 0.17. GRENTHE et al. (1992) considered this deviation as an appropriate uncertainty for the value calculated from the CODATA values and recommended

$$\log_{10}{}^*K°(5.19.10, 298.15\text{ K}) = -(6.99 \pm 0.17)$$

This value is only slightly different from NTB 91-18 ($\log_{10}{}^*K°$(5.19.10, 298.15 K) = - 6.980) and is adopted for the database update.

The dissociation of H_2S(aq) in NaCl solutions at 25°C was studied by ALMGREN et al. (1976) and HERSHEY et al. (1988), see THOENEN (in prep.) for a discussion. We used these data to determine $\log_{10}*K°$(5.19.10, 298.15 K) and $\Delta\varepsilon$(5.19.10, Na$^+$ + Cl$^-$) according to SIT, see Fig. 5.19.2. An unweighted linear regression resulted in

$$\log_{10}*K°(5.19.10, 298.15\ K) = -(6.98 \pm 0.02)$$

and

$$\Delta\varepsilon(5.19.10, Na^+ + Cl^-) = (0.142 \pm 0.009)\ kg \cdot mol^{-1}$$
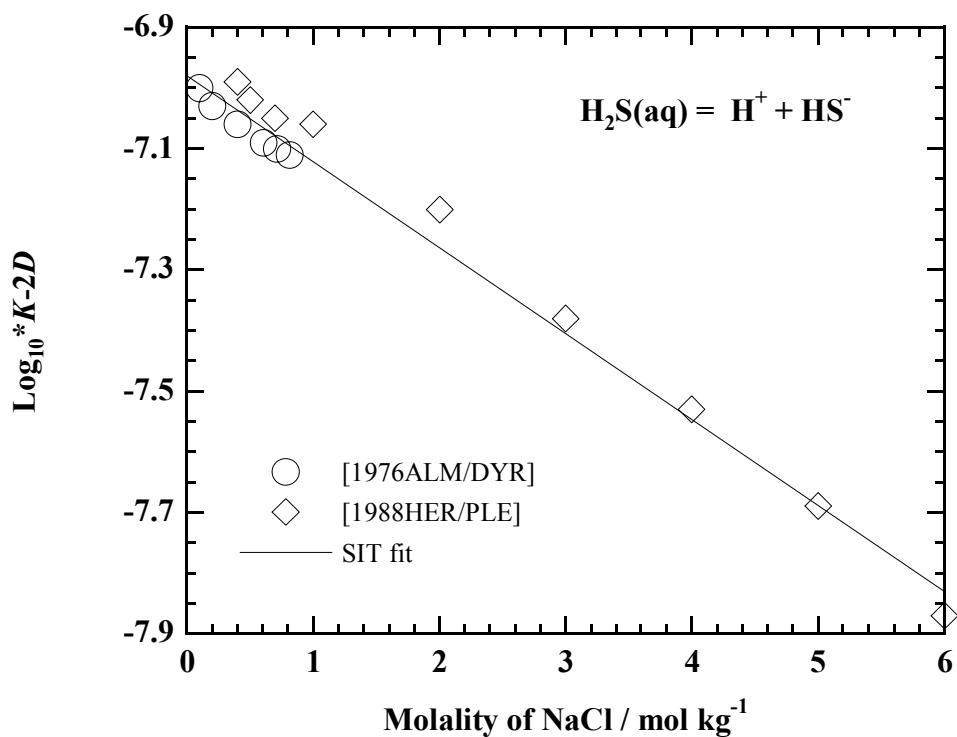
Fig. 5.19.2: Experimental data by ALMGREN et al. (1976) [1976ALM/DYR] and HERSHEY et al. (1988) [1988HER/PLE] for the reaction H_2S(aq) ⇔ H$^+$ + HS$^-$ in NaCl solutions at 25°C. The straight line represents an unweighted linear regression, resulting in $\log_{10}*K°$(5.19.10) = -(6.98 ± 0.02) and $\Delta\varepsilon$(5.19.10, Na$^+$ + Cl$^-$) = (0.142 ± 0.009) kg·mol^{-1}.
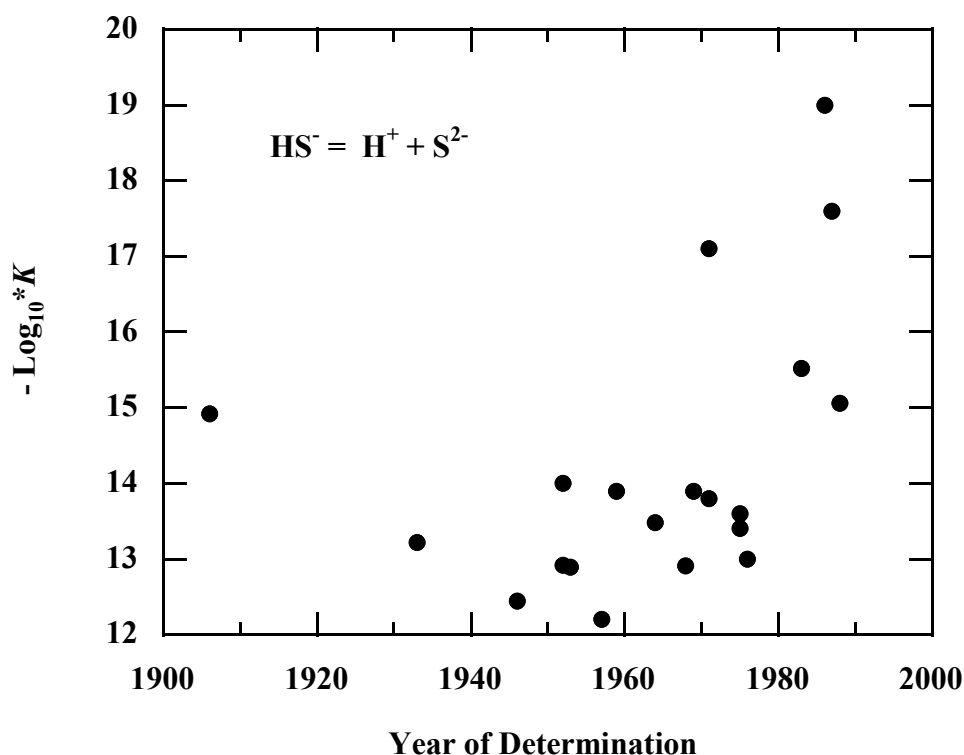
Fig. 5.19.3:   Values of the second dissociation constant of $H_2S(aq)$ as a function of the year of determination, see THOENEN (in prep.) for references. There is a trend for higher values from more recent determinations.

with uncertainties of 2σ determined from the fit. Within the uncertainty, the value for $\log_{10}*K°(5.19.10, 298.15\ K)$ is identical to the recommended one based on CODATA values.

From

$$\Delta\varepsilon(5.19.10, Na^+ + Cl^-) = \varepsilon(HS^-, Na^+) + \varepsilon(H^+, Cl^-) - \varepsilon(H_2S(aq), Na^+ + Cl^-)$$

follows that

$$\varepsilon(HS^-, Na^+) = (0.08 \pm 0.01)\ kg \cdot mol^{-1}$$

with $\varepsilon(H^+, Cl^-) = (0.12 \pm 0.01)\ kg \cdot mol^{-1}$ (RARD et al. 1999), $\Delta\varepsilon(5.19.10, Na^+ + Cl^-) = (0.142 \pm 0.009)\ kg \cdot mol^{-1}$, and $\varepsilon(H_2S(aq), Na^+ + Cl^-) = (0.055 \pm 0.004)\ kg \cdot mol^{-1}$.

The enthalpy of reaction

$$\Delta_r H_m°(5.19.10, 298.15\ K) = (22.3 \pm 2.1)\ kJ \cdot mol^{-1}$$

recommended by GRENTHE et al. (1992) was calculated from NEA auxiliary data (CODATA values), $\Delta_f H_m°(H_2S, aq, 298.15 \text{ K}) = - (38.6 \pm 1.5) \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_f H_m°(HS^-, aq, 298.15 \text{ K}) = - (16.3 \pm 1.5) \text{ kJ} \cdot \text{mol}^{-1}$. This value, apart from the uncertainty identical to the value from NTB 91-18, is adopted for the database update.

5.19.1.3 S^{2-}

The value of the second dissociation constant of $H_2S(aq)$ has been the subject of controversy for more than fifty years and proposed logarithmic values cover a span from -12.2 to -19, with a trend to more negative values from more recent determinations, see Fig. 5.19.3. The NEA review by GRENTHE et al. (1992) recommended

$$\log_{10}*K°(5.19.11, 298.15 \text{ K}) = - (19 \pm 2)$$

for

$$HS^- \Leftrightarrow H^+ + S^{2-} \qquad (5.19.11)$$

which we accept for the database update. It is obvious from this value that S^{2-} cannot be present in measurable quantities in aqueous solutions. Unfortunately, the solubility of sulfide minerals is usually reported in terms of the solubility product which is based on the non-observable quantity of S^{2-} and therefore implies that S^{2-} was calculated from measured amounts of $H_2S(aq)$ or HS^- using $\log_{10}*K°(5.19.11)$. It is essential that the same value for $\log_{10}*K°(5.19.11)$ is used for the recalculation of such a solubility product to a solubility constant involving $H_2S(aq)$ or HS^-. Otherwise, an error of several orders of magnitude may easily be introduced.

5.19.2   Redox Reactions

The Gibbs free energy of reaction for the sulfur/sulfide redox couple

$$S(\text{rhomb}) + H^+ + 2e^- \Leftrightarrow HS^- \qquad (5.19.12)$$

can be calculated from $\Delta_f G_m°(HS^-, aq, 298.15 \text{ K}) = (12.243 \pm 2.115) \text{ kJ} \cdot \text{mol}^{-1}$, see Section 5.19.1.2. Therefore,

$$\Delta_r G_m°(5.19.12, 298.15 \text{ K}) = (12.244 \pm 2.116) \text{ kJ} \cdot \text{mol}^{-1}$$

and consequently

$$\log_{10}*K°(5.19.12, 298.15 \text{ K}) = - (2.144 \pm 0.370)$$

This value is adopted for the database update.

The enthalpy of reaction for the sulfur/sulfide couple can be calculated from $\Delta_f H_m°$(HS⁻, aq, 298.15 K) = - (16.3 ± 1.5) kJ·mol⁻¹, see Section 5.19.1.2,

$$\Delta_r H_m°(5.19.12, 298.15 \text{ K}) = - (16.3 \pm 1.5) \text{ kJ·mol}^{-1}$$

This value is adopted for the database update.

The Gibbs free energy of reaction for the sulfate/sulfide redox couple

$$SO_4^{2-} + 9H^+ + 8e^- \Leftrightarrow HS^- + 4H_2O(l) \qquad\qquad (5.19.13)$$
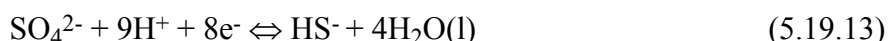
can be calculated from $\Delta_f G_m°$(SO₄²⁻, aq, 298.15 K) = - (744.004 ± 0.418) kJ·mol⁻¹ and $\Delta_f G_m°$(H₂O, l, 298.15 K) = - (237.140 ± 0.041) kJ·mol⁻¹, both NEA auxiliary data (RARD et al. 1999) based on CODATA, and from $\Delta_f G_m°$(HS⁻, aq, 298.15 K), see above, resulting in

$$\Delta_r G_m°(5.19.13, 298.15 \text{ K}) = - (192.31 \pm 2.16) \text{ kJ·mol}^{-1}$$

which leads to

$$\log_{10}{}^* K°(5.19.13, 298.15 \text{ K}) = (33.69 \pm 0.38)$$

This value is included in the database update.

From $\Delta_f H_m°$(SO₄²⁻, aq, 298.15 K) = - (909.34 ± 0.40) kJ·mol⁻¹ and $\Delta_f H_m°$(H₂O, l, 298.15 K) = -(285.83 ± 0.04), both NEA auxiliary data (RARD et al. 1999) taken from CODATA, and from $\Delta_f H_m°$(HS⁻, aq, 298.15 K), see above, we obtain

$$\Delta_r H_m°(5.19.13, 298.15 \text{ K}) = - (250.28 \pm 1.56) \text{ kJ·mol}^{-1}$$

which is included in the database update.

5.19.3   Actinides

For the purposes of the database update, we did not systematically survey the literature on thermodynamic data for actinide sulfides. Instead, we relied on the reviews by GRØNVOLD et al. (1984) (covering Th, U, Np, Pu, and Am), GRENTHE et al. (1992) (covering U), SILVA et al. (1995) (covering Am). Note that the review by LEMIRE et al. (2001) on the chemical thermodynamics of neptunium and plutonium does not consider any neptunium or plutonium sulfides.

All actinide sulfide solids known to date have only been synthesized at high temperatures in non-aqueous environments and none of them exist as minerals in natural environments. There appear to be no solubility data for sulfide solids and data for sulfide complexes are also missing. Because actinide cations are hard acids and the sulfide and bisulfide anions are soft bases, actinide (bi)sulfide complexes are expected to be very weak, if they exist at all.

5.19.3.1   Thorium

All thorium sulfide solids known to date (ThS(cr), Th_2S_3(cr), Th_7S_{12}(cr), ThS_2(cr), and Th_2S_5(cr)) appear to be high temperature syntheses (although the review by GRØNVOLD et al. 1984 does not give any information about preparative methods) and none of them occur as minerals in natural environments. There are no solubility studies and therefore no experimentally determined solubility constants. For this reason, no data were selected for the database update.

Thermodynamic data discussed and selected by GRØNVOLD et al. (1984) are presented in Table 5.19.2. We do not intend to discuss these selections at length (for more details the reader may refer to GRØNVOLD et al. 1984 and references therein) but rather give a short summary of the methods employed in producing these data.

ThS(cr): $\Delta_fH_m°$ was based on solution calorimetry of $ThS_{1.043}$(cr) (corrected for the compositional deviation), while $S_m°$ and $C_{p,m}°$ were determined from heat capacity measurements.

Th_2S_3(cr): $\Delta_fH_m°$ was obtained from solution calorimetry. $S_m°$ was calculated from a second-law evaluation of solid-state e.m.f. measurements of the overall cell reaction

$$Th(cr) + Th_2S_3(cr) \Leftrightarrow 3\ ThS(cr)$$
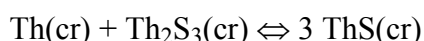
at temperatures between 825 and 925˚C. $C_{p,m}°$ was estimated.

Th_7S_{12}(cr): $\Delta_fH_m°$ and $S_m°$ were obtained from second- and third-law evaluations of solid-state e.m.f. measurements of the overall cell reaction

$$Th(cr) + Th_7S_{12}(cr) \Leftrightarrow 4\ Th_2S_3(cr)$$
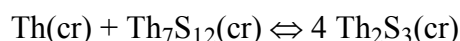
at temperatures between 825 and 925˚C.

ThS_2(cr): $\Delta_fH_m°$ was based on a third-law evaluation of solid-state e.m.f. measurements of the overall cell reaction

$$Th(cr) + 6\ ThS_2(cr) \Leftrightarrow Th_7S_{12}(cr)$$
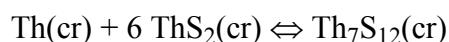
at temperatures between 825 and 925˚C. $S_m°$ and $C_{p,m}°$ were determined from heat capacity measurements.

Th₂S₅(cr): $\Delta_f H_m°$ was calculated from a thermodynamic cycle based on values for $\Delta_r G$ extracted from reported dissociation pressures for $ThS_{2.19}(cr)$ over the range 650-800˚C, assuming them to refer to the reaction

$$4\ ThS_{2.5}(cr) \Leftrightarrow 4\ ThS_2(cr) + S_2(g).$$
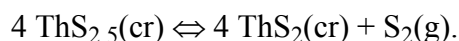
$S_m°$ was estimated.

Table 5.19.2: Thermodynamic data for thorium sulfide solids at 298.15 K as selected by GRØNVOLD et al. (1984), p. 13 (values recalculated from cal to J). None of these data were selected for the database update.

Solid	$\Delta_f G_m°$ (kJ · mol⁻¹)	$\Delta_f H_m°$ (kJ · mol⁻¹)	$S_m°$ (J · K⁻¹ · mol⁻¹)	$C_{p,m}°$ (J · K⁻¹ · mol⁻¹)
ThS(cr)	-395 ± 4	-400 ± 4	69.79 ± 0.33	47.74 ± 0.25
Th₂S₃(cr)	-1073 ± 13	-1084 ± 13	180 ± 17	{122 ± 8}
Th₇S₁₂(cr)	-4100 ± 146	-4130 ± 146	641 ± 59	-
ThS₂(cr)	-621.3 ± 42	-628 ± 42	96.2 ± 0.8	70.3 ± 0.25
Th₂S₅(cr)	{-1247 ± 84}	-1272 ± 84	{215 ± 17}	-

5.19.3.2　Uranium

All uranium sulfide solids known to date ($US(cr)$, $U_2S_3(cr)$, $U_3S_5(cr)$, $US_{1.90}(cr)$, $US_2(cr)$, $U_2S_5(cr)$, $US_3(cr)$) appear to be high temperature syntheses (although the reviews by GRØNVOLD et al. (1984) and GRENTHE et al. (1992) do not give any information about preparative methods) and none of them occur as minerals in natural environments (not even in connection with uranium ores). There are no solubility studies and therefore no experimentally determined solubility constants. For this reason, no data were selected for the database update. Thermodynamic data discussed and selected by GRENTHE et al. (1992) are presented in Table 5.19.3.

Table 5.19.3: Thermodynamic data for uranium sulfide solids at 298.15 K as selected by GRENTHE et al. (1992), Table V.32. None of these data were selected for the database update.

Solid	$\Delta_f G_m°$ (kJ · mol^{-1})	$\Delta_f H_m°$ (kJ · mol^{-1})	$S_m°$ (J · K^{-1} · mol^{-1})	$C_{p,m}°$ (J · K^{-1} · mol^{-1})
US(cr)	-320.9 ± 12.6	-322.2 ± 12.6	77.99 ± 0.21	50.54 ± 0.08
U_2S_3(cr)	-880 ± 67	-879 ± 67	199.2 ± 1.7	133.7 ± 0.8
U_3S_5(cr)	-1425 ± 100	-1431 ± 100	291 ± 25	-
US$_{1.90}$(cr)	-509.5 ± 20.9	-509.9 ± 20.9	109.66 ± 0.21	73.97 ± 0.13
US_2(cr)	-519.2 ± 8.0	-520.4 ± 8.0	110.42 ± 0.21	74.64 ± 0.13
U_2S_5(cr)	-	-	243 ± 25	-
US_3(cr)	-537.3 ± 12.6	-539.6 ± 12.6	138.49 ± 0.21	95.60 ± 0.25

5.19.3.3   Neptunium

Neptunium sulfides are not covered by LEMIRE et al. (2001).

All neptunium sulfide solids known to date (NpS(cr), Np_3S_{4+x}(cr), Np_2S_3(cr), Np_3S_5(cr), Np_2S_5(cr), and NpS_3(cr)) are high temperature syntheses. Preparative methods were summarized in the review by GRØNVOLD et al. (1984):

NpS(cr): NpS(cr) was obtained by heating Np_2S_3(cr) with neptunium metal at 1600˚C.

Np_2S_3(cr): Orthorhombic Np_2S_3(cr) was prepared by treating NpO_2(cr) with carbon disulfide and hydrogen sulfide at 1025 - 1525˚C. α-Np_2S_3(cr), an orthorhombic structural modification, was produced by thermally decomposing Np_3S_5(cr) at 925˚C. At about 1225˚C α-Np_2S_3(cr) transforms into tetragonal β-Np_2S_3(cr).

Np_3S_5(cr): Np_3S_5(cr) was formed by thermal decomposition of NpS_3(cr) at 500˚C.

Np_2S_5(cr): Np_2S_5(cr) was produced by heating Np_3S_5(cr) with sulfur at 500˚C.

NpS_3(cr): NpS_3(cr) was synthesized from metallic neptunium and sulfur at 500˚C.

There are no solubility studies and therefore no experimentally determined solubility constants.

According to the review by GRØNVOLD et al. (1984), there are no measured thermodynamic data. However, these authors have discussed and selected estimates of values which are presented in Table 5.19.4. These estimated data were not considered for the database update.

Table 5.19.4: Thermodynamic data for neptunium sulfide solids at 298.15 K as selected by GRØNVOLD et al. (1984), p. 105 (values recalculated from cal to J). None of these data were considered for the database update

Solid	$\Delta_f G_m°$	$\Delta_f H_m°$	$S_m°$
	(kJ · mol^{-1})	(kJ · mol^{-1})	(J · K^{-1} · mol^{-1})
NpS(cr)	{-343 ± 46}	{-343 ± 42}	{85.8 ± 8}
Np$_3$S$_{4+x}$(cr)	{-1255 ± 138}	{-1255 ± 126}	{276 ± 25}
Np$_2$S$_3$(cr)	{-912 ± 75}	{-912 ± 67}	{192 ± 25}
Np$_3$S$_5$(cr)	{-1406 ± 163}	{-1418 ± 151}	{289 ± 25}
Np$_2$S$_5$(cr)	{-996 ± 109}	{-1004 ± 100}	{238 ± 25}
NpS$_3$(cr)	{-506 ± 54}	{-510 ± 50}	{136 ± 13}

5.19.3.4 Plutonium

Plutonium sulfides are not covered by LEMIRE et al. (2001).

All plutonium sulfide and oxysulfide solids known to date (PuS(cr), Pu$_3$S$_{4+x}$(cr), Pu$_5$S$_{7+x}$(cr), Pu$_2$S$_3$(cr), PuS$_{1.8}$(cr), PuS$_{1.9-x}$(cr), PuS$_2$(cr), Pu$_2$O$_2$S(cr), Pu$_4$O$_4$S$_3$(cr), PuOS(cr)) are high temperature syntheses. Preparative methods for some of these solids were summarized in the reviews by CLEVELAND (1970), and GRØNVOLD et al. (1984):

PuS(cr): PuS(cr) was prepared by reacting plutonium with sulfur at 400-500˚C.

Pu$_2$S$_3$(cr): α-Pu$_2$S$_3$(cr) was obtained by thermal decomposition of PuS$_2$(cr) in vacuum above 600˚C. By heating α-Pu$_2$S$_3$(cr) under vacuum, it transforms to β-Pu$_2$S$_3$(cr) at 1350˚C, which itself is transformed to γ-Pu$_2$S$_3$(cr) at 1400˚C.

PuS$_2$(cr): PuS$_2$(cr) was prepared by heating stoichiometric quantities of plutonium and sulfur to 600˚C.

Apparently, there are no experimental studies involving the solubilities or thermodynamic properties of these solids and therefore, GRØNVOLD et al. (1984) report only estimated values (see Table 5.19.5). These estimated data were not considered for the database update.

Table 5.19.5: Thermodynamic data for plutonium sulfide solids at 298.15 K as selected by GRØNVOLD et al. (1984), p. 113 (values recalculated from cal to J). None of these data were considered for the database update.

Solid	$\Delta_f G_m^\circ$ (kJ · mol⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol⁻¹)	S_m° (J · K⁻¹ · mol⁻¹)
PuS(cr)	{-360 ± 42}	{-364 ± 38}	{75 ± 8}
Pu₃S₄₊ₓ(cr)	{-1356 ± 151}	{-1368 ± 138}	{264 ± 25}
Pu₅S₇₊ₓ(cr)	-	-	-
Pu₂S₃(cr)	{-979 ± 109}	{-987 ± 100}	{188 ± 17}
PuS₁.₉₋ₓ(cr)	{-519 ± 59}	{-523 ± 54}	{105 ± 8}
PuS₂(cr)	{-523 ± 59}	{-529 ± 54}	{107 ± 13}

5.19.3.5 Americium

Several americium sulfide and oxysulfide solids have been synthesized at high temperatures in non-aqueous environments (see the reviews by GRØNVOLD et al. 1984, SILVA et al. 1995, and references therein):

AmS(cr): AmS(cr) mixed with Am_3S_4(cr) was prepared by heating Am_2S_3(cr) in vacuum at 650˚C.

Am₃S₄(cr): Am_3S_4(cr), also referred to as γ-Am_2S_3(cr) (sic!), was obtained by thermal decomposition of Am_2S_3(cr) in vacuum at 1295˚C.

Am₂S₃(cr): Am_2S_3(cr) was prepared by heating americium hydride with the stoichiometric amount of sulfur at 500˚C. Orthorhombic α-Am_2S_3(cr) transforms to tetragonal β-Am_2S_3(cr) at about 1100˚C.

AmS₂(cr): AmS_2(cr) was formed by heating americium hydride with excess sulfur at 400˚C.

Am₂O₂S(cr): Am_2O_2S(cr) was obtained by reducing Am(III) oxysulfate, $Am_2O_2SO_4$(cr), in H_2/Ar at about 800˚C.

Am₁₀OS₁₄(cr): $Am_{10}OS_{14}$(cr) was prepared by heating Am_2S_3(cr) in vacuum at 850˚C.

According to the review by SILVA et al. (1995), there are no experimental studies involving the solubilities or thermodynamic properties of these solids and therefore, SILVA et al. (1995) report only some estimates for the standard entropies of AmS(cr) and Am_2S_3(cr), and for the standard heat capacity of Am_2S_3(cr), see Table 5.19.6. The estimated data for Am_2S_3(cr) are appreciably different from the experimental values for U_2S_3(cr) (see Table 5.19.3) and may therefore not be very reliable.

Table 5.19.6: Thermodynamic data for americium sulfide and oxysulfide solids at 298.15 K as reported by SILVA et al. (1995). None of these data were selected for the database update.

Solid	$\Delta_f G_m°$ (kJ · mol^{-1})	$\Delta_f H_m°$ (kJ · mol^{-1})	$S_m°$ (J · K^{-1} · mol^{-1})	$C_{p,m}°$ (J · K^{-1} · mol^{-1})
AmS(cr)	-	-	{92 ± 12}	-
Am$_3$S$_4$(cr)	-	-	-	-
Am$_2$S$_3$(cr)	-	-	{133}	{244}
AmS$_2$(cr)	-	-	-	-
Am$_2$O$_2$S(cr)	-	-	-	-
Am$_{10}$OS$_{14}$(cr)	-	-	-	-

5.19.4   Technetium

No technetium minerals are known. However, several technetium sulfide solids have been synthesized, namely TcS$_2$(am), TcS$_2$(cr), and Tc$_2$S$_7$(s). There are only a few experimental solubility studies, all of which have serious limitations that prevent the extraction of reliable solubility constants (see RARD et al. 1999 and THOENEN in prep. for references and more information). The data listed in NTB 91-18 are based on estimates and have to be deleted from the database (see below for a discussion)

Therefore, no thermodynamic data for technetium sulfide solids can be recommended.

Information on potential technetium (bi)sulfide complexes is missing.

5.19.4.1   Data in NTB 91-18

NTB 91-18 contains thermodynamic data for TcS$_2$(s), TcS$_3$(s), and Tc$_2$S$_7$(s) (see Table 5.19.7 for $\Delta_f G_m°$ and $\Delta_f H_m°$). $\Delta_f G_m°$ and $\Delta_f H_m°$ were extracted from $\log_{10} K_{s,0}°$ (see Table 5.19.15) and $\Delta_r H_m°$ of the reactions

$$TcS_2(s) + 9H_2O(l) \Leftrightarrow TcO^{2+} + 2SO_4^{2-} + 18H^+ + 16e^-$$

$$TcS_3(s) + 13H_2O(l) \Leftrightarrow TcO^{2+} + 3SO_4^{2-} + 26H^+ + 22e^-$$

and

$$Tc_2S_7(s) + 30H_2O(l) \Leftrightarrow 2TcO^{2+} + 7SO_4^{2-} + 60H^+ + 50e^-$$
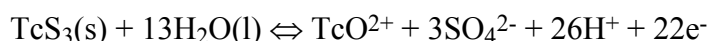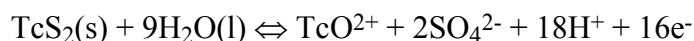
The values for $\log_{10}K_{s,0}^\circ$ and $\Delta_r H_m^\circ$ were taken from the HATCHES 3.0 database (CROSS & EWART 1991) which lists an NEA EQ3/6 database as reference. This NEA database could not be traced. However, it is almost certain that these values are ultimately based on the estimated data by MCDONALD & COBBLE (1962) which are discussed below. It is evident from Table 5.19.7 that there are huge differences between the values of $\Delta_f G_m^\circ$ and $\Delta_f H_m^\circ$ listed in NTB 91-18 and the values estimated by MCDONALD & COBBLE (1962), with the sole exception of $\Delta_f G_m^\circ$(TcS$_2$, s, 298.15 K). These differences must be due to serious errors during conversion of $\log_{10}K_{s,0}^\circ$ and $\Delta_r H_m^\circ$ into $\Delta_f G_m^\circ$ and $\Delta_f H_m^\circ$.

None of the data on technetium sulfide solids contained in NTB 91-18 are included in the database update.

Table 5.19.7: Thermodynamic data for technetium sulfide solids at 298.15 K and 1 bar as listed in NTB 91-18. Very likely, these data were ultimately based on the values estimated by MCDONALD & COBBLE (1962) which are given for comparison. The extreme deviations of the NTB 91-18 data are discussed in the text. None of these data were selected for the database update.

	NTB 91-18		MCDONALD & COBBLE (1962)	
	$\Delta_f G_m^\circ$ (kJ·mol^{-1})	$\Delta_f H_m^\circ$ (kJ·mol^{-1})	$\Delta_f G_m^\circ$ (kJ·mol^{-1})	$\Delta_f H_m^\circ$ (kJ·mol^{-1})
TcS$_2$(s)	-215.147	673.510	{-216}	{-224}
TcS$_3$(s)	1103.539	867.350	{-263}	{-276}
Tc$_2$S$_7$(s)	2051.927	1928.540	{-581}	{-615}

MCDONALD & COBBLE (1962) measured the heats of combustion of ReS$_2$(s) and Re$_2$S$_7$(s) by bomb calorimetry and calculated the corresponding $\Delta_f H_m^\circ$ at 298.15K by means of auxiliary data (not given in the paper). They estimated S_m° "from additivity rules and comparison with corresponding oxides" without mentioning any more details, calculated $\Delta_f S_m^\circ$ with auxiliary data (not given in the paper) and finally obtained values of $\Delta_f G_m^\circ$ for ReS$_2$(cr) and Re$_2$S$_7$(cr). Based on these experimental and estimated data, they derived values of $\Delta_f H_m^\circ$ and $\Delta_f G_m^\circ$ for Tc-, Ru-, Rh-, Pd-, Os-, and Ir-sulfide solids without further explanation (they merely stated that "these data also make it possible to estimate similar functions for neighboring sulfides which have not been available previously"). In the case of Tc, they estimated thermodynamic data for TcS$_2$(s), TcS$_3$(s), and Tc$_2$S$_7$(s). These data can certainly not be recommended for the database update.

5.19.5   Zirconium

There are no zirconium sulfide minerals and syntheses. Because the zirconium cation is a hard acid and the sulfide and bisulfide anions are soft bases, zirconium (bi)sulfide complexes are expected to be very weak, if they exist at all.

5.19.6   Tin

Only three tin sulfide minerals are known: SnS(cr) (herzenbergite), SnS_2(cr) (berndtite in two modifications), and Sn_2S_3(cr) (ottemannite). Solubility data are available for SnS(pr) [1] and SnS_2(pr) but only data for SnS(pr) were considered to be of sufficient quality to be included in the database update. For a discussion of the data that were not considered see THOENEN (in prep.). All of the data for tin sulfide solids in NTB 91-18 had to be rejected.

The oxidation state of Sn in aqueous solution is IV and II. There are some data on $Sn(IV)S_3^{2-}$, $Sn(IV)S_2(OH)^-$, $Sn(IV)S_4(H_2O)_2^{4-}$, and $Sn(IV)S_2(HS)^-$, but none of them are reliable enough to warrant inclusion into the database update, see THOENEN (in prep.) for more details. Information on potential Sn(II)-(bi)sulfide complexes is completely missing.

5.19.6.1   Data in NTB 91-18

NTB 91-18 contains thermodynamic data for SnS(s), Sn_3S_4(s), and Sn_2S_3(s). $\Delta_f G_m°$ and $\Delta_f H_m°$ (see Table 5.19.8) were calculated from $\log_{10}K_{s,0}°$ (see Table 5.19.15) and $\Delta_r H_m°$ values for the following reactions:

$$SnS(s) + 4H_2O(l) \Leftrightarrow Sn^{2+} + SO_4^{2-} + 8H^+ + 8e^-$$

$$Sn_3S_4(s) + 16H_2O(l) \Leftrightarrow 3Sn^{2+} + 4SO_4^{2-} + 32H^+ + 30e^-$$

$$Sn_2S_3(s) + 12H_2O(l) \Leftrightarrow 2Sn^{2+} + 3SO_4^{2-} + 24H^+ + 22e^-$$
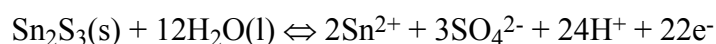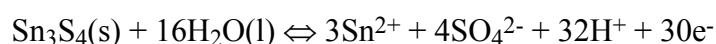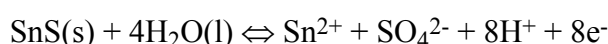
Values for $\log_{10}K_{s,0}°$ and $\Delta_r H_m°$ were taken from the HATCHES 3.0 database CROSS & EWART (1991), which further refers to "ex NEA EQ3/6". As we had no access to this database, the original sources for these data remain obscure. We suspect that these data are derived from high temperature experiments as are the corresponding data from version data0.com.R16 of the EQ3/6 database. It is revealing that Sn_3S_4(s) is not known as a mineral.

---

[1]   Precipitates without specified structure (amorphous, microcrystalline, or crystalline) are designated with (pr).

A comparison of the Sn-sulfide data from NTB 91-18 with the corresponding EQ3/6 data from version data0.com.R16 (see Table 5.19.8) reveals small differences for $\Delta_f G_m°$(Sn$_3$S$_4$, s, 298.15 K) and $\Delta_f G_m°$(Sn$_2$S$_3$, s, 298.15 K), and a large difference for $\Delta_f G_m°$(SnS, s, 298.15 K). The values of $\Delta_f H_m°$ for all three Sn-sulfides in NTB 91-18 are so wide off the mark that they appear to be some sort of random numbers.

We cannot recommend any of the data for SnS(s), Sn$_3$S$_4$(s), and Sn$_2$S$_3$(s) from NTB 91-18 and they are therefore not included in the database update.

Table 5.19.8: Thermodynamic data for tin sulfide solids at 298.15 K and 1 bar as listed in NTB 91-18. Data from the EQ3/6 database (version data0.com.R16) are given for comparison. None of these data were selected for the database update.

	NTB 91-18		EQ3/6 data0.com.R16 (kJ and kcal)			
	$\Delta_f G_m°$ (kJ·mol^{-1})	$\Delta_f H_m°$ (kJ·mol^{-1})	$\Delta_f G_m°$ (kJ·mol^{-1})	$\Delta_f H_m°$ (kJ·mol^{-1})	$\Delta_f G_m°$ (kcal·mol^{-1})	$\Delta_f H_m°$ (kcal·mol^{-1})
SnS(s)	-97.704	184.940	-104.696	-106.541	-25.023	-25.464
Sn$_3$S$_4$(s)	-356.482	816.055	-358.853	-370.284	-85.768	-88.5
Sn$_2$S$_3$(s)	-251.643	631.115	-253.408	-263.592	-60.566	-63

5.19.6.2   New Data

Solubility studies of Sn-sulfide solids appear to be very rare.

PEIFFERT & FREVERT (1987) prepared precipitates of SnS by adding 1 ml of 10^{-1} M Na$_2$S·9H$_2$O standard solution to 100 ml of 0.1 M SnCl$_2$. The ionic strength was adjusted to I = 0.1 M by adding an unspecified amount of 0.1 M NaCl [2]. After 5 days of equilibration, the pH was 1.8. The activity of H$_2$S(aq) was measured with a combined glass|Ag$_2$S electrode cell, resulting in pH$_2$S(aq) = 9.7. PEIFFERT & FREVERT (1987) do not provide an uncertainty for this value. We adopted an uncertainty of ± 0.3, based on the uncertainty of pH$_2$S(aq) = (14.2 ± 0.3) determined by these authors from seven experimental runs of solutions in equilibrium with PbS(pr). Note that the large decrease in pH after the 5 days of equilibration indicates an extensive oxidation of sulfide and the

---

[2] PEIFFERT & FREVERT (1987) write that "if sparingly soluble metal salts (PbCl$_2$, Sn(OH)$_2$, AgCl) were formed, the ionic strength was adjusted to I = 0.1 by adding 0.1 M NaCl". From these remarks we assume that in the course of the experiments with SnS(pr) there was also precipitation of Sn(OH)$_2$(pr) and that the salting in effect was used to redissolve the precipitated Sn(OH)$_2$(pr). However, PEIFFERT & FREVERT (1987) fail to mention whether SnS(pr) was analyzed for potential traces of Sn(OH)$_2$(pr).

oxidation products are very likely to have influenced the function of the sulfide electrode. The reported uncertainty is therefore probably underestimated.

For pSn^{2+}, PEIFFERT & FREVERT (1987) report a value of 1.6 calculated from $[Sn^{2+}]$, but unfortunately do not the specify the value of $[Sn^{2+}]$. Because it is unclear how they performed this calculation (they mention the use of the Davies approximation and accounting for the common ion effect but they do not explicitly state that Sn-chloride complexes were considered) we assign an uncertainty of $\pm$ 0.3 to this value. Using these data, PEIFFERT & FREVERT (1987) calculated $\log_{10}K_{s,0}°$ for the solubility reaction

$$SnS(pr) \Leftrightarrow Sn^{2+} + S^{2-} \tag{5.19.14}$$

from

$$pK_{s,0}°(5.19.14) = pSn^{2+} + pK(5.19.10, I = 0.1\ M) \tag{5.19.15}$$
$$+ pK(5.19.11, I = 0.1\ M) + pH_2S\ \text{-2pH}$$

where $pK(5.19.10, I = 0.1\ M)$ and $pK(5.19.11, I = 0.1\ M)$ are the conditional dissociation constants of $H_2S(aq)$. The use of these constants is clearly incorrect and they should be replaced by $pK°(5.19.10)$ and $pK°(5.19.10)$, respectively.

We prefer to calculate the equilibrium constant for

$$SnS(pr) + H^+ \Leftrightarrow Sn^{2+} + HS^- \tag{5.19.16}$$

according to

$$\log_{10}{*}K_s°(5.19.16) = -\ pSn^{2+} - pH_2S + 2pH + \log_{10}{*}K°(5.19.10) \tag{5.19.17}$$

With $pSn^{2+} = (1.6 \pm 0.3)$, pH = 1.8, $pH_2S = (9.7 \pm 0.3)$, and $\log_{10}{*}K°(5.19.10) = -\ (6.99 \pm 0.17)$

$$\log_{10}{*}K_s°(5.19.16) = -\ (14.7 \pm 0.5)$$

In the absence of more convincing solubility data (see THOENEN in prep. for more information) we recommend this value for the database update. We emphasize, however, that this solubility was determined from oversaturation only, that the precipitate was not characterized with respect to particle size and crystallinity and that it was not analyzed for potential traces of $Sn(OH)_2(pr)$. Furthermore, the reported pH drop during equilibration points to extensive oxidation of sulfide.

5.19.7 Radium

There is no information on radium sulfide solids and complexes, and they are not expected to exist.

5.19.8 Nickel

The known pure Ni-sulfide minerals are NiS(cr) (millerite), NiS_2(cr) (vaesite), Ni_3S_2(cr) (heazlewoodite), Ni_3S_4(cr) (polydymite), and Ni_7S_6(cr) (godlevskite). For a discussion of their natural formation environments see THOENEN (1999). The only solubility studies available are for NiS(s), all of which are unreliable and cannot be recommended for the database update (see THOENEN 1999 and THOENEN in prep. for details).

None of the data for Ni-sulfide solids in NTB 91-18 could be included in the database update.

Complexation data are available for $NiHS^+$, $Ni(HS)_2$(aq), $Ni_2(HS)^{3+}$, $Ni_3(HS)^{5+}$, NiS(aq), and $NiS(HS)^-$, but only data for $NiHS^+$ and $Ni(HS)_2$(aq) can be recommended for the database update (see THOENEN in prep. for a discussion of the rejected data).

5.19.8.1 Data in NTB 91-18

NTB 91-18 contains thermodynamic data for Ni_3S_2(s), NiS(s), Ni_3S_4(s), and NiS_2(s). $\Delta_f G_m°$ and $\Delta_f H_m°$ values (see Table 5.19.9) were supposedly calculated from $\log_{10} K_{s,0}°$ and $\Delta_r H_m°$ values reported by BAEYENS & MCKINLEY (1989) for the following reactions:
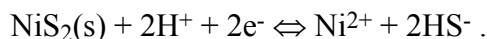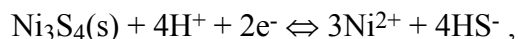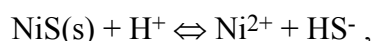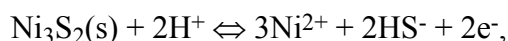
$$Ni_3S_2(s) + 2H^+ \Leftrightarrow 3Ni^{2+} + 2HS^- + 2e^-,$$

$$NiS(s) + H^+ \Leftrightarrow Ni^{2+} + HS^-,$$

$$Ni_3S_4(s) + 4H^+ + 2e^- \Leftrightarrow 3Ni^{2+} + 4HS^-,$$

$$NiS_2(s) + 2H^+ + 2e^- \Leftrightarrow Ni^{2+} + 2HS^-.$$

BAEYENS & MCKINLEY (1989) derived these $\log_{10} K_{s,0}°$ and $\Delta_r H_m°$ values from the corresponding values for $\Delta_f G_m°$ and $\Delta_f H_m°$ (see Table 5.19.9). Comparison of these data with those listed in NTB 91-18 reveals large differences which cannot be simply attributed to rounding errors, but rather point to serious errors during conversion of the values given by BAEYENS & MCKINLEY (1989) into the unreasonable values listed in NTB 91-18. The $\Delta_f G_m°$ and $\Delta_f H_m°$ data selected by BAEYENS & MCKINLEY (1989) can be traced back to the following references:

Ni$_3$S$_2$(s): Data for Ni$_3$S$_2$(s) were taken from the compilation by WAGMAN et al. (1982) which give no further references. Therefore, the quality of these data cannot be assessed and they cannot be recommended.

NiS(s): Data for NiS(s) were taken from the compilation by ROBIE et al. (1978) which refer to ROSENQVIST (1954) for $\Delta_f G_m°$ and $\Delta_f H_m°$. ROSENQVIST (1954) performed an experimental study of the phase relations in the Ni-S system at temperatures between 400 and 1200°C. A temperature dependent free energy of reaction for

$$2Ni(s) + S_2(g) \Leftrightarrow 2NiS(s) \tag{5.19.18}$$

was calculated from free energies of reaction for

$$3/2Ni(s) + H_2S(g) \Leftrightarrow 1/2Ni_3S_2(s) + H_2(g),$$

$$2Ni_3S_2 + H_2S(g) \Leftrightarrow Ni_6S_5(s) + H_2(g), \text{ and}$$

$$Ni_6S_5(s) + H_2S(g) \Leftrightarrow 6NiS + H2(g),$$
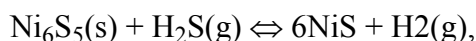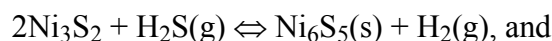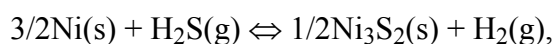
which were calculated from experimentally determined reaction properties at temperatures between 400 and 560°C. The Gibbs free energy of reaction for equation (5.19.18) was then extrapolated down to 25°C by using an assumed value for the integrated $\Delta_r C_p$ between 400°C and 25°C, and by using an estimated heat of transformation for the NiS(s) to millerite transformation. Combining this result with the Gibbs free energy of $S_2(g) \Leftrightarrow 2S(s, rhomb)$, ROSENQVIST (1954) finally obtained $\Delta_f G_m°$(NiS, s, 298.15 K) = -20.6 kcal · mol^{-1} and $\Delta_f H_m°$(NiS, s, 298.15 K) = -20.2 kcal · mol^{-1} (without explaining how he derived the latter).

These data, relying on estimates and a very long extrapolation from high temperature experiments cannot be recommended.

Ni$_3$S$_4$(s): Data for Ni$_3$S$_4$(s) were taken from the compilation by MILLS (1974) who chose $\Delta_f H_m°$(Ni$_3$S$_4$, s, 298.15 K) = - (26.0 ± 2.0) kcal · mol^{-1} as a value lying between one which was determined from electrochemical measurements on Ni$_3$S$_4$(am) and one which was derived from high temperature dissociation pressure experiments. $\Delta_f G_m°$(Ni$_3$S$_4$, s, 298.15 K) = -74.7 kcal · mol^{-1} was calculated by BAEYENS & MCKINLEY (1989) from $\Delta_f H_m°$(Ni$_3$S$_4$, s, 298.15 K) and $\Delta_f S_m°$(Ni$_3$S$_4$, s, 298.15 K) (see Table 5.19.10). The latter was calculated by using a value for $S_m°$(Ni$_3$S$_4$, s, 298.15 K) which was estimated by MILLS (1974).

These data, based on high temperature experiments and estimated data, cannot be recommended.

NiS$_2$(s): Data for NiS$_2$(s) were compiled by MILLS (1974) who chose $\Delta_f H_m°$(NiS$_2$, s, 298.15 K) = -(32.0 ± 2.0) kcal·mol^{-1} as an approximate mean of several values calculated from high temperature dissociation pressure data. $\Delta_f G_m°$(NiS$_2$, s, 298.15 K) = -30.2 kcal·mol^{-1} was calculated by BAEYENS & MCKINLEY (1989) from $\Delta_f H_m°$(NiS$_2$, s, 298.15 K) and $\Delta_f S_m°$(NiS$_2$, s, 298.15 K) (see Table 5.19.10). The latter was calculated by using a value for $S_m°$(NiS$_2$, s, 298.15 K) selected by MILLS (1974) which was also determined from high temperature dissociation pressure data.

These data, determined from high temperature experiments, cannot be recommended.

In summary, none of the data for Ni$_3$S$_2$(s), NiS(s), Ni$_3$S$_4$(s), and Ni$_3$S$_4$(s) listed in NTB 91-18 are included in the database update.

Table 5.19.9:   Thermodynamic data for nickel sulfide solids at 298.15 K and 1 bar as listed in NTB 91-18 compared with their source values. See text for discussion of discrepancies. None of these data were selected for the database update.

	NTB 91-18		BAEYENS & MCKINLEY (1989)	
	$\Delta_f G_m°$ (kJ·mol^{-1})	$\Delta_f H_m°$ (kJ·mol^{-1})	$\Delta_f G_m°$ (kJ·mol^{-1})	$\Delta_f H_m°$ (kJ·mol^{-1})
Ni$_3$S$_2$(s)	-310.333	-229.100	-197.1	-202.9
NiS(s)	-85.993	-70.460	-86.2	-84.9
Ni$_3$S$_4$(s)	-671.822	-325.200	-312.5	-326.4
NiS$_2$(s)	-248.586	-130.900	-126.2	-134

5.19.8.2   New Data

Conditional stability constants of Ni-bisulfide complexes have been experimentally determined by ZHANG & MILLERO (1994), LUTHER et al. (1996), and AL-FARAWATI & VAN DEN BERG (1999) in seawater and diluted seawater at pH = 8 (see below for a short description of the experiments). We used the conditional stability constants of all three experimental sets for the determination of the stability constant for

$$Ni^{2+} + HS^- \Leftrightarrow NiHS^+ \qquad (5.19.19)$$

by extrapolating the data to $I = 0$ using SIT. Note that AL-FARAWATI & VAN DEN BERG (1999) corrected their logarithmic conditional stability constants by adding a term accounting for the side reaction of Ni with the major anions of seawater. However, they reported only the values of the side-reaction coefficients (different for each salinity), without specifying which additional Ni-complexes they considered. We also added such corrections to the data by ZHANG & MILLERO (1994) and LUTHER et al. (1996).

Table 5.19.10: Thermodynamic data at 298.15 K and 1 bar compiled by MILLS (1974) as used by BAEYENS & MCKINLEY (1989). Note that there is an unexplained discrepancy between the value of $\Delta_f G_m°$(Pd$_4$S, s, 298.15 K) calculated from the data by MILLS (1974) and the value given by BAEYENS & MCKINLEY (1989). None of these data were selected for the database update.

	MILLS (1974)		calculated from the two columns at left		BAEYENS & MCKINLEY (1989)
	$\Delta_f H_m°$ (kcal·mol^{-1})	$S_m°$ (cal·K^{-1}·mol^{-1})	$\Delta_f S_m°$ (cal·K^{-1}·mol^{-1})	$\Delta_f G_m°$ (kcal·mol^{-1})	$\Delta_f G_m°$ (kcal·mol^{-1})
S(s,rhomb)	-	7.62	-	-	-
Pd(s)	-	9.06	-	-	-
Ni(s)	-	7.14	-	-	-
Ni$_3$S$_4$(s)	-78	40.95	-10.95	-74.7	-74.7
NiS$_2$(s)	-32	16.2	-6.18	-30.2	-30.2
Pd$_4$S(s)	-16.5	43.18	3.64	-17.6	-16.3
PdS(s)	-16.9	13.5	-3.18	-16.0	-15.9
PdS$_2$(s)	-18.7	21	-3.3	-17.7	-17.7

As the dilution of seawater does not change the relative amounts of dissolved salts, the concentration of one component (e.g. the molality of Cl$^-$) is sufficient to characterize the total composition of the diluted seawater and the SIT regression can be performed in terms of the molality of Cl$^-$ (see Section 5.19.11 for details). A weighted linear regression to the data corrected for side-reactions (see Table 5.19.11 for the data and Fig. 5.19.4 for the regression) results in our recommended value

$$\log_{10}\beta_1°(5.19.19, 298.15 \text{ K}) = (5.5 \pm 0.2)$$

with

$$\Delta\varepsilon(5.19.19, \text{seawater}) = -(1.2 \pm 0.4) \text{ kg·mol}^{-1}$$

A discussion of this $\Delta\varepsilon$ is given in the Appendix.

Only AL-FARAWATI & VAN DEN BERG (1999) provided conditional stability constants (corrected for side-reactions) for the reaction

$$Ni^{2+} + 2HS^- \Leftrightarrow Ni(HS)_2(aq) \tag{5.19.20}$$

A weighted linear regression to these data (see Table 5.19.12 for the data and Fig. 5.19.4 for the regression) results in our recommended value

$$\log_{10}\beta_2°(5.19.20, 298.15\ K) = (11.1 \pm 0.1)$$

with

$$\Delta\varepsilon(5.19.20, \text{seawater}) = -(1.3 \pm 0.3)\ \text{kg}\cdot\text{mol}^{-1}$$

A discussion of this $\Delta\varepsilon$ is given in the Appendix.

Table 5.19.11: Values for conditional stability constants of $NiHS^+$ used for extrapolation of the stability constants to $I = 0$ (see Fig. 5.19.4). $\log_{10}\beta_1'$ refers to the stability constant without consideration of side-reactions and $\log_{10}\alpha_{Ni}$ to the side-reaction coefficient. Original data in boldface type. See Appendix for the calculation of the ionic strength and the molality of Cl^- from the salinity, and for the conversion of the stability constants from molar to molal units. [1994ZHA/MIL]: ZHANG & MILLERO (1994), [1996LUT/RIC]: LUTHER et al. (1996), [1999AL-/VAN]: AL-FARAWATI & VAN DEN BERG (1999).

Source	Salinity	Cl^-	I	$\log_{10}\beta_1'$	$\log_{10}\alpha_{Ni}$	$\log_{10}\beta_1$	$\log_{10}\beta_1$
	[‰]	molal units	molal units	molar units	molar units	molar units	molal units
[1994ZHA/MIL]	35	0.563	0.72	**5.30 ± 0.10**	0.33	5.63 ± 0.10	5.62 ± 0.10
[1996LUT/RIC]	3.5	0.055	0.07	**4.94 ± 0.22**	0.30	5.24 ± 0.22	5.23 ± 0.22
[1996LUT/RIC]	17.5	0.276	0.35	**4.73 ± 0.23**	0.31	5.04 ± 0.23	5.03 ± 0.23
[1996LUT/RIC]	35	0.563	0.72	**4.97 ± 0.24**	0.33	5.30 ± 0.24	5.29 ± 0.24
[1999AL-/VAN]	**10.5**	0.165	0.21	**5.12 ± 0.90**	**0.30**	**5.42 ± 0.90**	5.42 ± 0.90
[1999AL-/VAN]	**21**	0.333	0.43	**4.83 ± 0.14**	**0.31**	**5.14 ± 0.14**	5.14 ± 0.14
[1999AL-/VAN]	**35**	0.563	0.72	**4.89 ± 0.39**	**0.33**	**5.22 ± 0.39**	5.21 ± 0.39
[1999AL-/VAN]	**35**	0.563	0.72	**4.69 ± 0.13**	**0.33**	**5.02 ± 0.13**	5.01 ± 0.13

Table 5.19.12: Values for conditional stability constants of Ni(HS)$_2$(aq) used for extrapolation of the stability constants to $I = 0$ (see Fig. 5.19.4). $\log_{10}\beta_2'$ refers to the stability constant without consideration of side-reactions and $\log_{10}\alpha_{Ni}$ to the side-reaction coefficient. Original data in boldface type. See Appendix for the calculation of the ionic strength and the molality of Cl$^-$ from the salinity, and for the conversion of the stability constants from molar to molal units. [1999AL-/VAN]: AL-FARAWATI & VAN DEN BERG (1999).

Source	Salinity	Cl$^-$	I	$\log_{10}\beta_2'$	$\log_{10}\alpha_{Ni}$	$\log_{10}\beta_2$	$\log_{10}\beta_2$
	[‰]	molal units	molal units	molar units	molar units	molar units	molal units
[1999AL-/VAN]	**10.5**	0.165	0.21	**10.41 ± 0.14**	**0.30**	**10.71 ± 0.14**	10.71 ± 0.14
[1999AL-/VAN]	**21**	0.333	0.43	**10.19 ± 0.07**	**0.31**	**10.50 ± 0.07**	10.49 ± 0.07
[1999AL-/VAN]	**35**	0.563	0.72	**10.25 ± 0.07**	**0.33**	**10.58 ± 0.07**	10.57 ± 0.07
[1999AL-/VAN]	**35**	0.563	0.72	**10.66 ± 0.14**	**0.33**	**10.99 ± 0.14**	10.98 ± 0.14
[1999AL-/VAN]	**35**	0.563	0.72	**10.46 ± 0.04**	**0.33**	**10.79 ± 0.04**	10.78 ± 0.04

5.19.8.3   Discussion of Selected References

ZHANG & MILLERO (1994) used voltammetric methods to determine conditional stability constants of metal bisulfide complexes for Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu$^+$, Cu^{2+}, Zn^{2+}, Ag$^+$, Cd^{2+}, Hg^{2+}, and Pb^{2+} in seawater at a pH of 8 (we assume that this seawater corresponds to a salinity of 35‰). For this purpose, seawater with an added metal (at concentrations between 0.5 and 1.5 μM) was titrated with sulfide (in concentrations from 0.25 to 0.5 μM that were low enough to prevent precipitation of sulfide minerals) and the concentration of free sulfide was measured with cathodic stripping square wave voltammetry. The decrease in free sulfide was attributed to the formation of metal bisulfide complexes and it was assumed that 1:1 and 1:2 complexes with HS$^-$ were formed. Values of the stability constants were then determined by regression of the titration data. In the case of Ni^{2+}, titration results could be fitted by assuming that only the 1:1 complex, NiHS$^+$, had formed. We assume that the reported conditional stability constants refer to molar units.

LUTHER et al. (1996) determined the stability constants of sulfide complexes of Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} in seawater and diluted seawater (ionic strengths of 0.7, 0.35, and 0.07 M) with sulfide concentrations between 1 to 10 μM. They titrated the solutions with metal (in concentrations between 1 to 10 μM) and monitored the concentration of free sulfide by square wave voltammetry. Acid-base titrations were used to determine the proton stoichiometry of the

complexes in order to distinguish between the ligands S^{2-} and HS^-. In the case of Ni^{2+}, titrations could be fitted by assuming that $NiHS^+$, $Ni_2(HS)^{3+}$, and $Ni_3(HS)^{5+}$ had formed. Note that the authors did not discuss the plausibility of such peculiar Ni-clusters with bisulfide centers. We assume that the reported conditional stability constants refer to molar units.

AL-FARAWATI & VAN DEN BERG (1999) determined the conditional stability constants in seawater of pH 8 at various salinities by flow-analysis with detection by cathodic stripping voltammetry (FA-CSV). Two methods were employed. The first method consists in titration of the sulfide by adding metals (Ag^+, Cd^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, and Al^{3+}) and detection of the remaining free sulfide by FA-CSV.

The second method was used for the detection of the bisulfide complexes of Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+}. It depends on the ligand competition between sulfide and oxine (8-hydroxyquinoline) for free metal ions. Metal oxine complexes are electroactive and are therefore detected by FA-CSV. After addition of sulfide, the signal of the metal oxine complex decreases as a result of the complexation of the metal by sulfide.

In the experiments with Ni, metal concentrations of 100 or 150 nM were used, and the maximum amount of added sulfide was about 10 µM. Curve fitting of the titration data resulted in conditional stability constants for $NiHS^+$ and $Ni(HS)_2(aq)$ at salinities of 10.5, 21, and 35 ‰. AL-FARAWATI & VAN DEN BERG (1999) corrected the conditional stability constants with a side-reaction coefficient to account for complexation of Ni with the major anions of seawater. However, they gave only the values of the side-reaction coefficients (different for each salinity), without specifying which additional Ni-complexes they considered. We assume that the reported conditional stability constants refer to molar units.
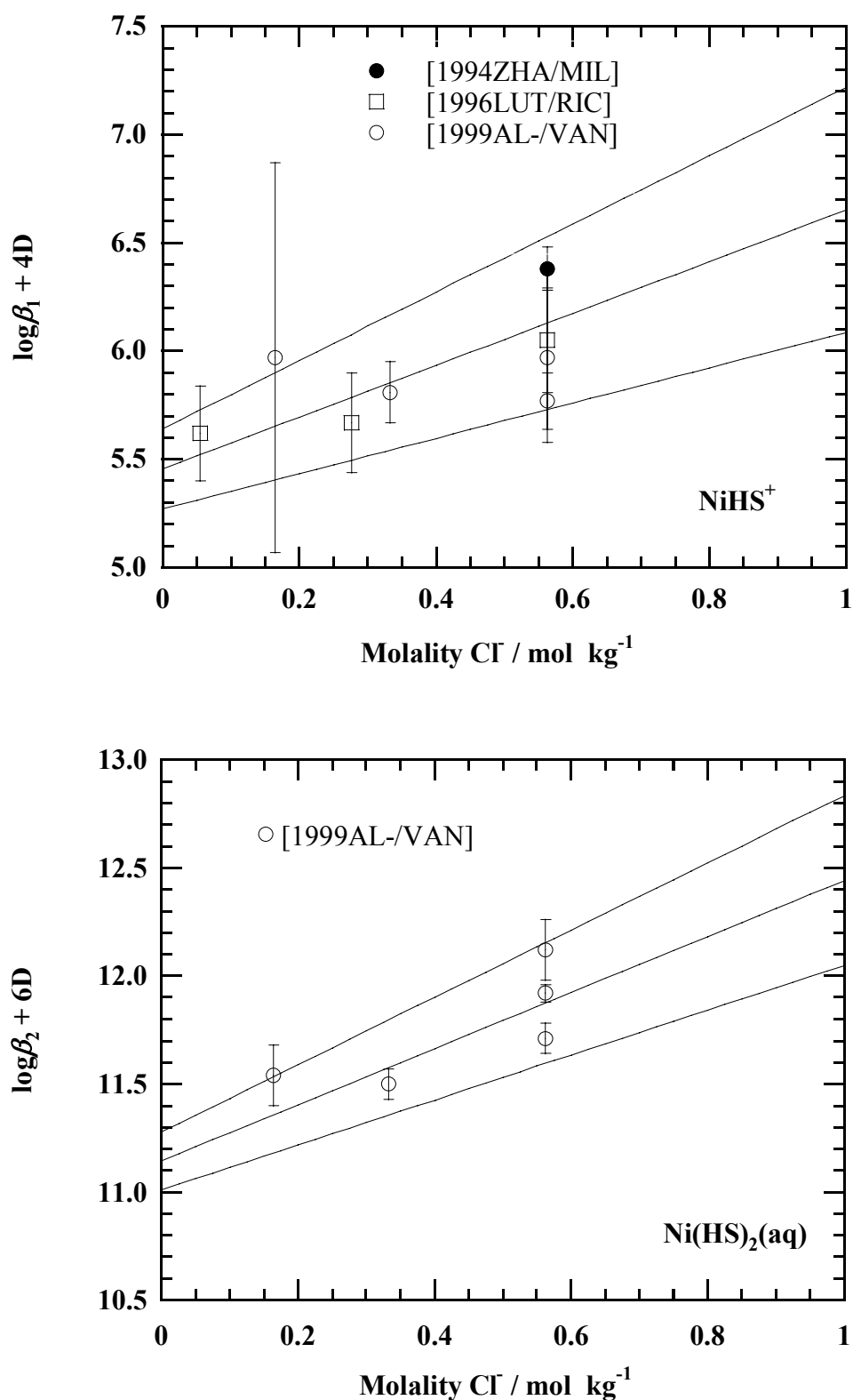
Fig. 5.19.4: Weighted linear regressions for the extrapolation to $I = 0$ of conditional stability constants determined in seawater for $NiHS^+$ (above) and $Ni(HS)_2(aq)$ (below). Experimental data by ZHANG & MILLERO (1994) [1994ZHA/MIL], LUTHER et al. (1996) [1996LUT/RIC], and AL-FARAWATI & VAN DEN BERG (1999) [1999AL-/VAN].

5.19.9 Palladium

Vysotskite, PdS(cr) is the only pure Pd-sulfide mineral. PdS_2(s) and Pd_4S(s) have been synthesized at high temperatures. Only a few low temperature solubility studies of PdS(s) have been performed, they are either inconclusive or unreliable (see THOENEN in prep. for a more detailed discussion). None of the data for Pd-sulfide solids in NTB 91-18 could be included in the database update.

Although several palladium bisulfide complexes such as $Pd(HS)^+$, $Pd(HS)_2$(aq), $Pd(HS)_3^-$, and $Pd(HS)_4^{2-}$ have been discussed in the literature, there is a lack of trustworthy low temperature data (see THOENEN in prep. for a discussion) and none can be recommended.

5.19.9.1 Data in NTB 91-18

NTB 91-18 contains thermodynamic data for Pd_4S(s), PdS(s), and PdS_2(s). $\Delta_f G_m°$ and $\Delta_f H_m°$ (see Table 5.19.13) were supposedly calculated from $\log_{10} K_{s,0}°$ and $\Delta_r H_m°$ reported by BAEYENS & MCKINLEY (1989) for the following reactions:
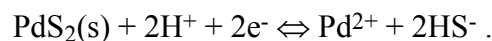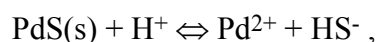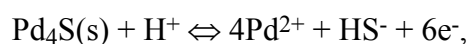
$$Pd_4S(s) + H^+ \Leftrightarrow 4Pd^{2+} + HS^- + 6e^-,$$

$$PdS(s) + H^+ \Leftrightarrow Pd^{2+} + HS^-,$$

$$PdS_2(s) + 2H^+ + 2e^- \Leftrightarrow Pd^{2+} + 2HS^-.$$

BAEYENS & MCKINLEY (1989) derived these $\log_{10} K_{s,0}°$ and $\Delta_r H_m°$ values from the corresponding values for $\Delta_f G_m°$ and $\Delta_f H_m°$ (see Table 5.19.13). The comparison of these data with those listed in NTB 91-18 reveals large differences which cannot be simply attributed to rounding errors but rather point to serious mistakes made during conversion of the values given by BAEYENS & MCKINLEY (1989) into the unreasonable $\Delta_f H_m°$ values listed in NTB 91-18. The $\Delta_f G_m°$ and $\Delta_f H_m°$ data selected by BAEYENS & MCKINLEY (1989) can be traced back to the following references:

Pd_4S(s): Data for Pd_4S(s) were taken from the compilation by MILLS (1974). This author derived $\Delta_f H_m°$(Pd_4S, s, 298.15 K) = - (16.5 ± 0.5) kcal·mol^{-1} from a third law evaluation of published free energy data for the reaction

$$4Pd(s) + H_2S(g) \Leftrightarrow Pd_4S(s) + H_2(g)$$
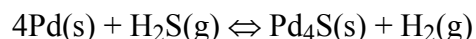
in the temperature range (638-795K) without giving any details of the calculation. MILLS (1974) selected a calorimetrically determined value for $S_m°$(Pd_4S, s, 298.15 K) which was used by BAEYENS & MCKINLEY (1989) to calculate $\Delta_f S_m°$(Pd_4S, s, 298.15 K) and $\Delta_f G_m°$(Pd_4S, s, 298.15 K) (see Table 5.19.10). Note that there is an unexplained discrepancy between the value for

$\Delta_f G_m°$(Pd$_4$S, s, 298.15 K) listed by BAEYENS & MCKINLEY (1989) and the one calculated from the data by MILLS (1974).

These data, based on high temperature experiments, cannot be recommended.

PdS(s): Data for PdS(s) were taken from the compilation by MILLS (1974). This author derived $\Delta_f H_m°$(PdS, s, 298.15 K) = - (16.9 ± 1.5) kcal · mol^{-1} from a third law evaluation of published free energy data for the reaction

$$Pd_4S(s) + 3H_2S(g) \Leftrightarrow 4Pd(s) + 3H_2(g)$$
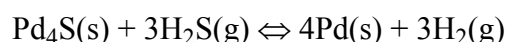
in the temperature range (612-795K) without giving any details of the calculation. MILLS (1974) selected an estimated value for $S_m°$(PdS, s, 298.15 K) which was used by BAEYENS & MCKINLEY (1989) to calculate $\Delta_f S_m°$(PdS, s, 298.15 K) and $\Delta_f G_m°$(PdS, s, 298.15 K) (see Table 5.19.10).

These data, based on high temperature experiments, cannot be recommended.

PdS$_2$(s): Data for PdS$_2$(s) were taken from the compilation by MILLS (1974). This author calculated $\Delta_f H_m°$(PdS$_2$) = - (18.9 ± 3.0) kcal · mol^{-1} from a reaction enthalpy value derived from high temperature dissociation pressure determinations for

$$PdS_2(s) \Leftrightarrow PdS(s) + 0.5S_2(g)$$

as well as value for $S_m°$(PdS$_2$, s, 298.15 K) without giving detailed explanations. These data were used by BAEYENS & MCKINLEY (1989) to calculate $\Delta_f S_m°$(PdS$_2$) and $\Delta_f G_m°$(PdS$_2$) (see Table 5.19.10).

These data, based on high temperature experiments, cannot be recommended.

In summary, none of the data for Pd$_4$S(s), PdS(s), and PdS$_2$(s) listed in NTB 91-18 are included in the database update.

5.19.10   Europium

There is no information on europium sulfide solids and complexes, and they are not expected to exist.

Table 5.19.13: Thermodynamic data for palladium sulfide solids at 298.15 K and 1 bar as listed in NTB 91-18 compared with their source values. See text for discussion of discrepancies. None of these data were considered for the database update.

	NTB 91-18		BAEYENS & McKINLEY (1989)	
	$\Delta_f G_m^\circ$	$\Delta_f H_m^\circ$	$\Delta_f G_m^\circ$	$\Delta_f H_m^\circ$
	$(kJ \cdot mol^{-1})$	$(kJ \cdot mol^{-1})$	$(kJ \cdot mol^{-1})$	$(kJ \cdot mol^{-1})$
$Pd_4S(s)$	-72.139	427.100	-68.2	-69
$PdS(s)$	-76.055	86.500	-66.7	-70.7
$PdS_2(s)$	-194.869	37.400	-74	-78.2

5.19.11 Appendix: SIT in Seawater

Calculation of ionic strength and molality of Cl⁻ from the salinity of seawater

Complexation experiments are often made in seawater diluted with various amounts of pure water. As the dilution of seawater does not change the relative amounts of dissolved salts, one parameter is sufficient to characterize the total composition of the diluted seawater. For the purpose of SIT regressions, it is useful to characterize the composition of seawater with the molality of Cl⁻.

If the composition of seawater is given in terms of the salinity, $S(‰)$, the corresponding chlorinity, $Cl(‰)$, can be calculated according to

$$Cl(‰) = S(‰)/1.8154 \qquad (5.19.21)$$

(see MILLERO 1996 for this equation and for a definition of salinity and chlorinity). From the chlorinity follows the ionic strength

$$I = 0.035989 \, Cl(‰) \qquad (5.19.22)$$

and the molinity (number of moles per kg of seawater) of Cl⁻

$$n_{Cl^-} = 0.028176 \, Cl(‰) \qquad (5.19.23)$$

see MILLERO (1996).

In these equations, $S(‰)$, $Cl(‰)$, I, and n_{Cl^-} all refer to 1 kg of seawater. Thus, the ionic strength given by equation (5.19.22) and the concentration of Cl⁻ given by equation (5.19.23) have to be converted from molinity to molality which is done by dividing the molinity by the weight fraction of pure H_2O in seawater, W_{H_2O},

$$\text{molality} = \frac{\text{molinity}}{W_{H_2O}} \qquad (5.19.24)$$

where

$$W_{H_2O} = 1\text{-}S(‰)/1000 \qquad (5.19.25)$$

Conversion of conditional stability constants from molarity to molality for seawater

Conditional stability constants are usually given in molar units. The conversion to molal units is done as follows: Noting that the molarity is calculated from the molinity by multiplying with the density of seawater, ρ,

Table 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 5.18.12 were performed. Seawater is abbreviated by sw.

$S(‰)$ $\left[\dfrac{g}{kg\,sw}\right]$	$Cl(‰)$ $\left[\dfrac{g}{kg\,sw}\right]$	$[Cl^-]$ $\left[\dfrac{mol}{kg\,sw}\right]$	I $\left[\dfrac{mol}{kg\,sw}\right]$	W_{H_2O} $\left[\dfrac{kg}{kg\,sw}\right]$	$\rho(25°C, 1\ bar)$ $\left[\dfrac{kg}{l}\right]$	$\log_{10}f$
3.5	1.928	0.054	0.07	0.9965	1.000	0.0016
10.5	5.784	0.333	0.21	0.9895	1.005	0.0024
17.5	9.640	0.163	0.35	0.9825	1.010	0.0033
21	11.57	0.326	0.42	0.9790	1.013	0.0037
35	19.28	0.543	0.69	0.9650	1.023	0.0054

$$\text{molarity} = \text{molinity} \cdot \rho \qquad (5.19.26)$$

and combining this with equation (5.19.24), one obtains

$$\text{molality} = f\ \text{molarity} \qquad (5.19.27)$$

with

$$f = \frac{1}{\rho W_{H_2O}} \qquad (5.19.28)$$

The density of seawater as a function of salinity, temperature, and pressure can be calculated from the international equation of state for seawater (MILLERO et al. 1980 and MILLERO & POISSON 1981), see also http://isitv.univ-tln.fr/~lecalve/oceano/ies80/index.html for a nice online calculator (by courtesy of Olivier Le Calvé).

With equations (5.19.27) and (5.19.28) and data from Table 5.19.14, the molar conditional stability constants for the nickel bisulfide complexes listed in Tables 5.19.11 and 5.19.12 can be converted into molal constants according to

$$\log_{10}\beta_1(5.19.19, \text{molal units}) = \log_{10}\beta_1(5.19.19, \text{molar units}) - \log_{10}f \qquad (5.19.29)$$

and

$$\log_{10}\beta_2(5.19.20, \text{molal units}) = \log_{10}\beta_2(5.19.20, \text{molar units}) - 2\log_{10}f \qquad (5.19.30)$$

Table 5.19.14 lists values for $Cl(‰)$, I, n_{Cl^-}, W_{H_2O}, $\rho(25°C, 1\text{ bar})$, and $\log_{10}f$ calculated from the above equations for the salinities at which the nickel bisulfide complexation experiments reported in Tables 5.19.11 and 5.19.12 were performed.

Determination of SIT interaction coefficients for seawater

The composition of seawater is dominated by Na^+, Mg^{2+}, Cl^-, and SO_4^{2-}. Therefore, activity coefficients for Ni^{2+}, $NiHS^+$, $Ni(HS)_2(aq)$, and HS^- can be expressed according to SIT as

$$\log_{10}\gamma_{Ni^{2+}} = -4D + \varepsilon(Ni^{2+},Cl^-)m_{Cl^-} + \varepsilon(Ni^{2+},SO_4^{2-})m_{SO_4^{2-}} \qquad (5.19.31)$$

$$\log_{10}\gamma_{NiHS^+} = -D + \varepsilon(NiHS^+,Cl^-)m_{Cl^-} + \varepsilon(NiHS^+,SO_4^{2-})m_{SO_4^{2-}} \qquad (5.19.32)$$

$$\log_{10}\gamma_{Ni(HS)_2(aq)} = \varepsilon(Ni(HS)_2(aq),Na^+)m_{Na^+} + \varepsilon(Ni(HS)_2(aq),Mg^{2+})m_{Mg^{2+}}$$
$$+ \varepsilon(Ni(HS)_2(aq),Cl^-)m_{Cl^-} + \varepsilon(Ni(HS)_2(aq),SO_4^{2-})m_{SO_4^{2-}} \qquad (5.19.33)$$

$$\log_{10}\gamma_{HS^-} = -D + \varepsilon(HS^-,Na^+)m_{Na^+} + \varepsilon(HS^-,Mg^{2+})m_{Mg^{2+}} \qquad (5.19.34)$$

The following ratios hold for seawater (see Table 2.5 in MILLERO 1996)

$$a \equiv \frac{m_{SO_4^{2-}}}{m_{Cl^-}} = 0.05173 \qquad (5.19.35)$$

$$b \equiv \frac{m_{Na^+}}{m_{Cl^-}} = 0.85929 \qquad (5.19.36)$$

$$c \equiv \frac{m_{Mg^{2+}}}{m_{Cl^-}} = 0.09676 \tag{5.19.37}$$

With equations (5.19.31), (5.19.32), (5.19.34), and (5.19.35)-(5.19.37), the equilibrium relation for

$$Ni^{2+} + HS^- \Leftrightarrow NiHS^+ \tag{5.19.19}$$

can be written as

$$\log_{10} \beta_1(5.19.19) + 4D = \log_{10} \beta_1°(5.19.19) - \Delta\varepsilon(5.19.19)m_{Cl^-} \tag{5.19.38}$$

where

$$\begin{aligned}
\Delta\varepsilon(5.19.19) = &+\varepsilon(NiHS^+,Cl^-) + \varepsilon(NiHS^+,SO_4^{2-})a \\
&-\varepsilon(Ni^{2+},Cl^-) - \varepsilon(Ni^{2+},SO_4^{2-})a \\
&-\varepsilon(HS^-,Na^+)b - \varepsilon(HS^-,Mg^{2+})c
\end{aligned} \tag{5.19.39}$$

In a similar manner, the equilibrium relation for

$$Ni^{2+} + 2HS^- \Leftrightarrow Ni(HS)_2(aq) \tag{5.19.20}$$

can be written as

$$\log_{10} \beta_2(5.19.20) + 6D = \log_{10} \beta_2°(5.19.20) - \Delta\varepsilon(5.19.20)m_{Cl^-} \tag{5.19.40}$$

where

$$\begin{aligned}
\Delta\varepsilon(5.19.20) = &+\varepsilon(Ni(HS)_2(aq),Na^+)b + \varepsilon(Ni(HS)_2(aq),Mg^{2+})c \\
&+\varepsilon(Ni(HS)_2(aq),Cl^-) + \varepsilon(Ni(HS)_2(aq),SO_4^{2-})a \\
&-\varepsilon(Ni^{2+},Cl^-) - \varepsilon(Ni^{2+},SO_4^{2-})a \\
&-2\varepsilon(HS^-,Na^+)b - 2\varepsilon(HS^-,Mg^{2+})c
\end{aligned} \tag{5.19.41}$$

Table 5.19.15: Selected thermodynamic data for sulfide solids and species at 298.15 K and 1 bar.

TDB Version 05/92   **TDB Version 01/01**

Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$S_m°$	Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$S_m°$	Species
HS-	12.240	-16.300	67	HS-	12.243 ± 2.115	-16.3 ± 1.5	67 ± 5	HS-

Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Reaction
-	-	-	HS-	33.69 ± 0.38	-250.28 ± 1.56	$SO_4^{2-} + 9H^+ + 8e^- \Leftrightarrow HS^- + 4H_2O(l)$
SO4-2/HS-:PE	4.212	-31.285	-	-	-	$0.125SO_4^{2-} + 1.125H^+ + e^- \Leftrightarrow$ $0.125HS^- + 0.5H_2O(l)$
-	-	-	H2S(g)	8.01 ± 0.17	-4.3 ± 2.6	$HS^- + H^+ \Leftrightarrow H_2S(g)$
H2S(AQ)	6.980	-22.300	H2S(aq)	6.99 ± 0.17	-22.3 ± 2.1	$HS^- + H^+ \Leftrightarrow H_2S(aq)$
-	-	-	S-2	-19 ± 2	-	$HS^- \Leftrightarrow S^{2-} + H^+$
-	-	-	Ni(HS)+	5.5 ± 0.2	-	$Ni^{2+} + HS^- \Leftrightarrow Ni(HS)^+$
-	-	-	Ni(HS)2(aq)	11.1 ± 0.1	-	$Ni^{2+} + 2HS^- \Leftrightarrow Ni(HS)_2(aq)$
Reaction						
NIS	-9.221	-	-	-	-	$NiS(s) + H^+ \Leftrightarrow Ni^{2+} + HS^-$
NIS2	-39.851	-	-	-	-	$NiS_2(s) + 2H^+ + 2e^- \Leftrightarrow Ni^{2+} + 2HS^-$
NI3S2	-34.691	-	-	-	-	$Ni_3S_2(s) + 2H^+ \Leftrightarrow 3Ni^{2+} + 2HS^- + 2e^-$
NI3S4	-102.311	-	-	-	-	$Ni_3S_4(s) + 4H^+ + 2e^- \Leftrightarrow 3Ni^{2+} + 4HS^-$
PDSS	-46.391	-	-	-	-	$PdS(s) + H^+ \Leftrightarrow Pd^{2+} + HS^-$
PDS2	-69.351	-	-	-	-	$PdS_2(s) + 2H^+ + 2e^- \Leftrightarrow Pd^{2+} + 2HS^-$
PD4S	-138.471	-	-	-	-	$Pd_4S(s) + H^+ \Leftrightarrow 4Pd^{2+} + HS^- + 6e^-$
SNS	-48.120	-	-	-	-	$SnS(s) + 4H_2O(l) \Leftrightarrow$ $Sn^{2+} + SO_4^{2-} + 8H^+ + 8e^-$
-	-	-	SnS(pr)	-14.7 ± 0.5	-	$SnS(pr) + H^+ \Leftrightarrow Sn^{2+} + HS^-$

Table 5.19.15: continued

TDB Version 05/92			TDB Version 01/01			
Name	$\log_{10}\beta°$	$\Delta_r H_m°$	**Name**	$\log_{10}\beta°$	$\Delta_r H_m°$	**Reaction**
SN2S3	-141.930	-	-	-	-	Sn_2S_3 (s) + 12H_2O(l) $\Leftrightarrow$ 2Sn^{2+} + 3SO_4^{2-} + 24H^+ + 22e^-
SN3S4	-191.300	-	-	-	-	Sn_3S_4(s) + 16H_2O(l) $\Leftrightarrow$ 3Sn^{2+} + 4SO_4^{2-} + 32H^+ + 30e^-
TCS2	-133.290	-	-	-	-	TcS_2(s) + 9H_2O(l) $\Leftrightarrow$ TcO^{2+} + 2SO_4^{2-} + 18H^+ + 16e^-
TCS3	61.900	-	-	-	-	TcS_3(s) + 13H_2O(l) $\Leftrightarrow$ TcO^{2+} + 3SO_4^{2-} + 26H^+ + 22e^-
TC2S7	60.780	-	-	-	-	Tc_2S_7(s) + 30H_2O(l) $\Leftrightarrow$ 2TcO^{2+} + 7SO_4^{2-} + 60H^+ + 50e^-
S0/HS-:PE	-1.072	-8.150	-	-	-	0.5S(rhomb) + 0.5H^+ + e^- $\Leftrightarrow$ 0.5HS^-
-	-	-	S(rhomb)	-2.144 ± 0.370	-16.3 ± 1.5	S(rhomb) + H^+ + 2e^- $\Leftrightarrow$ HS^-

5.19.12 References

AL-FARAWATI, R. & VAN DEN BERG, C.M.G. (1999): Metal-sulfide complexation in seawater. Marine Chemistry, 63, 331-352.

ALMGREN, T., DYRSSEN, D., ELGQUIST, B. & JOHANSSON, O. (1976): Dissociation of hydrogen sulphide in seawater and comparison of pH scales. Marine Chemistry, 4, 289-297.

BAEYENS, B. & MCKINLEY, I.G. (1989): A PHREEQE Database for Pd, Ni and Se. Nagra Technical Report NTB 88-28, Nagra, Wettingen, Switzerland, 59 pp.

BARRET, T.J., ANDERSON, G.M. & LUGOWSKI, J. (1988): The solubility of hydrogen sulphide in 0-5 m NaCl solutions at 25˚-95˚C and one atmosphere. Geochimica et Cosmochimica Acta, 52, 807-811.

CLEVELAND, J.M. (1970): The Chemistry of Plutonium. Gordon and Breach, New York. 653 pp.

CROSS, J.E. & EWART, F.T. (1991): HATCHES - A thermodynamic database and management system. Radiochimica Acta, 52/53, 421-422.

GAMSJÄGER, H. & SCHINDLER, P. (1969): Löslichkeiten und Aktivitätskoeffizienten von H_2S in Elektrolytmischungen. Helvetica Chimica Acta, 52, 1395-1402.

GRENTHE, I., FUGER, J., KONINGS, R.J.M., LEMIRE, R.J., MULLER, A.B., NGUYEN-TRUNG, C. & WANNER, H. (1992): Chemical Thermodynamics of Uranium. Chemical Thermodynamics, Vol. 1. North-Holland, Amsterdam. 715 pp.

GRENTHE, I., PLYASUNOV, A.V. & SPAHIU, K. (1997): Estimation of medium effects on thermodynamic data. In: GRENTHE, I. & PUIGDOMENECH, I. (eds.): Modelling in Aquatic Chemistry. NEA/OECD, 325-426.

GRØNVOLD, F., DROWART, J. & WESTRUM, E.F., JR. (1984): The Chemical Thermodynamics of Actinide Elements and Compounds, Part 4: The Actinide Chalcogenides (excluding Oxides). International Atomic Energy Agency, Vienna. 265 pp.

HERSHEY, J.P., PLESE, T. & MILLERO, F.J. (1988): The pK_1* for the dissociation of H_2S in various ionic media. Geochimica et Cosmochimica Acta, 52, 2047-2051.

LEMIRE, R.J., FUGER, J., NITSCHE, H., POTTER, P., RAND, M.H., RYDBERG, J., SPAHIU, K., SULLIVAN, J.C., ULLMAN, W.J., VITORGE, P. & WANNER, H. (2001): Chemical Thermodynamics of Neptunium & Plutonium. Chemical Thermodynamics, Vol. 4, NEA/OECD, Paris. 845 pp.

LUTHER, G.W., III , RICKARD, D.T., THEBERGE, S. & OLROYD, A. (1996): Determination of metal (bi)sulfide stability constants of Mn^{2+}, Fe^{2+}, Co2+, Ni^{2+}, Cu^{2+}, and Zn^{2+} by voltammetric methods. Environmental Science and Technology, 30, 671-679.

MCDONALD, J.E. & COBBLE, J.W. (1962): The heats of combustion of ReS_2 and Re_2S_7 and the thermodynamic functions for transition metal sulfides. Journal of Physical Chemistry, 66, 791-794.

MILLERO, F.J. (1996): Chemical Oceanography. CRC Press, Boca Raton, Florida. 469 pp.

MILLERO, F.J., CHEN, C.-T., BRADSHAW, A. & SCHLEICHER, K. (1980): A new high pressure equation of state for seawater. Deep-Sea Research, 27, 255-264.

MILLERO, F.J. & POISSON, A. (1981): International one-atmosphere equation of state of seawater. Deep-Sea Research, 28, 625-629.

MILLS, K.C. (1974): Thermodynamic data for inorganic sulphides, selenides and tellurides. Butterworths, London. 845 pp.

PEARSON, F.J., JR. & BERNER, U. (1991): Nagra Thermochemical Data Base I. Core Data. Nagra Technical Report NTB 91-17, Nagra, Wettingen, Switzerland, 70 pp.

PEARSON, F.J., JR., BERNER, U. & HUMMEL, W. (1992): Nagra Thermochemical Data Base II. Supplemental Data 05/92. Nagra Technical Report NTB 91-18, Nagra, Wettingen, Switzerland, 284 pp.

PEIFFERT, S. & FREVERT, T. (1987): Potentiometric determination of heavy metal sulphide solubilities using a pH_2S (glass|Ag°, Ag_2S) electrode cell. Analyst, 112, 951-954.

RARD, J.A., RAND, M.H., ANDEREGG, G. & WANNER, H. (1999): Chemical Thermodynamics of Technetium. Chemical Thermodynamics, Vol. 3, Elsevier, Amsterdam. 544 pp.

ROBIE, R.A., HEMINGWAY, B.S. & FISHER, J.R. (1978): Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pascals) pressure and at higher temperatures. United States Geological Survey Bulletin, 1452,

ROSENQVIST, T. (1954): A thermodynamic study of the iron, cobalt, and nickel sulphides. Journal of the Iron and Steel Institute, 176, 37-57.

SILVA, R.J., BIDOGLIO, G., RAND, M.H., ROBOUCH, P.B., WANNER, H. & PUIGDOMENECH, I. (1995): Chemical Thermodynamics of Americium. Chemical Thermodynamics, Vol. 2, North-Holland, Amsterdam. 374 pp.

THOENEN, T. (1999): Pitfalls in the use of solubility limits for radioactive waste disposal: The case of nickel in sulfidic environments. Nuclear Technology, 126, 75-87.

THOENEN, T. (in prep.): Chemical Thermodynamics of Sulfide in Aqueous Systems. PSI Report, Paul Scherrer Institut, Villigen.

WAGMAN, D.D., EVANS, W.H., PARKER, V.B., SCHUMM, R.H., HALOW, I., BAILEY, S.M., CHURNEY, K.L. & NUTTALL, R.L. (1982): The NBS tables of chemical thermodynamic properties: Selected values for inorganic and C_1 and C_2 organic substances in SI units. Journal of Physical and Chemical Reference Data, 11, Supplement No. 2, 1-392.

ZHANG, J.-Z. & MILLERO, F.J. (1994): Investigation of metal sulfide complexes in sea water using cathodic stripping square wave voltammetry. Analytica Chimica Acta, 284, 497-504.

5.20   Technetium

All information on technetium is taken from OECD NEA's book "Chemical Thermodynamics of Technetium" (RARD et al. 1999). However, not all recommended values of this NEA review are included in our database since NEA reviews are not restricted to data relevant for radioactive waste management or even environmental modelling in general. We tried to exclude from our database phases and complexes which most probably will never be relevant in environmental systems. The notation of formulae and symbols used in this chapter follows the NEA recommendations and practice.

5.20.1   Elemental technetium

The absolute entropy and heat capacity of Tc(cr) are given in Table 5.20.1 to quantify the thermochemical properties of elemental technetium. Technetium liquid and gas are not relevant under environmental conditions. Hence, none of these phases is included in the database.

5.20.2   Simple aqueous technetium ions of each oxidation state

Technetium has an extensive redox chemistry, and the most stable oxidation state in contact with air is pertechnetate(VII), TcO_4^-, in the entire pH range. TcO_4^- can therefore be used as a reference oxidation state. In aqueous solution, and in the absence of complexing anions other than hydroxide, technetium can assume oxidation numbers from +VII to +III.

5.20.2.1 TcO_4^-

Recommended values of thermodynamic properties of TcO_4^- at 298.15 K are

$$\Delta_f G_m^\circ (TcO_4^-, aq, 298.15 \text{ K}) \quad = \quad -(637.4 \pm 7.6) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_f H_m^\circ (TcO_4^-, aq, 298.15 \text{ K}) \quad = \quad -(729.4 \pm 7.6) \text{ kJ} \cdot \text{mol}^{-1}$$

$$S_m^\circ (TcO_4^-, aq, 298.15 \text{ K}) \quad = \quad (199.6 \pm 1.5) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{p,m}^\circ (TcO_4^-, aq, 298.15 \text{ K}) \quad = \quad -(15 \pm 8) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

5.20.2.2 TcO_4^{2-}

Because of the instability of TcO_4^{2-}, it is not meaningful to include a Tc(VII) / Tc(VI) reduction potential or the derived $\log_{10}K°$ value in a thermodynamic database, without including the rate constant for the disproportionation of TcO_4^{2-} at the same time. In practice, Tc(VI) is only of potential relevance in the area of chemical syntheses, and in elucidating the stepwise redox behaviour of technetium. It will never be a stable oxidation state in aqueous equilibrium systems.

5.20.2.3   Tc(V)

Tc(V) is not a stable species as it decomposes further, and its consideration in chemical equilibrium calculations is thus not necessary.

5.20.2.4   Tc(IV)

In contrast to Tc(VI) and Tc(V), Tc(IV) is a stable oxidation state. Tc(IV) is the most important oxidation state of technetium under reducing conditions. From the pH independence of the solubility of $TcO_2 \cdot xH_2O(s)$, it is evident that an uncharged Tc(IV) species dominates in non-complexing solutions in the pH range 3 < pH < 10. Possible chemical formulae of this uncharged Tc(IV) species are $Tc(OH)_4(aq)$, $TcO(OH)_2(aq)$ and $TcO_2(aq)$. It is fairly well established today that a maximum of two protons can be forced upon the uncharged Tc(IV) complex in the pH range of aqueous solutions. This leaves TcO^{2+} (and not the free Tc^{4+}) as an undissociable unit, and it is thus reasonable to follow the current practice and to use $TcO(OH)_2(aq)$ as the reference formula of the uncharged Tc(IV) complex.

The redox potential of the redox pair Tc(VII) / Tc(IV), derived from potentiometric redox measurements in the presence of $TcO_2 \cdot xH_2O(s)$, is given as a half cell involving aqueous species only:

$$TcO_4^- + 4\,H^+ + 3\,e^- \Leftrightarrow TcO(OH)_2(aq) + H_2O(l)$$
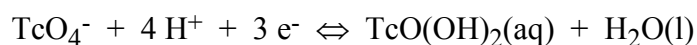
$$E° \,(298.15\ K) \quad = \quad 0.579 \pm 0.016\ V$$

$$\log_{10}K° \,(298.15\ K) \quad = \quad 29.4 \pm 0.8$$

5.20.2.5 Tc^{3+}

There is a total absence of thermodynamic data for the Tc(III) species. A value of $\Delta_f G_m°$ for Tc^{3+} is discussed by RARD et al. (1999) but it is not recommended. Thus, the state-of-the-art concerning Tc(III) is such that no data can be recommended for these systems, neither for any Tc(III) species, nor for any of the redox reactions connected with Tc(III).

5.20.2.6 Tc^{2+}

There is no experimental evidence for the existence of Tc^{2+} as a viable chemical species in aqueous solution.

5.20.3   Oxide and hydrogen compounds and complexes

5.20.3.1   Aqueous species formed by hydrolysis and protonation reactions

5.20.3.1.1   The acid / base chemistry of Tc(IV)

The existence of a species such as TcO^{2+} is not certain. Only a few solubility data are available between pH = 0 and pH = 3 for an estimate of the first two protonation constants of $TcO(OH)_2(aq)$. RARD et al. (1999) therefore preferred to select a limiting value for the equilibrium constant including the species TcO^{2+} and to use $TcO(OH)_2(aq)$ as the main Tc(IV) species.

Solubility measurements for $TcO_2 \cdot xH_2O(s)$ in aqueous 0.05 to 2.6 M NaCl solutions at pH = 6.9 to 9.3 revealed no significant variation of the solubility with chloride concentration. Since $TcO(OH)_2(aq)$ is the predominant aqueous species at low ionic strengths and at $3 < pH < 10$, the observed independence of solubility on chloride concentration implies that this species persists even in concentrated chloride solutions. Thus, chloride and mixed hydroxide-chloride complexes of Tc(IV) probably do not form in significant amounts in solutions with pH > 3.

The solubility of $TcO_2 \cdot xH_2O(s)$ increases at pH > 10. The few reported high pH data suggest a slope of 0.5 rather than 1 in a plot of Tc solubility versus pH (see Figure V.3 in RARD et al. 1999). However, the scarce data are insufficient to propose a more complex mechanism than the formation of $TcO(OH)_3^-$. The reactions are thus written as follows:

$$TcO(OH)_2(aq) \ + \ H^+ \ \Leftrightarrow \ TcO(OH)^+ \ + H_2O(l)$$

$$\log_{10}{}^*K° \ (298.15 \ K) \quad = \quad 2.5 \ \pm \ 0.3$$

$$TcO(OH)_2(aq) \ + \ 2 \ H^+ \ \Leftrightarrow \ TcO^{2+} \ + \ 2 \ H_2O(l)$$

$$\log_{10}{}^*K° \ (298.15 \ K) \quad < \quad 4$$

$$TcO(OH)_2(aq) \ + \ H_2O(l) \ \Leftrightarrow \ TcO(OH)_3^- \ + \ H^+$$
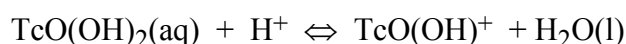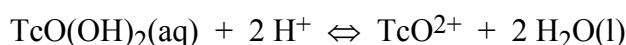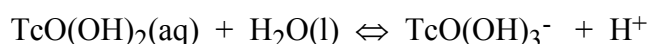
$$\log_{10}{}^*K° \ (298.15 \ K) \quad = \quad -10.9 \ \pm \ 0.4$$

5.20.3.1.2   The acid / base chemistry of other Tc oxidation states

RARD et al. (1999) do not consider any of the reported values for the protonation of TcO_4^- to be reliable. Aqueous solutions of $HTcO_4$ are thus considered to be fully dissociated by RARD et al. (1999).

Protonation constants of TcO_4^{2-} have been estimated based on pulse radiolysis at various pH values and variable ionic strength. However, the species $HTcO_4^-$ and $H_2TcO_4(aq)$ are of no relevance in equilibrium systems due to the instability of Tc(VI) (see 5.20.2.2).

5.20.3.2   Solid technetium oxides and their hydrates

$Tc_2O_7(cr)$: Tc(VII) oxide is hygroscopic and thus of no relevance for environmental systems.

$Tc_2O_7 \cdot xH_2O(s)$: This compound is compatible with the formulation of either $Tc_2O_7 \cdot xH_2O(s)$ or $HTcO_4(s)$. It is a very hygroscopic compound and thus of no relevance for environmental systems.

$TcO_3(s)$: Because the existence of $TcO_3(s)$ has not been established with certainty, RARD et al. (1999) do not recommend any estimated thermodynamic values for it.

$TcO_2(cr)$: There are several studies in which attempts were made to measure solubilities that could be used to calculate $\Delta_f G_m°$ of $TcO_2(cr)$. Some of these studies found the solubility of $TcO_2(cr)$ to be lower than that of $TcO_2 \cdot xH_2O(s)$ whereas others found it to be higher. Generally, amorphous or poorly crystalline hydrous oxides are more soluble than their corresponding anhydrous oxides. In addition, there is no way to be sure whether the surface layer of the $TcO_2(cr)$ remained unhydrated during the solubility experiments, and thus it is possible that the observed solubilities actually refer to a partially hydrated dioxide. Because of these uncertainties, RARD et al. (1999) based their evaluation of the thermodynamic properties of $TcO_2(cr)$ on calorimetric measurements. These data are not included in our database (see discussion below).

$TcO_2 \cdot xH_2O(s)$: There is considerable information about the hydrous oxides of Tc(IV). Since the exact value of x in $TcO_2 \cdot xH_2O(s)$ is of no importance in aqueous chemistry, a notation such as $TcO_2(s,hyd)$ for this compound would be a reasonable simplification. However, in order to visibly indicate in the chemical formula that the solid phase in question is hydrated, RARD et al. (1999) prefer to use the formula $TcO_2 \cdot 1.6H_2O(s)$ as 1.6 seems to be a reasonable average hydration number in spite of possible larger variations. From two reliable solubility studies of $TcO_2 \cdot 1.6H_2O(s)$ a recommended solubility constant has been derived:

$$TcO_2 \cdot 1.6H_2O(s) \Leftrightarrow TcO(OH)_2(aq) + 0.6\,H_2O(l)$$

$$\log_{10}K° \,(298.15\ K) \quad = \quad -8.4 \pm 0.5$$
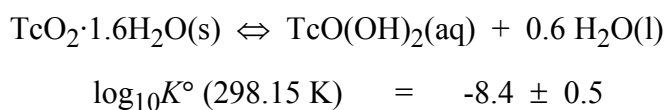
From this solubility constant and the Gibbs energy of formation of the solid, derived from measurements with the TcO_4^- / $TcO_2 \cdot 1.6H_2O(s)$ electrode,

$$\Delta_f G_m^\circ \text{ (TcO}_2 \cdot 1.6\text{H}_2\text{O, s, 298.15 K)} \quad = \quad -(758.5 \pm 8.4) \text{ kJ} \cdot \text{mol}^{-1}$$

RARD et al. (1999) derived the recommended Gibbs energy of formation for the uncharged Tc(IV) hydrolysis species:

$$\Delta_f G_m^\circ \text{ (TcO(OH)}_2\text{, aq, 298.15 K)} \quad = \quad -(568.2 \pm 8.8) \text{ kJ} \cdot \text{mol}^{-1}$$

Because of their large relative uncertainties, values of the assessed thermodynamic properties of $TcO_2(cr)$ and $TcO_2 \cdot 1.6H_2O(s)$ should not be used simultaneously in the thermodynamic calculations. The thermodynamic data for $TcO_2 \cdot 1.6H_2O(s)$ and the aqueous species are thermodynamically consistent, and thus it is the appropriate substance to be considered in aqueous solubility calculations. Hence, we decide to include $TcO_2 \cdot 1.6H_2O(s)$ in our database and to discard $TcO_2(cr)$.

Lower valence hydrous Tc oxides and mixed valence Tc oxides: The preparation of several lower valence and mixed valence hydrous oxides has been claimed, e.g. $Tc_4O_7(s)$, $Tc_3O_4(s)$, "$Tc(OH)_4(s)$", $Tc(OH)_3(s)$, $Tc(OH)_2(s)$, $TcOH(s)$ (CARTLEDGE 1971) and "$Tc_4O_5 \cdot xH_2O(s)$". The existence of these compounds is not proven. Further compounds such as "$Tc_2O_3(s)$" were postulated without characterisation. However, both Tc(III) solutions and the hydrous oxide of Tc(III) are quite unstable and tend to disproportionate at pH above 3 or 4. There are several published thermodynamic databases for technetium and several potential / pH diagrams which include $\Delta_f G_m^\circ$ values calculated from the E° values of CARTLEDGE (1971). These potential / pH diagrams predict that $Tc_3O_4(s)$ can be a solubility limiting phase for the $Tc-O_2-H_2O$ system under certain reducing conditions. However, in view of all of the available evidence, RARD et al. (1999) consider $Tc_3O_4(s)$ to be a questionable compound. It is more likely that $TcO_2 \cdot xH_2O(s)$, and probably Tc(cr) are the actual solubility limiting phases under various reducing conditions.

5.20.3.3   Gaseous technetium oxides

Gaseous technetium oxides are not relevant under environmental conditions. None of these phases is included in the database.

5.20.3.4   Technetium hydrides

Binary and ternary technetium hydrides decompose under normal environmental conditions. No thermodynamic data are available for these compounds.

5.20.4 Halogen compounds and complexes

5.20.4.1 Fluorine compounds and complexes

There are few studies in the literature on technetium complexation with fluoride anions. Only the $Tc(IV)F_6^{2-}$ complex has been identified, but no thermodynamic data are available.

No Gibbs energy of formation for any solid technetium fluoride is available.

5.20.4.2 Chlorine, bromine and iodine compounds and complexes

Whereas TcF_6^{2-} is stable even in water and dilute solutions of alkali hydroxide, $TcCl_6^{2-}$ could only be stabilised in concentrated Cl^- solutions and $TcBr_6^{2-}$ needs concentrated HBr solutions to remain stable. As discussed in 5.20.3.1.1, the formation of chloride and mixed hydroxide-chloride complexes of Tc(IV) in saline solutions with pH > 3 is unlikely. In addition, no equilibrium constant is recommended by RARD et al. (1999) relating $TcCl_6^{2-}$ to $TcO(OH)_2(aq)$ and consequently, no value for the Gibbs energy of formation has been selected. Hence, $TcCl_6^{2-}$ is not included in our database.

Although some compounds with stoichiometry $M_2TcX_6(cr)$ (with M = NH_4, K, Rb, Cs and X = Cl and Br) exhibit low solubility products, these compounds are not included in our database. Because of the instability of $TcCl_6^{2-}$ and $TcBr_6^{2-}$ under environmental conditions, these compounds are not relevant under environmental conditions.

5.20.5 Chalcogen compounds and complexes

5.20.5.1 Technetium sulphides

From measured combustion enthalpies for several rhenium sulphides, thermochemical data for $Tc_2S_7(s)$, $TcS_3(s)$ and $TcS_2(s)$ have been estimated. No direct thermochemical data are available for these technetium sulphides. In addition, there are no reports of the preparation of $TcS_3(s)$. There are no reliable solubilities for $Tc_2S_7(s)$. No thermodynamic data are recommended by RARD et al. (1999).

5.20.5.2 Technetium sulphates

No thermodynamic data are available for technetium sulphates. However, the results of several polarographic studies imply that SO_4^{2-} complexes of Tc(IV) and Tc(III) are weak or non-existent at pH > 4 owing to competition from hydrolysis.

5.20.6   Group 15 compounds and complexes

5.20.6.1   Nitrogen compounds and complexes

There are no experimental studies on the thermodynamic properties of technetium nitrogen compounds. A polarographic study of the reduction of NH_4TcO_4 in HNO_3 solutions provided no evidence for technetium nitrate complexes.

5.20.6.2   Phosphorous compounds and complexes

No thermodynamic data are available for technetium phosphate compounds or complexes. There are some indications on the formation of Tc(III) and Tc(IV) phosphate complexes but no single species has been identified.

5.20.7   Group 14 compounds and complexes

5.20.7.1   Carbon compounds and complexes

5.20.7.1.1   Technetium carbides

RARD et al. (1999) recommend thermodynamic data for TcC(g). However, gaseous monocarbide is not relevant under environmental conditions and is not included in our database.

5.20.7.1.2   Technetium carbonates

A solubility study for $TcO_2 \cdot xH_2O(s)$ as a function of pH in the absence and presence of carbonate revealed an increase of the solubility of $TcO_2 \cdot xH_2O(s)$ in the presence of $CO_2(g)$ at a partial pressure up to 1 bar in the pH range 6.3 to 8.6. These findings have been interpreted in terms of the formation of two hydroxide-carbonate complexes, a neutral and an anionic one:
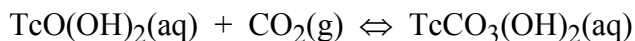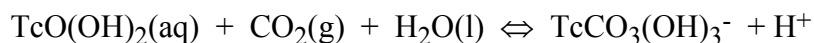
$$TcO(OH)_2(aq) + CO_2(g) \Leftrightarrow TcCO_3(OH)_2(aq)$$
$$\log_{10}K° \text{ (298.15 K)}   =   1.1 \pm 0.3$$
$$TcO(OH)_2(aq) + CO_2(g) + H_2O(l) \Leftrightarrow TcCO_3(OH)_3^- + H^+$$
$$\log_{10}K° \text{ (298.15 K)}   =   -7.2 \pm 0.6$$

Using the carbonate equilibrium constants selected in our review (see Chapter 4, Core Data) relating $CO_2(g)$ with CO_3^{2-} the above values have been converted to
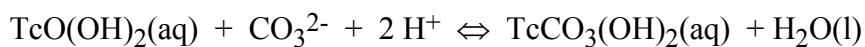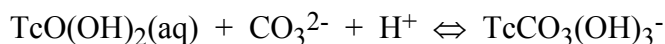
$$TcO(OH)_2(aq) + CO_3^{2-} + 2 H^+ \Leftrightarrow TcCO_3(OH)_2(aq) + H_2O(l)$$
$$\log_{10}{}^*K° \text{ (298.15 K)}   =   19.3 \pm 0.3$$
$$TcO(OH)_2(aq) + CO_3^{2-} + H^+ \Leftrightarrow TcCO_3(OH)_3^-$$
$$\log_{10}{}^*K° \text{ (298.15 K)}   =   11.0 \pm 0.6$$

These values are included in the database due to the relevance for environmental systems.

5.20.7.1.3   Technetium cyanides and oxycyanides

No thermodynamic data are available for these compounds and complexes.

5.20.7.2   Silicon compounds and complexes

There is no published study of the Tc-Si-O phase system. No information about silicon complexes of technetium could be located by RARD et al. (1999).

5.20.8   Pertechnetates and mixed oxides

The pertechnetate anion TcO_4^- has little tendency to form complexes with cations in aqueous solutions. However, a large number of pertechnetate salts has been prepared. The solubilities of these salts in general are very high (see Table V.36 in RARD et al. 1999): The dissolution of $NaTcO_4 \cdot 4H_2O(cr)$ gives 11.3 M pertechnetate solutions, $KTcO_4(cr)$ 0.1 M and $NH_4TcO_4(cr)$ 0.6 M solutions. A few salts with small solubility products are known, i.e. $AgTcO_4(cr)$ and $TlTcO_4(cr)$. However, under groundwater conditions the concentration of Ag or Tl is extremely low and consequently the pertechnetate concentration has to reach molar concentrations to precipitate these solids. None of these pertechnetate salts is relevant under environmental conditions and thus, none of these phases is included in the database.

Table 5.20.1: Selected technetium data. All data included in TDB Version 01/01 are taken from RARD et al. (1999).

TDB Version 05/92

TDB Version 01/01

Name	$\Delta_f G_m°$	$\Delta_f H_m°$	Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$S_m°$	$C_{p,m}°$	Species
TC(C)	-0.792	49.947	Tc(cr)	0.0	0.0	32.5 ± 0.7	24.9 ± 1.0	Tc(cr)
TCO(OH)2	-556.044	0	TcO(OH)2	-568.2 ± 8.8				$TcO(OH)_2$(aq)
TCO4-	-623.659	0	TcO4-	-637.4 ± 7.6	-729.4 ± 7.6	199.6 ± 1.5	-15 ± 8	TcO_4^-

Name	Redox	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Reaction
TC+3	III	8.7	0		-	-	$TcO(OH)_2$(aq) + 4 H$^+$ + e$^-$ $\Leftrightarrow$ Tc^{3+} + 3 H$_2$O(l)
TCO+2	IV	3.3	0	TcO+2	< 4		$TcO(OH)_2$(aq) + 2 H$^+$ $\Leftrightarrow$ TcO^{2+} + 2 H$_2$O(l)
TCO(OH)+	IV	2.2	0	TcO(OH)+	2.5 ± 0.3		$TcO(OH)_2$(aq) + H$^+$ $\Leftrightarrow$ TcO(OH)$^+$ + H$_2$O(l)
	IV	-	-	TcO(OH)3-	-10.9 ± 0.4		$TcO(OH)_2$(aq) + H$_2$O(l) $\Leftrightarrow$ TcO(OH)$_3^-$ + H$^+$
TCOOH22	IV	6.5	0		-	-	2 $TcO(OH)_2$(aq) $\Leftrightarrow$ (TcO(OH)$_2$(aq))$_2$
	IV	-	-	TcCO3(OH)2	19.3 ± 0.3		$TcO(OH)_2$(aq) + CO$_3^{2-}$ + 2H$^+$ $\Leftrightarrow$ TcCO$_3$(OH)$_2$(aq) + H$_2$O(l)
	IV	-	-	TcCO3(OH)3-	11.0 ± 0.6	-	$TcO(OH)_2$(aq) + CO$_3^{2-}$ + H$^+$ $\Leftrightarrow$ TcCO$_3$(OH)$_3^-$
TCO4-3	V	-50.0	0		-	-	$TcO(OH)_2$(aq) + H$_2$O(l) $\Leftrightarrow$ TcO$_4^{3-}$ + 4 H$^+$ + e$^-$
TCO4-2	VI	-40.0	0		-	-	$TcO(OH)_2$(aq) + H$_2$O(l) $\Leftrightarrow$ TcO$_4^{2-}$ + 4 H$^+$ + 2 e$^-$
HTCO4-	VI	8.7	0		-	-	TcO$_4^{2-}$ + H$^+$ $\Leftrightarrow$ HTcO$_4^-$
H2TCO4	VI	0.3	0		-	-	HTcO$_4^-$ + H$^+$ $\Leftrightarrow$ H$_2$TcO$_4$(aq)
TCO4-	VII	-29.7	0	TcO4-	-29.4 ± 0.8		$TcO(OH)_2$(aq) + H$_2$O(l) $\Leftrightarrow$ TcO$_4^-$ + 4 H$^+$ + 3 e$^-$

Table 5.20.1: continued

		TDB Version 05/92			TDB Version 01/01		
Name	Redox	$\log_{10}K_{s,0}°$	$\Delta_rH_m°$		$\log_{10}K_{s,0}°$	$\Delta_rH_m°$	Reaction
HTCO4(S)	VII	5.94	0		-	-	$HTcO_4(s) \Leftrightarrow TcO_4^- + H^+$
NATCO4	VII	1.56	0		-	-	$NaTcO_4(s) \Leftrightarrow TcO_4^- + Na^+$
KTCO4(S	VII	-2.22	0		-	-	$KTcO_4(s) \Leftrightarrow TcO_4^- + K^+$
TC2O7	VII	13.1	-6.4		-	-	$Tc_2O_7(s) \Leftrightarrow 2\ TcO_4^- + 2\ H^+$
TCO3	VI	-23.2	0		-	-	$TcO_3(s) + H_2O(l) \Leftrightarrow TcO_4^{2-} + 2\ H^+$
TCO2AM	IV	-7.5	0		-	-	$TcO_2 \cdot 2.0H_2O(s) \Leftrightarrow TcO(OH)_2(aq) + H_2O(l)$
	IV	-	-	TcO2:1.6H2O	-8.4 ± 0.5		$TcO_2 \cdot 1.6H_2O(s) \Leftrightarrow TcO(OH)_2(aq) + 0.6\ H_2O(l)$
TC4O7	IV/III	-36.8	0		-	-	$Tc_4O_7(s) + 6\ H^+ \Leftrightarrow 4\ TcO^{2+} + 3\ H_2O(l) + 2\ e^-$
TC3O4	III/II	-57.0	33.697		-	-	$Tc_3O_4(s) + 2\ H^+ \Leftrightarrow 3\ TcO^{2+} + H_2O(l) + 4\ e^-$
TCOH3(S)	III	-14.66	0		-	-	$Tc(OH)_3(s) + H^+ \Leftrightarrow TcO^{2+} + 2\ H_2O(l) + e^-$
TCOH2(S)	II	-21.63	33.697		-	-	$Tc(OH)_2(s) \Leftrightarrow TcO^{2+} + H_2O(l) + 2\ e^-$
TCOH(S)	I	-23.54	67.395		-	-	$Tc(OH)(s) \Leftrightarrow TcO^{2+} + 2\ e^-$ **(???)**
TC2S7	VII	60.78	280.98		-	-	$Tc_2S_7(s) + 30H_2O(l) \Leftrightarrow 2\ TcO^{2+} + 60\ H^+ + 50\ e^- + 7\ SO_4^{2-}$
TCS3	VI	61.90	120.42		-	-	$TcS_3(s) + 13\ H_2O(l) \Leftrightarrow TcO^{2+} + 26\ H^+ + 22\ e^- + 3\ SO_4^{2-}$
TCS2	IV	-133.29	80.28		-	-	$TcS_2(s) + 9\ H_2O(l) \Leftrightarrow TcO^{2+} + 18\ H^+ + 16\ e^- + 2\ SO_4^{2-}$

4.20.9   References

CARTLEDGE, G.H. (1971): Free energies of formation of hydrous oxides of technetium in its lower valencies. J. Electrochem. Soc., 118, 231-236.

RARD, J.A., RAND, M.H., ANEREGG, G., WANNER, H. (1999): Chemical Thermodynamics of Technetium. Elsevier, Amsterdam, 544p.

5.21   Thorium

In most cases, chemical systems relevant for radioactive waste management and/or environmental modelling have pH values above ~ 6 and exhibit ionic strengths not higher than that of sea-water. The most important solution species of Th in such systems are the hydrolysis products and the carbonate complexes (to a lesser extent also phosphates, sulphates and fluorides). Since thorium is sometimes used as an analogue for other actinide(IV) elements, its complexes and solids with hydroxide and carbonate are reviewed in more detail as would be expected for a "first step"-type review limited by rather narrow deadlines. To check for consistency, selected data for other actinide(IV) elements are compiled in Table 5.21.2.

5.21.1   Basic values

Entropy values were taken from COX et al. (1989):

$$S_m°(H_2(g), 298.15\ K) = \textbf{130.680} \pm \textbf{0.003 Jmol}^{-1}\textbf{K}^{-1}$$

$$S_m°(Th(cr), 298.15\ K) = \textbf{51.8} \pm \textbf{0.5 Jmol}^{-1}\textbf{K}^{-1}$$

Standard values for Th^{4+} are from FUGER & OETTING (1976):

$$\Delta_f G_m°(Th^{4+}, 298.15\ K) = \textbf{–704.6 kJmol}^{-1}\textbf{K}^{-1}$$

$$\Delta_f H_m°(Th^{4+}, 298.15\ K) = \textbf{–769.0 kJmol}^{-1}\textbf{K}^{-1}\textbf{.}$$

Using

$\Delta_f G_m°(Th^{4+}, 298.15\ K) = \Delta_f H_m°(Th^{4+}, 298.15\ K) - 298.15 \cdot \Delta_f S_m°(Th^{4+}, 298.15\ K)$ and

$\Delta_f S_m°(Th^{4+}, 298.15\ K) = S_m°(Th^{4+}, 298.15\ K) - S_m°(Th(cr), 298.15\ K) + 4/2 \cdot S_m°(H_2(g), 298.15\ K)$

one obtains

$$S_m°(\ Th^{4+}, 298.15\ K) = \textbf{–425.6 Jmol}^{-1}\textbf{K}^{-1}$$

5.21.2   Hydrolysis

Reviews on Th hydrolysis have been given by BAES & MESMER (1976) and BROWN et al. (1983). Very recently, a further review including additional information from LIBD (Laser Induced Breakdown Detection) has been presented by NECK & KIM (1999).

From these reviews and as pointed out by NECK & KIM (1999), it is evident that Th^{4+} shows a strong tendency to form polynuclear and/or colloidal species and that an unambiguous interpretation of the hydrolysis data is still missing.

It is widely accepted that neutral $Th(OH)_4(aq)$ is the predominant hydrolysis product at pH > 6. The most important solid which needs to be considered in systems relevant to waste management is ThO_2. Although other solids, particularly mixed phases or even solid solutions including Th may exist, no data are presently available for such phases and they are not considered in the present update. Naturally occurring thorium is often located in phosphates (monazites), but these phases are formed at very high temperature and are very resistant to metamorphisms (in fact monazite is used in geochronology to date the magmatic emplacement of metagranitic rocks). Therefore such phases are not considered in our update.

In aqueous systems above pH 6 the solubility of thorium can be predicted if the two equilibria

$$ThO_2(s) + 4\ H^+ \Leftrightarrow Th^{4+} + 2\ H_2O \quad (*K_{s,o}) \qquad (5.21.1)$$

and

$$Th^{4+} + 4\ H_2O \Leftrightarrow Th(OH)_4(aq) + 4\ H^+ \quad (*\beta_{14}) \qquad (5.21.2)$$
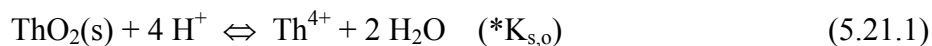
are known. The total dissolved thorium is then simply given by adding the equations:

$$ThO_2(s) + 2\ H_2O = Th(OH)_4(aq) \qquad \log_{10}{}^*K_{s,4} = \log_{10}{}^*K_{s,0} + \log_{10}{}^*\beta_{14} \qquad (5.21.3)$$
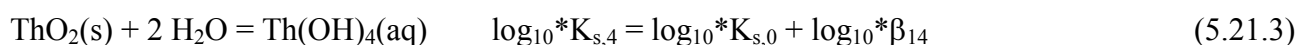
(see section 5.21.3 for systems including substantial amounts of carbonate). Independent studies have assumed different hydrolysis products (including monomers, dimers, tetramers and even hexamers with different numbers of associated hydroxides) in order to derive $*\beta_{14}°$ and $*K_{s,o}°$ (in media of varying ionic strength), but as GRENTHE & LAGERMANN (1991) state, at least $*\beta_{11}°$ and $*\beta_{14}°$ are well determined. NECK & KIM (1999) report on LIBD-experiments which indicate that colloidal particles are produced during the hydrolysis of Th^{4+}. This means that interpretations of former studies concerning the numerical value of $\log_{10}{}^*K_{s,o}°$ may be ambiguous.
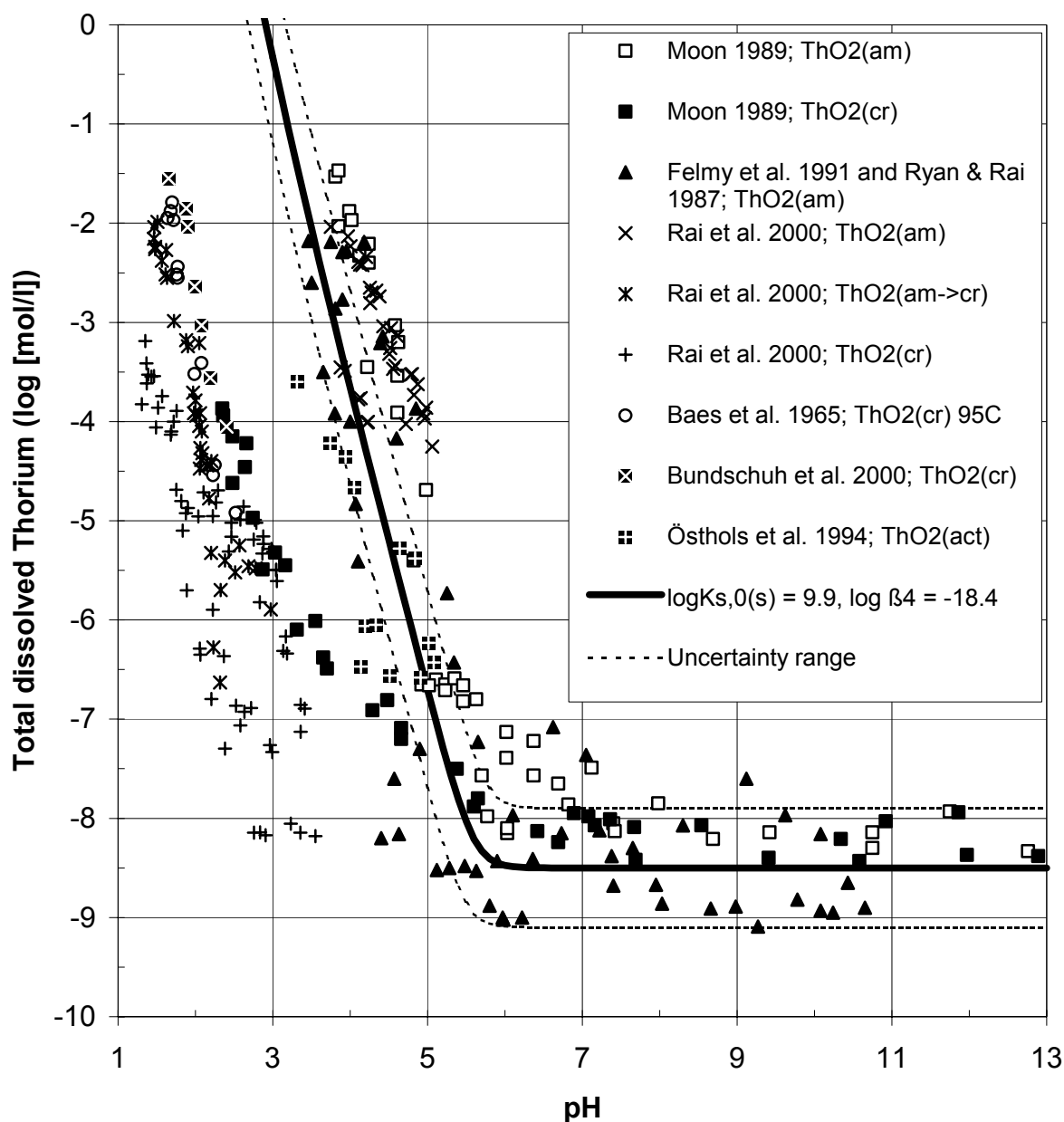
Fig. 5.21.1 Solubility of thorium dioxide as a function of pH from different authors. The solid line represents predictions made with the equilibria selected in this work.

There is no doubt that above pH ~ 6 the solubility of thorium is well described using the constant $\log_{10}{}^{*}K_{s,4}° = -8.5 \pm 0.6$ as proposed by NECK & KIM (1999) and as visualised in Fig. 5.21.1. This total Th solubility is confirmed by several authors (RYAN & RAI 1987, MOON 1989, FELMY et al. 1991, SERNE et al. 1996, WIERCZINSKY et al. 1998) and is even valid in 0.6 M NaCl and KCl (FELMY et al. 1991).

Although the total solubility fixes the sum of $\log_{10}*\beta_{14}°$ and $\log_{10}*K_{s,o}°$, it does not define an absolute value for either of the constants.

GRENTHE & LAGERMANN (1991) give -13.94 ± 0.31 for $\log_{10}*\beta_{14}°$ (recalculated from -16.65 ± 0.04 in 3 M NaClO₄, using SIT with $\epsilon(Th^{4+},ClO_4^-) = 0.67 ± 0.1$ as suggested by NECK & KIM (1999) and $\epsilon(H^+,ClO_4^-) = 0.14 ± 0.02$ (GRENTHE et al. 1992)), whereas EKBERG et al. (2000) give -16.93 ± 0.58 (recalculated from -19.4 ± 0.5 measured in 1 M NaClO₄ using identical ε's). NECK & KIM (1999) suggest to use -17.3 ± 1.2 (at I = 0), RYAN & RAI (1987) estimate <= -18.4 (recalculated from <= -19.7, measured in 0.1 M NaClO₄) and LANGMUIR & HERMAN (1980) report -15.9 for $\log_{10}*\beta_{14}°$.

Both, GRENTHE & LAGERMANN (1991) and EKBERG et al. (2000) give detailed data and clearly explain, how they derived the constants from their data. In addition to potentiometric data at lower pH, EKBERG et al. (2000) provide solvent extraction data at high pH. These solvent extraction data facilitate the evaluation of $\log_{10}*\beta_{14}°$, independent of polymer formation and/or ThO₂(s) precipitation. Although both papers are rated to be of high reliability, we cannot resolve the discrepancy of 3 orders of magnitude in $\log_{10}*\beta_{14}°$ without further independent information.

Similar discrepancies exist for $\log_{10}*K_{s,o}$. RYAN & RAI (1987) suggest 10.5 ± 0.5 (for 0.1 M NaClO₄; 9.2 ± 0.5 at I = 0 using the above given ε's), ÖSTHOLS et al. (1994) give 9.37 ± 0.13 (for 0.5 M NaClO₄; 7.3 ± 0.2 at I = 0 using the same ε's) and NECK & KIM (1999) propose 8.8 ± 1.0 (at I = 0). A second group of authors gives much lower values: 3.1 (MOON 1989, for 0.5 M NaClO₄), 3.6 ± 0.9 (NECK 1998, BUNDSCHUH 1999, at I = 0) and ≈6.6 (BAES & MESMER 1976, at I = 0?). The value of 5.3 from GRENTHE & LAGERMANN (1991) has been calculated from $\log_{10}*K_{s,4}$ and depends on their selection of $\log_{10}*\beta_{14}$. Note that also the value from ÖSTHOLS et al. (1994) has to be taken with care: according to the publication (Figure 1, therein) this value was derived from only a few experimental points and does not demonstrate convincing reliability.

The reasons for these large discrepancies become clear, when all available solubility data are plotted together (see Fig. 5.21.1). At pH values below ~ 6, two groups of data indicate the presence of two different solubility limiting thorium dioxides (obviously a crystalline and an amorphous modification). Indeed, RAI et al. (2000) very recently showed that the "higly" soluble amorphous ThO₂ converts to a sparingly soluble crystalline modification when heated to 90 °C. RAI et al. (2000) give $\log_{10}*K_{s,o}^0 \geq -0.9$ for ThO₂(cr) and $\log_{10}*K_{s,o}^0 = 11.1±0.5$ for ThO₂(am). For a partly crystallised product they give (at 90 °C) an intermediate value of $\log_{10}*K_{s,o} = 6.8±0.2$. From a thermodynamic point of view one could argue that crystalline ThO₂ is the stable phase which "finally" (whatever this means in terms of time) will define Th concentrations in solution. Unfortunately, the situation complicates if pH is raised above ~ 6. The dataset of MOON (1989)

clearly demonstrates that Th concentrations in solution are **independent** of the crystallinity of ThO_2 at higher pH. An important consequence of these findings is the fact that there is no unique dataset which describes all of the data compiled in Fig. 5.21.1. Or, with other words, we do not yet know which features/processes control the solubility of ThO_2 above pH ~ 6 (note that NECK & KIM 1999 attribute this to an amorphous hydoxide layer covering the surface of $ThO_2(s)$).

In the present update we prefer to start from measured solubilities (e.g. equation 5.21.3) in systems relevant for waste management and try to deduce a consistent pair of $*\beta_{14}°$ and $*K_{s,o}°$ in such a way, that predictions derived thereof will again reproduce the measured solubilities.

Unforunately, this decision faces us with the delicate problem of selecting a sensible pair of constants from the ranges $\log_{10}*\beta_{14}$ [-19.7 … -15.9] and $\log_{10}*K_{s,o}$ [–0.9 … 11.1] which, after appropriate recalculation to I = 0, must sum up to $–8.5 \pm 0.6$. We start the selection with examining $\log_{10}*\beta_{14}$, since independent information are available for this equilibrium. As a main problem we identified the recalculation to zero ionic strength using SIT in the case of highly charged ions like Th^{4+}. At higher ionic strength both, the Debye-Hückel term D and the interaction coefficient ε, give substantial contributions to the $\log_{10}K$ correction (although they may partly cancel). As stated above, NECK & KIM (1999) proposed to use $\varepsilon(Th^{4+}, ClO_4^-) = 0.67 \pm 0.1$, derived from $\varepsilon(U^{4+}, ClO_4^-) = 0.76 \pm 0.06$ (GRENTHE et al. 1992, note that ÖSTHOLS et al. 1994 used 0.76 to recalculate their values from 0.5 M $NaClO_4$ to I = 0).

By extrapolating $\log_{10}*\beta_{14}$ from GRENTHE & LAGERMANN (1991), EKBERG et al. (2000) and RYAN & RAI (1987) to I = 0 according to the procedure given in GRENTHE et al. (1992), we obtained a much larger $\varepsilon(Th^{4+}, ClO_4^-)$ (see Fig. 5.21.2). The slope $-\Delta\varepsilon = 1.49 \pm 0.17$ produces $\varepsilon(Th^{4+}, ClO_4^-) = 2.05 \pm 0.17$ when substituting $\varepsilon(H^+, ClO_4^-) = 0.14 \pm 0.02$ (GRENTHE et al. 1992) in $\Delta\varepsilon = 4 \cdot \varepsilon(H^+, ClO_4^-) – \varepsilon(Th^{4+}, ClO_4^-)$. This value is unusually high and is not consistent with the ε's $((U^{4+}, Np^{4+}, Pu^{4+}), ClO_4^-)$ of 0.76, 0.82 and 1.03 and with $\varepsilon(Th^{4+},(Cl^-, NO_3^-))$ of 0.25 and 0.11 as given by GRENTHE et al. (1992).

Unfortunately, we cannot resolve this problem based on the available data. There are no obvious reasons to discard either of the $\log_{10}*\beta_{14}$'s from GRENTHE & LAGERMANN (1991) or EKBERG et al. (2000), since both studies give a very careful analysis of the experimental data. Although GRENTHE & LAGERMANN (1991) used reasonable high $[Th^{4+}]_{tot}$ concentrations, they found a remarkable consistency of $\log_{10}*\beta_{14}$ among the set of models they tested (note that the models also include various combinations of polymeric species). Maybe the inconsistency is a consequence of the basic assumptions of the SIT approach (GRENTHE et al. 1992, see also GRENTHE & PUIGDOMENECH 1997) which

i) in its simplest form assumes concentration-independent interaction coefficients (which in turn has consequences for the denominator of the Debye-Hückel term),

ii) sets the interaction coefficients for uncharged solutes to zero. GRENTHE & PUIGDOMENECH (1997), on page 334 discuss interactions involving neutral species (in the present case $Th(OH)_4(aq)$) and state that …*interactions between uncharged species may be far from negligible*… , but it would require to set $\varepsilon(Th(OH)_4(aq),Na^++ClO_4^-)$ to -0.7 in order to obtain $\varepsilon(Th^{4+},ClO_4^-) = 0.67$ as proposed by NECK & KIM (1999). Unfortunately, this negative value contradicts the interaction coefficients tabulated by CIAVATTA (1990) for neutral solutes like $CdCl_2(aq)$, $CdI_2(aq)$, $Hg(OH)_2(aq)$, $HgCl_2(aq)$, $PbCl_2(aq)$.

iii) was "calibrated" using simple, low-charged ions. The square of the charge in the Debye-Hückel term has a substantial impact on the magnitude of the correction. Is it still justified to use the "full" charge for highly charged ions?
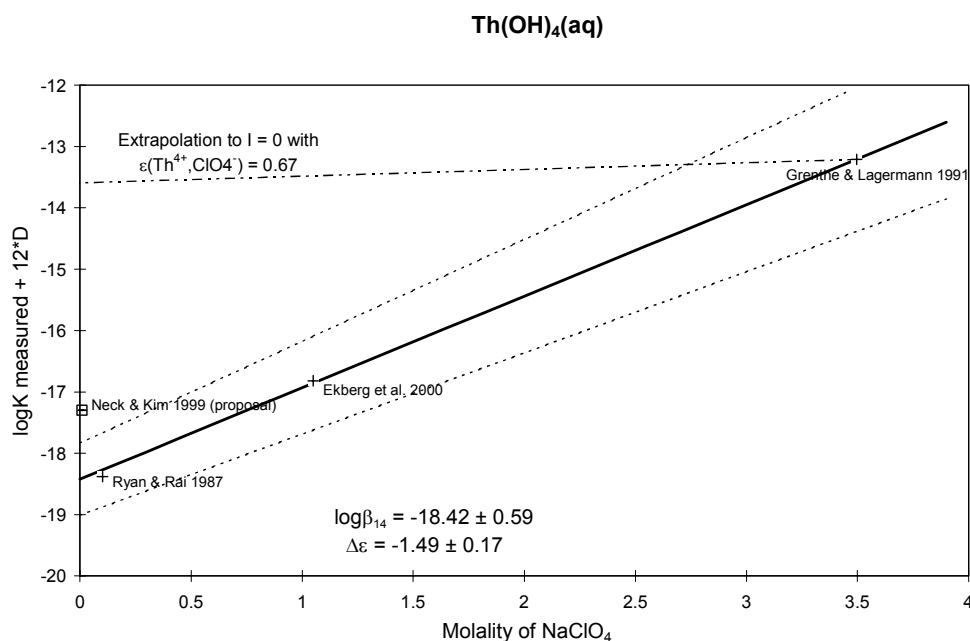
Th(OH)₄(aq)

Fig. 5.21.2 Evaluation of $\Delta\varepsilon$ for the reaction $Th^{4+} + 4\ H_2O \Leftrightarrow Th(OH)_4(aq) + 4\ H^+$ according to the procedure given in GRENTHE et al. (1992). The resulting slope corresponds to the difference $\varepsilon(Th^{4+},ClO_4^-) - 4\cdot\varepsilon(H^+,ClO_4^-)$ (note that the very small uncertainty ($\pm$ 0.04) associated with the GRENTHE & LAGERMANN (1991)-value does not significantly affect the result of the weighted regression). The dashed-dotted line indicates the strong influence of $\varepsilon(Th^{4+},ClO_4^-)$.

Note that GRENTHE & LAGERMANN (1991) also reported an unusual high interaction coefficient $(\varepsilon(Th_2(OH)_2^{6+},ClO_4^-) = 1.2 \pm 0.2)$, but did not comment on it further. However, the discussion on this topic is stopped here. We ascertain an inconsistency in either the experimental $\log_{10}*\beta_{14}$'s or in the SIT approach (or in both), and we hope that this issue will be resolved in subsequent discussions.

According to Fig. 5.21.2, $\log_{10}*\beta_{14}° = -18.42 \pm 0.59$ compares fairly well with NECK & KIM (1999)'s estimated $\log_{10}*\beta_{14}° = -17.3 \pm 1.2$ (not used in the regression). Our present decision is to rely on the careful potentiometric studies of EKBERG et al. (2000) and GRENTHE & LAGERMANN (1991) and on the solubility study of RYAN & RAI (1987) and we recommend to use

$$\log_{10}*\beta_{14}° = -18.4 \pm 0.6,$$

together with $\varepsilon(Th^{4+},ClO_4^-) = 2.05 \pm 0.17$. From $\log_{10}*K_{s,4}° = -8.5 \pm 0.6$ and $\log_{10}*\beta_{14}° = -18.4 \pm 0.6$ we derive according to eq. 5.21.3:

$$\log_{10}*K_{s,o}° = 9.9 \pm 0.8.$$

The consequences of selecting this particular combination of $*K_{s,0}°$ and $*\beta_{14}°$ are best explained with the help of Fig. 5.21.1. As expected, Th solubilities at high pH are very well reproduced. In the acidic region, the slope of -3 (including $Th(OH)^{3+}$, see below) produces a solubility curve close to the measurements for the more amporphous thorium dioxides, which in turn would support NECK & KIM (1999)'s presumtion of an amorphous surface hydroxide layer to be responsible for the solubility at high pH. Vice versa, it would require to decrease $*K_{s,o}°$ by some 8 orders of magnitude in order to describe the solubility of the crystalline oxide in the pH range [1 … 3]. This would, however, lead to extremely low solubilities at higher pH, not consistent with all observations. There is no chance to resolve this dilemma based on available data, but we justify our selection by the fact that it reproduces Th solubilities in a chemical environment relevant for waste management problems.

The present update does not make any attempts to review equilibrium constants for the second or third hydrolysis step ($\log_{10}*\beta_{12}°$ / $\log_{10}*\beta_{13}°$), nor does it comment on the most prominent polymeric hydrolysis products ($Th_2(OH)_2^{6+}$, $Th_4(OH)_8^{8+}$ and $Th_6(OH)_{15}^{9+}$, see BAES & MESMER 1976, GRENTHE & LAGERMANN 1991 and EKBERG et al. 2000). These species contribute to total dissolved Th only in the narrow pH range [4.5 … 6] at total Th concentrations exceeding about 10^{-5} mol/l. Since these ranges are not of primary importance for systems relevant to waste management, a detailed review of polymeric hydrolysis products is postponed to a later stage of the update. This is in principle also applicable to $Th(OH)^{3+}$, but from a point of view of chemical systematics the first hydrolysis constant is an important number. Therefore, this constant is discussed here in more detail.

Several authors give values for the first hydrolysis constant

$$Th^{4+} + H_2O \Leftrightarrow Th(OH)^{3+} + H^+ \qquad\qquad *\beta_{11}$$
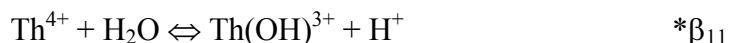
at different ionic strengths (see Table 5.21.2). The recalculation to zero ionic strength (see Fig. 5.21.3) leads to $\log_{10}*\beta_{11}° = -2.4 \pm 0.1$ and to $\varepsilon(ThOH^{3+},ClO_4^-) = 2.0 \pm 0.2$. The "fit" is very bad, but there is a fair agreement of the resulting constant with $\log_{10}*\beta_{11} = -2.98 \pm 0.01$ obtained by BROWN et al. (1983) in 0.1 M KNO_3 and with the proposal of NECK & KIM (1999) ($\log_{10}*\beta_{11}° = -2.3$; note that both values were not used in the extrapolation to $I = 0$).

To be honest, one should not use the term "fit" when inspecting Fig. 5.21.3. A term like "indication" would be much more appropriate. It is interesting to note that $\varepsilon(Th(OH)^{3+},ClO_4^-) = 2.0$ resulting from Fig. 5.21.3 (i.e., $\varepsilon(Th(OH)^{3+},ClO_4^-) = \Delta\varepsilon - \varepsilon(H^+,ClO_4^-) + \varepsilon(Th^{4+},ClO_4^-)$) suffers from the same inconsistency as does $\varepsilon(Th^{4+},ClO_4^-)$. Nevertheless, we recommend to use

$$\log_{10}*\beta_{11}° = -2.4 \pm 0.5$$

together with $\varepsilon(ThOH^{3+},ClO_4^-) = 2.0 \pm 0.2$. Note that we adopt an increased uncertainty of ± 0.5 log units (instead of ± 0.1) in order to account for the very bad quality of the "extrapolation" as shown in Fig. 5.21.3.
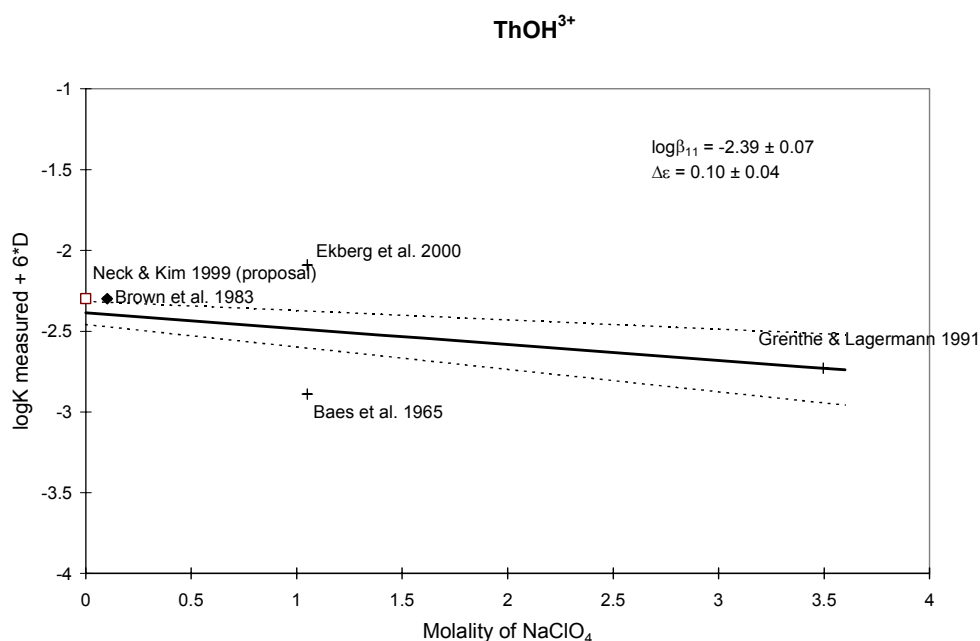
Fig. 5.21.3   Evaluation of $\Delta\varepsilon$ for the reaction $Th^{4+} + H_2O \Leftrightarrow Th(OH)^{3+} + H^+$ according to the procedure given in GRENTHE et al. (1992). The resulting slope of -0.10 corresponds to the difference $\varepsilon(Th^{4+},ClO_4^-) - \varepsilon(Th(OH)^{3+},ClO_4^-) - \varepsilon(H^+,ClO_4^-)$. Note that the points "NECK & KIM (1999)" and "BROWN et al. (1983)" do not contribute to the "fitted" line.

5.21.3   Carbonate complexes

Quantitative information on the formation of Th carbonate complexes has only been given by a few authors (JOÃO et al. 1987, ÖSTHOLS et al. 1994, RAI et al. 1995, FELMY et al. 1997, HESS et al. 1997). XAS spectroscopy (HESS et al. 1997) clearly revealed that the most prominent species at high carbonate concentrations (~0.15 up to >2 M) is the pentacarbonato thorate complex $Th(CO_3)_5{}^{6-}$. A mixed hydroxide carbonate complex becomes relevant at total carbonate concentrations below 0.1 M. However, the precise nature of this mixed complex is not yet resolved. Several authors (ÖSTHOLS et al. 1994, RAI et al. 1995 and FELMY et al. 1997) utilized a trihydroxide monocarbonato complex $(Th(OH)_3(CO_3)^-$ to successfully model measured solubilities, but HESS et al. (1997) concluded that a dihydroxide tricarbonato complex $(Th(CO_3)_3(OH)_2{}^{4-})$ is compatible with their spectroscopic findings. For the reaction

$$ThO_2(s) + 5CO_3{}^{2-} + 4H^+ \Leftrightarrow Th(CO_3)_5{}^{6-} + 2H_2O \qquad \log_{10}{}^*K_{s,50}$$

ÖSTHOLS et al. (1994) give $\log_{10}{}^*K_{s,50} = 42.12 \pm 0.32$ (in 0.5 M $NaClO_4$) and FELMY et al. (1997) give $\log_{10}{}^*K_{s,50}° = 37.6$ (derived from 0.05 to 2 M $Na_2CO_3/NaClO_4$ solutions using a Pitzer formalism; no uncertainties given). For the reaction

$$ThO_2(s) + CO_3{}^{2-} + H^+ + H_2O \Leftrightarrow Th(CO_3)(OH)_3{}^- \qquad \log_{10}{}^*K_{s,13}$$
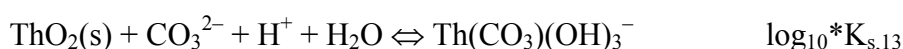
ÖSTHOLS et al. (1994) give $\log_{10}{}^*K_{s,13} = 6.11 \pm 0.19$ (in 0.5 M $NaClO_4$) and FELMY et al. (1997) give $\log_{10}{}^*K_{s,13}° = 6.78$ (derived from 0.05 to 2 M $Na_2CO_3/NaClO_4$ using a Pitzer formalism; no uncertainties given). The recalculation of the ÖSTHOLS et al. (1994)-values to I = 0 using SIT gives

$$\log_{10}{}^*K_{s,50}° = 39.7 \pm 0.4 \text{ and}$$

$$\log_{10}{}^*K_{s,13}° = 6.77 \pm 0.21$$

with

$\log_{10}{}^*K_{s,50}(molal) = 42.03 \pm 0.32$ $\quad(42.12 - 8{}^*\log_{10}(1.0256))$

$\log_{10}{}^*K_{s,13}(molal) = 6.10 \pm 0.19$ $\quad(6.11 - 1{}^*\log_{10}(1.0256))$

$\varepsilon(Th(CO_3)_5{}^{6-},Na^+) = -0.30 \pm 0.15$ $\quad$SILVA et al. (1995); analogy to $\varepsilon(U(CO_3)_5{}^{6-},Na^+)$

$\varepsilon(ThCO_3(OH)_3{}^-,Na^+) = 0.00 \pm 0.05$ $\quad$SILVA et al. (1995); analogy to $\varepsilon((UO_2)CO_3(OH)_3{}^-,Na^+)$

$\varepsilon(CO_3{}^{2-},Na^+) = -0.08 \pm 0.03$ $\quad$SILVA et al. (1995)

$\varepsilon(H^+,ClO_4{}^-) = 0.14 \pm 0.02$ $\quad$GRENTHE et al. (1992).

Note that ÖSTHOLS et al. (1994) give nearly identical $\log_{10}*K°$'s (39.64 ± 0.4, 6.78 ± 0.3) without explicitly giving the ε's they used to correct to $I = 0$. Indeed, and as pointed out by FELMY et al. (1997), there is an excellent agreement among the two studies.

In accordance with GRENTHE et al. (1992), SILVA et al. (1995) and LEMIRE et al. (2001) (see also Table 5.21.2) it is more convenient to express the carbonate complex formation for actinide(IV) elements as "homogeneous" reactions. This can simply be achieved by adding the inverse of equilibrium (5.21.1) to the corresponding carbonate equilibria involving $ThO_2(s)$.

We obtain[3]

$$Th^{4+} + 5CO_3^{2-} \Leftrightarrow Th(CO_3)_5^{6-} \qquad \mathbf{log_{10}\beta_{CO3,5}° = 29.8 \pm 1.1}$$
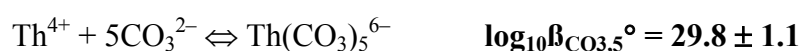
with $\log_{10}\beta_{CO3,5}° = \log_{10}*K_{s,50}° - \log_{10}*K_{s,0}°$, and

$$Th^{4+} + CO_3^{2-} + 3H_2O \Leftrightarrow Th(CO_3)(OH)_3^- + 3H^+ \qquad \mathbf{log_{10}*K_{13}° = -3.1 \pm 1.0}$$
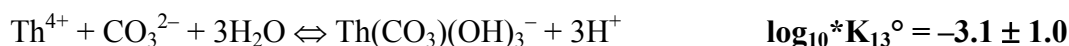
with $\log_{10}*K_{13}° = \log_{10}*K_{s,13}° - \log_{10}*K_{s,0}°$.

Hypothesis for thorium concentrations in natural environments

Combining hydrolysis- and carbonate data offers some interesting aspects concerning the total solubility of Th in natural environments:

In the presence of $ThO_2(s)$ the concentration of $Th(CO_3)(OH)_3^-$ may be expressed with

$$log[Th(CO_3)(OH)_3^-] = -11.38 (\pm 0.21) + log\, p_{CO2} + pH.$$

Based on about one thousand analyses of Swiss groundwaters HUMMEL et al. (2000, Figs. 23-25, p.997) demonstrate that the sum of $log\, p_{CO2} + pH$ (yielding a value of about 5.5) is more or less constant in the pH range [6...9]. $Th(OH)_4(aq)$ and $Th(CO_3)_5^{6-}$ do not substantially contribute to total dissolved Th under these conditions. Provided that $ThO_2(s)$ is the limiting solid, one thus

---

[3] Those who prefer to use HCO_3^- as a master species for carbonate may replace CO_3^{2-} with $\log_{10}\{CO_3^{2-}\} = -10.329 + \log_{10}\{HCO_3^-\} - \log_{10}\{H^+\}$ to obtain

$$Th^{4+} + 5HCO_3^- \Leftrightarrow Th(CO_3)_5^{6-} + 5H^+ \qquad \log_{10}\beta_{HCO3,5}° = -21.8 \pm 1.1$$

$$Th^{4+} + HCO_3^- + 3H_2O \Leftrightarrow Th(CO_3)(OH)_3^- + 4H^+ \qquad \log_{10}*K_{HCO3,13}° = -13.4 \pm 1.0$$
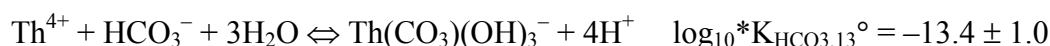
would expect similar maximum Th concentrations for all Swiss groundwaters, i.e.,
[Th(CO₃)(OH)₃⁻] ~ 10⁻⁶ mol/l.

We could locate only one measured concentration of Th in Swiss groundwater ~ 10⁻⁹ mol/l.
Thorium does not belong to the set of elements having routinely been measured in Nagra's
groundwater geochemistry programme. Anyway, this datum together with similar results from
natural analogue sites indicate much lower thorium concentrations than expected from laboratory
data. The conclusion is that ThO₂(s), the still poorly defined solid studied in laboratory experi-
ments, is not the solubility controlling phase in common groundwaters. Most probably Th forms
solid solutions with host minerals in these environments. However, ThO₂(s) may form in the vicinity
of a repository for radioactive waste. In such an environment ThO₂(s) represents the upper limit of
solubility controlling solid phases.

5.21.4 Complexes and solids with other ligands

Nearly all of the Th species/solids given in PEARSON et al. (1992) which include "other" ligands
(Cl^-, F^-, SO_4^{2-}, PO_4^{2-}, NO_3^-) had originally been taken from LANGMUIR & HERMAN (1980). Only a
small part of these data really need to be considered for systems relevant to waste management.

In order to become relevant in aqueous systems above pH 7, complexes of the form

$$Th^{4+} + nL^{x-} \Leftrightarrow Th(L)_n^{4-nx} \qquad\qquad log_{10}K_{Ln}$$
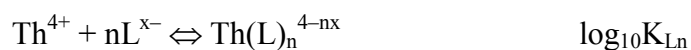
have to be present in concentrations exceeding about 1 % of the dominating hydrolysis species
$Th(OH)_4(aq)$. In the presence of $ThO_2(s)$ this may be expressed with

$$log_{10}[ThL_n] > log_{10}K_{s,4} - 2.$$

The above relation defines a lower limit for $log_{10}K_{Ln}$. Since

$$log_{10}[ThL_n] = log_{10}K_{Ln} + log_{10}[Th^{4+}] + n \cdot log_{10}[L_{free}]$$

and, in the presence of $ThO_2(s)$,

$$log_{10}[Th^{4+}] = 9.9 - 4 \cdot pH,$$

we arrive at

$$log_{10}K_{Ln} > -20.4 + 4 \cdot pH - n \cdot log_{10}[L_{free}].$$

By assuming that $[L_{free}]$ does not exceed 0.1 mol/l ($log_{10}[L_{free}] < -1$), we conclude that for systems
above pH 7

$log_{10}K_{Ln}$ needs to be larger than [8.6; 9.6; 10.6; 11.6] for n = [1; 2; 3; 4]

in order to produce relevant concentrations of [ThL_n] complexes. Such conditions are only fulfilled for the phosphates and, to a lesser extent, for the fluorides and sulphates. Due to "non-relevance", chloride and nitrate complexes are therefore not considered in this first update step.

5.21.5   Phosphate complexes

Based on data from MOSKVIN et al. (1967) measured in 0.35 M $HClO_4$, LANGMUIR & HERMAN (1980) proposed the equilibria:

Reaction		LANGMUIR & HERMAN (1980)	
$Th^{4+} + HPO_4^{2-} \Leftrightarrow ThHPO_4^{2+}$	$log_{10}K_{HPO4,1} =$	10.82	(i)
$Th^{4+} + 2HPO_4^{2-} \Leftrightarrow Th(HPO_4)_2(aq)$	$log_{10}\beta_{HPO4,2} =$	22.81	(ii)
$Th^{4+} + 3HPO_4^{2-} \Leftrightarrow Th(HPO_4)_3^{2-}$	$log_{10}\beta_{HPO4,3} =$	31.28	(iii)
$Th^{4+} + 2HPO_4^{2-} + 4H_2O(l) \Leftrightarrow Th(HPO_4)_2 \cdot 4H_2O(s)$	$log_{10}K_{HPO4,s} =$	26.88	(iv)

for I = 0.35. As discussed in GRENTHE et al. (1992), the degree of protonation of the ligand cannot be determined based on the MOSKVIN et al. (1967)-data alone. From data given by WAGMAN et al. (1977), LANGMUIR & HERMAN (1980) also give formation constants for

Reaction		LANGMUIR & HERMAN (1980)	
$Th^{4+} + H_2PO_4^- \Leftrightarrow ThH_2PO_4^{3+}$	$log_{10}K_{H2PO4,1} =$	4.64	(v)
$Th^{4+} + 2H_2PO_4^- \Leftrightarrow Th(H_2PO_4)_2^{2+}$	$log_{10}\beta_{H2PO4,2} =$	8.91	(vi)

and from data provided by KATZ & SEABORG (1957) at I = 2:

$Th^{4+} + H_3PO_4(aq) \Leftrightarrow ThH_3PO_4^{4+}$	$log_{10}K_{H3PO4,1} =$	1.9	(vii)

The equilibria (i) to (vii) are included in our original database (PEARSON et al. 1992).

Obviously, the phosphate complexes have only been investigated in strongly acidic media and without further information it becomes a difficult task to identify a correct complex stoichiometry. In our opinion there is no need to have all these complexes included in the update, since they were evaluated in strongly acidic solutions and their quality is not yet assured. We suggest to postpone a careful review of these equilibria to a later update. However, since the data indicate that phosphate complexes could become relevant at pH values below ~7 in systems including sufficient phosphate, we recommend to include just the potentially most relevant complex (equilibrium (i) from the above equations). An estimate based on SIT-parameters for 0.35 M $HClO_4$ leads to

$$\mathbf{log_{10}K_{HPO4,1}° = 13 \pm 1}.$$

Note that we do not recommend this value in the sense of "our best estimate" for Th phosphate complex formation. We understand this value in the sense of a placeholder for missing Th phosphate complexes or in the sense of a guard, watching model applications with Th in phosphate containing systems. The idea behind this selection is that the modeler should be warned about the possibility of phosphate complex formation in his particular system.

Note further that the combination of equilibrium (ii) and (iv) would lead to a pH-independent concentration of $\log_{10}[Th(HPO_4)_2(aq)] \cong -4 \pm 1$ in the presence of $Th(HPO_4)_2 \cdot 4H_2O(s)$. Such behavior has never been reported in the literature for systems relevant to waste management. Therefore, we exclude the solubility product (iv) from the present update.

5.21.6   Fluoride complexes

LANGMUIR & HERMAN (1980) refer to two independent studies and give the following data:

Reaction		WAGMAN et al. (1977)	BAUMANN (1970)
$Th^{4+} + F^- \Leftrightarrow ThF^{3+}$	$\log_{10}K_{F,1} =$	8.03	8.44
$Th^{4+} + 2F^- \Leftrightarrow ThF_2^{2+}$	$\log_{10}\beta_{F,2} =$	14.25	15.06
$Th^{4+} + 3F^- \Leftrightarrow ThF_3^+$	$\log_{10}\beta_{F,3} =$	18.93	19.81
$Th^{4+} + 4F^- \Leftrightarrow ThF_4(aq)$	$\log_{10}\beta_{F,4} =$	22.31	23.17

and

Reaction		WAGMAN et al. (1977)	
$Th^{4+} + 4F^- \Leftrightarrow ThF_4(c)$	$\log_{10}K_{F,s} =$	30.2	
$Th^{4+} + 4F^- + 2.5H_2O(l) \Leftrightarrow$ $ThF_4 \cdot 2.5H_2O(s)$	$\log_{10}K =$	33.1	(estimate)

The authors do not explicitly state why, but they recommend to use the data from WAGMAN et al. (1977). We presently have no obvious reasons to change this recommendation and thus remain with the fluoride complex formation constants as already given in PEARSON et al. (1992):

$$\mathbf{\log_{10}K_{F,1} = 8.0}$$

$$\mathbf{\log_{10}\beta_{F,2} = 14.2}$$

$$\mathbf{\log_{10}\beta_{F,3} = 18.9}$$

$$\mathbf{\log_{10}\beta_{F,4} = 22.3}$$

and

$$\mathbf{\log_{10}K_{F,s} = 30.2.}$$

Consistent with these values are the formation constants given by FELMY et al. (1993) for increased fluoride concentrations: $\log_{10}\beta_{F,5}° = 24.76$ and $\log_{10}\beta_{F,6}° = 25.56$.

Note also the fair agreement with fluoride formation constants as selected for other tetravalent actinides:

	Th(IV)	U(IV)	Np(IV)	Pu(IV)
	WAGMAN et al. (1977)	GRENTHE et al. (1992)	LEMIRE et al. (2001)	LEMIRE et al. (2001)
$\log_{10}K_{F,1}$	8.0	9.28 ± 0.09	8.96 ± 0.14	8.84 ± 0.10
$\log_{10}\beta_{F,2}$	14.2	16.23 ± 0.15	15.7 ± 0.3	15.7 ± 0.2
$\log_{10}\beta_{F,3}$	18.9	21.6 ± 1.0		
$\log_{10}\beta_{F,4}$	22.3	25.6 ± 1.0		

The formation constant of the hydrous fluoride $ThF_4 \cdot 2.5H_2O(s)$ is an estimate and we recommend to eliminate this equilibrium from the database.

5.21.7 Sulphate complexes

Data in PEARSON et al. (1992), based on the recommendation given in LANGMUIR & HERMAN (1980) originate from WAGMAN et al. (1977). Note that the original source of these WAGMAN et al. (1977) data was not known to the present reviewer, but from FELMY & RAI 1992 one learns that the data trace back to ALLEN & MCDOWELL (1963). From successive stability constants, obviously based on the same source LANGMUIR & HERMAN (1980) estimated a slightly different set of constants.

Reaction		WAGMAN et al. (1977)	LANGMUIR & HERMAN (1980)
$Th^{4+} + SO_4^{2-} \Leftrightarrow ThSO_4^{2+}$	$\log_{10}K_{SO4,1} =$	5.45	6.17
$Th^{4+} + 2SO_4^{2-} \Leftrightarrow Th(SO_4)_2(aq)$	$\log_{10}\beta_{SO4,2} =$	9.73	9.59
$Th^{4+} + 3SO_4^{2-} \Leftrightarrow Th(SO_4)_3^{2-}$	$\log_{10}\beta_{SO4,3} =$	10.50	10.34
$Th^{4+} + 4SO_4^{2-} \Leftrightarrow Th(SO_4)_4^{4-}$	$\log_{10}\beta_{SO4,4} =$	8.48	8.27

Since the estimation procedure of LANGMUIR & HERMAN (1980) offers some interesting features, it is briefly outlined below. From published stepwise stability constants, i.e.

$\Delta_4 \log_{10}K \ (\Rightarrow \log_{10}\beta_{SO4,4} - \log_{10}\beta_{SO4,3}) = \ -2.07$ ALLEN & MCDOWELL (1963); I = 0

$\Delta_3 \log_{10}K \ (\Rightarrow \log_{10}\beta_{SO4,3} - \log_{10}\beta_{SO4,2}) = \ \ 0.75$ ALLEN & MCDOWELL (1963); I = 0

$\Delta_2 \log_{10}K \ (\Rightarrow \log_{10}\beta_{SO4,2} - \log_{10}K_{SO4,1}) = \ \ 2.42$ AHRLAND et al. (1973); I = 2

$= \ \ 3.42$ (corrected to I = 0 by LANGMUIR & HERMAN 1980, no details of correction procedure given)

LANGMUIR & HERMAN (1980) constructed the following scheme:

$\Delta_x \log_{10}K$	$\Delta\Delta_x \log_{10}K$	estimate		
	2.75 (=(2.67+2.82)/2)	6.17	=(2.75+3.42)	$\log_{10}K_{SO4,1}$
x=2 3.42				
	2.67	9.59	=(6.17+3.42)	$\log_{10}\beta_{SO4,2}$
x=3 0.75				
	2.82	10.34	=(9.59+0.75)	$\log_{10}\beta_{SO4,3}$
x=4 −2.07				
		8.27	=(10.34−2.07)	$\log_{10}\beta_{SO4,4}$

This estimate does not include one single absolute $\log_{10}\beta_{SO4,x}$ - value. It is based on the hypothesis that the differences of $\log_{10}\beta_{SO4,x}$ - differences are more or less constant. Unfortunately, the quality of the correction of $\Delta_2\log_{10}K$ from AHRLAND et al. (1973) to I = 0 is completely unclear.

FELMY & RAI (1992) re-evaluated the thermodynamics of Th sulphate complexation including additional data from WIRTH (1912), BARRE (1912), ZEBROSKI et al. (1951), ZIELEN (1959), ALLEN & MCDOWELL (1963), LINKE (1965) and REARDON (1988) (the list from FELMY & RAI 1992 is given to facilitate a later update). Since this re-evaluation uses a Pitzer approach, it does not directly provide $\log_{10}\beta_{SO4,x}$-values. Further, a $\beta^{(1)}(Th^{4+}/SO_4^{2-})$ - parameter of zero as proposed by FELMY & RAI (1992) is not consistent with the expected ranges for this Pitzer-parameter (GRENTHE & PUIGDOMENECH 1997; p.378). Nevertheless, from the tabulated μ°/RT-values

$\mu°/RT(Th(SO_4)_2(aq)) \ = \ \ -911.69$

$\mu°/RT(Th(SO_4)_3^{2-}) \ \ = \ \ -1214.0$

$\mu°/RT(Th^{4+}) \ \ \ \ \ \ \ = \ \ -284.227$

$\mu°/RT(SO_4^{2-}) \ \ \ \ \ \ = \ \ -300.386$

one might recalculate

$$\log_{10}\beta_{SO4,2}° \qquad = \qquad 11.59$$

$$\log_{10}\beta_{SO4,3}° \qquad = \qquad 12.42,$$

which leads to $\Delta_3\log_{10}K° = 0.83$, in good agreement with the 0.75 evaluated by ALLEN & MCDOWELL (1963).

To our knowledge, FELMY & RAI 1992 is the only study which provides comprehensible values for the formation constants in question. Provided that a sensible estimate for the correction of $\Delta_2\log_{10}K$ to zero ionic strength is available, one could now directly (without assuming constant differences of differences) estimate $\log_{10}K_{SO4,1}°$ using $\Delta_2\log_{10}K$ (= $\log_{10}\beta_{SO4,2}-\log_{10}K_{SO4,1}$) from AHRLAND et al. (1973) and $\log_{10}\beta_{SO4,2}°$ from FELMY & RAI (1992). Following the formalism of SIT, $\Delta_2\log_{10}K°$ is given by

$$\Delta_2\log_{10}K(I_m) = \quad \Delta_2\log_{10}K° - 8{\cdot}D + (\epsilon(ThSO_4^{2+},ClO_4^-) + \epsilon(SO_4^{2+},Na^+)){\cdot}I_m$$

$$- \epsilon(Th(SO_4)_2(aq),Na^++ClO_4^-){\cdot}I_m^{\#}$$

with

$\epsilon(ThSO_4^{2+},ClO_4^-) = 0.3 \pm 0.1$ RARD et al. (1999); in analogy to USO_4^{2+}

$\epsilon(SO_4^{2-},Na^+) = -0.14 \pm 0.06$ RARD et al. (1999)

$\epsilon(Th(SO_4)_2(aq),Na^++ClO_4^-) = 0$ according to the rules given in GRENTHE et al. (1992)

$I_m^{\#} = 4.414$ mol/kg H_2O AHRLAND et al. (1973); the sum of $[Na^+]+[ClO_4^-]$, assuming that $NaClO_4$ was used as inert salt.

$\Delta_2\log_{10}K(I_m) = 2.42$ AHRLAND et al. (1973)

$I_m = 2.207$ mol/kg H_2O AHRLAND et al. (1973), assuming that $NaClO_4$ was used as inert salt.

$D = 0.2342$ Debye-Hückel term (GRENTHE et al. 1992)

one obtains $\Delta_2\log_{10}K° = 3.94 \pm 0.22$.

However, GRENTHE & PUIGDOMENECH (1997, p.334) state that the inclusion of interaction coefficients between uncharged and ionic species would lead to more correct results. Some interaction coefficients proposed by CIAVATTA (1990) indicate that $\epsilon(Th(SO_4)_2(aq),Na^++ClO_4^-)$ could be in the range 0.1 ± 0.1, which in turn would lead to $\Delta_2\log_{10}K° = 4.38 \pm 0.30$. Based on available data we cannot resolve the problem, but we believe that $\Delta_2\log_{10}K° = 4.0 \pm 0.5$ is an

appropriate estimate for the logK-difference in question. Based on this $\Delta_2 \log_{10} K°$ and on $\log_{10} \beta_{SO4,2}°$ from FELMY & RAI 1992, we recommend to use

$$\mathbf{\log_{10} K_{SO4,1}° = 7.6 \pm 0.5}.$$

This recommendation is strongly supported by the fact that similar formation constants and particularly nearly identical $\Delta_2 \log_{10} K$'s are proposed for the sulphate complexes of other tetravalent actinides:

	Th(IV)	U(IV)	Np(IV)	Pu(IV)
	FELMY & RAI (1992)	GRENTHE et al. (1992)	LEMIRE et al. (2001)	LEMIRE et al. (2001)
$\log_{10} K_{SO4,1}°$	7.6 ± 0.5 (this work)	6.6 ± 0.2	6.85 ± 0.16	6.89 ± 0.23
$\log_{10} \beta_{SO4,2}°$	11.59	10.5 ± 0.2	11.05 ± 0.27	11.14 ± 0.34

We end up with recommending the following constants for sulphate complexes:

$$\mathbf{\log_{10} K_{SO4,1}°} \quad = \quad \mathbf{7.6 \pm 0.5} \qquad \text{(this work)}$$
$$\mathbf{\log_{10} \beta_{SO4,2}°} \quad = \quad \mathbf{11.6} \qquad \text{FELMY \& RAI (1992)}$$
$$\mathbf{\log_{10} \beta_{SO4,3}°} \quad = \quad \mathbf{12.4} \qquad \text{FELMY \& RAI (1992)}$$

Since the tetrasulphato thorate ($Th(SO4)_4^{4-}$) is a very weak complex, it is no more included in the database. Solubility data on pure and mixed thorium sulphate solids listed in FELMY & RAI (1992) are not selected, because they are only relevant in very concentrated sulphate solutions. Such data may be subject of a later update.

Note that the Th sulphate complexes as given above do not perfectly fit into the "systematics" of the other tetravalent actinides. However, a debate on the systematics of sulfate complexation (extended to the whole database, i.e. mono-, di-, tri- and tetravalent cations; see also comments in the introduction and in section 5.2) is not yet fully resolved.

Table 5.21.1: Compilation of selected Th(IV) data.

TDB Version 05/92

TDB Version 01/01

Name	$\Delta_f G_m°$	$\Delta_f H_m°$	Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$S_m°$	Species
H2(G)			H2	**0.0**	**0.0**	**130.680±0.003**	$H_2(g)$
			Th(cr)	**0.0**	**0.0**	**51.8±0.5**	Th(cr)
TH+4	-705.0	-769.0	Th+4	**-704.6**	**-769.0** →	**-425.6**	Th^{4+}

Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	Reaction
THOH+3	-3.2	24.895	ThOH+3	**$-2.4±0.5$**	$Th^{4+} + H_2O(l) \Leftrightarrow ThOH^{3+} + H^+$
THOH2+2	-6.95	57.739			$Th^{4+} + 2\,H_2O(l) \Leftrightarrow Th(OH)_2^{2+} + 2\,H^+$
THOH3+	-11.7	85.354			$Th^{4+} + 3\,H_2O(l) \Leftrightarrow Th(OH)_3^+ + 3\,H^+$
THOH4	-15.9	103.345	Th(OH)4	**$-18.4±0.6$**	$Th^{4+} + 4\,H_2O(l) \Leftrightarrow Th(OH)_4(aq) + 4\,H^+$
TH2OH2+6	-6.1	61.923			$2\,Th^{4+} + 2\,H_2O(l) \Leftrightarrow Th_2(OH)_2^{6+} + 2\,H^+$
TH4OH8+8	-21.1	241.835			$4\,Th^{4+} + 8\,H_2O(l) \Leftrightarrow Th_4(OH)_8^{8+} + 8\,H^+$
TH6OH15+9	-36.7	453.546			$6\,Th^{4+} + 15\,H_2O(l) \Leftrightarrow Th_6(OH)_{15}^{9+} + 15\,H^+$
THCl+3	1.1	-0.837			$Th^{4+} + Cl^- \Leftrightarrow ThCl^{3+}$
THCl2+2	0.8	87.446			$Th^{4+} + 2\,Cl^- \Leftrightarrow ThCl_2^{2+}$

Table 5.21.1: continued

TDB Version 05/92   **TDB Version 01/01**

Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	Reaction
THCl3+	1.65	65.898			$Th^{4+} + 3\ Cl^- \Leftrightarrow ThCl_3^+$
THCl4	1.26	51.463			$Th^{4+} + 4\ Cl^- \Leftrightarrow ThCl_4(aq)$
THF+3	8	−5.858	ThF+3	**8.0**	$Th^{4+} + F^- \Leftrightarrow ThF^{3+}$
THF2+2	14.2	−8.786	ThF2+2	**14.2**	$Th^{4+} + 2\ F^- \Leftrightarrow ThF_2^{2+}$
THF3+	18.9	−12.552	ThF3+	**18.9**	$Th^{4+} + 3\ F^- \Leftrightarrow ThF_3^+$
THF4	22.3	−15.899	ThF4	**22.3**	$Th^{4+} + 4\ F^- \Leftrightarrow ThF_4(aq)$

Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	Reaction
THCO3+2	0.671	0			$Th^{4+} + HCO_3^- \Leftrightarrow ThCO_3^{2+} + H^+$
			Th(CO3)5-6	**29.8±1.1**	$Th^{4+} + 5\ CO_3^{2-} \Leftrightarrow Th(CO_3)_5^{6-}$
			Th(CO3)(OH)3-	**−3.1±1.0**	$Th^{4+} + CO_3^{2-} + 3\ H_2O(l) \Leftrightarrow Th(CO_3)(OH)_3^- + 3\ H^+$
THHPO4+2	13.199	−0.462	ThHPO4+2	**13±1**	$Th^{4+} + HPO_4^{2-} \Leftrightarrow ThHPO_4^{2+}$
THH2PO4+3	11.749	68.574			$Th^{4+} + HPO_4^{2-} + H^+ \Leftrightarrow ThH_2PO_4^{3+}$
THH3PO4+4	11.249	71.921			$Th^{4+} + HPO_4^{2-} + 2\ H^+ \Leftrightarrow ThH_3PO_4^{4+}$
THH2PO42	26.397	−13.686			$Th^{4+} + 2\ HPO_4^{2-} \Leftrightarrow Th(HPO_4)_2(aq)$

Table 5.21.1: continued

TDB Version 05/92			TDB Version 01/01		
Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	Reaction
THH4PO42+2	23.317	13.301			$Th^{4+} + 2\ HPO_4^{2-} + 2\ H^+ \Leftrightarrow Th(H_2PO_4)_2^{2+}$
THH3PO43-2	34.946	−21.889			$Th^{4+} + 3\ HPO_4^{2-} + \Leftrightarrow Th(HPO_4)_3^{2-}$
THNO3+3	0.94	0			$Th^{4+} + NO_3^- \Leftrightarrow ThNO_3^{3+}$
THNO32+2	1.97	0			$Th^{4+} + 2\ NO_3^- \Leftrightarrow Th(NO_3)_2^{2+}$
THSO4+2	5.45	15.481	ThSO4+2	**7.6±0.5**	$Th^{4+} + SO_4^{2-} \Leftrightarrow ThSO_4^{2+}$
THSO42	9.75	31.38	Th(SO4)2	**11.6**	$Th^{4+} + 2\ SO_4^{2-} \Leftrightarrow Th(SO_4)_2(aq)$
THSO43-2	10.5	48.953	Th(SO4)3-2	**12.4**	$Th^{4+} + 3\ SO_4^{2-} \Leftrightarrow Th(SO_4)_3^{2-}$
THSO44-4	8.5	54.81			$Th^{4+} + 4\ SO_4^{2-} \Leftrightarrow Th(SO_4)_4^{4-}$
Name	$\log_{10}K_{s,0}°$	$\Delta_f H_m°$	Name	$\log_{10}K_{s,0}°$	Reaction
THO2	6.3	−113.805	ThO2(s)	**9.9±0.8**	$ThO_2(s) + 4\ H^+ \Leftrightarrow Th^{4+} + 2\ H_2O(l)$
TH(OH)4CR	13.8	−31.38			$Th(OH)_4(cr) + 4\ H^+ \Leftrightarrow Th^{4+} + 4\ H_2O(l)$
THF4CR	−30.1	−11.715	ThF4(cr)	**−30.2**	$ThF_4(cr) \Leftrightarrow Th^{4+} + 4\ F^-$
THF4_AQ	−33.1	29.916			$ThF_4 \cdot 2.5H_2O(s) \Leftrightarrow Th^{4+} + 4\ F^- + 2.5\ H_2O(l)$
THH2PO42CR	−26.797	−20.832			$Th(HPO_4)_2 \cdot 4H_2O(s) \Leftrightarrow Th^{4+} + 2\ HPO_4^{2-} + 4\ H_2O(l)$

Table 5.21.2: Compilation of Th(IV) hydrolysis and carbonate data. For comparison and in order to check for consistency, a selection of additional actinide(IV) data is also given (those selected by the present review team are typed in bold face).

Reaction	Constant	Th(IV)		U(IV)		Np(IV)		Pu(IV)	
$AnO_2(am) + 2H_2O(l)$ $\Leftrightarrow An(OH)_4^0$ (solubility)	$\log_{10}*K_{s,4}$	**8.5 ± 0.6**	**NECK & KIM 1999**	-8.5 ± 1.0 **-9 ± 1** -8.7 ± 0.4	NECK & KIM 1999 **CHAPTER 5.23.3.1.3** YAJIMA et al. 1995	**–8.3 ± 0.3** < –9.0 –9.0 ± 1.0	**LEMIRE et al. 2001** NAKAYAMA et al. 1996 NECK & KIM 1999	–11.0 ± 1.1 –10.4 ± 0.5	NECK & KIM 1999 RAI et al. 1999A
$AnO_2(am) + 4H^+$ $\Leftrightarrow An^{4+} + 2H_2O(l)$	$\log_{10}*K_{s,0}$	8.8 ± 1.0 9.37 ± 0.13 10.5 ± 0.5 3.1 3.6 ± 0.9 5.3 6.3 ≈6.6	NECK & KIM 1999 (I = 0) ÖSTHOLS et al. 1994 (0.5 M NaClO4) RYAN & RAI 1987 (0.1 M NaClO4) MOON 1989 (0.5 M NaClO4) NECK 1998, BUNDSCHUH 1999 (I = 0) GRENTHE & LAGERMANN 1991, based on (–14.3/ –9.0) SMITH & MARTELL 1976 BAES & MESMER 1976 (I = 0 ?)	**0 ± 2** 0.8 ± 1.0 0.34 ± 0.4 2.56	**CHAPTER 5.23.3.1.3** NECK & KIM 1999 YAJIMA et al. 1995 RAI et al. 1998	**1.53 ± 1.00** –0.7 ± 0.5	**LEMIRE et al. 2001** NECK & KIM 1999	**–2.0 ± 1.0** –2.5 ± 1.1 –2.3 ± 0.5	**LEMIRE et al. 2001** NECK & KIM 1999 CAPDEVILA & VITORGE 1998
$An^{4+} + H_2O(l)$ $\Leftrightarrow An(OH)^{3+} + H^+$	$\log_{10}*\beta_{101}$	–2.3 –4.35±0.09 –3.2 –4.15±0.04 –3.3 ± 0.10 –2.98±0.01	NECK & KIM 1999 (I = 0) GRENTHE & LAGERMANN 1991 (3 M NaClO4) LANGMUIR & HERMAN 1980 BAES et al. 1965 (1 M NaClO4) EKBERG et al. 2000 (1 M NaClO4) BROWN et al. 1983 (0.1 M KNO3)	**–0.54±0.06** –0.4 ± 0.2	**GRENTHE et al. 1992** NECK & KIM 1999	**–0.29 ± 1.0** 0.5 ± 0.2	**LEMIRE et al. 2001** NECK & KIM 1999, from DUPLESSIS & GUILLAUMONT 1977	**–0.78±0.60** 0.6 ± 0.2	**LEMIRE et al. 2001** NECK & KIM 1999, from METIVIER & GUILLAUMONT 1972

Table 5.21.2: continued

Reaction	Constant	Th(IV)		U(IV)		Np(IV)		Pu(IV)	
$An^{4+} + 2H_2O(l)$ $\Leftrightarrow An(OH)_2^{2+} + 2H^+$	$\log_{10}{}^*\beta_{102}$	-5.5 ± 1.0 -7.81 -8.6 ± 0.1	NECK & KIM 1999 (I = 0) BAES & MESMER 1976 (1 M NaClO4) EKBERG et al. 2000 (1 M NaClO4)	(-0.5 ± 1.0)	NECK & KIM 1999 (estimate)	0.3 ± 0.3	NECK & KIM 1999, from DUPLESSIS & GUILLAUMONT 1977	0.6 ± 0.3	NECK & KIM 1999, from METIVIER & GUILLAUMONT 1972
$An^{4+} + 3H_2O(l)$ $\Leftrightarrow An(OH)_3^+ + 3H^+$	$\log_{10}{}^*\beta_{103}$	-10.5 ± 1.0 -14.2 -12.3 ± 0.2	NECK & KIM 1999 (I = 0) EKBERG et al. 2000 (1M NaClO4; estimated) GRENTHE & LAGERMANN 1991 (3 M NaClO4)	(-3.8 ± 1.0)	NECK & KIM 1999 (estimate)	(-2.8 ± 1.0)	NECK & KIM 1999 (estimate)	-2.3 ± 0.4	NECK & KIM 1999, from METIVIER & GUILLAUMONT 1972
$An^{4+} + 4H_2O(l)$ $\Leftrightarrow An(OH)_4^0 + 4H^+$	$\log_{10}{}^*\beta_{104}$	-17.3 ± 1.2 -16.65 ± 0.04 -15.9 -19.4 ± 0.5 < -19.7	NECK & KIM 1999 (I = 0) GRENTHE & LAGERMANN 1991 (3 M NaClO4) LANGMUIR & HERMAN 1980 EKBERG et al. 2000 (1 M NaClO4) RYAN & RAI 1987 (0.1 NaClO4)	$\mathbf{-9 \pm 2}$ -9.0 ± 0.5 -9.3 ± 1.4	**CHAPTER 5.23.3.1.3** YAJIMA et al. 1995 NECK & KIM 1999	-8.8 ± 1.0 $\mathbf{-9.8 \pm 1.1}$	NECK & KIM 1999 **LEMIRE** et al. **2001**	-8.5 ± 0.5	NECK & KIM 1999, from METIVIER & GUILLAUMONT 1972
$2An^{4+} + 2H_2O(l)$ $\Leftrightarrow An_2(OH)_2^{6+} + 2H^+$	$\log_{10}{}^*\beta_{202}$	-4.61 -5.10 ± 0.17	BAES & MESMER 1976 (1 m NaClO4) GRENTHE & LAGERMANN 1991 (3 M NaClO4)						
$4An^{4+} + 8H_2O(l)$ $\Leftrightarrow An_4(OH)_8^{8+} + 8H^+$	$\log_{10}{}^*\beta_{408}$	-19.01 -19.1 ± 0.1 -19.6 ± 0.2	BAES & MESMER 1976 (1 m NaClO4) EKBERG et al. 2000 (1 M NaClO4) GRENTHE & LAGERMANN 1991 (3 M NaClO4)						
$6An^{4+} + 15H_2O(l)$ $\Leftrightarrow An_6(OH)_{15}^{9+} + 15H^+$	$\log_{10}{}^*\beta_{6015}$	-36.76 -36.6 ± 0.2	BAES & MESMER 1976 (1 M NaClO4) EKBERG et al. 2000 (1 M NaClO4)						

Table 5.21.2: continued

Reaction	Constant	Th(IV)	U(IV)	Np(IV)	Pu(IV)
$AnO_2(am)+5CO_3^{2-}+4H^+$ $\Leftrightarrow An(CO_3)_5^{6-}+2H_2O(l)$	$\log_{10}{}^*K_{s,50}$	42.12±0.32 ÖSTHOLS et al. 1994 (0.5 M NaClO4) 37.6 FELMY et al. 1997 (I = 0)	33.8 RAI et al. 1998	34.85 RAI et al. 1999	33.32 RAI et al. 1999A
$An^{4+} + 4CO_3^{2-}$ $\Leftrightarrow An(CO_3)_4^{4-}$	$\log_{10}\beta_{40}$		**35.22±1.25 GRENTHE et al. 1992**	**36.69±1.11 LEMIRE et al. 2001** 34.3 ± 1.13 CAPDEVILA et al. 1996 34.5 NECK & KIM 2000	
$An^{4+} + 5CO_3^{2-}$ $\Leftrightarrow An(CO_3)_5^{6-}$	$\log_{10}\beta_{50}$	33.2 JOÃO et al. 1987 recalc. by ÖSTHOLS et al. 1994 32.75±0.35 ÖSTHOLS et al. 1994 (0.5 M NaClO4)	34.0 ± 0.9 GRENTHE et al. 1992 **34.1 ± 1.0 SILVA et al. 1995**	**35.62±1.15 LEMIRE et al. 2001** 32.8 NECK & KIM 2000	32.2 ± 2 VITORGE 1995 33.0 ± 1.3 CAPDEVILA et al. 1996 35.8 ± (>1) RAI et al. 1999A
$AnO_2(am)+ CO_3^{2-}$ $+H^++H_2O(l)$ $\Leftrightarrow An(OH)_3CO_3^-$	$\log_{10}{}^*K_{s,13}$	6.11 ± 0.19 ÖSTHOLS et al. 1994 (0.5 M NaClO4) 6.78 FELMY et al. 1997 (I = 0)			
$AnO_2(am) + 2HCO_3^-$ $\Leftrightarrow An(OH)_2(CO_3)_2^{2-}$	$\log_{10}{}^*K_{s,22}$		–4.8 RAI et al. 1998	–4.44 RAI et al. 1999	–4.75 RAI et al. 1999A

5.21.8 References

BAES JR C.F., MESMER R.E. (1976): The Hydrolysis of Cations. John Wiley and Sons, New York, Reprint Edition 1986.

BUNDSCHUH T., KNOPP R., MÜLLER R., KIM J.I., NECK V., FANGHÄNEL TH. (2000): Application of LIBD to the determination of the solubility product of thorium(IV)-colloids. Radiochimica Acta, 88, p.625-629.

COX J.D., WAGMAN D.D., MEDVEDEV V.A. (1989): CODATA Key Values for Thermodynamics. Hemisphere Publishing Corp., New York.

EKBERG C., ALBINSSON Y., COMARMOND M.J., BROWN P.L. (2000): Studies on the Complexation Behavior of Thorium(IV). 1. Hydrolysis Equilibria. J. Solution Chemistry, 29(1), p.63-86.

FELMY A.R., RAI D., MASON M.J. (1991): The Solubility of Thorium(IV) Oxide in Chloride Media: Development of an Aqueous Ion-Interaction Model. Radiochimica Acta, 55, 177-185.

FELMY A.R., RAI D., MASON M.J. (1993): Solid Phase Precipitates and Anionic Aqueous Thorium Fluoride Complexes in the Na-NH$_4$-Th-F-H$_2$O System to High Concentrations. Radiochimica Acta, 62, 133-139.

FELMY A.R., RAI D., STERNER S.M., MASON M.J., HESS N.J., CONRADSON S.D. (1997): Thermodynamic Models for Highly Charged Aqueous Species: Solubility of Th(IV) Hydrous Oxide in Concentrated NaHCO$_3$ and Na$_2$CO$_3$ Solutions. J. Solution Chemistry, 26/3, 233-248.

FELMY R., RAI D. (1992): An Aqueous Thermodynamic Model for a High Valence 4:2 Electrolyte Th^{4+}-SO$_4^{2-}$ in the System Na$^+$-K$^+$-Li$^+$-NH$_4^+$-Th^{4+}-SO$_4^{2-}$-HSO$_4^-$-H$_2$O to High Concentration. J. Solution Chemistry, 21/5, 407-423.

GRENTHE I., FUGER J., KONINGS R.J.M., LEMIRE R.J., MULLER A.B., NGUYEN-TRUNG C., WANNER H. (1992): Chemical Thermodynamics Vol. 1: Chemical Thermodynamics of Uranium. OECD/NEA, North-Holland Elsevier, ISBN 0 444 89381 4.

GRENTHE I., LAGERMANN B. (1991): Studies on Metal Carbonate Equilibria. 23. Complex Formation in the Th(IV)-H$_2$O-CO$_2$(g) System. Acta Chemica Scandinavia, 45, 231-238.

GRENTHE I., PUIGDOMENECH I. (1997): Modelling in Aquatic Chemistry. Nuclear Energy Agency, OECD Publications 725p.

HESS N.J., FELMY A.R., RAI D., CONRADSON S.D. (1997): Characterization of Th Carbonate Solutions Using XAS and Implications for Thermodynamic Modeling. Mat. Res. Soc. Symp. Proc., 465, 729-734.

HUMMEL W., GLAUS M.A., VAN LOON L.R. (2000): Trace metal-humate interactions. II. The "conservative roof" model and its application. Applied Geochemistry, 15, 975-1001.

LANGMUIR D., HERMAN J.S., (1980): The Mobility of Thorium in Natural Waters at Low Temperatures. Geochimica et Cosmochimica Acta, 44, 1753-1766.

LEMIRE R.J., FUGER J., NITSCHE H., POTTER P., RAND M.H., RYDBERG J., SPAHIU K., SULLIVAN J.C., ULLMAN W.J., VITORGE P., WANNER H. (2001): Chemical Thermodynamics of Neptunium & Plutonium. Chemical Thermodynamics, Vol. 4, NEA/OECD, Paris. 845 pp.

MOON H.C. (1989): Equilibrium Ultrafiltration of Hydrolysed Thorium(IV) Solutions. Bull. Korean Chem. Soc., 10, 270-272.

NECK V., KIM J.I. (1999): Solubility and Hydrolysis of Tetravalent Actinides. Forschungszentrum Karlsruhe, Wissenschaftliche Berichte FZKA 6350.
　　　Additional information on Th are provided in the very recent paper: NECK V., KIM J.I. (2001): Solubility and Hydrolysis of Tetravalent Actinides. Radiochimica Acta, 89,1-16.

NECK V., KIM J.I. (2000): An Electrostatic Approach for The Prediction of Actinide Complexation Constants with Inorganic Ligands – Application to Carbonate Complexes. Radiochimica Acta, 88, 815-822.

ÖSTHOLS E., BRUNO J., GRENTHE I. (1994): On the influence of carbonate mineral dissolution: III. The solubility of microcrystalline ThO_2 in CO_2-H_2O media. Geochimica et Cosmochimica Acta, 58, 613-623.

PEARSON F.J., BERNER U., HUMMEL W. (1992): Nagra Thermochemical Data Base II. Supplemental Data 05/92. Nagra Technical Report NTB 91-18, Nagra, Wettingen, Switzerland 284p.

RAI D., FELMY A.R., HESS N.J., MOORE D.A., YUI M. (1998): A Thermodynamic Model for the Solubility of UO_2(am) in the Aqueous K^+-Na^+-HCO_3^--CO_3^{2-}-OH^--H_2O system. Radiochimica Acta, 82, 17-25.

RAI D., FELMY A.R., MOORE D.A., MASON M.J. (1995): The Solubility of Th(IV) and U(IV) Hydrous Oxides in Concentrated $NaHCO_3$ and Na_2CO_3 Solutions. Mat. Res. Soc. Symp. Proc., 353, 1143-1150.

RAI D., HESS N.J., FELMY A.R., MOORE D.A., YUI M. (1999): A Thermodynamic Model for the Solubility of NpO_2(am) in the Aqueous K^+-HCO_3^--CO_3^--OH^--H_2O System, Radiochimica Acta, 84 p.159-170.

RAI D., HESS N.J., FELMY A.R., MOORE D.A., YUI M., VITORGE P. (1999A): A Thermodynamic Model for the Solubility of PuO_2(am) in the Aqueous K^+-HCO_3^--CO_3^--OH^--H_2O System. Radiochimica Acta, 86, 89-99.

RAI D., MOORE D.A., OAKES C.S., YUI M. (2000): Thermodynamic model for the solubility of thorium dioxide in the Na^+-Cl^--OH^--H_2O system at 23 °C and 90 °C. Radiochimica Acta, 88, 297-306.

RARD J.A., RAND M.H., ANDEREGG G., WANNER H. (1999): Chemical Thermodynamics Vol. 3: Chemical Thermodynamics of Technetium. OECD/NEA, North-Holland Elsevier, ISBN 0 444 50378-1.

RYAN J.L., RAI D. (1987): Thorium(IV) Hydrous Oxide Solubility. Inorganic Chemistry, 26, 4140-4142.

SERNE R.J., RAI D., MARTIN P.F., FELMY A.R., RAO L., UETA S. (1996): Leachability of Nd, U, Th, and Sr from Cements in a CO_2 free Atmosphere. Mat. Res. Soc. Symp. Proc., 412, 459-467.

SILVA R.J., BIDOGLIO G., RAND M.H., ROBUCH P., WANNER H., PUIGDOMENECH I. (1995): Chemical Thermodynamics Vol. 2: Chemical Thermodynamics of Americium. OECD/NEA, North-Holland Elsevier, ISBN 0 444 82281 X.

WIERCZINSKI B., HELFER S., OCHS M., SKARNEMARK G. (1998): Solubility measurements and sorption studies of thorium in cement pore water. J. Alloys and Compounds, 271-273, 272-276.

YAJIMA T., KAWAMURA Y., UETA S. (1995): Uranium(IV) solubility and hydrolysis constants under reduced conditions. Mat. Res. Soc. Symp. Proc., 353, 1137-1142.

Indirectly cited References

Some of the references were not available during writing of this chapter and were not explicitly studied (due to deadlines). These references were given as sources in the articles cited under the heading *references*. In order to facilitate the tracing back of data and to clearly point out which reports have been studied in detail and which not, these articles are given under the heading *indirectly cited references* .

AHRLAND S., LILJENZIN J.O., RYDBERG J. (1973): Solution chemistry (of the actinides). In: Comprehensive Inorganic Chemistry, Vol. 5, Actinides, Master Index. Pergamon Press p.645-635.

ALLEN K.A., MCDOWELL W.J. (1963): The thorium sulfate complexes from di-*n*-decylamine sulfate extraction equilibria. J. Phys. Chem., 65, 1139-1140.

BAES C.F., MEYER N.J., ROBERTS C.E. (1965). Inorganic Chemistry, 4, 518.

BARRE M. (1912). Bull. Soc. Chim., 4/11, 646.

BAUMANN E.W. (1970): Thermodynamic parameters of thorium-fluoride complexes from measurements with the fluoride-selective electrode at 5, 25 and 45 °C. J. Inorg. Nucl. Chem., 32, 3823-3830.

BROWN P.L., ELLIS J., SILVA R.N. (1983): The Hydrolysis of Metal Ions Part 5: Thorium(IV). J. Chem. Soc. Dalton Trans., 31.

BUNDSCHUH T. (1999): Entwicklung und Anwendung der Laser-induzierten Breakdown-detektion zur Quantifizierung aquatischer Kolloide und Actinidenkolloide. Thesis, Institut für Radiochemie, Technische Universität München, and, BUNDSCHUH T., KIM J.I. (1999): Report FZKA 6273, Forschungszentrum Karlsruhe.

CAPDEVILA H., VITORGE P. (1998): Solubility Product of Pu(OH)$_4$(am), Radiochimica Acta, 82, 11-16.

CAPDEVILA H., VITORGE P., GIFFAULT E., DELMAU L. (1996): Spectrophotometric Study of the Dissociation of the Pu(IV) Carbonate Limiting Complex. Radiochimica Acta, 74, 93.

CIAVATTA L. (1990): The specific interaction theory in equilibrium analysis: Some empirical rules for estimating interaction coefficients of metal ion complexes. Ann. Chim. Roma, 80, 255-263.

DUPLESSIS J., GUILLAUMONT R. (1977): Hydolyse du Neptunium tétravalent, Radiochem. Radioanal. Lett., 31, 293.

FUGER J., OETTING F.L. (1976): The Chemical Thermodynamics of Actinide Elements and Compounds Part 2: *The Actinide Aqueous Ions*. IAEA, Vienna.

JOÃO A., BIGOT S., FROMAGE F. (1987): Etudes des carbonates complexes des éléments IVB 1- Détermination de la constante de stabilité du pentacarbonatothorate(IV). Bull. Soc. Chim. Fr., 1, 42-44.

KATZ J.J., SEABORG G.T., MORSS L.R. (1957): The Chemistry of the Actinide Elements (2nd ed. 1986). Chapman and Hall, 1674p.

LINKE W.F. (1965): Solubilities of Inorganic and Metal Organic Compounds (4th ed.). Am. Chem. Soc. Washington D.C.

METIVIER H., GUILLAUMONT R., (1972): Hydrolyse du Plutonium tétravalent, Radiochem. Radioanal. Lett., 10, 27.

MOSKVIN A.I., ESSEN L.N., BUKHTIYAROVA T.N. (1967): The formation of thorium(IV) and uranium(IV) complexes in phosphate solutions. Russ. J. Inorg. Chem., 12, 1794-1795.

NAKAYAMA S., YAMAGUCHI T., SEKINE K. (1996): Solubility of Neptunium(IV) Hydrous Oxide in Aqueous Solutions. Radiochimica Acta, 74, 15-19.

NECK V. (1998): Solubility and Hydrolysis of Tetravalent Actinides. Statusseminar INE, Forschungszentrum Karlsruhe.

REARDON E.J. (1988). J. Phys. Chem., 92, 6426.

SMITH R.M., MARTELL A.E. (1976): Critical stability constants: Volume 4, Inorganic complexes. Plenum Press, New York.

VITORGE P. (1995): Neptunium en solution carbonate concentrée réductrice: bibliographie pour l'OECD-AEN-TDB. Report CEA-BIB-246, Centre d'Etudes Nucléaires de Fontenay-aux-Roses, Fontenay-aux-Roses, 95p.

WAGMAN D.D., SCHUMM R.H., PARKER V.B. (1977): A computer-assisted evaluation of the thermochemical data of compounds of thorium. NBSIR 77-1300, National Bureau of Standards, Department of Commerce, USA, 93p.

WIRTH F. (1912). Z. Anorg. Chem., 76, 174.

ZEBROSKI E.L., ALTER H.W., HEUMANN F.K. (1951). J. Am. Chem. Soc., 73, 5646.

ZIELEN A.J. (1959). J. Am. Chem. Soc., 81, 5022.

5.22   Tin

Most of the tin data compiled in the Nagra Thermochemical Database 05/92 (PEARSON et al. 1992) had been taken (as a block of data) from the HATCHES 3.0 database (CROSS & EWART 1991). All data from the HATCHES database have been discarded in this update. We primarily concentrate on data relevant for radioactive waste management and/or other environmental systems. In most cases, such chemical systems have pH values above 7 and an ionic strength not higher than about sea-water (~ 0.7 M).

The present chapter concentrates on a recent review of the thermodynamics of tin by LOTHENBACH et al. (1999), which serves as an excellent starting point for our update. It provides a very comprehensive summary of experimental data from which qualified estimates for many relevant tin equilibria can be derived. The following sections discuss our selections based on these data. Since proper documentation is a very important issue of our update, the references as listed in LOTHENBACH et al. (1999) are include where appropriate. We hope that this "redundancy" (instead of just saying "*according to references given in ....*") will substantially facilitate further steps in the update procedure.

5.22.1   Basic values

The very basic thermodynamic data,

$S_m° (H_2(g), 298.15\ K)$ $= 130.680 \pm 0.003$ $J\ mol^{-1}\ K^{-1}$,

$S_m° (Sn(cr), 298.15\ K)$ $= 51.18 \pm 0.08$ $J\ mol^{-1}\ K^{-1}$,

$S_m° (Sn^{2+}, aq, 298.15\ K)$ $= -16.7 \pm 4.0$ $J\ mol^{-1}\ K^{-1}$,

$\Delta_f H_m° (Sn^{2+}, aq, 298.15\ K)$ $= -8.9 \pm 1.0$ $kJ\ mol^{-1}$,

taken from COX et al. (1989) would lead to $\Delta_f G_m°(Sn^{2+}, aq, 298.15\ K) = -27.6 \pm 1.6\ kJ\ mol^{-1}$, the value reported by the NEA (SILVA et al. 1995). However, for the sake of consistency throughout the presented set of data in this report we prefer to select the value directly derived from reaction data (see section 5.22.2):

$\Delta_f G_m° (Sn^{2+}, aq, 298.15\ K)$ $= -26.43 \pm 0.46$ $kJ\ mol^{-1}$.

With the fundamental relation $\Delta_f G_m° = \Delta_f H_m° - T\cdot\Delta_f S_m°$ and using $\Delta_f S_m°(Sn^{2+},298.15\ K) = S_m°(Sn^{2+},298.15\ K) - S_m°(Sn(cr),298.15\ K) + S_m°(H_2(g),298.15\ K)$ we obtain

$\Delta_f H_m° (Sn^{2+}, aq, 298.15\ K)$ $= -7.7 \pm 1.3$ $kJ\ mol^{-1}$.

Note that from a statistical point of view both values ($\Delta_f G_m°$ and $\Delta_f H_m°$) do not differ from those given in COX et al. (1989).

5.22.2   Redox

Based on the data given in Table 5.22.2, LOTHENBACH et al. (1999) obtain $\log_{10} K° = -4.63$ for the equilibrium $Sn^{2+} + 2\ e^- \Leftrightarrow Sn(cr)$ using the SIT formalism. Their regression of $\log_{10} K - 4D$ vs. ionic strength results $\Delta\varepsilon = -0.25$, but the re-evaluation (Fig. 5.22.2; excluding the data point from RICCOBONI et al. (1949) measured in KCl, see Table 5.22.2) gives a different $\Delta\varepsilon$:

$$Sn^{2+} + 2\ e^- \Leftrightarrow Sn(cr) \quad \mathbf{\log_{10} K° = -4.63 \pm 0.08} \qquad \mathbf{\Delta\varepsilon(ClO_4^-) = -0.32 \pm 0.13}$$

Table 5.22.2: Experimental $\log_{10} K$ values for the reaction $Sn^{2+} + 2\ e^- \Leftrightarrow Sn(cr)$ as compiled in LOTHENBACH et al. (1999, Table 4.10.)

$\log_{10} K$	I(M)	Medium	Reference	Comments
–5.06	0.08	HClO$_4$	PRYTZ (1928)	logK recalc. by LOTHENBACH et al. (1999)
–5.11	0.2	HClO$_4$	PRYTZ (1928)	logK recalc. by LOTHENBACH et al. (1999)
–5.11	0.35	HClO$_4$	PRYTZ (1928)	logK recalc. by LOTHENBACH et al. (1999)
–5.24	1	KCl	RICCOBONI et al. (1949)	not used in regression
–5.13	1	NaClO$_4$ [1]	BOND & TAYLOR (1970)	logK recalc. by LOTHENBACH et al. (1999)

[1] Since the cation (Na^+) is not considered in the regression, $NaClO_4$ and $HClO_4$ are comparable.

Note that the uncertainties are a consequence of setting the uncertainty of each individual point to $\pm$ 0.1 (the difference of $\log_{10} K$-values measured in 1M KCl and in 1 M NaClO$_4$). The resulting $\Delta\varepsilon$ is equivalent to $-\varepsilon(Sn^{2+}, ClO_4^-)$ and we thus obtain $\mathbf{\varepsilon(Sn^{2+}, ClO_4^-) = 0.32 \pm 0.13}$, which is in good agreement with interaction coefficients for other divalent ions (GRENTHE et al. 1997). The stability constant for the same reaction, if derived from $\Delta_f G_m°(Sn^{2+}, aq, 298.15\ K) = -27.6 \pm 1.6\ kJmol^{-1}$ (COX et al. 1989), is $\log_{10} K° = -4.84 \pm 0.28$.

The relevant redox equilibrium in the tin system is the couple Sn^{2+}/Sn^{4+}. Unfortunately, corresponding data from HUEY & TARTAR (1934) measured in fairly concentrated HCl seem to suffer from the fact that the redox properties cannot be separated from complexation with chloride.

LOTHENBACH et al. (1999) state that a tentative value of $\log_{10}K \sim 5$ "*may be used*" for the equilibrium $Sn^{4+} + 2\ e^- \Leftrightarrow Sn^{2+}$, but they also admit that this value "*is debatable*" since chloride complex formation was not considered.

VASIL'EV et al. (1979) performed a careful emf-study of the $Sn^{4+} + 2\ e^- \Leftrightarrow Sn^{2+}$ equilibrium in 2, 3 and 4 M $HClO_4$. Unfortunately they used $SnCl_4(l)$ and $SnCl_2(cr)$ as starting materials, which again poses the problem of separating chloride complexation (and Sn(IV)-hydrolysis) from redox properties. We re-interpreted the VASIL'EV et al. (1979)-data (see Fig. 5.22.3 & 5.22.4) and obtained $E°(Sn^{4+}/Sn^{2+}) = +289 \pm 6$ mV. In order to perform the re-interpretation we used

i)   the tin(II) chloride complex formation constants as given in section 5.22.8,

ii) $\varepsilon(Cl^-,Na^+) = 0.03 \pm 0.01$,

iii) $\varepsilon(Cl^-,H^+) = 0.12 \pm 0.01$,

iv) $\varepsilon(SnCl_2(aq),\mathbf{Na}ClO_4(aq)) = \varepsilon(SnCl_2(aq),\mathbf{H}ClO_4(aq))$ and

v)   estimated that $\varepsilon(\ SnCl_3^-,\mathbf{H}^+) - \varepsilon(\ SnCl_3^-,\mathbf{Na}^+) = 0.10 \pm 0.05$.

Tin(IV)-hydrolysis at low pH was used as proposed in VASIL'EV et al. (1979). The above $E°(Sn^{4+}/Sn^{2+})$ redox potential leads to $\log_{10}K° = 9.8\pm0.2$ ($\Delta_fG_m°(Sn^{4+}$,aq, 298.15 K$) = +29.4\pm1.3$ kJ mol^{-1}) and the regression versus m_{ClO4} indicates a difference $\varepsilon(\mathbf{Sn^{4+}},ClO_4^-) - \varepsilon(\mathbf{Sn^{2+}},ClO_4^-)$ very close to zero.

Due to the obvious need for further clarification we do not select a formation constant for the basic redox equilibrium (although we would prefer the results derived from the measurements of VASIL'EV et al. (1979) in $HClO_4$). As a consequence of this "non-selection", one i) needs to define two independent master species for the same element (one for tin(II) and one for tin(IV)) and ii) cannot predict tin-behaviour as a function of the redox potential.

However, for the reader who wants to couple Sn(II) with Sn(IV)(OH)$_4$ (the most relevant tin(IV)-species in neutral to slightly alkaline environments) we provide the following additional information:

NAZARENKO et al. (1971) give $\log_{10}K = 0.87$ for the equilibrium $Sn(OH)_4(aq) + 4\ H^+ \Leftrightarrow Sn^{4+} + 4\ H_2O(l)$, measured at 25 °C in 1 M KNO_3, but the required SIT corrections to obtain $\log_{10}K°$ for this reaction are quite large. The $\Delta z^2 \cdot D$-term is about 2.5 $\log_{10}$-units and the $\Delta\varepsilon \cdot m_{ClO4}$-term about -0.2 $\log_{10}$-units. Thus, one ends up with $\log_{10}K° \sim -1.4 \pm x$ for the above hydrolysis reaction (not in-

cluded in the update, see section 5.22.3). When combining the hydrolysis equilibrium with Sn^{4+} + $H_2(g) \Leftrightarrow Sn^{2+} + 2\,H^+$ one obtains

$$Sn(OH)_4(aq) + 2\,H^+ + H_2(g) \Leftrightarrow Sn^{2+} + 4\,H_2O(l),$$
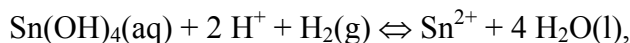
with either $\log_{10}K° \sim 3.6 \pm x$ ($\log_{10}K°(Sn^{4+}/Sn^{2+}) = 5$) or $\log_{10}K° \sim 8.4 \pm x'$ ($\log_{10}K°(Sn^{4+}/Sn^{2+}) = 9.8$). Note that the compilation of PHILLIPS et al. (1988) gives $\log_{10}K° = 4.41$ and that of HOUSE & KELSALL (1984) gives $\log_{10}K° = 7.02$ for this combined reaction. Nothing is known about the uncertainties x and x', but we estimate that the order of magnitude is ~1 for both.

5.22.3 Tin(IV) hydrolysis

The predominant species in the pH range [2 … 7] is $Sn(OH)_4(aq)$ and it makes sense to use this species as the master species for tin(IV). Only one study investigates the hydrolysis of tin(IV) under acidic conditions at ambient temperature (NAZARENKO et al. 1971). The present author agrees with LOTHENBACH et al. (1999)'s conclusion that the $\log_{10}\beta$ - values derived from this study can be considered as estimates, but not as values which fulfil the criteria for an updated database. Therefore, no formation constants for the species Sn^{4+}, $Sn(OH)^{3+}$, $Sn(OH)_2^{2+}$ and $Sn(OH)_3^+$ are proposed. Experimental data for tin(IV) hydrolysis above pH 7 are listed in Tables 5.22.3 & 5.22.4:

Table 5.22.3: Experimental $\log_{10}K$ values for the reaction $Sn(OH)_4(aq) + H_2O(l) \Leftrightarrow Sn(OH)_5^- + H^+$ as compiled in LOTHENBACH et al. (1999, Table 4.2).

$\log_{10}K$	I(M)	Medium	Reference	Comments
−12.4	0.2 - 2.5	NaOH	BARSUKOV & KLINTSOVA (1970)	extrapolated value
−9.06	dil.	NaOH	KURIL'CHIKOVA & BARSUKOV (1970)	T = 100 °C
−7.75	0.1	NaClO₄	AMAYA et al. (1997), ODA & AMAYA (1998)	

Table 5.22.4: Experimental $\log_{10}K$ values for the reaction $Sn(OH)_4(aq) + 2\,H_2O(l) \Leftrightarrow Sn(OH)_6^{2-} + 2\,H^+$ as compiled in LOTHENBACH et al. (1999, Table 4.2).

$\log_{10}K$	I(M)	Medium	Reference	Comments
−18.30	dil.	NaOH	KURIL'CHIKOVA & BARSUKOV (1970)	T = 100 °C
−20.77	dil.	self	KLINTSOVA & BARSUKOV (1973)	T = 200 °C
−20.43	0.25	NaOH	GABE & SRIPATR (1973)	estimate
−17.74	0.1	NaClO$_4$	AMAYA et al. (1997) ODA & AMAYA (1998)	

The most reliable studies seem to be those of AMAYA et al. (1997) and ODA & AMAYA (1998), who measured the solubility of $SnO_2(s)$ from over- and undersaturation in the pH range [2 … 12] in dilute NaClO$_4$ at 25 °C. LOTHENBACH et al. (1999) extrapolated these experimental values to I = 0 using SIT. Thereby, they assumed that $\Delta\varepsilon$ is close to zero for both hydrolysis reactions (actually, $\Delta\varepsilon$ for both equilibria is close to 0.1 and thus $\Delta\varepsilon\cdot I \sim 0.01$, which justifies this approximation). We follow the arguments of LOTHENBACH et al. (1999) and recommend to include

$$Sn(OH)_4(aq) + H_2O(l) \Leftrightarrow Sn(OH)_5^- + H^+ \qquad \mathbf{\log_{10}\beta_{1,5}° = -8.0 \pm 0.3}$$

and

$$Sn(OH)_4(aq) + 2\,H_2O(l) \Leftrightarrow Sn(OH)_6^{2-} + 2\,H^+ \qquad \mathbf{\log_{10}\beta_{1,6}° = -18.4 \pm 0.3}$$
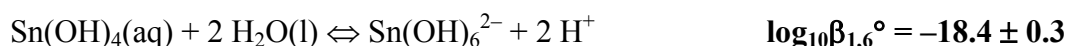
in our update (see Fig. 5.22.1). LOTHENBACH et al. (1999) do not give uncertainties for these equilibria, but since the values were derived from the solubility of $SnO_2(am)$ it seems appropriate to select a similar uncertainty (± 0.3 $\log_{10}$-units, see section 5.22.4). Note that an additional uncertainty arising from neglecting the $\Delta\varepsilon$-correction will not exceed ± 0.1 $\log_{10}$-units, provided that these equilibria are applied for predictions at **ionic strength below ~ 0.5 M.**
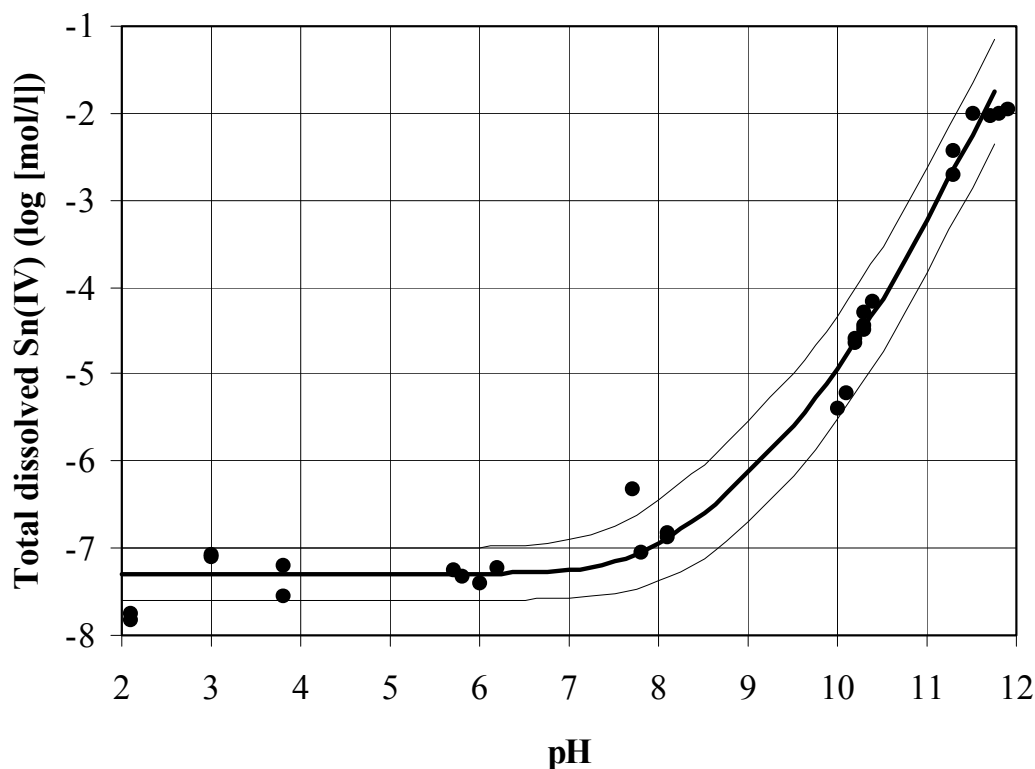
Fig. 5.22.1: Solubility of SnO_2(am). Experimental data (•) are from AMAYA et al. (1997), the solid lines are calculated for $I =$ 0.1M $NaClO_4$ using $\log_{10}K_{s0}^\circ = -7.3 \pm 0.3$, $\log_{10}\beta_{1,5}^\circ = -8.0 \pm 0.3$ and $\log_{10}\beta_{1,6}^\circ = -18.4 \pm 0.3$ selected in this review.

5.22.4 Tin(IV) oxides/hydroxides

According to several authors (FEITKNECHT & SCHINDLER 1963, KURIL'CHIKOVA & BARSUKOV 1970, AMAYA et al. 1997), freshly precipitated $Sn(OH)_4$(s) is amorphous and may exhibit a high solubility. Upon ageing, the precipitate turns into a poorly crystalline product. AMAYA et al. (1997) showed that the solubility of this poorly crystalline product in the pH range [2…7] is similar (within an order of magnitude) to the solubility of a crystalline SnO_2 (cassiterite), whose solubility, measured from undersaturation in the same pH range, was remarkably constant. At present, the study from AMAYA et al. (1997) seems to be the most reliable investigation of cassiterite solubility and LOTHENBACH et al. (1999) recommend to use

$$SnO_2(\text{cassiterite}) + 2\,H_2O(l) \Leftrightarrow Sn(OH)_4(aq) \qquad \qquad \mathbf{\log_{10}K_{so}^\circ = -8.0 \pm 0.2}.$$
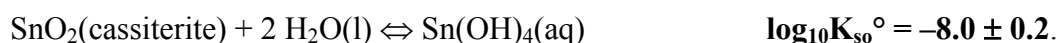
Acutally LOTHENBACH et al. (1999) do not provide an uncertainty, but from the constancy of AMAYA et al. (1997)'s experimental data we conclude that $\pm$ 0.2 $\log_{10}$-units would be an acceptable

value. According to LOTHENBACH et al. (1999), a solubility of –8.5 may be derived from FEITKNECHT & SCHINDLER (1963), based on unpublished results from EGGER (1957).

For precipitated SnO_2 (aged 1 month/ 6 months; amorphous, according to X-ray patterns) AMAYA et al. (1997) determined $\log_{10}K_{so}° = -7.46$ with "*a curve fitting calculation using the least squares method*". We re-analysed the pH-independent part of AMAYA et al. (1997)'s data (Table 5.22.5 and Fig. 5.22.1) and obtained $\log_{10}K_{so}° = -7.3 \pm 0.3$ (averaging the numbers provided in Table 5.22.5 produces $(4.90 \pm 2.36) \cdot 10^{-8}$ and the conversion to the log-scale gives –7.31 with the asymmetric uncertainty range +0.17/–0.29).

The same group of authors, ODA & AMAYA (1998), investigated the influence of dissolved NaCl and Na_2SO_4 on the solubility of the precipitate. Corresponding results are listed in Table 5.22.6, but it is not completely clear how these results should be interpreted. Both, chloride and sulfate may form complexes with Sn^{4+}, but it is unclear why the lowest solubility was found at the highest chloride concentration (the measurements in sulfate solutions show the expected trends, i.e., the highest solubility at the highest sulfate concentration).

Based on the facts that i) X-ray analyses confirmed the amorphous character of the precipitate and ii) Sn(IV) hydrolysis in the alkaline region relies on the same data (see section 5.22.3), we recommend to consider the AMAYA et al. (1997)-data for deriving the solubility of $SnO_2(am)$.

However, instead of adopting AMAYA et al. (1997)'s proposal we recommend to use

$$SnO_2(am) + 2\ H_2O(l) \Leftrightarrow Sn(OH)_4(aq) \qquad\qquad \mathbf{\log_{10}K_{so}° = -7.3 \pm 0.3,}$$
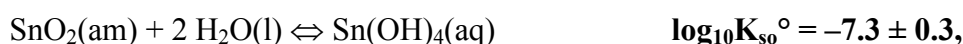
based on the data compiled in Table 5.22.5 and shown in Fig. 5.22.1. This selection is corroborated by the formation constants as given by ODA & AMAYA (1998) (Table 5.22.6): As a first approximation, the formation constant for $SnO_2(precip.) + 2\ H_2O(l) \Leftrightarrow Sn(OH)_4(aq)$ should not depend on ionic strength and, thus, solubilities at very low NaCl and $NaSO_4$ concentrations should compare well with the solubility in 0.1 M $NaClO_4$. Indeed, we again obtain $\log_{10}K_{so}° = -7.3 \pm 0.3$ from averaging the quoted values from Table 5.22.6.

Table 5.22.5: Excerpt of solubility measurements as taken from AMAYA et al. (1997). Total concentrations of tin according to SnO_2(precip.) + 2 H_2O(l) $\Leftrightarrow$ $Sn(OH)_4$(aq) are given for the pH range 2 to 7, where solubility does not depend on pH. Experiments were performed in 0.1 M $NaClO_4$ at 25 °C for one month (six months). Initial tin concentration was $1 \cdot 10^{-4}$ mol/l.

pH	measured tin concentration [mol/l]	
2.1	$(1.8 \pm 1.3) \cdot 10^{-8}$	
2.1	$(1.5 \pm 1.3) \cdot 10^{-8}$	
3.0	$(7.9 \pm 1.3) \cdot 10^{-8}$	
3.0	$(8.4 \pm 1.3) \cdot 10^{-8}$	
3.8	$(6.2 \pm 1.3) \cdot 10^{-8}$	
3.8	$(2.9 \pm 1.3) \cdot 10^{-8}$	
5.7	$(5.6 \pm 1.2) \cdot 10^{-8}$	
5.8	$(4.7 \pm 0.2) \cdot 10^{-8}$	six months
6.0	$(4.1 \pm 0.1) \cdot 10^{-8}$	six months
6.2	$(5.9 \pm 1.3) \cdot 10^{-8}$	

Table 5.22.6: Experimental $\log_{10}K$ values for SnO_2(precip.) + 2 H_2O(l) $\Leftrightarrow$ $Sn(OH)_4$(aq) as compiled in LOTHENBACH et al. (1999, Table 4.5). Influence of dissolved NaCl and Na_2SO_4.

$\log_{10}K$	I(M)	Medium	Reference	Comments
−7.46	0.1	$NaClO_4$	AMAYA et al. (1997)	
−7.46	0.1	$NaClO_4$	ODA & AMAYA (1998)	independence of data-point?
−6.88	0.53	$NaClO_4$	ODA & AMAYA (1998)	0.4 M $NaClO_4$? $\Rightarrow$ does not fit with given ionic strength.
−6.98	0.54	$NaClO_4$	ODA & AMAYA (1998)	0.004 M NaCl
−6.94	0.57	$NaClO_4$	ODA & AMAYA (1998)	0.04 M NaCl
−7.65	0.53	NaCl	ODA & AMAYA (1998)	0.4 M NaCl/ 0.13 M $NaClO_4$
−7.35	0.53	$NaClO_4$	ODA & AMAYA (1998)	0.001 M Na_2SO_4
−7.29	0.56	$NaClO_4$	ODA & AMAYA (1998)	0.01 M Na_2SO_4
−7.04	0.43	Na_2SO_4	ODA & AMAYA (1998)	0.1 M Na_2SO_4/ 0.13 M $NaClO_4$

5.22.5 Other tin(IV) complexes/compounds

Very recently, LOTHENBACH et al. (2000) reported on a sparingly soluble calcium stannate. In very alkaline solutions (pH range [11…13.1]) the solubility of $Ca[Sn(OH)_6](s)$ was investigated using both, over- and undersaturation techniques. Corresponding data are provided in Table 5.22.7. Results from over- and undersaturation experiments differ by about one order of magnitude, although LOTHENBACH et al. (2000) could not detect any difference in the XRD diffraction spectra of the solids after the experiment. It seems that the solubility differences have to be attributed to the kinetics of dissolution/precipitation processes or to the drying procedure for obtaining the solid for the dissolution experiments (or to both). However, following the nomenclature of LOTHENBACH et al. (2000) we recommend to include the solubility product for the "precipitate" in the database. According to the SIT regression (Fig. 5.22.5) we obtain

$$Ca[Sn(OH)_6](precip.) \Leftrightarrow Sn(OH)_6^{2-} + Ca^{2+} \qquad \mathbf{log_{10}K_{so}° = -9.7 \pm 0.1.}$$
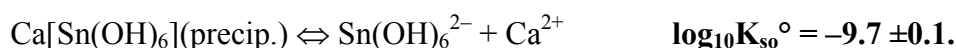
Note that LOTHENBACH et al. (2000) calculated $log_{10}K_{so}° = -9.85$ by performing an un-weighted regression (we estimated the uncertainty of the individual points from the standard deviation of the mean at given ionic strength). Only three points are available from dissolution experiments and the corresponding $log_{10}K_{so}°$ is -10.8 ± 0.1 (note that LOTHENBACH et al. 2000 called this solid "crystalline" and obtained $log_{10}K_{so}° = -10.93$ by performing an un-weighted regression). Rewriting the above equilibrium in terms of the master species $Sn(OH)_4(aq)$ gives:

$$Ca[Sn(OH)_6](s) + 2 H^+ \Leftrightarrow Sn(OH)_4(aq) + Ca^{2+} + 2 H_2O(l) \quad log_{10}*K_{so}° = 8.7 \pm 0.3.$$
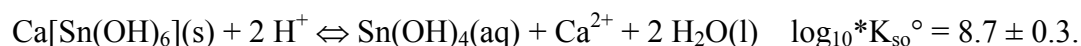
Only a limited amount of data of questionable reliability is available for other tin(IV) compounds and complexes. We follow LOTHENBACH et al. (1999)'s opinion and do not select any of these equilibria, but nevertheless give them as indicative numbers (Table 5.22.8).

Table 5.22.7: Experimental $\log_{10}K$ values for $CaSn(OH)_6(s) \Leftrightarrow Sn(OH)_6^{2-} + Ca^{2+}$ as compiled in LOTHENBACH et al. (2000).

$\log_{10}K$	I(M)	Medium	pH	Comments
−8.44	0.25	NaClO$_4$	12.5	Oversaturation (one week)
−8.60	0.25	NaClO$_4$	13.1	Oversaturation (one week)
−8.51	0.5	NaClO$_4$	12.5	Oversaturation (one week)
−8.71	0.5	NaClO$_4$	12.5	Oversaturation (one week)
−8.82	0.5	NaClO$_4$	13.1	Oversaturation (one week)
−8.89	0.5	NaClO$_4$	13.1	Oversaturation (one week)
−8.84	2.0	NaClO$_4$	12.5	Oversaturation (one week)
−8.49	2.0	NaClO$_4$	13.1	Oversaturation (one week)
−9.67	0.25	NaClO$_4$	12.0 - 13.1	Dissolution (4 months)
−9.99	0.5	NaClO$_4$	11.5 - 13.1	Dissolution (4 months)
−10.02	2.0	NaClO$_4$	11.1 - 13.1	Dissolution (4 months)

Table 5.22.8: Experimental formation constants for tin(IV) complexes compiled in LOTHENBACH et al. (1999, Table 4.7), which are not included in the update.

Reaction	Medium	$\log_{10}K$	Reference
$Sn^{4+} + Cl^- \Leftrightarrow SnCl^{3+}$	5 M HClO$_4$	3.71	FATOUROS & ROUELLE (1978)
$Sn^{4+} + 2\ Cl^- \Leftrightarrow SnCl_2^{2+}$	5 M HClO$_4$	6.46	FATOUROS & ROUELLE (1978)
$Sn^{4+} + 3\ Cl^- \Leftrightarrow SnCl_3^+$	5 M HClO$_4$	8.78	FATOUROS & ROUELLE (1978)
$Sn^{4+} + 4\ Cl^- \Leftrightarrow SnCl_4(aq)$	5 M HClO$_4$	9.48	FATOUROS & ROUELLE (1978)
$Sn^{4+} + 5\ Cl^- \Leftrightarrow SnCl_5^-$	5 M HClO$_4$	11.23	FATOUROS & ROUELLE (1978)
$Sn^{4+} + 6\ Cl^- \Leftrightarrow SnCl_6^{2-}$	5 M HClO$_4$	12.40	FATOUROS & ROUELLE (1978)
$Sn(OH)_4(aq) + CO_3^{2-} + H^+ \Leftrightarrow$ $Sn(OH)_3CO_3^- + H_2O(l)$	NaHCO$_3$ I = 0.1-0.5	7.71	KURIL'CHIKOVA & BARSUKOV (1971)
$SnO_2(aq) + 2\ H_2SO_4 \Leftrightarrow$ $SnSO_4^{2+} + SO_4^{2-} + 2\ H_2O(l)$	H$_2$SO$_4$	−1.30	BRUBAKER (1955) (30 °C)
$SnO_2(aq) + 2\ H_2SO_4 \Leftrightarrow$ $SnSO_4^{2+} + SO_4^{2-} + 2\ H_2O(l)$	H$_2$SO$_4$	−1.55	BRUBAKER (1955) (18 °C)
$SnS_2(s) + S^{2-} \Leftrightarrow SnS_3^{2-}$	0.1 M NaNO$_3$	5.31	HSEU & RECHNITZ (1968)[1]
$Sn(OH)_4(aq) + 2\ HS^- + 2\ H^+ \Leftrightarrow$ $SnS_2(s)+ 4\ H_2O(l)$	NaClO$_4$	36.45	KOCHETKOVA et al. (1984), based on $\Delta_fG°(Sn(OH)_4(aq)) =$ −944.16 kJ/mol

[1] This work seems to suffer from shortcomings in the calibration of the ion-selective electrode and information from this study should be taken with care.

5.22.6 Tin(II) hydrolysis

When extrapolating the data compiled in Table 5.22.9 according to the SIT formalism (Figs. 5.22.6 to 5.22.8) we obtain:

$$Sn^{2+} + H_2O(l) \Leftrightarrow SnOH^+ + H^+ \qquad \mathbf{log_{10}}{}^*\boldsymbol{\beta_{1,1}}^\circ = \mathbf{-3.8 \pm 0.2} \quad \Delta\varepsilon(NaNO_3) = -0.17$$

$$Sn^{2+} + 2\ H_2O(l) \Leftrightarrow Sn(OH)_2(aq) + 2\ H^+ \quad \mathbf{log_{10}}{}^*\boldsymbol{\beta_{1,2}}^\circ = \mathbf{-7.7 \pm 0.2} \quad \Delta\varepsilon(NaNO_3) = -0.31$$

$$Sn^{2+} + 3\ H_2O(l) \Leftrightarrow Sn(OH)_3^- + 3\ H^+ \qquad \mathbf{log_{10}}{}^*\boldsymbol{\beta_{1,3}}^\circ = \mathbf{-17.5 \pm 0.2} \quad \Delta\varepsilon(NaNO_3) = +0.09$$

The uncertainties were taken from the weighted regression according to GRENTHE et al. (1992) by giving each experimental point an estimated uncertainty of ± 0.2 log_{10}-units. This estimate was derived from the three points measured in 3 M NaClO$_4$ (Table 5.22.9a). Based on $\varepsilon(H^+, NO_3^-) = 0.07 \pm 0.01$ and $\varepsilon(Sn(OH)_2(aq), NaNO_3) = 0$ (GRENTHE et al. 1992), the $\Delta\varepsilon$ of -0.31 ± 0.30 as obtained for the reaction forming $Sn(OH)_2(aq)$ leads to $\boldsymbol{\varepsilon(Sn^{2+}, NO_3^-) = 0.45 \pm 0.30}$. Such an interaction coefficient seems reasonable if compared to corresponding interaction coefficients in ClO_4^- media. Note that ε-values for nitrate media tabulated in GRENTHE et al. (1992) (and associated references) do not show a very convincing chemical consistency. Therefore, it is important to point out that the above set of hydrolysis constants was derived by **neglecting** the possible formation of Sn(II) nitrate complexes. With the same assumptions one obtains $\varepsilon(SnOH^+, NO_3^-) = 0.21 \pm 0.42$ and $\varepsilon(Sn(OH)_3^-, Na^+) = 0.33 \pm 0.42$, but according to GRENTHE et al. (1997) it is debatable, whether the assumption $\varepsilon(Sn(OH)_2(aq), NaNO_3) = 0$ is really justified or not. Although this problem area lies far outside the scope of the present work, it should clearly be recognised as an issue for a next update step.

Table 5.22.9: Experimental $log_{10}K$ values for hydrolysis reactions of Sn(II) as compiled in LOTHENBACH et al. (1999, Table 4.13).

a) Equilibrium: $Sn^{2+} + H_2O(l) \Leftrightarrow SnOH^+ + H^+$; see Fig. 5.22.6 for SIT regression.

$log_{10}K$	I(M)	Medium	Reference	Comments
–4.10	0.1	NaNO$_3$	PETTINE et al. (1981)	
–3.80	0.5	NaNO$_3$	PETTINE et al. (1981)	
–4.10	1	NaNO$_3$	PETTINE et al. (1981)	
–3.92	3	NaClO$_4$	TOBIAS (1958)	not used in regression
–3.70	3	NaClO$_4$	GOBOM (1976)	not used in regression
–3.77	3	NaClO$_4$	SALVATORE et al. (1997)	not used in regression

b) Equilibrium: $Sn^{2+} + 2\,H_2O(l) \Leftrightarrow Sn(OH)_2(aq) + 2\,H^+$; see Fig. 5.22.7 for SIT regression.

$\log_{10}K$	I(M)	Medium	Reference	Comments
−7.90	0.1	$NaNO_3$	PETTINE et al. (1981)	
−7.90	0.5	$NaNO_3$	PETTINE et al. (1981)	
−7.80	1	$NaNO_3$	PETTINE et al. (1981)	

c) Equilibrium: $Sn^{2+} + 3\,H_2O(l) \Leftrightarrow Sn(OH)_3^- + 3\,H^+$; see Fig. 5.22.8 for SIT regression.

$\log_{10}K$	I(M)	Medium	Reference	Comments
−17.5	0.1	$NaNO_3$	PETTINE et al. (1981)	
−17.7	0.5	$NaNO_3$	PETTINE et al. (1981)	
−17.6	1	$NaNO_3$	PETTINE et al. (1981)	
−17.96	3	$NaClO_4$	MARK (1977)	not used in regression

d) Equilibrium: $3\,Sn^{2+} + 4\,H_2O(l) \Leftrightarrow Sn_3(OH)_4^{2+} + 4\,H^+$

$\log_{10}K$	I(M)	Medium	Reference	Comments
−6.77	3	$NaClO_4$	TOBIAS (1958)	
−6.81	3	$NaClO_4$	GOBOM (1976)	
−6.87	3	$NaClO_4$	SALVATORE et al. (1997)	

Three independent studies give remarkable consistent formation constants for $Sn_3(OH)_4^{2+}$ at high ionic strength ($\log_{10}*\beta_{3,4} = -6.8 \pm 0.1$; I = 3 M $NaClO_4$; see Table 5.22.9d). It seems worth to extrapolate this formation constant to zero ionic strength, although data from only one electrolyte concentration are available. With $\varepsilon(Sn^{2+},ClO_4^-) = 0.32 \pm 0.13$, $\varepsilon(H^+,ClO_4^-) = 0.14 \pm 0.02$ and $\varepsilon(Sn_3(OH)_4^{2+},ClO_4^-) = 0.45 \pm 0.20$ we obtain $\Delta\varepsilon = 0.05 \pm 0.45$. Note that the interaction coefficient for the polymeric species was estimated from a series of corresponding values provided in GRENTHE et al. (1997). Thus, the corrections for 3 M $NaClO_4$ (3.50 molal) are $\Delta z^2 \cdot D = -1.00$ and $\Delta\varepsilon \cdot m_{ClO4-} = 0.18 \pm 1.58$. The resulting $\log_{10}*\beta_{3,4}°$ is -5.62 ± 1.58.

$$3\,Sn^{2+} + 4\,H_2O(l) \Leftrightarrow Sn_3(OH)_4^{2+} + 4\,H^+ \qquad \mathbf{\log_{10}*\beta_{3,4}° = -5.6 \pm 1.6}.$$

Note that $Sn_3(OH)_4^{2+}$ becomes relevant only in acidic solutions at $[Sn(II)]_{tot} > 10^{-5}$ M.

5.22.7 Tin(II) oxides/hydroxides

The properties of potential solubility limiting oxides/hydroxides are not well established. The dehydration of $Sn(OH)_2$(precip.) to SnO(cr) is not well understood and some authors report on oxidation to SnO_2(cr). Solubility measurements in non-complexing aqueous solutions are very scarce. From the few constants compiled in Table 5.22.10, LOTHENBACH et al. (1999) derived

$$Sn^{2+} + H_2O(l) \Leftrightarrow SnO(cr) + 2\,H^+ \qquad \log_{10}{}^*K_{so}° = -2.41,\ \text{and}$$

$$Sn^{2+} + 2\,H_2O(l) \Leftrightarrow Sn(OH)_2(precip.) + 2\,H^+ \qquad \log_{10}{}^*K_{so}° = -2.82.$$
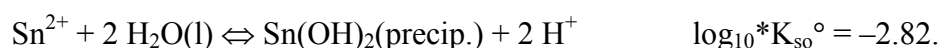
We are not very satisfied with this selection. In our opinion, the few available data and the poor characterizations of the solids do not justify a distinction among different oxidic precipitates of Sn^{2+}. On the other hand it's evident that such solids are formed. We propose to include a non-specific oxide SnO(s) in the database. A reasonable uncertainty, which reflects the lack of knowledge on the properties of the solid and which includes the available data, would be ± 0.5. Thus,

$$Sn^{2+} + 2\,H_2O(l) \Leftrightarrow SnO(s) + 2\,H^+ \qquad \mathbf{\log_{10}{}^*K_{so} = -2.5 \pm 0.5}.$$

Table 5.22.10: Experimental $\log_{10}K$ values for the solubility of Sn(II) oxides/hydroxides as compiled in LOTHENBACH et al. (1999, Table 4.16).

a) Equilibrium: $Sn^{2+} + H_2O(l) \Leftrightarrow SnO(cr) + 2\,H^+$

$\log_{10}K$	I(M)	Medium	Reference	Comments
–2.41	dil	water	GARRET & HEIKS (1941)	recalculated from a measured solubility of $5\cdot10^{-6}$ M with $\log_{10}{}^*\beta_{1,2}° = -7.71$.
-2.93	3	NaClO$_4$	MARK (1977)	

b) Equilibrium: $Sn^{2+} + H_2O(l) \Leftrightarrow SnO(precip.) + 2\,H^+$

$\log_{10}K$	I(M)	Medium	Reference	Comments
–2.84	dil	water	GOLDSCHMIDT & ECKHARDT (1906)	recalculated from a measured solubility of $1.35\cdot10^{-5}$ M with $\log_{10}{}^*\beta_{1,2}° = -7.71$.
-2.79	dil	water	PRYTZ (1928)	

5.22.8 Tin(II) chlorides

Many experimental data from independent studies are available for Sn(II) chloride complex formation (Table 5.22.11). The extrapolation of these data to I = 0 gives (Figs. 5.22.9 to 5.22.11):

$$Sn^{2+} + Cl^- \Leftrightarrow SnCl^+ \qquad \mathbf{log_{10}\beta_{1,1}° = 1.70 \pm 0.11} \quad \mathbf{\Delta\epsilon(NaClO_4) = -0.14 \pm 0.03}$$

$$Sn^{2+} + 2\ Cl^- \Leftrightarrow SnCl_2(aq) \quad \mathbf{log_{10}\beta_{1,2}° = 2.36 \pm 0.23} \quad \mathbf{\Delta\epsilon(NaClO_4) = -0.28 \pm 0.06}$$

$$Sn^{2+} + 3\ Cl^- \Leftrightarrow SnCl_3^- \qquad \mathbf{log_{10}\beta_{1,3}° = 2.1 \pm 0.4} \qquad \mathbf{\Delta\epsilon(NaClO_4) = -0.31 \pm 0.09}$$
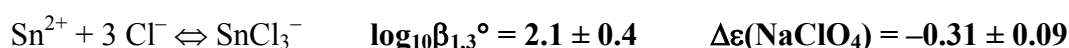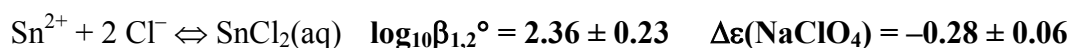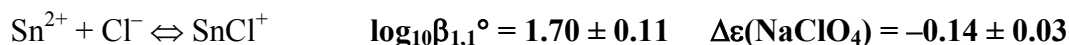
Single point uncertainties of ±0.2/±0.4 were estimated from the standard deviations of corresponding measurements at I = 1 M. Based on $\epsilon(Cl^-,Na^+) = 0.03\pm0.01$ and $\epsilon(SnCl_2(aq),NaClO_4) = 0$ (GRENTHE et al. 1992), the $\Delta\epsilon$ of -0.28 ± 0.06 as obtained for the reaction forming $SnCl_2(aq)$ leads to $\mathbf{\epsilon(Sn^{2+},ClO_4^-) = 0.22\pm0.06}$, $\epsilon(SnCl^+,ClO_4^-) = 0.11\pm0.07$ and $\epsilon(SnCl_3^-,Na^+) = 0.0\pm0.1$. Remember that $\epsilon(Sn^{2+},ClO_4^-) = 0.32\pm0.13$ was obtained from the reaction $Sn^{2+} + 2\ e^- \Leftrightarrow Sn(cr)$ (section 5.22.2). Associating the difference of 0.10 ± 0.14 to $\epsilon(SnCl_2(aq),NaClO_4)$ (instead of setting this interaction coefficient to zero) would very good match the interaction coefficients for neutral species as proposed by CIAVATTA (1990). This again provides evidence that NEA's decision to set interaction coefficients of neutral species to zero should possibly be reconsidered.

SnOHCl(aq): VANDERZEE & RHODES (1952) determined $log_{10}K = 1.04$ for $SnOH^+ + Cl^- \Leftrightarrow SnOHCl(aq)$ in 3 M $NaClO_4$, and PETTINE et al. (1981) determined $log_{10}K = 1.14$ in 0.5 M NaCl. In their Fig. 4.9, LOTHENBACH et al. (1999) show a regression with these two points (rewritten in terms of the equilibrium $Sn^{2+} + H_2O(l) + Cl^- \Leftrightarrow SnOHCl(aq) + H^+$) and give $log_{10}*K° = -2.27$. Since the two points are measured in different media, we are not very satisfied with this evaluation.

Instead, we prefer to combine the equilibrium measured by VANDERZEE & RHODES (1952) in 3 M $NaClO_4$ with the first hydrolysis equilibrium also measured in 3 M $NaClO_4$ by different authors (Table 5.22.9a; average = -3.80 ± 0.11). This leads to $Sn^{2+} + H_2O(l) + Cl^- \Leftrightarrow SnOHCl(aq) + H^+$; $log_{10}*K(3\ M\ NaClO_4) = -2.76 \pm 0.11$. From the reaction forming $SnCl_2(aq)$ (see above), we obtained the difference $\epsilon(Sn^{2+},ClO_4^-) - \epsilon(SnCl_2(aq),NaClO_4) = 0.22\pm0.06$. We introduce the approximation $\epsilon(Sn\mathbf{OH}Cl(aq),NaClO_4) \approx \epsilon(Sn\mathbf{Cl_2}(aq),NaClO_4)$ and use this difference to estimate $\Delta\epsilon = -0.11\pm0.06$ for the formation of the mixed complex ($\epsilon(H^+,ClO_4^-) = 0.14\pm0.02$; $\epsilon(Cl^-, Na^+) = 0.03\pm0.01$). Finally, we obtain

$$Sn^{2+} + H_2O(l) + Cl^- \Leftrightarrow SnOHCl(aq) + H^+ \qquad \mathbf{log_{10}*K° = -3.1 \pm 0.2}.$$
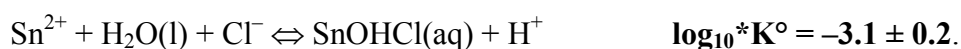
Table 5.22.11: Experimental $\log_{10}K$ values for Sn(II) chloride complex formation as compiled in LOTHENBACH et al. (1999, Table 4.19).

a) Equilibrium: $Sn^{2+} + Cl^- \Leftrightarrow SnCl^+$; see Fig. 5.22.9 for SIT regression.

$\log_{10}K$	I(M)	Medium	Reference	Comments
1.09	0.5	NaClO$_4$	FEDOROV et al. (1975)	
1.02	1	NaClO$_4$	FEDOROV et al. (1975)	
1.08	1	NaClO$_4$	SAMOILENKO et al. (1976)	
0.73	1	NaNO$_3$	PETTINE et al. (1981)	not used in regression
1.11	2	HClO$_4$ [1)]	DUKE & PINKERTON (1951)	
1.06	2	ClO$_4^-$ [2)]	RABIDEAU & MOORE (1961)	recalc. from DUKE & COUTNEY (1950)
1.14	3	NaClO$_4$	RABIDEAU & MOORE (1961)	recalc. from VANDERZEE & RHODES (1952)
1.18	3	NaClO$_4$	FEDOROV et al. (1975)	
1.45	4	H$_2$SO$_4$/HCl	HAIGHT et al. (1962)	not used in regression
1.34	4	NaClO$_4$	FEDOROV et al. (1975)	
1.80	6	NaClO$_4$	FEDOROV et al. (1975)	

b) Equilibrium: $Sn^{2+} + 2\,Cl^- \Leftrightarrow SnCl_2(aq)$; see Fig. 5.22.10 for SIT regression.

$\log_{10}K$	I(M)	Medium	Reference	Comments
1.36	0.5	NaClO$_4$	FEDOROV et al. (1975)	
1.13	1	NaClO$_4$	FEDOROV et al. (1975)	
1.85	1	NaClO$_4$	SAMOILENKO et al. (1976)	
1.08	1	NaNO$_3$	PETTINE et al. (1981)	not used in regression
1.72	2	ClO$_4^-$ [2)]	RABIDEAU & MOORE (1961)	recalc. from DUKE & COUTNEY (1950)
1.70	3	NaClO$_4$	RABIDEAU & MOORE (1961)	recalc. from VANDERZEE & RHODES (1952)
1.78	3	NaClO$_4$	FEDOROV et al. (1975)	
2.35	4	H$_2$SO$_4$/HCl	HAIGHT et al. (1962)	not used in regression
2.12	4	NaClO$_4$	FEDOROV et al. (1975)	
3.04	6	NaClO$_4$	FEDOROV et al. (1975)	

c) Equilibrium: $Sn^{2+} + 3\,Cl^- \Leftrightarrow SnCl_3^-$; see Fig. 5.22.11 for SIT regression.

$\log_{10}K$	I(M)	Medium	Reference	Comments
1.50	2	$ClO_4^{-\,2)}$	RABIDEAU & MOORE (1961)	recalc. from DUKE & COUTNEY (1950)
1.66	3	$NaClO_4$	RABIDEAU & MOORE (1961)	recalc. from VANDERZEE & RHODES (1952)
1.65	3	$NaClO_4$	FEDOROV et al. (1975)	
2.46	4	H_2SO_4/HCl	HAIGHT et al. (1962)	not used in regression
2.12	4	$NaClO_4$	FEDOROV et al. (1975)	
3.04	6	$NaClO_4$	FEDOROV et al. (1975)	

d) Equilibrium: $SnOH^+ + Cl^- \Leftrightarrow SnOHCl(aq)$.

$\log_{10}K$	I(M)	Medium	Reference	Comments
1.04	3	$NaClO_4$	VANDERZEE & RHODES (1952)	
1.14	0.5	NaCl	PETTINE et al. (1981)	

[1] Most likely DUKE & PINKERTON (1951) used a mixture of $NaClO_4/HClO_4$ as did DUKE & COUTNEY (1950)

[2] DUKE & COUTNEY (1950) used a mixture of $NaClO_4/HClO_4$.

Note that the data from PETTINE et al. (1981) measured in 0.5 M NaCl would lead to $\log_{10}*K° = -2.4$, but it is unclear, whether this value is corrected for chloride complex formation or not. Therefore, we discard the PETTINE et al. (1981)-value (see also the comments on nitrate complex formation in nitrate media in section 5.22.11).

5.22.9   SnOHCl(s)

LOTHENBACH et al. (1999) consider only the reference RANDALL & MURAKAMI (1930) as sufficiently reliable to derive the solubility product of SnOHCl(s). The experimental data, measured in dilute chloride media, were corrected by LOTHENBACH et al. (1999) for chloride complex formation (using constants which are very close to those given in section 5.22.8). Their regression according to the SIT formalism gives

$$Sn^{2+} + Cl^- + H_2O \Leftrightarrow SnOHCl(s) + H^+ \qquad \log_{10}*K_{so}° = 2.42 \qquad\qquad \Delta\varepsilon = +3.28.$$

Note that RANDALL & MURAKAMI (1930) suggested $\log_{10}*K_{so}° = 2.75$ using a Debye-Hückel-type extrapolation to I=0. Unfortunately, it is absolutely unclear what the resulting $\Delta\varepsilon$ of +3.28 should mean. In our opinion, and according to available information on the size of ε-values (GRENTHE et al. 1992), $\Delta\varepsilon$ for the above reaction should be in the range [–0.2…0] since $\varepsilon(H^+,Cl^-) = 0.12\pm0.03$, $\varepsilon(Cl^-,Na^+) = 0.03\pm0.01$, and, estimated from analogies, $\varepsilon(Sn^{2+},Cl^-) \sim [0.1…0.3]$. Therefore, we conclude that something is very unclear with respect to the interpretation of the original data or with the data themselves. At present we do not include this equilibrium in the update, but we suggest to perform a more comprehensive re-evaluation of the original data in a later update.

5.22.10 Tin(II) fluorides

Tin(II) fluoride complexes exist and have considerable stabilities. LOTHENBACH et al. (1999) recommend formation constants for SnF^+, $SnF_2(aq)$ and SnF_3^-, but in our opinion only the constant for SnF^+ is sufficiently well established. Corresponding experimental $\log_{10}K$'s are compiled in Table 5.22.12. With these data we evaluate according to the SIT formalism (Fig. 5.22.12):

$$Sn^{2+} + F^- \Leftrightarrow SnF^+ \qquad \mathbf{\log_{10}\beta_1° = 5.0 \pm 0.3} \qquad \mathbf{\Delta\varepsilon(NaClO_4) = -0.02 \pm 0.24}$$
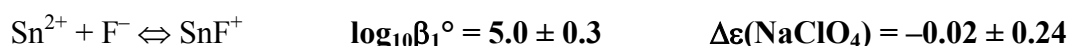
Note that the uncertainty of ±0.3 is a direct consequence of estimating the uncertainty of each point to be in the order of ±0.3 $\log_{10}$-units. Varying this uncertainty estimate does not influence $\log_{10}\beta_1°$ or $\Delta\varepsilon$ of the reaction. From $\Delta\varepsilon = -0.02\pm0.24$ and $\varepsilon(F^-,Na^+) = 0.02\pm0.02$ follows that $\varepsilon(SnF^+,ClO_4^-) - \varepsilon(Sn^{2+},ClO_4^-) = 0.00\pm0.24$. The comparison with the corresponding chloride complex formation reaction (section 5.22.8) reveals that the difference $\varepsilon(SnF^+,ClO_4^-) - \varepsilon(SnCl^+,ClO_4^-) = 0.11\pm0.24$ lies in a sensible range.

In contrast to LOTHENBACH et al. (1999) we do not recommend formation constants for $SnF_2(aq)$ and SnF_3^- due to the few available data. However, in the sense of an indication, corresponding "raw" data as compiled in LOTHENBACH et al. (1999) are provided in Tables 5.22.12b and 5.22.12c.

No data are available for the solubility product of $SnF_2(s)$.

Table 5.22.12: $Log_{10}K$ values for Sn(II) fluoride complex formation as compiled in LOTHENBACH et al. (1999, Table 4.22).

a) Equilibrium $Sn^{2+} + F^- \Leftrightarrow SnF^+$. See Fig. 5.22.12 for SIT regression.

$log_{10}K$	I(M)	Medium	Reference	Comments
3.60	0.1	NaF	NELSON & AMIN (1975)	not used in regression
4.14	0.5	$HClO_4$ [1]	CONNICK & PAUL (1961)	mean, no uncertainties
4.48	0.85	$NaClO_4$	BOND (1971)	recalc. from HALL & SLATER (1968)
4.00	1	$NaClO_4$	BOND & TAYLOR (1970)	
4.05	2	$HClO_4$ [1]	CONNICK & PAUL (1961)	mean, no uncertainties

b) Equilibrium $Sn^{2+} + 2 F^- \Leftrightarrow SnF_2(aq)$. Indicative values, no regression performed.

$log_{10}K$	I(M)	Medium	Reference	Comments
7.04	0.1	NaF	NELSON & AMIN (1975)	
8.18	0.85	$NaClO_4$	BOND (1971)	recalc. from HALL & SLATER (1968)
6.85	1	$NaClO_4$	BOND & TAYLOR (1970)	

c) Equilibrium $Sn^{2+} + 3 F^- \Leftrightarrow SnF_3^-$. Indicative values, no regression performed.

$log_{10}K$	I(M)	Medium	Reference	Comments
9.00	0.1	NaF	NELSON & AMIN (1975)	
10.30	0.85	$NaClO_4$	BOND (1971)	recalc. from HALL & SLATER (1968)
9.43	1	$NaClO_4$	BOND & TAYLOR (1970)	

[1] The variation of the cation was not considered in the regression. Actually this means that we implicitely made the approximation $\varepsilon(F^-,Na^+) = \varepsilon(F^-,H^+)$.

5.22.11 Tin(II) carbonates

No experimental data are available for tin(II) carbonate species.

5.22.12 Tin(II) nitrates

It's common knowledge that nitrate complexes are very weak and will hardly be relevant in geo-chemical systems. LOTHENBACH et al. (1999) consider formation constants measured in $NaNO_3$ solutions up to 6 M, based on data from ANDREEV et al. (1980). The regression of these data (Table 5.22.13) against the molality of NO_3^- gives:

$$Sn^{2+} + NO_3^- \Leftrightarrow SnNO_3^+ \qquad \log_{10}\beta_1° = 1.25 \quad \Delta\epsilon(NaNO_3) = 0.00,$$

$$Sn^{2+} + 2\ NO_3^- \Leftrightarrow Sn(NO_3)_2(aq) \qquad \log_{10}\beta_2° = 1.7 \quad \Delta\epsilon(NaNO_3) = 0.02 \text{ and}$$

$$Sn^{2+} + 3\ NO_3^- \Leftrightarrow Sn(NO_3)_3^- \qquad \log_{10}\beta_3° = 1.3 \quad \Delta\epsilon(NaNO_3) = 0.08.$$
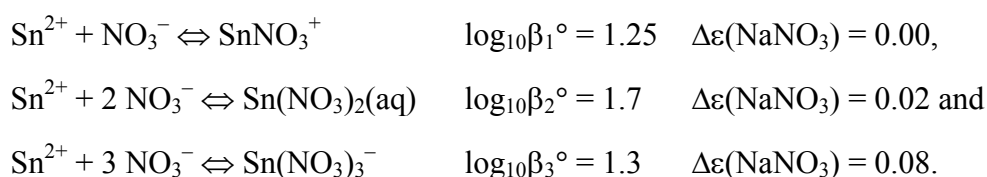
Using $\epsilon(Sn(NO_3)_2(aq),NaNO_3) = 0$ and $\epsilon(NO_3^-,Na^+) = -0.04$ (GRENTHE et al. 1992) we obtain

$$\epsilon(Sn^{2+},NO_3^-) = 0.06,$$

$$\epsilon(SnNO_3^+,NO_3^-) = 0.02 \text{ and}$$

$$\epsilon(Sn(NO_3)_3^-,Na^+) = 0.02.$$

This set of data opens a problem area which should be discussed in some more detail. The Sn(II) nitrate complexes were measured in $NaNO_3$ solutions. Therefore, the complex formation constants may interfere with the activity corrections caused by the medium. With other words, how to distinguish between real complex formation and medium effects? This question is particularly important for small constants as in the case of nitrate complexes. To give a typical example: how to distinguish between the complex formation $SnNO_3^+ + NO_3^- \Leftrightarrow Sn(NO_3)_2(aq)$ and the activity correction term $\epsilon(SnNO_3^+,NO_3^-)\cdot m_{NO_3^-}$? The activity correction terms in the SIT formalism may be quite substantial, i.e., $-z^2\cdot D \sim -1.0$ and $\epsilon(Sn^{2+},NO_3^-)\cdot m_{NO_3^-} \sim 2.1\pm1.4$ for Sn^{2+} in 4 M $NaNO_3$ (taking $\epsilon(Sn^{2+},NO_3^-) = 0.45\pm0.30$, see section 5.22.6). Since the formation constants as compiled in Table 5.22.13 have magnitudes comparable with, or even less than the uncertainties of the activity correction terms, they do not necessarily reflect true nitrate complex formation. Maybe, a detailed re-evaluation of the experimental data of ANDREEV et al. (1980) could demonstrate, whether these data would also be compatible with the hypothesis "no nitrate complexes formed" or not. However, based on presently available information we conclude that independent (spectroscopic, other) information is needed to show that Sn(II) nitrate complexes really exist. Sn(II) nitrate complexes seem to have stabilities similar to chloride complexes (see section 5.22.8) and it would be easy to

show this by conducting corresponding experiments in $NaClO_4$-solutions instead of $NaNO_3$-solutions.

In the present update we do not include Sn(II) nitrate complexes.

Table 5.22.13: Experimental $\log_{10}K$ values for Sn(II) nitrate complex formation as compiled in LOTHENBACH et al. (1999, Table 4.26).

a) Equilibrium: $Sn^{2+} + NO_3^- \Leftrightarrow SnNO_3^+$.

$\log_{10}K$	I(M)	Medium	Reference
0.44	1	$NaNO_3$	ANDREEV et al. (1980)
0.41	2	"	"
0.14	3	"	"
0.15	4	"	"
0.18	6	"	"

b) Equilibrium: $Sn^{2+} + 2\,NO_3^- \Leftrightarrow Sn(NO_3)_2(aq)$.

$\log_{10}K$	I(M)	Medium	Reference
0.45	2	$NaNO_3$	ANDREEV et al. (1980)
0.05	3	"	"
−0.06	4	"	"
0	6	"	"

c) Equilibrium: $Sn^{2+} + 3\,NO_3^- \Leftrightarrow Sn(NO_3)_3^-$.

$\log_{10}K$	I(M)	Medium	Reference
−0.35	3	$NaNO_3$	ANDREEV et al. (1980)
−0.58	4	"	"
−0.85	6	"	"

5.22.13 Tin(II) sulfates

According to LOTHENBACH et al. (1999), only PETTINE et al. (1981) determined complex formation with sulfate:

$$Sn^{2+} + SO_4^{2-} \Leftrightarrow Sn(SO_4)(aq) \qquad \log_{10}\beta_1(1 \text{ M NaNO}_3) = 1.29$$

$$Sn^{2+} + 2 \, SO_4^{2-} \Leftrightarrow Sn(SO_4)_2^{2-} \qquad \log_{10}\beta_2(1 \text{ M NaNO}_3) = 1.65$$
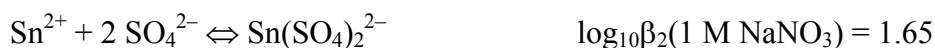
There is no information about the ionic strength dependency of these equilibria. Assuming that the **difference** $\varepsilon(\mathbf{Sn(SO_4)}(aq),NaNO_3) - \varepsilon(Sn^{2+},NO_3^-) = -0.45 \pm 0.30$ is equal to the difference $\varepsilon(\mathbf{Sn(OH)_2}(aq), NaNO_3) - \varepsilon(Sn^{2+},NO_3^-)$ (see section 5.22.6) and using $\varepsilon(SO_4^{2-},Na^+) = -0.12 \pm 0.06$ (GRENTHE et al. 1997) we obtain $\Delta\varepsilon = -0.33 \pm 0.31$ for the reaction forming the uncharged 1:1 complex. Thus,

$$Sn^{2+} + SO_4^{2-} \Leftrightarrow Sn(SO_4)(aq) \qquad \mathbf{\log_{10}\beta_1° = 2.6 \pm 0.3.}$$

Note that this formation constant is in very good agreement with many other $M(II)(SO_4)(aq)$ formation constants. We see mainly two reasons for not recommending a formation constant for the 1:2 complex: i) the 1:2 complex is very weak and becomes relevant only in fairly concentrated sulfate solutions where $[SO_4^{2-}] > [0.01…0.1]$ M, ii) the uncertainty introduced by the required SIT corrections is comparable with the successive $\log_{10}K_2$ itself (see also discussion on nitrates in the former section).

Solubility data for sparingly soluble tin(II) sulfates are not available. The constant provided in the PEARSON et al. (1992)-database, $\log_{10}K_{so}°(SnSO_4(s) \Leftrightarrow Sn^{2+} + SO_4^{2-}) = -23.93$ is completely wrong: A quick look to corresponding textbooks reveals that $SnSO_4(s)$ is hygroscopic and has a solubility of about 0.5 to 1 M at ambient temperature. This equilibrium has been dropped from the database. Most likely, the wrong number may be traced back to a simple typing error: –908.19 kJ/mol instead of –809.19 kJ/mol (GMELIN 1975) was compiled for $\Delta_f G°(SnSO_4(s))$ in the original source (CROSS & EWART 1991; HATCHES 3.0 database).

5.22.14 Tin(II) phosphates

No reliable data are available for tin(II) phosphates.

Table 5.22.1: Compilation of selected Tin data.

TDB Version 05/92   **TDB Version 01/01**

Name	$\Delta_f G_m°$	$\Delta_f H_m°$	Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$S_m°$	Species
H2(G)			H2	**0.0**	**0.0**	**130.680±0.003**	H_2
			Sn(cr)	**0.0**	**0.0**	**51.18±0.08**	Sn(cr)
SN+2	−26.7	−8.9	Sn+2	**−26.43±0.46**	**−7.7±1.3**	**−16.7±4.0**	Sn^{2+}

Tin(II)

Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	Reaction
SNOH+	−1.55	2.01	SnOH+	**−3.8±0.2**	$Sn^{2+} + H_2O(l) \Leftrightarrow SnOH^+ + H^+$
SNOH2	−7.06		Sn(OH)2	**−7.7±0.2**	$Sn^{2+} + 2\,H_2O(l) \Leftrightarrow Sn(OH)_2(aq) + 2\,H^+$
SNOH3-	−16.61		Sn(OH)3–	**−17.5±0.2**	$Sn^{2+} + 3\,H_2O(l) \Leftrightarrow Sn(OH)_3^- + 3\,H^+$
HSNO2-	−16.05				$Sn^{2+} + 2\,H_2O(l) \Leftrightarrow HSnO_2^- + 3\,H^+$
SN2OH2+2	−4.77				$2\,Sn^{2+} + 2\,H_2O(l) \Leftrightarrow Sn_2(OH)_2^{2+} + 2\,H^+$
SN3OH4+2	−6.88		Sn3(OH)4+2	**−5.6±1.6**	$3\,Sn^{2+} + 4\,H_2O(l) \Leftrightarrow Sn_3(OH)_4^{2+} + 4\,H^+$
SNCL+	0.62	2.67	SnCl+	**1.70±0.11**	$Sn^{2+} + Cl^- \Leftrightarrow SnCl^+$
SNCL2	1.43	3.21	SnCl2	**2.36±0.23**	$Sn^{2+} + 2\,Cl^- \Leftrightarrow SnCl_2(aq)$
SNCL3-	0.88	5.56	SnCl3–	**2.1±0.4**	$Sn^{2+} + 3\,Cl^- \Leftrightarrow SnCl_3^-$
			Sn(OH)Cl	**−3.1±0.2**	$Sn^{2+} + H_2O(l) + Cl^- \Leftrightarrow Sn(OH)Cl(aq) + H^+$
			SnF+	**5.0±0.3**	$Sn^{2+} + F^- \Leftrightarrow SnF^+$
			SnSO4	**2.6±0.3**	$Sn^{2+} + SO_4^{2-} \Leftrightarrow SnSO_4(aq)$

Table 5.22.1: continued

TDB Version 05/92			TDB Version 01/01		
Name	$\log_{10}K_{s,0}°$	$\Delta_f H_m°$	Name	$\log_{10}K_{s,0}°$	Reaction
SN(W)	4.77		Sn(cr)	**4.63±0.08**	$Sn(cr) \Leftrightarrow Sn^{2+} + 2\ e^-$
SNO	1.3	134.52	SnO(s)	**2.5±0.5**	$SnO(s) + 2\ H^+ \Leftrightarrow Sn^{2+} + H_2O(l)$
SNOH2(S)	1.84				$Sn(OH)_2(s) + 2\ H^+ \Leftrightarrow Sn^{2+} + 2\ H_2O(l)$
SNS	−48.12	40.14			$SnS(s) + 4\ H_2O(l) \Leftrightarrow Sn^{2+} + 8\ e^- + SO_4^{2-} + 8\ H^+$
SNSO4(S)	−23.93				$SnSO_4(s) \Leftrightarrow Sn^{2+} + SO_4^{2-}$

Tin(IV)

Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	Reaction
SN+4	−5.25	9.4			$Sn^{2+} \Leftrightarrow Sn^{4+} + 2\ e^-$
SNOH5-	−14.5				$Sn^{2+} + 5\ H_2O(l) \Leftrightarrow Sn(OH)_5^- + 2\ e^- + 5\ H^+$
			Sn(OH)5–	**−8.0±0.3**	$Sn(OH)_4(aq) + H_2O(l) \Leftrightarrow Sn(OH)_5^- + H^+$
SNOH6-2	−26.51				$Sn^{2+} + 6\ H_2O(l) \Leftrightarrow Sn(OH)_6^{2-} + 2\ e^- + 6\ H^+$
			Sn(OH)6–2	**−18.4±0.3**	$Sn(OH)_4(aq) + 2\ H_2O(l) \Leftrightarrow Sn(OH)_6^{2-} + 2\ H^+$
SNO3-2	−28.7				$Sn^{2+} + 3\ H_2O(l) \Leftrightarrow SnO_3^{2-} + 2\ e^- + 6\ H^+$

Name	$\log_{10}K_{s,0}°$	$\Delta_f H_m°$	Name	$\log_{10}K_{s,0}°$	Reaction
SNO2	−3.21	0.06			$SnO_2(s) + 2\ e^- + 4\ H^+ \Leftrightarrow Sn^{2+} + 2\ H_2O(l)$
			SnO2(cr)	**−8.0±0.2**	$SnO_2(cassiterite) + 2\ H_2O(l) \Leftrightarrow Sn(OH)_4(aq)$
SNOH4(S)	4.22				$Sn(OH)_4(s) + 2\ e^- + 4\ H^+ \Leftrightarrow Sn^{2+} + 4\ H_2O(l)$
			SnO2(am)	**−7.3±0.3**	$SnO_2(am) + 2\ H_2O(l) \Leftrightarrow Sn(OH)_4(aq)$
			CaSn(OH)6(s)	**−9.7±0.1**	$Ca[Sn(OH)_6](s) \Leftrightarrow Sn(OH)_6^{2-} + Ca^{2+}$
SNSO42(S)	21.21	−9.4			$Sn(SO_4)_2(s) + 2\ e^- \Leftrightarrow Sn^{2+} + 2\ SO_4^{2-}$

Table 5.22.1: continued

TDB Version 05/92   **TDB Version 01/01**

Tin(III/II) solids

Name	$\log_{10}K_{s,0}°$	$\Delta_f H_m°$	Name	$\log_{10}K_{s,0}°$	Reaction
SN2S3	−141.93	53.025			$Sn_2S_3(s) + 12\ H_2O(l) \Leftrightarrow 2\ Sn^{2+} + 22\ e^- + 24\ H^+ + 3\ SO_4^{2-}$
SN3S4	−191.3	93.165			$Sn_3S_4(s) + 16\ H_2O(l) \Leftrightarrow 3\ Sn^{2+} + 30\ e^- + 32\ H^+ + 4\ SO_4^{2-}$

5.22.15 References

AMAYA T., CHIBA T., SUZUKI K., ODA C., YOSHIKAWA H., YUI M. (1997): Solubility of Sn(IV) oxide in dilute $NaClO_4$ solution at ambient temperature. Mat. Res. Soc. Symp. Proc., 465, 751-758.

COX J.D., WAGMAN D.D., MEDVEDEV V.A. (1989): CODATA Key Values for Thermodynamics. Hemisphere Publishing Corp., New York 271p.

CROSS J.E., EWART F.T. (1991): HATCHES - a thermodynamic database and management system. Radiochimica Acta, 52/53, 421-422.

GRENTHE I., PLYASUNOV V., SPAHIU K. (1997): Estimations of medium effects on thermodynamic data. In: Modelling in aquatic chemistry (GRENTHE I. & PUIGDOMENECH I., eds.). Nuclear Energy Agency, OECD Publications, Paris, 724p., ISBN 92-64-15569-4.

GRENTHE, I., FUGER, J., KONINGS, R.J.M., LEMIRE, R.J., MULLER, A.B., NGUYEN-TRUNG, C., WANNER, H. (1992): Chemical Thermodynamics Vol. 1: Chemical Thermodynamics of Uranium. OECD/NEA, North-Holland Elsevier, ISBN 0 444 89381 4.

HSEU T.-M., RECHNITZ G.A. (1968): Analytical study of a sulfide ion-selective membrane electrode in alkaline solutions. Anal. Chem., 40, 1054-1060.

LOTHENBACH B., OCHS M., HAGER D. (2000): Thermodynamic data for the solubility of tin(IV) in aqueous cementitious environments. Radiochimica Acta 88, 521-526.

LOTHENBACH B., OCHS M., WANNER H., YUI M. (1999): Thermodynamic Data for the Speciation and Solubility of Pd, Pb, Sn, Sb, Nb and Bi in Aqueous Solution. Japan Nuclear Cycle Development Institute (JNC), TN8400 99-011.

PEARSON F.J., BERNER U., HUMMEL W. (1992): Nagra Thermochemical Data Base II. Supplemental Data 05/92. Nagra Technical Report NTB 91-18, Nagra, Wettingen, Switzerland, 284p.

SILVA R.J., BIDOGLIO G., RAND M.H., ROBUCH P., WANNER H., PUIGDOMENECH I. (1995): Chemical Thermodynamics Vol. 2: Chemical Thermodynamics of Americium. OECD/NEA, North-Holland Elsevier, ISBN 0 444 82281 X.

VASIL'EV V.P., GLAVINA S.R., TSCHOROCHOVA V.I. (1979): Potentiometric determination of energy of formation of tin(IV) ion in an aqueous solution (in Russian). Izv. Vyssh. Ucheb. Zaved. SSSR, Khim. I Khim. Tekhnol., 22, 1082-1085.

Indirectly cited References

Most of the references given in this chapter have not been explicitly studied, but were directly taken from LOTHENBACH et al. (1999). The simple reason for this unusual action is to keep this comprehensive list of references together in order to facilitate later work on this subject.

ANDREEV A.I., SAMSONOVA N.P., ROBOV A.M., FEDOROV V.A. (1980): Formation of nitrate complexes of tin(II) in aqueous solutions. Koordinationsonnaya Khimiya, 5, 1325-1327.

BARSUKOV V.L., KLINTSOVA A.P. (1970): Solubility of cassiterite in water and aqueous NaOH at 25 °C. Gheokhimiya, 1, 1268-1272.

BOND A.M. (1971): Some suggested calculation procedures and the variation in results obtained from different calculation methods for evaluation of concentration stability constants of metal ion complexes in aqueous solution. Coordin. Chem. Rev., 6, 377-405.

BOND A.M., TAYLOR R.J. (1970): Polarographic study of the fluoride complexes of tin(II) in neutral and acidic media. J. Electroanal. Chem., 28, 207-215.

BRUBAKER C.H. (1955): The hydrolysis of tin(IV) in sulfuric acid. J. Am. Chem. Soc., 77, 5265-5269.

CIAVATTA L. (1990): The specific ion interaction theory in equilibrium analysis: Some empirical rules for estimating interaction coefficients of metal ion complexes. Ann. Chim. Roma, 80, 255-263.

CONNICK R.E., PAUL A.D. (1961): The fluoride complexes of silver and stannous ions in aqueous solution. J. Phys. Chem., 65, 1216-1220.

DUKE F.R., COUTNEY W.G. (1950): The stannous chloride equilibrium. Iowa State J. Research, 24, 397-403.

DUKE F.R., PINKERTON F.C. (1951): The rôle of halide ions on the ferric-stannous reaction. J. Am. Chem. Soc., 73, 3045-3049.

EGGER K. (1957): Lic. work, University of Berne, cited in FEITKNECHT & SCHINDLER (1963).

FATOUROS N., ROUELLE F., CHEMLA M. (1978): Influence de la formation de complexes chlorures sur la réduction électrochimique de SnIV en milieu perchlorique acide. J. Chim. Phys. Physico-Chimie Biol., 75, 477-483.

FEDOROV V.A., BOL'SHAKOVA I.M., MOSKALENTO T.G. (1975): Formation of mixed bromo/chloro-complexes of tin(II) in aqueous solutions. Russ. J. Inorg. Chem., 20, 859-861.

FEITKNECHT W., SCHINDLER P. (1963): Solubility constants of metal oxides, metal hydroxides and metal hydroxide salts in aqueous solution. Pure Appl. Chem., 1, 130-199.

GABE D.R., SRIPATR P. (1973): Anode behaviour of tin during alkaline stannate palting. Trans. Inst. Metal Finishing, 51, 141-144.

GARRET A.B., HEIKS R.E. (1941): Equilibria in the stannous oxide-sodium hydroxide and in the stannous oxide-hydrochloric acid system at 25 °C. Analysis of dilute solutions of stannous tin. J. Am. Chem. Soc., 63, 562-567.

GMELIN-INSTITUT (1975): Gmelins Hanbuch der Anorganischen Chemie: Zinn. Teil C2, Springer-Verlag, Berlin, Heidelberg, New York, p.60.

GOBOM S. (1976): The hydrolysis of tin(II) ion. Acta Chem. Scand., A30, 745-750.

GOLDSCHMIDT H., ECKHARDT M. (1906): Über die Reduktion von Nitrokörpern durch alkalische Zinnoxydullösungen. Zeitschrift phys. Chemie, 56, 385-452.

HAIGHT G.P., ZOLTEWICZ J., EVANS W. (1962): Solubility studies on substituted ammonium salts of halide complexes. Acta Chem. Scand., 16, 311-322.

HALL F.M., SLATER S.J. (1968): Determination of the stability constants of the fluoride complexes of tin(II) using the fluoride electrode. Aust. J. Chem., 21, 2663-2667.

HOUSE C.I., KELSALL G.H. (1984): Potential-pH diagrams for the Sn/H_2O-Cl system. Electrochimica Acta, 29, 1459-1464.

HUEY C.S., TARTAR H.V. (1934): The stannous-stannic oxidation-reduction potential. J. Am. Chem. Soc., 56, 2585-2588.

KLINTSOVA A.P., BARSUKOV V.L. (1973): Solubility of cassiterite in water and aqueous NaOH at elevated temperatures. Gheokhimiya, 5, 701-709.

KOCHETKOVA N.V., TOPTYGINA G.M., KARPOV I.K., EDVOKIMOV V.I. (1984): Thermodynamic analysis of equilibria in the SnS_2-$CaCl_2$-H_2O system. Russ. J. Inorg. Chem., 29, 460-463.

KURIL'CHIKOVA G.E., BARSUKOV V.L. (1970): Stability of hydroxystannate complexes and experimental crystallization of cassiterite under hydrothermal conditions. Gheokhimiya, 1, 35-42.

KURIL'CHIKOVA G.Y., BARSUKOV V.L. (1971): Effects of CO_2 and of sodium and potassium bicarbonates and carbonates on the formation of Sn(IV) complexes in solution. Gheokhimiya, 6, 642-653.

MARK W. (1977): Hydrolysis of the tin(II) ion, Sn^{2+}, in alkaline solution. Acta Chem. Scand., A31, 157-162.

NAZARENKO V.A., ANTONOVICH V.P., NEVSKAYA E.M. (1971): Spectrophotometric determination of the hydrolysis constants of tin(IV) ions. Russ. J. Inorg. Chem., 15, 980-982.

NELSON K.G., AMIN K.N. (1975): Determination of stability constants of stannous fluoride complexes by potentiostatic titration. J. Pharmaceutical Sci., 64, 350-353.

ODA C., AMAYA T. (1998): Effects of ligands on the solubility of tin. JNC Technical Report, Japan, JNC TN8400 98-001.

PETTINE M., MILLERO F.J., MACCHI G. (1981): Hydrolysis of tin(II) in aqueous solutions. Anal. Chem., 53, 1039-1043.

PHILLIPS S.L., HALE F.V., SILVESTER L.F., SIEGEL L.D. (1988): Thermodynamic tables for nuclear waste isolation, an aqueous solutions database. Vol. 1, Lawrence Berkely Laboratory, California, USA, Report NUREG/CR-4864, LBL-22860, SAND87-0323.

PRYTZ M. (1928): Hydrolysemessungen in Stannosalzlösungen. Z. anorg. allg. Chemie, 172, 147-167.

RABIDEAU S.W., MOORE R.H. (1961): The application of high-speed computers to test least squares dertermination of the formation constants of the chloro-complexes of tin(II). J. Phys. Chem., 65, 371-373.

RANDALL M., MURAKAMI S. (1930): The free energy of stannous hydroxyl chloride and the activity coefficient of stannous chloride and stannous ion. J. Am. Chem. Soc., 52, 3967-3971.

RICCOBONI L., POPOFF P., ARICH G. (1949): Comportamento polarografico delle soluzione di stagno stannoso. Gazzetta Chimica Italiana, 79, 547-587.

SALVATORE F., FERRI D., TRIFUOGGI M., MANFREDI C., VASCA E. (1997): On the hydrolysis of the tin(II) ion. Annali di Chimica, 87, 477-481

SAMOILENKO V.M., LYASHENKO V.I., POLTORATSKOYA T.V. (1976): Halogeno- and thiocyanato-complexes of tin(II) in protonic and aprotic donor solvents. Russ. J. Inorg. Chem., 21, 1804-1807.

TOBIAS T.S. (1958): Studies on the hydrolysis of metal ions. 21. The hydrolysis of the tin(II) ion Sn^{2+}. Acta Chem. Scand., 12, 198-223.

VANDERZEE C.E., RHODES D.E. (1952): Thermodynamic data on the stannous chloride complexes from electromotive force measurement. J. Am. Chem. Soc., 74, 3552-3555.

Sn^{2+} + 2 e$^-$ <=> Sn(cr)

Weighted linear regression according to Grenthe et al. (1992), p.704

Medium	Molality	$\log_{10}K$ + 4 D			$1/\sigma_i^2$	m_i/σ_i^2	m_i^2/σ_i^2	X_i/σ_i^2	m_iX_i/σ_i^2
	m_i	X_i	σ_i						
$HClO_4$	0.081	-4.65	0.1		100	8.1	0.6561	-465	-37.665
$HClO_4$	0.202	-4.56	0.1		100	20.2	4.0804	-456	-92.112
$HClO_4$	0.357	-4.47	0.1		100	35.7	12.7449	-447	-159.579
$NaClO_4$	1.050	-4.31	0.1		100	104.99	110.229001	-431	-452.507
KCl	1.030	-4.42							
$\Sigma(i) =$					400	168.99	127.710401	-1799	-741.863

$$\Delta = \Sigma 1/\sigma_i^2\ \Sigma m_i^2/\sigma_i^2 - (\Sigma m_i/\sigma_i^2)^2 = 22526.54$$

$$\Sigma 1 = \Sigma m_i^2/\sigma_i^2\ \Sigma X_i/\sigma_i^2 = -229751$$

$$\Sigma 2 = \Sigma m_i/\sigma_i^2\ \Sigma m_iX_i/\sigma_i^2 = -125367$$

Intercept $\quad X^o = (\Sigma 1 - \Sigma 2) / \Delta = -4.63381 \qquad \sigma(X^o) = (\Sigma m_i^2/\sigma_i^2 / \Delta)^{0.5} = 0.075295$

$$\Sigma 3 = \Sigma 1/\sigma_i^2\ \Sigma m_iX_i/\sigma_i^2 = -296745$$

$$\Sigma 4 = \Sigma m_i/\sigma_i^2\ \Sigma X_i/\sigma_i^2 = -304013$$

Slope $\quad \Delta\varepsilon = (\Sigma 3 - \Sigma 4) / \Delta = 0.322635 \qquad \sigma(\Delta\varepsilon) = (\Sigma 1/\sigma_i^2 / \Delta)^{0.5} = 0.133255$

	$\log_{10}K$ + 4 D (calculated)		
Molality	mean	upper limit	lower limit
0	-4.63381	-4.55851	-4.7091
1.1	-4.27891	-4.05703	-4.50078
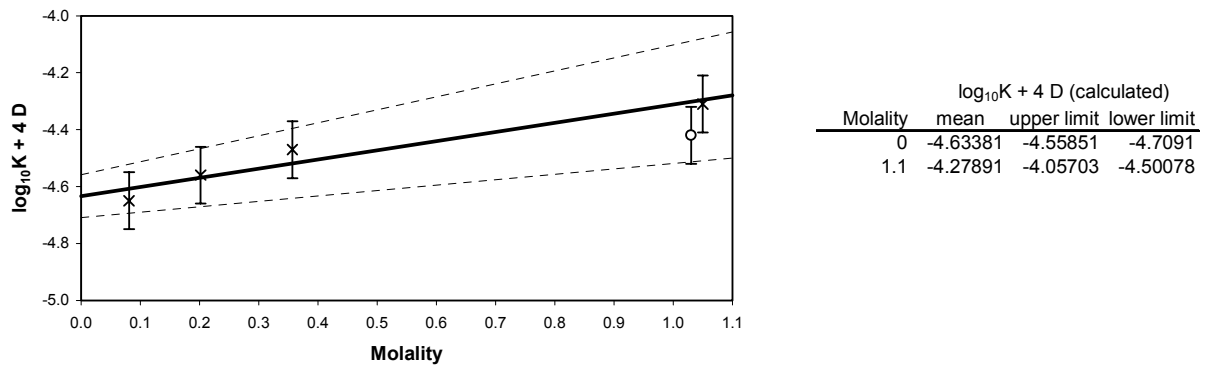
Fig. 5.22.2: SIT regression for the reaction Sn^{2+} + 2 e$^-$ $\Leftrightarrow$ Sn(cr); data from Table 5.22.2. The point measured in 1 M KCl (RICCOBONI et al. 1949) is not included in the regression.

emf - measurement in 2, 3 und 4 M $HClO_4$ at $25^{o}C$

Chain: Pt, H_2 | $HClO_4$(var.) || $SnCl_2$, $SnCl_4$, $HClO_4$(var.) | Hg, Pt

$HClO_4$ [mol/l]	$SnCl_4$(tot) [mol/l]	$SnCl_2$(tot) [mol/l]	$[Sn^{4+}]$-frei [mol/l]	E [V]	
2.000	1.013E-02	2.375E-02	2.689E-03	0.1634	
2.000	1.633E-02	1.331E-02	4.352E-03	0.1776	
2.000	1.935E-02	1.060E-02	5.161E-03	0.18309	
2.000	1.500E-02	1.868E-02	3.978E-03	0.1719	
3.000	9.208E-03	2.276E-02	3.423E-03	0.15194	
3.000	5.000E-03	2.184E-02	5.584E-03	0.1572	Mass balance unclear / Oxidation of Sn(II)?
3.000	7.489E-03	2.665E-02	2.783E-03	0.1465	
3.000	7.598E-03	2.879E-02	2.824E-03	0.1471	
3.000	1.740E-02	6.085E-03	6.481E-03	0.178	
4.000	2.593E-02	4.071E-03	1.112E-02	0.1788	
4.052	2.651E-02	3.595E-03	1.147E-02	0.1799	
4.000	2.650E-02	3.500E-03	1.136E-02	0.1796	
4.000	3.491E-03	2.362E-02	1.491E-03	0.12771	Probably outliner / point not considered
4.000	1.472E-02	7.791E-03	6.289E-03	0.1581	

Fig. 5.22.3:   Experimental data according to VASIL'EV et al. (1979).
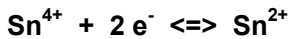
Sn^{4+} + 2 e$^-$ <=> Sn^{2+}   Weighted linear regression according to Grenthe et al. (1992), p.704

Medium	Molality	E$_0$ apparent			$1/\sigma_i^2$	m_i/σ_i^2	m_i^2/σ_i^2	X_i/σ_i^2	m_iX_i/σ_i^2
	m_i	X_i	σ_i						
HClO$_4$	2.2038	0.286246	0.006		27777.78	61216.6667	134909.29	7951.275	17523.02
HClO$_4$	2.2038	0.285234	0.006		27777.78	61216.6667	134909.29	7923.156	17461.05
HClO$_4$	2.2038	0.284481	0.006		27777.78	61216.6667	134909.29	7902.239	17414.95
HClO$_4$	2.2038	0.284966	0.006		27777.78	61216.6667	134909.29	7915.729	17444.68
HClO$_4$	3.4713	0.292288	0.0065		23668.64	82160.9467	285205.294	6918.048	24014.62
HClO$_4$	3.4713	0.292138	0.0065		23668.64	82160.9467	285205.294	6914.512	24002.35
HClO$_4$	3.4713	0.293088	0.0065		23668.64	82160.9467	285205.294	6936.988	24080.37
HClO$_4$	3.4713	0.289643	0.0065		23668.64	82160.9467	285205.294	6855.465	23797.38
HClO$_4$	4.8684	0.281922	0.008		15625	76068.75	370333.103	4405.028	21445.44
HClO$_4$	4.931689	0.280903	0.008		15625	77057.6438	380024.349	4389.105	21645.7
HClO$_4$	4.8684	0.280086	0.008		15625	76068.75	370333.103	4376.35	21305.82
HClO$_4$	4.8684	0.287147	0.008		15625	76068.75	370333.103	4486.672	21842.91
HClO$_4$	4.8684	0.300029	0.016						
				$\Sigma(i) =$	268285.7	878774.347	3171481.99	76974.57	251978.3

$$\Delta = \Sigma 1/\sigma_i^2 \, \Sigma m_i^2/\sigma_i^2 - (\Sigma m_i/\sigma_i^2)^2 = 7.86E+10$$
$$\Sigma 1 = \Sigma m_i^2/\sigma_i^2 \, \Sigma X_i/\sigma_i^2 = 2.44E+11$$
$$\Sigma 2 = \Sigma m_i/\sigma_i^2 \, \Sigma m_iX_i/\sigma_i^2 = 2.21E+11$$

Intercept $\mathbf{X^o} = (\Sigma 1 - \Sigma 2)/\Delta = 0.288625$ $\sigma(\mathbf{X^o}) = (\Sigma m_i^2/\sigma_i^2 / \Delta)^{0.5} = 0.006351$

$$\Sigma 3 = \Sigma 1/\sigma_i^2 \, \Sigma m_iX_i/\sigma_i^2 = 6.76E+10$$
$$\Sigma 4 = \Sigma m_i/\sigma_i^2 \, \Sigma X_i/\sigma_i^2 = 6.76E+10$$

Slope $\mathbf{\Delta\epsilon} = (\Sigma 3 - \Sigma 4)/\Delta = -0.00052$ $\sigma(\Delta\epsilon) = (\Sigma 1/\sigma_i^2 / \Delta)^{0.5} = 0.001847$

	E$_0$ apparent (calculated)		
Molality	mean	upper limit	lower limit
0	0.288625	0.294977	0.282274
5.4	0.285802	0.302129	0.269475
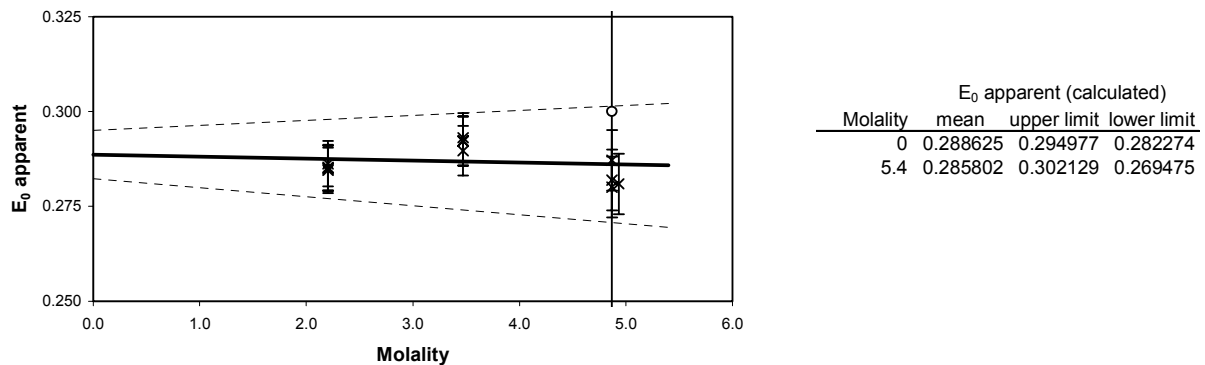
Fig. 5.22.4: SIT regression for the reaction Sn^{4+} + 2 e$^-$ ⇔ Sn^{2+}; data from VASIL'EV et al. (1979).
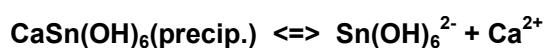
CaSn(OH)$_6$(precip.) <=> Sn(OH)$_6^{2-}$ + Ca^{2+}

Weighted linear regression according to Grenthe et al. (1992), p.704

Medium	Molality	log$_{10}$*K - 8 D			1 / σ$_i^2$	m$_i$/σ$_i^2$	m$_i^2$/σ$_i^2$	X$_i$/σ$_i^2$	m$_i$X$_i$/σ$_i^2$
	m$_i$	X$_i$	σ$_i$						
NaClO$_4$	0.2536	-9.61	0.11		82.64463	20.9586777	5.31512066	-794.215	-201.413
NaClO$_4$	0.2536	-9.77	0.11		82.64463	20.9586777	5.31512066	-807.438	-204.766
NaClO$_4$	0.5133	-9.92	0.17		34.60208	17.7612457	9.1168474	-343.253	-176.192
NaClO$_4$	0.5133	-10.12	0.17		34.60208	17.7612457	9.1168474	-350.173	-179.744
NaClO$_4$	0.5133	-10.23	0.17		34.60208	17.7612457	9.1168474	-353.979	-181.698
NaClO$_4$	0.5133	-10.36	0.17		34.60208	17.7612457	9.1168474	-358.478	-184.007
NaClO$_4$	2.2124	-10.71	0.25		16	35.3984	78.3154202	-171.36	-379.117
NaClO$_4$	2.2124	-10.36	0.25		16	35.3984	78.3154202	-165.76	-366.727
KCl	1.03	-4.83							
				Σ(i) =	335.6976	183.759138	203.728471	-3344.66	-1873.66

$\Delta = \Sigma 1/\sigma_i^2\ \Sigma m_i^2/\sigma_i^2 - (\Sigma m_i/\sigma_i^2)^2 =$ 34623.73

$\Sigma 1 = \Sigma m_i^2/\sigma_i^2\ \Sigma X_i/\sigma_i^2 =$ -681402

$\Sigma 2 = \Sigma m_i/\sigma_i^2\ \Sigma m_i X_i/\sigma_i^2 =$ -344303

Intercept $\quad X^o = (\Sigma 1 - \Sigma 2) / \Delta =$ -9.73606 $\qquad \sigma(X^o) = (\Sigma m_i^2/\sigma_i^2\ / \Delta)^{0.5} =$ 0.076708

$\Sigma 3 = \Sigma 1/\sigma_i^2\ \Sigma m_i X_i/\sigma_i^2 =$ -628984

$\Sigma 4 = \Sigma m_i/\sigma_i^2\ \Sigma X_i/\sigma_i^2 =$ -614611

Slope $\quad \Delta\epsilon = (\Sigma 3 - \Sigma 4) / \Delta =$ -0.41512 $\qquad \sigma(\Delta\epsilon) = (\Sigma 1/\sigma_i^2\ / \Delta)^{0.5} =$ 0.098466
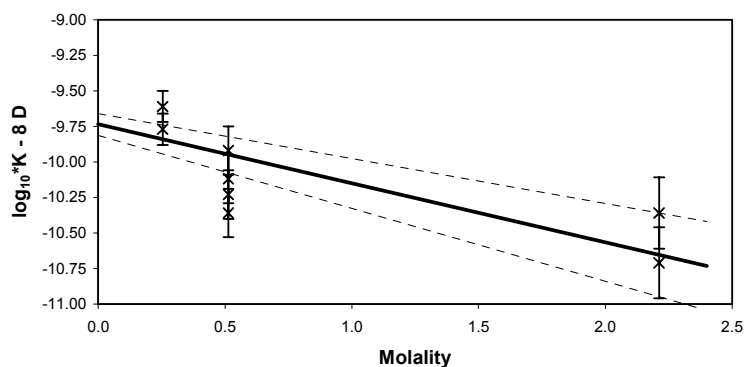
	log$_{10}$*K - 8 D (calculated)		
Molality	mean	upper limit	lower limit
0	-9.73606	-9.65936	-9.81277
2.4	-10.7324	-10.4193	-11.0454

Fig. 5.22.5:   SIT regression for the reaction CaSn(OH)$_6$(precip.) $\Leftrightarrow$ Sn(OH)$_6^{2-}$ + Ca^{2+}; data from LOTHENBACH et al. (2000).
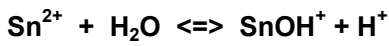
Sn^{2+} + H$_2$O <=> SnOH$^+$ + H$^+$ Weighted linear regression according to Grenthe et al. (1992), p.704

Medium	Molality	log$_{10}$K + 2 D			1 / σ_i^2	m_i/σ_i^2	m_i^2/σ_i^2	X_i/σ_i^2	m_iX_i/σ_i^2
	m_i	X_i	σ_i						
NaNO$_3$	0.1006	-3.88	0.2		25	2.515	0.253009	-97	-9.7582
NaNO$_3$	0.509	-3.45	0.2		25	12.725	6.477025	-86.25	-43.9013
NaNO$_3$	1.034	-3.69	0.2		25	25.85	26.7289	-92.25	-95.3865
NaClO$_4$	3.496	-3.2	0.11						
NaClO$_4$	3.496	-3.27	0.11						
NaClO$_4$	3.496	-3.42	0.11						
				$\Sigma(i) =$	75	41.09	33.458934	-275.5	-149.046

$$\Delta = \Sigma 1/\sigma_i^2 \, \Sigma m_i^2/\sigma_i^2 - (\Sigma m_i/\sigma_i^2)^2 = 821.0319$$

$$\Sigma 1 = \Sigma m_i^2/\sigma_i^2 \, \Sigma X_i/\sigma_i^2 = -9217.94$$

$$\Sigma 2 = \Sigma m_i/\sigma_i^2 \, \Sigma m_iX_i/\sigma_i^2 = -6124.3$$

Intercept $X^o = (\Sigma 1 - \Sigma 2) / \Delta = -3.76799$ $\sigma(X^o) = (\Sigma m_i^2/\sigma_i^2 / \Delta)^{0.5} = 0.201872$

$$\Sigma 3 = \Sigma 1/\sigma_i^2 \, \Sigma m_iX_i/\sigma_i^2 = -11178.4$$

$$\Sigma 4 = \Sigma m_i/\sigma_i^2 \, \Sigma X_i/\sigma_i^2 = -11320.3$$

Slope $\Delta\varepsilon = (\Sigma 3 - \Sigma 4) / \Delta = 0.172769$ $\sigma(\Delta\varepsilon) = (\Sigma 1/\sigma_i^2 / \Delta)^{0.5} = 0.302239$
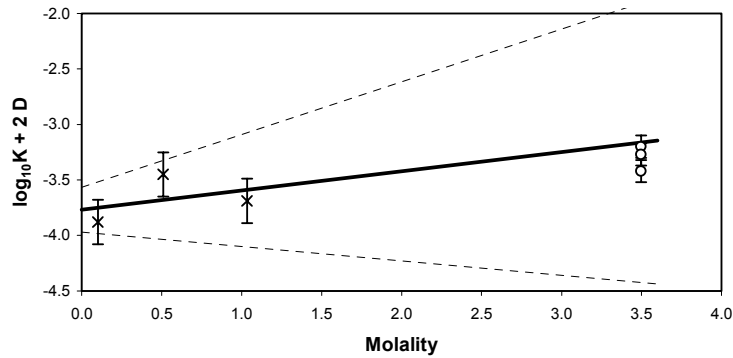
	log$_{10}$K + 2 D (calculated)		
Molality	mean	upper limit	lower limit
0	-3.76799	-3.56612	-3.96986
3.6	-3.14602	-1.85609	-4.43595

Fig. 5.22.6:   SIT regression for the reaction Sn^{2+} + H$_2$O(l) $\Leftrightarrow$ SnOH$^+$ + H$^+$; data from Table 5.22.9a. Points measured at 3.496 m NaClO$_4$ are not included in the regression.

Sn^{2+} + 2 H_2O <=> $Sn(OH)_2$(aq) + 2 H^+

Weighted linear regression according to Grenthe et al. (1992), p.704

Medium	Molality	$\log_{10}K$ + 2 D			$1/\sigma_i^2$	m_i/σ_i^2	m_i^2/σ_i^2	X_i/σ_i^2	m_iX_i/σ_i^2
	m_i	X_i	σ_i						
$NaNO_3$	0.1006	-7.68	0.2		25	2.515	0.253009	-192	-19.3152
$NaNO_3$	0.509	-7.55	0.2		25	12.725	6.477025	-188.75	-96.0738
$NaNO_3$	1.034	-7.39	0.2		25	25.85	26.7289	-184.75	-191.032
				$\Sigma(i) =$	75	41.09	33.458934	-565.5	-306.42

$$\Delta = \Sigma 1/\sigma_i^2\ \Sigma m_i^2/\sigma_i^2 - (\Sigma m_i/\sigma_i^2)^2 = 821.0319$$

$$\Sigma 1 = \Sigma m_i^2/\sigma_i^2\ \Sigma X_i/\sigma_i^2 = -18921$$

$$\Sigma 2 = \Sigma m_i/\sigma_i^2\ \Sigma m_iX_i/\sigma_i^2 = -12590.8$$

Intercept $\mathbf{X^o} = (\Sigma 1 - \Sigma 2)/\Delta = -7.71007$ $\sigma(X^o) = (\Sigma m_i^2/\sigma_i^2\ /\ \Delta)^{0.5} = 0.201872$

$$\Sigma 3 = \Sigma 1/\sigma_i^2\ \Sigma m_iX_i/\sigma_i^2 = -22981.5$$

$$\Sigma 4 = \Sigma m_i/\sigma_i^2\ \Sigma X_i/\sigma_i^2 = -23236.4$$

Slope $\mathbf{\Delta\epsilon} = (\Sigma 3 - \Sigma 4)/\Delta = 0.310416$ $\sigma(\Delta\epsilon) = (\Sigma 1/\sigma_i^2\ /\ \Delta)^{0.5} = 0.302239$
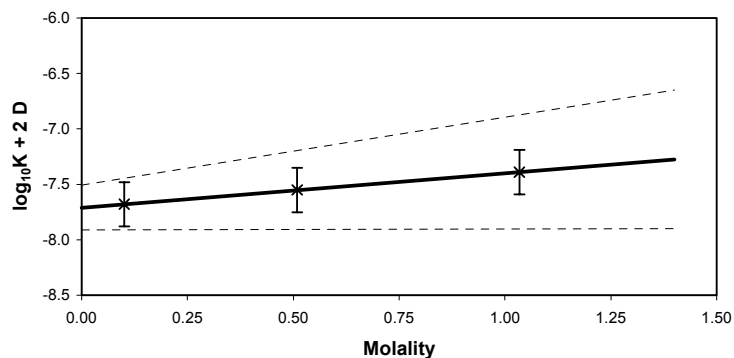
	$\log_{10}K$ + 2 D (calculated)		
Molality	mean	upper limit	lower limit
0	-7.71007	-7.50819	-7.91194
1.4	-7.27548	-6.65048	-7.90049

Fig. 5.22.7:   SIT regression for the reaction Sn^{2+} + 2 H_2O(l) $\Leftrightarrow$ $Sn(OH)_2$(aq) + 2 H^+; data from Table 5.22.9b

Sn^{2+} + 3 H_2O <=> $Sn(OH)_3^-$ + 3 H^+　　Weighted linear regression according to Grenthe et al. (1992), p.704

Medium	Molality m_i	$\log_{10}K$ X_i	σ_i	$1/\sigma_i^2$	m_i/σ_i^2	m_i^2/σ_i^2	X_i/σ_i^2	m_iX_i/σ_i^2
$NaNO_3$	0.1006	-17.5	0.2	25	2.515	0.253009	-437.5	-44.0125
$NaNO_3$	0.509	-17.7	0.2	25	12.725	6.477025	-442.5	-225.233
$NaNO_3$	1.034	-17.6	0.2	25	25.85	26.7289	-440	-454.96
$NaClO_4$	3.496	-17.96	0.2					
$\Sigma(i) =$				75	41.09	33.458934	-1320	-724.205

$$\Delta = \Sigma 1/\sigma_i^2 \, \Sigma m_i^2/\sigma_i^2 - (\Sigma m_i/\sigma_i^2)^2 = 821.0319$$
$$\Sigma 1 = \Sigma m_i^2/\sigma_i^2 \, \Sigma X_i/\sigma_i^2 = -44165.8$$
$$\Sigma 2 = \Sigma m_i/\sigma_i^2 \, \Sigma m_iX_i/\sigma_i^2 = -29757.6$$

Intercept　　$X^o = (\Sigma 1 - \Sigma 2)/\Delta = -17.5489$　　　$\sigma(X^o) = (\Sigma m_i^2/\sigma_i^2 / \Delta)^{0.5} = 0.201872$

$$\Sigma 3 = \Sigma 1/\sigma_i^2 \, \Sigma m_iX_i/\sigma_i^2 = -54315.4$$
$$\Sigma 4 = \Sigma m_i/\sigma_i^2 \, \Sigma X_i/\sigma_i^2 = -54238.8$$

Slope　　$\Delta\varepsilon = (\Sigma 3 - \Sigma 4)/\Delta = -0.09327$　　　$\sigma(\Delta\varepsilon) = (\Sigma 1/\sigma_i^2 / \Delta)^{0.5} = 0.302239$

	$\log_{10}K$ (calculated)		
Molality	mean	upper limit	lower limit
0	-17.5489	-17.347	-17.7508
3.6	-17.8847	-16.5947	-19.1746
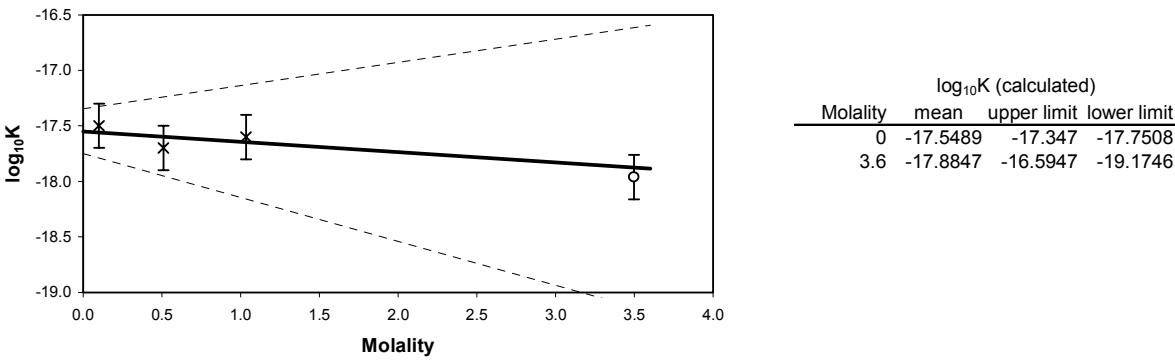
Fig. 5.22.8:　SIT regression for the reaction Sn^{2+} + 3 $H_2O(l) \Leftrightarrow Sn(OH)_3^- $ + 3 H^+; data from Table 5.22.9c. The point measured at 3.496 m $NaClO_4$ is not included in the regression.

$Sn^{2+} + Cl^- \Leftrightarrow SnCl^+$

Weighted linear regression according to Grenthe et al. (1992), p.704

Medium	Molality m_i	$\log_{10}K + 4D$ X_i	σ_i	$1/\sigma_i^2$	m_i/σ_i^2	m_i^2/σ_i^2	X_i/σ_i^2	m_iX_i/σ_i^2
$NaClO_4$	0.5128	1.79	0.2	25	12.82	6.574096	44.75	22.9478
$NaClO_4$	1.0499	1.9	0.2	25	26.2475	27.5572503	47.5	49.87025
$NaClO_4$	1.0499	1.84	0.2	25	26.2475	27.5572503	46	48.2954
$HClO_4$	2.2074	2.05	0.2	25	55.185	121.815369	51.25	113.1293
ClO_4^-	2.2074	2	0.2	25	55.185	121.815369	50	110.37
$NaClO_4$	3.4956	2.18	0.2	25	87.39	305.480484	54.5	190.5102
$NaClO_4$	3.4956	2.14	0.2	25	87.39	305.480484	53.5	187.0146
$NaClO_4$	4.9456	2.38	0.2	25	123.64	611.473984	59.5	294.2632
$NaClO_4$	8.1	2.9	0.2	25	202.5	1640.25	72.5	587.25
$NaNO_3$	1.0338	1.55	0.2					
H_2SO_4/HCl	4.4	2.48	0.2					
$\Sigma(i) =$				225	676.605	3168.00429	479.5	1603.651

$\Delta = \Sigma 1/\sigma_i^2\, \Sigma m_i^2/\sigma_i^2 - (\Sigma m_i/\sigma_i^2)^2 = 255006.6$

$\Sigma 1 = \Sigma m_i^2/\sigma_i^2\, \Sigma X_i/\sigma_i^2 = 1519058$

$\Sigma 2 = \Sigma m_i/\sigma_i^2\, \Sigma m_iX_i/\sigma_i^2 = 1085038$

Intercept $\quad X^o = (\Sigma 1 - \Sigma 2)\,/\,\Delta = 1.701995 \qquad \sigma(X^o) = (\Sigma m_i^2/\sigma_i^2\,/\,\Delta)^{0.5} = 0.11146$

$\Sigma 3 = \Sigma 1/\sigma_i^2\, \Sigma m_iX_i/\sigma_i^2 = 360821.4$

$\Sigma 4 = \Sigma m_i/\sigma_i^2\, \Sigma X_i/\sigma_i^2 = 324432.1$

Slope $\quad \Delta\varepsilon = (\Sigma 3 - \Sigma 4)\,/\,\Delta = 0.142699 \qquad \sigma(\Delta\varepsilon) = (\Sigma 1/\sigma_i^2\,/\,\Delta)^{0.5} = 0.029704$
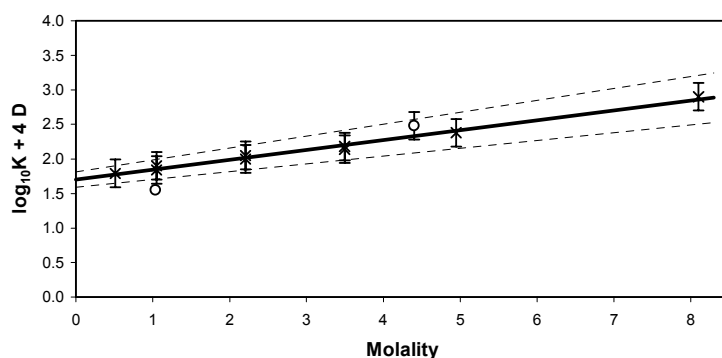
	$\log_{10}K + 4D$ (calculated)		
Molality	mean	upper limit	lower limit
0	1.701995	1.813454	1.590535
8.3	2.8864	3.244403	2.528397

Fig. 5.22.9:   SIT regression for the reaction $Sn^{2+} + Cl^- \Leftrightarrow SnCl^+$; data from Table 5.22.11a.

Sn^{2+} + 2 Cl$^-$ <=> SnCl$_2$(aq)   Weighted linear regression according to Grenthe et al. (1992), p.704

Medium	Molality	log$_{10}$K + 6 D			1 / σ$_i^2$	m$_i$/σ$_i^2$	m$_i^2$/σ$_i^2$	X$_i$/σ$_i^2$	m$_i$X$_i$/σ$_i^2$
	m$_i$	X$_i$	σ$_i$						
NaClO$_4$	0.5128	2.41	0.4		6.25	3.205	1.643524	15.0625	7.72405
NaClO$_4$	1.0499	3.08	0.4		6.25	6.561875	6.88931256	19.25	20.21058
NaClO$_4$	1.0499	2.36	0.4		6.25	6.561875	6.88931256	14.75	15.48603
ClO$_4^-$	2.2074	3.13	0.4		6.25	13.79625	30.4538423	19.5625	43.18226
NaClO$_4$	3.4956	3.2	0.4		6.25	21.8475	76.370121	20	69.912
NaClO$_4$	3.4956	3.28	0.4		6.25	21.8475	76.370121	20.5	71.6598
NaClO$_4$	4.9456	3.69	0.4		6.25	30.91	152.868496	23.0625	114.0579
NaClO$_4$	8.1	4.69	0.4		6.25	50.625	410.0625	29.3125	237.4313
NaNO$_3$	1.0338	2.31	0.4						
H$_2$SO$_4$/HCl	4.4	3.9	0.4						
				Σ(i) =	50	155.355	761.547229	161.5	579.6639

$\Delta = \Sigma 1/\sigma_i^2\, \Sigma m_i^2/\sigma_i^2 - (\Sigma m_i/\sigma_i^2)^2 =$ 13942.19

$\Sigma 1 = \Sigma m_i^2/\sigma_i^2\, \Sigma X_i/\sigma_i^2 =$ 122989.9

$\Sigma 2 = \Sigma m_i/\sigma_i^2\, \Sigma m_i X_i/\sigma_i^2 =$ 90053.68

Intercept $X^o = (\Sigma 1 - \Sigma 2) / \Delta =$ 2.362341 $\sigma(X^o) = (\Sigma m_i^2/\sigma_i^2 / \Delta)^{0.5} =$ 0.233713

$\Sigma 3 = \Sigma 1/\sigma_i^2\, \Sigma m_i X_i/\sigma_i^2 =$ 28983.19

$\Sigma 4 = \Sigma m_i/\sigma_i^2\, \Sigma X_i/\sigma_i^2 =$ 25089.83

Slope $\Delta\epsilon = (\Sigma 3 - \Sigma 4) / \Delta =$ 0.27925 $\sigma(\Delta\epsilon) = (\Sigma 1/\sigma_i^2 / \Delta)^{0.5} =$ 0.059885
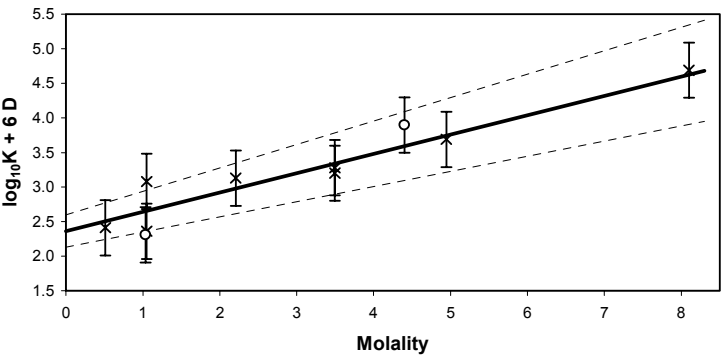
	log$_{10}$K + 6 D (calculated)		
Molality	mean	upper limit	lower limit
0	2.362341	2.596054	2.128628
8.3	4.680119	5.41088	3.949359

Fig. 5.22.10: SIT regression for the reaction Sn^{2+} + 2 Cl$^-$ $\Leftrightarrow$ SnCl$_2$(aq); data from Table 5.22.11b.

Sn^{2+} + 3 Cl$^-$ <=> SnCl$_3^-$ Weighted linear regression according to Grenthe et al. (1992), p.704

Medium	Molality	log$_{10}$K + 6 D			1 / σ$_i^2$	m$_i$/σ$_i^2$	m$_i^2$/σ$_i^2$	X$_i$/σ$_i^2$	m$_i$X$_i$/σ$_i^2$
	m$_i$	X$_i$	σ$_i$						
ClO$_4^-$	2.2074	2.91	0.4		6.25	13.79625	30.4538423	18.1875	40.14709
NaClO$_4$	3.4956	3.16	0.4		6.25	21.8475	76.370121	19.75	69.0381
NaClO$_4$	3.4956	3.15	0.4		6.25	21.8475	76.370121	19.6875	68.81963
NaClO$_4$	4.9456	3.69	0.4		6.25	30.91	152.868496	23.0625	114.0579
NaClO$_4$	8.1	4.69	0.4		6.25	50.625	410.0625	29.3125	237.4313
H$_2$SO$_4$/HCl	4.4	4.01	0.4						
				Σ(i) =	31.25	139.02625	746.12508	110	529.494

$$\Delta = \Sigma 1/\sigma_i^2\, \Sigma m_i^2/\sigma_i^2 - (\Sigma m_i/\sigma_i^2)^2 = 3988.111$$
$$\Sigma 1 = \Sigma m_i^2/\sigma_i^2\, \Sigma X_i/\sigma_i^2 = 82073.76$$
$$\Sigma 2 = \Sigma m_i/\sigma_i^2\, \Sigma m_i X_i/\sigma_i^2 = 73613.56$$

Intercept **X^o** = (Σ1 - Σ2) / Δ = 2.121355   **σ(X^o)** = (Σm$_i^2$/σ$_i^2$ / Δ)$^{0.5}$ = 0.432536

$$\Sigma 3 = \Sigma 1/\sigma_i^2\, \Sigma m_i X_i/\sigma_i^2 = 16546.69$$
$$\Sigma 4 = \Sigma m_i/\sigma_i^2\, \Sigma X_i/\sigma_i^2 = 15292.89$$

Slope **Δε** = (Σ3 - Σ4) / Δ = 0.314384   **σ(Δε)** = (Σ1/σ$_i^2$ / Δ)$^{0.5}$ = 0.08852
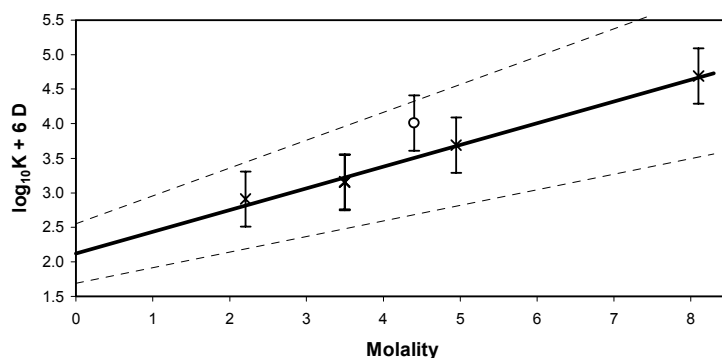
log$_{10}$K + 6 D (calculated)

Molality	mean	upper limit	lower limit
0	2.121355	2.553891	1.688819
8.3	4.730744	5.897996	3.563492

Fig. 5.22.11: SIT regression for the reaction Sn^{2+} + 3 Cl$^-$ ⇔ SnCl$_3^-$; data from Table 5.22.11c.
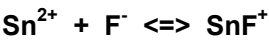
Sn^{2+} + F$^-$ <=> SnF$^+$ Weighted linear regression according to Grenthe et al. (1992), p.704

Medium	Molality	log$_{10}$K + 4 D			1 / σ$_i^2$	m$_i$/σ$_i^2$	m$_i^2$/σ$_i^2$	X$_i$/σ$_i^2$	m$_i$X$_i$/σ$_i^2$
	m$_i$	X$_i$	σ$_i$						
HClO$_4$	0.51	4.84	0.3		11.11111	5.66666667	2.89	53.77778	27.42667
HClO$_4$	0.886	5.27	0.3		11.11111	9.84444444	8.72217778	58.55556	51.88022
NaClO$_4$	1.05	4.82	0.3		11.11111	11.6666667	12.25	53.55556	56.23333
NaClO$_4$	2.16	4.98	0.3		11.11111	24	51.84	55.33333	119.52
NaF	0.1	4.04	0.4						

Σ(i) = 44.44444 51.1777778 75.7021778 221.2222 255.0602

$\Delta = \Sigma 1/\sigma_i^2 \ \Sigma m_i^2/\sigma_i^2 - (\Sigma m_i/\sigma_i^2)^2$ = 745.3763

$\Sigma 1 = \Sigma m_i^2/\sigma_i^2 \ \Sigma X_i/\sigma_i^2$ = 16747

$\Sigma 2 = \Sigma m_i/\sigma_i^2 \ \Sigma m_i X_i/\sigma_i^2$ = 13053.42

Intercept $X^o = (\Sigma 1 - \Sigma 2) / \Delta$ = 4.955334 $\sigma(X^o) = (\Sigma m_i^2/\sigma_i^2 / \Delta)^{0.5}$ = 0.318689

$\Sigma 3 = \Sigma 1/\sigma_i^2 \ \Sigma m_i X_i/\sigma_i^2$ = 11336.01

$\Sigma 4 = \Sigma m_i/\sigma_i^2 \ \Sigma X_i/\sigma_i^2$ = 11321.66

Slope $\Delta\varepsilon = (\Sigma 3 - \Sigma 4) / \Delta$ = 0.01925 $\sigma(\Delta\varepsilon) = (\Sigma 1/\sigma_i^2 / \Delta)^{0.5}$ = 0.244186
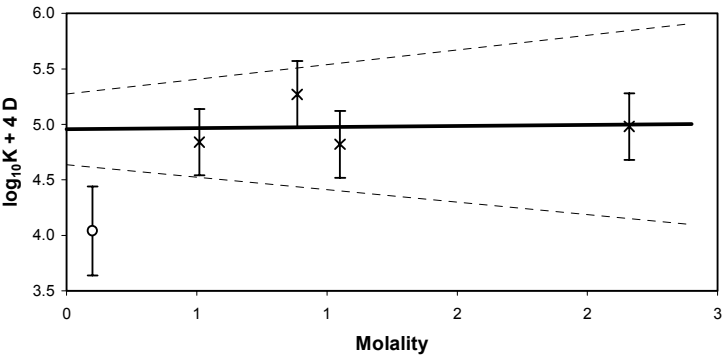
log$_{10}$K + 4 D (calculated)		
Molality	mean	upper limit lower limit
0	4.955334	5.274023 4.636646
2.4	5.001533	5.906268 4.096798

Fig. 5.22.12:   SIT regression for the reaction Sn^{2+} + F$^-$ $\Leftrightarrow$ SnF$^+$; data from Table 5.22.12.

5.23   Uranium

The information on uranium is taken from OECD NEA's books "Chemical Thermodynamics of Uranium" (GRENTHE et al. 1992), "Chemical Thermodynamics of Americium, Appendix D" (GRENTHE et al. 1995) and selected publications. Most inorganic complexes and solids of uranium included in the Nagra/PSI TDB 01/01 are recommended values taken from the NEA review. A few cases where we did not agree with the NEA data selection are documented extensively (marked by a vertical left borderline in this chapter). However, not all recommended values of the NEA review are included in our database. NEA reviews are not restricted to data relevant for radioactive waste management or even environmental modelling in general: All kinds of liquid and gas phases, high temperature solids and complexes with exotic ligands like azide are included. There are no formal guidelines which of these phases should be included in our database. In an attempt to focus our database on environmental modelling and to avoid overloading it with phases and complexes which most probably will never be relevant in environmental systems, all available thermodynamic data in the NEA reviews has been thoroughly scrutinised and underwent a careful selection procedure. Our decisions are documented in the following sections. The notation of formulae and symbols used in this text follows the NEA recommendations and practice.

5.23.1   Elemental uranium

Uranium metal and gas are not relevant under environmental conditions. Uranium gas is not included in the database. The absolute entropy and heat capacity of U(cr) is given in Table 5.23.1 for computational purposes only.

5.23.2   Simple uranium aqua ions

In aqueous media, uranium exists in oxidation states III, IV, V and VI.

UO_2^{2+}: Extensive and accurate data are available for UO_2^{2+}. Because of the thorough CODATA reviews, the CODATA value of

$$\Delta_f H_m° \ (UO_2^{2+}, aq, 298.15 \ K) \quad = \quad -(1019.0 \pm 1.5) \ kJ \cdot mol^{-1}$$

has been adopted by GRENTHE et al. (1992). As an expedient to assure maximum CODATA consistency, the CODATA value of the entropy of the UO_2^{2+} ion is recommended by GRENTHE et al. (1992):

$$S_m° \ (UO_2^{2+}, aq, 298.15 \ K) \quad = \quad -(98.2 \pm 3.0) \ J \cdot K^{-1} \cdot mol^{-1}$$

The Gibbs energy of formation is obtained from the above values

$$\Delta_f G_m° \ (UO_2^{2+}, aq, 298.15 \ K) \quad = \quad -(952.55 \pm 1.75) \ kJ \cdot mol^{-1}$$

G RENTHE et al. (1992) selected as value for the molar heat capacity of UO_2^{2+}:

$$C_{p,m}° \ (UO_2^{2+}, \ aq, \ 298.15 \ K) \quad = \quad (42.4 \pm 3.0) \ J \cdot K^{-1} \cdot mol^{-1}$$

UO_2^+: The pentavalent cation, UO_2^+, rapidly disproportionates to U(VI) and U(IV) under most environmental conditions. The regions in which UO_2^+ has been proposed as a significant species are at pH < 5. Only a single U(V) carbonate complex has been reported in the literature (see 5.23.7.1.2). Despite this very low significance of U(V) for geochemical modelling we decided to include UO_2^+ in our database for the sake of chemical systematics. The standard Gibbs energy of formation of UO_2^+ is obtained from the standard potential of the reaction

$$UO_2^{2+} + e^- \Leftrightarrow UO_2^+$$
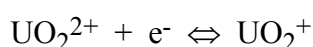
and the standard Gibbs energy of formation of UO_2^{2+} discussed above. The value of G RENTHE et al. (1992) for the UO_2^{2+}/UO_2^+ couple is:

$$\log_{10} K° \ (298.15 \ K) \quad = \quad 1.484 \pm 0.022$$

In the absence of experimental data, G RENTHE et al. (1992) selected an estimated entropy value

$$S_m° \ (UO_2^+, \ aq, \ 298.15 \ K) \quad = \quad -(25 \pm 8) \ J \cdot K^{-1} \cdot mol^{-1}$$

The enthalpy of formation is derived from the selected $\log_{10} K° \rightarrow \Delta_f G_m°$ and $S_m°$ values:

$$\Delta_f H_m° \ (UO_2^+, \ aq, \ 298.15 \ K) \quad = \quad -(1025.1 \pm 3.0) \ kJ \cdot mol^{-1}$$

The validity of this estimate is corroborated by a new experimental value of $-(60 \pm 11) \ J \cdot K^{-1} \cdot mol^{-1}$ for the partial molar heat capacity of Th^{4+} (H OVEY et al. 1997).

U^{4+}: The standard Gibbs energy of formation of U^{4+} is obtained from experimental data on the standard potential of the reaction

$$UO_2^{2+} + 4 \ H^+ + 2 \ e^- \Leftrightarrow U^{4+} + 2 \ H_2O(l)$$
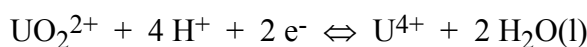
and the standard Gibbs energy of formation of UO_2^{2+} discussed above. The value selected by G RENTHE et al. (1992) is:

$$\log_{10} K° \ (298.15 \ K) \quad = \quad 9.038 \pm 0.041$$

The enthalpy of formation as selected by G RENTHE et al. (1992) is based on two series of experiments.

$$\Delta_f H_m° \ (U^{4+}, \ aq, \ 298.15 \ K) \quad = \quad -(591.2 \pm 3.3) \ kJ \cdot mol^{-1}$$

The entropy is derived from the selected $\log_{10} K° \rightarrow \Delta_f G_m°$ and $\Delta_f H_m°$ values:

$$S_m° \ (U^{4+}, \ aq, \ 298.15 \ K) \quad = \quad -(416.9 \pm 12.6) \ J \cdot K^{-1} \cdot mol^{-1}$$

Due to the absence of $C_{p,m}$ measurements for U^{4+}, GRENTHE et al. (1992) adopted an estimate, defined as the mean partial molal heat capacity from 298.15 to 473 K.

$$C_{p,m} \ (U^{4+}, \ aq, \ 298.15\text{-}473 \ K) \quad = \quad -(48 \pm 15) \ J \cdot K^{-1} \cdot mol^{-1}$$

U^{3+}: The trivalent cation, U^{3+}, is the lowest oxidation state of uranium which may be generated electrochemically in aqueous media. However, U^{3+} will be oxidised rapidly to higher oxidation states in any environmental system and no reliable U(III) complexation data have been reported in the literature. Therefore, we decided to exclude U^{3+} from our database.

5.23.3   Oxygen and hydrogen compounds

5.23.3.1 Aqueous uranium hydroxide complexes

5.23.3.1.1   U(VI) hydroxide complexes

The hydrolysis of U(VI) has been the subject of extensive study. However, the vast majority of experimental work was done in aqueous, slightly acidic ($2 < pH < 5$) media with total uranium concentrations above 10^{-4} M. For this range of conditions polymeric U(VI) species are predominant.

Thermodynamic data on U(VI) hydrolysis refer to the reaction

$$m \ UO_2^{2+} \ + \ n \ H_2O(l) \ \Leftrightarrow \ (UO_2)_m(OH)_n^{(2m-n)} \ + \ n \ H^+$$
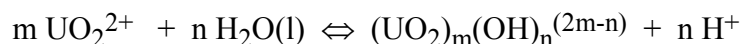
Polymeric U(VI) hydrolysis species: For slightly acidic media with total uranium concentrations above 10^{-4} M there is a general consensus that the dimer, $(UO_2)_2(OH)_2^{2+}$, is a major species. Two tri-uranyl species, $(UO_2)_3(OH)_5^+$ and $(UO_2)_3(OH)_4^{2+}$, are also reasonably well established. GRENTHE et al. (1992) selected the following standard equilibrium constants for these polymeric species:

$$\log_{10}{}^*\beta_{2,2}° \ (m = 2, \ n = 2, \ 298.15 \ K) \quad = \quad -5.62 \pm 0.04$$

$$\log_{10}{}^*\beta_{4,3}° \ (m = 3, \ n = 4, \ 298.15 \ K) \quad = \quad -11.9 \pm 0.3$$

$$\log_{10}{}^*\beta_{5,3}° \ (m = 3, \ n = 5, \ 298.15 \ K) \quad = \quad -15.55 \pm 0.12$$

The formation of $(UO_2)_2OH^{3+}$ was initially reported from potentiometric studies in which high uranium concentrations were used. In addition, there is good kinetic evidence for the existence of this species. GRENTHE et al. (1992) selected the value

$$\log_{10}{}^*\beta_{1,2}° \ (m = 2, \ n = 1, \ 298.15 \ K) \quad = \quad -2.7 \pm 1.0$$

Further polymeric cationic species have been proposed on the basis of potentiometric studies. Scrutinising the most careful studies GRENTHE et al. (1992) decided to recommend the species $(UO_2)_4(OH)_7^+$ with a selected value

$$\log_{10}{}^*\beta_{7,4}° \ (m = 4, n = 7, 298.15 \ K) \quad = \quad -21.9 \pm 1.0$$

In view of the strong qualitative evidence for a polymeric anionic hydrolysis species, GRENTHE et al. (1992) accepted the existence of $(UO_2)_3(OH)_7^-$, and a value of

$$\log_{10}{}^*\beta_{7,3}° \ (m = 3, n = 7, 298.15 \ K) \quad = \quad -31 \pm 2$$

UO_2OH^+: The existence of UO_2OH^+ and the equilibrium constant for its formation have been the subject of debate for almost forty years. The value of ${}^*\beta_1°$ is not really well defined by the experimental data, and estimation of activity coefficients for species such as UO_2OH^+ using sparse data is not a clear-cut procedure. Appraising all available data GRENTHE et al. (1992) finally decided to select a value of

$$\log_{10}{}^*\beta_1° \ (m = 1, n = 1, 298.15 \ K) \quad = \quad -5.2 \pm 0.3$$

Neutral and anionic U(VI) hydrolysis species: Several authors have hypothesised neutral and / or anionic hydrolysis species of U(VI) in an attempt to fit experimental data. The study of species in neutral and alkaline solutions of U(VI) is complicated by the formation of very insoluble uranate solids of varying compositions, and by the formation of very strong carbonate complexes $UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2-}$ (see 5.23.7.1.2). At very low total solution concentrations of uranium, it would be expected that monomeric species $UO_2(OH)_n^{2-n}$ would predominate over polymeric species. However, no direct evidence for such species has been found in neutral and weakly basic solutions.

$UO_2(OH)_2(aq)$: There is no unambiguous evidence to confirm the existence of $UO_2(OH)_2(aq)$, nevertheless, an upper limit can be assigned to the formation constant of this species. The maximum value for the equilibrium constant of the reaction

$$UO_3 \cdot 2H_2O(s) \iff UO_2(OH)_2(aq) + H_2O(l)$$
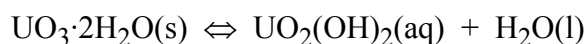
that is compatible with the 25°C solubility data of NIKITIN et al. (1972) is $\log_{10}K_{s,2} = -5.5$. The solubility product of $UO_3 \cdot H_2O(s)$ for the reaction

$$UO_3 \cdot 2H_2O(s) + 2 \ H^+ \iff UO_2^{2+} + 3 \ H_2O(l)$$
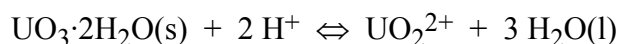
can be calculated from the selected Gibbs energy of formation ($\Delta_f G_m°$ ($UO_3 \cdot 2H_2O$, cr, 298.15 K), see 5.23.3.2.1) as $\log_{10}{}^*K_{s,0}° = 4.8 \pm 0.4$. Thus, a limiting value of $\log_{10}{}^*\beta_2° \leq -10.3$ has been selected by GRENTHE et al. (1992).

At this point, we disagree with GRENTHE et al. (1992). As discussed in the next section, we have preferably derived equilibrium constants for aqueous complexes from measured solubilities and not from $\Delta_f G_m°$ values originating from thermochemical data. As mentioned in GRENTHE et al. (1992), p.137, footnote 5, SANDINO (1991) determined the solubility product for schoepite, $UO_3 \cdot H_2O(s)$, and reported $\log_{10}{}^*K_{s,0}° = (5.96 \pm 0.18)$. If we use this value instead of the constant derived from $\Delta_f G_m°$ (see section 5.23.3.2.1 for further discussion), a limiting value of $\log_{10}{}^*\beta_2° \leq -11.5$ is derived from two sets of solubility data. As also mentioned in GRENTHE et al. (1992), p.113, footnote 4, a paper by CHOPPIN & MATHUR (1991), received after the draft of the NEA review was completed, reports $\log_{10}{}^*\beta_2 = -12.4 \pm 0.2$ in 0.1 M $NaClO_4$, suggesting a value of $\log_{10}{}^*\beta_2° = -12.0 \pm 0.2$. More recently, β_2 has been estimated based on experimental data of Pu(VI) hydrolysis (PASHALIDIS et al. 1995). On the assumption that the ratio between the stepwise equilibrium constants is approximately the same for the plutonyl and uranyl ions, an estimate of $\log_{10}{}^*\beta_2° = -12.6 \pm 0.4$ for the formation of $UO_2(OH)_2(aq)$ can be derived from the data given by PASHALIDIS et al. (1995) (Note that the ionic strength correction from $\beta_{1,2}$ to $\beta_{1,2}°$ has been done incorrectly in PASHALIDIS et al. (1995), the value of $\log_{10}{}^*\beta_2°$ has been re-estimated with corrected parameters.). As a tentative value we select the constant of CHOPPIN & MATHUR (1991) but with an increased uncertainty range in order to reflect the ambiguities in data selection.

$$\log_{10}{}^*\beta_2° \ (m = 1, n = 2, 298.15 \ K) \quad = \quad -12.0 \pm 0.5$$

$UO_2(OH)_3^-$ **:** The value of the equilibrium constant $\log_{10}{}^*\beta_3°$ derived from the phosphate complexation study of SANDINO (1991) has been accepted by GRENTHE et al. (1992), but the uncertainty has been increased to reflect the uncertainties in the model selection.

$$\log_{10}{}^*\beta_3° \ (m = 1, n = 3, 298.15 \ K) \quad = \quad -19.2 \pm 0.4$$

$UO_2(OH)_4^{2-}$ **:** MUSIKAS (1972) concluded that in very basic solutions a species with OH:U ratio approaching 4 is obtained above pH 13. If it is assumed that this species is $UO_2(OH)_4^{2-}$, a rough value of

$$\log_{10}{}^*\beta_4° \ (m = 1, n = 4, 298.15 \ K) \quad = \quad -33 \pm 2$$

can be estimated.

This estimate by GRENTHE et al. (1992) can be compared with a more recent value from the experimental study of YAMAMURA et al. (1998): $\log_{10}{}^*\beta_4° = -32.4 \pm 0.7$. The difference of 0.6 log units is small between the new study and the original NEA estimate considering their associated uncertainties. However, an unresolved and statistically significant difference of 1.7 log units remains between $\log_{10}{}^*\beta_3° = -19.2 \pm 0.4$ as recommended by GRENTHE et al. (1992) and $\log_{10}{}^*\beta_3° = -20.9 \pm 0.8$ as determined by YAMAMURA et al. (1998). We decided to retain the old NEA

recommended values for $UO_2(OH)_4^{2-}$ and $UO_2(OH)_3^-$ until the NEA uranium update becomes available.

Temperature dependence of U(VI) hydrolysis constants: Only a few studies investigated U(VI) hydrolysis at temperatures outside the range 20 to 30°C. The few available data on temperature dependence have been fitted by GRENTHE et al. (1992) assuming that $\Delta_r C_{p,m}$ is zero for each reaction. This is a very crude assumption; however, in no case does the precision of the available data warrant the use of an extra fitting parameter (GRENTHE et al. 1992). The resulting entropies are:

$$S_m° (UO_2OH^+, aq, 298.15\ K) \qquad = \quad (17 \pm 50)\ J \cdot K^{-1} \cdot mol^{-1}$$

$$S_m° ((UO_2)_2(OH)_2^{2+}, aq, 298.15\ K) \quad = \quad -(38 \pm 15)\ J \cdot K^{-1} \cdot mol^{-1}$$

$$S_m° ((UO_2)_3(OH)_5^+, aq, 298.15\ K) \quad = \quad (83 \pm 30)\ J \cdot K^{-1} \cdot mol^{-1}$$

5.23.3.1.2   U(V) hydroxide complexes

No aqueous models which need to call upon UO_2^+ hydroxide species have been proposed for interpreting experimental data. The regions in which UO_2^+ has been proposed as a significant species are at pH < 5. By analogy with NpO_2^+, no hydrolysis of UO_2^+ would be expected under these conditions. In higher pH regions, UO_2^+ hydroxide species are not expected to be found at significant concentrations because of the disproportionation of U(V). Therefore, GRENTHE et al. (1992) did not find credible UO_2^+ hydroxide species.

5.23.3.1.3   U(IV) hydroxide complexes

Hydrolysis of the U^{4+} ion is extensive except in strongly acidic solutions, and precipitation of extremely insoluble uranium dioxide or hydroxide occurs readily from U(IV) solutions as pH is increased. Even in strongly basic solutions (pH > 12), the equilibrium solution concentration of uranium over such solids remains very low. These factors have limited the number of reliable studies of the hydrolysis species and their equilibrium constants $^*\beta_{n,m}$ for the reactions

$$m\ U^{4+}\ +\ n\ H_2O(l) \Leftrightarrow U_m(OH)_n^{(4m-n)}\ +\ n\ H^+$$
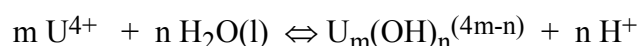
UOH^{3+}: Information about the (1,1) monomeric hydrolysis species UOH^{3+} has primaryly been derived from studies of acidic solutions of U(IV). The value selected by GRENTHE et al. (1992) was obtained from a linear regression of experimental data at different perchlorate concentrations to zero ionic strength.

$$\log_{10}{}^*\beta_1° (m = 1, n = 1, 298.15\ K) \qquad = \qquad -0.54 \pm 0.06$$

From the same experimental data, measured at different temperatures, the enthalpy and entropy of reaction have been selected, based on a weighted average of results, extrapolated to zero ionic strength.

$$\Delta_r H_m° \text{ (298.15 K)} \quad = \quad (46.9 \pm 9.0) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r S_m° \text{ (298.15 K)} \quad = \quad (147 \pm 30) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

U(OH)$_4$(aq): GRENTHE et al. (1992) recommended $\log_{10} {}^*\beta_4° = -4.5 \pm 1.4$ based on two solubility studies:

(1) PARKS & POHL (1988) measured the solubility of uraninite (UO$_2$) at temperatures from 100 to 300°C. They found that the temperature and pH dependence are statistically insignificant in the experimental results for all pH > 4, suggesting the predominance of a single species U(OH)$_4$(aq), and the dissolution equilibrium

$$UO_2(s) + 2 H_2O(l) \Leftrightarrow U(OH)_4(aq)$$
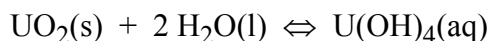
for which, at all temperatures from 100 to 300°C, $\log_{10} K_{s,4} = -9.47 \pm 0.56$. The solubility product of UO$_2$(cr) for the reaction

$$UO_2(cr) + 4 H^+ \Leftrightarrow U^{4+} + 2 H_2O(l)$$
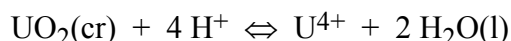
can be calculated from the selected Gibbs energy of formation ($\Delta_f G_m°$ (UO$_2$, cr, 298.15 K), see 5.23.3.2.2) as $\log_{10} {}^*K_{s,0}° = -4.85 \pm 0.36$. A value of $\log_{10} {}^*\beta_4° = \log_{10} K_{s,4} - \log_{10} {}^*K_{s,0}° = -4.6 \pm 0.7$ can be derived from these two numbers.

(2) BRUNO et al. (1987) measured the solubility of a so-called amorphous (actually partially crystalline) form of UO$_2$ at 25°C. The solubility of this material was $\log_{10} K_{s,4} = -4.4 \pm 0.4$, independent of pH between pH values of 5.5 to 10.0. The solubility product for a similarly prepared solid was determined potentiometrically by BRUNO et al. (1986) as $\log_{10} {}^*K_{s,0}° = 0.1 \pm 0.7$. A value of $\log_{10} {}^*\beta_4° = \log_{10} K_{s,4} - \log_{10} {}^*K_{s,0}° = -4.5 \pm 0.8$ can be derived from these two numbers.

GRENTHE et al. (1992) stated that the agreement of these values is unexpectedly good, especially considering the difficulties in characterising an amorphous solid as the one used by BRUNO et al. (1987). The uncertainty of the recommended value had been increased "to allow for uncertainties in the nature of the solids and for compatibility with the values for other hydrolysis species". However, the latter aspect prompted GRENTHE et al. (1992) to add a section entitled "A potential inconsistency" (GRENTHE et al. 1992, *pp*.129-131): The selected values for $\log_{10} {}^*\beta_1° = -0.54$ and $\log_{10} {}^*\beta_4° = -4.5$ imply equal concentrations of UOH^{3+} and U(OH)$_4$(aq) near pH = 1.8 (see solid line in Fig. 5.23.1), but there has been no experimental evidence that U(OH)$_4$(aq) occurs in acidic solutions of pH < 3. As a consequence, the stability of the neutral species U(OH)$_4$(aq) has been

overestimated by orders of magnitude. In GRENTHE et al. (1995) one reads: "Although it appears that the stability of U(OH)$_4$(aq) has been overestimated by orders of magnitude in GRENTHE et al. (1992), the inconsistencies mentioned by GRENTHE et al. (1992) still remain unresolved, and a re-examination of this system is being undertaken simultaneously with the neptunium and plutonium NEA-review." Apparently, this re-examination has been further postponed to the NEA-TDB update of the uranium review which will not be published before 2002.
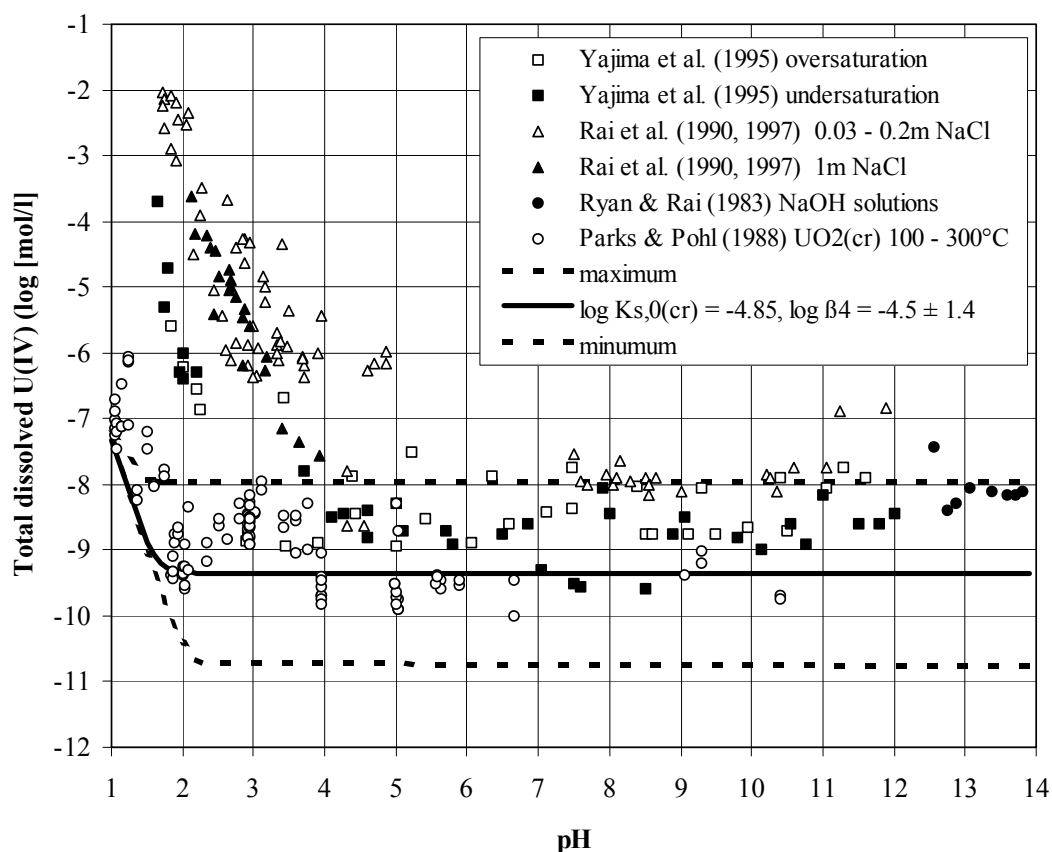
Fig. 5.23.1:   Solubility data of the system UO$_2$ - H$_2$O. The lines have been calculated using thermodynamic constants recommended by GRENTHE et al. (1992).

This inconsistency and a possible resolution has been discussed in detail by BERNER (1995). As discussed by RAI et al. (1990) and BERNER (1995), BRUNO et al. (1987) were not successful in effectively controlling the oxidation state of uranium and most probably their measurements reflect the solubility of "UO$_2$" in a partly oxidised environment. Appraising the experimental information available at the time of the preparation of his report, BERNER (1995) proposed to rely on the thermodynamic constants derived by RAI et al. (1990). Meanwhile, some more experimental data have been published and a re-evaluation of this problem is in place.

The short term experiments of RAI et al. (1990) (up to 8 days equilibrium time) resulted in uranium concentrations of about 10^{-8} M at pH > 4 (see Fig. 5.23.2). X-ray diffraction patterns of the solids separated from the equilibrated solutions indicated that the precipitates were amorphous UO_2. More recently, YAJIMA et al. (1995) studied the solubility of UO_2 in 0.1 M $NaClO_4$ from oversaturation and undersaturation between pH 2 and 12. At pH > 3 they found constant uranium concentrations (see Fig. 5.23.2). For experiments with 7 days oversaturation, the solubility of UO_2 was about 10^{-8} M and the diffraction patterns showed that the precipitate was amorphous UO_2. These findings are in accordance with the results reported by RAI et al. (1990). However, the results of 14 days and 28 days oversaturation experiments converge with the results of under saturation experiments at a somewhat lower value of log U = -8.7 ± 0.8. The diffraction peaks of solids extracted from these longer oversaturation experiments showed distinct peaks which became stronger and sharper with ageing time. The data reported by PARKS & POHL (1988) from their hydrothermal solubility experiments (100 to 300°C) partly overlap with the results of YAJIMA et al. (1995) but tend to a somewhat lower mean value of log U = -9.5 ± 0.6 (see Fig. 5.23.2). No temperature dependence has been observed between 100 to 300°C and therefore, we do not expect significant temperature effects between 100 and 25°C. However, the surface of the solids controlling the solubility in the hydrothermal experiments of PARKS & POHL (1988) might have been more crystalline than in the 25°C experiments of YAJIMA et al. (1995) and very long term experiments at 25°C might converge to values as found in the hydrothermal experiments. As long as there is no experimental evidence supporting this hypothesis we propose

$$\log_{10}K_{s,4}° \ (UO_2, s, 298.15 \ K) \ = \ -9 \pm 1$$

assuming that all dissolved uranium is present as $U(OH)_4(aq)$ and ionic strength effects for this neutral species are much smaller than the uncertainty in solubility data. The thick solid and dotted lines in Fig. 5.23.2 at pH > 4 represent our choice of $\log_{10}K_{s,4}° = -9$ and its associated uncertainty of ± one order of magnitude.
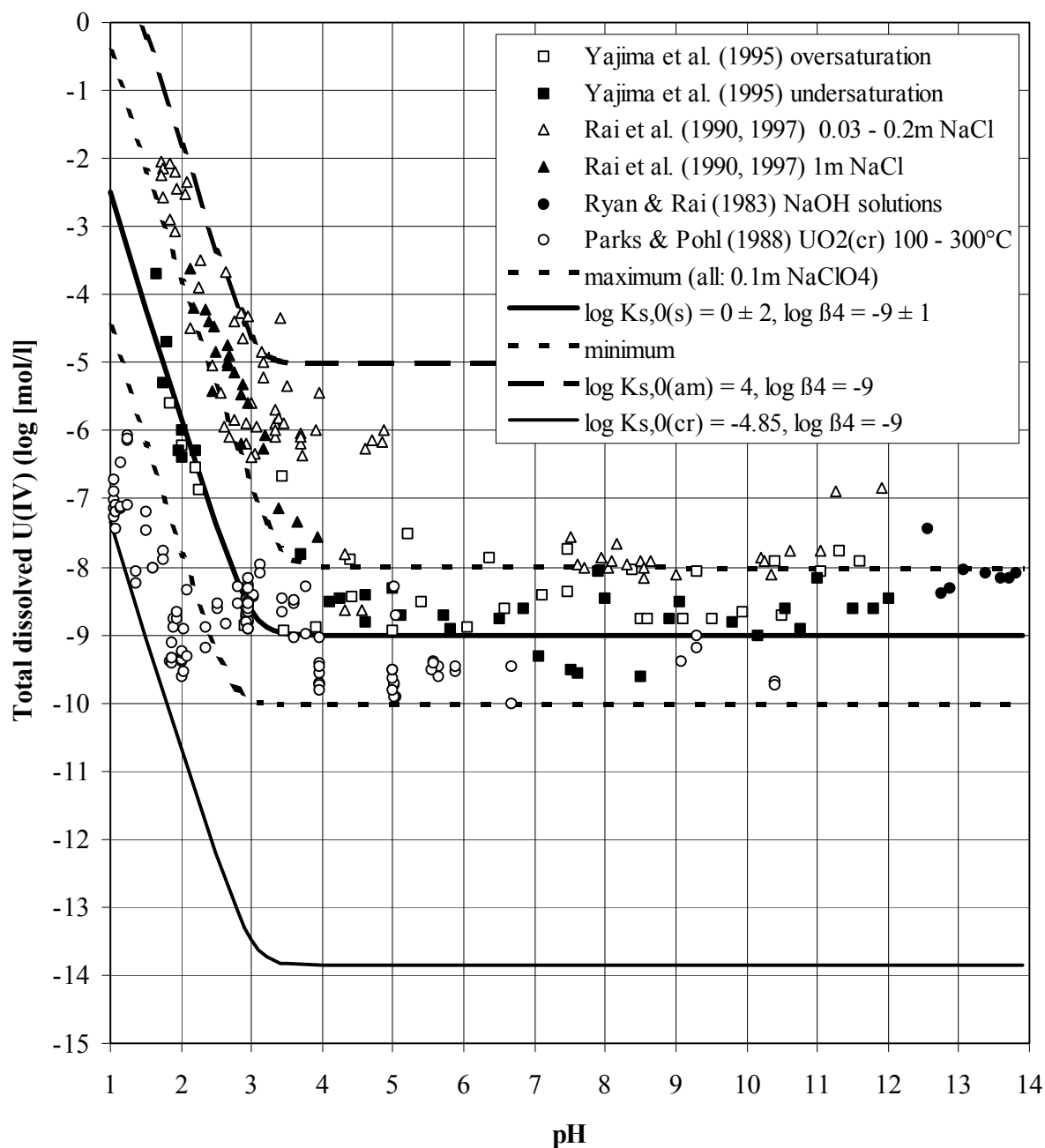
Fig. 5.23.2: Solubility data of the system UO_2 - H_2O. The thick solid line is calculated using thermodynamic constants estimated in this review. Dotted lines represent the estimated uncertainty. The dashed line is calculated using $\log_{10}{}^*K_{s,0}°(am) = 4$ given by RAI et al. (1990). The thin solid line is calculated using $\log_{10}{}^*K_{s,0}°(cr) = -4.85$ derived from $\Delta_f G_m°$ of $UO_2(cr)$ (GRENTHE et al. 1992).

The situation concerning the solubility product, $\log_{10}{}^*K_{s,0}°$, of UO_2 is much less clear-cut. RAI et al. (1990) derive from their short term experiments at pH < 4 a value of $\log_{10}{}^*K_{s,0}° = 4.0 \pm 1.6$.

They included the first hydrolysis constant as $\log_{10}{}^*\beta_1° = -0.50 \pm 0.06$ into their data analysis (dashed line in Fig. 5.23.2 at pH < 3). Recently, RAI et al. (1997) reported additional solubility experiments at pH < 4. In general, long term experiments (more than 30 days equilibrium time) resulted in systematically lower uranium concentrations. As stated by RAI et al. (1997), the value of the solubility product that best described their data was calculated to be $\log_{10}{}^*K_{s,0}° = 2.55$ (no error estimate given by the authors!). This value is about 1.5 orders of magnitude lower than that calculated from the low ionic strength and short term data of RAI et al. (1990), and RAI et al. (1997) believe that this value is more reflective of the solubility product for relatively aged UO_2(am). At pH < 3 YAJIMA et al. (1995) found a variation of log uranium concentration with pH with a slope of about -4. They derived a solubility product of $\log_{10}{}^*K_{s,0}° = 0.34 \pm 0.8$ without considering the first hydrolysis constant. However, regression analysis of the data reported by YAJIMA et al. (1995) reveals that the measured uranium concentrations in the range 10^{-7} to 10^{-4} M (10 data points) are very close to a slope -3 and only one data point at higher uranium concentration deviates from this trend. A re-evaluation of the data in the concentration range 10^{-7} to 10^{-4} M including the first hydrolysis constant ($\log_{10}{}^*\beta_1° = -0.54 \pm 0.06$) results in $\log_{10}{}^*K_{s,0}° = -0.5 \pm 0.6$ (see data close to the thick solid line in Fig. 5.23.2 at pH < 3). This value is about 3 orders of magnitude lower than that calculated from the long term data of RAI et al. (1997). Of course, the same difference is revealed directly by inspecting the two data sets in Fig. 5.23.2. BRUNO et al. (1986) measured the solubility product indirectly by using an emf method, i.e. they titrated UO_2(s) with $[UO_2^{2+}]$ and measured the resulting redox potential. From these measurements the concentration of $[U^{4+}]$ in equilibrium with UO_2(s) can be calculated. For an amorphous phase BRUNO et al. (1986) report $\log_{10}{}^*K_{s,0}° = 0.1 \pm 0.7$ (approximately represented by the thick solid line in Fig. 5.23.2 at pH < 3). For a more crystalline precipitate and a pellet of nuclear fuel they derived $\log_{10}{}^*K_{s,0}° = -1.6 \pm 0.8$. The data of PARKS & POHL (1988) at pH < 4 suggest an even lower solubility product. However, these low pH data show some peculiarities: a solubility minimum at pH 2 and a corresponding maximum at pH 3 (see Fig. 5.23.2). The maximum at pH 3 indicates fluorine contamination of the solutions as discussed by PARKS & POHL (1988). Probably the solid phase controlling the uranium concentration at pH < 3 is an uranium oxofluoride precipitate. Calculating a solubility product from the Gibbs energy of formation ($\Delta_f G_m°$ (UO_2, cr, 298.15 K), see section 3.2.2) as selected by GRENTHE et al. (1992) results in the lowest value of all: $\log_{10}{}^*K_{s,0}° = -4.85 \pm 0.36$.

The scatter of experimental solubility data at pH < 4 in Fig. 5.23.2 reveals a strong dependence of UO_2 solubility on crystallinity. Consequently, the range of solubility products from $\log_{10}{}^*K_{s,0}°$(cr) = -4.85 (GRENTHE et al. 1992) to $\log_{10}{}^*K_{s,0}°$(am) = 4.0 (RAI et al. 1990) spans 9 orders of magnitude! On the other hand, a maximum variation two orders of magnitude in UO_2 solubility has been observed at pH > 4 which can be represented by $\log_{10}K_{s,4}°$(s) = -9 ± 1 (Fig. 5.23.2). Both ranges are coupled by the (unknown) constant $\log_{10}{}^*\beta_4°$. Obviously, no unique set of constants

$\log_{10}{}^{*}K_{s,0}{}^{\circ} + \log_{10}{}^{*}\beta_4{}^{\circ} = \log_{10}K_{s,4}{}^{\circ}$ can be selected which is compatible with all experimental data. GRENTHE et al. (1992) attempted to resolve this dilemma by selecting $\log_{10}K_{s,4}{}^{\circ}(s)$ compatible with the experimental data of PARKS & POHL (1988) at pH > 4 and selecting $\log_{10}{}^{*}K_{s,0}{}^{\circ}(cr)$ derived from $\Delta_f G_m{}^{\circ}$ of $UO_2(cr)$. As a consequence, the value of $\log_{10}{}^{*}\beta_4{}^{\circ}$ has been overestimated by orders of magnitude. But what is a "more reasonable" value of $\log_{10}{}^{*}\beta_4{}^{\circ}$?

Expanding our reasoning from the $UO_2(s)$ - H_2O system to the more relevant system $UO_2(s)$ - H_2O - CO_2 we gain additional information which renders the choice of $\log_{10}{}^{*}\beta_4{}^{\circ}$ less arbitrary. RAI et al. (1998) recently demonstrated that in this system still $UO_2(s)$ is the solubility limiting solid and $U(CO_3)_5{}^{6-}$, which has been identified by UV-vis-IR and XAS techniques, is the most important aqueous complex. The logarithm of the thermodynamic equilibrium constant for the $UO_2(s)$ dissolution reaction

$$UO_2(s) \; + \; 5\,CO_3{}^{2-} \; + \; 4\,H^+ \; \Leftrightarrow \; U(CO_3)_5{}^{6-} \; + \; 2\,H_2O(l)$$
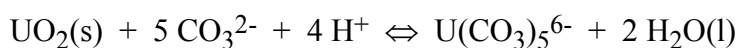
was found to be 33.8 (no error estimate given by RAI et al. (1998) !). From this value and the equilibrium

$$U^{4+} \; + \; 5\,CO_3{}^{2-} \; \Leftrightarrow \; U(CO_3)_5{}^{6-}$$
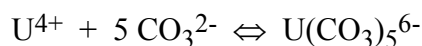
with $\log_{10}\beta_5{}^{\circ} = 34.1 \pm 1.0$, as recommended by GRENTHE et al. (1992) (see 5.23.7.1.2), we can derive a value for the solubility product which is compatible with the measured U(IV) solubilities in the system $UO_2(s)$ - H_2O at pH > 4 as well as with solubilities in the $UO_2(s)$ - H_2O - CO_2 system. Considering the large variations in reported solubility products we recommend a rough value with an increased uncertainty range

$$\log_{10}{}^{*}K_{s,0}{}^{\circ} = \; 0 \pm 2$$

and, derived therefrom,

$$\log_{10}{}^{*}\beta_4{}^{\circ} = \log_{10}K_{s,4} - \log_{10}{}^{*}K_{s,0}{}^{\circ} = -9 \pm 2$$

Note that by calculating the solubility of U(IV) in pure water from the selected values $\log_{10}{}^{*}K_{s,0}{}^{\circ}$ and $\log_{10}{}^{*}\beta_4{}^{\circ}$ the measured value of log U(tot) = -9 is reproduced but the individual uncertainties of $\log_{10}{}^{*}K_{s,0}{}^{\circ}$ and $\log_{10}{}^{*}\beta_4{}^{\circ}$ must not be recombined by erroneously assuming statistical independence of these highly correlated uncertainties.

To summarise this long story, the stability constant of $U(OH)_4(aq)$ has been derived from measured $UO_2(s)$ solubility data at pH > 4. In this parameter range the solubility data have been found to be independent of pH, suggesting the predominance of $U(OH)_4(aq)$, and several studies reported fairly consistent results. However, the solubility product of UO_2, which is needed to derive the stability constant of $U(OH)_4(aq)$ from solubility data, strongly depends on crystallinity and varies by nine orders of magnitude. As a pragmatic solution of this dilemma, a value for the solubility product of $UO_2(s)$ has been chosen which is compatible with the measured U(IV) solubilities not only in the

$UO_2(s)$ - H_2O system but also in the $UO_2(s)$ - H_2O - CO_2 system at pH > 4. Consequently, this data set cannot be used to represent the widely varying UO_2 solubility at pH < 3. Similar difficulties have been encountered for other tetra-valent actinides like Th. Several hypotheses have been considered but the dilemma of conflicting data remains unresolved (see section 3.2 for further discussion).

$U(OH)_5^-$: GRENTHE et al. (1992) estimated an upper limit of the stability of $U(OH)_5^-$ based on the assumption that the species $U(OH)_5^-$ may predominate at pH > 12. However, a synopsis of the data reported by YAJIMA et al. (1995), RAI et al. (1990) and RYAN & RAI (1983) reveals no evidence of amphoteric behaviour of $UO_2(s)$ up to pH 14 (see Fig. 5.23.2). Hence, we exclude the species $U(OH)_5^-$ from our database.

Other U(IV) hydrolysis species: An equilibrium constant for the polynuclear species $U_6(OH)_{15}^{9+}$ has been reported in GRENTHE et al. (1992) which is valid for 3 M $NaClO_4$ solutions between pH 1 and 2 and 0.01 M U(IV). No attempt has been made by GRENTHE et al. (1992) to extrapolate this constant to zero ionic strength. Anyway, the conditions pH < 2 and 0.01M U(IV) are not relevant for radioactive waste management and this species can safely be ignored in our database.

We expect that other monomeric hydrolysis species would be involved at low uranium concentrations. However, no unambiguous evidence for the formation of species like $U(OH)_2^{2+}$ and $U(OH)_3^+$ in acidic solutions has been reported. From the viewpoint of U(IV) solubility modelling the impact of these species is minimal: In acidic solutions between pH 1 and 4 the slope of the log U(IV) solubility curve would change more smoothly from -3 to zero compared with the present model comprising only the species UOH^{3+} and $U(OH)_4(aq)$. Between pH 3 and 4 the modelled uranium solubility probably would increase up to an order of magnitude. This uncertainty is negligible considering the large variations in measured solubilities in this pH range (Fig. 5.23.2).

5.23.3.2 Solid uranium oxides and hydroxides

5.23.3.2.1 U(VI) oxides and hydroxides

An entire series of oxides, hydrated oxides and hydroxides of U(VI) has been identified and their thermochemical properties (enthalpy, heat capacity, entropy) have been determined: α-$UO_3(cr)$, β-$UO_3(cr)$, γ-$UO_3(cr)$, $UO_3 \cdot 0.9H_2O(cr)$, α-$UO_3 \cdot H_2O(cr) \equiv \alpha$-$UO_2(OH)_2(cr)$, β-$UO_3 \cdot H_2O(cr) \equiv \beta$-$UO_2(OH)_2(cr)$, $UO_3 \cdot 2H_2O(cr)$. The stability of these phases at ambient conditions increases from α-$UO_3(cr)$ to $UO_3 \cdot 2H_2O(cr)$ with $UO_3 \cdot 2H_2O(cr)$ being the stable phase in aqueous solutions at 25°C. Based on precipitation studies, $UO_3 \cdot 2H_2O(cr)$ becomes unstable with respect to β-$UO_2(OH)_2(cr)$ at a temperature between 40 and 100°C. There are reports of at least partial

conversion of $UO_3 \cdot 2H_2O$(cr) in contact with liquid water to $\alpha\text{-}UO_3 \cdot H_2O$(cr) at temperatures below 100°C (GRENTHE et al. 1992).

For geochemical modelling in liquid water at temperatures ≤100°C the anhydrous forms of UO_3(cr) can safely be excluded from the database, whereas the hydrated oxides should be considered as relevant solids. The dihydrate usually is identified with the mineral schoepite. Actually, crystal structure data of schoepite (also named schoepite I or epiianthinite) lead to the formula $(UO_2)_8O_2(OH)_{12} \cdot 12H_2O \equiv UO_3 \cdot 2.25H_2O$. Meta-schoepite (or schoepite II) is reported with the formula $UO_3 \cdot 1\text{-}2H_2O$ and para-schoepite (or schoepite III) as "$UO_3 \cdot 2H_2O$ (?)". Yet another form of $UO_3 \cdot 2H_2O$ is known as the mineral masuyite. However, for geochemical modelling we may label the dihydrate "schoepite" and all the less hydrated oxides "dehydrated schoepites".

Comparing experimental solubility data with calculated values based on Gibbs energies in general leads to discrepancies. For example, using the Gibbs energy of formation as selected by GRENTHE et al. (1992), the solubility of $UO_3 \cdot 2H_2O$(cr) is calculated as $\log_{10}{}^*K_{s,0}° = 4.8 \pm 0.4$. On the other hand, SANDINO (1991) determined the solubility product of $UO_3 \cdot 2H_2O$ and reported $\log_{10}{}^*K_{s,0}° = 5.96 \pm 0.18$. The measured solubility product of this solid phase in contact with water is more than an order of magnitude higher than the value calculated from thermochemical data represennting the bulk porperties of the well-crystalline solid. However, as in the case of the bulk properties of UO_2(cr) and the solubility of UO_2(s) at pH > 4 (see 5.23.3.1.3) there is no prove that $UO_3 \cdot 2H_2O$(cr) used in calorimetric studies will reveal its calculated solubility when brought in contact with water. The main purpose of our database is calculating radionuclide solubilities for performance assessment of radioactive waste repositories. Therefore, in case of such unresolved ambiguities, we prefer to rely on measured solubility products rather than on using Gibbs energies derived from thermochemical cycles. We select the solubility product

$$UO_3 \cdot 2H_2O(s) \ + \ 2\,H^+ \ \Leftrightarrow \ UO_2{}^{2+} \ + \ 3\,H_2O(l)$$
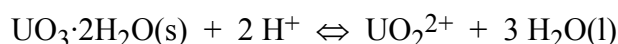
as reported by SANDINO (1991)

$$\log_{10}{}^*K_{s,0}° = 5.96 \pm 0.18$$

Note that the stability constant of $UO_2(OH)_2$(aq) selected in this review is compatible with the above selected solubility product (see 5.23.3.1.1.).

The enthalpy of formation as selected by GRENTHE et al. (1992) is based on the enthalpy of hydration of $\gamma\text{-}UO_3$(cr) to $UO_3 \cdot 2H_2O$(cr) which in turn is based on the differences in the enthalpies of solution of the two solids in aqueous HF or aqueous HNO_3:

$$\Delta_f H_m° \ (UO_3 \cdot 2H_2O,\ cr,\ 298.15\ K) \quad = \quad \text{-}(1826.1 \pm 1.7)\ kJ \cdot mol^{-1}$$

Calorimetric data are available for the determination of entropy and heat capacity of $UO_3 \cdot 2H_2O(cr)$ (GRENTHE et al. 1992) and the following values have been selected by GRENTHE et al. (1992):

$$S_m° (UO_3 \cdot 2H_2O, cr, 298.15 \text{ K}) \quad = \quad (188.54 \pm 0.38) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{p,m}°(UO_3 \cdot 2H_2O, cr, 298.15 \text{ K}) \quad = \quad (172.07 \pm 0.34) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

To be consistent with our arguments for preferring measured solubility products we have to discard either the entropy or the enthalpy recommendation of GRENTHE et al. (1992), or both. For the purpose of estimating the temperature dependence of "schoepite" solubility, we decided somewhat arbitrary to include the entropy (and heat capacity) value in our database. Consequently, $\Delta_f H_m°$ recalculated from $\log_{10}{}^*K_{s,0}°(s)$ and $S_m°$ differs from the recommendation of GRENTHE et al. (1992).

No reliable solubility products are reported for the other hydrated oxides, $UO_3 \cdot 0.9H_2O(cr)$, α-$UO_3 \cdot H_2O(cr)$ and β-$UO_3 \cdot H_2O(cr)$. We therefore exclude these solids from our database.

5.23.3.2.2   U(IV) oxides

Values for the entropy and enthalpy of formation of $UO_2(cr)$, uraninite, were assessed by CODATA. From these, the Gibbs energy has been calculated as $\Delta_f G_m°$ (UO_2, cr, 298.15 K) = -(1031.8 $\pm$ 1.0) kJ $\cdot$ mol^{-1}. This recommended value of GRENTHE et al. (1992) leads to a solubility product

$$UO_2(cr) \ + \ 4\,H^+ \ \Leftrightarrow \ U^{4+} \ + \ 2\,H_2O(l)$$
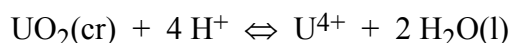
$$\log_{10}{}^*K_{s,0}° = -4.85 \pm 0.36$$

As discussed in 5.23.3.1.3 the scatter of experimental UO_2 solubility data at pH < 4 reveals a strong dependence of UO_2 solubility on crystallinity. Consequently, the range of solubility products reported in the literature spans 9 orders of magnitude, from $\log_{10}{}^*K_{s,0}°(cr) = -4.85$ (GRENTHE et al. 1992) to $\log_{10}{}^*K_{s,0}°(am) = 4.0$ (RAI et al. 1990). On the other hand, a maximum variation of two orders of magnitude in UO_2 solubility has been observed at pH > 4 which can be represented by $\log_{10}K_{s,4}°(s) = -9 \pm 1$ (Fig. 5.23.2). Both ranges are coupled by the (unknown) constant $\log_{10}{}^*\beta_4°$. Obviously, no unique set of constants $\log_{10}{}^*K_{s,0}° + \log_{10}{}^*\beta_4° = \log_{10}K_{s,4}°$ can be selected which is compatible with all experimental data. As a pragmatic solution of this dilemma, values for $\log_{10}{}^*\beta_4°$ and $\log_{10}{}^*K_{s,0}°(s)$, the solubility product of $UO_2(s)$, have been chosen which are compatible with the measured U(IV) solubilities not only in the $UO_2(s)$ - H_2O system but also in the $UO_2(s)$ - H_2O - CO_2 system at pH > 4. Note, that this data set cannot be used to represent the widely varying UO_2 solubility at pH < 3 (see section 3.2 for further discussion). Considering the

large variations in reported solubility products we recommend a rough value with an increased uncertainty range

$$UO_2(s) + 4\,H^+ \Leftrightarrow U^{4+} + 2\,H_2O(l)$$

$$\log_{10}{}^*K_{s,0}° = 0 \pm 2$$

The enthalpy of formation as selected by CODATA and accepted by GRENTHE et al. (1992) is based on the enthalpy of oxidation of UO_2(cr) to U_3O_8(cr):

$$\Delta_f H_m° \,(UO_2, cr, 298.15\,K) \quad = \quad -(1085.0 \pm 1.0)\,kJ \cdot mol^{-1}$$

Calorimetric data are available for the determination of entropy and heat capacity of UO_2(cr) (GRENTHE et al. 1992). The entropy as selected by CODATA and accepted by GRENTHE et al. (1992) and the heat capacity as selected by GRENTHE et al. (1992) are:

$$S_m° \,(UO_2, cr, 298.15\,K) \qquad = \qquad (77.03 \pm 0.20)\,J \cdot K^{-1} \cdot mol^{-1}$$

$$C_{p,m}° \,(UO_2, cr, 298.15\,K) \qquad = \qquad (63.60 \pm 0.08)\,J \cdot K^{-1} \cdot mol^{-1}$$

To be consistent with our arguments for preferring measured solubility products we have to discard either the entropy or the enthalpy recommendation of GRENTHE et al. (1992), or both. For the purpose of estimating the temperature dependence of UO_2(s) solubility, we decided somewhat arbitrary to include the entropy (and heat capacity) value in our database. Consequently, $\Delta_f H_m°$ recalculated from $\log_{10}{}^*K_{s,0}°$(s) and $S_m°$ differs from the recommendation of GRENTHE et al. (1992).

5.23.3.2.2   Mixed valence oxides

Values for the enthalpy of formation and entropy of U_3O_8(cr), U_3O_7(cr) and U_4O_9(cr) are recommended by GRENTHE et al. (1992). The enthalpy of formation, $\Delta_f H_m°$, of U_3O_8(cr) has been determined from the heat of combustion of uranium metal to U_3O_8, $\Delta_f H_m°$ of U_3O_7(cr) and U_4O_9(cr) has been derived from enthalpy of solution data. The absolute entropy, $S_m°$, of all solids is based on low temperature heat capacity measurements. No solubility measurements are reported for these mixed valence oxides.
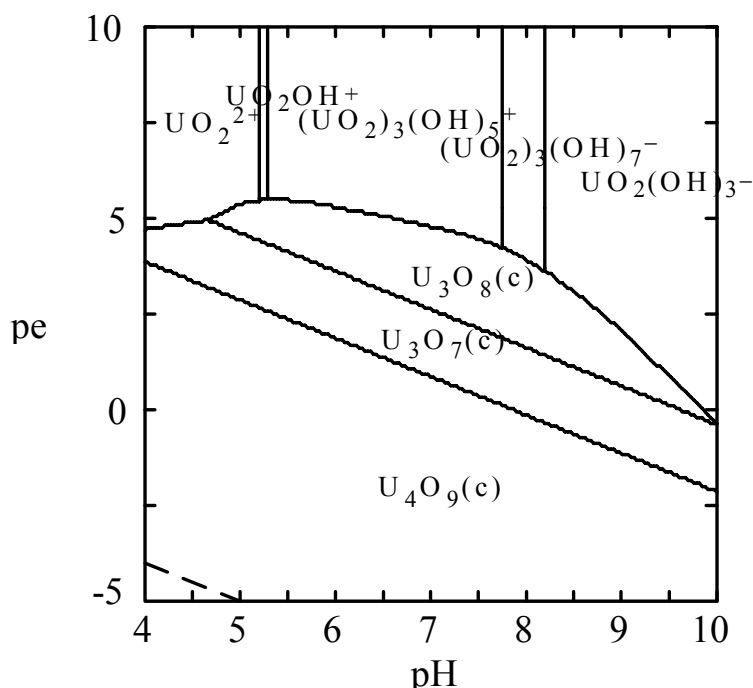
Fig. 5.23.3: Solubility and predominance diagram of the U(VI)/U(IV) hydroxide system at 25°C in the range 4 < pH < 10, as a function of the redox potential. Total dissolved uranium concentration is 10^{-5} M. The solubility limiting phases are $UO_3 \cdot 2H_2O(s)$ and $UO_2(s)$ as selected in this review and the mixed oxides $U_3O_8(cr)$, $U_3O_7(cr)$ and $U_4O_9(cr)$ as recommended by GRENTHE et al. (1992).

Combining calculated $\Delta_f G_m°$ values of any of these mixed valence oxides with our selected solubility products for "schoepite", $UO_3 \cdot 2H_2O(s)$, and "uraninite", $UO_2(s)$, invariably leads to grossly erroneous results in geochemical modelling. $UO_3 \cdot 2H_2O(s)$ and $UO_2(s)$ become unstable in speciation calculations due to the systematic discrepancies between solubility products derived from bulk calorimetric data and solubility measurements and the predominance ranges of the mixed valence oxides are "expanded" beyond any reasonable limits (compare Fig. V.8 in GRENTHE et al. (1992) with Fig. 5.23.3). Especially under reducing conditions, $U_4O_9(cr)$ will always be predicted as the stable solid phase instead of $UO_2(s)$ and the calculated uranium solubility may deviate by orders of magnitude from measured values (Fig. 5.23.3). Therefore, we decided to exclude all mixed valence oxides from our database. The error induced in solubility calculations by this exclusion is expected to be much smaller than by including them.

5.23.3.3 Uranium hydrides

$UH_3(cr)$ is not relevant under environmental conditions, this phase is not included in the database.

5.23.4   Halogen compounds and complexes

5.23.4.1 Aqueous halogen complexes

U(VI) fluorides: A sufficient number of equilibrium studies has been reported concerning U(VI) fluoride complexation. GRENTHE et al. (1992) recommended equilibrium constants for the reactions:

$$UO_2^{2+} + n\,F^- \Leftrightarrow UO_2F_n^{(2-n)}$$

$$\log_{10}\beta_1^\circ \; (n = 1, 298.15\ \text{K}) \quad = \quad 5.09 \pm 0.13$$

$$\log_{10}\beta_2^\circ \; (n = 2, 298.15\ \text{K}) \quad = \quad 8.62 \pm 0.04$$

$$\log_{10}\beta_3^\circ \; (n = 3, 298.15\ \text{K}) \quad = \quad 10.9 \pm 0.4$$

$$\log_{10}\beta_4^\circ \; (n = 4, 298.15\ \text{K}) \quad = \quad 11.7 \pm 0.7$$

In addition, enthalpy of reaction values are recommended by GRENTHE et al. (1992). The selected enthalpies of formation in GRENTHE et al. (1992) are derived therefrom.

$$\Delta_r H_m^\circ \; (n = 1, 298.15\ \text{K}) \quad = \quad (1.70 \pm 0.08)\ \text{kJ·mol}^{-1}$$

$$\Delta_r H_m^\circ \; (n = 2, 298.15\ \text{K}) \quad = \quad (2.10 \pm 0.19)\ \text{kJ·mol}^{-1}$$

$$\Delta_r H_m^\circ \; (n = 3, 298.15\ \text{K}) \quad = \quad (2.35 \pm 0.31)\ \text{kJ·mol}^{-1}$$

$$\Delta_r H_m^\circ \; (n = 4, 298.15\ \text{K}) \quad = \quad (0.29 \pm 0.47)\ \text{kJ·mol}^{-1}$$
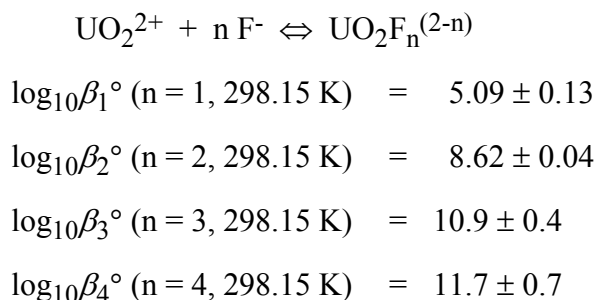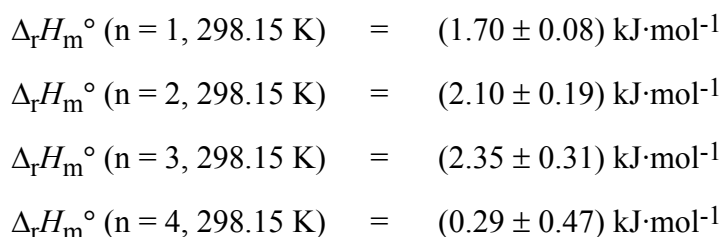
U(V) fluorides: No information exists on aqueous species of the form $UO_2F_n^{(1-n)}$, presumably due to the limited stability range of U(V) in aqueous media.

U(IV) fluorides: A fair number of equilibrium studies has been reported concerning U(IV) fluoride complexation. GRENTHE et al. (1992) recommended equilibrium constants for the reactions:

$$U^{4+} + n\,F^- \Leftrightarrow UF_n^{(4-n)}$$

$$\log_{10}\beta_1^\circ \; (n = 1, 298.15\ \text{K}) \quad = \quad 9.28 \pm 0.09$$

$$\log_{10}\beta_2^\circ \; (n = 2, 298.15\ \text{K}) \quad = \quad 16.23 \pm 0.15$$

$$\log_{10}\beta_3^\circ \; (n = 3, 298.15\ \text{K}) \quad = \quad 21.6 \pm 1.0$$

$$\log_{10}\beta_4^\circ \; (n = 4, 298.15\ \text{K}) \quad = \quad 25.6 \pm 1.0$$

$$\log_{10}\beta_5^\circ \; (n = 5, 298.15\ \text{K}) \quad = \quad 27.01 \pm 0.30$$

$$\log_{10}\beta_6^\circ \; (n = 6, 298.15\ \text{K}) \quad = \quad 29.08 \pm 0.18$$
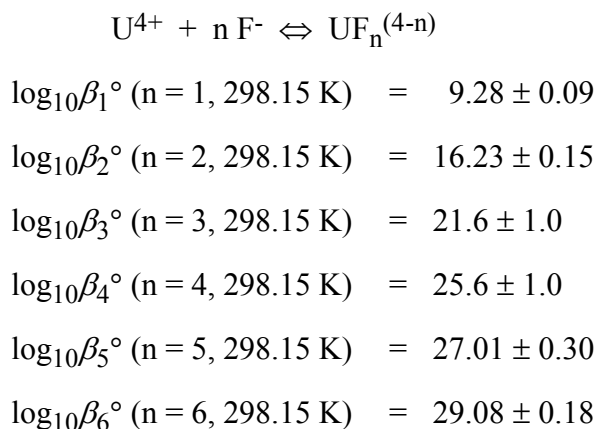
The only experimental study of anionic U(IV) fluoride complexes, UF_5^- and UF_6^{2-}, is a solubility study of $UF_4 \cdot 2.5H_2O$. It should be noted that the solubility product $\log_{10}K_{s,0}° = -(29.38 \pm 0.19)$, as used by GRENTHE et al. (1992) for the evaluation of $\log_{10}\beta_5°$ and $\log_{10}\beta_6°$ is different from the value of $-(33.5 \pm 1.2)$ which can be calculated from $\Delta_f G_m°$ ($UF_4 \cdot 2.5H_2O$, cr, 298.15 K) recommended by GRENTHE et al. (1992) (see 5.23.4.2).

In addition, enthalpy of reaction values are recommended by GRENTHE et al. (1992). The selected enthalpies of formation in GRENTHE et al. (1992) are derived therefrom.

$$\Delta_r H_m° \ (n = 1, 298.15 \ K) \quad = \quad -(5.6 \pm 0.5) \ kJ \cdot mol^{-1}$$

$$\Delta_r H_m° \ (n = 2, 298.15 \ K) \quad = \quad -(3.5 \pm 0.6) \ kJ \cdot mol^{-1}$$

$$\Delta_r H_m° \ (n = 3, 298.15 \ K) \quad = \quad (0.5 \pm 4.0) \ kJ \cdot mol^{-1}$$

No enthalpy of reaction is reported for UF_4(aq). GRENTHE et al. (1992) therefore estimated an entropy of reaction based on experimental data

$$\Delta_r S_m° \ (n = 4, 298.15 \ K) \quad = \quad (476 \pm 17) \ J \cdot K^{-1} \cdot mol^{-1}$$

GRENTHE et al. (1992) concluded that the enthalpies of reaction in the U^{4+} - F^- system are small, hence the corresponding equilibria are not strongly influenced by temperature.

U(VI) chlorides: The U(VI) chloride complexes are very weak. A sufficient number of experimental data is available which cover a wide range of ionic strengths, but especially in the case of the complex UO_2Cl_2(aq), it is in practice impossible to distinguish between complex formation and ionic strength effects. However, the observed ionic strength dependence of the experimental data seems to conform to the specific ion interaction theory, which is rather unexpected in view of the large medium changes necessary to study these weak complexes. Weighted linear regressions resulted in good extrapolations to zero ionic strength for the equilibria

$$UO_2^{2+} + n \ Cl^- \Leftrightarrow UO_2Cl_n^{(2-n)}$$
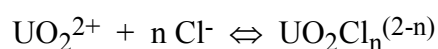
$$\log_{10}\beta_1° \ (n = 1, 298.15 \ K) \quad = \quad 0.17 \pm 0.02$$

$$\log_{10}\beta_2° \ (n = 2, 298.15 \ K) \quad = \quad -1.1 \pm 0.4$$

In addition, enthalpy of reaction values are recommended by GRENTHE et al. (1992). The selected enthalpies of formation in GRENTHE et al. (1992) are derived therefrom.

$$\Delta_r H_m° \ (n = 1, 298.15 \ K) \quad = \quad (8 \pm 2) \ kJ \cdot mol^{-1}$$

$$\Delta_r H_m° \ (n = 2, 298.15 \ K) \quad = \quad (15 \pm 6) \ kJ \cdot mol^{-1}$$

U(V) chlorides: No aqueous species of the form $UO_2Cl_n^{(1-n)}$ have been identified.

U(IV) chlorides: There are fairly few studies of chloride complexes of U(IV). GRENTHE et al. (1992) recommended an equilibrium constant for the reaction:

$$U^{4+} + n\, Cl^- \Leftrightarrow UCl_n^{(4-n)}$$

$$\log_{10}\beta_1^\circ\ (n = 1, 298.15\ K)\quad =\quad 1.27 \pm 0.13$$
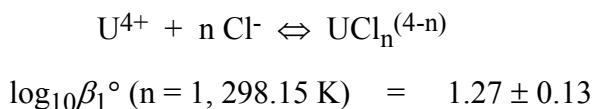
No reliable value of $\log_{10}\beta_2^\circ$ can be obtained from the only experimental work addressing this species. This reflects the general difficulty in determining accurate values for stability constants of weak complexes. Because of large variations in the composition of the test solutions, it is also difficult to assure constant activity factors in the equilibrium experiments.

From the available equilibrium data GRENTHE et al. (1992) calculated an enthalpy of reaction value. The selected enthalpy of formation in GRENTHE et al. (1992) is derived therefrom.

$$\Delta_r H_m^\circ\ (n = 1, 298.15\ K)\quad =\quad -(19 \pm 9)\ kJ \cdot mol^{-1}$$

Uranium chlorites: The formation of a weak ClO_2^- complex of U(VI) has been reported. This value is uncertain, and no selection has been made by GRENTHE et al. (1992). No aqueous complexes of U(V) are identified. GRENTHE et al. (1992) did not include any equilibrium data for U(IV) chlorite species.

Uranium chlorates: No data are available on the aqueous ClO_3^- complexes of either U(IV) or U(V). The formation of a weak $UO_2ClO_3^+$ complex has been reported and GRENTHE et al. (1992) selected an equilibrium constant. However, chlorate complexes are not thought to be of relevance for geochemical modelling and are not included in our database.

Uranium perchlorates: No data are available on the aqueous ClO_4^- complexes of either U(VI) or U(V). A very weak $UClO_4^{3+}$ complex has been reported. It is difficult to distinguish between the effects of complex formation and variations in the activity coefficients under conditions where such weak complexes may be formed. Therefore, GRENTHE et al. (1992) did not recommend equilibrium constants for uranium perchlorates.

Bromine and iodine complexes of uranium: GRENTHE et al. (1992) selected equilibrium constants for the generally rather weak complexes UO_2Br^+, UBr^{3+}, $UO_2BrO_3^+$, UI^{3+}, $UO_2IO_3^+$ and $UO_2(IO_3)_2(aq)$. However, bromine and iodine complexes of uranium are not thought to be of relevance for geochemical modelling and are not included in our database.

5.23.4.2 Uranium halide compounds

A large number of uranium halide compounds have been the subject of extensive thermochemical studies.

Uranium fluoride compounds: The calculated Gibbs energies of U(IV) fluorides and oxofluorides suggest that some of these compounds are sparingly soluble solids (see Table 5.23.1). According to these data the stable solid in aqueous solutions at 25°C is $UF_4 \cdot 2.5H_2O(cr)$. The only solubility study in the field of uranium fluoride compounds corroborates this conclusion, as the stable solid in this solubility study was identified as $UF_4 \cdot 2.5H_2O$. However, the solubility product of the reaction

$$UF_4 \cdot 2.5H_2O(cr) \Leftrightarrow U^{4+} + 4\,F^- + 2.5\,H_2O(l)$$
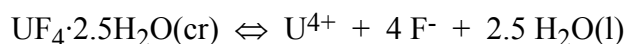
$$\log_{10}K_{s,0}° = -29.38 \pm 0.19$$

as derived from this solubility study and used by GRENTHE et al. (1992) for the evaluation of $\log_{10}\beta_5°$ and $\log_{10}\beta_6°$ of the complexes UF_5^- and UF_6^{2-}, respectively (see 5.23.4.1), differs by 4 orders of magnitude from the value of $-(33.5 \pm 1.2)$ which can be calculated from $\Delta_fG_m°$ ($UF_4 \cdot 2.5H_2O$, cr, 298.15 K). This observation is consistent with the differences found for UO_2 as discussed above. In the U(IV) - H_2O - HF system the strong aqueous U(IV) fluoride complexes can influence the U(IV) solubility at pH < 5. In similar solutions $UF_4 \cdot 2.5H_2O(cr)$ can precipitate and limit the U(IV) concentration in solution at pH < 4 (GRENTHE et al. 1992). These conditions are of little significance in geochemical modelling. However, the solubility product of $UF_4 \cdot 2.5H_2O$ is included in our database for the sake of consistency with the aqueous speciation model.

The enthalpy of formation as selected by GRENTHE et al. (1992) is based on the enthalpy of hydration of $UF_4(cr)$ to $UF_4 \cdot 2.5H_2O(cr)$:

$$\Delta_fH_m° \,(UF_4 \cdot 2.5H_2O, \text{ cr, } 298.15\text{ K}) = -(2671.5 \pm 4.3)\text{ kJ} \cdot \text{mol}^{-1}$$

The entropy and the heat capacity as estimated by GRENTHE et al. (1992) are:

$$S_m° \,(UO_3 \cdot 2H_2O, \text{ cr, } 298.15\text{ K}) = (263.5 \pm 15.0)\text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{p,m}° \,(UO_3 \cdot 2H_2O, \text{ cr, } 298.15\text{ K}) = (263.7 \pm 15.0)\text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

To be consistent with our arguments for preferring measured solubility products we have to discard either the entropy or the enthalpy recommendation of GRENTHE et al. (1992), or both. For the purpose of estimating the temperature dependence of $UF_4 \cdot 2.5H_2O(cr)$ solubility, we decided somewhat arbitrary to include the entropy (and heat capacity) value in our database. Consequently, $\Delta_fH_m°$ recalculated from $\log_{10}{}^*K_{s,0}°$ and $S_m°$ differs from the recommendation of GRENTHE et al. (1992).

Uranium chlorine compounds: The calculated Gibbs energies of uranium chlorides and oxochlorides suggest that all these compounds are highly soluble salts (see Table 5.23.1). The same conclusion can be deduced in a much simpler way from looking at the labels glued to the bottles of commercially available uranium chloride salts. The labels for $UCl_4(cr)$ and $UO_2Cl_2 \cdot 3H_2O(cr)$ state

"moisture sensitive" and "hygroscopic", respectively. None of these highly soluble salts is included in our database.

No evaluation of thermodynamic data on solid uranium chlorites or chlorates of any oxidation state has been made in the literature. No solid perchlorates of uranium at any oxidation state are credited by GRENTHE et al. (1992).

Bromine and iodine compounds of uranium: The calculated Gibbs energies of uranium bromides, oxobromides and uranium iodides suggest that all these compounds are highly soluble salts. The only measured solubility product concerns U(VI) iodate. According to the reported solubility product, this solid would only be of importance in solutions containing millimolar concentrations of iodate. None of these solids is included in our database.

5.23.5   Chalcogen compounds and complexes

5.23.5.1 Sulphur compounds and complexes

5.23.5.1.1   Uranium sulphides

No thermodynamic data are available for aqueous uranium sulphide complexes. Thermochemical data have been selected by GRENTHE et al. (1992) for a series of binary uranium sulphide solids. However, none of these solids is included in our database. For a more detailed discussion see Chapter 5.19.

5.23.5.1.2   Uranium sulphites

GRENTHE et al. (1992) recommended an equilibrium constant for a 1:1 uranium(VI) sulphite complex. No thermodynamic data are available for aqueous uranium(IV) sulphite complexes. In addition, thermochemical data for uranium(VI) and uranium(IV) sulphite solids have been selected by GRENTHE et al. (1992).

However, sulphite complexes and compounds are presently not included in our database.

5.23.5.1.3   Uranium sulphates

Aqueous U(VI) sulphates: The U(VI) - sulphate system has been extensively investigated with many different experimental methods. Conclusive quantitative evidence exists for the formation of the 1:1 and 1:2 complexes. Thus, GRENTHE et al. (1992) evaluated and recommended equilibrium constants for the reactions:

$$UO_2^{2+} + n\,SO_4^{2-} \Leftrightarrow UO_2(SO_4)_n^{(2-2n)}$$
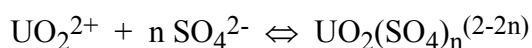
$$\log_{10}\beta_1° \ (n = 1, \ 298.15 \ K) \quad = \quad 3.15 \pm 0.02$$

$$\log_{10}\beta_2° \ (n = 2, \ 298.15 \ K) \quad = \quad 4.14 \pm 0.07$$

The enthalpy changes for these reactions were obtained calorimetrically by several studies. GRENTHE et al. (1992) selected the unweighted average of these data:

$$\Delta_r H_m° \ (n = 1, \ 298.15 \ K) \quad = \quad (19.5 \pm 1.6) \ kJ \cdot mol^{-1}$$

$$\Delta_r H_m° \ (n = 2, \ 298.15 \ K) \quad = \quad (35.1 \pm 1.0) \ kJ \cdot mol^{-1}$$

There is some evidence to suggest the existence of $UO_2(SO_4)_3{}^{4-}$. However, this complex is very weak (if formed at all), and GRENTHE et al. (1992) did not assign any thermodynamic data to this species.

Aqueous U(V) sulphates: No experimental information is available on aqueous U(V) sulphates.

Aqueous U(IV) sulphates: The U(IV) - sulphate system has been studied in strongly acidic solutions to avoid hydrolysis. The available experimental data are limited, and they refer to reactions of the type

$$U^{4+} \ + \ n \ HSO_4{}^- \ \Leftrightarrow \ U(SO_4)_n{}^{(4-2n)} \ + \ n \ H^+.$$

GRENTHE et al. (1992) obtained equilibrium constants for these reactions, and combining these equilibrium constants with the protonation constant for $SO_4{}^{2-}$ resulted in recommended values for the reactions:

$$U^{4+} \ + \ n \ SO_4{}^{2-} \ \Leftrightarrow \ U(SO_4)_n{}^{(4-2n)}$$
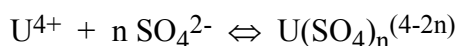
$$\log_{10}\beta_1° \ (n = 1, \ 298.15 \ K) \quad = \quad 6.58 \pm 0.19$$

$$\log_{10}\beta_2° \ (n = 2, \ 298.15 \ K) \quad = \quad 10.51 \pm 0.20$$

The enthalpy changes for these reactions were obtained by GRENTHE et al. (1992) from selected equilibrium constants at 10, 25 and 40°C :

$$\Delta_r H_m° \ (n = 1, \ 298.15 \ K) \quad = \quad (8.0 \pm 2.7) \ kJ \cdot mol^{-1}$$

$$\Delta_r H_m° \ (n = 2, \ 298.15 \ K) \quad = \quad (32.7 \pm 2.8) \ kJ \cdot mol^{-1}$$

No species above U(IV) disulphate have been credited by GRENTHE et al. (1992).

Uranium sulphate solids: Thermochemical data have been selected by GRENTHE et al. (1992) for $UO_2SO_4(cr)$, $UO_2SO_4 \cdot 2.5H_2O(cr)$, $UO_2SO_4 \cdot 3H_2O(cr)$ and $UO_2SO_4 \cdot 3.5H_2O(cr)$. Only the 2.5-hydrate is thermally stable at room temperature (GRENTHE et al. 1992). However, even the thermally stable solid $UO_2SO_4 \cdot 2.5H_2O(cr)$ exhibits a very high solubility: Osmotic coefficients and mean activity coefficients of U(VI) sulphate have been measured in solutions up to 6 mol·kg^{-1} salt

concentration, see Appendix 8.10, Tables 7 and 16, respectively, in ROBINSON & STOKES (1959). Hence, $UO_2SO_4 \cdot 2.5H_2O(cr)$ is not relevant under environmental conditions and is not included in the database.

On the other hand, uranium sulphates (zippeites) were among the first naturally occurring uranium minerals to be recognised and were known in the early part of the 19th century. Zippeite is a basic dioxouranium(VI) sulphate, $K_4(UO_2)_6(SO_4)_6(OH)_{10} \cdot 4H_2O$, first found in Joachimsthal. Potassium can be replaced by other cations to form sodium-, ammonium-, magnesium-, cobalt-, nickel- and zink-zippeite. Two papers reporting solubility products and standard Gibbs energies of formation of these zippeites were discussed and rejected by GRENTHE et al. (1992) and GRENTHE et al. (1995). They conclude that "further experimental studies with pH variations are needed to obtain reliable information on the behaviour of the zippeites in aqueous solutions" (GRENTHE et al. 1992).

When uranium(IV) sulphate solutions are hydrolysed, a sparingly soluble oxo or hydroxo sulphate is formed. Several compositions have been proposed in the literature for this solid. Appraising all available information, GRENTHE et al. (1992) considered $U(OH)_2SO_4(cr)$ as the most precise formula. The solubility product of a "basic uranium(IV) sulphate" has been reported in the literature and GRENTHE et al. (1992) accepted this value but with an increased uncertainty assuming that the solubility product corresponds the reaction

$$U(OH)_2SO_4(cr) \Leftrightarrow U^{4+} + 2\,OH^- + SO_4^{2-}$$

$$\log_{10}K_{s,0}° = -31.17 \pm 0.50$$
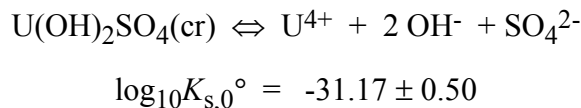
Thermochemical data have been selected by GRENTHE et al. (1992) for other uranium(IV) sulphate solids like $U(SO_4)_2(cr)$, $U(SO_4)_2 \cdot 4H_2O(cr)$ and $U(SO_4)_2 \cdot 8H_2O(cr)$. However, no solubility data of any of these solids have been reported and no information is provided by GRENTHE et al. (1992) regarding the stability of these solids in aqueous systems. Considering the solubility of $U(OH)_2SO_4(cr)$ and the thermochemical data of $U(SO_4)_2 \cdot nH_2O(cr)$, these latter solids are expected to form only in acidic solutions at pH < 3 (and strongly reducing conditions, of course). These conditions are of little significance in geochemical modelling and thus, thermochemical data of $U(SO_4)_2 \cdot nH_2O(cr)$ are not considered further.

5.23.5.1.4   Uranium thiosulphates

GRENTHE et al. (1992) accepted a tentative equilibrium constant for a 1:1 uranium(VI) thiosulphate complex. No thermodynamic data are available for aqueous uranium(IV) thiosulphate complexes. GRENTHE et al. (1992) did not find reliable evidence for the formation of uranium thiosulphate solids.

However, thiosulphate is presently not included in our database.

5.23.5.2 Selenium compounds and complexes

GRENTHE et al. (1992) selected thermochemical data for a series of binary uranium selenide solids. However, no solubility data of any of these solids have been reported and no information is provided by GRENTHE et al. (1992) regarding the stability of these solids in aqueous systems. None of these solids is known as a naturally occurring mineral. Hence, none of these solids is included in our database.

Enthalpy values for a uranium selenite and a uranium selenate solid have been selected by GRENTHE et al. (1992). None of these solids is included in our database.

No experimental information is available on selenium complexes with uranium.

5.23.5.3 Tellurium compounds

GRENTHE et al. (1992) selected an entropy value for a uranium telluride solid and an enthalpy value for a uranium tellurite. None of these solids is included in our database.

No experimental information is available on tellurium complexes with uranium.

5.23.6   Group 15 compounds and complexes

5.23.6.1 Nitrogen compounds and complexes

5.23.6.1.1   Uranium nitrides

GRENTHE et al. (1992) selected thermochemical data for several binary uranium nitride solids. However, binary uranium nitrides are not relevant under environmental conditions and are not included in our database.

5.23.6.1.2   Uranium azides

GRENTHE et al. (1992) evaluated stability constants for $UO_2(N_3)_n^{2-n}$ complexes with n = 1 to 4 from experimental studies on the complex formation between uranium(VI) and azide ions. However, azide complexes are not relevant under environmental conditions and are not included in our database.

5.23.6.1.3 Uranium nitrates

Aqueous U(VI) nitrates: The dioxouranium(VI) nitrate complexes are weak, and it is therefore difficult to distinguish between complex formation and changes in the activity factors of the solutes caused by the large changes in solute concentration. Hence, GRENTHE et al. (1992) relied only on the data obtained for the $UO_2NO_3^+$ species according to

$$UO_2^{2+} + NO_3^- \Leftrightarrow UO_2NO_3^+$$

$$\log_{10}\beta° \text{ (298.15 K)} = 0.30 \pm 0.15$$
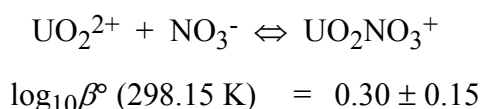
and considered that there is no reliable information on higher U(VI) nitrato complexes.

Aqueous U(IV) nitrates: The uranium(IV) nitrate system was studied by several investigators using spectrophotometry, distribution measurements and potentiometry. Using these data GRENTHE et al. (1992) evaluated equilibrium constants for the reaction

$$U^{4+} + n\,NO_3^- \Leftrightarrow U(NO_3)_n^{(4-n)}$$

$$\log_{10}\beta_1° \text{ (n = 1, 298.15 K)} = 1.47 \pm 0.13$$

$$\log_{10}\beta_2° \text{ (n = 2, 298.15 K)} = 2.30 \pm 0.35$$
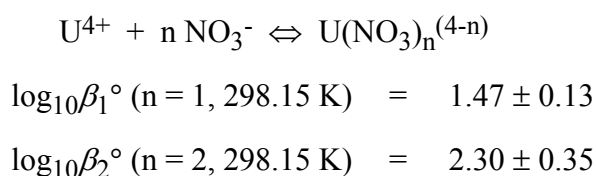
Solid uranium nitrates: Thermochemical data have been selected by GRENTHE et al. (1992) for a series of U(VI) nitrate solids. The calculated Gibbs energies suggest that all these compounds are highly soluble salts (see Table 5.23.1). The same conclusion can be deduced in a much simpler way from looking at the labels glued to the bottles of commercially available uranium nitrate salts: For $UO_2(NO_3)_2 \cdot 6H_2O(cr)$ it states "hygroscopic". Hence, none of these highly soluble salts is included in our database.

5.23.6.2 Phosphorous compounds and complexes

5.23.6.2.1 The aqueous uranium phosphorous system

The experimental studies of equilibria in the uranium - phosphoric acid system are complicated not only by the presence of several competing ligands (H_3PO_4(aq), $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}) but also by the formation of a number of sparingly soluble solid phases and the formation of ternary complexes of the type $MH_r(PO_4)_q$, where $M = UO_2^{2+}$ or U^{4+}. There are few precise studies available in the literature, and most of them refer to solutions of low pH and fairly high concentration of phosphoric acid. The only experimental study which extends into the pH range encountered in ground and surface waters is the thesis of SANDINO (1991), where the solubility of $(UO_2)_3(PO_4)_2 \cdot 4H_2O(cr)$ was measured in the range 6 < pH < 9.

Complex formation in the U(VI) - H₃PO₄ system: Appraising all available information, GRENTHE et al. (1992) considered only the following equilibria in acidic solution, with $H_3PO_4(aq)$ and $H_2PO_4^-$ as ligands, as sufficiently well established:

$$UO_2^{2+} + H_3PO_4(aq) \Leftrightarrow UO_2H_2PO_4^+ + H^+$$

$$\log_{10}\beta° \ (298.15\ K) \ = \ 1.12 \pm 0.06$$

$$UO_2^{2+} + H_3PO_4(aq) \Leftrightarrow UO_2H_3PO_4^{2+}$$

$$\log_{10}\beta° \ (298.15\ K) \ = \ 0.76 \pm 0.15$$

$$UO_2^{2+} + 2\ H_3PO_4(aq) \Leftrightarrow UO_2(H_2PO_4)_2(aq) + 2\ H^+$$

$$\log_{10}\beta° \ (298.15\ K) \ = \ 0.64 \pm 0.11$$

$$UO_2^{2+} + 2\ H_3PO_4(aq) \Leftrightarrow UO_2(H_2PO_4)(H_3PO_4)^+ + H^+$$
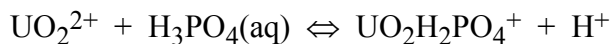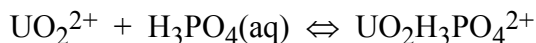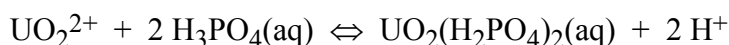
$$\log_{10}\beta° \ (298.15\ K) \ = \ 1.65 \pm 0.11$$

In neutral to basic solutions, a solubility study of $(UO_2)_3(PO_4)_2 \cdot 4H_2O(cr)$ in the pH range between 6 and 9 has been published by SANDINO (1991). Equilibrium data were reported for the formation of $UO_2HPO_4(aq)$, $UO_2PO_4^-$ and $UO_2(OH)_3^-$, in addition to the solubility product for the solid phase. The constant reported for $UO_2(OH)_3^-$ is consistent with the value selected in Section 5.23.3.1.1. GRENTHE et al. (1992) accepted Sandino's formation constants for $UO_2HPO_4(aq)$, $UO_2PO_4^-$ and according to the reactions

$$UO_2^{2+} + PO_4^{3-} \Leftrightarrow UO_2PO_4^-$$
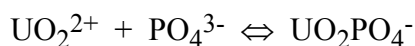
$$\log_{10}\beta_1° \ (298.15\ K) \ = 13.23 \pm 0.15$$

$$UO_2^{2+} + HPO_4^{2-} \Leftrightarrow UO_2HPO_4(aq)$$
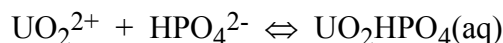
$$\log_{10}\beta_1° \ (298.15\ K) \ = \ 7.24 \pm 0.26$$

In view of the importance of the phosphate system for the modelling of dioxouranium(VI) in the environment, it is highly desirable to have additional experimental verification of the U(VI) phosphate system in the neutral and alkaline pH ranges.

Solubility equilibria in the U(VI) - H₃PO₄ system: The determinations of the solubility products of U(VI) phosphate solids were mainly carried out in acidic solutions. GRENTHE et al. (1992) credited data for the following reactions:

$$UO_2HPO_4 \cdot 4H_2O(cr) + 2\ H^+ \Leftrightarrow UO_2^{2+} + H_3PO_4(aq) + 4\ H_2O(l)$$

$$\log_{10}{}^*K_{s,0}° \ (298.15\ K) \qquad = -2.50 \pm 0.09$$

$$(UO_2)_3(PO_4)_2 \cdot 4H_2O(cr) + 6\,H^+ \iff 3\,UO_2^{2+} + 2\,H_3PO_4(aq) + 4\,H_2O(l)$$

$$\log_{10}{}^*K_{s,0}° \;(298.15\text{ K}) \qquad = -5.96 \pm 0.30$$
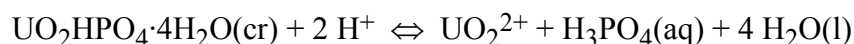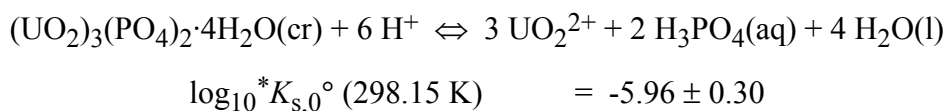
Note, that GRENTHE et al. (1992) consider the thermodynamic properties of $UO_2HPO_4 \cdot 4H_2O(cr)$ to be identical to those of $H_2(UO_2)_2(PO_4)_2 \cdot 8H_2O(cr)$. This phase is one out of five H-autunite phases, distinguished by their hydration numbers, as accepted by the NEA reviewers: $H_2(UO_2)_2(PO_4)_2 \cdot x$ $H_2O(cr)$ (x = 0, 2, 4, 8, 10). Hence, the solubility of $UO_2HPO_4 \cdot 4H_2O(cr)$ may represent those of the mineral chernikovite.

SANDINO (1991) reported the solubility product of a well defined $(UO_2)_3(PO_4)_2 \cdot 4H_2O(cr)$ phase, which is about four orders of magnitude lower than the value selected by GRENTHE et al. (1992). GRENTHE et al. (1992) stated that the most obvious reason for this discrepancy is a difference in the crystallinity between the two phases. GRENTHE et al. (1992) defended their selection by arguing (1) with a satisfying consistency check of their selected solubility products by comparing calculated and measured phosphoric acid concentrations in a system where $(UO_2)_3(PO_4)_2 \cdot 4H_2O(cr)$ and $UO_2HPO_4 \cdot 4H_2O(cr)$ are in equilibrium, and (2) with their preference of selecting data measured at lower ionic strength. The latter argument is somewhat enigmatic as the difference between 0.5 M $NaClO_4$ (SANDINO 1991) and 0.32 M $NaNO_3$ (GRENTHE et al. 1992) is negligible compared with the difference in solubility products of four orders of magnitude. Anyhow, we decided to stick to the recommendation of GRENTHE et al. (1992) as for safety assessments the higher solubility product is a conservative choice.

The solubility of $UO_2(H_2PO_4)_2 \cdot 3H_2O(cr)$ was measured in concentrated phosphoric acid solutions. GRENTHE et al. (1992) assessed an approximate value for the solubility product of this phase and concluded that $UO_2(H_2PO_4)_2 \cdot 3H_2O(cr)$ is not thermodynamically stable at low phosphoric acid concentrations. Hence, this phase is not relevant under environmental conditions and is not included in our database.

The aqueous U(IV) - H_3PO_4 system: There are few experimental studies of equilibria in the uranium(IV) - phosphate system. GRENTHE et al. (1992) credited data only for the following reaction:

$$U(HPO_4)_2 \cdot 4H_2O(cr) + 4\,H^+ \iff U^{4+} + 2\,H_3PO_4(aq) + 4\,H_2O(l)$$

$$\log_{10}{}^*K_{s,0}° \;(298.15\text{ K}) \qquad = -11.79 \pm 0.15$$
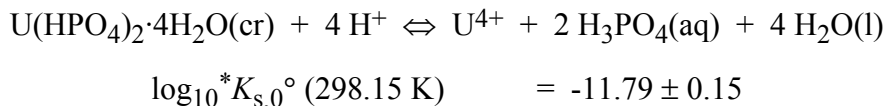
GRENTHE et al. (1992) found it impossible to obtain any reliable information on the composition of the aqueous uranium(IV) phosphate complexes and the numerical values of their formation constants. However, there is no doubt that very stable U(IV) phosphate complexes are formed and that additional investigations are needed. From this viewpoint it is pretty useless to include only the

solubility product of $U(HPO_4)_2 \cdot 4H_2O(cr)$ in our database without any U(IV) phosphate complexes: Speciation calculations in this system, except for strongly acidic solutions, will be grossly wrong.

Aqueous uranium pyrophosphates ($H_4P_2O_7$): GRENTHE et al. (1992) did not select any values for U(VI) or U(IV) pyrophosphate complexes or compounds. All published data have been discarded as insufficient or unreliable.

5.23.6.2.2 Solid uranium phosphorous compounds

Uranium phosphides: Thermochemical data have been selected by GRENTHE et al. (1992) for several binary uranium phosphide solids. However, phosphides are not relevant under environmental conditions and are not included in our database.

Uranium hypophosphites and phosphites: No thermodynamic data are available for these compounds.

Uranium metaphosphates: No thermodynamic data have been selected by GRENTHE et al. (1992) for these compounds.

Uranium(VI) orthophosphates: GRENTHE et al. (1992) selected thermodynamic data for $(UO_2)_3(PO_4)_2(cr)$, $(UO_2)_3(PO_4)_2 \cdot 4H_2O(cr)$ and $(UO_2)_3(PO_4)_2 \cdot 6H_2O(cr)$. The anhydrous solid $(UO_2)_3(PO_4)_2(cr)$ is not stable in aqueous solution and thus, it is not included in our database. According to dehydration experiments both, the tetra- and hexahydrates are stable at room temperature. A solubility product has been selected for $(UO_2)_3(PO_4)_2 \cdot 4H_2O(cr)$ by GRENTHE et al. (1992) and included in our database (see 5.23.6.2.1). Based on this solubility product and the assumption that the Gibbs energy of formation of the hexahydrate will not differ from the sum of the value of the tetrahydrate plus that of two moles of liquid water by more than a few $kJ \cdot mol^{-1}$, GRENTHE et al. (1992) estimated $\Delta_f G_m°$ of the hexahydrate. This estimated value is not included in our database.

Uranium(IV) orthophosphates: No thermodynamic data are available for these compounds.

Uranium pyrophosphates: Thermochemical data have been selected by GRENTHE et al. (1992) for several uranium pyrophosphate solids. Only in one case, $UP_2O_7(cr)$, these thermochemical data can be compared with solubility data. The solubility product calculated from $\Delta_f G_m°$ is ten (!) orders of magnitude lower than the solubility product derived from dissolution experiments. Note that the latter value has been discarded by GRENTHE et al. (1992) with the argument of an incomplete speciation model (see 5.23.6.2.1). In summary, none of these compounds is included in our database.

Other uranium phosphorous compounds: The only phases for which reliable data exist are $U(HPO_4)_2 \cdot 4H_2O(cr)$ and $UO_2HPO_4 \cdot 4H_2O(cr)$. Both are discussed in Section 5.23.6.2.1.

5.23.6.3 Arsenic compounds

Thermochemical data for several uranium arsenide and arsenate solids have been selected by GRENTHE et al. (1992). None of these solids is known as naturally occurring uranium mineral and no solubility data are available. Hence, none of these solids is included in our database.

5.23.6.4 Antimony compounds

Thermochemical data for several binary uranium antimonide solids have been selected by GRENTHE et al. (1992). None of these solids is known as naturally occurring uranium mineral and no solubility data are available. Hence, none of these solids is included in our database.

5.23.7 Group 14 compounds and complexes

5.23.7.1 Carbon compounds and complexes

5.23.7.1.1 Uranium carbides

Thermochemical data for several binary uranium carbide solids have been selected by GRENTHE et al. (1992). However, carbides are not relevant under environmental conditions and are not included in our database.

5.23.7.1.2 Uranium carbonates

Major U(VI) carbonate complexes: The stoichiometric compositions of the three mononuclear U(VI) carbonate complexes, $UO_2CO_3(aq)$, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$, are well established. The same is true for the trimer $(UO_2)_3(CO_3)_6^{6-}$. Appraising the available experimental data the NEA reviewers evaluated the following recommended values (GRENTHE et al. 1992 and GRENTHE et al. 1995):

$$UO_2^{2+} + n\,CO_3^{2-} \Leftrightarrow UO_2(CO_3)_n^{(2-2n)}$$
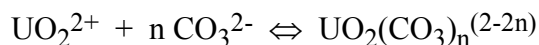
$$\log_{10}\beta_1° \ (n = 1, 298.15\ K) \quad = \quad 9.67 \pm 0.05$$

$$\log_{10}\beta_2° \ (n = 2, 298.15\ K) \quad = \quad 16.94 \pm 0.12$$

$$\log_{10}\beta_3° \ (n = 1, 298.15\ K) \quad = \quad 21.60 \pm 0.05$$

Enthalpy of reaction data are selected by GRENTHE et al. (1992) as follows:

$$\Delta_r H_m° \ (n = 1, 298.15\ K) \quad = \quad (5 \pm 2)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m° \ (n = 2, 298.15\ K) \quad = \quad (18.5 \pm 4.0)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m° \ (n = 3, 298.15\ K) \quad = \quad -(39.2 \pm 4.1)\ kJ \cdot mol^{-1}$$

Note a somewhat enigmatic inconsistency in the argumentation of GRENTHE et al. (1992) regarding their procedures to evaluate $\log_{10}\beta^\circ$ values. In the case of n = 1 they state that "there are only few experimental data" for this reaction and therefore each experimental value had been corrected individually to zero ionic strength (using a SIT interaction coefficient derived from tabulated values) and from the resulting values a weighted average had been selected. However, "an equally large number of experimental data are available" for the equilibria n = 2 and n = 3. But in these cases linear regressions had been done in order to evaluate the corresponding values of $\log_{10}\beta^\circ$. Why not linear regression in all three cases, with "equally large numbers of experimental data"? Well, in the case of n = 1 a linear regression would result in a SIT interaction coefficient of $UO_2CO_3(aq)$ which is significantly different from zero when using the tabulated SIT coefficients for UO_2^{2+} and CO_3^{2-}. This is a contradiction to the explicit assumption in all NEA reviews that SIT interaction coefficients of neutral species are taken as zero. The above described procedure disguises this inconsistency.

The trinuclear complex is characterised by the following well established constants:

$$3\ UO_2^{2+}\ +\ 6\ CO_3^{2-}\ \Leftrightarrow\ (UO_2)_3(CO_3)_6^{6-}$$

$$\log_{10}\beta_{6,3}^\circ\ (298.15\ K)\quad\quad =\quad 54.0 \pm 1.0$$

$$\Delta_r H_m^\circ\ (298.15\ K)\quad\quad\quad =\quad \text{-}(62.7 \pm 2.4)\ kJ\cdot mol^{-1}$$
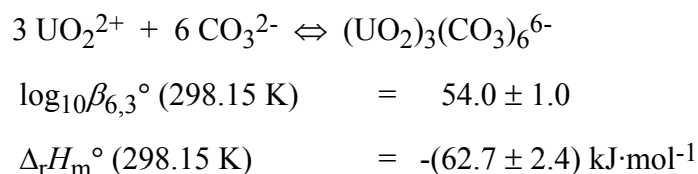
Mixed U(VI) hydroxide - carbonate complexes: These complexes are often minor species, and there are several different proposals for their composition. GRENTHE et al. (1992) conclude that there is good evidence for the formation of a highly polynuclear mixed hydroxide - carbonate complex:

$$11\ UO_2^{2+}\ +\ 6\ CO_2(g) + 18\ H_2O(l)\ \Leftrightarrow\ (UO_2)_{11}(CO_3)_6(OH)_{12}^{2-} + 24\ H^+$$
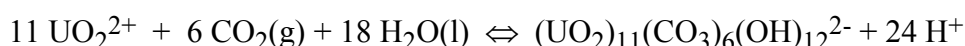
GRENTHE et al. (1992) selected

$$\log_{10}{}^*K\ (298.15\ K)\ =\ \text{-}72.5 \pm 2.0$$

as an average of equilibrium constants measured between 0.1 to 3.0 M $NaClO_4$, but they did not find it meaningful to extrapolate the data to I = 0 because the result is very sensitive even to small model errors due to the very large Debye-Hückel term. Considering this ambiguity and the fact that this large polynuclear complex represents, at most, 15% of the total uranium in rather concentrated solutions (GRENTHE et al. 1992), we decided not to include this complex in our database.

A further polynuclear complex, $(UO_2)_3O(OH)_2(HCO_3)^+$, also is never predominant, and it is difficult to establish its existence experimentally. However, as a guideline for the reaction

$$3\ UO_2^{2+} + CO_2(g) + 4\ H_2O(l) \Leftrightarrow (UO_2)_3O(OH)_2(HCO_3)^+ + 5\ H^+$$
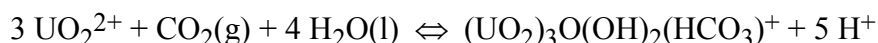
GRENTHE et al. (1992) propose the following constant, corrected to I = 0:

$$\log_{10}{}^*K^\circ\ (298.15\ \text{K}) = -17.5 \pm 0.5$$

Using the carbonate equilibrium constants selected in our review (see Chapter 4, Core Data) relating $CO_2(g)$ with CO_3^{2-} the above value has been converted to

$$3\ UO_2^{2+} + CO_3^{2-} + 3\ H_2O(l) \Leftrightarrow (UO_2)_3O(OH)_2(HCO_3)^+ + 3\ H^+$$
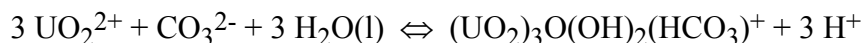
$$\log_{10}{}^*K^\circ\ (298.15\ \text{K}) = 0.66 \pm 0.50$$

Two studies support the formation of a mixed complex

$$2\ UO_2^{2+} + CO_2(g) + 4\ H_2O(l) \Leftrightarrow (UO_2)_2CO_3(OH)_3^- + 5\ H^+$$
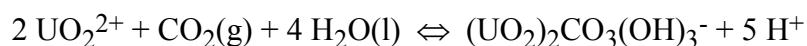
which is a major complex in addition to $UO_2(CO_3)_3^{4-}$. However, there is a fairly large difference between the values derived from the two studies (GRENTHE et al. 1992). This is clearly a case of conflicting evidence where additional experimental information is necessary to resolve the issue. For the time being, GRENTHE et al. (1992) preferred the value derived from the study which provides the most experimental data and the selected

$$\log_{10}{}^*K^\circ\ (298.15\ \text{K}) = -19.01 \pm 0.50$$

Using the carbonate equilibrium constants selected in our review (see Chapter 4, Core Data) relating $CO_2(g)$ with CO_3^{2-} the above value has been converted to

$$2\ UO_2^{2+} + CO_3^{2-} + 3\ H_2O(l) \Leftrightarrow (UO_2)_2CO_3(OH)_3^- + 3\ H^+$$
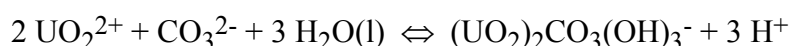
$$\log_{10}{}^*K^\circ\ (298.15\ \text{K}) = -0.86 \pm 0.50$$

Mixed U(VI), Np(VI) and Pu(VI) carbonate complexes: Carbonate is an excellent bridging ligand and the formation of polynuclear carbonate complexes containing one type of metal ion is well known. Such complexes may also contain two or more different types of metal ions. Known examples are carbonate complexes containing UO_2^{2+}, NpO_2^{2+} and PuO_2^{2+} as metal ions. These complexes are discussed in the neptunium and plutonium reviews, respectively.

U(V) carbonate complexes: Only one dioxouranium(V) carbonate complex, $UO_2(CO_3)_3^{5-}$, was identified in aqueous solution. Information about this species was obtained by using various electrochemical techniques. Appraising the available experimental information GRENTHE et al. (1992) selected for the reaction

$$UO_2^+ + 3 CO_3^{2-} \Leftrightarrow UO_2(CO_3)_3^{5-}$$
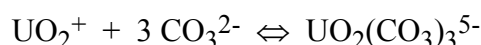
the following constant

$$\log_{10}\beta_3° \text{ (298.15 K)} = 7.41 \pm 0.27$$

Note that $UO_2(CO_3)_3^{5-}$ is the only known U(V) complex! No information on other U(V) complexes is available in the literature.

U(IV) carbonate complexes: There is considerably less information about the carbonate complexes of U(IV) than about U(VI). The uranium(IV) carbonate complexes were only investigated in solutions of rather high bicarbonate concentration. The chemical composition and the equilibrium constant of the limiting complex $U(CO_3)_5^{6-}$ are well established. However, the magnitude of the equilibrium constant depends on the value of the standard potential of $UO_2^{2+}/$ U^{4+} because it has to be determined via the redox potential of the reaction

$$UO_2(CO_3)_3^{4-} + 2 e^- + 2 CO_2(g) \Leftrightarrow U(CO_3)_5^{6-}$$
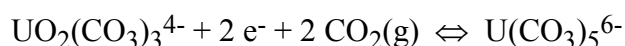
Using the selected standard potential of the UO_2^{2+}/U^{4+} couple (see 5.23.2) and β_3 for the formation of $UO_2(CO_3)_3^{4-}$, GRENTHE et al. (1992) calculated the equilibrium constant for the reaction

$$U^{4+} + 5 CO_3^{2-} \Leftrightarrow U(CO_3)_5^{6-}$$
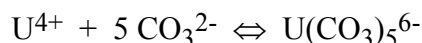
The selected value is

$$\log_{10}\beta_5° \text{ (298.15 K)} = 34.1 \pm 1.0$$

The enthalpy of this reaction has been determined experimentally as

$$\Delta_r H_m° \text{ (298.15 K)} = -(20 \pm 4) \text{ kJ·mol}^{-1}$$

The dissociation of the limiting complex $U(CO_3)_5^{6-}$ to $U(CO_3)_4^{4-}$ was studied in varying ionic media and these data were used to estimate (GRENTHE et al. 1992)

$$U(CO_3)_5^{6-} \Leftrightarrow U(CO_3)_4^{4-} + CO_3^{2-}$$

$$\log_{10}K_5° \text{ (298.15 K)} = 1.12 \pm 0.25$$

No information is available on the composition and equilibrium constants of U(IV) carbonate complexes in acidic solutions. However, based on studies on the corresponding Th(IV) system, GRENTHE et al. (1992) concluded that mixed hydroxide carbonate / bicarbonate complexes of U(IV) are likely to be formed at pH < 7, complexes that will affect both the speciation and the

solubility of uranium(IV). Experimental information on the complexes formed and their stability constants is badly needed. Such information should probably first be obtained for Th(IV), where the experimental difficulties seem less formidable.

$UO_2(CO_3)$(cr): The only known stable solid in the U - CO_2 - H_2O system is the simple U(VI) carbonate $UO_2(CO_3)$(cr). When naturally occurring, this yellow orthorhombic mineral is called rutherfordine. Four reliable values of the equilibrium constant for reaction

$$UO_2(CO_3)(cr) \Leftrightarrow UO_2^{2+} + CO_3^{2-}$$
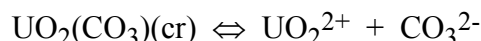
from references given in GRENTHE et al. (1992) have been credited. The weighted average of the values extrapolated to I = 0 is (GRENTHE et al. 1995, p.357):

$$\log_{10}K_{s,0}° (298.15 \text{ K}) = \quad -14.49 \pm 0.04$$

The entropy and heat capacity of $UO_2(CO_3)$(cr) were determined experimentally and GRENTHE et al. (1992) selected the following values:

$$S_m° (UO_2(CO_3), \text{cr}, 298.15 \text{ K}) \quad = \quad (144.2 \pm 0.3) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{p,m}°(UO_2(CO_3), \text{cr}, 298.15 \text{ K}) \quad = \quad (120.1 \pm 0.1) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Other uranium carbonates: Thermodynamic data exist for $Na_4UO_2(CO_3)_3$(cr), and for the minerals $Ca_2UO_2(CO_3)_3 \cdot 10H_2O$(cr) (liebigite), $CaMgUO_2(CO_3)_3 \cdot 12H_2O$(cr) (swartzite), $Mg_2UO_2(CO_3)_3 \cdot 10H_2O$(cr) (bayleyite), $CaNa_2UO_2(CO_3)_3 \cdot 6H_2O$(cr) (andersonite) (GRENTHE et al. 1992), $Ca_3NaUO_2(CO_3)_3FSO_4 \cdot 10H_2O$(cr) (schröckingerite) and $K_3NaUO_2(CO_3)_3 \cdot H_2O$(cr) (grimselite) (GRENTHE et al. 1995).

The solubility product of $Na_4UO_2(CO_3)_3$(cr) was measured at different ionic strengths and in different media. GRENTHE et al. (1992) used six values reported for $NaClO_4$ media up to I = 3 M for the reaction

$$Na_4UO_2(CO_3)_3(cr) \Leftrightarrow 4 Na^+ + UO_2(CO_3)_3^{4-}$$
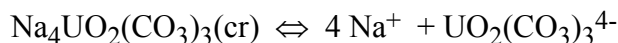
to make an extrapolation to I = 0. The resulting selected solubility constant is (GRENTHE et al. 1992)

$$\log_{10}K_{s,3}° (298.15 \text{ K}) = \quad -5.34 \pm 0.16$$

As can be seen from its solubility product, this solid will only precipitate in highly concentrated Na salt solutions. In ordinary ground and surface waters, this solid is unstable with respect to schoepite, $UO_3 \cdot 2H_2O$(s), and rutherfordine, $UO_2(CO_3)$(cr). As a consequence, $Na_4UO_2(CO_3)_3$(cr),

is not known as naturally occurring mineral. Hence, $Na_4UO_2(CO_3)_3(cr)$ is not relevant under environmental conditions and is not included in our database.

GRENTHE et al. (1992) did not select any thermodynamic data for liebigite, swartzite, bayleyite, andersonite, schröckingerite and grimselite, as the quality of the experimental data has been regarded as not adequate to include them in the selection procedure. For a detailed discussion see GRENTHE et al. (1992), p. 328, and GRENTHE et al. (1995), p.358.

5.23.7.1.3   Uranium thiocyanate complexes

Equilibrium constants for U(VI) thiocyanate complexes

$$UO_2^{2+} + n\ SCN^- \Leftrightarrow UO_2(SCN)_n^{(2-n)}$$
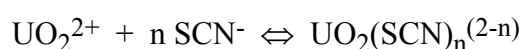
with n = 1,2 and 3, and for U(IV) thiocyanate complexes

$$U^{4+} + n\ SCN^- \Leftrightarrow U(SCN)_n^{(4-n)}$$
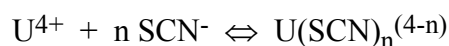
with n = 1 and 2 have been selected by GRENTHE et al. (1992).

However, thiocyanate complexes are presently not included in our database.

5.23.7.2 Silicon compounds and complexes

5.23.7.2.1   Aqueous uranium silicates

Experimental information on uranium silicate complexes refer to the reaction

$$UO_2^{2+} + Si(OH)_4(aq) \Leftrightarrow UO_2SiO(OH)_3^+ + H^+$$
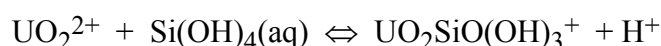
GRENTHE et al. (1992) stated that the experimental data clearly indicate that a complex formation takes place. However, the resulting stability constant has been regarded as unexpectedly large, indicating that the ligand must have a larger negative charge and that a chelate complex must be formed. Both these facts suggest that the complex contains a polynuclear silicate ligand. The experimental information on aqueous uranium silicate species is not sufficiently precise to define a stoichiometry and to evaluate an equilibrium constant. However, aqueous uranium silicate complexes may well exist in groundwater systems, and additional experimental investigations are necessary to decide the type of complexes formed and their stabilities (GRENTHE et al. 1992, p.334).

Within the last years more experimental studies on uranium silicate complexes have been published but unfortunately the situation has not improved concerning the stoichiometry and stability of these complexes and no value for U(VI) silicate complexation can be recommended. For a detailed discussion see 5.18.4.6.

5.23.7.2.2   Solid uranium silicates

$(UO_2)_2SiO_4\cdot2H_2O(cr)$: In the uranium(VI) - silicate group, $(UO_2)_2SiO_4\cdot2H_2O(cr)$, soddyite, is the only known compound. However, thermodynamic data for this solid phase have not been reported.

Coffinite, $USiO_4(cr)$, is an abundant mineral in reduced sedimentary uranium deposits. This mineral generally forms small crystals and is almost always associated with amorphous $USiO_4$, uraninite, $UO_2(cr)$, and auxiliary minerals. Coffinite minerals have been synthesised only with difficulty because many particular conditions are necessary: reducing media, basic pH ($7 < pH < 10$), solutions rich in dissolved silica. Coffinite minerals are always obtained in association with $UO_2(cr)$ and $SiO_2(cr)$. Therefore, it is very difficult to determine thermodynamic data for pure coffinite experimentally.

GRENTHE et al. (1992) accepted an estimation procedure proposed by LANGMUIR (1978) who assumed an average aqueous silica concentration of 10^{-3} M (60 ppm as SiO_2) for the coffinite – uraninite equilibrium

$$USiO_4(cr) \ + \ 2\,H_2O(l) \ \Leftrightarrow \ UO_2(cr) \ + \ Si(OH)_4(aq)$$
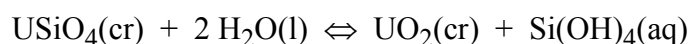
In this equilibrium the only aqueous species is $Si(OH)_4(aq)$ and thus, the equilibrium constant equals the assumed silica concentration of 10^{-3} M. The ionic strength dependence of an equilibrium involving only neutral species is minimal and as a good approximation we can assume

$$log_{10}K° \ (298.15 \ K) \ \ = \ \ \ \ \ \ -3.0$$

Considering that $\Delta_r G_m° = -R\cdot T\cdot ln\,(10)\cdot log_{10}K°$ we calculate $\Delta_r G_m° = 17.124$ kJ·mol^{-1}. Using this value and the Gibbs energy of formation of uraninite as well as auxiliary data for $H_2O(l)$ and $Si(OH)_4(aq)$ as recommended by GRENTHE et al. (1992)

$$\Delta_f G_m° \ (UO_2, \ cr, \ 298.15 \ K) \ \ \ \ = \ \ -(1031.833 \pm 1.004) \ kJ \cdot mol^{-1}$$

$$\Delta_f G_m° \ (H_2O, \ l, \ 298.15 \ K) \ \ \ \ \ \ \ = \ \ \ -(237.140 \pm 0.041) \ kJ \cdot mol^{-1}$$

$$\Delta_f G_m° \ (Si(OH)_4, \ aq, \ 298.15 \ K) = \ \ -(1307.735 \pm 1.156) \ kJ \cdot mol^{-1}$$

the Gibbs energy of formation of coffinite is calculated as

$$\Delta_f G_m^\circ \text{ (USiO}_4\text{, cr, 298.15 K)}   =   \text{-(1882.4} \pm \text{4.0) kJ} \cdot \text{mol}^{-1}$$

The uncertainty is given as estimated by GRENTHE et al. (1992). Note that this recalculation of the Gibbs energy of coffinite reveals an error of 1.2 kJ·mol^{-1} in the recommended value of GRENTHE et al. (1992), $\Delta_f G_m^\circ$ = -(1883.6 ± 4.0) kJ·mol^{-1}. The source of this error is unclear. However, this error is of no consequence for our data base because we have to deal with much larger differences induced by the changes in UO$_2$(s) and Si(OH)$_4$(aq) data, as indicated in the following paragraphs.

The Gibbs energy of formation of Si(OH)$_4$(aq) was changed by 1.45 kJ·mol^{-1} as a consequence of the change in the solubility of quartz (RIMSTIDT 1997, GUNNARSSON & ARNORSSON 2000) (see 5.18.3.2):

$$\Delta_f G_m^\circ \text{ (Si(OH)}_4\text{, aq, 298.15 K)} =   \text{-(1309.183} \pm \text{0.610) kJ} \cdot \text{mol}^{-1}$$

Note that in the most recent review GUNNARSSON & ARNORSSON (2000) do not give any uncertainty estimate for their recommended value of $\Delta_f G_m^\circ$(Si(OH)$_4$) which we have selected in our update. However, RIMSTIDT (1997) recommends in his earlier review, basically evaluating the same data as GUNNARSSON & ARNORSSON (2000), $\Delta_f G_m^\circ$ (Si(OH)$_4$, aq, 298.15 K) = -(1309.231 ± 0.610) kJ·mol^{-1}. This recommended value differs by only 0.052 kJ·mol^{-1} from the result of GUNNARSSON & ARNORSSON (2000) and thus, we have selected Rimstidt's uncertainty estimate in our update.

A much larger change was made concerning the thermodynamic parameters of UO$_2$(s). The Gibbs energy of formation of UO$_2$(s) changed by 27.9 kJ·mol^{-1} with respect to UO$_2$(cr) as a consequence of a re-evaluation of the system UO$_2$ - H$_2$O - CO$_2$ (see section 5.23.3.1.3). The thermodynamic constants selected for our database update do not refer to well defined uraninite, UO$_2$(cr), at very low pH but are based on U(IV) solubility data above pH 4. They consistently describe the system UO$_2$(s) – H$_2$O – CO$_2$ above pH 4 but refer to a poorly defined solid UO$_2$(s).

We now have two options. We can retain the Gibbs energy of formation of UO$_2$(cr) for calculating $\Delta_f G_m^\circ$(USiO$_4$). In that case, model calculations of the U(IV) system using our updated database including UO$_2$(s) would refer to an equilibrium concentration of log [Si(OH)$_4$(aq)] = -7.9. In other words, any model water containing silicate would either be grossly oversaturated by USiO$_4$(cr) or the dissolved silica would be lowered to trace concentrations by concomitant dissolution of all other silicate solids.

The second option is to retain the model assumption of an average dissolved silica concentration of 10^{-3} M for the USiO$_4$(s) – UO$_2$(s) equilibrium. Note that now both solids do not represent the well

defined crystalline phases. In that case we have to adapt the Gibbs energy of formation of $USiO_4(s)$ using the value

$$\Delta_f G_m^\circ (UO_2, s, 298.15\ K) \quad = \quad -(1004.1 \pm 11.4)\ kJ \cdot mol^{-1}$$

The uncertainty of $\Delta_f G_m^\circ(UO_2)$ results from the uncertainty of the solubility product of $UO_2(s)$, $\log_{10}{}^* K_{s,0}^\circ = 0 \pm 2$, as estimated in section 5.23.3.1.3. Using the new $\Delta_f G_m^\circ(Si(OH)_4)$ and the changed $\Delta_f G_m^\circ(UO_2)$ results in

$$\Delta_f G_m^\circ (USiO_4, s, 298.15\ K) \quad = \quad -(1856.1 \pm 11.4)\ kJ \cdot mol^{-1}$$

We have chosen the second option.

5.23.8   Alkali and alkaline-earth compounds

Thermochemical data have been selected by GRENTHE et al. (1992) for the entire series of alkali and alkaline-earth uranates. These solids potentially can play an important role as uranium bearing phases in highly alkaline cement pore waters. However, no solubility data are available and no indication is given to what extend any of these compounds might be stable in high pH aqueous systems. Scoping calculations using $\Delta_f G_m^\circ$ of $CaUO_4(cr)$ recommended by GRENTHE et al. (1992) resulted in dissolved uranium concentrations several orders of magnitude lower than actually measured in cement pore waters (J. Tits and E. Wieland, personal communication). It seems that we face the same difficulties as discussed in the case of $UO_2(cr)$ versus $UO_2(s)$ (see 5.23.3.1.3) and the mixed valence oxides (see 5.23.3.2.2). Hence, alkali and alkaline-earth uranates are presently not included in our database.

5.23.9   Uranium compounds and uranium minerals

A final remark on uranium compounds and uranium minerals: In the Uranium Book (GRENTHE et al. 1992) thermodynamic data for 197 uranium solids have been selected by the NEA reviewers. A comparably large number, 242, of naturally occurring uranium minerals have been "officially" recognised (MINERAL DATABASE 1997). However, the set of uranium minerals for which thermodynamic data have been selected is surprisingly small: 5 (!), i.e. uraninite UO_2, schoepite $UO_3 \cdot 2H_2O$, chernikovite $UO_2HPO_4 \cdot 4H_2O$, rutherfordine UO_2CO_3 and coffinite $USiO_4$. All these minerals are included in our database. In addition, solubility products of three solid phases have been included in our database which are thought to be of some relevance for environmental modelling: $UF_4 \cdot 2.5H_2O(cr)$, $U(OH)_2SO_4(cr)$ and $(UO_2)_3(PO_4)_2 \cdot 4H_2O(cr)$.
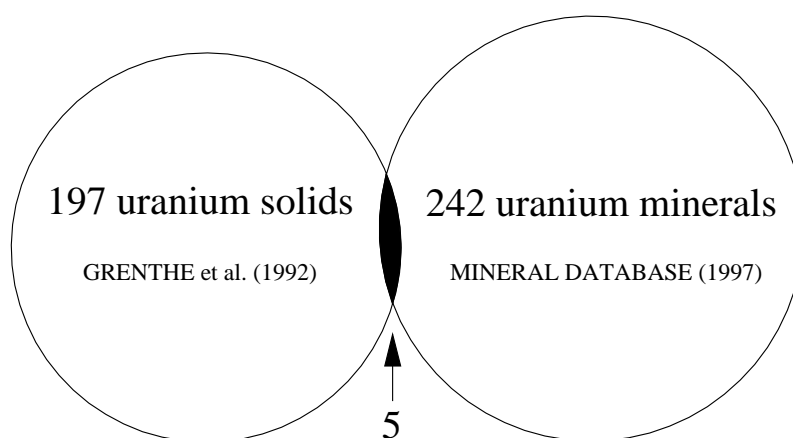
Fig. 5.23.4: Venn diagram representing the set of uranium solids in GRENTHE et al. (1992), the set of uranium minerals "officially" recognised (MINERAL DATABASE 1997) and the set of uranium minerals for which thermodynamic data have been selected.

Table 5.23.1: Selected uranium data. Numbers in ***bold face*** are selected in this review. They are at variance from the values recommended by GRENTHE et al. (1992). Arrows point to calculated values.

TDB Version 05/92   **TDB Version 01/01**

Name	$\Delta_f G_m°$	$\Delta_f H_m°$	Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$S_m°$	$C_{p,m}°$	Species
	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$		$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	
	-	-		0.0	0.0	50.2 ± 0.20	27.66 ± 0.05	U(cr)
UO2+2	-952.551	-1019.000		-952.551 ± 1.75 ←	-1019.0 ± 1.5	-98.2 ± 3.0	42.4 ± 3.0	UO_2^{2+}

Name	$\log_{10}K°$	$\Delta_f H_m°$	Name	$\log_{10}K°$	$\Delta_f H_m°$	$S_m°$	$C_{p,m}°$	Reaction
UO2+	1.484	-1025.127	UO2+2	1.484 ± 0.022	$-1025.127 \pm 0.3.0$ ←	-25 ± 8		$UO_2^{2+} + e^- \Leftrightarrow UO_2^+$
U+4	9.038	-591.200	U+4	9.038 ± 0.041	-591.2 ± 3.3	→ -416.896 ± 12.6	48 ± 15	$UO_2^{2+} + 4H^+ + 2e^- \Leftrightarrow U^{4+} + 2H_2O(l)$
U+3	-9.353	-489.100	U+3	-	-	-	-	$U^{4+} + e^- \Leftrightarrow U^{3+}$

Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	$\Delta_r S_m°$	$S_m°$	Reaction
ULOH+	-5.21	0	UO2OH+	-5.2 ± 0.3			17 ± 50	$UO_2^{2+} + H_2O(l) \Leftrightarrow UO_2OH^+ + H^+$
ULOH2	-10.31	0	UO2(OH)2	***-12.0 ± 0.5***				$UO_2^{2+} + 2 H_2O(l) \Leftrightarrow UO_2(OH)_2(aq) + 2 H^+$
ULOH3-	-19.21	0	UO2(OH)3-	-19.2 ± 0.4				$UO_2^{2+} + 3 H_2O(l) \Leftrightarrow UO_2(OH)_3^- + 3 H^+$
ULOH4-2	-33.01	0	UO2(OH)4-2	-33 ± 2				$UO_2^{2+} + 4 H_2O(l) \Leftrightarrow UO_2(OH)_4^{2-} + 4 H^+$
UL2OH+3	-2.72	0	(UO2)2OH+3	-2.7 ± 1.0				$2 UO_2^{2+} + H_2O(l) \Leftrightarrow (UO_2)_2OH^{3+} + H^+$
UL2OH2+2	-5.64	0	(UO2)2(OH)2+2	-5.62 ± 0.04			-38 ± 15	$2 UO_2^{2+} + 2 H_2O(l) \Leftrightarrow (UO_2)_2(OH)_2^{2+} + 2 H^+$
UL3OH4+2	-11.93	0	(UO2)3(OH)4+2	-11.9 ± 0.3				$3 UO_2^{2+} + 4 H_2O(l) \Leftrightarrow (UO_2)_3(OH)_4^{2+} + 4 H^+$
UL3OH5+	-15.58	0	(UO2)3(OH)5+	-15.55 ± 0.12			83 ± 30	$3 UO_2^{2+} + 5 H_2O(l) \Leftrightarrow (UO_2)_3(OH)_5^+ + 5 H^+$
UL3OH7-	-31.03	0	(UO2)3(OH)7-	-31 ± 2				$3 UO_2^{2+} + 7 H_2O(l) \Leftrightarrow (UO_2)_3(OH)_7^- + 7 H^+$
UL4OH7+	-21.901	0	(UO2)4(OH)7+	-21.9 ± 1.0				$4 UO_2^{2+} + 7 H_2O(l) \Leftrightarrow (UO_2)_4(OH)_7^+ + 7 H^+$
UOH+3	-0.53	46.903	UOH+3	-0.54 ± 0.06	46.91	←147 ± 30		$U^{4+} + H_2O(l) \Leftrightarrow UOH^{3+} + H^+$
UOH4	-4.53	0	U(OH)4	***-9 ± 2***				$U^{4+} + 4 H_2O(l) \Leftrightarrow U(OH)_4(aq) + 4 H^+$

Table 5.23.1: continued

Name	$\log_{10}\beta°$	$\Delta_rH_m°$	Name	$\log_{10}\beta°$	$\Delta_rH_m°$	$\Delta_rS_m°$	$S_m°$	Reaction
UOH5-	-16.54	0		-	-	-		$U^{4+} + 5\,H_2O(l) \Leftrightarrow U(OH)_5^- + 5\,H^+$
ULF+	5.09	0	UO2F+	5.09 ± 0.13	1.70 ± 0.08			$UO_2^{2+} + F^- \Leftrightarrow UO_2F^+$
ULF2	8.62	0	UO2F2	8.62 ± 0.04	2.10 ± 0.19			$UO_2^{2+} + 2\,F^- \Leftrightarrow UO_2F_2(aq)$
ULF3-	10.9	0	UO2F3-	10.9 ± 0.4	2.35 ± 0.31			$UO_2^{2+} + 3\,F^- \Leftrightarrow UO_2F_3^-$
ULF4-2	11.71	0	UO2F4-2	11.7 ± 0.7	0.29 ± 0.47			$UO_2^{2+} + 4\,F^- \Leftrightarrow UO_2F_4^{2-}$
UF+3	9.29	-5.648	UF+3	9.28 ± 0.09	-5.6 ± 0.5			$U^{4+} + F^- \Leftrightarrow UF^{3+}$
UF2+2	16.23	-3.515	UF2+2	16.23 ± 0.15	-3.5 ± 0.6			$U^{4+} + 2\,F^- \Leftrightarrow UF_2^{2+}$
UF3+	21.58	0.502	UF3+	21.6 ± 1.0	0.5 ± 4.0			$U^{4+} + 3\,F^- \Leftrightarrow UF_3^+$
UF4	25.52	-3.640	UF4	25.6 ± 1.0	$-4.206 \Leftarrow 476 \pm 17$			$U^{4+} + 4\,F^- \Leftrightarrow UF_4(aq)$
UF5-	27.03	0	UF5-	27.01 ± 0.30				$U^{4+} + 5\,F^- \Leftrightarrow UF_5^-$
UF6-2	29.11	0	UF6-2	29.08 ± 0.18				$U^{4+} + 6\,F^- \Leftrightarrow UF_6^{2-}$
ULCL+	0.07	0	UO2Cl+	0.17 ± 0.02	8 ± 2			$UO_2^{2+} + Cl^- \Leftrightarrow UO_2Cl^+$
ULCL2	-1.1	0	UO2Cl2	-1.1 ± 0.4	15 ± 6			$UO_2^{2+} + 2\,Cl^- \Leftrightarrow UO_2Cl_2(aq)$
UCL+3	1.72	-18.995	UCl+3	1.72 ± 0.13	-19 ± 9			$U^{4+} + Cl^- \Leftrightarrow UCl^{3+}$
ULSO4	3.14	0	UO2SO4	3.15 ± 0.02	19.5 ± 1.6			$UO_2^{2+} + SO_4^{2-} \Leftrightarrow UO_2SO_4(aq)$
ULSO42-2	4.14	0	UO2(SO4)2-2	4.14 ± 0.07	35.1 ± 1.0			$UO_2^{2+} + 2\,SO_4^{2-} \Leftrightarrow UO_2(SO_4)_2^{2-}$
USO4+2	6.58	7.950	USO4-2	6.58 ± 0.19	8.0 ± 2.7			$U^{4+} + SO_4^{2-} \Leftrightarrow USO_4^{2+}$
USO42	10.51	32.593	U(SO4)2	10.51 ± 0.20	32.7 ± 2.8			$U^{4+} + 2\,SO_4^{2-} \Leftrightarrow U(SO_4)_2(aq)$
ULNO3+	0.29	0	UO2NO3+	0.30 ± 0.15				$UO_2^{2+} + NO_3^- \Leftrightarrow UO_2NO_3^+$
UNO3+3	1.47	0	UNO3+3	1.47 ± 0.13				$U^{4+} + NO_3^- \Leftrightarrow UNO_3^{3+}$
UNO32+2	2.30	0	U(NO3)2+2	2.30 ± 0.35				$U^{4+} + 2\,NO_3^- \Leftrightarrow U(NO_3)_2^{2+}$

Table 5.23.1: continued

Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	$\Delta_r S_m°$	$S_m°$	Reaction
ULPO4	13.689	0	UO2PO4-	13.23 ± 0.15				$UO_2^{2+} + PO_4^{3-} \Leftrightarrow UO_2PO_4^-$
ULHPO4	7.719	0	UO2HPO4	7.24 ± 0.26				$UO_2^{2+} + HPO_4^{2-} \Leftrightarrow UO_2HPO_4(aq)$
ULH2PO4	1.128	0	UO2H2PO4+	1.12 ± 0.06				$UO_2^{2+} + H_3PO_4(aq) \Leftrightarrow UO_2H_2PO_4^+ + H^+$
ULH3PO4	0.779	0	UO2H3PO4+2	0.76 ± 0.15				$UO_2^{2+} + H_3PO_4(aq) \Leftrightarrow UO_2H_3PO_4^{2+}$
ULH4PO4	0.897	0	UO2(H2PO4)2	0.64 ± 0.11				$UO_2^{2+} + 2\ H_3PO_4(aq) \Leftrightarrow UO_2(H_2PO_4)_2(aq) + 2\ H^+$
ULH5PO4	1.717	0	UO2H2PO4H3PO4+	1.65 ± 0.11				$UO_2^{2+} + 2\ H_3PO_4(aq) \Leftrightarrow UO_2(H_2PO_4)(H_3PO_4)^+ + H^+$
ULCO30	9.62	0	UO2CO3	9.67 ± 0.05			5 ± 2	$UO_2^{2+} + CO_3^{2-} \Leftrightarrow UO_2CO_3(aq)$
ULCO3-2	16.99	0	UO2(CO3)2-2	16.94 ± 0.12			18.5 ± 4.0	$UO_2^{2+} + 2\ CO_3^{2-} \Leftrightarrow UO_2(CO_3)_2^{2-}$
ULCO3-4	21.62	0	UO2(CO3)3-4	21.60 ± 0.05			-39.2 ± 4.1	$UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow UO_2(CO_3)_3^{4-}$
UL3C36-6	53.981	0	(UO2)2(CO3)6-6	54.0 ± 1.0			-62.7 ± 2.4	$3\ UO_2^{2+} + 6\ CO_3^{2-} \Leftrightarrow (UO_2)_3(CO_3)_6^{6-}$
UL2OHC3	-19.029	0	(UO2)2CO3(OH)3-	-0.86 ± 0.50				$2\ UO_2^{2+} + CO_3^{2-} + 3\ H_2O(l) \Leftrightarrow (UO_2)_2CO_3(OH)_3^- + 3\ H^+$
UL3OH5C+	-17.389	0	(UO2)3O(OH)2HCO3+	0.66 ± 0.50				$3UO_2^{2+} + CO_3^{2-} + 3H_2O(l) \Leftrightarrow (UO_2)_3O(OH)_2(HCO_3)^+ + 3H^+$
UO2CO33-5	7.42	0	UO2(CO3)3-5	7.41 ± 0.27				$UO_2^+ + 3\ CO_3^{2-} \Leftrightarrow UO_2(CO_3)_3^{5-}$
UCO34-4	35.121	0	U(CO3)4-4	35.22 ± 1.03				$U^{4+} + 4\ CO_3^{2-} \Leftrightarrow U(CO_3)_4^{4-}$
UCO35-6	34.001	20.000	U(CO3)5-6	34.1 ± 1.0			-20 ± 4	$U^{4+} + 5\ CO_3^{2-} \Leftrightarrow U(CO_3)_5^{6-}$

Name	$\Delta_f G_m°$	$\log_{10}K_{s,0}°$	Name	$\log_{10}K_{s,0}°$	$S_m°$	$C_{p,m}°$	Reaction
UO2_CRYS	-1032.337	→ -4.94		-	-	-	$UO_2(cr) + 4\ H^+ \Leftrightarrow U^{4+} + 2\ H_2O(l)$
UO2_AMOR	-1003.569	→ 0.10	UO2(s)	$\mathit{0 \pm 2}$	77.03 ± 0.20	63.60 ± 0.08	$UO_2(s) + 4\ H^+ \Leftrightarrow U^{4+} + 2\ H_2O(l)$
U4O9	-4276.332	→-13.00		-	-	-	$U_4O_9(cr) + 14\ H^+ \Leftrightarrow 3\ U^{4+} + UO_2^{2+} + 7\ H_2O(l)$

Table 5.23.1: continued

Name	$\Delta_f G_m°$	$\log_{10}K_{s,0}°$	Name	$\log_{10}K_{s,0}°$	$S_m°$	$C_{p,m}°$	Reaction
U3O7-BE	-3241.716 →	-7.66	-		-	-	$\beta\text{-}U_3O_7 + 10\,H^+ \Leftrightarrow 2\,U^{4+} + UO_2^{2+} + 5\,H_2O(l)$
U3O8	-3369.471 →	2.46	-		-	-	$U_3O_8(cr) + 8\,H^+ \Leftrightarrow U^{4+} + 2\,UO_2^{2+} + 4\,H_2O(l)$
A_U3O8	-3369.421 →	2.47	-		-	-	$U_3O_8(am) + 8\,H^+ \Leftrightarrow U^{4+} + 2\,UO_2^{2+} + 4\,H_2O(l)$
UO3_ALF	-1140.375 →	8.64	-		-	-	$\alpha\text{-}UO_3 + 2\,H^+ \Leftrightarrow UO_2^{2+} + H_2O(l)$
UO3_BETA	-1142.258 →	8.31	-		-	-	$\beta\text{-}UO_3 + 2\,H^+ \Leftrightarrow UO_2^{2+} + H_2O(l)$
UO3_GAMM	-1145.626 →	7.72	-		-	-	$\gamma\text{-}UO_3 + 2\,H^+ \Leftrightarrow UO_2^{2+} + H_2O(l)$
UO3_ALF_	-1374.577 →	5.00	-		-	-	$\alpha\text{-}UO_3\cdot0.9H_2O + 2\,H^+ \Leftrightarrow UO_2^{2+} + 1.9\,H_2O(l)$
UO3_2H2O	-1636.459 →	4.82	Schoepite	5.96 ± 0.18	188.54 ± 0.38	172.07 ± 0.34	$UO_3\cdot2H_2O + 2\,H^+ \Leftrightarrow UO_2^{2+} + 3\,H_2O(l)$
A_NA2UO4	-1679.149 →	47.58 (?)	-		-	-	$\alpha\text{-}Na_2UO_4 + 4\,H^+ \Leftrightarrow UO_2^{2+} + 2\,H_2O(l) + 2\,Na^+$
UF3CR	-1434.620 →	-19.90	-		-	-	$UF_3(cr) \Leftrightarrow U^{3+} + 3\,F^-$
UF4CR	-1823.581 →	-29.37	-		-	-	$UF_4(cr) \Leftrightarrow U^{4+} + 4\,F^-$
UF4_2.5A	-2440.347 →	-33.56	UF4:2.5H2O(cr)	-29.38 ± 0.19	263.5 ± 15.0	263.7 ± 15.0	$UF_4\cdot2.5H_2O(cr) \Leftrightarrow$ $U^{4+} + 4\,F^- + 2.5\,H_2O(l)$
A_UF5	-2440.282 →	-13.04	-		-	-	$UF_5(cr) + 2\,H_2O(l) \Leftrightarrow UO_2^+ + 4\,H^+ + 5\,F^-$
UF6_CRYS	-1968.772 →	17.31	-		-	-	$UF_6(cr) + 2\,H_2O(l) \Leftrightarrow UO_2^{2+} + 4\,H^+ + 6\,F^-$
UUF9	-3812.160 →	-45.88	-		-	-	$U_2F_9(cr) + 2\,H_2O(l) \Leftrightarrow U^{4+} + UO_2^+ + 4\,H^+ + 9\,F^-$
UU3F17	-7464.231 →	-105.48	-		-	-	$U_4F_{17}(cr) + 2\,H_2O(l) \Leftrightarrow 3\,U^{4+} + UO_2^+$ $+ 4\,H^+ + 17\,F^-$
UOF2CR	-1434.095 →	-18.23	-		-	-	$UOF_2(cr) + 2\,H^+ \Leftrightarrow U^{4+} + 2\,F^- + H_2O(l)$
UOF2_1AQ	-1674.489 →	-18.80	-		-	-	$UOF_2\cdot H_2O(cr) + 2\,H^+ \Leftrightarrow U^{4+} + 2\,F^- + 2\,H_2O(l)$
UOFOH	-1342.625 →	-9.98	-		-	-	$UOFOH(cr) + 3\,H^+ \Leftrightarrow U^{4+} + F^- + 2\,H_2O(l)$
UOFOH_0.	-1458.113 →	-9.44	-		-	-	$UOFOH\cdot0.5H_2O(cr) + 3\,H^+ \Leftrightarrow U^{4+} + F^-$ $+ 2.5\,H_2O(l)$

Table 5.23.1: continued

Name	$\Delta_f G_m°$	$\log_{10}K_{s,0}°$	Name	$\log_{10}K_{s,0}°$	$S_m°$	$C_{p,m}°$	Reaction
UOF4	-1816.319 →	4.41		-	-	-	$UOF_4(cr) + H_2O(l) \Leftrightarrow UO_2^{2+} + 4\ F^- + 2\ H^+$
U2O3F6	-3373.920 →	-2.95		-	-	-	$U_2O_3F_6(cr) + H_2O(l) \Leftrightarrow 2\ UO_2^{2+} + 6\ F^- + 2\ H^+$
U3O5F8	-4889.511 →	-2.95		-	-	-	$U_3O_8F_8(cr) + H_2O(l) \Leftrightarrow 3\ UO_2^{2+} + 8\ F^- + 2\ H^+$
ULF2CR	-1557.316 →	-7.31		-	-	-	$UO_2F_2(cr) \Leftrightarrow UO_2^{2+} + 2\ F^-$
ULF2_3A	-2269.706 →	-7.48		-	-	-	$UO_2F_2 \cdot 3H_2O(cr) \Leftrightarrow UO_2^{2+} + 2\ F^- + 3\ H_2O(l)$
ULFOH_1	-1721.650 →	-2.33		-	-	-	$UO_2FOH \cdot H_2O(cr) + H^+ \Leftrightarrow UO_2^{2+} + F^- + 2\ H_2O(l)$
ULFOH_2	-1960.959 →	-2.71		-	-	-	$UO_2FOH \cdot 2H_2O(cr) + H^+ \Leftrightarrow UO_2^{2+} + F^- + 3\ H_2O(l)$
UCL3CR	-800.268 →	12.24		-	-	-	$UCl_3(cr) \Leftrightarrow U^{3+} + 3\ Cl^-$
UCL4CR	-929.623 →	21.92		-	-	-	$UCl_4(cr) \Leftrightarrow U^{4+} + 4\ Cl^-$
UCL5CR	-949.800 →	33.82		-	-	-	$UCl_5(cr) + 2\ H_2O(l) \Leftrightarrow UO_2^+ + 4\ H^+ + 5\ Cl^-$
UCL6	-951.371 →	55.05		-	-	-	$UCl_6(cr) + 2\ H_2O(l) \Leftrightarrow UO_2^{2+} + 4\ H^+ + 6\ Cl^-$
UOCLCR	-787.126 →	10.11		-	-	-	$UOCl(cr) + 2\ H^+ \Leftrightarrow U^{3+} + Cl^- + H_2O(l)$
UOCL2CR	-996.106 →	5.84		-	-	-	$UOCl_2(cr) + 2\ H^+ \Leftrightarrow U^{4+} + 2\ Cl^- + H_2O(l)$
UOCL3	-1068.853 →	8.53		-	-	-	$UOCl_3(cr) + H_2O(l) \Leftrightarrow UO_2^+ + 2\ H^+ + 3\ Cl^-$
UO2CLCR	-1095.323 →	-0.54		-	-	-	$UO_2Cl(cr) \Leftrightarrow UO_2^+ + Cl^-$
ULCL2CR	-1145.811 →	12.12		-	-	-	$UO_2Cl_2(cr) \Leftrightarrow UO_2^{2+} + 2\ Cl^-$
ULCL2_1	-1404.984 →	8.26		-	-	-	$UO_2Cl_2 \cdot H_2O(cr) \Leftrightarrow UO_2^{2+} + 2\ Cl^- + H_2O(l)$
ULCL2_3	-1894.618 →	5.57		-	-	-	$UO_2Cl_2 \cdot 3H_2O(cr) \Leftrightarrow UO_2^{2+} + 2\ Cl^- + 3\ H_2O(l)$
ULUO2CL3	-2234.799 →	12.69		-	-	-	$(UO_2)_2Cl_3(cr) \Leftrightarrow UO_2^+ + UO_2^{2+} + 3\ Cl^-$
UUO2CL5	-2037.332 →	19.21		-	-	-	$U_2O_2Cl_5(cr) \Leftrightarrow U^{4+} + UO_2^+ + 5\ Cl^-$
U5O12CL	-5517.971 →	-18.81		-	-	-	$U_5O_{12}Cl(cr) \Leftrightarrow 5\ UO_2^+ + Cl^- + 2\ H_2O(l)$
ULCLOH_	-1782.177 →	2.28		-	-	-	$UO_2ClOH \cdot 2H_2O(cr) + H^+ \Leftrightarrow UO_2^{2+}$ $+ Cl^- + 3\ H_2O(l)$

Table 5.23.1: continued

Name	$\Delta_f G_m°$	$\log_{10}K_{s,0}°$	Name	$\log_{10}K_{s,0}°$	$S_m°$	$C_{p,m}°$	Reaction
UCL3F	-1146.648 →	10.23	-	-	-	-	$UCl_3F(cr) \Leftrightarrow U^{4+} + 3\ Cl^- + F^-$
UCL2F2	-1376.060 →	-3.63	-	-	-	-	$UCl_2F_2(cr) \Leftrightarrow U^{4+} + 2\ Cl^- + 2\ F^-$
UCLF3	-1606.442 →	-17.66	-	-	-	-	$UClF_3(cr) \Leftrightarrow U^{4+} + Cl^- + 3\ F^-$
USO42CR	-2084.471 →	-11.67	-	-	-	-	$U(SO_4)_2(cr) \Leftrightarrow U^{4+} + 2\ SO_4^{2-}$
USO42_4A	-3033.260 →	-11.71	-	-	-	-	$U(SO_4)_2\cdot4H_2O(cr) \Leftrightarrow U^{4+} + 2\ SO_4^{2-} + 4\ H_2O(l)$
USO42_8A	-3987.870 →	-12.77	-	-	-	-	$U(SO_4)_2\cdot8H_2O(cr) \Leftrightarrow U^{4+} + 2\ SO_4^{2-} + 8\ H_2O(l)$
UOH2SO4	-1766.234 →	-3.17	U(OH)2SO4(cr)	-3.17 ± 0.50			$U(OH)_2SO_4(cr) + 2\ H^+ \Leftrightarrow U^{4+} + SO_4^{2-} + 2\ H_2O(l)$
ULSO4CR	-1685.763 →	1.89	-	-	-	-	$UO_2SO_4(cr) \Leftrightarrow UO_2^{2+} + SO_4^{2-}$
ULSO4_25	-2298.477 →	-1.59	-	-	-	-	$UO_2SO_4\cdot2.5H_2O(cr) \Leftrightarrow UO_2^{2+} + SO_4^{2-} + 2.5\ H_2O(l)$
ULSO4_3	-2416.533 →	-1.50	-	-	-	-	$UO_2SO_4\cdot3H_2O(cr) \Leftrightarrow UO_2^{2+} + SO_4^{2-} + 3\ H_2O(l)$
ULSO4_35	-2535.559 →	-1.58	-	-	-	-	$UO_2SO_4\cdot3.5H_2O(cr) \Leftrightarrow UO_2^{2+} + SO_4^{2-} + 3.5\ H_2O(l)$
ULNO32CR	-1106.036 →	11.93	-	-	-	-	$UO_2(NO_3)_2(cr) \Leftrightarrow UO_2^{2+} + 2\ NO_3^-$
ULNO32_H	-1362.925 →	8.47	-	-	-	-	$UO_2(NO_3)_2\cdot H_2O(cr) \Leftrightarrow UO_2^{2+} + 2\ NO_3^- + H_2O(l)$
ULNO322H	-1620.442 →	4.90	-	-	-	-	$UO_2(NO_3)_2\cdot2H_2O(cr) \Leftrightarrow UO_2^{2+} + 2\ NO_3^- + 2\ H_2O(l)$
ULNO323H	-1864.603 →	3.67	-	-	-	-	$UO_2(NO_3)_2\cdot3H_2O(cr) \Leftrightarrow UO_2^{2+} + 2\ NO_3^- + 3\ H_2O(l)$
ULNO326H	-2584.128 →	2.25	-	-	-	-	$UO_2(NO_3)_2\cdot6H_2O(cr) \Leftrightarrow UO_2^{2+} + 2\ NO_3^- + 6\ H_2O(l)$
ULCO3CR		-14.44	Rutherfordine	-14.49 ± 0.04	144.2 ± 0.31	20.1 ± 0.1	$UO_2CO_3(cr) \Leftrightarrow UO_2^{2+} + CO_3^{2-}$
UH2P424H	-3844.648 →	-11.83	-	-	-	-	$U(HPO_4)_2\cdot4H_2O(cr) + 4\ H^+ \Leftrightarrow U^{4+} + 2\ H_3PO_4(aq) + 4\ H_2O(l)$
UL3P42CR	-5116.058 →	7.06	-	-	-	-	$(UO_2)_3(PO_4)_2(cr) + 6\ H^+ \Leftrightarrow 3\ UO_2^{2+} + 2\ H_3PO_4(aq)$

Table 5.23.1: continued.

Name	$\Delta_f G_m°$	$\log_{10} K_{s,0}°$	Name	$\log_{10} K_{s,0}°$	$S_m°$	$C_{p,m}°$	Reaction
UL3P424H	-6138.992 → -5.97		(UO2)3(PO4)2:4H2O(cr)	-5.96 ± 0.30			$(UO_2)_3(PO_4)_2 \cdot 4H_2O(cr) + 6H^+ \Leftrightarrow$ $3UO_2^{2+} + 2H_3PO_4(aq) + 4H_2O(l)$
UL3P426H	-6618.067 → -6.81			-	-	-	$(UO_2)_3(PO_4)_2 \cdot 6H_2O(cr) + 6H^+ \Leftrightarrow$ $3UO_2^{2+} + 2H_3PO_4(aq) + 6H_2O(l)$
ULHPO4_	-3064.789 → -2.51		Chernikovite	-2.50 ± 0.09			$UO_2HPO_4 \cdot 4H_2O(cr) + 2H^+ \Leftrightarrow$ $UO_2^{2+} + H_3PO_4(aq) + 4H_2O(l)$
USIO4	-1882.288 → -7.83		USiO4(s)	***1856.1 ±11.4*** $(\Delta_f G_m°)$			$USiO_4(s) + 4H+ \Leftrightarrow U^{4+} + Si(OH)_4(aq)$

5.23.10 References

BERNER, U. (1995): Kristallin-I: Estimates of Solubility Limits for Safety Relevant Radionuclides. PSI-Bericht Nr. 95-07, Paul Scherrer Institute, Villigen, Switzerland, 58p.

BRUNO, J., CASAS, I., LAGERMANN, B., MUÑOZ, M. (1987): The determination of the solubility of amorphous $UO_2(s)$ and the mononuclear hydrolysis constants of uranium(IV) at 25°C. Mat. Res. Soc. Symp. Proc., 84, 153-160.

BRUNO, J., FERRI, D., GRENTHE, I., SALVATORE, F. (1986): Studies on metal carbonate equilibria: 13. On the solubility of uranium(IV) dioxide, $UO_2(s)$. Acta Chem. Scand., 40, 428-434.

CHOPPIN, G.R., MATHUR, J.N. (1991): Hydrolysis of actinyl(VI) cations. Radiochim. Acta, 53/54, 25-28.

GRENTHE, I., FUGER, J., KONINGS, R.J.M., LEMIRE, R.J., MULLER, A.B., NGUYEN-TRUNG, C., WANNER, H. (1992): Chemical Thermodynamics of Uranium. Elsevier, Amsterdam, 715p.

GRENTHE, I., PUIGDOMÈNECH, I., SANDINO, M.C.A., RAND, M.H. (1995): Corrections to the Uranium NEA-TDB review. In: SILVA, R.J., BIDOGLIO, G., RAND, M.H., ROBOUCH, P.B., WANNER, H., PUIGDOMÈNECH, I.: Chemical Thermodynamics of Americium, Elsevier, Amsterdam, Appendix D, 347-374.

GUNNARSSON, I. AND ARNORSSON, S. (2000): Amorphous silica solubility and the thermodynamic properties of $H_4SiO_4°$ in the range of 0° to 350°C at P_{sat}. Geochim. Cosmochim. Acta, 64, 2295-2307.

HOVEY, J.K. (1997): Thermodynamics of Hydration of a 4+ Aqueous Ion: Partial Molar Heat Capacities and Volumes of aqueous Thorium(IV) from 10 to 55°C. The Journal of Physical Chemistry B, 101, 4321-4334.

LANGMUIR, D. (1978): Uranium solution–mineral equilibria at low temperatures with applications to sedimentary ore deposits. Geochim. Cosmochim. Acta, 42, 547-569.

MINERAL DATABASE (1997), Version 97.2 - December 1997, Aleph Enterprises, P.O. Box 213, Livermore, CA 94551-0213, USA.

MUSIKAS, C. (1972): Formation d'uranates solubles par hydrolyse des ions uranyle(VI). Radiochem. Radioanal. Letters, 11, 307-316, in French.

NIKITIN, A.A., SERGEYEVA, E.I., KHODAKOVSKY, I.L., NAUMOV, G.B. (1972): Hydrolysis of uranyl in the hydrothermal region. Geokhimiya, 3, 297-307, in Russian.

PARKS, G.A., POHL, D.C. (1988): Hydrothermal solubility of uraninite. Geochim. Cosmochim. Acta, 52, 863-875.

PASHALIDIS, I., KIM, J.I., ASHIDA, T., GRENTHE, I. (1995): Spectroscopic study of the hydrolysis of PuO_2^{2+} in aqueous solution. Radiochim. Acta, 68, 99-104.

RAI, D., FELMY, A.R., HESS, N.J., MOORE, D.A., YUI, M. (1998): A thermodynamic model for the solubility of $UO_2(am)$ in the aqueous K^+-Na^+-HCO_3^--CO_3^{2-}-OH^--H_2O system. Radiochim. Acta, 82, 17-25.

RAI, D., FELMY, A.R., RYAN, J.L. (1990): Uranium(IV) hydrolysis constants and solubility product of $UO_2 \cdot xH_2O(am)$. Inorg. Chem., 29, 7852-7865.

RAI, D., FELMY, A.R., STERNER, S.M., MOORE, D.A., MASON, M.J., NOVAK, C.F. (1997): The solubility of Th(IV) and U(IV) hydrous oxides in concentrated NaCl and $MgCl_2$ solutions. Radiochim. Acta, 79, 239-247.

RIMSTIDT, J. D. (1997): Quartz solubility at low temperatures. Geochim. Cosmochim. Acta, 61, 2553-2558.

ROBINSON, R.A., STOKES, R.H. (1959): Electrolyte solutions. London, Butterworths, 2nd ed., 559p.

RYAN, J.L., RAI, D. (1983): The solubility of uranium(IV) hydrous oxide in in sodium hydroxide solutions under reducing conditions. Polyhedron, 2, 947-952.

SANDINO, M.C.A. (1991): Processes affecting the mobility of uranium in natural waters. Ph.D. thesis in inorganic chemistry, The Royal Institute of Technology, Stockholm, Sweden.

YAJIMA, T., KAWAMURA, Y., UETA, S. (1995): Uranium(IV) solubility and hydrolysis constants under reduced conditions. Mat. Res. Soc. Symp. Proc., 353, 1137-1142.

YAMAMURA, T., KITAMURA, A., FUKUI, A., NISHIKAWA, S., YAMAMOTO, T., MORIYAMA, H. (1998): Solubility of U(VI) in Highly Basic Solutions. Radiochimica Acta, 83, 139-146.

5.24   Zirconium

5.24.1   Introduction

In this chapter, thermodynamic data for Zr to be included in the Nagra/PSI TDB 01/01 are selected and discussed. Symbols and notation follow the guidelines given by GRENTHE & PUIGDOMENECH (1997). Through the report, uncertainties of composite quantities have been determined using conventional error propagation formulas (see BEVINGTON 1969, chapter 4). All selected data are summarised in Table 5.24.8.

In the previous version, the Nagra TDB 05/92, Zr data were taken over from the HATCHES 3.0 database without any detailed proofing (PEARSON et al. 1992, p.21) and need therefore to be re-evaluated. Unfortunately, in the CODATA compilation (COX et al. 1989) no thermodynamic data for Zr are given.

Because Zr thermodynamic data are currently being evaluated by an NEA review team, only a limited effort has been made for the present update. The major aim is (besides correcting constants which are clearly wrong and eliminating unreliable species) to derive equilibrium constants at zero ionic strength using the SIT formalism, based on conditional constants selected from the IUPAC database (IUPAC 1997). This procedure is not without risk, since the original data are not analysed in detail. However, in those cases where a sufficient number of independent studies over a wide range of ionic strengths exists, this approach proved to be successful. For the chloride and fluoride complexes and for Zr monosulphate this procedure yielded consistent results. Zirconium also forms strong carbonate and phosphate complexes, but the available data are insufficient to derive reliable formation constants.

A notable exception to the approach described above concerns hydrolysis equilibria, which are critical for any Zr aqueous speciation model. In this case, published data have been analysed in detail and recent solubility measurements of monoclinic ZrO_2, obtained at PSI, were integrated. These data are essential as they refer to an intermediate pH region where the solubility of this phase is low, while all constants given in the literature are based on measurements in strongly acidic or strongly alkaline solutions. We could ascertain that all acceptable experimental data on the solubility of monoclinic ZrO_2, including those obtained at intermediate pH, can be reproduced satisfactorily using the constants recommended by BAES & MESMER (1976).

5.24.2   Elemental zirconium

Metallic zirconium is important in nuclear reactor technology, but it is not relevant in environmental systems. The absolute entropy of Zr(cr) is given in Table 5.24.8 for reference state definition purposes (S_m^o = 39.0 J mol^{-1} K^{-1} , taken from WAGMAN et al. 1982). Zr as a gas phase plays no role in environmental systems and is not included in the database.

5.24.3   Free zirconium aqua ions

Under environmental conditions, zirconium always occurs in the oxidation state +IV. Due to its high charge, small size (ionic radius = 0.72 Å in octahedral coordination) and hard metal character, Zr^{4+} is hydrolysed already at pH=0, which means that the Zr^{4+} free aqua ion does not exist in natural environments.

The former view that the free aqueous species is the zirconyl ion (ZrO^{2+}) has now been abandoned. Evidence comes from the stoichiometry of basic Zr chlorides (SOLOVKIN & TSVETKOVA 1962). The formation of Zr hydroxo trichloride, $Zr(OH)Cl_3 \cdot n\ H_2O$, for instance, cannot be explained assuming that it contains the zirconyl ion. BAES & MESMER (1976) also cite crystallographic investigations which disprove the existence of zirconyl ions in various solids.

State function data given in the Nagra TDB 05/92 are:

$\Delta_f G_m^0$ (Zr^{4+}, aq, 298.15 K) = -524.5 kJ mol^{-1},

$\Delta_f H_m^0$ (Zr^{4+}, aq, 298.15 K) = 0 kJ mol^{-1}

Since CODATA gives no data for Zr, we calculated the properties of the free aqua ions as described below.

(a) From standard potential data (BARD et al. 1985):

$$\Delta_f G_m^0\ (Zr^{4+},\ aq,\ 298.15\ K) = E^0_{(red)}\ F\ n =$$

$$= \text{-1.55 V eq. x 96.4935 kJ (V eq.)}^{-1}\ x\ 4 = \text{-598.0 kJ mol}^{-1}.$$

It is important to note that the potential of -1.55 V given above is not the result of e.m.f. measurements but follows from thermodynamic calculations. Since Zr^{4+} hydrolyses even in concentrated acid solutions it is not possible to measure directly the standard potential of the reduction to metallic Zr:

$$Zr^{4+}(aq) + 4e^- = Zr(cr).$$
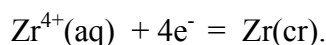
BARD et al. (1985) calculated the value of -1.55 V for the above half-cell from slightly adjusted thermodynamic data reported by LATIMER (1952) for the reaction:

$$Zr(OH)_4(cr) + 4H^+ = Zr^{4+}(aq) + 4\ H_2O\ (l).$$
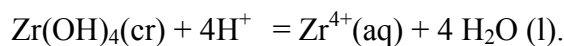
In their calculation, $\Delta_f G_m^o = -1550$ kJ mol^{-1} was assumed for $Zr(OH)_4(cr)$, a value now dismissed from compilations of thermodynamic data. In addition, a rough estimation of the solubility product ($K^0_s = 0.06$) was necessary to calculate the free energy of the reaction. The estimate is based on the assumption (LATIMER 1952, p.271) that Zr^{4+} is present as free cationic species in acid solutions and must therefore be rejected based on current knowledge.

The free energy determined from these data for $Zr^{4+}(aq)$ (-598.0 kJ mol^{-1}) is not acceptable, as it would lead to $\log_{10}*K^0_{s,0} = 5.2$ and thus to solubilities exceeding by several orders of magnitude the Zr concentrations measured in equilibrium with Zr oxides. For instance, a Zr equilibrium concentration exceeding 1 M would be predicted at pH 2, while measurements indicate concentrations between 10^{-5} and 10^{-4} M at that pH.

(b)   <u>From the solubility product of monoclinic zirconia selected for the TDB update</u> (see section 5.24.4.3) and $\Delta_f G_m^0(ZrO_2, cr) = -1042.79$ kJ mol^{-1} (WAGMAN et al. 1982):

$$ZrO_2\ (cr) + 4\ H^+ = Zr^{4+} + 2\ H_2O$$
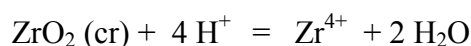
$$\Delta_f G_m^0\ {}_{(Zr^{4+},\ aq,\ 298.15\ K)} = \Delta_r G_m^0 - 2\ \Delta_f G_m^0(H_2O,l) + 4\ \Delta_f G_m^0(H^+,aq) + \Delta_f G_m^0\ (ZrO_2, cr) =$$

$$= -RT \ln *K^0_{s,0} - 2\ \Delta_f G_m^0(H_2O,l) + \Delta_f G_m^0\ (ZrO_2, cr) =$$

$$= -0.0083147 \times 298.15 \times \ln 10 \times (-1.9 \pm 0.5) - 2 \times (-237.1) + (-1042.79 \pm 10.4) =$$

$$= -557.7 \pm 10.8\ kJ\ mol^{-1}$$

Estimated uncertainties of half $\log_{10}$-unit (± 0.5) for $\log_{10}*K^0_{s,0} = -1.9$ and $\pm 1\%$ for $\Delta_f G_m^0(ZrO_2, cr)$ have been assumed to evaluate the uncertainty of $\Delta_f G_m^0\ (Zr^{4+}, aq, 298.15\ K)$. The latter value (-557.7 $\pm$ 10.8 kJ mol^{-1}), derived using the solubility product for crystalline ZrO_2 selected for the present update, is included in the database. Note that the selected free energy for Zr^{4+} is about 30 kJ mol^{-1} lower than the value given in the old database.

Since no entropy data are available for Zr^{4+}, aq, we used $S_m^0\ (Ce^{4+}, aq) = -301$ J K^{-1} mol^{-1} from WAGMAN et al. (1982) to obtain an estimated value of -300 $\pm$ 130 JK^{-1}mol^{-1} for $S_m^0\ (Zr^{4+}, aq)$. The

large uncertainty arises from considering the variations in the entropies of tetravalent actinides: Th^{4+} = -425.6, Pu^{4+} = -414.15, U^{4+} = -416.9 JK^{-1}mol^{-1} in the present update. Using the entropies of WAGMAN et al. (1982), the CODATA value for the molar entropy of hydrogen gas and the estimated value for S_m^0 (Zr^{4+}, aq) given above one obtains:

$$\Delta_f S_m^0{}_{(Zr^{4+}, aq)} = S_m^0{}_{(Zr^{4+}, aq)} + 2\ S_m^0{}_{(H_2, g)} - 4\ S_m^0{}_{(H^+, aq)} - S_m^0{}_{(Zr, cr)} =$$

$$\Delta_f S_m^0{}_{(Zr^{4+}, aq)} = -300\ (\pm 130) + 2 \times 130.68 - 4 \times 0 - 39.0 = -78 \pm 130\ \ JK^{-1}\ mol^{-1}$$

The following formation enthalpy is then obtained for the aqueous Zr^{4+} ion:

$$\Delta_f H_m^0{}_{(Zr^{4+}, aq)} = \Delta_f G_m^0{}_{(Zr^{4+}, aq)} + T^0\ \Delta_f S_m^0{}_{(Zr^{4+}, aq)} = -557.7 \pm 10.5\ + 298.15 \times (-0.078 \pm 0.13)$$

$$\Delta_f H_m^0{}_{(Zr^{4+}, aq)} = -581.0\ \pm\ 40.2\ \ kJ\ mol^{-1}$$

These values for $\Delta_f S_m^0$ (Zr^{4+}, aq) and $\Delta_f H_m^0$ (Zr^{4+}, aq) are proposed as rough estimates of these properties to enable calculations at temperatures other than 25 °C; they are however <u>not included</u> in the database update.

5.24.4 Oxygen and hydrogen compounds

5.24.4.1 Preliminary remarks

Hydrolysis of Zr starts already between pH 0 and 1 (JOLIVET 1994, p.98), so that solutions must be stored in 10 M HCl to guarantee the stability of monomeric species (SOLOVKIN & TSVETKOVA 1962).

The strong tendency to the formation of polymeric species and colloids complicates considerably hydrolysis studies of Zr (BAES & MESMER 1976). Other complicating factors are the unpredictable stoichiometry and the slow ageing of freshly precipitated hydrolysis products. According to JOLIVET (1994), p. 99-102, pure Zr hydroxide with formula $Zr(OH)_4$ is never stable, due to the strong polarisation of the OH-groups when coordinated to the highly charged Zr^{4+}. The first precipitate is an oxy-hydroxide with the generic formula $ZrO_{2-x}OH_{2x} \cdot y\ H_2O$, which is transformed upon ageing into monoclinic ZrO_2. Amorphous ZrO_2 apparently forms at pH 4-5 through condensation of the tetrameric species.

5.24.4.2 Analysis of hydrolysis data

Table 5.24.1 summarises thermodynamic constants for hydrolysis reactions from two sources: BAES & MESMER (1976) and BILINSKI et al. (1966). The two sets of constants show large discrepancies. In particular, the solubility product given for "$Zr(OH)_4$" by the data of BILINSKI et al. (1966) is 6-7 orders of magnitude higher than that for ZrO_2 proposed by BAES & MESMER (1976).

The solubility data of BILINSKI et al. (1966) refer to hydrolysis products separated from oversaturated solutions in the pH range 1.5 to 6.5. The experiments involved detection of the colloid precipitation by optical measurement of the solution turbidity (tindallometry). As mentioned in the previous section, such fresh precipitates derive from the condensation of dissolved polymers and are highly active. They are slowly transformed into crystalline anhydrous oxide through olation and oxolation, i.e. the removal of protons and hydroxo groups, respectively, from coordinating water molecules (JOLIVET 1994). The stable end-product is a monoclinic anhydrous oxide: monoclinic zirconia or *baddeleyite* as a mineral (see CURTI & HUMMEL 1999).

In contrast, the solubility product specified by BAES & MESMER (1976) refers to crystalline ZrO_2. Although determined with the help of calorimetric data (unfortunately it is not possible to reconstruct the detailed method of calculation), this solubility product yields results in good agreement with solubilities measured from undersaturation experiments (i.e. all data in Fig. 5.24.1 except those of BILINSKI et al. 1966).

The data of KOVALENKO & BAGDASAROV (1961) show a slight offset from the calculated solubility curve, which can be presumably explained by the short ageing time (24 hours) of the solid phase used in their dissolution experiments. In contrast, SHEKA & PEZVNER (1960) used a precipitate aged for 45 days (at 30-40 ^{o}C) for their solubility measurements in 1 to 10 M NaOH. The agreement between the data of SHEKA & PEZVNER (1960) and our model calculations is a logical consequence of the fact that these data were selected by BAES & MESMER (1976) to define the hydrolysis model adopted here. Nonetheless, it also indicates that our extrapolation procedure, performed using the SIT formalism, is equivalent to that applied by Baes & Mesmer (1976). It is also remarkable that our SIT correction well reproduces the curvature of Sheka and Pezvner's data, barely visible in Fig. 5.24.1.

Indications of the existence of the pentahydroxo complex rely exclusively on the data of SHEKA & PEZVNER (1960) and ADAIR et al. (1987). The experimental procedures used to obtain both datasets are unfortunately not well documented and can therefore be questioned, particularly regarding the possible contribution of carbonate complexes. Although the former investigators explicitly state to have taken precautions against CO_2 contamination, they do not specify which kind of precautions

they took. The experiments of ADAIR et al. (1987) were performed in air, so that CO_2 absorption by the solutions certainly occurred. However, even allowing equilibrium with the atmospheric CO_2, the very high hydroxide concentrations involved (above 1 M) should have prevented any carbonate complex to become predominant over $Zr(OH)_5^-$.

To complicate things, the experiments performed by KULMALA & HAKANEN (1993) (not included in Fig. 5.24.1) indicate very low Zr equilibrium concentrations at alkaline pH. In a first set of experiments, equilibrium was approached from oversaturation by mixing 0.1 M $ZrOCl_2$ and NaOH solutions. This yielded Zr concentrations between 3×10^{-8} and 5×10^{-7} M after 1-2 months equilibration time at pH ~ 13. In a second set of experiments, equilibrium was approached from undersaturation, by dissolving ZrO_2 in cement water (a Na-Ca-K-OH-SO$_4$-CO$_3$ brine). In this case, equilibrium concentration at pH ~ 13 were under the detection limit (2×10^{-9} M) and at least one order of magnitude lower than for analogous experiments conducted in a Na-Ca-Cl-SO$_4$ groundwater at pH ~ 8.5.

The results of these experiments cannot be included in our analysis of ZrO_2 solubility because of the many additional chemical components involved. We suspect that these data are related to the precipitation or dissolution of solids with complex composition, not of pure Zr oxy-hydroxides. It is for instance well-known that Zr forms oxychlorides with compositions varying from $ZrOCl_2.nH_2O$ through $ZrOHCl_2.nH_2O$ (SOLOVKIN & TSVETKOVA 1962). The solubility of such phases will decrease with increasing pH. Moreover, basic Zr carbonates readily precipitate upon mixing acid $ZrOCl_2$ and alkali carbonate solutions (MIKHAILOV & GRIGOR'EVA 1961).

In summary, we conclude that although the available data support the existence of the pentahydroxo complex, the question cannot be regarded as resolved. Further experiments under carefully controlled conditions are definitely needed.

Additional experimental data were considered for our analysis. The data reported in Fig. 5.24.1 from ADAIR et al. (1987) and POUCHON et al. (2001) refer both to experiments carried out from undersaturation with pure monoclinic zirconia and prove to be roughly consistent with the solubility curve predicted using the constants proposed by BAES & MESMER (1976). The study of POUCHON et al. (2001) is particularly important as it is (to the author's knowledge) the only one providing zirconia solubility data in an intermediate pH region relevant for environmental studies. The measurements should be trusted as they were obtained after equilibration times of 250 days through careful ICP-MS measurements, lying clearly above blank concentrations.

A striking feature of the analysed data is that, as far as equilibrium is approached from undersaturation, crystalline and fresh precipitates yield similar solubilities. In contrast, approaching

equilibrium from oversaturated solutions, as done by BILINSKI et al. (1966), leads to much higher Zr concentrations. This is a strong indication for the formation of polymers and colloidal suspensions. Such Zr solutions equilibrate very slowly and are quasi-metastable. As pointed out by SOLOVKIN & TSVETKOVA (1962) (p. 658) depolymerisation in acidic Zr solutions is strongly hindered and thus exceedingly slow. Equilibration times of only 24 hours were used by BILINSKI et al. (1966).
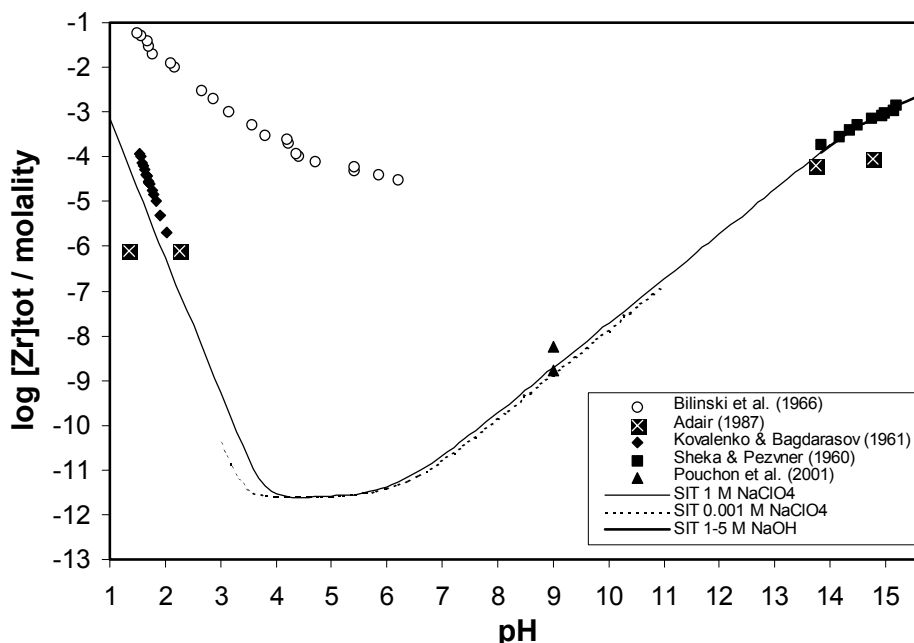
Fig. 5.24.1:   Solubility data for Zr oxides and hydrous oxides compared with predictions based on the hydrolysis constants selected by BAES & MESMER (1976). The data of BILINSKI et al. (1966) were obtained from strongly oversaturated solutions while all other data stem from equilibria reached from undersaturation.

5.24.4.3 Aqueous hydroxide complexes and solid oxy-hydroxides: data selection

Based on the discussion above, and considering that Zr equilibrium concentrations in natural aqueous solutions are always approached from undersaturation, the constants of BILINSKI et al. (1966) must be rejected and will therefore not be included in the database.

We also rejected the hydrolysis constants given in the recent review of AJA et al. (1995), according to which the solubility of monoclinic ZrO_2 would approach or even exceed the mM range at neutral pH (cf. Fig. 7 in cited reference). Such unreasonably high solubilities arise from a largely overestimated formation constant for $Zr(OH)_4(aq)$. A closer look to the numbers given by these authors reveals that the erroneous constant arises from a mistake in the manipulation of the original

literature data. In their Table 1, AJA et al. (1995) list for instance $\log_{10}\beta_4 = 52.0$ in 1.0 m $NaClO_4$ and refer this constant to "BILINSKI et al. (1961)". In their reference list, however, only the work of BILINSKI et al. (1966), also cited in the present report, is listed, from which we conclude that the considered constant was derived from the data given in the latter reference. BILINSKI et al. (1966) give, for the specified medium, the following conditional constants (see Table 2 in cited reference):

$\log_{10}{}^{*}K_{s,0} \cong 3.8$ $\qquad\qquad$ $Zr(OH)_4(s) + 4\ H^+ \Leftrightarrow Zr^{4+} + 4\ H_2O$

$\log_{10}K_{s,4} = -4.36$ $\qquad\qquad$ $Zr(OH)_4(s) \Leftrightarrow Zr(OH)_4(aq)$

$\log_{10}K_w = -13.94$ $\qquad\qquad$ $H_2O \Leftrightarrow H^+ + OH^-$
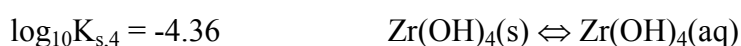
A linear combination of the above equilibria yields the required formation constant: $\log_{10}\beta_4 = \log_{10}K_{s,4} - \log_{10}{}^{*}K_{s,0} - 4\ \log_{10}K_w = 47.6$. The value of 52.0 given by AJA et al. (1995) differs from our result by exactly 4.4, suggesting that these authors forgot to add the $\log_{10}K_{s,4}$ term in the preceding calculation. This omission, combined with the adoption of Bilinski et al.'s solubility product (which is $\sim 5\ \log_{10}$ units higher than the value adopted here) leads to the huge discrepancy ($\sim 9\ \log_{10}$ units!) to the minimum Zr oxide solubility calculated using Baes and Mesmer's dataset.

In conclusion, the constants proposed by BAES & MESMER (1976) seem to be the most appropriate as they lead to results in reasonable agreement with all available solubility data obtained from undersaturation. They were thus selected for our database update (Table 5.24.1).

Note that the three hydroxo complexes $Zr(OH)^{3+}$, $Zr(OH)_4(aq)$ and $Zr(OH)_5^-$ are fully sufficient to reproduce all the selected solubility data. We decided to exclude from our database update the constants for the polymeric species $Zr_3(OH)_4^{8+}$ and $Zr_4(OH)_8^{8+}$, which had been included in the previous version, because these data are not well assessed and polymerisation of Zr species does not play a role in natural aqueous solutions.

As unique limiting solid we selected the monoclinic form of crystalline Zr oxide, which is demonstrably the stable form in low temperature aqueous systems (LUMPKIN 1999). The cubic form is stable only at very high temperatures (many hundreds degrees) and poorly aged hydrolysis products are invariably converted to monoclinic zirconia in aqueous solutions.

Table 5.24.1: Compilation of hydrolysis constants for Zr. The data in bold, selected by BAES & MESMER (1976) were included in the database update. The constants of BILINSKI et al. (1966) are conditional constants obtained in dilute solutions at 20 $^\circ$C .

Reaction	constant	BAES & MESMER (1976)	BILINSKI et al. (1966) [†]
$Zr^{4+} + H_2O \Leftrightarrow Zr(OH)^{3+} + H^+$	$\log_{10}*\beta^0_1$	**0.3**	-
$Zr^{4+} + 2\,H_2O \Leftrightarrow Zr(OH)_2^{2+} + 2\,H^+$	$\log_{10}*\beta^0_2$	-	-2.77
$Zr^{4+} + 3\,H_2O \Leftrightarrow Zr(OH)_3^+ + 3\,H^+$	$\log_{10}*\beta^0_3$	-	-4.33
$Zr^{4+} + 4\,H_2O \Leftrightarrow Zr(OH)_4\,(aq) + 4\,H^+$	$\log_{10}*\beta^0_4$	**-9.7**	-8.5
$Zr^{4+} + 5\,H_2O \Leftrightarrow Zr(OH)_5^- + 5\,H^+$	$\log_{10}*\beta^0_5$	**-16.0**	-
$Zr(OH)_4\,(s) + 4\,H^+ \Leftrightarrow Zr^{4+} + 4\,H_2O$	$\log_{10}*K^0_{s,0}$	-	4.6
$ZrO_2\,(s) + 4\,H^+ \Leftrightarrow Zr^{4+} + 2\,H_2O$	$\log_{10}*K^0_{s,0}$	**-1.9**	-

[†] the constants for the hydroxo complexes were calculated by combining appropriately the equilibrium constants given in the original reference.

5.24.5 Halogen compounds and complexes

5.24.5.1 Fluoride complexes and solids

Zr forms very stable complexes with F^-. The IUPAC database reports thermodynamic data from several experimental studies (mainly EMF and ISE measurements, see Table 5.24.2). Constants have been determined experimentally for mononuclear complexes up to a ligand number of 6. All the constants given in the literature are expressed using HF(aq) as reaction partner:

$$ZrF_{n-1}^{5-n} + HF(aq) \Leftrightarrow ZrF_n^{4-n} + H^+, \qquad \log_{10}*K_n$$

This may indicate that the studies were conducted at pH values below $pK_a(HF) = 3.18$, where hydrofluoric acid does not dissociate significantly. We extrapolated to zero ionic strength the conditional $\log_{10}*K_n$ values given in the IUPAC database using the SIT formalism (Figs. 5.24.2a and 5.24.2b). The resulting $\log_{10}*K^0_n$ were then converted to $\log_{10}\beta^0_n$ values (Table 5.24.3) by combining with the auxiliary equilibrium:

$$HF(aq) \Leftrightarrow H^+ + F^- \quad (pK_a = 3.18 \pm 0.02, \text{ see GRENTHE et al. 1992, p. 366}).$$
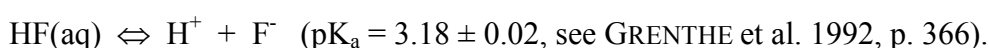
In spite of the many investigations on Zr fluoride complexes, the conditional constants were measured at two, in the best case at three ionic strengths, which is not favourable for computing

SIT linear regressions. Fortunately, in many cases measurements were redundant (several constant determinations at the same ionic strength by different methods) so that constructing a regression through only two ionic strengths has been considered acceptable.

Table 5.24.2: Conditional formation constants of Zr-fluoride complexes considered for SIT extrapolation (medium: $HClO_4$ or $HClO_4 / NaClO_4$ mixtures, $T = 20$ or 25 ^{o}C).

Reaction	Method	I(M)	Conditional constant	References
$Zr^{4+} + HF \Leftrightarrow ZrF^{3+} + H^+$	Solv Extr	2.0	$\log_{10}{}^*K_1 = 5.80$	CONNICK & MCVEY (1949)
	Ion Exch	2.0	$\log_{10}{}^*K_1 = 5.81$	KRYLOV et al. (1969)
	Ion Exch	4.0	$\log_{10}{}^*K_1 = 5.96$	AHRLAND et al. (1963)
	Solv Extr	4.0	$\log_{10}{}^*K_1 = 5.88$	NOREN (1969)
	ISE	4.0	$\log_{10}{}^*K_1 = 5.97$	NOREN (1973)
$ZrF^{3+} + HF \Leftrightarrow ZrF_2^{2+} + H^+$	Solv Extr	2.0	$\log_{10}{}^*K_2 = 4.32$	CONNICK & MCVEY (1949)
	EMF	4.0	$\log_{10}{}^*K_2 = 4.42$	NOREN (1967)
	Solv Extr	4.0	$\log_{10}{}^*K_2 = 4.36$	NOREN (1969)
	ISE	4.0	$\log_{10}{}^*K_2 = 4.4$	NOREN (1973)
$ZrF_2^{2+} + HF \Leftrightarrow ZrF_3^+ + H^+$	Conduct.	0.5	$\log_{10}{}^*K_3 = 2.7$	BUSLAEV (1962)
	Solv Extr	2.0	$\log_{10}{}^*K_3 = 2.83$	CONNICK & MCVEY (1949)
	EMF	4.0	$\log_{10}{}^*K_3 = 3.0$	NOREN (1967)
	Solv Extr	4.0	$\log_{10}{}^*K_3 = 3.0$	NOREN (1969)
$ZrF_3^+ + HF \Leftrightarrow ZrF_4(aq) + H^+$	Conduct.	0.5	$\log_{10}{}^*K_4 = 1.83$	BUSLAEV (1962)
	EMF	1.0	$\log_{10}{}^*K_4 = 2.8$	BUKHSH et al. (1966)
	EMF	4.0	$\log_{10}{}^*K_4 = 2.28$	NOREN (1967)
	Solv Extr	4.0	$\log_{10}{}^*K_4 = 2.3$	NOREN (1969)
$ZrF_4(aq) + HF \Leftrightarrow ZrF_5^- + H^+$	Conduct.	0.5	$\log_{10}{}^*K_5 = 1.51$	BUSLAEV (1962)
	EMF	1.0	$\log_{10}{}^*K_5 = 1.9$	BUKHSH et al. (1966)
	EMF	4.0	$\log_{10}{}^*K_5 = 1.53$	NOREN (1967)
$ZrF_5^- + HF \Leftrightarrow ZrF_6^{-2} + H^+$	Conduct.	0.5	$\log_{10}{}^*K_6 = 0.86$	BUSLAEV (1962)
	EMF	1.0	$\log_{10}{}^*K_6 = 1.35$	BUKHSH et al. (1966)
	EMF	4.0	$\log_{10}{}^*K_6 = 0.3$	NOREN (1967)
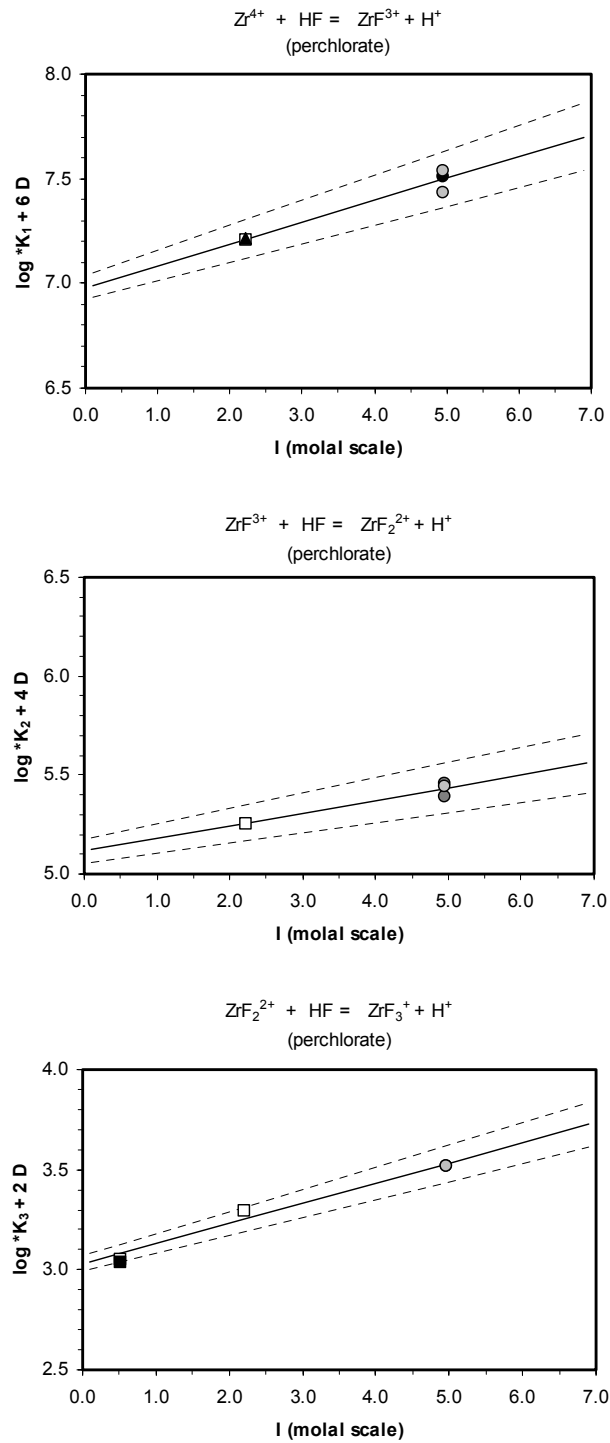
Fig. 5.24.2a: SIT plots for the determination of constants for ZrF^{3+}, ZrF_2^{2+}, ZrF_3^+ at $I = 0$.
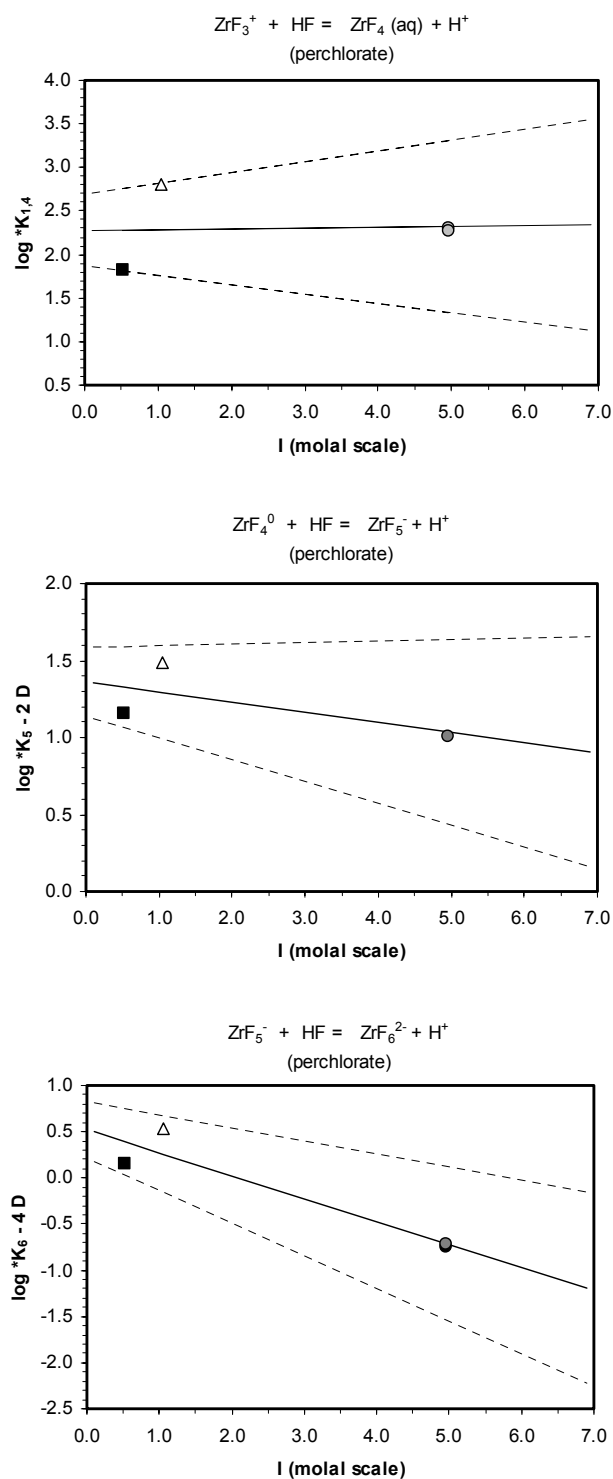
Fig. 5.24.2b: SIT plots for the determination of constants for $ZrF_4(aq)$, ZrF_5^-, ZrF_6^{2-} at $I = 0$.

Table 5.24.3 Formation constants of Zr fluoride complexes, extrapolated to zero ionic strength using the SIT formalism. Uncertainties (± 1σ) have been determined from the standard deviations of the unweighted regressions (Figs. 5.24.2a and 5.24.2b) using the error propagation formula given by BEVINGTON (1969).

Reaction	n	$\log_{10}\beta^0_n$	$\log_{10}K^0_n$
$Zr^{4+} + \; F^- \Leftrightarrow ZrF^{3+}$	1	10.2 ± 0.1	10.2 ± 0.1
$Zr^{4+} + 2\,F^- \Leftrightarrow ZrF_2^{2+}$	2	18.5 ± 0.1	8.3 ± 0.1
$Zr^{4+} + 3\,F^- \Leftrightarrow ZrF_3^{+}$	3	24.7 ± 0.2	6.2 ± 0.1
$Zr^{4+} + 4\,F^- \Leftrightarrow ZrF_4(aq)$	4	30.1 ± 0.5	5.5 ± 0.5
$Zr^{4+} + 5\,F^- \Leftrightarrow ZrF_5^{-}$	5	34.7 ± 0.6	4.6 ± 0.3
$Zr^{4+} + 6\,F^- \Leftrightarrow ZrF_6^{2-}$	6	38.4 ± 0.7	3.7 ± 0.4

The IUPAC database reports also the following reaction enthalpies from AHRLAND et al. (1990):

$$\Delta H(Zr^{4+} + HF(aq) \Leftrightarrow ZrF^{3+} + H^+) \quad = \quad 17.5 \text{ kJ mol}^{-1}$$

$$\Delta H(ZrF^{3+} + HF(aq) \Leftrightarrow ZrF_2^{2+} + H^+) \quad = \quad 16.8 \text{ kJ mol}^{-1}$$

$$\Delta H(ZrF_2^{2+} + HF(aq) \Leftrightarrow ZrF_3^{+} + H^+) \quad = \quad 11.2 \text{ kJ mol}^{-1}$$

$$\Delta H(ZrF_3^{+} + HF(aq) \Leftrightarrow ZrF_4(aq) + H^+) \quad = \quad 22 \text{ kJ mol}^{-1}$$

When combined with the reaction enthalpy for the formation of hydrofluoric acid ($\Delta H(H^+ + F^- \Leftrightarrow HF(aq)) = 12.2 \pm 0.3$ kJ mol^{-1}, NEA value from GRENTHE et al. 1992, p. 367) the following reaction enthalpies are obtained for reactions with the dissociated fluoride ion:

$$\Delta H(Zr^{4+} + F^- \Leftrightarrow ZrF^{3+}) \quad = \quad 29.7 \text{ kJ mol}^{-1}$$

$$\Delta H(ZrF^{3+} + F^- \Leftrightarrow ZrF_2^{2+}) \quad = \quad 29.0 \text{ kJ mol}^{-1}$$

$$\Delta H(ZrF_2^{2+} + F^- \Leftrightarrow ZrF_3^{+}) \quad = \quad 23.4 \text{ kJ mol}^{-1}$$

$$\Delta H(ZrF_3^{+} + F^- \Leftrightarrow ZrF_4(aq)) \quad = \quad 34.2 \text{ kJ mol}^{-1}$$

and:
$$\Delta H(Zr^{4+} + 2\,F^- \Leftrightarrow ZrF_2^{2+}) \quad = \quad 58.7 \text{ kJ mol}^{-1}$$

$$\Delta H(Zr^{4+} + 3\,F^- \Leftrightarrow ZrF_3^{+}) \quad = \quad 82.1 \text{ kJ mol}^{-1}$$

$$\Delta H(Zr^{4+} + 4\,F^- \Leftrightarrow ZrF_4(aq)) \quad = \quad 116.3 \text{ kJ mol}^{-1}$$

From the slopes of the unweighted SIT regressions shown in Figs. 5.24.2a and 5.24.2b we derived the following Δε values:

$$\Delta\epsilon(Zr^{4+}+HF\Leftrightarrow ZrF^{3+}+H^+) \quad = \quad -0.10 \pm 0.01$$

$$\Delta\epsilon(ZrF^{3+}+HF\Leftrightarrow ZrF_2^{2+}+H^+) \quad = \quad -0.06 \pm 0.01$$

$$\Delta\epsilon(ZrF_2^{2+}+HF\Leftrightarrow ZrF_3^{+}+H^+) \quad = \quad -0.10 \pm 0.01$$

$$\Delta\epsilon(ZrF_3^{+}+HF\Leftrightarrow ZrF_4(aq)+H^+) \quad = \quad -0.01 \pm 0.12$$

$$\Delta\epsilon(ZrF_4(aq)+HF\Leftrightarrow ZrF_5^{-}+H^+) \quad = \quad 0.07 \pm 0.08$$

$$\Delta\epsilon(ZrF_5^{-}+HF\Leftrightarrow ZrF_6^{2-}+H^+) \quad = \quad 0.25 \pm 0.10$$

The individual interaction coefficients of the Zr fluoride complexes were then derived from the following equations, assuming $\epsilon_{(j,k)} = 0$ for uncharged species and setting $\epsilon_{(H^+,ClO_4^-)} = 0.14 \pm 0.02$ (from GRENTHE et al. 1997):

$$\boldsymbol{\epsilon(ZrF_3^+,ClO_4^-) = \epsilon(H^+,ClO_4^-) - \Delta\epsilon(ZrF_3^{+}+HF=ZrF_4(aq)+H^+)}$$

$$\epsilon(ZrF_2^{2+},ClO_4^-) = \epsilon(H^+,ClO_4^-) + \epsilon(ZrF_3^+,ClO_4^-) - \Delta\epsilon(ZrF_2^{2+}+HF\Leftrightarrow ZrF_3^{+}+H^+)$$

$$\epsilon(ZrF^{3+},ClO_4^-) = \epsilon(H^+,ClO_4^-) + \epsilon(ZrF_2^{2+},ClO_4^-) - \Delta\epsilon(ZrF^{3+}+HF\Leftrightarrow ZrF_2^{2+}+H^+)$$

$$\epsilon(Zr^{4+},ClO_4^-) = \epsilon(H^+,ClO_4^-) + \epsilon(ZrF^{3+},ClO_4^-) - \Delta\epsilon(Zr^{4+}+HF\Leftrightarrow ZrF^{3+}+H^+)$$

$$\epsilon(ZrF_4(aq),ClO_4^-) = \epsilon(ZrF_4(aq),Na^+) = 0 \quad \text{(per definition, see GRENTHE et al. 1997)}$$

$$\boldsymbol{\epsilon(ZrF_5^-,Na^+) = \Delta\epsilon(ZrF_4(aq)+HF\Leftrightarrow ZrF_5^{-}+H^+) - \epsilon(H^+,ClO_4^-)}$$

$$\epsilon(ZrF_6^{2-},Na^+) = \Delta\epsilon(ZrF_5^{-}+HF\Leftrightarrow ZrF_6^{2-}+H^+) - \epsilon(H^+,ClO_4^-) + \epsilon(ZrF_5^-,Na+)$$

The determination of the individual interaction coefficients was possible because two of the studied reactions involve only a single unknown coefficient (equations marked in bold characters). Once $\epsilon_{(ZrF_3^+,ClO_4^-)}$ and $\epsilon_{(ZrF_5^-,Na^+)}$ are determined, the other interaction coefficients can be successively computed. The resulting interaction coefficients are listed in Table 5.24.4 and compared with the analogous coefficients for other tetravalent cations (taken from GRENTHE et al. 1997). There is a remarkably good correspondence with the interaction coefficients of Np(IV), Pu(IV), and particularly U(IV), thereby increasing our confidence in the selected Zr fluoride data up to ZrF_3^+. The interaction coefficients determined for the anionic complexes ZrF_5^- and ZrF_6^- have to be taken with care because comparative data are lacking.

In acid solutions Zr forms a relatively insoluble tetrafluoride (ZrF_4) and double fluoride salts with alkalis (particularly zirconium potassium hexafluoride, K_2ZrF_6). Rare Zr fluorosilicate minerals are reported, most of which containing Zr and F only as minor elements. The only exception is the recently discovered mineral *burpalite* (MERLINO et al. 1990), with formula $Na_8Ca_4Zr_4(Si_2O_7)_4F_8$. To our knowledge, no solubility data exist for these solids.

Table 5.24.4: Interaction coefficients ($\varepsilon_{(j,k)}$) for Zr^{4+} and fluoride complexes with perchlorate, computed with the help of the regressions shown in Figs. 5.24.2a and 5.24.2b. Corresponding interaction coefficients for other tetravalent cations, taken from GRENTHE et al. (1997), are given for comparison.

	$\varepsilon(M^{4+},ClO_4^-)$	$\varepsilon(MF^{3+},ClO_4^-)$	$\varepsilon(MF_2^{2+},ClO_4^-)$	$\varepsilon(MF_3^+,ClO_4^-)$	$\varepsilon(MF_5^-,Na^+)$	$\varepsilon(MF_6^{2-},Na^+)$
Zr(IV)	0.84 ± 0.12	0.59 ± 0.12	0.39 ± 0.12	0.15 ± 0.12	-0.07 ± 0.08	0.03 ± 0.13
U(IV)	0.76 ± 0.06	0.48 ± 0.08	0.3 ± 0.1	0.1 ± 0.1	-	-
Np(IV)	0.82 ± 0.05	-	-	-	-	-
Pu(IV)	1.03 ± 0.05	-	-	-	-	-

5.24.5.2   Zr chloride complexes and solids

Zr forms a series of mononuclear complexes with chloride ions. Although considerably weaker than fluoride complexes, chloride complexes could significantly contribute to zirconium speciation in saline groundwaters.

The IUPAC database reports a number of experimental studies on Zr chloride complexation. Conditional constants are given for the formation of the species $ZrCl^{3+}$, $ZrCl_2^{2+}$, $ZrCl_3^+$, and $ZrCl_4(aq)$ mostly in solutions of 2 M to 6.5 M perchloric acid. The available data proved to be sufficient to extrapolate a reliable zero ionic strength constant for the monochloride. For the higher complexes we were forced to reject the results of the extrapolations for the reasons explained later in this section.

The conditional constants considered for the SIT extrapolations are listed in Table 5.24.5 and the corresponding plots are shown in Fig. 5.24.3. The accepted constant and SIT parameters are summarised in Table 5.24.6. For $ZrCl^{3+}$, the SIT formalism yields:

$$\log_{10}K^0_1 = 1.5 \pm 0.3$$

which is included in the database update. Note that this value is more than one order of magnitude larger than the constant included in the previous version of the database ($\log_{10}K^0_1 = 0.2$).

Table 5.24.5: Data considered for the extrapolation of the formation constants for Zr chloride complexes at zero ionic strength (medium: $HClO_4$ or $HClO_4$ / $NaClO_4$ mixtures, $T = 20$ or $25\ ^{\circ}C$):

Reaction	Method	I(M)	Conditional constant	References
$Zr^{4+} + Cl^- \Leftrightarrow ZrCl^{3+}$	spectrophotometry	2.0	$\log_{10}K_1 = -0.02$	MAROV & RYABCHIKOV (1962)
	distribution	2.0	$\log_{10}K_1 = 0.08$	PRASILOVA & HAVLICEK (1970)
	distribution	2.0	$\log_{10}K_1 = 0.30$	CONNICK & MCVEY (1949)
	spectrophotometry	3.5	$\log_{10}K_1 = -0.50$	TRIBALAT & SCHRIVER (1972)
	spectrophotometry	4.0	$\log_{10}K_1 = 0.04$	MAROV & RYABCHIKOV (1962)
	distribution	6.54	$\log_{10}K_1 = 0.92$	SOLOVKIN (1957)
$ZrCl^{3+} + Cl^- \Leftrightarrow ZrCl_2^{2+}$	spectrophotometry	2.0	$\log_{10}K_2 = -0.20$	MAROV & RYABCHIKOV (1962)
	distribution	2.0	$\log_{10}K_2 = -0.62$	PRASILOVA & HAVLICEK (1970)
	spectrophotometry	4.0	$\log_{10}K_2 = -0.72$	MAROV & RYABCHIKOV (1962)
	distribution	6.54	$\log_{10}K_2 = 0.40$	SOLOVKIN (1957)
$ZrCl_2^{2+} + Cl^- \Leftrightarrow ZrCl_3^+$	spectrophotometry	2.0	$\log_{10}K_3 = -0.62$	MAROV & RYABCHIKOV (1962)
	distribution	2.0	$\log_{10}K_3 = -0.46$	PRASILOVA & HAVLICEK (1970)
	distribution	6.54	$\log_{10}K_3 = 0.19$	SOLOVKIN (1957)

Using $\Delta\varepsilon_{(Zr^{4+}+Cl^-\Leftrightarrow ZrCl^{3+})} = -0.15 \pm 0.06$ (as determined from the SIT regression), the auxiliary interaction coefficients $\varepsilon_{(Zr^{4+},ClO_4^-)} = 0.84 \pm 0.12$ (previously determined from the Zr-fluoride data) and $\varepsilon_{(Cl^-,H^+)} = \varepsilon_{(H^+,Cl^-)} = 0.12 \pm 0.01$ (from GRENTHE et al. 1997), we calculated the following interaction parameter for the Zr-monochloride complex:

$$\varepsilon_{(ZrCl^{3+},ClO_4^-)} = \varepsilon_{(Zr^{4+},ClO_4^-)} + \varepsilon_{(Cl^-,H^+)} + \Delta\varepsilon_{(Zr^{3+}+Cl^-=ZrCl^{3+})} = 0.81 \pm 0.18.$$

This value compares reasonably well with $\varepsilon_{(UCl^{3+},ClO_4^-)} = 0.59 \pm 0.10$ given in GRENTHE et al. (1997), considering the general trend to higher coefficients with decreasing ionic radius for highly charged cations.

From the SIT plots for $ZrCl_2^{2+}$ and $ZrCl_3^+$, the formal constants $\log_{10}K^0_2 = 0.5 \pm 0.4$ and $\log_{10}K^0_3 = 0.3 \pm 0.3$ were determined. These constants appear to be too small for a reliable determination in the framework of the SIT theory.

The basic assumption of a constant ionic medium cannot be fulfilled for the Zr dichloride and trichloride complexes, as exceedingly high total chloride concentrations are required (according to the conditional constants given in Table 5.24.5) in order for these complexes to become dominant. In other words, the determination of conditional constants for these complexes requires chloride concentrations far exceeding 1 M, which adds to the perchlorate, so that the condition of a background electrolyte at constant ionic strength cannot be met. It is in practice impossible to distinguish between ionic medium effects and complex formation in such cases. Therefore, one is forced to reject the above mentioned formation constants for Zr dichloride and trichloride. It should also be noted that these weak complexes would anyway be unimportant for the modelling of common aquatic systems.

Chloride forms various salts with Zr. The pure tetrachloride, $ZrCl_4$ (cr), is irrelevant for our database since it is unstable in water and even in fairly concentrated hydrochloric acid. It hydrolyses readily into hydroxychlorides of variable stoichiometry ($ZrOH_xCl_{4-x}$, where x ranges from zero to one). These products are easily soluble in water (REMY 1949) and will therefore play no role in limiting Zr concentrations in groundwaters. No solubility data could be found on these solids.

Table 5.24.6: Formation constant and SIT parameters of the Zr monochloride complex. Uncertainties have been determined from the standard deviations of the unweighted regression (Fig. 5.24.3).

Reaction	$\log_{10}K^0_1 = \log_{10}\beta^0_1$	$\Delta\varepsilon$	$\varepsilon_{(ZrCl3+,ClO4-)}$
$Zr^{4+} + Cl^- \Leftrightarrow ZrCl^{3+}$	1.5 ± 0.3	-0.15 ± 0.06	0.81 ± 0.18
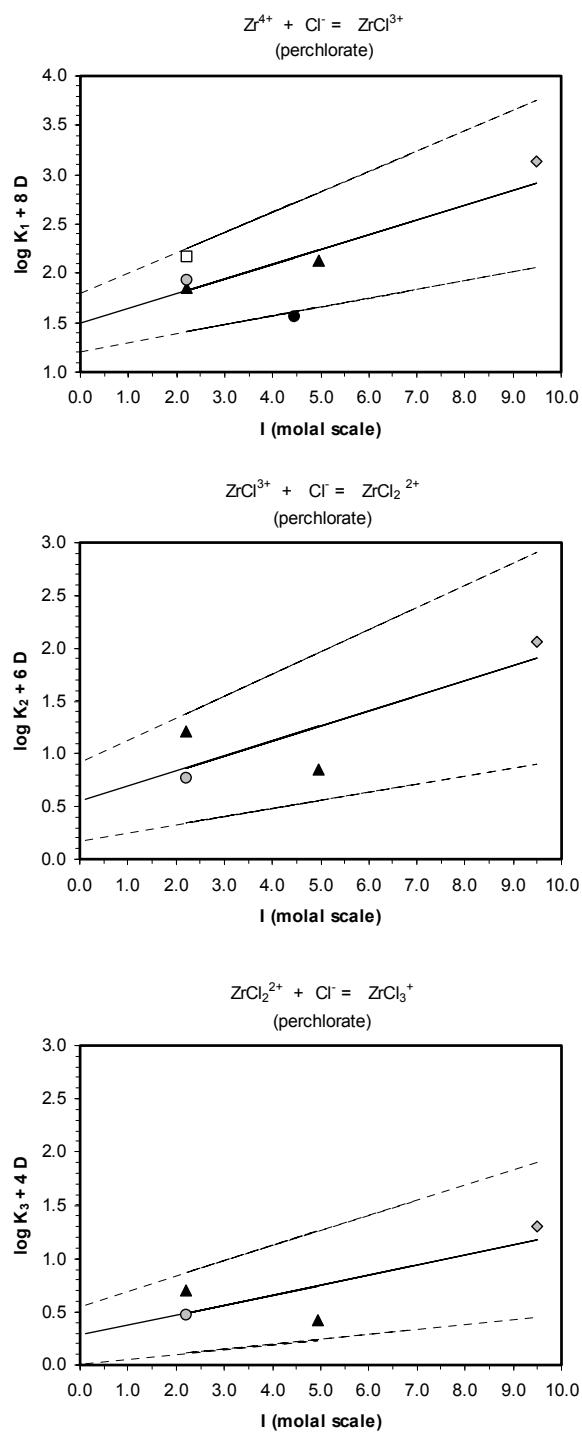
Fig. 5.24.3: SIT plots for the determination of constants for $ZrCl^{3+}$, $ZrCl_2^{2+}$, $ZrCl_3^+$ at $I = 0$.

5.24.6   Sulphate compounds and complexes

5.24.6.1 Zr sulphate complexes

Zr forms strong complexes with sulphate, and a considerable number of experimental studies exist, mostly carried out in concentrated perchloric acid. We considered the conditional constants reported in the IUPAC database (Table 5.24.7) to extrapolate to zero ionic strength the formation constants for Zr sulphate complexes, using the usual SIT formalism.

Since conditional constants are given in different forms (as $\log_{10}K$, $\log_{10}{}^*K$, $\log_{10}\beta$ and $\log_{10}{}^*\beta$ values), a reduction of the data to a common reaction scheme was necessary. Considering that the majority of the conditional constants are given in the original literature as equilibria with HSO_4^- (the prevailing free sulphate species in all experiments), we adopted the following reaction scheme for the SIT extrapolation procedure (charges omitted for clarity):

$$Zr(SO_4)_{n-1} + HSO_4^- \Leftrightarrow Zr(SO_4)_n + H^+, \qquad \log_{10}{}^*K_n$$
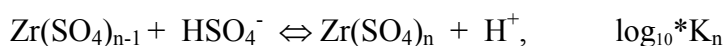
In order to transform the conditional constants expressed in terms of sulphate ions to constants corresponding to the above formalism, the second dissociation constant of sulphuric acid as a function of the $HClO_4$ concentration is needed (GRENTHE et al. 1997, p. 374):

$$HSO_4^- \Leftrightarrow H^+ + SO_4^{2-} \qquad\qquad pK = pK^0 - \Delta z^2\,D + \Delta\varepsilon\,m_k$$

where:

m_k is the molality of the background electrolyte ($HClO_4$) which coincides with the ionic strength $I(m)$,

$pK^0 = 1.987 \pm 0.009$ at 25 ^oC

$$D = 0.5091\,\frac{\sqrt{I(m)}}{1 + 1.5\sqrt{I(m)}}$$

$\Delta z^2 \quad = 4$

$\Delta\varepsilon \quad = \varepsilon_{(H^+,ClO_4^-)} + \varepsilon_{(SO_4^{2-},H^+)} - \varepsilon_{(HSO_4^-,H^+)} \cong \varepsilon_{(H^+,ClO_4^-)} + \varepsilon_{(SO_4^{2-},Na^+)} - \varepsilon_{(HSO_4^-,Na^+)} =$

$\qquad = 0.14\,(\pm 0.02) - 0.12\,(\pm 0.06) + 0.01\,(\pm 0.02) =$

$\qquad = 0.03 \pm 0.07$

Note that $\varepsilon_{(SO_4^{2-},H^+)}$ and $\varepsilon_{(HSO_4^-,H^+)}$ had to be approximated through $\varepsilon_{(SO_4^{2-},Na^+)}$ and $\varepsilon_{(HSO_4^-,Na^+)}$, respectively, since values for the former interaction coefficients could not be found in the literature. The transformation among the different types of constants was carried out with the help of the following relations:

$$\log_{10}*K_n = \log_{10}K_n - pK$$

$$\log_{10}*K_n = \log_{10}*\beta_n - \sum_{j=1}^{n-1} \log_{10}*K_j$$

$$\log_{10}*K_n = \log_{10}\beta_n - n\,pK - \sum_{j=1}^{n-1} \log_{10}*K_j$$

The SIT extrapolation was successful for the first Zr-sulphate complex, for which the unweighted regression (Fig. 5.24.4) yielded a precise value ($\log_{10}*K^0_1 = 4.99 \pm 0.05$). The small uncertainty arises from the relatively large number and consistent values of the conditional constants used in the regression.

Note that the constant determined by TRIBALAT & SCHRIVER (1976) was excluded from the regression as it differs from all other values by 2-3 orders of magnitude. By combining $\log_{10}*K^0_1$ with the pK^0 for the dissociation of HSO_4^-, we obtain:

$$\log_{10}K^0_1 = \log_{10}\beta^0_1 = 7.0 \pm 0.1$$

which is included in the database update.

From the slope of the regression shown in Fig. 5.24.4 and approximating $\varepsilon_{(HSO_4^-,H^+)} \cong \varepsilon_{(HSO_4^-,Na^+)}$, the following individual interaction coefficient for zirconium monosulphate in perchlorate is obtained:

$$\varepsilon_{(ZrSO_4^{2+},ClO_4^-)} \cong \varepsilon_{(Zr^{4+},ClO_4^-)} + \varepsilon_{(HSO_4^-,Na^+)} - \varepsilon_{(H^+,ClO_4^-)} + \Delta\varepsilon_{(Zr^{4+}+HSO4^-=ZrSO_4^{2+}+H^+)} =$$

$$= 0.84\,(\pm 0.12) - 0.01\,(\pm 0.02) - 0.14\,(\pm 0.02) - 0.19\,(\pm 0.02) = 0.50 \pm 0.12.$$

Table 5.24.7 Data considered in the extrapolation of formation constants for Zr sulphate complexes to zero ionic strength (medium: $HClO_4$ or $HClO_4$ / $NaClO_4$ mixtures, T = 20 or 25 ^oC):

Reaction	Method	I/M	Conditional constant	References
$Zr^{4+} + HSO_4^- \Leftrightarrow ZrSO_4^{2+} + H^+$	distrib.	2.0	$\log_{10}{}^*K_1 = 2.66$	CONNICK & MCVEY (1949)
$Zr^{4+} + HSO_4^- \Leftrightarrow ZrSO_4^{2+} + H^+$	distrib.	2.0	$\log_{10}{}^*K_1 = 2.6$	PRASILOVA & HAVLICEK (1970)
$Zr^{4+} + HSO_4^- \Leftrightarrow ZrSO_4^{2+} + H^+$	ion exch.	2.3	$\log_{10}{}^*K_1 = 2.56$	RYABCHIKOV et al. (1962)
$Zr^{4+} + HSO_4^- \Leftrightarrow ZrSO_4^{2+} + H^+$	ion exch.	2.3	$\log_{10}{}^*K_1 = 2.67$	RYABCHIKOV et al. (1964)
$Zr^{4+} + HSO_4^- \Leftrightarrow ZrSO_4^{2+} + H^+$	ion exch.	4.0	$\log_{10}{}^*K_1 = 2.85$	AHRLAND et al. (1963)
$Zr^{4+} + HSO_4^- \Leftrightarrow ZrSO_4^{2+} + H^+$	distrib.	4.0	$\log_{10}{}^*K_1 = 2.8$	NOREN (1969)
$Zr^{4+} + SO_4^{2-} \Leftrightarrow ZrSO_4^{2+}$	distrib.	2.0	$\log_{10} K_1 = 3.69$	WHITEKER & DAVIDSON (1953)
$Zr^{4+} + SO_4^{2-} \Leftrightarrow ZrSO_4^{2+}$	distrib.	4.0	$\log_{10} K_1 = 1.60$	TRIBALAT & SCHRIVER (1976)
$ZrSO_4^{2+} + HSO_4^- \Leftrightarrow Zr(SO_4)_2^0 + H^+$	distrib.	2.0	$\log_{10}{}^*K_2 = 1.72$	CONNICK & MCVEY (1949)
$ZrSO_4^{2+} + HSO_4^- \Leftrightarrow Zr(SO_4)_2^0 + H^+$	ion exch.	4.0	$\log_{10}{}^*K_2 = 1.85$	AHRLAND et al. (1963)
$ZrSO_4^{2+} + HSO_4^- \Leftrightarrow Zr(SO_4)_2^0 + H^+$	distrib.	4.0	$\log_{10}{}^*K_2 = 0.9$	NOREN (1969)
$Zr^{4+} + 2\,HSO_4^- \Leftrightarrow Zr(SO_4)_2^0 + 2\,H^+$	distrib.	2.0	$\log_{10}{}^*\beta_2 = 4.5$	PRASILOVA & HAVLICEK (1970)
$Zr^{4+} + 2\,HSO_4^- \Leftrightarrow Zr(SO_4)_2^0 + 2\,H^+$	ion exch.	2.3	$\log_{10}{}^*\beta_2 = 3.34$	RYABCHIKOV et al. (1962)
$Zr^{4+} + 2\,HSO_4^- \Leftrightarrow Zr(SO_4)_2^0 + 2\,H^+$	ion exch.	2.3	$\log_{10}{}^*\beta_2 = 3.54$	RYABCHIKOV et al. (1964)
$Zr^{4+} + 2\,SO_4^{2-} \Leftrightarrow Zr(SO_4)_2^0$	distrib.	2.0	$\log_{10} \beta_2 = 6.64$	WHITEKER & DAVIDSON (1953)
$Zr^{4+} + 2\,SO_4^{2-} \Leftrightarrow Zr(SO_4)_2^0$	distrib.	4.0	$\log_{10} \beta_2 = 2.72$	TRIBALAT & SCHRIVER (1976)
$Zr(SO_4)_2^0 + HSO_4^- = Zr(SO_4)_3^{2-} + H^+$	distrib.	2.0	$\log_{10}{}^*K_3 = 0.0$	CONNICK & MCVEY (1949)
$Zr(SO_4)_2^0 + HSO_4^- = Zr(SO_4)_3^{2-} + H^+$	distrib.	4.0	$\log_{10}{}^*K_3 = 0.3$	NOREN (1969)
$Zr^{4+} + 3\,HSO_4^- = Zr(SO_4)_3^{2-} + 3\,H^+$	distrib.	2.0	$\log_{10}{}^*\beta_3 = 5.5$	PRASILOVA & HAVLICEK (1970)
$Zr^{4+} + 3\,HSO_4^- = Zr(SO_4)_3^{2-} + 3\,H^+$	ion exch.	2.3	$\log_{10}{}^*\beta_3 = 5.61$	RYABCHIKOV et al. (1962)
$Zr^{4+} + 3\,HSO_4^- = Zr(SO_4)_3^{2-} + 3\,H^+$	ion exch.	2.3	$\log_{10}{}^*\beta_3 = 6.59$	RYABCHIKOV et al. (1964)

$$Zr^{4+} + HSO_4^- = ZrSO_4^{2+} + H^+$$
(perchlorate)

○ Prasilova and Havlicek (1970)   ◇ Ahrland et al. (1963)

▲ Whiteker and Davidson (1953)   ■ Noren (1969)

□ Connick and McVey (1949)   ▨ Ryabchikov et al. (1964)

                                         ◆ Ryabchikov et al. (1962)
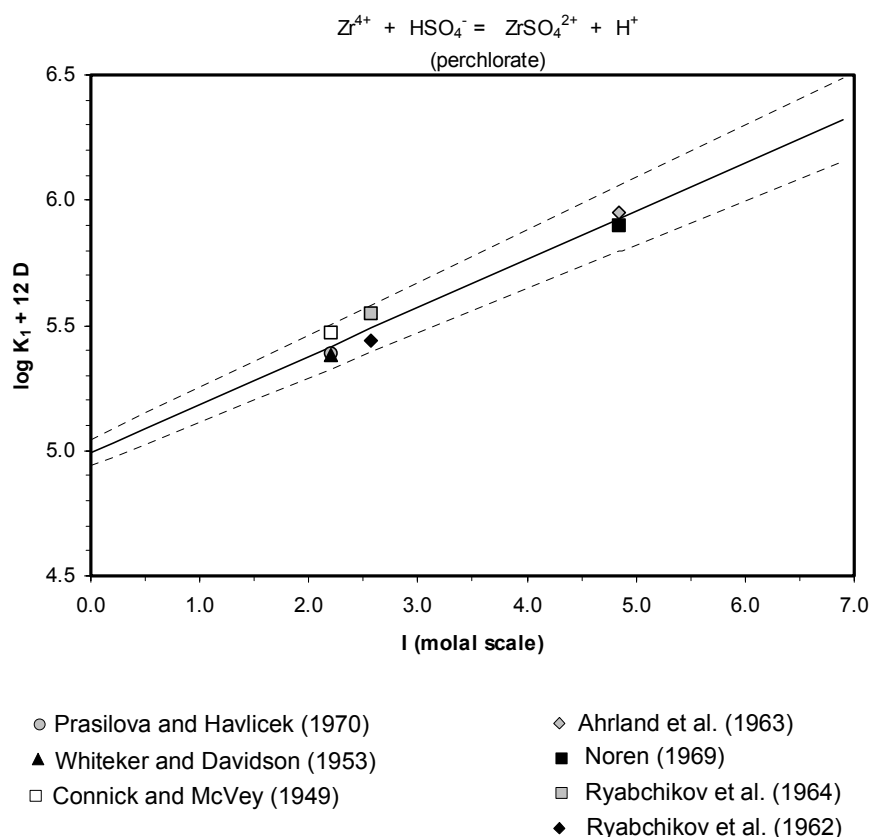
Fig. 5.24.4:   SIT plot for the determination of the constant for the formation of $Zr(SO_4)^{2+}$ at $I = 0$.

The above value fits well within the range of corresponding interaction coefficients for complexes with net charge +2 (GRENTHE et al. 1997).

The data for the di- and trisulphate complexes proved to be too inconsistent for any reasonable extrapolation to zero ionic strength. A reason lies probably in the different equilibrium formulations (and thus different values for the implied auxiliary constants) used by the investigators. Only a detailed review of each paper could help resolving these inconsistencies. We did not attempt a detailed analysis of the data, and thus no formation constants for $Zr(SO_4)_2^0$ and $Zr(SO_4)_3^{2-}$ are included in the database.

5.24.6.2 Zr sulphate solids

In strongly acidic solutions zirconium forms complex sulphate salts with different degrees of hydration. The anhydrous form, $Zr(SO_4)_2$, is unstable in water and converts readily to hydrated products (see REMY 1949, Vol. II, p. 70). A rare natural form is the mineral *zircosulphate*, $Zr(SO_4)_2$ · $4H_2O$. No solubility data could be found for any of the mentioned solids.

5.24.7   Zr carbonate compounds and complexes

5.24.7.1 Zr carbonate aqueous complexes

None of the reviews on the aqueous chemistry of Zr cited in the present report mentions complex formation with the ubiquitous and abundant carbonate species. However, there are unequivocal indications that Zr forms strong carbonate complexes, and even stability constants for pure and mixed Zr carbonato complexes have been published (KARLYSHEVA et al. 1982; JOÃO et al. 1987). Dissolution experiments with the mineral weloganite (a Na-Zr-Sr hydrous carbonate) yielded equilibrium Zr concentrations of about 10^{-4} M at pH ~ 8 (AJA et al. 1995). JOÃO et al. (1987) were able to prepare stable solutions at millimolar Zr concentrations in the presence of 0.5 to 1 M total carbonate (at pH 10). Finally, spectroscopic evidence of the existence of Zr-carbonate complexes was given by KARLYSHEVA et al. (1982).

Recent experiments carried out in our laboratory (POUCHON et al. 2001) confirmed these findings, indicating that the solubility of zirconia and of a Zr hydrous oxide increase by several orders of magnitude in the presence of 0.05 to 0.5 M $NaHCO_3$ at pH=9 (see Fig. 5.24.5). The results suggest the formation of a mononuclear tetra- or penta-carbonato complex but do not allow the derivation of thermodynamic constants. Specifically, solubility models assuming a (1,4) or (1,5) stoichiometry strongly overestimate equilibrium Zr concentrations in the 0.5 M $NaHCO_3$ solution (the rightmost data in Fig. 5.24.5). This may indicate precipitation of a basic Zr carbonate (see next section).

Due to the scarcity of data, the ambiguous stoichiometry of Zr-carbonate complexes and errors found in the derivation of the published constants (see CURTI & HUMMEL 1999, for details) we cannot accept the Zr-carbonate complexation constants proposed in the literature. However, we see a fair chance to determine in future the relevant complexes and relative formation constants through a careful and detailed analysis of all the raw data available, particularly those available from the Russian literature. In view of the ongoing NEA review, we did not attempt such analysis, and no data on Zr carbonate complexes are therefore included in the update.
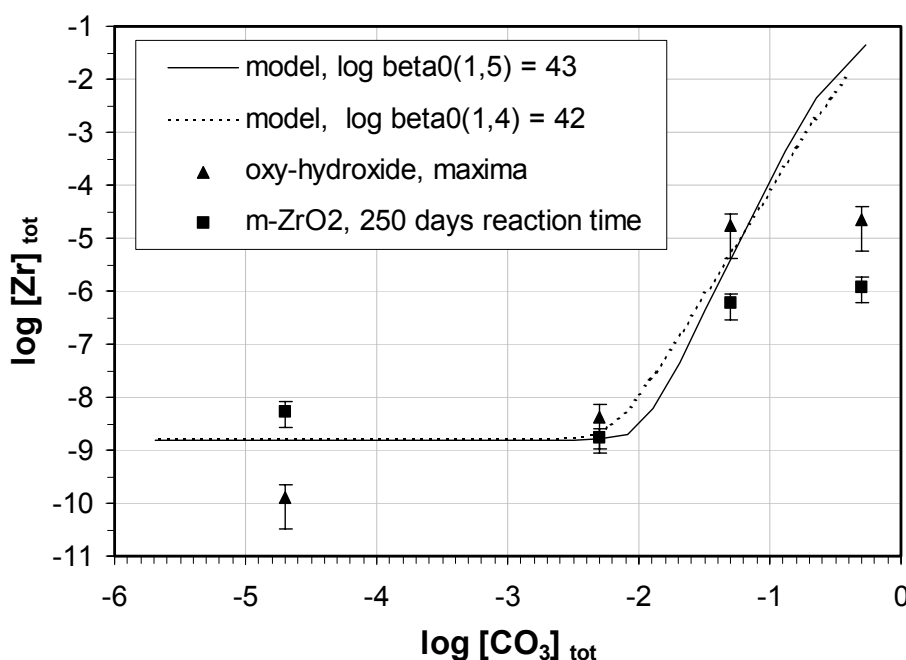
Figure 5.24.5: Solubility of monoclinic zirconia and of freshly precipitated Zr oxy-hydroxide as a function of total carbonate concentration: comparison of experimental data (^{95}Zr radiometric measurements for the oxy-hydroxide and ICP-MS for monoclinic zirconia) with computed solubility curves, after POUCHON et al. (2001). The data for monoclinic zirconia at carbonate concentrations less than 10^{-2} M have been included in the analysis of hydrolysis data (see Fig. 5.24.1).

5.24.7.2 Zr carbonate solids

In the laboratory, basic Zr carbonates readily precipitate through addition of alkali carbonate (Na_2CO_3 or K_2CO_3) in millimolar concentrations, beginning at pH values around 4 (MIKHAILOV & GRIGOR'EVA 1961). These precipitates are non-stoichiometric and frequently include alkali ions. These solids redissolve upon addition of alkali carbonate at pH's above 8-9, which is a further indication that stable carbonate complexes are formed. No thermodynamic data are available for such compounds.

In nature, very rare minerals resembling the above mentioned precipitates are found as hydrothermal alteration products in hyperalkaline intrusive rocks (*sabinaite*, $Na_4Zr_2TiO_4(CO_3)_4$, *voggite*, $Na_2Zr(PO_4)(CO_3)(OH)·2H_2O$ and *weloganite*, $Sr_3Na_2Zr(CO_3)_6 · 3H_2O$). Solubility data for weloganite have been published by AJA et al. (1995) but the solubility product determined by these authors cannot be included in our update since a state of thermodynamic equilibrium was clearly not reached in the experiments. Solids of this type, although uncommon in nature, could be solubility-limiting in cementitious repository environments.

5.24.8   Zr nitrate compounds and complexes

5.24.8.1 Zr nitrate aqueous complexes

Zirconium forms rather weak complexes with nitrate. A few formation constants for mononuclear species up to a ligand number of four are reported in the IUPAC database, mainly from the same investigators who determined formation constants for Zr halogenide and sulphate complexes. The values given for the first formation constant ($\log_{10}K_1$) in 2 or 4 M perchlorate vary from -0.1 to 0.3, indicating that the stability of Zr nitrate complexes is in the order of that of chloride complexes. Due to the scarcity of the available data we did not attempt an extrapolation of the formation constants to zero ionic strength. No data on Zr nitrate complexes are therefore included in the database update.

5.24.8.2 Zr nitrate solid compounds

Various Zr nitrate salts are formed from concentrated nitric acid (REMY 1949, Vol. I, p. 71). These products are invariably hydrated, strongly hygroscopic and hence easily soluble in water. They will play no role as solubility-limiting solids. No natural Zr nitrate was found up to date.

5.24.9   Zr phosphate compounds and complexes

5.24.9.1 Zr phosphate aqueous complexes

The IUPAC database reports only two investigations dealing with the formation of Zr phosphate complexes. This is too little to attempt any systematisation and therefore no constant is included in the update.

5.24.9.2 Zr phosphate solid compounds

Zirconium phosphate with the ideal formula $Zr_3(PO_4)_4$ precipitates easily from phosphoric acid or sodium phosphate solutions (REMY 1949, Vol. I, p. 71). Phosphate also reacts strongly with Zr hydrous oxides, oxychlorides and nitrates. Such reactions are so effective, that these solids are routinely used to separate phosphate from solution. This indicates a strong natural tendency of Zr to form insoluble phosphates, which is confirmed by the occurrence in nature of rare but numerous double phosphate salts (e.g. the minerals *mahlmoodite* $FeZr(PO_4)_2 \cdot 4H_2O$, *selwynite,* $NaK(Be,Al)Zr_2(PO_4)_4 \cdot 2H_2O$, *wycherproofite*, $NaAlZr(PO_4)_2(OH)_2 \cdot H_2O$). It is conceivable that Zr phosphates could control the solubility of this radionuclide in phosphate-rich environments (e.g.

vitrified waste and cast steel canisters) but no data could be retrieved on the solubility of any Zr phosphate.

5.24.10 Final remarks

Thermodynamic data for aqueous complexes and solid compounds of Zr are scarce and difficult to evaluate. This is due in a large measure to the peculiar chemical properties of this metal. With a radius of 0.72 Å in octahedral coordination and a valency of +IV, Zr behaves as a typical hard cation, forming stable complexes and solids with hydroxyl, sulphate, carbonate, phosphate and fluoride. Hydrolysis is very strong, but not sufficient to produce stable oxo-anions and oxo-acids (like silicic acid, sulphate, molybdate). Therefore, hydrolysis reactions always interfere with complexation by other ligands, unless the reaction occurs in strong acids.

It is therefore not surprising that most studies of Zr aqueous complexes were conducted in concentrated acid. This means that the selected constants must be extrapolated over many pH units when applied to determine Zr speciation in environmental systems. On the other hand, hydrolysis reactions will dominate over other Zr-ligand interactions in most environmental systems, as fluoride, sulphate and chloride complexes will become important only at very low pH. Exceptions are Zr carbonate and possibly phosphate complexes. Carbonate species can demonstrably become dominant at mildly alkaline pH values. Thus, we consider that hydrolysis and Zr carbonate complexation or precipitation are the critical reactions in environmental systems and future efforts to improve the database for Zr should go in this direction.

Table 5.24.8: Selection of thermodynamic data for Zr(IV) to be included in the Nagra/PSI TDB 01/01 (bold). The data included in the previous version of the database, Nagra TDB 05/92, are given for comparison (normal typing).

Zirconium

Name	$\Delta_f G_m^o$ [kJ mol^{-1}]	$\Delta_f H_m^o$ [kJ mol^{-1}]	S_m^o [J mol^{-1} K^{-1}]	Species/ Reaction
Zr(cr)	**0.0**	**0.0**	**39.0**	Zr(cr)
Zr+4	**-557.7 ± 10.8**			Zr^{4+}

Name	$\log_{10}{}^{(*)}\beta_{j,n}^o$ (new)	$\Delta_f H_m^o$ [kJ mol^{-1}]	$\log_{10}{}^{(*)}\beta_{j,n}^o$ (old)	Reaction
ZrOH+3	**0.3**	-	0.3	$Zr^{4+} + H_2O(l) \Leftrightarrow ZrOH^{3+} + H^+$
Zr(OH)4	**-9.7**	-	-9.7	$Zr^{4+} + 4 H_2O(l) \Leftrightarrow Zr(OH)_4(aq) + 4 H^+$
Zr(OH)5-	**-16**	-	-16	$Zr^{4+} + 5 H_2O(l) \Leftrightarrow Zr(OH)_5^- + 5 H^+$
	-	-	-0.6	$3 Zr^{4+} + 4 H_2O(l) \Leftrightarrow Zr_3(OH)_4^{8+} + 4 H^+$
	-	-	6	$4 Zr^{4+} + 8 H_2O \Leftrightarrow Zr_4(OH)_8^{8+} + 8 H^+$
ZrF+3	**10.2 ± 0.1**	**29.7**	-	$Zr^{4+} + F^- \Leftrightarrow ZrF^{3+}$
ZrF2+2	**18.5 ± 0.2**	**58.7**	-	$Zr^{4+} + 2 F^- \Leftrightarrow ZrF_2^{2+}$
ZrF3+	**24.7 ± 0.3**	**82.1**	-	$Zr^{4+} + 3 F^- \Leftrightarrow ZrF_3^+$
ZrF40	**30.1 ± 0.8**	**116.3**	-	$Zr^{4+} + 4 F^- \Leftrightarrow ZrF_4(aq)$
ZrF5-	**34.7 ± 1.1**	-	-	$Zr^{4+} + 5 F^- \Leftrightarrow ZrF_5^-$
ZrF6-2	**38.4 ± 1.5**	-	-	$Zr^{4+} + 6 F^- \Leftrightarrow ZrF_6^{2-}$
ZrSO4+2	**7.0 ± 0.1**	-	3.05	$Zr^{4+} + SO_4^{2-} \Leftrightarrow ZrSO_4^{2+}$
ZrCl+3	**1.5 ± 0.3**	-	0.2	$Zr^{4+} + Cl^- \Leftrightarrow ZrCl^{3+}$

Name	$\log_{10}{}^{(*)}K_{S,0}^o$ (new)	$\Delta_f H_m^o$ [kJ mol^{-1}]	$\log_1{}^{(*)}K_{S,0}^o$ (old)	Reaction
Baddeleyite	**-1.9**	-	-1.9	$ZrO_2(cr) + 4 H^+ \Leftrightarrow Zr^{4+} + 2 H_2O(l)$
	-	-	-37.53	$ZrCl_4(cr) \Leftrightarrow Zr^{4+} + 4 Cl^-$

5.24.11 References

ADAIR J.H., DENKEWICZ R.P. & ARRIAGADA F.J. (1987): Precipitation and in-situ transformation in the hydrothermal synthesis of crystalline zirconium dioxide. Ceramic Trans., 1, 135-145.

AHRLAND S., KARIPIDES D. & NOREN B. (1963): The fluoride and sulphate complexes of zirconium. Acta Chem. Scand., 17, 411-424.

AHRLAND S., HEFTER G. & NOREN B. (1990): A calorimetric study of the mononuclear fluoride complexes of zirconium(IV), hafnium(IV), thorium(IV) and uranium(IV). Acta Chem. Scand., 44, 1-7.

AJA S.U., WOOD S.A. & WILLIAMS-JONES A.E. (1995): The aqueous geochemistry of Zr and the solubility of Zr-bearing minerals. Applied Geochemistry, 10, 603-620.

BAES C.F., Jr. & MESMER R.E. (1976): The Hydrolysis of Cations. New York, John Wiley & Sons, 489p.

BARD A.J., PARSONS R. & JORDAN J. (1985): Standard potentials in aqueous solutions. Marcel Dekker, inc., New York and Basel, 834p.

BEVINGTON PH.R. (1969): Data reduction and error analysis for the physical sciences. Mc-Graw-Hill, New York, 336 p.

BILINSKI H., BRANICA M. & SILLEN L.G. (1966): Precipitation and hydrolysis of metallic ions II. Studies on the solubility of zirconium hydroxide in dilute solutions and in 1 M $NaClO_4$. Acta Chem. Scand., 20, 853-861.

BUKHSH M., FLEGENHEIMER J. et al. (1966): The chemistry of protactinium-VII. The fluoro-complexes. J. Inorg. Nucl. Chem., 28, 421-431.

BUSLAEV Y. (1962): Instability constants of complex zirconium fluorides. Zhur. Neorg. Khim., 7, 1204(E:619).

CONNICK R. & MCVEY W. (1949): The aqueous chemistry of zirconium. J. Am. Chem. Soc., 71, 3182-3191.

COX J.D., WAGMAN D.D. & MEDVEDEV V.A. (1989): CODATA key values for thermodynamics. Hemisphere Publishing Corporation, New York, 271 p.

CURTI E. & HUMMEL W. (1999): Modeling the solubility of zirconia in a repository for high-level radioactive waste. J. Nucl. Mat., 274, 189-196.

GRENTHE I., FUGER J., KONINGS R.J.M., LEMIRE R.J., MULLER A.B., NGUYEN-TRUNG C. & WANNER H. (1992): Chemical Thermodynamics of Uranium. Elsevier, Amsterdam, 715p.

GRENTHE I. & PUIGDOMENECH I. (1997): Symbols, Standards, and Conventions. In: Modelling in Aquatic Chemistry, I. GRENTHE & I. PUIGDOMENECH (eds.), 35-68. OECD, Nuclear Energy Agency, Paris.

GRENTHE I., SPAHIU K. & PLYASUNOV A. V. (1997): Estimations of medium effects on thermodynamic data. In: Modelling in Aquatic Chemistry, I. GRENTHE & I. PUIGDOMENECH (eds.), 325-426. OECD, Nuclear Energy Agency, Paris.

IUPAC (1997): Stability Constants Database. Academic Software, Timble, OTLEY, Yorkshire (U.K.).

JOÃO A., BIGOT S. & FROMAGE F. (1987): Etude des carbonates complexes des éléments IVB II - Détermination des constantes d'équilibre de formation des tétracarbonatozirconate (IV) et -hafnate (IV). Bull. Soc. Chim. France, 943-947.

JOLIVET J.P. (1994): De la solution à l' oxyde. Savoirs Actuels, InterEditions and CNRS Editions, Paris, 387 p.

KARLYSHEVA K.F., CHUMAKOVA L.S., MALINKO L.A. & SHEKA I.A. (1982): Reaction of zirconium and hafnium oxide chlorides with sodium carbonate in solution. Russ. J. Inorg. Chem., 27, 1582-1585.

KOVALENKO P.N. & BAGDASAROV K.N. (1961): The solubility of zirconium hydroxide. Russ J. Inorg. Chem., 6, 272-275.

KRYLOV V.N., KOMAROV E.V. & PUSHLENKOV M.F. (1969): Investigation of the complex formation of Zr(IV) with the fluoride ion in solutions of $HClO_4$ and HNO_3 by the method of ion exchange. Radiokhim., 11 , 460-462 (E:450).

KULMALA S. & HAKANEN M. (1993): The solubility of Zr, Nb and Ni in groundwater and concrete water, and sorption on crushed rock and cement. Nuclear Waste Commission of Finnish Power Companies (YIT), Helsinki.

LATIMER W.M. (1952): Oxidation potentials. Second Edition, Prentice-Hall, Inc. Englewood Cliffs, N.J, 392 p.

LUMPKIN G.R. (1999): Physical and chemical characteristics of baddeleyite (monoclinic zirconia) in natural environments: an overview and case study. J. Nucl. Mater., 274, 206-217.

MAROV I. & RYABCHIKOV D. (1962): Complex formation of Zr^{IV} and Hf^{IV} with chloride, nitrate and oxalate ions. Zhur. Neorg. Khim., 7, 1036 (E:533).

MERLINO S., PERCHIAZZI N. et al. (1990): Burpalite, a new mineral from Burpalinskii massif, north Transbajkal, USSR: its crystal structure and OD character. Eur. J. Mineral., 2, 177-185.

MIKHAILOV V.A. & GRIGOR'EVA E.F. (1961): Basic carbonates of zirconium. Russ. J. Inorg. Chem., 6, 760-762.

NOREN B. (1967): The fluoride complexes of zirconium. Acta Chem. Scand., 21, 2457-2462.

NOREN B. (1969): Solvent extraction studies of the formation of fluoride and sulphate complexes of zirconium(IV). Acta Chem. Scand., 23, 379-387.

NOREN B. (1973): The hydrolysis of Zr^{4+} and Hf^{4+}. Acta Chem. Scand., 27, 1369-1384.

PEARSON F.J., JR., BERNER U. & HUMMEL W. (1992): NAGRA thermochemical database - II. Supplemental data. Technical Report NTB 91-18, NAGRA, Wettingen, Switzerland.

POUCHON M. A., CURTI E., DEGUELDRE C. & TOBLER L. (2001): The influence of carbonate complexes on the solubility of zirconia: new experimental data. Progr. Nucl. Energy, 38, 443-446.

PRASILOVA J. & HAVLICEK J. (1970): Determination of stability constants of some complexes of zirconium using dinonyl naphtalene sulphonic acid as liquid ion exchanger. J. Inorg. Nucl. Chem., 32, 953-960.

REMY H. (1949): Lehrbuch der anorganischen Chemie. Akademische Verlagsgesellschaft Geest & Portig K.-G, Leipzig, 5th edition.

RYABCHIKOV D., ERMAKOV A. et al. (1962): Ion exchange study of complex formation by zirconium and hafnium with sulphate ions. Zhur. Neorg. Khim., 7, 69 (E:34).

RYABCHIKOV D., MAROV I. et al. (1964): Stability of some inorganic and organic complex compounds of zirconium and hafnium. J. Inorg. Nucl. Chem., 26, 965-980.

SHEKA I.A. & PEVZNER T.V. (1960): Solubility of zirconium and hafnium hydroxides in sodium hydroxide solutions. Russ. J. Inorg. Chem., 5, 1119-1121.

SOLOVKIN A.S. (1957): Determination of hydrolysis constants and of formation constants of Zr^{4+} with nitrate and chloride ions by extraction methods. Zhur. Neorg. Khim., 2, 611.

SOLOVKIN A.S. & TSETKOVA S.V. (1962): The chemistry of aqueous solutions of zirconium salts (does the zyrconyl ion exist ?). Russ. Chem. Rev., 31, 655-669.

TRIBALAT S. & SCHRIVER L. (1972): Le complexe thiocyanate de zirconium(IV), son utilisation comme indicateur de thiocyanate ou de zirconium (IV) libre. Compt. Rend. Acad. Sc. Paris, 274 C, 849-852.

T<small>RIBALAT</small> S. & S<small>CHRIVER</small> L. (1976): Use of chloroform extraction of isopropyltropolonates to study zirconium (+4) and hafnium (+4) complexes. J. Inorg. Nucl. Chem., 38, 145-148.

W<small>AGMAN</small> D.D., E<small>VANS</small> W.H. et al. (1982): The NBS tables of chemical thermodynamic properties. J. of Physical and Chemical Reference Data, 11 (Suppl. No. 2), 390 p.

W<small>HITEKER</small> R. & D<small>AVIDSON</small> N. (1953): Ion-Exchange and Spectrophotometric investigation of iron (III) sulfate complex ions. J. Am. Chem. Soc., 75, 3081-3085.

Appendix

The following tables (5.24.A1 to 5.24.A4) list the conditional constants and the background electrolyte data used in the SIT extrapolations.

Table 5.24.A1: Experimental data and calculated quantities for SIT regressions, referring to Figure 5.24.2a.

Medium	T / °C	A(T)	I(M)	molality factor	I(m)	$H=I^{0.5}/(1+1.5\,I^{0.5})$	$\log_{10}{}^{*}K_n$	$\log_{10}{}^{*}K_n - \Delta z^2 A\,H$	Reference
							n=1		**Figure 5.24.2a, top (ZrF^{3+})**
$(Na,H)ClO_4^-$	25	0.5091	2	1.1037	2.2074	4.60E-01	5.80	7.21	CONNICK & MCVEY (1949)
$(Na,H)ClO_4^-$	25	0.5091	2	1.1037	2.2074	4.60E-01	5.81	7.22	KRYLOV et al. (1969)
$(Na,H)ClO_4^-$	20	0.5050	4	1.2364	4.9456	5.13E-01	5.96	7.51	AHRLAND et al. (1963)
$(Na,H)ClO_4^-$	20	0.5050	4	1.2364	4.9456	5.13E-01	5.88	7.43	NOREN (1969)
$(Na,H)ClO_4^-$	25	0.5091	4	1.2364	4.9456	5.13E-01	5.97	7.54	NOREN (1973)
							n=2		**Figure 5.24.2a, middle (ZrF_2^{2+})**
$(Na,H)ClO_4^-$	25	0.5091	2	1.1037	2.2074	4.60E-01	4.32	5.49	CONNICK & MCVEY (1949)
$(Na,H)ClO_4^-$	20	0.5050	4	1.2364	4.9456	5.13E-01	4.42	5.72	NOREN (1967)
$(Na,H)ClO_4^-$	20	0.5050	4	1.2364	4.9456	5.13E-01	4.36	5.66	NOREN (1969)
$(Na,H)ClO_4^-$	25	0.5091	4	1.2364	4.9456	5.13E-01	4.40	5.71	NOREN (1973)
							n=3		**Figure 5.24.2a, bottom (ZrF_3^{+})**
$(Na,H)ClO_4^-$	25	0.5091	0.5	1.0256	0.5128	3.45E-01	2.7	3.05	BUSLAEV (1962)
$(Na,H)ClO_4^-$	25	0.5091	2	1.1037	2.2074	4.60E-01	2.83	3.30	CONNICK & MCVEY (1949)
$(Na,H)ClO_4^-$	20	0.5050	4	1.2364	4.9456	5.13E-01	3	3.52	NOREN (1967)
$(Na,H)ClO_4^-$	20	0.5050	4	1.2364	4.9456	5.13E-01	3	3.52	NOREN (1969)

Table 5.24.A2:   Experimental data and calculated quantities for SIT regressions, referring to Figure 5.24.2b.

Medium	T / $^{\circ}C$	A(T)	I(M)	molality factor	I(m)	$H=I^{0.5}$ $/(1+1.5\,I^{0.5})$	$\log_{10}{}^*K_n$	$\log_{10}{}^*K_n -$ $\Delta z^2 A\,H$	Reference
							n=4		**Figure 5.24.2b, top (ZrF$_4$(aq))**
(Na,H)ClO$_4^-$	20	0.5050	4	1.2364	4.9456	5.13E-01	2.30	2.30	NOREN (1969)
(Na,H)ClO$_4^-$	20	0.5050	4	1.2364	4.9456	5.13E-01	2.28	2.28	NOREN (1967)
(Na,H)ClO$_4^-$	25	0.5091	1	1.0499	1.0499	4.04E-01	2.80	2.80	BUKHSH et al. (1966)
(Na,H)ClO$_4^-$	25	0.5091	0.5	1.0256	0.5128	3.45E-01	1.83	1.83	BUSLAEV (1962)
							n=5		**Figure 5.24.2b, middle (ZrF$_5^-$)**
(Na,H)ClO$_4^-$	25	0.5091	0.5	1.0256	0.5128	3.45E-01	1.51	1.16	BUSLAEV (1962)
(Na,H)ClO$_4^-$	25	0.5091	1	1.0499	1.0499	4.04E-01	1.9	1.49	BUKHSH et al. (1966)
(Na,H)ClO$_4^-$	20	0.5050	4	1.2364	4.9456	5.13E-01	1.53	1.01	NOREN (1967)
							n=6		**Figure 5.24.2b, bottom (ZrF$_6^{2-}$)**
(Na,H)ClO$_4^-$	25	0.5091	0.5	1.0256	0.5128	3.45E-01	0.86	0.16	BUSLAEV (1962)
(Na,H)ClO$_4^-$	25	0.5091	1	1.0499	1.0499	4.04E-01	1.35	0.53	BUKHSH et al. (1966)
(Na,H)ClO$_4^-$	20	0.5050	4	1.2364	4.9456	5.13E-01	0.3	-0.74	NOREN (1967)

Table 5.24.A3: Experimental data and calculated quantities for SIT regressions, referring to Figure 5.24.3.

Medium	T / °C	A(T)	I(M)	molality factor	I(m)	$H=I^{0.5}$ $/(1+1.5\ I^{0.5})$	$\log_{10} {}^*K_n$	$\log_{10} {}^*K_n -$ $\Delta z^2 A\ H$	Reference
							n=1		**Figure 5.24.3, top (ZrCl^{3+})**
(Na,H)ClO$_4^-$	25 ?	0.5091	4	1.2364	4.9456	5.13E-01	0.04	2.13	MAROV & RYABCHIKOV (1962)
(Na,H)ClO$_4^-$	25 ?	0.5091	2	1.1037	2.2074	4.60E-01	-0.02	1.85	MAROV & RYABCHIKOV (1962)
(Na,H)ClO$_4^-$	25 ?	0.5050	3.5	1.2720	4.4520	5.07E-01	-0.5	1.56	TRIBALAT & SHRIVER (1972)
(Na,H)ClO$_4^-$	20	0.5050	2	1.1037	2.2074	4.60E-01	0.08	1.94	PRASILOVA & HAVLICEK (1970)
(Na,H)ClO$_4^-$	20	0.5050	6.54	1.45 [1]	9.4830	5.48E-01	0.92	3.13	SOLOVKIN (1957)
(Na,H)ClO$_4^-$	25	0.5091	2	1.1037	2.2074	4.60E-01	0.3	2.17	CONNICK & MCVEY (1949)
							n=2		**Figure5.24. 3, middle (ZrCl$_2^{2+}$)**
(Na,H)ClO$_4^-$	25 ?	0.5091	4	1.2364	4.9456	5.13E-01	-0.72	0.85	MAROV & RYABCHIKOV (1962)
(Na,H)ClO$_4^-$	25 ?	0.5091	2	1.1037	2.2074	4.60E-01	-0.20	1.21	MAROV & RYABCHIKOV (1962)
(Na,H)ClO$_4^-$	20	0.5050	6.54	1.45 [1]	9.4830	5.48E-01	0.40	2.06	SOLOVKIN (1957)
(Na,H)ClO$_4^-$	20	0.5050	2	1.1037	2.2074	4.60E-01	-0.62	0.77	PRASILOVA & HAVLICEK (1970)
							n=3		**Figure 5.24.3, bottom (ZrCl$_3^+$)**
(Na,H)ClO$_4^-$	25 ?	0.5091	4	1.2364	4.9456	5.13E-01	-0.62	0.42	MAROV & RYABCHIKOV (1962)
(Na,H)ClO$_4^-$	25 ?	0.5091	2	1.1037	2.2074	4.60E-01	-0.23	0.71	MAROV & RYABCHIKOV (1962)
(Na,H)ClO$_4^-$	20	0.5050	6.54	1.45 [1]	9.4830	5.48E-01	0.19	1.30	SOLOVKIN (1957)
(Na,H)ClO$_4^-$	20	0.5050	2	1.1037	2.2074	4.60E-01	-0.46	0.47	PRASILOVA & HAVLICEK (1970)

---

[1] Value estimated through linear extrapolation

Table 5.24.A4: Experimental data and calculated quantities for SIT regressions, referring to Figure 5.24.4.

Medium	T / $^{\circ}$C	A(T)	I(M)	molality factor	I(m)	$H = I^{0.5} / (1 + 1.5\, I^{0.5})$	$\log_{10}{}^{*}K_n$	$\log_{10}{}^{*}K_n - \Delta z^2 A\, H$	Reference
							n=1		**Figure 5.24.4 ($ZrSO_4^{2+}$)**
$(Na,H)ClO_4^{-}$	25	0.5091	2	1.1019	2.2038	4.60E-01	2.66	5.47	CONNICK & MCVEY (1949)
$(Na,H)ClO_4^{-}$	20	0.5050	2	1.0989	2.1978	4.60E-01	2.60	5.39	PRASILOVA & HAVLICEK (1970)
$(Na,H)ClO_4^{-}$	25	0.5091	2	1.1019	2.2038	4.60E-01	2.57	5.38	WHITEKER & DAVIDSON (1953)
$(Na,H)ClO_4^{-}$	25 ?	0.5091	2.3	1.1180	2.5714	4.71E-01	2.56	5.44	RYABCHIKOV et al. (1962)
$(Na,H)ClO_4^{-}$	25 ?	0.5091	2.3	1.1180	2.5714	4.71E-01	2.67	5.55	RYABCHIKOV et al. (1964)
$(Na,H)ClO_4^{-}$	20	0.5091	4	1.2122	4.8488	5.12E-01	2.85	5.95	AHRLAND et al. (1963)
$(Na,H)ClO_4^{-}$	20	0.5091	4	1.2122	4.8488	5.12E-01	2.80	5.90	NOREN (1969)

APPENDIX A: CALCULATION OF THERMODYNAMIC PROPERTIES

A.1   INTRODUCTION

The Nagra/PSI Chemical Thermodynamic Data Base 01/01 was set up and maintained by using PMATCHC, a **P**rogram to **MA**nage **T**hermo**CH**emical data, written in **C**++. This program (based on PMATCH, PEARSON et al. 1993, a code developed to support the development of the earlier Nagra Thermochemical Data Base, PEARSON & BERNER 1991, PEARSON et al. 1992) was developed and tested in collaboration with S. Dmytriyeva and D. Kulik. PMATCHC serves two main purposes:

1.   It is designed to derive the maximum amount of information following from whatever data have been entered into the database by the user, while maintaining internal consistency among the data. If, e.g., $\log_{10}K°$ of the formation reaction of an aqueous product species is entered, PMATCHC calculates $\Delta_r G°$ and, if values for $\Delta_f G°$ of all participating master species are contained in the data base, also $\Delta_f G°$ of that product species. Conversely, if $\Delta_f G°$ of a product species and all participating master species are known, $\Delta_r G°$ and consequently $\log_{10}K°$ are calculated. A large number of calculation pathways are necessary to allow for the various possible permutations and combinations of data which can be entered (see Table A1).

2.   It allows the output of stored data in a number of user-specified formats. Formatting commands can be collected in external script files that control output formatting and writing. The data tables presented in Appendix B were prepared by using PMATCHC with such script files.

The PMATCHC distribution package is posted on the web for free download at "http://les.web.psi.ch/Software/Index.htm". It includes the source code, executable files for Windows and Linux, a sample database, example script files, and the documentation.

A.2   THERMODYNAMIC QUANTITIES AND EQUILIBRIUM CONSTANTS

Selected thermodynamic data for reactions refer to the reference temperature $T°$ of 298.15 K (25°C) and reference pressure of 0.1 MPa (1 bar) and, for aqueous species, infinite dilution ($I = 0$).

A.2.1 Constants and Units

Thermodynamic data in PMATCHC can be entered, displayed and (or) output in J and kJ or in cal and kcal. Internally, the program calculates and stores data as J and kJ. In the equations below, units of J are used for illustration purposes.

The following constants and conversion factors are used in PMATCHC:

1 cal:	4.184 J
R (gas constant):	8.31451 $J \cdot mol^{-1} \cdot K^{-1}$
ln(10):	2.30259
$T°$:	298.15 K

A.2.2 Reactions, Elements, Solute Species, Minerals and Gases

The reaction parameters include

$\log_{10}K°$:	the equilibrium constant of the reaction (logarithmic)	
$\Delta_r G_m°$:	the molar Gibbs free energy of reaction	$(kJ \cdot mol^{-1})$
$\Delta_r H_m°$:	the molar enthalpy of reaction	$(kJ \cdot mol^{-1})$
$\Delta_r S_m°$:	the molar entropy of reaction	$(J \cdot K^{-1} \cdot mol^{-1})$
$\Delta_r C_{p,m}°$:	the molar heat capacity of reaction	$(J \cdot K^{-1} \cdot mol^{-1})$

The equilibrium constant, $K°$, is related to $\Delta_r G_m°$ according to the following relation,

$$\Delta_r G_m° = - R \cdot T° \cdot \ln(10) \cdot \log_{10}K° \tag{2.1}$$

and the molar quantities $\Delta_r G_m°$, $\Delta_r H_m°$ and $\Delta_r S_m°$ are related according to the Gibbs-Helmholtz equation:

$$\Delta_r G_m° = \Delta_r H_m° - T° \cdot \Delta_r S_m° \tag{2.2}$$

Thermodynamics of individual entities are tabulated using standard state properties of formation from the elements in their reference state,

$\Delta_f G_m°$:	the standard molar Gibbs free energy of formation	$(kJ \cdot mol^{-1})$
$\Delta_f H_m°$:	the standard molar enthalpy of formation	$(kJ \cdot mol^{-1})$
$\Delta_f S_m°$:	the standard molar entropy of formation	$(J \cdot K^{-1} \cdot mol^{-1})$
$\Delta_f C_{p,m}°$:	the standard molar heat capacity of formation	$(J \cdot K^{-1} \cdot mol^{-1})$

or the absolute quantities,

$S_m°$:   the standard molar entropy $(J \cdot K^{-1} \cdot mol^{-1})$

$C_{p,m}°$:   the standard molar heat capacity $(J \cdot K^{-1} \cdot mol^{-1})$

The properties of a reaction are calculated from the standard state properties of its reactants and products as follows:

$$\Delta_r X_m° = \sum \Delta_f X_m°(\text{products}) - \sum \Delta_f X_m°(\text{reactants}) \tag{2.3}$$

where X represents the thermodynamic property and $\sum$ throughout this appendix is the stoichiometric sum, the sum of the products of the property of the product or reactant times its stoichiometric coefficient.

The standard molar quantities $\Delta_f G_m°$, $\Delta_f H_m°$ and $\Delta_f S_m°$ are related according to the Gibbs-Helmholtz equation:

$$\Delta_f G_m° = \Delta_f H_m° - T° \cdot \Delta_f S_m° \tag{2.4}$$

For neutral species

$$\Delta_f S_m° = S_m° - \sum S_m°(\text{elements}) \tag{2.5}$$

$$\Delta_f C_{p,m}° = C_{p,m}° - \sum C_{p,m}°(\text{elements}) \tag{2.6}$$

and for charged species

$$\Delta_f S_m° = S_m° - \sum S_m°(\text{elements}) + n\, S_m°(e^-) \tag{2.7}$$

$$\Delta_f C_{p,m}° = C_{p,m}° - \sum C_{p,m}°(\text{elements}) + n\, C_{p,m}°(e^-) \tag{2.8}$$

in which n is the charge. The values of $S_m°(e^-)$ and $C_{p,m}°(e^-)$ are $1/2\, S_m°(H_2, g)$ and $1/2\, C_{p,m}°(H_2, g)$ because e^- and $H_2(g)$ are related by:

$$1/2\, H_2(g) - e^- = H^+ \tag{2.8a}$$

and all properties of H^+ are zero by convention (SILVA *et al.* 1995 Section II.1.6.5, WAGMAN *et al.* 1982 p. 2-22).

NOTE: In order to calculate correctly, the present version of PMATCHC requires that $S_m°(e^-)$ and $C_{p,m}°(e^-)$ equal the **negative** of $1/2 S_m°(H_2, g)$ and $1/2\, C_{p,m}°(H_2, g)$.

Some gas data are given at 1 atm (0.101325 MPa) in their original sources. The entropy values of gases are sensitive to pressure and were converted from 1 atm to 1 bar using equations given by WAGMAN *et al.* (1982, p. 2-23):

$$S_m°(\text{bar}) - S_m°(\text{atm}) = R \cdot \ln(1.01325/1.0) = 0.1094 \text{ J} \cdot K^{-1} \cdot mol^{-1} \qquad (2.9)$$

A.3   THERMODYNAMIC EQUATIONS

The equations given in this section are largely duplicates of those given above in Sections 2.1 through 2.3.

The equation of MAIER & KELLEY (1932) is widely used to express the variation of the molar heat capacity at constant pressure, $C_{p,m}°$, with absolute temperature, T. When applied to a reaction, this equation is written:

$$\Delta_r C_{p,m}°(T) = \Delta_r a + \Delta_r b \cdot T - \Delta_r c / T^2 \qquad (3.1)$$

where $\Delta_r a$, $\Delta_r b$ and $\Delta_r c$ are constants. It can also be applied to heat capacities of formation:

$$\Delta_f C_{p,m}°(T) = \Delta_f a + \Delta_f b \cdot T - \Delta_f c / T^2 \qquad (3.1a)$$

where $\Delta_f a$, $\Delta_f b$ and $\Delta_f c$ are constants.

Integration of equation (3.1) leads to the following equation relating $\log_{10} K°(T)$ values to temperature:

$$\log_{10} K°(T) = A + B \cdot T + C / T + D \cdot \log_{10}(T) + E / T^2 \qquad (3.2)$$

This equation is embodied in PMATCHC and PHREEQC (PARKHURST & APPELO 1999), and has been adopted for the Nagra/PSI Chemical Thermodynamic Data Base.

The following equations show the relations between the temperature dependent equilibrium constant, $\log_{10} K°(T)$, and such other thermodynamic properties of reaction as $\Delta_r G_m°$, $\Delta_r H_m°$, $\Delta_r S_m°$, $\Delta_r C_{p,m}°$ and $\Delta_r a$, $\Delta_r b$ and $\Delta_r c$ of the heat capacity equation.

$$\Delta_r G_m°(T) = - R \cdot T \cdot \ln(10) \cdot \log_{10} K°(T) \qquad (3.3)$$

$$\Delta_r G_m°(T) = - R \cdot \ln(10) \cdot (A \cdot T + B \cdot T^2 + C + D \cdot T \cdot \log_{10}(T) + E / T) \qquad (3.4)$$

$$\Delta_r H_m°(T) = R \cdot T^2 \cdot \ln(10) \cdot (\partial \log_{10} K°(T) / \partial T) \qquad (3.5)$$

$$\Delta_r H_m°(T) = R \cdot \ln(10) \cdot (B \cdot T^2 - C + D \cdot T / \ln(10) - 2 \cdot E / T) \qquad (3.6)$$

$$\Delta_r S_m°(T) = - \partial \Delta_r G_m°(T) / \partial T \qquad (3.7)$$

$$\Delta_r S_m{}^\circ(T) = R \cdot \ln(10) \cdot (A + 2 \cdot B \cdot T + D / \ln(10) \cdot (1 + \ln(T)) - E / T^2) \qquad (3.8)$$

$$\Delta_r C_{p,m}{}^\circ(T) = \partial \Delta_r H_m{}^\circ(T) / \partial T \qquad (3.9)$$

$$\Delta_r C_{p,m}{}^\circ(T) = R \cdot \ln(10) \cdot (2 \cdot B \cdot T + D / \ln(10) + 2 \cdot E / T^2) \qquad (3.10)$$

$$\Delta_r a = R \cdot D \qquad (3.11)$$

$$\Delta_r b = 2 \cdot R \cdot \ln(10) \cdot B \qquad (3.12)$$

$$\Delta_r c = -2 \cdot R \cdot \ln(10) \cdot E \qquad (3.13)$$

If sufficient experimental data are available to define all five coefficients A through E, the values of the Gibbs energy, enthalpy, entropy, heat capacity, and all three coefficients $\Delta_r a$, $\Delta_r b$ and $\Delta_r c$ of the heat capacity expression, can be found using the above equations. It is also necessary to be able to calculate values of the coefficients A through E of the $\log_{10} K^\circ(T)$ equation from thermodynamic properties of a reaction. If the coefficients $\Delta_r a$, $\Delta_r b$ and $\Delta_r c$ of the heat capacity equation are available, the coefficients B, D and E are calculated according to:

$$E = -\Delta_r c / (2 \cdot R \cdot \ln(10)) \qquad (3.14)$$

$$D = \Delta_r a / R \qquad (3.15)$$

$$B = \Delta_r b / (2 \cdot R \cdot \ln(10)) \qquad (3.16)$$

The coefficient C is calculated using $\Delta_r H_m{}^\circ$ at the reference temperature T°:

$$C = B \cdot T^{\circ 2} + D \cdot T^\circ / \ln(10) - 2 \cdot E / T^\circ - \Delta_r H_m{}^\circ(T^\circ) / (R \cdot \ln(10)) \qquad (3.17)$$

$$C = (\Delta_r b / 2 \cdot T^{\circ 2} + \Delta_r a \cdot T^\circ + \Delta_r c / T^\circ - \Delta_r H_m{}^\circ(T^\circ)) / (R \cdot \ln(10)) \qquad (3.18)$$

A is calculated from $\Delta_r S_m{}^\circ$ at the reference temperature T°:

$$A = \Delta_r S_m{}^\circ(T^\circ) / (R \cdot \ln(10)) - 2 \cdot B \cdot T^\circ \\ - D / \ln(10) \cdot (1 + \ln(T^\circ)) + E / T^{\circ 2} \qquad (3.19)$$

$$A = (\Delta_r S_m{}^\circ(T^\circ) - \Delta_r b \cdot T^{\circ 2} - \Delta_r a \cdot (1 + \ln(T^\circ)) \\ - \Delta_r c / (2 \cdot T^{\circ 2})) / (R \cdot \ln(10)) \qquad (3.20)$$

If $\Delta_r C_{p,m}{}^\circ$ is known only at the reference temperature T°, it is often assumed to be constant with temperature. In this case, $\Delta_r C_{p,m}{}^\circ = \Delta_r a$ and $\Delta_r b = \Delta_r c = 0$, so that B = E = 0, and the expression for $\log_{10} K^\circ(T)$ has the form:

$$\log_{10} K^\circ(T) = A + C / T + D \cdot \log_{10}(T) \qquad (3.21)$$

This equation is called the three-term approximation of temperature dependence. From the equations above it follows that:

$$D = \Delta_r C_{p,m}^{\circ} / R \tag{3.22}$$

$$C = (\Delta_r C_{p,m}^{\circ} \cdot T^{\circ} - \Delta_r H_m^{\circ}(T^{\circ})) / (R \cdot \ln(10)) \tag{3.23}$$

$$A = (\Delta_r S_m^{\circ}(T^{\circ}) - \Delta_r C_{p,m}^{\circ} \cdot (1 + \ln(T^{\circ}))) / (R \cdot \ln(10)) \tag{3.24}$$

For most reactions, $\Delta_r C_{p,m}^{\circ}$ is not known and it must be assumed that $\Delta_r H_m^{\circ}$ is constant with temperature. In this case, $B = D = E = 0$, and the expression for $\log_{10} K^{\circ}(T)$ has the form:

$$\log_{10} K^{\circ}(T) = A + C / T \tag{3.25}$$

This equation is called the two-term approximation of temperature dependence. From the equations above it follows that:

$$C = - \Delta_r H_m^{\circ}(T^{\circ}) / (R \cdot \ln(10)) \tag{3.26}$$

$$A = \Delta_r S_m^{\circ}(T^{\circ}) / (R \cdot \ln(10)) \tag{3.27}$$

$$\log_{10} K^{\circ}(T) = \log_{10} K^{\circ}(T^{\circ}) + \Delta_r H_m^{\circ}(T^{\circ}) / (R \cdot \ln(10)) \cdot (1 / T^{\circ} - 1 / T) \tag{3.28}$$

Equation (3.28) is the integrated van't Hoff equation as used in MINEQL (WESTALL et al. 1976), PHREEQC (PARKHURST & APPELO 1999) and other geochemical programs.

A.4   PMATCHC CALCULATION SCHEME

The calculation scheme in PMATCHC is designed to derive the maximum amount of information from whatever data have been entered into the database by the user, while maintaining the priority given to reaction data. Numerical records in PMATCHC are in one of three possible states: Entered, Calculated of Null (no data entered or calculated). Calculated values are flagged within the database (and indicated by an asterisk in the data tables in Appendix B) so they can be distinguished from data entered by the user.

A number of calculation pathways are necessary to allow for the various permutations and combinations of data which can be entered. These are summarised in Table A1. No attempt has been made to include all possible permutations and combinations of thermodynamic data entry in the calculation scheme. Rather, a user with a combination of data for a species, solid or gas that does not match any of the cases included in PMATCHC is expected to modify the form available for data entry to one of the existing cases by judicious addition of zero values or calculations external to PMATCHC. In any case, PMATCHC checks the data entered in the database and performs the first calculations for which sufficient data are available.

A.5   IMPLICIT ASSUMPTIONS

For the purposes of the Nagra/PSI Chemical Thermodynamic Data Base 01/01 it was decided to concentrate on the evaluation of thermodynamic data at 25°C. Therefore, no special efforts were made to gather data on the temperature dependence of equilibrium constants. This is reflected in the kind of data entered in PMATCHC. For the majority of secondary master species, aqueous product species, solids and gases (counting beans: 268 of a total 456, or 59%) only $\log_{10}K°$ was entered and in an additional 101 cases only $\log_{10}K°$ and either $\Delta_r H_m°$ or $\Delta_r S_m°$. Thus, for 369 of the 456 equilibria represented in the database (81%) there is no heat capacity information that would enable the rigorous extrapolation of equilibrium constants to temperatures higher than 25°C.

In the present version of PMATCHC the following assumptions are made if not enough heat capacity data are entered to represent the temperature dependence of an equilibrium constant (compare with Table A1):

1)   **Calculation cases 10, 15, 16, 17, 21a, and 22a:**

If only $\log_{10}K°$, $\Delta_r G_m°$, $\Delta_r H_m°$ and $\Delta_r S_m°$ of an equilibrium are known but no heat capacity data are given, it is assumed that $\Delta_r C_{p,m}°$ is zero and that it remains zero at any temperature (as a consequence $\Delta_r a$, $\Delta_r b$, and $\Delta_r c$ are also set to zero, see eq. 3.1). This ultimately leads to the integrated van't Hoff equation (also called two-term approximation) for the temperature dependence of the equilibrium constant and only the coefficients A and C of the temperature-dependent logK expression, see eq. (3.2), are non-zero.

If $\Delta_f C_{p,m}°$, or $\Delta_f a$, $\Delta_f b$ and $\Delta_f c$, see eq. (3.1a), are known for all master species participating in the reaction, values for the corresponding entities of the product species (aqueous product species, solid or gas) can be calculated from $\Delta_r C_{p,m}° = \Delta_r a = \Delta_r b = \Delta_r c = 0$.

Note that in this case, the values calculated for $\Delta_f C_{p,m}°$, $\Delta_f a$, $\Delta_f b$, and $\Delta_f c$ depend on how the formation reaction is written (i.e. which master species are used)! However, $\Delta_f C_{p,m}°$, $\Delta_f a$, $\Delta_f b$, and $\Delta_f c$ are properties of formation from the elements and **should be independent from how the formation reaction from master species is formulated**. These values are therefore dubious and are only correct if it can be shown that $\Delta_r C_{p,m}°$ of the formation reaction from the master species is actually zero or nearly so.

Table A1: Summary of PMATCHC calculation cases.

Property	PMATCHC Field Name	logK(T) Coefficients Entered				Properties of Reaction Entered				
		1	**2**	**3**	**4**	**6**	**7**	**8**	**9**	**10**
EQUILIBRIUM CONSTANT										
A Coef. logK(T) expression	ALGK	E	E	E	E	3.19	3.19	3.19	3.19	3.19
B Coef. logK(T) expression	BLGK	E	E	set to 0	set to 0	3.16	3.16	3.16 $\Rightarrow$ 0	3.16 $\Rightarrow$ 0	3.16 $\Rightarrow$ 0
C Coef. logK(T) expression	CLGK	E	E	E	E	3.17	3.17	3.17	3.17	3.17
D Coef. logK(T) expression	DLGK	E	E	E	set to 0	3.15	3.15	3.15	3.15	3.15 $\Rightarrow$ 0
E Coef. logK(T) expression	ELGK	E	set to 0	set to 0	set to 0	3.14	3.14 $\Rightarrow$ 0	3.14 $\Rightarrow$ 0	3.14 $\Rightarrow$ 0	3.14 $\Rightarrow$ 0
logK(25 °C)	LGK25	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2
PROPERTIES OF REACTION										
$\Delta_r G_m°$	DGR	3.4	3.4	3.4	3.4	E or 2.2	E or 2.2	E or 2.2	E or 2.2	E or 2.2
$\Delta_r H_m°$	DHR	3.6	3.6	3.6	3.6	E or 2.2	E or 2.2	E or 2.2	E or 2.2	E or 2.2
$\Delta_r S_m°$	DSR	3.8	3.8	3.8	3.8	E or 2.2	E or 2.2	E or 2.2	E or 2.2	E or 2.2
$\Delta_r C_{p,m}°$	D25CPR	3.1	3.1	3.1	3.1 $\Rightarrow$ 0	3.1	3.1	3.1	E	set to 0
$\Delta_r a$: Maier-Kelley	DACPR	3.11	3.11	3.11	3.11 $\Rightarrow$ 0	E	E	E	set to $\Delta_r C_{p,m}°$	set to 0
$\Delta_r b$: Maier-Kelley	DBCPR	3.12	3.12	3.12 $\Rightarrow$	3.12 $\Rightarrow$ 0	E	E	set to 0	set to 0	set to 0
$\Delta_r c$: Maier-Kelley	DCCPR	3.13	3.13 $\Rightarrow$	3.13 $\Rightarrow$	3.13 $\Rightarrow$ 0	E	set to 0	set to 0	set to 0	set to 0
PROPERTIES OF FORMATION OF ALL ENTITIES IN REACTION										
Reaction Stoichiometry	STOICH	E	E	E	E	E	E	E	E	E
$\Delta_f G_m°$	GF	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
$\Delta_f H_m°$	HF	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
$\Delta_f S_m°$	SF	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
$\Delta_f C_{p,m}°$	CP25F	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
a: Maier-Kelley	CPAF	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
b: Maier-Kelley	CPBF	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
c: Maier-Kelley	CPCF	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
ABSOLUTE PROPERTIES OF ALL ENTITIES IN REACTION										
$S_m°$	S0									
$C_{p,m}°$	CP0									

Legend:
E   Data entered
3.4   Calculated using eq. (3.4)
3.1 $\Rightarrow$ 0   Calculated to be zero from eq. (3.1)
--   Blank: Not entered or insufficient data to calculate

Table A1: continued

Property	PMATCHC Field Name	Properties of Formation Entered					Mixed and Single Value Properties Entered			
		11	**12**	**13**	**14**	**15**	**16**	**116a**	**116b**	**116c**
EQUILIBRIUM CONSTANT										
A Coef. logK(T) expression	ALGK	3.19	3.19	3.19	3.19	3.19	3.19	3.19	3.19	3.19
B Coef. logK(T) expression	BLGK	3.16	3.16	3.16	3.16	3.16 $\Rightarrow$ 0	3.16 $\Rightarrow$ 0	3.16	3.16	3.16 $\Rightarrow$ 0
C Coef. logK(T) expression	CLGK	3.17	3.17	3.17	3.17	3.17	3.17	3.17	3.17	3.17
D Coef. logK(T) expression	DLGK	3.15	3.15	3.15	3.15	3.15 $\Rightarrow$ 0	3.15 $\Rightarrow$ 0	3.15	3.15	3.15
E Coef. logK(T) expression	ELGK	3.14	3.14	3.14	3.14	3.14 $\Rightarrow$ 0	3.14 $\Rightarrow$ 0	3.14	3.14 $\Rightarrow$ 0	3.14 $\Rightarrow$ 0
logK(25°C)	LGK25	3.2	3.2	3.2	3.2	3.2	E	E	E	E
PROPERTIES OF REACTION										
$\Delta_r G_m°$	DGR	2.3	2.3	2.3	2.3	2.3	2.1	2.1	2.1	2.1
$\Delta_r H_m°$	DHR	2.3	2.3	2.3	2.3	2.3	E or 2.2	E or 2.2	E or 2.2	E or 2.2
$\Delta_r S_m°$	DSR	2.3	2.3	2.3	2.3	2.3	E or 2.2	E or 2.2	E or 2.2	E or 2.2
$\Delta_r C_{p,m}°$	D25CPR	3.1	3.1	3.1	3.1	set to 0	set to 0	3.1	3.1	3.1
$\Delta_r a$: Maier-Kelley	DACPR	2.3	2.3	2.3	2.3	set to 0	set to 0	E	E	E
$\Delta_r b$: Maier-Kelley	DBCPR	2.3	2.3	2.3	2.3	set to 0	set to 0	E	E	set to 0
$\Delta_r c$: Maier-Kelley	DCCPR	2.3	2.3	2.3	2.3	set to 0	set to 0	E	set to 0	set to 0
PROPERTIES OF FORMATION OF ALL ENTITIES IN REACTION										
Reaction Stoichiometry	STOICH	E	E	E	E	E	E	E	E	E
$\Delta_f G_m°$	GF	E or 2.4	E or 2.4	E or 2.4	E or 2.4	E or 2.4	2.3	2.3	2.3	2.3
$\Delta_f H_m°$	HF	E or 2.4	E or 2.4	E or 2.4	E or 2.4	E or 2.4	2.3	2.3	2.3	2.3
$\Delta_f S_m°$	SF	E or 2.4	E or 2.4	E or 2.4	E or 2.4	E or 2.4	2.3	2.3	2.3	2.3
$\Delta_f C_{p,m}°$	CP25F	3.1a	3.1a	3.1a	E	2.3	2.3	2.3	2.3	2.3
a: Maier-Kelley	CPAF	E	E	E	set to $\Delta_f C_{p,m}°$	2.3	2.3	2.3	2.3	2.3
b: Maier-Kelley	CPBF	E	E	set to 0	set to 0	2.3	2.3	2.3	2.3	2.3
c: Maier-Kelley	CPCF	E	set to 0	set to 0	set to 0	2.3	2.3	2.3	2.3	2.3
ABSOLUTE PROPERTIES OF ALL ENTITIES IN REACTION										
$S_m°$	S0									
$C_{p,m}°$	CP0									

Table A1: continued

Property	PMATCHC Field Name	Mixed and Single Value Properties Entered						
		116d	**17**	**117a**	**117b**	**117c**	**117d**	**17a**
EQUILIBRIUM CONSTANT								
A Coef. logK(T) expression	ALGK	3.19	3.19	3.19	3.19	3.19	3.19	3.19
B Coef. logK(T) expression	BLGK	3.16 ⇒ 0	3.16 ⇒ 0	3.16	3.16	3.16	3.16	3.16
C Coef. logK(T) expression	CLGK	3.17	3.17	3.17	3.17	3.17	3.17	3.17
D Coef. logK(T) expression	DLGK	3.15	3.15 ⇒ 0	3.15	3.15	3.15	3.15	3.15
E Coef. logK(T) expression	ELGK	3.14 ⇒ 0	3.14 ⇒ 0	3.14	3.14	3.14	3.14	3.14
logK(25 °C)	LGK25	E	E	E	E	E	E	E
PROPERTIES OF REACTION								
$\Delta_r G_m°$	DGR	2.1	2.1	2.1	2.1	2.1	2.1	2.1
$\Delta_r H_m°$	DHR	E or 2.2	2.3	2.3	2.3	2.3	2.3	2.3
$\Delta_r S_m°$	DSR	E or 2.2	2.3	2.3	2.3	2.3	2.3	2.2
$\Delta_r C_{p,m}°$	D25CPR	E	set to 0	3.1	3.1	3.1	3.1	3.1
$\Delta_r a$: Maier-Kelley	DACPR	set to $\Delta_r C_{p,m}°$	set to 0	2.3	2.3	2.3	2.3	2.3
$\Delta_r b$: Maier-Kelley	DBCPR	set to 0	set to 0	2.3	2.3	2.3	2.3	2.3
$\Delta_r c$: Maier-Kelley	DCCPR	set to 0	set to 0	2.3	2.3	2.3	2.3	2.3
PROPERTIES OF FORMATION OF ALL ENTITIES IN REACTION								
Reaction Stoichiometry	STOICH	E	E	E	E	E	E	E
$\Delta_f G_m°$	GF	2.3	2.3	2.3	2.3	2.3	2.3	2.3
$\Delta_f H_m°$	HF	2.3	E or 2.4	E or 2.4	E or 2.4	E or 2.4	E or 2.4	2.4
$\Delta_f S_m°$	SF	2.3	E or 2.4	E or 2.4	E or 2.4	E or 2.4	E or 2.4	E see Note
$\Delta_f C_{p,m}°$	CP25F	2.3	2.3	3.1a	3.1a	3.1a	E	E see Note
a: Maier-Kelley	CPAF	2.3	2.3	E	E	E	set to $\Delta_f C_{p,m}°$	set to 0 or $\Delta_f C_{p,m}°$
b: Maier-Kelley	CPBF	2.3	2.3	E	E	set to 0	set to 0	set to 0
c: Maier-Kelley	CPCF	2.3	2.3	E	set to 0	set to 0	set to 0	set to 0
ABSOLUTE PROPERTIES OF ALL ENTITIES IN REACTION								
$S_m°$	S0							E see Note
$C_{p,m}°$	CP0							E see Note

Note:
Values for $\Delta_f S_m°$ and $\Delta_f C_{p,m}°$ (designated SFE and CP25FE) can also be calculated from $S_m°$ and $C_{p,m}°$ data for elements and other entities using eqs. (2.7) or (2.8). If values for both SF and SFE, and for CP25F and CP25FE are present they are compared. If they differ by more than 0.01, an error message appears on the screen. For case 17a, SFE and possibly CP25FE are available and can be used to enter the missing SF and CP25F.

Table A1:   continued

Property	PMATCHC Field Name	Mixed and Single Value Properties Entered			Absolute Entropy (and Absolute Heat Capacity) Entered			
		18	19	20	21a	21b	22a	22b
EQUILIBRIUM CONSTANT								
A Coef. logK(T) expression	ALGK	set to logK (25°C)	set to logK (25°C)	set to logK (25°C)	3.19	3.19	3.19	3.19
B Coef. logK(T) expression	BLGK	--	--	--	3.16 ⇒ 0	3.16 ⇒ 0	3.16 ⇒ 0	3.16 ⇒ 0
C Coef. logK(T) expression	CLGK	--	--	--	3.17	3.17	3.17	3.17
D Coef. logK(T) expression	DLGK	--	--	--	3.15 ⇒ 0	3.15	3.15 ⇒ 0	3.15
E Coef. logK(T) expression	ELGK	--	--	--	3.14 ⇒ 0	3.14 ⇒ 0	3.14 ⇒ 0	3.14 ⇒ 0
logK(25 °C)	LGK25	E	2.1	2.1	3.2	3.2	3.2	3.2
PROPERTIES OF REACTION								
$\Delta_r G_m°$	DGR	2.1	E	2.3	2.2	2.2	2.3	2.3
$\Delta_r H_m°$	DHR	--	--	--	2.3	2.3	2.2	2.2
$\Delta_r S_m°$	DSR	--	--	--	2.12	2.12	2.12	2.12
$\Delta_r C_{p,m}°$	D25CPR	--	--	--	set to 0	2.13	set to 0	2.13
$\Delta_r a$: Maier-Kelley	DACPR	--	--	--	set to 0	set to $\Delta_r C_{p,m}°$	set to 0	set to $\Delta_r C_{p,m}°$
$\Delta_r b$: Maier-Kelley	DBCPR	--	--	--	set to 0	set to 0	set to 0	set to 0
$\Delta_r c$: Maier-Kelley	DCCPR	--	--	--	set to 0	set to 0	set to 0	set to 0
PROPERTIES OF FORMATION OF ALL ENTITIES IN REACTION								
Reaction Stoichiometry	STOICH	E	E	E	E	E	E	E
$\Delta_f G_m°$	GF	2.3	2.3	E	2.3	2.3	E	E
$\Delta_f H_m°$	HF	--	--	--	E	E	2.3	2.3
$\Delta_f S_m°$	SF	--	--	--	2.4	2.4	2.4	2.4
$\Delta_f C_{p,m}°$	CP25F	--	--	--	2.3	2.3	2.3	2.3
a: Maier-Kelley	CPAF	--	--	--	2.3	2.3	2.3	2.3
b: Maier-Kelley	CPBF	--	--	--	2.3	2.3	2.3	2.3
c: Maier-Kelley	CPCF	--	--	--	2.3	2.3	2.3	2.3
ABSOLUTE PROPERTIES OF ALL ENTITIES IN REACTION								
$S_m°$	S0				E	E	E	E
$C_{p,m}°$	CP0				--	E	--	E

Legend:
E   Data entered
3.4   Calculated using eq. (3.4)
3.1 ⇒ 0   Calculated to be zero from eq. (3.1)
--   Blank: Not entered or insufficient data to calculate

2) **Calculation cases 9, 116d, 21b, and 22b:**

If only $\log_{10}K°$, $\Delta_r G_m°$, $\Delta_r H_m°$, $\Delta_r S_m°$, and $\Delta_r C_{p,m}°$ of an equilibrium are known but no further heat capacity data are given, it is assumed that $\Delta_r C_{p,m}°$ is constant with temperature (as a consequence, $\Delta_r a$ is set to $\Delta_r C_{p,m}°$, and $\Delta_r b$ and $\Delta_r c$ are both set to zero). This leads to the three-term approximation of temperature dependence and only A, C, and D are non-zero.

If $\Delta_f C_{p,m}°$, or $\Delta_f a$, $\Delta_f b$ and $\Delta_f c$ are known for all master species participating in the reaction, values for the corresponding entities of the product species can be calculated from $\Delta_r C_{p,m}° = \Delta_r a$ and $\Delta_r b = \Delta_r c = 0$. These values of the product species are only correct if it can be shown that the three-term approximation gives a reasonable representation of the temperature dependence of the equilibrium constant.

3) **Calculation cases 14, 117d, and 17a:**

If only $\log_{10}K°$, $\Delta_r G_m°$, $\Delta_r H_m°$, and $\Delta_r S_m°$ of an equilibrium are known, as well as $\Delta_f C_{p,m}°$ of the product species and $\Delta_f a$, $\Delta_f b$, $\Delta_f c$, and $\Delta_f C_{p,m}°$ of all master species involved in the reaction, it is assumed that $\Delta_f C_{p,m}°$ for the product species is constant with temperature. As a consequence, $\Delta_f a$ for the product species is set to $\Delta_f C_{p,m}°$, and $\Delta_f b$ and $\Delta_f c$ are both set to zero. If $\Delta_f a$, $\Delta_f b$ and $\Delta_f c$ are known for all master species involved in the formation reaction of the product species, $\Delta_r a$, $\Delta_r b$, $\Delta_r c$, and $\Delta_r C_{p,m}°$ can be calculated.

Note that these calculation cases were not used in the preparation of the Nagra/PSI Chemical Thermodynamic Data Base 01/01.

4) **Calculation cases 18, 19, and 20:**

If only $\log_{10}K°$ and $\Delta_r G_m°$ of an equilibrium are known, all other properties of reaction are left blank. All temperature coefficients of the heat capacity equations are left blank except A, which is set to $\log_{10}K°$.

All aqueous species, solids and gases in the Nagra/PSI Chemical Thermodynamic Data Base 01/01 for which thermodynamic data were calculated according to the calculation cases discussed above (except cases 18, 19, and 20) are listed in Table A2.

Table A2:   List of aqueous species, solids and gases from the Nagra/PSI Chemical Thermo-dynamic Data Base 01/01 which are affected by the implicit assumptions of the present version of PMATCHC. Species for which heat capacity data of formation from the elements are calculated (see text for a discussion) are set bold. The numbers refer to the calculation cases of Table A1.

Secondary Master Species

Al(OH)4-	9	Eu+2	15	Fe+3	16	**U+4**	17
		HS-	15	H2PO4-	16	**UO2+**	17
		Np+3	15	H3PO4	16		
		Np+4	15	**NH3**	16		
		NpO2+	15	PO4-3	16		
		Pu+3	15	**SiO(OH)3-**	16		
		Pu+4	15	**SiO2(OH)2-2**	16		
		PuO2+	15				
		S2O3-2	15				
		SO3-2	15				

Product Species

Al(OH)2+	9	Fe(SO4)2-	16	NiSO4	16	SrSO4	16
Al(OH)3	9	Fe2(OH)2+4	16	Np(SO4)2	16	**U(CO3)5-6**	16
AlOH+2	9	Fe3(OH)4+5	16	NpF+3	16	**U(SO4)2**	16
		FeCl+2	16	NpO2(CO3)3-4	16	**UCl+3**	16
UF4	10	FeF+2	16	**NpO2(CO3)3-5**	16	**UF+3**	16
UOH+3	10	FeF2+	16	NpO2(SO4)2-2	16	**UF2+2**	16
		FeF3	16	NpO2SO4	16	**UF3+**	16
As(OH)4-	15	FeOH+	16	**NpO2SO4-**	16	**UO2(CO3)2-2**	16
AsO4-3	15	FeOH+2	16	NpSO4+2	16	**UO2(CO3)3-4**	16
H2AsO4-	15	FeSO4	16	Pu(SO4)2-	16	**UO2(SO4)2-2**	16
H3AsO4	15	FeSO4+	16	PuF+3	16	**UO2Cl+**	16
HSO3-	15	**H2S**	16	PuF2+2	16	**UO2Cl2**	16
		H2SeO3	16	PuO2(CO3)2-2	16	**UO2CO3**	16
(UO2)3(CO3)6-6	16	HSeO3-	16	PuO2(CO3)3-4	16	**UO2F+**	16
AlF+2	16	KSO4-	16	PuO2(CO3)3-5	16	**UO2F2**	16
AlF2+	16	MgF+	16	PuO2(SO4)2-2	16	**UO2F3-**	16
AlF3	16	MgSO4	16	PuO2OH+	16	**UO2F4-2**	16
AlF4-	16	**MnOH+**	16	PuO2SO4	16	**UO2SO4**	16
AlF5-2	16	**MnSO4**	16	PuOH+3	16	**USO4+2**	16
AlF6-3	16	NaCO3-	16	PuSO4+	16		
CaF+	16	NaSO4-	16	RaCl+	16	Ni(OH)2	17
CaSO4	16	Ni2OH+3	16	RaCO3	16	Ni(OH)3-	17
Fe(OH)2+	16	Ni4(OH)4+4	16	RaOH+	16	ZrF+3	17
Fe(OH)3	16	NiOH+	16	RaSO4	16	ZrF2+2	17
Fe(OH)4-	16	NiP2O7-2	16	SeO4-2	16	ZrF3+	17
						ZrF4	17

Solids

Gibbsite	9	**Graphite**	15	Brucite	16	Eu(OH)3(cr)	17
		Mo(cr)	15	Dolomite(dis)	16		
		Molybdite	15	Dolomite(ord)	16		
		Nb2O5(cr)	15	**Hausmannite**	16		
		NbO2(cr)	15	**Kaolinite**	16		
		Pd(cr)	15	**NpO2OH(am,ag)**	16		
		Quartz	15	**NpO2OH(am,fr)**	16		
		S(rhomb)	15	**Portlandite**	16		
		Se(cr)	15	**Pyrolusite**	16		
		Sn(cr)	15	RaCO3(cr)	16		
		Tugarinovite	15	RaSO4(cr)	16		
				SiO2(am)	16		

Gases

H2S(g)	16

A.6 REFERENCES

MAIER, C. G. & KELLEY, K. K. (1932): An Equation for the Representation of High-Temperature Heat Content Data. Journal of the American Chemical Society, 54, 3243-3246.

PARKHURST, D.L. & APPELO, C.A.J. (1999): User's Guide to PHREEQC (Version 2) - A Computer Program for Speciation, Batch-Reaction, One-Dimensional-Transport, and Inverse Geochemical Calculations. Water-Resources Investigations Report 99-4259, U.S. Geological Survey, Denver, CO, 312 pp.

PEARSON, F.J., JR. & BERNER, U. (1991): Nagra Thermochemical Data Base I. Core Data. Nagra Technical Report NTB 91-17, Nagra, Wettingen, Switzerland, 70 pp.

PEARSON, F.J., JR., BERNER, U. & HUMMEL, W. (1992): Nagra Thermochemical Data Base II. Supplemental Data 05/92. Nagra Technical Report NTB 91-18, Nagra, Wettingen, Switzerland, 284 pp.

PEARSON, F.J., JR, AVIS, J.D., NILSSON, K. & SKYTTE JENSEN, B. (1993): Geochemical databases - Part I: Pmatch: A program to manage thermochemical data - Part II: The experimental validation of geochemical computer models: Final Report EUR 14170 EN, Commission of the European Communities, Luxembourg, 397 pp.

SILVA, R.J., BIDOGLIO, G., RAND, M.H., ROBOUCH, P.B., WANNER, H. & PUIGDOMENECH, I. (1995): Chemical Thermodynamics of Americium. Chemical Thermodynamics, Vol. 2, North-Holland, Amsterdam, 374 pp.

WAGMAN, D.D., EVANS, W.H., PARKER, V.B., SCHUMM, R.H., HALOW, I., BAILEY, S.M., CHURNEY, K.L. & NUTTALL, R.L. (1982): The NBS tables of chemical thermodynamic properties: Selected values for inorganic and C_1 and C_2 organic substances in SI units. Journal of Physical and Chemical Reference Data, 11, Supplement No. 2, 1-392.

WESTALL, J.C., ZACHARY, J.L. & MOREL, F.M.M (1976): MINEQL - A computer program for the calculation of chemical equilibrium compositions of aqueous systems. Technical Note No. 18, Water Quality Laboratory, Ralph M. Parsons Laboratory for Water Resources and Environmental Engineering, Department for Civil Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, 91pp.

APPENDIX B: TABLES OF RECOMMENDED THERMODYNAMIC PROPERTIES

All data tables were created with PMATCHC, Version 1.1 for Win32, 3-9-2001 (see Appendix A) with only minor manual editing. Derived thermodynamic properties calculated by PMATCHC from "primary" thermodynamic properties, the latter of which are contained in the backup file AUG20.BAC, are followed by an asterisk (*).

Standard state data refer to 25˚C and 1 bar.

Explanations to Table B1:   Reaction properties

$\log_{10} K°$	Equilibrium constant	
$\Delta_r G_m°$	Gibbs free energy of reaction	kJ·mol^{-1}
$\Delta_r H_m°$	Enthalpy of reaction	kJ·mol^{-1}
$\Delta_r S_m°$	Entropy of reaction	J·mol^{-1}·K^{-1}
$\Delta_r C_{p,m}°$	Isobaric heat capacity of reaction	J·mol^{-1}·K^{-1}

Values of $\log_{10} K°$ set in *italics* were calculated from $\Delta_r G_m°$ and had to be entered manually into the table.

Explanations to Table B2:   Properties of formation from the elements and absolute properties

$\Delta_f G_m°$	Gibbs free energy of formation from the elements	kJ·mol^{-1}
$\Delta_f H_m°$	Enthalpy of formation from the elements	kJ·mol^{-1}
$\Delta_f S_m°$	Entropy of formation from the elements	J·mol^{-1}·K^{-1}
$S_m°$	Entropy	J·mol^{-1}·K^{-1}
$C_{p,m}°$	Isobaric heat capacity	J·mol^{-1}·K^{-1}
a, b	Extended Debye-Hückel or WATEQ a parameter,	

and WATEQ b parameter for the activity coefficient γ

$$\log_{10}\gamma = \frac{-Az^2\sqrt{I}}{1 + Ba\sqrt{I}} + bI$$

where A and B are constants at a given temperature,

z is the charge, and I the ionic strength

Explanations to Table B3: Parameters of temperature dependent equilibrium constants

A, B, C, D, E Coefficents of the temperature dependent $\log_{10}K$ equation

$$\log_{10}K(T) = A + BT + C/T + D \log_{10}T + E/T^2$$

Note that species and minerals or solids for which only A has a non-zero value were omitted from the table. Only non-zero values are shown, entries for coefficients with a value of zero were left blank.

Explanations to Table B4: Heat capacities and parameters for temperature dependent heat capacity equations

$\Delta_\mathrm{f}a, \Delta_\mathrm{f}b, \Delta_\mathrm{f}c$ Coefficients of the equation for the isobaric heat capacity of formation

from the elements

$$\Delta_\mathrm{f}C_{p,\mathrm{m}}(T) = \Delta_\mathrm{f}a + \Delta_\mathrm{f}b\ T - \Delta_\mathrm{f}c/T^2$$

$\Delta_\mathrm{r}a, \Delta_\mathrm{r}b, \Delta_\mathrm{r}c$ Coefficients of the equation for the isobaric heat capacity of reaction

$$\Delta_\mathrm{r}C_{p,\mathrm{m}}(T) = \Delta_\mathrm{r}a + \Delta_\mathrm{r}b\ T - \Delta_\mathrm{r}c/T^2$$

$\Delta_\mathrm{f}C_{p,\mathrm{m}}^{\circ}$ Isobaric heat capacity of formation from the elements $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$

$\Delta_\mathrm{r}C_{p,\mathrm{m}}^{\circ}$ Isobaric heat capacity of reaction $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$

Note that all species for which none of these parameters are known were omitted from the table. Values of $\Delta_\mathrm{f}C_{p,\mathrm{m}}^{\circ}$ set in *italics* were calculated from $\Delta_\mathrm{f}a, \Delta_\mathrm{f}b,$ and $\Delta_\mathrm{f}c$ and had to be entered manually into the table. Only non-zero values for the coefficients are shown, entries for coefficients with a value of zero were left blank.

Table B1:   Reaction Properties.

SECONDARY MASTER SPECIES

Name	Reaction	$\log_{10}K°$	$\Delta_r G_m°$	$\Delta_r H_m°$	$\Delta_r S_m°$	$\Delta_r C_{p,m}°$
Al(OH)4-	+1.0 Al+3 +4.0 H2O -4.0 H+ = Al(OH)4-	-22.879*	130.595	180.899	168.720*	-57.321
As(OH)3	+1.0 HAsO4-2 +4.0 H+ +2.0 e- -1.0 H2O = As(OH)3	28.441*	-162.344*	-121.693*	136.344*	31.827*
CH4	+1.0 HCO3- +9.0 H+ +8.0 e- -3.0 H2O = CH4	27.849*	-158.961*	-255.882*	-325.075*	429.061*
CO2	+1.0 H+ -1.0 H2O +1.0 HCO3- = CO2	6.352*	-36.257*	-9.109*	91.052*	366.658*
CO3-2	-1.0 H+ +1.0 HCO3- = CO3-2	-10.329*	58.958*	14.901*	-147.766*	-290.513*
Eu+2	+1.0 Eu+3 +1.0 e- = Eu+2	-5.920	33.800*	78.100*	148.583*	0.000*
Fe+3	+1.0 Fe+2 -1.0 e- = Fe+3	-13.020	74.319*	40.500	-113.428*	0.000*
H2	+2.0 H+ +2.0 e- = H2	-3.105*	17.726*	-4.039*	-73.000*	144.187*
H2PO4-	+1.0 HPO4-2 +1.0 H+ = H2PO4-	7.212	-41.166*	-3.600	125.998*	0.000*
H2Se	+1.0 SeO3-2 +8.0 H+ +6.0 e- -3.0 H2O = H2Se	57.390	-327.585*			
H3PO4	+1.0 HPO4-2 +2.0 H+ = H3PO4	9.352	-53.382*	4.880	195.410*	0.000*
HS-	+1.0 SO4-2 +9.0 H+ +8.0 e- -4.0 H2O = HS-	33.690	-192.313*	-250.280	-194.422*	0.000*
HSeO4-	+1.0 SeO3-2 +1.0 H2O -1.0 H+ -2.0 e- = HSeO4-	-25.580	146.012*			
I2	+2.0 I- -2.0 e- = I2	20.950	-119.583*			
N2	+2.0 NO3- +12.0 H+ +10.0 e- -6.0 H2O = N2	207.263*	-1183.064*	-1311.717*	-431.504*	689.398*
NH3	+1.0 NH4+ -1.0 H+ = NH3	-9.237	52.725*	52.090	-2.130*	0.000*
NH4+	+1.0 NO3- +10.0 H+ +8.0 e- -3.0 H2O = NH4+	119.134*	-680.024*	-783.900*	-348.402*	277.178*
Np+3	+1.0 NpO2+2 +4.0 H+ +3.0 e- -2.0 H2O = Np+3	33.500	-191.280*	-238.160*	-157.236*	0.000*
Np+4	+1.0 NpO2+2 +4.0 H+ +2.0 e- -2.0 H2O = Np+4	29.800	-170.180*	-266.960*	-324.602*	0.000*
NpO2+	+1.0 NpO2+2 +1.0 e- = NpO2+	19.590	-111.900*	-117.500*	-18.782*	0.000*
O2	+2.0 H2O -4.0 H+ -4.0 e- = O2	-85.984*	490.801*	559.601*	230.756*	136.132*
OH-	+1.0 H2O -1.0 H+ = OH-	-14.000*	79.910*	55.906*	-80.511*	-210.948*
PO4-3	+1.0 HPO4-2 -1.0 H+ = PO4-3	-12.350	70.494*	14.600	-187.470*	0.000*
Pu+3	+1.0 PuO2+2 +4.0 H+ +3.0 e- -2.0 H2O = Pu+3	50.970	-290.880*	-341.460*	-169.646*	0.000*
Pu+4	+1.0 PuO2+2 +4.0 H+ +2.0 e- -2.0 H2O = Pu+4	33.280	-189.880*	-289.560*	-334.328*	0.000*
PuO2+	+1.0 PuO2+2 +1.0 e- = PuO2+	15.820	-90.200*	-88.100*	7.043*	0.000*
S2O3-2	+2.0 SO4-2 +10.0 H+ +8.0 e- -5.0 H2O = S2O3-2	38.014*	-216.983*	-258.970*	-140.825*	0.000*
SiO(OH)3-	+1.0 Si(OH)4 -1.0 H+ = SiO(OH)3-	-9.810	55.996*	25.600	-101.948*	0.000*
SiO2(OH)2-2	+1.0 Si(OH)4 -2.0 H+ = SiO2(OH)2-2	-23.140	132.084*	75.000	-191.461*	0.000*
SO3-2	+1.0 SO4-2 +2.0 H+ +2.0 e- -1.0 H2O = SO3-2	-3.397*	19.392*	-11.990*	-105.256*	0.000*
TcO(OH)2	+1.0 TcO4- +4.0 H+ +3.0 e- -1.0 H2O = TcO(OH)2	29.400	-167.816*			
U+4	+1.0 UO2+2 +4.0 H+ +2.0 e- -2.0 H2O = U+4	9.038	-51.589*	-143.860*	-309.477*	0.000*
UO2+	+1.0 UO2+2 +1.0 e- = UO2+	1.484	-8.471*	-6.127*	7.861*	0.000*

PRODUCT SPECIES

Name	Reaction	$\log_{10}K°$	$\Delta_r G_m°$	$\Delta_r H_m°$	$\Delta_r S_m°$	$\Delta_r C_{p,m}°$
(NpO2)2(OH)2+2	+2.0 NpO2+2 +2.0 H2O -2.0 H+ = (NpO2)2(OH)2+2	-6.270	35.789*			
(NpO2)2CO3(OH)3-	+2.0 NpO2+2 +1.0 CO3-2 +3.0 H2O -3.0 H+ = (NpO2)2CO3(OH)3-	-2.870	16.382*			
(NpO2)3(CO3)6-6	+3.0 NpO2+2 +6.0 CO3-2 = (NpO2)3(CO3)6-6	49.840	-284.489*			
(NpO2)3(OH)5+	+3.0 NpO2+2 +5.0 H2O -5.0 H+ = (NpO2)3(OH)5+	-17.120	97.722*			
(PuO2)2(OH)2+2	+2.0 PuO2+2 +2.0 H2O -2.0 H+ = (PuO2)2(OH)2+2	-7.500	42.810*			
(UO2)2(OH)2+2	+2.0 UO2+2 +2.0 H2O -2.0 H+ = (UO2)2(OH)2+2	-5.620	32.079*			
(UO2)2CO3(OH)3-	+2.0 UO2+2 +3.0 H2O -3.0 H+ +1.0 CO3-2 = (UO2)2CO3(OH)3-	-0.860	4.909*			
(UO2)2NpO2(CO3)6-6	+2.0 UO2+2 +1.0 NpO2+2 +6.0 CO3-2 = (UO2)2NpO2(CO3)6-6	53.590	-305.894*			
(UO2)2OH+3	+2.0 UO2+2 +1.0 H2O -1.0 H+ = (UO2)2OH+3	-2.700	15.412*			
(UO2)2PuO2(CO3)6-6	+2.0 UO2+2 +1.0 PuO2+2 +6.0 CO3-2 = (UO2)2PuO2(CO3)6-6	52.700	-300.814*			
(UO2)3(CO3)6-6	+3.0 UO2+2 +6.0 CO3-2 = (UO2)3(CO3)6-6	54.000	-308.234*	-62.700	823.526*	0.000*
(UO2)3(OH)4+2	+3.0 UO2+2 +4.0 H2O -4.0 H+ = (UO2)3(OH)4+2	-11.900	67.926*			
(UO2)3(OH)5+	+3.0 UO2+2 +5.0 H2O -5.0 H+ = (UO2)3(OH)5+	-15.550	88.760*			
(UO2)3(OH)7-	+3.0 UO2+2 +7.0 H2O -7.0 H+ = (UO2)3(OH)7-	-31.000	176.949*			
(UO2)3O(OH)2HCO3+	+3.0 UO2+2 +1.0 CO3-2 +3.0 H2O -3.0 H+ = (UO2)3O(OH)2HCO3+	0.660	-3.767*			
(UO2)4(OH)7+	+4.0 UO2+2 +7.0 H2O -7.0 H+ = (UO2)4(OH)7+	-21.900	125.006*			
Al(OH)2+	+1.0 Al+3 +2.0 H2O -2.0 H+ = Al(OH)2+	-10.594*	60.471	98.282	126.819*	134.306
Al(OH)3	+1.0 Al+3 +3.0 H2O -3.0 H+ = Al(OH)3	-16.432*	93.797	144.704	170.743*	155.645

Table B1:   continued

Name	Reaction	$\log_{10}K°$	$\Delta_r G_m°$	$\Delta_r H_m°$	$\Delta_r S_m°$	$\Delta_r C_{p,m}°$
Al(OH)6SiO-	+1.0 Al(OH)4- +1.0 Si(OH)4 -1.0 H2O = Al(OH)6SiO-	3.600	-20.549*			
Al(SO4)2-	+1.0 Al+3 +2.0 SO4-2 = Al(SO4)2-	5.900	-33.677*			
AlF+2	+1.0 Al+3 +1.0 F- = AlF+2	7.080	-40.413*	4.800	151.645*	0.000*
AlF2+	+1.0 Al+3 +2.0 F- = AlF2+	12.730	-72.663*	8.100	270.882*	0.000*
AlF3	+1.0 Al+3 +3.0 F- = AlF3	16.780	-95.781*	8.900	351.102*	0.000*
AlF4-	+1.0 Al+3 +4.0 F- = AlF4-	19.290	-110.108*	10.100	403.180*	0.000*
AlF5-2	+1.0 Al+3 +5.0 F- = AlF5-2	20.300	-115.873*	7.000	412.119*	0.000*
AlF6-3	+1.0 Al+3 +6.0 F- = AlF6-3	20.300	-115.873*	0.500	390.318*	0.000*
AlOH+2	+1.0 Al+3 +1.0 H2O -1.0 H+ = AlOH+2	-4.957*	28.296	49.798	72.118*	127.194
AlSiO(OH)3+2	+1.0 Al+3 +1.0 SiO(OH)3- = AlSiO(OH)3+2	7.400	-42.240*			
AlSO4+	+1.0 Al+3 +1.0 SO4-2 = AlSO4+	3.900	-22.261*			
Am(CO3)2-	+1.0 Am+3 +2.0 CO3-2 = Am(CO3)2-	12.300	-70.209*			
Am(CO3)3-3	+1.0 Am+3 +3.0 CO3-2 = Am(CO3)3-3	15.200	-86.762*			
Am(OH)2+	+1.0 Am+3 +2.0 H2O -2.0 H+ = Am(OH)2+	-15.200	86.762*			
Am(OH)3	+1.0 Am+3 +3.0 H2O -3.0 H+ = Am(OH)3	-25.700	146.697*			
Am(SO4)2-	+1.0 Am+3 +2.0 SO4-2 = Am(SO4)2-	5.400	-30.823*			
AmCl+2	+1.0 Am+3 +1.0 Cl- = AmCl+2	1.050	-5.993*			
AmCO3+	+1.0 Am+3 +1.0 CO3-2 = AmCO3+	7.800	-44.523*			
AmF+2	+1.0 Am+3 +1.0 F- = AmF+2	3.400	-19.407*			
AmF2+	+1.0 Am+3 +2.0 F- = AmF2+	5.800	-33.107*			
AmH2PO4+2	+1.0 Am+3 +1.0 H2PO4- = AmH2PO4+2	3.000	-17.124*			
AmNO3+2	+1.0 Am+3 +1.0 NO3- = AmNO3+2	1.330	-7.592*			
AmOH+2	+1.0 Am+3 +1.0 H2O -1.0 H+ = AmOH+2	-7.300	41.669*			
AmSiO(OH)3+2	+1.0 Am+3 +1.0 SiO(OH)3- = AmSiO(OH)3+2	8.100	-46.235*			
AmSO4+	+1.0 Am+3 +1.0 SO4-2 = AmSO4+	3.850	-21.976*			
As(OH)4-	+1.0 As(OH)3 +1.0 H2O -1.0 H+ = As(OH)4-	-9.232*	52.696*	27.343*	-85.034*	0.000*
AsO4-3	+1.0 HAsO4-2 -1.0 H+ = AsO4-3	-11.603*	66.232*	18.200*	-161.100*	0.000*
B(OH)4-	+1.0 B(OH)3 +1.0 H2O -1.0 H+ = B(OH)4-	-9.235*	52.715*	14.053*	-129.672*	-196.602*
BaCO3	+1.0 Ba+2 -1.0 H+ +1.0 HCO3- = BaCO3	-7.616*	43.471*	29.743*	-46.043*	-190.954*
BaHCO3+	+1.0 Ba+2 +1.0 HCO3- = BaHCO3+	0.982*	-5.603*	23.263*	96.816*	156.046*
BaOH+	+1.0 Ba+2 +1.0 H2O -1.0 H+ = BaOH+	-13.470	76.887*			
BaSO4	+1.0 Ba+2 +1.0 SO4-2 = BaSO4	2.700	-15.412*			
CaCO3	+1.0 Ca+2 -1.0 H+ +1.0 HCO3- = CaCO3	-7.105*	40.554*	29.733*	-36.293*	330.347*
CaF+	+1.0 Ca+2 +1.0 F- = CaF+	0.940	-5.366*	17.238	75.813*	0.000*
CaHCO3+	+1.0 Ca+2 +1.0 HCO3- = CaHCO3+	1.106*	-6.311*	11.263*	58.945*	-408.288*
CaOH+	+1.0 Ca+2 +1.0 H2O -1.0 H+ = CaOH+	-12.780	72.949*			
CaSiO(OH)3+	+1.0 Ca+2 +1.0 SiO(OH)3- = CaSiO(OH)3+	1.200	-6.850*			
CaSiO2(OH)2	+1.0 Ca+2 +1.0 SiO2(OH)2-2 = CaSiO2(OH)2	4.600	-26.257*			
CaSO4	+1.0 Ca+2 +1.0 SO4-2 = CaSO4	2.300	-13.128*	6.904	67.188*	0.000*
Eu(CO3)2-	+1.0 Eu+3 +2.0 CO3-2 = Eu(CO3)2-	12.100	-69.067*			
Eu(OH)2+	+1.0 Eu+3 +2.0 H2O -2.0 H+ = Eu(OH)2+	-15.100	86.191*			
Eu(OH)3	+1.0 Eu+3 +3.0 H2O -3.0 H+ = Eu(OH)3	-23.700	135.281*			
Eu(OH)4-	+1.0 Eu+3 +4.0 H2O -4.0 H+ = Eu(OH)4-	-36.200	206.631*			
Eu(SiO(OH)3)2+	+1.0 Eu+3 +2.0 SiO(OH)3- = Eu(SiO(OH)3)2+	12.800	-73.063*			
Eu(SO4)2-	+1.0 Eu+3 +2.0 SO4-2 = Eu(SO4)2-	5.700	-32.536*			
EuCl+2	+1.0 Eu+3 +1.0 Cl- = EuCl+2	1.100	-6.279*			
EuCl2+	+1.0 Eu+3 +2.0 Cl- = EuCl2+	1.500	-8.562*			
EuCO3+	+1.0 Eu+3 +1.0 CO3-2 = EuCO3+	8.100	-46.235*			
EuF+2	+1.0 Eu+3 +1.0 F- = EuF+2	3.800	-21.691*			
EuF2+	+1.0 Eu+3 +2.0 F- = EuF2+	6.500	-37.102*			
EuOH+2	+1.0 Eu+3 +1.0 H2O -1.0 H+ = EuOH+2	-7.640	43.609*			
EuSiO(OH)3+2	+1.0 Eu+3 +1.0 SiO(OH)3- = EuSiO(OH)3+2	7.900	-45.094*			
EuSO4+	+1.0 Eu+3 +1.0 SO4-2 = EuSO4+	3.950	-22.547*			
Fe(OH)2+	+2.0 H2O -2.0 H+ +1.0 Fe+3 = Fe(OH)2+	-5.670	32.365*	71.548	131.420*	0.000*
Fe(OH)3	+3.0 H2O -3.0 H+ +1.0 Fe+3 = Fe(OH)3	-12.560	71.693*	103.764	107.568*	0.000*
Fe(OH)4-	+4.0 H2O -4.0 H+ +1.0 Fe+3 = Fe(OH)4-	-21.600	123.294*	133.471	34.134*	0.000*
Fe(SO4)2-	+2.0 SO4-2 +1.0 Fe+3 = Fe(SO4)2-	5.380	-30.709*	19.248	167.556*	0.000*
Fe2(OH)2+4	+2.0 H2O -2.0 H+ +2.0 Fe+3 = Fe2(OH)2+4	-2.950	16.839*	56.486	132.978*	0.000*
Fe3(OH)4+5	+4.0 H2O -4.0 H+ +3.0 Fe+3 = Fe3(OH)4+5	-6.300	35.961*	59.834	80.073*	0.000*
FeCl+	+1.0 Fe+2 +1.0 Cl- = FeCl+	0.140	-0.799*			
FeCl+2	+1.0 Cl- +1.0 Fe+3 = FeCl+2	1.480	-8.448*	23.432	106.924*	0.000*

Table B1:   continued

Name	Reaction				$\log_{10}K°$	$\Delta_r G_m°$	$\Delta_r H_m°$	$\Delta_r S_m°$	$\Delta_r C_{p,m}°$
FeCl2+	+2.0 Cl-	+1.0 Fe+3		= FeCl2+	2.130	-12.158*			
FeCl3	+3.0 Cl-	+1.0 Fe+3		= FeCl3	1.130	-6.450*			
FeCO3	+1.0 Fe+2	+1.0 HCO3-	-1.0 H+	= FeCO3	-5.949	33.957*			
FeF+	+1.0 Fe+2	+1.0 F-		= FeF+	1.000	-5.708*			
FeF+2	+1.0 F-	+1.0 Fe+3		= FeF+2	6.200	-35.390*	11.297	156.588*	0.000*
FeF2+	+2.0 F-	+1.0 Fe+3		= FeF2+	10.800	-61.647*	20.084	274.127*	0.000*
FeF3	+3.0 F-	+1.0 Fe+3		= FeF3	14.000	-79.913*	22.595	343.812*	0.000*
FeHCO3+	+1.0 Fe+2	+1.0 HCO3-		= FeHCO3+	2.000	-11.416*			
FeHSO4+	+1.0 Fe+2	+1.0 H+	+1.0 SO4-2	= FeHSO4+	3.068	-17.512*			
FeHSO4+2	+1.0 H+	+1.0 SO4-2	+1.0 Fe+3	= FeHSO4+2	4.468	-25.504*			
FeOH+	+1.0 Fe+2	+1.0 H2O	-1.0 H+	= FeOH+	-9.500	54.226*	55.229	3.362*	0.000*
FeOH+2	+1.0 H2O	-1.0 H+	+1.0 Fe+3	= FeOH+2	-2.190	12.501*	43.515	104.022*	0.000*
FeSiO(OH)3+2	+1.0 Fe+3	+1.0 SiO(OH)3-		= FeSiO(OH)3+2	9.700	-55.368*			
FeSO4	+1.0 Fe+2	+1.0 SO4-2		= FeSO4	2.250	-12.843*	13.514	88.403*	0.000*
FeSO4+	+1.0 SO4-2	+1.0 Fe+3		= FeSO4+	4.040	-23.060*	16.360	132.219*	0.000*
H2AsO4-	+1.0 HAsO4-2	+1.0 H+		= H2AsO4-	6.764*	-38.611*	-3.220*	118.702*	0.000*
H2S	+1.0 HS-	+1.0 H+		= H2S	6.990	-39.899*	-22.300	59.028*	0.000*
H2SeO3	+1.0 SeO3-2	+2.0 H+		= H2SeO3	11.200	-63.930*	12.090	254.973*	0.000*
H3AsO4	+1.0 HAsO4-2	+2.0 H+		= H3AsO4	9.027*	-51.527*	3.840*	185.702*	0.000*
HF	+1.0 H+	+1.0 F-		= HF	3.176*	-18.129*	13.307*	105.435*	144.356*
HF2-	+1.0 H+	+2.0 F-		= HF2-	3.620*	-20.663*	15.200*	120.285*	273.600*
HSe-	+1.0 H2Se	-1.0 H+		= HSe-	-3.800	21.691*			
HSeO3-	+1.0 SeO3-2	+1.0 H+		= HSeO3-	8.400	-47.948*	5.020	177.654*	0.000*
HSO3-	+1.0 H+	+1.0 SO3-2		= HSO3-	7.220*	-41.212*	120.950*	543.894*	0.000*
HSO4-	+1.0 H+	+1.0 SO4-2		= HSO4-	1.988*	-11.346*	16.128*	92.149*	239.237*
I3-	+1.0 I-	+1.0 I2		= I3-	2.870	-16.382*			
KOH	+1.0 K+	+1.0 H2O	-1.0 H+	= KOH	-14.460	82.538*			
KSO4-	+1.0 K+	+1.0 SO4-2		= KSO4-	0.850	-4.852*	9.414	47.848*	0.000*
LiOH	+1.0 Li+	+1.0 H2O	-1.0 H+	= LiOH	-13.640	77.858*			
LiSO4-	+1.0 Li+	+1.0 SO4-2		= LiSO4-	0.640	-3.653*			
MgCO3	+1.0 Mg+2	-1.0 H+	+1.0 HCO3-	= MgCO3	-7.349*	41.950*	26.252*	-52.648*	-214.368*
MgF+	+1.0 Mg+2	+1.0 F-		= MgF+	1.820	-10.389*	13.389	79.750*	0.000*
MgHCO3+	+1.0 Mg+2	+1.0 HCO3-		= MgHCO3+	1.068*	-6.097*	3.288*	31.480*	173.964*
MgOH+	+1.0 Mg+2	+1.0 H2O	-1.0 H+	= MgOH+	-11.440	65.300*			
MgSiO(OH)3+	+1.0 Mg+2	+1.0 SiO(OH)3-		= MgSiO(OH)3+	1.500	-8.562*			
MgSiO2(OH)2	+1.0 Mg+2	+1.0 SiO2(OH)2-2		= MgSiO2(OH)2	5.700	-32.536*			
MgSO4	+1.0 Mg+2	+1.0 SO4-2		= MgSO4	2.370	-13.528*	19.037	109.224*	0.000*
MnCl+	+1.0 Mn+2	+1.0 Cl-		= MnCl+	0.610	-3.482*			
MnCl2	+1.0 Mn+2	+2.0 Cl-		= MnCl2	0.250	-1.427*			
MnCl3-	+1.0 Mn+2	+3.0 Cl-		= MnCl3-	-0.310	1.769*			
MnCO3	+1.0 Mn+2	+1.0 HCO3-	-1.0 H+	= MnCO3	-5.429	30.989*			
MnF+	+1.0 Mn+2	+1.0 F-		= MnF+	0.840	-4.795*			
MnHCO3+	+1.0 Mn+2	+1.0 HCO3-		= MnHCO3+	1.950	-11.131*			
MnOH+	+1.0 Mn+2	+1.0 H2O	-1.0 H+	= MnOH+	-10.590	60.448*	60.250	-0.666*	0.000*
MnSO4	+1.0 Mn+2	+1.0 SO4-2		= MnSO4	2.250	-12.843*	14.100	90.368*	0.000*
NaCO3-	+1.0 Na+	-1.0 H+	+1.0 HCO3-	= NaCO3-	-9.059	51.709*	52.180	1.579*	0.000*
NaF	+1.0 Na+	+1.0 F-		= NaF	-0.240	1.370*			
NaHCO3	+1.0 Na+	+1.0 HCO3-		= NaHCO3	-0.250	1.427*			
NaOH	+1.0 Na+	+1.0 H2O	-1.0 H+	= NaOH	-14.180	80.940*			
NaSO4-	+1.0 Na+	+1.0 SO4-2		= NaSO4-	0.700	-3.996*	4.686	29.119*	0.000*
Nb(OH)4+	+1.0 NbO3-	+2.0 H+	+1.0 H2O	= Nb(OH)4+	6.896*	-39.360*			
Nb(OH)5	+1.0 NbO3-	+1.0 H+	+2.0 H2O	= Nb(OH)5	7.344*	-41.920*			
Ni(CO3)2-2	+1.0 Ni+2	+2.0 CO3-2		= Ni(CO3)2-2	6.000	-34.248*			
Ni(HS)2	+1.0 Ni+2	+2.0 HS-		= Ni(HS)2	11.100	-63.359*			
Ni(NH3)2+2	+1.0 Ni+2	+2.0 NH3		= Ni(NH3)2+2	4.900	-27.969*			
Ni(NH3)3+2	+1.0 Ni+2	+3.0 NH3		= Ni(NH3)3+2	6.500	-37.102*			
Ni(NH3)4+2	+1.0 Ni+2	+4.0 NH3		= Ni(NH3)4+2	7.600	-43.381*			
Ni(NH3)5+2	+1.0 Ni+2	+5.0 NH3		= Ni(NH3)5+2	8.300	-47.377*			
Ni(NH3)6+2	+1.0 Ni+2	+6.0 NH3		= Ni(NH3)6+2	8.200	-46.806*			
Ni(NO3)2	+1.0 Ni+2	+2.0 NO3-		= Ni(NO3)2	-0.600	3.425*			
Ni(OH)2	+1.0 Ni+2	+2.0 H2O	-2.0 H+	= Ni(OH)2	-18.000	102.745*	85.760*	-56.967*	0.000*

Table B1:   continued

Name	Reaction				$\log_{10}K°$	$\Delta_\mathrm{r}G_\mathrm{m}°$	$\Delta_\mathrm{r}H_\mathrm{m}°$	$\Delta_\mathrm{r}S_\mathrm{m}°$	$\Delta_\mathrm{r}C_{p,\mathrm{m}}°$
Ni(OH)3-	+1.0 Ni+2	+3.0 H2O	-3.0 H+	= Ni(OH)3-	-29.700	169.529*	120.590*	-164.142*	0.000*
Ni(OH)4-2	+1.0 Ni+2	+4.0 H2O	-4.0 H+	= Ni(OH)4-2	-44.900	256.291*			
Ni(SO4)2-2	+1.0 Ni+2	+2.0 SO4-2		= Ni(SO4)2-2	3.200	-18.266*			
Ni2OH+3	+2.0 Ni+2	+1.0 H2O	-1.0 H+	= Ni2OH+3	-9.800	55.939*	35.000	-70.229*	0.000*
Ni4(OH)4+4	+4.0 Ni+2	+4.0 H2O	-4.0 H+	= Ni4(OH)4+4	-27.900	159.254*	170.000	36.041*	0.000*
NiCl+	+1.0 Ni+2	+1.0 Cl-		= NiCl+	0.400	-2.283*			
NiCl2	+1.0 Ni+2	+2.0 Cl-		= NiCl2	0.960	-5.480*			
NiCO3	+1.0 Ni+2	+1.0 CO3-2		= NiCO3	4.000	-22.832*			
NiF+	+1.0 Ni+2	+1.0 F-		= NiF+	1.300	-7.420*			
NiH2PO4+	+1.0 Ni+2	+1.0 H2PO4-		= NiH2PO4+	1.544	-8.813*			
NiHCO3+	+1.0 Ni+2	+1.0 HCO3-		= NiHCO3+	1.000	-5.708*			
NiHP2O7-	+1.0 Ni+2	+2.0 HPO4-2	+1.0 H+ -1.0 H2O	= NiHP2O7-	9.258	-52.845*			
NiHPO4	+1.0 Ni+2	+1.0 HPO4-2		= NiHPO4	2.934	-16.747*			
NiHS+	+1.0 Ni+2	+1.0 HS-		= NiHS+	5.500	-31.394*			
NiNH3+2	+1.0 Ni+2	+1.0 NH3		= NiNH3+2	2.700	-15.412*			
NiNO3+	+1.0 Ni+2	+1.0 NO3-		= NiNO3+	0.400	-2.283*			
NiOH+	+1.0 Ni+2	+1.0 H2O	-1.0 H+	= NiOH+	-9.500	54.226*	50.000	-14.175*	0.000*
NiP2O7-2	+1.0 Ni+2	+2.0 HPO4-2	-1.0 H2O	= NiP2O7-2	3.088	-17.626*	9.917	92.381*	0.000*
NiPO4-	+1.0 Ni+2	+1.0 PO4-3		= NiPO4-	8.374	-47.799*			
NiSO4	+1.0 Ni+2	+1.0 SO4-2		= NiSO4	2.310	-13.186*	13.975	91.097*	0.000*
Np(CO3)4-4	+1.0 Np+4	+4.0 CO3-2		= Np(CO3)4-4	36.690	-209.428*			
Np(CO3)5-6	+1.0 Np+4	+5.0 CO3-2		= Np(CO3)5-6	35.620	-203.320*			
Np(OH)4	+1.0 Np+4	+4.0 H2O	-4.0 H+	= Np(OH)4	-9.800	55.939*			
Np(SO4)2	+1.0 Np+4	+2.0 SO4-2		= Np(SO4)2	11.050	-63.074*	55.400	397.363*	0.000*
NpCl+3	+1.0 Np+4	+1.0 Cl-		= NpCl+3	1.500	-8.562*			
NpF+3	+1.0 Np+4	+1.0 F-		= NpF+3	8.960	-51.144*	1.500	176.569*	0.000*
NpF2+2	+1.0 Np+4	+2.0 F-		= NpF2+2	15.700	-89.616*			
NpNO3+3	+1.0 Np+4	+1.0 NO3-		= NpNO3+3	1.900	-10.845*			
NpO2(CO3)2-2	+1.0 NpO2+2	+2.0 CO3-2		= NpO2(CO3)2-2	16.520	-94.297*			
NpO2(CO3)2-3	+1.0 NpO2+	+2.0 CO3-2		= NpO2(CO3)2-3	6.530	-37.274*			
NpO2(CO3)2OH-4	+1.0 NpO2+	+2.0 CO3-2	+1.0 H2O -1.0 H+	= NpO2(CO3)2OH-4	-5.300	30.253*			
NpO2(CO3)3-4	+1.0 NpO2+2	+3.0 CO3-2		= NpO2(CO3)3-4	19.370	-110.565*	-41.900	230.303*	0.000*
NpO2(CO3)3-5	+1.0 NpO2+	+3.0 CO3-2		= NpO2(CO3)3-5	5.500	-31.394*	-13.300	60.688*	0.000*
NpO2(HPO4)2-2	+1.0 NpO2+2	+2.0 HPO4-2		= NpO2(HPO4)2-2	9.500	-54.226*			
NpO2(OH)	+1.0 NpO2+	+1.0 H2O	-1.0 H+	= NpO2(OH)	-11.300	64.501*			
NpO2(OH)2-	+1.0 NpO2+	+2.0 H2O	-2.0 H+	= NpO2(OH)2-	-23.600	134.710*			
NpO2(OH)3-	+1.0 NpO2+2	+3.0 H2O	-3.0 H+	= NpO2(OH)3-	-19.000	108.453*			
NpO2(OH)4-2	+1.0 NpO2+2	+4.0 H2O	-4.0 H+	= NpO2(OH)4-2	-33.000	188.365*			
NpO2(SO4)2-2	+1.0 NpO2+2	+2.0 SO4-2		= NpO2(SO4)2-2	4.700	-26.828*	26.000	177.185*	0.000*
NpO2Cl+	+1.0 NpO2+2	+1.0 Cl-		= NpO2Cl+	0.400	-2.283*			
NpO2CO3	+1.0 NpO2+2	+1.0 CO3-2		= NpO2CO3	9.320	-53.199*			
NpO2CO3-	+1.0 NpO2+	+1.0 CO3-2		= NpO2CO3-	4.960	-28.312*			
NpO2F	+1.0 NpO2+	+1.0 F-		= NpO2F	1.200	-6.850*			
NpO2F+	+1.0 NpO2+2	+1.0 F-		= NpO2F+	4.570	-26.086*			
NpO2F2	+1.0 NpO2+2	+2.0 F-		= NpO2F2	7.600	-43.381*			
NpO2H2PO4+	+1.0 NpO2+2	+1.0 H2PO4-		= NpO2H2PO4+	3.320	-18.951*			
NpO2HPO4	+1.0 NpO2+2	+1.0 HPO4-2		= NpO2HPO4	6.200	-35.390*			
NpO2HPO4-	+1.0 NpO2+	+1.0 HPO4-2		= NpO2HPO4-	2.950	-16.839*			
NpO2OH+	+1.0 NpO2+2	+1.0 H2O	-1.0 H+	= NpO2OH+	-5.100	29.111*			
NpO2SO4	+1.0 NpO2+2	+1.0 SO4-2		= NpO2SO4	3.280	-18.722*	16.700	118.807*	0.000*
NpO2SO4-	+1.0 NpO2+	+1.0 SO4-2		= NpO2SO4-	0.440	-2.512*	23.200	86.237*	0.000*
NpOH+2	+1.0 Np+3	+1.0 H2O	-1.0 H+	= NpOH+2	-6.800	38.815*			
NpOH+3	+1.0 Np+4	+1.0 H2O	-1.0 H+	= NpOH+3	-0.290	1.655*			
NpSO4+2	+1.0 Np+4	+1.0 SO4-2		= NpSO4+2	6.850	-39.100*	29.800	231.092*	0.000*
Pd(NH3)2+2	+1.0 Pd+2	+2.0 NH3		= Pd(NH3)2+2	18.500	-105.599*			
Pd(NH3)3+2	+1.0 Pd+2	+3.0 NH3		= Pd(NH3)3+2	26.000	-148.409*			
Pd(NH3)4+2	+1.0 Pd+2	+4.0 NH3		= Pd(NH3)4+2	32.800	-187.224*			
Pd(OH)2	+1.0 Pd+2	-2.0 H+	+2.0 H2O	= Pd(OH)2	-4.000	22.832*			
Pd(OH)3-	+1.0 Pd+2	-3.0 H+	+3.0 H2O	= Pd(OH)3-	-15.500	88.475*			
PdCl+	+1.0 Pd+2	+1.0 Cl-		= PdCl+	5.100	-29.111*			
PdCl2	+1.0 Pd+2	+2.0 Cl-		= PdCl2	8.300	-47.377*			

Table B1:   continued

Name	Reaction	$\log_{10}K°$	$\Delta_rG_m°$	$\Delta_rH_m°$	$\Delta_rS_m°$	$\Delta_rC_{p,m}°$
PdCl2(OH)2-2	+1.0 Pd+2 +2.0 Cl- +2.0 H2O -2.0 H+ = PdCl2(OH)2-2	-7.000	39.956*			
PdCl3-	+1.0 Pd+2 +3.0 Cl- = PdCl3-	10.900	-62.218*			
PdCl3OH-2	+1.0 Pd+2 +3.0 Cl- +1.0 H2O -1.0 H+ = PdCl3OH-2	2.500	-14.270*			
PdCl4-2	+1.0 Pd+2 +4.0 Cl- = PdCl4-2	11.700	-66.784*			
PdNH3+2	+1.0 Pd+2 +1.0 NH3 = PdNH3+2	9.600	-54.797*			
Pu(CO3)4-4	+1.0 Pu+4 +4.0 CO3-2 = Pu(CO3)4-4	35.900	-204.919*			
Pu(CO3)5-6	+1.0 Pu+4 +5.0 CO3-2 = Pu(CO3)5-6	34.500	-196.927*			
Pu(OH)4	+1.0 Pu+4 +4.0 H2O -4.0 H+ = Pu(OH)4	-8.400	47.948*			
Pu(SO4)2	+1.0 Pu+4 +2.0 SO4-2 = Pu(SO4)2	11.140	-63.588*			
Pu(SO4)2-	+1.0 Pu+3 +2.0 SO4-2 = Pu(SO4)2-	5.700	-32.536*	12.000	149.374*	0.000*
PuCl+2	+1.0 Pu+4 +1.0 Cl- = PuCl+2	1.200	-6.850*			
PuCl+3	+1.0 Pu+3 +1.0 Cl- = PuCl+3	1.800	-10.274*			
PuF+3	+1.0 Pu+4 +1.0 F- = PuF+3	8.840	-50.459*	9.100	199.762*	0.000*
PuF2+2	+1.0 Pu+4 +2.0 F- = PuF2+2	15.700	-89.616*	11.000	337.469*	0.000*
PuH3PO4+4	+1.0 Pu+4 +1.0 H3PO4 = PuH3PO4+4	2.400	-13.699*			
PuNO3+3	+1.0 Pu+4 +1.0 NO3- = PuNO3+3	1.950	-11.131*			
PuO2(CO3)2-2	+1.0 PuO2+2 +2.0 CO3-2 = PuO2(CO3)2-2	14.600	-83.337*	-27.000	188.957*	0.000*
PuO2(CO3)3-4	+1.0 PuO2+2 +3.0 CO3-2 = PuO2(CO3)3-4	17.700	-101.032*	-38.600	209.399*	0.000*
PuO2(CO3)3-5	+1.0 PuO2+ +3.0 CO3-2 = PuO2(CO3)3-5	5.000	-28.540*	-19.110	31.629*	0.000*
PuO2(OH)2	+1.0 PuO2+2 +2.0 H2O -2.0 H+ = PuO2(OH)2	-13.200	75.346*			
PuO2(SO4)2-2	+1.0 PuO2+2 +2.0 SO4-2 = PuO2(SO4)2-2	4.400	-25.115*	43.000	228.460*	0.000*
PuO2Cl+	+1.0 PuO2+2 +1.0 Cl- = PuO2Cl+	0.700	-3.996*			
PuO2Cl2	+1.0 PuO2+2 +2.0 Cl- = PuO2Cl2	-0.600	3.425*			
PuO2CO3	+1.0 PuO2+2 +1.0 CO3-2 = PuO2CO3	9.300	-53.085*			
PuO2CO3-	+1.0 PuO2+ +1.0 CO3-2 = PuO2CO3-	5.120	-29.225*			
PuO2F+	+1.0 PuO2+2 +1.0 F- = PuO2F+	4.560	-26.029*			
PuO2F2	+1.0 PuO2+2 +2.0 F- = PuO2F2	7.250	-41.383*			
PuO2OH	+1.0 PuO2+ +1.0 H2O -1.0 H+ = PuO2OH	-9.730	55.539*			
PuO2OH+	+1.0 PuO2+2 +1.0 H2O -1.0 H+ = PuO2OH+	-5.500	31.394*	28.000	-11.384*	0.000*
PuO2SO4	+1.0 PuO2+2 +1.0 SO4-2 = PuO2SO4	3.380	-19.293*	16.100	118.709*	0.000*
PuOH+2	+1.0 Pu+3 +1.0 H2O -1.0 H+ = PuOH+2	-6.900	39.385*			
PuOH+3	+1.0 Pu+4 +1.0 H2O -1.0 H+ = PuOH+3	-0.780	4.452*	36.000	105.812*	0.000*
PuSO4+	+1.0 Pu+3 +1.0 SO4-2 = PuSO4+	3.900	-22.261*	17.200	132.354*	0.000*
PuSO4+2	+1.0 Pu+4 +1.0 SO4-2 = PuSO4+2	6.890	-39.328*			
RaCl+	+1.0 Ra+2 +1.0 Cl- = RaCl+	-0.100	0.571*	2.100	5.129*	0.000*
RaCO3	+1.0 Ra+2 +1.0 CO3-2 = RaCO3	2.500	-14.270*	4.480	62.888*	0.000*
RaOH+	+1.0 Ra+2 +1.0 OH- = RaOH+	0.500	-2.854*	4.600	25.001*	0.000*
RaSO4	+1.0 Ra+2 +1.0 SO4-2 = RaSO4	2.750	-15.697*	5.400	70.760*	0.000*
S-2	+1.0 HS- -1.0 H+ = S-2	-19.000	108.453*			
SeO4-2	+1.0 HSeO4- -1.0 H+ = SeO4-2	-1.800	10.274*	-23.800	-114.286*	0.000*
Sn(OH)2	+1.0 Sn+2 +2.0 H2O -2.0 H+ = Sn(OH)2	-7.700	43.952*			
Sn(OH)3-	+1.0 Sn+2 +3.0 H2O -3.0 H+ = Sn(OH)3-	-17.500	99.891*			
Sn(OH)5-	+1.0 Sn(OH)4 +1.0 H2O -1.0 H+ = Sn(OH)5-	-8.000	45.664*			
Sn(OH)6-2	+1.0 Sn(OH)4 +2.0 H2O -2.0 H+ = Sn(OH)6-2	-18.400	105.028*			
Sn3(OH)4+2	+3.0 Sn+2 +4.0 H2O -4.0 H+ = Sn3(OH)4+2	-5.600	31.965*			
SnCl+	+1.0 Sn+2 +1.0 Cl- = SnCl+	1.700	-9.704*			
SnCl2	+1.0 Sn+2 +2.0 Cl- = SnCl2	2.360	-13.471*			
SnCl3-	+1.0 Sn+2 +3.0 Cl- = SnCl3-	2.100	-11.987*			
SnF+	+1.0 Sn+2 +1.0 F- = SnF+	5.000	-28.540*			
SnOH+	+1.0 Sn+2 +1.0 H2O -1.0 H+ = SnOH+	-3.800	21.691*			
SnOHCl	+1.0 Sn+2 +1.0 H2O +1.0 Cl- -1.0 H+ = SnOHCl	-3.100	17.695*			
SnSO4	+1.0 Sn+2 +1.0 SO4-2 = SnSO4	2.600	-14.841*			
SrCO3	+1.0 Sr+2 -1.0 H+ +1.0 HCO3- = SrCO3	-7.524*	42.946*	36.729*	-20.852*	-144.091*
SrHCO3+	+1.0 Sr+2 +1.0 HCO3- = SrHCO3+	1.185*	-6.762*	25.301*	107.540*	169.723*
SrOH+	+1.0 Sr+2 +1.0 H2O -1.0 H+ = SrOH+	-13.290	75.860*			
SrSO4	+1.0 Sr+2 +1.0 SO4-2 = SrSO4	2.290	-13.071*	8.703	73.031*	0.000*
TcCO3(OH)2	+1.0 TcO(OH)2 +1.0 CO3-2 +2.0 H+ -1.0 H2O = TcCO3(OH)2	19.300	-110.165*			
TcCO3(OH)3-	+1.0 TcO(OH)2 +1.0 H+ +1.0 CO3-2 = TcCO3(OH)3-	11.000	-62.788*			
TcO(OH)+	+1.0 TcO(OH)2 +1.0 H+ -1.0 H2O = TcO(OH)+	2.500	-14.270*			
TcO(OH)3-	+1.0 TcO(OH)2 +1.0 H2O -1.0 H+ = TcO(OH)3-	-10.900	62.218*			
TcO+2	+1.0 TcO(OH)2 +2.0 H+ -2.0 H2O = TcO+2	4.000	-22.832*			

Table B1: continued

Name	Reaction					$\log_{10}K°$	$\Delta_r G_m°$	$\Delta_r H_m°$	$\Delta_r S_m°$	$\Delta_r C_{p,m}°$
Th(CO3)5-6	+1.0 Th+4	+5.0 CO3-2			= Th(CO3)5-6	29.800	-170.100*			
Th(OH)4	+1.0 Th+4	+4.0 H2O	-4.0 H+		= Th(OH)4	-18.400	105.028*			
Th(SO4)2	+1.0 Th+4	+2.0 SO4-2			= Th(SO4)2	11.600	-66.213*			
Th(SO4)3-2	+1.0 Th+4	+3.0 SO4-2			= Th(SO4)3-2	12.400	-70.780*			
ThCO3(OH)3-	+1.0 Th+4	+1.0 CO3-2	-3.0 H+	+3.0 H2O	= ThCO3(OH)3-	-3.100	17.695*			
ThF+3	+1.0 Th+4	+1.0 F-			= ThF+3	8.000	-45.664*			
ThF2+2	+1.0 Th+4	+2.0 F-			= ThF2+2	14.200	-81.054*			
ThF3+	+1.0 Th+4	+3.0 F-			= ThF3+	18.900	-107.882*			
ThF4	+1.0 Th+4	+4.0 F-			= ThF4	22.300	-127.289*			
ThHPO4+2	+1.0 Th+4	+1.0 HPO4-2			= ThHPO4+2	13.000	-74.205*			
ThOH+3	+1.0 Th+4	+1.0 H2O	-1.0 H+		= ThOH+3	-2.400	13.699*			
ThSO4+2	+1.0 Th+4	+1.0 SO4-2			= ThSO4+2	7.600	-43.381*			
U(CO3)4-4	+1.0 U+4	+4.0 CO3-2			= U(CO3)4-4	35.220	-201.037*			
U(CO3)5-6	+1.0 U+4	+5.0 CO3-2			= U(CO3)5-6	34.100	-194.644*	-20.000	585.760*	0.000*
U(NO3)2+2	+1.0 U+4	+2.0 NO3-			= U(NO3)2+2	2.300	-13.128*			
U(OH)4	+1.0 U+4	+4.0 H2O	-4.0 H+		= U(OH)4	-9.000	51.372*			
U(SO4)2	+1.0 U+4	+2.0 SO4-2			= U(SO4)2	10.510	-59.992*	32.700	310.889*	0.000*
UCl+3	+1.0 U+4	+1.0 Cl-			= UCl+3	1.720	-9.818*	-19.000	-30.797*	0.000*
UF+3	+1.0 U+4	+1.0 F-			= UF+3	9.280	-52.971*	-5.600	158.882*	0.000*
UF2+2	+1.0 U+4	+2.0 F-			= UF2+2	16.230	-92.642*	-3.500	298.982*	0.000*
UF3+	+1.0 U+4	+3.0 F-			= UF3+	21.600	-123.294*	0.500	415.206*	0.000*
UF4	+1.0 U+4	+4.0 F-			= UF4	25.600	-146.125*	-4.206	476.000	0.000*
UF5-	+1.0 U+4	+5.0 F-			= UF5-	27.010	-154.174*			
UF6-2	+1.0 U+4	+6.0 F-			= UF6-2	29.080	-165.990*			
UNO3+3	+1.0 U+4	+1.0 NO3-			= UNO3+3	1.470	-8.391*			
UO2(CO3)2-2	+1.0 UO2+2	+2.0 CO3-2			= UO2(CO3)2-2	16.940	-96.694*	18.500	386.363*	0.000*
UO2(CO3)3-4	+1.0 UO2+2	+3.0 CO3-2			= UO2(CO3)3-4	21.600	-123.294*	-39.200	282.052*	0.000*
UO2(CO3)3-5	+1.0 UO2+	+3.0 CO3-2			= UO2(CO3)3-5	7.410	-42.297*			
UO2(H2PO4)2	+1.0 UO2+2	+2.0 H3PO4	-2.0 H+		= UO2(H2PO4)2	0.640	-3.653*			
UO2(OH)2	+1.0 UO2+2	+2.0 H2O	-2.0 H+		= UO2(OH)2	-12.000	68.497*			
UO2(OH)3-	+1.0 UO2+2	+3.0 H2O	-3.0 H+		= UO2(OH)3-	-19.200	109.594*			
UO2(OH)4-2	+1.0 UO2+2	+4.0 H2O	-4.0 H+		= UO2(OH)4-2	-33.000	188.365*			
UO2(SO4)2-2	+1.0 UO2+2	+2.0 SO4-2			= UO2(SO4)2-2	4.140	-23.631*	35.100	196.986*	0.000*
UO2Cl+	+1.0 UO2+2	+1.0 Cl-			= UO2Cl+	0.170	-0.970*	8.000	30.087*	0.000*
UO2Cl2	+1.0 UO2+2	+2.0 Cl-			= UO2Cl2	-1.100	6.279*	15.000	29.251*	0.000*
UO2CO3	+1.0 UO2+2	+1.0 CO3-2			= UO2CO3	9.670	-55.197*	5.000	201.901*	0.000*
UO2F+	+1.0 UO2+2	+1.0 F-			= UO2F+	5.090	-29.054*	1.700	103.149*	0.000*
UO2F2	+1.0 UO2+2	+2.0 F-			= UO2F2	8.620	-49.203*	2.100	172.072*	0.000*
UO2F3-	+1.0 UO2+2	+3.0 F-			= UO2F3-	10.900	-62.218*	2.350	216.561*	0.000*
UO2F4-2	+1.0 UO2+2	+4.0 F-			= UO2F4-2	11.700	-66.784*	0.290	224.968*	0.000*
UO2H2PO4+	+1.0 UO2+2	+1.0 H3PO4	-1.0 H+		= UO2H2PO4+	1.120	-6.393*			
UO2H2PO4H3PO4+	+1.0 UO2+2	+2.0 H3PO4	-1.0 H+		= UO2H2PO4H3PO4+	1.650	-9.418*			
UO2H3PO4+2	+1.0 UO2+2	+1.0 H3PO4			= UO2H3PO4+2	0.760	-4.338*			
UO2HPO4	+1.0 UO2+2	+1.0 HPO4-2			= UO2HPO4	7.240	-41.326*			
UO2NO3+	+1.0 UO2+2	+1.0 NO3-			= UO2NO3+	0.300	-1.712*			
UO2OH+	+1.0 UO2+2	+1.0 H2O	-1.0 H+		= UO2OH+	-5.200	29.682*			
UO2PO4-	+1.0 UO2+2	+1.0 PO4-3			= UO2PO4-	13.230	-75.517*			
UO2SO4	+1.0 UO2+2	+1.0 SO4-2			= UO2SO4	3.150	-17.980*	19.500	125.710*	0.000*
UOH+3	+1.0 U+4	+1.0 H2O	-1.0 H+		= UOH+3	-0.540	3.082*	46.910	147.000	0.000*
USO4+2	+1.0 U+4	+1.0 SO4-2			= USO4+2	6.580	-37.559*	8.000	152.805*	0.000*
Zr(OH)4	+1.0 Zr+4	+4.0 H2O	-4.0 H+		= Zr(OH)4	-9.700	55.368*			
Zr(OH)5-	+1.0 Zr+4	+5.0 H2O	-5.0 H+		= Zr(OH)5-	-16.000	91.329*			
ZrCl+3	+1.0 Zr+4	+1.0 Cl-			= ZrCl+3	1.500	-8.562*			
ZrF+3	+1.0 Zr+4	+1.0 F-			= ZrF+3	10.200	-58.222*	0.000*	0.000*	0.000*
ZrF2+2	+1.0 Zr+4	+2.0 F-			= ZrF2+2	18.500	-105.599*	0.000*	0.000*	0.000*
ZrF3+	+1.0 Zr+4	+3.0 F-			= ZrF3+	24.700	-140.989*	0.000*	0.000*	0.000*
ZrF4	+1.0 Zr+4	+4.0 F-			= ZrF4	30.100	-171.812*	0.000*	0.000*	0.000*
ZrF5-	+1.0 Zr+4	+5.0 F-			= ZrF5-	34.700	-198.069*			
ZrF6-2	+1.0 Zr+4	+6.0 F-			= ZrF6-2	38.400	-219.189*			
ZrOH+3	+1.0 Zr+4	+1.0 H2O	-1.0 H+		= ZrOH+3	0.300	-1.712*			
ZrSO4+2	+1.0 Zr+4	+1.0 SO4-2			= ZrSO4+2	7.000	-39.956*			

Table B1:   continued

MINERALS AND SOLIDS

Name	Reaction	$\log_{10}K°$	$\Delta_r G_m°$	$\Delta_r H_m°$	$\Delta_r S_m°$	$\Delta_r C_{p,m}°$
(NH4)4NpO2(CO3)3(s)	+4.0 NH4+ +1.0 NpO2+2 +3.0 CO3-2 = (NH4)4NpO2(CO3)3	26.810	-153.033*			
(UO2)3(PO4)2:4H2O(cr)	+3.0 UO2+2 +2.0 H3PO4 +4.0 H2O -6.0 H+ = (UO2)3(PO4)2:4H2O	5.960	-34.020*			
Am(CO3)1.5(cr)	+1.0 Am+3 +1.5 CO3-2 = Am(CO3)1.5	16.700	-95.324*			
Am(OH)3(am)	+1.0 Am+3 +3.0 H2O -3.0 H+ = Am(OH)3	-17.000	97.037*			
Am(OH)3(cr)	+1.0 Am+3 +3.0 H2O -3.0 H+ = Am(OH)3	-15.200	86.762*			
AmCO3OH(cr)	+1.0 Am+3 +1.0 CO3-2 +1.0 OH- = AmCO3OH	21.200	-121.010*			
Anhydrite	+1.0 Ca+2 +1.0 SO4-2 = CaSO4	4.357*	-24.873*	7.156*	107.424*	580.644*
Aragonite	+1.0 Ca+2 -1.0 H+ +1.0 HCO3- = CaCO3	-1.993*	11.375*	25.735*	48.163*	4.584*
As(cr)	+1.0 HAsO4-2 +7.0 H+ +5.0 e- -4.0 H2O = As	40.989*	-233.968*	-236.980*	-10.102*	0.000*
Baddeleyite	+1.0 Zr+4 +2.0 H2O -4.0 H+ = ZrO2	1.900	-10.845*			
Barite	+1.0 Ba+2 +1.0 SO4-2 = BaSO4	9.970*	-56.911*	-26.575*	101.749*	404.044*
Brucite	+1.0 Mg+2 +2.0 H2O -2.0 H+ = Mg(OH)2	-16.840	96.123*	113.386	57.900*	0.000*
Calcite	+1.0 Ca+2 -1.0 H+ +1.0 HCO3- = CaCO3	-1.849*	10.554*	24.510*	46.808*	4.584*
CaSn(OH)6(s)	+1.0 Sn(OH)4 +2.0 H2O +1.0 Ca+2 -2.0 H+ = CaSn(OH)6	-8.700	49.660*			
Cassiterite	+1.0 Sn(OH)4 -2.0 H2O = SnO2	8.000	-45.664*			
Celestite	+1.0 Sr+2 +1.0 SO4-2 = SrSO4	6.632*	-37.855*	4.339*	141.519*	420.418*
Chernikovite	+1.0 UO2+2 +1.0 H3PO4 +4.0 H2O -2.0 H+ = UO2HPO4:4H2O	2.500	-14.270*			
Dolomite(dis)	+1.0 Ca+2 +1.0 Mg+2 -2.0 H+ +2.0 HCO3- = CaMg(CO3)2	-4.118	23.506*	76.202	176.744*	0.000*
Dolomite(ord)	+1.0 Ca+2 +1.0 Mg+2 -2.0 H+ +2.0 HCO3- = CaMg(CO3)2	-3.568	20.366*	69.282	164.064*	0.000*
Eu(OH)3(am)	+1.0 Eu+3 +3.0 H2O -3.0 H+ = Eu(OH)3	-17.600	100.462*			
Eu(OH)3(cr)	+1.0 Eu+3 +3.0 H2O -3.0 H+ = Eu(OH)3	-14.900	85.050*	124.390*	131.948*	0.000*
Eu2(CO3)3(cr)	+2.0 Eu+3 +3.0 CO3-2 = Eu2(CO3)3	35.000	-199.781*			
EuF3(cr)	+1.0 Eu+3 +3.0 F- = EuF3	17.400	-99.320*			
EuOHCO3(cr)	+1.0 Eu+3 +1.0 OH- +1.0 CO3-2 = EuOHCO3	21.700	-123.865*			
Fe(cr)	+1.0 Fe+2 +2.0 e- = Fe	-13.823*	78.900*	89.100*	34.211*	0.000*
Fe(OH)3(am)	+3.0 H2O -3.0 H+ +1.0 Fe+3 = Fe(OH)3	-5.000	28.540*			
Fe(OH)3(mic)	+3.0 H2O -3.0 H+ +1.0 Fe+3 = Fe(OH)3	-3.000	17.124*			
FeCO3(pr)	+1.0 Fe+2 +1.0 HCO3- -1.0 H+ = FeCO3	0.121*	-0.692*	14.901*	52.298*	-290.513*
Fluorite	+1.0 Ca+2 +2.0 F- = CaF2	10.600*	-60.503*	-19.642*	137.048*	210.116*
Gibbsite	+1.0 Al+3 +3.0 H2O -3.0 H+ = Al(OH)3	-7.756*	44.271	102.784	196.254*	-1.255
Goethite	+2.0 H2O -3.0 H+ +1.0 Fe+3 = FeOOH	1.000	-5.708*			
Graphite	+1.0 HCO3- +5.0 H+ +4.0 e- -3.0 H2O = C	21.819*	-124.545*	-167.275*	-143.317*	0.000*
Gypsum	+1.0 Ca+2 +1.0 SO4-2 +2.0 H2O = CaSO4:2H2O	4.581*	-26.148*	0.454*	89.225*	208.384*
Hausmannite	+3.0 Mn+2 +4.0 H2O -8.0 H+ -2.0 e- = Mn3O4	-61.030	348.362*	421.078	243.891*	0.000*
Hematite	+3.0 H2O -6.0 H+ +2.0 Fe+3 = Fe2O3	-1.120	6.393*			
K4NpO2(CO3)3(s)	+4.0 K+ +1.0 NpO2+2 +3.0 CO3-2 = K4NpO2(CO3)3	26.400	-150.692*			
Kaolinite	+2.0 Al+3 +2.0 Si(OH)4 +1.0 H2O -6.0 H+ = Al2Si2O5(OH)4	-7.435	42.439*	147.700	353.046*	0.000*
Magnesite	+1.0 Mg+2 -1.0 H+ +1.0 HCO3- = MgCO3	-2.041	11.650*			
Magnetite	+1.0 Fe+2 +4.0 H2O -8.0 H+ +2.0 Fe+3 = Fe3O4	-10.020	57.195*			
Manganite	+1.0 Mn+2 +2.0 H2O -3.0 H+ -1.0 e- = MnOOH	-25.340	144.642*			
Melanterite	+1.0 Fe+2 +1.0 SO4-2 +7.0 H2O = FeSO4:7H2O	2.209*	-12.611*	-20.537*	-26.585*	139.998*
Mo(cr)	+1.0 MoO4-2 +8.0 H+ +6.0 e- -4.0 H2O = Mo	*19.667*	-112.260*	-145.420*	-111.219*	0.000*
Molybdite	+1.0 MoO4-2 +2.0 H+ -1.0 H2O = MoO3	*12.055*	-68.810*	-33.020*	120.040*	0.000*
Na3NpO2(CO3)2(s)	+3.0 Na+ +1.0 NpO2+ +2.0 CO3-2 = Na3NpO2(CO3)2	14.700	-83.908*			
NaNpO2CO3(s,ag)	+1.0 Na+ +1.0 NpO2+ +1.0 CO3-2 = NaNpO2CO3	11.660	-66.556*			
NaNpO2CO3:3.5H2O(s,fr)	+1.0 Na+ +1.0 NpO2+ +1.0 CO3-2 +3.5 H2O = NaNpO2CO3:3.5H2O	11.160	-63.702*			
Nb2O5(cr)	+2.0 NbO3- +2.0 H+ -1.0 H2O = Nb2O5	*24.341*	-138.940*	0.000*	0.000*	0.000*
NbO2(cr)	+1.0 NbO3- +2.0 H+ +1.0 e- -1.0 H2O = NbO2	*7.978*	-45.540*	0.000*	0.000*	0.000*
NiCO3(cr)	+1.0 Ni+2 +1.0 CO3-2 = NiCO3	11.200	-63.930*			
NpO2(am,hyd)	+1.0 Np+4 +2.0 H2O -4.0 H+ = NpO2	-1.500	8.562*			
NpO2CO3(s)	+1.0 NpO2+2 +1.0 CO3-2 = NpO2CO3	14.600	-83.337*			
NpO2OH(am,ag)	+1.0 NpO2+ +1.0 H2O -1.0 H+ = NpO2OH	-4.700	26.828*	41.100	47.869*	0.000*
NpO2OH(am,fr)	+1.0 NpO2+ +1.0 H2O -1.0 H+ = NpO2OH	-5.300	30.253*	41.100	36.382*	0.000*
NpO3:H2O(cr)	+1.0 NpO2+2 +2.0 H2O -2.0 H+ = NpO3H2O	-5.470	31.223*			
Pd(cr)	+1.0 Pd+2 +2.0 e- = Pd	30.800	-175.800*	-177.200	-4.696*	0.000*
Pd(OH)2(s)	+1.0 Pd+2 -2.0 H+ +2.0 H2O = Pd(OH)2	3.300	-18.837*			
Portlandite	+1.0 Ca+2 +2.0 H2O -2.0 H+ = Ca(OH)2	-22.800	130.143*	129.704	-1.474*	0.000*
Pu(HPO4)2(am,hyd)	+1.0 Pu+4 +2.0 HPO4-2 = Pu(HPO4)2	30.450	-173.810*			

Table B1: continued

Name	Reaction					$\log_{10}K°$	$\Delta_r G_m°$	$\Delta_r H_m°$	$\Delta_r S_m°$	$\Delta_r C_{p,m}°$
Pu(OH)3(cr)	+1.0 Pu+3	+3.0 H2O	-3.0 H+		= Pu(OH)3	-15.800	90.187*			
PuO2(hyd,ag)	+1.0 Pu+4	+2.0 H2O	-4.0 H+		= PuO2	2.000	-11.416*			
PuO2(OH)2:H2O(cr)	+1.0 PuO2+2	+3.0 H2O	-2.0 H+		= PuO2(OH)2:H2O	-5.500	31.394*			
PuO2CO3(s)	+1.0 PuO2+2	+1.0 CO3-2			= PuO2CO3	14.200	-81.054*			
PuO2OH(am)	+1.0 PuO2+	+1.0 H2O	-1.0 H+		= PuO2OH	-5.000	28.540*			
PuPO4(s,hyd)	+1.0 Pu+3	+1.0 PO4-3			= PuPO4	24.600	-140.418*			
Pyrite	+1.0 Fe+2	+2.0 HS-	-2.0 H+	-2.0 e-	= FeS2	18.500	-105.599*			
Pyrochroite	+1.0 Mn+2	+2.0 H2O	-2.0 H+		= Mn(OH)2	-15.200	86.762*			
Pyrolusite	+1.0 Mn+2	+2.0 H2O	-4.0 H+	-2.0 e-	= MnO2	-41.380	236.199*	272.420	121.487*	0.000*
Quartz	+1.0 Si(OH)4	-2.0 H2O			= SiO2	3.746	-21.384*	-20.637	2.505*	0.000*
RaCO3(cr)	+1.0 Ra+2	+1.0 CO3-2			= RaCO3	8.300	-47.377*	-11.700	119.660*	0.000*
RaSO4(cr)	+1.0 Ra+2	+1.0 SO4-2			= RaSO4	10.260	-58.565*	-39.300	64.613*	0.000*
Rhodochrosite	+1.0 Mn+2	+1.0 HCO3-	-1.0 H+		= MnCO3	0.801*	-4.573*	20.884*	85.384*	-290.513*
Rhodochrosite(syn)	+1.0 Mn+2	+1.0 HCO3-	-1.0 H+		= MnCO3	0.061*	-0.349*	14.901*	51.149*	-290.513*
Rutherfordine	+1.0 UO2+2	+1.0 CO3-2			= UO2CO3	14.490	-82.710*			
S(rhomb)	+1.0 HS-	-1.0 H+	-2.0 e-		= S	2.144	-12.243*	16.300	95.734*	0.000*
Schoepite	+1.0 UO2+2	+3.0 H2O	-2.0 H+		= UO3:2H2O	-5.960	34.020*			
Se(cr)	+1.0 SeO3-2	+6.0 H+	+4.0 e-	-3.0 H2O	= Se	61.290	-349.820*	0.000*	0.000*	0.000*
Siderite	+1.0 Fe+2	+1.0 HCO3-	-1.0 H+		= FeCO3	0.561*	-3.203*	25.278*	95.525*	-290.513*
SiO2(am)	+1.0 Si(OH)4	-2.0 H2O			= SiO2	2.714	-15.492*	-14.594	3.011*	0.000*
Sn(cr)	+1.0 Sn+2	+2.0 e-			= Sn	-4.630	26.430*	7.700	-62.821*	0.000*
SnO(s)	+1.0 Sn+2	+1.0 H2O	-2.0 H+		= SnO	-2.500	14.270*			
SnO2(am)	+1.0 Sn(OH)4	-2.0 H2O			= SnO2	7.300	-41.669*			
SnS(pr)	+1.0 Sn+2	+1.0 HS-	-1.0 H+		= SnS	14.700	-83.908*			
Strontianite	+1.0 Sr+2	-1.0 H+	+1.0 HCO3-		= SrCO3	-1.058*	6.041*	16.576*	35.335*	179.975*
TcO2:1.6H2O(s)	+1.0 TcO(OH)2	+0.6 H2O			= TcO2:1.6(H2O)	8.400	-47.948*			
Theophrastite	+1.0 Ni+2	+2.0 H2O	-2.0 H+		= Ni(OH)2	-10.500	59.934*			
ThF4(cr)	+1.0 Th+4	+4.0 F-			= ThF4	30.200	-172.383*			
ThO2(s)	+1.0 Th+4	+2.0 H2O	-4.0 H+		= ThO2	-9.900	56.510*			
Troilite	+1.0 Fe+2	+1.0 HS-	-1.0 H+		= FeS	5.310	-30.310*			
Tugarinovite	+1.0 MoO4-2	+4.0 H+	+2.0 e-	-2.0 H2O	= MoO2	29.956*	-170.990*	-162.700*	27.805*	0.000*
U(OH)2SO4(cr)	+1.0 U+4	+1.0 SO4-2	+2.0 H2O	-2.0 H+	= U(OH)2SO4	3.170	-18.094*			
UF4:2.5H2O(cr)	+1.0 U+4	+4.0 F-	+2.5 H2O		= UF4:2.5H2O	29.380	-167.702*			
UO2(s)	+1.0 U+4	+2.0 H2O	-4.0 H+		= UO2	0.000	-0.000*			
USiO4(s)	+1.0 U+4	+1.0 Si(OH)4	-4.0 H+		= USiO4	2.988*	-17.057*			
Witherite	+1.0 Ba+2	-1.0 H+	+1.0 HCO3-		= BaCO3	-1.767*	10.087*	11.961*	6.285*	293.360*

GASES

Name	Reaction			$\log_{10}K°$	$\Delta_r G_m°$	$\Delta_r H_m°$	$\Delta_r S_m°$	$\Delta_r C_{p,m}°$
CH4(g)	+1.0 CH4		= CH4	2.856*	-16.305*	13.797*	100.962*	-207.470*
CO2(g)	+1.0 H+	-1.0 H2O	+1.0 HCO3-	= CO2	7.820*	-44.636*	10.875*	186.184*	188.054*
H2(g)	+1.0 H2		= H2	3.106*	-17.727*	4.040*	73.005*	-144.190*
N2(g)	+1.0 N2		= N2	3.186*	-18.188*	10.438*	96.011*	-221.073*
O2(g)	+1.0 O2		= O2	2.894*	-16.521*	12.060*	95.861*	-199.788*
H2S(g)	+1.0 HS-	+1.0 H+	= H2S	8.010	-45.721*	-4.300	138.928*	0.000*

Table B2: Properties of formation from the elements and absolute properties.

ELEMENTS

Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$\Delta_f S_m°$	$S_m°$	$C_{p,m}°$
Al	0.000	0.000	0.000	28.300	24.200
Am	0.000	0.000	0.000	55.400	
As	0.000	0.000	0.000	35.100	24.640
B	0.000	0.000	0.000	5.900	11.087
Ba	0.000	0.000	0.000	62.420	
Br	0.000	0.000	0.000	76.105	37.845
C	0.000	0.000	0.000	5.740	8.517
Ca	0.000	0.000	0.000	41.590	25.929
Cl	0.000	0.000	0.000	111.540	16.974
Cs	0.000	0.000	0.000	85.230	32.210
e	0.000	0.000	0.000	-65.340	-14.418
Eu	0.000	0.000	0.000	77.780	
F	0.000	0.000	0.000	101.395	15.652
Fe	0.000	0.000	0.000	27.280	25.100
H	0.000	0.000	0.000	65.340	14.418
I	0.000	0.000	0.000	58.070	27.219
K	0.000	0.000	0.000	64.680	29.600
Li	0.000	0.000	0.000	29.120	24.860
Mg	0.000	0.000	0.000	32.670	24.869
Mn	0.000	0.000	0.000	32.010	26.320
Mo	0.000	0.000	0.000	28.660	24.060
N	0.000	0.000	0.000	95.804	14.562
Na	0.000	0.000	0.000	51.300	28.230
Nb	0.000	0.000	0.000	36.400	24.600
Ni	0.000	0.000	0.000	29.870	
Np	0.000	0.000	0.000	50.460	29.620
O	0.000	0.000	0.000	102.576	14.689
P	0.000	0.000	0.000	41.090	23.824
Pd	0.000	0.000	0.000	37.820	25.360
Pu	0.000	0.000	0.000	54.460	31.490
Ra	0.000	0.000	0.000	71.000	
S	0.000	0.000	0.000	32.054	22.750
Se	0.000	0.000	0.000	42.270	25.030
Si	0.000	0.000	0.000	18.810	19.789
Sn	0.000	0.000	0.000	51.180	
Sr	0.000	0.000	0.000	55.700	
Tc	0.000	0.000	0.000	32.500	24.900
Th	0.000	0.000	0.000	51.800	
U	0.000	0.000	0.000	50.200	27.660
Zr	0.000	0.000	0.000	39.000	

PRIMARY MASTER SPECIES

Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$\Delta_f S_m°$	$S_m°$	$C_{p,m}°$	a	b
Al+3	-487.740	-538.424	-169.995*	-337.710	-133.070	6.65	0.19
Am+3	-598.700	-616.700	-60.372*	-201.000		9.00	0.00*
B(OH)3	-969.268	-1072.800	-347.248*	162.400			
Ba+2	-557.656	-534.800	76.659*	8.400		4.55	0.09
Br-	-103.850	-121.410	-58.897*	82.550		3.00	0.00*
Ca+2	-552.806	-543.000	32.889*	-56.200		4.86	0.15
Cl-	-131.217	-167.080	-120.285*	56.600		3.71	0.01
Cs+	-291.456	-258.000	112.212*	132.100		2.50	0.00*
e-	0.000	0.000	0.000*	0.000	0.000	0.00	0.00*
Eu+3	-555.100	-586.000	-103.639*	-222.000		9.00	0.00*
F-	-281.523	-335.350	-180.537*	-13.800		3.46	0.08
Fe+2	-78.900	-89.100	-34.211*	-137.700		5.08	0.16
H+	0.000	0.000	0.000*	0.000	0.000	9.00	0.00*
H2O	-237.140	-285.830	-163.307*	69.950	75.351		
HAsO4-2	-714.592	-906.340	-643.126*	-1.700		4.00	0.00*
HCO3-	-586.875	-690.215	-346.604*	98.400		5.40	0.00
HPO4-2	-1095.985	-1299.000	-680.916*	-33.500		4.00	0.00*
I-	-51.724	-56.780	-16.958*	106.450		3.00	0.00*
K+	-282.510	-252.140	101.861*	101.200		3.71	0.01
Li+	-292.918	-278.470	48.459*	12.240		4.76	0.20
Mg+2	-455.375	-467.000	-38.990*	-137.000		5.46	0.22

Table B2:   continued

Name	$\Delta_f G_m^\circ$	$\Delta_f H_m^\circ$	$\Delta_f S_m^\circ$	S_m°	$C_{p,m}^\circ$	a	b
Mn+2	-228.100	-220.750	24.652*	-73.600	50.000	7.04	0.22
MoO4-2	-836.300	-997.900	-542.009*	27.200		5.00	0.00*
Na+	-261.953	-240.340	72.490*	58.450		4.32	0.06
NbO3-	-932.100					3.00	0.00*
Ni+2	-45.500	-54.100	-28.845*	-130.000		5.51	0.22
NO3-	-110.794	-206.850	-322.173*	146.700		3.00	0.00*
NpO2+2	-795.900	-860.700	-217.340*	-92.400		4.00	0.00*
Pd+2	175.800	177.200	4.696*	-88.300		5.50	0.00*
PuO2+2	-762.400	-822.000	-199.899*	-71.200		4.00	0.00*
Ra+2	-561.500	-527.600	113.701*	54.000		5.00	0.00*
SeO3-2	-361.600					4.50	0.00*
Si(OH)4	-1309.183	-1461.723	-511.622*	178.851	237.370		
Sn(OH)4	-						
Sn+2	-26.430	-7.700	62.821*	-16.700		6.00	0.00*
SO4-2	-744.004	-909.340	-554.540*	18.500		5.31	-0.07
Sr+2	-563.864	-550.900	43.481*	-31.500		5.48	0.11
TcO4-	-637.400	-729.400	-308.570*	199.600	-15.000	3.50	0.00*
Th+4	-704.600	-769.000	-215.999*	-425.600		11.00	0.00*
UO2+2	-952.551	-1019.000	-222.871*	-98.200	42.400	4.00	0.00*
Zr+4	-557.700					11.00	0.00*

SECONDARY MASTER SPECIES

Name	$\Delta_f G_m^\circ$	$\Delta_f H_m^\circ$	$\Delta_f S_m^\circ$	S_m°	$C_{p,m}^\circ$	a	b
Al(OH)4-	-1305.705*	-1500.845*	-654.503*			4.00	0.00*
As(OH)3	-639.796*	-742.203*	-343.475*	195.000			
CH4	-34.416	-88.607	-181.758*				
CO2	-385.992*	-413.494*	-92.245*	119.360			
CO3-2	-527.917*	-675.314*	-494.370*	-50.000		5.40	0.00*
Eu+2	-521.300	-507.900	44.944*	-8.000		6.00	0.00*
Fe+3	-4.581*	-48.600*	-147.639*			9.00	0.00*
H2	17.726	-4.039	-73.000*				
H2PO4-	-1137.151*	-1302.600*	-554.917*	92.500		4.50	0.00*
H2Se	22.235*						
H3PO4	-1149.367*	-1294.120*	-485.505*	161.912			
HS-	12.243	-16.300	-95.734*	67.000		3.50	0.00*
HSeO4-	-452.728*					4.00	0.00*
I2	-223.031*						
N2	18.188	-10.437	-96.009*				
NH3	-26.673*	-81.170*	-182.784*	109.040			
NH4+	-79.398	-133.260	-180.654*	111.170		2.50	0.00*
Np+3	-512.900	-527.200	-47.962*	-193.600		9.00	0.00*
Np+4	-491.800	-556.000	-215.328*	-426.400		11.00	0.00*
NpO2+	-907.800	-978.200	-236.123*	-45.900	-4.000	4.00	0.00*
O2	16.521	-12.059	-95.858*				
OH-	-157.230*	-229.924*	-243.818*	-10.900		10.65	0.00*
PO4-3	-1025.491*	-1284.400*	-868.386*	-220.970		4.00	0.00*
Pu+3	-579.000	-591.800	-42.931*	-184.500		9.00	0.00*
Pu+4	-478.000	-539.900	-207.614*	-414.500		11.00	0.00*
PuO2+	-852.600	-910.100	-192.856*	1.000		4.00	0.00*
S2O3-2	-519.291	-648.500	-433.369*			4.00	0.00*
SiO(OH)3-	-1253.187*	-1436.123*	-613.570*			4.00	0.00*
SiO2(OH)2-2	-1177.099*	-1386.723*	-703.083*			4.00	0.00*
SO3-2	-487.472	-635.500	-496.488*			4.50	0.00*
TcO(OH)2	-568.200						
U+4	-529.860*	-591.200	-205.734*	-416.896	48.000	11.00	0.00*
UO2+	-961.022*	-1025.127	-215.010*	-25.000		4.00	0.00*

Table B2:   continued

PRODUCT SPECIES

Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$\Delta_f S_m°$	$S_m°$	$C_{p,m}°$	a	b
(NpO2)2(OH)2+2	-2030.291*					4.00	0.00*
(NpO2)2CO3(OH)3-	-2814.755*					4.00	0.00*
(NpO2)3(CO3)6-6	-5839.694*					4.00	0.00*
(NpO2)3(OH)5+	-3475.678*					3.00	0.00*
(PuO2)2(OH)2+2	-1956.270*					4.00	0.00*
(UO2)2(OH)2+2	-2347.303*	-2572.065*	-753.856*	-38.000		4.00	0.00*
(UO2)2CO3(OH)3-	-3139.531*					4.00	0.00*
(UO2)2NpO2(CO3)6-6	-6174.401*					6.00	0.00*
(UO2)2OH+3	-2126.830*					4.00	0.00*
(UO2)2PuO2(CO3)6-6	-6135.821*					6.00	0.00*
(UO2)3(CO3)6-6	-6333.392*	-7171.584*	-2811.309*			4.00	0.00*
(UO2)3(OH)4+2	-3738.287*					4.00	0.00*
(UO2)3(OH)5+	-3954.593*	-4389.086*	-1457.296*	83.000		4.00	0.00*
(UO2)3(OH)7-	-4340.684*					4.00	0.00*
(UO2)3O(OH)2HCO3+	-4100.758*					4.00	0.00*
(UO2)4(OH)7+	-5345.178*					4.00	0.00*
Al(OH)2+	-901.549*	-1011.802*	-369.790*			4.00	0.00*
Al(OH)3	-1105.363*	-1251.210*	-489.173*				
Al(OH)6SiO-	-2398.297*					4.00	0.00*
Al(SO4)2-	-2009.425*					4.00	0.00*
AlF+2	-809.676*	-868.974*	-198.887*			4.00	0.00*
AlF2+	-1123.449*	-1201.024*	-260.187*			4.00	0.00*
AlF3	-1428.090*	-1535.574*	-360.503*				
AlF4-	-1723.940*	-1869.724*	-488.961*			4.00	0.00*
AlF5-2	-2011.228*	-2208.174*	-660.559*			4.00	0.00*
AlF6-3	-2292.751*	-2550.024*	-862.897*			4.00	0.00*
AlOH+2	-696.584*	-774.456*	-261.184*			4.00	0.00*
AlSiO(OH)3+2	-1783.167*					4.00	0.00*
AlSO4+	-1254.005*					4.00	0.00*
Am(CO3)2-	-1724.744*					4.00	0.00*
Am(CO3)3-3	-2269.215*					4.00	0.00*
Am(OH)2+	-986.218*					4.00	0.00*
Am(OH)3	-1163.423*						
Am(SO4)2-	-2117.531*					4.00	0.00*
AmCl+2	-735.910*					4.00	0.00*
AmCO3+	-1171.140*					4.00	0.00*
AmF+2	-899.630*					4.00	0.00*
AmF2+	-1194.853*					4.00	0.00*
AmH2PO4+2	-1752.976*					4.00	0.00*
AmNO3+2	-717.086*					4.00	0.00*
AmOH+2	-794.171*					4.00	0.00*
AmSiO(OH)3+2	-1898.122*					4.00	0.00*
AmSO4+	-1364.680*					4.00	0.00*
As(OH)4-	-824.240	-1000.690	-591.816*			4.50	0.00*
AsO4-3	-648.360	-888.140	-804.226*	-162.800		4.00	0.00*
B(OH)4-	-1153.693*	-1344.577*	-640.227*			4.50	0.00*
BaCO3	-1101.060*	-1195.272*	-315.988*				
BaHCO3+	-1150.134*	-1201.752*	-173.129*			4.00	0.00*
BaOH+	-717.909*					4.00	0.00*
BaSO4	-1317.072*						
CaCO3	-1099.127*	-1203.482*	-350.008*				
CaF+	-839.695*	-861.112*	-71.834*			4.00	0.00*
CaHCO3+	-1145.992*	-1221.952*	-254.770*			4.00	0.00*
CaOH+	-716.997*					4.00	0.00*
CaSiO(OH)3+	-1812.843*					4.00	0.00*
CaSiO2(OH)2	-1756.162*						
CaSO4	-1309.938*	-1445.436*	-454.462*				
Eu(CO3)2-	-1680.002*					4.00	0.00*
Eu(OH)2+	-943.189*					4.00	0.00*
Eu(OH)3	-1131.239*						
Eu(OH)4-	-1297.029*					4.00	0.00*
Eu(SiO(OH)3)2+	-3134.537*					4.00	0.00*
Eu(SO4)2-	-2075.644*					4.00	0.00*
EuCl+2	-692.596*					4.00	0.00*
EuCl2+	-826.096*					4.00	0.00*
EuCO3+	-1129.253*					4.00	0.00*

Table B2:   continued

Name	$\Delta_fG_m°$	$\Delta_fH_m°$	$\Delta_fS_m°$	$S_m°$	$C_{p,m}°$	a	b
EuF+2	-858.314*					4.00	0.00*
EuF2+	-1155.248*					4.00	0.00*
EuOH+2	-748.631*					4.00	0.00*
EuSiO(OH)3+2	-1853.381*					4.00	0.00*
EuSO4+	-1321.651*					4.00	0.00*
Fe(OH)2+	-446.497*	-548.712*	-342.833*			4.00	0.00*
Fe(OH)3	-644.308*	-802.326*	-529.993*				
Fe(OH)4-	-829.848*	-1058.449*	-766.734*			4.00	0.00*
Fe(SO4)2-	-1523.299*	-1848.032*	-1089.163*			4.00	0.00*
Fe2(OH)2+4	-466.604*	-612.374*	-488.915*			4.00	0.00*
Fe3(OH)4+5	-926.343*	-1229.286*	-1016.073*			9.00	0.00*
FeCl+	-210.916*					4.00	0.00*
FeCl+2	-144.246*	-192.248*	-161.001*			4.00	0.00*
FeCl2+	-279.173*					4.00	0.00*
FeCl3	-404.682*						
FeCO3	-631.818*						
FeF+	-366.131*					4.00	0.00*
FeF+2	-321.494*	-372.653*	-171.588*			4.00	0.00*
FeF2+	-629.274*	-699.216*	-234.586*			4.00	0.00*
FeF3	-929.063*	-1032.055*	-345.437*				
FeHCO3+	-677.191*					4.00	0.00*
FeHSO4+	-840.416*					4.00	0.00*
FeHSO4+2	-774.089*					4.00	0.00*
FeOH+	-261.814*	-319.701*	-194.156*			4.00	0.00*
FeOH+2	-229.221*	-290.915*	-206.925*			4.00	0.00*
FeSiO(OH)3+2	-1313.136*					4.00	0.00*
FeSO4	-835.747*	-984.926*	-500.347*				
FeSO4+	-771.646*	-941.580*	-569.960*			4.00	0.00*
H2AsO4-	-753.203	-909.560	-524.424*	117.000		4.50	0.00*
H2S	-27.656*	-38.600*	-36.706*				
H2SeO3	-425.530*						
H3AsO4	-766.119	-902.500	-457.424*	184.000			
HF	-299.652*	-322.043*	-75.102*	88.000			
HF2-	-583.709	-655.500	-240.788*	92.683		4.00	0.00*
HSe-	44.000					3.50	0.00*
HSeO3-	-409.548*					4.00	0.00*
HSO3-	-528.684	-514.550	47.406*			4.00	0.00*
HSO4-	-755.350*	-893.212*	-462.390*	131.700		4.00	0.00*
I3-	-291.138*					4.00	0.00*
KOH	-437.112*						
KSO4-	-1031.366*	-1152.066*	-404.830*			4.00	0.00*
LiOH	-452.200*						
LiSO4-	-1040.575*					4.00	0.00*
MgCO3	-1000.300*	-1130.963*	-438.243*				
MgF+	-747.287*	-788.961*	-139.777*			4.00	0.00*
MgHCO3+	-1048.347*	-1153.927*	-354.115*			4.00	0.00*
MgOH+	-627.215*					4.00	0.00*
MgSiO(OH)3+	-1717.124*					4.00	0.00*
MgSiO2(OH)2	-1665.010*						
MgSO4	-1212.907*	-1357.303*	-484.306*				
MnCl+	-362.799*					4.00	0.00*
MnCl2	-491.961*						
MnCl3-	-619.982*					4.00	0.00*
MnCO3	-783.986*						
MnF+	-514.418*					4.00	0.00*
MnHCO3+	-826.106*					4.00	0.00*
MnOH+	-404.792*	-446.330*	-139.321*			4.00	0.00*
MnSO4	-984.947*	-1115.990*	-439.520*				
NaCO3-	-797.119*	-878.375*	-272.534*			4.00	0.00*
NaF	-542.106*						
NaHCO3	-847.401*						
NaOH	-418.153*						
NaSO4-	-1009.953*	-1144.994*	-452.931*			4.00	0.00*
Nb(OH)4+	-1208.600					4.00	0.00*
Nb(OH)5	-1448.300						
Ni(CO3)2-2	-1135.583*					4.00	0.00*
Ni(HS)2	-84.373*						
Ni(NH3)2+2	-126.815*					4.00	0.00*
Ni(NH3)3+2	-162.621*					4.00	0.00*

Table B2:   continued

Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$\Delta_f S_m°$	$S_m°$	$C_{p,m}°$	a	b
Ni(NH3)4+2	-195.572*					4.00	0.00*
Ni(NH3)5+2	-226.241*					4.00	0.00*
Ni(NH3)6+2	-252.343*					4.00	0.00*
Ni(NO3)2	-263.663*						
Ni(OH)2	-417.035*	-540.000	-412.426*				
Ni(OH)3-	-587.391*	-791.000	-682.907*			4.00	0.00*
Ni(OH)4-2	-737.769*					4.00	0.00*
Ni(SO4)2-2	-1551.774*					4.00	0.00*
Ni2OH+3	-272.201*	-359.030*	-291.225*			4.00	0.00*
Ni4(OH)4+4	-971.306*	-1189.720*	-732.565*			5.00	0.00*
NiCl+	-179.000*					4.00	0.00*
NiCl2	-313.414*						
NiCO3	-596.250*						
NiF+	-334.443*					4.00	0.00*
NiH2PO4+	-1191.465*					4.00	0.00*
NiHCO3+	-638.083*					4.00	0.00*
NiHP2O7-	-2053.175*					4.00	0.00*
NiHPO4	-1158.232*						
NiHS+	-64.651*					4.00	0.00*
NiNH3+2	-87.585*					4.00	0.00*
NiNO3+	-158.577*					4.00	0.00*
NiOH+	-228.414*	-289.930*	-206.327*			4.00	0.00*
NiP2O7-2	-2017.956*	-2356.353*	-1134.988*			4.00	0.00*
NiPO4-	-1118.790*					4.00	0.00*
NiSO4	-802.690*	-949.465*	-492.287*				
Np(CO3)4-4	-2812.898*					6.00	0.00*
Np(CO3)5-6	-3334.708*					9.00	0.00*
Np(OH)4	-1384.421*						
Np(SO4)2	-2042.882*	-2319.280*	-927.044*				
NpCl+3	-631.579*					6.00	0.00*
NpF+3	-824.467*	-889.850*	-219.295*			6.00	0.00*
NpF2+2	-1144.462*					4.00	0.00*
NpNO3+3	-613.439*					6.00	0.00*
NpO2(CO3)2-2	-1946.032*					4.00	0.00*
NpO2(CO3)2-3	-2000.908*					4.00	0.00*
NpO2(CO3)2OH-4	-2170.522*					4.00	0.00*
NpO2(CO3)3-4	-2490.217*	-2928.542*	-1470.148*			3.00	0.00*
NpO2(CO3)3-5	-2522.947*	-3017.442*	-1658.545*			4.00	0.00*
NpO2(HPO4)2-2	-3042.096*					4.00	0.00*
NpO2(OH)	-1080.439*	-1199.260*	-398.528*	25.000			
NpO2(OH)2-	-1247.370*	-1431.264*	-616.784*	40.000		4.00	0.00*
NpO2(OH)3-	-1398.867*					4.00	0.00*
NpO2(OH)4-2	-1556.095*					4.00	0.00*
NpO2(SO4)2-2	-2310.736*	-2653.380*	-1149.234*			4.00	0.00*
NpO2Cl+	-929.400*					4.00	0.00*
NpO2CO3	-1377.016*						
NpO2CO3-	-1464.029*					4.00	0.00*
NpO2F	-1196.173*						
NpO2F+	-1103.509*					4.00	0.00*
NpO2F2	-1402.327*						
NpO2H2PO4+	-1952.002*					4.00	0.00*
NpO2HPO4	-1927.275*						
NpO2HPO4-	-2020.624*					4.00	0.00*
NpO2OH+	-1003.929*					4.00	0.00*
NpO2SO4	-1558.626*	-1753.340*	-653.073*				
NpO2SO4-	-1654.316*	-1864.340*	-704.425*			4.00	0.00*
NpOH+2	-711.225*					5.00	0.00*
NpOH+3	-727.285*					4.00	0.00*
NpSO4+2	-1274.904*	-1435.540*	-538.775*			4.00	0.00*
Pd(NH3)2+2	16.856*					4.00	0.00*
Pd(NH3)3+2	-52.628*					4.00	0.00*
Pd(NH3)4+2	-118.115*					4.00	0.00*
Pd(OH)2	-275.648*						
Pd(OH)3-	-447.145*					4.00	0.00*
PdCl+	15.472*					4.00	0.00*
PdCl2	-134.011*						
PdCl2(OH)2-2	-520.958*					4.00	0.00*
PdCl3-	-280.069*					4.00	0.00*
PdCl3OH-2	-469.261*					4.00	0.00*

Table B2: continued

Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$\Delta_f S_m°$	$S_m°$	$C_{p,m}°$	a	b
PdCl4-2	-415.852*					4.00	0.00*
PdNH3+2	94.330*					4.00	0.00*
Pu(CO3)4-4	-2794.589*					4.00	0.00*
Pu(CO3)5-6	-3314.515*					6.00	0.00*
Pu(OH)4	-1378.612*						
Pu(SO4)2	-2029.596*						
Pu(SO4)2-	-2099.544*	-2398.480*	-1002.637*			4.00	0.00*
PuCl+2	-717.067*					4.00	0.00*
PuCl+3	-619.491*					4.00	0.00*
PuF+3	-809.982*	-866.150*	-188.388*			4.00	0.00*
PuF2+2	-1130.662*	-1199.600*	-231.218*			4.00	0.00*
PuH3PO4+4	-1641.066*					4.00	0.00*
PuNO3+3	-599.925*					4.00	0.00*
PuO2(CO3)2-2	-1901.572*	-2199.628*	-999.683*			4.00	0.00*
PuO2(CO3)3-4	-2447.185*	-2886.542*	-1473.611*			4.00	0.00*
PuO2(CO3)3-5	-2464.893*	-2955.152*	-1644.338*			4.00	0.00*
PuO2(OH)2	-1161.334*						
PuO2(SO4)2-2	-2275.523*	-2597.680*	-1080.519*			4.00	0.00*
PuO2Cl+	-897.613*					4.00	0.00*
PuO2Cl2	-1021.409*						
PuO2CO3	-1343.402*						
PuO2CO3-	-1409.743*					4.00	0.00*
PuO2F+	-1069.952*					4.00	0.00*
PuO2F2	-1366.829*						
PuO2OH	-1034.201*						
PuO2OH+	-968.146*	-1079.830*	-374.591*			4.00	0.00*
PuO2SO4	-1525.697*	-1715.240*	-635.730*				
PuOH+2	-776.755*					4.00	0.00*
PuOH+3	-710.688*	-789.730*	-265.109*			4.00	0.00*
PuSO4+	-1345.265*	-1483.940*	-465.117*			4.00	0.00*
PuSO4+2	-1261.332*					4.00	0.00*
RaCl+	-692.146*	-692.580*	-1.455*			4.00	0.00*
RaCO3	-1103.688*	-1198.434*	-317.781*				
RaOH+	-721.584*	-752.924*	-105.116*			4.00	0.00*
RaSO4	-1321.201*	-1431.540*	-370.078*				
S-2	120.696*					5.00	0.00*
SeO4-2	-442.454*					4.00	0.00*
Sn(OH)2	-456.758*						
Sn(OH)3-	-637.959*					4.00	0.00*
Sn(OH)5-	-					4.00	0.00*
Sn(OH)6-2	-					4.00	0.00*
Sn3(OH)4+2	-995.885*					4.00	0.00*
SnCl+	-167.351*					4.00	0.00*
SnCl2	-302.335*						
SnCl3-	-432.068*					4.00	0.00*
SnF+	-336.493*					4.00	0.00*
SnOH+	-241.879*					4.00	0.00*
SnOHCl	-377.092*						
SnSO4	-785.275*						
SrCO3	-1107.793*	-1204.386*	-323.975*				
SrHCO3+	-1157.501*	-1215.814*	-195.582*			4.00	0.00*
SrOH+	-725.144*					4.00	0.00*
SrSO4	-1320.939*	-1451.537*	-438.027*				
TcCO3(OH)2	-969.143*						
TcCO3(OH)3-	-1158.906*					4.00	0.00*
TcO(OH)+	-345.330*					4.00	0.00*
TcO(OH)3-	-743.122*					4.00	0.00*
TcO+2	-116.752*					4.50	0.00*
Th(CO3)5-6	-3514.287*					4.00	0.00*
Th(OH)4	-1548.132*						
Th(SO4)2	-2258.821*						
Th(SO4)3-2	-3007.392*					4.00	0.00*
ThCO3(OH)3-	-1926.243*					4.00	0.00*
ThF+3	-1031.787*					4.00	0.00*
ThF2+2	-1348.700*					4.00	0.00*
ThF3+	-1657.051*					4.00	0.00*
ThF4	-1957.981*						
ThHPO4+2	-1874.790*					4.00	0.00*
ThOH+3	-928.041*					4.00	0.00*

Table B2:   continued

Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$\Delta_f S_m°$	$S_m°$	$C_{p,m}°$	a	b
ThSO4+2	-1491.985*					4.00	0.00*
U(CO3)4-4	-2842.567*					4.00	0.00*
U(CO3)5-6	-3364.092*	-3987.770*	-2091.826*			4.00	0.00*
U(NO3)2+2	-764.577*					4.00	0.00*
U(OH)4	-1427.048*						
U(SO4)2	-2077.860*	-2377.180*	-1003.925*				
UCl+3	-670.895*	-777.280*	-356.817*			4.00	0.00*
UF+3	-864.354*	-932.150*	-227.389*			4.00	0.00*
UF2+2	-1185.548*	-1265.400*	-267.826*			4.00	0.00*
UF3+	-1497.723*	-1596.750*	-332.138*			4.00	0.00*
UF4	-1802.078*	-1936.806*	-451.881*				
UF5-	-2091.649*					4.00	0.00*
UF6-2	-2384.988*					4.00	0.00*
UNO3+3	-649.045*					4.00	0.00*
UO2(CO3)2-2	-2105.080*	-2351.128*	-825.248*			4.00	0.00*
UO2(CO3)3-4	-2659.597*	-3084.142*	-1423.930*			4.00	0.00*
UO2(CO3)3-5	-2587.071*					4.00	0.00*
UO2(H2PO4)2	-3254.937*						
UO2(OH)2	-1358.334*						
UO2(OH)3-	-1554.377*					4.00	0.00*
UO2(OH)4-2	-1712.746*					4.00	0.00*
UO2(SO4)2-2	-2464.190*	-2802.580*	-1134.965*			4.00	0.00*
UO2Cl+	-1084.738*	-1178.080*	-313.069*			4.00	0.00*
UO2Cl2	-1208.706*	-1338.160*	-434.190*				
UO2CO3	-1535.665*	-1689.314*	-515.340*				
UO2F+	-1263.128*	-1352.650*	-300.258*			4.00	0.00*
UO2F2	-1564.800*	-1687.600*	-411.872*				
UO2F3-	-1859.338*	-2022.700*	-547.920*			4.00	0.00*
UO2F4-2	-2145.427*	-2360.110*	-720.050*			6.00	0.00*
UO2H2PO4+	-2108.311*					4.00	0.00*
UO2H2PO4H3PO4+	-3260.702*					4.00	0.00*
UO2H3PO4+2	-2106.256*					4.00	0.00*
UO2HPO4	-2089.862*						
UO2NO3+	-1065.057*					4.00	0.00*
UO2OH+	-1160.009*	-1261.657*	-340.928*	17.000		4.00	0.00*
UO2PO4-	-2053.559*					4.00	0.00*
UO2SO4	-1714.535*	-1908.840*	-651.701*				
UOH+3	-763.918*	-830.120*	-222.041*			4.00	0.00*
USO4+2	-1311.423*	-1492.540*	-607.469*			4.00	0.00*
Zr(OH)4	-1450.892*						
Zr(OH)5-	-1652.071*					4.00	0.00*
ZrCl+3	-697.479*					4.00	0.00*
ZrF+3	-897.445*	29.700	3109.660*			4.00	0.00*
ZrF2+2	-1226.345*	58.700	4310.061*			4.00	0.00*
ZrF3+	-1543.258*	82.100	5451.476*			4.00	0.00*
ZrF4	-1855.604*	116.300	6613.799*				
ZrF5-	-2163.384*					4.00	0.00*
ZrF6-2	-2466.027*					4.00	0.00*
ZrOH+3	-796.552*					4.00	0.00*
ZrSO4+2	-1341.660*					4.00	0.00*

MINERALS AND SOLIDS

Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$\Delta_f S_m°$	$S_m°$	$C_{p,m}°$
(NH4)4NpO2(CO3)3(s)	-2850.277*				
(UO2)3(PO4)2:4H2O(cr)	-6138.966*				
Am(CO3)1.5(cr)	-1485.900*				
Am(OH)3(am)	-1213.083*				
Am(OH)3(cr)	-1223.358*				
AmCO3OH(cr)	-1404.858*				
Anhydrite	-1321.683*	-1445.184*	-414.226*		
Aragonite	-1128.306*	-1207.480*	-265.551*		
As(cr)	0.000	0.000	0.000*		
Baddeleyite	-1042.825*				
Barite	-1358.571*	-1470.715*	-376.131*		
Brucite	-833.532*	-925.274*	-307.704*		
Calcite	-1129.127*	-1208.705*	-266.907*		
CaSn(OH)6(s)	-				

Table B2: continued

Name	$\Delta_f G_m°$	$\Delta_f H_m°$	$\Delta_f S_m°$	$S_m°$	$C_{p,m}°$
Cassiterite	-				
Celestite	-1345.723*	-1455.901*	-369.539*		
Chernikovite	-3064.748*				
Dolomite(dis)	-2158.425*	-2314.228*	-522.565*		
Dolomite(ord)	-2161.565*	-2321.148*	-535.245*		
Eu(OH)3(am)	-1166.058*				
Eu(OH)3(cr)	-1181.470*	-1319.100	-461.613*		
Eu2(CO3)3(cr)	-2893.734*				
EuF3(cr)	-1498.988*				
EuOHCO3(cr)	-1364.112*				
Fe(cr)	0.000	0.000	0.000*		
Fe(OH)3(am)	-687.461*				
Fe(OH)3(mic)	-698.877*				
FeCO3(pr)	-666.467*	-764.414*	-328.517*		
Fluorite	-1176.355*	-1233.342*	-191.135*		
Gibbsite	-1154.889*	-1293.130*	-463.663*	68.440	91.720
Goethite	-484.569*				
Graphite	0.000	0.000	0.000*		
Gypsum	-1797.238*	-2023.546*	-759.039*		
Hausmannite	-1284.498*	-1384.492*	-335.382*		
Hematite	-714.190*				
K4NpO2(CO3)3(s)	-3660.385*				
Kaolinite	-3788.547*	-4138.424*	-1173.494*		
Magnesite	-1030.600*				
Magnetite	-979.428*				
Manganite	-557.738*				
Melanterite	-2495.495*	-3019.787*	-1758.485*		
Mo(cr)	0.000	0.000	0.000*		
Molybdite	-667.970	-745.090	-258.662*		
Na3NpO2(CO3)2(s)	-2833.402*				
NaNpO2CO3(s,ag)	-1764.226*				
NaNpO2CO3:3.5H2O(s,fr)	-2591.362*				
Nb2O5(cr)	-1766.000	-1899.500	-447.761*		
NbO2(cr)	-740.500	-796.200	-186.819*		
NiCO3(cr)	-637.348*				
NpO2(am,hyd)	-957.518*				
NpO2CO3(s)	-1407.155*				
NpO2OH(am,ag)	-1118.112*	-1222.930*	-351.561*		
NpO2OH(am,fr)	-1114.687*	-1222.930*	-363.048*		
NpO3:H2O(cr)	-1238.957*				
Pd(cr)	0.000	0.000	0.000*		
Pd(OH)2(s)	-317.317*				
Portlandite	-896.943*	-984.956*	-295.198*		
Pu(HPO4)2(am,hyd)	-2843.780*				
Pu(OH)3(cr)	-1200.233*				
PuO2(hyd,ag)	-963.696*				
PuO2(OH)2:H2O(cr)	-1442.426*				
PuO2CO3(s)	-1371.372*				
PuO2OH(am)	-1061.200*				
PuPO4(s,hyd)	-1744.909*				
Pyrite	-160.013*				
Pyrochroite	-615.618*				
Pyrolusite	-466.181*	-519.990*	-180.475*		
Quartz	-856.287	-910.700	-182.502*	41.460	44.602
RaCO3(cr)	-1136.794*	-1214.614*	-261.009*		
RaSO4(cr)	-1364.069*	-1476.240*	-376.225*		
Rhodochrosite	-819.548*	-890.081*	-236.568*		
Rhodochrosite(syn)	-815.324*	-896.064*	-270.803*		
Rutherfordine	-1563.178*	-1689.778*	-424.620*	144.200	120.100
S(rhomb)	0.000	0.000	0.000*		
Schoepite	-1629.951*	-1819.545*	-635.900*	188.540	172.070
Se(cr)	0.000	0.000	0.000*	42.270	25.030
Siderite	-668.978*	-754.037*	-285.290*		
SiO2(am)	-850.395*	-904.657*	-181.997*		
Sn(cr)	0.000	0.000	0.000*		
SnO(s)	-249.300*				
SnO2(am)	-				
SnS(pr)	-98.095*				
Strontianite	-1144.698*	-1224.539*	-267.788*		

Table B2:   continued

Name	$\Delta_f G_m^\circ$	$\Delta_f H_m^\circ$	$\Delta_f S_m^\circ$	S_m°	$C_{p,m}^\circ$
TcO2:1.6H2O(s)	-758.432*				
Theophrastite	-459.846*	-547.115*	-292.702*	73.000	
ThF4(cr)	-2003.075*				
ThO2(s)	-1122.370*				
Troilite	-96.967*				
Tugarinovite	-533.010	-588.940	-187.590*		
U(OH)2SO4(cr)	-1766.239*				
UF4:2.5H2O(cr)	-2416.505*	-2647.696*	-775.420*	263.500	263.700
UO2(s)	-1004.140*	-1057.307*	-178.322*	77.030	63.600
USiO4(s)	-1856.100				
Witherite	-1134.444*	-1213.054*	-263.659*		

GASES

Name	$\Delta_f G_m^\circ$	$\Delta_f H_m^\circ$	$\Delta_f S_m^\circ$	S_m°	$C_{p,m}^\circ$
CH4(g)	-50.721*	-74.810*	-80.796*		
CO2(g)	-394.371*	-393.510*	2.887*	213.785	37.135
H2(g)	-0.001*	0.001*	0.004*	130.680	28.836
H2S(g)	-33.478*	-20.600*	43.194*		
N2(g)	-0.000*	0.001*	0.002*	191.609	29.124
O2(g)	-0.000*	0.001*	0.003*	205.152	29.378

Table B3: Parameters of temperature dependent equilibrium constants.

SECONDARY MASTER SPECIES

Name	A	B	C	D	E
Al(OH)4-	2.88659E+01*		-1.03416E+04*	-6.89409E+00*	
As(OH)3	-4.01250E+00		6.85207E+03	3.82786E+00	
CH4	1.36686E+02*	4.10056E-02*	2.77799E+03*	-5.73080E+01*	1.01553E+06*
CO2	3.56309E+02	6.09196E-02	-2.18344E+04	-1.26834E+02	1.68492E+06
CO3-2	-1.07887E+02	-3.25285E-02	5.15179E+03	3.89256E+01	-5.63714E+05
Eu+2	7.76098E+00*		-4.07942E+03*		
Fe+3	-5.92475E+00*		-2.11545E+03*		
H2	-7.64510E+01*	-6.53305E-03	3.03719E+03*	2.63117E+01*	
H2PO4-	6.58131E+00*		1.88040E+02*		
H3PO4	1.02069E+01*		-2.54899E+02*		
HS-	-1.01553E+01*		1.30730E+04*		
N2	-2.63716E+02*		7.92516E+04*	8.29150E+01*	
NH3	-1.11279E-01*		-2.72083E+03*		
NH4+	-1.15166E+02*		4.52623E+04*	3.33367E+01*	
Np+3	-8.21297E+00*		1.24399E+04*		
Np+4	-1.69550E+01*		1.39442E+04*		
NpO2+	-9.81072E-01*		6.13742E+03*		
O2	-2.16371E+01*	4.10123E-03*	-2.74744E+04*	1.07417E+01*	
OH-	-2.83971E+02*	-5.06984E-02	1.33230E+04	1.02244E+02	-1.11967E+06
PO4-3	-9.79221E+00*		-7.62607E+02*		
Pu+3	-8.86118E+00*		1.78356E+04*		
Pu+4	-1.74631E+01*		1.51247E+04*		
PuO2+	3.67902E-01*		4.60176E+03*		
S2O3-2	-7.35576E+00*		1.35269E+04*		
SiO(OH)3-	-5.32510E+00*		-1.33717E+03*		
SiO2(OH)2-2	-1.00006E+01*		-3.91750E+03*		
SO3-2	-5.49786E+00*		6.26278E+02*		
U+4	-1.61650E+01*		7.51429E+03*		
UO2+	4.10602E-01*		3.20034E+02*		

PRODUCT SPECIES

Name	A	B	C	D	E
(UO2)3(CO3)6-6	4.30155E+01*		3.27503E+03*		
Al(OH)2+	-4.03611E+01*		-3.04200E+03*	1.61532E+01*	
Al(OH)3	-4.55320E+01*		-5.13445E+03*	1.87197E+01*	
AlF+2	7.92092E+00*		-2.50720E+02*		
AlF2+	1.41491E+01*		-4.23090E+02*		
AlF3	1.83392E+01*		-4.64877E+02*		
AlF4-	2.10594E+01*		-5.27557E+02*		
AlF5-2	2.15263E+01*		-3.65633E+02*		
AlF6-3	2.03876E+01*		-2.61167E+01*		
AlOH+2	-4.07303E+01*		-6.20276E+02*	1.52978E+01*	
As(OH)4-	-4.44162E+00*		-1.42821E+03*		
AsO4-3	-8.41479E+00*		-9.50646E+02*		
B(OH)4-	3.49600E+00	-1.72215E-02	-2.26492E+03		
BaCO3	-1.07774E+02	-2.38075E-02	5.15179E+03	3.89256E+01	-5.63714E+05
BaHCO3+	-3.09380E+00	1.36690E-02			
CaCO3	-1.33662E+03	-3.31972E-01	4.06645E+04	5.24744E+02	-5.63714E+05
CaF+	3.95996E+00*		-9.00402E+02*		
CaHCO3+	1.20912E+03	3.12940E-01	-3.47650E+04	-4.78782E+02	
CaSO4	3.50945E+00*		-3.60598E+02*		
Fe(OH)2+	6.86451E+00*		-3.73716E+03*		
Fe(OH)3	5.61862E+00*		-5.41995E+03*		
Fe(OH)4-	1.78292E+00*		-6.97162E+03*		
Fe(SO4)2-	8.75200E+00*		-1.00536E+03*		
Fe2(OH)2+4	6.94590E+00*		-2.95046E+03*		
Fe3(OH)4+5	4.18249E+00*		-3.12535E+03*		
FeCl+2	5.58500E+00*		-1.22391E+03*		
FeF+2	8.17914E+00*		-5.90080E+02*		
FeF2+	1.43185E+01*		-1.04905E+03*		
FeF3	1.79585E+01*		-1.18021E+03*		
FeOH+	1.75612E-01*		-2.88478E+03*		
FeOH+2	5.43340E+00*		-2.27292E+03*		
FeSO4	4.61759E+00*		-7.05898E+02*		

Table B3:   continued

Name	A	B	C	D	E
FeSO4+	6.90622E+00*		-8.54563E+02*		
H2AsO4-	6.20020E+00*		1.68191E+02*		
H2S	3.08323E+00*		1.16480E+03*		
H2SeO3	1.33181E+01*		-6.31501E+02*		
H3AsO4	9.69982E+00*		-2.00576E+02*		
HF	-2.03300E+00	1.26450E-02	4.29010E+02		
HF2-	-8.94327E+01*		3.46693E+03*	3.29063E+01*	
HSeO3-	9.27946E+00*		-2.62211E+02*		
HSO3-	2.84094E+01*		-6.31762E+03*		
HSO4-	-5.68890E+01	6.47300E-03	2.30790E+03	1.98858E+01	
KSO4-	2.49925E+00*		-4.91724E+02*		
MgCO3	-1.06896E+02	-2.58585E-02	5.15179E+03	3.89256E+01	-5.63714E+05
MgF+	4.16560E+00*		-6.99342E+02*		
MgHCO3+	-5.92150E+01		2.53746E+03	2.09230E+01	
MgSO4	5.70515E+00*		-9.94376E+02*		
MnOH+	-3.47869E-02*		-3.14704E+03*		
MnSO4	4.72021E+00*		-7.36494E+02*		
NaCO3-	8.24884E-02*		-2.72553E+03*		
NaSO4-	1.52096E+00*		-2.44770E+02*		
Ni(OH)2	-2.97558E+00*		-4.47953E+03*		
Ni(OH)3-	-8.57367E+00*		-6.29882E+03*		
Ni2OH+3	-3.66830E+00*		-1.82817E+03*		
Ni4(OH)4+4	1.88254E+00*		-8.87966E+03*		
NiOH+	-7.40429E-01*		-2.61167E+03*		
NiP2O7-2	4.82537E+00*		-5.17998E+02*		
NiSO4	4.75830E+00*		-7.29961E+02*		
Np(SO4)2	2.07556E+01*		-2.89373E+03*		
NpF+3	9.22279E+00*		-7.83500E+01*		
NpO2(CO3)3-4	1.20295E+01*		2.18858E+03*		
NpO2(CO3)3-5	3.16995E+00*		6.94703E+02*		
NpO2(SO4)2-2	9.25498E+00*		-1.35807E+03*		
NpO2SO4	6.20570E+00*		-8.72296E+02*		
NpO2SO4-	4.50444E+00*		-1.21181E+03*		
NpSO4+2	1.20707E+01*		-1.55655E+03*		
Pu(SO4)2-	7.80230E+00*		-6.26800E+02*		
PuF+3	1.04342E+01*		-4.75323E+02*		
PuF2+2	1.76271E+01*		-5.74567E+02*		
PuO2(CO3)2-2	9.86983E+00*		1.41030E+03*		
PuO2(CO3)3-4	1.09376E+01*		2.01621E+03*		
PuO2(CO3)3-5	1.65209E+00*		9.98179E+02*		
PuO2(SO4)2-2	1.19332E+01*		-2.24603E+03*		
PuO2OH+	-5.94640E-01*		-1.46253E+03*		
PuO2SO4	6.20058E+00*		-8.40956E+02*		
PuOH+3	5.52689E+00*		-1.88040E+03*		
PuSO4+	6.91329E+00*		-8.98413E+02*		
RaCl+	2.67902E-01*		-1.09690E+02*		
RaCO3	3.28486E+00*		-2.34005E+02*		
RaOH+	1.30588E+00*		-2.40273E+02*		
RaSO4	3.69603E+00*		-2.82060E+02*		
SeO4-2	-5.96956E+00*		1.24315E+03*		
SrCO3	-1.08906E+02	-1.97025E-02	5.15179E+03	3.89256E+01	-5.63714E+05
SrHCO3+	-3.24800E+00	1.48670E-02			
SrSO4	3.81464E+00*		-4.54572E+02*		
U(CO3)5-6	3.05962E+01*		1.04467E+03*		
U(SO4)2	1.62388E+01*		-1.70803E+03*		
UCl+3	-1.60864E+00*		9.92433E+02*		
UF+3	8.29893E+00*		2.92507E+02*		
UF2+2	1.56168E+01*		1.82817E+02*		
UF3+	2.16876E+01*		-2.61167E+01*		
UF4	2.48631E+01*		2.19693E+02*		
UO2(CO3)2-2	2.01810E+01*		-9.66316E+02*		
UO2(CO3)3-4	1.47325E+01*		2.04755E+03*		
UO2(SO4)2-2	1.02892E+01*		-1.83339E+03*		
UO2Cl+	1.57153E+00*		-4.17867E+02*		
UO2Cl2	1.52787E+00*		-7.83500E+02*		
UO2CO3	1.05460E+01*		-2.61167E+02*		
UO2F+	5.38783E+00*		-8.87966E+01*		
UO2F2	8.98790E+00*		-1.09690E+02*		
UO2F3-	1.13117E+01*		-1.22748E+02*		

Table B3: continued

Name	A	B	C	D	E
UO2F4-2	1.17508E+01*		-1.51477E+01*		
UO2SO4	6.56623E+00*		-1.01855E+03*		
UOH+3	7.67830E+00*		-2.45027E+03*		
USO4+2	7.98153E+00*		-4.17867E+02*		

MINERALS AND SOLIDS

Name	A	B	C	D	E
Anhydrite	-1.97520E+02		8.66880E+03	6.98350E+01	
Aragonite	6.40902E+01	4.54645E-02	2.24850E+03	-3.26694E+01	-5.63714E+05
As(cr)	-5.27677E-01*		1.23783E+04*		
Barite	-1.36035E+02		7.68041E+03	4.85950E+01	
Brucite	3.02432E+00*		-5.92255E+03*		
Calcite	6.40194E+01	4.54645E-02	2.31247E+03	-3.26694E+01	-5.63714E+05
Celestite	1.48060E+04	2.46609E+00	-7.56969E+05	-5.43636E+03	4.05536E+07
Dolomite(dis)	9.23194E+00*		-3.98028E+03*		
Dolomite(ord)	8.56961E+00*		-3.61883E+03*		
Eu(OH)3(cr)	6.89206E+00*		-6.49730E+03*		
Fe(cr)	1.78695E+00*		-4.65399E+03*		
FeCO3(pr)	-9.74371E+01	-3.25285E-02	5.15179E+03	3.89256E+01	-5.63714E+05
Fluorite	-6.63480E+01		4.29820E+03	2.52710E+01	
Gibbsite	1.06900E+01*		-5.38829E+03*	-1.50941E-01*	
Graphite	-7.48593E+00*		8.73733E+03*		
Gypsum	-6.82401E+01		3.22151E+03	2.50627E+01	
Hausmannite	1.27392E+01*		-2.19943E+04*		
Kaolinite	1.84408E+01*		-7.71486E+03*		
Melanterite	-1.44700E+00	4.15300E-03			2.14949E+05
Mo(cr)	-5.80935E+00*		7.59577E+03*		
Molybdite	6.27010E+00*		1.72474E+03*		
NpO2OH(am,ag)	2.50037E+00*		-2.14679E+03*		
NpO2OH(am,fr)	1.90037E+00*		-2.14679E+03*		
Pd(cr)	-2.45268E-01*		9.25574E+03*		
Portlandite	-7.69718E-02*		-6.77487E+03*		
Pyrolusite	6.34569E+00*		-1.42294E+04*		
Quartz	1.30868E-01*		1.07794E+03*		
RaCO3(cr)	6.25026E+00*		6.11130E+02*		
RaSO4(cr)	3.37498E+00*		2.05277E+03*		
Rhodochrosite	-9.57089E+01	-3.25285E-02	4.83926E+03	3.89256E+01	-5.63714E+05
Rhodochrosite(syn)	-9.74971E+01	-3.25285E-02	5.15179E+03	3.89256E+01	-5.63714E+05
S(rhomb)	5.00049E+00*		-8.51403E+02*		
Siderite	-9.51792E+01	-3.25285E-02	4.60979E+03	3.89256E+01	-5.63714E+05
SiO2(am)	1.57256E-01*		7.62293E+02*		
Sn(cr)	-3.28134E+00*		-4.02197E+02*		
Strontianite	-2.62918E+02	-3.25285E-02	1.23914E+04	9.55120E+01	-5.63714E+05
Tugarinovite	1.45234E+00*		8.49836E+03*		
Witherite	-7.15529E+02	-1.53626E-01	2.51630E+04	2.75420E+02	-5.63714E+05

GASES

Name	A	B	C	D	E
CH4(g)	7.80660E+01	6.22936E-05	-3.95720E+03	-2.50383E+01	
CO2(g)	2.47923E+02	4.10689E-02	-1.49148E+04	-8.63824E+01	1.01555E+06
H2(g)	7.64529E+01	6.53321E-03	-3.03728E+03	-2.63123E+01	
H2S(g)	7.25668E+00*		2.24603E+02*		
N2(g)	6.99069E+01	-3.66386E-03	-3.66236E+03	-2.15583E+01	
O2(g)	6.09665E+01	-4.10133E-03	-3.37671E+03	-1.83976E+01	

Table B4:   Heat capacities and parameters for temperature dependent heat capacity equations.

PRIMARY MASTER SPECIES

Name	$\Delta_f a$	$\Delta_f b$	$\Delta_f c$	$\Delta_f C_{p,m}°$
Al+3	-114.016*			-114.016*
Br-	-194.100			-194.100*
Ca+2	-278.470			-278.470*
Cl-	-167.800			-167.800*
F-	-136.800			-136.800*
H2O	31.826			31.826*
HCO3-	749.276	-1.57248E+00	3.88842E+07	-156.984*
Mn+2	52.516*			52.516*
NO3-	-159.600			-159.600*
Si(OH)4	101.153*			101.153*
SO4-2	-403.000			-403.000*
TcO4-	-113.074*			-113.074*
UO2+2	14.198*			14.198*

SECONDARY MASTER SPECIES

Name	$\Delta_f a$	$\Delta_f b$	$\Delta_f c$	$\Delta_f C_{p,m}°$	$\Delta_r a$	$\Delta_r b$	$\Delta_r c$	$\Delta_r C_{p,m}°$
Al(OH)4-	-44.033*			-44.033*	-57.321*			-57.321
As(OH)3	-	-	-	-	31.827*			31.827*
CH4	177.310	-2.38501E-03		176.599*	-476.488*	1.57009E+00*	-3.88842E+07*	429.061*
CO2	-337.112*	7.60118E-01*	-2.56307E+07*	177.848*	-1054.562*	2.33260E+00*	-6.45149E+07*	366.658*
CO3-2	1072.923*	-2.81799E+00*	6.04687E+07*	-447.497*	323.647*	-1.24551E+00*	2.15845E+07*	-290.513*
H2	218.769	-2.50149E-01		144.187*	218.769*	-2.50149E-01*		144.187*
HS-	-530.304*			*-530.304*				0.000*
N2	179.242	1.40285E-01		221.068*	689.398*			689.398*
NH3	22.100*			22.100*				0.000*
NH4+	22.100			22.100*	277.178*			277.178*
NpO2+	-48.580*			-48.580*				0.000*
O2	152.964	1.57035E-01		199.784*	89.312*	1.57035E-01*		136.132*
OH-	881.939*	-1.94123E+00*	4.28718E+07*	-179.122*	850.113*	-1.94123E+00*	4.28718E+07*	-210.948*
S2O3-2	-965.130*			*-965.130*				0.000*
SiO(OH)3-	101.153*			101.153*				0.000*
SiO2(OH)2-2	101.153*			101.153*				0.000*
SO3-2	-434.826*			*-434.826*				0.000*
U+4	-49.454*			-49.454*				0.000*
UO2+	14.198*			14.198*				0.000*

Table B4: continued

PRODUCT SPECIES

Name	$\Delta_f a$	$\Delta_f b$	$\Delta_f c$	$\Delta_f C_{p,m}°$	$\Delta_r a$	$\Delta_r b$	$\Delta_r c$	$\Delta_r C_{p,m}°$
(UO2)3(CO3)6-6	6480.134*	-1.69079E+01*	3.62812E+08*	-2642.388*				0.000*
Al(OH)2+	83.942*			83.942*	134.306*			134.306
Al(OH)3	137.107*			137.107*	155.645*			155.645
AlF+2	-250.816*			-250.816*				0.000*
AlF2+	-387.616*			-387.616*				0.000*
AlF3	-524.416*			-524.416*				0.000*
AlF4-	-661.216*			-661.216*				0.000*
AlF5-2	-798.016*			-798.016*				0.000*
AlF6-3	-934.816*			-934.816*				0.000*
AlOH+2	45.004*			45.004*	127.194*			127.194
B(OH)4-	-	-	-	-	0.000*	-6.59407E-01*		-196.602*
BaCO3	-	-	-	-	323.647*	-9.11582E-01*	2.15845E+07*	-190.954*
BaHCO3+	-	-	-	-	0.000*	5.23382E-01*		156.046*
CaCO3	4833.792*			4833.792*	4362.986*	-1.27111E+01*	2.15845E+07*	330.347*
CaF+	-415.270*			-415.270*				0.000*
CaHCO3+	-3510.032*			-3510.032*	-3980.838*	1.19824E+01*		-408.288*
CaSO4	-681.470*			-681.470*				0.000*
H2S	-530.304*			-530.304*				0.000*
HF	-136.800*			-136.800*	0.000*	4.84174E-01*		144.356*
HF2-	0.000			0.000*	273.600*			273.600*
HSO3-	-434.826*			-434.826*				0.000*
HSO4-	-237.659*			-237.659*	165.341*	2.47849E-01*		239.237*
MgCO3	-	-	-	-	323.647*	-9.90115E-01*	2.15845E+07*	-214.368*
MgF+	-	-	-	-				0.000*
MgHCO3+	-	-	-	-	173.964*			173.964*
MnOH+	84.342*			84.342*				0.000*
MnSO4	-350.484*			-350.484*				0.000*
NpO2(CO3)3-5	3170.190*	-8.45396E+00*	1.81406E+08*	-1391.071*				0.000*
NpO2SO4-	-451.580*			-451.580*				0.000*
SrCO3	-	-	-	-	323.647*	-7.54403E-01*	2.15845E+07*	-144.091*
SrHCO3+	-	-	-	-	0.000*	5.69253E-01*		169.723*
U(CO3)5-6	5315.163*	-1.40899E+01*	3.02343E+08*	-2286.939*				0.000*
U(SO4)2	-855.454*			-855.454*				0.000*
UCl+3	-217.254*			-217.254*				0.000*
UF+3	-186.254*			-186.254*				0.000*
UF2+2	-323.054*			-323.054*				0.000*
UF3+	-459.854*			-459.854*				0.000*
UF4	-596.654*			-596.654*				0.000*
UO2(CO3)2-2	2160.045*	-5.63597E+00*	1.20937E+08*	-880.796*				0.000*
UO2(CO3)3-4	3232.968*	-8.45396E+00*	1.81406E+08*	-1328.293*				0.000*
UO2(SO4)2-2	-791.802*			-791.802*				0.000*
UO2Cl+	-153.602*			-153.602*				0.000*
UO2Cl2	-321.402*			-321.402*				0.000*
UO2CO3	1087.121*	-2.81799E+00*	6.04687E+07*	-433.299*				0.000*
UO2F+	-122.602*			-122.602*				0.000*
UO2F2	-259.402*			-259.402*				0.000*
UO2F3-	-396.202*			-396.202*				0.000*
UO2F4-2	-533.002*			-533.002*				0.000*
UO2SO4	-388.802*			-388.802*				0.000*
UOH+3	-17.628*			-17.628*				0.000*
USO4+2	-452.454*			-452.454*				0.000*

Table B4: continued

MINERALS AND SOLIDS

Name	$\Delta_f a$	$\Delta_f b$	$\Delta_f c$	$\Delta_f C_{p,m}°$	$\Delta_r a$	$\Delta_r b$	$\Delta_r c$	$\Delta_r C_{p,m}°$
Anhydrite	-100.826*			*-100.826**	580.644*			580.644*
Aragonite	199.176*			*199.176**	-271.630*	1.74082E+00*	2.15845E+07*	4.584*
Barite	-	-	-	-	404.044*			404.044*
Calcite	199.176*			*199.176**	-271.630*	1.74082E+00*	2.15845E+07*	4.584*
Celestite	-	-	-	-	-45200.660*	9.44260E+01*	-1.55279E+09*	420.418*
FeCO3(pr)	-	-	-		323.647*	-1.24551E+00*	2.15845E+07*	-290.513*
Fluorite	-341.954*			*-341.954**	210.116*			210.116*
Gibbsite	-19.793*			-19.793*	-1.255*			-1.255
Graphite	653.798*	-1.57248E+00*	3.88842E+07*	-252.462*				0.000*
Gypsum	-409.434*			*-409.434**	208.384*			208.384*
Hausmannite	284.852*			284.852*				0.000*
Kaolinite	6.100*			6.100*				0.000*
Melanterite	-	-	-	-	0.000*	1.59017E-01*	-8.23034E+06*	139.998*
NpO2OH(am,ag)	-16.754*			-16.754*				0.000*
NpO2OH(am,fr)	-16.754*			-16.754*				0.000*
Portlandite	-214.818*			*-214.818**				0.000*
Pyrolusite	116.168*			116.168*				0.000*
Quartz	37.501*			37.501*				0.000*
Rhodochrosite	1125.439*	-2.81799E+00*	6.04687E+07*	-394.981*	323.647*	-1.24551E+00*	2.15845E+07*	-290.513*
Rhodochrosite(syn)	1125.439*	-2.81799E+00*	6.04687E+07*	-394.981*	323.647*	-1.24551E+00*	2.15845E+07*	-290.513*
Rutherfordine	10.478*			10.478*	-	-	-	
S(rhomb)	-530.304*			*-530.304**				0.000*
Schoepite	13.293*			13.293*	-	-	-	
Siderite	-	-	-	-	323.647*	-1.24551E+00*	2.15845E+07*	-290.513*
SiO2(am)	37.501*			37.501*				0.000*
Strontianite	-	-	-	-	794.135*	-1.24551E+00*	2.15845E+07*	179.975*
UF4:2.5H2O(cr)	64.619*			64.619*	-	-	-	
UO2(s)	6.562*			6.562*	-	-	-	
Witherite	-	-	-	-	2289.986*	-5.88232E+00*	2.15845E+07*	293.360*

GASES

Name	$\Delta_f a$	$\Delta_f b$	$\Delta_f c$	$\Delta_f C_{p,m}°$	$\Delta_r a$	$\Delta_r b$	$\Delta_r c$	$\Delta_r C_{p,m}°$
CH4(g)	-30.871*	1.96261E-07*		-30.871*	-208.181*	2.38521E-03*		-207.470*
CO2(g)	-0.777*	3.74729E-05*	-9.28920E+02*	-0.755*	-718.227*	1.57252E+00*	-3.88851E+07*	188.054*
H2(g)	-0.005*	5.97021E-06*		-0.003*	-218.774*	2.50155E-01*		-144.190*
H2S(g)	-530.304*			*-530.304**				0.000*
N2(g)	-0.004*	-3.43808E-06*		-0.005*	-179.246*	-1.40288E-01*		-221.073*
O2(g)	-0.003*	-3.73295E-06*		-0.004*	-152.967*	-1.57039E-01*		-199.788*