The PSI/Nagra Chemical Thermodynamic Database 12/07

Nuclear Energy and Safety Research Department
Laboratory for Waste Management (LES)

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Preface

The Laboratory for Waste Management of the Nuclear Energy and Safety Research Department of the Paul Scherrer Institut is performing work to develop and test models as well as to acquire specific data relevant to performance assessments of planned Swiss nuclear waste repositories. These investigations are undertaken in close co-operation with, and with the partial financial support of, the National Cooperative for the Disposal of Radioactive Waste (Nagra).

Abstract

The PSI/Nagra Chemical Thermodynamic Database 12/07 (PSI/Nagra TDB 12/07) is an update of the Nagra/PSI Chemical Thermodynamic Data Base 01/01 (Nagra/PSI TDB 01/01) and was prepared to support the ongoing safety assessments in the framework of the *Sachplan Geologische Tiefenlager* for the planned repositories for low- and intermediate-level and for high-level radioactive waste in Switzerland. It was carried out during Phase 1 of the Sachplan; starting in 2008, it was completed in 2009 with the implementation of the electronic versions of the PSI/Nagra TDB 12/07.

The update is mainly based on the OECD NEA's book series on "Chemical Thermodynamics" and has considered the volumes that appeared after publication of the Nagra/PSI TDB 01/01, namely the four volumes concerning the chemical thermodynamics of Ni, Se, Zr, and Th, as well as the update volume on U, Np, Pu, Am and Tc.

In addition, thermochemical data for Si compounds and complexes have been the subject of a thorough in-house review.

The present report is a supplement to the documentation of the Nagra/PSI TDB 01/01 and replaces the chapters on the data selection for U, Np, Pu, Am, Cm, Tc, Ni, Se, Zr, Th, and Si. All other data contained in the Nagra/PSI TDB 01/01 have been adopted without any change and are not further discussed. Thus, e.g., the data concerning Al, Eu, Pd and Sn that were the subject of extensive in-house reviews for the preparation of the Nagra/PSI TDB 01/01 remain unchanged.

As in the NEA review volumes and the Nagra/PSI TDB 01/01, the specific ion interaction theory (SIT) was used to extrapolate experimental data to zero ionic strength. In the documentation of the Nagra/PSI TDB 01/01, however, the SIT coefficients were in most cases not explicitly reported. For the present update, special care was given to the description of how the relevant SIT coefficients were obtained and the selected values are all tabulated.

For the application of SIT to environmental systems where the salinity is governed by NaCl, an estimation method was developed to fill the numerous gaps in the set of experimentally determined SIT coefficients in NaCl background media.

Zusammenfassung

Die PSI/Nagra Chemisch-thermodynamische Datenbank 12/07 (PSI/Nagra TDB 12/07) ist eine Aktualiserung der Nagra/PSI Chemisch-thermodynamischen Datenbank 01/01(Nagra/PSI TDB 01/01) und wurde im Rahmen des Sachplans Geologische Tiefenlager zur Unterstützung der Sicherheitsanalysen für die geplanten Tiefenlager zur dauerhaften Einlagerung von schwach- und mittelaktiven sowie von hochaktiven Abfällen erstellt. Die Aktualisierung wurde während der Phase 1 des Sachplans durchgeführt; sie begann 2008 und wurde 2009 mit der Implementierung der elektronischen Versionen der PSI/Nagra TDB 12/07 abgeschlossen.

Die Aktualisierung basiert vor allem auf der von der OECD NEA herausgegebenen Buchserie „Chemical Thermodynamics“ und berücksichtigt diejenigen Bände, die nach der Publikation der Nagra/PSI TDB 01/01 herausgekommen sind, namentlich die vier Bände über die chemische Thermodynamik von Ni, Se, Zr und Th, sowie den Band mit den aktualisierten Daten für U, Np, Pu, Am und Tc.

Zudem wurde eine eigene Evaluierung der thermochemischen Daten von Si durchgeführt.

Der vorliegende Bericht ergänzt die Dokumentation zur Nagra/PSI TDB 01/01 und ersetzt diejenigen Kapitel, welche die Datenauswahl für U, Np, Pu, Am, Cm, Tc, Ni, Se, Zr, Th und Si betreffen. Alle anderen Daten der Nagra/PSI TDB 01/01 wurden unverändert übernommen und werden nicht weiter besprochen. Dies betrifft insbesondere die Daten für Al, Eu, Pd, und Sn, die auf eigenen Reviews basierten.

In den NEA-Reviews und in der Nagra/PSI TDB 01/01 wurde die spezifische Ioneninteraktionstheorie (SIT) verwendet, um experimentelle Daten auf die Ionenstärke Null zu extrapolieren. In der Dokumentation zur Nagra/PSI TDB 01/01 wurden die SIT-Koeffizienten in der Regel nicht explizit angegeben. In der vorliegenden Aktualiserung hingegen wird besonderes Gewicht auf die Beschreibung der Herkunft der relevanten SIT-Koeffizienten gelegt und alle ausgewählten Koeffizienten werden auch tabellarisch aufgeführt.

Zur Anwendung der SIT auf die Modellierung von Umweltsystemen, bei denen NaCl die Salinität dominiert, wurde eine Schätzmethode entwickelt, um die zahlreichen Lücken in den experimentell bestimmten SIT-Koeffizienten für NaCl-Medien zu füllen.

Résumé

La base de données thermodynamique chimique PSI/Nagra TDB 12/07, qui est une mise à jour de la version précédente (Nagra/PSI TDB 01/01), a été réalisée dans le but de consolider les études de sûreté dans le contexte du *Sachplan Geologische Tiefenlager* pour les lieux de stockage de déchets radioactifs de faible, moyenne et haute activité, planifiés en Suisse. Cela a été réalisé durant la première phase du *Sachplan*, qui a débuté en 2008 et a été achevée en 2009 avec l'implémentation des versions électroniques de la PSI/Nagra TDB 12/07.

Cette mise à jour est principalement basée sur la série de livres de l'OECD NEA sur la « Chemical Thermodynamics », et les volumes parus après la publication de la Nagra/PSI TDB 01/01 ont été pris en compte, plus précisément les quatre volumes traitant de la thermodynamique chimique du Ni, Se, Zr, et Th, ainsi que le volume mis à jour concernant U, Np, Pu, Am et Tc.

De plus, les données thermochimiques pour les composants et les complexes du Si ont fait l'objet d'une revue maison approfondie.

Le présent rapport est un supplément de la documentation de la Nagra/PSI TDB 01/01 et remplace les chapitres concernant la sélection des données, pour U, Np, Pu, Am, Cm, Tc, Ni, Se, Zr, Th, et Si. Toutes les autres données contenues dans la Nagra/PSI TDB 01/01 ont été reprises sans aucune modification, et ne sont pas discutées par la suite. Ainsi, par exemple les données sur l'Al, Eu, Pd et Sn qui ont déjà fait l'objet d'une revue maison complète lors de la préparation de la Nagra/PSI TDB 01/01 demeurent inchangées.

Tout comme dans les volumes de revue du NEA et dans la Nagra/PSI TDB 01/01, la théorie d'interaction ionique spécifique (SIT) a été utilisée pour extrapoler les données expérimentales à une force ionique nulle. Cependant, dans la documentation de la Nagra/PSI TDB 01/01, les coefficients SIT n'ont pas été renseignés explicitement, dans la plupart des cas. Dans cette mise à jour, une attention spéciale a été apportée à la description de comment les coefficients SIT ont été obtenus, et les valeurs sélectionnées sont toutes indiquées dans des tableaux.

Pour l'application de la SIT aux systèmes environnementaux où la salinité est gouvernée par NaCl, une méthode d'estimation a été développée afin de combler les nombreux vides dans la collection de coefficients SIT déterminés expérimentalement en milieux dominés par NaCl.

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1 Introduction

1.1 Scope of the update

The Nagra/PSI Chemical Thermodynamic Data Base 01/01 (Nagra/PSI TDB 01/01, Hummel et al. 2002) has been updated to support the ongoing safety assessments in the framework of the *Sachplan Geologische Tiefenlager* for the planned repositories for low- and intermediate-level (L/ILW) and high-level (HLW) radioactive waste in Switzerland. The update from the Nagra/PSI Chemical Thermodynamic Data Base 01/01 to the PSI/Nagra Chemical Thermodynamic Database 12/07 (PSI/Nagra TDB 12/07) was prepared for Phase 1 of the Sachplan. It started in 2008 and was finished in 2009 with the preparation of the electronic versions for PHRREQC and GEMS-PSI.

The present update is mainly based on the OECD NEA's book series on "Chemical Thermodynamics". The following volumes that appeared after publication of the Nagra/PSI TDB 01/01, but not after 2009, have been considered:

1. Volume 5: "Update on the Chemical Thermodynamics of **Uranium**, **Neptunium**, **Plutonium**, **Americium** and **Technetium**" by Guillaumont et al. (2003)
2. Volume 6: "Chemical Thermodynamics of **Nickel**" by Gamsjäger et al. (2005)
3. Volume 7: "Chemical Thermodynamics of **Selenium**" by Olin et al. (2005)
4. Volume 8: "Chemical Thermodynamics of **Zirconium**" by Brown et al. (2005)
5. Volume 11: "Chemical Thermodynamics of **Thorium**" by Rand et al. (2008)

In addition, thermochemical data for **silicon** compounds and complexes have been the subject of an extensive in-house review.

The present report is a supplement to the documentation of the Nagra/PSI TDB 01/01 (Hummel et al. 2002) and replaces the chapters discussing the data selection for **U**, **Np**, **Pu**, **Am**, **Cm**, **Tc**, **Ni**, **Se**, **Zr**, **Th**, and **Si.** All other data contained in the Nagra/PSI TDB 01/01 have been adopted without any change and are neither listed nor discussed in the present report. Thus, e.g., the data concerning Al, Eu, Pd and Sn that were the subject of extensive in-house reviews for the preparation of the Nagra/PSI TDB 01/01 remain unchanged.

1.2 Data quality and data categories

The Nagra TDB version 05/92 (Pearson & Berner 1991, Pearson et al. 1992) distinguished two types of data, "core data" and "supplemental data".

Well-characterized aqueous species, minerals and gases of elements commonly found in significant quantities in natural waters were included as core data. These data were carefully selected and are widely accepted.

Supplemental, or auxiliary, data were added for elements that are found as minor components in natural waters, or elements that are of interest principally for the safety assessment of nuclear waste facilities. Supplemental aqueous species, and minerals, are usually less well-characterized than those in the core data.

In the Nagra TDB 05/92 the data for the aqueous species and minerals in the core subset were selected individually. In contrast, the supplemental data were selected (imported) in groups, each from one of several existing data sets, e.g. the HATCHES database, or the MINEQL-PSI and PHREEQE-PSI databases.

In the Nagra/PSI TDB 01/01 the classification of "core data" and "supplemental data" was retained although the supplemental data were selected individually, either taken from NEA TDB reviews or derived by in-house reviews.

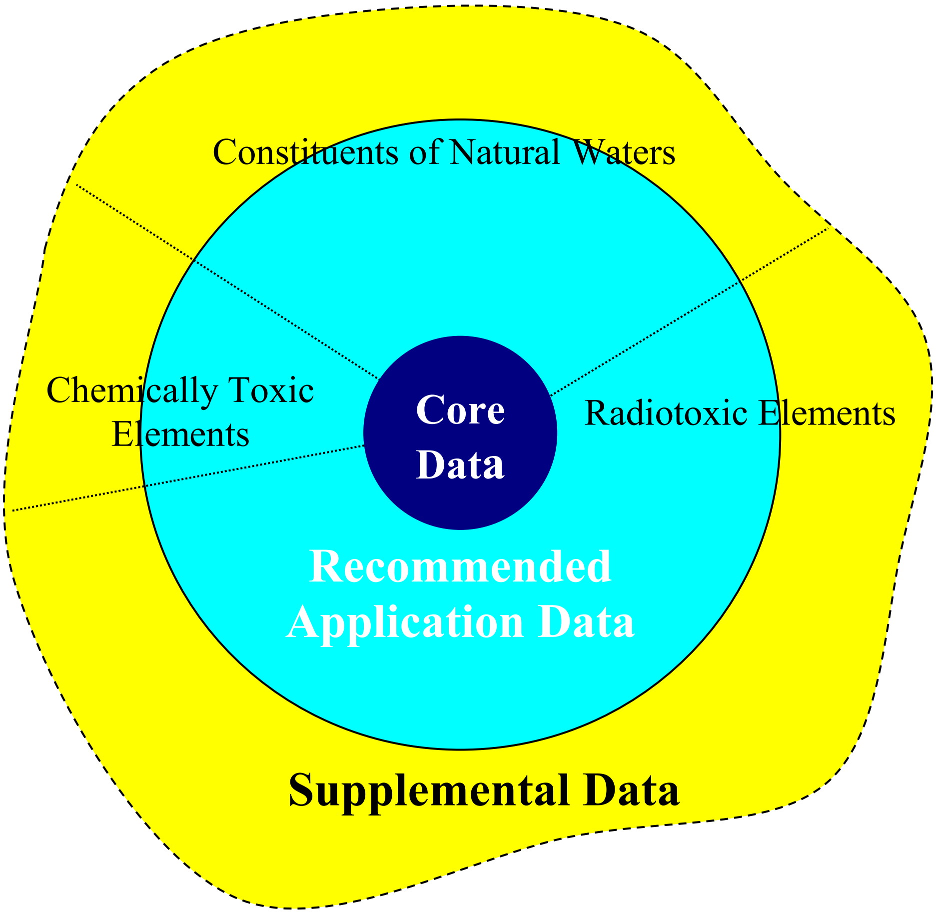

Fig. 1.1: Data types distinguished in the PSI/Nagra TDB 12/07. For a detailed explanation see text.

Meanwhile, after more than 20 years of NEA TDB review projects, resulting in the publication of presently thirteen volumes of "Chemical Thermodynamics", slowly emerging publications of IUPAC reviews, and seminal efforts of the present authors concerning in-house reviews for the PSI/Nagra TDB, as well as their participation in NEA and IUPAC review projects, the historic data categories have been redefined and extended. The PSI/Nagra TDB 12/07 distinguishes between three categories of data, i.e., **core data**, **recommended application data**, and **supplemental data**.

Core Data: Well-characterized aqueous species, minerals and gases of elements involved in almost any type of speciation calculation. These data have been carefully selected and are widely accepted in different fields of application. The core data basically comprise the CODATA key values (Cox et al. 1989) and some other values of similar quality and almost worldwide acceptance.

Recommended Application Data: Well-characterized aqueous species, minerals and gases of elements important in different fields of application. These fields of application are (a) modeling of ground and surface waters, (b) safety assessments of nuclear waste repositories and (c) pollution dynamics of chemically toxic substances. The boundaries of the three fields are fuzzy, e.g. Sr is a minor constituent of natural waters but also of interest as radiotoxic isotope ^{90}Sr, and the chemically toxic element Ni has also to be included in safety assessments of nuclear waste facilities as ^{59}Ni and ^{63}Ni. The recommended application data are of high quality and well established, but in contrast to the core data, which may not be revised in the foreseeable future, the recommended application data originate from rather active fields of environmental sciences and may be revised and improved over time. Sources for ground and surface water data are the reviews of Nordstrom et al. (1990), high quality data for radiotoxic elements come from the NEA TDB review projects (Mompeán & Wanner 2003) and our in-house reviews.

Supplemental Data: Supplemental aqueous species and minerals are less well-characterized than those in the recommended application data. They comprise uncertain data, not selected in the NEA TDB and other reviews but discussed there as suitable for scoping calculations and qualitative modeling. The numerical values either are accompanied by large ± uncertainties, or they are given as approximate ($\approx$) or limiting ($\leq$) values. Last but not least, estimates are provided for important species where experimental data are missing or unreliable, particularly in cases where omission of such estimated constants would lead to obviously unacceptable results. These estimates are based on chemical analogues, linear free energy relationships or other estimation methods found reliable by the reviewers.

As a visual aid for identifying the different types of data in tables of numerical values,

- the **core data** will be printed in **bold face**,
- whereas the recommended application data are shown in normal face,
- and the *supplemental data* are given in *italics*.

1.3 Solid compounds included in the database

The data concerning solid compounds in the PSI/NagraTDB 12/07 are restricted to pure phases. We envision to include data for solid solutions in future updates when there is an agreement on the use of solid solution models and, more importantly, when reliable thermodynamic data will become available for selected environmental systems. The current status of chemical thermodynamics of solid solutions is discussed by Bruno et al. (2007).

Solid compounds included in the PSI/NagraTDB 12/07 are supposed to attain thermodynamic equilibrium at conditions including surface environments as well as deep radioactive waste repository systems. Hence, thermodynamic data derived for mineral phases at hydrothermal conditions (T > 300°C and high pressure) are included only if there is convincing evidence that these phases may also reach equilibrium at ambient conditions, i.e. that solubility values calculated from these data are found in concentration ranges not in contradiction with experimental data. The same criteria apply for thermodynamic data of solid phases solely derived from high temperature calorimetry. In any case of doubt from an application point of view, data from these sources are not included in the PSI/NagraTDB 12/07.

Detailed discussion and inclusion of solid compounds are restricted in the PSI/NagraTDB 12/07 to the so-called "sparingly soluble" solids. These are the important solids governing the chemistry of most ground and surface waters and determining the solubility limits of radionuclides. There is no exact numerical definition of "sparingly soluble". However, data for highly soluble salts leading to solutions of molar concentrations at saturation are generally not included in the PSI/NagraTDB 12/07. This means that the PSI/NagraTDB 12/07 is not suited to model the evolution of salt lakes or radioactive waste repositories situated in salt domes.

1.4 Weak complexes and the dependence of the TDB on ionic strength correction models

This is an open and perhaps never-ending discussion. Unfortunately, this is not a purely academic discussion which could be ignored from an application point of view, since in the realm of weak complexes the TDB becomes model dependent.

If we use the original Extended Debye-Hückel ionic strength correction model, each ion is associated with its individual adjustable Debye-Hückel parameter. Modified variants of the Extended Debye-Hückel model use two or three adjustable parameters for each individual ion. In any case, if we consider a cation (Na^+, K^+, Mg^{2+}, Ca^{2+}, …) – anion (ClO_4^-, Cl^-, OH^-, …) matrix (Table 1.1) the mean activity data of only one cation-anion pair in each row can be described by these individual ion parameters alone, indicated by "-" in Table 1.1. For all other cation–anion combinations in this row we have in addition to assume ion pairs or (weak) complexes to describe the experimentally measured interactions by the Extended Debye-Hückel model in a formally consistent way.

Table 1.1: Ion-association model by Parkhurst (1990).
Each ion is characterized by three ion-activity-coefficient parameters. Stability constants have been fitted in addition for the complexes shown in the table.

	ClO_4^-	Cl^-	OH^-	SO_4^{2-}
Na^+	$NaClO_4(aq)$	-	$NaOH(aq)$	$NaSO_4^-$, $Na_2SO_4(aq)$
K^+	*(no data)*	-	$KOH(aq)$	KSO_4^-, $K_2SO_4(aq)$
Mg^{2+}	-	$MgCl^+$	$MgOH^+$	$MgSO_4(aq)$, $Mg(SO_4)_2^{2-}$
Ca^{2+}	-	$CaCl^+$	$CaOH^+$	$CaSO_4(aq)$, $Ca(SO_4)_2^{2-}$
Ba^{2+}	$BaClO_4^+$	-	$BaOH^+$	*(no data, "insoluble" salt)*

Table 1.2: Specific ion Interaction Theory (SIT) model used in NEA TDB reviews. Each cation - anion interaction is characterized by a specific SIT interaction parameter ε. Complexes have to be considered in addition as indicated in the table.

	ClO_4^-	Cl^-	OH^-	SO_4^{2-}
Na^+	$\varepsilon(Na^+,ClO_4^-)$	$\varepsilon(Na^+,Cl^-)$	$\varepsilon(Na^+,OH^-)$	$\varepsilon(Na^+,SO_4^{2-})$
K^+	*(no data)*	$\varepsilon(K^+,Cl^-)$	$\varepsilon(K^+,OH^-)$	$\varepsilon(K^+,SO_4^{2-})$
Mg^{2+}	$\varepsilon(Mg^{2+},ClO_4^-)$	$\varepsilon(Mg^{2+},Cl^-)$	$MgOH^+ + \varepsilon$	$MgSO_4(aq) + \varepsilon$
Ca^{2+}	$\varepsilon(Ca^{2+},ClO_4^-)$	$\varepsilon(Ca^{2+},Cl^-)$	$CaOH^+ + \varepsilon$	$CaSO_4(aq) + \varepsilon$
Ba^{2+}	$\varepsilon(Ba^{2+},ClO_4^-)$	$\varepsilon(Ba^{2+},Cl^-)$	$BaOH^+ + \varepsilon$	$BaSO_4(aq) + \varepsilon$

If we use the SIT model, the mean activity data in the above mentioned cation–anion matrix are described mainly by specific ion interaction parameters, the SIT ε - parameters, and in most cases there is no need to consider in addition weak complexes (Table 1.2). However, in cases where the ion interactions are strong, complexes (and their associated SIT ε - parameters) have to be explicitly considered in the SIT model, e.g. for Mg, Ca, Ba hydroxide and sulphate (Table 1.2). This boundary between weak and strong ion interactions is fuzzy and no consensus has yet been reached among the experts, when complexes have to be introduced in the SIT model and how their associated SIT ε parameters have to be evaluated in a consistent way.

The same considerations are valid if we use the Pitzer ion interaction model instead of the SIT model. The differences are that the fuzzy boundary, where complexes have to be considered explicitly, is shifted to stronger ion interactions, and there are more Pitzer parameters associated with each ion interaction which have to be evaluated in a consistent way.

In any case, the **number** of weak complexes to be included in a TDB and the **values** of their stability constants depend on the chosen ionic strength model.

In our Nagra/PSI TDB 01/01 we largely ignored this problem by not really discussing it, as it seems to be kind of a tradition in all other data bases too. Hence, we could simply continue this "tradition" and be in good company.

Perhaps the scientifically most satisfying option would be to develop a "SIT TDB" and a separate "Extended Debye-Hückel TDB" with two distinct sets of weak complexes and accompanying adjustable parameters. However, in order to really improve the consistency of our TDB this would imply a complete re-evaluation of the respective experimental data according to the two different ionic strength correction models. Considering our limited manpower and restricted time frame, this tremendous task is not feasible.

For the PSI/Nagra TDB 12/07 we took a pragmatic approach in-between the traditional "don't ask, don't tell" strategy and the unfeasible "complete re-evaluation from scratch" option and made remarks if we identified problem cases with respect to weak complexes, making the problem of weak complexes visible to the user without actually resolving it.

1.5 Discussion and presentation of the data selection

The final product of our TDB update project is a thermodynamic database available for the user in suitable electronic format for geochemical modeling codes (i.e., for GEMS-PSI and PHREEQC). However, the major scientific task of the TDB update consisted of detailed discussions of the data selection and the presentation of the results in tabular form.

When we relied on the NEA TDB reviews the discussion part is kept to a minimum, just presenting to the user of the database our reasoning for inclusion or rejection of data. In cases of disagreement with certain details of NEA TDB reviews or in the case of in-house reviews the discussion part was extended as necessary.

Compounds and complexes selected in NEA TDB reviews, but not included in our TDB because they are not relevant in environmental systems, are summarized in lists. Selected data are given in detailed tables. Previously selected data are also included in these tables in order to visualize the changes.

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2 Americium

Almost all information on americium is taken from OECD NEA's books "Chemical Thermodynamics of Americium" (Silva et al. 1995) and "Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium" (Guillaumont et al. 2003), the latter of which reviewed new literature published between 1993 and the end of 2001 that was not considered by Silva et al. (1995). However, not all recommended values of these NEA reviews are included in our database since NEA reviews are not restricted to data relevant for radioactive waste management or even environmental modeling in general. We excluded from our database phases and complexes which most probably will never be relevant in environmental systems. They are listed in Table 2.1. The notation of formulae and symbols used in this text follows the NEA recommendations.

It is well known that the coordination chemistry and complex formation reactions in aqueous solution are very similar for the trivalent actinides and for the lanthanides (an important exception being the redox properties). Thus, Guillaumont et al. (2003) made use of this analogy and included experimental data for Cm(III) in the evaluation of thermodynamic data for aqueous Am(III) complexes because experimental data for Cm(III) are often more accurate than for Am(III) and, due to the very sensitive time-resolved laser fluorescence spectroscopy (TRLFS), there is a large amount of accurate information available on the aqueous complex formation of Cm(III).

Guillaumont et al. (2003) noted that the differences in the activity coefficients and in the ion interaction coefficients of Am(III), Cm(III), Nd(III), and Eu(III) species are considered to be negligible and that the differences in the formation constants of the analogous complexes are mostly smaller than the experimental uncertainties. However, the solubility constants of isostructural solids can differ considerably.

2.1 Elemental americium

Americium metal, liquid and gas are not relevant under environmental conditions. The absolute entropy of Am(cr) selected by Silva et al. (1995)

$$S_m°(\text{Am, cr, 298.15 K}) = (55.4 \pm 2.0)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

appears in our database for computational purposes only (i.e. calculation of the entropy of formation of Am^{3+}). Data on other americium solids (β-Am and γ-Am), Am(l) and Am(g) selected by Silva et al. (1995) are not included in the database.

2.2 Simple americium aqua ions

In aqueous media, americium can occur in the di-, tri-, tetra-, penta-, and hexavalent state. Silva et al. (1995) cited evidence that Am^{2+} is formed in aqueous perchlorate media only transiently in pulse radiolysis experiments (with a half life of approximately 5 μs) and selected estimated values for $S_m°$ and $\Delta_f H_m°$.

Normally, americium exists as the trivalent ion except under strongly oxidizing conditions, where the penta- and hexavalent 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+}. Although AmO_2^+ is very unstable with respect to reduction and disproportionation, it becomes quite stable in carbonate solutions by forming carbonate complexes. Am^{4+}, too, is only stable in the presence of strongly complexing agents such as carbonate or fluoride.

Considering the fact that the only formation constants for Am(IV) and Am(VI) complexes recommended by Silva et al. (1995) and Guillaumont et al. (2003) are for $Am^{(IV)}(CO_3)_5^{6-}$ and $Am^{(VI)}O_2(CO_3)_3^{4-}$, and that Am(II) is only formed transiently, we decided to restrict our database to Am^{3+} and AmO_2^+.

2.2.1 AmO_2^+

The enthalpy of reaction for

$$Am^{3+} + 2\ H_2O(l) \Leftrightarrow AmO_2^+ + 4\ H^+ + 2\ e^-$$

$$\Delta_r H_m°(298.15\ K) = (384.1 \pm 5.2)\ kJ \cdot mol^{-1}$$

was calculated by Silva et al. (1995) from the measured enthalpy of reduction of AmO_2^+ to Am^{3+} by Fe^{2+} and from the enthalpy of Fe^{3+}/Fe^{2+} reduction and is accepted for our database. From this value and $\Delta_f H_m°(Am^{3+}, aq, 298.15\ K) = -(616.7 \pm 1.5)\ kJ \cdot mol^{-1}$ (derived below) the formation enthalpy for AmO_2^+ is

$$\Delta_f H_m°(AmO_2^+, aq, 298.15\ K) = -(804.3 \pm 5.4)\ kJ \cdot mol^{-1}$$

Following Fuger & Oetting (1976), Silva et al. (1995) estimated the molar entropy of AmO_2^+ by equating it to the molar entropy of NpO_2^+ and ignoring potential magnetic contributions to the entropy. Thus, Silva et al. (1995) selected $S_m°(AmO_2^+, aq, 298.15\ K) = S_m°(NpO_2^+, aq, 298.15\ K) = -(21 \pm 10)\ J \cdot K^{-1} \cdot mol^{-1}$. This value was also accepted by Guillaumont et al. (2003). Unfortunately, this leads to an inconsistency, since Lemire et al. (2001) and Guillaumont et al. (2003) selected a different value for $S_m°(NpO_2^+, aq, 298.15\ K)$:

$$S_m°(NpO_2^+, aq, 298.15\ K) = -(45.9 \pm 10.7)\ J \cdot K^{-1} \cdot mol^{-1}$$

Using this value as an estimate, we select

$$S_m°(AmO_2^+, aq, 298.15\ K) = -(45.9 \pm 10.7)\ J \cdot K^{-1} \cdot mol^{-1}$$

From this value and $S_m°(Am, cr, 298.15\ K) = (55.4 \pm 2.0)\ J \cdot K^{-1} \cdot mol^{-1}$, $S_m°(O_2, g, 298.15\ K) = (205.52 \pm 0.005)\ J \cdot K^{-1} \cdot mol^{-1}$, and $S_m°(H_2, g, 298.15\ K) = (130.680 \pm 0.003)\ J \cdot K^{-1} \cdot mol^{-1}$, the molar entropy of formation of AmO_2^+ can be calculated according to

$$\Delta_f S_m°(AmO_2^+, aq) = S_m°(AmO_2^+, aq) - S_m°(Am, cr) - S_m°(O_2, g) + \tfrac{1}{2} S_m°(H_2, g)$$

(Wagman et al. 1982, p. 2-22) resulting in

$$\Delta_f S_m°(AmO_2^+, aq, 298.15\ K) = -(241.1 \pm 10.9)\ J \cdot K^{-1} \cdot mol^{-1}$$

The molar Gibbs energy of formation can then be calculated from $\Delta_f H_m°(AmO_2^+, aq, 298.15\ K)$ and $\Delta_f S_m°(AmO_2^+, aq, 298.15\ K)$ as

$$\Delta_f G_m°(AmO_2^+, aq, 298.15\ K) = -(732.4 \pm 6.3)\ kJ \cdot mol^{-1}$$

which is selected for our database. This value, together with the selected values for $\Delta_f G_m°(Am^{3+}, aq, 298.15\ K)$, $\Delta_f G_m°(H_2O, l, 298.15)$, $\Delta_f G_m°(H^+, aq, 298.15)$, and $\Delta_f G_m°(e^-, aq, 298.15)$ – the latter two are by definition equal to zero – gives $\Delta_r G_m°$ (298.15 K) and $\log_{10}{}^*K°$for the reaction

$$Am^{3+} + 2\ H_2O(l) \Leftrightarrow AmO_2^+ + 4\ H^+ + 2\ e^-$$

$$\Delta_r G_m°(298.15\ K) = (340.6 \pm 7.9)\ kJ \cdot mol^{-1}$$

$$\log_{10}{}^*K°(298.15\ K) = -(59.7 \pm 1.4)$$

which are selected for our database.

Guillaumont et al. (2003) converted conditional formation constants of Am(V) carbonate complexes to zero ionic strength by using the selected ion interaction coefficients for the analogous Np(V) species (see Section 2.7.1.2 below). Thus, they assumed that $\varepsilon(AmO_2^+, Cl^-)$ = $\varepsilon(NpO_2^+, Cl^-)$ and set

$$\varepsilon(AmO_2^+, Cl^-) = (0.09 \pm 0.05)\ kg \cdot mol^{-1}$$

We select this value for our database (although no ion interaction coefficients for AmO_2^+ were selected by Guillaumont et al. 2003). By analogy, we assume $\varepsilon(AmO_2^+, ClO_4^-)$ to be equal to $\varepsilon(NpO_2^+, ClO_4^-)$ and select

$$\varepsilon(AmO_2^+, ClO_4^-) = (0.25 \pm 0.05)\ kg \cdot mol^{-1}$$

by using the corresponding value for NpO_2^+ selected by Grenthe et al. (1992) and Guillaumont et al. (2003).

2.2.2 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. For Am^{3+}, we accept the enthalpy value selected by Silva et al. (1995) (based on experimental data and extrapolated to zero ionic strength)

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

their estimated entropy value

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

and the Gibbs energy of formation calculated from the above values

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

Guillaumont et al. (2003) assumed $\varepsilon(Am^{3+}, Cl^-)$ to be equal to $\varepsilon(Nd^{3+}, Cl^-)$ and calculated a value for Nd^{3+} from trace activity coefficients of Nd^{3+} in 0 – 4 m NaCl, based on Pitzer parameters evaluated from osmotic coefficients in aqueous $NdCl_3$-NaCl and $NdCl_3$-$CaCl_2$ solutions. They obtained

$$\varepsilon(Am^{3+}, Cl^-) = (0.23 \pm 0.02)\ kg \cdot mol^{-1}$$

which is selected for our database.

Silva et al. (1995) selected

$$\varepsilon(Am^{3+}, ClO_4^-) = (0.49 \pm 0.03)\ kg \cdot mol^{-1}$$

by assuming it to be equal to $\varepsilon(Nd^{3+}, ClO_4^-)$. They did not cite any reference for the Nd^{3+} value, but, judging from the entry for $La^{3+} \rightarrow Lu^{3+}$ in their Table B.3 of ion interaction coefficients, it can be suspected that it was taken from Spahiu (1983). The value for $\varepsilon(Am^{3+}, ClO_4^-)$ selected by Silva et al. (1995) is selected for our database.

2.3 Oxygen and hydrogen compounds

2.3.1 Aqueous americium(V) hydroxide complexes

Runde & Kim (1994) measured the solubility of $AmO_2OH(am)$ over a wide range of H^+ concentrations ($8.0 < \log_{10}[H+] < 13.15$) in 5 M NaCl and obtained values for

$\log_{10}\beta_1$(AmO_2OH, aq, 5 M NaCl) and $\log_{10}\beta_2$($AmO_2(OH)_2^-$, 5 M NaCl) that were almost identical to those for $\log_{10}\beta_1$(NpO_2OH, aq, 5 M NaCl) and $\log_{10}\beta_2$($NpO_2(OH)_2^-$, 5 M NaCl) from analogous solubility measurements with an aged precipitate of Np(V) hydroxide. The extrapolation of these formation constants to $I = 0$ with SIT has a large uncertainty and there are no experimental data at low ionic strengths. Since the formation constants of the respective hydroxide complexes of Am(V) and Np(V) reported by Runde & Kim (1994) are the same within uncertainty limits, Guillaumont et al. (2003) decided to recommend the formation constants of $NpO_2OH(aq)$ and $NpO_2(OH)_2^-$ selected by Lemire et al. (2001) as reasonable estimates for the corresponding Am(V) hydroxide complexes. Thus,

$$AmO_2^+ + H_2O(l) \Leftrightarrow AmO_2OH(aq) + H^+$$

$$\log_{10}{}^*\beta_1^\circ\ (298.15\ K) = -(11.3 \pm 0.7)$$

$$AmO_2^+ + 2\ H_2O(l) \Leftrightarrow AmO_2(OH)_2^- + 2\ H^+$$

$$\log_{10}{}^*\beta_2^\circ\ (298.15\ K) = -(23.6 \pm 0.5)$$

Although $\log_{10}{}^*\beta_1^\circ$(298.15 K) and $\log_{10}{}^*\beta_2^\circ$(298.15 K) are not listed by Guillaumont et al. (2003) in the tables of selected americium data, we have included these constants in our database. We estimated a value for $\varepsilon(AmO_2(OH)_2^-, Na^+)$ by using the value by Guillaumont et al. (2003) for the corresponding Np(V) complex resulting in

$$\varepsilon(AmO_2(OH)_2^-, Na^+) = -(0.01 \pm 0.07)\ kg\cdot mol^{-1}$$

which is selected for our database.

2.3.2 Aqueous Am(III) and Cm(III) hydroxide complexes

The hydrolysis reactions of Am(III) can be described by

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

with n = 1, 2 and 3. 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. Various solubility studies in NaCl-NaOH, $NaClO_4$-NaOH, pure NaOH, and pure KOH solutions up to pH 14 have not shown any evidence for such a solubility increase (Neck et al. 2009). In solubility experiments of fresh and aged Am(III) precipitates at extremely alkaline KOH solutions ([OH-] > 3 M), however, Vitorge & Tran-The (1991) observed an increase in Am concentrations. These results were not evaluated by Silva et al. (1995) and Guillaumont et al. (2003) because of the very high and variable ionic strength of the experimental solutions. From these experiments, Neck et al. (2009) derived $\log_{10}K^\circ$ (298.15 K) = -(0.5 ± 0.4) for the reaction $Am(OH)_3(aq) + OH^- \Leftrightarrow Am(OH)_4^-$, with $\varepsilon(Am(OH)_4^-, K^+) = -(0.03 \pm 0.05)\ kg\cdot mol^{-1}$. $Am(OH)_4^-$ is presently not included in our database, but will be considered in the next update.

Polynuclear hydroxo- or oxo-complexes could conceivably form in the region immediately before precipitation, however, there is no evidence of their existence (this is to some extent due to the low concentrations of Am (III) used in the experiments).

According to Silva et al. (1995), the major difficulties in the experimental determination of equilibrium constants for Am(III) hydrolysis complexes generally are due to 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 neutral $Am(OH)_3(aq)$. Guillaumont et al. (2003) extended the review by Silva et al. (1995) and included experimental studies on curium(III). Based on the data already discussed by Silva et al. (1995) and a large amount of new experimental data for Am(III) and particularly

Cm(III) hydroxide complexes, Guillaumont et al. (2003) selected the following standard equilibrium constants which are included in our database:

$$An^{3+} + H_2O(l) \Leftrightarrow AnOH^{2+} + H^+$$

$$\log_{10}{}^*\beta_1^\circ(298.15\ K) = -(7.2 \pm 0.5)$$

$$\Delta\varepsilon_1 = -(0.15 \pm 0.06)\ kg\cdot mol^{-1}$$

$$An^{3+} + 2\ H_2O(l) \Leftrightarrow An(OH)_2^{+} + 2\ H^+$$

$$\log_{10}{}^*\beta_2^\circ(298.15\ K) = -(15.1 \pm 0.7)$$

$$\Delta\varepsilon_2 = -(0.26 \pm 0.20)\ kg\cdot mol^{-1}$$

$$An^{3+} + 3\ H_2O(l) \Leftrightarrow An(OH)_3(aq) + 3\ H^+$$

$$\log_{10}{}^*\beta_3^\circ(298.15\ K) = -(26.2 \pm 0.5)$$

where An stands for Am and Cm. Using the values for $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ together with $\varepsilon(An^{3+}, Cl^-) = (0.23 \pm 0.02)\ kg\cdot mol^{-1}$ and $\varepsilon(H^+, Cl^-) = (0.12 \pm 0.01)\ kg\cdot mol^{-1}$, Guillaumont et al. (2003) obtained

$$\varepsilon(AnOH^{2+}, Cl^-) = -(0.04 \pm 0.07)\ kg\cdot mol^{-1}$$

and

$$\varepsilon(An(OH)_2^{+}, Cl^-) = -(0.27 \pm 0.20)\ kg\cdot mol^{-1}$$

which are both included in our database.

Silva et al. (1995) estimated values for the corresponding ion interaction coefficients in perchlorate media based on the suggestion by Grenthe et al. (1992) that, since ions and complexes of the same charge have similar ion interaction coefficients with a given counterion, it is possible to estimate unknown ion interaction parameters within an error of at most ± 0.1 by adopting known values from other ions or complexes with the same charge. Therefore, Silva et al. (1995) assumed $\varepsilon(AmOH^{2+}, ClO_4^-) = \varepsilon(YHCO_3^{2+}, ClO_4^-) = (0.39 \pm 0.04)\ kg\cdot mol^{-1}$ and $\varepsilon(Am(OH)_2^{+}, ClO_4^-) = \varepsilon(YCO_3^{+}, ClO_4^-) = (0.17 \pm 0.04)\ kg\cdot mol^{-1}$ using values for the Y-complexes by Spahiu (1983). We adopt these values for our database but have increased their errors

$$\varepsilon(AmOH^{2+}, ClO_4^-) = (0.39 \pm 0.10)\ kg\cdot mol^{-1}$$

$$\varepsilon(Am(OH)_2^{+}, ClO_4^-) = (0.17 \pm 0.10)\ kg\cdot mol^{-1}$$

Data on $\Delta_r H_m$ for hydroxocomplexes are scarce and no recommended values were given by Silva et al. (1995) and Guillaumont et al. (2003).

2.3.3 Ternary calcium americium(III) hydroxide complexes

Rabung et al. (2008) used time-resolved laser fluorescence spectroscopy (TRLFS) to study Cm(III) solutions in 0.1–3.5 M $CaCl_2$ at pH_c from 10.8 to 11.9 and identified ternary Ca-Cm(III)-OH complexes. They reported standard formation constants and ion interaction coefficients for $CaCm(OH)_3^{2+}$, $Ca_2Cm(OH)_4^{3+}$, and $Ca_3Cm(OH)_6^{3+}$ that we consider as supplemental data for our database, see the discussion in Section 3.3.1 below. Due to the well-established similarity between Am(III) and Cm(III) complexes (see above) we adopt these constants and coefficients for the corresponding Ca-Am(III)-OH complexes and select

$$Ca^{2+} + Am^{3+} + 3\ H_2O(l) \Leftrightarrow CaAm(OH)_3^{2+} + 3\ H^+$$

$$\log_{10}\beta_{1,1,3}^\circ(CaAm(OH)_3^{2+}, 298.15\ K) = -(26.3 \pm 0.5)$$

$$\varepsilon(\mathrm{CaAm(OH)_3^{2+}, Cl^-}) = (0.05 \pm 0.04)\ \mathrm{kg{\cdot}mol^{-1}}$$

$$2\mathrm{Ca^{2+}} + \mathrm{Am^{3+}} + 4\ \mathrm{H_2O(l)} \Leftrightarrow \mathrm{Ca_2Am(OH)_4^{3+}} + 4\ \mathrm{H^+}$$

$$\log_{10}\beta_{2,1,4}^\circ(\mathrm{Ca_2Am(OH)_4^{3+}}, 298.15\ \mathrm{K}) = -(37.2 \pm 0.6)$$

$$\varepsilon(\mathrm{Ca_2Am(OH)_4^{3+}, Cl^-}) = (0.29 \pm 0.07)\ \mathrm{kg{\cdot}mol^{-1}}$$

$$3\mathrm{Ca^{2+}} + \mathrm{Am^{3+}} + 6\ \mathrm{H_2O(l)} \Leftrightarrow \mathrm{Ca_3Am(OH)_6^{3+}} + 6\ \mathrm{H^+}$$

$$\log_{10}\beta_{3,1,6}^\circ(\mathrm{Ca_3Am(OH)_6^{3+}}, 298.15\ \mathrm{K}) = -(60.7 \pm 0.5)$$

$$\varepsilon(\mathrm{Ca_3Am(OH)_6^{3+}, Cl^-}) = (0.00 \pm 0.06)\ \mathrm{kg{\cdot}mol^{-1}}$$

as supplemental data.

We estimated the ion interaction coefficient for chloride media according to the method described in Appendix A which is based on a statistical analysis of published SIT ion interaction coefficients and allows the estimation of such coefficients for cations with Cl^- and ClO_4^-, and for anions with Na^+ from the charge of the considered species. The estimated values

$$\varepsilon(\mathrm{CaAm(OH)_3^{2+}, ClO_4^-}) = (0.4 \pm 0.1)\ \mathrm{kg{\cdot}mol^{-1}}$$

$$\varepsilon(\mathrm{Ca_2Am(OH)_4^{3+}, ClO_4^-}) = (0.6 \pm 0.1)\ \mathrm{kg{\cdot}mol^{-1}}$$

$$\varepsilon(\mathrm{Ca_3Am(OH)_6^{3+}, ClO_4^-}) = (0.6 \pm 0.1)\ \mathrm{kg{\cdot}mol^{-1}}$$

are selected for our database as supplemental data.

2.3.4 Solid americium oxides and hydroxides

2.3.4.1 Americium oxides

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 modeling. Thus, AmO_2(cr) is excluded from our database.

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.

$BaAmO_3$(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.

2.3.4.2 Solid Am(V) hydroxides

There are only a few studies of the solubility of Am(V) precipitates in near neutral and alkaline solutions. In most of the studies, the solid was not characterized and it is also not clear whether the pH measurements were corrected for the liquid junction potential. For these reasons, Guillaumont et al. (2003) only considered the solubility measurements of X-ray amorphous Am(V) hydroxide precipitates at 295.15 K in 5 M NaCl by Runde & Kim (1994). The solubility constant calculated from the solubility data in the range $8.0 < \log_{10}[H^+] < 9.5$ is consistent with the thermodynamic data selected by Lemire et al. (2001) for freshly precipitated amorphous Np(V) hydroxide. Guillaumont et al. (2003) used the selected value for $\log_{10}{}^*K_{s,0}°(NpO_2OH$, am, fresh, 298.15 K) = (5.3 ± 0.2) as an estimate for the corresponding solubility constant of AmO_2OH(am). They increased the uncertainty to ± 0.5 $\log_{10}$ because there are no Am(V) solubility data at lower ionic strengths for comparison. Therefore

$$\log_{10}{}^*K_{s,0}°(AmO_2OH, \text{am}, 298.15\ \text{K}) = (5.3 \pm 0.5)$$

for the reaction

$$AmO_2OH(am) + H^+ \Leftrightarrow AmO_2^+ + H_2O(l)$$

2.3.4.3 Solid Am(III) hydroxides

$Am(OH)_3(s)$: 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 rationalized 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 behavior may not end with the most crystalline product. The amorphization 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. Guillaumont et al. (2003) remarked that the use of "crystalline" and "amorphous" to describe the structure of a solid phase may indicate a conceptual oversimplification. X-ray data give information on the bulk structure of the solid while solubility in equilibrium with a solid is determined by its surface characteristics, which may be very different from the bulk structure. This caveat notwithstanding, Guillaumont et al. (2003) selected solubility constants for well-characterized amorphous and crystalline americium hydroxide.

The solubility constants selected by Guillaumont et al. (2003) are:

$$\log_{10}{}^*K_{s,0}°(Am(OH)_3, \text{cr}, 298.15\ \text{K}) = (15.6 \pm 0.6)$$

for the reaction

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

and

$$\log_{10}{}^*K_{s,0}°(Am(OH)_3, \text{am}, 298.15\ \text{K}) = (16.9 \pm 0.8)$$

for the reaction

$$Am(OH)_3(am) + 3\ H^+ \Leftrightarrow Am^{3+} + 3\ H_2O(l)$$

Both of these values are selected for our database.

2.3.5 Americium hydrides

$AmH_2(cr)$ and $AmH_3(cr)$ are not relevant under environmental conditions. None of these phases is included in the database.

2.4 Halogen compounds and complexes

2.4.1 Aqueous halogen complexes

Am(III) fluorides: The number of experimental studies on Am(III) complexation with fluoride ions is relatively limited. Based on these data, Silva et al. (1995) recommended an equilibrium constant for AmF^{2+}

$$Am^{3+} + F^- \Leftrightarrow AmF^{2+}$$

$$\log_{10}\beta_1°(AmF^{2+}, 298.15\ K) = (3.4 \pm 0.4)$$

In addition to the experimental data on the fluoride complexation of Am(III), Guillaumont et al. (2003) also considered experimental data on the complexation of Cm(III) with fluoride. Including these data, Guillaumont et al. (2003) obtained the same value with a slightly smaller uncertainty for

$$An^{3+} + F^- \Leftrightarrow AnF^{2+}$$

$$\log_{10}\beta_1°(AnF^{2+}, 298.15\ K) = (3.4 \pm 0.3)$$

which is valid for Am(III) and Cm(III) and is selected for our database. Since no new data were available for other Am(III) and Cm(III) fluoride complexes, Guillaumont et al. (2003) retained the formation constant for AmF_2^+ recommended by Silva et al. (1995)

$$Am^{3+} + 2\ F^- \Leftrightarrow AmF_2^+$$

$$\log_{10}\beta_2°(AmF_2^+, 298.15\ K) = (5.8 \pm 0.2)$$

which is also selected for our database. Experimental data on the formation of $AmF_3(aq)$ were rejected by Silva et al. (1995) and no new data were reported by Guillaumont et al. (2003).

Silva et al. (1995) estimated values for the ion interaction coefficients of AmF^{2+} and AmF_2^+ in perchlorate media by assuming $\varepsilon(AmF^{2+}, ClO_4^-) = \varepsilon(YHCO_3^{2+}, ClO_4^-) = (0.39 \pm 0.04)\ kg\cdot mol^{-1}$ and $\varepsilon(AmF_2^+, ClO_4^-) = \varepsilon(YCO_3^+, ClO_4^-) = (0.17 \pm 0.04)\ kg\cdot mol^{-1}$ using values for the Y-complexes by Spahiu (1983), see the discussion in Section 2.3.2. We adopt these values for our database but have increased their errors

$$\varepsilon(AmF^{2+}, ClO_4^-) = (0.39 \pm 0.10)\ kg\cdot mol^{-1}$$

$$\varepsilon(AmF_2^+, ClO_4^-) = (0.17 \pm 0.10)\ kg\cdot mol^{-1}$$

We estimated the corresponding ion interaction coefficients for chloride media based on charge correlations (see Appendix A). The estimated values

$$\varepsilon(AmF^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg\cdot mol^{-1}$$

$$\varepsilon(AmF_2^+, Cl^-) = (0.05 \pm 0.10)\ kg\cdot mol^{-1}$$

are selected for our database.

Am(III) and Cm(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 $AmCl_4^-$.

According to Guillaumont et al. (2003), experimental studies on the chloride complexation of trivalent actinides can be divided into two groups. Most of the experimental data have been determined by the application of two-phase equilibria, such as ion exchange or liquid-liquid extraction. Another group of data was obtained from spectroscopic methods. While the extracted complexation constants are similar within each group, the spectroscopically determined ones are about two orders of magnitude smaller than those from two-phase equilibria. Guillaumont et al. (2003) preferred to rely only on complexation constants that were derived from spectroscopic studies. In contrast to spectroscopic methods, ion-exchange or liquid-liquid extraction methods are not able to distinguish between ion-ion interactions and inner-sphere complexation. Changes in activity coefficients caused by the successive replacement of the background electrolyte (e.g. $NaClO_4$) by a weak ligand like chloride are often misinterpreted as complex formation.

Several spectroscopic studies on Am(III), Np(III), and Pu(III) in concentrated HCl and LiCl solutions, as well as TRLFS (time resolved laser fluorescence spectroscopy) studies on Cm(III) in $CaCl_2$ solutions have indicated that inner-sphere chloride complexes with these actinides are only formed at very high chloride concentrations (> 4-5 molal). This contradicts the value for $\log_{10}\beta_1°(AmCl^{2+}, 298.15\ K) = (1.05 \pm 0.06)$ selected by Silva et al. (1995), which would result in the presence of about 50% of the monochloro complex in a 1 molal chloride solution. The TRLFS study by Fanghänel et al. (1995), however, did not detect any Cm(III) chloride complex formation even in 4 molal chloride solution.

Fanghänel et al. (1995) and Könnecke et al. (1997) derived a quantitative model of Cm(III) chloride complexation from their TRLFS data in chloride solutions over a wide range of concentrations using the Pitzer ion-interaction approach. The Pitzer approach was chosen because the range of ionic strengths covered in the experiments and the lowest ionic strength at which chloride complexation was found (about $I = 12\ mol\cdot kg^{-1}$) are far beyond the applicability of the SIT method. Guillaumont et al. (2003) selected the equilibrium constants and uncertainty estimates given by Könnecke et al. (1997) for the formation of $AnCl^{2+}$ and $AnCl_2^+$, both valid for Am(III) and Cm(III),

$$An^{3+} + Cl^- \Leftrightarrow AnCl^{2+}$$

$$\log_{10}\beta_1°(AnCl^{2+}, 298.15\ K) = (0.24 \pm 0.03)$$

$$An^{3+} + 2\ Cl^- \Leftrightarrow AnCl_2^+$$

$$\log_{10}\beta_2°(AnCl_2^+, 298.15\ K) = -(0.74 \pm 0.05)$$

These constants are also selected for our database.

We estimated the SIT ion interaction coefficients of $AmCl^{2+}$ and $AmCl_2^+$ for chloride media based on charge correlations (see Appendix A). The estimated values

$$\varepsilon(AmCl^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg\cdot mol^{-1}$$

$$\varepsilon(AmCl_2^+, Cl^-) = (0.05 \pm 0.10)\ kg\cdot mol^{-1}$$

are selected for our database.

Silva et al. (1995) estimated values for the ion interaction coefficients of $AmCl^{2+}$ and $AmCl_2^+$ in perchlorate media by assuming $\varepsilon(AmCl^{2+}, ClO_4^-) = \varepsilon(YHCO_3^{2+}, ClO_4^-) = (0.39 \pm 0.04)\ kg\cdot mol^{-1}$ and $\varepsilon(AmCl_2^+, ClO_4^-) = \varepsilon(YCO_3^+, ClO_4^-) = (0.17 \pm 0.04)\ kg\cdot mol^{-1}$ using values for the Y-complexes by Spahiu (1983), see the discussion in Section 2.3.2. Note that both of these values were selected by Silva et al. (1995) and listed in their Table B.3 of selected ion interaction coefficients. In all further NEA-reviews, however, $\varepsilon(AmCl_2^+, ClO_4^-)$ is omitted. We adopt the estimates by Silva et al. (1995) for our database but have increased their errors

$$\varepsilon(\mathrm{AmCl}^{2+}, \mathrm{ClO_4^-}) = (0.39 \pm 0.10)\ \mathrm{kg{\cdot}mol^{-1}}$$

$$\varepsilon(\mathrm{AmCl_2^+}, \mathrm{ClO_4^-}) = (0.17 \pm 0.10)\ \mathrm{kg{\cdot}mol^{-1}}$$

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) and Guillaumont et al. (2003) 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.

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 vapor 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.
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 by Silva et al. (1995) and Guillaumont et al. (2003).

In the case of AmF_3(cr), Silva et al. (1995) derived a solubility product from these estimated values and compared it 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 with amorphous (or even hydrated) trifluoride. Hence, the selection made by Silva et al. (1995) cannot be confirmed with solubility data. Guillaumont et al. (2003) emphasize that a definitive study of the AmF_3-H_2O system that includes well-defined solubility measurements is clearly required.

Considering these uncertainties, we decided that the estimated Gibbs free energies, enthalpies and entropies of AmF_3(cr), AmF_4(cr), $AmCl_3$(cr), AmOCl(cr), $Cs_2NaAmCl_6$(cr), $AmBr_3$(cr), AmOBr(cr) and AmI_3(cr) shall not be included in our database.

Guillaumont et al. (2003) selected values for $\Delta_f G_m°$ and $\Delta_f H_m°$ for AmF_3(g). Since AmF_3(g) is hardly relevant in natural environments, these data shall not be included in our database.

2.5 Chalcogen compounds and complexes

2.5.1 Americium chalcogenides

There are no experimental studies involving the thermodynamic properties for americium chalcogenides. Silva et al. (1995) summarized the preparative and structural data for these phases, and included estimated values for the entropies of the monochalcogenides AmS(cr), AmSe(cr), and AmTe(cr).

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

2.5.2 Aqueous americium sulphates

There are several quantitative studies available in the literature on the Am(III) sulphate system that used solvent extraction techniques, ion exchange, and electromigration. All of them refer to solutions of low pH (≤ 3.6). Based on these data, Silva et al. (1995) recommended equilibrium constants for the reactions

$$\mathrm{Am^{3+} + n\ SO_4^{2-} \Leftrightarrow Am(SO_4)_n^{(3-2n)}}$$

$$\log_{10}\beta_1^\circ(\mathrm{n = 1, 298.15\ K}) = (3.85 \pm 0.03)$$

$$\log_{10}\beta_2^\circ(\mathrm{n = 2, 298.15\ K}) = (5.4 \pm 0.7)$$

Paviet et al. (1996) and Neck et al. (1998) investigated sulphate complexes of Cm(III) and used TRLFS to identify the complexes $\mathrm{CmSO_4^+}$, $\mathrm{Cm(SO_4)_2^-}$, and $\mathrm{Cm(SO_4)_3^{3-}}$, the latter of which was only found at sulphate concentrations above 1 $\mathrm{mol \cdot kg^{-1}\ H_2O}$. Compared with formation constants derived from solvent extraction and ion exchange methods at similar ionic strengths, the formation constants obtained from the spectroscopic studies are about 0.6 log units smaller for $\mathrm{CmSO_4^+}$ and about 1.5–2 log units smaller for $\mathrm{Cm(SO_4)_2^-}$. This is a similar situation as discussed in the case of the Cm(III) chloride complexes above (see Section 2.4.1) and Guillaumont et al. (2003) concluded that also for sulphate complexation discrepancies in the results between spectroscopic and previous non-spectroscopic methods are not a result of chemical differences, but rather that the two different types of methods measure different phenomena. Therefore, Guillaumont et al. (2003) decided to rely entirely on spectroscopic data for Cm(III) for the derivation of formation constants of $\mathrm{CmSO_4^+}$ and $\mathrm{Cm(SO_4)_2^-}$ which they take to be also valid, by chemical analogy, for $\mathrm{AmSO_4^+}$ and $\mathrm{Am(SO_4)_2^-}$. They considered two sets of data, one by Neck et al. (1998) at pH 2–4 in 0.15 and 0.55 m $\mathrm{Na_2SO_4}$ solutions with appropriate additions of NaCl for varying I between about 1.5 and 5.8 $\mathrm{mol \cdot kg^{-1}\ H_2O}$ and another by Paviet et al. (1996) in 3 m $\mathrm{NaCl\text{-}Na_2SO_4}$ at varying sulphate concentrations ($[\mathrm{SO_4^{2-}}]$ = 0.03–0.37 m). SIT was used to extrapolate each set of data to zero ionic strength and the following mean values were selected by Guillaumont et al. (2003) which are also selected for our database

$$\mathrm{An^{3+} + SO_4^{2-} \Leftrightarrow AnSO_4^+}$$

$$\log_{10}\beta_1^\circ(\mathrm{AnSO_4^+, 298.15\ K}) = (3.30 \pm 0.15)$$

$$\mathrm{An^{3+} + 2\ SO_4^{2-} \Leftrightarrow An(SO_4)_2^-}$$

$$\log_{10}\beta_2^\circ(\mathrm{An(SO_4)_2^-, 298.15\ K}) = (3.70 \pm 0.15)$$

where An stands for Am and Cm. Since Guillaumont et al. (2003) were not able to determine specific ion interaction coefficients from the data in these $\mathrm{NaCl\text{-}Na_2SO_4}$ mixtures, we used the estimation based on charge correlations (see Appendix A) to obtain

$$\varepsilon(\mathrm{AmSO_4^+, Cl^-}) = (0.05 \pm 0.10)\ \mathrm{kg \cdot mol^{-1}}$$

Guillaumont et al. (2003) retained ε($AmSO_4^+$, ClO_4^-) that was derived by Silva et al. (1995) from experiments in perchlorate media

$$\varepsilon(AmSO_4^+, ClO_4^-) = (0.22 \pm 0.08)\ kg\cdot mol^{-1}$$

and they also retained ε($Am(SO_4)_2^-$, Na^+), which was estimated by Silva et al. (1995), who did not explain what this estimate is based on

$$\varepsilon(Am(SO_4)_2^-, Na^+) = -(0.05 \pm 0.05)\ kg\cdot mol^{-1}$$

All these values are also selected for our database.

There is no evidence of any americium hydrogen-sulphate complex formation.

2.6 Group 15 compounds and complexes

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

$$Am^{3+} + NO_3^- \Leftrightarrow AmNO_3^{2+}$$

$$\log_{10}\beta_1°(298.15\ K) = (1.33 \pm 0.20)$$

and considered that there is no clear evidence for the existence of higher complexes.

Note that the selected equilibrium constant for the Am(III) nitrate complex is probably too high, considering the discussion of Am(III) chloride complexation (see Section 2.4.1). No spectroscopic studies are available for the Am(III) nitrate system and the selection of a complexation constant based on solvent extraction studies only is inconsistent with the selected Am(III) chloride complexation constants. However, this inconsistency is not discussed by Guillaumont et al. (2003).

No value for ε($AmNO_3^{2+}$, Cl^-) was selected by Silva et al. (1995) and Guillaumont et al. (2003). We used a method based on charge correlations (see Appendix A) for estimating our selected value

$$\varepsilon(AmNO_3^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg\cdot mol^{-1}$$

Silva et al. (1995) estimated a value for the ion interaction coefficient of $AmNO_3^{2+}$ in perchlorate media by assuming $\varepsilon(AmNO_3^{2+}, ClO_4^-) = \varepsilon(YHCO_3^{2+}, ClO_4^-) = (0.39 \pm 0.04)$ $kg \cdot mol^{-1}$ using a value for the Y-complex by Spahiu (1983), see the discussion in Section 2.3.2. We adopt this estimate for our database with an increased error

$$\varepsilon(AmNO_3^{2+}, ClO_4^-) = (0.39 \pm 0.10)\ kg \cdot mol^{-1}$$

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 equilibria 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 reanalyzed. 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

$$Am^{3+} + H_2PO_4^- \Leftrightarrow AmH_2PO_4^{2+}$$

$$\log_{10}\beta_1^\circ(298.15\ K) = (3.0 \pm 0.5)$$

only the first equilibrium constant is recommended by Silva et al. (1995).

No value for $\varepsilon(AmH_2PO_4^{2+}, Cl^-)$ was selected by Silva et al. (1995) and Guillaumont et al. (2003). We used a method based on charge correlations (see Appendix A) for estimating our selected value

$$\varepsilon(AmH_2PO_4^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg \cdot mol^{-1}$$

Silva et al. (1995) estimated a value for the ion interaction coefficient of $AmH_2PO_4^{2+}$ in perchlorate media by assuming $\varepsilon(AmH_2PO_4^{2+}, ClO_4^-) = \varepsilon(YHCO_3^{2+}, ClO_4^-) = (0.39 \pm 0.04)$ $kg \cdot mol^{-1}$ using a value for the Y-complex by Spahiu (1983), see the discussion in Section 2.3.2. We adopt this estimate for our database with an increased error

$$\varepsilon(AmH_2PO_4^{2+}, ClO_4^-) = (0.39 \pm 0.10)\ kg \cdot mol^{-1}$$

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:

$$AmPO_4 \cdot xH_2O(am) \Leftrightarrow Am^{3+} + PO_4^{3-} + x\ H_2O(l)$$

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, hyd) 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.

2.6.3 Arsenic, antimony and bismuth compounds

No thermodynamic data are available for arsenides, arsenates, antimonides and bismuthides of americium.

2.7 Group 14 compounds and complexes

2.7.1 Carbon compounds and complexes

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.

2.7.1.2 Americium carbonate compounds and complexes

Am(V) carbonate complexes: The formation constants of the Am(V) carbonate complexes $AmO_2CO_3^-$, $AmO_2(CO_3)_2^{3-}$, and $AmO_2(CO_3)_3^{5-}$ were extracted from two studies dealing with the solubility of $NaAmO_2CO_3$(s) over a wide range of carbonate concentrations in 3, 4, and 5 M NaCl (Giffaut 1994, Runde & Kim 1994). Although the solid phases were not characterized by X-ray diffraction, there is enough evidence from analogous studies with Np(V), where solids were sufficiently characterized, that the measured solubilities actually refer to $NaAmO_2CO_3$(s). Guillaumont et al. (2003) used the reported conditional stepwise formation constants for the Am(V) carbonate complexes together with the SIT ion interaction coefficients selected by Lemire et al. (2001) for the analogous Np(V) complexes to calculate the formation constants at $I = 0$. Guillaumont et al. (2003) selected the weighted averages of the formation constants at $I = 0$, which correspond to the following overall formation constants

$$AmO_2^+ + CO_3^{2-} \Leftrightarrow AmO_2CO_3^-$$

$$\log_{10}\beta_1°(AmO_2CO_3^-, 298.15\text{ K}) = (5.1 \pm 0.5)$$

$$AmO_2^+ + 2\ CO_3^{2-} \Leftrightarrow AmO_2(CO_3)_2^{3-}$$

$$\log_{10}\beta_2°(AmO_2(CO_3)_2^{3-}, 298.15\text{ K}) = (6.7 \pm 0.8)$$

$$AmO_2^+ + 3\ CO_3^{2-} \Leftrightarrow AmO_2(CO_3)_3^{5-}$$

$$\log_{10}\beta_3°(AmO_2(CO_3)_3^{5-}, 298.15\text{ K}) = (5.1 \pm 1.0)$$

These are also selected for our database.

We adopted the above mentioned ion interaction coefficients of the Np(V) complexes as estimates for the corresponding Am(V) complexes and selected

$$\varepsilon(\mathrm{AmO_2CO_3^-, Na^+}) = -(0.18 \pm 0.15)\ \mathrm{kg \cdot mol^{-1}}$$

$$\varepsilon(\mathrm{AmO_2(CO_3)_2^{3-}, Na^+}) = -(0.33 \pm 0.17)\ \mathrm{kg \cdot mol^{-1}}$$

$$\varepsilon(\mathrm{AmO_2(CO_3)_3^{5-}, Na^+}) = -(0.53 \pm 0.19)\ \mathrm{kg \cdot mol^{-1}}$$

for our database. By analogy, we also selected

$$\varepsilon(\mathrm{AmO_2(CO_3)_3^{5-}, K^+}) = -(0.22 \pm 0.03)\ \mathrm{kg \cdot mol^{-1}}$$

Am(IV) and Am(VI) carbonate complexes: Measurements in 2 M $NaHCO_3/Na_2CO_3$ media have been interpreted by presuming that $Am(IV)(CO_3)_5^{6-}$ and $Am(VI)O_2(CO_3)_3^{4-}$ are the limiting complexes for the IV and VI oxidation states, as expected by analogy with U(IV), and U(VI)–Pu(VI), respectively. Equilibrium constants for these complexes were recommended by Silva et al. (1995). However, as these carbonate complexes are the only Am(IV) and Am(VI) species with a known equilibrium constant, they are not included in our database.

Am(III) carbonate complexes: Americium complexation by carbonate has been investigated with a number of different methods. For the reaction

$$\mathrm{Am^{3+} + n\ CO_3^{2-} \Leftrightarrow Am(CO_3)_n^{(3-2n)}}$$

these studies have demonstrated the existence of complexes with n = 1, 2 and 3. In addition to experimental data on Am(III), Guillaumont et al. (2003) also considered available spectroscopic data on the chemical analog Cm(III) which were obtained by TRLFS. They noted that the uncertainties of the different experimental methods (solubility measurements, solvent extraction, laser induced photoacoustic spectroscopy LIPAS, and TRLFS) are considerably larger than the chemical differences between Am(III) and Cm(III), such that experimental data for these two elements can be safely treated and weighted together. Thus, Guillaumont et al. (2003) extracted stepwise stability constants from various experimental data and converted them to $I = 0$ using SIT and recommended the following overall formation constants

$$\mathrm{An^{3+} + CO_3^{2-} \Leftrightarrow AnCO_3^+}$$

$$\log_{10}\beta_1°(\mathrm{AnCO_3^+}, 298.15\ \mathrm{K}) = (8.0 \pm 0.4)$$

$$\mathrm{An^{3+} + 2\ CO_3^{2-} \Leftrightarrow An(CO_3)_2^-}$$

$$\log_{10}\beta_2°(\mathrm{An(CO_3)_2^-}, 298.15\ \mathrm{K}) = (12.9 \pm 0.6)$$

$$\mathrm{An^{3+} + 3\ CO_3^{2-} \Leftrightarrow An(CO_3)_3^{3-}}$$

$$\log_{10}\beta_3°(\mathrm{An(CO_3)_3^{3-}}, 298.15\ \mathrm{K}) = (15.0 \pm 1.0)$$

where An stands for Am and Cm. All values are also selected for our database. From their SIT analysis, Guillaumont et al. (2003) obtained

$$\varepsilon(\mathrm{AnCO_3^+, Cl^-}) = (0.01 \pm 0.05)\ \mathrm{kg \cdot mol^{-1}}$$

$$\varepsilon(\mathrm{An(CO_3)_2^-, Na^+}) = -(0.14 \pm 0.06)\ \mathrm{kg \cdot mol^{-1}}$$

$$\varepsilon(\mathrm{An(CO_3)_3^{3-}, Na^+}) = -(0.23 \pm 0.07)\ \mathrm{kg \cdot mol^{-1}}$$

which are selected for our database. Silva et al. (1995) estimated a value for the ion interaction coefficient of $AmCO_3^+$ in perchlorate media by assuming $\varepsilon(AmCO_3^+, ClO_4^-) = \varepsilon(YCO_3^+, ClO_4^-) = (0.17 \pm 0.04)\ kg \cdot mol^{-1}$ using a value for the Y-complex by Spahiu (1983), see the discussion in Section 2.3.2. We adopt this estimate for our database with an increased error

$$\varepsilon(\mathrm{AmCO_3^+, ClO_4^-}) = (0.17 \pm 0.10)\ \mathrm{kg \cdot mol^{-1}}$$

The formation of the tetracarbonato complex $M(CO_3)_4^{5-}$ has been observed for Cm(III), Ce(III), and Eu(III). For chemical reasons one would expect the same behavior for Am(III), however, all of the available spectroscopic and solubility data provide no evidence for $Am(CO_3)_4^{5-}$ up to carbonate concentrations of 1 $mol \cdot L^{-1}$.

TRLFS studies have shown that chloride complexation with Cm^{3+} is negligible even in concentrated NaCl. Therefore, ternary carbonate-chloride complexes can be ruled out for Cm(III) and, by analogy, Am(III).

Am(III) and Cm(III) bicarbonate complexes: A spectroscopic TRLFS study of the first Cm(III) bicarbonate complex was made by Fanghänel et al. (1998) in 1 M NaCl solutions at pH 3–6 and CO_2 partial pressures of 0.5–11 bar. Guillaumont et al. (2003) converted the reported conditional formation constant to $I = 0$ using $\varepsilon(Cm^{3+}, Cl^-) = 0.23$, $\varepsilon(CmHCO_3^{2+}, Cl^-) = 0.16$, and $\varepsilon(HCO_3^-, Na^+) = 0.0$ $kg \cdot mol^{-1}$ and assumed the resulting formation constant to be equal to the analogous formation constant of the Am(III) bicarbonate complex. The selected value, which is also included in our database, is

$$An^{3+} + HCO_3^- \Leftrightarrow AnHCO_3^{2+}$$

$$\log_{10}\beta_1°(AnHCO_3^{2+}, 298.15\ K) = (3.1 \pm 0.3)$$

where An stands for Am and Cm. Note that the values for $\varepsilon(Cm^{3+}, Cl^-)$ and $\varepsilon(HCO_3^-, Na^+)$ used by Guillaumont et al. (2003) are selected NEA-values, but these authors did not explain how they derived the value for $\varepsilon(CmHCO_3^{2+}, Cl^-)$ and they also did not select it. Since this value is nearly identical to the value (0.15 ± 0.10) $kg \cdot mol^{-1}$ estimated on the basis of charge correlations (see Appendix A), we adopt it for $AmHCO_3^{2+}$ in our database, assuming an error of ± 0.10

$$\varepsilon(AmHCO_3^{2+}, Cl^-) = (0.16 \pm 0.10)\ kg \cdot mol^{-1}$$

For perchlorate media we applied a method based on charge correlations (see Appendix A) for estimating our selected value

$$\varepsilon(AmHCO_3^{2+}, ClO_4^-) = (0.4 \pm 0.1)\ kg \cdot mol^{-1}$$

The formation constant for the bicarbonate complex, $AmHCO_3^{2+}$, is about five orders of magnitude smaller than the carbonate complex, $AmCO_3^+$. As a consequence, the bicarbonate complex becomes dominant only under high CO_2 partial pressures above 1 bar.

Mixed Am(III) hydroxide-carbonate complexes: All of the available experimental data from studies claiming the existence of mixed Am(III) hydroxide-carbonate complexes can be re-interpreted with the assumption that only americium carbonate complexes and/or hydrolysis products are formed in aqueous solutions. This is supported by TRLFS studies of Cm(III) in carbonate-bicarbonate studies. Further experimental work is needed to confirm or deny the existence of mixed Am(III) hydroxy-carbonate complexes in aqueous solutions.

Am(III) hydroxycarbonate $AmOHCO_3 \cdot 0.5H_2O(cr)$: Silva & Nitsche (1984) measured the solubility of crystalline ^{243}Am(III) hydroxycarbonate, which was characterized by X-ray diffraction but not analyzed for crystal water. Merli & Fuger (1996) determined the standard enthalpy of formation of $^{241}AmOHCO_3 \cdot 0.5H_2O(cr)$ and estimated a value for the standard entropy. From these thermodynamic data, they calculated a solubility constant, which was recalculated by Guillaumont et al. (2003) by using a correction term for the entropy. Guillaumont et al. (2003) selected the mean value of their recalculated solubility constant of Merli & Fuger (1996) and the solubility constant determined by Silva & Nitsche (1984)

$$AmOHCO_3 \cdot 0.5H_2O(cr) \Leftrightarrow Am^{3+} + OH^- + CO_3^{2-} + 0.5\ H_2O(l)$$

$$\log_{10}K_{s,0}°(AmOHCO_3 \cdot 0.5H_2O, cr, 298.15\ K) = -(22.4 \pm 0.5)$$

The solubility constant measured by Runde et al. (1992) with $^{241}AmOHCO_3(s)$ was ascribed by Guillaumont et al. (2003) to an aged solid that was rendered amorphous by α-irradiation. Since there is no other data on amorphous $AmOHCO_3(s)$ available and since solubility data on amorphous solids are often scattered, Guillaumont et al. (2003) selected the solubility constant determined by Runde et al. (1992) with an increased uncertainty

$$AmOHCO_3(am, hyd) \Leftrightarrow Am^{3+} + OH^- + CO_3^{2-} + 0.5\ H_2O(l)$$

$$\log_{10}K_{s,0}°(AmOHCO_3, am, hyd, 298.15\ K) = -(20.2 \pm 1.0)$$

The solubility constants for both the crystalline and amorphous solids are selected for our database.

From $\log_{10}K_{s,0}°(AmOHCO_3 \cdot 0.5\ H_2O, cr, 298.15\ K)$, $\log_{10}{}^*K_{s,0}°(Am(OH)_3, cr, 298.15\ K)$, and auxiliary data the reaction

$$Am(OH)_3(cr) + CO_2(g) \Leftrightarrow AmOHCO_3 \cdot 0.5H_2O(cr) + 0.5\ H_2O(l)$$

can be calculated as

$$\log_{10}K_p°(298.15\ K) = (5.8 \pm 0.8)$$

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 $1 \cdot 10^{-5}$ bar > pCO_2 > $2.5 \cdot 10^{-7}$ bar (2 orders of magnitude as 95% confidence interval !).

Am(III) carbonate $Am_2(CO_3)_3$(am, hyd): The solubility of $Am_2(CO_3)_3 \cdot xH_2O(s)$ has been determined by several authors. The reported numbers of crystal water vary over a large range from x = 2 to 8. Since the solid in one study was described to be X-ray amorphous and the solids in the others were only identified from their solubility behavior, Guillaumont et al. (2003) ascribed the mean value of the reported conditional solubility constants recalculated to $I = 0$ by Silva et al. (1995) not to the well-defined crystalline solid $Am_2(CO_3)_3(cr)$ but rather to the amorphous and hydrated solid $Am_2(CO_3)_3 \cdot xH_2O$ (am), which will be referred to as $Am_2(CO_3)_3$(am, hyd) in our database. The selected value by Guillaumont et al. (2003)

$$0.5\ Am_2(CO_3)_3(am, hyd) \Leftrightarrow Am^{3+} + 1.5\ CO_3^{2-}$$

$$\log_{10}K_{s,0}°(Am_2(CO_3)_3, am, hyd, 298.15\ K) = -(16.7 \pm 1.1)$$

is included in our database.

From $\log_{10}K_{s,0}°(Am_2(CO_3)_3, am, hyd, 298.15\ K)$, $\log_{10}K_{s,0}°(AmOHCO_3 \cdot 0.5\ H_2O, cr, 298.15\ K)$, and auxiliary data the reaction

$$AmOHCO_3 \cdot 0.5H_2O(cr) + ½\ CO_2(g) \Leftrightarrow ½\ Am_2(CO_3)_3(am, hyd) + H_2O(l)$$

can be calculated with

$$\log_{10}K_p°(298.15\ K) = -(0.8 \pm 1.2)$$

which results in a very large range of $CO_2(g)$ equilibrium partial pressures for the equilibrium between the two solids of 10^4 bar > pCO_2 > $1.6 \cdot 10^{-1}$ bar (5 orders of magnitude as 95% confidence interval !).

The large uncertainties associated with the phase boundaries between the solids $Am_2(CO_3)_3$(am, hyd), $AmOHCO_3 \cdot 0.5H_2O(cr)$ and $Am(OH)_3(cr)$ pose serious obstacles in geochemical modeling. 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.

Na-Am(V) carbonate $NaAmO_2CO_3(s)$: The solubility of $NaAmO_2CO_3(s)$ has been studied by several authors. Although the solid has not been characterized by X-ray diffraction in any of the studies, the assumption of $NaAmO_2CO_3(s)$ as solubility limiting solid is justified, because the analogous solid $NaNpO_2CO_3(s)$, which was characterized by X-ray diffraction, is known to be stable under the conditions used in the solubility measurements of $NaAmO_2CO_3(s)$ and the solubility data for both solids are similar. Furthermore, the dependence of the solubility on $\log_{10}[CO_3^{2-}]$ is the same for Am(V) and Np(V), which suggests that the solubility limiting solids have comparable compositions. Guillaumont et al. (2003) selected

$$NaAmO_2CO_3(s) \Leftrightarrow Na^+ + AmO_2^+ + CO_3^{2-}$$

$$\log_{10}K_{s,0}°(NaAmO_2CO_3, s, 298.15 \text{ K}) = -(10.9 \pm 0.4)$$

which is also selected for our database.

Na-Am(III) carbonates $NaAm(CO_3)_2 \cdot xH_2O$ (s) and $Na_3Am(CO_3)_3 \cdot xH_2O$ (s): The solubility of $NaAm(CO_3)_2{\cdot}xH_2O(s)$ was determined by several authors. Runde & Kim (1994) used a well-characterized solid (by thermogravimetry, IR spectroscopy, and X-ray diffraction) in carbonate solutions containing 5 M NaCl for determining a conditional solubility constant. This conditional constant was recalculated to $I = 0$ by Guillaumont et al. (2003) using SIT by assuming the number of crystal water molecules to be x = (5 ± 1), since reported values for x in $NaAm(CO_3)_2{\cdot}xH_2O(s)$ and the analogous Eu and Nd solids are x = 4, x = 5, or x = 6. Guillaumont et al. (2003) selected

$$NaAm(CO_3)_2{\cdot}5H_2O(cr) \Leftrightarrow Na^+ + Am^{3+} + 2\ CO_3^{2-} + 5\ H_2O(l)$$

$$\log_{10}K_{s,0}°(NaAm(CO_3)_2 \cdot 5H_2O, cr, 298.15 \text{ K}) = -(21.0 \pm 0.5)$$

which is also selected for our database.

$Na_3Am(CO_3)_3{\cdot}xH_2O(s)$ has been synthesized, but thermodynamic data are not available.

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.

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 $AmSCN^{2+}$

$$Am^{3+} + SCN^- \Leftrightarrow AmSCN^{2+}$$

$$\log_{10}\beta_1°(AmSCN^{2+}, 298.15 \text{ K}) = (1.3 \pm 0.3)$$

which is also selected for our database. Silva et al. (1995) estimated a value for the ion interaction coefficient of $AmSCN^{2+}$ in perchlorate media by assuming that $\varepsilon(AmSCN^{2+}, ClO_4^-) = \varepsilon(YHCO_3^{2+}, ClO_4^-) = (0.39 \pm 0.04)$ kg·mol^{-1} using a value for $YHCO_3^{2+}$ by Spahiu (1983), see the discussion in Section 2.3.2. We adopt this estimated value for our database but have increased its error

$$\varepsilon(\mathrm{AmSCN}^{2+}, \mathrm{ClO_4^-}) = (0.39 \pm 0.10)\ \mathrm{kg \cdot mol^{-1}}$$

For chloride media we estimated

$$\varepsilon(\mathrm{AmSCN}^{2+}, \mathrm{Cl^-}) = (0.15 \pm 0.10)\ \mathrm{kg \cdot mol^{-1}}$$

according to an estimation method based on charge correlations (see Appendix A). This value is also selected for our database.

2.7.2 Silicon compounds and complexes

Thermodynamic data for silicon compounds and complexes contained in our database are discussed in Chapter 8.

2.8 Group 6 compounds and complexes

Am(III) molybdate compounds and complexes: Guillaumont et al. (2003) provided equilibrium constants for $\mathrm{Nd(MoO_4)_2^-}$, $\mathrm{Nd_2Mo_7O_{24}(aq)}$, $\mathrm{NaNd(MoO_4)_2(cr)}$, and $\mathrm{Nd_2(MoO_4)_3(s, hyd)}$ as guidance for modeling aqueous Am(III) molybdate complexes but selected none of them. These data have not been considered for our database.

Aqueous complexes with tungstophosphate and tungstosilicate heteropolyanions: The stabilization of Am(III), Am(IV), and Am(V) in aqueous solutions of polyphosphatotungstate has been described in several publications. Guillaumont et al. (2003) compiled a number of conditional formation constants for $\mathrm{Am(P_2W_{17}O_{61})^{7-}}$, $\mathrm{Am(P_2W_{17}O_{61})_2^{17-}}$, $\mathrm{Cm(PW_{11}O_{39})^{4-}}$, $\mathrm{Am(SiW_{11}O_{39})^{5-}}$, $\mathrm{Cm(SiW_{11}O_{39})^{5-}}$, $\mathrm{Am(SiW_{11}O_{39})_2^{13-}}$, $\mathrm{Am(P_2W_{17}O_{61})^{6-}}$, $\mathrm{Am(P_2W_{17}O_{61})_2^{16-}}$, $\mathrm{Am(SiW_{11}O_{39})^{4-}}$, and $\mathrm{Am(SiW_{11}O_{39})_2^{12-}}$. These data have not been considered for our database.

2.9 Ionic strength corrections

The selected SIT ion interaction coefficients for americium species are listed in Table 2.3. If available, the coefficients were taken from Silva et al. (1995) and Guillaumont et al. (2003). Missing interaction coefficients were estimated according to a method based on a statistical analysis of published SIT ion interaction coefficients that allows the estimation of interaction coefficients from the charge of the considered species (see Appendix A).

Table 2.1: Americium data selected by NEA (Silva et al. 1995 and Guillaumont et al. 2003) but not included in TDB Version 12/07. For explanations see text.

Gases	$\mathrm{Am(g)}^{ad}$, $\mathrm{AmF_3(g)}^{ad}$
Solids	β-Am ^{b}, γ-Am ^{b}, $\mathrm{AmO_2(cr)}^{a}$, $\mathrm{Am_2O_3(cr)}^{a}$, $\mathrm{AmH_2(cr)}^{a}$, $\mathrm{AmF_3(cr)}^{a}$, $\mathrm{AmF_4(cr)}^{a}$, $\mathrm{AmCl_3(cr)}^{a}$, $\mathrm{AmOCl(cr)}^{ac}$, $\mathrm{AmBr_3(cr)}^{a}$, $\mathrm{AmOBr(cr)}^{ac}$, $\mathrm{AmI_3(cr)}^{a}$, $\mathrm{AmS(cr)}^{b}$, $\mathrm{AmSe(cr)}^{b}$, $\mathrm{AmTe(cr)}^{b}$, $\mathrm{AmPO_4(am, hyd)}^{c}$, $\mathrm{Am_2C_3(cr)}^{a}$, $\mathrm{SrAmO_3(cr)}^{b}$, $\mathrm{BaAmO_3(cr)}^{b}$, $\mathrm{Cs_2NaAmCl_6(cr)}^{a}$
Liquids	$\mathrm{Am(l)}^{b}$
Aqueous species	$\mathrm{Am}^{2+\,ac}$, $\mathrm{Am}^{4+\,a}$, $\mathrm{AmO_2}^{2+\,ad}$, $\mathrm{AmN_3}^{2+\,ac}$, $\mathrm{AmNO_2}^{2+\,c}$, $\mathrm{AmO_2(CO_3)_3}^{4-\,c}$, $\mathrm{Am(CO_3)_5}^{6-\,ac}$

[a] Single species data including $\Delta_f G_m°$

[b] Single species data excluding $\Delta_f G_m°$

[c] Reaction data including $\log_{10}K°$

[d] Reaction data excluding $\log_{10}K°$

Table 2.2: Selected americium data. All data included in TDB Version 12/07 are taken from Silva et al. (1995) and Guillaumont et al. (2003), except where marked with an asterisk (*). Supplemental data are given in italics. New or changed data with respect to TDB Version 01/01 (Hummel et al. 2002) are shaded.

		TDB Version 01/01				TDB Version 12/07				
Name	**Redox**	$\Delta_\mathrm{f}G_\mathrm{m}^\circ$ $[\mathrm{kJ\cdot mol^{-1}}]$	$\Delta_\mathrm{f}H_\mathrm{m}^\circ$ $[\mathrm{kJ\cdot mol^{-1}}]$	S_m° $[\mathrm{J\cdot K^{-1}\cdot mol^{-1}}]$	$C_\mathrm{p,m}^\circ$ $[\mathrm{J\cdot K^{-1}\cdot mol^{-1}}]$	$\Delta_\mathrm{f}G_\mathrm{m}^\circ$ $[\mathrm{kJ\cdot mol^{-1}}]$	$\Delta_\mathrm{f}H_\mathrm{m}^\circ$ $[\mathrm{kJ\cdot mol^{-1}}]$	S_m° $[\mathrm{J\cdot K^{-1}\cdot mol^{-1}}]$	$C_\mathrm{p,m}^\circ$ $[\mathrm{J\cdot K^{-1}\cdot mol^{-1}}]$	**Species**
Am(cr)	0	0	0	55.4 ± 2.0	-	0	0	55.4 ± 2.0	-	Am(cr)
Am+3	III	-598.7 ± 4.8	-616.7 ± 1.5	-201 ± 15	-	-598.7 ± 4.8	-616.7 ± 1.5	-201 ± 15	-	$\mathrm{Am^{3+}}$
AmO2+	V	-	-	-	-	(-732.4 ± 6.3)*	-804.3 ± 5.4	(-45.9 ± 10.7)*	-	$\mathrm{AmO_2^+}$

		TDB Version 01/01		TDB Version 12/07		
Name	**Redox**	$\log_{10}\beta^\circ$	$\Delta_\mathrm{r}H_\mathrm{m}^\circ$ $[\mathrm{kJ\cdot mol^{-1}}]$	$\log_{10}\beta^\circ$	$\Delta_\mathrm{r}H_\mathrm{m}^\circ$ $[\mathrm{kJ\cdot mol^{-1}}]$	**Reaction**
AmO2+	III/V	-	-	(-59.7±1.4)*	384.1 ± 5.2	$\mathrm{Am^{3+} + 2\ H_2O(l) \Leftrightarrow AmO_2^+ + 4\ H^+ + 2\ e^-}$
AmO2OH	V	-	-	(-11.3 ± 0.7)^c	-	$\mathrm{AmO_2^+ + H_2O(l) \Leftrightarrow AmO_2OH(aq) + H^+}$
AmO2(OH)2-	V	-	-	(-23.6 ± 0.5)^c	-	$\mathrm{AmO_2^+ + 2\ H_2O(l) \Leftrightarrow AmO_2(OH)_2^- + 2\ H^+}$
AmO2CO3-	V	-	-	5.1 ± 0.5	-	$\mathrm{AmO_2^+ + CO_3^{2-} \Leftrightarrow AmO_2CO_3^-}$
AmO2(CO3)2-3	V	-	-	6.7 ± 0.8	-	$\mathrm{AmO_2^+ + 2\ CO_3^{2-} \Leftrightarrow AmO_2(CO_3)_2^{3-}}$
AmO2(CO3)3-5	V	-	-	5.1 ± 1.0	-	$\mathrm{AmO_2^+ + 3\ CO_3^{2-} \Leftrightarrow AmO_2(CO_3)_3^{5-}}$
AmOH+2	III	-7.3 ± 0.3	-	(-7.2 ± 0.5)^a	-	$\mathrm{Am^{3+} + H_2O(l) \Leftrightarrow AmOH^{2+} + H^+}$
Am(OH)2+	III	-15.2 ± 0.8	-	(-15.1 ± 0.7)^a	-	$\mathrm{Am^{3+} + 2\ H_2O(l) \Leftrightarrow Am(OH)_2^+ + 2\ H^+}$
Am(OH)3	III	-25.7 ± 0.5	-	(-26.2 ± 0.5)^a	-	$\mathrm{Am^{3+} + 3\ H_2O(l) \Leftrightarrow Am(OH)_3(aq) + 3\ H^+}$
CaAm(OH)3+2	III	-	-	*(-26.3 ± 0.5)**^{b}		$Ca^{2+} + Am^{3+} + 3\ H_2O(l) \Leftrightarrow CaAm(OH)_3^{2+} + 3\ H^+$
Ca2Am(OH)4+3	III	-	-	*(-37.2 ± 0.6)**^{b}		$2\ Ca^{2+} + Am^{3+} + 4\ H_2O(l) \Leftrightarrow Ca_2Am(OH)_4^{3+} + 4\ H^+$
Ca3Am(OH)6+3	III	-	-	*(-60.7 ± 0.5)**^{b}		$3\ Ca^{2+} + Am^{3+} + 6\ H_2O(l) \Leftrightarrow Ca_3Am(OH)_6^{3+} + 6\ H^+$
AmF+2	III	3.4 ± 0.4	-	(3.4 ± 0.3)^a	-	$\mathrm{Am^{3+} + F^- \Leftrightarrow AmF^{2+}}$
AmF2+	III	5.8 ± 0.2	-	5.8 ± 0.2	-	$\mathrm{Am^{3+} + 2\ F^- \Leftrightarrow AmF_2^+}$
AmCl+2	III	1.05 ± 0.06	-	(0.24 ± 0.03)^a	-	$\mathrm{Am^{3+} + Cl^- \Leftrightarrow AmCl^{2+}}$
AmCl2+	III	-	-	(-0.74 ± 0.05)^a	-	$\mathrm{Am^{3+} + 2\ Cl^- \Leftrightarrow AmCl_2^+}$
AmSO4+	III	3.85 ± 0.03	-	(3.30 ± 0.15)^b	-	$\mathrm{Am^{3+} + SO_4^{2-} \Leftrightarrow AmSO_4^+}$
Am(SO4)2-	III	5.4 ± 0.7	-	(3.70 ± 0.15)^b	-	$\mathrm{Am^{3+} + 2\ SO_4^{2-} \Leftrightarrow Am(SO_4)_2^-}$
AmNO3+2	III	1.33 ± 0.20	-	1.33 ± 0.20	-	$\mathrm{Am^{3+} + NO_3^- \Leftrightarrow AmNO_3^{2+}}$
AmH2PO4+2	III	3.0 ± 0.5	-	3.0 ± 0.5	-	$\mathrm{Am^{3+} + H_2PO_4^- \Leftrightarrow AmH_2PO_4^{2+}}$

		TDB Version 01/01		TDB Version 12/07		
Name	**Redox**	**$\log_{10}\beta°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**$\log_{10}\beta°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**Reaction**
AmCO3+	III	7.8 ± 0.3	-	(8.0 ± 0.4)[a]	-	$Am^{3+} + CO_3^{2-} \Leftrightarrow AmCO_3^+$
Am(CO3)2-	III	12.3 ± 0.4	-	(12.9 ± 0.4)[a]	-	$Am^{3+} + 2\ CO_3^{2-} \Leftrightarrow Am(CO_3)_2^-$
Am(CO3)3-3	III	15.2 ± 0.6	-	(15.0 ± 1.0)[a]	-	$Am^{3+} + 3\ CO_3^{2-} \Leftrightarrow Am(CO_3)_3^{3-}$
AmHCO3+2	III	-	-	(3.1 ± 0.3)[b]	-	$Am^{3+} + HCO_3^- \Leftrightarrow AmHCO_3^{2+}$
AmSCN+2	III	-	-	1.3 ± 0.3	-	$Am^{3+} + SCN^- \Leftrightarrow AmSCN^{2+}$

[a] Formation constant is based on combined Am and Cm data

[b] Formation constant is based on Cm data only

[c] Recommended by Guillaumont et al. (2003) as reasonable estimate

		TDB Version 01/01		TDB Version 12/07		
Name	**Redox**	**$\log_{10}K_{s,0}°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**$\log_{10}K_{s,0}°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**Reaction**
AmO2OH(am)	V	-	-	5.3 ± 0.5	-	$AmO_2OH(am) + H^+ \Leftrightarrow AmO_2^+ + H_2O(l)$
NaAmO2CO3(s)	V	-	-	-10.9 ± 0.4	-	$NaAmO_2CO_3(s) \Leftrightarrow Na^+ + AmO_2^+ + CO_3^{2-}$
Am(OH)3(cr)	III	15.2 ± 0.6	-	15.6 ± 0.6	-	$Am(OH)_3(cr) + 3\ H^+ \Leftrightarrow Am^{3+} + 3\ H_2O(l)$
Am(OH)3(am)	III	17.0 ± 0.6	-	16.9 ± 0.8	-	$Am(OH)_3(am) + 3\ H^+ \Leftrightarrow Am^{3+} + 3\ H_2O(l)$
AmOHCO3 (cr)	III	-21.2 ± 1.4	-	-	-	$AmOHCO_3\ (cr) \Leftrightarrow Am^{3+} + OH^- + CO_3^{2-}$
AmOHCO3:0.5H2O(cr)	III	-	-	-22.4 ± 0.5	-	$AmOHCO_3 \cdot 0.5H_2O(cr) \Leftrightarrow Am^{3+} + OH^- + CO_3^{2-} + 0.5\ H_2O(l)$
AmOHCO3(am, hyd)	III	-	-	-20.2 ± 1.0	-	$AmOHCO_3(am,\ hyd) \Leftrightarrow Am^{3+} + OH^- + CO_3^{2-}$
Am(CO3)1.5(am, hyd)[a]	III	-16.7 ± 1.1	-	-16.7 ± 1.1	-	$0.5\ Am_2(CO_3)_3(am,\ hyd) \Leftrightarrow Am^{3+} + 1.5\ CO_3^{2-}$
NaAm(CO3)2:5H2O(cr)	III	-	-	-21.0 ± 0.5	-	$NaAm(CO_3)_2 \cdot 5H_2O(cr) \Leftrightarrow Na^+ + Am^{3+} + 2\ CO_3^{2-} + 5\ H_2O(l)$

[a] This phase is referred to as Am(CO3)1.5(cr) in TDB Version 01/01, and as $Am_2(CO_3)_3 \cdot xH_2O$ (am) by Guillaumont et al. (2003)

Table 2.3: Selected SIT ion interaction coefficients $\varepsilon_{j,k}$ [kg·mol^{-1}] for americium species. The data included in TDB Version 12/07 are taken from Silva et al. (1995) and Guillaumont et al. (2003) unless indicated otherwise. Own data estimates based on charge correlations (see Appendix A) are shaded. Supplemental data are in italics.

***j* *k*→** **↓**	**Cl^-** $\varepsilon_{j,k}$	**ClO_4^-** $\varepsilon_{j,k}$	**NO_3^-** $\varepsilon_{j,k}$	**Li^+** $\varepsilon_{j,k}$	**Na^+** $\varepsilon_{j,k}$	**K^+** $\varepsilon_{j,k}$
Am+3	0.23 ± 0.02	0.49 ± 0.03	-	0	0	0
AmO2+	$(0.09 \pm 0.05)^{a,b}$	$(0.25 \pm 0.05)^{b,e}$	-	0	0	0
AmO2OH	0	0	0	0	0	0
AmO2(OH)2-	0	0	0	-	$(-0.01 \pm 0.07)^{b,e}$	-
AmO2CO3-	0	0	0	-	$(-0.18 \pm 0.15)^{b,e}$	-
AmO2(CO3)2-3	0	0	0	-	$(-0.33 \pm 0.17)^{b,e}$	-
AmO2(CO3)3-5	0	0	0	-	$(-0.53 \pm 0.19)^{b,e}$	$(-0.22 \pm 0.03)^{b,e}$
AmOH+2	-0.04 ± 0.07	$(0.39 \pm 0.10)^{f}$	-	0	0	0
Am(OH)2+	-0.27 ± 0.20	$(0.17 \pm 0.10)^{f}$	-	0	0	0
Am(OH)3	0	0	0	0	0	0
CaAm(OH)3+2	*$(0.05 \pm 0.04)^{c}$*	*0.4 ± 0.1*	-	*0*	*0*	*0*
Ca2Am(OH)4+3	*$(0.29 \pm 0.07)^{c}$*	*0.6 ± 0.1*	-	*0*	*0*	*0*
Ca3Am(OH)6+3	*$(0.00 \pm 0.06)^{c}$*	*0.6 ± 0.1*	-	*0*	*0*	*0*
AmF+2	0.15 ± 0.10	$(0.39 \pm 0.10)^{f}$	-	0	0	0
AmF2+	0.05 ± 0.10	$(0.17 \pm 0.10)^{f}$	-	0	0	0
AmCl+2	0.15 ± 0.10	$(0.39 \pm 0.10)^{f}$	-	0	0	0
AmCl2+	0.05 ± 0.10	$(0.17 \pm 0.10)^{f,g}$	-	0	0	0
AmSO4+	0.05 ± 0.10	0.22 ± 0.08	-	0	0	0
Am(SO4)2-	0	0	0	-	-0.05 ± 0.05	-
AmNO3+2	0.15 ± 0.10	$(0.39 \pm 0.10)^{f}$	-	0	0	0
AmH2PO4+2	0.15 ± 0.10	$(0.39 \pm 0.10)^{f}$	-	0	0	0
AmCO3+	0.01 ± 0.05	$(0.17 \pm 0.10)^{f}$	-	0	0	0
Am(CO3)2-	0	0	0	-	-0.14 ± 0.06	-
Am(CO3)3-3	0	0	0	-	-0.23 ± 0.07	-
AmHCO3+2	$(0.16 \pm 0.10)^{a,d,f}$	0.4 ± 0.1	-	0	0	0
AmSCN+2	0.15 ± 0.10	$(0.39 \pm 0.10)^{f}$	-	0	0	0

[a] Value discussed by Guillaumont et al. (2003) but not listed in their Table B-4

[b] Value taken from analogous Np(V) species or complex

[c] Value taken from analogous Cm(III) complex (Rabung et al. 2008)

[d] Value taken from analogous Cm(III) complex

[e] This work

[f] Increased error

[g] Value selected by Silva et al. (1995) but omitted in all further NEA-reviews

2.10 References

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3 Curium

We have not systematically reviewed thermodynamic data of curium solids or aqueous species. However, as already discussed in Chapter 2 on americium, it is well known that the coordination chemistry and complex formation reactions in aqueous solution are very similar for the trivalent actinides and for the lanthanides (an important exception being the redox properties). Thus, Guillaumont et al. (2003) made use of this analogy and included experimental data for Cm(III) in the evaluation of thermodynamic data for aqueous Am(III) complexes because experimental data for Cm(III) are often more accurate than for Am(III) and there is a large amount of accurate information available on the aqueous complex formation of Cm(III). This similarity can also be used vice versa and we have therefore included in our database formation constants of aqueous Cm(III) complexes by adopting the selected formation constants of the corresponding Am(III) complexes. In addition, we have selected thermodynamic data for Cm(cr), Cm^{3+}, $CaCm(OH)_3^{2+}$, $Ca_2Cm(OH)_4^{3+}$, $Ca_3Cm(OH)_6^{3+}$, and $Cm(OH)_3$(am, coll).

3.1 Elemental curium

Curium metal, liquid and gas are not relevant under environmental conditions. The value selected by Konings (2001) for $S_m°$(Cm, cr, 298.15 K) is given in Table 3.1 for computational purposes only, i.e. for the calculation of $\Delta_f S_m°$(Cm^{3+}, aq, 298.15 K) in order to obtain $\Delta_f G_m°$(Cm^{3+}, aq, 298.15 K).

3.2 Cm^{3+}

There are no solubility or other data from which the Gibbs free energies of the free curium ion can be related to any of the condensed phase compounds. The Gibbs free energy and related properties of the ion therefore depend on estimates of the entropy of the aqua ion, which are based on comparisons with other actinide and lanthanide ions. For Cm^{3+}, we have selected the enthalpy value derived by Konings (2001) from experimental data (enthalpy of solution of curium metal in 1M HCl) by Fuger et al. (1975) and extrapolated to zero ionic strength

$$\Delta_f H_m°(Cm^{3+}, aq, 298.15\ K) = -(615.0 \pm 6.0)\ kJ \cdot mol^{-1}$$

For the standard entropy we have selected the value by Konings (2001), which is an average of three estimates

$$S_m°(Cm^{3+}, aq, 298.15\ K) = -(191 \pm 10)\ J \cdot K^{-1} \cdot mol^{-1}$$

The Gibbs energy of formation can then be calculated from the above values

$$\Delta_f G_m°(Cm^{3+}, aq, 298.15\ K) = -(595.4 \pm 6.8)\ kJ \cdot mol^{-1}$$

which is comparable to $\Delta_f G_m°(Am^{3+}, aq, 298.15\ K) = -(598.7 \pm 4.8)\ kJ \cdot mol^{-1}$.

3.3 Curium(III) complexes

The majority of the selected formation constants of Cm(III) complexes in Table 3.1 have been adopted from the corresponding Am(III) complexes discussed in Chapter 2. It is marked in the table, whether the formation constant of the corresponding Am(III) complex is based on (a) combined Am and Cm data, (b) Cm data only, or (c) Am data only.

3.3.1 Ternary calcium curium(III) hydroxide complexes in equilibrium with $Cm(OH)_3$(am, coll)

Altmaier et al. (2008) observed unexpectedly high solubilities of Zr(IV), Th(IV) and Pu(IV) oxyhydroxide precipitates in alkaline $CaCl_2$ solutions that they explained by the formation of ternary Ca-M(IV)-OH complexes. These increased solubilities were found at $pH_c = 10–12$ and $[Ca^{2+}] > 0.05$ M for Zr[IV], at $pH_c = 11–12$ and $[Ca^{2+}] > 0.5$ M for Th[IV], while for Pu[IV] they were only found at $CaCl_2$ concentrations above 2 M. Note that the alkalinity of $CaCl_2$ solutions is limited to $pH_c < 12$ due to the formation of calcium hydroxides or hydroxychlorides in 0.1–4.5 M $CaCl_2$. From their experiments Altmaier et al. (2008) derived standard formation constants for $Ca_2[Zr(OH)_6]^{2+}$, $Ca_3[Zr(OH)_6]^{4+}$, $Ca_4[Th(OH)_8]^{4+}$, and estimated such constants for $Ca[Zr(OH)_6](aq)$ and $Ca_4[Pu(OH)_8]^{4+}$.

Rabung et al. (2008) observed similar increases in the solubility of Cm(III) in equilibrium with amorphous, colloidal curium-hydroxide in alkaline 0.1–3.5 M $CaCl_2$ solutions at pHc = 10.8–11.9. They used time-resolved laser fluorescence spectroscopy (TRLFS) to study the ternary Ca-Cm(III)-OH complexes and identified $CaCm(OH)_3^{2+}$, $Ca_2Cm(OH)_4^{3+}$, and $Ca_3Cm(OH)_6^{3+}$. They reported standard formation constants and ion interaction coefficients for these ternary complexes and a standard formation constant for $Cm(OH)_3$(am, coll) that were obtained from a not yet published comprehensive thermodynamic model for the solubility and hydrolysis of Nd(III), Cm(III) and Am(III) in dilute to concentrated NaCl, $MgCl_2$ and $CaCl_2$ solutions. We accept the following constants for our database

$$Ca^{2+} + Cm^{3+} + 3\ H_2O(l) \Leftrightarrow CaCm(OH)_3^{2+} + 3\ H^+$$

$$\log_{10}{}^*\beta^\circ_{1,1,3}(CaCm(OH)_3^{2+}, 298.15\ K) = -(26.3 \pm 0.5)$$

$$\varepsilon(CaCm(OH)_3^{2+}, Cl^-) = (0.05 \pm 0.04)\ kg \cdot mol^{-1}$$

$$2\ Ca^{2+} + Cm^{3+} + 4\ H_2O(l) \Leftrightarrow Ca_2Cm(OH)_4^{3+} + 4\ H^+$$

$$\log_{10}{}^*\beta^\circ_{2,1,4}(Ca_2Cm(OH)_4^{3+}, 298.15\ K) = -(37.2 \pm 0.6)$$

$$\varepsilon(Ca_2Cm(OH)_4^{3+}, Cl^-) = (0.29 \pm 0.07)\ kg \cdot mol^{-1}$$

$$3\ Ca^{2+} + Cm^{3+} + 6\ H_2O(l) \Leftrightarrow Ca_3Cm(OH)_6^{3+} + 6\ H^+$$

$$\log_{10}{}^*\beta^\circ_{3,1,6}(Ca_3Cm(OH)_6^{3+}, 298.15\ K) = -(60.7 \pm 0.5)$$

$$\varepsilon(Ca_3Cm(OH)_6^{3+}, Cl^-) = (0.00 \pm 0.06)\ kg \cdot mol^{-1}$$

$$Cm(OH)_3(am, coll) + 3\ H^+ \Leftrightarrow Cm^{3+} + 3\ H_2O(l)$$

$$\log_{10}{}^*K^\circ_{s,0}(Cm(OH)_3, am, coll, 298.15\ K) = (17.2 \pm 0.4)$$

however, as they are not yet published, we consider them as supplemental data. Note that Neck et al. (2009) reported the same data, but gave no further explanations.

3.4 Ionic strength corrections

The selected SIT ion interaction coefficients for curium species are listed in Table 3.2. If available, the coefficients were taken from the corresponding data for americium selected by Silva et al. (1995) and Guillaumont et al. (2003). Missing interaction coefficients were estimated according to a method based on a statistical analysis of published SIT ion interaction coefficients that allows the estimation of interaction coefficients from the charge of the considered species (see Appendix A).

Table 3.1: Selected curium data. All data included in TDB Version 12/07 are taken from the corresponding data for americium selected by Silva et al. (1995) and Guillaumont et al. (2003), except where marked with an asterisk (*). Supplemental data are given in italics. New or changed data with respect to TDB Version 01/01 (Hummel et al. 2002) are shaded.

		TDB Version 01/01				**TDB Version 12/07**				
Name	**Redox**	$\Delta_{\mathrm{f}}G_{\mathrm{m}}^\circ$ [kJ·mol^{-1}]	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^\circ$ [kJ·mol^{-1}]	S_{m}° [J·K^{-1}·mol^{-1}]	$C_{p,\mathrm{m}}^\circ$ [J·K^{-1}·mol^{-1}]	$\Delta_{\mathrm{f}}G_{\mathrm{m}}^\circ$ [kJ·mol^{-1}]	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^\circ$ [kJ·mol^{-1}]	S_{m}° [J·K^{-1}·mol^{-1}]	$C_{p,\mathrm{m}}^\circ$ [J·K^{-1}·mol^{-1}]	**Species**
Cm(cr)	0	-	-	-	-	0	0	(70.8 ± 3.0)*	-	Cm(cr)
Cm+3	III	-	-	-	-	(-595.4 ± 6.8)*	(-615.0 ± 6.0)*	(-191 ± 10)*	-	Cm^{3+}

		TDB Version 01/01		**TDB Version 12/07**		
Name	**Redox**	$\log_{10}\beta^\circ$	$\Delta_{\mathrm{r}}H_{\mathrm{m}}^\circ$ [kJ·mol^{-1}]	$\log_{10}\beta^\circ$	$\Delta_{\mathrm{r}}H_{\mathrm{m}}^\circ$ [kJ·mol^{-1}]	**Reaction**
CmOH+2	III	-	-	(-7.2 ± 0.5)[a]	-	$Cm^{3+} + H_2O(l) \Leftrightarrow CmOH^{2+} + H^+$
Cm(OH)2+	III	-	-	(-15.1 ± 0.7)[a]	-	$Cm^{3+} + 2\ H_2O(l) \Leftrightarrow Cm(OH)_2^+ + 2\ H^+$
Cm(OH)3	III	-	-	(-26.2 ± 0.5)[a]	-	$Cm^{3+} + 3\ H_2O(l) \Leftrightarrow Cm(OH)_3(aq) + 3\ H^+$
CaCm(OH)3+2	III	-	-	*(-26.3 ± 0.5)**		$Ca^{2+} + Cm^{3+} + 3\ H_2O(l) \Leftrightarrow CaCm(OH)_3^{2+} + 3\ H^+$
Ca2Cm(OH)4+3	III	-	-	*(-37.2 ± 0.6)**		$2Ca^{2+} + Cm^{3+} + 4\ H_2O(l) \Leftrightarrow Ca_2Cm(OH)_4^{3+} + 4\ H^+$
Ca3Cm(OH)6+3	III	-	-	*(-60.7 ± 0.5)**		$3Ca^{2+} + Cm^{3+} + 6\ H_2O(l) \Leftrightarrow Ca_3Cm(OH)_6^{3+} + 6\ H^+$
CmF+2	III	-	-	(3.4 ± 0.3)[a]	-	$Cm^{3+} + F^- \Leftrightarrow CmF^{2+}$
CmF2+	III	-	-	(5.8 ± 0.2)[c]	-	$Cm^{3+} + 2\ F^- \Leftrightarrow CmF_2^+$
CmCl+2	III	-	-	(0.24 ± 0.03)[a]	-	$Cm^{3+} + Cl^- \Leftrightarrow CmCl^{2+}$
CmCl2+	III	-	-	(-0.74 ± 0.05)[a]	-	$Cm^{3+} + 2\ Cl^- \Leftrightarrow CmCl_2^+$
CmSO4+	III	-	-	(3.30 ± 0.15)[b]	-	$Cm^{3+} + SO_4^{2-} \Leftrightarrow CmSO_4^+$
Cm(SO4)2-	III	-	-	(3.70 ± 0.15)[b]	-	$Cm^{3+} + 2\ SO_4^{2-} \Leftrightarrow Cm(SO_4)_2^-$
CmNO3+2	III	-	-	(1.33 ± 0.20)[c]	-	$Cm^{3+} + NO_3^- \Leftrightarrow CmNO_3^{2+}$
CmH2PO4+2	III	-	-	(3.0 ± 0.5)[c]	-	$Cm^{3+} + H_2PO_4^- \Leftrightarrow CmH_2PO_4^{2+}$
CmCO3+	III	-	-	(8.0 ± 0.4)[a]	-	$Cm^{3+} + CO_3^{2-} \Leftrightarrow CmCO_3^+$
Cm(CO3)2-	III	-	-	(12.9 ± 0.4)[a]	-	$Cm^{3+} + 2\ CO_3^{2-} \Leftrightarrow Cm(CO_3)_2^-$
Cm(CO3)3-3	III	-	-	(15.0 ± 1.0)[a]	-	$Cm^{3+} + 3\ CO_3^{2-} \Leftrightarrow Cm(CO_3)_3^{3-}$
CmHCO3+2	III	-	-	(3.1 ± 0.3)[b]	-	$Cm^{3+} + HCO_3^- \Leftrightarrow CmHCO_3^{2+}$
CmSCN+2	III	-	-	(1.3 ± 0.3)[c]		$Cm^{3+} + SCN^- \Leftrightarrow CmSCN^{2+}$

[a] Formation constant of the corresponding Am(III) complex is based on combined Am and Cm data

[b] Formation constant of the corresponding Am(III) complex is based on Cm data only

[c] Formation constant of the corresponding Am(III) complex is based on Am data only

		TDB Version 01/01		TDB Version 12/07		
Name	**Redox**	**$\log_{10}K_{s,0}°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**$\log_{10}K_{s,0}°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**Reaction**
Cm(OH)3(am, coll)	III	-	-	*(17.2 ± 0.4)**	-	$Cm(OH)_3(am, coll) + 3\ H^+ \Leftrightarrow Cm^{3+} + 3\ H_2O(l)$

Table 3.2: Selected SIT ion interaction coefficients $\varepsilon_{j,k}$ [kg·mol^{-1}] for curium species. The data included in TDB Version 12/07 are taken from the corresponding data for americium selected by Silva et al. (1995) and Guillaumont et al. (2003) unless indicated otherwise. Own data estimates based on charge correlations (see Appendix A) are shaded. Supplemental data are in italics.

j $k \rightarrow$ $\downarrow$	**Cl^-** $\varepsilon_{j,k}$	**ClO_4^-** $\varepsilon_{j,k}$	**NO_3^-** $\varepsilon_{j,k}$	**Li^+** $\varepsilon_{j,k}$	**Na^+** $\varepsilon_{j,k}$	**K^+** $\varepsilon_{j,k}$
Cm+3	0.23 ± 0.02	0.49 ± 0.03	-	0	0	0
CmOH+2	-0.04 ± 0.07	(0.39 ± 0.10)[a]	-	0	0	0
Cm(OH)2+	-0.27 ± 0.20	(0.17 ± 0.10)[a]	-	0	0	0
Cm(OH)3	0	0	0	0	0	0
CaCm(OH)3+2	*(0.05 ± 0.04)*[b]	*0.4 ± 0.1*	-	*0*	*0*	*0*
Ca2Cm(OH)4+3	*(0.29 ± 0.07)*[b]	*0.6 ± 0.1*	-	*0*	*0*	*0*
Ca3Cm(OH)6+3	*(0.00 ± 0.06)*[b]	*0.6 ± 0.1*	-	*0*	*0*	*0*
CmF+2	0.15 ± 0.10	(0.39 ± 0.10)[a]	-	0	0	0
CmF2+	0.05 ± 0.10	(0.17 ± 0.10)[a]	-	0	0	0
CmCl+2	0.15 ± 0.10	(0.39 ± 0.10)[a]	-	0	0	0
CmCl2+	0.05 ± 0.10	(0.17 ± 0.10)[a,c]	-	0	0	0
CmSO4+	0.05 ± 0.10	0.22 ± 0.08	-	0	0	0
Cm(SO4)2-	0	0	0	-	-0.05 ± 0.05	-
CmNO3+2	0.15 ± 0.10	(0.39 ± 0.10)[a]	-	0	0	0
CmH2PO4+2	0.15 ± 0.10	(0.39 ± 0.10)[a]	-	0	0	0
CmCO3+	0.01 ± 0.05	(0.17 ± 0.10)[a]	-	0	0	0
Cm(CO3)2-	0	0	0	-	-0.14 ± 0.06	-
Cm(CO3)3-3	0	0	0	-	-0.23 ± 0.07	-
CmHCO3+2	(0.16 ± 0.10)[a,d,e]	0.4 ± 0.1	-	0	0	0
CmSCN+2	0.15 ± 0.10	(0.39 ± 0.10)[a]	-	0	0	0

[a] Increased error

[b] Value taken from Cm(III) data by Rabung et al. 2008

[c] Value selected by Silva et al. (1995) but omitted in all further NEA-reviews

[d] Value originally from Cm(III) data

[e] Value discussed by Guillaumont et al. (2003) but not listed in their Table B-4

3.5 References

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4 Neptunium

All information is taken from OECD NEA's books "Chemical Thermodynamics of Neptunium & Plutonium" (Lemire et al. 2001) and "Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium" (Guillaumont et al. 2003), the latter of which reviewed new literature published between 1999 and the end of 2001 that could not be considered by Lemire et al. (2001). However, not all values recommended by Lemire et al. (2001) and Guillaumont et al. (2003) are included in our database since the NEA reviews (unlike our database) 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. They are listed in Table 4.1. The notation of formulae and symbols used in this text follows the NEA recommendations.

4.1 Elemental neptunium

Neptunium metal, liquid and gas are not relevant under environmental conditions. Hence, the thermodynamic data selected by Lemire et al. (2001) and Guillaumont et al. (2003) for β-Np(cr), γ-Np(cr), and Np(g) are not included in our database. However, the absolute entropy and heat capacity of Np(cr) 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.

$$S_m^\circ(\mathrm{Np, cr}, \alpha, 298.15\ \mathrm{K}) = (50.46 \pm 0.80)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

$$C_{p,m}^\circ(\mathrm{Np, cr}, \alpha, 298.15\ \mathrm{K}) = (29.62 \pm 0.80)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

4.2 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. 4.1. 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.

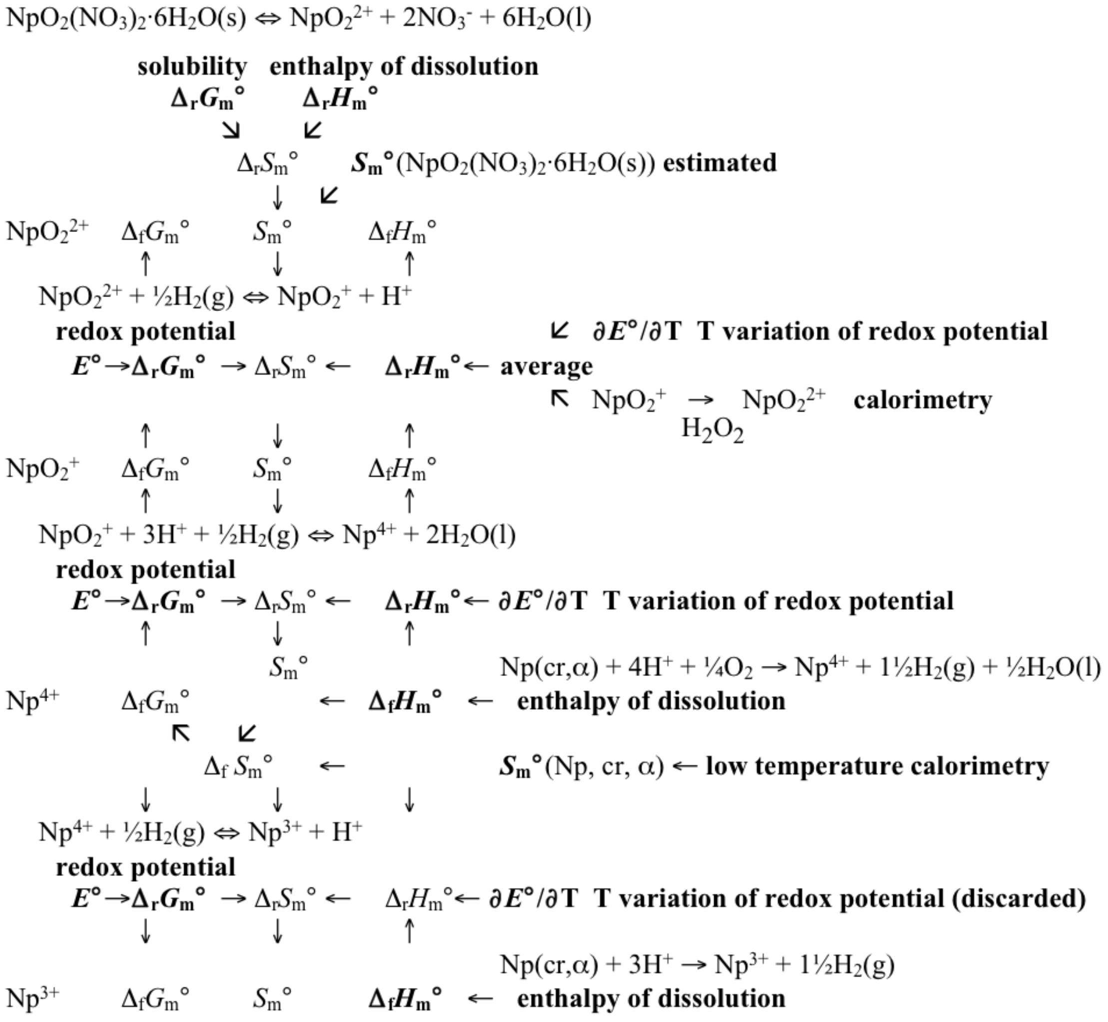

Fig. 4.1: Schematic representation of the selection and derivation process of thermodynamic quantities by Lemire et al. (2001) for Np^{3+}, Np^{4+}, NpO_2^+ and NpO_2^{2+}. Quantities in **bold face** are based on experimental data and an estimate, all others are calculated therefrom. Arrows indicate the links in the chain of thermodynamic calculations.

4.2.1 NpO_3^+

Heptavalent neptunium can be generated in alkaline solutions, the dominant species being $NpO_4(OH)_2^{3-}$, 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.

4.2.2 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

$$NpO_2(NO_3)_2 \cdot 6H_2O(s) \Leftrightarrow NpO_2^{2+} + 2\ NO_3^- + 6\ H_2O(l)$$

has been determined as $\log_{10}{}^*K_{s,0}° = (2.15 \pm 0.19)$ or $\Delta_rG_m° = -(12.30 \pm 1.09)$ 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 $\Delta_rH_m° = (18.83 \pm 1.67)$ kJ·mol^{-1}. From $\Delta_rG_m°$ and $\Delta_rH_m°$ a value of $\Delta_rS_m° = (104.4 \pm 7.6)$ 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, $\Delta_rS_m°$ and CODATA auxiliary values, determined

$$S_m°(NpO_2^{2+}, aq, 298.15\ K) = -(92.4 \pm 10.5)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

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

$$NpO_2^{2+} + ½\,H_2(g) \Leftrightarrow NpO_2^{+} + H^{+}$$

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

$$E°(298.15\ K) = (1.159 \pm 0.004)\ V$$

which corresponds to

$$\log_{10}K°(298.15\ K) = (19.59 \pm 0.07)$$

or

$$\Delta_rG_m°(298.15\ K) = -(111.8 \pm 0.4)\ kJ{\cdot}mol^{-1}$$

From the temperature dependence of this potential at 1 M $HClO_4$ $\Delta_rS_m(1M\ HClO_4) = \partial E°'/\partial T \cdot F = -(26.05 \pm 4.82)$ J·K^{-1}·mol^{-1} is obtained (F is the Faraday constant). Using this value and the accepted $\Delta_rG_m(1M\ HClO_4) = -(109.70 \pm 0.10)$ kJ·mol^{-1}, $\Delta_rH_m(1M\ HClO_4) = -(117.47 \pm 1.44)$ kJ·mol^{-1} is calculated. The enthalpy of transfer to infinite dilution is assumed to be zero and thus, the value of $\Delta_rH_m°$ is the same as $\Delta_rH_m(1M\ HClO_4)$.

A second, independent value of $\Delta_rH_m° = -(117.4 \pm 0.6)$ 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

$$\Delta_rH_m°(298.15\ K) = -(117.4 \pm 0.6)\ kJ{\cdot}mol^{-1}.$$

From $\Delta_rH_m°$ and the selected value of $\Delta_fH_m°(NpO_2^{+})$ (see Section 4.2.3) Lemire et al. (2001) determined the selected value

$$\Delta_fH_m°(NpO_2^{2+}, aq, 298.15\ K) = -(860.7 \pm 4.7)\ kJ{\cdot}mol^{-1}$$

Similarly, using $\Delta_rG_m°$ and the selected value of $\Delta_fG_m°(NpO_2^{+})$ (see Section 4.2.3) Lemire et al. (2001) determined the selected value

$$\Delta_fG_m°(NpO_2^{2+}, aq, 298.15\ K) = -(795.9 \pm 5.6)\ kJ{\cdot}mol^{-1}$$

Taking $\Delta_rG_m°$ and $\Delta_rH_m°$,

$$\Delta_rS_m° = -(18.9 \pm 2.3)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

is calculated. This value is required in the following Section 4.2.3.

Lemire et al. (2001) estimated a value for $\varepsilon(NpO_2^{2+}, ClO_4^{-})$ by assuming it to be equal to $\varepsilon(UO_2^{2+}, ClO_4^{-}) = (0.46 \pm 0.03)$ kg·mol^{-1}, which was determined by Ciavatta (1980) from isopiestic data. Lemire et al. (2001) selected this value for NpO_2^{2+} but increased the error, resulting in

$$\varepsilon(NpO_2^{2+}, ClO_4^-) = (0.46 \pm 0.05)\ kg\cdot mol^{-1}$$

which is also selected for our database.

We estimated the ion interaction coefficient for chloride media according to a method described in Appendix A, which is based on a statistical analysis of published SIT ion interaction coefficients and allows the estimation of such coefficients for cations with Cl^- and ClO_4^-, and for anions with Na^+ from the charge of the considered species. Our selected value is

$$\varepsilon(NpO_2^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg\cdot mol^{-1}$$

4.2.3 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 Section 4.2.2),

$$S_m°(NpO_2^+, aq, 298.15\ K) = -(45.9 \pm 10.7)\ J\cdot K^{-1}\cdot mol^{-1}$$

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.

$$NpO_2^+ + 3\ H^+ + ½\ H_2(g) \Leftrightarrow Np^{4+} + 2\ H_2O(l)$$

The formal potential (at 1 M $HClO_4$) selected by Lemire et al. (2001) has been extrapolated to zero ionic strength using SIT with $\Delta\varepsilon = +(0.17 \pm 0.09)\ kg\cdot mol^{-1}$ to obtain the standard potential

$$E°(298.15\ K) = (0.604 \pm 0.007)\ V$$

This corresponds to

$$\log_{10}K°(298.15\ K) = (10.21 \pm 0.12)$$

or

$$\Delta_r G_m°(298.15\ K) = -(58.3 \pm 0.7)\ kJ\cdot mol^{-1}$$

From the temperature dependence of this potential at 1 M $HClO_4$ $\Delta_r S_m(1M\ HClO_4) = \partial E°'/\partial T \cdot F = -(259.5 \pm 5.8)\ J\cdot K^{-1}\cdot mol^{-1}$ is obtained (F is the Faraday constant). Using this value and the accepted $\Delta_r G_m(1M\ HClO_4) = -(71.7 \pm 0.1)\ kJ\cdot mol^{-1}$, $\Delta_r H_m(1M\ HClO_4) = -(149.1 \pm 1.7)\ kJ\cdot mol^{-1}$ is calculated. The enthalpy of transfer to infinite dilution is assumed to be 0.42 $kJ\cdot mol^{-1}$. The reasoning for this correction is that it was done to account for the extent of the first hydrolysis reaction of Np^{4+} (see Section 4.2.4) but a similar correction for NpO_2^+ is negligible. Thus, the correction of 0.42 $kJ\cdot mol^{-1}$ can be applied directly to the accepted value of $\Delta_r H_m(1M\ HClO_4)$ to determine

$$\Delta_r H_m°(298.15\ K) = -(149.5 \pm 1.7)\ kJ\cdot mol^{-1}.$$

From $\Delta_r H_m°$ of the above reaction and the selected value of $\Delta_f H_m°(Np^{4+})$ (see Section 4.2.4) Lemire et al. (2001) determined the selected value

$$\Delta_f H_m°(NpO_2^+, \text{aq}, 298.15 \text{ K}) = -(978.2 \pm 4.6) \text{ kJ·mol}^{-1}$$

Similarly, using $\Delta_r G_m°$ and the selected value of $\Delta_f G_m°$ (Np^{4+}) (see Section 4.2.4) Lemire et al. (2001) determined the selected value

$$\Delta_f G_m°(NpO_2^+, \text{aq}, 298.15 \text{ K}) = -(907.8 \pm 5.6) \text{ kJ·mol}^{-1}$$

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 4.2.4.

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

$$C_{p,m}°(NpO_2^+, \text{aq}, 298.15 \text{ K}) = -(4 \pm 25) \text{ J·K}^{-1}\text{·mol}^{-1}$$

The heat capacity for NpO_2ClO_4(aq) selected by Lemire et al. (2001) is not considered in our database. 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 1.2.2, 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

$$NpO_2^{2+} + 4 H^+ + 2 e^- \Leftrightarrow Np^{4+} + 2 H_2O(l)$$

$$\log_{10}K°(298.15 \text{ K}) = (29.80 \pm 0.14)$$

Based on solubility studies of $NpO_2OH(s)$ in chloride media, Lemire et al. (2001) selected

$$\varepsilon(NpO_2^+, Cl^-) = (0.09 \pm 0.05) \text{ kg·mol}^{-1}$$

although they remarked that this value is not entirely consistent with the solubility of the Np(V) sodium carbonate solids. The value selected by Lemire et al. (2001) for $\varepsilon(NpO_2^+, ClO_4^-)$ was derived from potential measurements of the reaction

$$NpO_2^{2+} + \frac{1}{2} H_2(g) \Leftrightarrow NpO_2^+ + H^+$$

at different ionic strengths, with $\Delta\varepsilon = -(0.21 \pm 0.03)$ kg·mol^{-1}, where $\Delta\varepsilon = \varepsilon(NpO_2^+, ClO_4^-) - \varepsilon(NpO_2^{2+}, ClO_4^-)$. Note that there is no need to consider $\varepsilon(H^+, ClO_4^-)$ in the expression for $\Delta\varepsilon$, since H^+ represents the cation in the standard hydrogen electrode and is therefore already at standard conditions (see the discussion in Chapter B.1.3.2 by Lemire et al. 2001). Using the selected $\varepsilon(NpO_2^{2+}, ClO_4^-) = (0.46 \pm 0.05)$ kg·mol^{-1} with this $\Delta\varepsilon$, Lemire et al. (2001) obtained

$$\varepsilon(NpO_2^+, ClO_4^-) = (0.25 \pm 0.05) \text{ kg·mol}^{-1}$$

The values selected by Lemire et al. (2001) for $\varepsilon(NpO_2^+, Cl^-)$ and $\varepsilon(NpO_2^+, ClO_4^-)$ are both adopted for our database.

4.2.4 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:

$$Np(cr,\alpha) + 4 H^+ + 0.25 O_2(\text{dissolved}) \rightarrow Np^{4+} + 1.5 H_2(g) + 0.5 H_2O(l)$$

$$\Delta_f H_m°(Np^{4+}, \text{aq}, 298.15 \text{ K}) = -(556.0 \pm 4.2) \text{ kJ·mol}^{-1}$$

To evaluate other thermodynamic data in 1 M $HClO_4$ (see Sections 4.2.3 & 4.2.5) 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 ± 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 Section 4.2.3), and CODATA auxiliary data to give

$$S_m°(Np^{4+}, aq, 298.15\ K) = -(426.4 \pm 12.4)\ J\cdot K^{-1}\cdot mol^{-1}$$

Based on this, CODATA values and $S_m°$(Np, cr, α, 298.15 K) = (50.46 ± 0.80) $J\cdot K^{-1}\cdot mol^{-1}$ (see Section 4.1), $\Delta_f S_m°(Np^{4+})$ = -(215.5 ± 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

$$\Delta_f G_m°(Np^{4+}, aq, 298.15\ K) = -(491.8 \pm 5.6)\ kJ\cdot mol^{-1}$$

The value selected by Lemire et al. (2001) for $\varepsilon(Np^{4+}, ClO_4^-)$ was derived from potential measurements of the reaction

$$Np^{4+} + \tfrac{1}{2} H_2(g) \Leftrightarrow Np^{3+} + H^+$$

at different ionic strengths, with $\Delta\varepsilon$ = -(0.35 ± 0.03) $kg\cdot mol^{-1}$, where $\Delta\varepsilon = \varepsilon(Np^{3+}, ClO_4^-) - \varepsilon(Np^{4+}, ClO_4^-)$. Using the selected $\varepsilon(Np^{3+}, ClO_4^-)$ = (0.49 ± 0.05) $kg\cdot mol^{-1}$ (see discussion below) with this $\Delta\varepsilon$, Lemire et al. (2001) obtained

$$\varepsilon(Np^{4+}, ClO_4^-) = (0.84 \pm 0.06)\ kg\cdot mol^{-1}$$

We estimated the corresponding ion interaction coefficient for chloride media according to a method based on charge correlations (see Appendix A)

$$\varepsilon(Np^{4+}, Cl^-) = (0.35 \pm 0.10)\ kg\cdot mol^{-1}$$

Both of these values are selected for our database.

4.2.5 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:

$$Np(cr,\alpha) + 3\ H^+ \rightarrow Np^{3+} + 1.5\ H_2(g)$$

$$\Delta_f H_m°(Np^{3+}, aq, 298.15\ K) = -(527.2 \pm 2.1)\ kJ\cdot mol^{-1}$$

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

$$E°(298.15\ K) = (0.219 \pm 0.010)\ V$$

This corresponds to

$$\log_{10}K°(298.15\ K) = (3.70 \pm 0.17)$$

or

$$\Delta_r G_m°(298.15\ K) = -(21.1 \pm 1.0)\ kJ\cdot mol^{-1}$$

From the temperature dependence of this potential at 1M $HClO_4$, $\Delta_r S_m$(1M $HClO_4$) = $\partial E°'/\partial T \cdot F$ = (131.2 ± 4.8) $J\cdot K^{-1}\cdot mol^{-1}$ is obtained (F is the Faraday constant). Using this value and the accepted Δ_rG_m(1M $HClO_4$) = -(15.0 ± 0.1) kJ·mol^{-1}, Δ_rH_m(1M $HClO_4$) = (24.2 ± 1.5) kJ·mol^{-1} is calculated. Using Δ_fH_m(Np^{4+}, 1M $HClO_4$) = -(556.6 ± 4.2) kJ·mol^{-1} (see Section 4.2.4), the NEA reviewers calculated from electrochemical data Δ_fH_m(Np^{3+}, 1M $HClO_4$) = -(531.5 ± 12.3) kJ·mol^{-1}, and assumed that $\Delta_fH_m(Np^{3+}) \approx \Delta_fH_m°(Np^{3+})$. This value, -(531.5 ± 12.3) kJ·mol^{-1}, is somewhat more negative than the value based on calorimetric data, -(527.2 ± 2.1) kJ·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 $\Delta_fH_m°(Np^{4+})$ (see Section 4.2.4) and $\Delta_fH_m°(Np^{3+})$, $\Delta_rH_m°$ = (28.8 ± 4.7) kJ·mol^{-1} of the redox reaction is calculated. From this value and $\Delta_rG_m°$, $\Delta_rS_m°$ = (167.5 ± 16.0) J·K^{-1}·mol^{-1} is obtained. Hence, with CODATA auxiliary data and the previously selected value for $S_m°(Np^{4+})$ (see Section 4.2.4)

$$S_m°(Np^{3+}, aq, 298.15\ K) = -(193.6 \pm 20.3)\ J \cdot K^{-1} \cdot mol^{-1}$$

is calculated.

The standard Gibbs energy of formation

$$\Delta_fG_m°(Np^{3+}, aq, 298.15\ K) = -(512.9 \pm 5.7)\ kJ \cdot mol^{-1}$$

was obtained using $\Delta_rG_m°$ of the above reaction and $\Delta_fG_m°(Np^{4+})$ (see Section 4.2.4).

Note that for our database we combined the above $\log_{10}K°$ = (3.70 ± 0.17) with the Np(VI)/Np(V) equilibrium of Section 4.2.2, i.e. $\log_{10}K°$ = (19.59 ± 0.07), the Np(V)/Np(IV) equilibrium of Section 4.2.3, i.e. $\log_{10}K°$ = (10.21 ± 0.12), and $\log_{10}K°$ = 0 (by definition) for ½ $H_2(g) \Leftrightarrow H^+ + e^-$ in order to obtain

$$NpO_2^{2+} + 4\ H^+ + 3\ e^- \Leftrightarrow Np^{3+} + 2\ H_2O(l)$$

$$\log_{10}K°(298.15\ K) = (33.50 \pm 0.23)$$

Lemire et al. (2001) estimated a value for $\varepsilon(Np^{3+}, ClO_4^-)$ based on the suggestion by Grenthe et al. (1992) that, since ions and complexes of the same charge have similar ion interaction coefficients with a given counterion, it is possible to estimate unknown ion interaction coefficients within an error of at most ± 0.1 by adopting known values from other ions or complexes with the same charge. Therefore, Lemire et al. (2001) assumed $\varepsilon(Np^{3+}, ClO_4^-)$ = $\varepsilon(Ho^{3+}, ClO_4^-)$ = (0.49 ± 0.05) kg·mol^{-1} using the value for Ho^{3+} reported by Spahiu (1983) with an increased error. Thus

$$\varepsilon(Np^{3+}, ClO_4^-) = (0.49 \pm 0.05)\ kg \cdot mol^{-1}$$

We adopt this value for our database. For chloride media, we estimated the corresponding ion interaction coefficient according to a method based on charge correlations (see Appendix A) and select

$$\varepsilon(Np^{3+}, Cl^-) = (0.25 \pm 0.10)\ kg \cdot mol^{-1}$$

4.3 Neptunium oxygen and hydrogen compounds and complexes

4.3.1 Aqueous neptunium hydroxide complexes

4.3.1.1 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).

4.3.1.2 Neptunium(VI) hydroxide complexes

Np(VI) hydrolysis constants refer to the reaction

$$\mathrm{m\ NpO_2^{2+} + n\ H_2O(l) \Leftrightarrow (NpO_2)_m(OH)_n^{(2m-n)} + n\ H^+}$$

A self-consistent set of values derived from potentiometric measurements in 1 M aqueous $NaClO_4$ has been accepted by Lemire et al. (2001)

$$\mathrm{NpO_2^{2+} + H_2O(l) \Leftrightarrow NpO_2OH^+ + H^+}$$

$$\log_{10}{}^*\beta_1^\circ(298.15\ \mathrm{K}) = -(5.1 \pm 0.4)$$

$$\mathrm{2\ NpO_2^{2+} + 2\ H_2O(l) \Leftrightarrow (NpO_2)_2(OH)_2^{2+} + 2\ H^+}$$

$$\log_{10}{}^*\beta_{2,2}^\circ(298.15\ \mathrm{K}) = -(6.27 \pm 0.21)$$

$$\mathrm{3\ NpO_2^{2+} + 5\ H_2O(l) \Leftrightarrow (NpO_2)_3(OH)_5^{+} + 5\ H^+}$$

$$\log_{10}{}^*\beta_{5,3}^\circ(298.15\ \mathrm{K}) = -(17.12 \pm 0.22)$$

Ionic strength corrections leading to these standard state formation constants were performed by Lemire et al. (2001) using estimated values for the ion interaction coefficients of NpO_2OH^+, $(NpO_2)_2(OH)_2^{2+}$, and $(NpO_2)_3(OH)_5^+$ with ClO_4^-. These estimates were made by adopting the interaction coefficients of the corresponding UO_2^+ complexes that were selected by Grenthe et al. (1992) and adjusting their errors.

Grenthe et al. (1992) obtained $\Delta\varepsilon = -(0.4 \pm 3.7)$ kg·mol^{-1} for the reaction

$$\mathrm{UO_2^{2+} + H_2O(l) \Leftrightarrow UO_2OH^+ + H^+}$$

The extremely large uncertainty results from sparse data that in most cases were acquired at low ionic strengths. Using this Δε and the selected values $\varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$ kg·mol^{-1} and $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$ kg·mol^{-1}, Grenthe et al. (1992) calculated a value of -(0.06 ± 3.7) kg·mol^{-1} for $\varepsilon(UO_2OH^+, ClO_4^-)$. Note that using these numbers, one actually gets -(0.08± 3.7) kg·mol^{-1}. The discrepancy is probably due to rounding of the Δε-value. Lemire et al. (2001) adopted this $\varepsilon(UO_2OH^+, ClO_4^-)$ for NpO_2OH^+ but reduced the error to a "slightly more realistic value" and selected

$$\varepsilon(\mathrm{NpO_2OH^+, ClO_4^-}) = -(0.06 \pm 0.40)\ \mathrm{kg\cdot mol^{-1}}$$

which is also adopted for our database. Lemire et al. (2001) also tacitly reduced the error for $\varepsilon(UO_2OH^+, ClO_4^-)$ itself to the same reduced value. Therefore, $\varepsilon(UO_2OH^+, ClO_4^-) = -(0.06 \pm 0.40)$ kg·mol^{-1} appears in all subsequent NEA-reviews.

Grenthe et al. (1992) selected $\varepsilon((UO_2)_2(OH)_2^{2+}, ClO_4^-) = (0.57 \pm 0.07)$ kg·mol^{-1}, and $\varepsilon((UO_2)_3(OH)_5^+, ClO_4^-) = (0.45 \pm 0.15)$ kg·mol^{-1}. Lemire et al. (2001) used these values for the corresponding Np complexes but increased the errors and selected

$$\varepsilon(\mathrm{(NpO_2)_2(OH)_2^{2+}, ClO_4^-}) = (0.57 \pm 0.10)\ \mathrm{kg\cdot mol^{-1}}$$

$$\varepsilon(\mathrm{(NpO_2)_3(OH)_5^{+}, ClO_4^-}) = (0.45 \pm 0.20)\ \mathrm{kg\cdot mol^{-1}}$$

which are also selected for our database.

We estimated the corresponding ion interaction coefficients for chloride media based on charge correlations (see Appendix A) and select

$$\varepsilon(\mathrm{NpO_2OH^+, Cl^-}) = (0.05 \pm 0.10)\ \mathrm{kg\cdot mol^{-1}}$$

$$\varepsilon(\mathrm{(NpO_2)_2(OH)_2^{2+}, Cl^-}) = (0.15 \pm 0.10)\ \mathrm{kg\cdot mol^{-1}}$$

$$\varepsilon(\mathrm{(NpO_2)_3(OH)_5^{+}, Cl^-}) = (0.05 \pm 0.10)\ \mathrm{kg\cdot mol^{-1}}$$

for our database.

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 rationalized 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 favor of the other. If anionic polymers exist (as they have been found in the uranium system), both proposed constants for uranium may be regarded as limiting values for neptunium and are included in our database as supplemental data.

$$NpO_2^{2+} + 3\,H_2O(l) \Leftrightarrow NpO_2(OH)_3^- + 3\,H^+$$

$$\log_{10}{}^*\beta_3^\circ(298.15\text{ K}) \le -20$$

$$NpO_2^{2+} + 4\,H_2O(l) \Leftrightarrow NpO_2(OH)_4^{2-} + 4\,H^+$$

$$\log_{10}{}^*\beta_4^\circ(298.15\text{ K}) \le -32$$

We estimated the ion interaction coefficients of $NpO_2(OH)_3^-$ and $NpO_2(OH)_4^{2-}$ with Na^+ based on charge correlations (see Appendix A) and select

$$\varepsilon(NpO_2(OH)_3^-, Na^+) = -(0.05 \pm 0.10)\text{ kg}\cdot\text{mol}^{-1}$$

$$\varepsilon(NpO_2(OH)_4^{2-}, Na^+) = -(0.10 \pm 0.10)\text{ kg}\cdot\text{mol}^{-1}$$

as supplemental data.

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).

4.3.1.3 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 characterize. Under oxidizing 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. Lemire et al. (2001) derived the following constants

$$\mathrm{NpO_2^+ + H_2O(l) \Leftrightarrow NpO_2OH(aq) + H^+}$$

$$\log_{10}{}^*\beta_1^\circ(298.15\text{ K}) = -(11.3 \pm 0.7)$$

$$\mathrm{NpO_2^+ + 2\,H_2O(l) \Leftrightarrow NpO_2(OH)_2^- + 2\,H^+}$$

$$\log_{10}{}^*\beta_2^\circ(298.15\text{ K}) = -(23.6 \pm 0.5)$$

$$\varepsilon(\mathrm{NpO_2(OH)_2^-, Na^+}) = -(0.01 \pm 0.07)\text{ kg}\cdot\text{mol}^{-1}$$

In the absence of experimental data, estimated entropy values have been accepted by Lemire et al. (2001):

$$S_m°(NpO_2OH, aq, 298.15 K) = (25 \pm 60)\ J\cdot K^{-1}\cdot mol^{-1}$$

$$S_m°(NpO_2(OH)_2^-, aq, 298.15 K) = (40 \pm 100)\ J\cdot K^{-1}\cdot mol^{-1}$$

4.3.1.4 Calcium neptunium(V) hydroxide complexes

Recent studies of the solubility of trivalent and tetravalent actinides in alkaline $CaCl_2$ solutions have demonstrated the formation of ternary Ca-M(III)-OH and Ca-M(IV)-OH complexes. Rabung et al. (2008) published standard formation constants for $CaM(OH)_3^{2+}$, $Ca_2M(OH)_4^{3+}$ and $Ca_3M(OH)_6^{3+}$, where M = Cm, Nd, while Altmaier et al. (2008a) determined such constants for $CaZr(OH)_6(aq)$, $Ca_2Zr(OH)_6^{2+}$, $Ca_3Zr(OH)_6^{4+}$, $Ca_4Th(OH)_8^{4+}$, and $Ca_4Pu(OH)_8^{4+}$. Preliminary results by Altmaier et al. (2008) have shown that similar to the trivalent and tetravalent actinides, the hydrolysis of Np(V) in alkaline $CaCl_2$ solutions is also affected by strong interaction with Ca^{2+} cations, resulting in the formation of ternary Ca-Np(V)-OH complexes.

4.3.1.5 Neptunium(IV) hydroxide complexes

According to Guillaumont et al. (2003) the description of actinide (IV) hydrolysis in terms of thermodynamic constants is rather uncertain, due to various phenomena that are difficult to control in experiments, like the formation of colloids or changes in the solubility of solid phases as their structures evolve from amorphous to crystalline. Nevertheless, Guillaumont et al. (2003) selected equilibrium constants for $NpOH^{3+}$, $Np(OH)_2^{2+}$, and $Np(OH)_4(aq)$:

$$Np^{4+} + H_2O(l) \Leftrightarrow NpOH^{3+} + H^+$$

$$\log_{10}{}^*\beta_1°(298.15 K) = (0.55 \pm 0.20)$$

$$Np^{4+} + 2\ H_2O(l) \Leftrightarrow Np(OH)_2^{2+} + 2\ H^+$$

$$\log_{10}{}^*\beta_2°(298.15 K) = (0.35 \pm 0.30)$$

$$Np^{4+} + 4\ H_2O(l) \Leftrightarrow Np(OH)_4(aq) + 4\ H^+$$

$$\log_{10}{}^*\beta_4°(298.15 K) = -(8.3 \pm 1.1)$$

The values for $\log_{10}{}^*\beta_1°$ and $\log_{10}{}^*\beta_2°$ were derived from solvent extraction experiments, while $\log_{10}{}^*\beta_4°$ was calculated from solubility data (see below).

Lemire et al. (2001) estimated

$$\varepsilon(NpOH^{3+}, ClO_4^-) = (0.50 \pm 0.05)\ kg\cdot mol^{-1}$$

but gave no details on what their estimate is based on. We estimated the following ion interaction coefficients based on charge correlations (see Appendix A)

$$\varepsilon(NpOH^{3+}, Cl^-) = (0.25 \pm 0.10)\ kg\cdot mol^{-1}$$

$$\varepsilon(Np(OH)_2^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg\cdot mol^{-1}$$

$$\varepsilon(Np(OH)_2^{2+}, ClO_4^-) = (0.4 \pm 0.1)\ kg\cdot mol^{-1}$$

Neck & Kim (2001) estimated $\log_{10}{}^*\beta_3°$ for the formation of $Np(OH)_3^+$ based on two different estimation methods:

$$Np^{4+} + 3\ H_2O(l) \Leftrightarrow Np(OH)_3^+ + 3\ H^+$$

$$\log_{10}{}^*\beta_3°(298.15 K) = -(2.8 \pm 1.0)$$

This estimated value was not selected by Guillaumont et al. (2003) according to NEA TDB guidelines. It is included, however, in our database as supplemental data, for use in scoping calculations or qualitative modeling together with the ion interaction coefficients estimated according to a method based on charge correlations (see Appendix A)

$$\varepsilon(Np(OH)_3^+, Cl^-) = (0.05 \pm 0.10)\ kg{\cdot}mol^{-1}$$

$$\varepsilon(Np(OH)_3^+, ClO_4^-) = (0.2 \pm 0.1)\ kg{\cdot}mol^{-1}$$

Based on solubility data at pH below 3, Neck & Kim (2001) derived a solubility product for the amorphous hydrous oxide NpO_2(am, hyd), which was selected by Guillaumont et al. (2003):

$$NpO_2(am, hyd) + 4\ H^+ \Leftrightarrow Np^{4+} + 2\ H_2O(l)$$

$$\log_{10}{}^*K_{s,0}°(298.15\ K) = -(0.7 \pm 0.5)$$

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. These solubility data were represented by Neck & Kim (2001) as

$$\log_{10}[Np(OH)_4(aq)] = -(9 \pm 1) = \log_{10}{}^*K_{s,0}°(298.15\ K) + \log_{10}{}^*\beta_4°(298.15\ K)$$

Thus, with $\log_{10}{}^*K_{s,0}°(298.15\ K) = -(0.7 \pm 0.5)$ selected above, one obtains the value selected by Guillaumont et al. (2003) – already given above –

$$\log_{10}{}^*\beta_4°(298.15\ K) = -(8.3 \pm 1.1)$$

It is clear from the above mentioned solubility measurements that $Np(OH)_5^-$ is not an important hydrolysis species for Np(IV) up to very basic solutions. Thus, no value was proposed for this species by Lemire et al. (2001) and Guillaumont et al. (2003).

4.3.1.6 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. $\Delta\varepsilon = (0.04 \pm 0.09)\ kg{\cdot}mol^{-1}$. Lemire et al. (2001) recommended

$$\log_{10}{}^*\beta_1°(298.15\ K) = -(6.8 \pm 0.3)$$

We estimated the ion interaction coefficients for $NpOH^{2+}$ according to a method based on charge correlations (see Appendix A) and obtained

$$\varepsilon(NpOH^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg{\cdot}mol^{-1}$$

$$\varepsilon(NpOH^{2+}, ClO_4^-) = (0.4 \pm 0.1)\ kg{\cdot}mol^{-1}$$

Neither Lemire et al. (2001) nor Guillaumont et al. (2003) mention experimental data concerning the formation of $Np(OH)_2^+$ and $Np(OH)_3(aq)$. Hummel & Berner (2002) estimated values for $\log_{10}{}^*\beta_2°$ and $\log_{10}{}^*\beta_3°$ based on the chemical analogy of Np(III) with Am(III). They assumed the stepwise stability constants of $Np(OH)_2^+$ and $Np(OH)_3(aq)$ to be the same as those for $Am(OH)_2^+$ and $Am(OH)_3(aq)$ and thus obtained $\log_{10}{}^*\beta_2°(298.15\ K) = -14.7$ and $\log_{10}{}^*\beta_3°(298.15\ K) = -25.2$.

In the meantime, Guillaumont et al. (2003) have revised the data for Am(III) hydroxides, resulting in $\log_{10}{}^*K_2°(298.15\ K) = -7.9$ for $Am(OH)_2^+$ and in $\log_{10}{}^*K_3°(298.15\ K) = -11.1$ for

$Am(OH)_3(aq)$. With these stepwise stability constants and $\log_{10}{}^*\beta_1°(298.15\ K) = -(6.8 \pm 0.3)$ for $NpOH^{2+}$ the following estimates are obtained

$$Np^{3+} + 2\ H_2O(l) \Leftrightarrow Np(OH)_2^{+} + 2\ H^{+}$$

$$\log_{10}{}^*\beta_2°(298.15\ K) = -14.7$$

$$Np^{3+} + 3\ H_2O(l) \Leftrightarrow Np(OH)_3(aq) + 3\ H^{+}$$

$$\log_{10}{}^*\beta_3°(298.15\ K) = -25.8$$

These values are included in our database as supplemental data as well as the ion interaction coefficients for $Np(OH)_2^+$ estimated on the basis of charge correlations (see Appendix A)

$$\varepsilon(Np(OH)_2^{+}, Cl^{-}) = (0.05 \pm 0.10)\ kg{\cdot}mol^{-1}$$

$$\varepsilon(Np(OH)_2^{+}, ClO_4^{-}) = (0.2 \pm 0.1)\ kg{\cdot}mol^{-1}$$

4.3.2 Solid neptunium oxides and hydroxides

4.3.2.1 Neptunium(VII) oxides and hydroxides

No thermodynamic data for Np(VII) oxides and hydroxides are available.

4.3.2.2 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

$$\log_{10}{}^*K_{s,0}°(NpO_3{\cdot}H_2O, cr, 298.15\ K) = (5.47 \pm 0.40)$$

for the reaction

$$NpO_3{\cdot}H_2O(cr) + 2\ H^+ \Leftrightarrow NpO_2^{2+} + 2\ H_2O(l)$$

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

$$\Delta_f H_m°(NpO_2(OH)_2, cr, 298.15\ K) = -(1377 \pm 5)\ kJ{\cdot}mol^{-1}$$

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 $\Delta_f G_m°(NpO_2(OH)_2, cr)$ can be estimated as identical to that selected for $NpO_3{\cdot}H_2O$(cr):

$$\Delta_f G_m°(NpO_2(OH)_2, cr, 298.15\ K) \equiv \Delta_f G_m°(NpO_3{\cdot}H_2O, cr, 298.15\ K) = -(1239.0 \pm 6.4)\ kJ{\cdot}mol^{-1}$$

Combining this with the value derived for $\Delta_f H_m°(NpO_2(OH)_2, cr, 298.15\ K)$ and using $S_m°(Np, cr, \alpha, 298.15\ K)$ (see Section 4.1) and CODATA values leads to

$$S_m°(NpO_2(OH)_2, \text{cr}, 298.15 \text{ K}) = (129 \pm 28) \text{ J·K}^{-1}\text{·mol}^{-1}$$

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 $NpO_3·H_2O$(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 $NpO_3·H_2O$(cr), in favor 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).

4.3.2.3 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

$$\Delta_f H_m°(Np_2O_5, \text{cr}, 298.15 \text{ K}) = -(2162.7 \pm 9.5) \text{ kJ·mol}^{-1}$$

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

$$½ \, Np_2O_5(\text{cr}) + H^+ \Leftrightarrow NpO_2^+ + ½ \, H_2O(\text{l})$$

a value of

$$\log_{10}{}^*K_{s,0}°(Np_2O_5, \text{cr}, 298.15 \text{ K}) = (3.90 \pm 0.02)$$

From this value and the selected $\Delta_f H_m°$, $S_m°(Np_2O_5, \text{cr}, 298.15 \text{ K}) = (95 \pm 46) \text{ J·K}^{-1}\text{·mol}^{-1}$ 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-crystallized bulk Np_2O_5(cr). They accepted a mean value calculated from two previous estimates

$$S_m°(Np_2O_5, \text{cr}, 298.15 \text{ K}) = (174 \pm 20) \text{ J·K}^{-1}\text{·mol}^{-1}$$

as a value for "ideal", crystalline Np_2O_5(cr), and hence

$$\Delta_f G_m°(Np_2O_5, \text{cr}, 298.15 \text{ K}) = -(2031.6 \pm 11.2) \text{ kJ·mol}^{-1}$$

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:

$$C_{p,m}°(Np_2O_5, \text{cr}, 298.15 \text{ K}) = -(128.6 \pm 5.0) \text{ J·K}^{-1}\text{·mol}^{-1}$$

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 $\Delta_f G_m°(Np_2O_5, \text{cr}, 298.15 \text{ K})$ leads to a solubility product

$$\log_{10}{}^*K_{s,0}°(Np_2O_5, \text{cr}, 298.15 \text{ K}) = (1.9 \pm 1.0)$$

which is two orders of magnitude lower than the value derived from solubility measurements on Np_2O_5(cr) (which ultimately has 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 unrealistically 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 Section 4.3.1.3) 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

$$\log_{10}{}^*K_{s,0}°(NpO_2(OH), \text{am}, \text{"fresh"}, 298.15\ K) = (5.3 \pm 0.2)$$

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

$$\log_{10}{}^*K_{s,0}°(NpO_2(OH), \text{am}, \text{"aged"}, 298.15\ K) = (4.7 \pm 0.5)$$

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" $NpO_2(OH)$:

$$\Delta_r H_m°(NpO_2(OH), \text{am}, 298.15\ K) = -(41.1 \pm 3.0)\ kJ \cdot mol^{-1}$$

In the absence of any experimental data, Lemire et al. (2001) recommended an estimated value for the heat capacity of $NpO_2(OH)(am)$. However, we prefer not to include this estimate into our database.

4.3.2.4 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

$$\Delta_f H_m°(NpO_2, \text{cr}, 298.15\ K) = -(1074.0 \pm 2.5)\ kJ \cdot mol^{-1}$$

and, derived from low temperature heat capacity measurements, values for the entropy and heat capacity have been recommended by Lemire et al. (2001)

$$S_m°(NpO_2, \text{cr}, 298.15\ K) = (80.3 \pm 0.4)\ J \cdot K^{-1} \cdot mol^{-1}$$

$$C_{p,m}°(NpO_2, \text{cr}, 298.15\ K) = (66.2 \pm 0.5)\ J \cdot K^{-1} \cdot mol^{-1}$$

These thermochemical data result in

$$\Delta_f G_m°(NpO_2, \text{cr}, 298.15\ K) = -(1021.7 \pm 2.5)\ kJ \cdot mol^{-1}$$

which in turn can be interpreted as a solubility product of the reaction

$$NpO_2(cr) + 4\ H^+ \Leftrightarrow Np^{4+} + 2\ H_2O(l)$$

$$\log_{10}{}^*K_{s,0}^\circ(\mathrm{NpO_2, cr, 298.15\ K}) = -(9.8 \pm 0.4)$$

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. 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(am, hyd): The selected value for $\log_{10}{}^*K_{s,0}^\circ$ discussed above

$$\mathrm{NpO_2(am, hyd) + 4\ H^+ \Leftrightarrow Np^{4+} + 2\ H_2O(l)}$$

$$\log_{10}{}^*K_{s,0}^\circ(298.15\ \mathrm{K}) = -(0.7 \pm 0.5)$$

is smaller than the value suggested for the corresponding uranium compound ($\log_{10}{}^*K_{s,0}^\circ = 1.5 \pm 1.0$), and larger than the value suggested for the corresponding plutonium solid ($\log_{10}{}^*K_{s,0}^\circ = -2.33 \pm 0.52$). 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 behavior between the three actinide systems.

4.3.2.5 Neptunium(III) oxides and hydroxides

No chemical thermodynamic quantities have been selected by Lemire et al. (2001) or Guillaumont et al. (2003) for $Np_2O_3(s)$. No thermodynamic data for $Np(OH)_3(s)$ have been reported.

4.4 Halogen compounds and complexes

4.4.1 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) and Guillaumont et al. (2003) also selected thermochemical data for the following liquid and gaseous halides:

Liquid fluorides: $NpF_6(l)$

Liquid chlorides: $NpCl_6(l)$

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 liquids and gases are hardly relevant for aqueous environmental systems and are therefore excluded from our database update.

4.4.2 Aqueous neptunium fluoride complexes

4.4.2.1 Aqueous Np(VI) fluorides

The investigation of fluoride complexation of Np(VI) is complicated by the fact that NpO_2^{2+} has oxidizing properties, and that reduction to Np(IV) is favored 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 (i.e. $\Delta\varepsilon$) from the corresponding U(VI) fluoride equilibria and recommended the following weighted averages, which are also included in our database:

$$NpO_2^{2+} + F^- \Leftrightarrow NpO_2F^+$$

$$\log_{10}\beta_1°(298.15\ K) = (4.57 \pm 0.07)$$

$$NpO_2^{2+} + 2\ F^- \Leftrightarrow NpO_2F_2(aq)$$

$$\log_{10}\beta_2°(298.15\ K) = (7.60 \pm 0.08)$$

Lemire et al. (2001) estimated

$$\varepsilon(NpO_2F^+, ClO_4^-) = (0.29 \pm 0.12)\ kg \cdot mol^{-1}$$

from $\Delta\varepsilon = -(0.03 \pm 0.09)\ kg \cdot mol^{-1}$ for the reaction $NpO_2^{2+} + HF(aq) \Leftrightarrow NpO_2F^+ + H^+$, and the selected values $\varepsilon(NpO_2^{2+}, ClO_4^-) = (0.46 \pm 0.05)\ kg \cdot mol^{-1}$ and $(H^+, ClO_4^-) = (0.14 \pm 0.02)\ kg \cdot mol^{-1}$. The value for $\Delta\varepsilon$ was assumed by Lemire et al. (2001) to be equal to that determined by Grenthe et al. (1992) for the corresponding U(VI) system. To account for the estimate, Lemire et al. (2001) increased the reported uncertainty by 0.05 $kg \cdot mol^{-1}$. For the chloride system, we estimated the ion interaction coefficient based on charge correlations (see Appendix A) and obtained

$$\varepsilon(NpO_2F^+, Cl^-) = (0.05 \pm 0.10)\ kg \cdot mol^{-1}$$

Both estimates of ε for NpO_2F^+ are included in our database.

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).

4.4.2.2 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

$$NpO_2^+ + F^- \Leftrightarrow NpO_2F(aq)$$

$$\log_{10}\beta_1°(298.15\ K) = (1.2 \pm 0.3)$$

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 $\log_{10}\beta_1°$.

4.4.2.3 Aqueous Np(IV) fluorides

All experiments were carried out in strongly acidic solutions, and thus the relevant equilibrium is

$$\mathrm{Np^{4+} + n\,HF(aq) \Leftrightarrow NpF_n^{(4-n)} + n\,H^+}$$

The values for $\log_{10}{}^*\beta_1$ are in good agreement and Lemire et al. (2001) could do a simultaneous determination of $\log_{10}{}^*\beta_1^\circ = (5.78 \pm 0.14)$ and $\Delta\varepsilon = -(0.12 \pm 0.04)$ kg·mol^{-1} by weighted linear regression of the experimental data. The value of $\log_{10}{}^*\beta_2^\circ = (9.34 \pm 0.29)$ has been obtained by extrapolating the reported constants to zero ionic strength using $\Delta\varepsilon = -(0.18 \pm 0.15)$ kg·mol^{-1} from the corresponding U(IV) fluoride system (see Grenthe et al. 1992), where the uncertainty has been increased by 0.05 kg·mol^{-1}, 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

$$\mathrm{Np^{4+} + n\,F^- \Leftrightarrow NpF_n^{(4-n)}}$$

with n = 1 and 2:

$$\mathrm{Np^{4+} + F^- \Leftrightarrow NpF^{3+}}$$

$$\log_{10}\beta_1^\circ(\mathrm{n = 1, 298.15\ K}) = (8.96 \pm 0.14)$$

$$\mathrm{Np^{4+} + 2\,F^- \Leftrightarrow NpF_2^{2+}}$$

$$\log_{10}\beta_2^\circ(\mathrm{n = 2, 298.15\ K}) = (15.7 \pm 0.3)$$

These constants are accepted for our database. Lemire et al. (2001) calculated

$$\varepsilon(\mathrm{NpF^{3+}, ClO_4^-}) = (0.58 \pm 0.07)\ \mathrm{kg{\cdot}mol^{-1}}$$

$$\varepsilon(\mathrm{NpF_2^{2+}, ClO_4^-}) = (0.38 \pm 0.17)\ \mathrm{kg{\cdot}mol^{-1}}$$

from the $\Delta\varepsilon$-values mentioned above and from the selected $\varepsilon(\mathrm{Np^{4+}, ClO_4^-}) = (0.84 \pm 0.06)$ kg·mol^{-1} and $(\mathrm{H^+, ClO_4^-}) = (0.14 \pm 0.02)$ kg·mol^{-1}. We estimated the corresponding ε values for the chloride system based on charge correlations (see Appendix A) and obtained

$$\varepsilon(\mathrm{NpF^{3+}, Cl^-}) = (0.25 \pm 0.10)\ \mathrm{kg{\cdot}mol^{-1}}$$

$$\varepsilon(\mathrm{NpF_2^{2+}, Cl^-}) = (0.15 \pm 0.10)\ \mathrm{kg{\cdot}mol^{-1}}$$

These four values for ε are also included in our database.

From equilibrium constants measured at 10, 25 and 40°C it is possible to extract an enthalpy of reaction for the 1:1 complex:

$$\Delta_r H_m^\circ(\mathrm{n = 1, 298.15\ K}) = (1.5 \pm 2.0)\ \mathrm{kJ{\cdot}mol^{-1}}$$

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 coefficients 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 $\mathrm{NpF_3^+}$ and $\mathrm{NpF_4(aq)}$.

4.4.2.4 Aqueous Np(III) fluorides

No fluoride complexes of $\mathrm{Np^{3+}}$ have been identified. Hummel & Berner (2002) estimated stability constants for $\mathrm{NpF^{2+}}$ and $\mathrm{NpF_2^+}$, by adopting the values for the corresponding Am(III) fluoride complexes. From the data selected by Lemire et al. (2001) the following estimates are obtained

$$Np^{3+} + F^- \Leftrightarrow NpF^{2+}$$

$$log_{10}\beta_1^\circ(298.15\ K) = 3.4$$

$$Np^{3+} + 2\,F^- \Leftrightarrow NpF_2^+$$

$$log_{10}\beta_2°(298.15\ K) = 5.8$$

These values are included in our database as supplemental data. We estimated the ion interaction coefficients for these fluoride complexes in chloride and perchlorate media using a method based on charge correlations (see Appendix A) and obtained

$$\varepsilon(NpF^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg\cdot mol^{-1}$$

$$\varepsilon(NpF^{2+}, ClO_4^-) = (0.4 \pm 0.1)\ kg\cdot mol^{-1}$$

$$\varepsilon(NpF_2^+, Cl^-) = (0.05 \pm 0.10)\ kg\cdot mol^{-1}$$

$$\varepsilon(NpF_2^+, ClO_4^-) = (0.2 \pm 0.1)\ kg\cdot mol^{-1}$$

These values are also included in our database as supplemental data.

4.4.3 Aqueous neptunium chloride complexes

4.4.3.1 Aqueous Np(VI) chlorides

Experimental data for the Np(VI) chloride system have been reported in perchloric acid solutions, but a statistical treatment of these data seems difficult. Lemire et al. (2001) therefore adopted the SIT interaction coefficient that they evaluated for the corresponding Pu(VI) system and increased its uncertainty by 0.05, i.e. $\Delta\varepsilon = -(0.08 \pm 0.13)\ \mathrm{kg\cdot mol^{-1}}$, to extrapolate the experimental data to zero ionic strength, and selected the weighted average of the resulting values

$$\mathrm{NpO_2^{2+} + Cl^- \Leftrightarrow NpO_2Cl^+}$$

$$\log_{10}\beta_1°(\mathrm{n} = 1, 298.15\ \mathrm{K}) = (0.40 \pm 0.17)$$

which is included in our database. Using the estimated value for Δε and the selected values $\varepsilon(\mathrm{NpO_2^{2+}, ClO_4^-}) = (0.46 \pm 0.05)\ \mathrm{kg\cdot mol^{-1}}$ and $\varepsilon(\mathrm{Cl^-, H^+}) = (0.12 \pm 0.01)\ \mathrm{kg\cdot mol^{-1}}$, Lemire et al. (2001) estimated

$$\varepsilon(\mathrm{NpO_2Cl^+, ClO_4^-}) = (0.50 \pm 0.14)\ \mathrm{kg\cdot mol^{-1}}$$

which is selected for our database. We estimated

$$\varepsilon(\mathrm{NpO_2Cl^+, Cl^-}) = (0.05 \pm 0.10)\ \mathrm{kg\cdot mol^{-1}}$$

according to a method based on charge correlations (see Appendix A). This value is included in our database.

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 $\mathrm{NpO_2Cl_2(aq)}$, and did not select any value.

4.4.3.2 Aqueous Np(V) chlorides

Some authors have published formation constants for $\mathrm{NpO_2Cl(aq)}$ and $\mathrm{NpO_2Cl_2^-}$ at ionic strengths from 2 to 5 M. The stability of these complexes is very low and some results can equally well be 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.

4.4.3.3 Aqueous Np(IV) chlorides

The value selected by Lemire et al. (2001) 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 in mixed chloride/perchlorate media with $\Delta\varepsilon = -(0.15 \pm 0.18)$ kg·mol^{-1}

$$\log_{10}\beta_1°(298.15 \text{ K}) = (1.5 \pm 0.3)$$

and is included in our database. Using $\Delta\varepsilon$ together with the selected $\varepsilon(Np^{4+}, ClO_4^-) = (0.84 \pm 0.06)$ kg·mol^{-1} and $\varepsilon(Cl^-, H^+) = (0.12 \pm 0.01)$ kg·mol^{-1}, Lemire et al. (2001) determined

$$\varepsilon(NpCl^{3+}, ClO_4^-) = (0.81 \pm 0.19) \text{ kg·mol}^{-1}$$

which is accepted for our database. Note that in their Table B-4 Guillaumont et al. (2003) gave an uncertainty of ± 0.09 kg·mol^{-1} for $\varepsilon(NpCl^{3+}, ClO_4^-)$, and this typographical error has been perpetuated in all following NEA-reviews. From an estimation method based on charge correlations (see Appendix A) follows our selected

$$\varepsilon(NpCl^{3+}, Cl^-) = (0.25 \pm 0.10) \text{ kg·mol}^{-1}$$

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 artifacts due to medium changes, and Lemire et al. (2001) did not select any thermodynamic data for these complexes.

4.4.3.4 Aqueous Np(III) chlorides

There is only one quantitative study on chloride complexation of Np^{3+}. However, due to the very high and varying ionic strength (LiCl) used in the experiments, Lemire et al. (2001) could not select any value for zero ionic strength. Hummel & Berner (2002) estimated a stability constant for $NpCl^{2+}$ by adopting the value for the corresponding Am(III) chloride complex selected by Lemire et al. (2001). In the meantime, Guillaumont et al. (2003) have revised the data for $AmCl^{2+}$ and also provided an equilibrium constant for $AmCl_2^+$. Using these data leads to the following estimates

$$Np^{3+} + Cl^- \Leftrightarrow NpCl^{2+}$$

$$\log_{10}\beta_1°(298.15 \text{ K}) = 0.24$$

$$Np^{3+} + 2\,Cl^- \Leftrightarrow NpCl_2^+$$

$$\log_{10}\beta_2°(298.15 \text{ K}) = -0.74$$

These values are included in our database as supplemental data together with the ion interaction coefficients of $NpCl^{2+}$ and $NpCl_2^+$ in chloride and perchlorate media that we estimated with a method based on charge correlations (see Appendix A)

$$\varepsilon(NpCl^{2+}, Cl^-) = (0.15 \pm 0.10) \text{ kg·mol}^{-1}$$

$$\varepsilon(NpCl^{2+}, ClO_4^-) = (0.4 \pm 0.1) \text{ kg·mol}^{-1}$$

$$\varepsilon(NpCl_2^+, Cl^-) = (0.05 \pm 0.10) \text{ kg·mol}^{-1}$$

$$\varepsilon(NpCl_2^+, ClO_4^-) = (0.2 \pm 0.1) \text{ kg·mol}^{-1}$$

4.4.4 Aqueous neptunium bromide complexes

No thermodynamic data for aqueous neptunium bromide complexes have been selected by Lemire et al. (2001).

4.4.5 Aqueous neptunium iodide and iodate complexes

Lemire et al. (2001) selected equilibrium constants for the generally rather weak complexes NpI^{3+}, $NpO_2IO_3(aq)$ and $NpO_2IO_3^+$. Iodide complexation by Np^{4+} was investigated in three studies by solvent extraction in 2 M perchloric acid solutions. Lemire et al. (2001) used SIT to extrapolate the data to zero ionic strength by adopting $\Delta\varepsilon = -(0.15 \pm 0.25)\ kg\cdot mol^{-1}$, from the corresponding Np(IV) chloride system (with the uncertainty increased by $0.07\ kg\cdot mol^{-1}$) and selected the weighted average

$$Np^{4+} + I^- \Leftrightarrow NpI^{3+}$$

$$\log_{10}\beta_1°(298.15\ K) = (1.5 \pm 0.4)$$

which is also included in our database. In order to calculate $\varepsilon(NpI^{3+}, ClO_4^-)$ from $\Delta\varepsilon$, Lemire et al. (2001) assumed that $\varepsilon(I^-, H^+) = \varepsilon(I^-, Na^+) = (0.08 \pm 0.02)\ kg\cdot mol^{-1}$ and used the selected value $\varepsilon(Np^{4+}, ClO_4^-) = (0.84 \pm 0.06)\ kg\cdot mol^{-1}$ to obtain $\varepsilon(NpI^{3+}, ClO_4^-) = (0.77 \pm 0.26)\ kg\cdot mol^{-1}$. Hummel et al. (2005) provided $\varepsilon(I^-, H^+) = (0.19 \pm 0.01)\ kg\cdot mol^{-1}$, which they derived from mean activity data. Using this value instead of the estimate by Lemire et al. (2001) results in

$$\varepsilon(NpI^{3+}, ClO_4^-) = (0.88 \pm 0.26)\ kg\cdot mol^{-1}$$

which is selected for our database, as well as

$$\varepsilon(NpI^{3+}, Cl^-) = (0.25 \pm 0.10)\ kg\cdot mol^{-1}$$

which was estimated according to a method based on charge correlations (see Appendix A).

Based on a solvent extraction and a spectrophotometric study in 2 M $H(IO_3, ClO_4)$, Lemire et al. (2001) used SIT to extrapolate two equilibrium constants for the reaction

$$NpO_2^+ + IO_3^- \Leftrightarrow NpO_2IO_3(aq)$$

to zero ionic strength by using a $\Delta\varepsilon$ that was calculated with ion interaction coefficients adopted from the corresponding U(V) species. They selected the average of the equilibrium constants

$$\log_{10}\beta_1°(298.15\ K) = (0.5 \pm 0.3)$$

which is also included in our database.

A formation constant for the Np(VI)-iodate 1:1 complex was reported from a spectrophotometric study in a 0.3 M $(HClO_4, NaIO_3)$ solution. Lemire et al. (2001) extrapolated this constant to zero ionic strength and selected

$$NpO_2^{2+} + IO_3^- \Leftrightarrow NpO_2IO_3^+$$

$$\log_{10}\beta_1°(298.15\ K) = (1.2 \pm 0.3)$$

For the extrapolation they estimated a value for $\Delta\varepsilon$ that was based on the following assumptions: $\varepsilon(NpO_2^{2+}, ClO_4^-) = \varepsilon(UO_2^{2+}, ClO_4^-)$, $\varepsilon(IO_3^-, H^+) = \varepsilon(IO_3^-, Na^+)$, and $\varepsilon(NpO_2IO_3^+, ClO_4^-) = \varepsilon(UO_2IO_3^+, ClO_4^-)$. Thus,

$$\varepsilon(NpO_2IO_3^+, ClO_4^-) = (0.33 \pm 0.04)\ kg\cdot mol^{-1}$$

is selected for our database. For the chloride system, we applied an estimation method based on charge correlations (see Appendix A) and include

$$\varepsilon(NpO_2IO_3^+, Cl^-) = (0.05 \pm 0.10)\ kg\cdot mol^{-1}$$

in our database.

4.5 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.

4.5.1 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

$$NpO_2^{2+} + n\ SO_4^{2-} \Leftrightarrow NpO_2(SO_4)_n^{(2-2n)}$$

with n =1 and n = 2:

$$NpO_2^{2+} + SO_4^{2-} \Leftrightarrow NpO_2SO_4(aq)$$

$$\log_{10}\beta_1^\circ(n = 1, 298.15\ K) = (3.28 \pm 0.06)$$

$$\Delta_r H_m^\circ(n = 1, 298.15\ K) = (16.7 \pm 0.5)\ kJ\cdot mol^{-1}$$

$$NpO_2^{2+} + 2\ SO_4^{2-} \Leftrightarrow NpO_2(SO_4)_2^{2-}$$

$$\log_{10}\beta_2^\circ(n = 2, 298.15\ K) = (4.70 \pm 0.10)$$

$$\Delta_r H_m^\circ(n = 2, 298.15\ K) = (26.0 \pm 1.2)\ kJ\cdot mol^{-1}$$

We estimated the selected

$$\varepsilon(NpO_2(SO_4)_2^{2-}, Na^+) = -(0.10 \pm 0.10)\ kg\cdot mol^{-1}$$

by following a method based on charge correlations (see Appendix A).

4.5.2 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

$$\Delta_r H_m^\circ(298.15\ K) = (23.2 \pm 7.2)\ kJ\cdot mol^{-1}$$

We applied an estimation method based on charge correlations (see Appendix A) for obtaining

$$\varepsilon(NpO_2SO_4^-, Na^+) = -(0.05 \pm 0.10)\ kg\cdot mol^{-1}$$

and include this value in our database.

4.5.3 Aqueous Np(IV) sulphates

There are seven reliable studies describing the Np(IV) sulphate complexes. Because of concerns regarding interference due to hydrolysis, all Np(IV) experiments were performed in strong acid media (up to 4.6 m $HClO_4$). 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, Lemire et al. (2001) found the recommended values to be

$$Np^{4+} + HSO_4^- \Leftrightarrow NpSO_4^{2+} + H^+$$

$$\log_{10}\beta_1°(q = 1, 298.15\text{ K}) = (4.87 \pm 0.15)$$

$$Np^{4+} + 2\,HSO_4^- \Leftrightarrow Np(SO_4)_2(aq) + 2\,H^+$$

$$\log_{10}\beta_2°(q = 2, 298.15\text{ K}) = (7.09 \pm 0.25)$$

with $\Delta\varepsilon(q = 1) = -(0.19 \pm 0.06)$ kg·mol^{-1} and $\Delta\varepsilon(q = 2) = -(0.29 \pm 0.11)$ kg·mol^{-1}. Using the selected values $\varepsilon(Np^{4+}, ClO_4^-) = (0.84 \pm 0.06)$ kg·mol^{-1} and $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$ kg·mol^{-1}, and assuming that $\varepsilon(HSO_4^-, H^+) = \varepsilon(HSO_4^-, Na^+) = -(0.01 \pm 0{,}07)$ kg·mol^{-1}, where the uncertainty has been increased by 0.05 kg·mol^{-1}, Lemire et al. (2001) calculated $\varepsilon(NpSO_4^{2+}, ClO_4^-) = (0.48 \pm 0.11)$ kg·mol^{-1} from $\Delta\varepsilon(q = 1)$. Note that this value is slightly incorrect and should rather be

$$\varepsilon(NpSO_4^{2+}, ClO_4^-) = (0.50 \pm 0.11)\text{ kg·mol}^{-1}$$

For the chloride system we used a method based on charge correlations (see Appendix A) for estimating

$$\varepsilon(NpSO_4^{2+}, Cl^-) = (0.15 \pm 0.10)\text{ kg·mol}^{-1}$$

Both of these ion interaction coefficients are included in our database.

The enthalpies of the complexation reactions were determined by Lemire et al. (2001) from measured temperature variations

$$\Delta_r H_m°(q = 1, 298.15\text{ K}) = (7.38 \pm 8.8)\text{ kJ·mol}^{-1}$$

$$\Delta_r H_m°(q = 2, 298.15\text{ K}) = (10.5 \pm 3.6)\text{ kJ·mol}^{-1}$$

For our database update, these complex formation reactions were rewritten in terms of SO_4^{2-} instead of HSO_4^- as

$$Np^{4+} + n\,SO_4^{2-} \Leftrightarrow Np(SO_4)_n^{(4-2n)}$$

using the NEA recommended protonation equilibrium constant (1.98 ± 0.05) and enthalpy (22.44 ± 1.1) kJ·mol^{-1}. The selected equilibrium constants are

$$Np^{4+} + SO_4^{2-} \Leftrightarrow NpSO_4^{2+}$$

$$\log_{10}\beta_1°(n = 1, 298.15\text{ K}) = (6.85 \pm 0.16)$$

$$Np^{4+} + SO_4^{2-} \Leftrightarrow Np(SO_4)_2(aq)$$

$$\log_{10}\beta_2°(n = 2, 298.15\text{ K}) = (11.05 \pm 0.27)$$

and the selected standard reaction enthalpies

$$\Delta_r H_m°(n = 1, 298.15\text{ K}) = (29.8 \pm 8.9)\text{ kJ·mol}^{-1}$$

$$\Delta_r H_m°(n = 2, 298.15\text{ K}) = (55.4 \pm 3.9)\text{ kJ·mol}^{-1}$$

4.5.4 Aqueous Np(III) sulphates

No experimental evidence for the stability of Np(III) sulphate complexes was found by Lemire et al. (2001) and Guillaumont et al. (2003). Hummel & Berner (2002) estimated stability constants for $NpSO_4^+$ and $Np(SO_4)_2^-$ by adopting the values for the corresponding Am(III) sulphate complexes. Using the revised data by Guillaumont et al. (2003) for these complexes results in the following estimates

$$Np^{3+} + SO_4^{2-} \Leftrightarrow NpSO_4^+$$

$$\log_{10}\beta_1^\circ(298.15\text{ K}) = 3.3$$

$$Np^{3+} + 2\,SO_4^{2-} \Leftrightarrow Np(SO_4)_2^-$$

$$\log_{10}\beta_1^\circ(298.15\text{ K}) = 3.7$$

These values are included in our database as supplemental data as well as the ion interaction coefficients

$$\varepsilon(NpSO_4^+, Cl^-) = (0.05 \pm 0.10)\ kg\cdot mol^{-1}$$

$$\varepsilon(NpSO_4^+, ClO_4^-) = (0.2 \pm 0.1)\ kg\cdot mol^{-1}$$

$$\varepsilon(Np(SO_4)_2^-, Na^+) = -(0.05 \pm 0.10)\ kg\cdot mol^{-1}$$

that we estimated based on charge correlations (see Appendix A).

4.6 Group 15 compounds and complexes

4.6.1 Nitrogen compounds and complexes

Np nitrides: Thermochemical data for NpN(cr) have been selected by Lemire et al. (2001) and Guillaumont et al. (2003). 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, $\Delta_r G_m^\circ$ has been calculated. This value has been used in determining the value of $S_m^\circ(NpO_2^{2+}, aq, 298.15\text{ K})$ (see Section 4.2.2). 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

$$Np^{4+} + NO_3^- \Leftrightarrow NpNO_3^{3+}$$

$$\log_{10}\beta_1°(298.15 \text{ K}) = (1.90 \pm 0.15)$$

Using a method based on charge correlations (see Appendix A) we estimated

$$\varepsilon(NpNO_3^{3+}, Cl^-) = (0.25 \pm 0.10) \text{ kg·mol}^{-1}$$

$$\varepsilon(NpNO_3^{3+}, ClO_4^-) = (0.6 \pm 0.1) \text{ kg·mol}^{-1}$$

All of these data for $NpNO_3^{3+}$ are included in our database

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".

4.6.2 Phosphorous compounds and complexes

Aqueous Np(VI) phosphates: For the Np(VI) phosphate system there is only one study (solvent extraction at 25°C and 1M $NaClO_4$), 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 were accepted by Lemire et al. (2001) with substantially increased uncertainty limits and were extrapolated to zero ionic strength using SIT with selected or estimated ion interaction coefficients.

$$NpO_2^{2+} + H_2PO_4^- \Leftrightarrow NpO_2H_2PO_4^+$$

$$\log_{10}\beta_1°(298.15 \text{ K}) = (3.32 \pm 0.50)$$

$$NpO_2^{2+} + HPO_4^{2-} \Leftrightarrow NpO_2HPO_4(aq)$$

$$\log_{10}\beta_1°(298.15 \text{ K}) = (6.2 \pm 0.7)$$

$$NpO_2^{2+} + 2\ HPO_4^{2-} \Leftrightarrow NpO_2(HPO_4)_2^{2-}$$

$$\log_{10}\beta_2\ (298.15 \text{ K}) = (9.5 \pm 1.0)$$

These constants are also accepted for our database. For their SIT extrapolation, Lemire et al. (2001) estimated

$$\varepsilon(NpO_2(HPO_4)_2^{2-}, Na^+) = -(0.1 \pm 0.1) \text{ kg·mol}^{-1}$$

but did not indicate on what this estimate is based on. Nevertheless, this value is also included in our database. We estimated

$$\varepsilon(NpO_2H_2PO_4^+, Cl^-) = (0.05 \pm 0.10) \text{ kg·mol}^{-1}$$

$$\varepsilon(NpO_2H_2PO_4^+, ClO_4^-) = (0.2 \pm 0.1) \text{ kg·mol}^{-1}$$

by applying an estimation method based on charge correlations (see Appendix A).

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):

$$NpO_2^+ + HPO_4^{2-} \Leftrightarrow NpO_2HPO_4^-$$

$$\log_{10}\beta_1°(298.15\ K) = (2.95 \pm 0.10)$$

Since Lemire et al. (2001) did not report any ion interaction coefficients for $NpO_2HPO_4^-$, we estimated

$$\varepsilon(NpO_2HPO_4^-, Na^+) = -(0.05 \pm 0.10)\ kg \cdot mol^{-1}$$

according to a method based on charge correlations (see Appendix A).

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(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(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).

4.6.3 Neptunium antimony compounds

Thermochemical data for NpSb(cr) have been selected by Guillaumont et al. (2003) . However, this phase is hardly relevant to environmental systems and is therefore not included in our database.

4.7 Group 14 compounds and complexes

4.7.1 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.

4.7.2 Neptunium carbonates

4.7.2.1 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.

4.7.2.1.1 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 polymerization 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 $K_4NpO_2(CO_3)_3(s)$, $(NH_4)_4NpO_2(CO_3)_3(s)$ 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

$$E°(298.15 \text{ K}) = (0.338 \pm 0.006) \text{ V}$$

with

$$\Delta\varepsilon(298.15 \text{ K}) = -(0.14 \pm 0.04) \text{ kg}\cdot\text{mol}^{-1}$$

From $\Delta\varepsilon$ and $\varepsilon(NpO_2(CO_3)_3^{5-}, Na^+) = -(0.53 \pm 0.19)$ kg·mol^{-1} (see below), Lemire et al. (2001) obtained

$$\varepsilon(NpO_2(CO_3)_3^{4-}, Na^+) = -(0.40 \pm 0.19) \text{ kg}\cdot\text{mol}^{-1}$$

which is selected for our database as well as

$$\varepsilon(NpO_2(CO_3)_3^{4-}, K^+) = -(0.62 \pm 0.42) \text{ kg}\cdot\text{mol}^{-1}$$

which Lemire et al. (2001) determined from equilibria with solid Np(VI) carbonates (see below).

The $E°$ value was combined with the standard potential for the NpO_2^{2+}/NpO_2^+ redox couple (see Section 4.2.2) and the formation constant for the species $NpO_2(CO_3)_3^{5-}$ (see below) to calculate

$$NpO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{4-}$$

$$\log_{10}\beta_3°(298.15 \text{ K}) = (19.37 \pm 0.19)$$

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 was done using SIT coefficients of the corresponding U(VI) system and resulted in

$$\mathrm{NpO_2^{2+} + 2\,CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_2^{2-}}$$

$$\log_{10}\beta_2^\circ(298.15\text{ K}) = (16.52 \pm 0.73)$$

$$\mathrm{NpO_2^{2+} + CO_3^{2-} \Leftrightarrow NpO_2CO_3(aq)}$$

$$\log_{10}\beta_1^\circ(298.15\text{ K}) = (9.32 \pm 0.61)$$

The ion interaction coefficient

$$\varepsilon(\mathrm{NpO_2(CO_3)_2^{2-}, Na^+}) = -(0.02 \pm 0.14)\ \mathrm{kg{\cdot}mol^{-1}}$$

estimated and selected by Lemire et al. (2001) corresponds to the value selected by Grenthe et al. (1995) for $\varepsilon(\mathrm{UO_2(CO_3)_2^{2-}, Na^+})$ with an uncertainty increased by 0.05 $\mathrm{kg{\cdot}mol^{-1}}$ [1].

The carbonate trinuclear Np(VI) complex: The polymerization reaction

$$\mathrm{3\,NpO_2(CO_3)_3^{4-} \Leftrightarrow 3\,CO_3^{2-} + (NpO_2)_3(CO_3)_6^{6-}}$$

is well established, but there are still only two values (at 1 and 3 M $\mathrm{NaClO_4}$) 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, Lemire et al. (2001) used the only two available data to calculate a value with a large uncertainty

$$\log_{10}K^\circ(298.15\text{ K}) = -(8.27 \pm 1.45)$$

for which

$$\Delta\varepsilon(298.15\text{ K}) = (0.49 \pm 0.50)\ \mathrm{kg{\cdot}mol^{-1}}$$

Lemire et al. (2001) used this $\Delta\varepsilon$, together with the selected values $\varepsilon(\mathrm{NpO_2(CO_3)_3^{4-}, Na^+}) = -(0.40 \pm 0.19)\ \mathrm{kg{\cdot}mol^{-1}}$ and $\varepsilon(\mathrm{CO_3^{2-}, Na^+}) = -(0.08 \pm 0.03)\ \mathrm{kg{\cdot}mol^{-1}}$ to determine

$$\varepsilon(\mathrm{(NpO_2)_3(CO_3)_6^{6-}, Na^+}) = -(0.46 \pm 0.73)\ \mathrm{kg{\cdot}mol^{-1}}$$

which is selected for our database.

Combining $\mathrm{3\,NpO_2(CO_3)_3^{4-} \Leftrightarrow 3\,CO_3^{2-} + (NpO_2)_3(CO_3)_6^{6-}}$ with $\mathrm{NpO_2^{2+} + 3\,CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{4-}}$ results in the selected equilibrium

$$\mathrm{3\,NpO_2^{2+} + 6\,CO_3^{2-} \Leftrightarrow (NpO_2)_3(CO_3)_6^{6-}}$$

$$\log_{10}\beta_{6,3}^\circ(298.15\text{ K}) = (49.84 \pm 1.56)$$

with $\log_{10}\beta_{6,3}^\circ$calculated from the values of $\log_{10}K^\circ$ and $\log_{10}\beta_3^\circ$ selected above.

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 $\mathrm{NaClO_4}$ for the reaction

$$\mathrm{2\,NpO_2(CO_3)_3^{4-} + 7\,H^+ \Leftrightarrow (NpO_2)_2CO_3(OH)_3^- + 5\,CO_2(g) + 7\,H_2O(l)}$$

---

[1] As discussed in Section 11.8.1.2, we selected $\varepsilon(\mathrm{UO_2(CO_3)_2^{2-}, Na^+}) = -(0.15 \pm 0.08)\ \mathrm{kg{\cdot}mol^{-1}}$. We retained, however, $\varepsilon(\mathrm{NpO_2(CO_3)_2^{2-}, Na^+}) = -(0.02 \pm 0.14)\ \mathrm{kg{\cdot}mol^{-1}}$ and the corresponding $\log_{10}\beta_2^\circ(298.15\text{ K}) = (16.52 \pm 0.73)$.

$$\log_{10}K\,(1\text{M NaClO}_4,\ 298.15\text{ K}) = (41.75 \pm 1.46)$$

Using data selected in Lemire et al. (2001) and SIT coefficients of the corresponding uranium system, this corresponds to

$$2\ \text{NpO}_2^{2+} + \text{CO}_3^{2-} + 3\ \text{H}_2\text{O(l)} \Leftrightarrow (\text{NpO}_2)_2\text{CO}_3(\text{OH})_3^- + 3\ \text{H}^+$$

$$\log_{10}K°(298.15\text{ K}) = -(2.87 \pm 1.64)$$

Lemire et al. (2001) estimated the selected

$$\varepsilon((\text{NpO}_2)_2\text{CO}_3(\text{OH})_3^-, \text{Na}^+) = (0.00 \pm 0.05)\ \text{kg}\cdot\text{mol}^{-1}$$

by adopting the selected value for $\varepsilon((\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-, \text{Na}^+)$, which itself was estimated by Grenthe et al. (1992).

Mixed actinide carbonate complexes: A re-evaluation by Lemire et al. (2001) of data discussed earlier in Grenthe et al. (1992) considering the selected Np constants resulted in

$$2\ \text{UO}_2^{2+} + \text{NpO}_2^{2+} + 6\ \text{CO}_3^{2-} \Leftrightarrow (\text{UO}_2)_2\text{NpO}_2(\text{CO}_3)_6^{6-}$$

$$\log_{10}K°(298.15\text{ K}) = (53.59 \pm 2.70)$$

Lemire et al. (2001) estimated

$$\varepsilon((\text{UO}_2)_2\text{NpO}_2(\text{CO}_3)_6^{6-}, \text{Na}^+) = (0.09 \pm 0.71)\ \text{kg}\cdot\text{mol}^{-1}$$

from the weighted mean 2/3 $\varepsilon((\text{UO}_2)_3(\text{CO}_3)_6^{6-}, \text{Na}^+)$ + 1/3 $\varepsilon((\text{NpO}_2)_3(\text{CO}_3)_6^{6-}, \text{Na}^+)$, with $\varepsilon((\text{UO}_2)_3(\text{CO}_3)_6^{6-}, \text{Na}^+) = (0.37 \pm 0.11)$ and $\varepsilon((\text{NpO}_2)_3(\text{CO}_3)_6^{6-}, \text{Na}^+) = -(0.46 \pm 0.73)\ \text{kg}\cdot\text{mol}^{-1}$. Note, that based on the uncertainties of these values, the uncertainty of the weighted mean should be 0.25 $\text{kg}\cdot\text{mol}^{-1}$, but Lemire et al. (2001) did not comment on why they chose 0.71 $\text{kg}\cdot\text{mol}^{-1}$ as uncertainty.

4.7.2.1.2 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 ($\text{NpO}_2(\text{CO}_3)_n^{(1-2n)}$, 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 $\text{NpO}_2\text{CO}_3^-$, 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

$$\text{NpO}_2^+ + \text{CO}_3^{2-} \Leftrightarrow \text{NpO}_2\text{CO}_3^-$$

$$\log_{10}\beta_1°(298.15\text{ K}) = (4.96 \pm 0.06)$$

$$\text{NpO}_2\text{CO}_3^- + \text{CO}_3^{2-} \Leftrightarrow \text{NpO}_2(\text{CO}_3)_2^{3-}$$

$$\log_{10}K_2°(298.15\text{ K}) = (1.57 \pm 0.08)$$

$$NpO_2(CO_3)_2^{3-} + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-}$$

$$\log_{10}K_3°(298.15\ K) = -(1.03 \pm 0.11)$$

with $\Delta\varepsilon_1 = -(0.35 \pm 0.14)\ kg\cdot mol^{-1}$, $\Delta\varepsilon_2 = -(0.07 \pm 0.05)\ kg\cdot mol^{-1}$ and $\Delta\varepsilon_3 = -(0.12 \pm 0.06)\ kg\cdot mol^{-1}$, respectively. Lemire et al. (2001) used $\Delta\varepsilon_1$ and $\varepsilon(CO_3^{2-}, Na^+) = -(0.08 \pm 0.13)\ kg\cdot mol^{-1}$ to obtain

$$\varepsilon(NpO_2CO_3^-, Na^+) = -(0.18 \pm 0.15)\ kg\cdot mol^{-1}$$

From this, $\Delta\varepsilon_2$ and $\varepsilon(CO_3^{2-}, Na^+)$ they then calculated

$$\varepsilon(NpO_2(CO_3)_2^{3-}, Na^+) = -(0.33 \pm 0.17)\ kg\cdot mol^{-1}$$

and, finally,

$$\varepsilon(NpO_2(CO_3)_3^{5-}, Na^+) = -(0.53 \pm 0.19)\ kg\cdot mol^{-1}$$

from $\Delta\varepsilon_3$, $\varepsilon(NpO_2(CO_3)_2^{3-}, Na^+)$, and $\varepsilon(CO_3^{2-}, Na^+)$.

As will be discussed below, Guillaumont et al. (2003) derived

$$\varepsilon(NpO_2(CO_3)_3^{5-}, K^+) = -(0.22 \pm 0.03)\ kg\cdot mol^{-1}$$

All these ion interaction coefficients are included in our database.

From the selected $\beta_1°$, $K_2°$ and $K_3°$ values the cumulative stability constants are calculated

$$\log_{10}\beta_2°(298.15\ K) = (6.53 \pm 0.10)$$

$$\log_{10}\beta_3°(298.15\ K) = (5.50 \pm 0.15)$$

The values for $\log_{10}\beta_1°$, $\log_{10}\beta_2°$, and $\log_{10}\beta_3°$ selected by Lemire et al. (2001) are also selected for our database.

Lemire et al. (2001) concluded that no reliable experimental data are available concerning the temperature dependence of Np(V) carbonate complexation. However, from $\Delta_rH_m°(NpO_2(CO_3)_3^{4-} + e^- \Leftrightarrow NpO_2(CO_3)_3^{5-}) = -(88.8 \pm 2.9)\ kJ\cdot mol^{-1}$, $\Delta_rH_m°(NpO_2^{2+} + 3CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{4-}) = -(41.9 \pm 4.1)\ kJ\cdot mol^{-1}$ and $\Delta_rH_m°(NpO_2^{2+} + ½\ H_2(g) \Leftrightarrow NpO_2^+ + H^+) = -(117.4 \pm 0.6)\ kJ\cdot mol^{-1}$, Lemire et al. (2001) calculated the enthalpy for the reaction

$$NpO_2^+ + 3\ CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-}$$

$$\Delta_rH_m°(298.15\ K) = -(13.3 \pm 5.1)\ kJ\cdot mol^{-1}$$

Using $\Delta_fH_m°(NpO_2^+) = -(978.2 \pm 4.6)\ kJ\cdot mol^{-1}$ (see Section 4.2.3) and $\Delta_fH_m°(CO_3^{2-}) = -(675.23 \pm 0.25)\ kJ\cdot mol^{-1}$, $\Delta_fH_m°(NpO_2(CO_3)_3^{5-}, aq, 298.15\ K) = -(3017.12 \pm 6.89)\ kJ\cdot mol^{-1}$ is calculated (and used in 1.7.2.1.3 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 $NpO_2CO_3(OH)_2^{3-}$. Scrutinizing all the published data, Lemire et al. (2001) selected for the reaction

$$NpO_2(CO_3)_3^{5-} + OH^- \Leftrightarrow NpO_2(CO_3)_2OH^{4-} + CO_3^{2-}$$

$$\log_{10}K°(298.15\ K) = (3.20 \pm 1.16)$$

after correction of the ionic strength using SIT with the selected values for $\varepsilon(NpO_2(CO_3)_3^{5-}, Na^+)$, $\varepsilon(OH^-, Na^+)$, $\varepsilon(CO_3^{2-}, Na^+)$, and the assumption that $\varepsilon(NpO_2(CO_3)_2OH^{4-}, Na^+) = \varepsilon(NpO_2(CO_3)_3^{4-}, Na^+) = -(0.40 \pm 0.19)\ kg\cdot mol^{-1}$. The value for $\log_{10}K°(298.15\ K)$ is also accepted for our database. The estimated value

$$\varepsilon(NpO_2(CO_3)_2OH^{4-}, Na^+) = -(0.40 \pm 0.19) \text{ kg·mol}^{-1}$$

was selected by Lemire et al. (2001) and is also included in our database.

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) and $\log_{10}\beta°(H_2O(l) \Leftrightarrow H^+ + OH^-) = -14.0$ we have reformulated the reaction $NpO_2(CO_3)_3^{5-} + OH^- \Leftrightarrow NpO_2(CO_3)_2OH^{4-} + CO_3^{2-}$ for inclusion in our database, resulting in

$$NpO_2^+ + 2\,CO_3^{2-} + H_2O(l) \Leftrightarrow NpO_2(CO_3)_2OH^{4-} + H^+$$

$$\log_{10}{}^*K°(298.15 \text{ K}) = -(5.30 \pm 1.17).$$

4.7.2.1.3 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 four steps:

(1) Reanalysis of data from a spectrophotometric study of the dissociation of the limiting Np(IV) carbonate complex resulted in

$$Np(CO_3)_4^{4-} + CO_3^{2-} \Leftrightarrow Np(CO_3)_5^{6-}$$

$$\log_{10}K_5°(298.15 \text{ K}) = -(1.07 \pm 0.30).$$

This value was selected by Lemire et al. (2001) as the best estimate of $\log_{10}K_5°(298.15 \text{ K})$.

(2) Rai et al. (1999) studied the solubility of $NpO_2(am)$ in the aqueous K^+-HCO_3^--CO_3^{2-}-OH^--H_2O system and interpreted it in terms of the dominant species $Np(CO_3)_5^{6-}$, according to the reaction

$$NpO_2(am, hyd) + 5\,CO_3^{2-} + 2\,H_2O(l) \Leftrightarrow Np(CO_3)_5^{6-} + 4\,OH^-$$

At low concentrations of K_2CO_3, the calculated solubilities were too low, which was interpreted in terms of the formation of a new complex, $Np(OH)_2(CO_3)_2^{2-}$ from the dissociation of $Np(CO_3)_5^{6-}$, as the carbonate concentration was reduced. Inclusion of this complex did not remedy the situation in all experimental series and Lemire et al. (2001) remarked that it is not possible to determine whether the observed differences between calculated and observed solubilities result from the assumption made in the data analysis as to what species were present, or if the differences are the result of ionic strength effects. Since data from other sources had been interpreted by Lemire et al. (2001) in terms of the species $Np(CO_3)_4^{4-}$ and $Np(CO_3)_5^{6-}$, they reinterpreted the data by Rai et al. (1999) in a similar manner and, based on the selected value of $\log_{10}K_5°(298.15 \text{ K}) = -(1.07 \pm 0.30)$ for the formation of $Np(CO_3)_5^{6-}$, they obtained

$$NpO_2(am, hyd) + 4\,CO_3^{2-} + 2\,H_2O(l) \Leftrightarrow Np(CO_3)_4^{4-} + 4\,OH^-$$

$$\log_{10}K_{s,4}°(NpO_2, \text{am, hyd}, 298.15 \text{ K}) = -(17.79 \pm 0.22).$$

Lemire et al. (2001) selected this value as formation constant for $Np(CO_3)_4^{4-}$.

(3) Using the solubility product for

$$\mathrm{NpO_2(am, hyd)} + 4\,\mathrm{H^+} \Leftrightarrow \mathrm{Np^{4+}} + 2\,\mathrm{H_2O(l)}$$

as selected by Lemire et al. (2001), $\log_{10}{}^*K_{s,0}^\circ$ = (1.53 ± 1.00), a complex formation constant can be calculated for the reaction

$$\mathrm{Np^{4+}} + 4\,\mathrm{CO_3^{2-}} \Leftrightarrow \mathrm{Np(CO_3)_4^{4-}}$$

$$\log_{10}\beta_4^\circ(298.15\ \mathrm{K}) = (36.69 \pm 1.03)$$

(4) Combining the values of $\log_{10}K_5^\circ$ and $\log_{10}\beta_4^\circ$ results in

$$\mathrm{Np^{4+}} + 5\,\mathrm{CO_3^{2-}} \Leftrightarrow \mathrm{Np(CO_3)_5^{6-}}$$

$$\log_{10}\beta_5^\circ(298.15\ \mathrm{K}) = (35.62 \pm 1.06).$$

These values for $\log_{10}\beta_4^\circ$(298.15 K) and $\log_{10}\beta_5^\circ$(298.15 K) were selected by Hummel et al. (2002) for our previous database and they correspond to the values selected by Lemire et al. (2001) for $\Delta_f G_m^\circ$($\mathrm{Np(CO_3)_4^{4-}}$, aq, 298.15 K) and $\Delta_f G_m^\circ$($\mathrm{Np(CO_3)_5^{6-}}$, aq, 298.15 K).

Guillaumont et al. (2003) retained these standard Gibbs energies of formation for $\mathrm{Np(CO_3)_4^{4-}}$ and $\mathrm{Np(CO_3)_5^{6-}}$. Since these values are ultimately based on the solubility product for $\mathrm{NpO_2}$(am, hyd), see Section 4.3.2.4 above, they are inconsistent with the changed solubility product selected by Guillaumont et al. (2003), $\log_{10}{}^*K_{s,0}^\circ$ = -(0.7 ± 0.5) (see Section 4.3.1.5 above), which is also selected for our database. Accepting this value, the resulting standard formation constant of $\mathrm{Np(CO_3)_4^{4-}}$ is

$$\log_{10}\beta_4^\circ(298.15\ \mathrm{K}) = (38.9 \pm 0.5)$$

and that for $\mathrm{Np(CO_3)_5^{6-}}$

$$\log_{10}\beta_5^\circ(298.15\ \mathrm{K}) = (37.8 \pm 0.6).$$

These values, at variance with Guillaumont et al. (2003), are selected for our database.

Note that Guillaumont et al. (2003) made errata and corrigenda available for their update report (http://www.oecd-nea.org/dbtdb/info/publications/, accessed 1.12.2014). In these errata they write:

"The *Update* did not make any new selections for Np(IV) carbonate complexes. The $\Delta_f G_m^\circ$ values for $\mathrm{Np(CO_3)_4^{4-}}$ and $\mathrm{Np(CO_3)_5^{6-}}$ selected in [2001LEM/FUG] are adopted in the *Update*. However, the equilibrium constant for the reaction: $4\,\mathrm{CO_3^{2-}} + 2\,\mathrm{H_2O(l)} + \mathrm{NpO_2(am,hyd)} \Leftrightarrow \mathrm{Np(CO_3)_4^{4-}} + 4\,\mathrm{OH^-}$, $\log_{10}K^\circ = \log_{10}K_{s,0}^\circ(\mathrm{NpO_2}$, (am,hyd) + $\log_{10}\beta_4^\circ$, depends on the selection for $\log_{10}{}^*K_{s,0}^\circ(\mathrm{NpO_2(am,hyd)})$, which has been updated from (1.5 ± 1.0) in [2001LEM/FUG] to –(0.7 ± 0.5) in the *Update*. As a result, the value shown in the book $\log_{10}K^\circ$ = -17.79, is not consistent with the $\Delta_f G_m^\circ$ selections in the *Update*"

As is obvious from the discussion above, this is not true; rather it is the other way round, $\log_{10}\beta_4^\circ$, depends on the changed selection for $\log_{10}{}^*K_{s,0}^\circ(\mathrm{NpO_2(am,hyd)})$ and the values for $\log_{10}\beta_4^\circ$(298.15 K), $\log_{10}\beta_5^\circ$(298.15 K), $\Delta_f G_m^\circ$($\mathrm{Np(CO_3)_4^{4-}}$, 298.15 K), and $\Delta_f G_m^\circ$($\mathrm{Np(CO_3)_5^{6-}}$, 298.15 K) are not consistent with the unchanged value of $\log_{10}K^\circ$ = -17.79 for the reaction $4\,\mathrm{CO_3^{2-}} + 2\,\mathrm{H_2O(l)} + \mathrm{NpO_2(am,hyd)} \Leftrightarrow \mathrm{Np(CO_3)_4^{4-}} + 4\,\mathrm{OH^-}$. Guillaumont et al. (2003) continue:

"The reaction above should have been replaced by the reaction:

$$\mathrm{Np^{4+}} + 4\,\mathrm{CO_3^{2-}} \Leftrightarrow \mathrm{Np(CO_3)_4^{4-}}$$

together with reaction

$$\mathrm{Np^{4+}} + 5\,\mathrm{CO_3^{2-}} \Leftrightarrow \mathrm{Np(CO_3)_5^{6-}}$$

whose equilibrium constants can be calculated from $\Delta_f G_m°$ selections in [2001LEM/FUG] (cf. *Update*, p. 327)." Therefore, the selection by Guillaumont et al. (2003) for these constants is erroneous and different from ours. The opaqueness of the original discussion in Lemire et al. (2001) seems to have caused some confusion in the update by Guillaumont et al. (2003) which got from bad to worse in the errata to the update.

Lemire et al. (2001) derived a value for $\varepsilon(Np(CO_3)_5^{6-}, K^+)$ as follows. From the reanalysis of data for

$$Np(CO_3)_4^{4-} + CO_3^{2-} \Leftrightarrow Np(CO_3)_5^{6-}$$

and for

$$NpO_2(am, hyd) + 4\ CO_3^{2-} + 2\ H_2O(l) \Leftrightarrow Np(CO_3)_4^{4-} + 4\ OH^-$$

Lemire et al. (2001) obtained $\Delta\varepsilon = (0.45 \pm 0.68)\ kg \cdot mol^{-1}$ for the combined reaction

$$NpO_2(am, hyd) + 5\ CO_3^{2-} + 2\ H_2O(l) \Leftrightarrow Np(CO_3)_5^{6-} + 4\ OH^-$$

From this $\Delta\varepsilon$ and the selected values for $\varepsilon(OH^-, K^+)$ and $\varepsilon(CO_3^{2-}, K^+)$, Lemire et al. (2001) calculated

$$\varepsilon(Np(CO_3)_5^{6-}, K^+) = -(0.73 \pm 0.68)\ kg \cdot mol^{-1}$$

which we accept for our database, although we were not able to reproduce this value, but rather got a value of $-(0.71 \pm 0.69)\ kg \cdot mol^{-1}$.

We estimated

$$\varepsilon(Np(CO_3)_4^{4-}, Na^+) = -(0.20 \pm 0.30)\ kg \cdot mol^{-1}$$

$$\varepsilon(Np(CO_3)_5^{6-}, Na^+) = -(0.30 \pm 0.50)\ kg \cdot mol^{-1}$$

by using a method based on charge correlations (see Appendix A) and include these values in our database.

4.7.2.1.4 Ternary Np(IV) hydroxide-carbonate complexes

The increase in the solubility of NpO_2(am, hyd) in carbonate solutions compared to carbonate-free solutions was interpreted by three experimental studies in terms of the formation of one or two of the ternary complexes $Np(OH)_3(CO_3)^-$, $Np(OH)_4(CO_3)^{2-}$, $Np(OH)_4(CO_3)_2^{4-}$, and $Np(OH)_2(CO_3)_2^{2-}$. Guillaumont et al. (2003) selected none of the equilibrium constants of these ternary complexes because of the uncertainty of the solubility products of the solids used in the experiments. Further experimental investigations are needed to close this gap of chemical knowledge.

Hummel & Berner (2002) estimated maximum feasible values for ternary hydroxide-carbonate complexes of U(IV), Np(IV), and Pu(IV) at low bicarbonate concentrations. They assumed that $AnCO_3(OH)_3^-$ is the dominant mixed actinide hydroxide-carbonate complex and adjusted the formation constants to the maximal feasible values that are still consistent with the available experimental solubility data. In the case of $NpCO_3(OH)_3^-$ they obtained

$$Np^{4+} + CO_3^{2-} + 3\ H_2O(l) \Leftrightarrow NpCO_3(OH)_3^- + 3\ H^+$$

$$\log_{10}{}^*K°(298.15\ K) = 2$$

We estimated the value for the ion interaction coefficient

$$\varepsilon(NpCO_3(OH)_3^-, Na^+) = -(0.05 \pm 0.10)\ kg \cdot mol^{-1}$$

based on charge correlations (see Appendix A). Both of these estimated values for $NpCO_3(OH)_3^-$ are included in our database as supplemental data.

4.7.2.1.5 Np(III) carbonate complexes

Np^{3+} can be prepared and stabilized 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 stabilize neptunium in the +4 oxidation state, and Np(III) is usually oxidized 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) and Guillaumont et al. (2003). Hummel & Berner (2002) estimated stability constants for $NpCO_3^+$, $Np(CO_3)_2^-$, and $Np(CO_3)_3^{3-}$ by adopting the values for the corresponding Am(III) carbonate complexes. From the revised data by Guillaumont et al. (2003) for these complexes the following estimates are obtained

$$Np^{3+} + CO_3^{2-} \Leftrightarrow NpCO_3^+$$

$$\log_{10}\beta_1°(298.15\ K) = 8.0$$

$$Np^{3+} + 2\ CO_3^{2-} \Leftrightarrow Np(CO_3)_2^-$$

$$\log_{10}\beta_2°(298.15\ K) = 12.9$$

$$Np^{3+} + 3\ CO_3^{2-} \Leftrightarrow Np(CO_3)_3^{3-}$$

$$\log_{10}\beta_3°(298.15\ K) = 15.0$$

These values are included in our database as supplemental data together with the ion interaction coefficients

$$\varepsilon(NpCO_3^+, Cl^-) = (0.01 \pm 0.05)\ kg\cdot mol^{-1}$$

$$\varepsilon(NpCO_3^+, ClO_4^-) = (0.17 \pm 0.05)\ kg\cdot mol^{-1}$$

$$\varepsilon(Np(CO_3)_2^-, Na^+) = -(0.14 \pm 0.06)\ kg\cdot mol^{-1}$$

$$\varepsilon(Np(CO_3)_3^{3-}, Na^+) = -(0.23 \pm 0.07)\ kg\cdot mol^{-1}$$

that we estimated by adopting the values of the corresponding Am(III) carbonate complexes, see Section 2.7.1.2.

4.7.2.2 Solid neptunium carbonates

4.7.2.2.1 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 characterized. 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

$$(NH_4)_4NpO_2(CO_3)_3(s) \Leftrightarrow 4\,NH_4^+ + NpO_2^{2+} + 3\,CO_3^{2-}$$

$$\log_{10}K_{s,0}°(298.15\text{ K}) = -(26.81 \pm 0.35)$$

$$K_4NpO_2(CO_3)_3(s) \Leftrightarrow 4\,K^+ + NpO_2^{2+} + 3\,CO_3^{2-}$$

$$\log_{10}K_{s,0}°(298.15\text{ K}) = -(26.40 \pm 0.90)$$

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 Section 4.7.2.1.1) and corrected to zero ionic strength

$$NpO_2CO_3(s) \Leftrightarrow NpO_2^{2+} + CO_3^{2-}$$

$$\log_{10}K_{s,0}°(298.15\text{ K}) = -(14.60 \pm 0.47)$$

The latter three equilibria are included in our database.

4.7.2.2.2 Solid Np(V) carbonates

Sodium neptunium(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 they suspected a solid phase dehydration transformation 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, one for $NaNpO_2CO_3\cdot3.5H_2O$(s, fresh), and one for $NaNpO_2CO_3$(s, aged). Guillaumont et al. (2003) revised this choice and based their own selection of a single solubility product for $NaNpO_2CO_3\cdot3.5H_2O(cr)$ on five experimental studies in 0.1 and 1 M $NaClO_4$ and 0.1, 1.0, and 3.0 M NaCl that were exclusively done with well-characterized crystalline compounds aged at least for several weeks, and not with fresh, gelatinous precipitates. They selected the following solubility product

$$NaNpO_2CO_3\cdot3.5H_2O(cr) \Leftrightarrow Na^+ + NpO_2^+ + CO_3^{2-} + 3.5\,H_2O(l)$$

$$\log_{10}K_{s,0}°(298.15\text{ K}) = -(11.00 \pm 0.24)$$

which is also included in our database.

The solubility product for $Na_3NpO_2(CO_3)_2(cr)$ selected by Guillaumont et al. (2003)

$$Na_3NpO_2(CO_3)_2(cr) \Leftrightarrow 3\,Na^+ + NpO_2^+ + 2\,CO_3^{2-}$$

$$\log_{10}K_{s,0}°(\,298.15\text{ K}) = -(14.22 \pm 0.50)$$

was derived from solubility data of a well-characterized solid (X-ray diffraction) in 5 M NaCl and extrapolated to $I = 0$ using SIT. It is also included in our database.

Potassium neptunium(V) carbonates: Two experimental studies investigated the solubility of $KNpO_2CO_3\cdot xH_2O(s)$ in aqueous KCl-K_2CO_3 solutions with m(KCl) > m(K_2CO_3) and of $K_3NpO_2(CO_3)_2\cdot xH_2O(s)$ in pure K_2CO_3 solutions. Based on the experiments with $KNpO_2CO_3(s)$, Guillaumont et al. (2003) obtained the following equilibrium constant using SIT

$$KNpO_2CO_3(s) + 2\,CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-} + K^+$$

$$\log_{10}K_{s,3}°(298.15\ \text{K}) = -(17.65 \pm 0.11)$$

with

$$\Delta\varepsilon(298.15\ \text{K}) = -(0.25 \pm 0.06)\ \text{kg}\cdot\text{mol}^{-1}$$

From this value for Δε, Guillaumont et al. (2003) calculated $\varepsilon(\text{NpO}_2(\text{CO}_3)_3^{5-}, \text{K}^+) = -(0.22 \pm 0.03)$ kg · mol^{-1} by using the selected values $\varepsilon(\text{CO}_3^{2-}, \text{K}^+) = (0.02 \pm 0.01)$ kg·mol^{-1} and $\varepsilon(\text{K}^+, \text{Cl}^-) = (0.00 \pm 0.01)$ kg·mol^{-1}.

The SIT analysis by Guillaumont et al. (2003) for the experiments with $\text{K}_3\text{NpO}_2(\text{CO}_3)_2\cdot x\text{H}_2\text{O(s)}$ resulted in

$$\text{K}_3\text{NpO}_2(\text{CO}_3)_2\text{(s)} + \text{CO}_3^{2-} \Leftrightarrow \text{NpO}_2(\text{CO}_3)_3^{5-} + 3\ \text{K}^+$$

$$\log_{10}K_{s,3}°(298.15\ \text{K}) = -(9.96 \pm 0.06)$$

with

$$\Delta\varepsilon(298.15\ \text{K}) = -(0.22 \pm 0.02)\ \text{kg}\cdot\text{mol}^{-1}$$

From this Δε and the selected $\varepsilon(\text{CO}_3^{2-}, \text{K}^+)$, Guillaumont et al. (2003) obtained a second value for $\varepsilon(\text{NpO}_2(\text{CO}_3)_3^{5-}, \text{K}^+) = -(0.23 \pm 0.02)$ kg·mol^{-1}; note that we could not reproduce this value but obtained -(0.26 ± 0.04 kg·mol^{-1}). Averaging both values for $\varepsilon(\text{NpO}_2(\text{CO}_3)_3^{5-}, \text{K}^+)$, Guillaumont et al. (2003) selected

$$\varepsilon(\text{NpO}_2(\text{CO}_3)_3^{5-}, \text{K}^+) = -(0.22 \pm 0.03)\ \text{kg}\cdot\text{mol}^{-1}$$

which is also selected for our database.

Combining $\log_{10}K_{s,3}°(298.15\ \text{K})$ for $\text{KNpO}_2\text{CO}_3\text{(s)} + 2\ \text{CO}_3^{2-} \Leftrightarrow \text{NpO}_2(\text{CO}_3)_3^{5-} + \text{K}^+$ or $\log_{10}K_{s,3}°(298.15\ \text{K})$ for $\text{K}_3\text{NpO}_2(\text{CO}_3)_2\text{(s)} + \text{CO}_3^{2-} \Leftrightarrow \text{NpO}_2(\text{CO}_3)_3^{5-} + 3\ \text{K}^+$ with $\log_{10}\beta_3°$ for $\text{NpO}_2^+ + 3\ \text{CO}_3^{2-} \Leftrightarrow \text{NpO}_2(\text{CO}_3)_3^{5-}$ results in

$$\text{KNpO}_2\text{CO}_3\text{(s)} \Leftrightarrow \text{K}^+ + \text{NpO}_2^+ + \text{CO}_3^{2-}$$

$$\log_{10}K_{s,0}°(298.15\ \text{K}) = -(13.15 \pm 0.19)$$

and

$$\text{K}_3\text{NpO}_2(\text{CO}_3)_2\text{(s)} \Leftrightarrow 3\ \text{K}^+ + \text{NpO}_2^+ + 2\ \text{CO}_3^{2-}$$

$$\log_{10}K_{s,0}°(298.15\ \text{K}) = -(15.46 \pm 0.16)$$

which are included in our database.

Note that Guillaumont et al. (2003) neglected the water contents in the solids, since they are not exactly known. The solubility of the potassium dioxoneptunium(V) carbonates is roughly two orders of magnitude lower than that of the corresponding sodium dioxoneptunium(V) carbonates. Therefore the solubility of Np(V) in Na-K-Cl-CO_3 solutions will be controlled by $\text{KNpO}_2\text{CO}_3\text{(s)}$, even if the concentration of Na^+ is much higher than that of K^+ (Al Mahamid et al., 1998).

4.7.2.2.3 Solid Np(IV) carbonates

Np(IV) solubility in neutral media is $10^{-(9\pm1)}$ M and was interpreted in terms of the equilibrium

$$\text{NpO}_2\text{(am, hyd)} + 2\ \text{H}_2\text{O(l)} \Leftrightarrow \text{Np(OH)}_4\text{(aq)}$$

(see Section 4.3.1.5). 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 $\text{Np(CO}_3)_4^{4-}$ and $\text{Np(CO}_3)_5^{6-}$ 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).

4.7.3 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.

4.7.4 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 the following data for these complexes, which are also included in our database:

$$Np^{4+} + SCN^- \Leftrightarrow NpSCN^{3+}$$

$$\log_{10}\beta_1°(298.15\text{ K}) = (3.0 \pm 0.3)$$

$$\Delta_r H_m°(298.15\text{ K}) = -(7 \pm 3)\text{ kJ}\cdot\text{mol}^{-1}$$

$$Np^{4+} + 2\ SCN^- \Leftrightarrow Np(SCN)_2^{2+}$$

$$\log_{10}\beta_2°(298.15\text{ K}) = (4.1 \pm 0.5)$$

$$\Delta_r H_m°(298.15\text{ K}) = -(9 \pm 9)\text{ kJ}\cdot\text{mol}^{-1}$$

$$Np^{4+} + 3\ SCN^- \Leftrightarrow Np(SCN)_3^{+}$$

$$\log_{10}\beta_3°(298.15\text{ K}) = (4.8 \pm 0.5)$$

$$\Delta_r H_m°(298.15\text{ K}) = -(13 \pm 9)\text{ kJ}\cdot\text{mol}^{-1}$$

These data are based on solvent extraction experiments in 2 M $(H, Na)ClO_4$ solutions at 10, 25 and 40°C. Lemire et al. (2001) used SIT to extrapolate the experimental data to I = 0, the reaction enthalpies, however, were assumed to be independent of ionic strength.

For the 1:1 complex they assumed that $\Delta\varepsilon_1$ is identical to the value reported by Grenthe et al. (1992) for the corresponding U(IV) system. In order to extrapolate experimental data for the reaction $U^{4+} + SCN^- \Leftrightarrow USCN^{3+}$ to zero ionic strength, Grenthe et al. (1992) used $\Delta\varepsilon_1 = -(0.13 \pm 0.05)\text{ kg}\cdot\text{mol}^{-1}$, which they adopted from the corresponding reaction with Cl^-, see their Chapter V.7.1.4.1.c (note that there is an inconsistency in Grenthe et al. 1992, which we could not resolve, as these authors also report a value of $\Delta\varepsilon_1 = -(0.29 \pm 0.08)\text{ kg}\cdot\text{mol}^{-1}$ in their Chapter V.4.2.1.2.c on U(IV) chloride complexes). Thus, in the end, the value $\Delta\varepsilon_1 = -(0.13 \pm 0.10)\text{ kg}\cdot\text{mol}^{-1}$ used by Lemire et al. (2001) for $Np^{4+} + SCN^- \Leftrightarrow NpSCN^{3+}$ is actually the $\Delta\varepsilon_1$ value determined by Grenthe et al. (1992) for $U^{4+} + Cl^- \Leftrightarrow UCl^{3+}$ with the uncertainty increased by ± 0.05 to account for the estimation. Lemire et al. (2001) did not comment on why they did not use instead the value $\Delta\varepsilon_1 = -(0.15 \pm 0.18)\text{ kg}\cdot\text{mol}^{-1}$ that they derived from experiments for the reaction $Np^{4+} + Cl^- \Leftrightarrow NpCl^{3+}$.

For the SIT extrapolation of data for the 1:2 complex, Lemire et al. (2001) assumed that $\Delta\varepsilon_2$, too, is identical to the value of the corresponding U(IV) system. Grenthe et al. (1992) calculated $\Delta\varepsilon_2 = -(0.56 \pm 0.14)\text{ kg}\cdot\text{mol}^{-1}$ for the reaction $U^{4+} + 2\ SCN^- \Leftrightarrow U(SCN)_2^{2+}$ from the selected values $\varepsilon(U^{4+}, ClO_4^-) = -(0.76 \pm 0.06)\text{ kg}\cdot\text{mol}^{-1}$, $\varepsilon(SCN^-, Na^+) = (0.05 \pm 0.01)\text{ kg}\cdot\text{mol}^{-1}$, and $\varepsilon(U(SCN)_2^{2+}, ClO_4^-)$, which they assumed to be equal to $\varepsilon(UF_2^{2+}, ClO_4^-) = (0.3 \pm 0.1)\text{ kg}\cdot\text{mol}^{-1}$.

Lemire et al. (2001) increased the uncertainty for the calculated value of $\Delta\varepsilon_2$ by ± 0.05 to account for the estimation, resulting in $\Delta\varepsilon_2 = -(0.56 \pm 0.19)\ \text{kg}\cdot\text{mol}^{-1}$.

From their values for $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$, and from the selected values $\varepsilon(\text{Np}^{4+}, \text{ClO}_4^-) = (0.84 \pm 0.06)\ \text{kg}\cdot\text{mol}^{-1}$ and $\varepsilon(\text{SCN}^-, \text{Na}^+) = (0.05 \pm 0.01)\ \text{kg}\cdot\text{mol}^{-1}$, Lemire et al. (2001) obtained and selected

$$\varepsilon(\text{NpSCN}^{3+}, \text{ClO}_4^-) = (0.76 \pm 0.12)\ \text{kg}\cdot\text{mol}^{-1}$$

$$\varepsilon(\text{Np(SCN)}_2^{2+}, \text{ClO}_4^-) = (0.38 \pm 0.20)\ \text{kg}\cdot\text{mol}^{-1}$$

which are also included in our database. Note that in their Table B-4, Rand et al. (2008) mistook $\varepsilon(\text{NpSCN}^{3+}, \text{ClO}_4^-)$ for $\varepsilon(\text{NpSCN}^{3+}, \text{Cl}^-)$.

In order to calculate $\Delta\varepsilon_3$ for $\text{Np}^{4+} + 3\ \text{SCN}^- \Leftrightarrow \text{Np(SCN)}_3^+$, Lemire et al. (2001) assumed that $\varepsilon(\text{Np(SCN)}_3^+, \text{ClO}_4^-) = \varepsilon(\text{AmF}_2^+, \text{ClO}_4^-)$ and selected

$$\varepsilon(\text{Np(SCN)}_3^+, \text{ClO}_4^-) = (0.17 \pm 0.04)\ \text{kg}\cdot\text{mol}^{-1}$$

which is also selected for our database.

We estimated the corresponding ion interaction coefficients for the chloride system based on charge correlations (see Appendix A) and accept

$$\varepsilon(\text{NpSCN}^{3+}, \text{Cl}^-) = (0.25 \pm 0.10)\ \text{kg}\cdot\text{mol}^{-1}$$

$$\varepsilon(\text{Np(SCN)}_2^{2+}, \text{Cl}^-) = (0.15 \pm 0.10)\ \text{kg}\cdot\text{mol}^{-1}$$

$$\varepsilon(\text{Np(SCN)}_3^+, \text{Cl}^-) = (0.05 \pm 0.10)\ \text{kg}\cdot\text{mol}^{-1}$$

for our database.

For Np(V) an equilibrium constant for $\text{NpO}_2\text{SCN(aq)}$ was given as a guideline by Lemire et al. (2001) and is considered as supplemental data in our database:

$$NpO_2^+ + SCN^- \Leftrightarrow NpO_2SCN(aq)$$

$$\log_{10}\beta_1^\circ(298.15\ K) = (0.08 \pm 0.30)$$

4.7.5 Neptunium silicon compounds and complexes

Thermodynamic data for silicon compounds and complexes contained in our database are discussed in Chapter 8.

4.8 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 $\text{Sr}_3\text{NpO}_6\text{(cr)}$, $\text{Ba}_3\text{NpO}_6\text{(cr)}$, $\text{Ba}_2\text{MgNpO}_6\text{(cr)}$, $\text{Ba}_2\text{CaNpO}_6\text{(cr)}$, $\text{Ba}_2\text{SrNpO}_6\text{(cr)}$, $\text{Li}_2\text{NpO}_4\text{(cr)}$, $\alpha\text{-Na}_2\text{NpO}_4$, $\beta\text{-Na}_2\text{NpO}_4$, $\beta\text{-Na}_4\text{NpO}_5$, $\text{Na}_2\text{Np}_2\text{O}_7\text{(cr)}$, $\text{K}_2\text{NpO}_4\text{(cr)}$, $\text{K}_2\text{Np}_2\text{O}_7\text{(cr)}$, $\text{Rb}_2\text{Np}_2\text{O}_7\text{(cr)}$ and $\text{Cs}_2\text{NpO}_4\text{(cr)}$. There are no solubility products or $\Delta_f G_m^\circ$ values for any of these phases. They are not included in our database.

Table 4.1: Neptunium data selected by NEA (Lemire et al. 2001 and Guillaumont et al. 2003) but not included in TDB Version 12/07. For explanations see text.

Gases	Np(g) [a d], NpF(g) [a], NpF_2(g) [a], NpF_3(g) [a], NpF_4(g) [a d], NpF_6(g) [a d], $NpCl_3$(g) [a d], $NpCl_4$(g) [a d]
Solids	β-Np [b], γ-Np [b], NpO_2(cr) [a], Np_2O_5(cr) [a], $NpO_2(OH)_2$(cr) [a], NpF_3(cr) [a], NpF_4(cr) [a d], NpF_5(cr) [a] , NpF_6(cr) [a d], NpO_2F_2(cr) [b], $NpCl_3$(cr) [a d], $NpCl_4$(cr) [a d], $NpOCl_2$(cr) [a], $NpBr_3$(cr) [a], $NpBr_4$(cr) [a], $NpOBr_2$(cr) [a], NpI_3(cr) [a], NpN(cr) [a], $NpO_2(NO_3)_2\cdot 6H_2O$(s) [a], NpSb(cr) [b], $NpC_{0.91}$(cr) [a], Np_2C_3(cr) [a], Sr_3NpO_6(cr) [b], Ba_3NpO_6(cr) [b], Ba_2MgNpO_6(cr) [b], Ba_2CaNpO_6(cr) [b], Ba_2SrNpO_6(cr) [b], Li_2NpO_4(cr) [b], α-Na_2NpO_4 [b], β-Na_2NpO_4 [b], β-Na_4NpO_5 [b], $Na_2Np_2O_7$(cr) [b], Na_3NpF_8(cr) [a c], K_2NpO_4(cr) [b], $K_2Np_2O_7$(cr) [b], $Rb_2Np_2O_7$(cr) [b], Cs_2NpO_4(cr) [b], Cs_2NpCl_6(cr) [a], $Cs_2NpO_2Cl_4$(cr) [b], $Cs_3NpO_2Cl_4$(cr) [b], Cs_2NpBr_6(cr) [a], $Cs_2NaNpCl_6$(cr) [b]
Liquids	NpF_6(l) [b], $NpCl_4$(l) [b]
Aqueous species	NpO_2ClO_4(aq) [b]

[a] Single species data including $\Delta_f G_m°$

[b] Single species data excluding $\Delta_f G_m°$

[c] Reaction data including $\log_{10}K°$

[d] Reaction data excluding $\log_{10}K°$

Table 4.2: Selected neptunium data. All data included in TDB Version 12/07 are taken from Lemire et al. (2001) and Guillaumont et al. (2003) with the exception of those marked with an asterisk (*). Supplemental data are in italics. New or changed data with respect to TDB Version 01/01 (Hummel et al. 2002) are shaded.

		TDB Version 01/01				**TDB Version 12/07**				
Name	**Redox**	$\Delta_f G_m^\circ$ [$kJ \cdot mol^{-1}$]	$\Delta_f H_m^\circ$ [$kJ \cdot mol^{-1}$]	S_m° [$J \cdot K^{-1} \cdot mol^{-1}$]	$C_{p,m}^\circ$ [$J \cdot K^{-1} \cdot mol^{-1}$]	$\Delta_f G_m^\circ$ [$kJ \cdot mol^{-1}$]	$\Delta_f H_m^\circ$ [$kJ \cdot mol^{-1}$]	S_m° [$J \cdot K^{-1} \cdot mol^{-1}$]	$C_{p,m}^\circ$ [$J \cdot K^{-1} \cdot mol^{-1}$]	**Species**
Np(cr)	0	0.0	0.0	50.46 ± 0.80	29.62 ± 0.80	0.0	0.0	50.46 ± 0.80	29.62 ± 0.80	Np(cr)
Np+3	III	-512.9 ± 5.7	-527.2 ± 2.1	-193.6 ± 20.3	-	-512.9 ± 5.7	-527.2 ± 2.1	-193.6 ± 20.3	-	Np^{3+}
Np+4	IV	-491.8 ± 5.6	-556.0 ± 4.2	-426.4 ± 12.4	-	-491.8 ± 5.6	-556.0 ± 4.2	-426.4 ± 12.4	-	Np^{4+}
NpO2+	V	-907.8 ± 5.6	-978.2 ± 4.6	-45.9 ± 10.7	-4 ± 25	-907.8 ± 5.6	-978.2 ± 4.6	-45.9 ± 10.7	-4 ± 25	NpO_2^+
NpO2+2	VI	-795.9 ± 5.6	-860.7 ± 4.7	-92.4 ± 10.5	-	-795.9 ± 5.6	-860.7 ± 4.7	-92.4 ± 10.5	-	NpO_2^{2+}

		TDB Version 01/01		**TDB Version 12/07**		
Name	**Redox**	$\log_{10}\beta^\circ$	$\Delta_r H_m^\circ$ [$kJ \cdot mol^{-1}$]	$\log_{10}\beta^\circ$	$\Delta_r H_m^\circ$ [$kJ \cdot mol^{-1}$]	**Reaction**
NpO2OH+	VI	-5.1 ± 0.4	-	-5.1 ± 0.4	-	$NpO_2^{2+} + H_2O(l) \Leftrightarrow NpO_2OH^+ + H^+$
NpO2(OH)3-	VI	≤ -19	-	*(≤ -20)**	-	$NpO_2^{2+} + 3\ H_2O(l) \Leftrightarrow NpO_2(OH)_3^- + 3\ H^+$
NpO2(OH)4-2	VI	≤ -33	-	*(≤ -32)**	-	$NpO_2^{2+} + 4\ H_2O(l) \Leftrightarrow NpO_2(OH)_4^{2-} + 4\ H^+$
(NpO2)2(OH)2+2	VI	-6.27 ± 0.21	-	-6.27 ± 0.21	-	$2\ NpO_2^{2+} + 2\ H_2O(l) \Leftrightarrow (NpO_2)_2(OH)_2^{2+} + 2\ H^+$
(NpO2)3(OH)5+	VI	-17.12 ± 0.22	-	-17.12 ± 0.22	-	$3\ NpO_2^{2+} + 5\ H_2O(l) \Leftrightarrow (NpO_2)_3(OH)_5^+ + 5\ H^+$
NpO2F+	VI	4.57 ± 0.07	-	4.57 ± 0.07	-	$NpO_2^{2+} + F^- \Leftrightarrow NpO_2F^+$
NpO2F2	VI	7.60 ± 0.08	-	7.60 ± 0.08	-	$NpO_2^{2+} + 2\ F^- \Leftrightarrow NpO_2F_2(aq)$
NpO2Cl+	VI	0.40 ± 0.17	-	0.40 ± 0.17	-	$NpO_2^{2+} + Cl^- \Leftrightarrow NpO_2Cl^+$
NpO2IO3+	VI	-	-	1.2 ± 0.3	-	$NpO_2^{2+} + IO_3^- \Leftrightarrow NpO_2IO_3^+$
NpO2SO4	VI	3.28 ± 0.06	16.7 ± 0.5	3.28 ± 0.06	16.7 ± 0.5	$NpO_2^{2+} + SO_4^{2-} \Leftrightarrow NpO_2SO_4(aq)$
NpO2(SO4)2-2	VI	4.70 ± 0.10	26.0 ± 1.2	4.70 ± 0.10	26.0 ± 1.2	$NpO_2^{2+} + 2\ SO_4^{2-} \Leftrightarrow NpO_2(SO_4)_2^{2-}$
NpO2H2PO4+	VI	3.32 ± 0.50	-	3.32 ± 0.50	-	$NpO_2^{2+} + H_2PO_4^- \Leftrightarrow NpO_2H_2PO_4^+$
NpO2HPO4	VI	6.2 ± 0.7	-	6.2 ± 0.7	-	$NpO_2^{2+} + HPO_4^{2-} \Leftrightarrow NpO_2HPO_4(aq)$
NpO2(HPO4)2-2	VI	9.5 ± 1.0	-	9.5 ± 1.0	-	$NpO_2^{2+} + 2\ HPO_4^{2-} \Leftrightarrow NpO_2(HPO_4)_2^{2-}$
NpO2CO3	VI	9.32 ± 0.61	-	9.32 ± 0.61	-	$NpO_2^{2+} + CO_3^{2-} \Leftrightarrow NpO_2CO_3(aq)$
NpO2(CO3)2-2	VI	16.52 ± 0.73	-	16.52 ± 0.73	-	$NpO_2^{2+} + 2\ CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_2^{2-}$
NpO2(CO3)3-4	VI	19.37 ± 0.19	-41.9 ± 4.1	19.37 ± 0.19	-41.9 ± 4.1	$NpO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{4-}$
(NpO2)3(CO3)6-6	VI	49.84 ± 1.56	-	49.84 ± 1.56	-	$3\ NpO_2^{2+} + 6\ CO_3^{2-} \Leftrightarrow (NpO_2)_3(CO_3)_6^{6-}$

		TDB Version 01/01		**TDB Version 12/07**		
Name	**Redox**	**$\log_{10}\beta°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**$\log_{10}\beta°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**Reaction**
(NpO2)2CO3(OH)3-	VI	-2.87 ± 1.64	-	-2.87 ± 1.64	-	$2NpO_2^{2+} + CO_3^{2-} + 3H_2O(l) \Leftrightarrow (NpO_2)_2CO_3(OH)_3^- + 3H^+$
(UO2)2NpO2(CO3)6-6	VI	53.59 ± 2.70	-	53.59 ± 2.70	-	$2\ UO_2^{2+} + NpO_2^{2+} + 6\ CO_3^{2-} \Leftrightarrow (UO_2)_2NpO_2(CO_3)_6^{6-}$
NpO2+	VI/V	19.59 ± 0.07	-	19.59 ± 0.07	-	$NpO_2^{2+} + e^- \Leftrightarrow NpO_2^+$
NpO2(OH)	V	-11.3 ± 0.7	S_m° 25 ± 60	-11.3 ± 0.7	S_m° 25 ± 60	$NpO_2^+ + H_2O(l) \Leftrightarrow NpO_2OH(aq) + H^+$
NpO2(OH)2-	V	-23.6 ± 0.5	S_m° 40 ± 100	-23.6 ± 0.5	S_m° 40 ± 100	$NpO_2^+ + 2\ H_2O(l) \Leftrightarrow NpO_2(OH)_2^- + 2\ H^+$
NpO2F	V	1.2 ± 0.3	-	1.2 ± 0.3	-	$NpO_2^+ + F^- \Leftrightarrow NpO_2F(aq)$
NpO2IO3	V	-	-	0.5 ± 0.3	-	$NpO_2^+ + IO_3^- \Leftrightarrow NpO_2IO_3(aq)$
NpO2SO4-	V	0.44 ± 0.27	23.2 ± 7.2	0.44 ± 0.27	23.2 ± 7.2	$NpO_2^+ + SO_4^{2-} \Leftrightarrow NpO_2SO_4^-$
NpO2HPO4-	V	2.95 ± 0.10	-	2.95 ± 0.10	-	$NpO_2^+ + HPO_4^{2-} \Leftrightarrow NpO_2HPO_4^-$
NpO2CO3-	V	4.96 ± 0.06	-	4.96 ± 0.06	-	$NpO_2^+ + CO_3^{2-} \Leftrightarrow NpO_2CO_3^-$
NpO2(CO3)2-3	V	6.53 ± 0.10	-	6.53 ± 0.10	-	$NpO_2^+ + 2\ CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_2^{3-}$
NpO2(CO3)3-5	V	5.50 ± 0.15	-13.3 ± 5.1	5.50 ± 0.15	-13.3 ± 5.1	$NpO_2^+ + 3\ CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-}$
NpO2(CO3)2OH-4	V	-5.30 ± 1.17	-	-5.30 ± 1.17	-	$NpO_2^+ + 2\ CO_3^{2-} + H_2O(l) \Leftrightarrow NpO_2(CO_3)_2OH^{4-} + H^+$
NpO2SCN	V	-	-	*(0.08 ± 0.30)*[a]	-	$NpO_2^+ + SCN^- \Leftrightarrow NpO_2SCN(aq)$
Np+4	VI/IV	29.80 ± 0.14	-	29.80 ± 0.14	-	$NpO_2^{2+} + 4\ H^+ + 2\ e^- \Leftrightarrow Np^{4+} + 2\ H_2O(l)$
NpOH+3	IV	-0.29 ± 1.00	-	0.55 ± 0.20	-	$Np^{4+} + H_2O(l) \Leftrightarrow NpOH^{3+} + H^+$
Np(OH)2+2	IV	-	-	0.35 ± 0.30	-	$Np^{4+} + 2\ H_2O(l) \Leftrightarrow Np(OH)_2^{2+} + 2\ H^+$
Np(OH)3+	IV	-	-	*(-2.8 ± 1.0)**	-	$Np^{4+} + 3\ H_2O(l) \Leftrightarrow Np(OH)_3^+ + 3\ H^+$
Np(OH)4	IV	-9.8 ± 1.1	-	-8.3 ± 1.1	-	$Np^{4+} + 4\ H_2O(l) \Leftrightarrow Np(OH)_4(aq) + 4\ H^+$
NpF+3	IV	8.96 ± 0.14	1.5 ± 2.0	8.96 ± 0.14	1.5 ± 2.0	$Np^{4+} + F^- \Leftrightarrow NpF^{3+}$
NpF2+2	IV	15.7 ± 0.3	-	15.7 ± 0.3	-	$Np^{4+} + 2\ F^- \Leftrightarrow NpF_2^{2+}$
NpCl+3	IV	1.5 ± 0.3	-	1.5 ± 0.3	-	$Np^{4+} + Cl^- \Leftrightarrow NpCl^{3+}$
NpI+3	IV	-	-	1.5 ± 0.4	-	$Np^{4+} + I^- \Leftrightarrow NpI^{3+}$
NpSO4+2	IV	6.85 ± 0.16	29.8 ± 8.9	6.85 ± 0.16	29.8 ± 8.9	$Np^{4+} + SO_4^{2-} \Leftrightarrow NpSO_4^{2+}$
Np(SO4)2	IV	11.05 ± 0.27	55.4 ± 3.9	11.05 ± 0.27	55.4 ± 3.9	$Np^{4+} + 2\ SO_4^{2-} \Leftrightarrow Np(SO_4)_2(aq)$
NpNO3+3	IV	1.90 ± 0.15	-	1.90 ± 0.15	-	$Np^{4+} + NO_3^- \Leftrightarrow NpNO_3^{3+}$
Np(CO3)4-4	IV	(36.69 ± 1.03)[b]	-	(38.9 ± 0.5)*	-	$Np^{4+} + 4\ CO_3^{2-} \Leftrightarrow Np(CO_3)_4^{4-}$
Np(CO3)5-6	IV	(35.62 ± 1.06)[c]	-	(37.8 ± 0.6)*	-	$Np^{4+} + 5\ CO_3^{2-} \Leftrightarrow Np(CO_3)_5^{6-}$
NpCO3(OH)3-	IV	-	-	*(2)**	-	$Np^{4+} + CO_3^{2-} + 3\ H_2O(l) \Leftrightarrow NpCO_3(OH)_3^- + 3\ H^+$
NpSCN+3	IV	-	-	3.0 ± 0.3	-7 ± 3	$Np^{4+} + SCN^- \Leftrightarrow NpSCN^{3+}$

		TDB Version 01/01		**TDB Version 12/07**		
Name	**Redox**	**$\log_{10}\beta°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**$\log_{10}\beta°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**Reaction**
Np(SCN)2+2	IV	-	-	4.1 ± 0.5	-9 ± 9	$Np^{4+} + 2\ SCN^- \Leftrightarrow Np(SCN)_2^{2+}$
Np(SCN)3+	IV	-	-	4.8 ± 0.5	-13 ± 9	$Np^{4+} + 3\ SCN^- \Leftrightarrow Np(SCN)_3^{+}$
Np+3	VI/III	33.50 ± 0.23	-	33.50 ± 0.23	-	$NpO_2^{2+} + 4\ H^+ + 3\ e^- \Leftrightarrow Np^{3+} + 2\ H_2O(l)$
NpOH+2	III	-6.8 ± 0.3	-	-6.8 ± 0.3	-	$Np^{3+} + H_2O(l) \Leftrightarrow NpOH^{2+} + H^+$
Np(OH)2+	III	-	-	*(-14.7)**	-	$Np^{3+} + 2\ H_2O(l) \Leftrightarrow Np(OH)_2^{+} + 2\ H^+$
Np(OH)3	III	-	-	*(-25.8)**	-	$Np^{3+} + 3\ H_2O(l) \Leftrightarrow Np(OH)_3(aq) + 3\ H^+$
NpF+2	III	-	-	*(3.4)**	-	$Np^{3+} + F^- \Leftrightarrow NpF^{2+}$
NpF2+	III	-	-	*(5.8)**	-	$Np^{3+} + 2\ F^- \Leftrightarrow NpF_2^{+}$
NpCl+2	III	-	-	*(0.24)**	-	$Np^{3+} + Cl^- \Leftrightarrow NpCl^{2+}$
NpCl2+	III	-	-	*(-0.74)**	-	$Np^{3+} + 2\ Cl^- \Leftrightarrow NpCl_2^{+}$
NpSO4+	III	-	-	*(3.3)**	-	$Np^{3+} + SO_4^{2-} \Leftrightarrow NpSO_4^{+}$
Np(SO4)2-	III	-	-	*(3.7)**	-	$Np^{3+} + 2\ SO_4^{2-} \Leftrightarrow Np(SO_4)_2^{-}$
NpCO3+	III	-	-	*(8.0)**	-	$Np^{3+} + CO_3^{2-} \Leftrightarrow NpCO_3^{+}$
Np(CO3)2-	III	-	-	*(12.9)**	-	$Np^{3+} + 2\ CO_3^{2-} \Leftrightarrow Np(CO_3)_2^{-}$
Np(CO3)3-3	III	-	-	*(15.0)**	-	$Np^{3+} + 3\ CO_3^{2-} \Leftrightarrow Np(CO_3)_3^{3-}$

[a] Value given by Lemire et al. (2001) as a guideline only

[b] Value of uncertainty (± 1.11) given by Hummel et al. (2002) was incorrect

[c] Value of uncertainty (± 1.15) given by Hummel et al. (2002) was incorrect

TDB Version 01/01				**TDB Version 12/07**			
Name	**Redox**	**$\log_{10}K_{s,0}°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**Name**	**$\log_{10}K_{s,0}°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**Reaction**
NpO3:H2O(cr)	VI	5.47 ± 0.40	-	NpO3:H2O(cr)	5.47 ± 0.40	-	$NpO_3{\cdot}H_2O(cr) + 2\ H^+ \Leftrightarrow NpO_2^{2+} + 2\ H_2O(l)$
NpO2CO3(s)	VI	-14.60 ± 0.47	-	NpO2CO3(s)	-14.60 ± 0.47	-	$NpO_2CO_3(s) \Leftrightarrow NpO_2^{2+} + CO_3^{2-}$
K4NpO2(CO3)3(s)	VI	-26.40 ± 0.90	-	K4NpO2(CO3)3(s)	-26.40 ± 0.90	-	$K_4NpO_2(CO_3)_3(s) \Leftrightarrow 4\ K^+ + NpO_2^{2+} + 3\ CO_3^{2-}$
(NH4)4NpO2(CO3)3(s)	VI	-26.81 ± 0.35	-	(NH4)4NpO2(CO3)3(s)	-26.81 ± 0.35	-	$(NH_4)_4NpO_2(CO_3)_3(s) \Leftrightarrow 4\ NH_4^+ + NpO_2^{2+} + 3\ CO_3^{2-}$
NpO2OH(am)(fr)	V	5.3 ± 0.2	-41.1 ± 3.0	NpO2OH(am)(fr)	5.3 ± 0.2	-41.1 ± 3.0	$NpO_2OH(am, fr) + H^+ \Leftrightarrow NpO_2^{+} + H_2O(l)$
NpO2OH(am)(ag)	V	4.7 ± 0.5	-41.1 ± 3.0	NpO2OH(am)(ag)	4.7 ± 0.5	-41.1 ± 3.0	$NpO_2OH(am, ag) + H^+ \Leftrightarrow NpO_2^{+} + H_2O(l)$
NaNpO2CO3:3.5H2O(s)(fr)	V	-11.16 ± 0.35	-	NaNpO2CO3:3.5H2O(cr)	-11.0 ± 0.24	-	$NaNpO_2CO_3{\cdot}3.5H_2O(cr) \Leftrightarrow$ $Na^+ + NpO_2^{+} + CO_3^{2-} + 3.5\ H_2O(l)$
NaNpO2CO3(s)(ag)	V	-11.66 ± 0.50	-	-	-	-	$NaNpO_2CO_3(s, ag) \Leftrightarrow Na^+ + NpO_2^{+} + CO_3^{2-}$
Na3NpO2(CO3)2(s)	V	-14.70 ± 0.66	-	Na3NpO2(CO3)2(cr)	-14.22 ± 0.50	-	$Na_3NpO_2(CO_3)_2(cr) \Leftrightarrow 3\ Na^+ + NpO_2^{+} + 2\ CO_3^{2-}$

TDB Version 01/01				**TDB Version 12/07**			
Name	**Redox**	**$\log_{10}K_{s,0}°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**Name**	**$\log_{10}K_{s,0}°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**Reaction**
KNpO2CO3(s)	V	-	-	KNpO2CO3(s)	-13.15 ± 0.19	-	$KNpO_2CO_3(s) \Leftrightarrow K^+ + NpO_2^+ + CO_3^{2-}$
K3NpO2(CO3)2(s)	V	-	-	K3NpO2(CO3)2(s)	-15.46 ± 0.16	-	$K_3NpO_2(CO_3)_2(s) \Leftrightarrow 3 K^+ + NpO_2^+ + 2 CO_3^{2-}$
NpO2(am)(hyd)	IV	1.5 ± 1.0	-	NpO2(am)(hyd)	-0.7 ± 0.5	-	$NpO_2(am, hyd) + 4 H^+ \Leftrightarrow Np^{4+} + 2 H_2O(l)$

Table 4.3: Selected SIT ion interaction coefficients $\varepsilon_{j,k}$ [kg·mol^{-1}] for neptunium species. All data included in TDB Version 12/07 are taken from Lemire et al. (2001) and Guillaumont et al. (2003) unless indicated otherwise. Own data estimates based on charge correlations (see Appendix A) are shaded. Supplemental data are in italics.

j k→	**Cl$^-$**	**ClO$_4^-$**	**NO$_3^-$**	**Li$^+$**	**Na$^+$**	**K$^+$**
↓	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$
NpO2+2	0.15 ± 0.10	0.46 ± 0.05	-	0	0	0
NpO2OH+	0.05 ± 0.10	-0.06 ± 0.40	-	0	0	0
NpO2(OH)3-	*0*	*0*	*0*	-	*-0.05 ± 0.10*	-
NpO2(OH)4-2	*0*	*0*	*0*	-	*-0.10 ± 0.10*	-
(NpO2)2(OH)2+2	0.15 ± 0.10	0.57 ± 0.10	-	0	0	0
(NpO2)3(OH)5+	0.05 ± 0.10	0.45 ± 0.20	-	0	0	0
NpO2F+	0.05 ± 0.10	0.29 ± 0.12	-	0	0	0
NpO2F2	0	0	0	0	0	0
NpO2Cl+	0.05 ± 0.10	0.50 ± 0.14	-	0	0	0
NpO2IO3+	0.05 ± 0.10	0.33 ± 0.04	-	0	0	0
NpO2SO4	0	0	0	0	0	0
NpO2(SO4)2-2	0	0	0	-	-0.10 ± 0.10	-
NpO2H2PO4+	0.05 ± 0.10	0.2 ± 0.10	-	0	0	0
NpO2HPO4	0	0	0	0	0	0
NpO2(HPO4)2-2	0	0	0	-	-0.1 ± 0.1	-
NpO2CO3	0	0	0	0	0	0
NpO2(CO3)2-2	0	0	0	-	-0.02 ± 0.14	-
NpO2(CO3)3-4	0	0	0	-	-0.40 ± 0.19	-0.62 ± 0.42
(NpO2)3(CO3)6-6	0	0	0	-	-0.46 ± 0.73	-
(NpO2)2CO3(OH)3-	0	0	0	-	0.00 ± 0.05	-
(UO2)2NpO2(CO3)6-6	0	0	0	-	0.09 ± 0.71	-
NpO2+	0.09 ± 0.05	0.25 ± 0.05	-	0	0	0
NpO2(OH)	0	0	0	0	0	0
NpO2(OH)2-	0	0	0	-	-0.01 ± 0.07	-
NpO2F	0	0	0	0	0	0
NpO2IO3	0	0	0	0	0	0
NpO2SO4-	0	0	0	-	-0.05 ± 0.10	-
NpO2HPO4-	0	0	0	-	-0.05 ± 0.10	-
NpO2CO3-	0	0	0	-	-0.18 ± 0.15	-
NpO2(CO3)2-3	0	0	0	-	-0.33 ± 0.17	-
NpO2(CO3)3-5	0	0	0	-	-0.53 ± 0.19	-0.22 ± 0.03
NpO2(CO3)2OH-4	0	0	0	-	-0.40 ± 0.19	-
NpO2SCN	*0*	*0*	*0*	*0*	*0*	*0*
Np+4	0.35 ± 0.10	0.84 ± 0.06	-	0	0	0
NpOH+3	0.25 ± 0.10	0.50 ± 0.05	-	0	0	0
Np(OH)2+2	0.15 ± 0.10	0.4 ± 0.1	-	0	0	0
Np(OH)3+	*0.05 ± 0.10*	*0.2 ± 0.1*	-	*0*	*0*	*0*
Np(OH)4	0	0	0	0	0	0
NpF+3	0.25 ± 0.10	0.58 ± 0.07	-	0	0	0
NpF2+2	0.15 ± 0.10	0.38 ± 0.17	-	0	0	0
NpCl+3	0.25 ± 0.10	(0.81 ± 0.19)[a]	-	0	0	0

j k→ ↓	Cl^-	ClO_4^-	NO_3^-	Li^+	Na^+	K^+
	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$
NpI+3	0.25 ± 0.10	(0.88 ± 0.26)[b]	-	0	0	0
NpSO4+2	0.15 ± 0.10	(0.50 ± 0.11)[c]	-	0	0	0
Np(SO4)2	0	0	0	0	0	0
NpNO3+3	0.25 ± 0.10	0.6 ± 0.1	-	0	0	0
Np(CO3)4-4	0	0	0	-	-0.20 ± 0.30	-
Np(CO3)5-6	0	0	0	-	-0.30 ± 0.50	-0.73 ± 0.68
NpCO3(OH)3-	*0*	*0*	*0*	-	*-0.05 ± 0.10*	-
NpSCN+3	0.25 ± 0.10	0.76 ± 0.12	-	0	0	0
Np(SCN)2+2	0.15 ± 0.10	0.38 ± 0.20	-	0	0	0
Np(SCN)3+	0.05 ± 0.10	0.17 ± 0.04	-	0	0	0
Np+3	0.25 ± 0.10	0.49 ± 0.05	-	0	0	0
NpOH+2	0.15 ± 0.10	0.4 ± 0.1	-	0	0	0
Np(OH)2+	*0.05 ± 0.10*	*0.2 ± 0.1*	-	*0*	*0*	*0*
Np(OH)3	*0*	*0*	*0*	*0*	*0*	*0*
NpF+2	*0.15 ± 0.10*	*0.4 ± 0.1*	-	*0*	*0*	*0*
NpF2+	*0.05 ± 0.10*	*0.2 ± 0.1*	-	*0*	*0*	*0*
NpCl+2	*0.15 ± 0.10*	*0.4 ± 0.1*	-	*0*	*0*	*0*
NpCl2+	*0.05 ± 0.10*	*0.2 ± 0.1*	-	*0*	*0*	*0*
NpSO4+	*0.05 ± 0.10*	*0.2 ± 0.1*	-	*0*	*0*	*0*
Np(SO4)2-	*0*	*0*	*0*	-	*-0.05 ± 0.10*	-
NpCO3+	*(0.01 ± 0.05)*[d]	*(0.17 ± 0.10)*[d]	-	*0*	*0*	*0*
Np(CO3)2-	*0*	*0*	*0*	-	*-(0.14 ± 0.06)*[d]	-
Np(CO3)3-3	*0*	*0*	*0*	-	*-(0.23 ± 0.07)*[d]	-

[a] Typographical error in Guillaumont et al. (2003) and in all following NEA-reviews: Uncertainty given as ± 0.09 instead of ± 0.19 kg·mol^{-1}

[b] Recalculated by using ε(I$^-$, H$^+$) from Hummel et al. (2005) instead of the assumption ε(I$^-$, H$^+$) ≈ ε(I$^-$, Na$^+$) by Lemire et al. (2001)

[c] The original value by Lemire et al. (2001), (0.48 ± 0.11) kg·mol^{-1}, is slightly incorrect

[d] This work, estimated by adopting values from the corresponding Am(III) carbonate complexes, see Section 2.7.1.2.

4.9 References

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5 Nickel

Almost all information on inorganic compounds and complexes of nickel reported here was taken from the NEA review of the "Chemical Thermodynamics of Nickel" by Gamsjäger et al. (2005). Data for nickel sulphide complexes were selected by an in-house review. Data for nickel ammine complexes were taken from the work of Bjerrum (1941).

However, not all values recommended by Gamsjäger et al. (2005) 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. Ni data selected by NEA but not included in our database are summarized in Table 5.4. The data selected for the database update are listed in Table 5.5.

5.1 Elemental nickel

Pure Ni metal is defined as the nickel reference phase. As such, its Gibbs energy of formation and enthalpy of formation are zero by definition at 298.15 K and 0.1 MPa. The absolute entropy and heat capacity of Ni(cr) are well established. The entropy value selected by NEA

$$S_m°(\text{Ni, cr, 298.15 K}) = (29.87 \pm 0.20)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

is essentially the same as the value given in the NIST-JANAF Thermochemical Tables (Chase 1998), (29.87 ± 0.21) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and qualifies as core data value.

The heat capacity selected by NEA

$$C_{p,m}°(\text{Ni, cr, 298.15 K}) = (26.07 \pm 0.10)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

is also included in our database.

The melting point of Ni(cr) at (1726 ± 4) K indicates that nickel liquid, Ni(l), and nickel gas, Ni(g), are not relevant under environmental conditions. Although Gamsjäger et al. (2005) selected thermochemical data for both, none of these phases is included in our database (Table 5.4).

5.2 Simple nickel aqua ion

In aqueous media, the nickel aqua ion exists only in the divalent oxidation state Ni(II). Although the trivalent state of Ni can be stabilized by certain arrangement of donor ligands, no stable aqua ion of Ni(III) appears to exist in dilute aqueous solutions at ambient conditions.

The standard Gibbs energy of formation of Ni^{2+} can be obtained directly from potentiometric data, most accurately from measuring the standard electrode potential of $Ni^{2+} \mid Ni$ in a cell without liquid junction, such as $Ni \mid NiSO_4 \mid Hg_2SO_4 \mid Hg$. The NEA selected value is

$$\Delta_f G_m°(\text{Ni}^{2+}, \text{298.15 K}) = -(45.77 \pm 0.77)\ \text{kJ}\cdot\text{mol}^{-1}$$

The partial molar entropy of Ni^{2+} has been derived from experimental data about the solubility, the standard enthalpy of the dissolution reaction and low temperature calorimetry of $NiSO_4\cdot 7H_2O(cr)$:

$$S_m°(\text{Ni}^{2+}, \text{298.15 K}) = -(131.8 \pm 1.4)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

The enthalpy of formation of Ni^{2+} has been calculated from the above selected values as

$$\Delta_f H_m°(\text{Ni}^{2+}, \text{298.15 K}) = -(55.01 \pm 0.88)\ \text{kJ}\cdot\text{mol}^{-1}$$

The heat capacity of Ni^{2+} was derived from reported apparent molar heat capacity values for several nickel salts in aqueous solution. An unweighted average of the values discussed by Gamsjäger et al. (2005) was selected:

$$C_{p,m}°(Ni^{2+}, 298.15\ K = -(46.1 \pm 7.5)\ J\cdot K^{-1}\cdot mol^{-1}$$

All these NEA selected values were included in our database.

The SIT ion interaction coefficient for Ni^{2+} in ClO_4^- media has been evaluated by Gamsjäger et al. (2005). They selected the mean value of entirely independent measurements (emf measurements and isopiestic measurements)

$$\varepsilon(Ni^{2+}, ClO_4^-) = (0.37 \pm 0.03)\ kg\cdot mol^{-1}.$$

The ion interaction coefficient $\varepsilon(Ni^{2+}, NO_3^-)$ has also been derived by Gamsjäger et al. (2005) from the osmotic and mean activity coefficients of $Ni(NO_3)_2$ solutions. From a fit to experimental data up to an ionic strength of 15 kg·mol^{-1} they selected

$$\varepsilon(Ni^{2+}, NO_3^-) = (0.182 \pm 0.010)\ kg\cdot mol^{-1}.$$

The ion interaction coefficient $\varepsilon(Ni^{2+}, Cl^-)$ has been taken from Grenthe et al. (1992):

$$\varepsilon(Ni^{2+}, Cl^-) = (0.17 \pm 0.02)\ kg\cdot mol^{-1}.$$

It is also based on osmotic and mean activity coefficients of $NiCl_2$ solutions.

5.3 (Hydr)oxide compounds and complexes

5.3.1 Aqueous nickel hydroxo complexes

The hydrolysis of Ni(II) has mainly been studied by potentiometric titrations, although some solubility, kinetic and calorimetric studies have also been reported. According to these studies, the formation of five water soluble hydroxo complexes of Ni(II) is generally recognized: $NiOH^+$, $Ni(OH)_2(aq)$, $Ni(OH)_3^-$, Ni_2OH^{3+} and $Ni_4(OH)_4^{4+}$.

In acidic or near neutral solutions, hydrolysis of Ni^{2+} is weak, and in publications before 1965, the experimental data were interpreted only in terms of formation of the mononuclear $NiOH^+$ complex. However, at Ni(II) concentrations higher than 0.005 M, the $Ni_4(OH)_4^{4+}$ complex is dominant in the acidic pH region. The dinuclear Ni_2OH^{3+} species is always a minor component, and its formation is considered to account for small deviations between the observed and calculated titration curves. A re-analysis of all reliable experimental data lead to the following NEA data selection:

$$Ni^{2+} + H_2O(l) \Leftrightarrow NiOH^+ + H^+$$

$$\log_{10}{}^*\beta_1°(298.15\ K) = -(9.54 \pm 0.14)$$

$$\Delta_r H_m°(298.15\ K) = (53.8 \pm 1.7)\ kJ\cdot mol^{-1}$$

$$2\ Ni^{2+} + H_2O(l) \Leftrightarrow Ni_2OH^{3+} + H^+$$

$$\log_{10}{}^*\beta_{21}°(298.15\ K) = -(10.6 \pm 1.0)$$

$$\Delta_r H_m°(298.15\ K) = (45.9 \pm 6.0)\ kJ\cdot mol^{-1}$$

$$4\ Ni^{2+} + 4\ H_2O(l) \Leftrightarrow Ni_4(OH)_4^{4+} + 4\ H^+$$

$$\log_{10}{}^*\beta_{44}°(298.15\ K) = -(27.52 \pm 0.15)$$

$$\Delta_r H_m°(298.15\ K) = (190 \pm 10)\ kJ\cdot mol^{-1}$$

The SIT ion interaction coefficient for $NiOH^+$ in ClO_4^- and Cl^- has been evaluated by Gamsjäger et al. (2005) from their SIT analyses of experimental data in $NaClO_4$ and NaCl media:

$$\varepsilon(NiOH^+, ClO_4^-) = (0.14 \pm 0.07)\ kg \cdot mol^{-1}$$

and

$$\varepsilon(NiOH^+, Cl^-) = -(0.01 \pm 0.07)\ kg \cdot mol^{-1}.$$

No value was selected by Gamsjäger et al. (2005) for $\varepsilon(NiOH^+, NO_3^-)$.

The SIT ion interaction coefficient for $Ni_4(OH)_4^{4+}$ in ClO_4^- and Cl^- has been evaluated by Gamsjäger et al. (2005) from their SIT analyses of experimental data in perchlorate and NaCl:

$$\varepsilon(Ni_4(OH)_4^{4+}, ClO_4^-) = (1.08 \pm 0.08)\ kg \cdot mol^{-1}$$

and

$$\varepsilon(Ni_4(OH)_4^{4+}, Cl^-) = (0.43 \pm 0.08)\ kg \cdot mol^{-1}.$$

In the case of Ni_2OH^{3+} Gamsjäger et al. (2005) did extrapolations to $I = 0$ by assuming

$$\varepsilon(Ni_2OH^{3+}, ClO_4^-) = (0.50 \pm 0.15)\ kg \cdot mol^{-1}$$

based on the estimated value for $\varepsilon(Be_2OH^{3+}, ClO_4^-) = (0.50 \pm 0.05)\ kg \cdot mol^{-1}$.

Three further complexes have been reported to form in Ni(II) solutions above pH = 9, $Ni(OH)_2(aq)$, $Ni(OH)_3^-$ and $Ni(OH)_4^{2-}$, based on the increasing solubility of $Ni(OH)_2(cr)$ in alkaline solutions. Values of the respective hydrolysis constants selected by previous reviews are based on a few experimental points of a single paper by Gayer & Garrett (1949). The data situation has not improved, but these experimental points can be equally well described when only $Ni(OH)_3^-$ is assumed to be present. The numerical value of this third hydrolysis constant remains within its error limits whether $Ni(OH)_2(aq)$ is taken into account or not, and the NEA reviewers did not find any convincing evidence for formation of $Ni(OH)_4^{2-}$. A re-evaluation of the data reported by Gayer & Garrett (1949) resulted in the following NEA selected value:

$$Ni^{2+} + 3\ H_2O(l) \Leftrightarrow Ni(OH)_3^- + 3\ H^+$$

$$\log_{10}{}^*\beta_3°(298.15\ K) = -(29.2 \pm 1.7)$$

No thermodynamic quantities for the species $Ni(OH)_2(aq)$ are selected in the NEA review, though the reviewers state that for the reaction $Ni(OH)_2(cr) \Leftrightarrow Ni(OH)_2(aq)$ $\log_{10}K \le -7$ can be tentatively assigned as its upper limit. Together with the solubility product selected for $Ni(OH)_2(cr)$ (see 5.3.2) this results in the following supplemental data:

$$Ni^{2+} + 2\ H_2O(l) \Leftrightarrow Ni(OH)_2(aq) + 2\ H^+$$

$$\log_{10}{}^*\beta_2°(298.15\ K) \le -18$$

From the temperature dependence of $\log_{10}{}^*\beta_2°$ and $\log_{10}{}^*\beta_3°$ measured between 150 and 300°C, rough estimates for their standard reaction enthalpies can be derived as $\Delta_rH_m°(298.15\ K) \approx$ *90* and *(121.2 ± 6.5)* kJ·mol^{-1}, respectively.

5.3.2 Solid nickel oxides and hydroxides

5.3.2.1 Ni(II) oxide

Bunsenite (NiO) is an extremely rare mineral. It has been discovered as early as 1868 in Johanngeorgenstadt, Erzgebirge, Saxony, Germany in a hydrothermal Ni-U vein.

A very accurate technique for the determination of the standard entropy of a solid crystalline compound is the integration of low-temperature heat capacity data between 0 and 298.15 K. In the case of nickel oxide several publications dealing with heat capacity measurements in the temperature range 3.2–477.8 K are available. Based on a simultaneous evaluation of five independent experimental studies of comparable accuracy Gamsjäger et al. (2005) selected the standard entropy of NiO as

$$S_m°(\text{NiO, cr, 298.15 K}) = (38.4 \pm 0.4)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

Based on these studies and two high-temperature heat capacity studies Gamsjäger et al. (2005) selected

$$C_{p,m}°(\text{NiO, cr, 298.15 K}) = (44.4 \pm 0.1)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

The enthalpy of formation of nickel oxide was determined directly by means of combustion calorimetry as

$$\Delta_f H_m°(\text{NiO, cr, 298.15 K}) = -(239.7 \pm 0.4)\ \text{kJ·mol}^{-1}$$

Gamsjäger et al. (2005) state: "When the selected data for Ni(cr), the calorimetric value for the standard enthalpy of formation of NiO, … the heat capacity function and the standard entropy of NiO (selected above) are used, the predicted temperature dependence of the Gibbs energy of formation agrees remarkably well with experimental data obtained from various high-temperature electrochemical measurements." Thus, the NEA reviewer selected the standard enthalpy of formation from combustion calorimetry and calculated a value for the Gibbs energy of formation from the above selected values as

$$\Delta_f G_m°(\text{NiO, cr, 298.15 K}) = -(211.66 \pm 0.42)\ \text{kJ·mol}^{-1}$$

Gamsjäger et al. (2005) further state: "Due to the kinetically inert nature of nickel oxide with respect to its dissolution in aqueous media the solubility of NiO has been studied only at elevated temperatures so far. These studies are not suitable for the calculation of any thermodynamic properties of NiO because of the high uncertainty of the measured solubilities compared to the high-temperature emf data and the low-temperature heat capacity data discussed above. Moreover, the evaluation of the solubility experiments performed at hydrothermal conditions may cause an additional uncertainty for the solubility constant of NiO owing to the lack of heat capacity functions for the ionic species including the hydroxo species. Thus, the calculated value for the solubility constant of NiO at 298.15 K, according to the reaction:

$$\text{NiO(cr)} + 2\,\text{H}^+ \Leftrightarrow \text{Ni}^{2+} + \text{H}_2\text{O(l)}$$

derived from the thermodynamic data accepted in the present assessment, is :

$$\log_{10}{}^*K_{s,0}°(\text{NiO, cr, 298.15 K}) = (12.48\ \pm 0.15).\text{“}$$

The values selected for $\log_{10}{}^*K_{s,0}°$, $S_m°$ and $C_{p,m}°$ by Gamsjäger et al. (2005) are included in our database.

5.3.2.2 Ni(II) hydroxides, $Ni(OH)_2$

Theophrastite, β-$Ni(OH)_2$, is a gangue mineral in ore consisting of magnetite (Fe_3O_4), chromite ($FeCr_2O_4$) and Ni-sulphide as minor component. Theophrastite is formed from Ni-bearing solutions between $80 \le T(°C) \le 115$ in alkaline moderately oxidizing media.

Other varieties of crystallized divalent nickel hydroxide, α-$Ni(OH)_2$ and α^*-$Ni(OH)_2$, differ from the thermodynamically stable β-form by the presence of a layer of water in the van der Waals gap. Proposed formulae are α-$3Ni(OH)_2·2H_2O$ and α^*-$Ni(OH)_2·0.75H_2O$. Although the

α-form plays an important role in the charge/discharge cycle of nickel batteries (see below) no thermodynamic data can definitely be assigned to it. The natural occurrence of α-Ni(OH)$_2$ has never been reported as it is probably too unstable to persist under ambient conditions.

The heat capacity of Ni(OH)$_2$(cr) has been measured at low temperatures and these data have been used to determine the standard entropy $S_m°$(298.15 K) and $C_{p,m}°$(298.15 K). Gamsjäger et al. (2005) selected

$$S_m°(\text{Ni(OH)}_2, \beta, 298.15\text{ K}) = (80.0 \pm 0.8)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

$$C_{p,m}°(\text{Ni(OH)}_2, \beta, 298.15\text{ K}) = (82.0 \pm 0.3)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

Both values are included in our database.

Gamsjäger et al. (2005) state that actually most solubility data of Ni(OH)$_2$(cr) reported so far suffer from an uncertainty in the physical state of the solid investigated. They continue "apart from the well defined β-Ni(OH)$_2$, a number of basic salts of changing composition exist. When nickel hydroxide is precipitated from aqueous NiCl$_2$, Ni(NO$_3$)$_2$, or NiSO$_4$ with NaOH or KOH solutions it is always contaminated with basic salts. The solubility of the latter varies depending on the anion and the molar ratio OH/Ni. This means that solubility studies on poorly defined nickel hydroxide or the representative basic salts are useless as an experimental basis to derive accurate thermodynamic functions of nickel hydroxide. They may, however, serve to find out relevant information concerning removal of Ni^{2+} from radioactive effluents."

The value selected by Gamsjäger et al. (2005) for the reaction

$$\beta\text{-Ni(OH)}_2 + 2\text{ H}^+ \Leftrightarrow \text{Ni}^{2+} + 2\text{ H}_2\text{O(l)}$$

$$\log_{10}{}^{*}K_{s,0}°(\text{Ni(OH)}_2, \beta, 298.15\text{ K}) = (11.02 \pm 0.20)$$

is based on the new experimental study of Gamsjäger et al. (2002). This value is included in our database.

According to the present thermodynamic model the equilibrium temperature for

$$\beta\text{-Ni(OH)}_2 \Leftrightarrow \text{NiO(cr)} + \text{H}_2\text{O(l)}$$

amounts to $T = (503 \pm 31)$ K.

5.3.2.3 Ni(III, IV) hydroxides

Nickel hydroxides of oxidation state two and higher have been used as the active material in the positive electrodes of several alkaline batteries for more than a hundred years:

$$\begin{tikzcd}
& \text{charge} \rightarrow & \leftarrow \text{discharge} & \\
& \beta\text{-Ni(OH)}_2 \arrow[r, phantom, "\Leftrightarrow"] & \beta\text{-NiOOH} \arrow[d, "\text{overcharge}"] & \\
& \alpha\text{-Ni(OH)}_2 \arrow[u, "\text{dehydration}"] \arrow[r, phantom, "\Leftrightarrow"] & \gamma\text{-NiOOH} &
\end{tikzcd}$$

The charge and discharge cycles of nickel batteries involve two different pairs of solid phases. Oxidation of β-Ni(OH)$_2$ produces β-NiOOH, oxidation of α-Ni(OH)$_2$ produces γ-NiOOH. The end-products of these cycles are interconnected by dehydration and overcharge. In order to complicate things further, the so-called "α-Ni(OH)$_2$ | γ-NiOOH" system forms regular solid solutions of Ni(II) and Ni(IV) compounds in the whole range of compositions between α-Ni(OH)$_2$ and NiO$_2$·xH$_2$O, without any participation of Ni(III) oxide hydroxides.

No thermodynamic data for any of these compounds are recommended by Gamsjäger et al. (2005).

5.4 Halogen compounds and complexes

5.4.1 Nickel halide compounds

The solubility and the thermochemical properties of nickel halide compounds have been studied extensively since the end of the 19th century, and the relevant literature was reviewed in detail by Gamsjäger et al. (2005).

The anhydrous forms NiF_2(cr), $NiCl_2$(cr), $NiBr_2$(cr) and NiI_2(cr) are unstable in aqueous systems. They are sold with the label "hygroscopic" on the bottle, implying hydration and instantaneous dissolution in contact with water.

A number of hydrated $NiCl_2$ solids have been studied. In contact with saturated aqueous solutions at ambient pressure, the hexahydrate $NiCl_2 \cdot 6H_2O$(cr) was reported to be the stable form to approximately 36°C, with a solubility of 4.9 $mol \cdot kg^{-1}$, and the dehydration of the tetrahydrate $NiCl_2 \cdot 4H_2O$(cr) to the dihydrate $NiCl_2 \cdot 2H_2O$(cr) occurs above 60°C.

Anhydrous nickel iodate, β-$Ni(IO_3)_2$, is unstable in aqueous systems, and the most stable form near room temperature, the hydrated compound $Ni(IO_3)_2 \cdot 2H_2O$(cr), is highly soluble in water.

In summary, all these nickel halide solids are either unstable in aqueous systems or they are highly soluble salts. None of them is included in our database (Table 5.3).

5.4.2 Aqueous nickel halide complexes

Halide ions, with the exception of fluoride, form rather unstable complexes with Ni(II) in aqueous solution. This is mostly due to the strong hydration of Ni(II). Thus, water can efficiently compete with the essentially electrostatic Ni(II)-halide interaction. Consequently, high and varying excesses of ligand anions over Ni(II) have been used to assess the stability of the complexes formed. As it is almost impossible to distinguish between a medium effect and the formation of higher complexes, for lack of solid evidence, only NiX^+ species were accepted by Gamsjäger et al. (2005).

A considerable number of stability constants have been reported for the reaction

$$Ni^{2+} + F^- \Leftrightarrow NiF^+$$

The majority of data were obtained in $NaClO_4$ solutions using a fluoride selective electrode, but some pH-metric, kinetic and polarographic data were published, too. Gamsjäger et al. (2005) did a weighted linear regression using 11 data points and obtained the selected value of

$$\log_{10}\beta_1°(298.15\ K) = (1.43 \pm 0.08).$$

The resulting Δε value is -(0.049 ± 0.060) $kg \cdot mol^{-1}$. Using the selected values for $\varepsilon(Ni^{2+}, ClO_4^-)$ and $\varepsilon(Na^+, F^-)$ leads to a value of

$$\varepsilon(NiF^+, ClO_4^-) = (0.34 \pm 0.08)\ kg \cdot mol^{-1}.$$

In the absence of an experimental value for $\varepsilon(NiF^+, Cl^-)$ an estimate based on charge correlations (see Appendix A) is included in our database:

$$\varepsilon(NiF^+, Cl^-) = (0.05 \pm 0.15)\ kg \cdot mol^{-1}.$$

Published reaction enthalpy values for the formation of the NiF^+ complex were evaluated by Gamsjäger et al. (2005) and they selected a value of

$$\Delta_r H_m°(298.15 \text{ K}) = (9.5 \pm 3.0) \text{ kJ·mol}^{-1}.$$

All these values are included in our database.

The formation of higher complexes (NiF_n^{2-n}, $n > 1$) is not reported in the literature, not even in the presence of more than a thousand-fold excess of fluoride over Ni(II).

The derivation of a stability constant for the reaction

$$Ni^{2+} + Cl^- \Leftrightarrow NiCl^+$$

proved to be a bumpy road as described by Gamsjäger et al. (2005).

Gamsjäger et al. (2005) did not consider a number of reported data for reasons discussed in their Appendix A and stated further: "Most of the accepted data are, however, also subject to substantial experimental errors, due to the medium effect, and in such cases we assigned significantly higher uncertainty to the selected constants than reported in the original literature."

Gamsjäger et al. (2005) then started their analysis by stating: "The data in Libus & Tialowska (1975) are free of significant medium effects, and this is the only data set where the systematic errors can be assumed identical for each point. Therefore, these data were used to determine the ion interaction coefficient between $NiCl^+$ and ClO_4^-, in spite of the fact that the applied ionic strength (I_m = 3–9 m) is well above of the recommended range for the SIT analysis." The results of the linear regression are: $\log_{10}\beta_1°$(298.15 K) = -(0.37 ± 0.27) and $\Delta\varepsilon$ = -(0.073 ± 0.040) kg·mol^{-1}. However, deriving a value for $\varepsilon(NiCl^+, ClO_4^-)$ is difficult as $Ni(ClO_4)_2$ was used as a constant ionic medium (with a chloride content of ≈0.01 m) and $\Delta\varepsilon$ has to be calculated as $\Delta\varepsilon = \varepsilon(NiCl^+, ClO_4^-) - \varepsilon(Ni^{2+}, Cl^-) - \varepsilon(Ni^{2+}, ClO_4^-)$. Using the selected value $\varepsilon(Ni^{2+}, ClO_4^-)$ = (0.37 ± 0.03) kg·mol^{-1} is no problem, but what value should be used for $\varepsilon(Ni^{2+}, Cl^-)$? The NEA selected value $\varepsilon(Ni^{2+}, Cl^-)$ = (0.17 ± 0.02) kg·mol^{-1} was derived from isopiestic measurements and thus already implicitly includes the effects of nickel chloride complexation. It should be replaced by $\varepsilon(Ni^{2+}, ClO_4^-)$ in all calculations when chloride is part of the ionic medium. Doing so, a value $\varepsilon(NiCl^+, ClO_4^-)$ = (0.67 ± 0.06) kg·mol^{-1} can be calculated. Gamsjäger et al. (2005) discussed this but concluded: "This value of $\varepsilon(NiCl^+, ClO_4^-)$ is too high, taking into account the relatively accurate value for $\varepsilon(NiF^+, ClO_4^-)$." They decided to use $\varepsilon(Ni^{2+}, Cl^-)$ = (0.17 ± 0.02) kg·mol^{-1} which leads to a value of:

$$\varepsilon(NiCl^+, ClO_4^-) = (0.47 \pm 0.06) \text{ kg·mol}^{-1}.$$

Gamsjäger et al. (2005) then used the remaining (accepted) experimental values for $NaClO_4$ media for a second SIT analysis. As a result only $\Delta\varepsilon$ = (0.11 ± 0.06) kg·mol^{-1} is given in the text. The stability constant extrapolated to I = 0 is nowhere mentioned in the text and can only guessed as $\log_{10}\beta_1°$(298.15 K) ≈ (0.92 ± 0.22) from Figure V-23 in Gamsjäger et al. (2005). In this case $\Delta\varepsilon$ has to be calculated as $\Delta\varepsilon = \varepsilon(NiCl^+, ClO_4^-) - \varepsilon(Na^+, Cl^-) - \varepsilon(Ni^{2+}, ClO_4^-)$. Using the selected values for $\varepsilon(Ni^{2+}, ClO_4^-)$ and $\varepsilon(Na^+, Cl^-)$ results in $\varepsilon(NiCl^+, ClO_4^-)$ = 0.51 kg·mol^{-1}. Gamsjäger et al. (2005) stated: "This may support the value calculated using $\varepsilon(Ni^{2+}, Cl^-)$ from the data in Libus & Tialowska (1975), however, this is not particularly convincing because most of the remaining data in the other papers have relatively low accuracy, due to substantial medium effects." Consequently, $\log_{10}\beta_1°$(298.15 K) ≈ (0.92 ± 0.22) is not considered by Gamsjäger et al. (2005).

Instead, Gamsjäger et al. (2005) used their selected $\varepsilon(NiCl^+, ClO_4^-)$ = (0.47 ± 0.06) kg·mol^{-1} to extrapolate the remaining accepted data in $(H/Li/Na)ClO_4$ and KCl media to I = 0 with the caveat that due to medium effects, most of the constants derived by this extrapolation represent only the upper limits of the true values. The average of these data is reported as $\log_{10}\beta_1°$(298.15 K) = (0.52 ± 0.38).

Finally, Gamsjäger et al. (2005) took the average of the two values $\log_{10}\beta_1°$(298.15 K) = -(0.37 ± 0.27) and $\log_{10}\beta_1°$(298.15 K) = (0.52 ± 0.38) as their selected value

$$\log_{10}\beta_1°(298.15\ \text{K}) = (0.08 \pm 0.60).$$

Despite some doubts about the validity of the NEA selection procedure we included the selected values for $\log_{10}\beta_1°$ and ε($NiCl^+$, ClO_4^-) in our database. Note that ε($NiCl^+$, Cl^-) = ε($NiCl^+$, ClO_4^-), although the derivation of ε($NiCl^+$, ClO_4^-) itself is inconsistent as discussed above.

Several authors reported equilibrium constants K_2 for the reaction $NiCl^+ + Cl^- \Leftrightarrow NiCl_2(aq)$. However, Gamsjäger et al. (2005) did not find it justified to select a recommended value for K_2.

Only a few studies have reported reaction enthalpies for the formation of $NiCl^+$ species, but no value was selected by Gamsjäger et al. (2005).

Only a few studies are available concerning the complex formation between Ni(II) and bromide ions. Gamsjäger et al. (2005) evaluated data for the reaction $Ni^{2+} + Br^- \Leftrightarrow NiBr^+$ and reported a value $\log_{10}\beta_1°$(298.15 K) = -(0.03 ± 1.30) but stated: "Taking into account this large uncertainty, the above value cannot be recommended, but can be used as the most probable value, until more precise data are published." This value is not included in our database.

Finally, no quantitative data are available for the formation of NiI_n^{2-n} complexes.

5.5 Chalcogen compounds and complexes

5.5.1 Nickel sulphides

5.5.1.1 Nickel sulphide compounds

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).

Millerite, NiS(cr), is a low temperature hydrothermal mineral found in cavities in carbonate rocks and as an alteration product of other nickel minerals. Furthermore, it should be mentioned that millerite is the only nickel sulphide identified so far in natural low-temperature anoxic sulphidic environments according to Thoenen (1999).

The only solubility studies available are for NiS(s), e.g. Thiel & Gessner (1914) (for a detailed discussion see 5.5.1.3), all of which are unreliable and no data can be recommended for inclusion in our database.

Furthermore, thermochemical data selected by Gamsjäger et al. (2005) for α-NiS, β-NiS, NiS_2(cr), Ni_3S_2(cr) and Ni_9S_8(cr), which are all based on calorimetric data, e.g. Rosenqvist (1954) (for a detailed discussion see 5.5.1.3), were not included in our database (Table 5.4).

5.5.1.2 Aqueous nickel sulphide complexes

Complexation data are available for $NiHS^+$, $Ni(HS)_2(aq)$, $Ni_2(HS)^{3+}$, $Ni_3(HS)^{5+}$, NiS(aq), and $NiS(HS)^-$ (see Table below), but only data for $NiHS^+$ and $Ni(HS)_2(aq)$ are included in our database.

Complex	References
$Ni(HS)^+$	Dyrssen (1988) Luther et al. (1996) Zhang & Millero (1994) Al-Farawati & van den Berg (1999)
$Ni_2(HS)^{3+}$	Luther et al. (1996)
$Ni_3(HS)^{5+}$	Luther et al. (1996)
$NiS(HS)^-$	Dyrssen & Wedborg (1980) Dyrssen (1985) Dyrssen & Kremling (1990)
NiS(aq)	Dyrssen (1988) Dyrssen (1989)
$Ni(HS)_2(aq)$	Dyrssen & Wedborg (1980) Dyrssen (1985) Dyrssen (1988) Al-Farawati & van den Berg (1999)

Apart from theoretical estimations of the stability constants of aqueous nickel sulphide complexes by Dyrssen & Wedborg (1980), Dyrssen (1985; 1988; 1989) and Dyrssen & Kremling (1990), 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 5.5.1.3 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

$$Ni^{2+} + HS^- \Leftrightarrow NiHS^+ \qquad (5.1)$$

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). 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 5.5.1.4 for details). A weighted linear regression to the data corrected for side-reactions (see Table 5.1 for the data and Fig. 5.1 for the regression) results in our recommended value

$$\log_{10}\beta_1^\circ(5.1, 298.15\ \mathrm{K}) = (5.5 \pm 0.2)$$

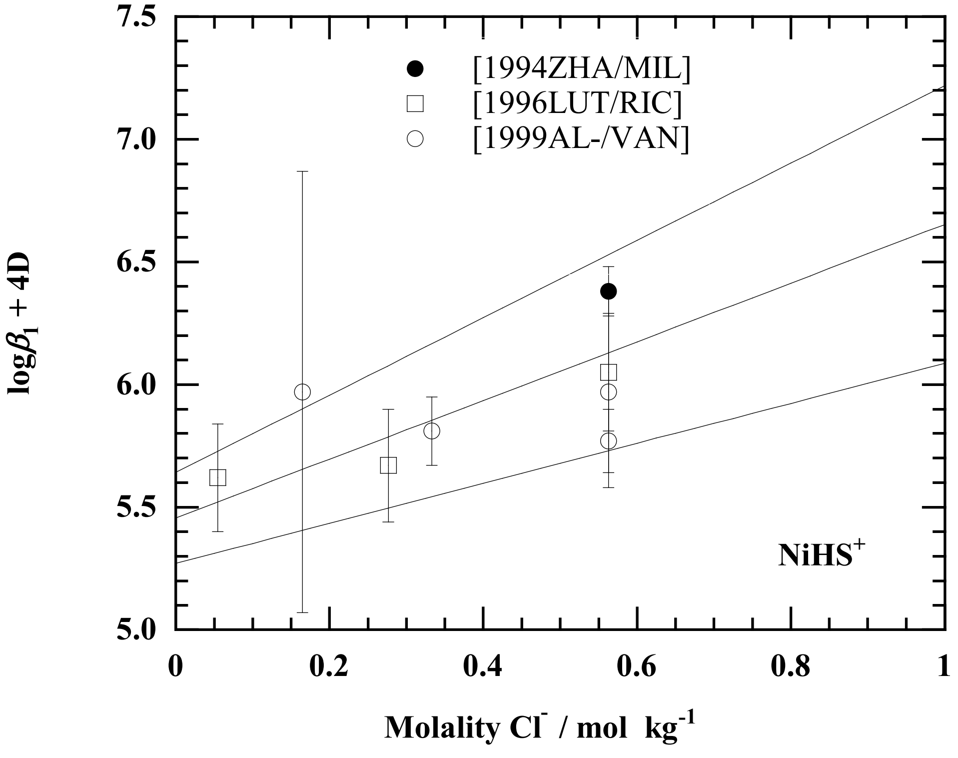
with

$$\Delta\varepsilon(5.1, \mathrm{seawater}) = -\,(1.2 \pm 0.4)\ \mathrm{kg{\cdot}mol^{-1}}$$

A discussion of this $\Delta\varepsilon$ is given in Section 5.5.1.4.

Table 5.1: Values for conditional stability constants of $NiHS^+$ used for extrapolation of the stability constants to $I = 0$ (see Fig. 5.1). $\log_{10}\beta_1'$ 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 Section 5.5.1.4 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^- molal units**	**I molal units**	**$\log_{10}\beta_1'$ molar units**	**$\log_{10}\alpha_{Ni}$ molar units**	**$\log_{10}\beta_1$ molar units**	**$\log_{10}\beta_1$ 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



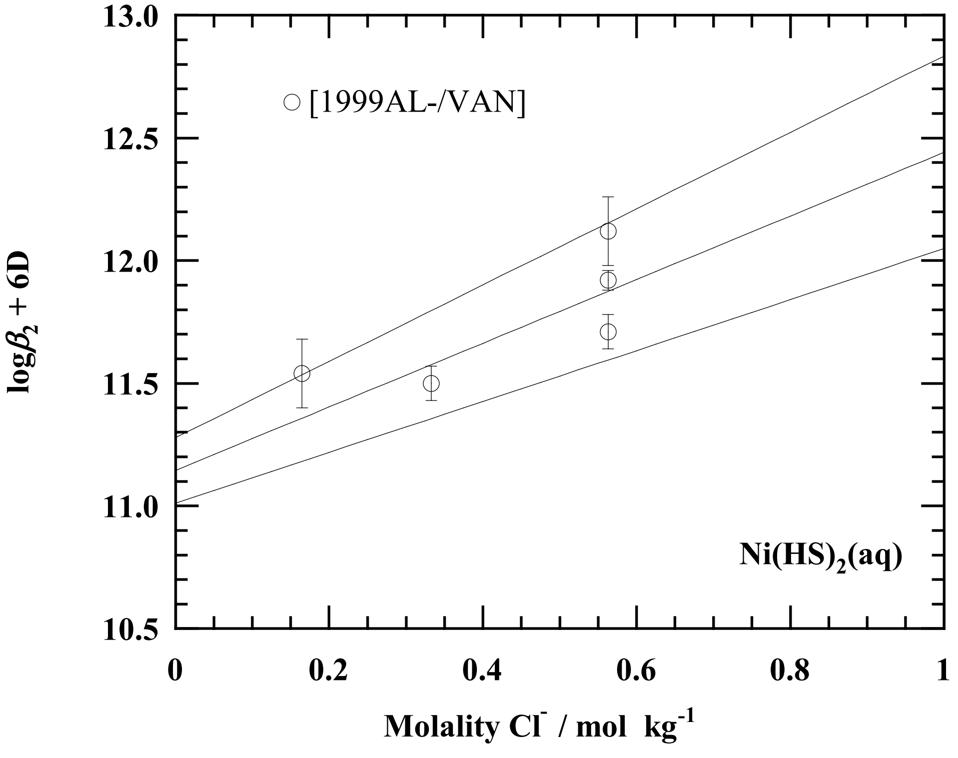


Fig. 5.1: Weighted linear regressions for the extrapolation to $I = 0$ of conditional stability constants determined in seawater for NiHS$^+$ (above) and Ni(HS)$_2$(aq) (below). Experimental data by Zhang & Millero (1994) [1994ZHA/MIL], Luther et al. (1996) [1996LUT/RIC], and Al-Farawati & van den Berg (1999) [1999AL-/VAN].

Only Al-Farawati & van den Berg (1999) provided conditional stability constants (corrected for side-reactions) for the reaction

$$\mathrm{Ni^{2+} + 2HS^{-} \Leftrightarrow Ni(HS)_2(aq)} \qquad (5.2)$$

A weighted linear regression to these data (see Table 5.2 for the data and Fig. 5.1 for the regression) results in our recommended value

$$\log_{10}\beta_2^\circ(5.2,\ 298.15\ \mathrm{K}) = (11.1 \pm 0.1)$$

with

$$\Delta\varepsilon(5.2,\ \text{seawater}) = -(1.3 \pm 0.3)\ \mathrm{kg\cdot mol^{-1}}$$

A discussion of this Δε is given in Section 5.5.1.4.

Table 5.2: Values for conditional stability constants of $\mathrm{Ni(HS)_2(aq)}$ used for extrapolation of the stability constants to $I = 0$ (see Fig. 5.1). $\log_{10}\beta_2'$ refers to the stability constant without consideration of side-reactions and $\log_{10}\alpha_{\mathrm{Ni}}$ to the side-reaction coefficient. Original data in boldface type. See Section 5.5.1.4 for the calculation of the ionic strength and the molality of $\mathrm{Cl^-}$ 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** [‰]	**$\mathrm{Cl^-}$** molal units	**I** molal units	**$\log_{10}\beta_2'$** molar units	**$\log_{10}\alpha_{\mathrm{Ni}}$** molar units	**$\log_{10}\beta_2$** molar units	**$\log_{10}\beta_2$** 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

Note that Gamsjäger et al. (2005) missed the publication of Al-Farawati & van den Berg (1999) in their review, and thus based their data evaluation only on Zhang & Millero (1994) and Luther et al. (1996). They did SIT regression analyses for the reactions

$\mathrm{Ni^{2+} + HS^{-} \Leftrightarrow NiHS^{+}}$ $\log_{10}\beta_1^\circ = (5.18 \pm 0.20)$ $\Delta\varepsilon = -(0.97 \pm 0.39)\ \mathrm{kg\cdot mol^{-1}}$

$\mathrm{2\ Ni^{2+} + HS^{-} \Leftrightarrow Ni_2HS^{3+}}$ $\log_{10}\beta_2^\circ = (9.92 \pm 0.10)$ $\Delta\varepsilon = -(0.05 \pm 0.22)\ \mathrm{kg\cdot mol^{-1}}$

$\mathrm{3\ Ni^{2+} + HS^{-} \Leftrightarrow Ni_3HS^{5+}}$ $\log_{10}\beta_3^\circ = (14.01 \pm 0.10)$ $\Delta\varepsilon = (0.59 \pm 0.22)\ \mathrm{kg\cdot mol^{-1}}$

It is unclear how Gamsjäger et al. (2005) did their SIT analyses for data in seawater. The only information given is found in the caption of Figure A-39 of Gamsjäger et al. (2005), "logarithm of solubility constants of nickel bisulphide complexes in seawater (NaCl solutions) plus the Debye-Hückel term for ionic strength correction plotted as a function of ionic strength."

Nevertheless, the results reported by Gamsjäger et al. (2005) for the first reaction, based on Zhang & Millero (1994) and Luther et al. (1996) only, are consistent with our recommended values within their associated uncertainties.

The SIT analyses for the second and third reaction were solely based on the data reported by Luther et al. (1996). Gamsjäger et al. (2005) calculated the distribution of nickel sulphide complexes as a function of total molality of nickel(II) in aqueous solutions and found that “the uncommon complexes Ni_2HS^{3+} and Ni_3HS^{5+} become the most dominant species in aqueous solution. As this situation seems to be unrealistic and no studies on the structure of these complexes are reported in the literature, we select thermodynamic data only for the aqueous species $NiHS^+$.”

We agree with this judgment not to consider the uncommon complexes Ni_2HS^{3+} and Ni_3HS^{5+}. However, we prefer $\log_{10}\beta_1°(5.1, 298.15 \text{ K}) = (5.5 \pm 0.2)$ evaluated in this review because this value is based on more experimental data and a clearly defined procedure for extrapolation to $I = 0$.

Gamsjäger et al. (2005) reported a value $\varepsilon(NiHS^+, ClO_4^-) = (0.85 \pm 0.39)$ kg·mol^{-1} in their Table B-4 with the footnote “see details in Section V.5.1.1.2”. However, there are no details in Section V.5.1.1.2 of Gamsjäger et al. (2005) except the value $\Delta\varepsilon = -(0.97 \pm 0.39)$ kg·mol^{-1} given in Table V-22. We do not include this coefficient $\varepsilon(NiHS^+, ClO_4^-)$ in our database. Furthermore, $\Delta\varepsilon(5.1, \text{seawater}) = -(1.2 \pm 0.4)$ kg·mol^{-1} cannot be deconvoluted because of the lack of necessary SIT interaction coefficients (see Eq. (5.21) in Section 5.5.1.4). As substitutes, estimate values based on charge correlations (see Appendix A) are included in our database.

5.5.1.3 Discussion of selected references

Thiel & Gessner (1914) studied the solubility of freshly precipitated NiS in order to explain why some NiS-precipitates are much more soluble in dilute acids than others. They concluded that there must exist three modifications of NiS which they named NiS(α), NiS(β), and NiS(γ). The evidence was circumstantial as the structural properties of these modifications could not be investigated at that time. Thiel & Gessner (1914) measured the solubility (unreversed, from undersaturation) of NiS(α), NiS(β), and NiS(γ) at room temperature in HCl-solutions saturated with $H_2S(g)$ under atmospheric pressure, and determined values for K_{s0} of 3×10^{-21}, 10^{-26}, and 2×10^{-28}, respectively. In their calculations, Thiel & Gessner (1914) used a value of 0.91×10^{-7} for K_{1,H_2S} ($\log K_{1,H_2S} = -7.04$) and a value of 1.2×10^{-15} for K_{2,H_2S} ($\log K_{2,H_2S} = -14.92$).

Thiel & Gessner (1914) explicitly stated that their solubility product constants were crude estimates that were only meant to give some idea of their order of magnitude: "Es kommt hier gar nicht darauf an, eine recht grosse Genauigkeit der Löslichkeitsbestimmung zu erzielen, sondern nur darauf, einen Anhalt für die Grössenordnung der Löslichkeit der drei Formen zu gewinnen. Wir kommen daher mit einer gröberen Schätzung aus; mehr ist auch bei der zum Teil noch recht erheblichen Unsicherheit der Grundlage vorläufig nicht möglich."

Ironically, these dubious constants were included in the "Critical Stability Constants" by Smith & Martell (1976). Any solubility product for NiS(α), NiS(β), or NiS(γ) found in compilations is ultimately based on Thiel & Gessner (1914).

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

$$2\ Ni(s) + S_2(g) \Leftrightarrow 2NiS(s) \qquad \text{(a)}$$

was calculated from free energies of reaction for

$$3/2\ Ni(s) + H_2S(g) \Leftrightarrow ½\ Ni_3S_2(s) + H_2(g),$$

$$2\ Ni_3S_2 + H_2S(g) \Leftrightarrow Ni_6S_5(s) + H_2(g), \text{ and}$$

$$Ni_6S_5(s) + H_2S(g) \Leftrightarrow 6\ NiS + H_2(g),$$

which were calculated from experimentally determined reaction properties at temperatures between 400 and 560°C. The Gibbs free energy of reaction for equation (a) 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) ⇔ 2S(s, rhomb), Rosenqvist (1954) finally obtained $\Delta_f G_m^\circ$(NiS, s, 298.15 K) = -20.6 kcal·mol^{-1} and $\Delta_f H_m^\circ$(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.

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_2HS^{3+}, and Ni_3HS^{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.

5.5.1.4 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

$$\mathrm{Cl}(‰) = \mathrm{S}(‰)/1.8154 \tag{5.3}$$

(see Millero 1996 for this equation and for a definition of salinity and chlorinity). From the chlorinity follows the ionic strength

$$I = 0.035989\ \mathrm{Cl}(‰) \tag{5.4}$$

and the molinity (number of moles per kg of seawater) of Cl^-

$$n_{\mathrm{Cl}^-} = 0.028176\ \mathrm{Cl}(‰) \tag{5.5}$$

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 (5.4) and the concentration of Cl^- given by equation (5.5) 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, $W_{\mathrm{H_2O}}$,

$$\text{molality} = \frac{\text{molinity}}{W_{\mathrm{H_2O}}} \tag{5.6}$$

where

$$W_{\mathrm{H_2O}} = 1\text{-}\mathrm{S}(‰)/1000 \tag{5.7}$$

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,

$$\text{molarity} = \text{molinity} \,.\, \rho \tag{5.8}$$

and combining this with equation (5.6), one obtains

$$\text{molality} = f\ \text{molarity} \tag{5.9}$$

with

$$f = \frac{1}{\rho W_{\mathrm{H_2O}}} \tag{5.10}$$

Table 5.3: Various compositional parameters of seawater as calculated from the salinities at which the nickel bisulfide complexation experiments reported in Tables 5.1 and 5.2 were performed. Seawater is abbreviated by sw.

S(‰) **[g·(kg$_{sw}$)$^{-1}$]**	**Cl(‰)** **[g·(kg$_{sw}$)$^{-1}$]**	**[Cl$^-$]** **[mol·(kg$_{sw}$)$^{-1}$]**	**I** **[mol·(kg$_{sw}$)$^{-1}$]**	**W_{H_2O}** **[kg·(kg$_{sw}$)$^{-1}$]**	**ρ(25°C, 1 bar)** **[kg·l^{-1}]**	**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

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).

With equations (5.9) and (5.10) and data from Table 5.3, the molar conditional stability constants for the nickel bisulfide complexes listed in Tables 5.1 and 5.2 can be converted into molal constants according to

$$\log_{10}\beta_1(5.1, \text{molal units}) = \log_{10}\beta_1(5.1, \text{molar units}) - \log_{10}f \qquad (5.11)$$

and

$$\log_{10}\beta_2(5.2, \text{molal units}) = \log_{10}\beta_2(5.2, \text{molar units}) - 2\log_{10}f \qquad (5.12)$$

Table 5.3 lists values for Cl(‰), I, n_{Cl^-}, $W_{\text{H}_2\text{O}}$, ρ(25°C, 1 bar), and log$_{10}f$ calculated from the above equations for the salinities at which the nickel bisulfide complexation experiments reported in Tables 5.1 and 5.2 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^+, $\text{Ni(HS)}_2\text{(aq)}$, and HS^- can be expressed according to SIT as

$$\log_{10}\gamma_{\text{Ni}^{2+}} = -4D + \varepsilon(\text{Ni}^{2+},\text{Cl}^-)m_{\text{Cl}^-} + \varepsilon(\text{Ni}^{2+},\text{SO}_4^{2-})m_{\text{SO}_4^{2-}} \qquad (5.13)$$

$$\log_{10}\gamma_{\text{NiHS}^+} = -D + \varepsilon(\text{NiHS}^+,\text{Cl}^-)m_{\text{Cl}^-} + \varepsilon(\text{NiHS}^+,\text{SO}_4^{2-})m_{\text{SO}_4^{2-}} \qquad (5.14)$$

$$\begin{aligned}\log_{10}\gamma_{\text{Ni(HS)}_2\text{(aq)}} &= \varepsilon(\text{Ni(HS)}_2\text{(aq)},\text{Na}^+)m_{\text{Na}^+} + \varepsilon(\text{Ni(HS)}_2\text{(aq)},\text{Mg}^{2+})m_{\text{Mg}^{2+}} \\ &\quad + \varepsilon(\text{Ni(HS)}_2\text{(aq)},\text{Cl}^-)m_{\text{Cl}^-} + \varepsilon(\text{Ni(HS)}_2\text{(aq)},\text{SO}_4^{2-})m_{\text{SO}_4^{2-}}\end{aligned} \qquad (5.15)$$

$$\log_{10}\gamma_{\text{HS}^-} = -D + \varepsilon(\text{HS}^-,\text{Na}^+)m_{\text{Na}^+} + \varepsilon(\text{HS}^-,\text{Mg}^{2+})m_{\text{Mg}^{2+}} \qquad (5.16)$$

The following ratios hold for seawater (see Table 2.5 in Millero 1996)

$$\mathrm{a} \equiv \frac{m_{\mathrm{SO_4^{2-}}}}{m_{\mathrm{Cl^-}}} = 0.05173 \qquad (5.17)$$

$$\mathrm{b} \equiv \frac{m_{\mathrm{Na^+}}}{m_{\mathrm{Cl^-}}} = 0.85929 \qquad (5.18)$$

$$\mathrm{c} \equiv \frac{m_{\mathrm{Mg^{2+}}}}{m_{\mathrm{Cl^-}}} = 0.09676 \qquad (5.19)$$

With equations (5.13), (5.14), (5.16), and (5.17)-(5.19), the equilibrium relation for

$$\mathrm{Ni^{2+} + HS^- \Leftrightarrow NiHS^+} \qquad (5.1)$$

can be written as

$$\log_{10}\beta_1(5.1) + 4D = \log_{10}\beta_1^\circ(5.1) - \Delta\varepsilon(5.1)m_{\mathrm{Cl^-}} \qquad (5.20)$$

where

$$\begin{aligned}\Delta\varepsilon(5.1) = &+ \varepsilon(\mathrm{NiHS^+,Cl^-}) + \varepsilon(\mathrm{NiHS^+,SO_4^{2-}})\cdot \mathrm{a}\\ &- \varepsilon(\mathrm{Ni^{2+},Cl^-}) - \varepsilon(\mathrm{Ni^{2+},SO_4^{2-}})\cdot \mathrm{a}\\ &- \varepsilon(\mathrm{HS^-,Na^+})\cdot \mathrm{b} - \varepsilon(\mathrm{HS^-,Mg^{2+}})\cdot \mathrm{c}\end{aligned} \qquad (5.21)$$

In a similar manner, the equilibrium relation for

$$\mathrm{Ni^{2+} + 2HS^- \Leftrightarrow Ni(HS)_2(aq)} \qquad (5.2)$$

can be written as

$$\log_{10}\beta_2(5.2) + 6D = \log_{10}\beta_2^\circ(5.2) - \Delta\varepsilon(5.2)m_{\mathrm{Cl^-}} \qquad (5.22)$$

where

$$\begin{aligned}\Delta\varepsilon(5.2) = &+ \varepsilon(\mathrm{Ni(HS)_2(aq),Na^+})\cdot \mathrm{b} + \varepsilon(\mathrm{Ni(HS)_2(aq),Mg^{2+}})\cdot \mathrm{c}\\ &+ \varepsilon(\mathrm{Ni(HS)_2(aq),Cl^-}) + \varepsilon(\mathrm{Ni(HS)_2(aq),SO_4^{2-}})\cdot \mathrm{a}\\ &- \varepsilon(\mathrm{Ni^{2+},Cl^-}) - \varepsilon(\mathrm{Ni^{2+},SO_4^{2-}})\cdot \mathrm{a}\\ &- 2\varepsilon(\mathrm{HS^-,Na^+})\cdot \mathrm{b} - 2\varepsilon(\mathrm{HS^-,Mg^{2+}})\cdot \mathrm{c}\end{aligned} \qquad (5.23)$$

5.5.2 Nickel sulphates

5.5.2.1 Nickel sulphate compounds

Several hydrated nickel sulphate solids from $\mathrm{NiSO_4\cdot 7H_2O}$ to $\mathrm{NiSO_4\cdot H_2O}$, including two forms of $\mathrm{NiSO_4\cdot 6H_2O}$, a tetrahydrate, and a dihydrate have been reported.

The heptahydrate, $\mathrm{NiSO_4\cdot 7H_2O}$, is the stable nickel sulphate hydrate at 298.15 K. Its solubility at 25°C is m(sat) = (2.62 ± 0.05) $\mathrm{mol\cdot kg^{-1}}$ $\mathrm{NiSO_4\cdot 7H_2O(cr)}$.

In contact with saturated solutions, the α-hexahydrate becomes the stable nickel sulphate near 302 K, and is transformed to the β-hexahydrate at approximately 327 K. Solubility data indicate that β-$\mathrm{NiSO_4\cdot 6H_2O}$ is the stable solid in contact with saturated solutions of nickel sulphate in water for temperatures between 327 and 358 K. There is evidence for the decomposition of the β-hexahydrate to a tetrahydrate at temperatures near 400 K and to the monohydrate near 440 K. The monohydrate does not readily lose water below 500 K.

All these nickel sulphate hydrates are highly soluble salts. $NiSO_4(cr)$ is unstable in water. They are not relevant under environmental conditions and thus, thermodynamic data selected by Gamsjäger et al. (2005) are not included in our database (Table 5.4).

5.5.2.2 Aqueous nickel sulphate complexes

The complexation reactions of Ni^{2+} with SO_4^{2-} have been the subject of a large number of investigations. For the reaction

$$Ni^{2+} + SO_4^{2-} \Leftrightarrow NiSO_4(aq)$$

Gamsjäger et al. (2005) re-analyzed conductance and emf data and selected a weighted average of these two data sets:

$$\log_{10}K°(298.15 \text{ K}) = (2.35 \pm 0.03).$$

Gamsjäger et al. (2005) stated further: "At high sulphate concentrations, there is some evidence for formation of $Ni(SO_4)_2^{2-}$ in several studies. However, the evidence is reasonably ambiguous, and may only reflect systematic errors in the experiment. No value is selected for $K_2°$ in the present review."

There have been several studies of the temperature dependence of the formation constant of the complex $NiSO_4(aq)$, as well as a determination of the enthalpy of reaction at 25°C by a titration calorimetric method. Gamsjäger et al. (2005) accepted the weighted average of the results from the calorimetric study and two determinations of the temperature dependence of $\log_{10}K°$:

$$\Delta_rH_m°(298.15 \text{ K}) = (5.66 \pm 0.81) \text{ kJ·mol}^{-1}.$$

We included both values, $\log_{10}K°$ and $\Delta_rH_m°$, in our database.

5.6 Group 15 compounds and complexes

5.6.1 Nitrogen compounds and complexes

5.6.1.1 Nickel nitrate compounds

The hydrated nickel nitrate solids have been the subject of sporadic thermodynamic studies over the last 150 years, but the basic thermodynamic quantities for these materials are not well defined.

The stable hydrate in equilibrium with a solution saturated in nickel nitrate at 298.15 K is $Ni(NO_3)_2·6H_2O(cr)$. The solid can easily lose water on exposure to dry air, but has also been reported to be slightly deliquescent in moist air. In a closed system, the hydrate begins to melt (or partially dissolve in its water of hydration) at 328K.

Dehydration of the hexahydrate leads to several lower hydrates, but the hydrate formed seems to depend markedly on the method used to carry out the dehydration. In few of the experiments were the dehydrated solids thoroughly characterized, nor was it established that the solids were stable over long periods.

All these nickel nitrate hydrates are highly soluble salts. They are not relevant under environmental conditions and thus, thermodynamic data selected by Gamsjäger et al. (2005) are not included in our database (Table 5.4).

5.6.1.2 Aqueous nickel nitrate complexes

For the reaction

$$Ni^{2+} + NO_3^- \Leftrightarrow NiNO_3^+$$

Gamsjäger et al. (2005) re-evaluated a data set measured in 1–4 M $Li(ClO_4, NO_3)$ taking into account only the formation of the $NiNO_3^+$ species. To minimize the medium effect, only half of the experimental data, for which $[NO_3^-] \leq [ClO_4^-]$, were taken into account. A weighted linear SIT regression resulted in the values $\log_{10}\beta_1°(298.15\ K) = (0.49 \pm 0.45)$ and $\Delta\varepsilon(LiClO_4) = -(0.08 \pm 0.14)\ kg\cdot mol^{-1}$. Gamsjäger et al. (2005) stated, without any further explanation, that from the latter value $\varepsilon(NiNO_3^+, ClO_4^-) = (0.44 \pm 0.14)\ kg\cdot mol^{-1}$ can be derived. How this derivation was done remains unclear. For the system analyzed $\Delta\varepsilon$ has to be calculated as $\Delta\varepsilon = \varepsilon(NiNO_3^+, ClO_4^-) - \varepsilon(Li^+, NO_3^-) - \varepsilon(Ni^{2+}, ClO_4^-)$. Using the selected values $\varepsilon(Ni^{2+}, ClO_4^-) = (0.37 \pm 0.03)\ kg\cdot mol^{-1}$ and $\varepsilon(Li^+, NO_3^-) = (0.08 \pm 0.01)\ kg\cdot mol^{-1}$ the correct result is

$$\varepsilon(NiNO_3^+, ClO_4^-) = (0.37 \pm 0.14)\ kg\cdot mol^{-1}.$$

This value is included in our database, together with an estimate $\varepsilon(NiNO_3^+, Cl^-) = (0.05 \pm 0.10)\ kg\cdot mol^{-1}$ based on charge correlations (see Appendix A).

For $\log_{10}\beta_1°$ Gamsjäger et al. (2005) selected the result of their SIT analysis with an increased uncertainty :

$$\log_{10}\beta_1°(298.15\ K) = (0.5 \pm 1.0).$$

This value is also included in our database.

5.6.1.3 Aqueous nickel ammine complexes

Aqueous nickel ammine 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 ammine complexes are taken from the seminal work of Bjerrum (1941).

We assumed that the ionic strength dependence of the isocoulombic reactions

$$Ni^{2+} + n\ NH_3(aq) \Leftrightarrow Ni(NH_3)_n^{2+} \qquad (n = 1\text{–}6)$$

can be neglected and thus, $\log_{10}\beta_n \approx \log_{10}\beta_n°$. We included the values of Bjerrum (1941) as supplemental data in our database.

In the absence of experimental data at varying ionic strength we used $\varepsilon(Ni(NH_3)_n^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg\cdot mol^{-1}$ and $\varepsilon(Ni(NH_3)_n^{2+}, ClO_4^-) = (0.4 \pm 0.1)\ kg\cdot mol^{-1}$ as estimates based on charge correlations (see Appendix A) and included them as supplemental data in our database.

5.6.2 Phosphorous compounds and complexes

5.6.2.1 Nickel phosphate compounds

A number of nickel phosphate solids have been reported, such as $Ni_3(PO_4)_2\cdot 8H_2O$, $Ni_3(PO_4)_2\cdot 7H_2O$, $Ni_3(PO_4)_2\cdot 1.25H_2O$, $NiHPO_4\cdot 3H_2O$, $(NiHPO_4)_2\cdot 3H_2O$, $Ni(H_2PO_4)_2\cdot 2H_2O$ and $Ni_3(PO_4)_2$. Nevertheless, chemical thermodynamic data for these solids are almost non-existent.

The most thoroughly studied solid is $Ni_3(PO_4)_2\cdot 8H_2O$.

However, Gamsjäger et al. (2005) concluded: "Though solubility measurements have been reported for $Ni_3(PO_4)_2 \cdot 8H_2O$, $Ni_3(PO_4)_2 \cdot 7H_2O$ and $NiHPO_4$, none are of adequate quality to allow chemical thermodynamic quantities to be calculated for these solids."

5.6.2.2 Aqueous nickel phosphate complexes

The literature on complex formation between phosphate and Ni(II) ions in solution is not extensive. Under most conditions the complexes are weak, and difficult to identify unambiguously because of protonation equilibria involving both the ligand and the complexes.

Most of the studies were inspired by the possible parallels between phosphate complexation and biochemical interactions between phosphate esters and metal ions. These studies have been carried out over a fairly limited pH range (usually between 4 and 6) at low ionic strength (≤ 0.2 M). Most authors interpreted their results in terms of a single complex, $NiHPO_4(aq)$,

$$Ni^{2+} + HPO_4^{2-} \Leftrightarrow NiHPO_3(aq).$$

Gamsjäger et al. (2005) corrected these values to $I = 0$, and selected a weighted average of three results at 25°C:

$$\log_{10}K°(298.15\ K) = (3.05 \pm 0.09).$$

This value is included in our database.

As in the NEA-TDB uranium review (Grenthe et al. 1992), the only polyphosphate(V) species considered by Gamsjäger et al. (2005) are the pyrophosphates (diphosphato complexes). Other polyphosphoric acid species have negligible equilibrium concentrations at total phosphate concentrations $< 0.045\ mol \cdot dm^{-3}$ and at temperatures below 200°C.

The complexes of the highly charged pyrophosphate ion with nickel are generally stronger than the phosphate complexes, but interpretation of the experiments is beset by the same difficulties as the interpretation of the phosphate studies with respect to unambiguous identification of the species.

Gamsjäger et al. (2005) selected the following values:

$$Ni^{2+} + P_2O_7^{4-} \Leftrightarrow NiP_2O_7^{2-}$$

$$\log_{10}K°(298.15\ K) = (8.73 \pm 0.25)$$

$$\Delta_r H_m°(298.15\ K) = (30.6 \pm 10.0)\ kJ \cdot mol^{-1}$$

$$Ni^{2+} + HP_2O_7^{3-} \Leftrightarrow NiHP_2O_7^{-}$$

$$\log_{10}K°(298.15\ K) = (5.14 \pm 0.25)$$

$$\Delta_r H_m°(298.15\ K) = (47.9 \pm 15.0)\ kJ \cdot mol^{-1}$$

The $\log_{10}K°$ values were derived from a single reliable study at 25°C in 0.1 M $(CH_3)_4NCl$ medium. The values for the enthalpies of reactions were derived from a single reliable study by analyzing the temperature dependence of formation constants between 5 to 35°C in 0.1 M KNO_3. Gamsjäger et al. (2005) accepted $\Delta_r H_m$ to be the same as $\Delta_r H_m°$ at $I = 0$ without correction for either ionic strength or association of K^+ with pyrophosphate and estimated their uncertainties.

All these values are included in our database, together with the estimates $\varepsilon(NiP_2O_7^{2-}, Na^+) = -(0.10 \pm 0.10)\ kg \cdot mol^{-1}$ and $\varepsilon(NiHP_2O_7^{-}, Na^+) = -(0.05 \pm 0.10)\ kg \cdot mol^{-1}$ based on charge correlations (see Appendix A).

Gamsjäger et al. (2005) further stated: "It must be emphasized that the values selected in this review for formation for $NiHP_2O_7^-$ and $NiP_2O_7^{2-}$ should not be used for solutions more than 0.01 M in alkali metal ions unless explicit values are introduced for the pyrophosphate-alkali metal ion association constants."

5.6.3 Arsenic compounds and complexes

5.6.3.1 Nickel arsenide compounds

Gamsjäger et al. (2005) selected enthalpy of formation values for NiAs(cr), $NiAs_2$(cr), Ni_5As_2(cr), $Ni_{11}As_8$(cr), as well as entropy values for NiAs(cr), Ni_5As_2(cr), $Ni_{11}As_8$(cr), and heat capacity functions for NiAs(cr) and $Ni_{11}As_8$(cr). No information is available about the behaviour of these compounds in aqueous systems under environmental conditions and hence, the thermochemical data selected by Gamsjäger et al. (2005) are not included in our database (Table 5.4).

5.6.3.2 Nickel arsenate compounds

Gamsjäger et al. (2005) evaluated published values for the solubility of $Ni_3(AsO_4)_2\cdot 8H_2O$(cr) (annabergite) for:

$$Ni_3(AsO_4)_2\cdot 8H_2O(cr) \Leftrightarrow 3\ Ni^{2+} + 2\ AsO_4^{3-} + 8\ H_2O(l)$$

using their selected auxiliary data and considering the effect of formation of the complex $NiHAsO_4$(aq) (see Section 5.6.3.3) and selected:

$$\log_{10}K^\circ(298.15\ K) = -(28.1 \pm 0.5).$$

This value is included in our database.

5.6.3.3 Aqueous nickel arsenate complexes

Langmuir et al. (1999) reported an estimated value of $\log_{10}K = 2.90$ for

$$Ni^{2+} + HAsO_4^{2-} \Leftrightarrow NiHAsO_3(aq).$$

Gamsjäger et al. (2005) argued that this value is similar to the value (3.05 ± 0.09) for the corresponding phosphate complex (see Section 5.6.2.2), and is an acceptable analogue value. They selected the value from Langmuir et al. (1999), but because of the unavailability of experimental values for comparison they assigned an uncertainty of ± 0.3,

$$\log_{10}K^\circ(298.15\ K) = (2.9 \pm 0.3).$$

Usually, estimated values are included in our database as supplemental data. However, as Gamsjäger et al. (2005) used the above estimated value in their evaluation of the solubility product of $Ni_3(AsO_4)_2\cdot 8H_2O$(cr) (annabergite) (see Section 5.6.3.2), these values should be used together in geochemical modelling and hence, both values are included as recommended values in our database.

5.6.3.4 Nickel arsenite compounds

Gamsjäger et al. (2005) used reported nickel concentrations, obtained from dissolution experiments of samples of nickel orthoarsenite in dilute nitric acid solutions at 20°C over 12 hours, assumed that the dissolution of the solid corresponds to the reaction:

$$Ni_3(AsO_3)_2\cdot xH_2O(cr, hydr.) + 6\ H^+ \Leftrightarrow 3\ Ni^{2+} + 2\ HAsO_2(aq) + (2 + x)\ H_2O(l)$$

and calculated an equilibrium constant:

$$\log_{10}K°(298.15 \text{ K}) = (28.7 \pm 0.7).$$

Considering the limited data available, the assumptions made by the reviewers, and the lack of a corresponding nickel arsenite complex, this value is included in our database as supplemental data.

5.7 Group 14 compounds and complexes

5.7.1 Carbon compounds and complexes

5.7.1.1 Nickel carbonate compounds

$NiCO_3$(cr), gaspéite, is the nickel end member of the solid solution (Ni,Mg)CO_3(cr). Gamsjäger et al. (2005) analyzed solubility data of synthetic $NiCO_3$(cr) for the reaction:

$$NiCO_3(cr) + 2 H^+ \Leftrightarrow Ni^{2+} + CO_2(g) + H_2O(l)$$

and selected

$$\log_{10}{}^*K°(298.15 \text{ K}) = (7.16 \pm 0.18).$$

They stated that this value obtained from solubility measurements of pure synthetic $NiCO_3$(cr) falls well within the error limits of values re-evaluated from decomposition studies, $NiCO_3(s) \Leftrightarrow NiO(s) + CO_2(g)$, but clearly is more precise.

Recalculation of this value for the reaction

$$NiCO_3(cr) \Leftrightarrow Ni^{2+} + CO_3^{2-}$$

using the selected values for the carbonic acid system results in

$$\log_{10}K°(298.15 \text{ K}) = -(11.00 \pm 0.18).$$

It seems that there is only one low temperature heat capacity study of $NiCO_3$(cr), and Gamsjäger et al. (2005) selected from this source

$$S_m°(NiCO_3, cr, 298.15 \text{ K}) = (85.4 \pm 2.0) \text{ J·K}^{-1}\text{·mol}^{-1}$$

$$C_{p,m}°(NiCO_3, cr, 298.15 \text{ K}) = (90.3 \pm 4.1) \text{ J·K}^{-1}\text{·mol}^{-1}$$

All these values are included in our database.

$NiCO_3 \cdot 5.5H_2O$(cr), hellyerite, has been prepared by a new method, and solubility measurements were carried out at different temperatures at I = 1.0 m (Na)ClO_4, as well as solubility data have been determined at 25°C and different ionic strengths. In either case the pH variation method was used to study the dissolution reaction according to:

$$NiCO_3 \cdot 5.5H_2O(cr) + 2 H^+ \Leftrightarrow Ni^{2+} + CO_2(g) + 6.5 H_2O(l)$$

Gamsjäger et al. (2005) selected

$$\log_{10}{}^*K°(298.15 \text{ K}) = (10.63 \pm 0.10)$$

from these new studies. A re-evaluation of two very old experimental data sets by Gamsjäger et al. (2005) resulted in $\log_{10}{}^*K° = (10.56 \pm 0.10)$, which compares favourably with the new data.

Recalculation of this value for the reaction

$$NiCO_3 \cdot 5.5H_2O(cr) \Leftrightarrow Ni^{2+} + CO_3^{2-} + 5.5 H_2O(l)$$

using the selected values for the carbonic acid system results in

$$\log_{10}K°(298.15 \text{ K}) = -(7.53 \pm 0.10).$$

From the weak temperature dependence of the solubility constant Gamsjäger et al. (2005) calculated the enthalpy of reaction and the entropy of $NiCO_3 \cdot 5.5H_2O(cr)$ using a non-linear least squares optimization routine. They selected:

$$S_m°(NiCO_3 \cdot 5.5H_2O, \text{cr}, 298.15 \text{ K}) = (311.1 \pm 10.0) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Apparently no experimental low-temperature heat capacity data of $NiCO_3 \cdot 5.5H_2O(cr)$ have been reported so far. Gamsjäger et al. (2005) obtained a crude estimate by analogy to magnesium carbonate and its hydrates:

$$C_{p,m}°(NiCO_3 \cdot 5.5H_2O, \text{cr}, 298.15 \text{ K}) = (405.4 \pm 50.0) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

All these values are included in our database.

5.7.1.2 Aqueous nickel carbonate complexes

Gamsjäger et al. (2005) start this section with:

"The formation of carbonato complexes in the system Ni^{2+}–H_2O–CO_2 has been critically discussed and re-evaluated in a seminal review by Hummel & Curti (2003).

So far only one paper has been published (Emara et al. 1987) describing an attempt to experimentally determine the equilibrium constant, β_1, of the reaction

$$Ni^{2+} + HCO_3^- \Leftrightarrow NiHCO_3^+$$

Emara et al. (1987) clearly misinterpreted their data and did not provide enough information to allow recalculation. Consequently, the stability constant of $NiHCO_3^+$ reported in Emara et al. (1987) cannot be included in this review."

Values of equilibrium constants for the above reaction estimated by various procedures differ considerably: $0.96 \leq \log_{10}\beta_1° \leq 3.08$.

The stability constant of the carbonato complex according to reaction

$$Ni^{2+} + CO_3^{2-} \Leftrightarrow NiCO_3(aq)$$

has also been estimated leading to an even larger discrepancy: $2.56 \leq \log_{10}K_1° \leq 6.87$.

For the reaction

$$NiCO_3(aq) + CO_3^{2-} \Leftrightarrow Ni(CO_3)_2^{2-}$$

one estimate exists for its equilibrium constant ($\log_{10}K_2° = 3.24$).

As the basis of the individual estimation procedures is rather dubious, variations of up to more than four log-units in these stability constants are to be expected (Hummel & Curti 2003). Again neither of these values appeared Gamsjäger et al. (2005) suitable to be included in their review.

Hummel & Curti (2003) proposed estimating K_1 using either the good correlation between the equilibrium constants of Ni(II) and Co(II) complexes and the poor data available for K_1 of $CoCO_3(aq)$ or the rather poor correlation between Ni(II) and Zn(II) complexes and the excellent data for K_1 of $ZnCO_3(aq)$. Both methods result in similar lower and upper bounds: $4 < \log_{10}K_1° < 5.5$.

A comparison of the stabilities of transition metal hydrogen carbonato as well as carbonato complexes led to $1 < \log_{10}\beta_1° < 2$ and $\log_{10}K_2° < (\log_{10}K_1° - 2)$ (Hummel & Curti 2003).

Gamsjäger et al. (2005) then concluded that "even the careful and competent guesswork of Hummel & Curti (2003) resulted in rough estimates only."

Gamsjäger et al. (2005) continued: "Fortunately, in a recent paper, Baeyens et al. (2003) investigated Ni-carbonato and -oxalato complexes by an ion exchange method. Ni-carbonato complexes were investigated at constant ionic strength I = 0.5 M $NaClO_4/NaHCO_3$ and (22 ± 1)°C. The experimentally obtained complexation constant, $\log_{10}K_1(295.12\ K) = (2.9 \pm 0.3)$, was extrapolated to $I = 0$ with the SIT approach to give

$$\log_{10}K_1°(298.15\ K) = (4.2 \pm 0.4).$$

This result was finally selected for the present review. The somewhat higher uncertainty was assigned, because Baeyens et al. (2003) carried out their measurements at 22°C instead of 25°C, and used a relatively simple approximation to extrapolate $\log_{10}K_1°$ to $I = 0$."

This value is included in our database.

Gamsjäger et al. (2005) further stated: "Only upper bounds can be given for the stabilities of $NiHCO_3^+$ and $Ni(CO_3)_2^{2-}$: $\log_{10}\beta_1°(298.15\ K) < 1.4$ and $\log_{10}K_2°(298.15\ K) < 2$ (Baeyens et al. 2003). Both upper bounds compare well with the lower limits of the range predicted by Hummel & Curti (2003), but do not qualify for being included in the list of selected values in this review."

We included in our database the values $\log_{10}\beta_1°(298.15\ K) \approx 1$ and $\log_{10}\beta_2°(298.15\ K) < 6$ as supplemental data.

In the absence of experimentally determined SIT interaction coefficients, we included the estimates $\varepsilon(NiHCO_3^+, Cl^-) = (0.05 \pm 0.10)\ kg\cdot mol^{-1}$, $\varepsilon(NiHCO_3^+, ClO_4^-) = (0.2 \pm 0.1)\ kg\cdot mol^{-1}$ and $\varepsilon(Ni(CO_3)_2^{2-}, Na^+) = -(0.10 \pm 0.10)\ kg\cdot mol^{-1}$ based on charge correlations (see Appendix A).

5.7.1.3 Aqueous nickel cyanide complexes

Most authors have agreed that the formation of $NiCN^+$, $Ni(CN)_2(aq)$ and $Ni(CN)_3^-$ cannot be detected in the equilibrated solutions. Reliable values were reported for the equilibrium

$$Ni^{2+} + 4\ CN^- \Leftrightarrow Ni(CN)_4^{2-}$$

Gamsjäger et al. (2005) found that although only a limited number of data are available in $NaClO_4$ media, the precision of the constants is assumed to be good enough to perform an SIT analysis. The weighted linear regression using five data points yielded the selected value of:

$$\log_{10}\beta_4°(298.15\ K) = (30.20 \pm 0.12).$$

From the slope of the SIT regression line, $\Delta\varepsilon(NaClO_4) = -(0.465 \pm 0.045)\ kg\cdot mol^{-1}$ can be calculated. Using the selected value for $\varepsilon(Ni^{2+}, ClO_4^-)$ and $\varepsilon(Na^+, CN^-) = (0.07 \pm 0.03)\ kg\cdot mol^{-1}$ leads to a value of

$$\varepsilon(Na^+, Ni(CN)_4^{2-}) = (0.185 \pm 0.081)\ kg\cdot mol^{-1}.$$

The reaction enthalpy of the formation of the tetracyano complex has been studied calorimetrically. Gamsjäger et al. (2005) selected:

$$\Delta_rH_m°(298.15\ K) = -(180.7 \pm 4.0)\ kJ\cdot mol^{-1}.$$

Since the pentacyano complex is rather unstable, high cyanide concentrations were used to achieve its formation, which resulted in considerable replacement of the original background electrolyte by NaCN. Due to this medium effect, Gamsjäger et al. (2005) assigned considerably higher uncertainties to the equilibrium constants than originally reported. The SIT analysis of the constants determined in $NaClO_4$ media for the reaction:

$$\mathrm{Ni(CN)_4^{2-} + CN^- \Leftrightarrow Ni(CN)_5^{3-}}$$

resulted in

$$\log_{10}K_5°(298.15\ \mathrm{K}) = -(1.70 \pm 0.36)$$

and $\Delta\varepsilon(\mathrm{NaClO_4}) = (0.00 \pm 0.11)\ \mathrm{kg \cdot mol^{-1}}$. From the latter value,

$$\varepsilon(\mathrm{Na^+, Ni(CN)_5^{3-}}) = (0.25 \pm 0.14)\ \mathrm{kg \cdot mol^{-1}}$$

can be derived. Using the equilibrium constant $\log_{10}\beta_4°$ from above, the overall formation constant of the $\mathrm{Ni(CN)_5^{3-}}$ species is

$$\mathrm{Ni^{2+} + 5\ CN^- \Leftrightarrow Ni(CO)_5^{3-}}$$

$$\log_{10}\beta_5°(298.15\ \mathrm{K}) = (28.5 \pm 0.5).$$

Neglecting the ionic strength dependence, $\Delta_r H_m°(298.15\ \mathrm{K}) = -(10.4 \pm 4.0)\ \mathrm{kJ \cdot mol^{-1}}$ can be estimated from the temperature variation of $\log_{10}K_5$. The combination of the above two enthalpy values yielded for the overall formation reaction:

$$\Delta_r H_m°(298.15\ \mathrm{K}) = -(191.1 \pm 8.0)\ \mathrm{kJ \cdot mol^{-1}}.$$

These values have been included in our database.

5.7.1.4 Aqueous nickel thiocyanide complexes

In the aqueous nickel thiocyanide system, depending on the ligand-to-metal ratio, the formation of four species is generally recognized:

$$\mathrm{Ni^{2+}} + q\ \mathrm{SCN^-} \Leftrightarrow \mathrm{Ni(SCN)}_q^{2-q}$$

with $q = 1$–4. A majority of the experimental data accepted by Gamsjäger et al. (2005) refers to the formation of the $\mathrm{NiSCN^+}$ species in perchlorate media. SIT analysis of these data showed acceptable consistency, and the weighted linear regression using 12 data points yielded the selected value of:

$$\log_{10}\beta_1°(q = 1, 298.15\ \mathrm{K}) = (1.81 \pm 0.04).$$

From the slope of the SIT regression line, $\Delta\varepsilon(q = 1, \mathrm{ClO_4^-}) = -(0.109 \pm 0.025)\ \mathrm{kg \cdot mol^{-1}}$ can be calculated. Since no experimental data are available $\varepsilon(\mathrm{H^+, CN^-})$ and $\varepsilon(\mathrm{Li^+, CN^-})$ were assumed to be equal to $\varepsilon(\mathrm{Na^+, CN^-})$. Using the selected values for $\varepsilon(\mathrm{Ni^{2+}, ClO_4^-})$ and $\varepsilon(\mathrm{Na^+, CN^-})$, $\Delta\varepsilon(q = 1, \mathrm{ClO_4^-})$ leads to a value of

$$\varepsilon(\mathrm{NiSCN^+, ClO_4^-}) = (0.31 \pm 0.03)\ \mathrm{kg \cdot mol^{-1}}.$$

Less data are available for the formation of the $\mathrm{Ni(SCN)_2(aq)}$ and $\mathrm{Ni(SCN)_3^-}$ species. The SIT treatment of the data accepted by Gamsjäger et al. (2005) resulted in the following selected thermodynamic formation constants:

$$\log_{10}\beta_2°(q = 2, 298.15\ \mathrm{K}) = (2.69 \pm 0.07),$$

$$\log_{10}\beta_3°(q = 3, 298.15\ \mathrm{K}) = (3.02 \pm 0.18).$$

From the slopes, $\Delta\varepsilon(q = 2, \mathrm{ClO_4^-}) = -(0.091 \pm 0.043)\ \mathrm{kg \cdot mol^{-1}}$ and $\Delta\varepsilon(q = 3, \mathrm{ClO_4^-}) = -(0.14 \pm 0.12)\ \mathrm{kg \cdot mol^{-1}}$ can be derived. These parameters lead to the values:

$$\varepsilon(\mathrm{Ni(SCN)_2(aq), Na^+ + ClO_4^-}) = (0.38 \pm 0.06)\ \mathrm{kg \cdot mol^{-1}},$$

$$\varepsilon(\mathrm{Na^+, Ni(SCN)_3^-}) = (0.66 \pm 0.13)\ \mathrm{kg \cdot mol^{-1}}.$$

Several experimental values are published for $\log_{10}\beta_4$ or $\log_{10}K_4$. However, Gamsjäger et al. (2005) concluded that, although there is good evidence for the existence of $Ni(SCN)_4^{2-}$, the available data cannot be used to derive a selected value.

Gamsjäger et al. (2005) found five reliable reports for the reaction enthalpies of the formation of $Ni(SCN)_q^{2-q}$ (q = 1–3) complexes. These data do not allow a correct evaluation of the ionic strength dependence, therefore it was assumed that the reaction enthalpies are independent of the ionic strength. Gamsjäger et al. (2005) selected the following weighted averages:

$$\Delta_r H_m^\circ(q = 1, 298.15\text{ K}) = -(11.8 \pm 5.0)\text{ kJ}\cdot\text{mol}^{-1},$$

$$\Delta_r H_m^\circ(q = 2, 298.15\text{ K}) = -(21 \pm 8)\text{ kJ}\cdot\text{mol}^{-1},$$

$$\Delta_r H_m^\circ(q = 3, 298.15\text{ K}) = -(29 \pm 10)\text{ kJ}\cdot\text{mol}^{-1}.$$

All these values have been included in our database.

5.7.2 Silicate compounds and complexes

Nickel silicate compounds and complexes are discussed in Chapter 8.

Table 5.4: Ni data selected by NEA (Gamsjäger et al. 2005) but not included in TDB 12/07. For explanations see text.

Gas	$Ni(g)$
Liquid	$Ni(l)$
Solids	$NiF_2(cr)$, $NiCl_2(cr)$, $NiCl_2\cdot 2H_2O(cr)$, $NiCl_2\cdot 4H_2O(cr)$, $NiCl_2\cdot 6H_2O(cr)$, $NiBr_2(cr)$, $NiI_2(cr)$, β-$Ni(IO_3)_2$, $Ni(IO_3)_2\cdot 2H_2O(cr)$, α-NiS, β-NiS, $NiS_2(cr)$, $Ni_3S_2(cr)$, $Ni_9S_8(cr)$, $NiSO_4(cr)$, α-$NiSO_4\cdot 6H_2O$, β-$NiSO_4\cdot 6H_2O$, $NiSO_4\cdot 7H_2O(cr)$, $Ni(NO_3)_2\cdot 2H_2O(cr)$, $Ni(NO_3)_2\cdot 4H_2O(cr)$, $Ni(NO_3)_2\cdot 6H_2O(cr)$, $NiAs(cr)$, $NiAs_2(cr)$, $Ni_5As_2(cr)$, $Ni_{11}As_8(cr)$

Table 5.5: Selected nickel data. All data included in TDB Version 12/07 are taken from Gamsjäger et al. (2005) with the exception of those marked with an asterisk (*). Core data are bold and supplemental data are in italics. New or changed data with respect to TDB Version 01/01 (Hummel et al., 2002) are shaded.

		TDB Version 01/01				TDB Version 12/07				
Name	**Redox**	$\Delta_f G_m^\circ$ [kJ·mol^{-1}]	$\Delta_f H_m^\circ$ [kJ·mol^{-1}]	S_m° [J·K^{-1}·mol^{-1}]	$C_{p,m}^\circ$ [J·K^{-1}·mol^{-1}]	$\Delta_f G_m^\circ$ [kJ·mol^{-1}]	$\Delta_f H_m^\circ$ [kJ·mol^{-1}]	S_m° [J·K^{-1}·mol^{-1}]	$C_{p,m}^\circ$ [J·K^{-1}·mol^{-1}]	**Species**
Ni(cr)	0	0.0	0.0	**29.87 ± 0.21**	-	0.0	0.0	**29.87 ± 0.20**	26.07 ± 0.10	Ni(cr)
Ni+2	II	-45.5 ± 3.4	-54.1 ± 2.5	-130 ± 3	-	-45.77 ± 0.77	-55.01 ± 0.88	-131.8 ± 1.4	-46.1 ± 7.5	Ni^{2+}

		TDB Version 01/01		TDB Version 12/07		
Name	**Redox**	$\log_{10}\beta^\circ$	$\Delta_r H_m^\circ$ [kJ·mol^{-1}]	$\log_{10}\beta^\circ$	$\Delta_r H_m^\circ$ [kJ·mol^{-1}]	**Reaction**
NiOH+	II	-9.50 ± 0.36	50 ± 21	-9.54 ± 0.14	53.8 ± 1.7	$Ni^{2+} + H_2O(l) \Leftrightarrow NiOH^+ + H^+$
Ni(OH)2	II	-18.0 ± 1.0	86 ± 13	*(≤ -18)*[a]	*(≈ 90)*[a]	$Ni^{2+} + 2\ H_2O(l) \Leftrightarrow Ni(OH)_2(aq) + 2\ H^+$
Ni(OH)3-	II	-29.7 ± 1.5	121 ± 18	-29.2 ± 1.7	*(121.2 ± 6.5)*[a]	$Ni^{2+} + 3\ H_2O(l) \Leftrightarrow Ni(OH)_3^- + 3\ H^+$
Ni(OH)4-2	II	-44.9 ± 0.6	-	-	-	$Ni^{2+} + 4\ H_2O(l) \Leftrightarrow Ni(OH)_4^{2-} + 4\ H^+$
Ni2OH+3	II	-9.8 ± 1.2	35 ± 17	-10.6 ± 1.0	45.9 ± 6.0	$2\ Ni^{2+} + H_2O(l) \Leftrightarrow Ni_2OH^{3+} + H^+$
Ni4(OH)4+4	II	-27.9 ± 1.0	170 ± 17	-27.52 ± 0.15	190 ± 10	$4\ Ni^{2+} + 4\ H_2O(l) \Leftrightarrow Ni_4(OH)_4^{4+} + 4\ H^+$
NiF+	II	1.3	-	1.43 ± 0.08	9.5 ± 3.0	$Ni^{2+} + F^- \Leftrightarrow NiF^+$
NiCl+	II	0.40	-	0.08 ± 0.60	-	$Ni^{2+} + Cl^- \Leftrightarrow NiCl^+$
NiCl2	II	0.96	-	-	-	$Ni^{2+} + 2\ Cl^- \Leftrightarrow NiCl_2(aq)$
NiHS+	II	5.5 ± 0.2	-	(5.5 ± 0.2)*	-	$Ni^{2+} + HS^- \Leftrightarrow NiHS^+$
Ni(HS)2	II	11.1 ± 0.1	-	(11.1 ± 0.1)*	-	$Ni^{2+} + 2\ HS^- \Leftrightarrow Ni(HS)_2(aq)$
NiSO4	II	2.31	13.975	2.35 ± 0.03	5.66 ± 0.81	$Ni^{2+} + SO_4^{2-} \Leftrightarrow NiSO_4(aq)$
Ni(SO4)2-2	II	3.2	-	-	-	$Ni^{2+} + 2\ SO_4^{2-} \Leftrightarrow Ni(SO_4)_2^{2-}$
NiNO3+	II	0.4	-	0.5 ± 1.0	-	$Ni^{2+} + NO_3^- \Leftrightarrow NiNO_3^+$
Ni(NO3)2	II	-0.6	-	-	-	$Ni^{2+} + 2\ NO_3^- \Leftrightarrow Ni(NO_3)_2(aq)$
NiNH3+2	II	2.7	-	*(2.7)**	-	$Ni^{2+} + NH_3(aq) \Leftrightarrow NiNH_3^{2+}$
Ni(NH3)2+2	II	4.9	-	*(4.9)**	-	$Ni^{2+} + 2\ NH_3(aq) \Leftrightarrow Ni(NH_3)_2^{2+}$
Ni(NH3)3+2	II	6.5	-	*(6.5)**	-	$Ni^{2+} + 3\ NH_3(aq) \Leftrightarrow Ni(NH_3)_3^{2+}$
Ni(NH3)4+2	II	7.6	-	*(7.6)**		$Ni^{2+} + 4\ NH_3(aq) \Leftrightarrow Ni(NH_3)_4^{2+}$
Ni(NH3)5+2	II	8.3	-	*(8.3)**	-	$Ni^{2+} + 5\ NH_3(aq) \Leftrightarrow Ni(NH_3)_5^{2+}$

		TDB Version 01/01		**TDB Version 12/07**		
Name	**Redox**	**$\log_{10}\beta°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**$\log_{10}\beta°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**Reaction**
Ni(NH3)6+2	II	8.2	-	*(8.2)**	-	*$Ni^{2+} + 6\ NH_3(aq) \Leftrightarrow Ni(NH_3)_6^{2+}$*
NiH2PO4+	II	1.544	-	-	-	$Ni^{2+} + H_2PO_4^- \Leftrightarrow NiH_2PO_4^+$
NiHPO4	II	2.934	-	3.05 ± 0.09	-	$Ni^{2+} + HPO_4^{2-} \Leftrightarrow NiHPO_4(aq)$
NiPO4-	II	8.374	-	-	-	$Ni^{2+} + PO_4^{3-} \Leftrightarrow NiPO_4^-$
NiHP2O7-	II	9.258	-	-	-	$Ni^{2+} + 2\ HPO_4^{2-} + H^+ \Leftrightarrow NiHP_2O_7^- + H_2O(l)$
NiHP2O7-	II	-	-	5.14 ± 0.25	47.9 ± 15.0	$Ni^{2+} + HP_2O_7^{3-} \Leftrightarrow NiHP_2O_7^-$
NIP2O7-2	II	3.088	9.917	-	-	$Ni^{2+} + 2\ HPO_4^{2-} \Leftrightarrow NiP_2O_7^{2-} + H_2O(l)$
NiP2O7-2	II	-	-	8.73 ± 0.25	30.6 ± 10.0	$Ni^{2+} + P_2O_7^{4-} \Leftrightarrow NiP_2O_7^{2-}$
NiHAsO4	II	-	-	2.9 ± 0.3	-	$Ni^{2+} + HAsO_4^{2-} \Leftrightarrow NiHAsO_4(aq)$
NiCO3	II	4.0 ± 0.3	-	4.2 ± 0.4	-	$Ni^{2+} + CO_3^{2-} \Leftrightarrow NiCO_3(aq)$
Ni(CO3)2-2	II	< 6	-	*(< 6)**	-	*$Ni^{2+} + 2\ CO_3^{2-} \Leftrightarrow Ni(CO_3)_2^{2-}$*
NiHCO3+	II	≈ 1	-	*(≈ 1)**	-	*$Ni^{2+} + HCO_3^- \Leftrightarrow NiHCO_3^+$*
Ni(CN)4-2	II	-	-	30.2 ± 0.12	-180.7 ± 4.0	$Ni^{2+} + 4\ CN^- \Leftrightarrow Ni(CN)_4^{2-}$
Ni(CN)5-3	II	-	-	28.5 ± 0.5	-191.1 ± 8.0	$Ni^{2+} + 5\ CN^- \Leftrightarrow Ni(CN)_5^{3-}$
NiSCN+	II	-	-	1.81 ± 0.04	-11.8 ± 5.0	$Ni^{2+} + SCN^- \Leftrightarrow NiSCN^+$
Ni(SCN)2	II	-	-	2.69 ± 0.07	-21 ± 8	$Ni^{2+} + 2\ SCN^- \Leftrightarrow Ni(SCN)_2(aq)$
Ni(SCN)3-	II	-	-	3.02 ± 0.18	-29 ± 10	$Ni^{2+} + 3\ SCN^- \Leftrightarrow Ni(SCN)_3^-$

[a] Derived from data reported but not selected by Gamsjäger et al. (2005)

		TDB Version 01/01		TDB Version 12/07			
Name	**Redox**	**$\log_{10}K_{s,0}°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**$\log_{10}K_{s,0}°$**	**$S_m°$** [J·K^{-1}·mol^{-1}]	**$C_{p,m}°$** [J·K^{-1}·mol^{-1}]	**Reaction**
Ni(OH)2(cr, β)[a]	II	10.5 ± 0.5	73 ± 10	11.02 ± 0.20	80.0 ± 0.8	82.0 ± 0.3	$Ni(OH)_2(cr, \beta) + 2 H^+ \Leftrightarrow Ni^{2+} + 2 H_2O(l)$
NiO(cr)	II	-	-	12.48 ± 0.15	38.4 ± 0.4	44.4 ± 0.1	$NiO(cr) + 2 H^+ \Leftrightarrow Ni^{2+} + H_2O(l)$
NiCO3(cr)	II	-11.2 ± 0.3	-	-11.00 ± 0.18	85.4 ± 2.0	90.3 ± 4.1	$NiCO_3(cr) \Leftrightarrow Ni^{2+} + CO_3^{2-}$
NiCO3:5.5H2O(s)	II	-	-	-7.53 ± 0.10	311.1 ± 10	405.4 ± 50	$NiCO_3 \cdot 5.5H_2O(s) \Leftrightarrow Ni^{2+} + CO_3^{2-} + 5.5 H_2O(l)$
Ni3(AsO4)2:8H2O(s)	II	-	-	-28.1 ± 0.5	540.8 ± 73.3	-	$Ni_3(AsO_4)_2 \cdot 8H_2O(s) \Leftrightarrow 3 Ni^{2+} + 2 AsO_4^{3-} + 8 H_2O(l)$
Ni3(AsO3)2:xH2O(s)	II	-	-	*28.7 ± 0.7*	-	-	$Ni_3(AsO_3)_2 \cdot xH_2O(s) + 6H^+ \Leftrightarrow 3 Ni^{2+} + 2As(OH)_3(aq) + x H_2O(l)$

[a] TDB Version 01/01: Theophrastite

Table 5.6: Selected SIT ion interaction coefficients $\varepsilon_{j,k}$ [kg·mol^{-1}] for updated auxiliary data. The data included in TDB Version 12/07 are taken from Gamsjäger et al. (2005). Own data estimates based on charge correlations (see Appendix A) are shaded.

j ***k*** → ↓	**Cl$^-$**	**ClO$_4^-$**	**NO$_3^-$**	**Na$^+$ + ClO$_4^-$**	**Na$^+$**	**K$^+$**
	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$
Ni+2	0.17 ± 0.02	0.37 ± 0.03	0.182 ± 0.010	0	0	0
NiOH+	-0.01 ± 0.07	0.14 ± 0.07	-	0	0	0
Ni(OH)2	0	0	0	0	0	0
Ni(OH)3-	0	0	0	0	-0.05 ± 0.20	-
Ni2OH+3	0.25 ± 0.10	0.59 ± 0.15	-	0	0	0
Ni4(OH)4+4	0.43 ± 0.08	1.08 ± 0.08	-	0	0	0
NiF+	0.05 ± 0.10	0.34 ± 0.08	-	0	0	0
NiCl+	(0.47 ± 0.06)[a]	(0.47 ± 0.06)[a]	-	0	0	0
NiHS+	0.05 ± 0.10	0.2 ± 0.1	-	0	0	0
Ni(HS)2	0	0	0	0	0	0
NiSO4	0	0	0	0	0	0
NiNO3+	0.05 ± 0.10	0.37 ± 0.14	-	0	0	0
NiNH3+2	*0.15 ± 0.10*	*0.4 ± 0.1*	-	0	0	0
Ni(NH3)2+2	*0.15 ± 0.10*	*0.4 ± 0.1*	-	0	0	0
Ni(NH3)3+2	*0.15 ± 0.10*	*0.4 ± 0.1*	-	0	0	0
Ni(NH3)4+2	*0.15 ± 0.10*	*0.4 ± 0.1*	-	0	0	0
Ni(NH3)5+2	*0.15 ± 0.10*	*0.4 ± 0.1*	-	0	0	0
Ni(NH3)6+2	*0.15 ± 0.10*	*0.4 ± 0.1*	-	0	0	0
NiHPO4	0	0	0	0	0	0
NiHP2O7-	0	0	0	0	*-0.05 ± 0.10*	-
NiP2O7-2	0	0	0	0	*-0.10 ± 0.10*	-
NiHAsO4	0	0	0	0	0	0
NiCO3	0	0	0	0	0	0
Ni(CO3)2-2	0	0	0	0	*-0.10 ± 0.10*	-
NiHCO3+	*0.05 ± 0.10*	*0.2 ± 0.1*	-	0	0	0

j ***k*** → ↓	**Cl^-** $\varepsilon_{j,k}$	**ClO_4^-** $\varepsilon_{j,k}$	**NO_3^-** $\varepsilon_{j,k}$	**$Na^+ + ClO_4^-$** $\varepsilon_{j,k}$	**Na^+** $\varepsilon_{j,k}$	**K^+** $\varepsilon_{j,k}$
Ni(CN)4-2	0	0	0	0	0.185 ± 0.081	-
Ni(CN)5-3	0	0	0	0	0.25 ± 0.14	-
NiSCN+	*0.05 ± 0.10*	0.31 ± 0.04	-	0	0	0
Ni(SCN)2	0	0	0	0.38 ± 0.08	0	0
Ni(SCN)3-	0	0	0	0	0.66 ± 0.13	-

[a] In combination with $\varepsilon(Ni^{2+}, Cl^-) = (Ni^{2+}, ClO_4^-) = (0.37 \pm 0.03)\ kg \cdot mol^{-1}$

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6 Plutonium

6.1 Introduction

Almost all information on plutonium contained in this report was taken (in large parts verbatim) from the NEA review of the "Chemical Thermodynamics of Neptunium & Plutonium" by Lemire et al. (2001) and from the “Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium” by Guillaumont et al. (2003), the latter of which reviewed new literature on plutonium published between 1999 and the end of 2001 that could not be considered by Lemire et al. (2001). However, not all values recommended by Lemire et al. (2001) and Guillaumont et al. (2003) are included in our database since the NEA reviews (unlike our database) are not restricted to data relevant for radioactive waste management or even environmental modeling in general. We tried to exclude from our database all phases and complexes that most probably will never be relevant in environmental systems (see Table 6.1). All data selected for our database are listed in Table 6.2.

Due to a lack of experimental data, several ion interaction coefficients for cationic plutonium species with chloride are unknown. We filled these gaps by applying an estimation method described in Appendix A, which is based on a statistical analysis of published SIT ion interaction coefficients and which allows the estimation of such coefficients for the interaction of cations with Cl^- and ClO_4^-, and for the interaction of anions with Na^+ from the charge of the considered cations or anions. The selected ion interaction coefficients for plutonium species are listed in Table 6.3.

6.2 Elemental plutonium

Plutonium metal, liquid and gas are not relevant under environmental conditions. Therefore, the thermodynamic data selected by Lemire et al. (2001) for β-Pu(cr), δ-Pu(cr), δ'-Pu(cr), γ-Pu(cr), ε-Pu(cr), and Pu(g) are 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:

$$C_{p,\mathrm{m}}°(\mathrm{Pu, cr}, \alpha, 298.15\ \mathrm{K}) = (31.49 \pm 0.40)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

$$S_\mathrm{m}°(\mathrm{Pu, cr}, \alpha, 298.15\ \mathrm{K}) = (54.46 \pm 0.80)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

6.3 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, 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:

$$\mathrm{PuO_2^{2+} + 4H^+ + 3e^- \Leftrightarrow Pu^{3+} + 2H_2O(l)} \quad (\textit{cf.}\ \text{Section 6.3.1})$$

$$\mathrm{PuO_2^{2+} + 4H^+ + 2e^- \Leftrightarrow Pu^{4+} + 2H_2O(l)} \quad (\textit{cf.}\ \text{Section 6.3.3})$$

$$\mathrm{PuO_2^{2+} + e^- \Leftrightarrow PuO_2^{+}} \quad (\textit{cf.}\ \text{Section 6.3.2})$$

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 1.1 to 1.4.

6.3.1 PuO_2^{2+}

Derivation of $\log_{10}{}^*K°$(6.1, 298.15 K), $\Delta_f G_m°(PuO_2^{2+}$, 298.15 K), $\varepsilon(PuO_2^{2+}, ClO_4^-)$, and $\varepsilon(PuO_2^{2+}, Cl^-)$

$\Delta_r G_m$(6.1, 1 M $HClO_4$, 298.15 K) for the reaction

$$\mathrm{PuO_2^{2+} + 4H^+ + 3e^- \Leftrightarrow Pu^{3+} + 2H_2O(l)} \tag{6.1}$$

was calculated by combining the Gibbs free energy of reaction for the Pu^{4+} disproportionation equilibrium

$$\mathrm{3Pu^{4+} + 2H_2O(l) \Leftrightarrow PuO_2^{2+} + 2Pu^{3+} + 4H^+} \tag{6.2}$$

with the Gibbs free energy of reaction corresponding to the Pu^{4+}/Pu^{3+} redox potential of

$$\mathrm{Pu^{4+} + e^- \Leftrightarrow Pu^{3+}} \tag{6.3}$$

$\Delta_r G_m$(6.1, 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^-, Lemire et al. (2001) used the corresponding values of the homologous ions Nd^{3+} and UO_2^{2+}:

$$\varepsilon(\mathrm{Pu^{3+}, ClO_4^-}) = \varepsilon(\mathrm{Nd^{3+}, ClO_4^-})^{2} = (0.49 \pm 0.05)\ \mathrm{kg \cdot mol^{-1}}$$

$$\varepsilon(\mathrm{PuO_2^{2+}, ClO_4^-}) = \varepsilon(\mathrm{UO_2^{2+}, ClO_4^-})^{3} = (0.46 \pm 0.05)\ \mathrm{kg \cdot mol^{-1}}$$

Since there are no data available for chloride systems, we estimated

$$\varepsilon(\mathrm{PuO_2^{2+}, Cl^-}) = (0.15 \pm 0.10)\ \mathrm{kg \cdot mol^{-1}}$$

based on charge correlations (see Appendix A). From the resulting $\Delta_r G_m°$(6.1, 298.15 K) follows

$$\log_{10}{}^*K°(6.1,\ 298.15\ \mathrm{K}) = (50.97 \pm 0.15)$$

$\Delta_f G_m°(PuO_2^{2+}$, 298.15 K) was calculated from $\Delta_r G_m°$(6.1, 298.15 K) together with the selected $\Delta_f G_m°(Pu^{3+}$, aq, 298.15 K), *cf.* Section 6.3.4, and CODATA auxiliary data:

$$\Delta_f G_m°(\mathrm{PuO_2^{2+}},\ 298.15\ \mathrm{K}) = -(762.4 \pm 2.8)\ \mathrm{kJ \cdot mol^{-1}}$$

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[2] Lemire et al. (2001) cite Spahiu (1983) as reference for $\varepsilon(Nd^{3+}, ClO_4^-)$. Spahiu (1983) gave the range 0.47 – 0.52 kg·mol^{-1} (without uncertainties) for the series $\varepsilon(La^{3+}, ClO_4^-)$ - $\varepsilon(Lu^{3+}, ClO_4^-)$ but did not mention how these values were obtained. According to Spahiu (1985), they were derived from the isopiestic measurements by Rard et al. (1977) of activity coefficients of rare earth perchlorate solutions.

[3] The value $\varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$ kg·mol^{-1} was selected by Grenthe et al. (1992) as derived by Ciavatta (1980) from isopiestic data. For the estimate, Lemire et al. (2001) increased the uncertainty to ± 0.05 kg·mol^{-1}.

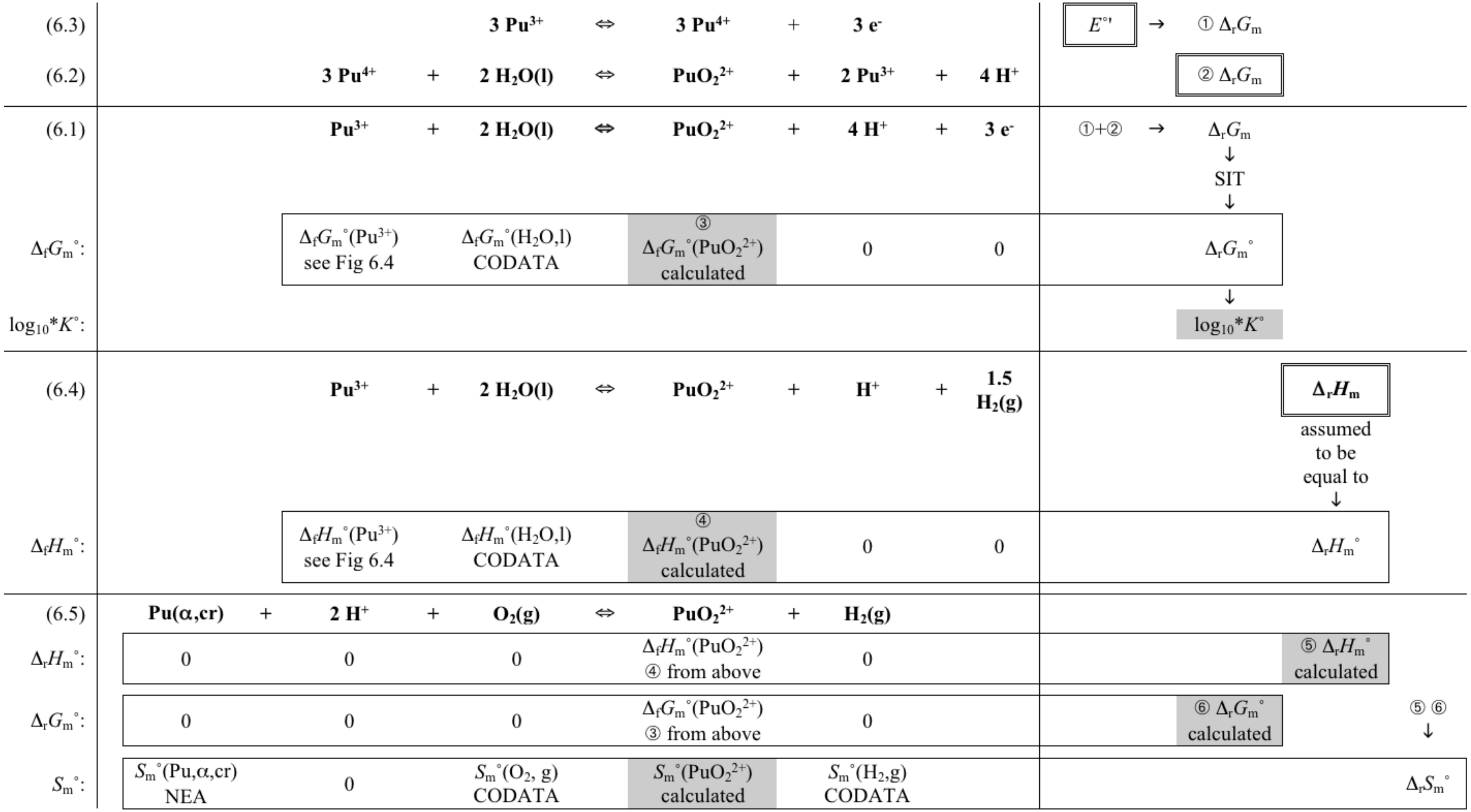

Fig. 6.1: Schematic representation of the derivation and selection process of thermodynamic data for PuO_2^{2+} by Lemire et al. (2001).

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

$$Pu^{3+} + 2\ H_2O(l) \Leftrightarrow PuO_2^{2+} + H^+ + 3/2\ H_2(g) \quad (6.4)$$

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 6.3.4) 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)

$\Delta_r S_m°$(6.5, 298.15 K) for the reaction

$$Pu(cr, \alpha) + 2\ H^+ + O_2(g) \Leftrightarrow PuO_2^{2+} + H_2(g) \quad (6.5)$$

was calculated from the Gibbs-Helmholtz equation (G = H - TS) applied to reaction (6.5), using $\Delta_r G_m°$(6.5, 298.15 K), which is equivalent to the selected value for $\Delta_f G_m°(PuO_2^{2+}$, 298.15 K), and $\Delta_r H_m°$(6.5, 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 $\Delta_r S_m°$(6.5, 298.15 K) of the reaction using the selected $S_m°$(Pu, cr, α, 298.15 K), *cf.* Section 6.2, and CODATA auxiliary values.

6.3.2 PuO_2^+

Derivation of $\log_{10}K°$(6.7, 298.15 K), $\Delta_f G_m°(PuO_2^+$, 298.15 K), $\varepsilon(PuO_2^+, ClO_4^-)$, and $\varepsilon(PuO_2^+, Cl^-)$

The standard potential of the reaction

$$PuO_2^{2+} + ½\ H_2(g) \Leftrightarrow PuO_2^+ + H^+ \quad (6.6)$$

was derived from formal potentials measured in 1 M $HClO_4$ which were extrapolated to standard conditions using SIT. The corresponding equilibrium constant is

$$\log_{10}{}^*K°(6.6, 298.15\ K) = (15.82 \pm 0.09)$$

The extrapolation was done by Lemire et al. (2001) by using $\Delta\varepsilon = \varepsilon(PuO_2^{2+}, ClO_4^-) - \varepsilon(PuO_2^+, ClO_4^-) = (0.22 \pm 0.03)\ kg{\cdot}mol^{-1}$, a value determined by Capdevila & Vitorge (1995) from redox potential measurements in 0–3.5 m perchlorate solutions. Note that the resulting standard potential was not considered by Lemire et al. (2001) due to the relatively large uncertainty of the reported measurements. From Δε and the selected $\varepsilon(PuO_2^{2+}, ClO_4^-) = (0.46 \pm 0.05)\ kg{\cdot}mol^{-1}$ follows

$$\varepsilon(PuO_2^+, ClO_4^-) = (0.24 \pm 0.05)\ kg{\cdot}mol^{-1}$$

Since there are no data available for chloride systems, we estimated

$$\varepsilon(PuO_2^+, Cl^-) = (0.05 \pm 0.10)\ kg{\cdot}mol^{-1}$$

based on charge correlations (see Appendix A).

Note that the value of $\log_{10}{}^*K°$(6.6, 298.15 K), as well as the values for $\Delta_r G_m°$(6.3, 298.15 K) and $\Delta_r H_m°$(6.6, 298.15 K), also apply to the reaction

$$PuO_2^{2+} + e^- \Leftrightarrow PuO_2^+ \qquad (6.7)$$

because reaction (6.7) can be obtained by subtracting

$$½ \, H_2(g) \Leftrightarrow H^+ + e^- \qquad (6.8)$$

from reaction (6.6), and because $\Delta_r G_m°$(6.8, 298.15 K) and $\Delta_r H_m°$(6.8, 298.15 K) are both equal to zero. Thus

$$\log_{10}K°(6.7, 298.15 \text{ K}) = (15.82 \pm 0.09)$$

$\Delta_f G_m°(PuO_2^+$, 298.15 K) was calculated from $\Delta_r G_m°$(6.6, 298.15 K) corresponding to the selected $\log_{10}{}^*K°$(6.6, 298.15 K) and from the selected $\Delta_f G_m°(PuO_2^{2+}$, 298.15 K), *cf.* Section 6.3.1

$$\Delta_f G_m°(PuO_2^+, 298.15 \text{ K}) = -(852.6 \pm 2.9) \text{ kJ·mol}^{-1}$$

Derivation of $\Delta_f H_m°(PuO_2^+$, 298.15 K)

$\Delta_r H_m°$(6.6, 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

$$\Delta_f H_m°(PuO_2^+, 298.15 \text{ K}) = -(910.1 \pm 8.9) \text{ kJ·mol}^{-1}$$

was then obtained from $\Delta_r H_m°$(6.6, 298.15 K) by using the selected value for $\Delta_f H_m°(PuO_2^{2+}$, 298.15 K), *cf.* Section 6.3.1.

Derivation of $S_m°(PuO_2^+$, 298.15 K)

$\Delta_r S_m°$(6.6, 298.15 K) was obtained from the Gibbs-Helmholtz equation, using $\Delta_r G_m°$(6.6, 298.15 K) corresponding to the selected value of $\log_{10}K°$(6.6, 298.15 K) and from $\Delta_r H_m°$(6.6, 298.15 K).

$S_m°(PuO_2^+$, 298.15 K) was then calculated from $\Delta_r S_m°$(6.6, 298.15 K) using the selected value for $S_m°(PuO_2^{2+}$, 298.15 K), *cf.* Section 6.3.1, and CODATA auxiliary data

$$S_m°(PuO_2^+, 298.15 \text{ K}) = (1 \pm 30) \text{ J·K}^{-1}\text{·mol}^{-1}$$

6.3.3 Pu^{4+}

Derivation of $\log_{10}K°$(6.10, 298.15 K), $\Delta_f G_m°(Pu^{4+}$, 298.15 K), $\varepsilon(Pu^{4+}, ClO_4^-)$, and $\varepsilon(Pu^{4+}, Cl^-)$

The standard potential of the reaction

$$Pu^{4+} + ½ \, H_2(g) \Leftrightarrow Pu^{3+} + H^+ \qquad (6.9)$$

was derived from experimental determinations of the Pu^{4+}/Pu^{3+} potential in 1 M $HClO_4$, $E°'$(6.9, 1 M $HClO_4$, 298.15 K), that were extrapolated to $I = 0$ using SIT. The selected value

$$\log_{10}{}^*K°(6.9, 298.15 \text{ K}) = (17.69 \pm 0.04)$$

was then calculated from the standard potential. The extrapolation was done by Lemire et al. (2001) by using $\Delta\varepsilon = \varepsilon(Pu^{4+}, ClO_4^-) - \varepsilon(Pu^{3+}, ClO_4^-) = (0.33 \pm 0.035)$ kg·mol^{-1}, a value determined by Capdevila & Vitorge (1995) from redox potential measurements in 0–3.5 m perchlorate solutions. The uncertainty was estimated by Lemire et al. (2001). From $\Delta\varepsilon$ and the selected $\varepsilon(Pu^{3+}, ClO_4^-) = (0.49 \pm 0.03)$ kg·mol^{-1} then follows, according to Lemire et al. (2001), $\varepsilon(Pu^{4+}, ClO_4^-) = (0.82 \pm 0.06)$ kg·mol^{-1}. Note that Guillaumont et al. (2003) listed a slightly different uncertainty of ± 0.07 kg·mol^{-1}, and this value was kept in all the following NEA-reviews and is also adopted for our database.

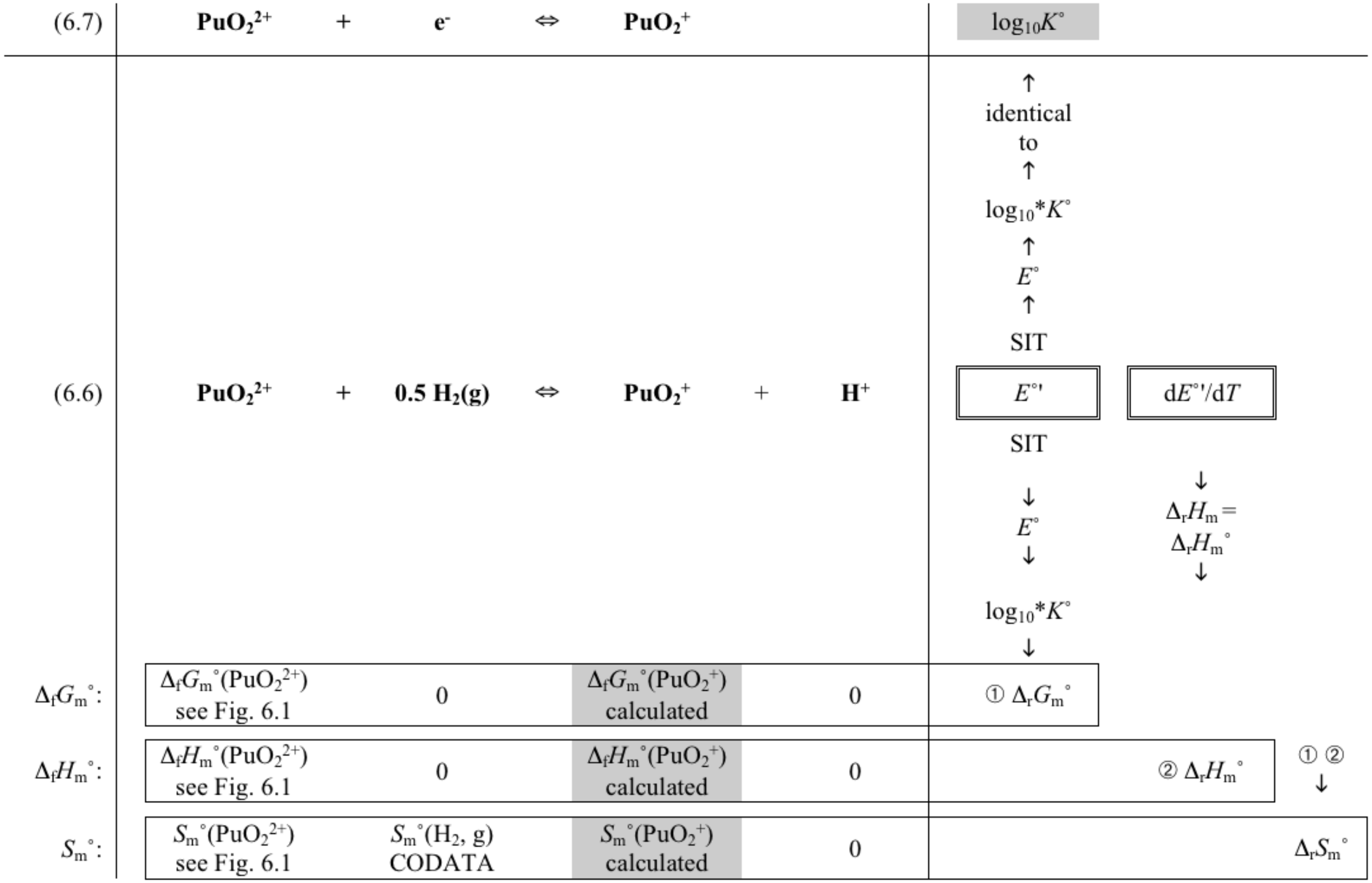

Fig. 6.2: Schematic representation of the derivation and selection process of thermodynamic data for PuO_2^+ by Lemire et al. (2001).

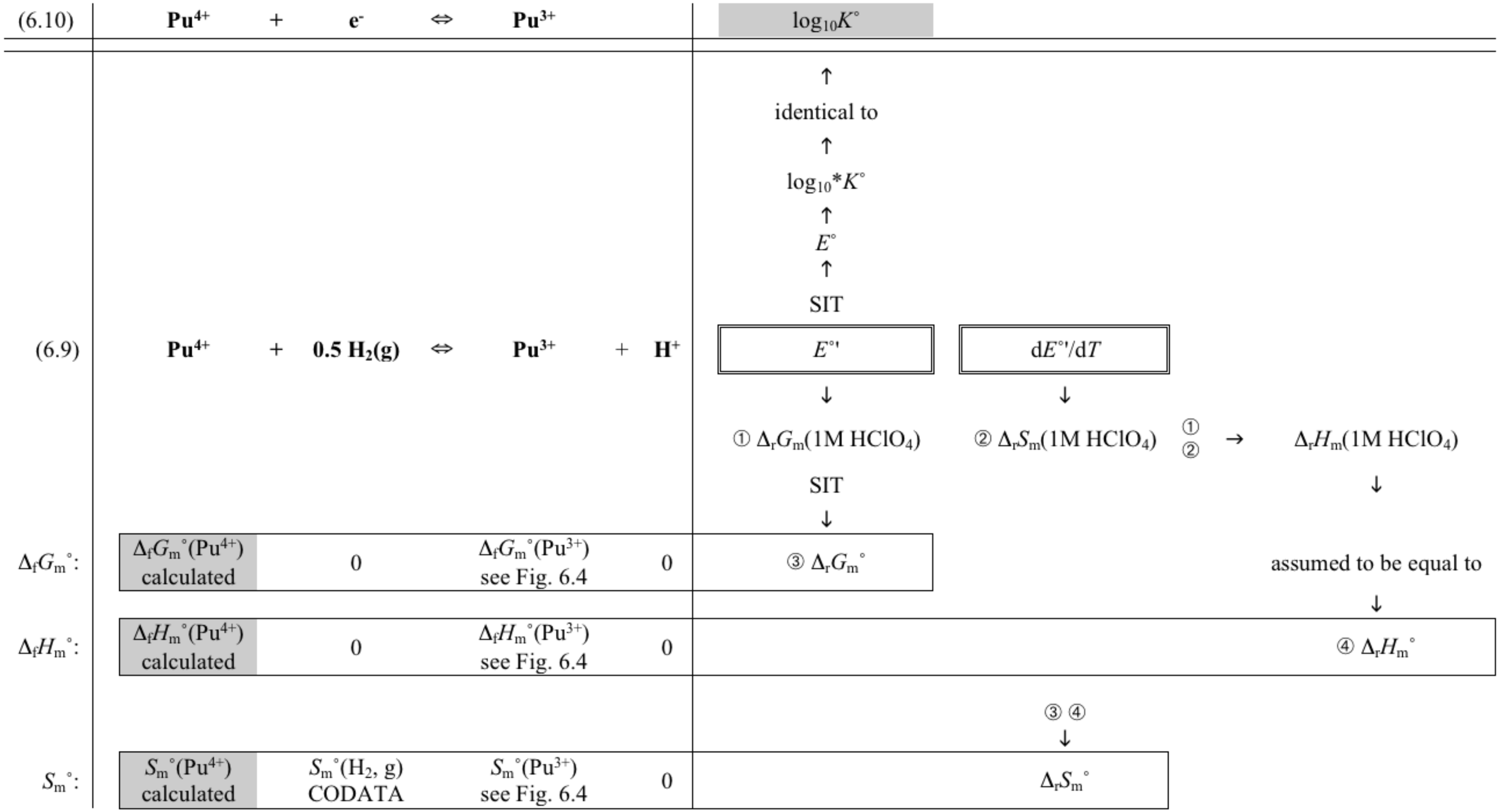

Fig. 6.3: Schematic representation of the derivation and selection process of thermodynamic data for Pu^{4+} by Lemire et al. (2001).

Thus,

$$\varepsilon(Pu^{4+}, ClO_4^-) = (0.82 \pm 0.07)\ kg \cdot mol^{-1}$$

In order to estimate $\varepsilon(Th^{4+}, Cl^-)$ from known values for $\varepsilon(Pu^{4+}, Cl^-)$, $\varepsilon(Np^{4+}, Cl^-)$, and $\varepsilon(U^{4+}, Cl^-)$, Rand et al. (2008) derived

$$\varepsilon(Pu^{4+}, Cl^-) = (0.37 \pm 0.05)\ kg \cdot mol^{-1}$$

from $\Delta\varepsilon = \varepsilon(Pu^{3+}, Cl^-) - \varepsilon(Pu^{4+}, Cl^-) = -(0.14 \pm 0.04)\ kg \cdot mol^{-1}$ obtained from $\log_{10}K$ values for $Pu^{4+} + e^- \Leftrightarrow Pu^3$ at $I = 0$ and in 1.02 m HCl. Rand et al. (2008) assumed that $\varepsilon(Pu^{3+}, Cl^-) = \varepsilon(Am^{3+}, Cl^-) = (0.23 \pm 0.02)\ kg \cdot mol^{-1}$.

Analogous to the PuO_2^{2+}/PuO_2^+ couple discussed above, $\log_{10}{}^*K°(6.9, 298.15\ K)$ is identical to $\log_{10}K°(6.10, 298.15\ K)$ for the reaction

$$Pu^{4+} + e^- \Leftrightarrow Pu^{3+} \qquad (6.10)$$

Therefore

$$\log_{10}K°(6.10, 298.15\ K) = (17.69 \pm 0.04)$$

$\Delta_rG_m°(6.9, 298.15\ K)$ was obtained from $\log_{10}{}^*K°(6.9, 298.15\ K)$ and used together with the selected value for $\Delta_fG_m°(Pu^{3+}, 298.15\ K)$, *cf.* Section 6.3.4, for the calculation of

$$\Delta_fG_m°(Pu^{4+}, 298.15\ K) = -(478.0 \pm 2.7)\ kJ \cdot mol^{-1}$$

Pu^{4+} can be expressed in terms of the primary master species PuO_2^{2+} by subtracting reaction (6.10) from reaction (6.1), resulting in

$$PuO_2^{2+} + 4\ H^+ + 2e^- \Leftrightarrow Pu^{4+} + 2H_2O(l)$$

with

$$\log_{10}K°(298.15\ K) = (33.28 \pm 0.15)$$

calculated from $\log_{10}K°(6.10, 298.15\ K) = (17.69 \pm 0.04)$ and $\log_{10}K°(6.1, 298.15\ K) = (50.97 \pm 0.15)$.

Derivation of $\Delta_fH_m°(Pu^{4+}, 298.15\ K)$

$\Delta_rG_m(6.9, 1\ M\ HClO_4, 298.15\ K)$ was calculated from $E°'(6.9, 1\ M\ HClO_4, 298.15\ K)$ while $\Delta_rS_m(6.9, 1\ M\ HClO_4, 298.15\ K)$ was obtained from measured temperature coefficients of the Pu^{4+}/Pu^{3+} potential. $\Delta_rG_m(6.9, 1\ M\ HClO_4, 298.15\ K)$ and $\Delta_rS_m(6.9, 1\ M\ HClO_4, 298.15\ K)$ were then used for the calculation of $\Delta_rH_m(6.9, 1\ M\ HClO_4, 298.15\ K)$ which was assumed to be equal to $\Delta_rH_m°(6.9, 298.15\ K)$. Finally,

$$\Delta_fH_m°(Pu^{4+}, 298.15\ K) = -(539.9 \pm 3.1)\ kJ \cdot mol^{-1}$$

was obtained from $\Delta_rH_m°(6.9, 298.15\ K)$ and the selected $\Delta_fH_m°(Pu^{3+}, 298.15\ K)$, *cf.* Section 6.3.4.

Derivation of $S_m°(Pu^{4+}, 298.15\ K)$

The standard entropy of reaction (6.9) was derived from $\Delta_rG_m°(6.9, 298.15\ K)$ and $\Delta_rH_m°(6.9, 298.15\ K)$ and was used together with $S_m°(Pu^{3+}, 298.15\ K)$, *cf.* Section 6.3.4, and CODATA auxiliary data for the calculation of

$$S_m°(Pu^{4+}, 298.15\ K) = -(414.5 \pm 10.2)\ J \cdot K^{-1} \cdot mol^{-1}$$

6.3.4 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

$$PuCl_3·6H_2O(cr) \rightarrow Pu^{3+} + 3Cl^- + 6H_2O(l) \qquad (6.11)$$

and using the Gibbs-Helmholtz equation, $\Delta_rS_m°$(6.11, 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 $S_m°(PuCl_3·6H_2O$, cr, 298.15 K). Thus

$$S_m°(Pu^{3+}, 298.15 K) = -(184.5 \pm 6.2) J·K^{-1}·mol^{-1}$$

Note that $PuCl_3·6H_2O(cr)$, is not contained in our database.

Derivation of $\Delta_fH_m°(Pu^{3+}$, 298.15 K)

$\Delta_fH_m°(Pu^{3+}$, 298.15 K) was derived from calorimetric measurements of the enthalpies of solution of Pu(cr, α) and $PuCl_3(cr)$ in HCl(aq). The selected value is

$$\Delta_fH_m°(Pu^{3+}, aq, 298.15 K) = -(591.8 \pm 2.0) kJ·mol^{-1}$$

Derivation of $\Delta_fG_m°(Pu^{3+}$, 298.15 K), ε(Pu^{4+}, ClO_4^-), and ε(Pu^{4+}, Cl^-)

$\Delta_rS_m°$(6.12, 298.15 K) for

$$Pu(cr, \alpha) + 3H^+ \Leftrightarrow Pu^{3+} + 3/2 H_2(g) \qquad (6.12)$$

was calculated from $S_m°(Pu^{3+}$, 298.15 K) and $S_m°$(Pu, cr, α, 298.15 K), *cf.* Section 6.2. $\Delta_rS_m°$(6.12, 298.15 K) is identical to $\Delta_fS_m°(Pu^{3+}$, 298.15 K). The latter was used together with the selected value for $\Delta_fH_m°(Pu^{3+}$, 298.15 K) to calculate

$$\Delta_fG_m°(Pu^{3+}, aq, 298.15 K) = -(579.0 \pm 2.7) kJ·mol^{-1}$$

according to the Gibbs-Helmholtz equation.

As discussed above, the value for ε(Pu^{3+}, ClO_4^-) was estimated by Lemire et al. (2001) as

$$\varepsilon(Pu^{3+}, ClO_4^-) = \varepsilon(Nd^{3+}, ClO_4^-) = (0.49 \pm 0.05) kg·mol^{-1}$$

Lemire et al. (2001) and Guillaumont et al. (2003) did not select any value for ε(Pu^{3+}, Cl^-). Since Rand et al. (2008) used the estimate

$$\varepsilon(Pu^{3+}, Cl^-) = \varepsilon(Am^{3+}, Cl^-) = (0.23 \pm 0.02) kg·mol^{-1}$$

for their derivation of ε(Th^{4+}, Cl^-) discussed above, we include it in our database.

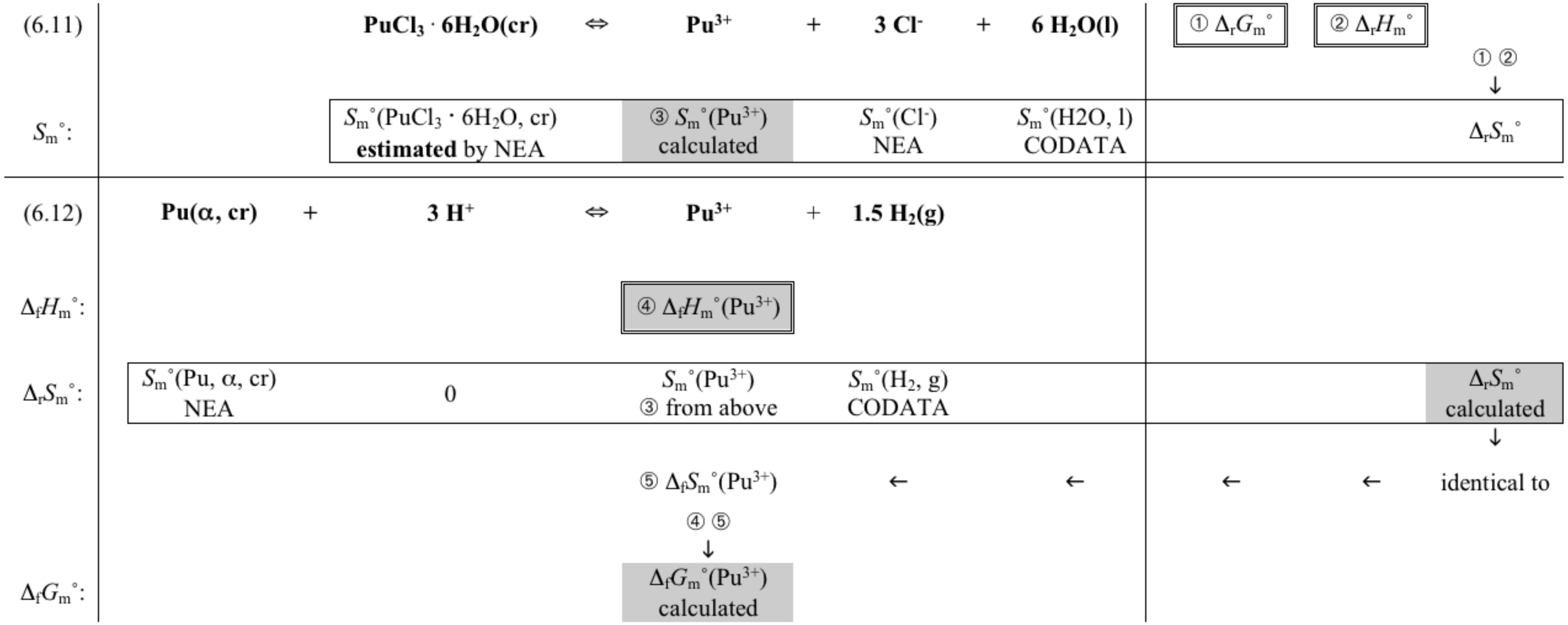

Fig. 6.4: Schematic representation of the derivation and selection process of thermodynamic data for Pu^{3+} by Lemire et al. (2001).

6.4 Plutonium oxygen and hydrogen compounds and complexes

6.4.1 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 6.4.5, 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:

$$PuO_2^{2+} + H_2O(l) \Leftrightarrow PuO_2OH^+ + H^+ \qquad (6.13)$$

$$2\ PuO_2^{2+} + 2\ H_2O(l) \Leftrightarrow (PuO_2)_2(OH)_2^{2+} + 2\ H^+ \qquad (6.14)$$

$$PuO_2^{2+} + 2\ H_2O(l) \Leftrightarrow PuO_2(OH)_2(aq) + 2\ H^+ \qquad (6.15)$$

The selected constants are

$$\log_{10}{}^*\beta_1^\circ(6.13,\ 298.15\ \text{K}) = -(5.5 \pm 0.5)$$

$$\Delta_r H_m^\circ(6.13,\ 298.15\ \text{K}) = (28 \pm 15)\ \text{kJ}\cdot\text{mol}^{-1}$$

$$\log_{10}{}^*\beta_{2,2}^\circ(6.14,\ 298.15\ \text{K}) = -\left(7.5\ {}^{+0.5}_{-1.0}\right), \text{ and } \log_{10}{}^*\beta_{2,1}^\circ(6.15,\ 298.15\ \text{K}) = -\left(13.2\ {}^{+0.5}_{-1.5}\right).$$

For our database update 01/01, we preferred to replace the unsymmetrical by symmetrical uncertainties. Thus

$$\log_{10}{}^*\beta_{2,2}^\circ(6.14,\ 298.15\ \text{K}) = -(7.5 \pm 1.0)$$

$$\log_{10}{}^*\beta_{2,1}^\circ(6.15,\ 298.15\ \text{K}) = -(13.2 \pm 1.5)$$

The same uncertainties are given by Guillaumont et al. (2003). Since neither Lemire et al. (2001) nor Guillaumont et al. (2003) discussed any ion interaction parameters for PuO_2OH^+ and $(PuO_2)_2(OH)_2^{2+}$, we estimated

$$\varepsilon(PuO_2OH^+,\ Cl^-) = (0.05 \pm 0.10)\ \text{kg}\cdot\text{mol}^{-1}$$

$$\varepsilon(PuO_2OH^+,\ ClO_4^-) = (0.2 \pm 0.1)\ \text{kg}\cdot\text{mol}^{-1}$$

$$\varepsilon((PuO_2)_2(OH)_2^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg\cdot mol^{-1}$$

$$\varepsilon((PuO_2)_2(OH)_2^{2+}, ClO_4^-) = (0.4 \pm 0.1)\ kg\cdot mol^{-1}$$

based on charge correlations (see Appendix A).

6.4.2 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

$$PuO_2^+ + H_2O(l) \Leftrightarrow PuO_2OH(aq) + H^+ \qquad (6.16)$$

can be gained from experimental data. The selected limiting value for the first hydrolysis constant is

$$\log_{10}{}^*\beta_1^\circ(6.16, 298.15\ K) \leq -9.73$$

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.

6.4.3 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). Stability constants have been proposed for the following hydrolysis reactions.

$$Pu^{4+} + H_2O(l) \Leftrightarrow PuOH^{3+} + H^+ \qquad (6.17)$$

$$Pu^{4+} + 2\ H_2O(l) \Leftrightarrow Pu(OH)_2^{2+} + 2\ H^+ \qquad (6.18)$$

$$Pu^{4+} + 3\ H_2O(l) \Leftrightarrow Pu(OH)_3^{+} + 3\ H^+ \qquad (6.19)$$

$$Pu^{4+} + 4\ H_2O(l) \Leftrightarrow Pu(OH)_4(aq) + 4\ H^+ \qquad (6.20)$$

For the first hydrolysis constant Lemire et al. (2001) obtained $\log_{10}{}^*\beta_1^\circ(6.17, 298.15\ K) = -(0.78 \pm 0.60)$ by taking the mean of three independent spectroscopic determinations in perchlorate media extrapolated to $I = 0$ using SIT. They concluded that none of the available studies provide good thermodynamic data for higher hydrolysis species of Pu(IV)

In contrast to Lemire et al. (2001), Hummel et al. (2002) chose to include $Pu(OH)_4(aq)$ in their database, since ignoring $Pu(OH)_4(aq)$ would lead to unrealistically low solubilities for $PuO_2(s)$, see Section 6.4.5. Based on experimental data by Lierse & Kim (1986), Rai et al. (1999), and Neck & Kim (2001), they selected $\log_{10}{}^*\beta_4^\circ(6.20, 298.15\ K) = -(8.4 \pm 1.1)$.

Guillaumont et al. (2003) adopted the values proposed in the review by Neck & Kim (2001), $\log_{10}{}^*\beta_1^\circ(6.17, 298.15\ K) = (0.6 \pm 0.2)$, $\log_{10}{}^*\beta_2^\circ(6.18, 298.15\ K) = (0.6 \pm 0.3)$, $\log_{10}{}^*\beta_3^\circ(6.19, 298.15\ K) = -(2.3 \pm 0.4)$, and $\log_{10}{}^*\beta_4^\circ(6.20, 298.15\ K) = -(8.5 \pm 0.5)$.

In a careful study, Yun et al. (2007) investigated the hydrolysis of Pu(IV) by a combination of absorption spectroscopy and redox potential measurements in 0.5 M HCl/NaCl in the concentration range from 10^{-5} to 4 x 10^{-4} M at pH 0.3–2.1 and (23 ± 2)°C. Using SIT to correct the determined hydrolysis constants to zero ionic strength, they obtained $\log_{10}{}^*\beta_1°(6.17, 298.15 \text{ K}) = (0.0 \pm 0.2)$, $\log_{10}{}^*\beta_2°(6.18, 298.15 \text{ K}) = -(1.2 \pm 0.6)$, and $\log_{10}{}^*\beta_3°(6.19, 298.15 \text{ K}) = -(3.1 \pm 0.9)$. These values are selected for our database. Yun et al. (2007) did not provide a value for the formation constant of $Pu(OH)_4(aq)$, since their measurements were made at very low pH and the method used in their study is not applicable beyond the acidic pH range. They remarked that in the light of their experimental results, the values for the first three hydrolysis constants given by Neck & Kim (2001) and selected by Guillaumont et al. (2003) were overestimated and probably also the value for the fourth hydrolysis constant selected by Guillaumont et al. (2003). Yun et al. (2007) noted that the latter was derived from the stepwise stability constant determined in a solvent extraction study and that even if the stepwise stability constant between $Pu(OH)_3^+$ and $Pu(OH)_4(aq)$ were correct, this would result in a maximum value of -(9.3 ± 0.5) for $\log_{10}{}^*\beta_4°(6.20, 298.15 \text{ K})$. This is the value we prefer to that selected by Guillaumont et al. (2003). Taking $\log_{10}{}^*\beta_4°(6.20, 298.15 \text{ K}) = -(9.3 \pm 0.5)$ as an upper limit and combining it with the solubility product $\log_{10}K_{s,0}°(PuO_2(am, hyd), 298.15 \text{ K}) = -(58.33 \pm 0.52)$ discussed below, the maximum concentration of $Pu(OH)_4(aq)$ is calculated to be $\log[Pu(OH)_4(aq)] < -(11.6 \pm 1.0)$. Yun et al. (2007) compared this with the experimentally determined solubility of PuO_2(am, hyd) in neutral and alkaline solutions, log[Pu] = -(10.4 ± 0.5) (Lierse & Kim 1986, Rai et al. 1999) and concluded that this solubility is probably not caused by the mononuclear species $Pu(OH)_4(aq)$ but rather by small polynuclear species $Pu_m(OH)_n^{4m-n}$ or by Pu species at other oxidation states. However, there is no information on the types of polynuclear species present and stability constants are not known.

In summary, the values included in our database for the hydrolysis constants of Pu(IV) are

$$\log_{10}{}^*\beta_1°(6.17, 298.15 \text{ K}) = (0.0 \pm 0.2)$$

$$\log_{10}{}^*\beta_2°(6.18, 298.15 \text{ K}) = -(1.2 \pm 0.6)$$

$$\log_{10}{}^*\beta_3°(6.19, 298.15 \text{ K}) = -(3.1 \pm 0.9)$$

$$\log_{10}{}^*\beta_4°(6.20, 298.15 \text{ K}) = -(9.3 \pm 0.5)$$

They are all different from those selected by Guillaumont et al. (2003).

Yun et al. (2007) used the following ion interaction coefficients for extrapolating the conditional stability constants to zero ionic strength

$$\varepsilon(PuOH^{3+}, Cl^-) = (0.2 \pm 0.1) \text{ kg·mol}^{-1}$$

$$\varepsilon(Pu(OH)_2^{2+}, Cl^-) = (0.1 \pm 0.1) \text{ kg·mol}^{-1}$$

$$\varepsilon(Pu(OH)_3^{+}, Cl^-) = (0.05 \pm 0.10) \text{ kg·mol}^{-1}$$

These were estimated by Neck & Kim (2001) according to known values for ions of equal charge, similar size and structure, systematics in the tetravalent actinide series, and differences between the interaction coefficients of cations with chloride and perchlorate. They are also included in our database, as well as

$$\varepsilon(PuOH^{3+}, ClO_4^-) = (0.50 \pm 0.05) \text{ kg·mol}^{-1}$$

which was estimated by Lemire et al. (2001) without explanation on how this estimation was obtained. Based on charge correlations (see Appendix A), we estimated

$$\varepsilon(Pu(OH)_2^{2+}, ClO_4^-) = (0.4 \pm 0.1) \text{ kg·mol}^{-1}$$

$$\varepsilon(Pu(OH)_3^{+}, ClO_4^-) = (0.2 \pm 0.1) \text{ kg·mol}^{-1}$$

for inclusion in our database.

6.4.4 Pu(III) hydroxide complexes

Pu(III) is unstable in aqueous solution with respect to oxidation by air. The hydrolysis constant

$$\log_{10}{}^*\beta_1°(298.15\ \text{K}) = -(6.9 \pm 0.3)$$

selected by Lemire et al. (2001) for

$$\text{Pu}^{3+} + \text{H}_2\text{O(l)} \Leftrightarrow \text{PuOH}^{2+} + \text{H}^+$$

was based on an average value of four potentiometric measurements at $I \leq 0.05$ 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 $\Delta\varepsilon = (0.04 \pm 0.05)$ kg·mol^{-1}. This value for $\Delta\varepsilon$ was calculated from the estimate

$$\varepsilon(\text{PuOH}^{2+}, \text{ClO}_4^-) = \varepsilon(\text{YHCO}_3^{2+}, \text{ClO}_4^-)^{4} = (0.39 \pm 0.04)\ \text{kg·mol}^{-1}$$

(an analogy suggested by Silva et al. (1995) for $\varepsilon(\text{AmOH}^{2+}, \text{ClO}_4^-)$), and from the selected $\varepsilon(\text{H}^+, \text{ClO}_4^-) = (0.39 \pm 0.04)$ kg·mol^{-1} and $\varepsilon(\text{Pu}^{3+}, \text{ClO}_4^-) = (0.49 \pm 0.05)$ kg·mol^{-1}. Although used by Lemire et al. (2001), they did not list their estimated value for $\varepsilon(\text{PuOH}^{2+}, \text{ClO}_4^-)$ in their table of selected values for ion interaction coefficients. It is, however, included in our database.

Since data in chloride media are missing, we estimated

$$\varepsilon(\text{PuOH}^{2+}, \text{Cl}^-) = (0.15 \pm 0.10)\ \text{kg·mol}^{-1}$$

based on charge correlations (see Appendix A).

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 ± 0.2). Note that the consistency is even better with the revised value by Guillaumont et al. (2003) for Am(III) of -(7.2 ± 0.5).

Neither Lemire et al. (2001) nor Guillaumont et al. (2003) mention experimental data concerning the formation of Pu(OH)_2^+ and $\text{Pu(OH)}_3\text{(aq)}$. Hummel & Berner (2002) estimated values for $\log_{10}{}^*\beta_2°$ and $\log_{10}{}^*\beta_3°$ based on the chemical analogy of Pu(III) with Am(III). They assumed the stepwise stability constants of Pu(OH)_2^+ and $\text{Pu(OH)}_3\text{(aq)}$ to be the same as those for Am(OH)_2^+ and $\text{Am(OH)}_3\text{(aq)}$ and thus obtained $\log_{10}{}^*\beta_2°(298.15\ \text{K}) = -14.8$ and $\log_{10}{}^*\beta_3°(298.15\ \text{K}) = -25.3$. In the meantime, Guillaumont et al. (2003) revised the data for Am(III) hydroxides, resulting in $\log_{10}{}^*K_2°(298.15\ \text{K}) = -7.9$ for Am(OH)_2^+ and in $\log_{10}{}^*K_3°(298.15\ \text{K}) = -11.1$ for $\text{Am(OH)}_3\text{(aq)}$. With these stepwise stability constants and $\log_{10}{}^*\beta_1°(298.15\ \text{K}) = -6.9 \pm 0.3$ for PuOH^{2+} the following estimates are obtained

$$Pu^{3+} + 2\ H_2O(l) \Leftrightarrow Pu(OH)_2^+ + 2\ H^+$$

$$\log_{10}{}^*\beta_2°(298.15\ K) = -14.8$$

$$Pu^{3+} + 3\ H_2O(l) \Leftrightarrow Pu(OH)_3(aq) + 3\ H^+$$

$$\log_{10}{}^*\beta_3°(298.15\ K) = -25.9$$

These values are included in our database as supplemental data, as well as the ion interaction coefficients

$$\varepsilon(Pu(OH)_2^+, Cl^-) = (0.05 \pm 0.10)\ kg·mol^{-1}$$

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[4] Value (without uncertainty) determined by Spahiu (1983) and Spahiu (1985) using an SIT analysis of experimentally derived formation constants for the yttrium bicarbonate complex.

$$\varepsilon(Pu(OH)_2^{+}, ClO_4^{-}) = (0.2 \pm 0.1)\ kg \cdot mol^{-1}$$

estimated based on charge correlations (see Appendix A).

6.4.5 Calcium Pu(IV) hydroxide complexes

Altmaier et al. (2008) studied the solubility of Zr(IV), Th(IV), and Pu(IV) oxyhydroxide precipitates in alkaline $CaCl_2$ and $Ca(ClO_4)_2$ solutions. In the case of Pu(IV), the experiments were carried out in 1.0, 2.0, and 4.0 M $CaCl_2$ with PuO_{2+x}(am, hyd) or $Pu(OH)_4$(am) that contained about 0.5% of oxidized Pu. pH was varied between 8 and 12. The solubility of Pu measured after 7–132 days in 1.0 M $CaCl_2$ is similar to that in NaCl and $NaClO_4$ across the experimental pH range and is on the order of 10^{-10} to 10^{-9} M (after 1.5–2 nm ultrafiltration). At pH 11–12 in 2.0 and 4.0 M $CaCl_2$, however, the Pu solubility increases sharply up to values of 10^{-8} M and 10^{-7} M, respectively. Altmaier et al. (2008) assumed that this solubility increase is caused by a species analogous to the ternary $Ca_4Th(OH)_8^{4+}$ complex. The solubility increase is well described by the equilibrium

$$Pu(OH)_4(am) + 4\ OH^- + 4\ Ca^{2+} \Leftrightarrow Ca_4Pu(OH)_8^{4+}$$

with log $K^\circ_{s(4,1,8)}$(298.15) = -(2.0 ± 0.5) and the SIT interaction coefficient $\varepsilon(Ca_4Pu(OH)_8^{4+}, Cl^-)$ = -(0.01 ± 0.10) kg·mol^{-1} as determined for the corresponding ternary thorium complex. Combining log $K^\circ_{s(4,1,8)}$ (298.15 K) with the solubility product $\log_{10}K_{s,0}^\circ$(298.15 K) = -(58.33 ± 0.32) for $PuO_2(hyd, ag) + 2H_2O(l) \Leftrightarrow Pu^{4+} + 4OH^-$ (see Section 6.4.6.3 below) or, equivalently, $Pu(OH)_4(am) \Leftrightarrow Pu^{4+} + 4OH^-$, leads to

$$Pu^{4+} + 8\ OH^- + 4\ Ca^{2+} \Leftrightarrow Ca_4Pu(OH)_8^{4+}$$

with $\log\beta^\circ_{(4,1,8)}$(298.15 K) = (56.3 ± 0.7). Combining this with the dissociation equilibrium for water finally results in

$$4\ Ca^{2+} + Pu^{4+} + 8\ H_2O(l) \Leftrightarrow Ca_4Pu(OH)_8^{4+} + 8\ H^+$$

$$\log_{10}{}^*\beta^\circ_{(4,1,8)}(298.15\ K) = -(55.7 \pm 0.7)$$

which we include in our database as supplemental data, as well as the estimated ion interaction coefficients

$$\varepsilon(Ca_4Pu(OH)_8^{4+}, Cl^-) \approx \varepsilon(Ca_4Th(OH)_8^{4+}, Cl^-) = -(0.01 \pm 0.10)\ kg \cdot mol^{-1}$$

$$\varepsilon(Ca_4Pu(OH)_8^{4+}, ClO_4^-) \approx \varepsilon(Ca_4Th(OH)_8^{4+}, ClO_4^-) = -(0.21 \pm 0.17)\ kg \cdot mol^{-1}$$

Altmaier et al. (2008) remarked that under the chosen experimental conditions, aqueous Pu(III) species are of no importance, but as the solid phase is in equilibrium with both Pu(IV) and Pu(V), the potential formation of ternary Ca-Pu(V)-OH or even Ca-Pu(VI)-OH complexes cannot be ruled out. Without further experiments under more reducing conditions, the observed solubility increasing effect of the proposed $Ca_4Pu(OH)_8^{4+}$ complex must be considered as an upper limit. For this reason, the selected data for $Ca_4Pu(OH)_8^{4+}$ are included in our database only as supplemental data.

6.4.6 Solid plutonium oxides and hydroxides

Lemire et al. (2001) recommended values of S_m° and $\Delta_fH_m^\circ$ for PuO_2(cr), Pu_2O_3(cr), and $PuO_{1.61}$(bcc), from which they calculated values for $\Delta_fG_m^\circ$. As there are no solubility studies of these solids, they are not included in our database.

6.4.6.1 Plutonium(VI) oxides and hydroxides

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

$$PuO_2(OH)_2 \cdot H_2O(cr) + 2\,H^+ \Leftrightarrow PuO_2^{2+} + 3H_2O(l)$$

the selected solubility constant is

$$\log_{10}{}^*K_{s,0}^\circ(298.15\text{ K}) = (5.5 \pm 1.0)$$

There are no experimentally determined values for the entropy or enthalpy of formation of $PuO_2(OH)_2(cr)$ or its hydrates. The value

$$S_m^\circ(PuO_2(OH)_2 \cdot H_2O\text{, cr, }298.15\text{ K}) = (190 \pm 40)\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

was selected by analogy with $UO_3 \cdot 2H_2O(cr)$ for which $S_m^\circ(298.15\text{ K})$ was reported to be $(188.54 \pm 38)\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. In the absence of any heat capacity determinations, the value

$$C_{p,m}^\circ(PuO_2(OH)_2 \cdot H_2O\text{, cr, }298.15\text{ K}) = (170 \pm 20)\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

was selected based on a Kopp's rule calculation and by analogy with the experimental value of $(172 \pm 0.34)\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for $C_{p,m}^\circ(UO_3 \cdot H_2O\text{, cr, }298.15\text{ K})$. 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 $S_m^\circ(PuO_2(OH)_2 \cdot H_2O\text{, cr})$ and for $C_{p,m}^\circ(PuO_2(OH)_2 \cdot H_2O\text{, cr})$ were based on estimates only, they are not included in our database.

6.4.6.2 Plutonium(V) oxides and hydroxides

A value of

$$\log_{10}{}^*K_{s,0}^\circ(298.15\text{ K}) = (5.0 \pm 0.5)$$

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

$$S_m^\circ(PuO_2OH\text{, am, }298.15\text{ K}) = (97 \pm 15)\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

was estimated as the sum of $S_m^\circ(PuO_2)$ and the entropy contribution of an OH^- group attached to a singly charged metal ion. The selected value

$$C_{p,m}^\circ(PuO_2OH\text{, am, }298.15\text{ K}) = (86 \pm 20)\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

was estimated from a Kopp's rule calculation.

Because both values for $S_m^\circ(PuO_2OH\text{, am, }298.15\text{ K})$ and $C_{p,m}^\circ(PuO_2OH\text{, am, }298.15\text{ K})$ were based on estimates only, they are not included in our database.

6.4.6.3 Plutonium(IV) oxides and hydroxides

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.

Pu(IV) solutions often contain a colloidal plutonium species, probably finely dispersed $PuO_2 \cdot xH_2O$, which can lead to high apparent solubilities (see below).

Based on two solubility experiments on well-aged hydrous PuO_2, or $Pu(OH)_4(am)$, which appear to have coped most successfully with the experimental difficulties, Lemire et al. (2001) selected a value of $\log_{10}K_{s,0}°(298.15\text{ K}) = -(58 \pm 1)$ for the reaction

$$PuO_2(\text{hyd, ag}) + 2\ H_2O(l) \Leftrightarrow Pu^{4+} + 4OH^-$$

Guillaumont et al. (2003) reviewed several more recent studies, which agreed well with the value selected by Lemire et al. (2001), but with reduced uncertainty. Taking the unweighted average of four investigations that used three different and independent methods, Guillaumont et al. (2003) selected

$$\log_{10}K_{s,0}°(298.15\text{ K}) = -(58.33 \pm 0.52)$$

For our database the solubility of PuO_2(hyd, ag)[5] is written as

$$PuO_2(\text{hyd, ag}) + 4\ H^+ \Leftrightarrow Pu^{4+} + 2H_2O(l) \qquad (6.21)$$

and the solubility product is accordingly recalculated to

$$\log_{10}{}^*K_{s,0}°(6.21, 298.15\text{ K}) = -(2.33 \pm 0.52)$$

using the dissociation constant of water.

This solubility product only applies to precipitated solids that were aged for several months near room temperature. Freshly precipitated solids may be more soluble.

In an experimental study on the solubility and redox reactions of hydrous Pu(IV) oxide, Neck et al. (2007) pointed out that small Pu(IV) colloids or polymers play an important role for the redox reactions between Pu(IV) and Pu(V). While the aqueous redox couples Pu^{3+}/Pu^{4+} and PuO_2^+/PuO_2^{2+} are reversible, this is not the case for Pu^{4+} and PuO_2^+. These ions and their hydroxide complexes (the system studied by Neck et al. 2007 did not contain additional ligands) are not in direct equilibrium with each other but only indirectly by their reactions with solid and colloidal or polymeric Pu(IV). Neck et al. (2007) measured a pH-independent concentration (at pH 8–13) $\log[Pu(IV)]_{coll}$ which may be expressed by the reaction

$$PuO_2(am, hyd) \Leftrightarrow PuO_2(coll, hyd)$$

with

$$\log_{10}K°(298.15\text{ K}) = -(8.3 \pm 1.0)$$

which belongs in our database to the supplemental data.

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[5] Note that this solid was referred to as PuO_2(am, hydr.) by Guillaumont et al. (2003)

6.4.6.4 Plutonium(III) oxides and hydroxides

Experimental studies of the solubility of actinide(III) hydroxides are very rare. The selected value of

$$\log_{10}{}^*K_{s,0}°(298.15\ K) = (15.8 \pm 1.5)$$

for the reaction

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

was based on a solubility experiment done in deionized water. This solubility product is consistent with the values selected by Guillaumont et al. (2003) for $Am(OH)_3(am)$, $\log_{10}{}^*K_{s,0}°(298.15\ K) = (16.9 \pm 0.8)$, and for $Am(OH)_3(cr)$, $\log_{10}{}^*K_{s,0}°(298.15\ K) = (15.6 \pm 0.6)$.

6.5 Solid and gaseous 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), $PuCl_3\cdot 6H_2O$(cr), $PuCl_4$(cr), PuOCl(cr), $Cs_2NaPuCl_6$(cr), Cs_3PuCl_6(cr), $CsPu_2Cl_7$(cr), Cs_2PuCl_6(cr)

Solid bromides: $PuBr_3$(cr), PuOBr(cr), Cs_2PuBr_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 our database.

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 our database.

6.6 Aqueous plutonium fluoride complexes

No fluoride complexes of PuO_2^+ have been identified.

6.6.1 Pu(III) 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 our database. Hummel & Berner (2002) estimated stability constants for PuF^{2+} and PuF_2^+, by adopting the values for the corresponding Am(III) fluoride complexes. From the data selected by Lemire et al. (2001) the following estimates are obtained

$$Pu^{3+} + F^- \Leftrightarrow PuF^{2+}$$

$$\log_{10}\beta_1°(298.15\ K) = 3.4$$

$$Pu^{3+} + 2\,F^- \Leftrightarrow PuF_2^+$$

$$log_{10}\beta_2°(298.15\ K) = 5.8$$

We estimated

$$\varepsilon(PuF^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg{\cdot}mol^{-1}$$

$$\varepsilon(PuF^{2+}, ClO_4^-) = (0.4 \pm 0.1)\ kg{\cdot}mol^{-1}$$

$$\varepsilon(PuF_2^+, Cl^-) = (0.05 \pm 0.10)\ kg{\cdot}mol^{-1}$$

$$\varepsilon(PuF_2^+, ClO_4^-) = (0.2 \pm 0.1)\ kg{\cdot}mol^{-1}$$

based on charge correlations (see Appendix A).

These estimates for the stability constants and for the ion interaction coefficients are included in our database as supplemental data.

6.6.2 Pu(IV) fluoride complexes

Experimentally determined concentration constants have been published for the reaction

$$Pu^{4+} + HF(aq) \Leftrightarrow PuF^{3+} + H^+ \qquad (6.22)$$

As the considered constants from 6 experimental studies refer only to two different ionic strength values (I = 1 M and I = 2 M $HClO_4$), a linear SIT fit was not thought to be feasible and the constants were extrapolated to I = 0 by using $\Delta\varepsilon$ = -(0.12 ± 0.09) kg·mol^{-1} from the corresponding Np(IV) fluoride system (uncertainty increased by 0.05). The weighted average of the values for $\log_{10}{}^*\beta_1°$(6.22, 298.15 K) was then converted to $\log_{10}\beta_1°$(6.23, 298.15 K) for

$$Pu^{4+} + F^- \Leftrightarrow PuF^{3+} \qquad (6.23)$$

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

$$\log_{10}\beta_1°(6.23, 298.15\ K) = (8.84 \pm 0.10)$$

For the reaction

$$Pu^{4+} + 2\ HF(aq) \Leftrightarrow PuF_2^{2+} + 2H^+ \qquad (6.24)$$

concentration constants from 4 experimental studies (at I = 1 M and I = 2 M $HClO_4$) 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 $\Delta\varepsilon$ = -(0 .18 ± 0 .15) kg·mol^{-1} from the corresponding U(IV) fluoride system (uncertainty increased by 0.05). The weighted average of the values for $\log_{10}{}^*\beta_2°$(6.24, 298.15 K) were then converted to $\log_{10}\beta_2°$(6.25, 298.15 K) for

$$Pu^{4+} + 2F^- \Leftrightarrow PuF_2^{2+} \qquad (6.25)$$

by using the selected protonation constant of fluoride. The resulting selected value is

$$\log_{10}\beta_2°(6.25, 298.15\ K) = (15.7 \pm 0.2)$$

The estimated

$$\varepsilon(PuF^{3+}, ClO_4^-) = (0.56 \pm 0.11)\ kg{\cdot}mol^{-1}$$

$$\varepsilon(PuF_2^{2+}, ClO_4^-) = (0.36 \pm 0.17)\ kg{\cdot}mol^{-1}$$

follow from the estimated values for $\Delta\varepsilon$ mentioned above and the selected $\varepsilon(Pu^{4+}, ClO_4^-)$ = (0.82 ± 0.07) kg·mol^{-1} and $\varepsilon(H^+, ClO_4^-)$ = (0.14 ± 0.02) kg·mol^{-1}. For use in chloride media, we estimated

$$\varepsilon(\mathrm{PuF^{3+}, Cl^-}) = (0.25 \pm 0.10)\ \mathrm{kg \cdot mol^{-1}}$$

$$\varepsilon(\mathrm{PuF_2^{2+}, Cl^-}) = (0.15 \pm 0.10)\ \mathrm{kg \cdot mol^{-1}}$$

based on charge correlations (see Appendix A).

From equilibrium constants measured at 1, 7.5, 15 and 25°C reported in one study, $\Delta_r H_m°$(6.22, 298.15 K) and $\Delta_r H_m°$(6.24, 298.15 K) were extracted and combined with the enthalpy of protonation of the fluoride ion, resulting in the following selected values

$$\Delta_r H_m°(6.23,\ 298.15\ \mathrm{K}) = (9.1 \pm 2.2)\ \mathrm{kJ \cdot mol^{-1}}$$

$$\Delta_r H_m°(6.25,\ 298.15\ \mathrm{K}) = (11 \pm 5)\ \mathrm{kJ \cdot mol^{-1}}$$

Data for the 1:3 and 1:4 complexes were published in one study but were rejected by Lemire et al. (2001).

6.6.3 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

$$\mathrm{PuO_2^{2+} + HF(aq) \Leftrightarrow PuO_2F^+ + H^+} \qquad (6.26)$$

and

$$\mathrm{PuO_2^{2+} + 2\ HF(aq) \Leftrightarrow PuO_2F_2(aq) + 2H^+} \qquad (6.27)$$

or to

$$\mathrm{PuO_2^{2+} + F^- \Leftrightarrow PuO_2F^+} \qquad (6.28)$$

and

$$\mathrm{PuO_2^{2+} + 2\ F^- \Leftrightarrow PuO_2F_2(aq)} \qquad (6.29)$$

depending on the experimental conditions. Only two experimental studies on the 1:1 complex were deemed reliable (one data point at 0.1 M and two at 1 M $NaClO_4$), both referring to Reaction (6.28), and the constants were corrected to $I = 0$ using $\Delta\varepsilon = -(0.19 \pm 0.10)\ \mathrm{kg \cdot mol^{-1}}$ from the corresponding Np(VI) system. The selected value

$$\log_{10}\beta_1°(6.28,\ 298.15\ \mathrm{K}) = (4.56 \pm 0.20)$$

is a weighted average of the three 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). From the estimated value for $\Delta\varepsilon$ mentioned above and the selected $\varepsilon(\mathrm{PuO_2^{2+}, ClO_4^-}) = (0.46 \pm 0.05)\ \mathrm{kg \cdot mol^{-1}}$ and $\varepsilon(\mathrm{F^-, Na^+}) = (0.02 \pm 0.02)\ \mathrm{kg \cdot mol^{-1}}$ follows the estimate

$$\varepsilon(\mathrm{PuO_2F^+, ClO_4^-}) = (0.29 \pm 0.11)\ \mathrm{kg \cdot mol^{-1}}$$

For chloride media we estimated

$$\varepsilon(\mathrm{PuO_2F^+, Cl^-}) = (0.05 \pm 0.10)\ \mathrm{kg \cdot mol^{-1}}$$

based on charge correlations (see Appendix A).

There is only one credible study for the 1:2 complex (at 0.1 M and 1 M $NaClO_4$). The constants for Reaction (6.29) 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 value for $\Delta\varepsilon$ 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.

$$\log_{10}\beta_2°(6.29, 298.15 \text{ K}) = (7.25 \pm 0.45)$$

Reported formation constants for the 1:3 complex, $PuO_2F_3^-$, were rejected by Lemire et al. (2001).

6.7 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.

6.7.1 Pu(III) chloride complexes

From several experimental studies of 1:1 complexes, only data of a single study (in 0.207 M - 1.0 M HCl) were found to be reliable. The four concentration constants for the reaction

$$Pu^{3+} + Cl^- \Leftrightarrow PuCl^{2+}$$

were extrapolated to $I = 0$ by adopting $\Delta\varepsilon = -(0.22 \pm 0.15)$ kg·mol^{-1} from the corresponding Am(III) system in H(ClO_4, Cl) media[6]. The weighted average of the resulting values for $\log_{10}\beta_1°$(298.15 K) was selected by Lemire et al. (2001) with an increased uncertainty due to the fact that the value is based on a single study

$$\log_{10}\beta_1°(298.15 \text{ K}) = (1.2 \pm 0.2)$$

Guillaumont et al. (2003) rejected this value since it is not based on EXAFS data[7]. We retain it in our database but relegate it to the supplemental dataset.

Lemire et al. (2001) calculated

$$\varepsilon(PuCl^{2+}, ClO_4^-) = (0.39 \pm 0.16) \text{ kg·mol}^{-1}$$

from the $\Delta\varepsilon$ value mentioned above and from the selected $\varepsilon(Pu^{3+}, ClO_4^-) = (0.49 \pm 0.05)$ kg·mol^{-1} and $\varepsilon(Cl^-, H^+) = (0.12 \pm 0.01)$ kg·mol^{-1}.

Following the discussion by Hummel et al. (2005) in their Chapter V.4 on weak complexes versus strong specific ion interaction, we used the value of $\varepsilon(PuCl^{2+}, ClO_4^-)$ for

$$\varepsilon(PuCl^{2+}, Cl^-) = \varepsilon(PuCl^{2+}, ClO_4^-) = (0.39 \pm 0.16) \text{ kg·mol}^{-1}$$

It is important to keep in mind that in order to be consistent, this value for $\varepsilon(PuCl^{2+}, Cl^-)$ should only be used in combination with $\varepsilon(Pu^{3+}, Cl^-) = \varepsilon(Pu^{3+}, ClO_4^-) = (0.49 \pm 0.05)$ kg·mol^{-1}.

6.7.2 Pu(IV) chloride complexes

The selected value for the formation constant of

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[6] Note that this $\Delta\varepsilon$ value for the corresponding Am(III) system in H(ClO_4, Cl) media is based on an estimate and was not obtained from an SIT regression. It was calculated by Silva et al. (1995) from the estimated $\varepsilon(AmCl^{2+}, ClO_4^-) \approx \varepsilon(YHCO_3^{2+}, ClO_4^-) = (0.39 \pm 0.04)$ kg·mol^{-1} and $\varepsilon(Am^{3+}, ClO_4^-) \approx \varepsilon(Nd^{3+}, ClO_4^-) = (0.49 \pm 0.03)$ kg·mol^{-1}, and from $\varepsilon(Cl^-, H^+) = (0.12 \pm 0.01)$ kg·mol^{-1}.

[7] Note that despite the rejection by Guillaumont et al. (2003) of the value for $\log_{10}\beta_1°(PuCl^{2+}$, 298.15 K), a value for $\Delta_f G_m°(PuCl^{2+}$, 298.15 K) derived from the rejected $\log_{10}\beta_1°$ still appears in Table 5-1 of selected plutonium data in Guillaumont et al. (2003).

$$Pu^{4+} + Cl^- \Leftrightarrow PuCl^{3+}$$

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)

$$\log_{10}\beta_1°(298.15 \text{ K}) = (1.8 \pm 0.3)$$

with $\Delta\varepsilon = -(0.09 \pm 0.07)$ kg·mol^{-1}. From this $\Delta\varepsilon$ and the selected $\varepsilon(Pu^{4+}, ClO_4^-) = (0.82 \pm 0.07)$ kg · mol^{-1} and $\varepsilon(Cl^-, H^+) = (0.12 \pm 0.01)$ kg·mol^{-1} follows

$$\varepsilon(PuCl^{3+}, ClO_4^-) = (0.85 \pm 0.09) \text{ kg·mol}^{-1}$$

Following the discussion by Hummel et al. (2005) in their Chapter V.4 on weak complexes versus strong specific ion interaction, we used the value of $\varepsilon(PuCl^{3+}, ClO_4^-)$ for

$$\varepsilon(PuCl^{3+}, Cl^-) = \varepsilon(PuCl^{3+}, ClO_4^-) = (0.85 \pm 0.09) \text{ kg·mol}^{-1}$$

It is important to keep in mind that in order to be consistent, this value for $\varepsilon(PuCl^{3+}, Cl^-)$ should only be used in combination with $\varepsilon(Pu^{4+}, Cl^-) = \varepsilon(Pu^{4+}, ClO_4^-) = (0.82 \pm 0.07)$ kg·mol^{-1}.

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.

6.7.3 Pu(VI) chloride complexes

The formation constant $\log_{10}\beta_1°(298.15 \text{ K}) = (0.70 \pm 0.13)$ selected by Lemire et al. (2001) for

$$PuO_2^{2+} + Cl^- \Leftrightarrow PuO_2Cl^+$$

was based on experimental data by Giffaut (1994)[8] for mixed H(Cl, ClO$_4$) solutions at $I = 2.2$ m and $I = 3.5$ m (HCl was kept constant at 1 M) extrapolated to $I = 0$ by SIT. Guillaumont et al. (2003) preferred the experimental data by Runde et al. (1999) whose spectroscopic measurements were carried out in NaCl solutions with I ranging from 0.25 to 3.5 m. The SIT-regression resulted in the formation constant selected by Guillaumont et al. (2003) and included in our database

$$\log_{10}\beta_1°(298.15 \text{ K}) = (0.23 \pm 0.03)$$

with $\Delta\varepsilon = -(0.13 \pm 0.03)$ kg·mol^{-1}. From this value of $\Delta\varepsilon$, the selected $\varepsilon(Cl^-, Na^+) = (0.03 \pm 0.01)$ kg·mol^{-1}, and the estimated $\varepsilon(PuO_2^{2+}, Cl^-) = \varepsilon(UO_2^{2+}, Cl^-) = (0.21 \pm 0.02)$ kg·mol^{-1}, Runde et al. (1999) derived $\varepsilon(PuO_2Cl^+, Cl^-) = (0.11 \pm 0.04)$ kg·mol^{-1} which was selected by Guillaumont et al. (2003) but was not listed in their Table B-4 of selected ion interaction coefficients, nor in the corresponding tables of any of the following NEA review volumes. For our database, we did not accept this value for $\varepsilon(PuO_2Cl^+, Cl^-)$ derived by Runde et al. (1999) because the estimate $\varepsilon(PuO_2^{2+}, Cl^-) = \varepsilon(UO_2^{2+}, Cl^-) = (0.21 \pm 0.02)$ kg·mol^{-1} is unfortunate, since the value for $\varepsilon(UO_2^{2+}, Cl^-)$ was derived by Ciavatta (1980) from isopiestic measurements without explicitly taking chloride complexation into account, i.e., the effect of chloride complexation is implicitly included in the value of the ion interaction coefficient. It is more reasonable to assume $\varepsilon(PuO_2^{2+}, Cl^-) = \varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.05)$ kg·mol^{-1}, since perchlorate has the same charge as Cl$^-$, but forms no complexes. Thus, from $\Delta\varepsilon$, the selected $\varepsilon(Cl^-, Na^+)$ and our estimate for $\varepsilon(PuO_2^{2+}, Cl^-)$ follows

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[8] We had no access to this thesis.

$$\varepsilon(PuO_2^{2+}, Cl^-) = (0.36 \pm 0.06)\ kg \cdot mol^{-1}$$

which is included in our database. For perchlorate media, Guillaumont et al. (2003) retained the value $\Delta\varepsilon = -(0.08 \pm 0.08)\ kg \cdot mol^{-1}$ obtained by Giffaut (1994). From the selected $\varepsilon(PuO_2^{2+}, ClO_4^-) = (0.46 \pm 0.05)\ kg \cdot mol^{-1}$ and $\varepsilon(Cl^-, H^+) = (0.12 \pm 0.01)$ then follows

$$\varepsilon(PuO_2Cl^+, ClO_4^-) = (0.50 \pm 0.09)\ kg \cdot mol^{-1}$$

which is also included in our database.

The formation constant $\log_{10}\beta_2°(298.15\ K) = -(0.6 \pm 0.2)$ selected by Lemire et al. (2001) for

$$PuO_2^{2+} + 2\ Cl^- \Leftrightarrow PuO_2Cl_2\ (aq)$$

was also based on the experimental data by Giffaut (1994). In addition to these, Guillaumont et al. (2003) also accepted the experimental data by Runde et al. (1999) with $\log_{10}\beta_2°(298.15\ K) = -(1.7 \pm 0.2)$ and selected the average of the two values

$$\log_{10}\beta_2°(298.15\ K) = -(1.15 \pm 0.30)$$

with an increased uncertainty. This formation constant is also included in our database.

6.8 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.

6.9 Aqueous plutonium bromide complexes

The selected data for $PuBr^{3+}$ is not included in the database because the complex is very weak and bromide is not relevant under environmental conditions.

6.10 Aqueous plutonium iodine complexes

Lemire et al. (2001) provided a formation constant for PuI^{2+} as a guideline, based on a single experimental determination. This constant is not included in our database because the complex is very weak and not relevant under environmental conditions.

6.11 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.

6.11.1 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

$$PuO_2^{2+} + HSO_4^{2-} \Leftrightarrow PuO_2SO_4(aq) + H^+ \qquad (6.30)$$

The value was extrapolated to $\log_{10}\beta_1°(6.30, 298.15 \text{ K})$ 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

$$PuO_2^{2+} + SO_4^{2-} \Leftrightarrow PuO_2SO_4(aq) \qquad (6.31)$$

The measured values were extrapolated to $\log_{10}\beta_1°(6.31, 298.15 \text{ K})$ by means of an SIT fit. $\log_{10}\beta_1°(6.30, 298.15 \text{ K})$ 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 $\log_{10}\beta_1°(6.30, 298.15 \text{ K})$ to the selected value

$$\log_{10}\beta_1°(6.31, 298.15 \text{ K}) = (3.38 \pm 0.20)$$

The selected formation constant for

$$PuO_2^{2+} + 2\ SO_4^{2-} \Leftrightarrow PuO_2(SO_4)_2^{2-} \qquad (6.32)$$

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

$$\log_{10}\beta_2°(6.32, 298.15 \text{ K}) = (4.4 \pm 0.2)$$

For sodium media, we estimated

$$\varepsilon(PuO_2(SO_4)_2^{2-}, Na^+) = -(0.10 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$$

based on charge correlations (see Appendix A). The selected reaction enthalpies were determined in a calorimetric study:

$$\Delta_r H_m°(6.31, 298.15 \text{ K}) = (16.1 \pm 0.6) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_r H_m°(6.32, 298.15 \text{ K}) = (43 \pm 9) \text{ kJ}\cdot\text{mol}^{-1}$$

6.11.2 Pu(IV) sulfate complexes

There are 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:

$$Pu^{4+} + HSO_4^- \Leftrightarrow PuSO_4^{2+} + H^+ \qquad (6.33)$$

$$Pu^{4+} + 2\ HSO_4^- \Leftrightarrow Pu(SO_4)_2(aq) + 2\ H^+ \qquad (6.34)$$

The most reliable value of $\log_{10}{}^*\beta_1°(6.33, 298.15 \text{ K})$ at I = 2.2 M $HClO_4$ or $(H,Na)ClO_4$ is the weighted average of several independent experimental determinations at I = 2.2 M. The average was extrapolated by Lemire et al. (2001) to standard conditions by using SIT with $\Delta\varepsilon(6.33) = -(0.31 \pm 0.12)$ kg·mol^{-1} estimated[9] by Grenthe et al. (1992) for the analogous U(IV) system, resulting in the selected value

$$\log_{10}{}^*\beta_1°(6.33, 298.15 \text{ K}) = (4.91 \pm 0.22)$$

Lemire et al. (2001) did not report any value for $\varepsilon(PuSO_4^{2+}, ClO_4^-)$. An estimate can be derived from the estimated $\Delta\varepsilon(6.33)$ and $\varepsilon(HSO_4^-, H^+) = \varepsilon(HSO_4^-, Na^+) = -(0.01 \pm 0.02)$ kg·mol^{-1}, and the selected $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$ kg·mol^{-1} and $\varepsilon(Pu^{4+}, ClO_4^-) = (0.82 \pm 0.07)$ kg·mol^{-1}, resulting in

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[9] Grenthe et al. (1992) estimated $\Delta\varepsilon$ for $U^{4+} + HSO_4^- \Leftrightarrow USO_4^{2+} + H^+$ from the selected $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$ kg mol^{-1} and $\varepsilon(U^{4+}, ClO_4^-) = (0.76 \pm 0.06)$ kg·mol^{-1} and from the estimated $\varepsilon(HSO_4^-, H^+) = \varepsilon(HSO_4^-, Na^+) = -(0.01 \pm 0.02)$ kg·mol^{-1} and $\varepsilon(USO_4^{2+}, ClO_4^-) = (0.3 \pm 0.1)$ kg·mol^{-1}. Grenthe et al. (1992) did not explain how they estimated $\varepsilon(USO_4^{2+}, ClO_4^-)$.

$$\varepsilon(PuSO_4^{2+}, ClO_4^-) = (0.36 \pm 0.14)\ kg \cdot mol^{-1}$$

In the absence of data for the chloride system, we estimated

$$\varepsilon(PuSO_4^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg \cdot mol^{-1}$$

based on charge correlations (see Appendix A).

The selected value

$$\log_{10}{}^*\beta_2°(6.34, 298.15\ K) = (7.18 \pm 0.32)$$

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 our database, these complex formation reactions were rewritten in terms of SO_4^{2-} instead of HSO_4^-:

$$Pu^{4+} + SO_4^{2-} \Leftrightarrow PuSO_4^{2+} \quad (6.35)$$

$$Pu^{4+} + 2\ SO_4^{2-} \Leftrightarrow Pu(SO_4)_2(aq) \quad (6.36)$$

Therefore, $\log_{10}{}^*\beta_1°(6.33, 298.15\ K)$ and $\log_{10}{}^*\beta_2°(6.34, 298.15\ K)$ were recalculated by adding once or twice the selected protonation constant of SO_4^{2-}, $\log_{10}{}^*\beta_1° = (1.98 \pm 0.05)$

$$\log_{10}\beta_1°(6.35, 298.15\ K) = (6.89 \pm 0.23)$$

$$\log_{10}\beta_2°(6.36, 298.15\ K) = (11.14 \pm 0.34)$$

6.11.3 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:

$$Pu^{3+} + HSO_4^- \Leftrightarrow PuSO_4^+ + H^+ \quad (6.37)$$

$$Pu^{3+} + 2\ HSO_4^- \Leftrightarrow Pu(SO4)_2^- + 2\ H^+ \quad (6.38)$$

The selected values for the reaction enthalpies

$$\Delta_r H_m°(6.37, 298.15\ K) = -(5.2 \pm 2.0)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m°(6.38, 298.15\ K) = -(33 \pm 16)\ kJ \cdot mol^{-1}$$

were calculated from reported temperature variations of $\log_{10}{}^*\beta_1°(6.37)$ and $\log_{10}{}^*\beta_1°(6.38)$.

Lemire et al. (2001) used a rather peculiar procedure to extract $\log_{10}{}^*\beta_1°(6.37)$ 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 $\log_{10}{}^*\beta_1°(6.37)$ of one of these studies was further extrapolated from 28 to 25°C by using the selected value for $\Delta_r H_m°(6.37, 298.15\ K)$. An average of these four formation constants resulted in the selected

$$\log_{10}{}^*\beta_1°(6.37, 298.15\ K) = (1.93 \pm 0.61)$$

The selected value for

$$\log_{10}{}^*\beta_2°(6.38, 298.15\ K) = (1.74 \pm 0.76)$$

was derived in a similar fashion from the same studies. Since Lemire et al. (2001) did not report any ion interaction coefficients for $PuSO_4^+$ and $Pu(SO_4)_2^-$, we used an estimation method based on charge correlations (see Appendix A) to obtain the missing coefficients

$$\varepsilon(PuSO_4^+, Cl^-) = (0.05 \pm 0.10)\ kg\cdot mol^{-1}$$

$$\varepsilon(PuSO_4^+, ClO_4^-) = (0.2 \pm 0.1)\ kg\cdot mol^{-1}$$

$$\varepsilon(Pu(SO_4)_2^-, Na^+) = -(0.05 \pm 0.10)\ kg\cdot mol^{-1}$$

For our database, the complex formation reactions were cast in terms of SO_4^{2-} instead of HSO_4^-:

$$Pu^{3+} + SO_4^{2-} \Leftrightarrow PuSO_4^+ \quad (6.39)$$

$$Pu^{3+} + 2\ SO_4^{2-} \Leftrightarrow Pu(SO_4)^{2-} \quad (6.40)$$

Therefore, $\log_{10}{}^*\beta_1°(6.37, 298.15\ K)$ and $\log_{10}{}^*\beta_2°(6.38, 298.15\ K)$ were recalculated by adding once or twice the selected protonation constant of SO_4^{2-}, $\log_{10}{}^*\beta_1° = (1.98 \pm 0.05)$:

$$\log_{10}\beta_1°(6.39, 298.15\ K) = (3.9 \pm 0.6)$$

$$\log_{10}\beta_2°(6.40, 298.15\ K) = (5.7 \pm 0.8)$$

In a similar fashion, $\Delta_rH_m°(6.37, 298.15\ K)$ and $\Delta_rH_m°(6.38, 298.15\ K)$ were recalculated by adding once or twice $\Delta_rH_m°(6.41, 298.15\ K)$, the enthalpy of protonation (see below), resulting in

$$\Delta_rH_m°(6.39, 298.15\ K) = (17.2 \pm 2.3)\ kJ\cdot mol^{-1}$$

$$\Delta_rH_m°(6.40, 298.15\ K) = (12 \pm 16)\ kJ\cdot mol^{-1}$$

$\Delta_rH_m°(6.41, 298.15\ K) = (22.44 \pm 1.08)$ for the protonation of SO_4^{2-}

$$SO_4^{2-} + H^+ \Leftrightarrow HSO_4^- \quad (6.41)$$

was calculated from selected auxiliary data:

$$\Delta_fH_m°(SO_4^{2-}, 298.15\ K) = -(909.340 \pm 0.400)\ kJ\cdot mol^{-1}$$

$$\Delta_fH_m°(HSO_4^-, 298.15\ K) = -(886.900 \pm 1.000)\ kJ\cdot mol^{-1}$$

6.12 Solid plutonium arsenic, antimony, and bismuth compounds

In addition to plutonium nitrogen compounds and complexes (Section 6.13) and to plutonium phosphorous compounds and complexes (Section 6.14), 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 $\Delta_fG_m°$ 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 our database.

6.13 Plutonium nitrogen compounds and complexes

In addition to plutonium nitrates which are discussed in Section 6.13.1, 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, it was not included in our database.

6.13.1 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 our database.

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 in mixed perchloric/nitric acid media were used to determine $\log_{10}\beta_1°(298.15\ K)$ by applying an SIT fit to the data, resulting in a selected value of

$$\log_{10}\beta_1°(298.15\ K) = (1.95 \pm 0.15)$$

with $\Delta\varepsilon = -(0.19 \pm 0.05)\ kg \cdot mol^{-1}$. Lemire et al. (2001) did not report any interaction coefficient for $PuNO_3^{3+}$. A value for $\varepsilon(PuNO_3^{3+}, ClO_4^-)$ can be derived from $\Delta\varepsilon$ and the selected $\varepsilon(Pu^{4+}, ClO_4^-) = (0.82 \pm 0.07)\ kg \cdot mol^{-1}$ and $\varepsilon(NO_3^-, H^+) = (0.07 \pm 0.01)\ kg \cdot mol^{-1}$, leading to

$$\varepsilon(PuNO_3^{3+}, ClO_4^-) = (0.70 \pm 0.09)\ kg \cdot mol^{-1}$$

For chloride media we estimated

$$\varepsilon(PuNO_3^{3+}, Cl^-) = (0.25 \pm 0.10)\ kg \cdot mol^{-1}$$

based on charge correlations (see Appendix A).

There is evidence that anionic complexes form at very high nitrate concentrations in acidic solutions but no thermodynamic data are available.

6.14 Plutonium phosphorous compounds and complexes

Besides PuP(cr), which is irrelevant in environmental systems and has therefore not been included in our database, PuPO4(s, hyd), and $Pu(HPO_4)_2(am)$, only aqueous plutonium phosphorous complexes were discussed by Lemire et al. (2001).

6.14.1 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

$$\log_{10}K_{s,0}°(298.15 \text{ K}) = -(24.6 \pm 0.8)$$

6.14.2 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

$$Pu(HPO_4)_2 \cdot xH_2O(s) \Leftrightarrow Pu^{4+} + 2\ HPO_4^{2-} + x\ H_2O(l)$$

For our database, this solubility reaction was written as

$$Pu(HPO_4)_2(am, hyd) \Leftrightarrow Pu^{4+} + 2\ HPO_4^{2-}$$

Since Lemire et al. (2001) did not report any ion interaction coefficients for $PuH_3PO_4^{4+}$, we estimated

$$\varepsilon(PuH_3PO_4^{4+}, Cl^-) = (0.35 \pm 0.10) \text{ kg} \cdot \text{mol}^{-1}$$

$$\varepsilon(PuH_3PO_4^{4+}, ClO_4^-) = (0.8 \pm 0.1) \text{ kg} \cdot \text{mol}^{-1}$$

based on charge correlations (see Appendix A).

6.14.3 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.

6.14.4 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.

6.15 Plutonium carbides

Lemire et al. (2001) selected thermodynamic data for $PuC_{0.84}$(cr), Pu_2C_3(cr), and Pu_3C_2(cr). However, carbides are not relevant for environmental systems and are therefore not included in our database.

6.16 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, accessed 1-12-2014).

6.16.1 Pu(VI) carbonate complexes

6.16.1.1 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

$$PuO_2(OH)_2(aq) + HCO_3^- \Leftrightarrow PuO_2CO_3OH^- + H_2O(l) \qquad (6.42)$$

as $\log_{10}\beta_1$(6.42, 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):

$$PuO_2(OH)_2(aq) + HCO_3^- \Leftrightarrow PuO_2CO_3(aq) + OH^- + H_2O(l) \qquad (6.43)$$

Therefore, the reported $\log_{10}\beta_1$(6.42, 0.1 M $NaClO_4$, 298.15 K) by Sullivan & Woods (1982) was assumed to refer to reaction (6.43) and thus $\log_{10}{}^*\beta_1$(6.43, 0.1 M $NaClO_4$, 298.15 K) = (2.67 ± 0.60). The SIT correction is very small, and $\log_{10}{}^*\beta_1°$(6.43, 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 6.4.1, and the auxiliary data for the stability of water and dissociation of bicarbonate, Lemire et al. (2001) calculated the equilibrium constant for the reaction

$$PuO_2^{2+} + CO_3^{2-} \Leftrightarrow PuO_2CO_3(aq) \qquad (6.44)$$

and obtained $\log_{10}\beta_1°$(6.44, 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 6.4.1.

Robouch & Vitorge (1987) determined the value of $\log_{10}\beta_1$(6.44, 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 $\varepsilon(UO_2^{2+}, ClO_4^-)$

= (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 $\log_{10}\beta_1°(6.44, 20°C) = (9.3 \pm 0.5)$. This result was assumed to apply also to 25°C. Because the discrepancy between the two values for $\log_{10}\beta_1°(6.44)$ is large, Lemire et al. (2001) selected their unweighted mean $\log_{10}\beta_1°(6.44, 298.15 K) = (11.6 \pm 3.0)$ as recommended value.

In our previous database update (Hummel et al. 2002) we did not agree with this choice. A discrepancy of more than four orders of magnitude between the two values for $\log_{10}\beta_1°(6.44)$ is too large to justify the simple selection of the mean (even if unweighted), and a decision had to be made. We chose to select the value $\log_{10}\beta_1°(6.44, 298.15 K) = (9.3 \pm 0.5)$ based on Robouch & Vitorge (1987) 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 $\log_{10}\beta_1° = 9.1$, $\log_{10}\beta_2° = 15.0$, and $\log_{10}\beta_3° = 17.9$ estimated with the semi-empirical electrostatic approach by Neck & Kim (2000) for the prediction of actinide complexation constants.

Guillaumont et al. (2003) re-evaluated the experimental data discussed by Lemire et al. (2001) and based their selected

$$\log_{10}\beta_1°(6.44, 298.15 K) = (9.5 \pm 0.5)$$

on the average of the values (extrapolated with SIT to $I = 0$) determined by Robouch & Vitorge (1987), Ullman & Schreiner (1988), Pashalidis et al. (1993), and Pashalidis et al. (1997). This value is included in our database

6.16.1.2 Dicarbonato complex

The association constant for

$$PuO_2^{2+} + 2\ CO_3^{2-} \Leftrightarrow PuO_2(CO_3)_2^{2-}$$

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 $\Delta_rH_m°(298.15 K)$ based on enthalpy titrations by Ullman & Schreiner (1988)

$$\Delta_rH_m°(298.15 K) = -(27 \pm 4)\ kJ\cdot mol^{-1}$$

Thus, $\log_{10}\beta_2°(298.15 K) = (13.9 \pm 1.4)$ was obtained.

Ullman & Schreiner (1988) determined $\log_{10}\beta_2°(298.15 K) = (15.1 \pm 1.2)$ 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 $\log_{10}\beta_2°(298.15 K) = (15.1 \pm 2.2)$.

Lemire et al. (2001) selected $\log_{10}\beta_2°(298.15 K) = (14.5 \pm 2.6)$, which is the unweighted average of the two values based on Robouch & Vitorge (1987) and on Ullman & Schreiner (1988).

In our previous database update (Hummel et al. 2002) we did 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 our previous database, resulting in

$$\log_{10}\beta_2°(298.15\ K) = (14.6 \pm 0.9).$$

Re-evaluating the experimental data discussed by Lemire et al. (2001), Guillaumont et al. (2003) accepted the experimental data by Robouch & Vitorge (1987), Ullman & Schreiner (1988), Pashalidis et al. (1993), and Pashalidis et al. (1997) and extrapolated the data to $I = 0$ with SIT. They selected the average value

$$\log_{10}\beta_2°(298.15\ K) = (14.7 \pm 0.5)$$

which is also included in our database. Since Guillaumont et al. (2003) gave no information on their SIT-extrapolation and did not report any ion interaction parameter for $PuO_2(CO_3)_2^{2-}$, we estimated

$$\varepsilon(PuO_2(CO_3)_2^{2-}, Na^+) = -(0.10 \pm 0.10)\ kg \cdot mol^{-1}$$

based on charge correlations (see Appendix A).

6.16.1.3 Tricarbonato complex

The stability constant for

$$PuO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow PuO_2(CO_3)_3^{4-} \qquad (6.45)$$

was estimated by Lemire et al. (2001) 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 $\varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$ kg· mol^{-1} as an estimate for $\varepsilon(PuO_2^{2+}, ClO_4^-)$, but with errors expanded to ± 0.5, and $\varepsilon(PuO_2(CO_3)_3^{4-}, Na^+) = -(0.2 \pm 0.3)$ kg· 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 $\Delta_r H_m°(6.45, 298.15\ K)$ based on enthalpy titrations

$$\Delta_r H_m°(6.45, 298.15\ K) = -(38.6 \pm 2.0)\ kJ \cdot mol^{-1}$$

Lemire et al. (2001) selected the weighted average of the resulting $\log_{10}\beta_3°(298.15\ K)$ and the value determined by another experiment (with increased uncertainties to account for unorthodox calculation procedures): $\log_{10}\beta_3°(6.45, 298.15\ K) = (17.7 \pm 0.9)$.

As for $PuO_2CO_3(aq)$ and $PuO_2(CO_3)_2^{2-}$, Guillaumont et al. (2003) relied on the experimental data by Robouch & Vitorge (1987), Ullman & Schreiner (1988), Pashalidis et al. (1993), and Pashalidis et al. (1997). They extrapolated the data to $I = 0$ with SIT (but gave no details on the procedure) and selected the average of the values

$$\log_{10}\beta_3°(6.45, 298.15\ K) = (18.0 \pm 0.5)$$

Because Guillaumont et al. (2003) did not report any ion interaction parameter for $PuO_2(CO_3)_3^{4}$, we estimated

$$\varepsilon(PuO_2(CO_3)_3^{4-}, Na^+) = -(0.20 \pm 0.30)\ kg \cdot mol^{-1}$$

based on charge correlations (see Appendix A).

6.16.1.4 Dicarbonato trimer

In an experimental study, spectrophotometric and potentiometric data were interpreted in terms of the reaction

$$3\ PuO_2(CO_3)_3^{4-} \Leftrightarrow (PuO_2)_3(CO_3)_6^{6-} + 3\ CO_3^{2-} \qquad (6.46)$$

with $\log_{10}K(6.46, I = 3\ M\ NaClO_4, 22°C) = -(7.5 \pm 0.5)$. 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 $\log_{10}K(6.46, I = 3$ 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 Δε of reaction (6.45), $\log_{10}\beta_3°(6.45, 298.15$ K) was extrapolated to $I = 3$ M $NaClO_4$ and 22°C, resulting in $\log_{10}\beta_3(6.45, I = 3$ M $NaClO_4$, 22°C) = (19.2 ± 1.4). This was used to calculate the stability of the dicarbonato trimer

$$3\ PuO_2^{2+} + 6\ CO_3^{2-} \Leftrightarrow (PuO_2)_3(CO_3)_6^{6-} \qquad (6.47)$$

with $\log_{10}\beta_{6,3}(6.47, I = 3$ 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 our database.

6.16.1.5 Mixed U(VI) Pu(VI) carbonate complexes

Grenthe et al. (1995) reported

$$\log_{10}K°(6.48, 298.15\ K) = -(8.2 \pm 1.3)$$

for

$$2\ UO_2(CO_3)_3^{4-} + PuO_2(CO_3)_3^{4-} \Leftrightarrow (UO_2)_2(PuO_2)(CO_3)_6^{6-} + 3\ CO_3^{2-} \qquad (6.48)$$

based on an extrapolation to $I = 0$ of experimental data at (22 ± 1)°C in 3 M $NaClO_4$, assuming that Δε for this reaction equals Δε = (0.16 ± 0.36) $kg\cdot mol^{-1}$ determined for the reaction 3 $UO_2(CO_3)_3^{4-} \Leftrightarrow (UO_2)_3(CO_3)_6^{6-} + 3\ CO_3^{2-}$. Since neither Lemire et al. (2001) nor Guillaumont et al. (2003) reported any value for $\varepsilon(PuO_2(CO_3)_3^{4-}, Na^+)$ we assumed one in order to derive a value for $\varepsilon((UO_2)_2PuO_2(CO_3)_6^{6-}, Na^+)$. An obvious choice is $\varepsilon(PuO_2(CO_3)_3^{4-}, Na^+) = \varepsilon(UO_2(CO_3)_3^{4-}, Na^+)$ and therefore

$$\varepsilon((UO_2)_2PuO_2(CO_3)_6^{6-}, Na^+) \approx \varepsilon((UO_2)_3(CO_3)_6^{6-}, Na^+) = (0.37 \pm 0.11)\ kg\cdot mol^{-1}$$

which is included in our database.

The selected value

The value $\log_{10}K°(6.48, 298.15$ K) = -(8.2 ± 1.3) was accepted by Lemire et al. (2001) but they recommended that this value be used with caution at ionic strengths much different form that of the original experiment.

For our database we wrote the formation of $(UO_2)_2(PuO_2)(CO_3)_6^{6-}$ as

$$2\ UO_2^{2+} + PuO_2^{2+} + 6\ CO_3^{2-} \Leftrightarrow (UO_2)_2(PuO_2)(CO_3)_6^{6-} \qquad (6.49)$$

The selected value

$$\log_{10}K°(6.49, 298.15\ K) = (53.5 \pm 1.4)$$[10]

was calculated from $\log_{10}K°(6.48, 298.15$ K), $\log_{10}\beta_3°(6.45, 298.15$ K) and from the selected

$$\log_{10}\beta_3°(6.50, 298.15\ K) = (21.84 \pm 0.04)$$

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[10] Note that in Thoenen (2012) and in the electronic versions of TDB 12/07 for PHREEQC and GEMS-PSI released before December 2014, the value was by mistake not updated. It has changed from (52.7 ± 1.6) to (53.5 ± 1.4) due to the updated values for $\log_{10}\beta_3°(6.45, 298.15$ K) and $\log_{10}\beta_3°(6.50, 298.15$ K).

for the reaction

$$UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow UO^2(CO_3)_3^{4-} \qquad (6.50)$$

6.16.2 Pu(V) carbonate complexes

A stability constant for

$$PuO_2^{+} + CO_3^{2-} \Leftrightarrow PuO_2CO_3^{-} \qquad (6.51)$$

was determined by laser photoacoustic spectrometry at I = 0.5 M $NaClO_4$ and 23°C. It was extrapolated to I = 0 using SIT, assuming that

$$\varepsilon(PuO_2CO_3^-, Na^+) = \varepsilon(NpO_2CO_3^-, Na^+) = -(0.18 \pm 0.18)\ kg\cdot mol^{-1}$$

the recommended value of with the uncertainty expanded from 0.15 to 0.18 kg·mol^{-1}. Assuming that measurements at 23°C are equally valid at 25°C, the selected constant is

$$\log_{10}\beta_1°(6.51, 298.15\ K) = (5.12 \pm 0.14)$$

This value is statistically identical to the value selected for the Np system $\log_{10}\beta_1°(NpO_2CO_3^-$, 298.15 K) = (4.96 ± 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

$$PuO_2(CO_3)_3^{4-} + e^- \Leftrightarrow PuO_2(CO_3)_3^{5-} \qquad (6.52)$$

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 (6.52) 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 (6.52), $E°$(6.52, 298.15 K) = (186 ± 10) mV was then converted into $\Delta_rG_m°$(6.52, 298.15 K) = -(17.9 ± 1.0) kJ·mol^{-1} and used with the selected $\Delta_rG_m°$ for the reactions

$$PuO_2^{2+} + e^- \Leftrightarrow PuO_2^{+} \qquad (6.7)$$

$$PuO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow PuO_2(CO_3)_3^{4-} \qquad (6.45)$$

$\Delta_rG_m°$(6.7, 298.15 K) = -(90.29 ± 0.52) kJ·mol^{-1} and $\Delta_rG_m°$(6.45, 298.15 K) = -(101 ± 5) kJ·mol^{-1} to calculate $\Delta_rG_m°$(6.53, 298.1) for

$$PuO_2^{+} + 3\ CO_3^{2-} \Leftrightarrow PuO_2(CO_3)_3^{5-} \qquad (6.53)$$

resulting in $\Delta_rG_m°$(6.53, 298.1) = -(28.68 ± 5.25) kJ·mol^{-1} and

$$\log_{10}\beta_3°(6.53, 298.15\ K) = (5.03 \pm 0.92)$$

Since no ion interaction coefficients were reported by Lemire et al. (2001) for $PuO_2(CO_3)_3^{5-}$, we estimated

$$\varepsilon(PuO_2(CO_3)_3^{5-}, Na^+) = -(0.25 \pm 0.40)\ kg\cdot mol^{-1}$$

based on charge correlations (see Appendix A).

$\Delta_r S_m°(6.52, 298.15\ K)$ was estimated at infinite dilution based on the temperature dependence of the reduction potential at each of the four ionic strengths. $\Delta_r S_m°(6.52, 298.15\ K)$ was used together with $\Delta_r G_m°(6.52, 298.15\ K)$, the latter of which was obtained from the standard potential of reaction (6.52), for the calculation of $\Delta_r H_m°(6.52, 298.15\ K)$. Finally,

$$\Delta_r H_m°(6.53, 298.15\ K) = -(19.11 \pm 8.50)\ kJ\cdot mol^{-1}$$

was calculated from $\Delta_r H_m°(6.52, 298.15\ K)$ using the selected enthalpy data for reactions (6.7) and (6.45).

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 $PuO_2(CO_3)_2^{3-}$.

6.16.3 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 coordinated 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

$$Pu(CO_3)_4^{4-} + CO_3^{2-} \Leftrightarrow Pu(CO_3)_5^{6-} \qquad (6.54)$$

at $I = 0$ from experiments performed between $I = 0.2$ to 4.5 m at (22 ± 1)°C. Their value was accepted by Lemire et al. (2001) as the best estimate for

$$\log_{10}K_5°(6.54, 298.15\ K) = -(1.36 \pm 0.09)$$

This value was also accepted by Guillaumont et al. (2003). Capdevila et al. (1996) assigned a value of

$$\log_{10}\beta_5(6.55, I = 3\ M\ NaClO_4, 22°C) = (35.8 \pm 1.3)$$

to the reaction

$$Pu^{4+} + 5\ CO_3^{2-} \Leftrightarrow Pu(CO_3)_5^{6-} \qquad (6.55)$$

According to Lemire et al. (2001), insufficient independent evidence is available to extrapolate this value to $I = 0$ and they did not recommend any stability constant for $Pu(CO_3)_5^{6-}$.

For our previous database update (Hummel et al. 2002) we attempted to estimate a value for $\log_{10}\beta_5°(6.55)$ using SIT with $\Delta\varepsilon(6.55) = -(0.42 \pm 0.54)\ kg\cdot mol^{-1}$, calculated from the selected values $\varepsilon(Pu^{4+}, ClO_4^-) = (0.82 \pm 0.06)\ kg\cdot mol^{-1}$ and $\varepsilon(CO_3^{2-}, Na^+) = -(0.08 \pm 0.03)\ kg\cdot mol^{-1}$. 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 $\Delta z^2(6.43) = 0$, $\log_{10}\beta_5°(6.55)$ can be calculated from

$$\log_{10}\beta_5°(6.55) = \log_{10}\beta_5(6.55) + \Delta\varepsilon(6.55)\, I$$

Neglecting the small temperature difference of 3°C and expanding the uncertainty from 2.37 to 2.5

$$\log_{10}\beta_5°(6.55, 298.15 \text{ K}) = (34.5 \pm 2.5)$$

which we selected for our previous database update. For the reaction

$$Pu^{4+} + 4\ CO_3^{2-} \Leftrightarrow Pu(CO_3)_4^{4-} \qquad (6.56)$$

$\log_{10}\beta_4°(6.56, 298.15 \text{ K})$ was then calculated from $\log_{10}\beta_5°(6.55, 298.15 \text{ K})$ and $\log_{10}K_5°(6.54, 298.15 \text{ K})$. The selected value for the previous database update was therefore

$$\log_{10}\beta_4°(6.56, 298.15 \text{ K}) = (35.9 \pm 2.5)$$

Guillaumont et al. (2003) accepted the experimental data by Rai et al. (1999) who studied the solubility of $PuO_2(am)$ in carbonate/bicarbonate solutions spanning a wide pH and concentration range. The limiting complex $Pu(CO_3)_5^{6-}$ was observed to predominate over a large concentration range and was characterized by EXAFS. From the experimental data, Guillaumont et al. (2003) derived

$$\log_{10}\beta_5°(6.55, 298.15 \text{ K}) = (35.65 \pm 1.13)$$

which is included in our database. Combining this value with $\log_{10}K_5°(6.54, 298.15 \text{ K}) = -(1.36 \pm 0.09)$ discussed above, Guillaumont et al. (2003) obtained

$$\log_{10}\beta_4°(6.56, 298.15 \text{ K}) = (37.0 \pm 1.1)$$

which is also included in our database. Since Guillaumont et al. (2003) did not report any ion interaction coefficients for $Pu(CO_3)_4^{4-}$ and $Pu(CO_3)_5^{6-}$, we estimated

$$\varepsilon(Pu(CO_3)_4^{4-}, Na^+) = -(0.20 \pm 0.30) \text{ kg·mol}^{-1}$$

$$\varepsilon(Pu(CO_3)_5^{6-}, Na^+) = -(0.30 \pm 0.50) \text{ kg·mol}^{-1}$$

based on charge correlations (see Appendix A).

6.16.4 Ternary Pu(IV) hydroxide-carbonate complexes

There appear to be no reliable experimental data on ternary Pu(IV) hydroxide-carbonate complexes. However, scoping calculations (Hummel & Berner 2002) showed that such complexes can be of importance in environmental modeling. Hummel & Berner (2002) estimated maximum feasible values for ternary hydroxide-carbonate complexes of U(IV), Np(IV), and Pu(IV) at low bicarbonate concentrations. They assumed that $AnCO_3(OH)_3^-$ is the dominant mixed hydroxide-carbonate complex and adjusted the formation constants to the maximal feasible values that are still consistent with the available experimental solubility data. In the case of $PuCO_3(OH)_3^-$ they obtained

$$Pu^{4+} + CO_3^{2-} + 3\ H_2O(l) \Leftrightarrow PuCO_3(OH)_3^- + 3\ H^+$$

$$\log_{10}{}^*K°(298.15 \text{ K}) = 6$$

This value is included in our database as supplemental data together with

$$\varepsilon(PuCO_3(OH)_3^-, Na^+) = -(0.05 \pm 0.10) \text{ kg·mol}^{-1}$$

that we estimated based on charge correlations (see Appendix A).

6.16.5 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). Hummel & Berner (2002) estimated stability constants for $PuCO_3^+$, $Pu(CO_3)_2^-$, and $Pu(CO_3)_3^{3-}$ by adopting the values for the corresponding Am(III) carbonate complexes. From the revised data by Guillaumont et al. (2003) for these complexes the following revised estimates are obtained

$$Pu^{3+} + CO_3^{2-} \Leftrightarrow PuCO_3^+$$

$$log_{10}\beta_1°(298.15\ K) = 8.0$$

$$Pu^{3+} + 2\ CO_3^{2-} \Leftrightarrow Pu(CO_3)_2^-$$

$$log_{10}\beta_2°(298.15\ K) = 12.9$$

$$Pu^{3+} + 3\ CO_3^{2-} \Leftrightarrow Pu(CO_3)_3^{3-}$$

$$log_{10}\beta_3°(298.15\ K) = 15.0$$

These values are included in our database as supplemental data, as well as the corresponding ion interaction coefficients

$$\varepsilon(PuCO_3^+, Cl^-) = (0.05 \pm 0.10)\ kg \cdot mol^{-1}$$

$$\varepsilon(PuCO_3^+, ClO_4^-) = (0.2 \pm 0.1)\ kg \cdot mol^{-1}$$

$$\varepsilon(Pu(CO_3)_2^-, Na^+) = -(0.10 \pm 0.10)\ kg \cdot mol^{-1}$$

$$\varepsilon(Pu(CO_3)_3^{3-}, Na^+) = -(0.15 \pm 0.20)\ kg \cdot mol^{-1}$$

that we estimated based on charge correlations (see Appendix A).

6.17 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 two studies in 0.1 and 3 M $NaClO_4$. and in a third study in 0.1 to 5.6 m NaCl and in 5.6 m $NaClO_4$. For each of these studies, Guillaumont et al. (2003) extrapolated the measured solubility constants to $I = 0$ by using SIT. They selected the unweighted mean values of these constants and obtained

$$\log_{10}K_{s,0}°(298.15\ K) = -(14.65 \pm 0.47)$$

for

$$PuO_2CO_3(s) \Leftrightarrow PuO_2^{2+} + CO_3^{2-}$$

which is also adopted for our database.

6.18 Plutonium thiocyanate complexes

Lemire et al. (2001) discussed thiocyanate complexes of Pu(III), namely $PuSCN^{2+}$, $Pu(SCN)_2^+$, and $Pu(SCN)_3(aq)$, which are all quite weak. Formation constants for the 1:1 complex were obtained in four different experimental studies for 1 M, 2 M, and 3 M $NaClO_4$ and for 1 M NH_4ClO_4. Lemire et al. (2001) extrapolated each of these values to $I = 0$ by using SIT, assuming that

$$\varepsilon(PuSCN^{2+}, ClO_4^-) \approx \varepsilon(AmSCN^{2+}, ClO_4^-)^{11} = (0.39 \pm 0.04)\ kg \cdot mol^{-1}$$

They selected the unweighted average of the extrapolated values

$$\log_{10}\beta_1°(298.15\ K) = (1.3 \pm 0.4)$$

for

$$Pu^{+3} + SCN^- \Leftrightarrow PuSCN^{2+}$$

which is also selected for our database, including the estimate for $\varepsilon(PuSCN^{2+}, ClO_4^-)$. As there are no data for chloride media, we estimated

$$\varepsilon(PuSCN^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg \cdot mol^{-1}$$

based on charge correlations (see Appendix A).

Lemire et al. (2001) did not select any constants for the higher Pu(III) thiocyanate complexes.

6.19 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 $\Delta_f G_m°$ values for any of these phases.

6.20 Plutonium alkaline-earth compounds

Several ternary oxides of alkaline earths elements with plutonium have been reported, but thermodynamic data are limited. Data were selected by Lemire et al. (2001) for $Sr_3PuO_6(cr)$, $Ba_3PuO_6(cr)$, $BaPuO_3(cr)$, $Ba_2MgPuO_6(cr)$, $Ba_2CaPuO_6(cr)$, and $Ba_2SrPuO_6(cr)$, but there are no solubility product or $\Delta_f G_m°$ values for any of these phases.

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[11] Note that $\varepsilon(AmSCN^{2+}, ClO_4^-)$ itself was estimated by Silva et al. (1995): $\varepsilon(AmSCN^{2+}, ClO_4^-) \approx \varepsilon(AmOH^{2+}, ClO_4^-) \approx \varepsilon(YHCO_3^{2+}, ClO_4^-) = (0.39 \pm 0.04)\ kg \cdot mol^{-1}$. The latter value (without uncertainty) was determined by Spahiu (1983) and Spahiu (1985) using an SIT analysis of experimentally derived formation constants for the yttrium bicarbonate complex.

Table 6.1: Pu data selected by NEA (Lemire et al. 2001 and Guillaumont et al. 2003) but not included in TDB Version 12/07. For explanations see text.

Gases	Pu(g)[ad], PuF(g)[a], PuF_2(g)[a], PuF_3(g)[ad], PuF_4(g)[ad], PuF_6(g)[ad], $PuCl_3$(g)[ad], $PuCl_4$(g)[ad], $PuBr_3$(g)[ac], PuI_3(g)[a]
Solids	β-Pu(cr)[b], δ-Pu(cr)[b], δ'-Pu(cr)[b], γ-Pu(cr)[b], ε-Pu(cr)[b], $PuO_{1.61}$(cr, bcc)[a], PuO_2(cr)[a], Pu_2O_3(cr)[a], PuF_3(cr)[ad], PuF_4(cr)[ad], PuF_6(cr)[ad], PuOF(cr)[a], $PuCl_3$(cr)[ad], $PuCl_4$(cr)[a], PuOCl(cr)[ad], $PuCl_3 \cdot 6H_2O$(cr)[a], $PuBr_3$(cr)[ac], PuOBr(cr)[ac], PuI_3(cr)[a], PuOI(cr)[a], PuSe(cr)[b], PuTe(cr)[b], PuN(cr)[a], $PuO_2(NO_3)_2 \cdot 6H_2O$(cr)[a], PuP(cr)[a], PuAs(cr)[a], PuSb(cr)[a], PuBi(cr)[a], $PuBi_2$(cr)[a], $PuC_{0.84}$(cr)[a], Pu_3C_2(cr)[a], Pu_2C_3(cr)[a], Sr_3PuO_6(cr)[b], $BaPuO_3$(cr)[b], Ba_3PuO_6(cr)[b], Ba_2MgPuO_6(cr)[b], Ba_2CaPuO_6(cr)[b], Ba_2SrPuO_6(cr)[b], Cs_2PuCl_6(cr)[a], Cs_3PuCl_6(cr)[ac], $CsPu_2Cl_7$(cr)[ac], Cs_2PuBr_6(cr)[a], $Cs_2NaPuCl_6$(cr)[a]
Aqueous species	$PuBr^{3+}$[ac], PuI^{2+}[ac]

[a] Single species data including $\Delta_f G_m°$

[b] Single species data excluding $\Delta_f G_m°$

[c] Reaction data including $\log_{10}K°$

[d] Reaction data excluding $\log_{10}K°$

Table 6.2: Selected plutonium data. All data included in TDB Version 12/07 are taken from Lemire et al. (2001) or Guillaumont et al. (2003), except where marked with an asterisk (*). Supplemental data are in italics. New or changed data with respect to TDB Version 01/01 (Hummel et al., 2002) are shaded.

		TDB Version 01/01				**TDB Version 12/07**				
Name	**Redox**	$\Delta_f G_m°$ [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}]	$\Delta_f G_m°$ [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}]	**Species**
Pu(cr)	0	0.0	0.0	54.46 ± 0.80	31.49 ± 0.40	0.0	0.0	54.46 ± 0.80	31.49 ± 0.40	Pu(cr, α)
Pu+3	III	-579.0 ± 2.7	-591.8 ± 2.0	-184.5 ± 6.2	-	-579.0 ± 2.7	-591.8 ± 2.0	-184.5 ± 6.2	-	Pu^{3+}
Pu+4	IV	-478.0 ± 2.7	-539.9 ± 3.1	-414.5 ± 10.2	-	-478.0 ± 2.7	-539.9 ± 3.1	-414.5 ± 10.2	-	Pu^{4+}
PuO2+	V	-852.6 ± 2.9	-910.1 ± 8.9	1 ± 30	-	-852.6 ± 2.9	-910.1 ± 8.9	1 ± 30	-	PuO_2^+
PuO2+2	VI	-762.4 ± 2.8	-822.0 ± 6.6	-71.2 ± 22.1	-	-762.4 ± 2.8	-822.0 ± 6.6	-71.2 ± 22.1	-	PuO_2^{2+}

		TDB Version 01/01		**TDB Version 12/07**		
Name	**Redox**	$\log_{10}\beta°$	$\Delta_r H_m°$ [kJ·mol^{-1}]	$\log_{10}\beta°$	$\Delta_r H_m°$ [kJ·mol^{-1}]	**Reaction**
PuO2OH+	VI	-5.5 ± 0.5	28 ± 15	-5.5 ± 0.5	28 ± 15	$PuO_2^{2+} + H_2O(l) \Leftrightarrow PuO_2OH^+ + H^+$
PuO2(OH)2	VI	-13.2 ± 1.5	-	-13.2 ± (1.5)*	-	$PuO_2^{2+} + 2\ H_2O(l) \Leftrightarrow PuO_2(OH)_2(aq) + 2\ H^+$
(PuO2)2(OH)2+2	VI	-7.5 ± 1.0	-	-7.5 ± (1.0)*	-	$2\ PuO_2^{2+} + 2\ H_2O(l) \Leftrightarrow (PuO_2)_2(OH)_2^{2+} + 2\ H^+$
PuO2F+	VI	4.56 ± 0.20	-	4.56 ± 0.20	-	$PuO_2^{2+} + F^- \Leftrightarrow PuO_2F^+$
PuO2F2	VI	7.25 ± 0.45	-	7.25 ± 0.45	-	$PuO_2^{2+} + 2\ F^- \Leftrightarrow PuO_2F_2(aq)$
PuO2Cl+	VI	0.70 ± 0.13	-	0.23 ± 0.03	-	$PuO_2^{2+} + Cl^- \Leftrightarrow PuO_2Cl^+$
PuO2Cl2	VI	-0.6 ± 0.2	-	-1.15 ± 0.30	-	$PuO_2^{2+} + 2\ Cl^- \Leftrightarrow PuO_2Cl_2(aq)$
PuO2SO4	VI	3.38 ± 0.20	16.1 ± 0.6	3.38 ± 0.20	16.1 ± 0.6	$PuO_2^{2+} + SO_4^{2-} \Leftrightarrow PuO_2SO_4(aq)$
PuO2(SO4)2-2	VI	4.4 ± 0.2	43 ± 9	4.4 ± 0.2	43 ± 9	$PuO_2^{2+} + 2\ SO_4^{2-} \Leftrightarrow PuO_2(SO_4)_2^{2-}$

		TDB Version 01/01		**TDB Version 12/07**		
Name	**Redox**	$\log_{10}\beta°$	$\Delta_r H_m°$ [kJ·mol^{-1}]	$\log_{10}\beta°$	$\Delta_r H_m°$ [kJ·mol^{-1}]	**Reaction**
PuO2CO3	VI	9.3 ± 0.5	-	9.5 ± 0.5	-	$PuO_2^{2+} + CO_3^{2-} \Leftrightarrow PuO_2CO_3(aq)$
PuO2(CO3)2-2	VI	14.6 ± 0.9	-27 ± 4	14.7 ± 0.5	-27 ± 4	$PuO_2^{2+} + 2\ CO_3^{2-} \Leftrightarrow PuO_2(CO_3)_2^{2-}$
PuO2(CO3)3-4	VI	17.7 ± 0.9	-38.6 ± 2.0	18.0 ± 0.5	-38.6 ± 2.0	$PuO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow PuO_2(CO_3)_3^{4-}$
(UO2)2PuO2(CO3)6-6	VI	52.7 ± 1.6	-	(53.5 ± 1.4)[a]	-	$2\ UO_2^{2+} + PuO_2^{2+} + 6\ CO_3^{2-} \Leftrightarrow (UO_2)_2PuO_2\ (CO_3)_3^{6-}$
PuO2+	VI/V	15.82 ± 0.09	-	15.82 ± 0.09	-	$PuO_2^{2+} + e^- \Leftrightarrow PuO_2^+$
PuO2OH	V	≤ -9.73	-	≤ -9.73	-	$PuO_2^+ + H_2O(l) \Leftrightarrow PuO_2OH(aq) + H^+$
PuO2CO3-	V	5.12 ± 0.14	-	5.12 ± 0.14	-	$PuO_2^+ + CO_3^{2-} \Leftrightarrow PuO_2CO_3^-$
PuO2(CO3)3-5	V	(5.03 ± 0.92)[b]	-19.11 ± 8.50	5.03 ± 0.92	-19.11 ± 8.50	$PuO_2^+ + 3\ CO_3^{2-} \Leftrightarrow PuO_2(CO_3)_3^{5-}$
Pu+4	VI/IV	33.28 ± 0.15	-	33.28 ± 0.15	-	$PuO_2^{2+} + 4\ H^+ + 2\ e^- \Leftrightarrow Pu^{4+} + 2\ H_2O(l)$
PuOH+3	IV	-0.78 ± 0.60	36 ± 10	(0.0 ± 0.2)*	-	$Pu^{4+} + H_2O(l) \Leftrightarrow PuOH^{3+} + H^+$
Pu(OH)2+2	IV	-	-	(-1.2 ± 0.6)*	-	$Pu^{4+} + 2\ H_2O(l) \Leftrightarrow Pu(OH)_2^{2+} + 2\ H^+$
Pu(OH)3+	IV	-	-	(-3.1 ± 0.9)*	-	$Pu^{4+} + 3\ H_2O(l) \Leftrightarrow Pu(OH)_3^+ + 3\ H^+$
Pu(OH)4	IV	-8.4 ± 1.1	-	(-9.3 ± 0.5)*	-	$Pu^{4+} + 4\ H_2O(l) \Leftrightarrow Pu(OH)_4(aq) + 4\ H^+$
Ca4Pu(OH)8+4	IV	-	-	*(-55.7 ± 0.7)**	-	$4\ Ca^{2+} + Pu^{4+} + 8\ H_2O(l) \Leftrightarrow Ca_4Pu(OH)_8^{4+} + 8\ H^+$
PuF+3	IV	8.84 ± 0.10	9.1 ± 2.2	8.84 ± 0.10	9.1 ± 2.2	$Pu^{4+} + F^- \Leftrightarrow PuF^{3+}$
PuF2+2	IV	15.7 ± 0.2	11 ± 5	15.7 ± 0.2	11 ± 5	$Pu^{4+} + 2\ F^- \Leftrightarrow PuF_2^{2+}$
PuCl+3	IV	1.8 ± 0.3	-	1.8 ± 0.3	-	$Pu^{4+} + Cl^- \Leftrightarrow PuCl^{3+}$
PuSO4+2	IV	6.89 ± 0.23	-	6.89 ± 0.23	-	$Pu^{4+} + SO_4^{2-} \Leftrightarrow PuSO_4^{2+}$
Pu(SO4)2	IV	11.14 ± 0.34	-	11.14 ± 0.34	-	$Pu^{4+} + 2\ SO_4^{2-} \Leftrightarrow Pu(SO_4)_2(aq)$
PuNO3+3	IV	1.95 ± 0.15	-	1.95 ± 0.15	-	$Pu^{4+} + NO_3^- \Leftrightarrow PuNO_3^{3+}$

		TDB Version 01/01		**TDB Version 12/07**		
Name	**Redox**	**$\log_{10}\beta°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**$\log_{10}\beta°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**Reaction**
PuH3PO4+4	IV	2.4 ± 0.3	-	2.4 ± 0.3	-	$Pu^{4+} + H_3PO_4(aq) \Leftrightarrow PuH_3PO_4^{4+}$
Pu(CO3)4-4	IV	35.9 ± 2.5	-	37.0 ± 1.1	-	$Pu^{4+} + 4\ CO_3^{2-} \Leftrightarrow Pu(CO_3)_4^{4-}$
Pu(CO3)5-6	IV	34.5 ± 2.5	-	35.65 ± 1.13	-	$Pu^{4+} + 5\ CO_3^{2-} \Leftrightarrow Pu(CO_3)_5^{6-}$
PuCO3(OH)3-	IV	-	-	*(6)**	-	$Pu^{4+} + CO_3^{2-} + 3\ H_2O(l) \Leftrightarrow PuCO_3(OH)_3^{-} + 3\ H^{+}$
Pu+3	VI/III	50.97 ± 0.15	-	50.97 ± 0.15	-	$PuO_2^{2+} + 4\ H^{+} + 3\ e^{-} \Leftrightarrow Pu^{3+} + 2\ H_2O(l)$
PuOH+2	III	-6.9 ± 0.3	-	-6.9 ± 0.3	-	$Pu^{3+} + H_2O(l) \Leftrightarrow PuOH^{2+} + H^{+}$
Pu(OH)2+	III	-	-	*(-14.8)**	-	$Pu^{3+} + 2\ H_2O(l) \Leftrightarrow Pu(OH)_2^{+} + 2\ H^{+}$
Pu(OH)3	III	-	-	*(-25.9)**	-	$Pu^{3+} + 3\ H_2O(l) \Leftrightarrow Pu(OH)_3(aq) + 3\ H^{+}$
PuF+2	III	-	-	*(3.4)**	-	$Pu^{3+} + F^{-} \Leftrightarrow PuF^{2+}$
PuF2+	III	-	-	*(5.8)**	-	$Pu^{3+} + 2\ F^{-} \Leftrightarrow PuF_2^{+}$
PuCl+2	III	1.2 ± 0.2	-	*(1.2 ± 0.2)**	-	$Pu^{3+} + Cl^{-} \Leftrightarrow PuCl^{2+}$
PuSO4+	III	3.9 ± 0.6	17.2 ± 2.3	3.9 ± 0.6	17.2 ± 2.3	$Pu^{3+} + SO_4^{2-} \Leftrightarrow PuSO_4^{+}$
Pu(SO4)2-	III	5.7 ± 0.8	12 ± 16	5.7 ± 0.8	12 ± 16	$Pu^{3+} + 2\ SO_4^{2-} \Leftrightarrow Pu(SO_4)_2^{-}$
PuCO3+	III	-	-	*(8.0)**	-	$Pu^{3+} + CO_3^{2-} \Leftrightarrow PuCO_3^{+}$
Pu(CO3)2-	III	-	-	*(12.9)**	-	$Pu^{3+} + 2\ CO_3^{2-} \Leftrightarrow Pu(CO_3)_2^{-}$
Pu(CO3)3-3	III	-	-	*(15.0)**	-	$Pu^{3+} + 3\ CO_3^{2-} \Leftrightarrow Pu(CO_3)_3^{3-}$
PuSCN+2	III	-	-	1.3 ± 4		$Pu^{3+} + SCN^{-} \Leftrightarrow PuSCN^{2+}$

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[a] Note that in Thoenen (2012) and in the electronic versions of TDB 12/07 for PHREEQC and GEMS-PSI released before December 2014, the value 52.7 ± 1.6 was by mistake not updated to 53.5 ± 1.4.

[b] Note that in the electronic versions of TDB 01/01 for PHREEQC and GEMS-PSI the value was erroneously entered as 5.00.

		TDB Version 01/01		**TDB Version 12/07**		
Name	**Redox**	**$\log_{10}K_{s,0}°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**$\log_{10}K°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**Reaction**
PuO2(coll, hyd)	IV	-	-	*(-8.3 ± 1.0)**	-	*$PuO_2(am, hyd) \Leftrightarrow PuO_2(coll, hyd)$*

		TDB Version 01/01		**TDB Version 12/07**		
Name	**Redox**	**$\log_{10}K_{s,0}°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**$\log_{10}K_{s,0}°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**Reaction**
PuO2(OH)2:H2O(cr)	VI	5.5 ± 1.0	-	5.5 ± 1.0	-	$PuO_2(OH)_2\cdot H_2O(cr) + 2 H^+ \Leftrightarrow PuO_2^{2+} + 3 H_2O(l)$
PuO2CO3(s)	VI	-14.2 ± 0.3	-	-14.65 ± 0.47	-	$PuO_2CO_3(s) \Leftrightarrow PuO_2^{2+} + CO_3^{2-}$
PuO2OH(am)	V	5.0 ± 0.5	-	5.0 ± 0.5	-	$PuO_2OH(am) + H^+ \Leftrightarrow PuO_2^+ + H_2O(l)$
PuO2(hyd,ag)[a]	IV	-2.0 ± 1.0	-	-2.33 ± 0.52	-	$PuO_2(hyd, aged) + 4 H^+ \Leftrightarrow Pu^{4+} + 2 H_2O(l)$
Pu(HPO4)2(am,hyd)	IV	-30.45 ± 0.51	-	-30.45 ± 0.51	-	$Pu(HPO_4)_2(am, hyd) \Leftrightarrow Pu^{4+} + 2 HPO_4^{2-}$
Pu(OH)3(cr)	III	15.8 ± 1.5	-	15.8 ± 1.5	-	$Pu(OH)_3(cr) + 3 H^+ \Leftrightarrow Pu^{3+} + 3 H_2O(l)$
PuPO4(s,hyd)	III	-24.6 ± 0.8	-	-24.6 ± 0.8	-	$PuPO_4(s, hyd) \Leftrightarrow Pu^{3+} + PO_4^{3-}$

[a] Referred to as PuO_2(am, hydr.) by Guillaumont et al. (2003)

Table 6.3: Selected SIT ion interaction coefficients $\varepsilon_{j,k}$ [kg·mol^{-1}] for plutonium species. Data included in TDB Version 12/07 are taken from Lemire et al. (2001) or Guillaumont et al. (2003) unless indicated otherwise. Own data estimates based on charge correlations (see Appendix A) are shaded. Supplemental data are in italics.

j ↓ k →	Cl^- $\varepsilon_{j,k}$	ClO_4^- $\varepsilon_{j,k}$	NO_3^- $\varepsilon_{j,k}$	Li^+ $\varepsilon_{j,k}$	Na^+ $\varepsilon_{j,k}$	K^+ $\varepsilon_{j,k}$
PuO2+2	0.15 ± 0.10	0.46 ± 0.05	-	0	0	0
PuO2OH+	0.05 ± 0.10	0.2 ± 0.1	-	0	0	0
PuO2(OH)2	0	0	0	0	0	0
(PuO2)2(OH)2+2	0.15 ± 0.10	0.4 ± 0.1	-	0	0	0
PuO2F+	0.05 ± 0.10	0.29 ± 0.11	-	0	0	0
PuO2F2	0	0	0	0	0	0
PuO2Cl+	(0.36 ± 0.06)[a]	0.50 ± 0.09	-	0	0	0
PuO2Cl2	0	0	0	0	0	0
PuO2SO4	0	0	0	0	0	0
PuO2(SO4)2-2	0	0	0	-	-0.10 ± 0.10	-
PuO2CO3	0	0	0	0	0	0
PuO2(CO3)2-2	0	0	0	-	-0.10 ± 0.10	-
PuO2(CO3)3-4	0	0	0	-	-0.20 ± 0.30	-
(UO2)2PuO2(CO3)6-6	0	0	0	-	(0.37 ± 0.11)[b]	-
PuO2+	0.05 ± 0.10	0.24 ± 0.05	-	0	0	0
PuO2OH	0	0	0	0	0	0
PuO2CO3-	0	0	0	-	-0.18 ± 0.18	-
PuO2(CO3)3-5	0	0	0	-	-0.25 ± 0.40	-
Pu+4	(0.37 ± 0.05)[c]	0.82 ± 0.07	-	0	0	0
PuOH+3	(0.2 ± 0.1)[d]	0.50 ± 0.05	-	0	0	0
Pu(OH)2+2	(0.1 ± 0.1)[d]	0.4 ± 0.1	-	0	0	0
Pu(OH)3+	(0.05 ± 0.10)[d]	0.2 ± 0.1	-	0	0	0
Pu(OH)4	0	0	0	0	0	0
Ca4Pu(OH)8+4	*(-0.01 ± 0.10)*[e]	*(0.21 ± 0.17)*[f]	-	*0*	*0*	*0*
PuF+3	0.25 ± 0.10	0.56 ± 0.11	-	0	0	0
PuF2+2	0.15 ± 0.10	0.36 ± 0.17	-	0	0	0
PuCl+3	(0.85 ± 0.09)[g]	0.85 ± 0.09	-	0	0	0
PuSO4+2	0.15 ± 0.10	(0.36 ± 0.14)[h]	-	0	0	0
Pu(SO4)2	0	0	0	0	0	0
PuNO3+3	0.25 ± 0.10	(0.70 ± 0.09)[h]	-	0	0	0
PuH3PO4+4	0.35 ± 0.10	0.8 ± 0.1	-	0	0	0

j k→ ↓	**Cl^-** $\varepsilon_{j,k}$	**ClO_4^-** $\varepsilon_{j,k}$	**NO_3^-** $\varepsilon_{j,k}$	**Li^+** $\varepsilon_{j,k}$	**Na^+** $\varepsilon_{j,k}$	**K^+** $\varepsilon_{j,k}$
Pu(CO3)4-4	0	0	0	-	-0.20 ± 0.30	-
Pu(CO3)5-6	0	0	0	-	-0.30 ± 0.50	-
PuCO3(OH)3-	*0*	*0*	*0*	-	*-0.05 ± 0.10*	-
Pu+3	(0.23 ± 0.02)[c]	0.49 ± 0.05	-	0	0	0
PuOH+2	0.15 ± 0.10	(0.39 ± 0.04)[i]	-	0	0	0
Pu(OH)2+	*0.05 ± 0.10*	*0.2 ± 0.1*	-	*0*	*0*	*0*
Pu(OH)3	*0*	*0*	*0*	*0*	*0*	*0*
PuF+2	*0.15 ± 0.10*	*0.4 ± 0.1*	-	*0*	*0*	*0*
PuF2+	*0.05 ± 0.10*	*0.2 ± 0.1*	-	*0*	*0*	*0*
PuCl+2	*(0.39 ± 0.16)*[j]	*0.39 ± 0.16*	-	*0*	*0*	*0*
PuSO4+	0.05 ± 0.10	0.2 ± 0.1	-	0	0	0
Pu(SO4)2-	0	0	0	-	-0.05 ± 0.10	-
PuCO3+	*0.05 ± 0.10*	*0.2 ± 0.1*	-	*0*	*0*	*0*
Pu(CO3)2-	*0*	*0*	*0*	-	*-0.10 ± 0.10*	-
Pu(CO3)3-3	*0*	*0*	*0*	-	*-0.15 ± 0.20*	-
PuSCN+2	0.15 ± 0.10	0.39 ± 0.04	-	0	0	0

[a] This work, to be used in combination with $\varepsilon(PuO_2^{2+}, Cl^-) = \varepsilon(PuO_2^{2+}, ClO_4^-) = (0.46 \pm 0.05)$ kg·mol^{-1}

[b] This work, estimated to be equal to $\varepsilon((UO_2)_3(CO_3)_6^{6-}, Na^+)$

[c] Rand et al. (2008)

[d] Neck & Kim (2001)

[e] Altmaier et al. (2008), same coefficient as for the corresponding Th-complex

[f] This work, same coefficient as for the corresponding Th-complex

[g] This work, to be used in combination with $\varepsilon(Pu^{4+}, Cl^-) = \varepsilon(Pu^{4+}, ClO_4^-) = (0.82 \pm 0.07)$ kg·mol^{-1}

[h] This work

[i] Value estimated and used by Lemire et al. (2001) but not listed in their Table B.3 of selected ion interaction coefficients

[j] This work, to be used in combination with $\varepsilon(Pu^{3+}, Cl^-) = \varepsilon(Pu^{3+}, ClO_4^-) = (0.49 \pm 0.05)$ kg·mol^{-1}

6.21 References

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7 Selenium

7.1 Introduction

Intermediate updates of the Nagra/PSI Chemical Thermodynamic Data Base 01/01 (Hummel et al. 2002) concerning selenium had been performed mainly based on a comprehensive review of Séby et al. (2001), but was never reported as a separate TDB update report. In the meantime the OECD NEA Thermodynamic Database (TDB) project on selenium has finished (Olin et al. 2005). The present chapter provides and discusses the equilibria selected from Olin et al. (2005) for the PSI/Nagra Chemical Thermodynamic Database 12/07.

The compilation of Séby et al. (2001) and the NEA report Olin et al. (2005) list a large number of "solubility products" for metal selenates, -selenites and -selenides. However, selenates and selenites often have high solubilities and it is questionable, whether such solids will ever be solubility limiting phases in environmental systems or not. We therefore restricted our selection to solubility products for use in systems relevant to radioactive waste management. On the other hand, many metal selenides are reported to have extremely low solubility products (similar to the sulfides; the winner in this list is PtSe with a $\log_{10}K_{s,0}°$ of -81.4!). In database applications these low solubility products have then to be "compensated" with rather high complex formation constants for the neutral complexes, in order to describe expected/measured solute concentrations. We do not think that such data should flow into the update in their present state, particularly when reliable solubility data for neutral complexes are missing (note that exceptions were made in the report for silver- and mercury selenides).

The NEA review volumes provide tables with selected SIT coefficients for the interaction of cations with Cl^-, ClO_4^-, and NO_3^-, and of anions with Li^+, Na^+, and K^+. Since numerous ion interaction coefficients of selenium species are not known, we used in such cases an estimation method based on charge correlations (see Appendix A) to fill the gaps. The selected ion interaction coefficients are listed in Table 7.2.

7.2 Elemental selenium

Based on Gaur et al. (1981), Olin et al. (2005) recommend

$$S_m°(\text{Se, trigonal, 298.15 K}) = (42.09 \pm 0.33)\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1},$$

$$C_{p,m}°(\text{Se, trigonal, 298.15 K}) = (25.09 \pm 0.30)\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}.$$

for the trigonal elemental selenium, also termed Se(cr). The unusual analytical heat capacity expression from the original source was re-evaluated to the standard form:

$$C_{p,m}°(\text{Se, trigonal, 298.15 – 500 K}) =$$

$$= (24.8014 + 1.2859\cdot10^{-3}\ T + 9.9273\cdot10^{-6}\ T^2 - 0.8713\cdot10^5\ T^{-2})\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}.$$

Note that an earlier recommendation by Grenthe et al. (1992), based on the work of Grønvold et al. (1984), provided (42.27 ± 0.05) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for $S_m°$(Se, trigonal, 298.15 K), the molal entropy of elemental selenium.

7.2.1 Solubility of elemental selenium

Earlier applications of the thermodynamic data for selenium (Berner 2002, 2002a) demonstrate a rather deep minimum of calculated selenium solubilities between the stability fields of Se(-II) and Se(IV) (Figure 7.1). Such behavior is chemically unreasonable and most likely indicates missing solution species. A reasonable candidate for such a missing species is $Se^0_x(aq)$. Indeed,

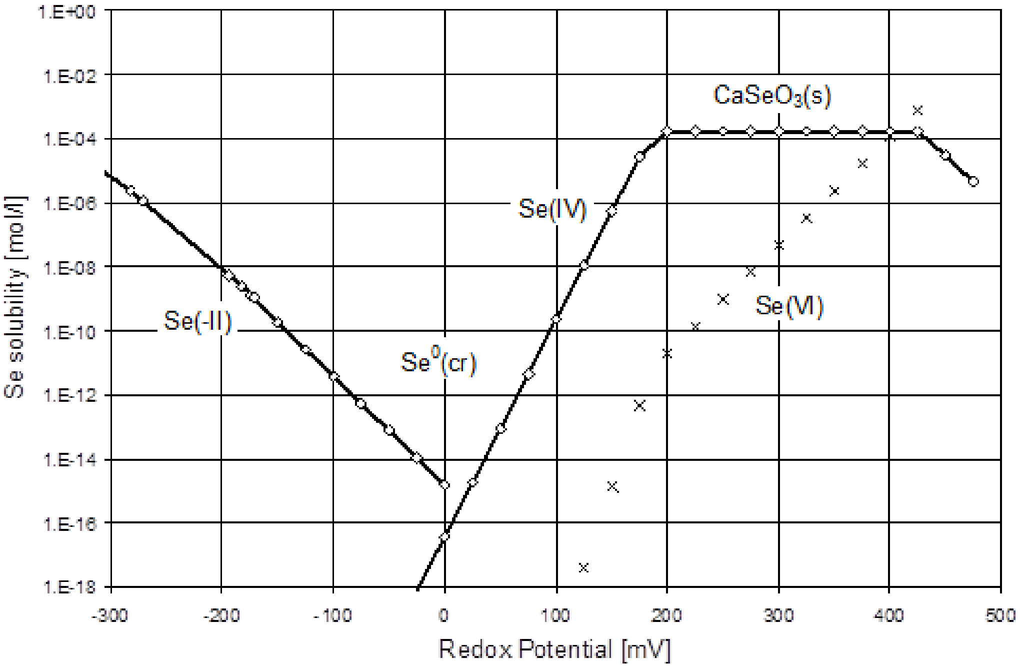

Fig. 7.1: Solubility of Se in bentonite pore water at pH 7.3 as a function of system Eh, taken from Berner (2002). All solution parameters except Eh were kept constant.

Hummel (2013) found evidence in the literature that a few elements (metals) from the groups 11 to 16 (exhibiting a B-type character) may dissolve in aqueous solution as neutral species. Olin et al. (2005) debate on the formation of the polyselenides Se_2^{2-}, Se_3^{2-}, and Se_4^{2-} in equilibrium with Se(cr) and provide a model and thermodynamic data (see below). They do, however, not mention the potential formation of Se_8^0(aq) in equilibrium with Se(cr).

In the chemically similar sulfur system the solubility of elemental sulfur is well established. In contact with solid sulfur S_8(s), Boulegue (1978) and Kamishny Jr. (2009) measured S_8^0(aq) solubilities of $(1.9 \pm 0.6)\cdot 10^{-8}$ and $(3.01 \pm 1.04)\cdot 10^{-8}$ $mol\cdot kg^{-1}$ in water. With $(2.63 \pm 0.04)\cdot 10^{-8}$ $mol\cdot L^{-1}$ Wang & Tessier (2009) reported a value between the former two solubilities. Taking the average of these values, the solubility of elemental sulfur may be estimated with a rather high precision ($(2.63 \pm 0.13)\cdot 10^{-8}$ $mol\cdot kg^{-1}$ of S_8^0(aq)).

For many processes the analogy among sulfur and selenium is well established. If this analogy is also applied to the solubility of selenium, one obtains

$$Se(s) \Leftrightarrow Se_8^0(aq) \tag{7.1}$$

$$K_s°(7.1) = (2.63 \pm 0.13)\cdot 10^{-8}$$

Solid selenium forms a modification with a (distorted) structure similar to that of rhomboedric $S_8(\alpha)$.The formation of Se_8(aq) is not confirmed by experimental studies but may be surmised from the polyselenide model accepted by Olin et al. (2005). It should be noted that the few experimental studies justifying the polyselenide model were conducted at millimolar solutions of selenide. This means that trace concentrations of neutral Se_8^0(aq) would disappear as undetectable within the analytical error. However, if compared to the formerly calculated minimum of about 10^{-15} $mol\cdot kg^{-1}$ (Figure 7.1), trace concentrations of about 10^{-7} $mol\cdot kg^{-1}$ constitute an increase of about 8 orders of magnitude in the Eh range of ~0 mV. From a point of view of applying thermodynamic data to real systems the assumption of a species $Se_8^0(aq)$ would consistently meet the requirements of the missing species.

For practical use and in analogy to the sulfur system, it is suggested to establish an equilibrium of the form

$$Se(cr) \Leftrightarrow Se^0(aq) \qquad (7.2)$$

with

$$K_s(7.2) = 2 \cdot 10^{-7}$$

The uncertainty of this value is unclear, from $K_s(7.1)$ one would estimate $(\pm 0.1) \cdot 10^{-7}$. The value of $K_s(7.2)$ is in the range from $\sim 10^{-9}$ mol·kg^{-1} to about $2 \cdot 10^{-7}$ mol·kg^{-1} and we propose using the upper end of this range for the solubility of elemental selenium.

From equilibrium (7.2), using $\Delta_f G_m°$(Se, cr, 298.15 K) = 0, one derives

$$\Delta_f G_m°(Se^0, aq, 298.15 \text{ K}) = 38.24 \text{ kJ·mol}^{-1},$$

or, similarly,

$$\Delta_f G_m°(Se_8^0, aq, 298.15 \text{ K}) = (43.27 \pm 0.12) \text{ kJ·mol}^{-1}.$$

The equilibrium (7.2) (as well as the corresponding $\Delta_f G_m°$-values) are not included in the TDB 12/07. It is, however, recommended to use equilibrium (7.2) to fill an obvious gap in the database when the calculation of selenium solubilities becomes an important task.

7.3 Redox equilibria in the selenium system

There are nearly no studies concerning the redox equilibria among the relevant oxidation states Se(IV)/Se(VI) and Se(IV)/Se(0), which seems to be a consequence of slow reaction rates. Additionally, it has been demonstrated by Runnels et al. (1987) that redox potentials measured by Pt electrodes are not affected by the ratio of Se(IV)/Se(VI) present in solution. Hence, one should not be astonished by the fact that Olin et al. (2005) were forced to base their evaluation on a single experimental investigation for each redox couple.

7.3.1 The Se(IV)/Se(0) couple

For the equilibrium

$$Se(s) + 2\, I_2(cr) + 3\, H_2O(l) \Leftrightarrow H_2SeO_3(aq) + 4\, I^- + 4\, H^+ \qquad (7.3)$$

Olin et al. (2005) evaluated $\log_{10}K°(7.3, 298.15 \text{ K}) = -(13.831 \pm 0.021)$**,** based on data from Schott et al. (1928), activity coefficients for hydroiodic acid taken from Pearce et al. (1923) and based on corrections for side reactions including the solubility of iodine, the formation of tri-iodide and the dissociation of $H_2SeO_3(aq)$. Olin et al. (2005) observed that improving the equilibria for the side reactions did not significantly change the resulting constant. They further noted an inconsistency with the state of solid selenium, which was probably not in its standard state. However, based on their assessment of the experimental procedure they concluded that "*the specimen was most likely close enough to the standard state activity*". Additional re-evaluations using activity data from Harned & Robinson (1941) and using an SIT approach with $\varepsilon(H^+, ClO_4^-) = 0.12$, $\varepsilon(H^+, I^-) = 0.18$ kg·mol^{-1} and $\varepsilon(H^+, ClO_4^-) = 0.014$ kg·mol^{-1} gave similar results for $\log_{10}K°(7.3)$. Therefore, Olin et al (2005) selected

$$\log_{10}K°(7.3, 298.15 \text{ K}) = -(13.90 \pm 0.10).$$

Subtracting the reaction 2 $I_2(cr) + 2\ H_2(g) \Leftrightarrow 4\ I^- + 4\ H^+$ from reaction (7.3) and reversing the result, one obtains (assuming that Se(s) and Se(cr) are thermodynamically equivalent)

$$H_2SeO_3(aq) + 2\ H_2(g) \Leftrightarrow Se(cr) + 3\ H_2O(l). \qquad (7.4)$$

From $\log_{10}K°(7.3, 298.15\ K)$ and $\Delta_fG_m°(I^-, 298.15\ K) = -(51.734 \pm 0.112)\ kJ\cdot mol^{-1}$ then follows

$$\Delta_rG_m°(7.4, 298.15\ K) = -(286.24 \pm 0.84)\ kJ\cdot mol^{-1}, \text{ or}$$

$$\log_{10}K°(7.4, 298.15\ K) = (50.15 \pm 0.15).$$

The standard electrode potential for the redox couple $H_2SeO_3(aq) + 4\ H^+ + 4\ e^- \Leftrightarrow Se(cr) + 3\ H_2O(l)$ is thus $E°(298.15\ K) = (0.742 \pm 0.002)$ V, which agrees with the 0.740 V from Latimer (1956) and with (0.745 ± 0.004) V from Osman-Zade & Vagramyan (1966). Séby et al. (2001) reported an additional independent study (Nevskii et al. 1968) that seems to confirm the above results, but this last study was not considered in Olin et al. (2005).

Combining $\Delta_rG_m°(7.4, 298.15\ K)$ with $\Delta_fG_m°(H_2O, l, 298.15\ K) = -(237.140 \pm 0.041)\ kJ\cdot mol^{-1}$ produces

$$\Delta_fG_m°(H_2SeO_3, aq, 298.15\ K) = -(425.18 \pm 0.85)\ kJ\cdot mol^{-1}.$$

7.3.2 The Se(VI)/Se(IV) couple

Sherill & Izard (1928) investigated the reactions

$$Cl_2(g) + H_2SeO_3(aq) + H_2O(l) \Leftrightarrow HSeO_4^- + 3\ H^+ + 2\ Cl^- \qquad (7.5)$$

and

$$Br_2(l) + H_2SeO_3(aq) + H_2O(l) \Leftrightarrow HSeO_4^- + 3\ H^+ + 2\ Br^- \qquad (7.6)$$

in 7 to 8 m HCl and 0.2 to 0.4 m HBr, respectively, and measured the equilibrium concentrations by chemical analysis. They made assumptions on the relative acidity constants of $H_2SeO_3(aq)$ and H_2SeO4^-, neglected the activity of uncharged species, took mean activity coefficients (based on HCl or HBr) for monovalent ions and used the water activity from vapour pressure data (which were later on confirmed by data from Harned et al. 1936 and Åkerlöf & Teare 1937). Obviously, Olin et al. (2005) accepted the results given by Sherill & Izard (1928) as were, because the reference is not further discussed in their chapter "Appendix A: discussion of selected references". For the further evaluation, Olin et al. (2005) used $\log_{10}K°(7.5, 298.15\ K) = -(9.148 \pm 0.057)$ ($\Delta_rG_m° = -52.217 \pm 0.325\ kJ\cdot mol^{-1}$) and $\log_{10}K°(7.6, 298.15\ K) = -(0.0560 \pm 0.0256)$ ($\Delta_rG_m° = 0.320 \pm 0.146\ kJ\cdot mol^{-1}$), respectively. With $\Delta_rG_m°(½Cl_2(g)/Cl^-, 298.15\ K) = -(131.22 \pm 0.12)\ kJ\cdot mol^{-1}$ and $\Delta_rG_m°(½Br_2(aq)/Br^-, 298.15\ K) = -(106.30 \pm 0.53)\ kJ\cdot mol^{-1}$ (Grenthe et al. 1992) one calculates $\Delta_rG_m°(7.7, 298.15\ K) = -(210.223 \pm 0.404)\ kJ\cdot mol^{-1}$ and $\Delta_rG_m°(7.7, 298.15\ K) = -(212.920 \pm 1.070)\ kJ\cdot mol^{-1}$, respectively for reaction (7.7):

$$HSeO_4^- + 3\ H^+ + 2\ e^- \Leftrightarrow H_2SeO_3(aq) + H_2O(l) \qquad (7.7)$$

Based on more recent Raman measurements Olin et el. (2005) concluded that side reactions of the type $H_2SeO_3(aq) + H^+ + Cl^-/Br^- \Leftrightarrow H_2SeO_2Cl/Br(aq) + H_2O(l)$ cannot be ruled out at elevated halogenide ion concentrations above about 4 M, although the resulting complexes seem to be rather weak (i.e, $\log_{10}K$'s are below 1.0). Hence, Olin et al. (2005) preferred selecting the results for reaction (7.6), because this experiment was performed at substantially lower halogenide ion concentrations than experiment (7.5) conducted in high chloride medium. It was thus expected that the reaction in the bromine/bromide system is potentially less affected by side reactions. The present assessment accepts this view and adopts

$$\Delta_rG_m°(7.7, 298.15\ K) = -(212.920 \pm 1.070)\ kJ\cdot mol^{-1}$$

$$\log_{10}K°(7.7, 298.15\text{ K}) = (37.30 \pm 0.19)$$

$$E°(7.7, 298.15\text{ K}) = (1.103 \pm 0.006)\text{ V}$$

Note the small difference in $\Delta_rG_m°$(7.7, 298.15 K) given by Olin et al. (2005) (i.e. $\Delta_rG_m°$(7.7, Olin et al. 2005, 298.15 K) = -(212.85 ± 1.00) kJ·mol^{-1}), which is most likely a consequence of rounding errors: Calculating back from $E°$(7.7, 298.15 K) = (1.103 ± 0.006) V to $\Delta_rG_m°$(7.7, 298.15 K) indeed produces -212.85 kJ·mol^{-1}, but it is not necessary to truncate the real value of $E°$ (1.10338 V) to three digits. Although the very small difference is only relevant for consistency reasons, it will induce similar tiny differences in the Gibbs free energies of all species including the unit "Se(VI)O_4^{2-}" .

Using $\log_{10}K°$(7.49) = (1.75 ± 0.10) for the protonation of the selenate ion (see below) leads to

$$\Delta_fG_m°(HSeO_4^-, 298.15\text{ K}) = -(449.4 \pm 1.4)\text{ kJ·mol}^{-1}$$

and

$$\Delta_fG_m°(SeO_4^{2-}, 298.15\text{ K}) = -(439.4 \pm 1.5)\text{ kJ·mol}^{-1}$$

7.3.3 The Se(0)/Se(-II) couples

Lyons & Young (1986) reported on the formal redox equilibria and on UV-visible molar absorptivity of the equilibria (7.8) to (7.10)

$$1/2\ Se_2^{2-} + e^- \Leftrightarrow Se^{2-} \quad (7.8)$$

$$1/3\ Se_3^{2-} + 4/3\ e^- \Leftrightarrow Se^{2-} \quad (7.9)$$

$$1/4\ Se_4^{2-} + 3/2\ e^- \Leftrightarrow Se^{2-} \quad (7.10)$$

at the non-standard conditions (1 M KOH, 304 K). Using $\log_{10}K_w(I = 1\text{ M}, 304\text{ K}) = -13.79$ and $\log_{10}K_1(HSe^- \Leftrightarrow H^+ + Se^{2-}, I = 1\text{ M}, 304\text{ K}) = 13.97$, Olin et al. (2005) corrected these values to

$$\log_{10}K(7.8, 1\text{ M KOH}, 304\text{ K}) = -(11.97 \pm 0.10),$$

$$\log_{10}K(7.9, 1\text{ M KOH}, 304\text{ K}) = -(15.74 \pm 0.14),$$

$$\log_{10}K(7.10, 1\text{ M KOH}, 304\text{ K}) = -(17.24 \pm 0.15),$$

in good agreement with independent values reported by Licht & Forouzan (1995). The problem was now to connect these equilibria to Se(cr), i.e., to find a constant for the reaction

$$Se(cr) + 2e^- \Leftrightarrow Se^{2-} \quad (7.11)$$

Based on the experimental observation of both Lyons & Young (1986) and Licht & Forouzan (1995), that the resulting polyselenide solutions reached equilibrium with elemental Se(cr) at a ratio of $Se(0)_{tot}/Se(-II)_{tot}$ = (2.8 ± 0.05), Olin et al. (2005) performed a mass balance iteration with the equilibria (7.8) to (7.10) and found $\log_{10}K$(7.11, 1 M KOH, 304 K) = -(21.08 ± 0.15).

Finally, the recalculation to I = 0 with the estimate $\varepsilon(Se_n^{2-}, K^+) \approx -0.06$ kg·mol^{-1} produced $\Delta_rG_m°$(7.11, 298.15 K) ≡ $\Delta_fG_m°(Se^{2-}$, 298.15 K) = (127.9 ± 1.9) kJ·mol^{-1}, corresponding to $\log_{10}K°$(7.11, 298.15 K) = -(22.4 ± 0.3). Note that the estimate $\varepsilon(Se_n^{2-}, K^+) \approx -0.06$ kg·mol^{-1} is based on the average o f $\varepsilon(X^{2-}, K^+)$ data presented in Olin et al. (2005, Table B-5). The Gibbs free energy of Se^{2-} derived in this way is in good agreement with $\Delta_fG_m°(Se^{2-}$, 298.15 K) = (129.4 ± 2.3) kJ·mol^{-1} derived from the dissociation of H_2Se(aq) and based on the selected data of H_2Se(g) (see below). Olin et al. (2005) selected the average of the two values according to the rules of the NEA reviews, which is also accepted in this assessment.

$$\Delta_fG_m°(Se^{2-}, 298.15\text{ K}) = (128.6 \pm 3.0)\text{ kJ·mol}^{-1}$$

$$\log_{10}K°(7.11, 298.15\text{ K}) = -(22.5 \pm 0.5)$$

$$E°(7.11, 298.15) = -(0.666 \pm 0.010)\text{ V}$$

For the polyselenide equilibria the finally selected constants are

$$E°(7.8, 298.15) = -(0.749 \pm 0.010)\text{ V}$$

$$\log_{10}K°(7.8, 298.15\text{ K}) = -(12.6 \pm 0.2)$$

$$E°(7.9, 298.15) = -(0.739 \pm 0.010)\text{ V}$$

$$\log_{10}K°(7.9, 298.15\text{ K}) = -(16.7 \pm 0.2)$$

$$E°(7.10, 298.15) = -(0.720 \pm 0.010)\text{ V}$$

$$\log_{10}K°(7.10, 298.15\text{ K}) = -(18.3 \pm 0.3)$$

and the corresponding Gibbs free energies of formation are

$$\Delta_f G_m°(Se_2^{2-}, 298.15\text{ K}) = (112.7 \pm 6.3)\text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m°(Se_3^{2-}, 298.15\text{ K}) = (100.6 \pm 9.2)\text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m°(Se_4^{2-}, 298.15\text{ K}) = (97.6 \pm 12.1)\text{ kJ}\cdot\text{mol}^{-1}$$

In their final Table III-2 (Olin et al. 2005, p.53) represent reactions (7.8) to (7.10) with integer numbers of stoichiometric reaction coefficients, i.e., multiples of the reactions (7.8) to (7.10) as presented above. The values for $\log_{10}K°$ and $\Delta_r G_m°$ are adjusted correctly, but the uncertainties for reactions (7.9) and (7.10) are not consistent with the uncertainties associated with the Gibbs free energies of the polymeric species. Hence, it is recommended to use

$$Se_2^{2-} + 2\text{ e}^- \Leftrightarrow 2Se^{2-} \tag{7.8'}$$

$$\Delta_r G_m°(7.8') = (144.53 \pm 1.90)\text{ kJ}\cdot\text{mol}^{-1}$$

$$\log_{10}K°(7.8') = -(25.32 \pm 0.33)$$

$$Se_3^{2-} + 4\text{ e}^- \Leftrightarrow 3Se^{2-} \tag{7.9'}$$

$$\Delta_r G_m°(7.9') = (285.21 \pm 3.86)\text{ kJ}\cdot\text{mol}^{-1}$$

$$\log_{10}K°(7.9') = -(49.97 \pm 0.68)$$

$$Se_4^{2-} + 6\text{ e}^- \Leftrightarrow 4Se^{2-} \tag{7.10'}$$

$$\Delta_r G_m°(7.10') = (416.82 \pm 5.79)\text{ kJ}\cdot\text{mol}^{-1}$$

$$\log_{10}K°(7.10') = -(73.02 \pm 1.01)$$

7.4 Selenide species and solids

7.4.1 Aqueous (and gaseous) selenide species

From molecular parameters in Lane et al. (1984), Olin et al. (2005) selected:

$$C_{p,m}°(H_2Se, g, 298.15\text{ K}) = (34.7 \pm 0.1)\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

$$S_m°(H_2Se, g, 298.15\text{ K}) = (219.0 \pm 0.1)\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}, \text{ and}$$

$$\Delta_f S_m°(H_2Se, g, 298.15\text{ K}) = (46.2 \pm 0.2)\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

From several studies investigating the formation of $H_2Se(g)$ from $H_2(g)$ and elemental selenium Olin et al. (2005) selected

$$\Delta_f H_m°(H_2Se, g, 298.15\ K) = (29.0 \pm 2.0)\ kJ\cdot mol^{-1}$$

and calculated

$$\Delta_f G_m°(H_2Se, g, 298.15\ K) = (15.2 \pm 2.0)\ kJ\cdot mol^{-1}.$$

The *Henry constant* for the solubility of $H_2Se(g)$, i.e. the equilibrium

$$H_2Se(g) \Leftrightarrow H_2Se(aq), \tag{7.12}$$

was evaluated based on two studies (McAmis & Felsing 1925, Dubeau & Sisi 1971) at a partial pressure of 1 atm $H_2Se(g)$ under the assumption that the first dissociation constant of $H_2Se(aq)$ is $10^{-(3.85 \pm 0.05)}$. This assumption was necessary because both studies measured total dissolved selenium (i.e., the sum of $H_2Se(aq)$ and HSe^-) by precipitation with silver, $Ag_2Se(s)$. Olin et al. (2005) took the average of the two studies and selected

$$\log_{10}K°(7.12, 298.15\ K) = -(1.10 \pm 0.01)$$

The enthalpy of reaction $\Delta_r H_m°(7.12, 298.15\ K) = -(14.7 \pm 0.3)\ kJ\cdot mol^{-1}$ was selected from Dubeau & Sisi (1971) with an increased uncertainty due to the fact that Dubeau & Sisi (1971) did not consider the dissociation of $H_2Se(aq)$ in their evaluation.

The first hydrolysis

$$H_2Se(aq) \Leftrightarrow H^+ + HSe^- \tag{7.13}$$

was evaluated from two conductometric (Bruner-Krakau 1913, de Hlasko 1923) and one potentiometric study (Hagisawa 1941). However, the evaluation of the two conductance measurements depended on the "assumption" of a solubility value for $H_2Se(aq)$ at $p_{H2Se(g)} = 1$ atm and were re-evaluated by Olin et al. (2005) using the value for the *Henry constant* as given above. There is, however, some feedback from the assumption made for evaluating $\log_{10}K°(7.12)$ to the hydrolysis reaction (7.13) and vice versa, but this is not further investigated here. The re-evaluated results from the two conductometric studies compared sufficiently well with the potentiometric study by Hagisawa (1941), and Olin et al. (2005) selected the average:

$$\log_{10}K°(7.13, 298.15\ K) = -(3.85 \pm 0.05).$$

For the second hydrolysis reaction

$$HSe^- \Leftrightarrow H^+ + Se^{2-} \tag{7.14}$$

Olin et al. (2005) in principle accepted $\log_{10}K°(7.14, 298.15\ K) = -(15.05 \pm 0.20)$ as "*by far the most reliable value of* $\log_{10}K°(7.14)$". This value can be traced back to UV-spectrometric studies in concentrated KOH solutions by Lyons & Young (1986) and Levy & Myers (1990), where hydroxide concentrations were systematically varied. From the constants (7.13), (7.14) and from the selected value of $\Delta_f G_m°(H_2Se, g, 298.15\ K) = (15.2 \pm 2.0)\ kJ\cdot mol^{-1}$ (see above), Olin et al. (2005) selected

$$\Delta_f H_m°(H_2Se, aq, 298.15\ K) = (14.3 \pm 2.0)\ kJ\cdot mol^{-1},$$

$$\Delta_f S_m°(H_2Se, aq, 298.15\ K) = -(24.1 \pm 9.5)\ J\cdot K^{-1}\cdot mol^{-1},$$

$$\Delta_f G_m°(H_2Se, aq, 298.15\ K) = (21.5 \pm 2.0)\ kJ\cdot mol^{-1} \text{ and}$$

$$\Delta_f G_m°(HSe^-, 298.15\ K) = (43.5 \pm 2.0)\ kJ\cdot mol^{-1}.$$

From $\Delta_f S_m°(H_2Se, aq, 298.15\ K) = -(24.1 \pm 9.5)\ J\cdot K^{-1}\cdot mol^{-1}$, the present work calculates $S_m°(H_2Se, aq, 298.15\ K) = (148.7 \pm 9.5)\ J\cdot K^{-1}\cdot mol^{-1}$. However, Olin et al. (2005) calculated $S_m°(H_2Se, aq, 298.15\ K)$ from $\Delta_r S_m°(7.12, 298.15\ K) = (70.4 \pm 1.0)\ J\cdot K^{-1}\cdot mol^{-1}$, which leads to the selected

$$S_m°(H_2Se, aq, 298.15\ K) = (148.6 \pm 1.0)\ J\cdot K^{-1}\cdot mol^{-1}.$$

Note that the corresponding value for $\Delta_f G_m°(\mathrm{Se}^{2-}$, 298.15 K) of (129.4 ± 2.3) kJ·mol^{-1} was not selected. Instead, Olin et al. (2005) selected the mean of this value and that independently evaluated from the redox studies in the poly-selenide systems (i.e., (127.9 ± 1.9) kJ·mol^{-1}, see above) to obtain

$$\Delta_f G°_m(\mathrm{Se}^{2-}, 298.15\ \mathrm{K}) = (128.6 \pm 3.0)\ \mathrm{kJ \cdot mol^{-1}}.$$

This selected Gibbs free energy of formation for Se^{2-} in turn corresponds to

$$\log_{10}K°(7.14, 298.15\ \mathrm{K}) = -(14.91 \pm 0.20).$$

The present review prefers selecting this somewhat larger $\log_{10}K°(7.14)$, because this value is consistent with the selected $\Delta_f G_m°(\mathrm{Se}^{2-}$, 298.15 K) and with the free energies of the species as given above.

7.4.2 Solid selenide species

7.4.2.1 Mercury selenides

Mercury is not included in the TDB update but is one of the cases where low solubility products seem to be compensated with moderate to strong complex formation, finally leading to noticeable concentrations of neutral complexes in solution. That is why the section of mercury selenide solubility/complex formation is added here anyway.

$$\mathrm{HgSe(s)} + 2\ \mathrm{H^+} \Leftrightarrow \mathrm{Hg^{2+}} + \mathrm{H_2Se(aq)} \qquad (7.15)$$

Olin et al. (2005) combined solubility measurements according to reaction (7.15) from Mehra (1968), performed below pH 3 ($\log_{10}K$(7.15, 1 M $\mathrm{NaClO_4}$, 298.15 K) = -(41.65 ± 04.5)), with various high temperature measurements on HgSe(s,α) to obtain a selected free energy of formation of

$$\Delta_f G_m°(\mathrm{HgSe}, \alpha, 298.15\ \mathrm{K}) = -(51.2 \pm 4.0)\ \mathrm{kJ \cdot mol^{-1}}$$

and a standard enthalpy of formation of

$$\Delta_f H_m°(\mathrm{HgSe}, \alpha, 298.15\ \mathrm{K}) = -(57.0 \pm 4.1)\ \mathrm{kJ \cdot mol^{-1}}$$

based on

$$\Delta S_m°(\mathrm{HgSe}, \alpha, 298.15\ \mathrm{K}) = (98.5 \pm 3.0)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}.$$

Olin et al. (2005) did not explicitly select an equilibrium constant for reaction (7.15), but they recalculated $\log_{10}K_{s,0}°$(HgSe, s, 298.15 K) = -(60.7 ± 0.5), obviously using $\varepsilon(\mathrm{Hg^{2+}}, \mathrm{ClO_4^-}) = 0.34$ kg·mol^{-1}. This value is sufficiently close to the value which is obtained from the selected $\Delta_f G_m°$(HgSe, α, 298.15 K) and the present assessment decides to neglect a potential inconsistency in the nature of the solid (i.e., between HgSe(s) and HgSe(α)). Hence,

$$\log_{10}K_{s,0}°(\mathrm{HgSe, s}, 298.15\ \mathrm{K}) \approx \log_{10}K_{s,0}°(\mathrm{HgSe}, \alpha, 298.15\ \mathrm{K}) = -(60.35 \pm 0.70).$$

Mehra & Gübeli (1971) interpreted their solubility measurements with the formation of the complexes Hg(HSe)(OH)(aq) (pH 0 to 3), $\mathrm{Hg(HSe)_2(OH)^-}$ (pH 4 to 5.5) and $\mathrm{Hg(HSe)_2(OH)_2^{2-}}$ (pH > 7). Olin et al. (2005) preferred a different notation without the $\mathrm{OH^-}$-ion. Using $\Delta\varepsilon = 0.04$ kg·mol^{-1} they recalculated for reaction

$$\mathrm{HgSe(s)} + \mathrm{HSe^-} \Leftrightarrow \mathrm{HgSe_2^{2-}} + \mathrm{H^+} \qquad (7.16)$$

$$\log_{10}K°(7.16, 298.15\ \mathrm{K}) = -(12.8 \pm 0.6),$$

which corresponds to

$$\Delta_f G_m°(HgSe_2^{2-}, 298.15\ K) = -(65.3 \pm 5.6)\ kJ\cdot mol^{-1}.$$

For the solubility of the neutral species

$$HgSe(s) \Leftrightarrow HgSe(aq) \qquad (7.17)$$

Olin et al. (2005) provide the constant $\log_{10}K$(7.17, 1 M $NaClO_4$, 298.15 K) = -(7.84 ± 0.44), but they claim that this constant is "*most likely too large due to the rather simple method used for the separation of the solid from the aqueous phase. It is tentatively included due to its potential importance in connection with the mobility of mercury from repositories*". Since no charge is involved, reaction (7.17) is not subject to ionic strength corrections in the presently valid implementation of the SIT framework. Hence, and following the arguments of Olin et al. (2005), in the present assessment the constant (7.17) is selected with a somewhat increased uncertainty (as in the case of reaction (7.16)):

$$\log_{10}K°(7.17, 298.15\ K) = -(7.8 \pm 0.6),$$

Note that $\Delta_f G_m°(Hg^{2+}$, 298.15 K) = -(164.667 ± 0.313) $kJ\cdot mol^{-1}$ should be used for all calculations involving the Hg^{2+}-cation.

7.4.2.2 Silver selenides

A similar problem as in the case of mercury is observed in the case of silver: Several high temperature data are available for $Ag_2Se(s,\alpha)$, but there are only two relevant studies that performed solubility measurements with not further specified solids termed $Ag_2Se(s)$. The solubility product is very low, but noticeable concentrations of neutral complexes may exist in aqueous solution. Since silver may be of some relevance in radioactive waste systems it was decided to report available data (as well as a recommendation for practical use) anyway. From the Mehra (1968) and Mehra & Gübeli (1971) data measured in different pH ranges, Olin et al. (2005) finally "accepted" for the reaction

$$Ag_2Se(s) \Leftrightarrow 2\ Ag^+ + Se^{2-} \qquad (7.18)$$

$\Delta_f G_m°(Ag_2Se$, s, 298.15 K) = -(46.3 ± 4.1) $kJ\cdot mol^{-1}$ or $\log_{10}K_{s,0}°$(7.18, 298.15 K) = -(57.65 ± 0.50), based on $\varepsilon(H^+,ClO_4^-)$ = (0.14 ± 0.02) $kg\cdot mol^{-1}$ and $\varepsilon(Ag^+,ClO_4^-)$ = (0.00 ± 0.01) $kg\cdot mol^{-1}$. However, they also selected

$$\Delta_f G_m°(Ag_2Se, \alpha, 298.15\ K) = -(46.9 \pm 1.3)\ kJ\cdot mol^{-1},$$

$$\Delta_f H_m°(Ag_2Se, \alpha, 298.15\ K) = -(40.1 \pm 1.3)\ kJ\cdot mol^{-1},$$

$$S_m°(Ag_2Se, \alpha, 298.15\ K) = (149.9 \pm 0.5)\ J\cdot K^{-1}\cdot mol^{-1}.$$

which, by neglecting a certain inconsistency in the nature of the solid and by associating a somewhat increased uncertainty, gives the solubility product recommended by this assessment:

$$\log_{10}K_{s,0}°(Ag_2Se, s, 298.15\ K) \approx \log_{10}K_{s,0}°(Ag_2Se, \alpha, 298.15\ K) = -(57.8 \pm 0.6).$$

Note that this solubility product is consistent with both, the free energy of formation of $Ag_2Se(s,\alpha)$ and the measured solubility of $Ag_2Se(s)$. Note further that $\Delta_f G_m°(Ag^+$, 298.15 K) = -(77.096 ± 0.156) $kJ\cdot mol^{-1}$ should be used for applications involving equilibrium (7.18).

Olin at al. (2005) discussed the formation of aqueous silver (I) selenide complexes based on the measurements of Mehra & Gübeli (1971). These authors found "*constant dissolved*" silver selenide concentrations in the range $6\cdot 10^{-8}$ to $8\cdot 10^{-9}$ $mol\cdot L^{-1}$ at pH > 10, independent of the total Se(-II) concentration in the test solution. Mehra & Gübeli (1971) interpreted their findings with a species having the formula $Ag_2(HSe)(OH)(aq)$, which is formally equivalent to $Ag_2Se(aq)$. Olin et al. (2005) did not accept Mehra & Gübeli's (1971) interpretation and did not select the proposed species. From the data of Mehra (1968) Olin et al. (2005) re-evaluated the equilibrium

$$Ag_2Se(s) \Leftrightarrow Ag_2Se(aq) \qquad (7.19)$$

and obtained $\log_{10}K$(7.19, 1 M $NaClO_4$, 298.15 K) = -(7.66 ± 0.48). Combining the equilibria (7.18) and (7.19) and neglecting the fact that equilibrium (7.19) is valid in 1 M $NaClO_4$ formally leads to a formation constant for the equilibrium

$$2\ Ag^+ + Se^{2-} \Leftrightarrow Ag_2Se(aq) \qquad (7.19a)$$

of

$$\log_{10}K(7.19a, 298.15\ K) = (50.14 \pm 0.77).$$

By using equilibrium (7.14) one further may calculate

$$\log_{10}K(7.19b, 298.15\ K) = (35.1 \pm 0.8)$$

for the equilibrium

$$2Ag^+ + HSe^- \Leftrightarrow Ag_2Se(aq) + H^+. \qquad (7.19b)$$

The formal constant (7.19b) is very high and means that the dissociation of $Ag_2Se(aq)$ into Ag^+ and HSe^- actually does not take place. At pH = 8 and measured $Ag_2Se(aq)$ concentrations of $\sim 6 \cdot 10^{-8}$ $mol \cdot L^{-1}$ the free HSe^- concentration is calculated to be less than $\sim 1 \cdot 10^{-17}$ $mol \cdot L^{-1}$. The present evaluation does not recommend using the equilibria (7.18), (7.19a), and (7.19b) as selected data, but for practical use and for estimating silver/selenium solubilities it is recommended to use equilibrium (7.19).

7.4.2.3 Manganese selenides

From experimental data of Mehra & Gübeli (1970) and Mehra (1968) using radioactively labelled Mn Olin et al. (2005) calculated

$$\log_{10}K(7.20, 1\ M\ NaClO_4, 298.15\ K) = -(0.52 \pm 0.70)$$

for the equilibrium

$$MnSe(s) + H^+ \Leftrightarrow Mn^{2+} + HSe^-. \qquad (7.20)$$

This corresponds to

$$\Delta_f G_m°(MnSe, s, 298.15\ K) = -(190.8 \pm 6.8)\ kJ \cdot mol^{-1}$$

when using $\Delta_f G_m°(Mn^{2+}$, 298.15 K) = -228.1 $kJ \cdot mol^{-1}$ from Wagman et al. (1982). From equilibra (7.20), using $\Delta\varepsilon$ = 0.25 $kg \cdot mol^{-1}$, and (7.14) Olin et al. (2005) evaluated $\log_{10}K_{s,0}°$(MnSe, s, 298.15 K) = -(16.0 ± 0.8). The solubility of MnSe(s) is not included in the TDB 12/07, but for estimates or scoping calculations, particularly at elevated pH, $\log_{10}K$(7.20) may be used to estimate maximum HSe^- concetrations in the presence of manganese.

Olin et al. (2005) do not provide or select data for any other metal selenide solids related to aqueous solutions.

7.5 Selenite species and solids

7.5.1 Aqueous selenious acid

Olin et al. (2005) discussed a series of studies proposing the formation of several polymeric species of the type $H_x(SeO_3)_2^y$ with variable charge, but based on converse studies not indicating the polymers, they did not accept the formation of polymeric species in their assessment. Note, however, that Walrafen (1962) confirmed the presence of polymers by Raman spectroscopy in extremely concentrated aqueous solutions of H_2SeO_3.

For the protonation constants

$$SeO_3^{2-} + H^+ \Leftrightarrow HSeO_3^- \quad (7.21)$$

$$HSeO_3^- + H^+ \Leftrightarrow H_2SeO_3(aq) \quad (7.22)$$

Olin et al. (2005) accepted studies from Kawassiades et al. (1967), Sekine et al. (1969), Salomaa et al. (1969), Vesala & Koskinen (1975), Fowless & Stranks (1977), Ozeki et al. (1988), and Dasgupta & Nara (1990) and found

$$\log_{10}K_1°(7.21, 298.15 \text{ K}) = (8.36 \pm 0.23)$$

$$\log_{10}K_{2,1}°(7.22, 298.15 \text{ K}) = (2.64 \pm 0.14).$$

With $\Delta_f G_m°(H_2SeO_3, aq, 298.15 \text{ K}) = -(425.18 \pm 0.85) \text{ kJ}\cdot\text{mol}^{-1}$ (see Section 7.3.1) the formation constants (7.21) and (7.22) yield

$$\Delta_f G_m°(HSeO_3^-, 298.15 \text{ K}) = -(410.1 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}.$$

$$\Delta_f G_m°(SeO_3^{2-}, 298.15 \text{ K}) = -(362.39 \pm 1.76) \text{ kJ}\cdot\text{mol}^{-1}.$$

Using the above selected protolysis constants, Olin et al. (2005) calculated the enthalpy change of the dissolution of $H_2SeO_3(cr)$ from measurements of Selivanova & Pakhorukov (1961) to finally obtain

$$\Delta_f H_m°(H_2SeO_3, aq, 298.15 \text{ K}) = -(505.32 \pm 0.65) \text{ kJ}\cdot\text{mol}^{-1},$$

and, consequently,

$$\Delta_f H_m°(HSeO_3^-, 298.15 \text{ K}) = -(512.3 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1},$$

$$\Delta_f H_m°(SeO_3^{2-}, 298.15 \text{ K}) = -(507.2 \pm 1.1) \text{ kJ}\cdot\text{mol}^{-1},$$

$$S_m°(SeO_3^{2-}, 298.15 \text{ K}) = (5.1 \pm 7.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}\text{[12]}.$$

Corresponding entropies of formation can be calculated from $\Delta_f G_m° = \Delta_f H_m° - T\Delta_f S_m°$ to yield $\Delta_f S_m°(H_2SeO_3, aq, 298.15 \text{ K}) = -(268.79 \pm 3.59) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $\Delta_f S_m°(HSeO_3^-, 298.15 \text{ K}) = -(342.78 \pm 6.62) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $\Delta_f S_m°(SeO_3^{2-}, 298.15 \text{ K}) = -(485.66 \pm 7.08) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. The molal entropies $S_m°(i, 298.15 \text{ K})$ should then be calculated from consistent elemental entropies according to $\Delta_f S_m°(i, 298.15 \text{ K}) = S_m°(i, 298.15 \text{ K}) - \Sigma\ S°(\text{element}, 298.15 \text{ K}) + Z/2\cdot S°(H_2)$ (where Z = 0, ±1, ±2…). From Cox et al. (1989) the present work used $S_m°(O_2, g, 298.15 \text{ K}) = (205.152 \pm 0.005) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and $S_m°(H_2, g, 298.15 \text{ K}) = (130.68 \pm 0.003) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

It is interesting to note that Olin et al. (2005) did not consider the evaluation of Séby et al. (2001) based on polyselenite equilibria from Barcza & Sillén (1971), nor did they consider these data.

7.5.2 Solid selenite species

Solid selenite species are known for many aqueous cations, but the present work primarily concentrates on elements relevant for geochemical radioactive waste systems and on elements included in the PSI/Nagra TDB. Therefore, only a subset of selenite solids is discussed here.

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[12] Note that our calculations resulted in $(5.2 \pm 7.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

7.5.2.1 Magnesium selenites

A number of studies measured the solubility product of solids denoted with $MgSeO_3(s)$. Olin et al. (2005) assume that the various determinations pertain to the hexadydrate and formulate the equilibrium as

$$MgSeO_3 \cdot 6H_2O(cr) \Leftrightarrow Mg^{2+} + SeO_3^{2-} + 6\ H_2O(l) \qquad (7.23)$$

Based on the measurements of Savenko (1995) (which was considered by Olin et al. 2005 to be the most reliable determination), neglecting hydrolysis of Mg^{2+} and using the equilibria (7.21, 7.22) Olin et al. (2005) estimated

$$\log_{10}K_{s,0}°(7.23,\ 298.15\ K) = -(5.82 \pm 0.25),$$

with the uncertainty also estimated by Olin et al. (2005).

From enthalpy changes in reactions between $Na_2SeO_3(cr)$, magnesium sulfate solutions and $MgSeO_3 \cdot 6H_2O(cr)$ performed by Leshchinskaya & Selivanova (1966) Olin et al. (2005) derived

$$\Delta_f H_m°(MgSeO_3 \cdot 6H_2O,\ cr,\ 298.15\ K) = -(2707.21 \pm 1.30)\ kJ \cdot mol^{-1},$$

and, consequently,

$$\Delta_f G_m°(MgSeO_3 \cdot 6H_2O,\ cr,\ 298.15\ K) = -(2273.83 \pm 2.60)\ kJ \cdot mol^{-1}$$

$$S_m°(MgSeO_3 \cdot 6H_2O,\ cr,\ 298.15\ K) = (328.5 \pm 9.8)\ J \cdot K^{-1} \cdot mol^{-1}.$$

7.5.2.2 Calcium selenites

From studies in the system $CaSeO_3$-SeO_2-H_2O (Dumm & Brown 1997, Ebert & Havlicek 1981) Olin et al. (2005) concluded that the solid phase studied in solubility experiments has the composition $CaSeO_3 \cdot H_2O$ and wrote the equilibrium

$$CaSeO_3 \cdot H_2O(cr) \Leftrightarrow Ca^{2+} + SeO_3^{2-} + H_2O(l). \qquad (7.24)$$

Due to shortcomings in the paper of Sharmasarkar et al. (1996) Olin et al. (2005) gave no weight to that evaluation but considered the work of Savenko (1995) to be the most "satisfactory". They selected

$$\log_{10}K_{s,0}°(7.24,\ 298.15\ K) = -(6.40 \pm 0.25).$$

From calorimetric measurements of Leshchinskaya & Selivanova (1963) and in good agreement with Wagman et al. (1982) Olin et al. (2005) adopted

$$\Delta_f H_m°(CaSeO_3 \cdot H_2O,\ cr,\ 298.15\ K) = -(1324.83 \pm 2.81)\ kJ \cdot mol^{-1},$$

and, consequently,

$$\Delta_f G_m°(CaSeO_3 \cdot H_2O,\ cr,\ 298.15\ K) = -(1188.90 \pm 2.50)\ kJ \cdot mol^{-1}$$

$$S_m°(CaSeO_3 \cdot H_2O,\ cr,\ 298.15\ K) = (168.8 \pm 12.6)\ J \cdot K^{-1} \cdot mol^{-1}.$$

Note that the above values of $\Delta_f H_m°(CaSeO_3 \cdot H_2O$, cr, 298.15 K) and $S_m°(CaSeO_3 \cdot H_2O$, cr, 298.15 K) are not selected values but considered as "*best values currently available*". Particularly, the value for $S_m°$ is considered to be "*somewhat too large*" in the opinion of Olin et.al (2005) and the authors recommend performing additional measurements with better control of the solid phase composition.

7.5.2.3 Strontium selenites

From chemical analyses performed by Selivanova & Leshchinskaya (1963) and Leshchinskaya et al. (1965) Olin et al. (2005) concluded that the solid phase in aquesous solubility studies is best represented by $SrSeO_3(cr)$, in contrast to the composition $SrSeO_3 \cdot 6H_2O(cr)$ reported by Ebert & Havlicek (1982). Olin et al. (2005) adopt the equilibrium

$$SrSeO_3(cr) \Leftrightarrow Ca^{2+} + SeO_3^{2-} \qquad (7.25)$$

and evaluated

$$\log_{10}K_{s,0}°(7.25, 298.15\ K) = -(6.30 \pm 0.50)$$

from experimental data measured by Chukhlantsev (1956). From enthalpy changes during the formation of $SrSeO_3(cr)$ in aqueous $SrCl_2 \cdot 6H_2O$-Na_2SeO_3 mixtures investigated by Selivanova & Leshchinskaya (1963) Olin et al. (2005) evaluated

$$\Delta_f H_m°(SrSeO_3, cr, 298.15\ K) = -(1051.9 \pm 2.7)\ kJ \cdot mol^{-1}.$$

Wagman et al. (1982) reported -1047.7 $kJ \cdot mol^{-1}$ for this $\Delta_f H_m°$-value. The difference could be ascribed to changes in the strontium data made by Grenthe et al. (1992). Consequently, Olin et al. (2005) calculated

$$\Delta_f G_m°(SrSeO_3, cr, 298.15\ K) = -(962.2 \pm 3.40)\ kJ \cdot mol^{-1}$$

$$S_m°(SrSeO_3, cr, 298.15\ K) = (104.7 \pm 14.6)\ J \cdot K^{-1} \cdot mol^{-1}.$$

7.5.2.4 Barium selenites

From the phase diagram of the system $BaSeO_3$-SeO_2-H_2O at 298.15 K Neall & McCrosky (1938) concluded $BaSeO_3$ and $BaSe_2O_5$ to be the solids formed.

Ripan & Vericeanu (1968) studied the solubility of $BaSeO_3(s)$ in pure water at 291 K and found a mean solubility value of $7.92 \cdot 10^{-4}\ mol \cdot L^{-1}$. For the equilibrium

$$BaSeO_3(cr) \Leftrightarrow Ca^{2+} + SeO_3^{2-} \qquad (7.26)$$

Olin et al. (2005) evaluated $\log_{10}K_{s,0}°(7.26, 291\ K) = -(6.43 \pm 0.10)$. Leshchinskaya et al. (1965) prepared crystalline barium selenite and measured the solubility at 298.15, leading to $\log_{10}K_{s,0}°(7.26, 291\ K) = -6.58$ at $I = 0$ (no uncertainties, only one single experiment). From these experiments Olin et al. (2005) selected

$$\log_{10}K_{s,0}°(7.26, 298.15\ K) = -(6.50 \pm 0.25).$$

Leshchinskaya et al. (1963) measured the enthalpy change of the the reaction between equimolar quantities of $BaCl_2 \cdot 2H_2O(cr)$ and $Na_2SeO_3(aq)$ with the formation of crystalline $BaSeO_3$. From these data Olin et al. (2005) calculated

$$\Delta_f H_m°(BaSeO_3, cr, 298.15\ K) = -(1036.7 \pm 2.9)\ kJ \cdot mol^{-1}.$$

Wagman et al. (1982) reported -1040.6 $kJ \cdot mol^{-1}$ for this $\Delta_f H_m°$-value. As in the case of strontium, the difference could partly be ascribed to changes in the barium data made by Grenthe et al. (1992). Consequently, Olin et al. (2005) calculated

$$\Delta_f G_m°(BaSeO_3, cr, 298.15\ K) = -(957.2 \pm 3.40)\ kJ \cdot mol^{-1}$$

$$S_m°(BaSeO_3, cr, 298.15\ K) = (145.6 \pm 15.0)\ J \cdot K^{-1} \cdot mol^{-1}.$$

7.5.2.5 Manganese selenites

A phase diagram for the system $MnSeO_3$-SeO_2-H_2O does not seem to exist. There is actually only one experimental study that was accepted by Olin et al. (2005). Chukhlantsev & Tomashevsky (1957) precipitated ampophous $MnSeO_3$ and aged the mixture for a long time to obtain a crystalline product. No X-ray diffraction was performed but chemical analysis confirmed the 1:1 ratio between Mn(II) and Se(IV). Based on an independent preparative study by Leshchinskaya & Selivanova (1966a) Olin et al. (2995) concluded that the composition of the solid was $MnSeO_3\cdot 2H_2O$.

$$MnSeO_3\cdot 2H_2O(cr) \Leftrightarrow Ca^{2+} + SeO_3^{2-} + 2\ H_2O \qquad (7.27)$$

From the data of Chukhlantsev & Tomashevsky (1957) at 293.15 K Olin et al. (2005) evaluated $\log_{10}K_{s,0}°(7.27, 293.15\ K) = -(7.64 \pm 0.08)$. From the more recent study of Sharmasarkar et al. (1996) they obtained $\log_{10}K_{s,0}°(7.27, 298.15\ K) = -7.11$, but as in the case of calcium they gave no weight to this determination. Olin et al. (2005) selected

$$\log_{10}K_{s,0}°(7.27, 293.15\ K) = -(7.6 \pm 1.0),$$

and, recalculated from Leshchinskaya & Selivanova (1966a)

$$\Delta_f H_m°(MnSeO_3\cdot 2H_2O, cr, 298.15\ K) = -(1280.7 \pm 2.6)\ kJ\cdot mol^{-1}.$$

Consequently,

$$\Delta_f G_m°(MnSeO_3\cdot 2H_2O, cr, 298.15\ K) = -(1108.2 \pm 7.7)\ kJ\cdot mol^{-1}$$

$$S_m°(SrSeO_3\cdot H_2O, cr, 298.15\ K) = (269.3 \pm 24.1)\ J\cdot K^{-1}\cdot mol^{-1}.$$

7.5.2.6 Iron selenites

Complexes and solids of iron was not subject of the present TDB update. Iron is foreseen to be updated later on, when the next issue from the NEA review series on iron is completed. Note that volume 13a of this series (Lemire et al. 2013) does not yet include selenium complexes and solids. Hovever, an exception was made for aqueous complexes with iron(III). Rai et al. (1995) studied the solubility of $Fe_2(SeO_3)_3\cdot 6H_2O(cr)$ (the stable phase in aqueous solution at pH < 4). Note that above this pH-value the selenie starts transforming into another phase of not yet known composition. Rai et al. (1995) used two equilibria (the solubility constant and the 1:1 complex) to explain measured data. From this work Olin et al. (2005) selected the solubility constant and the formation constant

$$Fe^{3+} + SeO_3^{2-} \Leftrightarrow FeSeO_3^{+} \qquad (7.28)$$

$$\log_{10}\beta_1°(7.28, 296\ K) = (11.15 \pm 0.11)$$

The present review adopts equilibrium 7.28, the solubility constant (see equilibrium 7.31) is noted below.

7.5.2.7 Nickel selenites

Ebert et al. (1982) established the phase diagram in the system $NiSeO_3$-SeO_2-H_2O at 298.15 K and found the solid phases $NiSeO_3\cdot 2H_2O$, $Ni(HeSO_3)_2\cdot 2H_2O$ and H_2SeO_3. From the chemical analysis of Chukhlantsev & Tomashevsky (1957) (no X-ray data but 1:1 ratio between Ni(II) and Se(IV)) Olin et al. (2005) assumed the solid phase to be $NiSeO_3\cdot 2H_2O$.

$$NiSeO_3\cdot 2H_2O(cr) \Leftrightarrow Ni^{2+} + SeO_3^{2-} + 2\ H_2O(l) \qquad (7.29)$$

Chukhlantsev (1956), Chukhlantsev & Tomashevsky (1957) and Ripan & Vericeanu (1968) measured the solubiliy of $NiSeO_3$ at 293 and 291 K (about 2.25 $mol\cdot L^{-1}$). Olin et al. (2005)

argued that under these conditions Ni(II) is partly hydrolysed and re-evaluated the experimental data accordingly. Their rather large associated uncertainty reflects the variance from the solubility measurements:

$$\log_{10}K_{s,0}°(7.29, 298.15\ \text{K}) = -(5.80 \pm 1.0).$$

The enthalpy $\Delta_f H_m°(NiSeO_3 \cdot 2H_2O, cr, 298.15\ K)$ was derived from measurements of Selivanova et al. (1963) and Olin et al. (2005) selected

$$\Delta_f H_m°(\text{NiSeO}_3\cdot 2\text{H}_2\text{O, cr, 298.15 K}) = -(1109.33 \pm 2.83)\ \text{kJ}\cdot\text{mol}^{-1}.$$

Wagman et al. (1982) provide -1134.32 $kJ \cdot mol^{-1}$ for the same entity. However, Olin et al. (2005) do not further discuss this large difference but just say that they do not accept the Wagman et al. (1981) - value. They refer to their "*Appendix A*", but this cross reference seems to be rather empty. Nevertheless, Olin et al. (2005) selected:

$$\Delta_f G_m°(\text{NiSeO}_3\cdot 2\text{H}_2\text{O, cr, 298.15 K}) = -(915.56 \pm 6.02)\ \text{kJ}\cdot\text{mol}^{-1}$$

$$S_m°(\text{SrSeO}_3\cdot \text{H}_2\text{O, cr, 298.15 K}) = (169.3 \pm 22.3)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

7.5.2.8 Other selenite equilibria

Olin et al. (2005) list a variety of selenite solid solubilities for elements that were not subject of the PSI/Nagra database update. However, some of these equilibria may be useful for specific purposes and/or may be relevant for a subsequent database update. These selenite equilibria are assembled in the following subsection, following the atomic number of elements. An indication is given of whether Olin et al. (2005) have "noted" or "selected" the equilibrium.

Aluminium:

$$\text{Al}_2(\text{SeO}_3)_3\cdot 6\text{H}_2\text{O(cr)} \Leftrightarrow 2\ \text{Al}^{3+} + 3\ \text{SeO}_3^{2-} + 6\text{H}_2\text{O(l)} \tag{7.30}$$

$$\log_{10}K_{s,0}°(7.30, 298.15\ \text{K}) = -3.11 \qquad \text{(noted)}$$

Iron:

$$\text{Fe}_2(\text{SeO}_3)_3\cdot 6\text{H}_2\text{O(cr)} \Leftrightarrow 2\ \text{Fe}^{3+} + 3\ \text{SeO}_3^{2-} + 6\ \text{H}_2\text{O(l)} \tag{7.31}$$

$$\log_{10}K_{s,0}°(7.31, 296\ \text{K}) = -(41.58 \pm 0.11) \qquad \text{(selected)}$$

Cobalt:

$$\text{CoSeO}_3\cdot 2\text{H}_2\text{O(cr)} \Leftrightarrow \text{Co}^{2+} + \text{SeO}_3^{2-} + 2\ \text{H}_2\text{O(l)} \tag{7.32}$$

$$\log_{10}K_{s,0}°(7.32, 298.15\ \text{K}) = -(7.9 \pm 0.4) \qquad \text{(selected)}$$

Copper:

$$\text{CuSeO}_3\cdot 2\text{H}_2\text{O(s)} \Leftrightarrow \text{Cu}^{2+} + \text{SeO}_3^{2-} + 2\ \text{H}_2\text{O(l)} \tag{7.33}$$

$$\log_{10}K_{s,0}°(7.33, 298.15\ \text{K}) = -(9.5 \pm 1.5) \qquad \text{(noted)}$$

Zinc:

$$\text{ZnSeO}_3\cdot[\text{H}_2\text{O}]\text{(cr)} \Leftrightarrow \text{Zn}^{2+} + \text{SeO}_3^{2-} + [\text{H}_2\text{O(l)}] \tag{7.34}$$

$$\log_{10}K_{s,0}°(7.34, 298.15\ \text{K}) = \leq -7.25 \qquad \text{(noted)}$$

Gallium:

$$\text{Ga}_2(\text{SeO}_3)_3\cdot 6\text{H}_2\text{O(cr)} \Leftrightarrow 2\ \text{Ga}^{3+} + 3\ \text{SeO}_3^{2-} + 6\ \text{H}_2\text{O(l)} \tag{7.35}$$

$$\log_{10}K_{s,0}°(7.35, 298.15\ \text{K}) = -(37.0 \pm 2.0) \qquad \text{(selected)}$$

Silver:

$$Ag_2SeO_3(cr) \Leftrightarrow 2\ Ag^{+} + SeO_3^{2-} \qquad (7.36)$$

$$\log_{10}K_{s,0}°(7.36, 298.15\ K) = -(15.8 \pm 0.3) \qquad \text{(selected)}$$

Cadmium:

$$CdSeO_3(cr) \Leftrightarrow Cd^{2+} + SeO_3^{2-} \qquad (7.37)$$

$$\log_{10}K_{s,0}°(7.37, 298.15\ K) = -(9.3 \pm 1.2) \qquad \text{(selected)}$$

Indium:

$$In_2(SeO_3)_3\cdot 6H_2O(cr) \Leftrightarrow 2\ In^{3+} + 3\ SeO_3^{2-} + 6\ H_2O(l) \qquad (7.38)$$

$$\log_{10}K°_{s,0}(7.38, 298.15\ K) = -(39.0 \pm 2.0) \qquad \text{(selected)}$$

Lanthanum:

$$La_2(SeO_3)_3(s) \Leftrightarrow 2\ La^{3+} + 3\ SeO_3^{2-} \qquad (7.39)$$

$$\log_{10}K_{s,0}°(7.39, 298.15\ K) = -(31.0 \pm 2.0) \qquad \text{(noted)}$$

Cerium:

$$Ce_2(SeO_3)_3(s) \Leftrightarrow 2\ Ce^{3+} + 3\ SeO_3^{2-} \qquad (7.40)$$

$$\log_{10}K_{s,0}°(7.40, 298.15\ K) = -(31.17 \pm 0.30) \qquad \text{(noted)}$$

Praseodymium:

$$Pr_2(SeO_3)_3(s) \Leftrightarrow 2\ Pr^{3+} + 3\ SeO_3^{2-} \qquad (7.41)$$

$$\log_{10}K_{s,0}°(7.41, 298.15\ K) = -(34.0 \pm 2.0) \qquad \text{(noted)}$$

Neodymium:

$$Nd_2(SeO_3)_3(s) \Leftrightarrow 2\ Nd^{3+} + 3\ SeO_3^{2-} \qquad (7.42)$$

$$\log_{10}K_{s,0}°(7.42, 298.15\ K) = -(30.0 \pm 2.0) \qquad \text{(noted)}$$

Samarium:

$$Sm_2(SeO_3)_3(s) \Leftrightarrow 2\ Sm^{3+} + 3\ SeO_3^{2-} \qquad (7.43)$$

$$\log_{10}K_{s,0}°(7.43, 298.15\ K) = -(35.0 \pm 2.0) \qquad \text{(noted)}$$

Mercury(I):

$$Hg_2SeO_3(cr) \Leftrightarrow Hg_2^{2+} + SeO_3^{2-} \qquad (7.44)$$

$$\log_{10}K_{s,0}°(7.44, 298.15\ K) = -(15.2 \pm 1.0) \qquad \text{(selected)}$$

Mercury(II):

$$HgSeO_3(cr) \Leftrightarrow Hg^{2+} + SeO_3^{2-} \qquad (7.45)$$

$$\log_{10}K_{s,0}°(7.45, 298.15\ K) = -(15.98 \pm 0.30) \qquad \text{(noted)}$$

$$HgSeO_3(cr) + SeO_3^{2-} \Leftrightarrow Hg(SeO_3)_2^{2-} \qquad (7.46)$$

$$\log_{10}K_{s,2}°(7.46, 298.15\ K) = -(1.35 \pm 0.15) \qquad \text{(selected)}$$

Lead:

$$PbSeO_3(cr) \Leftrightarrow Pb^{2+} + SeO_3^{2-} \qquad (7.47)$$

$$\log_{10}K_{s,0}°(7.47, 298.15\ K) = -(12.5 \pm 1.0) \qquad \text{(selected)}$$

Uranium:

$$UO_2SeO_3(s) \Leftrightarrow UO_2^{2+} + SeO_3^{2-} \qquad (7.48)$$

$$\log_{10}K_{s,0}°(7.48, 298.15\text{ K}) = -(12.5 \pm 1.0) \qquad \text{(noted)}$$

7.6 Selenate species and solids

7.6.1 Aqueous selenic acid

Selenic acid H_2SeO_4 is a strong acid, comparable with sulfuric acid (H_2SO_4). The species H_2SeO_4(aq) needs not being considered below total aqueous concentrations of 11 to 12 mol·L^{-1}. Hence, only the equilibrium

$$SeO_4^{2-} + H+ \Leftrightarrow HSeO_4^{2-} \qquad (7.49)$$

is relevant in aqueous solution. Several authors (Nair 1964, Covington & Dobson 1965, Ghosh & Nair 1970, Baes & Mesmer 1976) found $\log_{10}K$-values in the narrow range from 1.66 to 1.78, depending on the esitmates for the activity coefficients. Olin et al. (2005) based their selected value of

$$\log_{10}K_1°(7.49, 298.15\text{ K}) = (1.75 \pm 0.10).$$

solely on the work of Nair (1964) and Ghosh & Nair (1970). This value differs slightly from the value selected by Grenthe et al. (1992) $\log_{10}K_1°$(7.49, 298.15 K, Grenthe et al. 1992) = (1.80 ± 0.14). For the SIT calculation Olin et al. (2005) introduced the approximations $\varepsilon(H^+, HSeO_4^-) = \varepsilon(H^+, Cl^-) = 0.12$ kg·mol^{-1}, $\varepsilon(Na^+, HSeO_4^-) = \varepsilon(Na^+, HSO_4^-) = -(0.01 \pm 0.02)$ kg·mol^{-1}, and $\varepsilon(Na^+, SeO_4^{2-}) = \varepsilon(Na^+, SO_4^{2-}) = -(0.12 \pm 0.06)$ kg·mol^{-1} and took the numerical values from Grenthe et al. (1992).

From nine experiments between 273 and 318 K of Nair (1964), Olin et al. (2005) evaluated $\Delta_rH_m°$(7.49, 298.15 K) = 24.2 kJ·mol^{-1} using $\log_{10}K_1°(7.49, T) = a + bT^{-1} + C \ln T$ and Ghosh & Nair (1970) obtained $\Delta_rH_m°$(7.49, 298.15 K) = (24.0 ± 1.5) kJ·mol^{-1} from seven experiments between 273 and 318 K. From an analogous investigation of the protonation of the sulfate ion Nair & Nancollas (1958) obtained $\Delta_rH_m°$ of 23.4 kJ·mol^{-1}, similar to the value of 22.4 kJ·mol^{-1} selected by Cox et al. (1989). For $\Delta_rH_m°$(7.49, 298.15 K) Wagman et al. (1982) indicate a value of only 17.5 kJ·mol^{-1} based on measurements of Thomsen (1882). It is not fully obvious why Olin et al. (2005) gave the high weight to the measurements of Thomsen (1882), but they finally selected the mean of Ghosh & Nair (1970) and Thomsen (1882) to obtain

$$\Delta_rH_m°(7.49, 298.15\text{ K}) = (20.80 \pm 3.20)\text{ kJ·mol}^{-1}.$$

Olin et al. (2005) finally recommended

$$\Delta_fG_m°(HSeO_4^-, 298.15\text{ K}) = -(449.5 \pm 1.3)\text{ kJ·mol}^{-1}\text{ and}$$

$$\Delta_fH_m°(HSeO_4^-, 298.15\text{ K}) = -(582.7 \pm 4.7)\text{ kJ·mol}^{-1},$$

$$S_m°(HSeO_4^-, 298.15\text{ K}) = (136.2 \pm 16.4)\text{ J·K}^{-1}\text{·mol}^{-1},$$

and,

$$\Delta_fG_m°(SeO_4^{2-}, 298.15\text{ K}) = -(439.5 \pm 1.4)\text{ kJ·mol}^{-1}\text{ and}$$

$$\Delta_fH_m°(SeO_4^{2-}, 298.15\text{ K}) = -(603.5 \pm 3.5)\text{ kJ·mol}^{-1},$$

$$S_m°(SeO_4^{2-}, 298.15\text{ K}) = (33.0 \pm 12.7)\text{ J·K}^{-1}\text{·mol}^{-1}.$$

7.6.2 Solid and aqueous selenate species

Like in the case of selenite species this section starts with equilibria that were considered to be subject of the database update 12/07. Many other equilibria, also assessed by Olin et al. (2005), will be summarized under the heading "other selenate equilibria".

7.6.2.1 Magnesium selenates

Phase diagrams of the type $MgSeO_4$-(M(I),M(II)SeO_4-H_2O were investigated by at least ten different authors over the last seventy years. Isopiestic data from Ojkova & Staneva (1989) at 298.15 K have independently been evaluated by Kumov & Batyreva (1990) and Christov (1997). For the equilibrium

$$MgSeO_4\cdot 6H_2O(cr) \Leftrightarrow Mg^{2+} + SeO_4^{2-} + 6\ H_2O(l) \tag{7.50}$$

selected

$$\log_{10}K_{s,0}°(7.50, 298.15\ K) = (1.133 \pm 0.044).$$

Parker et al. (1997) cited the value of the equilibrium constant

$$Mg^{2+} + SeO_4^{2-} \Leftrightarrow MgSeO_4(aq) \tag{7.51}$$

$$log_{10}\beta_1°(7.5, 298.15\ K) = (2.2 \pm 0.2)$$

based on a "thesis by Quinn" that was not available to Olin et al. (2005). This value was selected by Olin et al. (2005) since it is consistent with the corresponding sulfate complex. The present update accepts the selection but puts the value into "supplemental data".

From Selivanova et al. (1961) Olin et al. (2005) evaluated and selected (in agreement with Wagman et al. 1982)

$$\Delta_f H_m°(MgSeO_4\cdot 6H_2O, cr, 298.15\ K) = -(2781.4 \pm 2.4)\ kJ\cdot mol^{-1},$$

and, consequently,

$$\Delta_f G_m°(MgSeO_4\cdot 6H_2O, cr, 298.15\ K) = -(2324.20 \pm 2.00)\ kJ\cdot mol^{-1}$$

$$S_m°(MgSeO_4\cdot 6H_2O, cr, 298.15\ K) = (351.1 \pm 10.5)\ J\cdot K^{-1}\cdot mol^{-1}.$$

7.6.2.2 Calcium selenates

From solubility data of Meyer & Aulich (1928) and Welton & King (1939) Olin et al. (2005) selected the mean solubility m($CaSeO4\cdot 2H_2O$, cr, aq sat, 298.15 K) = (0.380 ± 0.025) $mol\cdot kg^{-1}$, and from this value the solubility product

$$CaSeO_4\cdot 2H_2O(cr) \Leftrightarrow Ca^{2+} + SeO_4^{2-} + 2\ H_2O(l) \tag{7.52}$$

$$\log_{10}K_{s,0}°(7.52, 298.15\ K) = -(2.68 \pm 0.25).$$

Olin et al. (2005) based the extrapolation of $\log_{10}K(7.52)$ to $I = 0$ on the mean activity coefficient of $MgSO_4$, $\gamma_\pm = 0.12$, and on only moderate variations of mean activity coefficients observed by Ojkova & Staneva (1989) for aqueous selenates.

Parker et al. (1997) investigated the equilibrium

$$Ca^{2+} + SeO_4^{2-} \Leftrightarrow CaSeO_4(aq), \tag{7.53}$$

with

$$\log_{10}\beta_1°(7.53, 298.15\ K) = (2.00 \pm 0.10).$$

Olin et al. (2005) accepted and selected this value based on the fact that the similarly determined value for the sulfate complex agreed with literature data. From Selivanova & Shneider (1959) Olin et al. (2005) evaluated and selected

$$\Delta_f H_m°(\text{CaSeO}_4\cdot 6\text{H}_2\text{O, cr, 298.15 K}) = -(1709.0 \pm 2.6)\ \text{kJ}\cdot\text{mol}^{-1},$$

and, consequently

$$\Delta_f G_m°(\text{CaSeO}_4\cdot 6\text{H}_2\text{O, cr, 298.15 K}) = -(1481.9 \pm 2.3)\ \text{kJ}\cdot\text{mol}^{-1},$$

$$S_m°(\text{CaSeO}_4\cdot 6\text{H}_2\text{O, cr, 298.15 K}) = (198.8 \pm 11.7)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

7.6.2.3 Barium selenates

For the equilibrium

$$\text{BaSeO}_4(\text{cr}) \Leftrightarrow \text{Ba}^{2+} + \text{SeO}_4^{2-} + 2\ \text{H}_2\text{O(l)} \quad (7.54)$$

Olin et al. (2005) selected $\log_{10}K_{s,0}°(298.15\ \text{K}) = -(7.56 \pm 0.10)$ for this equilibrium, based on data from Selivanova & Shneider (1958). However, very recently Rai et al. (2014) in a very careful study investigated the solubility of BaSO_4(cr) from under- and oversaturation in Na_2SeO_4 solutions from 0.04 up to 4.1 $\text{mol}\cdot\text{kg}^{-1}$. The solids formed were investigated by XRD to be BaSeO_4(cr) and β-Na_2SeO_4 (above 1.0 $\text{mol}\cdot\text{kg}^{-1}$ of Na_2SeO_4). Rai et al. (2014) used both, a Pitzer- as well as a SIT-model to evaluate the experimental data and obtained

$$\log_{10}K_{s,0}°(7.54,\ 298.15\ \text{K}) = -(7.25 \pm 0.11)$$

for the SIT model. This study prefers using the Rai et al. (2014) value, based on the very careful and comprehensive thermodynamic analysis provided in the paper[13]. This preference is further corroborated by the fact that Rai et al.'s (2014) model is also capable to describe independent solubility data of BaSeO_4(cr) in a wide range from pH 1.4 to 13.8 described by Hata et al. (2004).

Consequently,

$$\Delta_f G_m°(\text{BaSeO}_4\text{, cr, 298.15 K}) = -(1038.54 \pm 0.64)\ \text{kJ}\cdot\text{mol}^{-1},$$

compared to -(1040.3 ± 3.0) $\text{kJ}\cdot\text{mol}^{-1}$ provided by Olin et al. (2005).

The model of Rai et al. (2014) requires the species $\text{Ba(SeO}_4)_2^{2-}$ when applying an SIT approach to the experimental data (the species is not necessary in the Pitzer-approach) above Na_2SeO_4 concentrations of ~0.1 $\text{mol}\cdot\text{kg}^{-1}$. For the equilibrium

$$\text{Ba}^{2+} + 2\text{SeO}_4^{2-} \Leftrightarrow \text{Ba(SeO}_4)_2^{2-} \quad (7.55)$$

Rai et al. (2014) provide

$$\log_{10}\beta_2°(7.55,\ 298.15\ \text{K}) = (3.44 \pm 0.12).$$

The species BaSeO_4(aq) has no region of dominance in the experiments of Rai et al. (2014) and the authors adopt a maximum value of $\log_{10}\beta_1 < 2.15$ for the stability of BaSeO_4(aq), in accordance with the corresponding stabilities for Mg ($\log_{10}\beta_1°(298.15\ \text{K}) = (2.2 \pm 0.2)$) and Ca ($\log_{10}\beta_1°(298.15\ \text{K}) = (2.00 \pm 0.10)$).

A relevant parameter in the experiments and the modelling of Rai et al. (2014) is the SIT interaction parameter $\varepsilon(\text{Na}^+, \text{SeO}_4^{2-})$. Rai et al. (2014) performed a comprehensive sensitivity analysis for this parameter, whose range must fall into the range $0.00 > \varepsilon(\text{Na}^+, \text{SeO}_4^{2-}) > -0.26$,

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[13] Since this improved solubility product by Rai et al. (2014) was discovered by us at a very late stage of the reporting process, it is not yet included in TDB 12/07, but will be considered in the next update.

when following the arguments of the authors (the lower border has been reported by Philipini et al. 2009). Rai et al. (2014) conclude that ε(Na^+, SeO_4^{2-}) = -0.12 kg·mol^{-1} (the value provided by Olin et al. 2005, see above) best fits the experimental data.

From Selinova et al. (1959) Olin et al. (2005) adopted

$$\Delta_f H_m°(\mathrm{BaSeO_4}, \mathrm{cr}, 298.15\ \mathrm{K}) = -(1144.0 \pm 5.0)\ \mathrm{kJ \cdot mol^{-1}},$$

which leads to $\Delta_f S_m° = (\Delta_f G°_m - \Delta_f H°_m)/(-298.15) = -(353.71 \pm 16.9)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, and, consequently to the selection of

$$S_m°(\mathrm{BaSeO_4}, \mathrm{cr}, 298.15\ \mathrm{K}) = (161.1 \pm 16.9)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}.$$

Note that Olin et al. (2005) gave $S_m°(\mathrm{BaSeO_4}, \mathrm{cr}, 298.15\ \mathrm{K}) = (167.0 \pm 19.6)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$.

7.6.2.4 Manganese selenates

The stable selenate solid in aqueous solution is the pentahydrate $MnSeO_4 \cdot 5H_2O$(cr), which is not stable against oxidation. The solubility of the salt is high. From several references Olin et al. (2005) selected the mean solubility m($MnSeO_4 \cdot 5H_2O$, cr, aq sat, 298.15 K) = (2.86 ± 0.08) mol·kg^{-1}, and from Kumov & Batyreva (1990) they adopted the equilibrium

$$\mathrm{MnSeO_4 \cdot 5H_2O(cr)} \Leftrightarrow \mathrm{Mn^{2+}} + \mathrm{SeO_4^{2-}} + 5\ \mathrm{H_2O(l)} \tag{7.56}$$

$$\log_{10} K_{s,0}°(7.56, 298.15\ \mathrm{K}) = -(2.05 \pm 0.03),$$

which was not selected by Olin et al. (2005) nor by this review due to the high resulting concentrations.

For the equilibrium

$$\mathrm{Mn^{2+}} + \mathrm{SeO_4^{2-}} \Leftrightarrow \mathrm{MnSeO_4(aq)}, \tag{7.57}$$

determined by Ghosh & Nair (1970) using potentiometric measurements, Olin et al. (2005) accepted and selected

$$\log_{10} \beta_1°(7.57, 298.15\ \mathrm{K}) = (2.43 \pm 0.05).$$

7.6.2.5 Nickel selenates

Below 355 K $NiSeO_4 \cdot 6H_2O$ is the stable phase. From Ojkova et al. (1998) Olin et al. (2005) selected a solubility of m($NiSeO_2 \cdot 6H_2O$, cr, aq sat, 298.15 K) = (1.92 ± 0.05) mol·kg^{-1}, and for the equilibrium

$$\mathrm{NiSeO_4 \cdot 6H_2O(cr)} \Leftrightarrow \mathrm{Ni^{2+}} + \mathrm{SeO_4^{2-}} + 6\ \mathrm{H_2O(l)}, \tag{7.58}$$

based on the isopiestic measurements of Ojkova & Stanev (1989) they selected

$$\log_{10} K_{s,0}°(7.58, 298.15\ \mathrm{K}) = -(1.381 \pm 0.045).$$

Due to very high resulting concentrations equilibrium (7.58) is not included in the update.

For the equilibrium

$$\mathrm{Ni^{2+}} + \mathrm{SeO_4^{2-}} \Leftrightarrow \mathrm{NiSeO_4(aq)}, \tag{7.59}$$

determined by Ghosh & Nair (1970) using potentiometric measurements at various temperatures, Olin et al. (2005) accepted and selected

$$\log_{10} \beta_1°(7.59, 298.15\ \mathrm{K}) = (2.67 \pm 0.05).$$

They did, however, not accept $\Delta_r H_m°(7.59, 298.15\ K) = (14.7 \pm 1.3)\ kJ\cdot mol^{-1}$, which may be used as an indication.

7.6.2.6 Uranium selenates

With $m(UO_2SeO_4\cdot 4H_2O, cr, aq\ sat, 298.15\ K) = 5.31\ mol\cdot kg^{-1}$ the solubility of uranium selenate is very high. The solubility product $UO_2SeO_4\cdot 4H_2O(cr) \Leftrightarrow UO_2^{2+} + SeO_4^{2-} + 4\ H_2O(l)$, $\log_{10}K_{s,0}°(298.15\ K) = -(2.25 \pm 0.04)$, reported by Kumov & Batyreva (1990) was not accepted by Olin et al. (2005), but is noted here if for specific reasons there is a need to assess the solubility of UO_2SeO_4.

For the enthalpy of formation Olin et al. (2005) adopted and selected the value from Grenthe at al. (1992):

$$\Delta_f H_m°(UO_2SeO_4, cr, 298.15\ K) = -(1539.3 \pm 3.3)\ kJ\cdot mol^{-1},$$

but no standard enthalpy of formation was available for $UO_2SeO_4\cdot 4H_2O(cr)$.

From spectrophotometric/potentiometric studies in 3 M $Na^+(ClO_4^-, SeO_4^{2-})$ solutions at (298.2 ± 0.5) K by Lubal & Havel (1997) and from a voltammetric study of the same system at (296 ± 2) K by Djogic et al. (1999) Olin et al. (2005) concluded a convincing evidence for the existence of the aqueous species $UO_2SeO_4(aq)$ and $UO_2(SeO_4)_2^{2-}$.

From these studies and by using $\varepsilon(UO_2^{2+}, SeO_4^{2-}) = -(0.34 \pm 0.07)\ kg\cdot mol^{-1}$ Olin et al. (2005) derived and selected a mean of

$$\log_{10}\beta_1°(7.60, 298.15\ K) = (2.74 \pm 0.25)$$

for the equilibrium

$$UO_2^{2+} + SeO_4^{2-} \Leftrightarrow UO_2SeO_4(aq), \qquad (7.60)$$

and,

$$\Delta_f G_m°(UO_2SeO_4, aq, 298.15\ K) = -(1407.7 \pm 2.7)\ kJ\cdot mol^{-1}.$$

For the equilibrium

$$UO_2^{2+} + 2SeO_4^{2-} \Leftrightarrow UO_2(SeO_4)_2^{2-} \qquad (7.60a)$$

Olin et al. (2005) derived

$$\log_{10}\beta°_2(7.60a) = (3.10 \pm 0.50),$$

but did not select the value because they ascertained a lack of supporting data in the long extrapolation procedure. From Lubal & Havel (1997) they indicate that $\log_{10}\beta°_2$ does not exceed 3.4. The present update accepts equilibrium (7.60a) as supplemental data.

7.6.2.7 Other selenate equilibria

Olin et al. (2005) list a variety of selenate solid solubilities (and complexes) for elements that are not contained in the PSI/Nagra TDB 12/07. However, some of these equilibria may be useful for specific purposes and/or may be relevant for a subsequent database update. These selenate equilibria are assembled in the following subsection, following the atomic number of elements. An indication is given of whether Olin et al. (2005) have "noted" or "selected" the equilibrium.

Beryllium:

$$BeSeO_4\cdot 4H_2O(cr) \Leftrightarrow Be^{2+} + SeO_4^{2-} + 4\ H_2O(l) \qquad (7.61)$$

$\log_{10}K_{s,0}°(7.61, 298.15\text{ K}) = -(2.94 \pm 0.06)$ (noted)

Ammonium:

$(NH_4)_2SeO_4(cr) \Leftrightarrow 2\ NH_4^+ + SeO_4^{2-}$ (7.62)

$\log_{10}K_{s,0}°(7.62, 298.15\text{ K}) = (0.911 \pm 0.065)$ (seleced)

Lithium:

$Li_2SeO_4 \cdot H_2O(cr) \Leftrightarrow 2\ Li^+ + SeO_4^{2-} + H_2O(l)$ (7.63)

$\log_{10}K_{s,0}°(7.63, 298.15\text{ K}) = (1.762 \pm 0.087)$ (seleced)

Sodium:

$Na_2SeO_4 \cdot 10H_2O(cr) \Leftrightarrow 2\ Na^+ + SeO_4^{2-} + 10\ H_2O(l)$ (7.64)

$\log_{10}K_{s,0}°(7.64, 298.15\text{ K}) = -(0.681 \pm 0.087)$ (seleced)

Potassium:

$K_2SeO_4(cr) \Leftrightarrow 2\ K^+ + SeO_4^{2-}$ (7.65)

$\log_{10}K_{s,0}°(7.65, 298.15\text{ K}) = (0.904 \pm 0.065)$ (seleced)

Scandium:

$Sc^{3+} + SeO_4^{2-} \Leftrightarrow ScSeO_4^+$ (7.66)

$\log_{10}\beta_1(7.66, 0.5\text{ M NaClO}_4, 298.15\text{ K}) = (1.65 \pm 0.20)$ (noted)

Cobalt:

$CoSeO_4 \cdot 6H_2O(cr) \Leftrightarrow Co^{2+} + SeO_4^{2-} + 6\ H_2O(l)$ (7.67)

$\log_{10}K_{s,0}°(7.67, 298.15\text{ K}) = -(1.759 \pm 0.043)$ (selected)

$Co^{2+} + SeO_4^{2-} \Leftrightarrow CoSeO_4(aq)$ (7.68)

$\log_{10}\beta_1°(7.68, 298.15\text{ K}) = (2.70 \pm 0.05)$ (selected)

Copper:

$CuSeO_4 \cdot 5H_2O(cr) \Leftrightarrow Cu^{2+} + SeO_4^{2-} + 5\ H_2O(l)$ (7.69)

$\log_{10}K_{s,0}°(7.69, 298.15\text{ K}) = -(2.44 \pm 0.20)$ (selected)

$Cu^{2+} + SeO_4^{2-} \Leftrightarrow CuSeO_4(aq)$ (7.70)

$\log_{10}\beta_1°(7.70, 298.15\text{ K}) < 2.2$ (noted)

Zinc:

$ZnSeO_4 \cdot 6H_2O(cr) \Leftrightarrow Zn^{2+} + SeO_4^{2-} + 6\ H_2O(l)$ (7.71)

$\log_{10}K_{s,0}°(7.71, 298.15\text{ K}) = -(1.538 \pm 0.064)$ (selected)

$Zn^{2+} + SeO_4^{2-} \Leftrightarrow ZnSeO_4(aq)$ (7.72)

$\log_{10}\beta_1°(7.72, 298.15\text{ K}) = (2.19 \pm 0.06)$ (selected)

$Zn^{2+} + 2\ SeO_4^{2-} \Leftrightarrow Zn(SeO_4)_2^{2-}$ (7.73)

$\log_{10}\beta_2°(7.73, 298.15\text{ K}) = (2.76 \pm 0.12)$ (noted)

For the neutral complex $ZnSeO_4(aq)$ Olin et al. (2005) further selected

$$\Delta_f G_m°(\text{ZnSeO}_4\text{, aq, 298.15 K}) = -(599.0 \pm 1.5)\ \text{kJ·mol}^{-1},$$

$$\Delta_f H_m°(\text{ZnSeO}_4\text{, aq, 298.15 K}) = -(752.3 \pm 5.3)\ \text{kJ·mol}^{-1}\text{, and}$$

$$S_m°(\text{ZnSeO}_4\text{, aq, 298.15 K}) = -(20.1 \pm 18.5)\ \text{kJ·mol}^{-1}.$$

Rubidium:

$$\text{Rb}_2\text{SeO}_4\text{(cr)} \Leftrightarrow 2\text{Rb}^+ + \text{SeO}_4^{2-} \qquad (7.74)$$

$$\log_{10}K_{s,0}°(7.74, 298.15\ \text{K}) = (0.430 \pm 0.065) \qquad \text{(seleced)}$$

Strontium:

$$\text{SrSeO}_4 \Leftrightarrow \text{Sr}^{2+} + \text{SeO}_4^{2-} \qquad (7.75)$$

$$\log_{10}K_{s,0}°(7.75, 298.15\ \text{K}) = -(4.35 \pm 0.15) \qquad \text{(noted)}$$

Cesium:

$$\text{Cs}_2\text{SeO}_4\text{(cr)} \Leftrightarrow 2\ \text{Cs}^+ + \text{SeO}_4^{2-} \qquad (7.76)$$

$$\log_{10}K_{s,0}°(7.76, 298.15\ \text{K}) = (0.636 \pm 0.065) \qquad \text{(seleced)}$$

Thallium(I):

$$\text{Tl}_2\text{SeO}_4\text{(cr)} \Leftrightarrow 2\ \text{Tl}^+ + \text{SeO}_4^{2-} \qquad (7.77)$$

$$\log_{10}K_{s,0}°(7.77, 298.15\ \text{K}) = -(3.90 \pm 0.15) \qquad \text{(seleced)}$$

Lead:

$$\text{PbSeO}_4\text{(cr)} \Leftrightarrow \text{Pb}^{2+} + \text{SeO}_4^{2-} \qquad (7.78)$$

$$\log_{10}K_{s,0}°(7.78, 298.15\ \text{K}) = -(6.90 \pm 0.25) \qquad \text{(selected)}$$

$$\text{Pb}^{2+} + \text{SeO}_4^{2-} \Leftrightarrow \text{PbSeO}_4\text{(aq)} \qquad (7.79)$$

$$\log_{10}\beta_1°(7.79, 298.15\ \text{K}) < 2.2 \qquad \text{(noted)}$$

7.7 Selenocyanate species

Due to their potential importance in radioactive waste systems the database update includes species for Ni-selenocyanate complexes. Further, specific types of radioactive wastes may include cyanide complexes (Prussian blue), leading to the formation of cyanoselenate ligands. Hence, this section first explains, how thermodynamic data for the selenocyanate ion SeCN^- is extracted from Olin et al. (2005). The selenocyanate ion SeCN^- is an ambidentate complexing agent which may coordinate to metal ions via either the nitrogen atom (to “hard” metal ions) or the selenium atom (to “soft” metal ions).

Olin et al. (2005) “partly” selected the thermodynamic values provided by Hamada (1961) (particulary they disagreed with $S_m°(\text{SeCN}^-, 298.15\ \text{K}) = 8.3\ \text{kJ·mol}^{-1}$ because it is inconsistent with corresponding values for OCN^- and SCN^- provided by Wagman et al. (1982)).

For the equilibrium

$$\text{SeCN}^- + \text{H}^+ \Leftrightarrow \text{Se(monoclinic)} + \text{HCN(aq)} \qquad (7.80)$$

Olin et al. (2005) accepted

$$\log_{10}K°(7.80, 298.15\ \text{K}) = (3.6 \pm 0.5)$$

and derived

$$\Delta_f G_m°(\text{SeCN}^-, 298.15\ \text{K}) = (136.1 \pm 3.8)\ \text{kJ·mol}^{-1}.$$

From Wunderlich & Chu (1980) and Gaur et al. (1981) Olin et al. (2005) evaluated and selected

$$\Delta_f H_m°(\text{Se, monoclinic}, 298.15\ \text{K}) = (2.4 \pm 1.10)\ \text{kJ·mol}^{-1},$$

$$S_m°(\text{Se, monoclinic}, 298.15\ \text{K}) = (44.97 \pm 0.40)\ \text{J·K}^{-1}\text{·mol}^{-1},$$

and, consequently derived

$$\Delta_f G_m°(\text{Se, monoclinic}, 298.15\ \text{K}) = (1.28 \pm 0.18)\ \text{kJ·mol}^{-1},$$

which, with $\Delta_f G_m°$(Se, cr, 298.15 K) = (0.00 ± 0.00) kJ·mol^{-1}, may be reformulated as

$$\text{Se(cr)} \Leftrightarrow \text{Se(monoclinic)} \qquad (7.81)$$

$$\log_{10}K°(7.81, 298.15\ \text{K}) = -(0.224 \pm 0.032).$$

We express the formation of $SeCN^-$ as a reaction in homogenous aqueous solution by an appropriate combination of the equilibria 7.4, 7.21, 7.22, 7.80, 7.81 and 4 H^+ + 4 e^- ⇔ 2 H_2(g):

$H_2SeO_3(aq) + 2\ H_2(g) \Leftrightarrow Se(cr) + 3H_2O(l)$ (7.4, $\log_{10}K°$ = (50.15 ± 0.15))
$SeO_3^{2-} + H^+ \Leftrightarrow HSeO_3^-$ (7.21, $\log_{10}K°$ = (8.36 ± 0.23))
$HSeO_3^- + H^+ \Leftrightarrow H_2SeO_3(aq)$ (7.22, $\log_{10}K°$ = (2.64 ± 0.14))
$Se(monoclinic) + HCN(aq) \Leftrightarrow SeCN^- + H^+$ (inv. 7.80, $\log_{10}K°$ = -(3.6 ± 0.5))
$Se(cr) \Leftrightarrow Se(monoclinic)$ (7.81, $\log_{10}K°$ = -(0.224 ± 0.032))
$4\ H^+ + 4e^- \Leftrightarrow 2\ H_2(g)$ (base definition, $\log_{10}K°$ = (0.0 ± 0.0)).

By adding these equilibria we obtain

$$SeO_3^{2-} + HCN(aq) + 5\ H^+ + 4\ e^- \Leftrightarrow SeCN^- + 3\ H_2O(l) \qquad (7.82)$$

$$\log_{10}K°(7.82, 298.15\ \text{K}) = (57.3 \pm 0.6).$$

Note that equilibrium (7.82) strongly favours the formation of $SeCN^-$ from SeO_3^{2-} and CN^- under conditions relevant for radioactive waste systems (i.e. pH 7.5, Eh -200 mV). On the other hand, $SeCN^-$ rapidly decomposes to Se(monoclinic) and HCN when acidified with HCl (Boughton & Keller 1966). This observation conversely supports the arguments provided in section 7.2.1 on the solubility of elemental selenium.

For SIT evaluations and based on Ciavatta (1980) Olin et al. (2005) propose to use the interaction coefficient $\varepsilon(SeCN^-, Na^+) \approx \varepsilon(SCN^-, Na^+)$ = (0.05 ± 0.01) kg·mol^{-1}, in analogy to the interaction of the thiocyanate ion SCN^- with sodium.

7.7.1 Nickel selenocyanates

Kulberg (1974) and Satyanarayana et al. (1975) studied the formation of Ni-SeCN complexes. Olin et al. (2005) did not fully agree with the evaluation of Satyanarayana et al. (1975), but selected from Kulberg (1974):

$$Ni^{2+} + SeCN^- \Leftrightarrow NiSeCN^+ \qquad (7.83)$$

$$\log_{10}\beta_1°(7.83, 298.15\ \text{K}) = (1.77 \pm 0.06)$$

and

$$Ni^{2+} + 2\ SeCN^- \Leftrightarrow Ni(SeCN)_2(aq) \qquad (7.84)$$

$$\log_{10}\beta_2°(7.84, 298.15\ \text{K}) = (2.24 \pm 0.14).$$

Note that Kulberg (1974) did not give sufficient evidence to establish the complex $Ni(SeCN)_3^-$. Equilibrium data were extrapolated from I = 1M $NaClO_4$ to I = 0 using $\Delta\varepsilon$ values of cadmium thiocaynate complexes provided by Bahta et al. (1997).

Kulberg (1974) provided his calorimetric measurements for 1 M $NaClO_4$ solutions. Olin et al. (2005) assumed that these data are also valid at I = 0, but accounted for this assumption by doubling the associated uncertainties. They selected

$$\Delta_r H_m°(7.83, 298.15\ \text{K}) = -(12.8 \pm 0.4)\ \text{kJ·mol}^{-1}, \text{ and}$$

$$\Delta_r H_m°(7.84, 298.15\ \text{K}) = -(25 \pm 4)\ \text{kJ·mol}^{-1}.$$

For the Gibbs energy of Ni^{2+} Olin et al. (2005) used $\Delta_f G_m°(Ni^{2+}, 298.15\ K) = -(45.773 \pm 0.771)$ kJ·mol^{-1} as taken from Gamsjäger et al. (2005) and calculated

$$\Delta_f G_m°(\text{NiSeCN}^-, 298.15\ \text{K}) = (80.2 \pm 3.9)\ \text{kJ·mol}^{-1}, \text{ and,}$$

$$\Delta_f G_m°(\text{Ni(SeCN)}_2, \text{aq}, 298.15\ \text{K}) = (213.5 \pm 7.7)\ \text{kJ·mol}^{-1}.$$

7.7.2 Other selenocyanates equilibria

Olin et al. (2005) list a variety of cyanoselenate equlibria for elements that are not contained in the PSI/Nagra TDB. However, some of these equilibria may be useful for specific purposes and/or may be relevant for a subsequent database update. These cyanoselenate equilibria are assembled in the following subsection, following the atomic number of elements. An indication is given of whether Olin et al. (2005) have "noted" or "selected" the equilibrium.

Cobalt:

$$Co^{2+} + SeCN^- \Leftrightarrow CoSeCN^+ \quad (7.85)$$

$$\log_{10}\beta_1°(7.85, 298.15\ \text{K}) = (1.5 \pm 0.3) \quad \text{(noted)}$$

Copper(I):

CuSeCN(s, cr) solids seems to be sparingly soluble in aqueous solution, but complexes disproportionate to Se(0) and Cu(I) cyanide complexes.

Zinc:

$$Zn^{2+} + SeCN^- \Leftrightarrow ZnSeCN^+ \quad (7.86)$$

$$\log_{10}\beta_1°(7.86, 298.15\ \text{K}) = (1.21 \pm 0.06) \quad \text{(selected)}$$

Extrapolated from 1 M $NaClO_4$, using $\Delta\varepsilon = -(0.026 \pm 0.058)$

$$Zn^{2+} + 2\ SeCN^- \Leftrightarrow Zn(SeCN)_2(aq) \quad (7.87)$$

$$\log_{10}\beta_2°(7.87, 298.15\ \text{K}) = (1.68 \pm 0.11) \quad \text{(selected)}$$

Extrapolated from 1 M $NaClO_4$, using $\Delta\varepsilon = -(0.145 \pm 0.094)$ kg·mol^{-1}.

Silver:

$$Ag^+ + 3\ SeCN^- \Leftrightarrow Ag(SeCN)_3^- \quad (7.88)$$

$$\log_{10}\beta_3°(7.88, 298.15\ \text{K}) = (13.85 \pm 0.30) \quad \text{(selected)}$$

$$Ag(SeCN)(cr) \Leftrightarrow Ag^+ + SeCN^- \quad (7.89)$$

$$\log_{10}K_{s,0}°(7.89, 298.15 \text{ K}) = -(14.0 \pm 0.5) \qquad \text{(selected)}$$

Cadmium:

$$Cd^{2+} + SeCN^- \Leftrightarrow CdSeCN^+ \qquad (7.90)$$

$$\log_{10}\beta_1°(7.90, 298.15 \text{ K}) = (2.24 \pm 0.06) \qquad \text{(selected)}$$

Extrapolated from 1 M $NaClO_4$, using $\Delta\varepsilon = -(0.026 \pm 0.058)$ kg·mol^{-1}.

$$Cd^{2+} + 2\ SeCN^- \Leftrightarrow Cd(SeCN)_2(aq) \qquad (7.91)$$

$$\log_{10}\beta_2°(7.91, 298.15 \text{ K}) = (3.34 \pm 0.12) \qquad \text{(selected)}$$

Extrapolated from 1 M $NaClO_4$, using $\Delta\varepsilon = -(0.145 \pm 0.094)$ kg·mol^{-1}.

$$Cd^{2+} + 3\ SeCN^- \Leftrightarrow Cd(SeCN)_3^- \qquad (7.92)$$

$$\log_{10}\beta_3°(7.92, 298.15 \text{ K}) = (3.81 \pm 0.21) \qquad \text{(selected)}$$

Extrapolated from 1 M $NaClO_4$, using $\Delta\varepsilon = -(0.202 \pm 0.134)$ kg·mol^{-1}.

$$Cd^{2+} + 4\ SeCN^- \Leftrightarrow Cd(SeCN)_4^{2-} \qquad (7.93)$$

$$\log_{10}\beta_4°(7.93, 298.15 \text{ K}) = (4.60 \pm 0.11) \qquad \text{(selected)}$$

Extrapolated from 1 M $NaClO_4$, using $\Delta\varepsilon = -(0.173 \pm 0.099)$ kg·mol^{-1}.

$$Cd(SeCN)_2(cr) \Leftrightarrow Ag^+ + 2\ SeCN^- \qquad (7.94)$$

$$\log_{10}K_{s,0}°(7.94, 298.15 \text{ K}) = -(5.7 \pm 0.5) \qquad \text{(selected)}$$

Mercury:

$$Hg^{2+} + 2\ SeCN^- \Leftrightarrow Hg(SeCN)_2(aq) \qquad (7.95)$$

$$\log_{10}\beta_2°(7.95, 298.15 \text{ K}) = (22.3 \pm 1.0) \qquad \text{(noted)}$$

$$Hg^{2+} + 3\ SeCN^- \Leftrightarrow Hg(SeCN)_3^- \qquad (7.96)$$

$$\log_{10}\beta_3°(7.96, 298.15 \text{ K}) = (26.8 \pm 1.0) \qquad \text{(noted)}$$

$$Hg^{2+} + 4\ SeCN^- \Leftrightarrow Hg(SeCN)_4^{2-} \qquad (7.97)$$

$$\log_{10}\beta_4°(7.97, 298.15 \text{ K}) = (29.3 \pm 0.5) \qquad \text{(noted)}$$

Thallium:

$$Tl^+ + SeCN^- \Leftrightarrow TlSeCN(aq) \qquad (7.98)$$

$$\log_{10}\beta_1°(7.98, 298.15 \text{ K}) = (1.75 \pm 0.2) \qquad \text{(noted)}$$

Table 7.1: Selected selenium data. All data included in TDB Version 12/07 are taken from Olin et al. (2005), except where marked with an asterisk (*). Supplemental data are in italics. New or changed data with respect to TDB Version 01/01 (Hummel et al. 2002) are shaded.

		TDB Version 01/01				**TDB Version 12/07**				
Name	**Redox**	$\Delta_f G_m^\circ$ [kJ·mol^{-1}]	$\Delta_f H_m^\circ$ [kJ·mol^{-1}]	S_m° [J·K^{-1}·mol^{-1}]	$C_{p,m}^\circ$ [J·K^{-1}·mol^{-1}]	$\Delta_f G_m^\circ$ [kJ·mol^{-1}]	$\Delta_f H_m^\circ$ [kJ·mol^{-1}]	S_m° [J·K^{-1}·mol^{-1}]	$C_{p,m}^\circ$ [J·K^{-1}·mol^{-1}]	**Species**
HSeO4-	VI	-	-	-	-	-449.5 ± 1.3	-582.7 ± 4.7	136.2 ± 16.4	-	$HSeO_4^-$
SeO3-2	IV	-361.60 ± 1.47	-	-	-	-362.39 ± 1.76	-507.2 ± 1.1	5.1 ± 7.0	-	SeO_3^{2-}
Se(cr)	0	0.0	0.0	42.27 ± 0.05	25.03 ± 0.05	0.0	0.0	42.09 ± 0.33	25.09 ± 0.30	Se(cr)
H2Se	-II	-	-	-	-	21.5 ± 2.0	14.3 ± 2.0	148.6 ± 1.0	-	$H_2Se(aq)$

		TDB Version 01/01		**TDB Version 12/07**		
Name	**Redox**	$\log_{10}\beta^\circ$	$\Delta_r H_m^\circ$ [kJ·mol^{-1}]	$\log_{10}\beta^\circ$ $\log_{10}K^\circ$	$\Delta_r H_m^\circ$ [kJ·mol^{-1}]	**Reaction**
HSeO4-	IV/VI	-25.58	-	(-26.3 ± 0.3)[a]	-	$SeO_3^{2-} + H_2O(l) \Leftrightarrow HSeO_4^- + H^+ + 2\ e^-$
H2Se	IV/-II	57.39	-	(57.4 ± 0.6)[b]	-	$SeO_3^{2-} + 8\ H^+ + 6\ e^- \Leftrightarrow H_2Se(aq) + 3\ H_2O(l)$
SeO4-2	VI	-1.80 ± 0.14	-23.8 ± 5.0	-1.75 ± 0.10	-20.80 ± 3.20	$HSeO_4^- \Leftrightarrow SeO_4^{2-} + H^+$
NiSeO4	VI	-	-	2.67 ± 0.05	-	$Ni^{2+} + SeO_4^{2-} \Leftrightarrow NiSeO_4(aq)$
MnSeO4	VI	-	-	2.43 ± 0.05	-	$Mn^{2+} + SeO_4^{2-} \Leftrightarrow MnSeO_4(aq)$
UO2SeO4	VI	-	-	2.74 ± 0.25	-	$UO_2^{2+} + SeO_4^{2-} \Leftrightarrow UO_2SeO_4(aq)$
UO2(SeO4)2-2	VI	-	-	*(3.10 ± 0.50)*[c]	-	$UO_2^{2+} + 2\ SeO_4^{2-} \Leftrightarrow UO_2(SeO_4)_2^{2-}$
MgSeO4	VI	-	-	*2.2 ± 0.2*	-	$Mg^{2+} + SeO_4^{2-} \Leftrightarrow MgSeO_4(aq)$
CaSeO4	VI	-	-	2.00 ± 0.10	-	$Ca^{2+} + SeO_4^{2-} \Leftrightarrow CaSeO_4(aq)$
(HSeO3-)[b]	IV	8.4 ± 0.1	5.02 ± 0.50	8.36 ± 0.23	-	$SeO_3^{2-} + H^+ \Leftrightarrow HSeO_3^-$

		TDB Version 01/01		TDB Version 12/07		
Name	**Redox**	**$\log_{10}\beta°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**$\log_{10}\beta°$** **$\log_{10}K°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**Reaction**
(H2SeO3)[c]	IV	2.8 ± 0.2	7.07 ± 0.5	2.64 ± 0.14	-	$HSeO_3^- + H^+ \Leftrightarrow H_2SeO_3(aq)$
FeSeO3+	IV	-	-	11.15 ± 0.11	-	$Fe^{3+} + SeO_3^{2-} \Leftrightarrow FeSeO_3^+$
SeCN-	0	-	-	57.3 ± 0.6	-	$HCN(aq) + SeO_3^{2-} + 5\ H^+ + 4\ e^- \Leftrightarrow SeCN^- + 3\ H_2O(l)$
NiSeCN+	0	-	-	1.77 ± 0.06	-12.8 ± 0.4	$Ni^{2+} + SeCN^- \Leftrightarrow NiSeCN^+$
Ni(SeCN)2	0	-	-	2.24 ± 0.14	-25 ± 4	$Ni^{2+} + 2\ SeCN^- \Leftrightarrow Ni(SeCN)_2(aq)$
Se2-2	0|-II	-	-	25.32 ± 0.33	-	$2\ Se^{2-} \Leftrightarrow Se_2^{2-} + 2\ e^-$
Se3-2	0|-II	-	-	(49.97 ± 0.68)[f]	-	$3\ Se^{2-} \Leftrightarrow Se_3^{2-} + 4\ e^-$
Se4-2	0|-II	-	-	(73.02 ± 1.01)[f]	-	$4\ Se^{2-} \Leftrightarrow Se_4^{2-} + 6\ e^-$
HSe-	-II	-3.8 ± 0.3	-	-3.85 ± 0.05	-	$H_2Se(aq) \Leftrightarrow HSe^- + H^+$
Se-2	-II	-	-	(-14.91 ± 0.20)*	-	$HSe^- \Leftrightarrow Se^{2-} + H^+$

[a] $\log_{10}K°$ and reaction derived from combining equilibria (7.7), (7.21) and (7.22)

[b] $\log_{10}K°$ and reaction derived from combining equilibria (7.4), (7.21), (7.22), (7.11), -(7.14), -(7.13) and $4\ H^+ + 4\ e^- \Leftrightarrow 2\ H_2(g)$

[c] Value reported but not selected by Olin et al. (2005)

[d] Note that in TDB Version 01/01 the formation reaction was formulated the other way round (formation of SeO_3^{2-} in terms of $HSeO_3^-$)

[e] Note that in TDB Version 01/01 the formation reaction was formulated the other way round (formation of $HSeO_3^-$ in terms of $H_2SeO_3(aq)$)

[f] Note that that the uncertainty differs from that given by Olin et al. (2005)

		TDB Version 01/01		TDB Version 12/07		
Name	**Redox**	**$\log_{10}K_{s,0}°$** **$\log_{10}K°$**	**$\Delta_f H_m°$** [kJ·mol^{-1}]	**$\log_{10}K_{s,0}°$** **$\log_{10}K°$**	**$\Delta_f H_m°$** [kJ·mol^{-1}]	**Reaction**
Se(cr)	0/IV	-61.29	-	-61.15 ± 0.31	-	$Se(cr) + 3\ H_2O(l) \Leftrightarrow SeO_3^{2-} + 6\ H^+ + 4\ e^-$
BaSeO4(cr)	VI	-	-	(-7.56 ± 0.10)[a]	(-1144.0 ± 5.0)[a]	$BaSeO_4(cr) \Leftrightarrow Ba^{2+} + SeO_4^{2-}$
NiSeO3:2H2O(cr)	IV	-	-	-5.80 ± 1.0	-	$NiSeO3\cdot 2H_2O(cr) \Leftrightarrow Ni^{2+} + SeO_3^{2-} + 2\ H_2O(l)$
MnSeO3:2H2O(cr)	IV	-	-	-7.6 ± 1.0	-	$MnSeO3\cdot 2H_2O(cr) \Leftrightarrow Mn^{2+} + SeO_3^{2-} + 2\ H_2O(l)$

		TDB Version 01/01		**TDB Version 12/07**		
Name	**Redox**	**$\log_{10}K_{s,0}°$** **$\log_{10}K°$**	**$\Delta_fH_m°$** [kJ·mol^{-1}]	**$\log_{10}K_{s,0}°$** **$\log_{10}K°$**	**$\Delta_fH_m°$** [kJ·mol^{-1}]	**Reaction**
MgSeO3:6H2O(cr)	IV	-	-	-5.82 ± 0.25	-2707.21 ± 1.30	MgSeO3·6H_2O(cr) ⇔ Mg^{2+} + SeO_3^{2-} + 6 H_2O(l)
CaSeO3:H2O(cr)	IV	-	-	-6.40 ± 0.25	-	CaSeO3·H_2O(cr) ⇔ Ca^{2+} + SeO_3^{2-} + H_2O(l)
SrSeO3(cr)	IV	-	-	-6.30 ± 0.50	-1051.9 ± 2.7	SrSeO3(cr) ⇔ Sr^{2+} + SeO_3^{2-}
BaSeO3(cr)	IV	-	-	-6.50 ± 0.25	-1036.7 ± 2.9	BaSeO3(cr) ⇔ Ba^{2+} + SeO_3^{2-}
H2Se(g)	-II	-	-	-1.10 ± 0.01	-14.7 ± 0.3	H_2Se(g) ⇔ H_2Se(aq)

[a] The improved (and preferred) solubility product of -7.25 ± 0.11 by Rai et al. (2014) was discovered by us at a very late stage of the reporting process. It will replace the value by Olin et al. (2005) in the next update. Note that Rai et al. (2014) did not provide values for $\Delta_fH_m°$.

Table 7.2: Selected SIT ion interaction coefficients $\varepsilon_{j,k}$ [kg·mol^{-1}] for selenium species. All data included in TDB Version 12/07 are taken from Olin et al. (2005). Own data estimates based on charge correlations (see Appendix A) are shaded. Supplemental data are in italics.

j k→ **↓**	**Cl^-**	**ClO_4^-**	**NO_3^-**	**Li^+**	**Na^+**	**K^+**
	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$
H2Se	0	0	0	0	0	0
HSeO4-	0	0	0	-	-0.01 ± 0.02	-
SeO4-2	0	0	0	-	-0.12 ± 0.06	-
NiSeO4	0	0	0	0	0	0
MnSeO4	0	0	0	0	0	0
UO2SeO4	0	0	0	0	0	0
UO2(SeO4)2-2	*0*	*0*	*0*	-	*-0.10 ± 0.1*	-
MgSeO4	*0*	*0*	*0*	*0*	*0*	*0*
CaSeO4	0	0	0	0	0	0
H2SeO3	0	0	0	0	0	0
HSeO3-	0	0	0	-	-0.05 ± 0.1	-
SeO3-2	0	0	0	-	-0.10 ± 0.1	-
FeSeO3+	0.05 ± 0.1	0.2 ± 0.1	-	0	0	0
SeCN-	0	0	0	-	0.05 ± 0.01	-
NiSeCN+	0.05 ± 0.1	0.2 ± 0.1	-	0	0	0
Ni(SeCN)2	0	0	0	0	0	0
Se2-2	0	0	0	-	-0.10 ± 0.1	(-0.06)[a]
Se3-2	0	0	0	-	-0.10 ± 0.1	(-0.06)[a]
Se4-2	0	0	0	-	-0.10 ± 0.1	(-0.06)[a]
HSe-	0	0	0	-	-0.05 ± 0.1	-
Se-2	0	0	0	-	-0.10 ± 0.1	-

[a] Value given by Olin et al. (2005) in text but not in Tables B.3 of selected ion interaction coefficients

7.8 References

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8. Silica and silicates

8.1 Elemental silicon

Silicon metal and gas are not relevant under environmental conditions. Hence, the gas phase Si(g) is not included in the data base. For the same reason $SiF_4(g)$, selected by Grenthe et al. (1992), is also 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).

$$S_m°(\text{Si, cr, 298.15 K}) = (18.810 \pm 0.08)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$C_{p,m}°(\text{Si, cr, 298.15 K}) = (19.789 \pm 0.030)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

8.2 Silica (quartz)

The selected values for $SiO_2(cr)$, quartz, are taken from CODATA (Cox et al. 1989).

$$\Delta_f H_m°(\text{SiO}_2\text{, cr, 298.15 K}) = -(910.700 \pm 1.0)\ \text{kJ}\cdot\text{mol}^{-1}$$

$$S_m°(\text{SiO}_2\text{, cr, 298.15 K}) = (41.460 \pm 0.20)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$C_{p,m}°(\text{SiO}_2\text{, cr, 298.15 K}) = (44.602 \pm 0.30)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

and the Gibbs energy of formation calculated from the above values and $S_m°$(Si, cr, 298.15 K)

$$\Delta_f G_m°(\text{SiO}_2\text{, cr, 298.15 K}) = -(856.287 \pm 1.0)\ \text{kJ}\cdot\text{mol}^{-1}$$

8.3 Silica compounds and aqueous species

8.3.1 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

$$\text{SiO}_2(\text{s}) + 2\ \text{H}_2\text{O(l)} \Leftrightarrow \text{Si(OH)}_4(\text{aq})$$

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

$$K_s = \text{m}_{\text{Si(dissolved)}}$$

where m is the measured concentration of dissolved silica in moles/kg H_2O.

New solubility data for quartz at 21, 50, 75 and 96°C have been reported by Rimstidt (1997). Note, that the duration of his solubility experiments at 21°C lasted for more than 13 years! These solubility data show excellent internal consistency and fit a straight line (Rimstidt 1997):

$$\log_{10}\text{m}_{\text{Si(dissolved)}} = -0.076 - 1093.711\ /\ \text{T}$$

This means that in the temperature range 21–96°C a two-term approximation of temperature dependence is sufficient, i.e. the integrated van't Hoff equation including only $\log_{10}K_s°$ and $\Delta_r H_m°$:

$$\log_{10}K_s°(\text{Quartz, cr, 298.15 K}) = -3.744$$

$$\Delta_r H_m°(\text{Quartz, cr, 298.15 K}) = 20.939\ \ \text{kJ}\cdot\text{mol}^{-1}$$

Rimstidt (1997) critically evaluated all the quartz solubility data from the literature and fitted all reliable literature data up to 300°C together with his own results to the van't Hoff equation:

$$\log_{10}m_{Si(dissolved)} = -(0.0254 \pm 0.0247) - (1107.12 \pm 10.77) \;/\; T$$

This function predicts that the solubility of quartz at 25°C is 11.0 ± 1.1 ppm "SiO_2". Note that all uncertainties given by Rimstidt (1997) are expressed as ± 1 standard deviation. This results in:

$$\log_{10}K_s^\circ(\text{Quartz, cr, 298.15 K}) = -(3.739 \pm 0.087)$$

$$\Delta_r H_m^\circ(\text{Quartz, cr, 298.15 K}) = (21.196 \pm 0.41) \text{ kJ}\cdot\text{mol}^{-1}$$

where the uncertainties are now expressed as 2 standard deviations (95% confidence level).

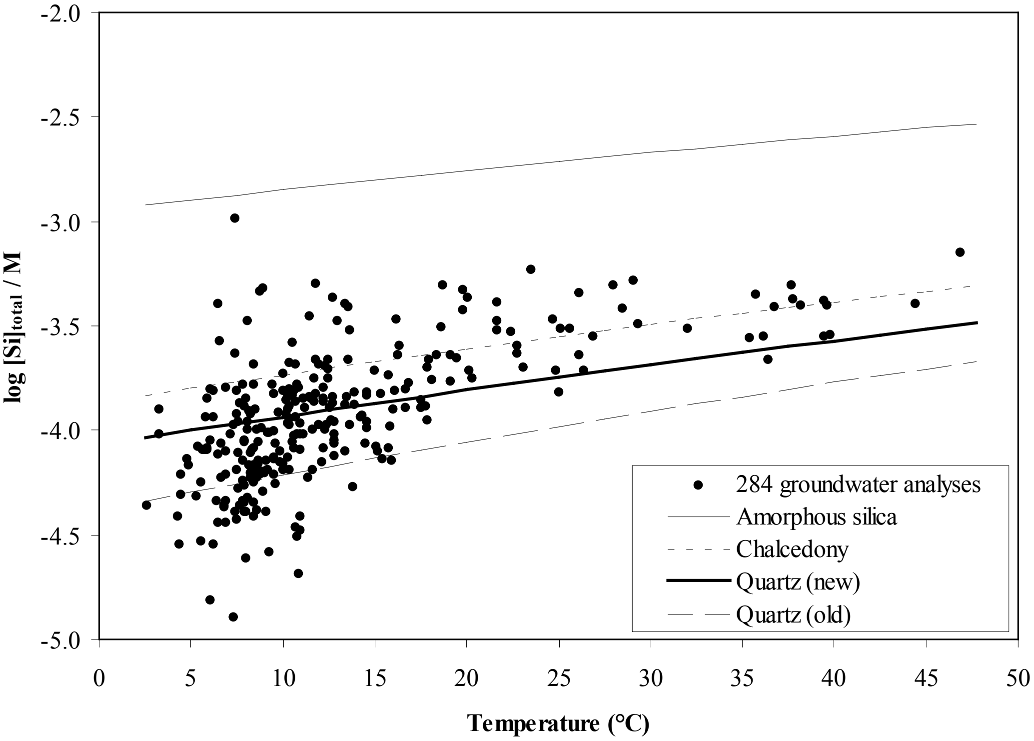

Fig. 8.1: Temperature dependence of total dissolved silica in Swiss groundwaters. The solubility of amorphous silica and quartz (new) is calculated with the integrated van't Hoff equation using $\log_{10}K_s^\circ$ and $\Delta_r H_m^\circ$ selected in this review. Note that the four term temperature 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).

Gunnarsson & Arnorsson (2000) discussed and simultaneously fitted the new data of Rimstidt (1997), their own experiments on amorphous silica, and all reliable published solubility data of quartz and amorphous silica in pure water in the temperature range 0 to 350°C at 1 bar below 100°C and at P_{sat} at higher temperatures. Their results are:

$$\log_{10}K_s\,(\text{Quartz, cr}) = -34.188 + 197.47 \;/\; T - 5.851\cdot10^{-6}\,T^2 + 12.245 \log_{10}T$$

$$\log_{10}K_s\,(\text{Silica, am}) = -8.476 - 485.24 \;/\; T - 2.268\cdot10^{-6}\,T^2 + 3.068 \log_{10}T$$

which results in:

$$\log_{10}K_s°(\text{Quartz, cr, 298.15 K}) = -(3.746 \pm 0.087)$$

$$\log_{10}K_s°(\text{Silica, am, 298.15 K}) = -(2.714 \pm 0.044)$$

$$\Delta_r H_m°(\text{Quartz, cr, 298.15 K}) = (20.637 \pm 0.41)\ \text{kJ}\cdot\text{mol}^{-1}$$

$$\Delta_r H_m°(\text{Silica, am, 298.15 K}) = (14.594 \pm 0.21)\ \text{kJ}\cdot\text{mol}^{-1}$$

No uncertainty estimates are given by Gunnarsson & Arnorsson (2000) except the information that the residuals of the data points used for the regressions are all within 500 $\text{J}\cdot\text{mol}^{-1}$ for amorphous silica whereas the quartz residuals are within 1000 $\text{J}\cdot\text{mol}^{-1}$. As the quartz data fitted by Gunnarsson & Arnorsson (2000) are essentially the same as the ones used by Rimstidt (1997) we used the uncertainty estimates of Rimstidt (1997) for the quartz parameters and half the quartz uncertainties as uncertainty estimates for amorphous silica parameters.

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).

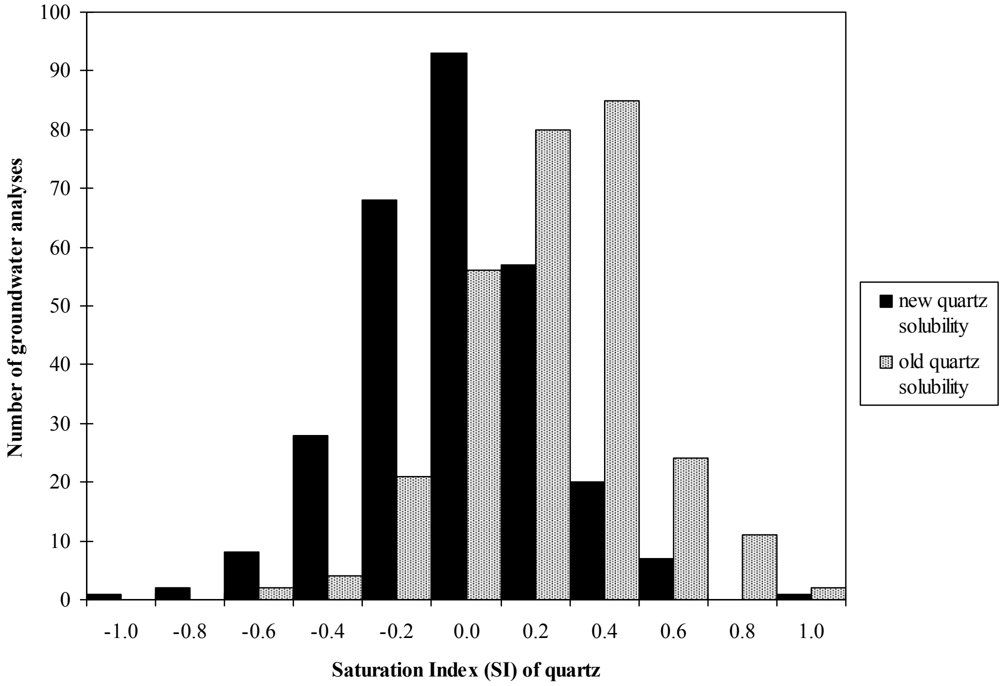

Fig. 8.2: Histogram of quartz saturation indices calculated for 284 Swiss groundwater analyses shown in Fig. 8.1.

Based on the old quartz solubility almost all groundwaters had been calculated to be significantly supersaturated with respect to quartz (Figs. 8.1 and 8.2). 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. 8.1 and 8.2). Hence, the dubious value of chalcedony solubility has been removed from the data base.

8.3.2 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 Si(cr) (see Section 8.1), $SiO_2(cr)$ (see Section 8.2), $H_2O(l)$, $O_2(g)$, $H_2(g)$ with their given uncertainties
- and the temperature dependent solubility of quartz, $SiO_2(cr) + 2\ H_2O(l) \Leftrightarrow Si(OH)_4(aq)$, expressed as $\log_{10}K_s(T) = A + B / T - C \cdot T^2 + D \cdot \log_{10}T$ with uncertainty estimates as discussed above (see Section 8.3.1).

They are calculated as follows ($R = 8.314510\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ and $T^o = 298.15\ K$):

$\log_{10}K_s(T°) = -(3.74634 \pm 0.08715)$

$\Delta_r G_m° = -R \cdot T^o \cdot \ln(10) \cdot \log_{10}K_s(T^o) = (21.3843 \pm 0.4975)\ kJ{\cdot}mol^{-1}$

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

$= R \cdot (-\ln(10) \cdot B + 2 \cdot \ln(10) \cdot C \cdot (T^o)^3 + D \cdot T^o) = (20.6368 \pm 0.4124)\ kJ{\cdot}mol^{-1}$

$\Delta_r S_m° = (\Delta_r H_m° - \Delta_r G_m°) / T^o \cdot 1000 = -(2.5071 \pm 2.1672)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_r C_{p,m}° = \partial \Delta_r H_m(T)/\partial T = R\ (6 \cdot \log_e 10 \cdot C \cdot (T^o)^2 + D) \cdot 1000 = 42.0659\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f G_m°(Si(OH)_4(aq)) = \Delta_r G_m° + \Delta_f G_m°(Quartz) + 2 \cdot \Delta_f G_m°(H_2O(l))$

$= (21.384 \pm 0.498) - (856.287 \pm 1.002) - 2 \cdot (237.140 \pm 0.041)$

$= -(1309.183 \pm 1.120)\ kJ{\cdot}mol^{-1}$

$\Delta_f H_m°(Si(OH)_4(aq)) = \Delta_r H_m° + \Delta_f H_m°(Quartz) + 2 \cdot \Delta_f H_m°(H_2O(l))$

$= (20.637 \pm 0.412) - (910.700 \pm 1.000) - 2 \cdot (285.830 \pm 0.040)$

$= -(1461.723 \pm 1.082)\ kJ{\cdot}mol^{-1}$

$\Delta_f S_m°(Si(OH)_4(aq)) = \Delta_r S_m° + \Delta_f S_m°(Quartz) + 2 \cdot \Delta_f S_m°(H_2O(l))$

$= -(2.507 \pm 2.167) - (182.502 \pm 0.200) - 2 \cdot (163.307 \pm 0.030)$

$= -(511.623 \pm 2.177)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$S_m°(Si(OH)_4(aq)) = \Delta_f S_m°(Si(OH)_4(aq)) + S_m°(Si(cr)) + 2 \cdot S_m°(O_2(g)) + 2 \cdot S_m°(H_2(g))$

$= -(511.623 \pm 2.177) + (18.810 \pm 0.080) + 2 \cdot (205.152 \pm 0.005) + 2 \cdot (130.680 \pm 0.003)$

$= (178.851 \pm 2.178)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f C_{p,m}°(Si(OH)_4(aq)) = \Delta_r C_{p,m}° + \Delta_f C_{p,m}°(Quartz) + 2 \cdot \Delta_f C_{p,m}°(H_2O(l))$

$= 42.066 - 4.565 + 2 \cdot 31.826 = 101.153\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$C_{p,m}°(Si(OH)_4(aq)) = \Delta_f C_{p,m}°(Si(OH)_4(aq)) + C_{p,m}°(Si(cr)) + 2{\cdot} C_{p,m}°(O_2(g)) + 2{\cdot} C_{p,m}°(H_2(g))$

$= 101.153 + 19.789 + 2 \cdot 29.378 + 2 \cdot 28.836 = 237.370\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

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):

$$Si(OH)_4(aq) \Leftrightarrow SiO(OH)_3^- + H^+$$

$$\log_{10}\beta_1° = -(9.81 \pm 0.02)$$

$$\Delta_r H_m° = (25.6 \pm 2.0)\ kJ\cdot mol^{-1}$$

$$Si(OH)_4(aq) \Leftrightarrow SiO_2(OH)_2^{2-} + 2\ H^+$$

$$\log_{10}\beta_2° = -(23.14 \pm 0.09)$$

$$\Delta_r H_m° = (75 \pm 15)\ kJ\cdot mol^{-1}$$

Both $\log_{10}\beta°$ values result from extrapolations to $I = 0$ of experimental data in NaCl media using SIT. From the slopes of these extrapolations Grenthe et al. (1992) obtained $\Delta\varepsilon = (0.04 \pm 0.03)$ kg·mol^{-1} and (0.14 ± 0.07) kg·mol^{-1}, respectively. Assuming $\varepsilon(Si(OH)_4(aq), NaCl) = 0$ Grenthe et al. (1992) derived $\varepsilon(SiO(OH)_3^-, Na^+) = -(0.08 \pm 0.03)$ kg·mol^{-1} and $\varepsilon(SiO_2(OH)_2^{2-}, Na^+) = -(0.10 \pm 0.07)$ kg·mol^{-1} and commented the results as follows: “The first value is more negative than would be expected from comparison with other ion interaction coefficients for species of the same charge and similar size.”

However, measurements of the solubility of amorphous silica in 1 and 3 M NaCl (Zarubin & Nemkina 1990) indicate that the assumption $\varepsilon(Si(OH)_4(aq), NaCl) = 0$ is not valid.

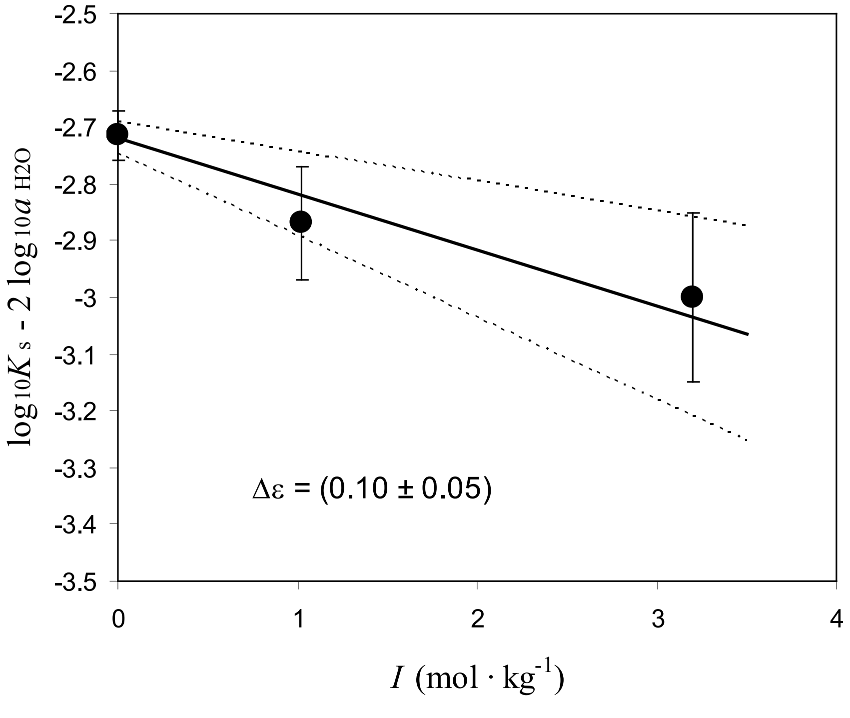

Fig. 8.3: Evaluation of the ion interaction coefficient of $Si(OH)_4(aq)$ in NaCl media using solubility data of amorphous silica of Zarubin & Nemkina (1990) (1 and 3 M NaCl) and Gunnarsson & Arnorsson (2000) ($I = 0$).

Table 8.1: Data for the reaction $SiO_2(am) + 2 H_2O(l) \Leftrightarrow Si(OH)_4(aq)$ in NaCl media.

I (M)	I (m)	$\log_{10}K_s$ (M)	± (est.)	$\log_{10}K_s$ (m)	$\log_{10}K_s$ (m) – 2 $\log_{10} a_{H2O}$	Reference
0	0	-2.714	0.044	-2.714	-2.714	Gunnarsson & Arnorsson (2000)
1	1.02	-2.88	0.10	-2.898	-2.869	Zarubin & Nemkina (1990)
3	3.20	-3.05	0.15	-3.106	-3.000	Zarubin & Nemkina (1990)

For the reaction

$$SiO_2(am) + 2 H_2O(l) \Leftrightarrow Si(OH)_4(aq)$$

the solubility data of Zarubin & Nemkina (1990) and Gunnarsson & Arnorsson (2000) were used to evaluate the SIT interaction coefficient of $Si(OH)_4(aq)$ according to the equation

$$\log_{10}K_s - 2 \log_{10}a_{H2O} = \log_{10}K_s° - \Delta\varepsilon \cdot I \text{ (m)}.$$

The values of $\log_{10}K_s$ (M) in 1 and 3 M NaCl were estimated from total dissolved silica measured at pH 8.5 (Zarubin & Nemkina 1990) assuming that about 10% of dissolved silica is $SiO(OH)_3^-$ in that pH range. The values given in Table 8.1 are numerically identical with $[Si(OH)_4(aq)]$ values calculated at pH < 7 by extrapolating a polynomial fit of experimental data in the range 8.3 < pH < 10.2 given by Zarubin & Nemkina (1990).

Rather large uncertainties were assigned to the $\log_{10}K_s$ (M) values in 1 and 3 M NaCl because of the mentioned estimation and extrapolation procedures and the small experimental data set they are based on.

The $\log_{10}K_s$ value at $I = 0$ from Gunnarsson & Arnorsson (2000) is more precise than the other two values (Table 8.1) and essentially acts as a fixed value in the SIT regression procedure. Hence, the only new result of the weighted linear regression (Fig. 8.3) is the slope $\Delta\varepsilon = \varepsilon(Si(OH)_4(aq), NaCl) = (0.10 \pm 0.05)$ kg·mol^{-1}. Using this value the SIT interaction coefficients of $SiO(OH)_3^-$ and $SiO_2(OH)_2^{2-}$ were re-evaluated resulting in:

$$\varepsilon(Si(OH)_4(aq), NaCl) = (0.10 \pm 0.05) \text{ kg·mol}^{-1}$$

$$\varepsilon(SiO(OH)_3^-, Na^+) = (0.02 \pm 0.05) \text{ kg·mol}^{-1}$$

$$\varepsilon(SiO_2(OH)_2^{2-}, Na^+) = (0.00 \pm 0.08) \text{ kg·mol}^{-1}$$

In the pH range above 10.5, and 10 millimolar and higher concentrations of dissolved silica, polymeric silicate species predominate.

In the first reliable potentiometric study of this system published half a century ago (Lagerström 1959) the results were interpreted in terms of dimeric and tetrameric silicate species, where $Si_4O_8(OH)_4^{4-}$ was the dominating species at pH > 11.

Stability constants for six polymeric species, i.e. two dimers, two trimers, and two tetramers have been reported and accepted by NEA as auxiliary data (Grenthe et al. 1992). The NEA data selection is based on the seminal paper of Sjöberg et al. (1985) who did a combined potentiometric and ^{29}Si NMR study. Sjöberg et al. (1985) conclude that "within the concentration ranges studied, the main polysilicate complex is tetrameric." In the pH range 11.0–12.2 "the prevailing species are the tetramer and the monomer $SiO(OH)_3^-$." Hence, the two equilibrium constants reported for the reaction

$$4 Si(OH)_4(aq) \Leftrightarrow Si_4O_8(OH)_4^{4-} + 4 H^+ + 4 H_2O(l)$$

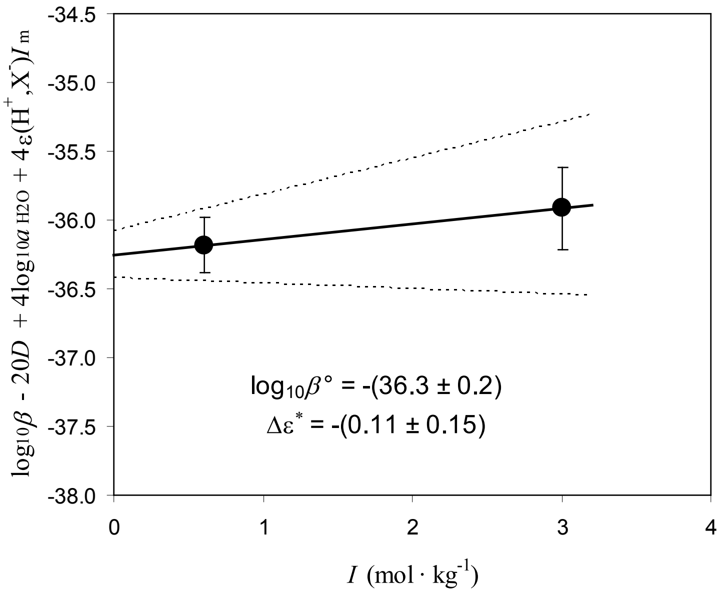

Fig. 8.4: Extrapolation to $I = 0$ of experimental data for the formation of $Si_4O_8(OH)_4^{4-}$ using SIT. The data are taken from Lagerström (1959) (3 m $NaClO_4$) and Sjöberg et al. (1985). (0.6 M NaCl)

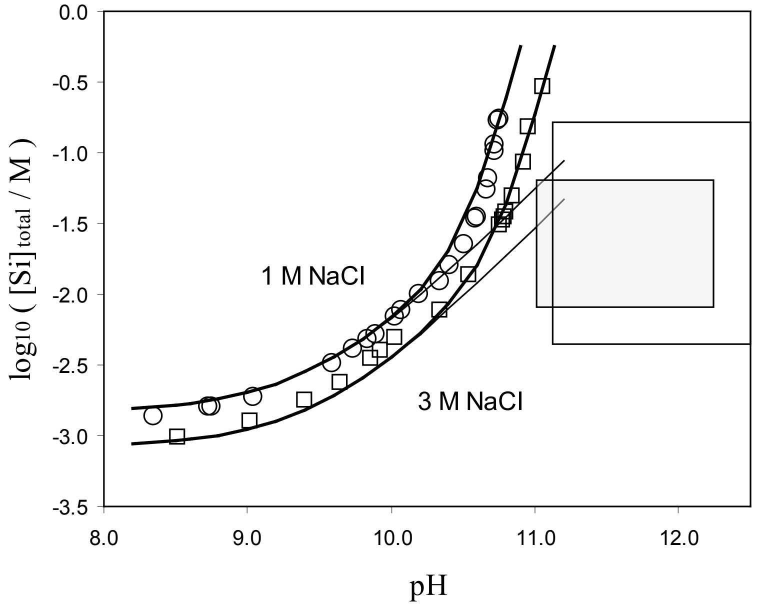

Fig. 8.5: Solubility of SiO_2(am) in NaCl media. Experimental data taken from Zarubin & Nemkina (1990), 1 M NaCl: circles, 3 M NaCl: squares. Thin solid lines: Calculated solubility using only the monomeric species $Si(OH)_4$(aq) and $SiO(OH)_3^-$ with stability constants and SIT parameters selected here. Thick solid lines: The tetrameric species $Si_4O_8(OH)_4^{4-}$ is added. White (larger) rectangle: Range of experimental study of Lagerström (1959). Grey (smaller) rectangle: Range of experimental study of Sjöberg et al. (1985).

in 3 m (molal) $NaClO_4$, $\log_{10}\beta = -32.48$ (Lagerström 1959) and in 0.6 M NaCl, $\log_{10}\beta = -32.81$ (Sjöberg et al. 1985) were extrapolated to $I = 0$ using SIT with uncertainties assigned in the present review (Fig. 8.4). Note that the resulting stability constant

$$\log_{10}\beta° = -(36.3 \pm 0.2)$$

is the same as the one selected by Grenthe et al. (1992). From the slope $\Delta\varepsilon^* = \Delta\varepsilon + 4\ \varepsilon(H^+, X^-) = \varepsilon(Si_4O_8(OH)_4^{4-}, Na^+) - 4\ \varepsilon(Si(OH)_4(aq), NaCl) = -(0.11 \pm 0.15)$ kg·mol^{-1} the SIT interaction coefficient for the tetramer was obtained assuming that $\varepsilon(Si(OH)_4(aq), NaCl) = \varepsilon(Si(OH)_4(aq), NaClO_4) = (0.10 \pm 0.04)$ kg·mol^{-1}:

$$\varepsilon(Si_4O_8(OH)_4^{4-}, Na^+) = (0.29 \pm 0.17)\ \text{kg·mol}^{-1}$$

Using a very simple model comprising only the monomeric species $Si(OH)_4(aq)$ and $SiO(OH)_3^-$ and the tetramer $Si_4O_8(OH)_4^{4-}$ with stability constants and SIT interaction coefficients derived in this review the solubility of $SiO_2(am)$ in NaCl media (Zarubin & Nemkina 1990) is reproduced sufficiently well (Fig. 8.5).

Adding the other polymeric species selected by Grenthe et al. (1992) to the model with SIT interaction coefficients adjusted in analogy to the new evaluations discussed above does not significantly change the overall picture shown in Fig. 8.5. Depending on the choice of the estimated SIT interaction coefficients the measured silica solubilities are slightly to significantly overestimated. However, as already discussed by Sjöberg et al. (1985) all these other polymers were found to remain minor species in the entire range of experimental studies indicated in Fig. 8.5.

A more recent paper proposing an aqueous thermodynamic model for polymerized silica species (Felmy et al. 2001) includes nine polymeric silicate species, i.e. two dimers, two trimers, four tetramers and one hexamer. The reasoning for the selection of this set of species is based on new ^{29}Si NMR data, whereas the actual stability constants were fitted to the $SiO_2(am)$ solubility data of Zarubin & Nemkina (1990) using the Pitzer formalism for ionic strength effects. A good fit is reported for the 3 M NaCl data, whereas the model calculations for 1 M NaCl deviate from experimental data at pH > 10.5, increasingly underestimating the measured solubilities with increasing pH.

The effect of the highly charged polymeric silica species on the speciation model strongly depends on the chosen ionic strength correction model and the estimated SIT or Pitzer parameters. On the other hand, dissolved silica concentrations in natural waters seldom exceed 0.1 mol even when contacted with highly basic solutions, because of the precipitation of calcium or other silicate-containing solid phases. Hence, the very simple model used in this review, including only one polymeric species, $Si_4O_8(OH)_4^{4-}$, besides the monomeric species $Si(OH)_4(aq)$, $SiO(OH)_3^-$ and $SiO_2(OH)_2^{2-}$ seems to be sufficient for all practical purposes of environmental modelling.

8.4 Metal silicate compounds and complexes

8.4.1 Calcium and magnesium

8.4.1.1 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:

$$M^{2+} + SiO(OH)_3^- \Leftrightarrow MSiO(OH)_3^+ \quad (a)$$

$$M^{2+} + SiO_2(OH)_2^{2-} \Leftrightarrow MSiO_2(OH)_2(aq) \quad (b)$$

Values for the stability constants are extrapolated from 1 M $NaClO_4$ to zero ionic strength by the SIT formalism using $\varepsilon(Ca^{2+}, ClO_4^-) = (0.27 \pm 0.03)$ kg·mol^{-1} and $\varepsilon(Mg^{2+}, ClO_4^-) = (0.33 \pm 0.03)$ kg·mol^{-1} (Grenthe et al. 1992), and $\varepsilon(SiO(OH)_3^-, Na^+) = 0.02 \pm 0.05$ kg·mol^{-1} and $\varepsilon(SiO_2(OH)_2^{2-}, Na^+) = (0.00 \pm 0.08)$ kg·mol^{-1} derived in this review and the following guesses for $\varepsilon(CaSiO(OH)_3^+, ClO_4^-) = (0.3 \pm 0.1)$ kg·mol^{-1}, $\varepsilon(MgSiO(OH)_3^+, ClO_4^-) = (0.4 \pm 0.2)$ kg·mol^{-1} and $\varepsilon(MSiO_2(OH)_2(aq), NaClO_4) = (0.2 \pm 0.2)$ kg·mol^{-1}. Note that the results presented below depend on these guesses.

Ca	$\log_{10}K°(\text{eq. a}) = (1.2 \pm 0.1)$	and	$\log_{10}K°(\text{eq. b}) = (4.6 \pm 0.2)$
Mg	$\log_{10}K°(\text{eq. a}) = (1.5 \pm 0.2)$	and	$\log_{10}K°(\text{eq. b}) = (5.7 \pm 0.2)$

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. If these complexes are found to be of crucial importance in some systems, additional experimental studies are recommended.

8.4.1.2 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 aluminum silicate hydrates (CASH) are important solid phases in cementitious systems. However, these phases form solid solutions (Kulik & Kersten 2001) and their appropriate thermodynamic representation is the subject of ongoing research (e.g. Lothenbach et al. 2008; www.empa.ch/cemdata/, accessed 1-12-2014).

8.4.2 Nickel

8.4.2.1 Aqueous nickel silicates

The complexation behavior of Ni^{2+} with $Si(OH)_4(aq)$ has been studied as a function of ionic strength from 0.20 to 1.00 M ($NaClO_4$) at pH 4.55 and 25°C by a solvent extraction technique (Pathak & Choppin 2006a). The authors concluded that Ni^{2+} forms a 1:1 complex, $NiSiO(OH)_3^+$, as the predominant species and interpreted their data in terms of the equilibrium

$$Ni^{2+} + SiO(OH)_3^- \Leftrightarrow NiSiO(OH)_3^+$$

The equilibrium constants $\log_{10}\beta$ derived at different ionic strengths have been fitted by Pathak & Choppin (2006a) with an extended Debye-Hückel expression similar to the SIT formalism and the authors obtained a value of $\log_{10}\beta° = (6.34 \pm 0.03)$ at zero ionic strength.

An analogous complexation study of Co^{2+} with $Si(OH)_4(aq)$ using the same method under the same conditions (Pathak & Choppin 2006b) resulted in $\log_{10}\beta° = (5.61 \pm 0.03)$ for $CoSiO(OH)_3^+$.

Re-analyses of the experimental data published by Pathak & Choppin (2006a, 2006b) in the present review using the SIT formalism (Fig. 8.6) resulted in:

$$\log_{10}\beta° = (6.34 \pm 0.10) \text{ and } \Delta\varepsilon = (0.18 \pm 0.13) \text{ kg·mol}^{-1} \text{ for } NiSiO(OH)_3^+$$

$$\log_{10}\beta° = (5.62 \pm 0.11) \text{ and } \Delta\varepsilon = (0.30 \pm 0.13) \text{ kg·mol}^{-1} \text{ for } CoSiO(OH)_3^+$$

Using $\varepsilon(Ni^{2+}, ClO_4^-) = (0.37 \pm 0.03)$ kg·mol^{-1} (Gamsjäger et al. 2005), $\varepsilon(Co^{2+}, ClO_4^-) = (0.34 \pm 0.03)$ kg·mol^{-1} (Grenthe et al. 1992) and $\varepsilon(SiO(OH)_3^-, Na^+) = (0.02 \pm 0.05)$ kg·mol^{-1} derived in this review we calculate

$$\varepsilon(NiSiO(OH)_3^+, ClO_4^-) = (0.57 \pm 0.15) \text{ kg·mol}^{-1}$$

$$\varepsilon(CoSiO(OH)_3^+, ClO_4^-) = (0.66 \pm 0.15) \text{ kg·mol}^{-1}$$

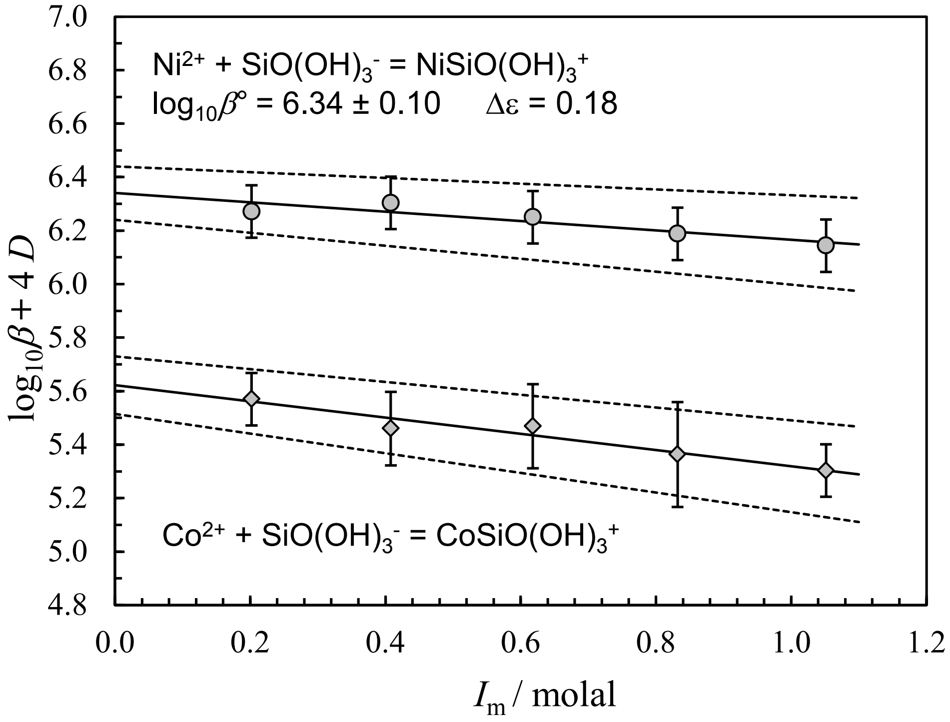

Fig. 8.6: Extrapolation to $I = 0$ of experimental data for the formation of $NiSiO(OH)_3^+$ and $CoSiO(OH)_3^+$ using SIT. The data are taken from Pathak & Choppin (2006a, 2006b).

The equilibrium constants reported by Pathak & Choppin (2006a, 2006b) are not unreasonable compared with other metal-silicate complexes, but as we have not yet any independent confirmation of these results, the complex $NiSiO(OH)_3^+$ has been included in our data base as "supplemental data" with a value of $\log_{10}\beta° = 6.3$.

8.4.2.2 Solid nickel silicates

Thermodynamic data for Ni_2SiO_4(cr) have been selected by Gamsjäger et al. (2005). The thermodynamic data have been derived from heat capacity measurements in the temperature range from 270 to 1570 K and from solution calorimetry in a molten oxide solvent at 965 K. There is no indication that Ni_2SiO_4(cr) forms at ambient conditions and consequently, no solution study in aqueous media is known.

Liebenbergite (Ni_2SiO_4) is an end-member of a complex solid-solution system known as the olivine group of minerals of the general formula X_2SiO_4, where X is a divalent metal cation (Mg, Fe, Mn, Ni, Ca and Co). The pure nickel olivine does not occur naturally; only liebenbergite of an approximate formula $Ni_{1.5}Mg_{0.5}SiO_4$ has been reported (Gamsjäger et al. 2005).

We conclude that liebenbergite is of no importance for thermodynamic models at ambient conditions and thus, the thermodynamic data for Ni_2SiO_4(cr) are not included in our data base.

8.4.3 Aluminum

8.4.3.1 Aqueous aluminum silicates

Several studies have been published reporting experimental data on Al silicate complexation.

Browne & Driscoll (1992) applied a fluorescent probe technique to study trace level concentrations of Al(III) (0.3–10 μM) with $[Si(OH)_4]_{tot}$ varying between 0.10 and 0.27 mM at pH 4.0–5.5 and 0.01 M ionic strength. At pH 4–5 the data were interpreted in terms of the following mononuclear reaction:

$$Al^{3+} + Si(OH)_4(aq) \Leftrightarrow AlSiO(OH)_3^{2+} + H^+$$

They reported $\log_{10}K° = -(1.07 \pm 0.06)$ at infinite dilution. At pH 5.5 the authors inferred in addition two dinuclear Al-Si stoichiometries from the experimental data.

Farmer & Lumsdon (1994) measured the shift in $\log[H^+]$ in Al(III) solutions with and without added silicic acid in 0.1 M $NaClO_4$. In this study, more concentrated solutions were used ($[Al]_{tot}$ = 0.5–2.0 mM and $[Si(OH)_4]_{tot}$ =1.33 mM) and the pH range was quite narrow (pH 3.75–4.11). They reported $\log_{10}K° = -(2.50 \pm 0.05)$ at infinite dilution, a value more than one magnitude lower than the one published by Browne & Driscoll (1992).

Pokrovski et al. (1996) studied the formation of $AlSiO(OH)_3^{2+}$ by measuring the pH variation of a 0.005 M silicic acid solution as a slightly acidic Al^{3+} solution was added. This allowed a wider concentration range in Al(III) to be studied (3 points with $[Al]_{tot}$ = 0.023, 0.0100 and 0.0160 M). Again a limited pH range was studied (pH = 3.710–3.448) in 0.1 M KCl medium. The reported stability constant at $I = 0$ is $\log_{10}K° = -(2.38 \pm 0.10)$.

Spadini et al. (2005) studied the Al–Si complexation by potentiometric titrations in 0.6 M NaCl using a hydrogen electrode with OH^- ions being generated coulometrically. The total concentrations were varied within the limits $0.3 < [Si]_{tot} < 2.5$ mM, $0.5 < [Al]_{tot} < 2.6$ mM and $2 \le -\log[H^+] \le 4.2$. A complex formation constant $\log_{10}K = -(2.75 \pm 0.1)$ was reported for $I = 0.6$ M NaCl and 25.0°C.

The data of Farmer & Lumsdon (1994), Pokrovski et al. (1996) and Spadini et al. (2005) were used in the present review for a SIT analysis (Fig. 8.7). As can be seen in Fig. 8.7 the data of Browne & Driscoll (1992) is far away of all the others and has not been considered in the final SIT analysis. The results are

$$\log_{10}K° = -(2.39 \pm 0.12) \text{ and } \Delta\varepsilon = -(0.61 \pm 0.36) \text{ kg·mol}^{-1}.$$

For the equilibrium

$$Al^{3+} + SiO(OH)_3^- \Leftrightarrow AlSiO(OH)_3^{2+}$$

we calculate a stability constant of $\log_{10}\beta° = (7.42 \pm 0.12)$ from the above result.

Using $\varepsilon(H^+, Cl^-) = (0.12 \pm 0.01)$ kg·mol^{-1} and $\varepsilon(Al^{3+}, Cl^-) = (0.33 \pm 0.02)$ kg·mol^{-1} (Grenthe et al. 1992), and $\varepsilon(Si(OH)_4(aq), NaCl) = (0.10 \pm 0.05)$ kg·mol^{-1} derived in this review we calculate

$$\varepsilon(AlSiO(OH)_3^{2+}, Cl^-) = -(0.30 \pm 0.36) \text{ kg·mol}^{-1}$$

Pokrovski et al. (1996) studied in addition the temperature dependence of the equilibrium $Al^{3+} + Si(OH)_4(aq) \Leftrightarrow AlSiO(OH)_3^{2+} + H^+$ at 25, 90 and 150°C and found a linear dependence of $\log_{10}K$ on reciprocal temperature, $\log_{10}K = -3473$ K/T + 9.25, which results in $\Delta_rH_m° = (66.6 \pm 3.0)$ kJ·mol^{-1}.

This value was later confirmed by measurements at 300°C (Salvi et al. 1998).

Hence, we accept this result and using $\Delta_rH_m° = (25.6 \pm 2.0)$ kJ·mol^{-1} for $Si(OH)_4(aq) \Leftrightarrow SiO(OH)_3^- + H^+$ we calculate $\Delta_rH_m° = (41.0 \pm 3.0)$ kJ·mol^{-1} for $Al^{3+} + SiO(OH)_3^- \Leftrightarrow AlSiO(OH)_3^{2+}$.

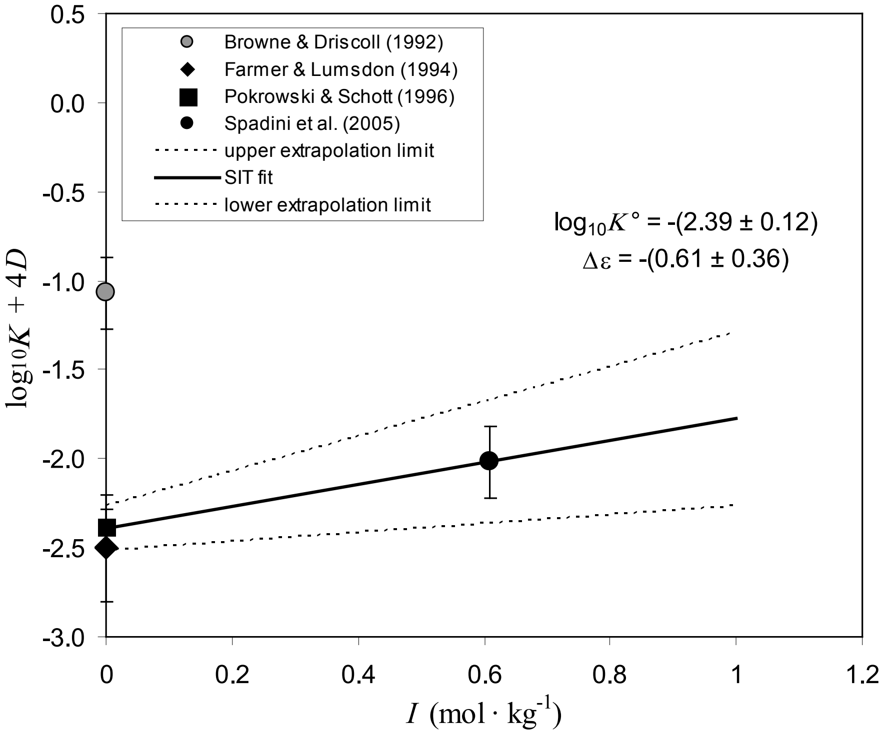

Fig. 8.7: SIT analysis of the equilibrium $Al^{3+} + Si(OH)_4(aq) \Leftrightarrow AlSiO(OH)_3^{2+} + H^+$. The data of Browne & Driscoll (1992) has not been included in the regression analysis.

All the studies discussed so far have been carried out in the acidic pH range $3.5 < pH < 5.5$.

The first study of aluminum silicate complexation by potentiometric titrations in the alkaline region, $9 < pH < 13$, at 25 and 75°C was mentioned by Pokrovski et al. (1998). In this extended abstract the authors claim to be able to interpret their (not yet published) experimental data in terms of the equilibrium

$$Al(OH)_4^- + Si(OH)_4(aq) \Leftrightarrow Al(OH)_3SiO(OH)_3^- + H_2O(l)$$

with $\log_{10}K° = (3.64 \pm 0.20)$.

The same group also claims to have found this complex to be the dominating aqueous aluminum-silicate species in the neutral to basic pH region at 300°C (Salvi et al. 1998).

Hence, we decided to include this complex in the previous version of our data base (TDB Version 01/01) as guidelines for modelers, or as "supplemental data" as this data category is named in the present version.

To the best of our knowledge, the potentiometric data and their interpretation mentioned in the extended abstract (Pokrovski et al. 1998) have never been published as a full paper.

However, shortly after the finalization of TDB Version 01/01 the same group published a Raman spectroscopic study of aluminum-silicate complexes at 20°C in basic solutions, $12.4 < \text{pH} < 14.3$ (Gout et al. 2000).

The measurements in "ultra basic solutions" at pH about 14 have been interpreted by Gout et al. (2000) in terms of the equilibrium

$$Al(OH)_4^- + SiO_2(OH)_2^{2-} \Leftrightarrow SiAlO_3(OH)_4^{3-} + H_2O(l)$$

The value of the apparent equilibrium constant for this reaction (for $I = 1.2$ M) was calculated by the authors as $K = (3.4 \pm 0.2)$. We did not make any attempt to extrapolate this value to zero ionic strength, but included the value $\log_{10}K = 0.53$ as "supplemental data" in the present version of our data base.

In their section "basic pH (≈ 12.5)" Gout et al. (2000) write that "calculations using the equilibrium constant of the reaction derived above imply that the complex $SiAlO_3(OH)_4^{3-}$ is minor in these solutions and, therefore, cannot account for the observed amounts of complexes Al and Si. Thus, the important quantities of complexed Al and Si at pH 12.5 are due to the formation of other complexes, between $SiO(OH)_3^-$ and $SiO_2(OH)_2^{2-}$ and $Al(OH)_4^-$. However, it was impossible to derive the stoichiometry and charge of these complexes from our measurements, because the amount of complexed and free Al and Si do not show any regular dependence on component concentrations. This strongly suggests the formation of several, likely polymerized, Al–Si species. This conclusion is also in agreement with our potentiometric and NMR measurements which demonstrated the existence of different polynuclear Al–Si complexes at $m_{(Al,Si)} > 0.006$ m (Pokrovski et al. 1998). Complementary studies are necessary to determine the nature of these complexes and their stabilities."

Although Gout et al. (2000) never mention it explicitly, in their statement cited above they implicitly retract the complex $Al(OH)_3SiO(OH)_3^-$ and its associated stability constant $\log_{10}K° = (3.64 \pm 0.20)$ published in their extended abstract (Pokrovski et al. 1998). Consequently, we removed this complex and its stability constant from our data base.

We are left with some sobering statements concerning Al–Si complexation: The complex $AlSiO(OH)_3^{2+}$ is fairly well established in acidic solutions, but as it predominates at pH < 5 it is of little importance for groundwater modelling. The complex $SiAlO_3(OH)_4^{3-}$ was identified in "ultra basic solutions" at pH about 14; it may hardly be of any importance in environmental modelling. In neutral to basic solutions there is qualitative evidence of polynuclear Al–Si complexes but no quantitative data are available.

8.4.3.2 Solid aluminum silicates

Thermodynamic data are available for the mineral kaolinite ($Al_2Si_2O_5(OH)_4$) (Nordstrom et al. 1990):

$$Al_2Si_2O_5(OH)_4(s) + 6\,H^+ \Leftrightarrow 2\,Al^{3+} + 2\,Si(OH)_4(aq) + H_2O(l)$$

$$\log_{10}{}^{*}K_{s,0}^{\circ}\ (\text{Kaolinite, cr, 298.15 K}) = 7.435$$

$$\Delta_r H_m^{\circ}(\text{Kaolinite, cr, 298.15 K}) = -35.3\ \text{kcal}\cdot\text{mol}^{-1} \rightarrow -147.7\ \text{kJ}\cdot\text{mol}^{-1}$$

The stability constant for kaolinite is derived from measured solubilities (May et al. 1986) and thus, the kaolinite data were included in our data base.

Aluminum silicate minerals, especially clay minerals, are of great importance in determining the chemistry of water in many rock types. A number of characteristics of these minerals renders excessively difficult the collection of reliable thermodynamic data and their proper use in geochemical modelling.

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 many clay minerals have highly variable chemical compositions and they are never found in nature in bigger crystals than the nanometer scale. Based on these facts and on thermodynamic reasoning Lippmann (1982) concluded that "virtually all clay minerals are more or less metastable or even completely unstable. Nevertheless, they persist through geological times. They owe their existence and their many-varied properties not to thermodynamic equilibrium but to the kinetic inhibitions inherent in ordinary-temperature conditions".

Thirty years later Lippmann's (1982) conclusions seem still to be valid and we decided not to include in our data base the many thermodynamic data derived from calorimetric measurements (Gailhanou et al. 2007, 2009, 2012, 2013).

8.4.4 Iron

Four studies have been published reporting experimental data on Fe(III) silicate complexation: absorbance measurements with a spectrophotometer at $I = 0.1$ M (Weber & Stumm 1965; Porter & Weber 1971), spectrophotometric analyses at $I = 0.1$ M and polarography at $I = 0.15$ M (Olson & O'Melia 1973), and determination of amorphous silica solubility in acidified ferric nitrate solutions at $I < 0.08$ M (Reardon 1979). For the equilibrium

$$Fe^{3+} + SiO(OH)_3^- \Leftrightarrow FeSiO(OH)_3^{2+}$$

the following constants are derived for zero ionic strength: $\log_{10}K^{\circ} = 10.0$ (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 $\log_{10}K^{\circ} = (9.7 \pm 0.3)$.

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 $Fe(OH)_nSiO(OH)_3^{2-n}$ dominates in neutral and alkaline groundwater in analogy with Al.

No thermodynamic data concerning Fe(II) silicate complexation have been found in the literature.

8.4.5 Europium, americium and curium

Silicate complexation of europium, americium and curium often has been studied by the same groups using the same experimental methods and hence, they are discussed together in this section.

Jensen & Choppin (1996) studied the interaction of Eu(III) with silicic acid in aqueous solutions of 0.1 M ionic strength by solvent extraction. 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 reported (Table 1 in Jensen & Choppin 1996): at pH 4 and 0.1 M NaCl $\log_{10}\beta_1 = (7.16 \pm 0.34)$, at pH 6 and 0.1 M $NaClO_4$ $\log_{10}\beta_1 = (7.36 \pm 0.15)$ and at pH 9 and 0.1 M $NaClO_4$ $\log_{10}\beta_1 = (7.25 \pm 0.13)$ and $\log_{10}\beta_2 = (11.7 \pm 0.4)$. Extrapolating these values to zero ionic strength gives: $\log_{10}\beta_1° = (7.82 \pm 0.34)$, (8.02 ± 0.15) and (7.91 ± 0.15), and $\log_{10}\beta_2° = (12.8 \pm 0.4)$.

For the complex $EuSiO(OH)_3^{2+}$ a mean value $\log_{10}\beta_1° = (7.92 \pm 0.20)$ is obtained from the reported results.

The existence of the complex $Eu(SiO(OH)_3)_2^+$ at pH 9 could not be confirmed by other studies carried out in the neutral and basic pH range (Steinle et al. 1997; Panak et al. 2005; Wang et al. 2005). Hence, this complex and its stability constant has been removed in the current version of our database.

Steinle et al. (1997) studied the interaction of Cm(III) with orthosilicic acid in aqueous solutions of ionic strength 0.1 M $NaClO_4$ by time-resolved laser fluorescence spectroscopy (TRLFS). Data obtained in the pH range 5.0–5.5 were interpreted in terms of the equilibrium

$$Cm^{3+} + SiO(OH)_3^- \Leftrightarrow CmSiO(OH)_3^{2+}$$

with $\log_{10}\beta_1 = (7.4 \pm 0.2)$, extrapolated to zero ionic strength: $\log_{10}\beta_1° = (8.1 \pm 0.2)$.

Above pH 5.5 a further Cm species was detected which the authors interpreted as probably due to sorption of Cm to a polymeric silicate species.

Wadsak et al. (2000) reported experimental data on Am(III) silicate complexation. The authors interpreted the results of their solvent extraction study, carried out at pH 3.0–3.8 in 0.1 M $NaClO_4$ solutions, 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 reported for zero ionic strength: $\log_{10}\beta_1° = (8.20 \pm 0.04)$ (1 σ).

Panak et al. (2005) investigated the complexation of Cm(III) with aqueous silicic acid in the pH range 1.5–9.0 in 0.03 M NaCl by time-resolved laser fluorescence spectroscopy (TRLFS). The silicate concentration was varied from under- to over-saturation with respect to the solubility of amorphous silica. Three different complexation products were observed: Cm-silicate(I), Cm-silicate(II) and Cm-silicate(III).

Cm-silicate(I) appears in both, under- and over-saturation of silicic acid only as a minor fraction at pH 4–7 and could be interpreted in terms of the equilibrium

$$Cm^{3+} + SiO(OH)_3^- \Leftrightarrow CmSiO(OH)_3^{2+}$$

with $\log_{10}\beta_1 = (7.32 \pm 0.08)$, extrapolated to zero ionic strength: $\log_{10}\beta_1° = (7.74 \pm 0.08)$. Considering its assigned uncertainty, this value is quite different from the value reported earlier from the same lab using the same experimental method (Steinle et al. 1997). This discrepancy is not discussed and although two co-authors are identical, the earlier publication of Steinle et al. (1997) is not even mentioned by Panak et al. (2005).

Cm-silicate(II) and Cm-silicate(III) were found to be colloidal. Cm-silicate(II) shows spectroscopic characteristics varying with the experimental conditions, whereas Cm-silicate(III), which formed exclusively with polysilicic acid, remained consistent and stable. The existence of a species $Cm(SiO(OH)_3)_2^+$, in analogy to the species $Eu(SiO(OH)_3)_2^+$ proposed by Jensen & Choppin (1996), could not be confirmed.

Wang et al. (2005) studied the complexation of Cm(III) and Eu(III) with dissolved silica by solubility measurement and time-resolved laser fluorescence spectroscopy (TRLFS) in basic solutions (pH 7.5–12) over a range of total silica concentrations at different electrolyte ($NaNO_3$) concentrations. The authors conclude: “The increase in solubility of the $Eu(OH)_3$/silica precipitates at high pH values indicated the possible formation of strong Eu-silicate aqueous complexes. The presence of these strong complexes was confirmed by TRLFS measurements of both Eu(III) and Cm(III) silicate solutions. The complexes present at the high pH values appeared to be fully coordinated with silicates and possibly nitrates in concentrated $NaNO_3$. The changes in fluorescence lifetime, fluorescence intensity and the concentrations of the monomeric and polymeric silicates suggested that the Cm(III) complex(es) in basic solution mostly involve polysilicates.”

Pathak & Choppin (2006c) measured the complex formation of silicate with U(VI), Cm(III) and Eu(III) in the temperature range 5–45°C in an aqueous medium of 0.20 M ($NaClO_4$) ionic strength and pH ≈ 3.5 by solvent extraction. Enthalpies of reaction were derived from the temperature variation of the obtained stability constants.

The stability constants at 25°C and 0.2 M $NaClO_4$ reported for the equilibria

$$Cm^{3+} + SiO(OH)_3^- \Leftrightarrow CmSiO(OH)_3^{2+}$$

$$Eu^{3+} + SiO(OH)_3^- \Leftrightarrow EuSiO(OH)_3^{2+}$$

are $\log_{10}\beta_1 = (7.83 \pm 0.02)$ and (7.79 ± 0.01), respectively (Table 1 in Pathak & Choppin 2006c). A re-evaluation in the present review of the experimental data given in graphical form in Figs. 2 and 3 of Pathak & Choppin (2006c) resulted in $\log_{10}\beta_1 = (7.82 \pm 0.02)$ and (7.79 ± 0.02) (1 σ), respectively. Considering the errors induced by digitizing graphical data the results are identical with the values published by Pathak & Choppin (2006c). Extrapolation of these values to zero ionic strength using the SIT equation with the Debye-Hückel term only yielded $\log_{10}\beta_1° = (8.64 \pm 0.04)$ and (8.61 ± 0.04) (2 σ), respectively.

In their Table 2 Pathak & Choppin (2006c) reported enthalpies of reaction for Cm(III) and Eu(III) as $\Delta_rH_m = (15.8 \pm 2.0)$ and (14.5 ± 1.0) $kJ\cdot mol^{-1}$, respectively. A re-evaluation in the present review by least squares fits of the experimental data given in Table 1 of Pathak & Choppin (2006c) resulted in $\log_{10}\beta_1$ (25°C) = (7.86 ± 0.02) $kJ\cdot mol^{-1}$ and $\Delta_rH_m = (15.8 \pm 1.9)$ $kJ\cdot mol^{-1}$ (1 σ), for Cm(III) and $\log_{10}\beta_1$ (25°C) = (7.78 ± 0.01) and $\Delta_rH_m = (14.1 \pm 0.8)$ kJ mol^{-1} (1 σ) for Eu(III). Within the statistical uncertainties these re-evaluated values are identical with the values published by Pathak & Choppin (2006c).

Hence, the values $\Delta_rH_m = (15.8 \pm 4.0)$ $kJ\cdot mol^{-1}$ (2 σ) for Cm(III) and $\Delta_rH_m = (14.5 \pm 2.0)$ $kJ\cdot mol^{-1}$ (2 σ) for Eu(III) are included as supplemental data in our database. In addition, an estimate $\Delta_rH_m \approx 15$ $kJ\cdot mol^{-1}$ for Am(III), Pu(III) and Np(III) is added as supplemental data to our database.

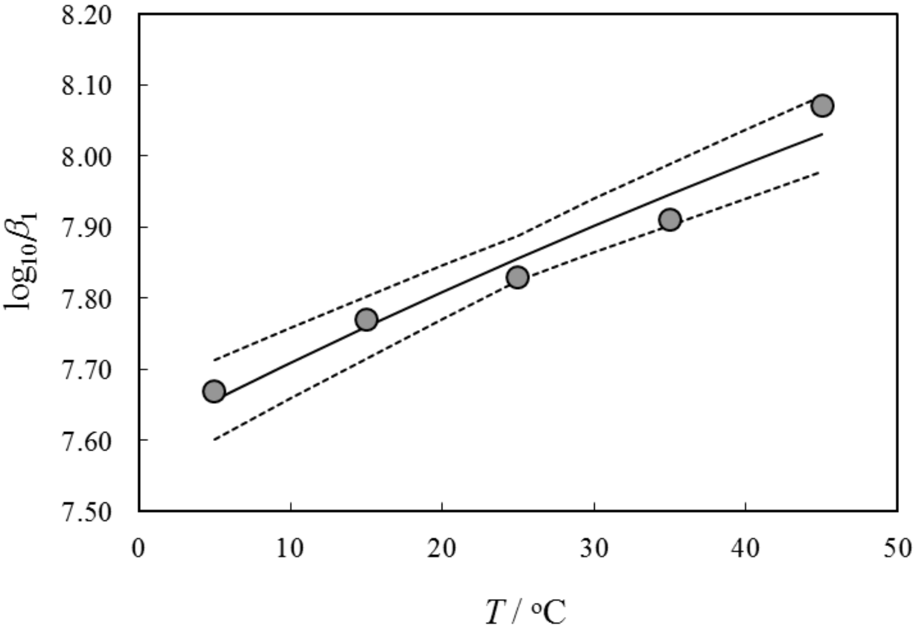

Fig. 8.8: Temperature dependence of the stability constant for the equilibrium Cm^{3+} + $SiO(OH)_3^-$ ⇔ $CmSiO(OH)_3^{2+}$. Data taken from Table 1 in Pathak & Choppin (2006c). An unweighted least squares fit gives: $\log_{10}\beta_1$ (25°C) = (7.86 ± 0.02) and $\Delta_r H_m$ = (15.8 ± 1.9) kJ·mol^{-1}. The dotted lines are the 1 σ standard deviations extrapolated from 25°C to lower and higher temperatures.

Thakur et al. (2007) measured the complex formation of silicate with Am(III), Cm(III) and Eu(III) at pH 3.5 and in ionic strengths of 0.20–1.00 M ($NaClO_4$) by the solvent extraction method. Hence, they used the same experimental set-up as Pathak & Choppin (2006c) in order to study the same equilibria. Instead of temperature variation at constant ionic strength (Pathak & Choppin 2006c) now the ionic strength was varied at constant temperature.

The authors reported for I = 0.20 M $\log_{10}\beta_1$ = (8.02 ± 0.10), (7.78 ± 0.08) and (7.81 ± 0.11) for Am(III), Cm(III) and Eu(III), respectively. While the values reported for Cm(III) and Eu(III) are virtually the same as the values reported by Pathak & Choppin (2006c), the stability constant of Am(III) is higher than the others. Experimental solvent extraction data for I = 0.20 M are given in graphical form in Fig. 3 of Thakur et al. (2007). These data were digitized and the stability constants re-evaluated in the present review. The results are: $\log_{10}\beta_1$ = (7.77 ± 0.06), (7.79 ± 0.03) and (7.83 ± 0.03) for Am(III), Cm(III) and Eu(III), respectively. Considering their assigned uncertainties all these values are the same, especially the stability constants of Am(III) and Cm(III) are undistinguishable. However, while the values for Cm(III) and Eu(III) re-evaluated in this review are the same as reported by Thakur et al. (2007), the value for Am(III) is at variance. Assuming that the experimental data shown in Fig. 3 of Thakur et al. (2007) are correct, the $\log_{10}\beta_1$ value for Am(III) given in Table 1 of Thakur et al. (2007) is incorrect.

Unfortunately, experimental solvent extraction data are published only for I = 0.20 M (Fig. 3 in Thakur et al. 2007) but no experimental data are published for I = 0.50, 0.75 and 1.00 M. Hence, the $\log_{10}\beta_1$ values given for these higher ionic strengths in Table 1 of Thakur et al. (2007) cannot be checked for correctness by re-evaluating the original experimental data. Inspecting Table 1 of Thakur et al. (2007) one recognizes that the $\log_{10}\beta_1$ values for Cm(III) and Eu(III) are very similar at all ionic strengths, differing by not more than 0.03 log units, while the Am(III) values are all systemically higher, differing from the Cm(III) data by 0.24, 0.27, 0.28 and 0.30 log units with increasing ionic strength. It seems that all $\log_{10}\beta_1$ values reported for Am(III) in

Table 1 are affected by the same systematic error in data evaluation and thus, they are not considered further in this review.

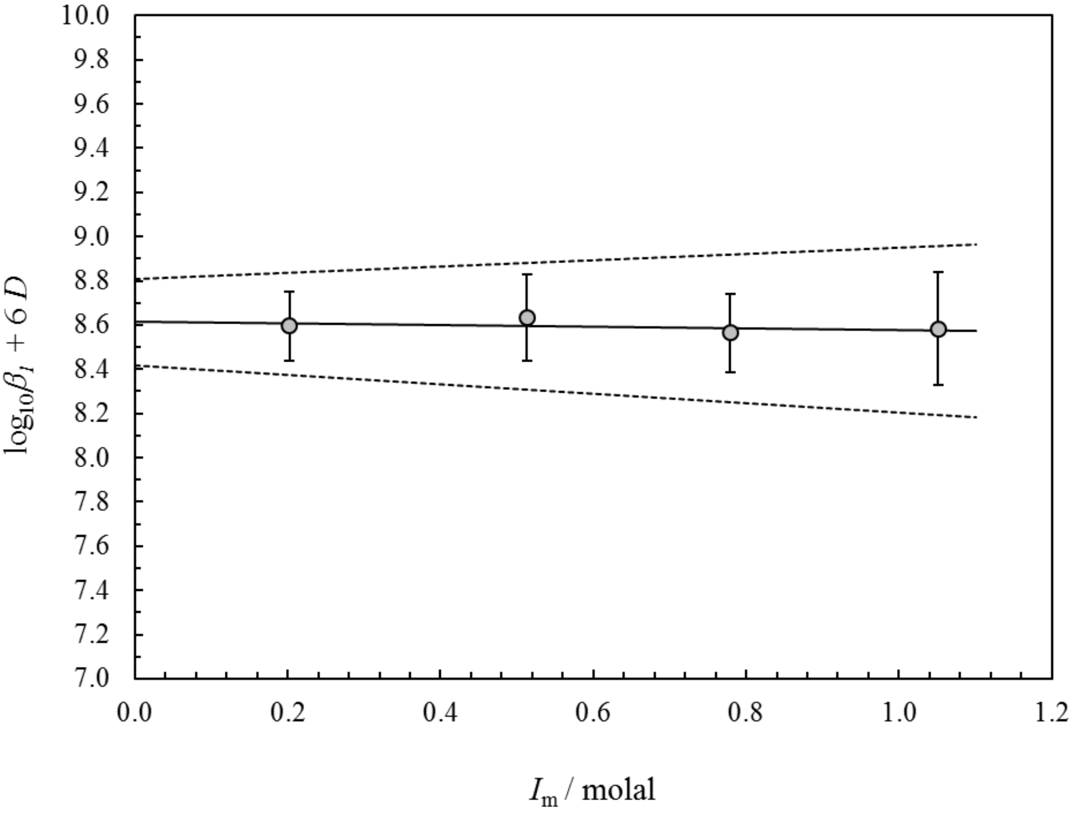

Fig. 8.9: Extrapolation to $I = 0$ of experimental data for the formation of $Cm^{3+} + SiO(OH)_3^- \Leftrightarrow CmSiO(OH)_3^{2+}$ using SIT. The data are taken from Thakur et al. (2007).

The $\log_{10}\beta_1$ values for Cm(III) and Eu(III) given in Table 1 of Thakur et al. (2007) were used for SIT regression analyses in the present review (Fig. 8.9). The results are for

$$Cm^{3+} + SiO(OH)_3^- \Leftrightarrow CmSiO(OH)_3^{2+}$$

$$Eu^{3+} + SiO(OH)_3^- \Leftrightarrow EuSiO(OH)_3^{2+}$$

$$\log_{10}\beta_1° = (8.61 \pm 0.19) \text{ and } \Delta\varepsilon = (0.04 \pm 0.31) \text{ kg·mol}^{-1} \text{ for } CmSiO(OH)_3^{2+}$$

$$\log_{10}\beta_1° = (8.67 \pm 0.24) \text{ and } \Delta\varepsilon = (0.07 \pm 0.37) \text{ kg·mol}^{-1} \text{ for } EuSiO(OH)_3^{2+}$$

Using $\varepsilon(Cm^{3+}, ClO_4^-) = \varepsilon(Eu^{3+}, ClO_4^-) = \varepsilon(Am^{3+}, ClO_4^-) = (0.49 \pm 0.03)$ kg·mol^{-1} (Gamsjäger et al. 2005), and $\varepsilon(SiO(OH)_3^-, Na^+) = (0.02 \pm 0.05)$ kg·mol^{-1} derived in this review we calculate

$$\varepsilon(CmSiO(OH)_3^{2+}, ClO_4^-) = (0.55 \pm 0.32) \text{ kg·mol}^{-1}$$

$$\varepsilon(EuSiO(OH)_3^{2+}, ClO_4^-) = (0.58 \pm 0.38) \text{ kg·mol}^{-1}$$

Using the value $\log_{10}\beta_1 = (7.77 \pm 0.06)$ re-evaluated for Am(III) at $I = 0.20$ M in this review, $\log_{10}\beta_1° = (8.59 \pm 0.2)$ is estimated for $I = 0$.

Note that the $\log_{10}\beta_1°$ values reported in Thakur et al. (2007), i.e. (8.23 ± 0.09), (7.94 ± 0.06) and (8.04 ± 0.08) for Am(III), Cm(III) and Eu(III), respectively, are incorrect. Probably the authors neglected the term Δz^2 in the extended Debye-Hückel expression and thus effectively used $\Delta z^2 = -1$ instead of the correct value $\Delta z^2 = -6$. By chance, these incorrectly extrapolated values "agree well with the reported values at $I = 0.00$" for Am(III), (8.20 ± 0.04) (Wadsak et al. 2000), for Cm(III), (7.74 ± 0.08) (Panak et al. 2005), and Eu(III), (7.98 ± 0.06) (Jensen & Choppin 1996), and the error went unnoticed.

Table 8.2: Stability constants $\log_{10}\beta_1°$ for the reaction $Me^{3+} + SiO(OH)_3^- \Leftrightarrow MeSiO(OH)_3^{2+}$ (Me = Eu, Am, Cm) extrapolated to zero ionic strength.

			$\log_{10}\beta_1°$		
Reference	Lab	Method	Eu(III)	Am(III)	Cm(III)
Jensen & Choppin (1996)	Choppin's lab	Solvent extr.	7.92 ± 0.20		
Pathak & Choppin (2006c)	Choppin's lab	Solvent extr.	8.61 ± 0.04		8.64 ± 0.04
Thakur et al. (2007)	Choppin's lab	Solvent extr.	8.67 ± 0.24	8.59 ± 0.2	8.61 ± 0.19
Wadsak et al. (2000)	University Vienna	Solvent extr.		8.20 ± 0.08	
Steinle et al. (1997)	INE Karlsruhe	TRLFS			8.1 ± 0.2
Panak et al. (2005)	INE Karlsruhe	TRLFS			7.74 ± 0.08

An overview over the stability constants discussed here for the equilibrium $Me^{3+} + SiO(OH)_3^- \Leftrightarrow MeSiO(OH)_3^{2+}$ (Me = Eu, Am, Cm) (Table 8.2) reveals two contradicting results:

On the one hand, stability constants obtained by the same method for different metal cations do not show any statistically significant difference or trend with respect to Eu(III), Am(III) and Cm(III) (Pathak & Choppin 2006c, Thakur et al. 2007).

On the other hand, values reported from the same lab, obtained with the same experimental method for the same metal cation show statistically significant differences, for Eu(III) (Jensen & Choppin (1996) versus Pathak & Choppin (2006c) and Thakur et al. (2007)) as well as for Cm(III) (Steinle et al. (1997) versus Panak et al. (2005)). In both cases, these differences are not discussed or not even mentioned in subsequently published papers.

In summary, based on the available data there is no reason to discern between Eu(III), Am(III) and Cm(III) with respect to the reaction $Me^{3+} + SiO(OH)_3^- \Leftrightarrow MeSiO(OH)_3^{2+}$. If we take just one of the almost identical values from Pathak & Choppin (2006c) and Thakur et al. (2007), in order not to give them too much weight, and average this value with the other values given in Table 8.2, a common value $\log_{10}\beta_1° = (8.1 \pm 0.4)$ is obtained. This value is included in our database for Eu(III), Am(III) and Cm(III), and as an estimate (supplemental data) for Pu(III) and Np(III).

8.4.6 Zirconium

No information about aqueous zirconium silicate complexes could be found in the literature during the present review.

Thermodynamic data for twelve zirconium silicate compounds have been selected in the NEA review of zirconium (Brown et al. 2005). However, none of these data are included in our data base (see Table 8.4) for reasons discussed in section 12.8.2.

8.4.7 Thorium

Rai et al. (2008) studied the solubility of $ThO_2(am)$ in alkaline silica solutions, pH 10–13.3, at room temperature (22 ± 2°C) in a controlled atmosphere chamber containing an inert gas. Freshly precipitated $ThO_2(am)$ was washed and the precipitate then suspended in appropriate Na_2SiO_3 solutions. Either the sodium silicate concentration was varied at constant pH or the pH was varied at constant sodium silicate concentration. The solubility experiments from undersaturation lasted from 7 to 487 days. The maximum Na concentration measured in these experiments was 0.4 M.

The experimental data were interpreted by Rai et al. (2008) in terms of the equilibrium

$$ThO_2(am) + 3\ Si(OH)_4(aq) + H_2O \Leftrightarrow Th(OH)_3(SiO(OH)_3)_3^{2-} + 2\ H^+$$

with $\log_{10}{}^*K_{s,0}° = -(18.5 \pm 0.7)$. Note that the solubility product $\log_{10}K_{s,0}° = -46.7$ is numerically identical with the solubility product $\log_{10}{}^*K_{s,0}° = (9.3 \pm 0.9)$ for $ThO_2(am, hyd, fr) + 4\ H^+ \Leftrightarrow Th^{4+} + 2\ H_2O$ selected by Rand et al. (2008) and included in our data base.

In the present review the solubility products given above were used together with equilibrium constants for $SiO(OH)_3^-$, $SiO_2(OH)_2^{2-}$ and $Th(OH)_4(aq)$, and the solubility of $SiO_2(am)$ as included in our data base in order to calculate the solubility of $ThO_2(am)$ (Figs. 8.10 and 8.11). The tetramer $Si_4O_8(OH)_4^{4-}$ was not included in this simplified speciation model as Fig. 6 in Rai et al. (2008) shows that polymeric silica species contribute less than 10% to the total silica speciation at these low total silica concentrations. The agreement between measured data points and calculated Th concentration is good in Fig. 8.10 and poor in Fig. 8.11.

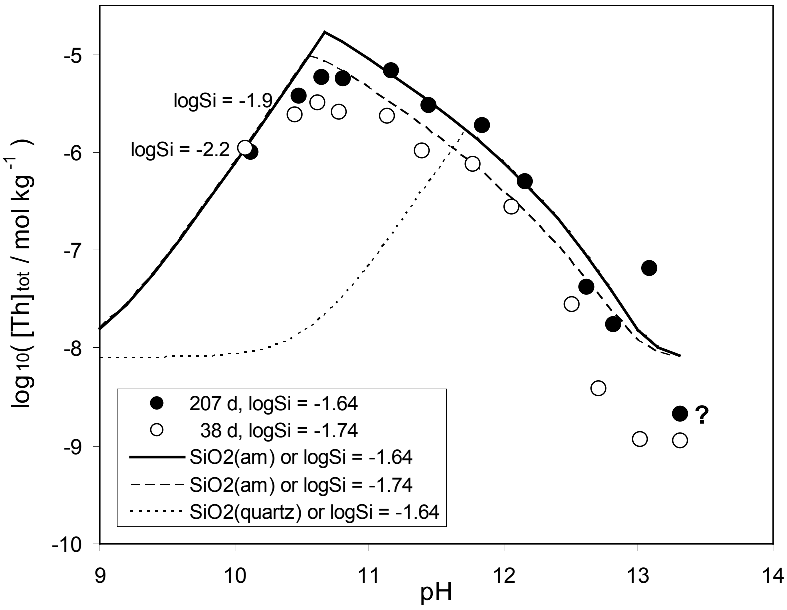

Fig. 8.10: Solubility of $ThO_2(am)$ as a function of pH and time at fixed aqueous Na_2SiO_3 concentration of approximately 0.018 mol·dm^{-3} (38 days reaction time) or 0.023 mol·dm^{-3} (207 days reaction time), except where shown explicitly otherwise. Data points taken from Table 11 in Rai et al. (2008). Data point with question mark refers to log[Th] given as < -8.677. Lines calculated in the present review with a simplified speciation model discussed in the text.

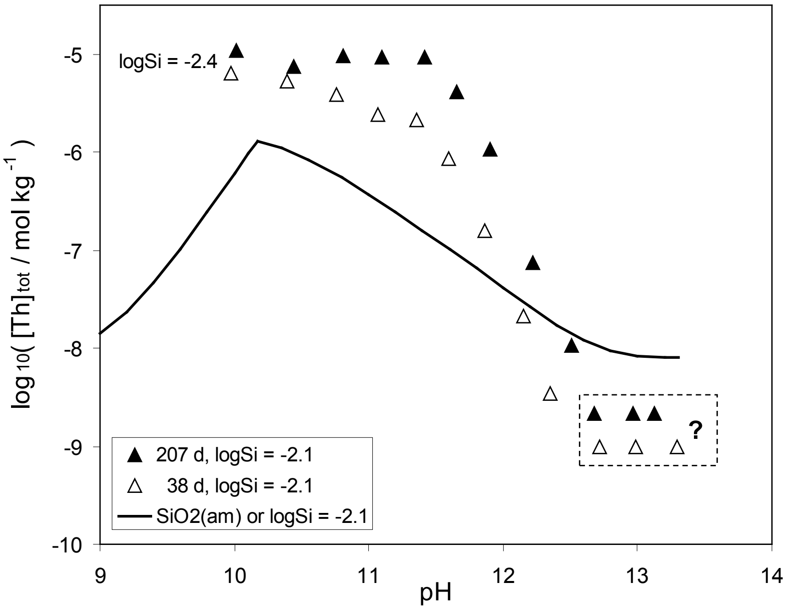

Fig. 8.11: Solubility of ThO_2(am) as a function of pH and time at fixed aqueous Na_2SiO_3 concentration of approximately 0.008 mol·dm^{-3}, except where shown explicitly otherwise. Data points taken from Table 12 in Rai et al. (2008). Data points in the dashed box with question mark refers to log[Th] given as < -8.667 and < -9.000. Lines calculated in the present review with a simplified speciation model discussed in the text.

Rai et al. (2008) assumed $\log_{10}K_{s,0}° = -46.7$ for the solubility product $ThO_2(am) + 2\ H_2O \Leftrightarrow Th^{4+} + 4\ OH^-$ and obtained for

$$Th^{4+} + 3\ Si(OH)_4(aq) + 3\ H_2O \Leftrightarrow Th(OH)_3(SiO(OH)_3)_3^{2-} + 6\ H^+$$

$$\log_{10}K° = -(27.8 \pm 0.7)$$

The data points with question marks in Figs. 8.10 and 8.11 refer to the unresolved question of detection limits. Rai et al. (2008) state that their detection limit for measured Th concentrations is $10^{-9.67}$, and indeed in their Table 9 (Set II) several numbers log[Th] < -9.67 appear. On the other hand, in Table 8 (Set I) log[Th] goes as low as -10.363. No detection limits in Set I? In Table 11 (Set III) we find one number log[Th] < -8.677 (question mark in Fig. 8.10). Does this indicate a detection limit one order of magnitude higher than stated in the text? In Table 12 (Set IV) we find three numbers log[Th] < -8.667 and three numbers log[Th] < -9.000 (dashed box with question mark in Fig. 8.11). Yet other detection limits? All these data should perhaps not be included in thermodynamic modelling.

The thermodynamic interpretation of experimental data by Rai et al. (2008) has several further shortcomings.

First of all, measurements at generally low ionic strength (the maximum Na concentration was 0.4 M) were interpreted in terms of both, the Pitzer and SIT formalism. The authors were aware of the fact that the results of the speciation calculations are insensitive to the Pitzer or SIT coefficients used. Nevertheless, they give Pitzer and SIT coefficients for $Th(OH)_3(SiO(OH)_3)_3^{2-}$ which are mere guesses. The SIT coefficient is not included in our data base.

Secondly, the authors claim to have included the solubility of quartz in their speciation model (Table 4 in Rai et al. (2008)). This cannot be correct. Using the solubility of quartz in our simplified speciation model results in calculated total silica incompatible with measurements and totally wrong Th solubility at pH < 11 (dotted line in Fig. 8.10).

Thirdly, the calculated Th concentration shown in Fig. 6 of Rai et al. (2008) could be reproduced in the present review only in the pH range 11.5–13. Below pH 11.5 the calculated curve of Rai et al. (2008) exhibits a parabolic shape which is incompatible with the effect of SiO_2(am) solubility which leads to the sharp edge in Fig 8.10 and a solubility limited total Si concentration at pH < 10.7. The measured log[Si] numbers shown in Fig. 8.10 are in perfect agreement with concentrations calculated with our simplified speciation model. This is not mentioned and was probably not recognized by Rai et al. (2008).

Last but not least there is a discrepancy of measured and calculated Th concentrations in data set IV (Fig. 8.11) and Rai et al. (2008) comment "it was surprising to find disagreement in this set, and exact reasons for this are not known". A closer look at Fig. 8.11 here and Fig. 11 in Rai et al. (2008) reveals even stranger disagreements. In Fig. 11 again the parabolic line appears, with a maximum Th concentration at pH 10.5 about one order of magnitude lower than calculated with our simplified speciation model (Fig. 8.11). The only difference between calculations shown in Fig. 8.10 and Fig. 8.11 is the total concentration of dissolved silica. Hence, it is unclear why we calculated something totally different than Rai et al. (2008) in this case, whereas the calculated curves in the first case (Fig. 8.10) agree well, at least at pH > 11.5. But the data shown in Fig. 8.11 may hide some more fundamental problems than differences in speciation calculations. The long-term solubility experiments (207 days) result in almost the same dissolved Th concentrations as the data shown in Fig. 8.10 although the total dissolved silica concentration differs by a factor of four. Furthermore, although the measured silica concentration at pH 10 (log[Si] = -2.4) agrees well with the one calculated as a result of solubility limitation by SiO_2(am), the total dissolved Th concentration is not lower than the other values at higher pH, in contrast to the effects seen in Fig. 8.10. Both effects cannot be explained by the formation of a single thorium silicate complex.

In summary, the experimental data of Rai et al. (2008) show strong thorium silicate complex formation in alkaline solutions, and their thermodynamic interpretation is not unreasonable. We included their equilibrium constant in our data base, but because of the shortcomings discussed above, as "supplemental data".

Rand et al. (2008) selected in their NEA review of thorium standard molar enthalpies of formation for the minerals $ThSiO_4$(huttonite) and $ThSiO_4$(thorite). Neither solubility products nor standard molar Gibbs free energies of formation are known for these solids and Rand et al. (2008) concluded that both compounds are metastable towards quartz and thorium dioxide under standard conditions. Therefore, they are not included in our data base (see Table 8.4).

8.4.8 Uranium

8.4.8.1 Aqueous uranium silicates

Seven papers have been published until 2007 reporting experimental data on U(VI) silicate complexation (Table 8.3). Five of these papers, i.e. Porter & Weber (1971), Satoh & Choppin (1992), Jensen & Choppin (1998), Moll et al. (1998) and Hrnecek & Irlweck (1999) have been discussed in detail and some data re-evaluated by Guillaumont et al. (2003). The experimental data in these papers have been interpreted in terms of the equilibrium

$$UO_2^{2+} + Si(OH)_4(aq) \Leftrightarrow UO_2SiO(OH)_3^+ + H^+$$

and the equilibrium constants reported ($\log_{10}{}^*K$) and extrapolated to zero ionic strength ($\log_{10}{}^*K^\circ$) by Guillaumont et al. (2003) are shaded in Table 8.3. For the equilibrium

$$UO_2^{2+} + SiO(OH)_3^- \Leftrightarrow UO_2SiO(OH)_3^+$$

$\log_{10}\beta_1°$ values were calculated using $\log_{10}\beta° = -(9.81 \pm 0.02)$ for $Si(OH)_4(aq) \Leftrightarrow SiO(OH)_3^- + H^+$ (last column in Table 8.3).

Table 8.3: Equilibrium constants $\log_{10}{}^*K$ for the reaction $UO_2^{2+} + Si(OH)_4(aq) \Leftrightarrow UO_2SiO(OH)_3^+ + H^+$ and $\log_{10}\beta_1$ for the reaction $UO_2^{2+} + SiO(OH)_3^- \Leftrightarrow UO_2SiO(OH)_3^+$. Data taken from Table 9-34 of Guillaumont et al. (2003) are shaded.

Reference	Ionic medium $NaClO_4$	T (°C)	$\log_{10}{}^*K$	$\log_{10}{}^*K°$	$\log_{10}\beta_1$	$\log_{10}\beta_1°$
Porter & Weber (1971)	0.2 M	25	-1.98 ± 0.13	-1.71 ± 0.13		8.10 ± 0.13
Satoh & Choppin (1992)	0.2 M	25	-2.01 ± 0.09	-1.74 ± 0.09		8.07 ± 0.09
Jensen & Choppin (1998)	0.1 M	25	-2.92 ± 0.06	-2.65 ± 0.06		7.16 ± 0.06
Moll et al. (1998)	0.3 M	20	-1.74 ± 0.20	-1.44 ± 0.20		8.37 ± 0.20
Hrnecek & Irlweck (1999)	0.2 M	25	-2.21 ± 0.06	-1.94 ± 0.06		7.87 ± 0.06
Yusov & Fedoseev (2005)	0.2 M	?	-2.56 ± 0.09	-2.29 ± 0.09		7.52 ± 0.09
Pathak & Choppin (2006c)	0.2 M	25			6.87 ± 0.04	7.42 ± 0.04

Yusov & Fedoseev (2005) studied the interaction of UO_2^{2+} ions with orthosilicic acid $Si(OH)_4$ and polymeric silicic acids in solutions of $I = 0.1–0.2$ M $NaClO_4$ in the pH range 1.7–4.3 by spectrophotometry. They reported a value of $\log_{10}{}^*K = -(2.56 \pm 0.09)$ at $I = 0.2$ and $\log_{10}{}^*K° = -(2.29 \pm 0.09)$ extrapolated to zero ionic strength, converted to $\log_{10}\beta_1° = (7.52 \pm 0.09)$.

Yusov & Fedoseev (2005) found that for the monomers and oligomers with $n \leq 4$, ${}^*K$ is the same within the determination error. For polymeric silicic acids with $n > 100$ the data varied beyond the error limits; the apparent constant ${}^*K$ decreased with an increase of polymerization. Based on these results the authors state that "the inconsistency of the data from different papers (see Table 8.3) cannot be attributed to the polymerization of $Si(OH)_4$. In particular, the lowest and the highest $\log_{10}{}^*K$ values (-2.92, Jensen & Choppin 1998, and -1.74, Moll et al. 1998) were obtained in experiments with monomeric $Si(OH)_4$. The inconsistency is apparently associated with the procedures used." Yusov & Fedoseev (2005) conclude: "We believe that the observed discrepancies are due to the complexity of the system under consideration; it is difficult to adequately take into account all the factors. This is especially difficult in experiments with trace amounts of a radionuclide when its behavior can also be affected by sorption and other difficult-to-control factors."

Pathak & Choppin (2006c) measured the complex formation of silicate with U(VI) in the temperature range 5–45°C in an aqueous medium of 0.20 M ($NaClO_4$) ionic strength and pH ≈ 3.5 by solvent extraction. The enthalpy of reaction was derived from the temperature variation of the obtained stability constants.

The stability constant at 25°C and 0.2 M $NaClO_4$ reported for the equilibrium

$$UO_2^{2+} + SiO(OH)_3^- \Leftrightarrow UO_2SiO(OH)_3^+$$

is $\log_{10}\beta_1$ = (6.87 ± 0.02) (Table 1 in Pathak & Choppin 2006c). A re-evaluation in the present review of the experimental data given in graphical form in Fig. 1 of Pathak & Choppin (2006c) resulted in $\log_{10}\beta_1$ = (6.85 ± 0.02) (1 σ). Considering the errors induced by digitizing graphical data this result is identical with the value published by Pathak & Choppin (2006c).

In their Table 2 Pathak & Choppin (2006c) reported the enthalpy of reaction for U(VI) as $\Delta_r H_m$ = (8.3 ± 0.7) kJ·mol^{-1}. A re-evaluation in the present review by least squares fits of the experimental data given in Table 1 of Pathak & Choppin (2006c) resulted in $\log_{10}\beta_1$ (25°C) = (6.88 ± 0.02) and $\Delta_r H_m$ = (8.8 ± 0.7) kJ·mol^{-1} (1 σ) (Fig. 8.12). Within the statistical uncertainties these re-evaluated values are identical with the values published by Pathak & Choppin (2006c).

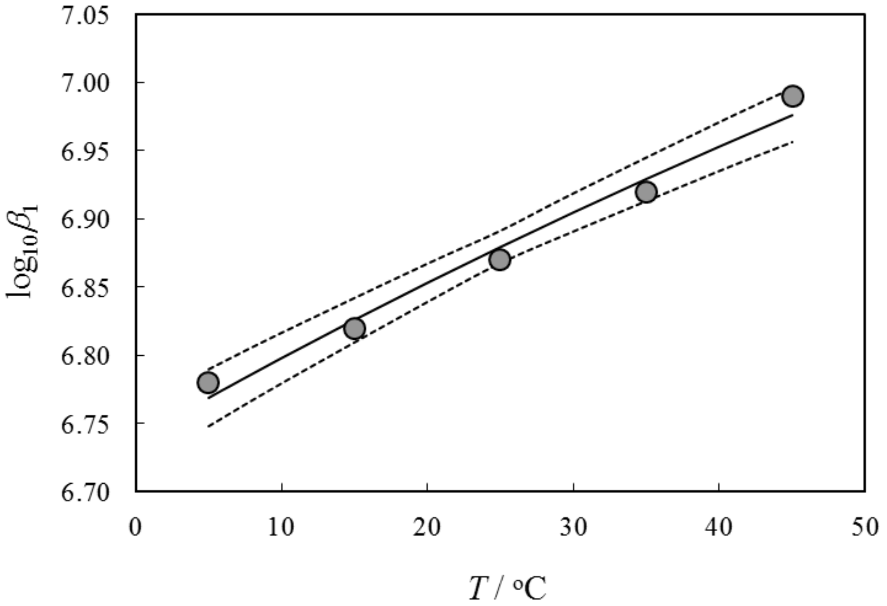

Fig. 8.12: Temperature dependence of the stability constant for the equilibrium UO_2^{2+} + $SiO(OH)_3^-$ ⇔ $UO_2SiO(OH)_3^+$. Data taken from Table 1 in Pathak & Choppin (2006c). An unweighted least squares fit gives: $\log_{10}\beta_1$ (25°C) = (6.88 ± 0.02) and $\Delta_r H_m$ = (8.8 ± 0.7) kJ·mol^{-1} (1 σ). The dotted lines are the 1 σ standard deviations extrapolated from 25°C to lower and higher temperatures.

Hence, the value $\Delta_r H_m$ = (8.3 ± 2.0) kJ·mol^{-1} (2 σ) is included as supplemental data in our database.

Considering the discussion of Yusov & Fedoseev (2005) about possible reasons for the observed discrepancies in reported equilibrium constants there seems no convincing argument to exclude any value given in Table 8.3, despite the variation of more than one order of magnitude. Furthermore, there is no good argument for any weighting scheme and thus, an unweighted average of the values in Table 8.3 was calculated: $\log_{10}\beta_1°$ = (7.8 ± 0.4).

8.4.8.2 Solid uranium silicates

Guillaumont et al. (2003) discuss solubility data for a number of solid U(VI) silicates, i.e. $(UO_2)_2SiO_4\cdot 2H_2O$ (soddyite), $Ca(UO_2)_2(SiO_3OH)_2\cdot 5H_2O$ (uranophane), $Na(UO_2)(SiO_3OH)\cdot 2H_2O$ (sodium boltwoodite) and $Na_2(UO_2)_2(Si2O_5)_3\cdot 4H_2O$ (sodium weeksite).

In all cases, no solubility constant was included in their tables of selected values.

In the case of soddyite, Guillaumont et al. (2003) conclude "in view of the non-concordant solubility constants (of two studies), this review does not recommend a value, but suggests that the average value … with increased uncertainty … may be used as a guideline until it has been confirmed. The estimated uncertainty covers the uncertainty ranges of the two studies."

For the other three U(VI) silicates, Guillaumont et al. (2003) also provide solubility constants with the proviso "for reasons discussed in Appendix A concerning the purity of the phases and the calculations, and the fact that the solutions are probably supersaturated with respect to silica, these values are not selected, but can be used in scoping calculations."

All four solubility constants given in the text of Guillaumont et al. (2003, p. 254–257) are included as supplemental data in our database (Table 8.6).

Coffinite, $USiO_4(s)$, 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, $UO_2(s)$, and auxiliary minerals. Coffinite minerals have been synthesized 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 $UO_2(s)$ and $SiO_2(s)$. Therefore, it is very difficult to determine thermodynamic data for pure coffinite experimentally.

Langmuir (1978) proposed an estimation procedure where he assumed an average aqueous silica concentration of 10^{-3} M (60 ppm as SiO_2) for the coffinite–uraninite equilibrium

$$USiO_4(s) + 2\,H_2O(l) \Leftrightarrow UO_2(s) + Si(OH)_4(aq)$$

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

$$\log_{10}K^\circ(298.15\text{ K}) = -3.0$$

In order to derive from this equilibrium a solubility constant for coffinite a further assumption has to be made about the nature of the involved U(IV) oxide and its associated solubility constant. Following the discussion in Guillaumont et al. (2003) about the solubility of U(IV) oxide this review chose $UO_2(am,hyd)$ as the appropriate solid and the solubility constant $\log_{10}K_{s,0}^\circ = (1.5 \pm 1.0)$ given by Guillaumont et al. (2003) for the equilibrium

$$UO_2(am,hyd) + 4\,H^+ \Leftrightarrow U^{4+} + 2\,H_2O$$

Combining this solubility equilibrium with the above described $USiO_4(s)$–$UO_2(s)$ equilibrium this review obtained for the solubility equilibrium

$$USiO_4(s) + 4\,H^+ \Leftrightarrow U^{4+} + Si(OH)_4(aq)$$

the new equilibrium constant $\log_{10}K_{s,0}^\circ = -(1.5 \pm 1.0)$ which is included as supplemental data in our database.

8.4.9 Neptunium and plutonium

Silicate complexation of neptunium and plutonium often has been studied using the same experimental methods by the same groups and hence, they are discussed together in this section.

No information about aqueous Np(III) and Pu(III) silicate complexes could be found in the literature during the present review. On the other hand, silicate complexation with Eu(III), Am(III) and Cm(III) is well established (see section 8.4.5) and these elements are considered as reasonably good chemical analogues for Pu(III) and Np(III). Therefore, we included the values

$$\log_{10}\beta_1° = (8.1 \pm 0.4) \text{ and } \Delta_r H_m° \approx 15 \text{ kJ}\cdot\text{mol}^{-1}$$

as estimates (supplemental data) in our database for the equilibria

$$Np^{3+} + SiO(OH)_3^- \Leftrightarrow NpSiO(OH)_3^{2+}$$

$$Pu^{3+} + SiO(OH)_3^- \Leftrightarrow PuSiO(OH)_3^{2+}$$

The first paper reporting experimental data on Pu(IV) silicate complexation was published by Pazukhin et al. (1990). The system Pu(IV) nitrate–sodium silicate was studied by potentiometric and spectrophotometric methods. Addition of sodium silicate to a Pu(IV) solution is proposed to form a complex in which the mole ratio Pu:silicate is 1:8 at pH 1.36. The authors report a value $K = 5$. However, the equilibrium this value refers to and the stoichiometry of the complex are not defined in the paper. Shilov & Fedoseev (2003) later comment on this paper: "we think that the authors dealt with colloid solutions in which Pu(IV) was sorbed on polysilicic acid particles". The paper of Pazukhin et al. (1990) is not considered further in this review.

Yusov et al. (2004) studied the hydrolysis and interaction of Np(IV) and Pu(IV) with orthosilicic acid, $Si(OH)_4(aq)$, in 0.1–1.0 M $(H,Na)ClO_4$ solutions. Spectrophotometry was used to study the reactions at about 10^{-4} M Np(IV) and Pu(IV) concentrations. Formation of the complexes $NpSiO(OH)_3^{3+}$ and $PuSiO(OH)_3^{3+}$ is demonstrated in the presence of 0.005–0.016 M $Si(OH)_4(aq)$ in the $p[H^+]$ range 1.0–2.2 and 0.3–1.4, respectively. Equilibrium constants at different ionic strengths are given in Table 2 of Yusov et al. (2004). From these data this review calculated by SIT analysis (Fig. 8.13)

$$\log_{10}K° = (1.34 \pm 0.18) \text{ and } \Delta\varepsilon = -(0.29 \pm 0.29) \text{ kg}\cdot\text{mol}^{-1}$$

for the reaction

$$Np^{4+} + Si(OH)_4(aq) \Leftrightarrow NpSiO(OH)_3^{3+} + H^+$$

Using $\varepsilon(Np^{4+}, ClO_4^-) = (0.84 \pm 0.06)$ kg·mol^{-1} (Guillaumont et al. 2003), $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$ kg·mol^{-1} (Grenthe et al. 1992) and $\varepsilon(SiO(OH)_4(aq), NaClO_4) = \varepsilon(SiO(OH)_4(aq), NaCl) = (0.10 \pm 0.05)$ kg·mol^{-1} derived in this review we calculate

$$\varepsilon(NpSiO(OH)_3^{3+}, ClO_4^-) = (0.51 \pm 0.30) \text{ kg}\cdot\text{mol}^{-1}.$$

Likewise, from the data given in Table 2 of Yusov et al. (2004) this review calculated by SIT analysis (Fig. 8.13)

$$\log_{10}K° = (2.07 \pm 0.18) \text{ and } \Delta\varepsilon = -(0.16 \pm 0.27) \text{ kg}\cdot\text{mol}^{-1}$$

for the reaction

$$Pu^{4+} + Si(OH)_4(aq) \Leftrightarrow PuSiO(OH)_3^{3+} + H^+$$

Using $\varepsilon(Pu^{4+}, ClO_4^-) = (0.82 \pm 0.07)$ kg·mol^{-1} (Guillaumont et al. 2003), and the other values as above we calculate

$$\varepsilon(PuSiO(OH)_3^{3+}, ClO_4^-) = (0.62 \pm 0.28) \text{ kg}\cdot\text{mol}^{-1}.$$

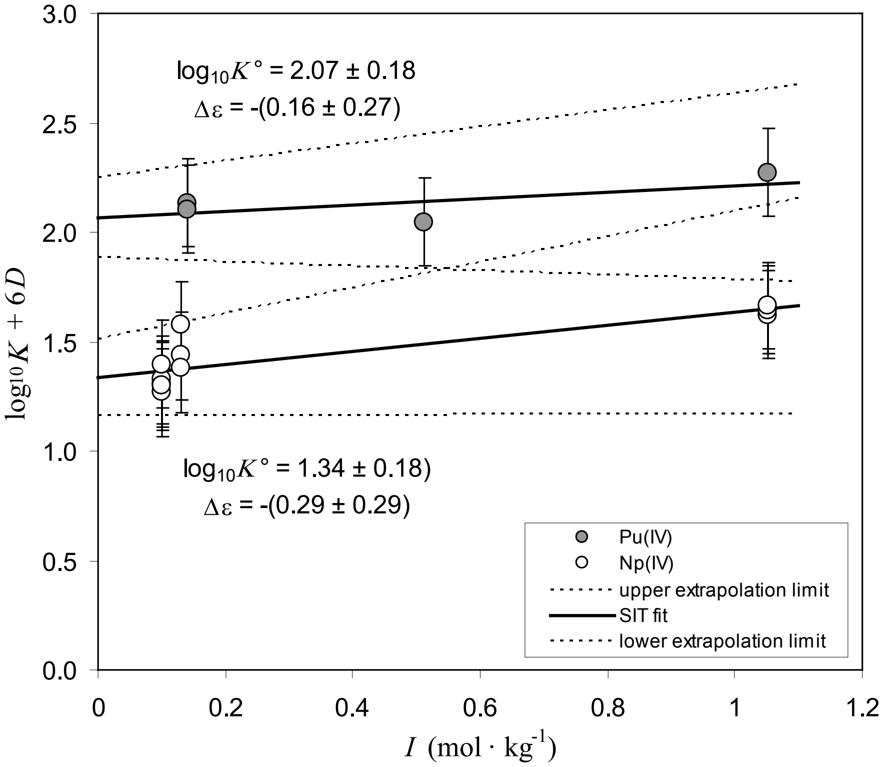

Fig. 8.13: SIT analysis of the equilibrium $An^{4+} + Si(OH)_4(aq) \Leftrightarrow AnSiO(OH)_3^{3+} + H^+$ where An is Np(IV) or Pu(IV). The experimental data are taken from Yusov et al. (2004).

For the reactions

$$Np^{4+} + SiO(OH)_3^- \Leftrightarrow NpSiO(OH)_3^{3+}$$

$$Pu^{4+} + SiO(OH)_3^- \Leftrightarrow PuSiO(OH)_3^{3+}$$

this review calculated $\log_{10}\beta_1° = (11.15 \pm 0.18)$ for Np(IV) and $\log_{10}\beta_1° = (11.88 \pm 0.18)$ for Pu(IV) using $\log_{10}\beta_1° = (9.81 \pm 0.02)$ for $SiO(OH)_3^- + H^+ \Leftrightarrow Si(OH)_4(aq)$ as ancillary data.

The values estimated by Yusov et al. (2004), $\log_{10}\beta_1° = 11.2$ for Np(IV) and $\log_{10}\beta_1° = 11.8$ for Pu(IV), are consistent with the SIT analysis in this review. Because no independent confirmation of these results is yet available the values estimated by Yusov et al. (2004) were included in our data base as "supplemental data".

Shilov & Fedoseev (2003) studied radiometrically the solubility of hydrated Pu(IV) oxide in 0.09–0.9 M NaOH containing 0.01–1 M Na_2SiO_3 and in 0.1–0.2 M $NaClO_4$ containing 0.01–0.09 M Na_2SiO_3 (pH 11 and 9). They stated that the experimental log-log dependence of the Pu(IV) solubility in 0.90 and 0.09 M NaOH (pH 13.8 an 12.8) on the silicate concentration "is almost linear" and interpreted these data in terms of the equilibrium

$$Pu(IV) + n\ SiO_3^{2-} \Leftrightarrow Pu^{IV}(SiO_3^{2-})_n$$

with n = 0.7 and 1.2, respectively. They further stated that "although the plutonium solubility at pH 11 also increased with increasing Na_2SiO_3 concentration, strong scattering of the experimental points was observed. At pH 9, the solubility was almost independent of the Na_2SiO_3 concentration".

A plot of all experimental data published in Table 2 (after filtration) of Shilov & Fedoseev (2003) shows (Fig. 8.14) that “almost linear” in the cases pH 13.8 and 12.8 and “almost independent” at pH 9 are euphemisms.

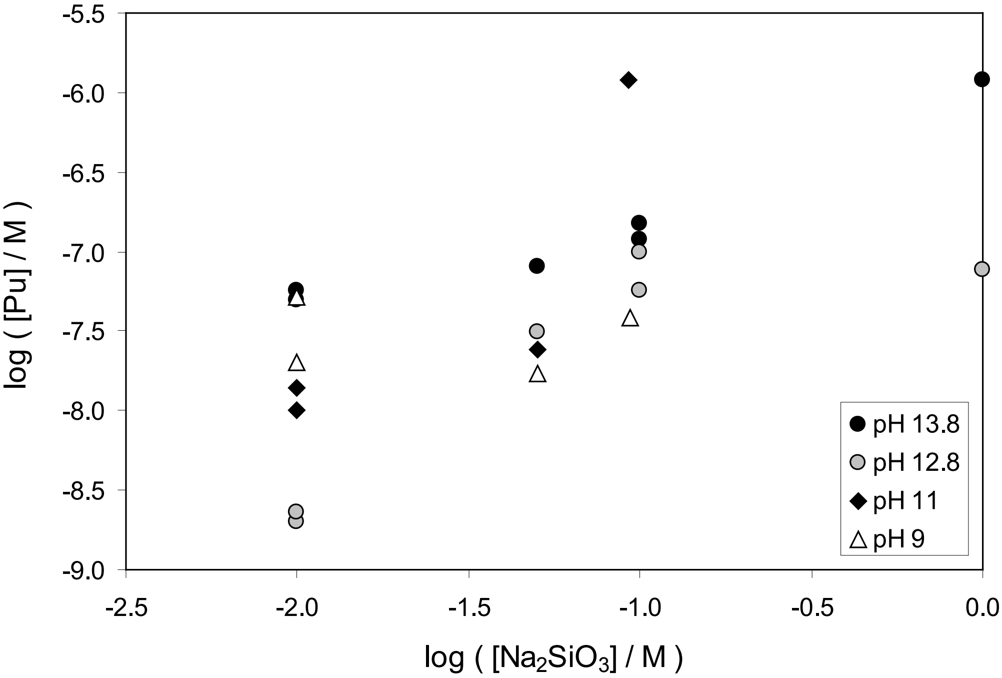

Fig. 8.14: Plutonium(IV) concentration in Na_2SiO_3 solution after filtration at different pH values. Data taken from Table 2 of Shilov & Fedoseev (2003).

The data at 0.01 M Na_2SiO_3 concentration do not show any systematic pH dependence, and the log mean value of the measured Pu(IV) concentrations is -(7.8 ± 0.5). This is the same value as measured without addition of Na_2SiO_3 (-7.9 ± 0.5, derived from Table 1 in Shilov & Fedoseev 2003). With increasing Na_2SiO_3 concentration there seems to be a systematic increase in measured Pu concentrations, which could be due to Pu silicate complex formation. However, the scatter and some erratic data points (Fig. 8.14) prevent any meaningful interpretation of these data in terms of a simple thermodynamic equilibrium.

Pathak & Choppin (2007) studied the complexation behavior of NpO_2^+ with silicic acid using solvent extraction at ionic strengths varying from 0.10 to 1.00 M $NaClO_4$ at $p[H^+]$ (3.68 ± 0.08) and 25°C. The stability constant value for the 1:1 complex

$$NpO_2^+ + SiO(OH)_3^- \Leftrightarrow NpO_2SiO(OH)_3(aq)$$

was found to decrease with increase in ionic strength. The values have been fitted in the SIT model expression and the results obtained by the authors are

$$\log_{10}\beta_1° = (7.04 \pm 0.02) \text{ and } \Delta\varepsilon = (0.14 \pm 0.03) \text{ kg·mol}^{-1}.$$

Using $\varepsilon(NpO_2^+, ClO_4^-) = (0.25 \pm 0.05)$ kg·mol^{-1} (Guillaumont et al. 2003) and $\varepsilon(SiO(OH)_3^-, Na^+) = (0.02 \pm 0.05)$ kg·mol^{-1} derived in this review we calculate

$$\varepsilon(NpO_2SiO(OH)_3(aq), NaClO_4) = (0.41 \pm 0.06) \text{ kg·mol}^{-1}.$$

Compared with stability constants for the analogous U(VI), Np(VI) and Pu(VI) silicate complexes (Table 8.6) the stability constant obtained by Pathak & Choppin (2007) seems exceptionally high. Also the SIT coefficient derived for the neutral species $NpO_2SiO(OH)_3(aq)$ seems a bit high.

According to a speciation diagram given by Pathak & Choppin (2007) for 1×10^{-3} M silicate and 1×10^{-4} M carbonate the species $NpO_2SiO(OH)_3(aq)$ predominates, at least up to pH 8. On the other hand, Shilov et al. (2003) who also attempted to study the complex formation of Np(V) with silicate ions could not detect any interaction of Np(V) with silicate at pH 10.3. They found only the complex $NpO_2CO_3^-$ by spectrophotometry and state that "the presence of this complex is caused by an impurity of dissolved CO_2; … under the conditions studied, only Np(V) carbonate and hydroxide complexes were revealed".

Considering this conflicting evidence about the complexation strength of Np(V) silicate we included the value obtained by Pathak & Choppin (2007) as supplemental data ($\log_{10}\beta_1° = 7.0$) in our data base.

Yusov & Fedoseev (2003) studied the reaction of Pu(VI) with orthosilicic acid (at concentrations 0.004–0.025 $mol\cdot dm^{-3}$) in a 0.2 M $NaClO_4$ solution at pH 3–8 by spectrophotometry.

Data in the pH range 4.5–5.5 were interpreted by the authors in terms of the equilibrium

$$PuO_2^{2+} + Si(OH)_4(aq) \Leftrightarrow PuO_2SiO(OH)_3^+ + H^+$$

with $\log_{10}K_1 = -(3.91 \pm 0.17)$. They combined this value obtained at $I = 0.2$ M $NaClO_4$ with $\log_{10}\beta_1° = -(9.81 \pm 0.02)$ for $Si(OH)_4(aq) \Leftrightarrow SiO(OH)_3^- + H^+$ at $I = 0$ and reported $\log_{10}\beta_1 = 5.90$ for

$$PuO_2^{2+} + SiO(OH)_3^- \Leftrightarrow PuO_2SiO(OH)_3^+$$

This erroneous value was later corrected (without any comment) to $\log_{10}\beta_1° = (6.17 \pm 0.17)$ (Yusov et al. 2005).

"For comparison with the spectrophotometric data, we (Yusov & Fedoseev 2003) performed the experiment on estimation of the stability constant of the Pu(VI) complex with $OSi(OH)_3^-$ by the potentiometric method like Pokrovski et al. (1996) studied the Al(III) complexes with $OSi(OH)_3^-$." They obtained $\log_{10}K_1 = -3.53$ and -3.71 in two experiments in a 0.207 M $NaClO_4$ solution (which gives $\log_{10}\beta_1° = 6.55$ and 6.37, respectively) and state "though these values somewhat exceed the values of the constants obtained from spectrophotometric data, they show reasonable agreement with them."

Considering that (a) these values are considerably lower than the stability constants obtained for the analogous U(VI) and Np(VI) complexes, (b) this is the only study reporting Pu(VI) complexation data and (c) the authors seem to trust their spectrophotometric data more than their potentiometric "estimation", we decided to include a value of $\log_{10}\beta_1° \approx 6$ as supplemental data in our database.

At pH > 5.5 Yusov & Fedoseev (2003) interpreted their spectrophotometric data in terms of the formation of either $PuO_2SiO_2(OH)_2(aq)$ or $PuO_2(OH)SiO(OH)_3(aq)$. Since the formation of these complexes differs just by the absence or presence of one water molecule and hence, the equilibrium constant should be the same, it is unclear why Yusov & Fedoseev (2003) report $\log_{10}\beta_2 \approx 12.6$ for

$$PuO_2^{2+} + SiO_2(OH)_2^{2-} \Leftrightarrow PuO_2SiO_2(OH)_2(aq)$$

but $\log_{10}\beta_2 \approx 13$ for

$$PuO_2^{2+} + SiO_2(OH)_2^{2-} + H_2O \Leftrightarrow PuO_2(OH)SiO(OH)_3(aq).$$

The first value (≈12.6) is obtained with the same mix of data at $I = 0.2$ M and $I = 0$ as above and thus should be ≈12.9. The derivation of the second value (≈13) is unclear. Nevertheless, the value ≈12.6, as given in the abstract of Yusov & Fedoseev (2003), is included as a "placeholder" in our database.

Shilov et al. (2004) studied the complexation of Np(VI) in silicate solutions in the presence of carbonate at pH 10.5–12.0 by spectrophotometry. The authors conclude from optical density data the occurrence of a fast competition reaction between carbonate and silicate

$$NpO_2(CO_3)_3^{4-} + SiO_3^{2-} \Leftrightarrow NpO_2SiO_3(aq) + 3\ CO_3^{2-}$$

and reported $\log_{10}\beta = 16.5$ at pH 10.13 in 0.1 M $NaClO_4$ solution for the equilibrium

$$NpO_2^{2+} + SiO_3^{2-} \Leftrightarrow NpO_2SiO_3(aq)$$

In order to obtain this value they used $\log_{10}\beta_3 = 20.41$ ($I = 0.1$) for the equilibrium $NpO_2^{2+} + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{4-}$, which is one order of magnitude at variance with the value selected in our database ($\log_{10}\beta_3 = 19.04$ at $I = 0.1$). In addition, while their dissociation constants of carbonic acid are almost identical with our values, the cumulative dissociation constant of "metasilicic acid" taken from a Russian "Chemist's Handbook", $\log_{10}\beta_2° = -21.45$, is two orders of magnitude different from our established value $\log_{10}\beta_2° = -(23.14 \pm 0.09)$. It is not clear what "dissociation constants of metasilicic acid" means, as Shilov et al. (2004) write in the introductory part of their paper about "silicate solutions in which both metasilicate SiO_3^{2-} and orthosilicate SiO_4^{4-} ions (and protonated species of the latter) can exist."

Hence, the value $\log_{10}\beta = 16.5$ might be grossly wrong but it is the only one reported so far for Np(VI) complexation with silicic acid at high pH, and thus the value $\log_{10}\beta \approx 16.5$ is included for the equilibrium $NpO_2^{2+} + SiO_2(OH)_2^{2-} \Leftrightarrow NpO_2SiO_2(OH)_2(aq)$ as a "placeholder" in our database.

In the last paper of this series, Yusov et al. (2005) studied the complexation of Np(VI) in silicate solutions in the acid and neutral pH range by spectrophotometry. The interaction at pH < 4.5 is described by the equilibrium

$$NpO_2^{2+} + Si(OH)_4(aq) \Leftrightarrow NpO_2SiO(OH)_3^{+} + H^{+}$$

with $\log_{10}K_1 = -(2.88 \pm 0.12)$ at ionic strength $I = 0.1–0.2$ ($\log_{10}K_1° = -(2.61 \pm 0.12)$ recalculated to $I = 0$). Using the dissociation constant $\log_{10}\beta_1° = -(9.81 \pm 0.02)$ for $Si(OH)_4(aq) \Leftrightarrow SiO(OH)_3^{-} + H^{+}$ the authors obtained $\log_{10}\beta_1 = (7.20 \pm 0.12)$ for

$$NpO_2^{2+} + SiO(OH)_3^{-} \Leftrightarrow NpO_2SiO(OH)_3^{+}$$

The value $\log_{10}\beta_1 = 7.2$ is included in our database as supplemental data.

Yusov et al. (2005) further write: "We attempted to reveal the neutral complex with monomeric silicic acid, $NpO_2SiO_2(OH)_2(aq)$. However, in the solution containing 4.5×10^{-4} M Np(VI) and 0.002 M $Si(OH)_4$ [at such concentration, $Si(OH)_4$ does not polymerize] and pH ≈ 7.5, we failed to detect the complexation because of the strong effect of the hydrolysis." This result sheds doubts on results reported earlier by the same group (Yusov & Fedoseev 2003) for $PuO_2SiO_2(OH)_2(aq)$ at pH > 5.5 using the same experimental set-up (see above). The hydrolysis effects of Np(VI) and Pu(VI) are rather similar, and the stability constants reported for Np(VI)-silicate complexes are even higher than for Pu(VI). So why should hydrolysis prevent the detection of a $NpO_2SiO_2(OH)_2(aq)$ complex, while under very similar conditions a stability constant for the (perhaps weaker?) $PuO_2SiO_2(OH)_2(aq)$ complex was reported?

The discussion in Yusov et al. (2005) becomes even stranger in the section "Regular trends in interaction of actinide ions with silicate ions in the series U(VI)–Np(VI)–Pu(VI)": "As we reported (Shilov et al. 2004), at pH > 10 Np(VI) forms the silicate complex $NpO_2SiO_3(aq)$ with the stability constant $\log_{10}\beta$ = 16.5 (I = 0.1). … Similar experiments with Pu(VI) gave an appreciably lower value: $\log_{10}\beta$ = 14.4, which is close to the stability constant of the Pu(VI) complex with another double-charged anion, $SiO_2(OH)_2^{2-}$, arising at pH ≈ 7: $\log_{10}\beta$ = 12.6 (I = 0.2) (Yusov & Fedoseev 2003)."

The value $\log_{10}\beta$ = 14.4 for a complex $PuO_2SiO_3(aq)$ appears here out of the blue, without any further comment or reference. And the authors seem to be convinced that SiO_3^{2-} and $SiO_2(OH)_2^{2-}$ are structurally different anions really existing in silicate solutions and forming metal-silicate complexes with rather different stabilities. However, there is no indication of a ligand SiO_3^{2-} existing in aqueous solution where silicon is coordinated to just three oxygen atoms (like in CO_3^{2-}) instead of four as in $SiO_2(OH)_2^{2-}$. Sometimes in the chemical thermodynamic literature SiO_3^{2-} is used as an alternative expression to $SiO_2(OH)_2^{2-}$ where formally one H_2O is "subtracted". The stability constants for equilibria formulated with these alternative expressions are the same, only $\Delta_f G_m$ values derived therefrom are different because of the inclusion or exclusion of the formal H_2O. Hence, the value $\log_{10}\beta$ = 14.4 referring to "$PuO_2SiO_3(aq)$" is not considered in our database.

Table 8.4: Silicon and silicate data selected by NEA (Grenthe et al. 1992; Brown et al. 2005; Gamsjäger et al. 2005; Rand et al. 2008) but not included in TDB Version 12/07. For explanations see text.

Gases	$Si(g)$, $SiF_4(g)$
Solids	$Ni_2SiO_4(cr)$, $ZrSiO_4(cr)$, $Ca_2ZrSi_3O_{12}(cr)$, $Ca_3ZrSi_2O_9(cr)$, $Sr_6ZrSi_5O_{18}(cr)$, $SrZrSi_2O_7(cr)$, $Na_2ZrSiO_5(cr)$, $Na_2ZrSi_2O_7(cr)$, $Na_4Zr_2Si_3O_{12}(cr)$, $Na_2ZrSi_3O_9\cdot 2H_2O(cr)$, $Na_2ZrSi_4O_{11}(cr)$, $Na_2ZrSi_6O_{15}\cdot 3H_2O(cr)$, $Cs_2ZrSi_2O_7(cr)$, $ThSiO_4$(huttonite), $ThSiO_4$(thorite),
Aqueous species	$Si_2O_3(OH)_4^{2-}$, $Si_2O_2(OH)_5^{-}$, $Si_3O_6(OH)_3^{3-}$, $Si_3O_5(OH)_5^{3-}$, $Si_4O_7(OH)_5^{3-}$

8.5 Summary

A graphical summary of aqueous silica species and metal silicate complexes finally included in the PSI/Nagra TDB 12/07 is shown in Table 8.5.

The monomeric aqueous silica species are well established and cover the entire pH range of interest for modelling in aquatic chemistry. The experimentally determined solubility of amorphous silica, $SiO_2(am)$, can be reproduced sufficiently well up to pH 11 by including a single polymeric silica species, $Si_4O_8(OH)_4^{4-}$, in the model (see Section 8.3.2).

Aqueous metal silicate complexes of the type $MSiO(OH)_3^{(n-1)}$ are known for a number of metal cations M^{n+} (Table 8.7). However, most of them have been studied in acidic solutions at pH < 5 and their range of predominance generally is restricted to pH < 7.

Aqueous metal silicate complexes of the type $MSiO_2(OH)_2^{(n-2)}$, predominating in the neutral pH range (5–9), have been reported for Ca^{2+} and Mg^{2+} (Santschi & Schindler 1974), and PuO_2^{2+} (Yusov & Fedoseev 2003). However, the species $PuO_2SiO_2(OH)_2(aq)$, as well as $NpO_2SiO_2(OH)_2(aq)$ claimed to be found in alkaline solutions (pH 10.5–12) (Shilov et al. 2004), are included as "placeholders" only in our TDB as the reported evidence for their formation is contradictory and needs confirmation. The species $Th(OH)_3(SiO(OH)_3)_3^{2-}$ has been proposed (Rai et al. 2008) to interpret a solubility study of $ThO_2(am)$ in alkaline silica solutions (pH 10–13.3). This species also needs confirmation.

The fate of the species $Al(OH)_3SiO(OH)_3^-$ is a special case. This species has been proposed in an extended abstract (Pokrovski et al. 1998) to interpret (not yet published) experimental data in the alkaline region, 9 < pH < 13. We decided to include this complex in the previous version of our database (Nagra/PSI TDB 01/01) as guideline for modellers. In a later paper from the same group (Gout et al. 2000) the authors implicitly retracted the complex $Al(OH)_3SiO(OH)_3^-$. Consequently, we removed this complex and its stability constant from our data base.

In summary, the complex $AlSiO(OH)_3^{2+}$ is fairly well established in acidic solutions, but as it predominates at pH < 5 it is of little importance for groundwater modelling. The complex $SiAlO_3(OH)_4^{3-}$ was identified in "ultra basic solutions" at pH about 14 (Gout et al. 2000); it may hardly be of any importance in environmental modelling. In neutral to basic solutions there is qualitative evidence of polynuclear Al–Si complexes but no quantitative data are available.

Table 8.5: Aqueous silica species and metal silicate complexes in the PSI/Nagra TDB 12/07. The positions of the formulae indicate the pH range of their experimental determination and/or their supposed predominance. Species with supplemental data are in italics, strikethrough indicates removal of the species.

	acidic pH < 5	neutral 5–9	alkaline 9–13	hyperalkaline > 13
H^+		$Si(OH)_4(aq)$	$SiO(OH)_3^-$ $Si_4O_8(OH)_4^{4-}$	$SiO_2(OH)_2^{2-}$
Ca^{2+}	$CaSiO(OH)_3^+$	$CaSiO_2(OH)_2(aq)$		
Mg^{2+}	$MgSiO(OH)_3^+$	$MgSiO_2(OH)_2(aq)$		
Fe^{2+}				
Ni^{2+}	*$NiSiO(OH)_3^+$*			
Al^{3+}	$AlSiO(OH)_3^{2+}$		~~*$Al(OH)_3SiO(OH)_3^-$*~~	*$AlSiO_3(OH)_4^{3-}$*
Fe^{3+}	$FeSiO(OH)_3^{2+}$			
Eu^{3+}	$EuSiO(OH)_3^{2+}$			
Np^{3+}	*$NpSiO(OH)_3^{2+}$*			
Pu^{3+}	*$PuSiO(OH)_3^{2+}$*			
Am^{3+}	$AmSiO(OH)_3^{2+}$			
Cm^{3+}	$CmSiO(OH)_3^{2+}$			
Th^{4+}			*$Th(OH)_3(SiO(OH)_3)_3^{2-}$*	
U^{4+}				
Np^{4+}	*$NpSiO(OH)_3^{3+}$*			
Pu^{4+}	*$PuSiO(OH)_3^{3+}$*			
NpO_2^+	*$NpO_2SiO(OH)_3(aq)$*			
PuO_2^+				
UO_2^{2+}	$UO_2SiO(OH)_3^+$			
NpO_2^{2+}	*$NpO_2SiO(OH)_3^+$*		*$NpO_2SiO_2(OH)_2(aq)$*	
PuO_2^{2+}	*$PuO_2SiO(OH)_3^+$*	*$PuO_2SiO_2(OH)_2(aq)$*		

Table 8.6: Selected silica and silicate data. Core data are bold and supplemental data in italics. New or changed data with respect to TDB Version 01/01 (Hummel et al. 2002) are shaded.

	TDB Version 01/01				TDB Version 12/07				
Name	$\Delta_f G_m°$ [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}]	$\Delta_f G_m°$ [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}]	**Species**
Si(cr)	0.0	0.0	**18.810 ± 0.08**	**19.789 ± 0.030**	0.0	0.0	**18.810 ± 0.08**	**19.789 ± 0.030**	Si(cr)
Quartz	**-856.287 ± 1.0**	**-910.700 ± 1.0**	**41.460 ± 0.20**	**44.602 ± 0.30**	**-856.287 ± 1.0**	**-910.700 ± 1.0**	**41.460 ± 0.20**	**44.602 ± 0.30**	Quartz
Si(OH)4	-1309.183	-1461.723	178.851	237.370	-1309.183 ± 1.1	-1461.723 ± 1.1	178.851 ± 2.2	237.370	$Si(OH)_4(aq)$

	TDB Version 01/01		TDB Version 12/07		
Name	$\log_{10}\beta°$	$\Delta_r H_m°$ [kJ·mol^{-1}]	$\log_{10}\beta°$	$\Delta_r H_m°$ [kJ·mol^{-1}]	**Reaction**
SiO(OH)3-	-9.81 ± 0.02	25.6 ± 2.0	-9.81 ± 0.02	25.6 ± 2.0	$Si(OH)_4(aq) \Leftrightarrow SiO(OH)_3^- + H^+$
SiO2(OH)2-2	-23.14 ± 0.09	75 ± 15	-23.14 ± 0.09	75 ± 15	$Si(OH)_4(aq) \Leftrightarrow SiO_2(OH)_2^{2-} + 2\ H^+$
Si4O8(OH)4-4	-	-	-36.3 ± 0.2	-	$4\ Si(OH)_4(aq) \Leftrightarrow Si_4O_8(OH)_4^{4-} + 4\ H^+ + 4\ H_2O(l)$
CaSiO(OH)3+	1.2 ± 0.1	-	1.2 ± 0.1	-	$Ca^{2+} + SiO(OH)_3^- \Leftrightarrow CaSiO(OH)_3^+$
CaSiO2(OH)2	4.6 ± 0.2	-	4.6 ± 0.2	-	$Ca^{2+} + SiO_2(OH)_2^{2-} \Leftrightarrow CaSiO_2(OH)_2(aq)$
MgSiO(OH)3+	1.5 ± 0.2	-	1.5 ± 0.2	-	$Mg^{2+} + SiO(OH)_3^- \Leftrightarrow MgSiO(OH)_3^+$
MgSiO2(OH)2	5.7 ± 0.2	-	5.7 ± 0.2	-	$Mg^{2+} + SiO_2(OH)_2^{2-} \Leftrightarrow MgSiO_2(OH)_2(aq)$
NiSiO(OH)3+	-	-	*6.3*	-	*$Ni^{2+} + SiO(OH)_3^- \Leftrightarrow NiSiO(OH)_3^+$*
AlSiO(OH)3+2	7.4 ± 0.2	-	7.4 ± 0.1	41.0 ± 3.0	$Al^{3+} + SiO(OH)_3^- \Leftrightarrow AlSiO(OH)_3^{2+}$
Al(OH)6SiO-	3.6 ± 0.2	-	-	-	$Al(OH)_4^- + Si(OH)_4(aq) \Leftrightarrow Al(OH)_3SiO(OH)_3^- + H_2O(l)$
AlSiO3(OH)4-3	-	-	*0.53*	-	*$Al(OH)_4^- + SiO_2(OH)_2^{2-} \Leftrightarrow AlSiO_3(OH)_4^{3-} + H_2O(l)$*
FeSiO(OH)3+2	9.7 ± 0.3	-	9.7 ± 0.3	-	$Fe^{3+} + SiO(OH)_3^- \Leftrightarrow FeSiO(OH)_3^{2+}$

	TDB Version 01/01		**TDB Version 12/07**		
Name	**$\log_{10}\beta^\circ$**	**$\Delta_r H_m^\circ$** [kJ·mol^{-1}]	**$\log_{10}\beta^\circ$**	**$\Delta_r H_m^\circ$** [kJ·mol^{-1}]	**Reaction**
EuSiO(OH)3+2	7.9 ± 0.2	-	8.1 ± 0.4	*14.5 ± 2.0*	$Eu^{3+} + SiO(OH)_3^- \Leftrightarrow EuSiO(OH)_3^{2+}$
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	-	8.1 ± 0.4	*15*	$Am^{3+} + SiO(OH)_3^- \Leftrightarrow AmSiO(OH)_3^{2+}$
CmSiO(OH)3+2	-	-	8.1 ± 0.4	*15.8 ± 4.0*	$Cm^{3+} + SiO(OH)_3^- \Leftrightarrow CmSiO(OH)_3^{2+}$
PuSiO(OH)3+2	-	-	*8.1 ± 0.4*	*15*	$Pu^{3+} + SiO(OH)_3^- \Leftrightarrow PuSiO(OH)_3^{2+}$
NpSiO(OH)3+2	-	-	*8.1 ± 0.4*	*15*	$Np^{3+} + SiO(OH)_3^- \Leftrightarrow NpSiO(OH)_3^{2+}$
UO2SiO(OH)3+	-	-	7.8 ± 0.4	*8.3 ± 2.0*	$UO_2^{2+} + SiO(OH)_3^- \Leftrightarrow UO_2SiO(OH)_3^+$
NpO2SiO(OH)3+	-	-	*7.2*	-	$NpO_2^{2+} + SiO(OH)_3^- \Leftrightarrow NpO_2SiO(OH)_3^+$
NpO2SiO2(OH)2	-	-	*≈16.5*	-	$NpO_2^{2+} + SiO_2(OH)_2^{2-} \Leftrightarrow NpO_2SiO_2(OH)_2(aq)$
PuO2SiO(OH)3+	-	-	*≈ 6*	-	$PuO_2^{2+} + SiO(OH)_3^- \Leftrightarrow PuO_2SiO(OH)_3^+$
PuO2SiO2(OH)2	-	-	*≈12.6*	-	$PuO_2^{2+} + SiO_2(OH)_2^{2-} \Leftrightarrow PuO_2SiO_2(OH)_2(aq)$
NpO2SiO(OH)3	-	-	*7.0*	-	$NpO_2^+ + SiO(OH)_3^- \Leftrightarrow NpO_2SiO(OH)_3(aq)$
NpSiO(OH)3+3	-	-	*11.2*	-	$Np^{4+} + SiO(OH)_3^- \Leftrightarrow NpSiO(OH)_3^{3+}$
PuSiO(OH)3+3	-	-	*11.8*	-	$Pu^{4+} + SiO(OH)_3^- \Leftrightarrow PuSiO(OH)_3^{3+}$
Th(OH)3(SiO(OH)3)3-2	-	-	*-27.8 ± 0.7*	-	$Th^{4+} + 3\ Si(OH)_4(aq) + 3\ H_2O(l) \Leftrightarrow Th(OH)_3(SiO(OH)_3)_3^{2-} + 6\ H^+$

	TDB Version 01/01		**TDB Version 12/07**		
Name	$\mathbf{log_{10}}\boldsymbol{K}_{\mathbf{s,0}}\mathbf{°}$	$\boldsymbol{\Delta_r H_m}\mathbf{°}$ [kJ·mol^{-1}]	$\mathbf{log_{10}}\boldsymbol{K}_{\mathbf{s,0}}\mathbf{°}$	$\boldsymbol{\Delta_r H_m}\mathbf{°}$ [kJ·mol^{-1}]	**Reaction**
Quartz	(-3.746)[a]	20.637	(-3.746)[a]	20.637	$SiO_2(cr) + 2\ H_2O(l) \Leftrightarrow Si(OH)_4(aq)$
SiO2(am)	(-2.714)[b]	14.594	(-2.714)[b]	14.594	$SiO_2(am) + 2\ H_2O(l) \Leftrightarrow Si(OH)_4(aq)$
Kaolinite	7.435	-147.7	7.435	-147.7	$Al_2Si_2O_5(OH)_4 + 6H^+ \Leftrightarrow 2\ Al^{3+} + 2\ Si(OH)_4(aq) + H_2O(l)$
Soddyite	-	-	*6.2 ± 1.0*	-	$(UO_2)_2SiO_4{\cdot}2H_2O(cr) + 4\ H^+ \Leftrightarrow 2\ UO_2^{2+} + Si(OH)_4(aq) + 2\ H_2O(l)$
Uranophane	-	-	*9.4 ± 0.5*	-	$Ca(H_3O)_2(UO_2)_2(SiO_4)_2{\cdot}3H_2O(cr) + 6\ H^+ \Leftrightarrow Ca^{2+} + 2\ UO_2^{2+} + 2\ Si(OH)_4(aq) + 5\ H_2O(l)$
Na-Boltwoodite	-	-	*> 5.8*	-	$Na(H_3O)UO_2SiO_4{\cdot}H_2O(cr) + 3\ H^+ \Leftrightarrow Na^+ + UO_2^{2+} + Si(OH)_4(aq) + 2\ H_2O(l)$
Na-Weeksite	-	-	*1.5 ± 0.1*	-	$Na_2(UO_2)_2(Si_2O_5)_3{\cdot}4H_2O(cr) + 6\ H^+ + 5\ H_2O(l) \Leftrightarrow 2\ Na^+ + 2\ UO_2^{2+} + 6\ Si(OH)_4(aq)$
USiO4(s)	(-3.0)[c]	-	*-1.5 ± 1.0*	-	$USiO_4(s) + 4\ H^+ \Leftrightarrow U^{4+} + Si(OH)_4(aq)$

[a] Temperature dependence of $\log_{10}K_{s,0}$ (Quartz, cr) = $-34.188 + 197.47 / T - 5.851{\cdot}10^{-6}\ T^2 + 12.245 \log_{10}T$

[b] Temperature dependence of $\log_{10}K_{s,0}$ (Silica, am) = $-8.476 - 485.24 / T - 2.268{\cdot}10^{-6}\ T^2 + 3.068 \log_{10}T$

[c] Based on ($\Delta_f G_m°$, $USiO_4$, s) = $-(1856.1 \pm 11.4)$ kJ·mol^{-1}

Table 8.7: Selected SIT ion interaction coefficients $\varepsilon_{j,k}$ [kg·mol^{-1}] for silicate species. All data included in TDB Version 12/07 are derived or estimated in this review. Own data estimates based on charge correlations (see Appendix A) are shaded. Supplemental data are in italics.

j k→ **↓**	**Cl$^-$** $\varepsilon_{j,k}$	**ClO$_4^-$** $\varepsilon_{j,k}$	**Na$^+$** $\varepsilon_{j,k}$	**K$^+$** $\varepsilon_{j,k}$	**NaCl** $\varepsilon_{j,k}$	**NaClO$_4$** $\varepsilon_{j,k}$
Si(OH)4	0	0	0	0	0.10 ± 0.05	0
SiO(OH)3-	0	0	0.02 ± 0.05	-	0	0
SiO2(OH)2-2	0	0	0.00 ± 0.08	-	0	0
Si4O8(OH)4-4	0	0	0.29 ± 0.17	-	0	0
CaSiO(OH)3+	0.05 ± 0.10	*0.3 ± 0.1*	0	0	0	0
CaSiO2(OH)2	0	0	0	0	0	*0.2 ± 0.2*
MgSiO(OH)3+	0.05 ± 0.10	*0.4 ± 0.2*	0	0	0	0
MgSiO2(OH)2	0	0	0	0	0	*0.2 ± 0.2*
NiSiO(OH)3+	*0.05 ± 0.10*	*0.57 ± 0.15*	*0*	*0*	*0*	*0*
AlSiO(OH)3+2	-0.30 ± 0.36	0	0	0	0	0
AlSiO3(OH)4-3	*0*	*0*	*-0.15 ± 0.10*	-	*0*	*0*
FeSiO(OH)3+2	0.15 ± 0.10	0.4 ± 0.1	0	0	0	0
EuSiO(OH)3+2	0.15 ± 0.10	0.58 ± 0.32	0	0	0	0
AmSiO(OH)3+2	0.15 ± 0.10	*0.55 ± 0.3*	0	0	0	0
CmSiO(OH)3+2	0.15 ± 0.10	0.55 ± 0.32	0	0	0	0
PuSiO(OH)3+2	*0.15 ± 0.10*	*0.55 ± 0.3*	*0*	*0*	*0*	*0*
NpSiO(OH)3+2	*0.15 ± 0.10*	*0.55 ± 0.3*	*0*	*0*	*0*	*0*
UO2SiO(OH)3+	0.05 ± 0.10	0.2 ± 0.1	0	0	0	0
NpO2SiO(OH)3+	*0.05 ± 0.10*	*0.2 ± 0.1*	*0*	*0*	*0*	*0*
NpO2SiO2(OH)2	*0*	*0*	*0*	*0*	*0*	*0.41 ± 0.06*
PuO2SiO(OH)3+	*0.05 ± 0.10*	*0.2 ± 0.1*	*0*	*0*	*0*	*0*
PuO2SiO2(OH)2	*0*	*0*	*0*	*0*	*0*	*0*
NpO2SiO(OH)3	*0*	*0*	*0*	*0*	*0*	*0*
NpSiO(OH)3+3	*0.25 ± 0.10*	*0.51 ± 0.30*	*0*	*0*	*0*	*0*
PuSiO(OH)3+3	*0.25 ± 0.10*	*0.62 ± 0.28*	*0*	*0*	*0*	*0*
Th(OH)3(SiO(OH)3)3-2	*0*	*0*	*-0.10 ± 0.10*	-	*0*	*0*

8.6 References

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9 Technetium

This report provides an update of the Nagra/PSI Thermochemical Database 01/01 (Hummel et al. 2002) with respect to technetium. All data for technetium in the Nagra/PSI TDB 01/01 were taken from OECD NEA's book "Chemical Thermodynamics of Technetium" by Rard et al. (1999). In the "Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium" by Guillaumont et al. (2003), all the literature on technetium was reviewed that was published between 1997 and the end of 2001. The update resulted in no changes in the values selected by Rard et al. (1999) and no new data were selected.

Therefore, the thermochemical data for technetium selected in the Nagra/PSI Chemical Thermodynamic Database 01/01 have been adopted for the PSI/Nagra Chemical Thermodynamic Database 12/07 without any changes, and the present report generally provides only minor textual revisions to Chapter 5.20 on technetium in Hummel et al. (2002).

Note, however, that not all recommended values by Rard et al. (1999) are included in our database since NEA reviews are not restricted to data relevant for radioactive waste management or even environmental modelling in general. Therefore, we tried to exclude from our database all the phases and complexes which most probably will never be relevant in environmental systems. They are all listed in Table 9.1.

The notation of formulae and symbols used in this chapter follows the NEA recommendations and practice.

9.1 Elemental technetium

The absolute entropy and heat capacity of Tc(cr) are given in Table 9.2 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.

9.2 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.

9.2.1 TcO_4^-

Recommended values of thermodynamic properties of TcO_4^- at 298.15 K are

$$\Delta_f G_m°(TcO_4^-, aq, 298.15\ K) = -(637.4 \pm 7.6)\ kJ\cdot mol^{-1}$$

$$\Delta_f H_m°(TcO_4^-, aq, 298.15\ K) = -(729.4 \pm 7.6)\ kJ\cdot mol^{-1}$$

$$S_m°(TcO_4^-, aq, 298.15\ K) = (199.6 \pm 1.5)\ J\cdot K^{-1}\cdot mol^{-1}$$

$$C_{p,m}°(TcO_4^-, aq, 298.15\ K) = -(15 \pm 8)\ J\cdot K^{-1}\cdot mol^{-1}$$

9.2.2 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 behavior of technetium. It will never be a stable oxidation state in aqueous equilibrium systems and is therefore not included in our database.

9.2.3 Tc(V)

Tc(V) is not a stable species as it decomposes further, and its consideration in chemical equilibrium calculations is thus not necessary.

9.2.4 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:

$$TcO_4^- + 4\,H^+ + 3\,e^- \Leftrightarrow TcO(OH)_2(aq) + H_2O(l)$$

$$E°(298.15\text{ K}) = (0.579 \pm 0.016)\text{ V}$$

$$\log_{10}K°(298.15\text{ K}) = (29.4 \pm 0.8)$$

9.2.5 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).

9.2.6 Tc^{2+}

There is no experimental evidence for the existence of Tc^{2+} as a viable chemical species in aqueous solution.

9.3 Oxide and hydrogen compounds and complexes

9.3.1 Aqueous species formed by hydrolysis and protonation reactions

9.3.1.1 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:

$$TcO(OH)_2(aq) + H^+ \Leftrightarrow TcO(OH)^+ + H_2O(l)$$

$$\log_{10}{}^*K^\circ(298.15\text{ K}) = (2.5 \pm 0.3)$$

$$TcO(OH)_2(aq) + 2\,H^+ \Leftrightarrow TcO^{2+} + 2\,H_2O(l)$$

$$\log_{10}{}^*K^\circ(298.15\text{ K}) < 4$$

$$TcO(OH)_2(aq) + H_2O(l) \Leftrightarrow TcO(OH)_3^- + H^+$$

$$\log_{10}{}^*K^\circ(298.15\text{ K}) = -(10.9 \pm 0.4)$$

9.3.1.2 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 Section 9.2.2).

9.3.2 Solid technetium oxides and their hydrates

$Tc_2O_7(cr)$: Tc(VII) oxide is hygroscopic and thus of no relevance for environmental systems and is therefore not included in our database.

$Tc_2O_7 \cdot xH_2O(s)$: 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 and is not included in our database.

$TcO_3(s)$: 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 $\Delta_f G_m^\circ$ 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:

$$TcO_2 \cdot 1.6H_2O(s) \Leftrightarrow TcO(OH)_2(aq) + 0.6\ H_2O(l)$$

$$\log_{10}K°(298.15\ K) = -(8.4 \pm 0.5)$$

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,

$$\Delta_f G_m°(TcO_2 \cdot 1.6H_2O,\ s,\ 298.15\ K) = -(758.5 \pm 8.4)\ kJ \cdot mol^{-1}$$

Rard et al. (1999) derived the recommended Gibbs energy of formation for the uncharged Tc(IV) hydrolysis species:

$$\Delta_f G_m°(TcO(OH)_2,\ aq,\ 298.15\ K) = -(568.2 \pm 8.8)\ kJ \cdot mol^{-1}$$

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 characterization. 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 $\Delta_f G_m°$ 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.

9.3.3 Gaseous technetium oxides

Gaseous technetium oxides are not relevant under environmental conditions and are therefore not included in our database.

9.3.4 Technetium hydrides

Binary and ternary technetium hydrides decompose under normal environmental conditions. No thermodynamic data are available for these compounds.

9.4 Halogen compounds and complexes

9.4.1 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.

Rard et al. (1999) recommended an equilibrium constant for the reaction TcF_6(cr, cubic) ⇔ TcF_6(g). Since $\Delta_f G_m°$ is not known for both phases, they cannot be related to any other technetium species or phases. In addition, this reaction is hardly relevant under environmental conditions. These fluoride phases are therefore not included in our database.

The same is true for TcO_3F(g) which is also not included in our database, all the more so as Rard et al. (1999) only recommended values for $S_m°$ and $C_{p,m}°$.

9.4.2 Chlorine, bromine and iodine compounds and complexes

TcO_3Cl(g) is not included in our database, since Rard et al. (1999) only recommended values for $S_m°$ and $C_{p,m}°$ and gaseous technetium compounds are irrelevant under environmental conditions.

9.4.2.1 Aqueous Tc(IV) halides

Whereas TcF_6^{2-} is stable even in water and dilute solutions of alkali hydroxide, $TcCl_6^{2-}$ could only be stabilized in concentrated Cl^- solutions and $TcBr_6^{2-}$ needs concentrated HBr solutions to remain stable. As discussed in 1.3.1.1, 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.

9.4.2.2 Aqueous Tc(V) halides

The Tc(V) oxychloride $TcOCl_5^{2-}$ has been shown to exist in aqueous solution by spectroscopic methods. Rard et al. (1999) discussed kinetic studies of the hydrolysis of $TcOCl_5^{2-}$, which were interpreted by use of the following reaction

$$TcOCl_5^{2-} + H_2O(l) \Leftrightarrow TcO_2Cl_4^{3-} + 2H^+ + Cl^-$$

Rard et al. (1999) raised doubts about the validity of this reaction and stated that "Further clarification of the equilibrium reaction is necessary before the value of $\log_{10}K°$ ... can be recommended". Consequently, the Tc(V) oxychlorides are not included in our database. Note, however, that a $\log_{10}K°$ for the reaction is erroneously listed by Rard et al. (1999) in Table 7-2 of selected thermodynamic data for reactions involving technetium compounds and complexes.

9.5 Chalcogen compounds and complexes

9.5.1 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).

Rard et al. (1999) recommend thermodynamic data for TcS(g). However, gaseous technetium sulphide is not relevant under environmental conditions and is not included in our database.

9.5.2 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.

9.6 Group 15 compounds and complexes

9.6.1 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.

9.6.2 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.

9.7 Group 14 compounds and complexes

9.7.1 Carbon compounds and complexes

9.7.1.1 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.

9.7.1.2 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:

$$TcO(OH)_2(aq) + CO_2(g) \Leftrightarrow TcCO_3(OH)_2(aq)$$

$$\log_{10}K°(298.15\ K) = (1.1 \pm 0.3)$$

$$TcO(OH)_2(aq) + CO_2(g) + H_2O(l) \Leftrightarrow TcCO_3(OH)_3^- + H^+$$

$$\log_{10}K°(298.15\ K) = -(7.2 \pm 0.6)$$

Using the selected carbonate equilibrium constants relating $CO_2(g)$ with CO_3^{2-}

$$HCO_3^- + H^+ \Leftrightarrow CO_2(g) + H_2O(l)$$

$$\log_{10}K°(298.15\ K) = 7.82$$

$$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+$$

$$\log_{10}K°(298.15\ K) = -10.329$$

the above values have been converted to

$$TcO(OH)_2(aq) + CO_3^{2-} + 2\ H^+ \Leftrightarrow TcCO_3(OH)_2(aq) + H_2O(l)$$

$$\log_{10}{}^*K°(298.15\ K) = (19.3 \pm 0.3)$$

$$TcO(OH)_2(aq) + CO_3^{2-} + H^+ \Leftrightarrow TcCO_3(OH)_3^-$$

$$\log_{10}{}^*K°(298.15\ K) = (11.0 \pm 0.6)$$

These values are included in the database due to the relevance for environmental systems.

9.7.1.3 Technetium cyanides and oxycyanides

No thermodynamic data are available for these compounds and complexes.

9.7.2 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).

9.8 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. $CsTcO_4(cr)$ has a solubility product similar to that of $AgTcO_4(cr)$. The precipitation of $CsTcO_4(cr)$ would require at least a concentration of $2 \times 10^{-2}\ mol \cdot kg^{-1}$ for either Cs^+ or TcO_4^-, which is unrealistically high under environmental conditions, even in the near-field of a radioactive waste repository. Therefore, $CsTcO_4(cr)$ is also not included in the database.

9.9 Ionic strength corrections

Neither Rard et al. (1999) nor Guillaumont et al. (2003) selected any SIT ion interaction coefficients, therefore, we estimated the ion interaction coefficients of our selected technetium species listed in Table 9.3 with a method based on charge correlations (see Appendix A).

Table 9.1: Technetium data selected by NEA (Rard et al. 1999 and Guillaumont et al. 2003) but not included in TDB Version 12/07. For explanations see text.

Gases	Tc(g) [ad], TcO(g) [a], Tc_2O_7(g) [ad], TcF_6(g) [bc], TcO_3F(g) [b], TcO_3Cl(g) [b], TcS(g) [a], TcC(g) [a]
Solids	TcO_2(cr) [a], Tc_2O_7(cr) [ad], $Tc_2O_7\cdot H_2O$(s) [ad], TcF_6(cr, cubic) [bc], NH_4TcO_4(cr) [ac], $(NH_4)_2TcCl_6$(cr) [c], $(NH_4)_2TcBr_6$(cr) [c], $TlTcO_4$(cr) [ac], $AgTcO_4$(cr) [ac], $NaTcO_4\cdot 4H_2O$(s) [ac], $KTcO_4$(cr) [ac], K_2TcCl_6(cr) [c], K_2TcBr_6(cr) [c], Rb_2TcCl_6(cr) [c], Rb_2TcBr_6(cr) [c], $CsTcO_4$(cr) [ac], Cs_2TcCl_6(cr) [c], Cs_2TcBr_6(cr) [c]
Aqueous species	TcO_4^{2-} [ac], $TcO_2Cl_4^{3-}$ [c], $TcOCl_5^{2-}$ [c], $TcCl_6^{2-}$ [c], $TcBr_6^{2-}$ [c]

[a] Single species data including $\Delta_f G_m°$

[b] Single species data excluding $\Delta_f G_m°$

[c] Reaction data including $\log_{10}K°$

[d] Reaction data excluding $\log_{10}K°$

Table 9.2: Selected technetium data. All data included in TDB Version 12/07 are taken from Rard et al. (1999), which are identical with the data by Guillaumont et al. (2003). TDB Version 01/01 refers to Hummel et al. (2002).

		TDB Version 01/01				**TDB Version 12/07**				
Name	**Redox**	$\Delta_f G_m^\circ$ [kJ·mol^{-1}]	$\Delta_f H_m^\circ$ [kJ·mol^{-1}]	S_m° [J·K^{-1}·mol^{-1}]	$C_{p,m}^\circ$ [J·K^{-1}·mol^{-1}]	$\Delta_f G_m^\circ$ [kJ·mol^{-1}]	$\Delta_f H_m^\circ$ [kJ·mol^{-1}]	S_m° [J·K^{-1}·mol^{-1}]	$C_{p,m}^\circ$ [J·K^{-1}·mol^{-1}]	**Species**
Tc(cr)	0	0	0	32.5 ± 0.7	24.9 ± 1.0	0	0	32.5 ± 0.7	24.9 ± 1.0	Tc(cr)
TcO(OH)2	IV	-568.2 ± 8.8	-	-	-	-568.2 ± 8.8	-	-	-	$TcO(OH)_2(aq)$
TcO4-	VII	-637.4 ± 7.6	-729.4 ± 7.6	199.6 ± 1.5	-15 ± 8	-637.4 ± 7.6	-729.4 ± 7.6	199.6 ± 1.5	-15 ± 8	TcO_4^-

		TDB Version 01/01		**TDB Version 12/07**		
Name	**Redox**	$\log_{10}\beta^\circ$	$\Delta_r H_m^\circ$ [kJ·mol^{-1}]	$\log_{10}\beta^\circ$	$\Delta_r H_m^\circ$ [kJ·mol^{-1}]	**Reaction**
TcO+2	IV	< 4	-	< 4	-	$TcO(OH)_2(aq) + 2 H^+ \Leftrightarrow TcO^{2+} + 2 H_2O(l)$
TcO(OH)+	IV	2.5 ± 0.3	-	2.5 ± 0.3	-	$TcO(OH)_2(aq) + H^+ \Leftrightarrow TcO(OH)^+ + H_2O(l)$
TcO(OH)3-	IV	-10.9 ± 0.4	-	-10.9 ± 0.4	-	$TcO(OH)_2(aq) + H_2O(l) \Leftrightarrow TcO(OH)_3^- + H^+$
TcCO3(OH)2	IV	19.3 ± 0.3	-	19.3 ± 0.3	-	$TcO(OH)_2(aq) + CO_3^{2-} + 2H^+ \Leftrightarrow TcCO_3(OH)_2(aq) + H_2O(l)$
TcCO3(OH)3-	IV	11.0 ± 0.6	-	11.0 ± 0.6	-	$TcO(OH)_2(aq) + CO_3^{2-} + H^+ \Leftrightarrow TcCO_3(OH)_3^-$
TcO4-	VII	-29.4 ± 0.8	-	-29.4 ± 0.8	-	$TcO(OH)_2(aq) + H_2O(l) \Leftrightarrow TcO_4^- + 4 H^+ + 3 e^-$

		TDB Version 01/01		**TDB Version 12/07**		
Name	**Redox**	$\log_{10}K_{s,0}^\circ$	$\Delta_r H_m^\circ$ [kJ·mol^{-1}]	$\log_{10}K_{s,0}^\circ$	$\Delta_r H_m^\circ$ [kJ·mol^{-1}]	**Reaction**
TcO2:1.6H2O	IV	-8.4 ± 0.5	-	-8.4 ± 0.5	-	$TcO_2 \cdot 1.6H_2O(s) \Leftrightarrow TcO(OH)_2(aq) + 0.6 H_2O(l)$

Table 9.3: Selected SIT ion interaction coefficients $\varepsilon_{j,k}$ [kg·mol^{-1}] for technetium species. Neither Rard et al. (1999) nor Guillaumont et al. (2003) selected any ion interaction coefficients. Own data estimates based on charge correlations (see Appendix A) are shaded.

j $k\rightarrow$	**Cl^-**	**ClO_4^-**	**NO_3^-**	**Li^+**	**Na^+**	**K^+**
$\downarrow$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$
TcO+2	0.15 ± 0.1	0.4 ± 0.1	-	0	0	0
TcO(OH)+	0.05 ± 0.1	0.2 ± 0.1	-	0	0	0
TcO(OH)2	0	0	0	0	0	0
TcO(OH)3-	0	0	0	-	-0.05 ± 0.1	-
TcCO3(OH)2	0	0	0	0	0	0
TcCO3(OH)3-	0	0	0	-	-0.05 ± 0.1	-
TcO4-	0	0	0	-	-0.05 ± 0.1	-

9.10 References

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10 Thorium

10.1 Introduction

The information contained in this Chapter on thorium is taken almost exclusively from OECD NEA's review "Chemical Thermodynamics of Thorium" (Rand et al. 2008). However, not all values recommended by Rand et al. (2008) are included in our database since the NEA reviews (unlike our database) 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. They are listed in Table 10.1 and the selected data in Table 10.2.

NEA chose the specific ion interaction theory (SIT) for the extrapolation of experimental data to zero ionic strength, see, e.g., Grenthe et al. (1997). Rand et al. (2008) used the strict ion interaction approach to determine ion interaction coefficients and standard formation constants for hydroxide, fluoride, and carbonate complexes in chloride and nitrate media. Thus, the formation of weak ion pairs or complexes of Th with chloride or nitrate is taken account of implicitly.

Due to a lack of experimental data, several ion interaction coefficients for cationic thorium species with chloride are unknown. We filled these gaps by applying an estimation method, which is based on a statistical analysis of published SIT ion interaction coefficients and which allows the estimation of such coefficients for the interaction of cations with Cl^- and ClO_4^-, and for the interaction of anions with Na^+ from the charge of the considered cations or anions (see Appendix A). The selected ion interaction coefficients for thorium species are listed in Table 10.3.

The notation of formulae and symbols used in this text follows the NEA recommendations.

For some systems, Rand et al. (2008) used a fitting code called NONLINT-SIT in order to fit and optimize dimensionless standard molar Gibbs free energy values ($\Delta_f G_m°/RT$) for solids and aqueous species, together with SIT coefficients, using experimental data gained from solubility, ion-exchange and solvent extraction studies.

10.2 Elemental Thorium

Elemental thorium metal, liquid, and gas are not relevant under environmental conditions, therefore, the selected data by Rand et al. (2008) for Th(g) are not considered for our database. Since the absolute entropy and the isobaric heat capacity of thorium metal are needed for the calculation of certain reaction properties of thorium species, the selected values by Rand et al. (2008) for Th(cr, α), the Th(cr) polymorph stable at 298.15 K, have been adopted for our database:

$$S_m°(\text{Th, cr, }\alpha\text{, 298.15 K}) = (52.64 \pm 0.50)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$C_{p,m}°(\text{Th, cr, }\alpha\text{, 298.15 K}) = (26.23 \pm 0.50)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

10.3 Thorium aqua ions (Th^{4+})

According to Rand et al. (2008) there is little evidence for valency states other than Th^{4+}. The standard molar enthalpy of solution for Th^{4+} was obtained by Rand et al. (2008) from the linear extrapolation to zero ionic strength of enthalpy of solution data for β-$ThCl_4$ as a function of HCl molality. The resulting $\Delta_{sol}H_m°(\text{ThCl}_4\text{, cr, }\beta\text{, 298.15 K})$ for the reaction

$$\text{ThCl}_4(\text{cr, }\beta) \Leftrightarrow \text{Th}^{4+} + 4\ \text{Cl}^-$$

was used by Rand et al. (2008) together with the selected values for $\Delta_f H_m°(ThCl_4$, cr, β, 298.15 K) and $\Delta_f H_m°(Cl^-$, 298.15 K) to calculate the selected standard molar enthalpy of solution for Th^{4+}:

$$\Delta_f H_m°(Th^{4+}, 298.15 \text{ K}) = -(768.7 \pm 2.3) \text{ kJ·mol}^{-1}$$

The standard molar entropy of Th^{4+} was obtained by Rand et al. (2008) from the measured enthalpy of solution $\Delta_{sol}H_m°(Th(NO_3)_4 \cdot 5H_2O$, cr, 298.15 K) and solubility data for

$$Th(NO_3)_4·5H_2O(cr) \Leftrightarrow Th^{4+} + 4\ NO_3^- + 5\ H_2O(l)$$

in the following way: $\Delta_r G_m°$ for this reaction was calculated from the solubility and from activity coefficient data and was combined with $\Delta_{sol}H_m°$ to obtain $\Delta_r S_m°$, according to $\Delta_r S_m° = (\Delta_{sol}H_m° - \Delta_r G_m°)/T$. A measured value of $S_m°(Th(NO_3)_4 \cdot 5H_2O$, cr, 298.15 K) was then used with selected auxiliary data for $S_m°(NO_3^-$, 298.15 K) and for $S_m°(H_2O$, l, 298.15 K) to calculate the selected standard molar entropy for Th^{4+}:

$$S_m°(Th^{4+}, 298.15 \text{ K}) = -(423.1 \pm 16.0) \text{ J·K}^{-1}\text{·mol}^{-1}$$

$\Delta_f S_m°(Th^{4+}$, 298.15 K) was calculated by Rand et al. (2008) from $\Delta_f S_m°(Th^{4+}$, 298.15 K) = $S_m°(Th^{4+}$, 298.15 K) - $S_m°$(Th, cr, α, 298.15 K) + 4/2 $S_m°(H_2$, g, 298.15 K) using the values for $S_m°(Th^{4+}$, 298.15 K) and $S_m°$(Th, cr, α, 298.15 K) selected above and $S_m°(H_2$, g, 298.15 K) = (130.680 ± 0.003) $\text{J·K}^{-1}\text{·mol}^{-1}$ resulting in $\Delta_f S_m°(Th^{4+}$, 298.15 K) = (214.38 ± 16.00) $\text{J·K}^{-1}\text{·mol}^{-1}$. Using G = H - TS, this value was then combined with that for $\Delta_f H_m°(Th^{4+}$, 298.15 K) selected above to obtain the selected

$$\Delta_f G_m°(Th^{4+}, 298.15 \text{ K}) = -(704.783 \pm 5.298) \text{ kJ·mol}^{-1}$$

The standard molar heat capacity selected by Rand et al. (2008)

$$C_{p,m}°(Th^{4+}, 298.15 \text{ K}) = -(224 \pm 15) \text{ J·K}^{-1}\text{·mol}^{-1}$$

was adopted from an experimental study using flow microcalorimetry to measure the apparent molar heat capacity of bare and uncomplexed Th^{4+}.

The values for $S_m°$, $\Delta_f G_m°$, and $C_{p,m}°$ are all included in our database.

The ion interaction coefficient of Th^{4+} with Cl^-, selected by all previous NEA-reviews and confirmed by Rand et al. (2008),

$$\varepsilon(Th^{4+}, Cl^-) = (0.25 \pm 0.03) \text{ kg·mol}^{-1}$$

was calculated by Ciavatta (1980) from isopiestic measurements and osmotic coefficients for $ThCl_4$ solutions.

Rand et al. (2008) selected an estimated a value of

$$\varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.10) \text{ kg·mol}^{-1}$$

based on the linear correlation of $\varepsilon(Pu^{4+}, ClO_4^-)$, $\varepsilon(Np^{4+}, ClO_4^-)$, and $\varepsilon(U^{4+}, ClO_4^-)$ with the ionic radii for eight-fold coordination of the corresponding actinides. This estimated value is identical (although with a slightly larger uncertainty) with $\varepsilon(Th^{4+}, ClO_4^-)$ = (0.70 ± 0.06) kg·mol^{-1} determined by Neck et al. (2006), who used a solvent extraction method for the determination of the Th^{4+} trace activity coefficients in NaCl and $NaNO_3$ solutions. For our database we included the value by Rand et al. (2008), which can be interpreted as the measured value by Neck et al. (2006) with an increased uncertainty. For $NaNO_3$ solutions Neck et al. (2006) obtained

$$\varepsilon(Th^{4+}, NO_3^-) = (0.31 \pm 0.12) \text{ kg·mol}^{-1}$$

which was selected by Rand et al. (2008) and is also included in our database.

10.4 Thorium oxygen and hydrogen compounds and complexes

Rand et al. (2008) relied on numerous potentiometric and a few solvent extraction studies to derive stability constants for aqueous thorium hydroxide complexes which they then used to determine solubility products from solubility data for crystalline and anhydrous, and for amorphous and hydrous thorium oxide solids.

10.4.1. Aqueous thorium hydroxide complexes

Rand et al. (2008) used SIT to extrapolate conditional stability constants of aqueous complexes to zero ionic strength. If sufficient data at different ionic strengths of the background electrolyte were available, a linear SIT regression was made, resulting in a value each for $\log_{10}{}^*\beta^\circ$ and $\Delta\varepsilon$. In some cases, where stability constants were determined in various background electrolytes, Rand et al. (2008) applied a simultaneous SIT regression, resulting in a single value for $\log_{10}{}^*\beta^\circ$ and a $\Delta\varepsilon$ value for each background electrolyte. The $\Delta\varepsilon$ values obtained from the regressions can be used to calculate the ion interaction coefficients of the complexes by using known ion interaction coefficients of the other aqueous species taking part in the complex formation reactions. In the case of thorium hydroxide complexes, which can be described by

$$\text{m Th}^{4+} + \text{n H}_2\text{O(l)} \Leftrightarrow \text{Th}_\text{m}(\text{OH})_\text{n}^{4\text{m}-\text{n}} + \text{n H}^+$$

Rand et al. (2008) made use of the following selected ion interaction coefficients: $\varepsilon(\text{Th}^{4+}, \text{Cl}^-) = (0.25 \pm 0.03)$ kg·mol^{-1}, $\varepsilon(\text{Th}^{4+}, \text{ClO}_4^-) = (0.70 \pm 0.10)$ kg·mol^{-1}, and $\varepsilon(\text{Th}^{4+}, \text{NO}_3^-) = (0.31 \pm 0.12)$ kg·mol^{-1} for Th^{4+}, and $\varepsilon(\text{H}^+, \text{Cl}^-) = (0.12 \pm 0.01)$ kg·mol^{-1}, $\varepsilon(\text{H}^+, \text{ClO}_4^-) = (0.14 \pm 0.01)$ kg·mol^{-1}, and $\varepsilon(\text{H}^+, \text{NO}_3^-) = (0.07 \pm 0.01)$ kg·mol^{-1} for H$^+$.

Dinuclear complexes: Rand et al. (2008) accepted data from eight potentiometric studies reporting the formation of $\text{Th}_2(\text{OH})_2^{6+}$. The formation constants were measured in chloride (3.0 M NaCl and 0.5–3.0 M NaCl, LiCl, and KCl), perchlorate (1.0 and 3.0 M NaClO_4) and nitrate media (0.5–4.0 NaNO_3, 3.0 M LiNO_3 and KNO_3). Rand et al. (2008) performed a simultaneous SIT regression of the chloride, perchlorate, and nitrate data and obtained

$$2\ \text{Th}^{4+} + 2\ \text{H}_2\text{O(l)} \Leftrightarrow \text{Th}_2(\text{OH})_2^{6+} + 2\ \text{H}^+$$

$$\log_{10}{}^*\beta^\circ_{2,2}(\text{Th}_2(\text{OH})_2^{6+}, 298.15\ \text{K}) = -(5.9 \pm 0.5)$$

with $\Delta\varepsilon_{2,2}$ (Cl$^-$) = (0.14 ± 0.15) kg·mol^{-1}, $\Delta\varepsilon_{2,2}$ (ClO_4^-) = (0.10 ± 0.14) kg·mol^{-1}, and $\Delta\varepsilon_{2,2}$ (NO_3^-) = (0.21 ± 0.11) kg·mol^{-1}. From these $\Delta\varepsilon_{2,2}$ values then follow

$$\varepsilon(\text{Th}_2(\text{OH})_2^{6+}, \text{Cl}^-) = (0.40 \pm 0.16)\ \text{kg·mol}^{-1}$$

$$\varepsilon(\text{Th}_2(\text{OH})_2^{6+}, \text{ClO}_4^-) = (1.22 \pm 0.24)\ \text{kg·mol}^{-1}$$

$$\varepsilon(\text{Th}_2(\text{OH})_2^{6+}, \text{NO}_3^-) = (0.69 \pm 0.26)\ \text{kg·mol}^{-1}$$

These data for $\text{Th}_2(\text{OH})_2^{6+}$ selected by Rand et al. (2008) are also included in our database.

For the formation of $\text{Th}_2(\text{OH})_3^{5+}$, Rand et al. (2008) accepted potentiometric data from three studies in alkali metal chloride media (0.5–3.0 LiCl, NaCl, and KCl) and from one study in alkaline earth chloride media (0.25–1.5 M MgCl_2, CaCl_2, SrCl_2, and BaCl_2). Separate SIT regressions of data in the alkali metal chloride and in the alkaline earth chloride media gave consistent results, and Rand et al. (2008) selected the average values

$$2\ \text{Th}^{4+} + 3\ \text{H}_2\text{O(l)} \Leftrightarrow \text{Th}_2(\text{OH})_3^{5+} + 3\ \text{H}^+$$

$$\log_{10}{}^*\beta^\circ_{3,2}(\text{Th}_2(\text{OH})_3^{5+}, 298.15\ \text{K}) = -(6.8 \pm 0.2)$$

and $\Delta\varepsilon_{3,2}$(Cl$^-$) = (0.15 ± 0.06) kg·mol^{-1}. The value for $\Delta\varepsilon_{3,2}$(Cl$^-$) leads to the selected

$$\varepsilon(Th_2(OH)_3^{5+}, Cl^-) = (0.29 \pm 0.09)\ kg \cdot mol^{-1}$$

The selected value for $\log_{10}{}^*\beta^\circ_{3,2}(Th_2(OH)_3^{5+}$, 298.15 K) was combined by Rand et al. (2008) with two conditional constants measured in 3.44 m KNO_3 and 3.50 m $NaClO_4$ for deriving $\Delta\varepsilon_{3,2}(ClO_4^-) = -(0.07 \pm 0.06)\ kg \cdot mol^{-1}$ and $\Delta\varepsilon_{3,2}(NO_3^-) = (0.28 \pm 0.06)\ kg \cdot mol^{-1}$ and, as a consequence,

$$\varepsilon(Th_2(OH)_3^{5+}, ClO_4^-) = (0.91 \pm 0.21)\ kg \cdot mol^{-1}$$

$$\varepsilon(Th_2(OH)_3^{5+}, NO_3^-) = (0.69 \pm 0.25)\ kg \cdot mol^{-1}$$

These data for $Th_2(OH)_3^{5+}$ are all included in our database.

The dinuclear complexes $Th_2(OH)^{7+}$ (proposed in two studies) and $Th_2(OH)_4^{4+}$ (proposed in one study) were not accepted by Rand et al. (2008) and are also not included in our database.

Trinuclear complexes: The trinuclear complexes $Th_3(OH)_6^{6+}$, $Th_3(OH)_5^{7+}$, $Th_3(OH)_3^{9+}$, and $Th_3(OH)^{11+}$ proposed in a few studies were not considered by Rand et al. (2008), either because they were not well supported by the experimental data, or the data could equally well be described without them. Furthermore, there is no structural evidence for trinuclear complexes.

Tetranuclear complexes: Rand et al. (2008) analyzed potentiometric data for $Th_4(OH)_8^{8+}$ in 1.0 M $NaClO_4$ (three studies), 3.0 M $NaClO_4$ (one study), and 4.0 M $NaClO_4$ (one study). Their SIT regression resulted in the selected

$$4\ Th^{4+} + 8\ H_2O(l) \Leftrightarrow Th_4(OH)_8^{8+} + 8\ H^+$$

$$\log_{10}{}^*\beta^\circ_{8,4}(Th_4(OH)_8^{8+}, 298.15\ K) = -(20.4 \pm 0.4)$$

with $\Delta\varepsilon_{8,4}(ClO_4^-) = (0.01 \pm 0.08)\ kg \cdot mol^{-1}$ and

$$\varepsilon(Th_4(OH)_8^{8+}, ClO_4^-) = (1.69 \pm 0.42)\ kg \cdot mol^{-1}$$

A conditional stability constant measured in 3.0 M NaCl and the selected value for $\log_{10}{}^*\beta^\circ_{8,4}(Th_4(OH)_8^{8+}$, 298.15 K) were used by Rand et al. (2008) for the calculation of $\Delta\varepsilon_{8,4}(Cl^-) = (0.66 \pm 0.14)\ kg \cdot mol^{-1}$ and

$$\varepsilon(Th_4(OH)_8^{8+}, Cl^-) = (0.70 \pm 0.20)\ kg \cdot mol^{-1}$$

Similarly, conditional stability constants measured in 3.0 M $LiNO_3$ and KNO_3, and the selected value for $\log_{10}{}^*\beta^\circ_{8,4}(Th_4(OH)_8^{8+}$, 298.15 K) led to $\Delta\varepsilon_{8,4}(NO_3^-) = (0.91 \pm 0.14)\ kg \cdot mol^{-1}$ and

$$\varepsilon(Th_4(OH)_8^{8+}, NO_3^-) = (1.59 \pm 0.51)\ kg \cdot mol^{-1}$$

According to Rand et al. (2008), measured stability constants for $Th_4(OH)_{12}^{4+}$ are scarce, since this tetranuclear complex is predominant at pH values close to the onset of precipitation of thorium oxyhydroxides (pH 3.5–4.5) and potentiometric measurements in the thorium hydroxide system are usually carried out at lower pH in order to avoid such precipitation. Rand et al. (2008) accepted three conditional stability constants for 3.0 NaClO4, 0.1 M KNO3, and 4.0 M NaNO3 and used an SIT regression to obtain

$$4\ Th^{4+} + 12\ H_2O(l) \Leftrightarrow Th_4(OH)_{12}^{4+} + 12\ H^+$$

$$\log_{10}{}^*\beta^\circ_{12,4}(Th_4(OH)_{12}^{4+}, 298.15\ K) = -(26.6 \pm 0.2)$$

with $\Delta\varepsilon_{12,4}(ClO_4^-) = -(0.56 \pm 0.06)\ kg \cdot mol^{-1}$, $\Delta\varepsilon_{12,4}(NO_3^-) = (0.02 \pm 0.05)\ kg \cdot mol^{-1}$, and accordingly

$$\varepsilon(Th_4(OH)_{12}^{4+}, ClO_4^-) = (0.56 \pm 0.42)\ kg \cdot mol^{-1}$$

$$\varepsilon(Th_4(OH)_{12}^{4+}, NO_3^-) = (0.42 \pm 0.50)\ kg \cdot mol^{-1}$$

In the absence of experimental data for chloride media, Rand et al. (2008) estimated

$$\varepsilon(\mathrm{Th_4(OH)_{12}}^{4+}, \mathrm{Cl^-}) = (0.25 \pm 0.20)\ \mathrm{kg{\cdot}mol^{-1}}$$

from a non-linear correlation of $\varepsilon(\mathrm{Th_m(OH)_n}^{4m-n}, \mathrm{Cl^-})$ with the charge of the complex.

These data for $\mathrm{Th_4(OH)_8}^{8+}$ and $\mathrm{Th_4(OH)_{12}}^{4+}$ are all included in our database.

Hexanuclear complexes: Two types of hexanuclear complexes were found to be predominant in potentiometric studies, either $\mathrm{Th_6(OH)_{15}}^{9+}$ (in 1.0 M $\mathrm{NaClO_4}$, 0.1 and 3.0 M $\mathrm{KNO_3}$, and 0.5–3.0 M $\mathrm{NaNO_3}$) or $\mathrm{Th_6(OH)_{14}}^{10+}$ (in 3.0 M NaCl). From the data of an additional study by Grenthe & Lagerman (1991) in 3.0 M $\mathrm{NaClO_4}$ it was not possible to distinguish between the two complexes and Grenthe & Lagerman (1991) proposed different speciation models, either including $\mathrm{Th_6(OH)_{15}}^{9+}$, or including $\mathrm{Th_6(OH)_{14}}^{10+}$, but not both.

An SIT regression of conditional constants for $\mathrm{Th_6(OH)_{15}}^{9+}$ (including one by Grenthe & Lagerman, 1991, in 3.0 M $\mathrm{NaClO_4}$) provided

$$6\ \mathrm{Th^{4+}} + 15\ \mathrm{H_2O(l)} \Leftrightarrow \mathrm{Th_6(OH)_{15}}^{9+} + 15\ \mathrm{H^+}$$

$$\log_{10}{}^*\beta^\circ_{15,6}(\mathrm{Th_6(OH)_{15}}^{9+}, 298.15\ \mathrm{K}) = -(36.8 \pm 1.5)$$

with $\Delta\varepsilon_{15,6}(\mathrm{ClO_4^-}) = -(0.25 \pm 0.40)\ \mathrm{kg{\cdot}mol^{-1}}$, $\Delta\varepsilon_{15,6}(\mathrm{NO_3^-}) = (1.39 \pm 0.23)\ \mathrm{kg{\cdot}mol^{-1}}$, and

$$\varepsilon(\mathrm{Th_6(OH)_{15}}^{9+}, \mathrm{ClO_4^-}) = (1.85 \pm 0.74)\ \mathrm{kg{\cdot}mol^{-1}}$$

$$\varepsilon(\mathrm{Th_6(OH)_{15}}^{9+}, \mathrm{NO_3^-}) = (2.20 \pm 0.77)\ \mathrm{kg{\cdot}mol^{-1}}$$

For chloride media Rand et al. (2008) estimated

$$\varepsilon(\mathrm{Th_6(OH)_{15}}^{9+}, \mathrm{Cl^-}) = (0.72 \pm 0.30)\ \mathrm{kg{\cdot}mol^{-1}}$$

from the mentioned correlation.

$\mathrm{Th_6(OH)_{14}}^{10+}$ was observed as major species only in 3.0 M NaCl, but, as mentioned above, was also proposed as an alternative to $\mathrm{Th_6(OH)_{15}}^{9+}$ in the experiments by Grenthe & Lagerman (1991) in 3.0 M $\mathrm{NaClO_4}$. In order to extrapolate both conditional constants for

$$6\ \mathrm{Th^{4+}} + 14\ \mathrm{H_2O(l)} \Leftrightarrow \mathrm{Th_6(OH)_{14}}^{10+} + 14\ \mathrm{H^+}$$

to zero ionic strength, Rand et al. (2008) estimated

$$\varepsilon(\mathrm{Th_6(OH)_{14}}^{10+}, \mathrm{Cl^-}) = (0.83 \pm 0.30)\ \mathrm{kg{\cdot}mol^{-1}}$$

and

$$\varepsilon(\mathrm{Th_6(OH)_{14}}^{10+}, \mathrm{ClO_4^-}) = (2.2 \pm 0.3)\ \mathrm{kg{\cdot}mol^{-1}}$$

from the said correlation. Combining these with the values for $\varepsilon(\mathrm{H^+}, \mathrm{Cl^-})$ and $\varepsilon(\mathrm{H^+}, \mathrm{ClO_4^-})$ given above, they obtained $\Delta\varepsilon_{14,6}(\mathrm{Cl^-})$ and $\Delta\varepsilon_{14,6}(\mathrm{ClO_4^-})$, finally leading to $\log_{10}{}^*\beta^\circ_{14,6}(\mathrm{Th_6(OH)_{14}}^{10+}, 298.15\ \mathrm{K}) = -(36.7 \pm 1.0)$ and $-(36.9 \pm 1.1)$ for 3.0 M NaCl and 3.0 M $\mathrm{NaClO_4}$, respectively and selected the average of both values

$$\log_{10}{}^*\beta^\circ_{14,6}(\mathrm{Th_6(OH)_{14}}^{10+}, 298.15\ \mathrm{K}) = -(36.8 \pm 1.2)$$

with a slightly enlarged uncertainty[14].

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[14] Note that it is in fact inconsistent to use the same potentiometric data by Grenthe & Lagerman (1991) both for $\mathrm{Th_6(OH)_{15}}^{9+}$ and for $\mathrm{Th_6(OH)_{14}}^{10+}$, as have done Rand et al. (2008), since these hexanuclear complexes are mutually exclusive in the speciation models proposed by Grenthe & Lagerman (1991) (this is not to say, however, that it is inconsistent to include both hexanuclear complexes in a database and perform speciation calculations with both of them). Since both values for $\log_{10}{}^*\beta^\circ_{14,6}(\mathrm{Th_6(OH)_{14}}^{10+}, 298.15\ \mathrm{K})$ are practically

For lack of experiments in nitrate media, Rand et al. (2008) estimated

$$\varepsilon(Th_6(OH)_{14}^{10+}, NO_3^-) = (2.9 \pm 0.5)\ kg\cdot mol^{-1}$$

from a non-linear correlation of $\varepsilon(Th_m(OH)_n^{4m-n}, NO_3^-)$ with the charge of the complex.

These data selected by Rand et al. (2008) for $Th_6(OH)_{15}^{9+}$ and $Th_6(OH)_{14}^{10+}$ are all included in our database.

Mononuclear complexes: Rand et al. (2008) selected standard stability constants for the mononuclear complexes $ThOH^{3+}$, $Th(OH)_2^{2+}$, and $Th(OH)_4(aq)$. Although $Th(OH)_3^+$ was reported in several studies (however, only as minor species), Rand et al. (2008), did not recommend a stability constant, because they considered the reported values as unreliable.

For the SIT analysis of experimental data, Rand et al. (2008) estimated $\varepsilon(ThOH^{3+}, ClO_4^-)$ by analogy with the corresponding U(IV) complex

$$\varepsilon(ThOH^{3+}, ClO_4^-) \approx \varepsilon(UOH^{3+}, ClO_4^-) = (0.48 \pm 0.08)\ kg\cdot mol^{-1}$$

and the following ion interaction coefficients from a non-linear correlation of $\varepsilon(Th_m(OH)_n^{4m-n}, Cl^-)$ with the charge of the complex:

$$\varepsilon(ThOH^{3+}, Cl^-) = (0.19 \pm 0.05)\ kg\cdot mol^{-1}$$

$$\varepsilon(ThOH^{3+}, NO_3^-) = (0.20 \pm 0.15)\ kg\cdot mol^{-1}$$

$$\varepsilon(Th(OH)_2^{2+}, Cl^-) = (0.13 \pm 0.05)\ kg\cdot mol^{-1}$$

$$\varepsilon(Th(OH)_2^{2+}, ClO_4^-) = (0.33 \pm 0.10)\ kg\cdot mol^{-1}$$

$$\varepsilon(Th(OH)_2^{2+}, NO_3^-) = (0.10 \pm 0.15)\ kg\cdot mol^{-1}$$

For $ThOH^{3+}$, Rand et al. (2008) accepted three conditional stability constants measured in 1.0 M $NaClO_4$, one measured in 3.0 M $NaClO_4$, and one measured in 0.10 KNO_3, all five from potentiometric studies. In addition, they also accepted a stability constant measured in 0.50 M KNO_3 with 0.01 M $Th(NO_3)_4$ from a solvent extraction study. From the selected ion interaction coefficients for Th^{4+} mentioned above and those estimated for $ThOH^{3+}$, Rand et al. (2008) calculated $\Delta\varepsilon_{1,1}(ClO_4^-) = -(0.08 \pm 0.13)\ kg\cdot mol^{-1}$ and $\Delta\varepsilon_{1,1}(NO_3^-) = -(0.04 \pm 0.19)\ kg\cdot mol^{-1}$ to extrapolate the conditional stability constants to zero ionic strength, obtaining values between -2.96 and -2.16. They selected

$$Th^{4+} + H_2O(l) \Leftrightarrow ThOH^{3+} + H^+$$

$$\log_{10}{}^*\beta^{\circ}_{1,1}(ThOH^{3+}, 298.15\ K) = -(2.5 \pm 0.5)$$

as an average, with the uncertainty covering the whole range of values.

In the case of $Th(OH)_2^{2+}$, Rand et al. (2008) accepted only two conditional constants from potentiometric measurements in 1.0 M $NaClO_4$. As for $ThOH^{3+}$, they calculated $\Delta\varepsilon_{2,1}(ClO_4^-) = -(0.09 \pm 0.14)\ kg\cdot mol^{-1}$ from the selected ion interaction coefficients for Th^{4+} and those estimated for $Th(OH)_2^{2+}$ and took the average from the resulting stability constants, again with an average that covers the whole range of expectation for the two values. Hence, they selected

$$Th^{4+} + 2\ H_2O(l) \Leftrightarrow Th(OH)_2^{2+} + 2\ H^+$$

$$\log_{10}{}^*\beta^{\circ}_{2,1}(Th(OH)_2^{2+}, 298.15\ K) = -(6.2 \pm 0.5)$$

$Th(OH)_4(aq)$ occurs only as a minor species in the pH range (pH < 5) where potentiometric measurements were carried out and solvent extraction studies report stability constants orders of

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identical, one can pretend that the value selected by Rand et al. (2008) was not based on the data by Grenthe & Lagerman (1991).

magnitude lower than those estimated from potentiometry. For this reason, Rand et al. (2008) relied on stability constants derived from the pH-independent solubility of amorphous and hydrous ThO_2(am, hyd), also designated as $Th(OH)_4$(am), under neutral and alkaline conditions, where $Th(OH)_4$(aq) is predominant. The stability constant selected by Rand et al. (2008) for $Th(OH)_4$(aq)

$$Th^{4+} + 4\ H_2O(l) \Leftrightarrow Th(OH)_4(aq) + 4\ H^+$$

$$\log_{10}{}^*\beta^\circ_{4,1}(Th(OH)_4,\ aq,\ 298.15\ K) = -(17.4 \pm 0.7)$$

therefore depends on the solubility of ThO_2(am, hyd) or $Th(OH)_4$(am) and is discussed in Section 10.4.3 below.

The data selected by Rand et al. (2008) for the mononuclear thorium hydroxide complexes are all included in our database.

Enthalpies of reaction: Enthalpies of reaction for thorium hydrolysis can be obtained from calorimetry or from the temperature dependence of thorium hydrolysis constants. Calorimetrically measured enthalpies of reaction are much more precise than those obtained from temperature dependence and are to be preferred. Only one study, however, provided calorimetric data and was restricted to $Th_2(OH)_2^{6+}$ and $Th_2(OH)_3^{5+}$. Rand et al. (2008) did not accept these data, because no experimental details were reported and possible errors and uncertainties could not be evaluated. Therefore, Rand et al. (2008) had to rely on two studies reporting the temperature dependence of the formation constants of $ThOH^{3+}$, $Th(OH)_2^{2+}$, $Th_2(OH)_2^{6+}$, $Th_4(OH)_8^{8+}$, and $Th_6(OH)_{15}^{9+}$ in 1 M $NaClO_4$. One was carried out at 0, 25, and 95°C, the other at 15, 25 and 35°C. Rand et al. (2008) calculated the enthalpies of reaction from the slopes of van't Hoff plots of the data and extrapolated them to zero ionic strength according to Grenthe et al. (1997). They obtained the following standard molar enthalpies of reaction

$$\Delta_r H_m^\circ{}_{1,1}(ThOH^{3+},\ 298.15\ K) = (44.2 \pm 6.3)\ kJ\cdot mol^{-1}$$

$$\Delta_r H_m^\circ{}_{2,1}(Th(OH)_2^{2+},\ 298.15\ K) = (85.7 \pm 41.4)\ kJ\cdot mol^{-1}$$

$$\Delta_r H_m^\circ{}_{2,2}(Th_2(OH)_2^{6+},\ 298.15\ K) = (58.3 \pm 5.7)\ kJ\cdot mol^{-1}$$

$$\Delta_r H_m^\circ{}_{8,4}(Th_4(OH)_8^{8+},\ 298.15\ K) = (243.0 \pm 21.3)\ kJ\cdot mol^{-1}$$

$$\Delta_r H_m^\circ{}_{15,6}(Th_6(OH)_{15}^{9+},\ 298.15\ K) = (472.8 \pm 22.0)\ kJ\cdot mol^{-1}$$

These standard molar enthalpies of formation are all included in our database.

10.4.2. Aqueous calcium thorium hydroxide complexes

Altmaier et al. (2008) studied the solubility of Zr(IV), Th(IV), and Pu(IV) oxyhydroxide precipitates in alkaline $CaCl_2$ and $Ca(ClO_4)_2$ solutions. Concerning Th, they measured the solubility of $ThO_2{\cdot}xH_2O$(pr) or, equivalently, $Th(OH)_4$(pr) in alkaline $CaCl_2$ (0.2–4.5 M) and $Ca(ClO_4)_2$ (2 M) solutions. Concentrations of Th in 0.2 M $CaCl_2$ turned out to be independent of pH ($\log_{10}[Th]_m = -8.5 \pm 0.5$), consistent with the formation of neutral $Th(OH)_4$(aq) monomers or $Th_m(OH)_{4m}$(aq) oligomers. At higher concentrations of $CaCl_2$ and $pH_c < 11$, Th concentrations remain at the same value. At $pH_c > 11$, however, Th concentrations show a steep linear increase with a slope of 4 ($\log_{10}$[Th] vs. pH_c), indicating the formation of a Th hydroxide complex with 8 OH^- ligands. EXAFS spectra show that this complex is stabilized by Ca^{2+}, in such a way that four Ca^{2+} ions are bound to the edges of the $Th(OH)_8^{4-}$ polyhedron. Thus, the solubility increase of $Th(OH)_4$(pr) in alkaline $CaCl_2$ solutions was described by Altmaier et al. (2008) as

$$Th(OH)_4(pr) + 4\ Ca^{2+} + 4\ OH^- \Leftrightarrow Ca_4Th(OH)_8^{4+}$$

with $\log_{10}K_{s(4,1,8)}{}^\circ(298.15\ K) = (1.8 \pm 0.5)$ and

$$\varepsilon(Ca_4Th(OH)_8^{4+}, Cl^-) = -(0.01 \pm 0.10)\ kg\cdot mol^{-1}$$

following from their SIT regression analysis. The stability constant of this complex was calculated by Altmaier et al. (2008) from $\log_{10}K_{s(4,1,8)}°(298.15\ K)$ by using $Th(OH)_4(pr) \Leftrightarrow Th^{4+} + 4\ OH^-$ with $\log_{10}K_{s,0}°(298.15\ K) = -(47.8 \pm 0.3)$, leading to

$$4\ Ca^{2+} + Th^{4+} + 8\ OH^- \Leftrightarrow Ca_4Th(OH)_8^{4+}$$

$\log_{10}\beta°_{8,1,4}(Ca_4Th(OH)_8^{4+}, 298.15\ K) = (49.6 \pm 0.6)$

For inclusion in our database, we used the dissociation constant of water to express this reaction in terms of $H_2O(l)$ and H^+ instead of OH^-. Thus

$$4\ Ca^{2+} + Th^{4+} + 8\ H_2O(l) \Leftrightarrow Ca_4Th(OH)_8^{4+} + 8\ H^+$$

$$\log_{10}{}^*\beta°_{8,1,4}(Ca_4Th(OH)_8^{4+}, 298.15\ K) = -(62.4 \pm 0.6)$$

Combining $\log_{10}K_{s(4,1,8)}°(298.15\ K)$ from the experimental data in $CaCl_2$ with the corresponding conditional constant from the solubility experiment in 2.0 M $Ca(ClO_4)_2$ and using $\varepsilon(OH^-, Ca^{2+}) = -(0.45 \pm 0.03)\ kg\cdot mol^{-1}$ and $\varepsilon(Ca^{2+}, ClO_4^-) = (0.27 \pm 0.03)$, Altmaier et al. (2008) obtained

$$\varepsilon(Ca_4Th(OH)_8^{4+}\ ClO_4^-) = (0.21 \pm 0.17)\ kg\cdot mol^{-1}$$

This value, together with that for $\varepsilon(Ca_4Th(OH)_8^{4+}, Cl^-) = -(0.01 \pm 0.10)\ kg\cdot mol^{-1}$ mentioned above is included in our database. Note that these values appear to be relatively low compared to $\varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.10)\ kg\cdot mol^{-1}$ and $\varepsilon(Th^{4+}, Cl^-) = (0.25 \pm 0.03)\ kg\cdot mol^{-1}$. Altmaier et al. (2008) explain this with the different charge distribution in the ternary complex where there is no high local positive charge as in Th^{4+}, but charge is rather distributed among the four Ca^{2+} cations that surround the central $Th(OH)_8^{4-}$ complex.

10.4.3 Solid thorium oxides and hydroxides

Based on calorimetric measurements, Rand et al. (2008) selected $\Delta_fH_m°$, $C_{p,m}°$, and $S_m°$ values for thorianite, $ThO_2(cr)$, which lead to $\Delta_fG_m°(ThO_2, cr, 298.15) = -(1169.0 \pm 3.5)\ kJ\cdot mol^{-1}$. Using this value together with the selected $\Delta_fG_m°(Th^{4+}, 298.15)$ and $\Delta_fG_m°(H_2O, l, 298.15) = -(237.140 \pm 0.041)$, Rand et al. (2008) obtained $\log_{10}{}^*K_{s,0}°(ThO_2, cr, 298.15\ K) = (1.77 \pm 1.11)$ for the reaction $ThO_2(cr) + 4\ H^+ \Leftrightarrow Th^{4+} + 2\ H_2O(l)$. For reasons discussed below, the calorimetric data and the solubility constant derived there from are not included in our database.

Rand et al. (2008) discussed the experimental solubility of well-crystallized $ThO_2(cr)$, thorianite, of microcrystalline $ThO_2(micr)$, and of amorphous and hydrous $ThO_2(am, hyd)$ or $Th(OH)_4(am)$. The solubility of these solids as a function of pH is clearly divided into two regions: In acidic solutions (pH < about 5), where Th^{4+} is predominant, the solubility decreases steeply with increasing pH (almost linearly in a $\log_{10}[Th]$ vs. pH plot), while under near-neutral and alkaline conditions (pH 6–14), where $Th(OH)_4(aq)$ is predominant, the solubility remains constant.

The solubility of $ThO_2(cr)$ at room temperature is affected by very slow dissolution kinetics. The solubility studies at room temperature and low pH reviewed by Rand et al. (2008) did not reach equilibrium from undersaturation. A striking example is the dissolution study by Neck et al. (2003) who added anhydrous and well-crystallized $ThO_2(cr)$ to 0.1 and 0.5 M HCl-NaCl solutions at room temperature in the pH-range 1–3. H^+ and Th concentrations were measured after 79, 169, and 318 days. The Th concentrations measured after 318 days were not higher than those measured at 169 days. Still, equilibrium was clearly not attained, as the Th concentrations showed only a very slight dependence on pH, and not a slope of -4 in $\log_{10}[Th]$ vs. pH diagram as expected from the dominant species Th^{4+} at low pH. In contrast, Neck et al. (2003) were able to reach an equilibrium state at room temperature from oversaturation. Their coulometric titration of Th nitrate solutions at pH 1-2.5 (0.5 M HCl-NaCl) led to the formation of hydrated microcrystalline ThO_2(micr, hyd) which agglomerated to a precipitate. According to Rand et al. (2008), the $\log_{10}{}^*K_{s,0}°$ value for this precipitate is about one log-unit higher than $\log_{10}{}^*K_{s,0}°(ThO_2$, cr, 298.15 K) = (1.77 ± 1.11) calculated from thermochemical data. Both values are in excellent agreement when considering the effect of particle size on the solubility constant.

The reported experimental solubilities of ThO_2(cr) in near-neutral to alkaline conditions (measured after ultrafiltration or ultracentrifugation to remove colloidal particles) have an average of $\log_{10}$[Th] = -(9.3 ± 1.4) (10 solubilities from 6 studies) and are very close to those determined for aged amorphous ThO_2(am, hyd, ag), with $\log_{10}K_{s,4}°(ThO_2$(am, hyd, ag) ⇔ $Th(OH)_4$(aq), 298.15 K)[15] = -(8.5 ± 1.0) ≈ $\log_{10}$[Th], see below. Rand et al. (2008) compared these measured solubilities with the value calculated from calorimetric data for ThO_2(cr). For this purpose, they combined $\log_{10}{}^*K_{s,0}°(ThO_2$, cr, 298.15 K) = (1.8 ± 1.1) with $\log_{10}{}^*\beta°_{4,1}(Th(OH)_4$, aq, 298.15 K) = -(17.4 ± 0.7), resulting in $\log_{10}K_{s,4}°(ThO_2$(cr) + 2 H_2O(l) ⇔ $Th(OH)_4$(aq), 298.15 K) = -(15.6 ± 1.3) ≈ $\log_{10}$[Th]. The calculated solubility is thus 6 orders of magnitude lower than the measured one. This discrepancy has been explained by small amounts of more soluble amorphous material present in the crystalline solid. Another explanation is that the solubility of ThO_2(cr) is determined by a hydrated surface layer in contact with aqueous solution and not by the crystalline bulk beneath the surface.

Rand et al. (2008) recalculated solubility data from eleven studies for ThO_2(am, hyd) or $Th(OH)_4$(am) in acidic solutions at room temperature using the selected formation constants for thorium hydroxide complexes presented above. They determined a mean value of $\log_{10}{}^*K_{s,0}°(ThO_2$, am, hyd, 298.15 K) = (8.9 ± 1.1) for the reaction ThO_2(am, hyd) + 4 H^+ ⇔ Th^{4+} + 2 H_2O(l).

The solubilities of ThO_2(am, hyd) or $Th(OH)_4$(am) at room temperature in near-neutral to alkaline solutions reported by Rand et al. (2008) differ markedly when comparing their values before and after ultrafiltration or ultracentrifugation for removing colloidal ThO_2(am, hyd). The average of nine measurements after ultrafiltration or -centrifugation corresponds to $\log_{10}K_{s,4}°(ThO_2$(am, hyd) ⇔ $Th(OH)_4$(aq), 298.15 K) = -(8.5 ± 1.0), while the values for $\log_{10}K_{s,4}°$(298.15 K) before such treatment vary between –(5.7 ± 1.1) and –(6.8 ± 0.2).

The particle size of ThO_2(am, hyd) usually varies in the range of 2 to 20 nm. This size variation has a very large impact on the free surface energy and consequently on the Gibbs free energy and solubility of the particles. This has been demonstrated by several solubility experiments at pH < 5 with various equilibration times (at pH > 6, where Th concentrations are low, there is no clear variation of solubility as a function of time). Rand et al. (2008) recalculated the data of nine studies using the selected formation constants for thorium hydroxide complexes. Values for $\log_{10}{}^*K_{s,0}°$(298.15 K) for "fresh" ThO_2(am, hyd), equilibrated for less than 25 days, vary between (8.4 ± 0.6) and (9.8 ± 0.3), while those for "aged" ThO_2(am, hyd), equilibrated for more than 70 days, vary between (8.0 ± 0.6) and (9.2 ± 0.4). Although the $\log_{10}{}^*K_{s,0}°$ values of both categories overlap somewhat, Rand et al. (2008) selected

$$ThO_2(\text{am, hyd, fr}) + 4\ H^+ \Leftrightarrow Th^{4+} + 2\ H_2O(l)$$

$$\log_{10}{}^*K_{s,0}°(ThO_2, \text{am, hyd, fr, 298.15 K}) = (9.3 \pm 0.9)$$

as a representative for a fresh, and

$$ThO_2(\text{am, hyd, ag}) + 4\ H^+ \Leftrightarrow Th^{4+} + 2\ H_2O(l)$$

$$\log_{10}{}^*K_{s,0}°(ThO_2, \text{am, hyd, ag, 298.15 K}) = (8.5 \pm 0.9)$$

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[15] H_2O is neglected in this reaction. It can also be written as $Th(OH)_4$(am) ⇔ $Th(OH)_4$(aq).

as a representative for an aged amorphous hydrous thorium oxide. We include both in our database.

The latter constant was selected by Rand et al. (2008) from solubility studies with solids aged for more than two months or from solids that were dried at room temperature. They recommend this constant for modelling the solubility of thorium in natural systems, since, as seen above, the thermodynamically stable ThO_2(cr) is not expected to control solubility in near-neutral to alkaline conditions. For this reason, ThO_2(cr) is also not included in our database.

Based on the solubility studies discussed so far, Rand et al. (2008) selected the value for $\log_{10}{}^*\beta^\circ_{4,1}$($Th(OH)_4$, aq, 298.15 K) as follows: The mean value of the solubilities determined for ThO_2(am, hyd) or $Th(OH)_4$(am) at near-neutral to alkaline conditions after ultrafiltration or -centrifugation corresponds to $\log_{10}K_{s,4}^\circ$(ThO_2(am, hyd) ⇔ $Th(OH)_4$(aq), 298.15 K) = -(8.5 ± 1.0). Combining this value with the $\log_{10}{}^*K_{s,0}^\circ$($ThO_2$, am, hyd, 298.15 K) = (8.9 ± 0.9), the mean of $\log_{10}{}^*K_{s,0}^\circ$($ThO_2$, am, hyd, fr, 298.15 K) and $\log_{10}{}^*K_{s,0}^\circ$($ThO_2$, am, hyd, ag, 298.15 K), they obtained

$$Th^{4+} + 4\ H_2O(l) \Leftrightarrow Th(OH)_4(aq) + 4\ H^+$$

$$\log_{10}{}^*\beta^\circ_{4,1}(Th(OH)_4,\ aq,\ 298.15\ K) = -(17.4 \pm 0.7)$$

which is included in our database.

As already discussed above, the solubilities of ThO_2(am, hyd) or $Th(OH)_4$(am) at room temperature in near-neutral to alkaline solutions before ultrafiltration or -centrifugation vary between -(5.7 ± 1.1) and -(6.8 ± 0.2). These concentrations correspond to the equilibrium between ThO_2(am, hyd) or $Th(OH)_4$(am) and a colloidal form of ThO_2(am, hyd) which can be written as ThO_2(am, hyd) ⇔ ThO_2(am, hyd, coll). We decided to include in our database the solubility value determined by Altmaier et al. (2004) in the presence of colloids

$$ThO_2(am,\ hyd) \Leftrightarrow ThO_2(am,\ hyd,\ coll)$$

$$\log_{10}K^\circ(ThO_2,\ am,\ hyd,\ coll,\ 298.15\ K) = -(6.3 \pm 0.5)$$

as supplemental data for calculating the maximum "equilibrium" concentration of thorium in the near-neutral and alkaline region. As Altmaier et al. (2004) have remarked, these colloids may be considered on the one hand as small solid particles that have properties like the bulk solid but on the other hand, they can also be considered as large aqueous species that contribute to the total concentration of Th in solution and a mutual equilibrium between the bulk solid phase, the colloids and the aqueous species can be assumed. For geochemical modelling it is important to keep in mind that the equilibrium concentration of ThO_2(am, hyd, coll) is tied to the precipitated ThO_2(am, hyd). Therefore calculations that involve ThO_2(am, hyd, coll) always require the presence of ThO_2(am, hyd). Due to the equilibrium between ThO_2(am, hyd, coll) and aqueous thorium species, ThO_2(am, hyd) ⇔ ThO_2(am, hyd, coll) can formally also be written as $ThO_2(coll,\ hyd) + 4\ H^+ \Leftrightarrow Th^{4+} + 2\ H_2O(l)$ with $\log_{10}K^\circ(298.15\ K) = -(14.8 \pm 1.0)$ where $ThO_2(am,\ hyd) \Leftrightarrow ThO_2(am,\ hyd,\ coll)$ has been combined with ThO_2(am, hyd, ag) + 4 H^+ ⇔ Th^{4+} + 2 H_2O(l).

10.4.4. Solid thorium hydrides

Solid thorium hydrides do not form under environmental conditions. The thermodynamic data selected by Rand et al. (2008) for ThH_2(cr), ThD_2(cr), ThT_2(cr), $ThH_{3.75}$(cr), $ThD_{3.75}$(cr), $ThT_{3.75}$(cr) are therefore not accepted for our database.

10.4.5 Gaseous thorium oxides and hydrides

Gaseous thorium oxides and hydrides are not relevant under environmental conditions. For this reason, the thermodynamic data selected by Rand et al. (2008) for ThO(g) , ThO_2(g), and ThH(g) are not considered in our database.

10.5 Thorium halogen compounds and complexes

10.5.1 Fluorine compounds and complexes

10.5.1.1 Aqueous fluorine complexes

Complexation of thorium with fluoride is strong and complexes of the type ThF_n^{4-n} have been reported with n ranging from one to six. An experimental difficulty with thorium stems from its strong tendency to hydrolyze and experiments have to be made in acid solutions to prevent the formation of thorium hydroxo complexes. In their analysis of thorium fluoride complexes, Rand et al. (2008) relied on stability constants for ThF^{3+}, ThF_2^{2+}, and ThF_3^+ that are based on liquid-liquid distribution and potentiometric data. At fluoride concentrations sufficiently high to promote the formation of thorium fluoride complexes with $n \geq 4$, it is not possible to obtain reliable stability constants from these methods because of the precipitation of $ThF_4{\cdot}xH_2O$(pr). Hence, for such complexes, Rand et al. (2008) only considered solubility data.

Rand et al. (2008) reviewed 10 experimental studies that reported stability constants for ThF^{3+}, 8 for ThF_2^{2+}, and 3 for ThF_3^+.

They accepted 10 conditional stability constants for ThF^{3+}, measured in 0.5 M $NaClO_4$, in 0.5, 1.0, and 4 M $HClO_4$, in 0.5 M (Na, H)ClO_4, in 2.0 M H(ClO_4, Cl), in 3 M (H, Na)(ClO_4, F), in 1 M (NaF, $HClO_4$), and in 4 M HNO_3. Due to this diversity of ionic media, a classical SIT regression is not possible, and Rand et al. (2008) extrapolated each conditional constant to zero ionic strength by using selected and estimated ion interaction parameters (see below for a discussion of these parameters). The unweighted average of the extrapolated values

$$Th^{4+} + F^- \Leftrightarrow ThF^{3+}$$

$$\log_{10}\beta^\circ_1(ThF^{3+}, 298.15\text{ K}) = (8.87 \pm 0.15)$$

was selected by Rand et al. (2008) and is also included in our database.

Rand et al. (2008) used a similar procedure for selecting the stability constant for ThF_2^{2+}. They accepted 7 conditional constants, measured in 0.5 M $NaClO_4$, in 0.5 and 4 M $HClO_4$, in 0.5 M (Na, H)ClO_4, in 3 M (H, Na)(ClO_4, F), in 1 M (NaF, $HClO_4$), and in 4 M HNO_3. As for ThF^{3+}, they extrapolated each conditional constant to zero ionic strength and selected

$$Th^{4+} + 2\,F^- \Leftrightarrow ThF_2^{2+}$$

$$\log_{10}\beta^\circ_2(ThF_2^{2+}, 298.15\text{ K}) = (15.63 \pm 0.23)$$

the unweighted average of the extrapolated values, which is also included in our database. For ThF_3^+, finally, Rand et al. (2008) accepted 4 conditional constants, measured in 0.5 M (Na, H)ClO_4, in 3 M (H, Na)(ClO_4, F), in 1 M (NaF, $HClO_4$), and. in 4 M HNO_3 and arrived at the selected value

$$Th^{4+} + 3\,F^- \Leftrightarrow ThF_3^+$$

$$\log_{10}\beta^\circ_3(ThF_3^+, 298.15\text{ K}) = (20.67 \pm 0.16)$$

by the same procedure as they used for ThF^{3+} and ThF_2^{2+}. This value, too, is included in our database.

For the extrapolation of the conditional stability constants to zero ionic strength, Rand et al. (2008) estimated the interaction coefficients of ThF^{3+}, ThF_2^{2+}, and ThF_3^+ with ClO_4^- from the selected values of the corresponding U(IV) fluoride complexes. Hence

$$\varepsilon(ThF^{3+}, ClO_4^-) = \varepsilon(UF^{3+}, ClO_4^-) = (0.48 \pm 0.08)\ kg\cdot mol^{-1}$$

$$\varepsilon(ThF_2^{2+}, ClO_4^-) = \varepsilon(UF_2^{2+}, ClO_4^-) = (0.3 \pm 0.1)\ kg\cdot mol^{-1}$$

$$\varepsilon(ThF_3^{+}, ClO_4^-) = \varepsilon(UF_3^{+}, ClO_4^-) = (0.1 \pm 0.1)\ kg\cdot mol^{-1}$$

The interaction coefficients with NO_3^- were estimated by Rand et al. (2008) using a linear correlation between $\varepsilon(M^{Z+}, ClO_4^-)$ and $\varepsilon(M^{Z+}, NO_3^-)$ for uncomplexed cations M^{Z+}, assuming that this correlation also holds for cationic complexes. From this correlation, Rand et al. (2008) obtained

$$\varepsilon(ThF^{3+}, NO_3^-) = (0.25 \pm 0.20)\ kg\cdot mol^{-1}$$

$$\varepsilon(ThF_2^{2+}, NO_3^-) = (0.15 \pm 0.20)\ kg\cdot mol^{-1}$$

$$\varepsilon(ThF_3^{+}, NO_3^-) = (0.0 \pm 0.2)\ kg\cdot mol^{-1}$$

The interaction coefficients of ThF^{3+}, ThF_2^{2+}, and ThF_3^+, with ClO_4^- and NO_3^- are also included in our database.

In addition to these estimates, Rand et al. (2008) also used the selected values for $\varepsilon(H^+, ClO_4^-)$, $\varepsilon(Th^{4+}, ClO_4^-)$, $\varepsilon(Na^+, F^-)$, $\varepsilon(NH_4^+, F^-)$, $\varepsilon(NH_4^+, NO_3^-)$, $\varepsilon(H^+, NO_3^-)$, and $\varepsilon(Th^{4+}, NO_3^-)$.

Rand et al. (2008) also reviewed two solubility studies that served to determine a stability constant for $ThF_4(aq)$. They relied on only one of them, since the other study was conducted at high ionic strength (4.56 m HNO_3) where it is uncertain if the SIT model is applicable and reliable SIT parameters for the HNO_3 medium are missing. Rand et al. (2008) reevaluated the experimental solubility data of $ThF_4(cr, hyd)$ in dilute NH_4F and NaF solutions (< 0.01 M) using NONLINT-SIT. They kept $\Delta_f G_m°/RT$ for ThF^{3+}, ThF_2^{2+}, and ThF_3^+ fixed at values calculated from the selected stability constants. The selected $\varepsilon(Na^+, F^-) = (0.02 \pm 0.02)\ kg\cdot mol^{-1}$ was also kept constant, as well as $\varepsilon(NH_4^+, F^-) = (0.03 \pm 0.02)\ kg\cdot mol^{-1}$, which was assumed to be identical to the selected value for $\varepsilon(K^+, F^-)$. From the least squares fit, Rand et al. (2008) obtained

$$Th^{4+} + 4\ F^- \Leftrightarrow ThF_4(aq)$$

$$\log_{10}\beta°_4(ThF_4, aq, 298.15\ K) = (25.58 \pm 0.18)$$

which is included in our database.

Only one study was carried out at fluoride concentrations high enough for the potential formation of the anionic thorium fluoride complexes ThF_5^- and ThF_6^{2-}. Rand et al. (2008) reinterpreted the solubility data of the thorium double salts $ThF_4\cdot NaF\cdot H_2O(cr)$ in NaF and $ThF_4\cdot NH_4F(cr)$ in NH_4F solutions using NONLINT-SIT. The $\Delta_f G_m°/RT$ values for ThF^{3+}, ThF_2^{2+}, ThF_3^+, and $ThF_4(aq)$ were kept constant according to the selected values of the formation constants. In addition, the ion interaction coefficients $\varepsilon(Na^+, F^-)$ and $\varepsilon(NH_4^+, F^-)$ were also kept constant at their selected values (see above). Several attempts were made to fit the $\Delta_f G_m°/RT$ values for $ThF_4(cr, hyd)$, $ThF_4\cdot NaF\cdot H_2O(cr)$, $ThF_4\cdot NH_4F(cr)$, ThF_5^-, and/or ThF_6^{2-} to the solubility data. The best fit was obtained with a value for $\Delta_f G_m°/RT(ThF_6^{2-}, 298.15\ K)$ that corresponds to $\log_{10}\beta°_6(ThF_6^{2-}, 298.15\ K) = (29.23 \pm 0.62)$, while ThF_5^- never became important enough to determine $\Delta_f G_m°/RT$ for ThF_5^- with sufficient certainty. Due to assumptions made in the fit of the solubility data and difficulties encountered in the interpretation, and because no supporting information is available, Rand et al. (2008) did not select the data for ThF_6^{2-}, but noted that they may be used for scoping calculations. For this reason, the data for ThF_6^{2-} obtained by Rand et al. (2008) with NONLINT-SIT

$$Th^{4+} + 6F^- \Leftrightarrow ThF_6^{2-}$$

$$\log_{10}\beta°_6(ThF_6^{2-}, 298.15\ K) = (29.23 \pm 0.62)$$

$$\varepsilon(ThF_6^{2-}, Na^+) = -(0.30 \pm 0.06)\ kg\cdot mol^{-1}$$

are included in our database only as supplemental data. Note that the value for $\varepsilon(ThF_6^{2-}, Na^+)$ appears in Table B.3 of the recommended ion interaction coefficients by Rand et al. (2008), even though $\log_{10}\beta°_6$ is not recommended. According to Table VIII-8 by Rand et al. (2008), the values for $\varepsilon(ThF_6^{2-}, Na^+)$ and $\varepsilon(ThF_6^{2-}, NH_4^+)$ used in the calculations were assumed to be equal to the selected value for $\varepsilon(UF_6^{2-}, Na^+)$.

Since no experimental data on thorium fluoride complexes are available for chloride media, we estimated the ion interaction coefficients of the cationic thorium fluoride complexes with chloride based on charge correlations (see Appendix A) and include

$$\varepsilon(ThF^{3+}, Cl^-) = (0.25 \pm 0.10)\ kg\cdot mol^{-1}$$

$$\varepsilon(ThF_2^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg\cdot mol^{-1}$$

$$\varepsilon(ThF_3^{+}, Cl^-) = (0.05 \pm 0.10)\ kg\cdot mol^{-1}$$

in our database.

Rand et al. (2008) reviewed five studies dealing with the determination of the enthalpy of reaction for ThF^{3+}, ThF_2^{2+}, ThF_3^+, and $ThF_4(aq)$. Three studies used the van't Hoff equation and two used calorimetric methods. Rand et al. (2008) accepted only calorimetric data, since enthalpies of reaction determined from the van't Hoff equation are much less accurate. The data selected by Rand et al. (2008)

$$\Delta_r H_m°_1(ThF^{3+}, 298.15\ K) = -\ (0.4 \pm 2.0)\ kJ\cdot mol^{-1}$$

$$\Delta_r H_m°_2(ThF_2^{2+}, 298.15\ K) = -\ (3.3 \pm 0.4)\ kJ\cdot mol^{-1}$$

are based on one study in the case of ThF_2^{2+} and on two studies in the case of ThF^{3+}. Although the measured reaction enthalpies for ThF^{3+} differ considerably, (1.6 ± 0.3) and -(2.4 ± 0.1) $kJ\cdot mol^{-1}$, Rand et al. (2008) accepted both and selected their average, remarking that the difference is probably due to the different ionic media used (0.5 M $NaClO_4$ and 4 M $HClO_4$, resp.) and that there is no reason to prefer one value over the other. We accept the choice by Rand et al. (2008) and include the standard molar reaction enthalpies for ThF^{3+} and ThF_2^{2+} in our database.

10.5.1.2 Solid and gaseous fluorides

Thorium fluoride solids: Based on two studies, Rand et al. (2008) reinterpreted solubility data for ThF_4(cr, hyd) in NaF, NH_4F, and HNO_3 solutions using NONLINT-SIT. They selected the average of the $\Delta_f G_m°/RT(ThF_4, cr, hyd)$ values based on the experimental data from the NaF and NH_4F systems. From $\Delta_f G_m°/RT(ThF_4, cr, hyd) = -(811.860 \pm 0.915)$ at 25°C and the selected $\Delta_f G_m°(Th^{4+}, 298.15\ K)$ and $\Delta_f G_m°(HF, aq, 298.15\ K) = -(299.675 \pm 0.702)\ kJ\cdot mol^{-1}$ they obtained

$$ThF_4(cr, hyd) + 4\ H^+ \Leftrightarrow Th^{4+} + 4\ HF(aq)$$

$$\log_{10}{}^*K_{s,0}°(ThF_4, cr, hyd, 298.15) = -(19.11 \pm 0.40)$$

For inclusion in our database (replacing ThF_4(cr) selected in the previous version of our database), we used $\log_{10}{}^*\beta^\circ_1(H^+ + F^- \Leftrightarrow HF$, aq, 298.15 K) = (3.18 ± 0.02) to reformulate the reaction in terms of F^-, leading to

$$ThF_4(\text{cr, hyd}) \Leftrightarrow Th^{4+} + 4\ F^-$$

$$\log_{10}K_{s,0}^\circ(ThF_4, \text{cr, hyd}, 298.15) = -(31.8 \pm 0.4)$$

This solid is highly soluble in water and was included in our database only by mistake. It can be safely neglected (as well as the thorium fluoride solid that was replaced by it).

The standard molar Gibbs free energies of formation selected by Rand et al. (2008) for ThF_4(cr) and $ThOF_2$(cr) were calculated from calorimetric data. As these solids are also soluble in water, they are not included in our database.

Thorium fluoride gases: Rand et al. (2008) selected thermodynamic data for the gaseous thorium fluorides and oxyfluorides ThF(g), ThF_2(g), ThF_3(g), ThF_4(g), and ThOF(g). These gases are not relevant under environmental conditions and are therefore not included in our database.

10.5.2 Chlorine compounds and complexes

10.5.2.1 Aqueous thorium chloride complexes

Aqueous thorium chloride complexes are much weaker than the fluoride complexes discussed above. In systems where weak complexes are formed it is very difficult to distinguish between the formation of complexes and variations in activity coefficients, and experimental data can be equally well described by the specific ion interaction theory, whether weak complexes are explicitly considered or not. In the previous volumes of the NEA series on "Chemical Thermodynamics", chloride complexes were explicitly considered and, for the sake of consistency, Rand et al. (2008) followed their example. For comparison, however, they used both approaches and found that the experimental data for the reaction $Th^{4+} + Cl^- \Leftrightarrow ThCl^{3+}$ is somewhat better described with the chloride complexation model at low ionic strength and chloride concentrations below 0.5 M, while in perchlorate-chloride mixtures of high ionic strength and chloride concentration, the strict ion interaction approach excluding chloride complexation fares equally well.

The experimental studies reviewed by Rand et al. (2008) reported stability constants for $ThCl^{3+}$, $ThCl_2^{2+}$, $ThCl_3^+$, $ThCl_4$(aq), and $ThCl_5^-$. They only accepted those for $ThCl^{3+}$, mainly because the constants for the higher complexes were obtained under conditions where a large part of perchlorate ions of the ionic background medium were replaced by chloride. For this reason, Rand et al. (2008) considered these constants merely as fitting parameters that have no meaning. For $ThCl^{3+}$, Rand et al. (2008) considered four liquid-liquid extraction studies in 0.5–6.0 M (Na^+, H^+)(Cl^-, ClO_4^-). Their SIT regression of 9 experimental data points lead to

$$Th^{4+} + Cl^- \Leftrightarrow ThCl^{3+}$$

$$\log_{10}\beta^\circ_1(ThCl^{3+}, 298.15\ K) = (1.70 \pm 0.10)$$

with $\Delta\varepsilon = -(0.11 \pm 0.05)$ kg·mol^{-1}. From this value and $\varepsilon(Th^{4+}, Cl^-) = \varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.10)$ kg·mol^{-1}, and $\varepsilon(Cl^-, Na^+) = (0.03 \pm 0.01)$ kg·mol^{-1} follows[16]

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[16] When using the complexation model, the interaction coefficient of Th^{4+} in chloride solution is taken to be equal to the value in non-complexing perchlorate solution $\varepsilon(Th^{4+}, Cl^-) = \varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.10)$ kg·mol^{-1}. The selected value $\varepsilon(Th^{4+}, Cl^-) = (0.25 \pm 0.03)$ kg·mol^{-1} (see Section 10.3) obtained from isopiestic measurements implicitly accounts for thorium chloride complexes and is not to be used in explicit complexation models.

$$\varepsilon(\text{ThCl}^{3+}, \text{Cl}^-) = \varepsilon(\text{ThCl}^{3+}, \text{ClO}_4^-) = (0.62 \pm 0.11)\ \text{kg}\cdot\text{mol}^{-1}$$

These data for ThCl^{3+} are included in our database.

10.5.2.2 Aqueous thorium chlorate complexes

Chlorate complexes are weak and chlorate is not relevant under environmental conditions. Therefore the stability constant selected by Rand et al. (2008) for ThClO_3^{3+} is not considered in our database.

10.5.2.3 Thorium chloride solids and gases

The thorium chloride and oxychloride solids β-ThCl_4, $\text{ThCl}_4\cdot2\text{H}_2\text{O(cr)}$, $\text{ThCl}_4\cdot4\text{H}_2\text{O(cr)}$, $\text{ThCl}_4\cdot7\text{H}_2\text{O(cr)}$, $\text{ThCl}_4\cdot8\text{H}_2\text{O(cr)}$, and $\text{ThOCl}_2\text{(cr)}$ are all soluble in water. The thermodynamic data selected by Rand et al. (2008) for these solids are therefore not included in our database. Note, however, that the solution enthalpy of β-ThCl_4 was used by Rand et al. (2008) for the calculation of $\Delta_f H_m^\circ(\text{Th}^{4+}, 298.15\ \text{K})$, see Section 10.3.

Thorium chloride gases are not relevant for natural aqueous environments and the thermodynamic data selected by Rand et al. (2008) for ThCl(g), $\text{ThCl}_2\text{(g)}$, $\text{ThCl}_3\text{(g)}$, and $\text{ThCl}_4\text{(g)}$ are not included in our database.

10.5.3 Bromine compounds and complexes

Rand et al. (2008) selected thermodynamic data for the thorium bromide complex ThBr^{3+}, for the thorium bromate complex ThBrO_3^{3+}, for the soluble thorium bromide solids β-ThBr_4, $\text{ThBr}_4\cdot7\text{H}_2\text{O(cr)}$, $\text{ThBr}_4\cdot10\text{H}_2\text{O(cr)}$, $\text{ThBr}_4\cdot12\text{H}_2\text{O(cr)}$, and $\text{ThOBr}_2\text{(cr)}$, and for the thorium bromide gases ThBr(g), $\text{ThBr}_2\text{(g)}$, $\text{ThBr}_3\text{(g)}$, and $\text{ThBr}_4\text{(g)}$. Bromine is not relevant for geochemical modeling of groundwaters and is not included in our database.

10.5.4 Iodine compounds and complexes

According to Rand et al. (2008) there is no experimental information available on the formation of thorium iodide complexes.

10.5.4.1 Iodate complexes

The formation of thorium iodate complexes was investigated in a single experimental study using liquid-liquid extraction. The experiments were performed in a 0.5 M $\text{H(ClO}_4, \text{IO}_3)$ medium and conditional formation constants were reported for ThIO_3^{3+}, $\text{Th(IO}_3)_2^{2+}$, and $\text{Th(IO}_3)_3^{+}$. Rand et al. (2008) accepted these constants and extrapolated them to zero ionic strength using the SIT and the following estimates for the ion interaction coefficients:

$$\varepsilon(\text{Th}^{4+}, \text{IO}_3^-) = \varepsilon(\text{Th}^{4+}, \text{ClO}_4^-) = (0.70 \pm 0.10)\ \text{kg}\cdot\text{mol}^{-1}$$

$$\varepsilon(\text{H}^+, \text{IO}_3^-) = \varepsilon(\text{H}^+, \text{ClO}_4^-) = (0.14 \pm 0.02)\ \text{kg}\cdot\text{mol}^{-1},$$

$$\varepsilon(\text{ThIO}_3^{3+}, \text{IO}_3^-) = \varepsilon(\text{ThIO}_3^{3+}, \text{ClO}_4^-) = \varepsilon(\text{ThNO}_3^{3+}, \text{ClO}_4^-) = (0.56 \pm 0.14)\ \text{kg}\cdot\text{mol}^{-1}$$

$$\varepsilon(\text{Th(IO}_3)_2^{2+}, \text{IO}_3^-) = \varepsilon(\text{Th(IO}_3)_2^{2+}, \text{ClO}_4^-) = \varepsilon(\text{Th(NO}_3)_2^{2+}, \text{ClO}_4^-) = (0.43 \pm 0.18)\ \text{kg}\cdot\text{mol}^{-1}$$

$$\varepsilon(\text{Th(IO}_3)_3^{+}, \text{IO}_3^-) = \varepsilon(\text{Th(IO}_3)_3^{+}, \text{ClO}_4^-) = \varepsilon(\text{Th(NO}_3)_3^{+}, \text{ClO}_4^-) = (0.25 \pm 0.15)\ \text{kg}\cdot\text{mol}^{-1}$$

With these ion interaction coefficients, Rand et al. (2008) obtained

$$Th^{4+} + IO_3^- \Leftrightarrow ThIO_3^{3+}$$

$$\log_{10}\beta°_1(ThIO_3^{3+}, 298.15 \text{ K}) = (4.14 \pm 0.10)$$

$$Th^{4+} + 2\ IO_3^- \Leftrightarrow Th(IO_3)_2^{2+}$$

$$\log_{10}\beta°_2(Th(IO_3)_2^{2+}, 298.15 \text{ K}) = (6.97 \pm 0.12)$$

$$Th^{4+} + 3\ IO_3^- \Leftrightarrow Th(IO_3)_3^{+}$$

$$\log_{10}\beta°_3(Th(IO_3)_3^{+}, 298.15 \text{ K}) = (9.87 \pm 0.11)$$

These stability constants are included in our database, as well as the estimated ion interaction parameters $\varepsilon(ThIO_3^{3+}, ClO_4^-)$, $\varepsilon(Th(IO_3)_2^{2+}, ClO_4^-)$, and $\varepsilon(Th(IO_3)_3^{+}, ClO_4^-)$.

Since no experiments were performed in chloride background media, we estimated the corresponding ion interaction coefficients based on charge correlations (see Appendix A)

$$\varepsilon(ThIO_3^{3+}, Cl^-) = (0.25 \pm 0.10) \text{ kg·mol}^{-1}$$

$$\varepsilon(Th(IO_3)_2^{2+}, Cl^-) = (0.15 \pm 0.10) \text{ kg·mol}^{-1}$$

$$\varepsilon(Th(IO_3)_3^{+}, Cl^-) = (0.05 \pm 0.10) \text{ kg·mol}^{-1}$$

and include them in our database.

10.5.4.2 Iodine solids and gases

Thorium iodide solids: The standard molar Gibbs free energy of formation selected by Rand et al. (2008) for $ThI_4(cr)$ is based on enthalpy of solution measurements and estimated standard molar entropies. $ThI_4(cr)$ is soluble in water and is not included in our database.

Only a value for the enthalpy of formation for $ThOI_2(cr)$ was selected by Rand et al. (2008), for this reason, this solid is not included in our database.

Thorium iodide gases: Thorium iodide gases are not relevant under environmental conditions and the thermodynamic data selected by Rand et al. (2008) for $ThI(g)$, $ThI_2(g)$, $ThI_3(g)$, and $ThI_4(g)$ are not included in our database.

10.6 Thorium group 16 compounds and complexes

10.6.1 Sulphur compounds and complexes

10.6.1.1 Aqueous sulphate complexes

Experimental data on the formation of thorium sulphate complexes have been acquired using solvent extraction and ion exchange methods. Most of them (four studies) were obtained at relatively high acidities (1.7 to 2 M) and nearly constant ionic strength (1.7 to 2 M) in various media ($HClO_4$, $H(ClO_4, HSO_4)$, $(H, Na)ClO_4$). Under these conditions the predominant complexes are $ThSO_4^{2+}$ and $Th(SO_4)_2(aq)$. Only one study was carried out at acidities low enough and sulphate concentrations high enough to promote the formation of the higher complexes $Th(SO_4)_3^{2-}$ and $Th(SO_4)_4^{4-}$. Moreover, a study reported the mixed complex $Th(HSO_4)(SO_4)^+$ and another one the ternary thorium-nitrate-sulphate complexes $Th(NO_3)(SO_4)^+$ and $Th(NO_3)_2(SO_4)(aq)$; the stability constants of these, however, were deemed unreliable by Rand et al. (2008) and were not accepted.

For the analysis of the reported conditional stability constants, Rand et al. (2008) proceeded as follows. The conditional constants for $Th^{4+} + HSO_4^- \Leftrightarrow ThSO_4^{2+} + H^+$ and $Th^{4+} + 2\ HSO_4^- \Leftrightarrow$

$Th(SO_4)_2(aq) + 2H^+$ were extrapolated to zero ionic strength using SIT. Since the constants were all measured at nearly the same ionic strength, a classical SIT regression was not possible and Rand et al. (2008) extrapolated each conditional stability constant to zero ionic strength (using estimated ion interaction coefficients for the complexes) and took the unweighted average of the extrapolated values. They then combined these averages with the selected value for the protonation of sulphate and found

$$Th^{4+} + SO_4^{2-} \Leftrightarrow ThSO_4^{2+}$$

$$\log_{10}\beta^\circ_1(ThSO_4^{2+}, 298.15\ K) = (6.17 \pm 0.32)$$

$$Th^{4+} + 2\ SO_4^{2-} \Leftrightarrow Th(SO_4)_2(aq)$$

$$\log_{10}\beta^\circ_2(Th(SO_4)_2, aq, 298.15\ K) = (9.69 \pm 0.27)$$

which are also accepted for our database. For the SIT extrapolations, Rand et al. (2008) assumed that $\varepsilon(ThSO_4^{2+}, ClO_4^-)$ can be approximated by the selected $\varepsilon(USO_4^{2+}, ClO_4^-) = (0.3 \pm 0.1)\ kg{\cdot}mol^{-1}$, $\varepsilon(Th^{4+}, HSO_4^-)$ by the selected $\varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.10)\ kg{\cdot}mol^{-1}$, and $\varepsilon(H^+, HSO_4^-)$ by the selected $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)\ kg{\cdot}mol^{-1}$. In addition, they used the selected $\varepsilon(Na^+, HSO_4^-) = -(0.01 \pm 0.02)$. Since no experiments were performed in chloride media, Rand et al. (2008) estimated the interaction coefficient of $ThSO_4^{2+}$ with Cl^- using a linear correlation between $\varepsilon(M^{Z+}, ClO_4^-)$ and $\varepsilon(M^{Z+}, Cl^-)$ for uncomplexed cations M^{Z+}, assuming that this correlation also holds for cationic complexes. Thus, the estimate of $\varepsilon(ThSO_4^{2+}, Cl^-)$ is based on an estimate of $\varepsilon(ThSO_4^{2+}, ClO_4^-)$. The estimated values

$$\varepsilon(ThSO_4^{2+}, ClO_4^-) = (0.3 \pm 0.1)\ kg{\cdot}mol^{-1}$$

$$\varepsilon(ThSO_4^{2+}, Cl^-) = (0.14 \pm 0.15)\ kg{\cdot}mol^{-1}$$

are also included in our database. The single study reporting the formation of the higher complexes $Th(SO_4)_3^{2-}$ and $Th(SO_4)_4^{4-}$ used a liquid ion-exchange method and was made in a mixed H_2SO_4-Na_2SO_4 medium with varying ionic strength. The experimental data were reinterpreted by Rand et al. (2008) by means of NONLINT-SIT. For this purpose, Rand et al. (2008) assumed that $\varepsilon(H^+, Th(SO_4)_3^{2-})$ is equal to the selected $\varepsilon(Li^+, SO_4^{2-})$[17]. The values for $\Delta_f G_m^\circ/RT(Th(SO_4)_3^{2-}, 298.15\ K)$ and $\varepsilon(Th(SO_4)_3^{2-}, Na^+)$ were fitted to the experimental data using the ion interaction coefficients for $ThSO_4^{2+}$ and $Th(SO_4)_3^{2-}$ and the other species just discussed, and keeping $\Delta_f G_m^\circ/RT(ThSO_4^{2+}, 298.15\ K)$ and $\Delta_f G_m^\circ/RT(Th(SO_4)_2, aq, 298.15\ K)$ at the values corresponding to $\log_{10}\beta^\circ_1(ThSO_4^{2+}, 298.15\ K)$ and $\log_{10}\beta^\circ_2(Th(SO_4)_2, aq, 298.15\ K)$. The NONLINT-SIT fit provided

$$Th^{4+} + 3\ SO_4^{2-} \Leftrightarrow Th(SO_4)_3^{2-}$$

$$\log_{10}\beta^\circ_3(Th(SO_4)_3^{2-}, 298.15\ K) = (10.748 \pm 0.076)$$

$$\varepsilon(Th(SO_4)_3^{2-}, Na^+) = -(0.091 \pm 0.038)\ kg{\cdot}mol^{-1}$$

These values were selected by Rand et al. (2008) and are also included in our database. Including $Th(SO_4)_4^{4-}$ did not improve the fits, therefore, Rand et al. (2008) did not consider this species. Rand et al. (2008) assumed that the value derived for $\varepsilon(Th(SO_4)_3^{2-}, Na^+)$ is also valid for the interaction of $Th(SO_4)_3^{2-}$ with K^+ and

$$\varepsilon(Th(SO_4)_3^{2-}, K^+) = -(0.091 \pm 0.038)\ kg{\cdot}mol^{-1}$$

is also included in our database.

The reaction enthalpies selected by Rand et al. (2008)

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[17] $\varepsilon(Li^+, SO_4^{2-}) = \varepsilon_1(Li^+, SO_4^{2-}) + \varepsilon_2(Li+, SO_4^{2-}) \log_{10}I_m$, with $\varepsilon_1(Li^+, SO_4^{2-}) = -(0.068 \pm 0.003)\ kg{\cdot}mol^{-1}$ and $\varepsilon_2(Li^+, SO_4^{2-}) = (0.093 \pm 0.007)\ kg{\cdot}mol^{-1}$

$$\Delta_r H_m{}^\circ{}_1(\mathrm{ThSO_4}^{2+}, 298.15\ \mathrm{K}) = (20.92 \pm 0.74)\ \mathrm{kJ \cdot mol^{-1}}$$

$$\Delta_r H_m{}^\circ{}_2(\mathrm{Th(SO_4)_2}, \mathrm{aq}, 298.15\ \mathrm{K}) = (40.38 \pm 1.08)\ \mathrm{kJ \cdot mol^{-1}}$$

are based on a calorimetric study that was performed in a 2.2 m $HClO_4$ background electrolyte. Rand et al. (2008) assumed that these enthalpies are a good approximation of the values at zero ionic strength. They are also included in our database. Another study determined the reaction enthalpies from the temperature dependence of the equilibrium constants. Since such data are less accurate than those from calorimetry, they were not accepted by Rand et al. (2008).

10.6.1.2 Thorium sulphide and sulphate solids

Thorium sulphides: Rand et al. (2008) calculated the standard molar Gibbs free energy of formation of ThS(cr) from calorimetrically determined values for the standard molar enthalpy of formation and for the standard molar entropy. These data are not included in our database since it is very unlikely that this synthetic solid forms in low-temperature aqueous environments. For the same reason and also because both solubility products and Gibbs free energies of formation are unknown, thermodynamic data selected by Rand et al. (2008) for ThS_2(cr), Th_2S_3(cr), and ThOS(cr) are not considered for our database.

Thorium sulphates: Rand et al. (2008) selected a standard molar heat capacity of formation for $Th(SO_4)_2$(cr). They did not accept the standard molar Gibbs free energy of formation derived from reported decomposition pressures for the reaction $Th(SO_4)_2(cr) \Leftrightarrow ThO_2(cr) + 2\ SO_2(g) + O_2(g)$ from 908–1057 K, since it would lead to unrealistically low solubilities for $Th(SO_4)_2$(cr). Therefore, $Th(SO_4)_2$(cr) is not included in our database.

There are at least three hydrates $Th(SO_4)_2 \cdot nH_2O$(cr), with n = 4, 8, and 9. These hydrates are highly soluble and the solubility product selected by Rand et al. (2008) for $Th(SO_4)_2 \cdot 9H_2O$(cr) is therefore not included in our database. Solubility products for $Th(SO_4)_2 \cdot 4H_2O$(cr) and for $Th(SO_4)_2 \cdot 8H_2O$(cr) were not accepted by Rand et al. (2008) because of the inapplicability of the SIT at the high ionic strengths of the saturated solutions. The standard molar enthalpy of reaction for $Th(SO_4)_2 \cdot 4H_2O(cr) + 4\ H_2O(l) \Leftrightarrow Th(SO_4)_2 \cdot 8H_2O(cr)$ selected by Rand et al. (2008) (discussed and selected in the text but not listed in their Table III-2) is not included in our database.

Rand et al. (2008) also selected solubility products (discussed and selected in the text but not listed in their Table III-2) for the hydrated double salts $Th(SO_4)_2 \cdot Na_2SO_4 \cdot 6H_2O$(cr), $Th(SO_4)_2 \cdot K_2SO_4 \cdot 4H_2O$(cr), $Th(SO_4)_2 \cdot 2K_2SO_4 \cdot 2H_2O$(cr), $Th(SO_4)_2 \cdot 3.5K_2SO_4$(cr), and $Th(SO_4)_2 \cdot (NH_4)_2SO_4 \cdot 4H_2O$(cr). These solids are only formed in concentrated sulphate solutions. Because of this, they are not included in our database.

10.6.2 Selenium compounds

Rand et al. (2008) selected thermodynamic data for ThOSe(cr), $Th(SeO_3)_2$(cr), and $Th(SeO_3)_2 \cdot H_2O$(cr) . Since only the heat capacity was measured for ThOSe(cr), this solid is not included in our database. A measured solubility product constant for $Th(SeO_3)_2$(cr) was not accepted by Rand et al. (2008) and is therefore not included in our database. Rand et al. (2008) selected $\Delta_r H_m{}^\circ$(298.15 K) and $\Delta_r S_m{}^\circ$(298.15 K) values for the dehydration reaction $Th(SeO_3)_2 \cdot H_2O(cr) \Leftrightarrow Th(SeO_3)_2(cr) + H_2O(l)$. This equilibrium is irrelevant for aqueous systems without the solubility product constant for $Th(SeO_3)_2$(cr) and is not included in our database.

10.7 Thorium group 15 compound and complexes

10.7.1 Nitrogen compounds and complexes

10.7.1.1 Aqueous nitrate complexes

Thorium nitrate complexes are weak and the thorium nitrate system (like the thorium chloride system discussed above) can be equally well described by using a complex formation or a specific ion interaction model. According to Rand et al. (2008), experimental mean activity coefficients of thorium nitrate solutions can be well reproduced by a strict SIT model without assuming complexes up to nitrate concentrations of 3.5 m. Large-angle X-ray diffraction data from nitrate solutions, however, indicate that inner-sphere Th nitrate complexes are formed. For this reason and in order to be compatible with the older volumes of the NEA series, Rand et al. (2008) decided to continue the use of the complex formation model. Experimental data on thorium nitrate complexation indicate the formation of $Th(NO_3)_n^{4-n}$, with n ranging from one to six. Rand et al. (2008) considered seven experimental studies, but accepted data from only one of these which is based on solvent extraction. Rand et al. (2008) interpreted the data (distribution coefficients of Th between an organic phase and aqueous solutions of 0.05–3 M $NaNO_3$ with 0.02 M HNO_3) using the complexation model and derived stability constants for $ThNO_3^{3+}$, $Th(NO_3)_2^{2+}$, and $Th(NO_3)_3^{+}$. For the first two complexes they obtained

$$Th^{4+} + NO_3^- \Leftrightarrow ThNO_3^{3+}$$

$$\log_{10}\beta^\circ_1(ThNO_3^{3+}, 298.15\ K) = (1.3 \pm 0.2)$$

$$\varepsilon(ThNO_3^{3+}, ClO_4^-) = \varepsilon(ThNO_3^{3+}, NO_3^-) = (0.56 \pm 0.14)\ kg\cdot mol^{-1}$$

$$Th^{4+} + 2\ NO_3^- \Leftrightarrow Th(NO_3)_2^{2+}$$

$$\log_{10}\beta^\circ_2(Th(NO_3)_2^{2+}, 298.15\ K) = (2.3 \pm 0.4)$$

$$\varepsilon(Th(NO_3)_2^{2+}, ClO_4^-) = \varepsilon(Th(NO_3)_2^{2+}, NO_3^-) = (0.43 \pm 0.18)\ kg\cdot mol^{-1}$$

which are included in our database. The ion interaction coefficients were calculated by Rand et al. (2008) using $\varepsilon(Th^{4+}, NO_3^-)$[18] = $\varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.10)\ kg\cdot mol^{-1}$ and the selected $\varepsilon(NO_3^-, Na^+) = -(0.04 \pm 0.03)\ kg\cdot mol^{-1}$. In the absence of experimental data for chloride media, we estimated

$$\varepsilon(ThNO_3^{3+}, Cl^-) = (0.25 \pm 0.10)\ kg\cdot mol^{-1}$$

$$\varepsilon(Th(NO_3)_2^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg\cdot mol^{-1}$$

based on charge correlations (see Appendix A) and include these data in our database.

Rand et al. (2008) also determined $\log_{10}\beta^\circ_3(Th(NO_3)_3^+, 298.15\ K) = (3.0 \pm 0.5)$ for $Th^{4+} + 3\ NO_3^- \Leftrightarrow Th(NO_3)_3^+$ with $\varepsilon(Th(NO_3)_3^+, ClO_4^-) = \varepsilon(Th(NO_3)_3^+, NO_3^-) = (0.25 \pm 0.15)\ kg\cdot mol^{-1}$ but did not select these data. Unfortunately, they gave no explanation why. A reason might be that $Th(NO_3)_3^+$ becomes important only at nitrate concentrations larger than 2 M. Since such nitrate concentrations are very unlikely under environmental conditions, data for this complex are not included in our database, not even as supplemental data.

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[18] When using the complexation model, the interaction coefficient of Th^{4+} in nitrate solution is taken to be equal to the value in non-complexing perchlorate solution $\varepsilon(Th^{4+}, NO_3^-) = \varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.10)\ kg\cdot mol^{-1}$. The selected value $\varepsilon(Th^{4+}, NO_3^-) = (0.31 \pm 0.12)\ kg\cdot mol^{-1}$ (see Section 10.3) implicitly accounts for the effect of thorium chloride complexes and is not to be used in explicit complexation models.

The formation of $Th(NO_3)_4(aq)$, $Th(NO_3)_5^-$, and $Th(NO_3)_6^{2-}$ was suggested by an experimental study measuring the distribution of trace amounts of Th between a nitrate loaded anion exchanger and aqueous nitrate solutions. Rand et al. (2008) did not accept their stability constants, mainly because the ionic strength was not held constant throughout the experiments.

10.7.1.2 Aqueous thorium azide complexes

The thermodynamic data selected by Rand et al. (2008) for ThN_3^{3+} and $Th(N_3)_2^{2+}$ are not included in our database as azides do not form under environmental conditions.

10.7.1.3 Solid nitrides and nitrites

Thorium nitride solids: Since the semimetal compound ThN(cr) and the Th(IV) compound $Th_3N_4(cr)$ are not formed under environmental conditions, the thermodynamic data selected by Rand et al. (2008) for these synthetic solids are not included in our database.

Thorium nitrate solids: Thorium nitrate solids are very soluble and are not formed in natural environments. Therefore the thermodynamic data selected by Rand et al. (2008) for $Th(NO_3)_4\cdot 4H_2O(cr)$ and $Th(NO_3)_4\cdot 5H_2O(cr)$ are not considered in our database.

10.7.2 Phosphorous compounds and complexes

10.7.2.1 Aqueous phosphate complexes

In their review of the aqueous Th-phosphate system, Rand et al. (2008) considered two liquid-liquid extraction and six solubility studies. The most precise data were acquired with the liquid-liquid extraction method, and Rand et al. (2008) accepted data from only one of these, which was made with trace amounts of Th, varying amounts of phosphoric acid, 2.00 M (Na, H)ClO_4 (with [H+] varying from 0.25–2.0 M) and an organic extractant. Since the extraction experiments were carried out at only one ionic strength, Rand et al. (2008) had to estimate ion interaction coefficients for $ThH_2PO_4^{3+}$, $ThH_3PO_4^{4+}$, $Th(H_2PO_4)_2^{2+}$, and $Th(H_3PO_4)(H_2PO_4)^{3+}$ in order to extrapolate their conditional stability constants to zero ionic strength with SIT. Their estimates are based on an analogy with like charged cations, hence

$$\varepsilon(ThH_2PO_4^{3+}, ClO_4^-) = \varepsilon(M^{3+}, ClO_4^-) \cong (0.5 \pm 0.1)\ kg\cdot mol^{-1}$$

$$\varepsilon(ThH_3PO_4^{4+}, ClO_4^-) = \varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.10)\ kg\cdot mol^{-1}$$

$$\varepsilon(Th(H_2PO_4)_2^{2+}, ClO_4^-) = \varepsilon(M^{2+}, ClO_4^-) \cong (0.4 \pm 0.1)\ kg\cdot mol^{-1}$$

$$\varepsilon(Th(H_3PO_4)(H_2PO_4)^{3+}, ClO_4^-) = \varepsilon(M^{3+}, ClO_4^-) \cong (0.5 \pm 0.1)\ kg\cdot mol^{-1}$$

From these estimated coefficients (which we adopted for our database) combined with the selected $\varepsilon(Th^{+4}, ClO_4^-) = (0.7 \pm 0.10)\ kg\cdot mol^{-1}$ and $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)\ kg\cdot mol^{-1}$ follow the stability constants selected by Rand et al. (2008)

$$Th^{4+} + H_3PO_4(aq) \Leftrightarrow ThH_2PO_4^{3+} + H^+$$

$$\log_{10}{}^*\beta^\circ(ThH_2PO_4^{3+}, 298.15\ K) = (3.45 \pm 0.32)$$

$$Th^{4+} + H_3PO_4(aq) \Leftrightarrow ThH_3PO_4^{4+}$$

$$\log_{10}\beta^\circ(ThH_3PO_4^{4+}, 298.15\ K) = (1.89 \pm 0.31)$$

$$Th^{4+} + 2\ H_3PO_4(aq) \Leftrightarrow Th(H_2PO_4)_2^{2+} + 2\ H^+$$

$$\log_{10}{}^*\beta^\circ(Th(H_2PO_4)_2^{2+}, 298.15\ K) = (6.20 \pm 0.32)$$

$$\mathrm{Th^{4+} + 2\ H_3PO_4(aq) \Leftrightarrow Th(H_3PO_4)(H_2PO_4)^{3+} + H^+}$$

$$\log_{10}{}^*\beta^\circ(\mathrm{Th(H_3PO_4)(H_2PO_4)^{3+}}, 298.15\ \mathrm{K}) = (5.42 \pm 0.32)$$

which are included in our database.

For chloride systems we estimated

$$\varepsilon(\mathrm{ThH_2PO_4^{3+}, Cl^-}) = (0.25 \pm 0.10)\ \mathrm{kg{\cdot}mol^{-1}}$$

$$\varepsilon(\mathrm{ThH_3PO_4^{4+}, Cl^-}) = (0.35 \pm 0.10)\ \mathrm{kg{\cdot}mol^{-1}}$$

$$\varepsilon(\mathrm{Th(H_2PO_4)_2^{2+}, Cl^-}) = (0.15 \pm 0.10)\ \mathrm{kg{\cdot}mol^{-1}}$$

$$\varepsilon(\mathrm{Th(H_3PO_4)(H_2PO_4)^{3+}, Cl^-}) = (0.25 \pm 0.10)\ \mathrm{kg{\cdot}mol^{-1}}$$

based on charge correlations (see Appendix A) and include them in our database.

10.7.2.2 Solid thorium phosphates

Thorium phosphate: The solubility of phosphate solids has been the subject of several studies. Measured solubility products for $Th(HPO_4)_2(s)$, $Th(HPO_4)_2(s, hyd)$, $Th(HPO_4)_2{\cdot}4H_2O(s)$, and $Th_2(PO_4)_2(HPO_4){\cdot}H_2O(s)$ were all not accepted by Rand et al. (2008). While they also did not select the solubility product of well characterized $Th_3(PO_4)_4(s)$ determined in 0.01–1 M perchloric acid, they reported it for use in scoping calculations. The solubility product was not selected because the procedure of how it was extrapolated to zero ionic strength was not described by the authors of the study. Therefore, we include

$$Th_3(PO_4)_4(s) \Leftrightarrow 3\ Th^{4+} + 4\ PO_4^{3-}$$

$$\log_{10}K_{s,0}^\circ(Th_3(PO_4)_4, s, 298.15\ K) = -(112.0 \pm 2.1)$$

in our database only as supplemental data.

Thorium phosphate diphosphate: A standard molar heat capacity value for the synthetic solid $Th_4(PO_4)_4P_2O_7(cr)$ was selected by Rand et al. (2008). Neither solubility product nor standard molar Gibbs free energy of formation are known. This solid is therefore not considered in our database.

10.7.3 Solid thorium arsenides, antimonides and bismuthides

Thorium arsenides: Rand et al. (2008) selected standard molar entropies and heat capacities of the intermetallic compounds ThAs(cr) and $Th_3As_4(cr)$. Since these solids are of no relevance for environmental systems and neither solubility products nor standard molar Gibbs free energies of formation are known, they are not included in our database.

Thorium antimonides: Rand et al. (2008) selected a temperature function of the Gibbs free energy of formation for the intermetallic compound $ThSb_2(cr)$ in the temperature range 939–1093 K. Since $ThSb_2(cr)$ does not exist in natural environments and these temperatures are way outside the range of applicability of our low-temperature database, $ThSb_2(cr)$ is not considered.

Thorium bismuthides: Rand et al. (2008) selected standard molar enthalpies of formation for the alloys ThBi(cr), $ThBi_2(cr)$, $Th_3Bi_4(cr)$, and $Th_5Bi_3(cr)$. These alloys are of no relevance for environmental systems and neither solubility constants nor standard molar Gibbs free energies of formation are known. Therefore, they are not included in our database.

10.8 Thorium group 14 compounds and complexes

10.8.1 Carbon compounds and complexes

10.8.1.1 Aqueous carbonate complexes

The thermodynamic data for aqueous carbonate complexes selected by Rand et al. (2008) are mainly based on solubility data. According to Rand et al. (2008), studies of the thorium carbonate system are complicated by the formation of sparingly soluble solid phases and the formation of ternary Th(IV)-hydroxide-carbonate complexes. Since HCO_3^- is a very weak ligand compared to CO_3^{2-} and OH^-, the formation of Th-bicarbonate complexes can be neglected and the ternary complexes can be described as

$$Th^{4+} + y\ OH^- + z\ CO_3^{2-} \Leftrightarrow Th(OH)_y(CO_3)_z^{4-y-2z}$$

Rand et al. (2008) analyzed 19 sets of solubility data for ThO_2(am, hyd) in carbonate solutions under widely varying conditions. They found that the solubility at pH 4.5–13, carbonate concentrations up to 2 M, and ionic strength varying from 0.1–4.0 M is well described by only a few ternary complexes, namely $ThOH(CO_3)_4^{5-}$, $Th(OH)_2(CO_3)_2^{2-}$, and $Th(OH)_4CO_3^{2-}$. For these, they selected

$$Th^{4+} + OH^- + 4\ CO_3^{2-} \Leftrightarrow ThOH(CO_3)_4^{5-}$$

$$\log_{10}\beta^{\circ}_{114}(ThOH(CO_3)_4^{5-}, 298.15\ K) = (35.6 \pm 0.5)$$

$$\varepsilon(ThOH(CO_3)_4^{5-}, Na^+) = -(0.22 \pm 0.13)\ kg\cdot mol^{-1}$$

$$Th^{4+} + 2\ OH^- + 2\ CO_3^{2-} \Leftrightarrow Th(OH)_2(CO_3)_2^{2-}$$

$$\log_{10}\beta^{\circ}_{122}(Th(OH)_2(CO_3)_2^{2-}, 298.15\ K) = (36.8 \pm 0.5)$$

$$\varepsilon(Th(OH)_2(CO_3)_2^{2-}, Na^+) = -(0.1 \pm 0.2)\ kg\cdot mol^{-1}$$

$$Th^{4+} + 4\ OH^- + CO_3^{2-} \Leftrightarrow Th(OH)_4CO_3^{2-}$$

$$\log_{10}\beta^{\circ}_{141}(Th(OH)_4CO_3^{2-}, 298.15\ K) = (40.4 \pm 0.6)$$

$$\varepsilon(Th(OH)_4CO_3^{2-}, Na^+) = -(0.1 \pm 0.2)\ kg\cdot mol^{-1}$$

which are also included in our database.

The complexes $Th(OH)_2CO_3$(aq) and $Th(OH)_3CO_3^-$ are only relevant at low carbonate concentrations near the solubility minimum range at pH 5–6 where they contribute at most 30 to 50% to the solubility. Rand et al. (2008) did not select

$$Th^{4+} + 2\ OH^- + CO_3^{2-} \Leftrightarrow Th(OH)_2CO_3(aq)$$

$$\log_{10}\beta^{\circ}_{121}(Th(OH)_2CO_3, aq, 298.15\ K) = (30.5 \pm 0.6)$$

$$Th^{4+} + 3\ OH^- + CO_3^{2-} \Leftrightarrow Th(OH)_3CO_3^-$$

$$\log_{10}\beta^{\circ}_{131}(Th(OH)_3CO_3^-, 298.15\ K) = (38.3 \pm 0.7)$$

$$\varepsilon(Th(OH)_3CO_3^-, Na^+) = -(0.05 \pm 0.20)\ kg\cdot mol^{-1}$$

but recommended these data as guidance. They are included in our database as supplemental data.

Note that, except for $ThOH(CO_3)_4^{5-}$, it was not possible for Rand et al. (2008) to evaluate the stability constants and the ion interaction coefficients at the same time, and they estimated the unknown coefficients for $Th(OH)_2(CO_3)_2^{2-}$, $Th(OH)_4CO_3^{2-}$, and $Th(OH)_3CO_3^-$ according to

Altmaier et al. (2005)[19]. The selected value of -(0.22 ± 0.13) kg·mol^{-1} for ε($ThOH(CO_3)_4^{5-}$, Na^+) was calculated by Rand et al. (2008) from Δε = (0.22 ± 0.05) kg·mol^{-1} for the reaction $Th(OH)_4$(am) + 4 CO_3^{2-} ⇔ $ThOH(CO_3)_4^{5-}$ + 3 OH^- combined with the selected values ε(OH^-, Na^+) = (0.04 ± 0.01) kg·mol^{-1} and ε(CO_3^{2-}, Na^+) = -(0.08 ± 0.03) kg·mol^{-1}.

In the experiments used to derive thermodynamic data for the ternary complexes discussed so far, the limiting pentacarbonate complex $Th(CO_3)_5^{6-}$ is never dominant. Rand et al. (2008) remarked that all these experiments were either performed at carbonate concentrations too low (C_{tot} ≤ 0.1 M) for the pentacarbonate complex to become dominant, or at pH > 12, where it is the ternary complexes that become dominant due to the competition between the OH^- and CO_3^{2-} ligands, even at high carbonate concentrations. Various EXAFS studies have shown that in the intermediate region (0.2 M < C_{tot} < 2 M and pH = 8–11) $Th(CO_3)_5^{6-}$ is the dominant species. Data for deriving its stability constant, however, are scarce. Rand et al. (2008) combined solubility data for ThO_2(am, hyd) at I = 0.5 M in NaCl and $NaClO_4$ from two studies with EXAFS data from two other studies and concluded that (30.8 ± 0.5) < $\log_{10}\beta°_{105}$($Th(CO_3)_5^{6-}$, 298.15 K) < (31.2 ± 0.5), assuming that ε($Th(CO_3)_5^{6-}$, Na^+) = ε($U(CO_3)_5^{6-}$, Na^+) = -(0.30 ± 0.15) kg·mol^{-1}. On this basis, Rand et al. (2008) selected

$$Th^{4+} + 5\ CO_3^{2-} \Leftrightarrow Th(CO_3)_5^{6-}$$

$$\log_{10}\beta°_{105}(Th(CO_3)_5^{6-},\ 298.15\ K) = (31.0 \pm 0.7)$$

$$\varepsilon(Th(CO_3)_5^{6-},\ Na^+) = -(0.30 \pm 0.15)\ kg\cdot mol^{-1}$$

which are also included in our database.

10.8.1.2 Carbonate and carbide solids

Thorium carbonate solids: According to Rand et al. (2008) recent solubility studies have shown that the solubility limiting solids of tetravalent actinides in carbonate solutions are An(IV) hydrous oxides and not An(IV) carbonate solids like $An(OH)_2CO_3\cdot xH_2O$(s) or $AnOCO_3\cdot xH_2O$(s) that were proposed in earlier studies. Attempts to prepare the postulated $Th(OH)_2CO_3\cdot 6H_2O$(s) or $ThOCO_3\cdot 8H_2O$(s) in sodium and potassium carbonate solutions resulted in the formation of $Na_6Th(CO_3)_5\cdot 12H_2O$(cr) and $K_6Th(CO_3)_5\cdot 12H_2O$(cr), respectively.

There are two experimental solubility studies of $Na_6Th(CO_3)_5\cdot 12H_2O$(cr) in sodium carbonate and bicarbonate solutions. Rand et al. (2008) reinterpreted the results of these studies and obtained three solubility products from experiments in 0.79–2.8 m Na_2CO_3, in Na_2CO_3-$NaNO_3$ solutions with [Na^+] = 2.0 M and [CO_3^{2-}] = 0.15–1.0 M, and in 2 M $NaHCO_3$-$NaNO_3$ with [HCO_3^-] = 0.2 - 1.0 M, by using the SIT to extrapolate to zero ionic strength. The mean of the three solubility products was selected by Rand et al. (2008), leading to

$$Na_6Th(CO_3)_5\cdot 12H_2O(cr) \Leftrightarrow 6\ Na^+ + Th(CO_3)_5^{6-} + 12\ H_2O(l)$$

$$\log_{10}K_{s,0}°(Na_6Th(CO_3)_5\cdot 12H_2O,\ cr,\ 298.15\ K) = -(11.2 \pm 0.4)$$

For inclusion in our database, we recalculated this equilibrium constant in terms of Th^{4+} and CO_3^{2-} by using $\log_{10}\beta°_{105}$($Th(CO_3)_5^{6-}$, 298.15 K) = (31.0 ± 0.7). Hence

$$Na_6Th(CO_3)_5\cdot 12H_2O(cr) \Leftrightarrow 6\ Na^+ + Th^{4+} + 5\ CO_3^{2-} + 12\ H_2O(l)$$

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[19] For ε($complex^Z$, Na^+), Altmaier et al. (2005) estimated -0.05 kg·mol^{-1} for Z = -1, -0.1 kg·mol^{-1} for Z = -2, -0.15 kg·mol^{-1} for Z = -3, -0.2 kg·mol^{-1} for Z = -4, -0.25 kg·mol^{-1} for Z = -5, and -0.3 kg·mol^{-1} for Z = -6, based on values selected by NEA for actinide complexes of analogous charge and similar size.

$$\log_{10}K_{s,0}^{\circ}(\text{Na}_6\text{Th(CO}_3)_5 \cdot 12\ \text{H}_2\text{O, cr, 298.15 K}) = -(42.2 \pm 0.8)$$

Thorium carbide solids: Rand et al. (2008) selected thermodynamic data for the thorium carbide solids $ThC_{0.97}$(cr) and $ThC_{1.94}$(cr). Thorium carbides do not form under natural conditions (no minerals are known) and are therefore not considered in our database.

10.8.1.3 Aqueous thiocyanate complexes

There are relatively few experimental studies on the formation of thorium thiocyanate complexes. Rand et al. (2008) selected

$$\text{Th}^{4+} + \text{SCN}^- \Leftrightarrow \text{ThSCN}^{3+}$$

$$\log_{10}\beta^{\circ}_1(\text{ThSCN}^{3+}, 298.15\ \text{K}) = (2.0 \pm 0.5)$$

$$\text{Th}^{4+} + 2\ \text{SCN}^- \Leftrightarrow \text{Th(SCN)}_2^{2+}$$

$$\log_{10}\beta^{\circ}_2(\text{Th(SCN)}_2^{2+}, 298.15\ \text{K}) = (3.4 \pm 0.8)$$

based on a liquid-liquid extraction study in a 3.0 M perchlorate solution. Rand et al. (2008) extrapolated the conditional constants to zero ionic strength by assuming $\varepsilon(\text{ThSCN}^{3+}, \text{ClO}_4^-)$ = (0.50 ± 0.10) $\text{kg}\cdot\text{mol}^{-1}$ (no explanations given for this estimate) and $\varepsilon(\text{Th(SCN)}_2^{2+}, \text{ClO}_4^-) = \varepsilon(\text{Np(SCN)}_2^{2+}, \text{ClO}_4^-)$ = (0.38 ± 0.20) $\text{kg}\cdot\text{mol}^{-1}$ and by using the selected $\varepsilon(\text{Th}^{4+}, \text{ClO}_4^-)$ = (0.70 ± 0.10) $\text{kg}\cdot\text{mol}^{-1}$ and $\varepsilon(\text{Na}^+, \text{SCN}^-)$ = (0.05 ± 0.01) $\text{kg}\cdot\text{mol}^{-1}$. The formation constants as well as the estimated

$$\varepsilon(\text{ThSCN}^{3+}, \text{ClO}_4^-) = (0.50 \pm 0.10)\ \text{kg}\cdot\text{mol}^{-1}$$

$$\varepsilon(\text{Th(SCN)}_2^{2+}, \text{ClO}_4^-) = (0.38 \pm 0.20)\ \text{kg}\cdot\text{mol}^{-1}$$

are included in our database. For chloride media, we include

$$\varepsilon(\text{ThSCN}^{3+}, \text{Cl}^-) = (0.25 \pm 0.10)\ \text{kg}\cdot\text{mol}^{-1}$$

$$\varepsilon(\text{Th(SCN)}_2^{2+}, \text{Cl}^-) = (0.15 \pm 0.10)\ \text{kg}\cdot\text{mol}^{-1}$$

in our database, estimated on the basis of charge correlations (see Appendix A).

10.8.2 Silicon compounds and complexes

10.8.2.1 Aqueous thorium silicate complexes

According to Rand et al. (2008) there are no thermodynamic data available for thorium silicate complexes, but these authors mentioned that X-ray absorption studies of aqueous solutions of Si and Th under acidic conditions as well as solubility studies of $ThO2\cdot xH_2O$(cr) in silicate solutions under highly alkaline conditions suggest the formation of fairly strong complexes. Based on an experimental study that was not yet available to Rand et al. (2008), we selected the formation constant for $Th(OH)_3(SiO(OH)_3)_3^{2-}$ as supplemental data

$$Th^{4+} + 3\ Si(OH)_4(aq) + 3\ H_2O(l) \Leftrightarrow Th(OH)_3(SiO(OH_3)_3^{2-} + 6\ H^+$$

$$log_{10}K^{\circ}(298.15\ K) = -(27.8 \pm 0.7)$$

for our database. This is further discussed in Section 8.4.7.

10.8.2.2 Thorium-silicon solids

Rand et al. (2008) selected standard molar enthalpies of formation for the intermetallic phase $ThSi_2$(cr), and for the minerals $ThSiO_4$ (huttonite) and $ThSiO_4$ (thorite). Neither solubility products nor standard molar Gibbs free energies of formation are known for these solids, therefore they are not included in our database.

10.8.3 Thorium-tin solids

A calorimetrically determined standard molar enthalpy of formation for the binary alloy Th_5Sn_3(cr) was selected by Rand et al. (2008). Since such alloys do not occur in natural environments and no other thermodynamic data are known (solubility product or standard molar Gibbs free energy of formation), this alloy is not included in our database.

10.9 Thorium-titanium solids

Brannerite is a naturally occurring mineral of general composition (U, Ca, Ce)(Ti, Fe)$_2$O$_6$. Thorium frequently substitutes for uranium, and the ideal endmember $ThTi_2O_6$(cr) is sometimes referred to as Th-brannerite. Rand et al. (2008) selected a calorimetrically determined value for the standard molar formation enthalpy of $ThTi_2O_6$(cr), but noted that this solid may only form at high temperatures. For this reason and because no other thermodynamic data are known (solubility product or standard molar Gibbs free energy of formation), $ThTi_2O_6$(cr) is omitted in our database.

Table 10.1: Thorium data selected by NEA (Rand et al. 2008, Tables III-1 and III-2) but not included in TDB Version 12/07. For explanations see text.

Gases	$Th(g)$ [ad], $ThO(g)$ [ad], $ThO_2(g)$ [a], $ThH(g)$ [b], $ThF(g)$ [a], $ThF_2(g)$ [a], $ThF_3(g)$ [a], $ThF_4(g)$ [ad], $ThOF(g)$ [a], $ThCl(g)$ [a], $ThCl_2(g)$ [a], $ThCl_3(g)$ [a], $ThCl_4(g)$ [ad], $ThBr(g)$ [ad], $ThBr_2(g)$ [a], $ThBr_3(g)$ [a], $ThBr_4(g)$ [a], $ThI(g)$ [b], $ThI_2(g)$ [b], $ThI_3(g)$ [b], $ThI_4(g)$ [ad]
Solids	$ThO_2(cr)$ [a], $ThH_2(cr)$ [a], $ThD_2(cr)$ [b], $ThT_2(cr)$ [b], $ThH_{3.75}(cr)$ [a], $ThD_{3.75}(cr)$ [b], $ThT_{3.75}(cr)$ [b], $ThOF_2(cr)$ [a], $ThF_4(cr)$ [a], β-$ThCl_4$ [a], $ThCl_4\cdot 2H_2O(cr)$ [b], $ThCl_4\cdot 4H_2O(cr)$ [b], $ThCl_4\cdot 7H_2O(cr)$ [b], $ThCl_4\cdot 8H_2O(cr)$ [b], $ThOCl_2(cr)$ [a], β-$ThBr_4$ [a], $ThBr_4\cdot 7H_2O(cr)$ [b], $ThBr_4\cdot 10H_2O(cr)$ [b], $ThBr_4\cdot 12H_2O(cr)$ [b], $ThOBr_2(cr)$ [b], $ThI_4(cr)$ [a], $ThOI_2(cr)$ [b], $ThS(cr)$ [a], $ThS_2(cr)$ [b], $Th_2S_3(cr)$ [b], $ThOS(cr)$ [b], $Th(SO_4)_2(cr)$ [b], $Th(SO_4)_2\cdot 4H_2O(cr)$ [de], $Th(SO_4)_2\cdot 8H_2O(cr)$ [de], $Th(SO_4)_2\cdot 9H_2O(cr)$ [ac], $Th(SO_4)_2\cdot Na_2SO_4\cdot 6H_2O(cr)$ [ce], $Th(SO_4)_2\cdot K_2SO_4\cdot 4H_2O(cr)$ [ce], $Th(SO_4)_2\cdot 2K_2SO_4\cdot 2H_2O(cr)$ [ce], $Th(SO_4)_2\cdot 3.5K_2SO_4(cr)$ [ce], $Th(SO_4)_2\cdot (NH_4)_2SO_4\cdot 4H_2O(cr)$ [ce], $ThOSe(cr)$ [b], $Th(SeO_3)_2(cr)$ [c], $Th(SeO_3)_2\cdot H_2O(cr)$ [c], $ThN(cr)$ [a], $Th_3N_4(cr)$ [a], $Th(NO_3)_4\cdot 4H_2O(cr)$ [b], $Th(NO_3)_4\cdot 5H_2O(cr)$ [a], $Th_4(PO_4)_4P_2O_7(cr)$ [b], $ThAs(cr)$ [b], $Th_3As_4(cr)$ [b], $ThSb_2(cr)$ [ae], $ThBi(cr)$ [b], $ThBi_2(cr)$ [b], $Th_3Bi_4(cr)$ [b], $Th_5Bi_3(cr)$ [b], $Th_5Sn_3(cr)$ [b], $ThC_{0.97}(cr)$ [a], $ThC_{1.94}(cr)$ [a], $ThSi_2(cr)$ [b], $ThSiO_4$(huttonite) [b], $ThSiO_4$(thorite) [b], $ThTi_2O_6(cr)$ [b]
Liquids	-
Aqueous species	$ThClO_3^{3+}$ [ac], $ThBr^{3+}$ [ac], $ThBrO_3^{3+}$ [ac], ThN_3^{3+} [ac], $Th(N_3)_2^{2+}$ [ac]

[a] Single species data including $\Delta_f G_m°$

[b] Single species data excluding $\Delta_f G_m°$

[c] Reaction data including $\log_{10}K°$

[d] Reaction data excluding $\log_{10}K°$

[e] Data discussed and selected by Rand et al. (2008), but not listed in their Tables III-1 and III-2

Table 10.2: Selected thorium data. All data included in TDB Version 12/07 are taken from Rand et al. (2008) with the exception of those marked with an asterisk (*). Supplemental data are in italics. New or changed data with respect to TDB Version 01/01 (Hummel et al., 2002) are shaded.

		TDB Version 01/01				TDB Version 12/07				
Name	**Redox**	**$\Delta_f G_m°$** [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}]	**$\Delta_f G_m°$** [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}]	**Species**
Th(cr, α)[a]	0	0.0	0.0	51.8 ± 0.5	-	0.0	0.0	52.64 ± 0.50	26.23 ± 0.50	Th(cr, α)
Th+4	IV	-704.6	-769.0	-425.6	-	-704.783 ± 5.298	-768.7 ± 2.3	-423.1 ± 16.0	-224 ± 15	Th^{4+}

[a] TDB Version 01/01: Th(cr)

		TDB Version 01/01		TDB Version 12/07		
Name	**Redox**	**$\log_{10}\beta°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**$\log_{10}\beta°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**Reaction**
ThOH+3	IV	-2.4 ± 0.5	-	-2.5 ± 0.5	44.2 ± 6.3	$Th^{4+} + H_2O(l) \Leftrightarrow ThOH^{3+} + H^+$
Th(OH)2+2	IV	-	-	-6.2 ± 0.5	85.7 ± 41.4	$Th^{4+} + 2\ H_2O(l) \Leftrightarrow Th(OH)_2^{2+} + 2\ H^+$
Th(OH)4	IV	-18.4 ± 0.6	-	-17.4 ± 0.7	-	$Th^{4+} + 4\ H_2O(l) \Leftrightarrow Th(OH)_4(aq) + 4\ H^+$
Th2(OH)2+6	IV	-	-	-5.9 ± 0.5	58.3 ± 5.7	$2\ Th^{4+} + 2\ H_2O(l) \Leftrightarrow Th_2(OH)_2^{6+} + 2\ H^+$
Th2(OH)3+5	IV	-	-	-6.8 ± 0.2	-	$2\ Th^{4+} + 3\ H_2O(l) \Leftrightarrow Th_2(OH)_3^{5+} + 3\ H^+$
Th4(OH)8+8	IV	-	-	-20.4 ± 0.4	243.0 ± 21.3	$4\ Th^{4+} + 8\ H_2O(l) \Leftrightarrow Th_4(OH)_8^{8+} + 8\ H^+$
Th4(OH)12+4	IV	-	-	-26.6 ± 0.2	-	$4\ Th^{4+} + 12\ H_2O(l) \Leftrightarrow Th_4(OH)_{12}^{4+} + 12\ H^+$
Th6(OH)14+10	IV	-	-	-36.8 ± 1.2	-	$6\ Th^{4+} + 14\ H_2O(l) \Leftrightarrow Th_6(OH)_{14}^{10+} + 14\ H^+$
Th6(OH)15+9	IV	-	-	-36.8 ± 1.5	472.8 ± 22.0	$6\ Th^{4+} + 15\ H_2O(l) \Leftrightarrow Th_6(OH)_{15}^{9+} + 15\ H^+$
Ca4Th(OH)8+4	IV	-	-	(-62.4 ± 0.6)*	-	$4\ Ca^{2+} + Th^{4+} + 8\ H_2O(l) \Leftrightarrow Ca_4Th(OH)_8^{4+} + 8\ H^+$
ThF+3	IV	8.0	-	8.87 ± 0.15	-0.4 ± 2.0	$Th^{4+} + F^- \Leftrightarrow ThF^{3+}$
ThF2+2	IV	14.2	-	15.63 ± 0.23	-3.3 ± 0.4	$Th^{4+} + 2\ F^- \Leftrightarrow ThF_2^{2+}$
ThF3+	IV	18.9	-	20.67 ± 0.16	-	$Th^{4+} + 3\ F^- \Leftrightarrow ThF_3^+$
ThF4	IV	22.3	-	25.58 ± 0.18	-	$Th^{4+} + 4\ F^- \Leftrightarrow ThF_4(aq)$
ThF6-2	IV	-	-	*(29.23 ± 0.62)*[a]	-	$Th^{4+} + 6F^- \Leftrightarrow ThF_6^{2-}$
ThCl+3	IV	-	-	1.70 ± 0.10	-	$Th^{4+} + Cl^- \Leftrightarrow ThCl^{3+}$
ThIO3+3	IV	-	-	4.14 ± 0.10	-	$Th^{4+} + IO_3^- \Leftrightarrow ThIO_3^{3+}$
Th(IO3)2+2	IV	-	-	6.97 ± 0.12	-	$Th^{4+} + 2\ IO_3^- \Leftrightarrow Th(IO_3)_2^{2+}$

		TDB Version 01/01		TDB Version 12/07		
Name	**Redox**	**$\log_{10}\beta°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**$\log_{10}\beta°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**Reaction**
Th(IO3)3+	IV	-	-	9.87 ± 0.11	-	$Th^{4+} + 3\ IO_3^- \Leftrightarrow Th(IO_3)_3^+$
ThSO4+2	IV	7.6 ± 0.5	-	6.17 ± 0.32	20.92 ± 0.74	$Th^{4+} + SO_4^{2-} \Leftrightarrow ThSO_4^{2+}$
Th(SO4)2	IV	11.6	-	9.69 ± 0.27	40.38 ± 1.08	$Th^{4+} + 2\ SO_4^{2-} \Leftrightarrow Th(SO_4)_2(aq)$
Th(SO4)3-2	IV	12.4	-	10.748 ± 0.076	-	$Th^{4+} + 3\ SO_4^{2-} \Leftrightarrow Th(SO_4)_3^{2-}$
ThNO3+3	IV	-	-	1.3 ± 0.2	-	$Th^{4+} + NO_3^- \Leftrightarrow ThNO_3^{3+}$
Th(NO3)2+2	IV	-	-	2.3 ± 0.4	-	$Th^{4+} + 2\ NO_3^- \Leftrightarrow Th(NO_3)_2^{2+}$
ThHPO4+2	IV	13 ± 1	-	-	-	$Th^{4+} + HPO_4^{2-} \Leftrightarrow ThHPO_4^{2+}$
ThH2PO4+3	IV	-	-	3.45 ± 0.32	-	$Th^{4+} + H_3PO_4(aq) \Leftrightarrow ThH_2PO_4^{3+} + H^+$
ThH3PO4+4	IV	-	-	1.89 ± 0.31	-	$Th^{4+} + H_3PO_4(aq) \Leftrightarrow ThH_3PO_4^{4+}$
Th(H2PO4)2+2	IV	-	-	6.20 ± 0.32	-	$Th^{4+} + 2\ H_3PO_4(aq) \Leftrightarrow Th(H_2PO_4)_2^{2+} + 2\ H^+$
Th(H3PO4)(H2PO4)+3	IV	-	-	5.42 ± 0.32	-	$Th^{4+} + 2\ H_3PO_4(aq) \Leftrightarrow Th(H_3PO_4)(H_2PO_4)^{3+} + H^+$
Th(CO3)5-6	IV	29.8 ± 1.1	-	31.0 ± 0.7	-	$Th^{4+} + 5\ CO_3^{2-} \Leftrightarrow Th(CO_3)_5^{6-}$
ThOH(CO3)4-5	IV	-	-	35.6 ± 0.5	-	$Th^{4+} + OH^- + 4\ CO_3^{2-} \Leftrightarrow ThOH(CO_3)_4^{5-}$
Th(OH)2CO3	IV	-	-	*(30.5 ± 0.6)*[a]	-	*$Th^{4+} + 2\ OH^- + CO_3^{2-} \Leftrightarrow Th(OH)_2CO_3(aq)$*
Th(OH)2(CO3)2-2	IV	-	-	36.8 ± 0.5	-	$Th^{4+} + 2\ OH^- + 2\ CO_3^{2-} \Leftrightarrow Th(OH)_2(CO_3)_2^{2-}$
Th(OH)3CO3-	IV	(38.9 ± 1.0)[b]	-	*(38.3 ± 0.7)*[a]	-	*$Th^{4+} + 3\ OH^- + CO_3^{2-} \Leftrightarrow Th(OH)_3CO_3^-$*
Th(OH)4CO3-2	IV	-	-	40.4 ± 0.6	-	$Th^{4+} + 4\ OH^- + CO_3^{2-} \Leftrightarrow Th(OH)_4CO_3^{2-}$
ThSCN+3	IV	-	-	2.0 ± 0.5	-	$Th^{4+} + SCN^- \Leftrightarrow ThSCN^{3+}$
Th(SCN)2+2	IV	-	-	3.4 ± 0.8	-	$Th^{4+} + 2\ SCN^- \Leftrightarrow Th(SCN)_2^{2+}$

[a] Not selected by Rand et al. (2008) but supplied by them for guidance or for scoping calculations

[b] Recalculated from $\log_{10}\beta° = -(3.1 \pm 1.0)$ for $Th^{4+} + CO_3^{2-} + 3\ H_2O(l) \Leftrightarrow Th(OH)_3CO_3^- + 3\ H^+$

		TDB Version 01/01		TDB Version 12/07			
Name	**Redox**	**$\log_{10}K_{s,0}°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**Name**	**$\log_{10}K_{s,0}°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**Reaction**
ThO2(coll, hyd)	IV	-	-	*ThO2(coll, hyd)*[a]	*14.8 ± 1.0*		*$ThO_2(coll, hyd) + 4\ H^+ \Leftrightarrow Th^{4+} + 2\ H_2O(l)$*

[a] The equilibrium constant of this colloid is only valid in the presence of ThO_2(am, hyd, fr) or ThO_2(am, hyd, ag)

		TDB Version 01/01		TDB Version 12/07			
Name	**Redox**	**$\log_{10}K_{s,0}°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**Name**	**$\log_{10}K_{s,0}°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**Reaction**
ThO2(s)	IV	9.9 ± 0.8	-	-	-	-	$ThO_2(s) + 4 H^+ \Leftrightarrow Th^{4+} + 2 H_2O(l)$
ThO2(am, hyd, fr)	IV	-	-	ThO2(am, hyd, fr)	9.3 ± 0.9	-	$ThO_2(am, hyd, fr) + 4 H^+ \Leftrightarrow Th^{4+} + 2 H_2O(l)$
ThO2(am, hyd, ag)	IV	-	-	ThO2(am, hyd, ag)	8.5 ± 0.9	-	$ThO_2(am, hyd, ag) + 4 H^+ \Leftrightarrow Th^{4+} + 2 H_2O(l)$
ThF4(cr)	IV	-30.2	-	-	-	-	$ThF_4(cr) \Leftrightarrow Th^{4+} + 4 F^-$
ThF4(cr, hyd)	IV	-	-	ThF4(cr, hyd)	-31.8 ± 0.4	-	$ThF_4(cr, hyd) \Leftrightarrow Th^{4+} + 4 F^-$
Th3(PO4)4(s)	IV	-	-	*Th3(PO4)4(s)*	*(-112.0 ± 2.1)*[a]	-	$Th_3(PO_4)_4(s) \Leftrightarrow 3 Th^{4+} + 4 PO_4^{3-}$
Na6Th(CO3)5:12H2O(cr)	IV	-	-	Na6Th(CO3)5:12H2O(cr)	-42.2 ± 0.8	-	$Na_6Th(CO_3)_5 \cdot 12H_2O(cr)$ $\Leftrightarrow 6 Na^+ + Th^{4+} + 5 CO_3^{2-} + 12 H_2O(l)$

[a] Not selected by Rand et al. (2008) but supplied by them for guidance or for scoping calculations

Table 10.3: Selected SIT ion interaction coefficients $\varepsilon_{j,k}$ [kg·mol^{-1}] for thorium species. All data included in TDB Version 12/07 are taken from Rand et al. (2008) unless indicated otherwise. Own data estimates based on charge correlations (see Appendix A) are shaded. Supplemental data are in italics.

j k→ ↓	**Cl$^-$** $\varepsilon_{j,k}$ [kg·mol^{-1}]	**ClO$_4^-$** $\varepsilon_{j,k}$ [kg·mol^{-1}]	**NO$_3^-$** $\varepsilon_{j,k}$ [kg·mol^{-1}]	**Li$^+$** $\varepsilon_{j,k}$ [kg·mol^{-1}]	**Na$^+$** $\varepsilon_{j,k}$ [kg·mol^{-1}]	**K$^+$** $\varepsilon_{j,k}$ [kg·mol^{-1}]
Th+4	0.25 ± 0.03	0.70 ± 0.10	0.31 ± 0.12	0	0	0
ThOH+3	0.19 ± 0.05	0.48 ± 0.08	0.20 ± 0.15	0	0	0
Th(OH)2+2	0.13 ± 0.05	0.33 ± 0.10	0.10 ± 0.15	0	0	0
Th(OH)4	0	0	0	0	0	0
Th2(OH)2+6	0.40 ± 0.16	1.22 ± 0.24	0.69 ± 0.26	0	0	0
Th2(OH)3+5	0.29 ± 0.09	0.91 ± 0.21	0.69 ± 0.25	0	0	0
Th4(OH)8+8	0.70 ± 0.20	1.69 ± 0.42	1.59 ± 0.51	0	0	0
Th4(OH)12+4	0.25 ± 0.20	0.56 ± 0.42	0.42 ± 0.50	0	0	0
Th6(OH)14+10	0.83 ± 0.30	2.2 ± 0.3	2.9 ± 0.5	0	0	0
Th6(OH)15+9	0.72 ± 0.30	1.85 ± 0.74	2.20 ± 0.77	0	0	0
Ca4Th(OH)8+4	(-0.01 ± 0.10)[a]	(0.21 ± 0.17)[a]	-	0	0	0
ThF+3	0.25 ± 0.10	0.48 ± 0.08	0.25 ± 0.20	0	0	0
ThF2+2	0.15 ± 0.10	0.3 ± 0.1	0.15 ± 0.20	0	0	0
ThF3+	0.05 ± 0.10	0.1 ± 0.1	0.0 ± 0.2	0	0	0
ThF4	0	0	0	0	0	0
ThF6-2	*0*	*0*	*0*	-	*-0.30 ± 0.06*	-
ThCl+3	(0.62 ± 0.11)[b]	(0.62 ± 0.11)[b]	-	0	0	0
ThIO3+3	0.25 ± 0.10	(0.56 ± 0.14)[c]	-	0	0	0
Th(IO3)2+2	0.15 ± 0.10	(0.43 ± 0.18)[c]	-	0	0	0
Th(IO3)3+	0.05 ± 0.10	(0.25 ± 0.15)[c]	-	0	0	0
ThSO4+2	0.14 ± 0.15	0.3 ± 0.1	-	0	0	0
Th(SO4)2	0	0	0	0	0	0
Th(SO4)3-2	0	0	0	(-0.068 ± 0.003)[d]	-0.091 ± 0.038	-0.091 ± 0.038
ThNO3+3	0.25 ± 0.10	(0.56 ± 0.14)[e]	-	0	0	0
Th(NO3)2+2	0.15 ± 0.10	(0.43 ± 0.18)[e]	-	0	0	0
ThH2PO4+3	0.25 ± 0.10	0.5 ± 0.1	-	0	0	0
ThH3PO4+4	0.35 ± 0.10	0.7 ± 0.1	-	0	0	0
Th(H2PO4)2+2	0.15 ± 0.10	0.4 ± 0.1	-	0	0	0
Th(H3PO4)(H2PO4)+3	0.25 ± 0.10	0.5 ± 0.1	-	0	0	0
Th(CO3)5-6	0	0	0	-	-0.30 ± 0.15	-
ThOH(CO3)4-5	0	0	0	-	-0.22 ± 0.13	-
Th(OH)2CO3	*0*	*0*	*0*	*0*	*0*	*0*
Th(OH)2(CO3)2-2	0	0	0	-	-0.1 ± 0.2	-
Th(OH)3CO3-	*0*	*0*	*0*	-	*-0.05 ± 0.20*	-
Th(OH)4CO3-2	0	0	0	-	-0.1 ± 0.2	-
ThSCN+3	0.25 ± 0.10	0.50 ± 0.10	-	0	0	0
Th(SCN)2+2	0.15 ± 0.10	0.38 ± 0.20	-	0	0	0

[a] Altmaier et al. (2008)

[b] In combination with $\varepsilon(\mathrm{Th}^{4+}, \mathrm{Cl}^-) = \varepsilon(\mathrm{Th}^{4+}, \mathrm{ClO}_4^-) = (0.70 \pm 0.10)$ kg·mol^{-1}

[c] Data given by Rand et al. (2008) in text but not in Table B-4

[d] In combination with $\varepsilon_2 = (0.093 \pm 0.007)$ kg·mol^{-1}

[e] In combination with $\varepsilon(\mathrm{Th}^{4+}, \mathrm{ClO}_4^-) = \varepsilon(\mathrm{Th}^{4+}, \mathrm{NO}_3^-) = (0.70 \pm 0.10)$ kg·mol^{-1}

10.10 References

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11 Uranium

11.1 Introduction

Almost all 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 "Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium" (Guillaumont et al. 2003), the latter of which reviewed new literature published between 1990 and the end of 2001 that was not considered by Grenthe et al. (1992) and (Grenthe et al. 1995). Most inorganic complexes and solids of uranium included in the PSI/Nagra Chemical Thermodynamic Database 12/07 are recommended values taken from the NEA reviews. 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 modeling 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 as to which of these phases should be included in our database. In an attempt to focus our database on environmental modeling 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 have been thoroughly scrutinized and undergone a careful selection procedure. Our decisions are documented in the following sections. Compounds and species for which NEA has selected thermodynamic data but are not included in our database are listed in Table 11.2. All data selected for our database are listed in Table 11.3.

Due to a lack of experimental data, several ion interaction coefficients for cationic uranium species with chloride are unknown. We filled these gaps by applying the estimation method described in Appendix A, which is based on a statistical analysis of published SIT ion interaction coefficients and which allows the estimation of such coefficients for the interaction of cations with Cl^- and ClO_4^-, and for the interaction of anions with Na^+ from the charge of the considered cations or anions. The selected ion interaction coefficients for uranium species are listed in Tables 11.4 and 11.5.

The notation of formulae and symbols used in this text follows the NEA recommendations and practice.

11.2 Elemental uranium

Uranium metal and gas are not relevant under environmental conditions. Therefore, U(g) is not included in the database. The absolute entropy and heat capacity of U(cr) is given in Table 11.2 for computational purposes only.

11.3 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

$$\Delta_f H_m^\circ(UO_2^{2+}, \text{aq}, 298.15\ \text{K}) = -(1019.0 \pm 1.5)\ \text{kJ} \cdot \text{mol}^{-1}$$

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):

$$S_m^\circ(UO_2^{2+}, \text{aq}, 298.15\ \text{K}) = -(98.2 \pm 3.0)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

The Gibbs energy of formation is obtained from the above values

$$\Delta_f G_m°(UO_2^{2+}, aq, 298.15\ K) = -(952.55 \pm 1.75)\ kJ\cdot mol^{-1}$$

Grenthe et al. (1992) selected as value for the molar heat capacity of UO_2^{2+}:

$$C_{p,m}°(UO_2^{2+}, aq, 298.15\ K) = (42.4 \pm 3.0)\ J\cdot K^{-1}\cdot mol^{-1}$$

All these data are included in our database. Ciavatta (1980) evaluated SIT ion interaction coefficients from isopiestic mean activity coefficient data and obtained

$$\varepsilon(UO_2^{2+}, Cl^-) = (0.21 \pm 0.02)\ kg\cdot mol^{-1}$$

$$\varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)\ kg\cdot mol^{-1}$$

$$\varepsilon(UO_2^{2+}, NO_3^-) = (0.24 \pm 0.03)\ kg\cdot mol^{-1}$$

As discussed by Grenthe et al. (1992), Ciavatta (1980) did not explicitly consider the formation of complexes of the metal cations (e.g., UO_2^{2+}) with the background electrolyte anions (e.g., Cl^- and NO_3^-). It is known, however, that numerous metal cations form weak complexes with chloride and nitrate (but not with perchlorate), which is reflected in the smaller ion interaction coefficients compared with those involving the non-complexing perchlorate anion. Since Grenthe et al. (1992) did explicitly consider the weak complexation of UO_2^{2+} with chloride and nitrate (if these anions were part of the background electrolyte), they used

$$\varepsilon(UO_2^{2+}, Cl^-) = \varepsilon(UO_2^{2+}, NO_3^-) = \varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)\ kg\cdot mol^{-1}$$

for all calculations involving chloride or nitrate in the background electrolytes. With this approach, the medium dependence of the activity coefficients is accounted for by a combination of an ion pairing model with a specific ion interaction model (Grenthe et al, 1992).

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 Section 11.8.1.2). Despite this very low significance of U(V) for geochemical modeling we decided to include UO_2^+ in our database for the sake of chemical systematics. The standard Gibbs energy of formation of UO_2^+, $-(961.0 \pm 1.8)\ kJ\cdot mol^{-1}$, 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 Grenthe et al. (1992) for the UO_2^{2+}/UO_2^+ couple in perchlorate media is:

$$\log_{10}K°(298.15\ K) = (1.484 \pm 0.022)$$

with

$$\Delta\varepsilon = -(0.20 \pm 0.01)\ kg\cdot mol^{-1}$$

resulting in $\varepsilon(UO_2^+, ClO_4^-) = (0.26 \pm 0.03)\ kg\cdot mol^{-1}$ by using the value for $\varepsilon(UO_2^{2+}, ClO_4^-)$ selected above. Since data for chloride systems are missing, we estimated

$$\varepsilon(UO_2^+, Cl^-) = (0.05 \pm 0.10)\ kg\cdot mol^{-1}$$

based on charge correlations (see Appendix A).

In the absence of experimental data, Grenthe et al. (1992) selected an estimated entropy value

$$S_m°(UO_2^+, aq, 298.15\ K) = -(25 \pm 8)\ J\cdot K^{-1}\cdot mol^{-1}$$

The enthalpy of formation is derived from the selected $\log_{10}K° \rightarrow \Delta_f G_m°$ and $S_m°$ values:

$$\Delta_f H_m^\circ(UO_2^+, aq, 298.15 K) = -(1025.1 \pm 3.0) kJ\cdot mol^{-1}$$

The validity of this estimate is corroborated by the experimental value of -(60 ± 11) $J\cdot K^{-1}\cdot mol^{-1}$ for the partial molar heat capacity of Th^{4+} (Hovey et al. 1997).

U^{4+}: The standard Gibbs energy of formation of U^{4+}, -(529.9 ± 1.8) $kJ\cdot mol^{-1}$, 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 calculated and selected by Grenthe et al. (1992) from measurements in sulphate, perchlorate, and chloride media is:

$$\log_{10}K^\circ(298.15 K) = (9.038 \pm 0.041)$$

From

$$\Delta\varepsilon = -(0.02 \pm 0.03) kg\cdot mol^{-1}$$

determined from

$$UO_2^{2+} + H_2(g) + 2 H^+ \Leftrightarrow U^{4+} + 2 H_2O(l)$$

Grenthe et al. (1992) calculated

$$\varepsilon (U^{4+}, ClO_4^-) = (0.76 \pm 0.06) kg\cdot mol^{-1}$$

using the value for $\varepsilon(UO_2^{2+}, ClO_4^-)$ selected above and the selected $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$ $kg\cdot mol^{-1}$. Since neither Grenthe et al. (1992) nor Guillaumont et al. (2003) reported any value for the chloride system, we estimated

$$\varepsilon(U^{4+}, Cl^-) = (0.35 \pm 0.10) kg\cdot mol^{-1}$$

based on charge correlations (see Appendix A).

The enthalpy of formation as selected by Grenthe et al. (1992) is based on two series of experiments.

$$\Delta_f H_m^\circ(U^{4+}, aq, 298.15 K) = -(591.2 \pm 3.3) kJ\cdot mol^{-1}$$

The entropy is derived from the selected $\log_{10}K^\circ \rightarrow \Delta_f G_m^\circ$ and $\Delta_f H_m^\circ$ values:

$$S_m^\circ(U^{4+}, aq, 298.15 K) = -(416.9 \pm 12.6) J\cdot K^{-1}\cdot mol^{-1}$$

Due to the absence of $C_{p,m}$ measurements for U^{4+}, Guillaumont et al. (2003) adopted an estimate, based on a measured value for $C_{p,m}^\circ(Th^{4+}, aq, 298.15 K)$

$$C_{p,m}^\circ(U^{4+}, aq, 298.15 K) = -(220 \pm 50) J\cdot K^{-1}\cdot mol^{-1}$$

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 oxidized 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.

11.4 Oxygen and hydrogen compounds

Gaseous uranium oxide compounds are not relevant under environmental conditions. Thus, thermodynamic data selected by Grenthe et al. (1992) and Guillaumont et al. (2003) for UO(g), UO_2(g), and UO_3(g) are not considered in our database.

11.4.1 Aqueous uranium hydroxide complexes

11.4.1.1 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. For these polymeric species, Grenthe et al. (1992) selected the following standard equilibrium constants and Δε values:

$$2\,UO_2^{2+} + 2\,H_2O(l) \Leftrightarrow (UO_2)_2(OH)_2^{2+} + 2\,H^+$$

$$\log_{10}{}^*\beta_{2,2}^\circ(m = 2, n = 2, 298.15\text{ K}) = -(5.62 \pm 0.04)$$

$$\Delta\varepsilon((UO_2)_2(OH)_2^{2+}, Cl^-) = (0.01 \pm 0.03)\text{ kg·mol}^{-1}$$

$$\Delta\varepsilon((UO_2)_2(OH)_2^{2+}, ClO_4^-) = -(0.07 \pm 0.02)\text{ kg·mol}^{-1}$$

$$\Delta\varepsilon((UO_2)_2(OH)_2^{2+}, NO_3^-) = -(0.29 \pm 0.07)\text{ kg·mol}^{-1}$$

$$3\,UO_2^{2+} + 4\,H_2O(l) \Leftrightarrow (UO_2)_3(OH)_4^{2+} + 4\,H^+$$

$$\log_{10}{}^*\beta_{4,3}^\circ(m = 3, n = 4, 298.15\text{ K}) = -(11.9 \pm 0.3)$$

$$\Delta\varepsilon((UO_2)_3(OH)_4^{2+}, Cl^-) = -(0.40 \pm 0.15)\text{ kg·mol}^{-1}$$

$$\Delta\varepsilon((UO_2)_3(OH)_4^{2+}, ClO_4^-) = (0.1 \pm 0.2)\text{ kg·mol}^{-1}$$

$$\Delta\varepsilon((UO_2)_3(OH)_4^{2+}, NO_3^-) = -(0.4 \pm 1.0)\text{ kg·mol}^{-1}$$

$$3\,UO_2^{2+} + 5\,H_2O(l) \Leftrightarrow (UO_2)_3(OH)_5^{+} + 5\,H^+$$

$$\log_{10}{}^*\beta_{5,3}^\circ(m = 3, n = 5, 298.15\text{ K}) = -(15.55 \pm 0.12)$$

$$\Delta\varepsilon((UO_2)_3(OH)_5^{+}, Cl^-) = (0.03 \pm 0.13)\text{ kg·mol}^{-1}$$

$$\Delta\varepsilon((UO_2)_3(OH)_5^{+}, ClO_4^-) = -(0.23 \pm 0.07)\text{ kg·mol}^{-1}$$

$$\Delta\varepsilon((UO_2)_3(OH)_5^{+}, NO_3^-) = -(0.6 \pm 0.2)\text{ kg·mol}^{-1}$$

Using these Δε values together with the selected values $\varepsilon(UO_2^{2+}, Cl^-) = \varepsilon(UO_2^{2+}, NO_3^-) = \varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)\text{ kg·mol}^{-1}$, $\varepsilon(H^+, Cl^-) = (0.12 \pm 0.01)\text{ kg·mol}^{-1}$, $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)\text{ kg·mol}^{-1}$, and $\varepsilon(H^+, NO_3^-) = (0.07 \pm 0.01)\text{ kg·mol}^{-1}$, Grenthe et al. (1992) derived the following selected ion interaction coefficients

$$\varepsilon((UO_2)_2(OH)_2^{2+}, Cl^-) = (0.69 \pm 0.07)\text{ kg·mol}^{-1}$$

$$\varepsilon((UO_2)_2(OH)_2^{2+}, ClO_4^-) = (0.57 \pm 0.07)\text{ kg·mol}^{-1}$$

$$\varepsilon((UO_2)_2(OH)_2^{2+}, NO_3^-) = (0.49 \pm 0.09)\text{ kg·mol}^{-1}$$

$$\varepsilon((UO_2)_3(OH)_4^{2+}, Cl^-) = (0.50 \pm 0.18)\text{ kg·mol}^{-1}$$

$$\varepsilon((UO_2)_3(OH)_4^{2+}, ClO_4^-) = (0.89 \pm 0.23) \text{ kg}\cdot\text{mol}^{-1}$$

$$\varepsilon((UO_2)_3(OH)_4^{2+}, NO_3^-) = (0.72 \pm 1.00) \text{ kg}\cdot\text{mol}^{-1}$$

$$\varepsilon((UO_2)_3(OH)_5^{+}, Cl^-) = (0.81 \pm 0.17) \text{ kg}\cdot\text{mol}^{-1}$$

$$\varepsilon((UO_2)_3(OH)_5^{+}, ClO_4^-) = (0.45 \pm 0.15) \text{ kg}\cdot\text{mol}^{-1}$$

$$\varepsilon((UO_2)_3(OH)_5^{+}, NO_3^-) = (0.41 \pm 0.22) \text{ kg}\cdot\text{mol}^{-1}$$

For $\varepsilon((UO_2)_3(OH)_4^{2+}, ClO_4^-)$,$\varepsilon((UO_2)_3(OH)_4^{2+}, NO_3^-)$, and $\varepsilon((UO_2)_3(OH)_5^{+}, NO_3^-)$ we obtained the following slightly different values than Grenthe et al. (1992), (0.94 ± 0.23), (0.70 ± 1.00), and (0.43 ± 0.22) kg·mol^{-1}, resp., but we retain the values reported by Grenthe et al. (1992) for our database.

Guillaumont et al. (2003) discussed a multitude of new experiments providing data on the formation of $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^{+}$ and one new experiment on $(UO_2)_3(OH)_4^{2+}$, which all confirmed the values selected by Grenthe et al. (1992). 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

$$2\ UO_2^{2+} + H_2O(l) \Leftrightarrow (UO_2)_2OH^{3+} + H^+$$

$$\log_{10}{}^*\beta_{1,2}^\circ(m = 2, n = 1, 298.15\text{ K}) = -(2.7 \pm 1.0)$$

No SIT ion interaction coefficients were recommended for $(UO_2)_2OH^{3+}$ by Grenthe et al. (1992). Therefore, we estimated the coefficients for chloride and perchlorate media based on charge correlations (see Appendix A). Our selected values are

$$\varepsilon((UO_2)_2OH^{3+}, Cl^-) = (0.25 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$$

$$\varepsilon((UO_2)_2OH^{3+}, ClO_4^-) = (0.6 \pm 0.1) \text{ kg}\cdot\text{mol}^{-1}$$

Further polymeric cationic species have been proposed on the basis of potentiometric studies. Scrutinizing the most careful studies Grenthe et al. (1992) decided to recommend the species $(UO_2)_4(OH)_7^{+}$ with a selected value

$$4\ UO_2^{2+} + 7\ H_2O(l) \Leftrightarrow (UO_2)_4(OH)_7^{+} + 7\ H^+$$

$$\log_{10}{}^*\beta_{7,4}^\circ(m = 4, n = 7, 298.15\text{ K}) = -(21.9 \pm 1.0)$$

We estimated

$$\varepsilon((UO_2)_4(OH)_7^{+}, Cl^-) = (0.05 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$$

$$\varepsilon((UO_2)_4(OH)_7^{+}, ClO_4^-) = (0.2 \pm 0.1) \text{ kg}\cdot\text{mol}^{-1}$$

based on charge correlations (see Appendix A).

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 selected a value that was later revised by Guillaumont et al. (2003) due to a reinterpretation of the original data. The revised value selected by Guillaumont et al. (2003)

$$3\ UO_2^{2+} + 7\ H_2O(l) \Leftrightarrow (UO_2)_3(OH)_7^{-} + 7\ H^+$$

$$\log_{10}{}^*\beta_{7,3}^\circ(m = 3, n = 7, 298.15\text{ K}) = -(32.2 \pm 0.8)$$

is included in our database, as well as

$$\varepsilon((UO_2)_3(OH)_7^-, Na^+) = -(0.05 \pm 0.10) \text{ kg·mol}^{-1}$$

which we estimated based on charge correlations (see Appendix A).

UO_2OH^+: Grenthe et al. (1992) noted: "The existence of UO_2OH^+ and the equilibrium constant for its formation have been the subject of debate for almost forty years." and "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 selected a value of $\log_{10}*\beta_1°$(298.15 K) = -(5.2 ± 0.3) for the reaction

$$UO_2^{2+} + H_2O(l) \Leftrightarrow UO_2OH^+ + H^+$$

with $\Delta\varepsilon(UO_2OH^+, ClO_4^-)$ = -(0.4 ± 3.7) kg·mol^{-1} and $\Delta\varepsilon(UO_2OH^+, NO_3^-)$ = (0.1 ± 1.4) kg·mol^{-1}, the large uncertainties reflecting the scarcity of data. Using these values for $\Delta\varepsilon$ together with the selected values for $\varepsilon(H^+, ClO_4^-)$ and $\varepsilon(H^+, NO_3^-)$, and $\varepsilon(UO_2^{2+}, ClO_4^-) = \varepsilon(UO_2^{2+}, NO_3^-)$ = (0.46 ± 0.03) kg·mol^{-1}, Grenthe et al. (1992) obtained $\varepsilon(UO_2OH^+, ClO_4^-)$ = -(0.06 ± 0.40) kg·mol^{-1} and $\varepsilon(UO_2OH^+, NO_3^-)$ = (0.51 ± 1.40) kg·mol^{-1} (our calculations with these data resulted in -(0.08 ± 3.7) and (0.59 ± 1.40) kg·mol^{-1}, resp.). Note that the uncertainties in $\Delta\varepsilon(UO_2OH^+, ClO_4^-)$ and $\varepsilon(UO_2OH^+, ClO_4^-)$ reported by Grenthe et al. (1992) are not compatible, they should be about the same, since the uncertainties in $\varepsilon(H^+, ClO_4^-)$ and $\varepsilon(UO_2^{2+}, ClO_4^-)$ are much smaller. Guillaumont et al. (2003) considered newer experimental studies and decided to select the weighted average of the value recommended by Grenthe et al. (1992) and the values obtained from two different experimental studies,

$$\log_{10}*\beta_1°(\text{ 298.15 K}) = -(5.25 \pm 0.24)$$

which we select for our database. Guillaumont et al. (2003) did not revise the values for $\varepsilon(UO_2OH^+, ClO_4^-)$ and $\varepsilon(UO_2OH^+, ClO_4^-)$ selected by Grenthe et al. (1992).

$$\varepsilon(UO_2OH^+, ClO_4^-) = -(0.06 \pm 0.40) \text{ kg·mol}^{-1}$$

$$\varepsilon(UO_2OH^+, NO_3^-) = (0.51 \pm 1.40) \text{ kg·mol}^{-1}$$

which we adopt for our database, despite the problem with the uncertainty for $\varepsilon(UO_2OH^+, ClO_4^-)$. We also selected

$$\varepsilon(UO_2OH^+, Cl^-) = (0.05 \pm 0.10) \text{ kg·mol}^{-1}$$

as estimated based on charge correlations (see Appendix A).

Neutral and anionic U(VI) hydrolysis species: Several authors have hypothesized 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 Section 11.8.1.2). 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. Despite these problems, Grenthe et al. (1992) selected formation constants for the neutral or anionic monomeric species $UO_2(OH)_2(aq)$, $UO_2(OH)_3^-$, and $UO_2(OH)_4^{2-}$, which were revised by Guillaumont et al. (2003). Except for $(UO_2)_3(OH)_7^-$ discussed above, no other anionic polymeric species were selected by Grenthe et al. (1992) and Guillaumont et al. (2003). The existence of the proposed trimers $(UO_2)_3(OH)_8^{2-}$ and $(UO_2)_3(OH)_{10}^{4-}$, e.g., was deemed to be not sufficiently established by potentiometric methods.

$UO_2(OH)_2(aq)$: 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

$$UO_3\cdot 2H_2O(s) \Leftrightarrow UO_2(OH)_2(aq) + H_2O(l)$$

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

$$UO_3\cdot 2H_2O(s) + 2\,H^+ \Leftrightarrow UO_2^{2+} + 3\,H_2O(l)$$

can be calculated from the selected Gibbs energy of formation ($\Delta_f G_m°$ ($UO_3\cdot 2H_2O$, cr, 298.15 K), see Section 11.4.2.1) as $\log_{10}{}^*K_{s,0}° = (4.8 \pm 0.4)$. Thus, a limiting value of $\log_{10}{}^*\beta_2° \leq -10.3$ was selected by Grenthe et al. (1992).

In their documentation of the Nagra/PSI Thermochemical Data Base 01/01, Hummel et al. (2002) made the following comments:

"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 $\Delta_f G_m°$ [...], 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."

Thus, Hummel et al. (2002) selected $\log_{10}{}^*\beta_2°(m = 1, n = 2, 298.15\text{ K}) = -(12.0 \pm 0.5)$ for

$$UO_2^{2+} + 2\,H_2O(l) \Leftrightarrow UO_2(OH)_2(aq) + 2\,H^+$$

Like Hummel et al. (2002), Guillaumont et al. (2003) considered the experimental data by Choppin & Mathur (1991) and selected

$$\log_{10}{}^*\beta_2°(m = 1, n = 2, 298.15\text{ K}) = -(12.15 \pm 0.07)$$

which is the weighted average value of the constants reported by Choppin & Mathur (1991). We adopt this value for our database. Note that it was considered as an upper limit by Guillaumont et al. (2003) in the discussion of the data by Choppin & Mathur (1991) in the appendix, but the qualification as an upper limit was dropped in all other occurrences of this value in Guillaumont et al. (2003).

$UO_2(OH)_3^-$: The value of the equilibrium constant $\log_{10}{}^*\beta_3°$ selected by Grenthe et al. (1992) was based on the experimental data by Sandino (1991). Guillaumont et al. (2003) selected the weighted average of the values given by Sandino & Bruno (1992), who reported the same data as Sandino (1991), and Yamamura et al. (1998)

$$UO_2^{2+} + 3\,H_2O(l) \Leftrightarrow UO_2(OH)_3^- + 3\,H^+$$

$$\log_{10}{}^*\beta_3^\circ(\text{m} = 1, \text{n} = 3, 298.15\ \text{K}) = -(20.25 \pm 0.42)$$

which is also included in our database. The source of the value for the ion interaction coefficient

$$\varepsilon(\text{UO}_2(\text{OH})_3^-, \text{Na}^+) = -(0.09 \pm 0.05)\ \text{kg·mol}^{-1}$$

selected by Grenthe et al. (1992) and retained by Guillaumont et al. (2003) is obscure. This value is listed by Grenthe et al. (1992) in their Table B.4 (p. 696) of the ion interaction coefficients for anions and it is marked as "estimated in this review". However, Grenthe et al. (1992) also wrote (on p. 113):

"It appears that $\log_{10}{}^*\beta_3 = -(19.09 \pm 0.27)$ from the phosphate complexation study of Sandino [91SAN] is a well defined value. The value was corrected by Sandino [91SAN] to $I = 0$ using the ion interaction coefficients $\varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = 0.46$, $\varepsilon(\text{UO}_2(\text{OH})_3^-, \text{Na}^+) = -0.09$ and $\varepsilon(\text{H}^+, \text{ClO}_4^-) = 0.14$. This extrapolation resulted in $\log_{10}{}^*\beta_3^\circ = -(19.18 \pm 0.29)$. This value of the equilibrium constant is accepted in this review..."

In their Table V.7 on p. 107, Grenthe et al. (1992) listed $\Delta\varepsilon(\text{UO}_2(\text{OH})_3^-, \text{Na}^+) = -(0.13 \pm 0.08)$ kg·mol^{-1} and marked it as an estimated value. This value is exactly reproducible by using $\varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = (0.46 \pm 0.03)$ kg·mol^{-1}, $\varepsilon(\text{H}^+, \text{ClO}_4^-) = (0.14 \pm 0.02)$ kg·mol^{-1}, both selected by Grenthe et al. (1992), and $\varepsilon(\text{UO}_2(\text{OH})_3^-, \text{Na}^+) = -(0.09 \pm 0.05)$ kg·mol^{-1} chosen by Sandino (1991).

Thus it appears, that Grenthe et al. (1992) adopted the value used by Sandino (1991). The experiments carried out by Sandino (1991) and also reported by Sandino & Bruno (1992) made use of a background electrolyte of NaClO_4 at $I = 0.5$ mol·dm^{-3}. Concerning the extrapolation of the equilibrium constants to zero ionic strength, Sandino & Bruno (1992) wrote:

"These equilibrium constants have been extrapolated to the infinite dilution standard state by using the SIT theory (Grenthe and Wanner, 1989). The interaction coefficients used in these calculations are $\varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = 0.46 \pm 0.03$, $\varepsilon(\text{HPO}_4^{2-}, \text{Na}^+) = -0.15 \pm 0.06$, $\varepsilon(\text{PO}_4^{3-}, \text{Na}^+) = -0.25 \pm 0.03$, $\varepsilon(\text{UO}_2\text{PO}_4^-, \text{Na}^+) = \varepsilon(\text{UO}_2(\text{OH})_3^-, \text{Na}^+) = -0.09 \pm 0.05$ (Grenthe and Wanner, 1989)."

Going back to Grenthe & Wanner (1989), one finds no values whatsoever for $\varepsilon(\text{UO}_2\text{PO}_4^-, \text{Na}^+)$ and $\varepsilon(\text{UO}_2(\text{OH})_3^-, \text{Na}^+)$ and the source for $\varepsilon(\text{UO}_2(\text{OH})_3^-, \text{Na}^+) = -(0.09 \pm 0.05)$ kg·mol^{-1} remains a mystery. Despite its uncertain origin, we include this value in our database, since it appears to be reasonable, lying within the uncertainty of the estimate -(0.05 ± 0.10) kg·mol^{-1} based on charge correlations (see Appendix A).

$\text{UO}_2(\text{OH})_4^{2-}$: Based on the experimental data by Yamamura et al. (1998), Guillaumont et al. (2003) selected

$$\text{UO}_2^{2+} + 4\ \text{H}_2\text{O(l)} \Leftrightarrow \text{UO}_2(\text{OH})_4^{2-} + 4\ \text{H}^+$$

$$\log_{10}{}^*\beta_4^\circ(\text{m} = 1, \text{n} = 4, 298.15\ \text{K}) = -(32.40 \pm 0.68)$$

which is included in our database.

Since Guillaumont et al. (2003) did not select any ion interaction coefficients, we estimated

$$\varepsilon(\text{UO}_2(\text{OH})_4^{2-}, \text{Na}^+) = -(0.10 \pm 0.10)\ \text{kg·mol}^{-1}$$

based on charge correlations (see Appendix A).

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:

$$S_m°(UO_2OH^+, aq, 298.15 K) = (17 \pm 50) J·K^{-1}·mol^{-1}$$

$$S_m°((UO_2)_2(OH)_2^{2+}, aq, 298.15 K) = -(38 \pm 15) J·K^{-1}·mol^{-1}$$

$$S_m°((UO_2)_3(OH)_5^+, aq, 298.15 K) = (83 \pm 30) J·K^{-1}·mol^{-1}$$

11.4.1.2 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.

11.4.1.3 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 primarily 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, resulting in

$$\log_{10}*\beta_1°(m = 1, n = 1, 298.15 K) = -(0.54 \pm 0.06)$$

with $\Delta\varepsilon = -(0.14 \pm 0.05)$ kg·mol^{-1}. From this value and the selected $\varepsilon(U^{4+}, ClO_4^-) = (0.76 \pm 0.06)$ kg·mol^{-1} and $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$ kg·mol^{-1} follows

$$\varepsilon(UOH^{3+}, ClO_4^-) = (0.48 \pm 0.08) kg·mol^{-1}$$

For use in chloride media we estimated

$$\varepsilon(UOH^{3+}, Cl^-) = (0.25 \pm 0.10) kg·mol^{-1}$$

based on charge correlations (see Appendix A).

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.

$$\Delta_r H_m°(298.15 K) = (46.9 \pm 9.0) kJ·mol^{-1}$$

$$\Delta_r S_m°(298.15 K) = (147 \pm 30) J·K^{-1}·mol^{-1}$$

$U(OH)_4(aq)$: Hummel et al. (2002) presented an extensive discussion of the solubility of $UO_2(s)$ (note that in the following quotation, which is marked in italics, the sections and figures have been renumbered to correspond to the present report):

Grenthe et al. (1992) recommended $\log_{10}{}^*\beta_4^\circ = -4.5 \pm 1.4$ *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 ($\Delta_fG_m^\circ$ *(*UO_2*, cr, 298.15 K), see Section 11.4.2.2) as* $\log_{10}{}^*K_{s,0}^\circ = -4.85 \pm 0.36$*. A value of* $\log_{10}{}^*\beta_4^\circ = \log_{10}K_{s,4} - \log_{10}{}^*K_{s,0}^\circ = -4.6 \pm 0.7$ *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* $\log_{10}{}^*K_{s,0}^\circ = 0.1 \pm 0.7$*. A value of* $\log_{10}{}^*\beta_4^\circ = \log_{10}K_{s,4} - \log_{10}{}^*K_{s,0}^\circ = -4.5 \pm 0.8$ *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 $\log_{10}{}^*\beta_1^\circ = -0.54$ *and* $\log_{10}{}^*\beta_4^\circ = -4.5$ *imply equal concentrations of* UOH^{3+} *and* $U(OH)_4(aq)$ *near pH = 1.8 (see solid line in Fig. 11.1), 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. 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 oxidized 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. 11.2). 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.*

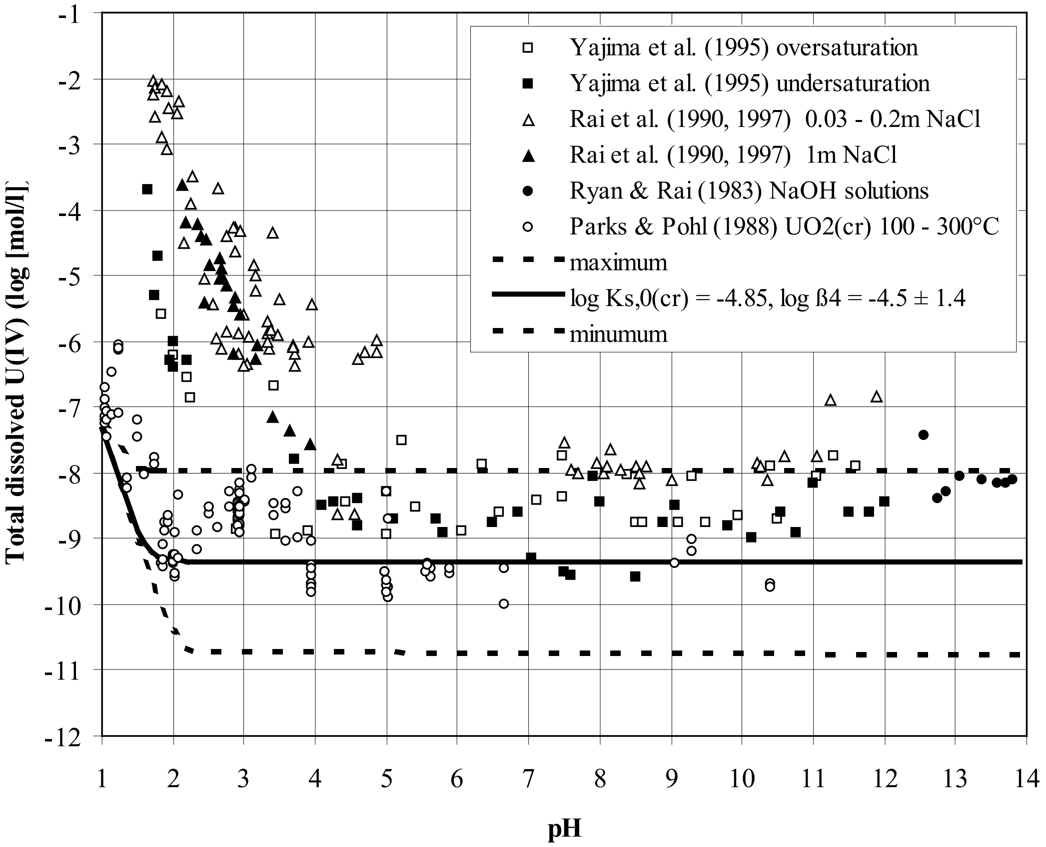

Fig. 11.1: *Solubility data of the system UO_2 - H_2O. The lines have been calculated using thermodynamic constants recommended by Grenthe et al. (1992).*

At pH > 3 they found constant uranium concentrations (see Fig. 11.2). 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. 11.2). 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

$$\log_{10}K_{s,4}^{\circ}\ (UO_2, s, 298.15\ K) = -9 \pm 1$$

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. 11.2 at pH > 4 represent our choice of $\log_{10}K_{s,4}^{\circ}$ = -9 and its associated uncertainty of ± one order of magnitude.

The situation concerning the solubility product, $\log_{10}{}^*K_{s,0}^\circ$, of UO_2 is much less clear-cut. Rai et al. (1990) derive from their short term experiments at pH < 4 a value of $\log_{10}{}^*K_{s,0}^\circ = 4.0 \pm 1.6$. They included the first hydrolysis constant as $\log_{10}{}^*\beta_1^\circ = -0.50 \pm 0.06$ into their data analysis (dashed line in Fig. 11.2 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 $\log_{10}{}^*K_{s,0}^\circ = 2.55$ (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 $\log_{10}{}^*K_{s,0}^\circ = 0.34 \pm 0.8$ 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 ($\log_{10}{}^*\beta_1^\circ = -0.54 \pm 0.06$) results in $\log_{10}{}^*K_{s,0}^\circ = -0.5 \pm 0.6$ (see data close to the thick solid line in Fig. 11.2 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. 11.2. 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 $\log_{10}{}^*K_{s,0}^\circ = 0.1 \pm 0.7$ (approximately represented by the thick solid line in Fig. 11.2 at pH < 3). For a more crystalline precipitate and a pellet of nuclear fuel they derived $\log_{10}{}^*K_{s,0}^\circ = -1.6 \pm 0.8$. 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. 11.2). 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 ($\Delta_f G_m^\circ$ (UO_2, cr, 298.15 K), see Section 11.4.2.2) as selected by Grenthe et al. (1992) results in the lowest value of all: $\log_{10}{}^*K_{s,0}^\circ = -4.85 \pm 0.36$. The scatter of experimental solubility data at pH < 4 in Fig. 11.2 reveals a strong dependence of UO_2 solubility on crystallinity. Consequently, the range of solubility products from $\log_{10}{}^*K_{s,0}^\circ(cr) = -4.85$ (Grenthe et al. 1992) to $\log_{10}{}^*K_{s,0}^\circ(am) = 4.0$ (Rai et al. 1990) spans 9 orders of magnitude! On the other hand, a maximum variation two orders of magnitude in UO_2 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 solubility has been observed at pH > 4 which can be represented by $\log_{10}K_{s,4}^\circ(s) = -9 \pm 1$ (Fig. 11.2). Both ranges are coupled by the (unknown) constant $\log_{10}{}^*\beta_4^\circ$. Obviously, no unique set of $\log_{10}K_{s,4}^\circ(s)$ 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 $\log_{10}{}^*\beta_4^\circ$?

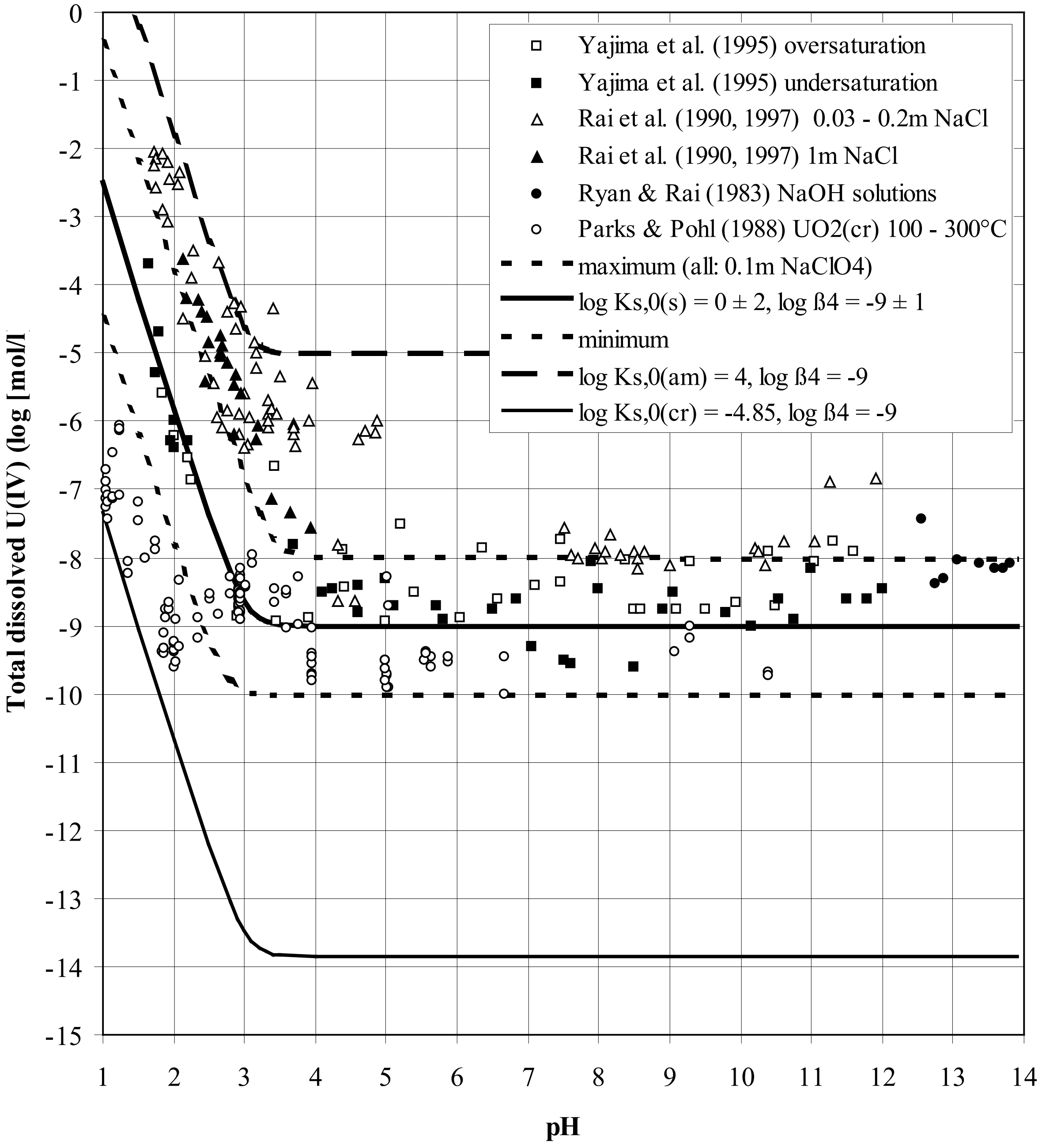

Fig. 11.2: *Solubility data of the system UO_2 - H_2O. The thick solid line is calculated using thermodynamic constants estimated in this review. Dotted lines represent the estimated uncertainty. The dashed line is calculated using $\log_{10}{}^*K_{s,0}^\circ(am)$ = 4 given by Rai et al. (1990). The thin solid line is calculated using $\log_{10}{}^*K_{s,0}^\circ(cr)$ = -4.85 derived from $\Delta_f G_m^\circ$ of $UO_2(cr)$ (Grenthe et al. 1992).*

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 $log_{10}\beta_5° = 34.1 \pm 1.0$*, as recommended by Grenthe et al. (1992) (see Section 11.8.1.2), 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*

$$log_{10}{}^*K_{s,0}° = 0 \pm 2$$

and, derived therefrom,

$$log_{10}{}^*\beta_4° = log_{10}K_{s,4} - log_{10}{}^*K_{s,0}° = -9 \pm 2$$

Note that by calculating the solubility of U(IV) in pure water from the selected values $log_{10}{}^*K_{s,0}°$ *and* $log_{10}{}^*\beta_4°$ *the measured value of log U(tot) = -9 is reproduced but the individual uncertainties of* $log_{10}{}^*K_{s,0}°$ *and* $log_{10}{}^*\beta_4°$ *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 tetravalent actinides like Th.*

Thus, Hummel et al. (2002) selected

$$UO_2(s) + 2\,H_2O(l) \Leftrightarrow U(OH)_4(aq)$$

$$\log_{10}K_{s,4}°(298.15\text{ K}) = -(9 \pm 1)$$

and

$$UO_2(s) + 4\,H^+ \Leftrightarrow U^{4+} + 2\,H_2O(l)$$

$$\log_{10}{}^*K_{s,0}°(298.15\text{ K}) = (0 \pm 2)$$

From $\log_{10}K_{s,4}°(298.15\text{ K})$ and $\log_{10}{}^*K_{s,0}°(298.15\text{ K})$ follows

$$U^{4+} + 4\,H_2O(l) \Leftrightarrow U(OH)_4(aq) + 4\,H^+$$

$$\log_{10}{}^*\beta_4°(298.15\text{ K}) = \log_{10}K_{s,4}°(298.15\text{ K}) - \log_{10}{}^*K_{s,0}°(298.15\text{ K}) = -(9 \pm 2)$$

In a study concerning the solubility and hydrolysis of tetravalent actinides, Neck & Kim (2001) argued in a similar manner as Hummel et al. (2002) and derived

$$UO_2(s) + 2\,H_2O(l) \Leftrightarrow U(OH)_4(aq)$$

$$\log_{10}K_{s,4}°(298.15\text{ K}) = -(8.5 \pm 1)$$

$$U^{4+} + 4\ H_2O(l) \Leftrightarrow U(OH)_4(aq) + 4\ H^+$$

$$\log_{10}{}^*\beta_4^\circ(298.15\ K) = -(10 \pm 1.4)$$

$$UO_2(s) + 4\ H^+ \Leftrightarrow U^{4+} + 2\ H_2O(l)$$

$$\log_{10}{}^*K_{s,0}^\circ(298.15\ K) = (1.5 \pm 1.0)$$

These values were adopted by Guillaumont et al. (2003) and are also included in our database, replacing the very similar values selected by Hummel et al. (2002). Guillaumont et al. (2003) referred to $UO_2(s)$ as $UO_2(am, hyd)$ and we have followed this nomenclature, deleting $UO_2(s)$ from our database. Thus, our database now contains

$$U^{4+} + 4\ H_2O(l) \Leftrightarrow U(OH)_4(aq) + 4\ H^+$$

$$\log_{10}{}^*\beta_4^\circ(298.15\ K) = -(10 \pm 1.4)$$

with

$$UO_2(am, hyd) + 4\ H^+ \Leftrightarrow U^{4+} + 2\ H_2O(l)$$

$$\log_{10}{}^*K_{s,0}^\circ(298.15\ K) = (1.5 \pm 1.0)$$

$U(OH)_5^-$: 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 behavior of $UO_2(s)$ up to pH 14. 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 0.01 M 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 modeling 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 modeled 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.

Neck & Kim (2001) estimated stability constants for $U(OH)_2^{2+}$ and $U(OH)_3^+$ from two different methods. One is based on a correlation of the formation constants of actinide hydroxide complexes with the electrostatic interaction energy between the actinide and the hydroxide ions, and the other on an electrostatic approach, correlating the mononuclear complexation constants for a given actinide cation with an inter-ligand electrostatic repulsion energy term. For $U(OH)_2^{2+}$ and $U(OH)_3^+$, Neck & Kim (2001) chose the mean values from both estimation methods and obtained

$$U^{4+} + 2\ H_2O(l) \Leftrightarrow U(OH)_2^{2+} + 2\ H^+$$

$$\log_{10}{}^*\beta_2^\circ(298.15\ K) = -(1.1 \pm 1.0)$$

$$U^{4+} + 3\ H_2O(l) \Leftrightarrow U(OH)_3^{+} + 3\ H^+$$

$$log_{10}{}^*\beta_3°(298.15\ K) = -(4.7 \pm 1.0)$$

These estimates were not selected by Guillaumont et al. (2003) in accordance with the NEA TDB guidelines. They are included, however, in our database as supplemental data (for use in scoping calculations or qualitative modeling), together with the following ion interaction coefficients estimated based on charge correlations (see Appendix A)

$$\varepsilon(U(OH)_2^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg{\cdot}mol^{-1}$$

$$\varepsilon(U(OH)_2^{2+}, ClO_4^-) = (0.4 \pm 0.1)\ kg{\cdot}mol^{-1}$$

$$\varepsilon(U(OH)_3^{+}, Cl^-) = (0.05 \pm 0.10)\ kg{\cdot}mol^{-1}$$

$$\varepsilon(U(OH)_3^{+}, ClO_4^-) = (0.2 \pm 0.1)\ kg{\cdot}mol^{-1}$$

11.4.2 Solid uranium oxides and hydroxides

11.4.2.1 U(VI) oxides, hydroxides and peroxides

An entire series of oxides, hydrated oxides and hydroxides of U(VI) has been identified and their thermochemical properties (enthalpy of formation, heat capacity, entropy) have been determined and have been selected by Grenthe et al. (1992): α-UO_3(cr), β-UO_3(cr), γ-UO_3(cr), δ-UO_3(cr) (only enthalpy of formation), ε-UO_3(cr) (only enthalpy of formation), α-$UO_3{\cdot}0.9H_2O$(cr), β-$UO_3{\cdot}H_2O$(cr) ≡ β-$UO_2(OH)_2$(cr), γ-$UO_3{\cdot}H_2O$(cr) ≡ γ-$UO_2(OH)_2$(cr) (only enthalpy of formation), $UO_3{\cdot}2H_2O$(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 β-$UO_3{\cdot}H_2O$(cr) at temperatures below 100°C (Grenthe et al. 1992).

For geochemical modeling in liquid water at temperatures ≤ 100°C the anhydrous forms of UO_3(cr) can safely be excluded from the database, as well as the hydrogen insertion compound δ-$UO_3H_{0.83}$(cr), for which Guillaumont et al. (2003) selected a value for the standard enthalpy of formation, whereas the hydrated oxides should be considered as relevant solids. According to Brugger et al. (2011), natural and synthetic hydrated oxides have an empirical chemical formula of $UO_3{\cdot}xH_2O$ (x = 0.8–2.25). There are several naturally occurring hydrated uranyl oxides which belong to the schoepite subgroup. Brugger et al. (2011) distinguish between three minerals, schoepite, $(UO_2)_8O_2(OH)_{12}{\cdot}12H_2O$(cr) or $UO_3{\cdot}2.25H_2O$(cr), metaschoepite, $(UO_2)_8O_2(OH)_{12}{\cdot}10H_2O$(cr) or $UO_3{\cdot}2H_2O$(cr), and their recently discovered paulscherrerite, $UO_2(OH)_2$(cr) or $UO_3{\cdot}H_2O$(cr). Solubility data are only known for metaschoepite.

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 representing the bulk properties 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 Section 11.4.1.3) there is no proof 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)

$$\log_{10}{}^*K_{s,0}^\circ = (5.96 \pm 0.18)$$

Note that the stability constant of $UO_2(OH)_2(aq)$ selected in this review is compatible with the above selected solubility product (see Section 11.4.1.1.).

Guillaumont et al. (2003) discussed a series of new solubility experiments that were published after the review by Grenthe et al. (1992) but retained the value selected by Grenthe et al. (1992).

The enthalpy of formation as selected by Grenthe et al. (1992) is based on the enthalpy of hydration of γ-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:

$$\Delta_f H_m^\circ(UO_3\cdot 2H_2O\text{, cr, 298.15 K}) = -(1826.1 \pm 1.7)\ \text{kJ}\cdot\text{mol}^{-1}$$

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):

$$S_m^\circ(UO_3\cdot 2H_2O\text{, cr, 298.15 K}) = (188.54 \pm 0.38)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$C_{p,m}^\circ(UO_3\cdot 2H_2O\text{, cr, 298.15 K}) = (172.07 \pm 0.34)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

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 arbitrarily to include the entropy (and heat capacity) value in our database. Consequently, $\Delta_f H_m^\circ$ recalculated from $\log_{10}{}^*K_{s,0}^\circ(s)$ 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); and for $UO_3\cdot 0.393H_2O$(cr), $UO_3\cdot 0.648H_2O$(cr), and α-$UO_3\cdot 0.85H_2O$ (cr) only enthalpies of formation are known. We therefore exclude these solids from our database.

Grenthe et al. (1992) selected enthalpies of formation for the U(VI) peroxides $UO_4\cdot 2H_2O$(cr) and $UO_4\cdot 4H_2O$(cr). No solubility or Gibbs free energy data are available for these compounds. Hence, they are not included in our database.

11.4.2.2 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 $\Delta_f G_m^\circ$ (UO_2, cr, 298.15 K) = -(1031.8 ± 1.0) $\text{kJ}\cdot\text{mol}^{-1}$. This recommended value of Grenthe et al. (1992), which was retained by Guillaumont et al. (2003) leads to a solubility product

$$UO_2(cr) + 4\,H^+ \Leftrightarrow U^{4+} + 2\,H_2O(l)$$

$$\log_{10}{}^*K_{s,0}^\circ = -(4.85 \pm 0.36)$$

As discussed in Section 11.4.1.3 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 $\log_{10}{}^*K_{s,0}^\circ(cr)$ =

-4.85 (Grenthe et al. 1992) to $\log_{10}{}^*K_{s,0}°(\text{am}) = 4.0$ (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 $\log_{10}K_{s,4}°(\text{s}) = -(8.5 \pm 1)$ (Fig. 11.2). 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 to this dilemma, values for $\log_{10}{}^*\beta_4°$ and $\log_{10}{}^*K_{s,0}°$ 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. As discussed in Section 11.4.1.3, the selected solubility product is

$$UO_2(\text{am, hyd}) + 4\ H^+ \Leftrightarrow U^{4+} + 2\ H_2O(l)$$

$$\log_{10}{}^*K_{s,0}° = (1.5 \pm 1.0)$$

11.4.2.3 Mixed valence oxides

Values for the enthalpy of formation and entropy of $U_3O_8(\text{cr}) \equiv 3\cdot UO_{2.6667}(\text{cr})$, β-U_3O_7(cr,) ≡ 3·β-$UO_{2.3333}$(cr)[20] , $U_4O_9(\text{cr}) \equiv 4\cdot UO_{2.25}(\text{cr})$, and β-$U_4O_9$(cr) ≡ 4·β-$UO_{2.25}$(cr) (higher-temperature polymorph) were 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 β-U_3O_7(cr), U_4O_9(cr) and β-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. Guillaumont et al. (2003) selected a value for the enthalpy of formation of an additional mixed valence oxide, α-$UO_{2.95}$(cr). Again, no solubility measurements are reported.

Combining calculated $\Delta_f G_m°$ values of any of these mixed valence oxides with our selected solubility products for metaschoepite, $UO_3\cdot 2H_2O$(cr), and "uraninite", UO_2(am, hyd), invariably leads to grossly erroneous results in geochemical modeling. $UO_3\cdot 2H_2O$(cr) and UO_2(am, hyd) 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. Especially under reducing conditions, U_4O_9(cr) will always be predicted as the stable solid phase instead of UO_2(am, hyd) and the calculated uranium solubility may deviate by orders of magnitude from measured values. 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.

For the hydrated mixed valence oxides $UO_{2.86}\cdot 0.5H_2O$(cr) and $UO_{2.86}\cdot 1.5H_2O$(cr), Grenthe et al. (1992) selected standard enthalpies of formation. Since additional data are missing, the hydrated mixed valence oxides are also not included in our database.

11.4.3 Uranium hydrides

β-UH_3(cr) is not relevant under environmental conditions, this phase is not included in the database.

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[20] Grenthe et al. (1992) also selected values for the heat capacity and entropy of α-U_3O_7(cr) ≡ 3 · α-$UO_{2.3333}$(cr), but none for the enthalpy of formation.

11.5 Halogen compounds and complexes

11.5.1 Aqueous halogen complexes

U(VI) fluorides: Guillaumont et al. (2003) recommended stability constants for

$$UO_2^{2+} + n\,F^- \Leftrightarrow UO_2F_n^{(2-n)}$$

with n = 1–4 based on Ferri et al. (1993) who studied the complex formation of U(VI) with fluoride in 3.00 M $NaClO_4$ using potentiometric methods. From an SIT regression of their conditional stability constants and those by Ahrland & Kullberg (1971), which were measured in 1.00 M $NaClO_4$, Ferri et al. (1993) derived

$$\varepsilon(UO_2F^+, ClO_4^-) = (0.28 \pm 0.04)\ kg{\cdot}mol^{-1}$$

$$\varepsilon(UO_2F_2(aq), Na^+ \text{ or } ClO_4^-) = (0.13 \pm 0.05)\ kg{\cdot}mol^{-1}$$

$$\varepsilon(UO_2F_3^-, Na^+) = -(0.14 \pm 0.05)\ kg{\cdot}mol^{-1}$$

$$\varepsilon(UO_2F_4^{2-}, Na^+) = -(0.30 \pm 0.06)\ kg{\cdot}mol^{-1}$$

by means of the selected $\varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)\ kg{\cdot}mol^{-1}$ and $\varepsilon(F^-, Na^+) = (0.02 \pm 0.02)\ kg{\cdot}mol^{-1}$. From these ion interaction coefficients and the conditional stability constants at 3.00 M $NaClO_4$, Guillaumont et al. (2003) obtained their selected standard stability constants

$$UO_2^{2+} + F^- \Leftrightarrow UO_2F^+$$

$$\log_{10}\beta_1°(n = 1, 298.15\ K) = (5.16 \pm 0.06)$$

$$UO_2^{2+} + 2\,F^- \Leftrightarrow UO_2F_2(aq)$$

$$\log_{10}\beta_2°(n = 2, 298.15\ K) = (8.83 \pm 0.08)$$

$$UO_2^{2+} + 3\,F^- \Leftrightarrow UO_2F_3^-$$

$$\log_{10}\beta_3°(n = 3, 298.15\ K) = (10.90 \pm 0.10)$$

$$UO_2^{2+} + 4\,F^- \Leftrightarrow UO_2F_4^{2-}$$

$$\log_{10}\beta_4°(n = 4, 298.15\ K) = (11.84 \pm 0.11)$$

which are all included in our database together with the corresponding ion interaction coefficients. Note, however, that the stability constants and the ion interaction coefficients are not very well constrained, since they were all derived from linear SIT-regressions of only two data points per reaction. It is also noteworthy that Ferri et al. (1993) provided an ion interaction coefficient for a neutral species, $\varepsilon(UO_2F_2(aq), Na^+ + ClO_4^-)$. Guillaumont et al. (2003) did not comment on this and tacitly excluded $\varepsilon(UO_2F_2(aq), Na^+ + ClO_4^-)$ from the list of selected ion interaction coefficients. In contrast to Guillaumont et al. (2003), we chose to include it in our database, since it is too large to be assumed to be equal to zero and since ion interaction coefficients for neutral species have been selected in the later NEA-reviews by Gamsjäger et al. (2005) and Hummel et al. (2005).

In their Table B.3 of selected ion interaction coefficients, Grenthe et al. (1992) listed a value of (0.04 ± 0.07) $kg{\cdot}mol^{-1}$ for $\varepsilon(UO_2F^+, Cl^-)$. The source of this value is mysterious. A footnote to $\varepsilon(UO_2F^+, Cl^-)$, and also to $\varepsilon(NpO_2^+, ClO_4^-)$, $\varepsilon(PuO_2^+, ClO_4^-)$, $\varepsilon(Np^{4+}, ClO_4^-)$ and $\varepsilon(Pu^{4+}, ClO_4^-)$, in Table B.3 says: "Taken from Riglet, Robouch and Vitorge [89RIG/ROB], where the following assumptions were made: $\varepsilon(Np^{3+}, ClO_4^-) \approx \varepsilon(Pu^{3+}, ClO_4^-) = 0.49$ as for other (M^{3+}, ClO_4^-) interactions, and $\varepsilon(NpO_2^{2+}, ClO_4^-) \approx \varepsilon(PuO_2^{2+}, ClO_4^-) \approx \varepsilon(UO_2^{2+}, ClO_4^-) = 0.46$". This clearly has little to do with $\varepsilon(UO_2F^+, Cl^-)$. In addition, the value of (0.04 ± 0.07) $kg{\cdot}mol^{-1}$ for

$\varepsilon(UO_2F^+, Cl^-)$ appears nowhere else in Grenthe et al. (1992), while on p.639, they make use of the estimate $\varepsilon(UO_2F^+, Cl^-) \approx \varepsilon(UO_2F^+, ClO_4^-) = (0.29 \pm 0.05)$ kg·mol^{-1}. Due to its dubious origin, we did not include the value for $\varepsilon(UO_2F^+, Cl^-)$ selected by Grenthe et al. (1992) in our database. Instead, we estimated

$$\varepsilon(UO_2F^+, Cl^-) = (0.05 \pm 0.10)\ \text{kg·mol}^{-1}$$

based on charge correlations (see Appendix A), which, incidentally, is not much different anyway.

Equilibrium constants were also reported for the formation of $UO_2F_5^{3-}$, but none were recommended by Guillaumont et al. (2003). The presence of $UO_2F_5^{3-}$ was clearly demonstrated by NMR, however, the complex is very weak and is therefore only stable in concentrated fluoride solutions.

Enthalpy of reaction values were recommended by Grenthe et al. (1992) and retained by Guillaumont et al. (2003). The selected enthalpies of formation in Grenthe et al. (1992) are derived therefrom.

$$\Delta_r H_m^\circ(n = 1, 298.15\ K) = (1.70 \pm 0.08)\ \text{kJ·mol}^{-1}$$

$$\Delta_r H_m^\circ(n = 2, 298.15\ K) = (2.10 \pm 0.19)\ \text{kJ·mol}^{-1}$$

$$\Delta_r H_m^\circ(n = 3, 298.15\ K) = (2.35 \pm 0.31)\ \text{kJ·mol}^{-1}$$

$$\Delta_r H_m^\circ(n = 4, 298.15\ K) = (0.29 \pm 0.47)\ \text{kJ·mol}^{-1}$$

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: Several equilibrium studies have been reported concerning U(IV) fluoride complexation in perchlorate media (a chloride medium was only used by a single study). The available experimental data were interpreted by Grenthe et al. (1992) and Guillaumont et al. (2003) in terms of

$$U^{4+} + n\ HF(aq) \Leftrightarrow UF_n^{(4-n)} + n\ H^+$$

with n = 1–4. Since the experiments were performed at only a few different ionic strengths, a simultaneous determination of $\log_{10}{}^*\beta_n^\circ$ and $\Delta\varepsilon$ by SIT regression was deemed unreliable by Grenthe et al. (1992) and by Guillaumont et al. (2003). Instead, they estimated $\Delta\varepsilon$, extrapolated each conditional stability constant to zero ionic strength and took their weighted average. The values for $\Delta\varepsilon$ were estimated as follows: $\Delta\varepsilon = -(0.14 \pm 0.05)$ kg·mol^{-1} for $U^{4+} + H_2O(l) \Leftrightarrow UOH^{3+} + H^+$ was used as an estimate of the corresponding $\Delta\varepsilon$ for $U^{4+} + HF(aq) \Leftrightarrow UF^{3+} + H^+$. With the selected $\varepsilon(U^{4+}, ClO_4^-) = (0.76 \pm 0.06)$ kg·mol^{-1} and $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$ kg·mol^{-1} one then obtains

$$\varepsilon(UF^{3+}, ClO_4^-) = (0.48 \pm 0.08)\ \text{kg·mol}^{-1}$$

The ion interaction coefficients for UF_2^{2+} and UF_3^+ were directly estimated according to

$$\varepsilon(UF_2^{2+}, Cl^-)^{[21]} \approx \varepsilon(M^{2+}, ClO_4^-) = (0.3 \pm 0.1)\ \text{kg·mol}^{-1}$$

$$\varepsilon(UF_3^+, Cl^-) \approx \varepsilon(M^+, ClO_4^-) = (0.1 \pm 0.1)\ \text{kg·mol}^{-1}$$

(note that Grenthe et al. (1992) never explain how these estimates were derived) and ε for $UF_4(aq)$ was assumed to be equal to zero. These values were then used together with the

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[21] Note that $\varepsilon(UF_2^{2+}, Cl^-) = (0.3 \pm 0.1)$ kg·mol^{-1} does not appear in the list of selected ion interactions coefficients by Grenthe et al. (1992) (nor in any of the following NEA reviews), although this estimate was apparently used by them (see their p. 630).

selected ε(U^{4+}, ClO_4^-) and ε(H^+, ClO_4^-) for the calculation of the corresponding Δε. After the extrapolation to zero ionic strength, the resulting values of $\log_{10}{}^*\beta_n°$ were converted to $\log_{10}\beta_n°$ for the reaction

$$U^{4+} + n\,F^- \Leftrightarrow UF_n^{(4-n)}$$

by adding the selected $\log_{10}\beta° = (3.18 \pm 0.02)$ for $H^+ + F^- \Leftrightarrow HF(aq)$.

In this way, Guillaumont et al. (2003) obtained the following recommended equilibrium constants:

$$U^{4+} + F^- \Leftrightarrow UF^{3+}$$

$$\log_{10}\beta_1°(n = 1, 298.15\text{ K}) = (9.42 \pm 0.51)$$

$$U^{4+} + 2\,F^- \Leftrightarrow UF_2^{2+}$$

$$\log_{10}\beta_2°(n = 2, 298.15\text{ K}) = (16.56 \pm 0.71)$$

$$U^{4+} + 3\,F^- \Leftrightarrow UF_3^{+}$$

$$\log_{10}\beta_3°(n = 3, 298.15\text{ K}) = (21.89 \pm 0.83)$$

$$U^{4+} + 4\,F^- \Leftrightarrow UF_4(aq)$$

$$\log_{10}\beta_4°(n = 4, 298.15\text{ K}) = (26.34 \pm 0.96)$$

These constants and the ion interaction coefficients mentioned above are included in our database, as well as

$$\varepsilon(UF^{3+}, Cl^-) = (0.25 \pm 0.10)\text{ kg}\cdot\text{mol}^{-1}$$

estimated based on charge correlations (see Appendix A).

The only experimental study of anionic U(IV) fluoride complexes, UF_5^- and UF_6^{2-}, is a solubility study of $UF_4\cdot 2.5H_2O$, see Section 11.5.2. Following Grenthe et al. (1992), the solubility product $\log_{10}K_{s,0}° = -(30.12 \pm 0.70)$ derived from this study was used by Guillaumont et al. (2003) for the evaluation of $\log_{10}\beta_5°$ and $\log_{10}\beta_6°$ and is selected for our database. Note, however, that this experimental solubility product is different from that of -(33.5 ± 1.2), which can be calculated from the value for $\Delta_fG_m°(UF_4\cdot 2.5H_2O$, cr, 298.15 K) recommended by Grenthe et al. (1992) and Guillaumont et al. (2003), which is based on thermochemical data (see Section 11.5.2). For the formation of UF_5^- and UF_6^{2-}, Guillaumont et al. (2003) selected

$$U^{4+} + 5\,F^- \Leftrightarrow UF_5^{-}$$

$$\log_{10}\beta_5°(n = 5, 298.15\text{ K}) = (27.73 \pm 0.74)$$

$$U^{4+} + 6\,F^- \Leftrightarrow UF_6^{2-}$$

$$\log_{10}\beta_6°(n = 6, 298.15\text{ K}) = (29.80 \pm 0.70)$$

which are also included in our database. The solubility experiments concerning $UF_4 \cdot 2.5H_2O$ were carried out at very low ionic strengths. For this reason, measured solubility constants were corrected to zero ionic strength using SIT but neglecting the ion interaction parameters. In the absence of these parameters, we estimated

$$\varepsilon(UF_5^-, Na^+) = -(0.05 \pm 0.10)\text{ kg}\cdot\text{mol}^{-1}$$

$$\varepsilon(UF_6^{2-}, Na^+) = -(0.10 \pm 0.10)\text{ kg}\cdot\text{mol}^{-1}$$

based on charge correlations (see Appendix A).

For some of the formation reactions, standard enthalpy of reaction values were recommended by Grenthe et al. (1992) and retained by Guillaumont et al. (2003). The selected enthalpies of formation in Grenthe et al. (1992) are derived therefrom.

$$\Delta_r H_m°(n = 1, 298.15 \text{ K}) = -(5.6 \pm 0.5) \text{ kJ·mol}^{-1}$$

$$\Delta_r H_m°(n = 2, 298.15 \text{ K}) = -(3.5 \pm 0.6) \text{ kJ·mol}^{-1}$$

$$\Delta_r H_m°(n = 3, 298.15 \text{ K}) = (0.5 \pm 4.0) \text{ kJ·mol}^{-1}$$

No enthalpy of reaction is reported for $UF_4(aq)$. Grenthe et al. (1992) therefore estimated an entropy of reaction based on experimental data

$$\Delta_r S_m°(n = 4, 298.15 \text{ K}) = (476 \pm 17) \text{ J·K}^{-1}\text{·mol}^{-1}$$

Grenthe et al. (1992) concluded that the enthalpies of reaction in the U^{4+}-F^- system are small, hence the corresponding equilibria are not expected to be strongly influenced by temperature.

U(VI) chlorides: The U(VI) chloride complexes are very weak, but an EXAFS study has shown such complexes to form at very high chloride concentrations. A sufficient number of experimental data is available which cover a wide range of ionic strengths in mixed chloride/perchlorate media, 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 by Grenthe et al. (1992) resulted in good extrapolations to zero ionic strength for the equilibria

$$UO_2^{2+} + n\,Cl^- \Leftrightarrow UO_2Cl_n^{(2-n)}$$

with n = 1 and n = 2. Thus, Grenthe et al. (1992) selected

$$UO_2^{2+} + Cl^- \Leftrightarrow UO_2Cl^+$$

$$\log_{10}\beta_1°(n = 1, 298.15 \text{ K}) = (0.17 \pm 0.02)$$

with $\Delta\varepsilon = -(0.25 \pm 0.02)$ kg·mol^{-1} and

$$UO_2^{2+} + 2\,Cl^- \Leftrightarrow UO_2Cl_2(aq)$$

$$\log_{10}\beta_2°(n = 2, 298.15 \text{ K}) = -(1.1 \pm 0.4)$$

with $\Delta\varepsilon = -(0.62 \pm 0.17)$ kg·mol^{-1}.

From $\Delta\varepsilon$ for UO_2Cl^+ and the selected $\varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$ kg·mol^{-1} and $\varepsilon(Cl^-, H^+) = (0.12 \pm 0.01)$ kg·mol^{-1}, Grenthe et al. (1992) calculated

$$\varepsilon(UO_2Cl^+, ClO_4^-) = (0.33 \pm 0.04) \text{ kg·mol}^{-1}$$

Following the discussion by Hummel et al. (2005) in their Chapter V.4 on weak complexes versus strong specific ion interaction, we used the value of $\varepsilon(UO_2Cl^+, ClO_4^-)$ for estimating

$$\varepsilon(UO_2Cl^+, Cl^-) = \varepsilon(UO_2Cl^+, ClO_4^-) = (0.33 \pm 0.04) \text{ kg·mol}^{-1}$$

It is important to keep in mind that in order to be consistent, this value for $\varepsilon(UO_2Cl^+, Cl^-)$ should only be used in combination with $\varepsilon(UO_2^{2+}, Cl^-) = \varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$ kg·mol^{-1}.

Enthalpy of reaction values were also recommended by Grenthe et al. (1992). The selected enthalpies of formation in Grenthe et al. (1992) were derived therefrom.

$$\Delta_r H_m°(n = 1, 298.15 \text{ K}) = (8 \pm 2) \text{ kJ·mol}^{-1}$$

$$\Delta_r H_m°(n = 2, 298.15 \text{ K}) = (15 \pm 6) \text{ kJ·mol}^{-1}$$

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). For UCl^{3+}, Grenthe et al. (1992) recommended

$$U^{4+} + Cl^- \Leftrightarrow UCl^{3+}$$

$$\log_{10}\beta_1°(298.15\ K) = (1.72 \pm 0.13)^{22}$$

based on experiments in mixed chloride/perchlorate media (six data points in H(Cl, ClO_4), one data point in 0.6 M $HClO_4$ and 0.4 M $NaClO_4$, and one data point in (Na, H)(Cl, ClO_4)). Guillaumont et al. (2003) retained the value of $\log_{10}\beta_1°(298.15\ K)$ but pointed out that it could be too high. From the SIT-regression, Grenthe et al. (1992) obtained $\Delta\varepsilon = -(0.29 \pm 0.08)$ kg·mol^{-1}. They used this value together with the selected $\varepsilon(U^{4+}, ClO_4^-) = (0.76 \pm 0.06)$ kg·mol^{-1} and $\varepsilon(Cl^-, H^+) = (0.12 \pm 0.01)$ kg·mol^{-1} for deriving

$$\varepsilon(UCl^{3+}, ClO_4^-) = (0.59 \pm 0.10)\ kg{\cdot}mol^{-1}$$

Guillaumont et al. (2003) claimed that this value is erroneous and replaced it with (0.50 ± 0.10) kg·mol^{-1}. Apparently, they used $\varepsilon(Cl^-, Na^+)$ instead of $\varepsilon(Cl^-, H^+)$ in deriving $\varepsilon(UCl^{3+}, ClO_4^-)$ from $\Delta\varepsilon$. For our database, we retained the value by Grenthe et al. (1992). Since six out of eight measurements were made in Na-free media, it is more reasonable to use $\varepsilon(Cl^-, H^+)$ than $\varepsilon(Cl^-, Na^+)$.

Following the discussion by Hummel et al. (2005) in their Chapter V.4 on weak complexes versus strong specific ion interaction, we used the value of (UCl^{3+}, ClO_4^-) for estimating

$$\varepsilon(UCl^{3+}, Cl^-) = \varepsilon(UCl^{3+}, ClO_4^-) = (0.59 \pm 0.10)\ kg{\cdot}mol^{-1}$$

It is important to keep in mind that in order to be consistent, this value for $\varepsilon(UCl^{3+}, Cl^-)$ should only be used in combination with $\varepsilon(U^{4+}, Cl^-) = \varepsilon(U^{4+}, ClO_4^-) = (0.76 \pm 0.06)$ kg·mol^{-1}.

From the equilibrium data of one study at 10, 25, and 40°C, Grenthe et al. (1992) calculated a value for the enthalpy of reaction. The selected enthalpy of formation in Grenthe et al. (1992) is derived therefrom.

$$\Delta_r H_m°(n = 1, 298.15\ K) = -(19 \pm 9)\ kJ{\cdot}mol^{-1}$$

No reliable value of $\log_{10}\beta_2°$ 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.

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 modeling 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

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[22] Note that on p. 462 in Hummel et al. (2002), this value was erroneously written as 1.27 ± 0.13. The electronic versions of TDB 01/01 contain the correct value.

where such weak complexes may be formed. Therefore, Grenthe et al. (1992) did not recommend equilibrium constants for uranium perchlorates.

Bromine complexes of uranium: Grenthe et al. (1992) selected equilibrium constants for the generally rather weak complexes UO_2Br^+, UBr^{3+}, and $UO_2BrO_3^+$. However, bromine complexes of uranium are not thought to be of relevance for geochemical modeling and are not included in our database.

Iodine complexes of uranium: Grenthe et al. (1992) selected equilibrium constants for a U(IV) iodide, UI^{3+}, and for the U(VI) iodates $UO_2IO_3^+$ and $UO_2(IO_3)_2(aq)$ which are included in our database:

$$U^{4+} + I^- \Leftrightarrow UI^{3+}$$

$$\log_{10}\beta_1°(298.15 \text{ K}) = (1.25 \pm 0.30)$$

$$UO_2^{2+} + IO_3^- \Leftrightarrow UO_2IO_3^+$$

$$\log_{10}\beta_1°(298.15 \text{ K}) = (2.00 \pm 0.02)$$

$$UO_2^{2+} + 2\ IO_3^- \Leftrightarrow UO_2(IO_3)_2(aq)$$

$$\log_{10}\beta_2°(298.15 \text{ K}) = (3.59 \pm 0.15)$$

The conditional stability constant for UI^{3+} in 2.5 M (Na, H)ClO_4 was extrapolated by Grenthe et al. (1992) to $I = 0$ by assuming that $\Delta\varepsilon(U^{4+} + I^- \Leftrightarrow UI^{3+}) \approx \Delta\varepsilon(U^{4+} + Cl^- \Leftrightarrow UCl^{3+}) = -(0.29 \pm 0.08)$ kg·mol^{-1}. From this and the selected $\varepsilon(U^{4+}, ClO_4^-) = (0.76 \pm 0.06)$ kg·mol^{-1} and $\varepsilon(I^-, Na^+) = (0.08 \pm 0.06)$ kg·mol^{-1} then follows

$$\varepsilon(UI^{3+}, ClO_4^-) = (0.55 \pm 0.10) \text{ kg·mol}^{-1}$$

The conditional stability constant for $UO_2IO_3^+$ in 0.1 M $NaClO_4$ was extrapolated by Grenthe et al. (1992) to $I = 0$ by assuming that

$$\varepsilon(UO_2IO_3^+, ClO_4^-) \approx \varepsilon(UO_2Cl^+, ClO_4^-) = (0.33 \pm 0.04) \text{ kg·mol}^{-1}$$

and $\varepsilon(IO_3^-, Na^+) \approx \varepsilon(BrO_3^-, Na^+) = -(0.06 \pm 0.02)$ kg·mol^{-1}. From these estimates and the selected $\varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$ kg·mol^{-1}, Grenthe et al. (1992) then calculated $\Delta\varepsilon$ for the extrapolation. The conditional stability constant for $UO_2(IO_3)_2(aq)$ was determined in a solubility study of $UO_2(IO_3)_2(cr)$ in 0.2 M NH_4Cl. Correction to $I = 0$ was made by Grenthe et al. (1992) by assuming that $\varepsilon(IO_3^-, NH_4^+) \approx \varepsilon(BrO_3^-, Na^+) = -(0.06 \pm 0.02)$ kg·mol^{-1} and $\varepsilon(UO_2(IO_3)_2(aq), NH_4^+ + Cl^-) = 0$. These estimates and the selected $\varepsilon(UO_2^{2+}, Cl^-) = \varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$ kg·mol^{-1} lead to the required $\Delta\varepsilon$ for the extrapolation.

Based on charge correlations (see Appendix A), we estimated for chloride media

$$\varepsilon(UI^{3+}, Cl^-) = (0.25 \pm 0.10) \text{ kg·mol}^{-1}$$

$$\varepsilon(UO_2IO_3^+, Cl^-) = (0.05 \pm 0.10) \text{ kg·mol}^{-1}$$

Grenthe et al. (1992) did not accept data for $UO_2(IO_3)_3^-$, due to the large changes in the ionic medium that occurred during the experiment in the concentration range where this complex is formed.

11.5.2 Uranium halide compounds

A large number of uranium halide compounds have been the subject of extensive thermochemical studies.

Uranium fluoride compounds: The Gibbs energies of U(IV) fluorides and oxofluorides calculated from thermochemical data suggest that some of these compounds are sparingly soluble solids. 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 $UF_4 \cdot 2.5H_2O(cr)$. The solubility of this solid was reported in terms of the reaction

$$UF_4\cdot 2.5H_2O(cr) \Leftrightarrow UF_n^{(4-n)} + (4-n)\ F^- + 2.5\ H_2O(l)$$

with $\log_{10}K^\circ_{s,n}$ for n = 2–6. Following Grenthe et al. (1992), Guillaumont et al. (2003) used the selected values for $\log_{10}\beta_2^\circ$, $\log_{10}\beta_3^\circ$, and $\log_{10}\beta_4^\circ$ with $\log_{10}K^\circ_{s,2}$, $\log_{10}K^\circ_{s,3}$, and $\log_{10}K^\circ_{s,4}$, to calculate three values for the solubility product

$$UF_4\cdot 2.5H_2O(cr) \Leftrightarrow U^{4+} + 4\ F^- + 2.5\ H_2O(l)$$

Taking the average, they obtained the selected

$$\log_{10}K_{s,0}^\circ = -(30.12 \pm 0.70)$$

and used this value to derive $\log_{10}\beta_5^\circ$ and $\log_{10}\beta_6^\circ$ for UF_5^- and UF_6^{2-} from $\log_{10}K^\circ_{s,5}$, and $\log_{10}K^\circ_{s,6}$ (see Section 11.5.1). The selected solubility product differs by 3 orders of magnitude from the value of -(33.5 ± 1.2) which is calculated from $\Delta_fG_m^\circ$ ($UF_4\cdot 2.5H_2O$, cr, 298.15 K), a value selected by Grenthe et al. (1992) and retained by Guillaumont et al. (2003). 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 modeling. 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), but not included in our database (see the following discussion), is based on the enthalpy of hydration of $UF_4(cr)$ to $UF_4\cdot 2.5H_2O(cr)$: $\Delta_fH_m^\circ(UF_4\cdot 2.5H_2O$, cr, 298.15 K) = -(2671.5 ± 4.3) $kJ\cdot mol^{-1}$

The entropy and the heat capacity as estimated by Grenthe et al. (1992) are:

$$S_m^\circ(UF_4\cdot 2.5H_2O,\ cr,\ 298.15\ K) = (263.5 \pm 15.0)\ J\cdot K^{-1}\cdot mol^{-1}$$

$$C_{p,m}^\circ(UF_4\cdot 2.5H_2O,\ cr,\ 298.15\ K) = (263.7 \pm 15.0)\ J\cdot K^{-1}\cdot mol^{-1}$$

In order 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 the solubility of $UF_4\cdot 2.5H_2O(cr)$, we decided somewhat arbitrarily to include the entropy (and heat capacity) value in our database. Consequently, $\Delta_fH_m^\circ$ recalculated from $\log_{10}{}^*K_{s,0}^\circ$ and S_m° differs from the recommendation of Grenthe et al. (1992).

The data selected by Grenthe et al. (1992) for $UF_3(cr)$, $UF_4(cr)$, α-$UF_5(cr)$, β-$UF_5(cr)$, $UF_6(cr)$, $U_2F_9(cr)$, $U_4F_{17}(cr)$, $UOF_2(cr)$, $UOF_4(cr)$, $UO_2F_2(cr)$, $U_2O_3F_6(cr)$, $U_3O_5F_8(cr)$, $H_3OUF_6(cr)$, $UOFOH(cr)$, $UOFOH\cdot 0.5H_2O(cr)$, $UOF_2\cdot H_2O(cr)$, $UF_4\cdot 2.5H_2O(cr)$, $UO_2FOH\cdot H_2O(cr)$, $UO_2FOH\cdot 2H_2O(cr)$, and $UO_2F_2\cdot 3H_2O(cr)$ are all based on thermochemical measurements and are not included in our database.

Uranium chlorine compounds: Grenthe et al. (1992) selected thermochemical data for the following uranium chloride, oxochloride, and hydroxochloride solids: $UCl_3(cr)$, $UCl_4(cr)$, $UCl_5(cr)$, $UCl_6(cr)$, $UOCl(cr)$, $UOCl_2(cr)$, $UOCl_3(cr)$, $UO_2Cl(cr)$, $UO_2Cl_2(cr)$, $U_2O_2Cl_5(cr)$, $(UO_2)_2Cl_3(cr)$, $U_5O_{12}Cl(cr)$, $UO_2Cl_2\cdot H_2O(cr)$, $UO_2Cl_2\cdot 3H_2O(cr)$, and $UO_2ClOH\cdot 2H_2O(cr)$. The calculated Gibbs energies of these compounds suggest that they are all highly soluble salts. The same conclusion can be drawn 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).

Mixed fluorine and chlorine compounds of uranium: The thermochemical data selected by Grenthe et al. (1992) for the highly soluble salts UCl_3F(cr), UCl_2F_2(cr), $UClF_3$(cr) are not included in our database.

Bromine and iodine compounds of uranium: Grenthe et al. (1992) selected thermochemical data for UBr_3(cr), UBr_4(cr), UBr_5(cr), $UOBr_2$(cr), $UOBr_3$(cr), UO_2Br_2(cr), $UO_2Br_2 \cdot H_2O$(cr), $UO_2BrOH \cdot 2H_2O$(cr), $UO_2Br_2 \cdot 3H_2O$(cr), UI_3(cr), and UI_4(cr). The calculated Gibbs free energies of these solids suggest that they are all highly soluble salts. The only measured solubility product concerns U(VI) iodate, $UO_2(IO_3)_2$(cr). 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.

Mixed chlorine, bromine, and iodine compounds of uranium: Likewise, the thermochemical data selected by Grenthe et al. (1992) for UBr_2Cl(cr), UBr_3Cl(cr), $UBrCl_2$(cr), UBr_2Cl_2(cr), $UBrCl_3$(cr), $UClI_3$(cr), UCl_2I_2(cr), UCl_3I(cr), $UBrI_3$(cr), UBr_2I_2(cr), and UBr_3I(cr) suggest that these mixed solids are also highly soluble. For this reason, they are not considered in our database.

11.5.3 Uranium halogen gases

Grenthe et al. (1992) selected thermodynamic data for the following uranium halogen gases:

Uranium fluoride gases: UF(g), UF_2(g), UF_3(g), UF_4(g), UF_5(g), UF_6(g), U_2F_{10}(g), UOF_4(g), UO_2F_2(g)

Uranium chloride gases: UCl(g), UCl_2(g), UCl_3(g), UCl_4(g), UCl_5(g), UCl_6(g), U_2Cl_{10}(g), UO_2Cl_2(g)

Uranium bromide gases: UBr(g), UBr_2(g), UBr_3(g), UBr_4(g), UBr_5(g)

Uranium iodide gases: UI(g), UI_2(g), UI_3(g), UI_4(g)

Since these gases are not relevant for geochemical modeling of groundwaters, they are not included in our database.

11.6 Chalcogen compounds and complexes

11.6.1 Sulphur compounds and complexes

11.6.1.1 Uranium sulphides

No thermodynamic data are available for aqueous uranium sulphide complexes. Thermochemical data have been selected by Grenthe et al. (1992) for the binary uranium sulphide solids US(cr), $US_{1.90}$(cr), US_2(cr), US_3(cr), U_2S_3(cr), U_2S_5(cr), and U_3S_5(cr). However, none of these solids is included in our database.

11.6.1.2 Uranium sulphites

Grenthe et al. (1992) recommended an equilibrium constant for the 1:1 uranium(VI) sulphite complex $UO_2SO_3(aq)$. No thermodynamic data are available for aqueous uranium(IV) sulphite complexes. In addition, thermochemical data for the uranium(VI) and uranium(IV) sulphite solids $UO_2SO_3(cr)$, $UO_2SO_4(cr)$, and $U(SO_3)_2(cr)$ have been selected by Grenthe et al. (1992).

However, sulphite complexes and compounds are presently not included in our database.

11.6.1.3 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, 1:2, and 1:3 complexes. Thus, Grenthe et al. (1992) and Guillaumont et al. (2003) evaluated and recommended equilibrium constants for the reactions:

$$UO_2^{2+} + n\,SO_4^{2-} \Leftrightarrow UO_2(SO_4)_n^{(2-2n)}$$

with n = 1, 2, and 3. Grenthe et al. (1992) extrapolated the conditional formation constants for $UO_2^{2+} + SO_4^{2-} \Leftrightarrow UO_2SO_4(aq)$ in $NaClO_4$ and NH_4ClO_4 media to $I = 0$ with $\Delta\varepsilon(n = 1) = -(0.34 \pm 0.07)$ kg·mol^{-1} calculated from the selected $\varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$ kg·mol^{-1} and $\varepsilon(SO_4^{2-}, NH_4^+) \approx \varepsilon(SO_4^{2-}, Na^+) = -(0.12 \pm 0.06)$ kg·mol^{-1} and assuming that the interaction coefficient of $UO_2SO_4(aq)$ is equal to zero. Conditional formation constants for $UO_2^{2+} + HSO_4^- \Leftrightarrow UO_2SO_4(aq) + H^+$ in $HClO_4$ were extrapolated with $\Delta\varepsilon(n = 1) = -(0.31 \pm 0.04)$ kg·mol^{-1}[23], which was calculated from the selected values $\varepsilon(UO_2^{2+}, ClO_4^-)$, $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$ kg·mol^{-1} and $\varepsilon(HSO_4^-, H^+) = -(0.01 \pm 0.02)$ kg·mol^{-1}[24], again assuming that the interaction coefficient of $UO_2SO_4(aq)$ is equal to zero. The latter constants were then expressed in terms of SO_4^{2-} by using $\log_{10}K° = (1.98 \pm 0.05)$ for $SO_4^{2-} + H^+ \Leftrightarrow HSO_4^-$. By taking the average of all accepted constants, Grenthe et al. (1992) obtained the selected

$$UO_2^{2+} + SO_4^{2-} \Leftrightarrow UO_2SO_4(aq)$$

$$\log_{10}\beta_1°(n = 1, 298.15\ K) = (3.15 \pm 0.02)$$

The formation of $UO_2(SO_4)_2^{2-}$ was studied in $NaClO_4$ and NH_4ClO_4 media. Conditional formation constants were extrapolated to $I = 0$ by Grenthe et al. (1992) using $\Delta\varepsilon(n = 2) = -(0.34 \pm 0.14)$ kg·mol^{-1} calculated from the selected $\varepsilon(UO_2^{2+}, ClO_4^-)$ and the estimates $\varepsilon(UO_2(SO_4)_2^{2-}, NH_4^+) \approx \varepsilon(SO_4^{2-}, NH_4^+) \approx \varepsilon(UO_2(SO_4)_2^{2-}, Na^+) \approx \varepsilon(SO_4^{2-}, Na^+) = -(0.12 \pm 0.06)$ kg·mol^{-1}. Grenthe et al. (1992) took the mean of the accepted formation constants, resulting in the selected

$$UO_2^{2+} + 2\,SO_4^{2-} \Leftrightarrow UO_2(SO_4)_2^{2-}$$

$$\log_{10}\beta_2°(n = 2, 298.15\ K) = (4.14 \pm 0.07)$$

These values for $\log_{10}\beta_1°$ and $\log_{10}\beta_2°$ as well as the estimated

$$\varepsilon(UO_2(SO_4)_2^{2-}, Na^+) = -(0.12 \pm 0.06)\ \text{kg·mol}^{-1}$$

are included in our database.

Grenthe et al. (1992) did not accept any data for the formation of $UO_2(SO_4)_3^{4-}$. Guillaumont et al. (2003) accepted data from a later study, which reported stability constants for $UO_2SO_4(aq)$, $UO_2(SO_4)_2^{2-}$, and $UO_2(SO_4)_3^{4-}$. Guillaumont et al. (2003) selected

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[23] Incorrect value of -(0.33 ± 0.04) kg·mol^{-1} given on p. 244 in Grenthe et al. (1992). The correct value is given on p. 558 and 638.

[24] Estimated according to $\varepsilon(HSO_4^-, H^+) \approx \varepsilon(HSO_4^-, Na^+) = -(0.01 \pm 0.02)$ kg·mol^{-1}

$$UO_2^{2+} + 3\ SO_4^{2-} \Leftrightarrow UO_2(SO_4)_3^{4-}$$

$$\log_{10}\beta_3°(n = 3, 298.15\ K) = (3.02 \pm 0.38)$$

but retained $\log_{10}\beta_1°$ and $\log_{10}\beta_2°$ selected by Grenthe et al. (1992). The conditional stability constants for $UO_2(SO_4)_3^{4-}$ were recalculated by the authors of the experimental study to zero ionic strength by using $\varepsilon(UO_2^{2+}, ClO_4^-) = 0.46$ kg·mol^{-1}, $\varepsilon(SO_4^{2-}, Na^+) = -0.12$ kg·mol^{-1} and the estimate $\varepsilon(UO_2(SO_4)_3^{4-}, Na^+) \approx \varepsilon(P_2O_7^{4-}, Na^+) = -0.24$ kg·mol^{-1}. The former two are identical to the selected values by NEA, $\varepsilon(P_2O_7^{4-}, Na^+) = -(0.26 \pm 0.05)$ kg·mol^{-1} selected by NEA is slightly different. Guillaumont et al. (2003) did not select any value for $\varepsilon(UO_2(SO_4)_3^{4-}, Na^+)$. For our database, we chose to include the estimate based on the NEA-value for $\varepsilon(P_2O_7^{4-}, Na^+)$. Thus,

$$\varepsilon(UO_2(SO_4)_3^{4-}, Na^+) \approx \varepsilon(P_2O_7^{4-}, Na^+) = -(0.26 \pm 0.05)\ kg \cdot mol^{-1}$$

The enthalpy changes for the first two of these reactions were obtained calorimetrically by several studies. Grenthe et al. (1992) selected the unweighted average of these data:

$$\Delta_r H_m°(n = 1, 298.15\ K) = (19.5 \pm 1.6)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m°(n = 2, 298.15\ K) = (35.1 \pm 1.0)\ kJ \cdot mol^{-1}$$

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

$$U^{4+} + n\ HSO_4^- \Leftrightarrow U(SO_4)_n^{(4-2n)} + n\ H^+.$$

with n = 1 and n = 2. Grenthe et al. (1992) extrapolated the conditional stability constants for USO_4^{2+} to zero ionic strength using $\Delta\varepsilon(n = 1) = -(0.31 \pm 0.12)$ kg·mol^{-1} calculated from the selected $\varepsilon(U^{4+}, ClO_4^-) = (0.76 \pm 0.06)$ kg·mol^{-1}, $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$ kg·mol^{-1}, $\varepsilon(HSO_4^-, H^+) = -(0.01 \pm 0.02)$ kg·mol^{-1}, and the estimated

$$\varepsilon(USO_4^{2+}, ClO_4^-) \approx \varepsilon(M^{2+}, ClO_4^-) = (0.3 \pm 0.1)\ kg \cdot mol^{-1}$$

For chloride media, we estimated

$$\varepsilon(USO_4^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg \cdot mol^{-1}$$

based on charge correlations (see Appendix A).

The conditional stability constants for $U(SO_4)_2(aq)$ were extrapolated by Grenthe et al. (1992) with $\Delta\varepsilon(n = 2) = -(0.46 \pm 0.08)$ kg·mol^{-1}, following from the selected $\varepsilon(U^{4+}, ClO_4^-)$, $\varepsilon(H^+, ClO_4^-)$, and $\varepsilon(HSO_4^-, H^+)$, and from the assumption that ion interaction coefficients of neutral species are zero.

Grenthe et al. (1992) combined the resulting equilibrium constants with the protonation constant for SO_4^{2-}, $\log_{10}K° = (1.98 \pm 0.05)$ and obtained stability constants for the reactions

$$U^{4+} + n\ SO_4^{2-} \Leftrightarrow U(SO_4)_n^{(4-2n)}$$

with n = 1 and n = 2. The values selected by Grenthe et al. (1992) are

$$U^{4+} + SO_4^{2-} \Leftrightarrow USO_4^{2+}$$

$$\log_{10}\beta_1°(n = 1, 298.15\ K) = (6.58 \pm 0.19)$$

$$U^{4+} + 2\ SO_4^{2-} \Leftrightarrow U(SO_4)_2(aq)$$

$$\log_{10}\beta_2°(n = 2, 298.15\ K) = (10.51 \pm 0.20)$$

The enthalpy changes for these reactions were obtained by Grenthe et al. (1992) from selected equilibrium constants at 10, 25 and 40°C :

$$\Delta_r H_m°(n = 1, 298.15\ K) = (8.0 \pm 2.7)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m°(n = 2, 298.15\ K) = (32.7 \pm 2.8)\ kJ \cdot mol^{-1}$$

No species above U(IV) disulphate have been credited by Grenthe et al. (1992).

Ternary U(VI) hydroxide-sulphate complexes: According to Guillaumont et al. (2003), the formation of ternary U(VI) hydroxide-sulphate complexes was reported by Grenthe & Lagerman (1993), Comarmond & Brown (2000), Moll et al. (2000), and Ciavatta et al. (2003). These authors measured stability constants for reactions of the type

$$m\ UO_2^{2+} + n\ H_2O(l) + r\ SO_4^{2-} \Leftrightarrow (UO_2)_m(OH)_n(SO_4)_r^{2m-n-2r} + n\ H^+$$

but observed different ternary complexes. Grenthe & Lagerman (1993) combined their potentiometric data measured in 0.500 M Na_2SO_4 + 2.00 M $NaClO_4$ with a reinterpretation of the potentiometric data measured by Peterson (1961) in 1.5 M Na_2SO_4 (who did not consider the possible formation of ternary complexes) and came up with stability constants for the ternary complexes with m:n:r equaling 2:2:2, 3:4:3, 3:4:4, and 5:8:6. For their EXAFS, NMR and potentiometric experiments, Moll et al. (2000) used the same background media as Peterson (1961) and Grenthe & Lagerman (1993), but extended the measurements to larger ranges of pH and uranyl concentrations. They reported stability constants for 2:2:2, 3:4:3, 4:7:4, and 5:8:6 complexes. Comarmond & Brown (2000) performed potentiometric experiments in 0.10 and 1.0 M Na_2SO_4 and combined their data with those of Peterson (1961), Grenthe & Lagerman (1993), and Moll et al. (2000) and interpreted the data in terms of 1:0:1, 1:0:2, 2:2:2, 3:4:3, 4:7:4, and 5:8:4 complexes. Ciavatta et al. (2003), finally, used potentiometry in 3.0 M $NaClO_4$ to determine stability constants for 2:1:1, 2:1:2, 2:2:2, 3:4:1, 3:5:1, and 4:6:2 complexes. Guillaumont et al. (2003) noted that the SIT analyses by Grenthe & Lagerman (1993) and Comarmond & Brown (2000) are different, which is reflected by different sulphate stoichiometries for the 5:8:r complexes and different equilibrium constants. They also noted that of all the ternary complexes proposed by Ciavatta et al. (2003) only the 2:2:2 complex is consistent with those of the previous studies. For these reasons, Guillaumont et al. (2003) did not select any stability constants for ternary uranyl hydroxide-sulphate complexes.

For qualitative modeling or scoping calculations, we suggest to use the data by Comarmond & Brown (2000) as supplemental data

$$2\ UO_2^{2+} + 2\ H_2O(l) + 2\ SO_4^{2-} \Leftrightarrow (UO_2)_2(OH)_2(SO_4)_2^{2-} + 2\ H^+$$

$$\log_{10}{}^*\beta_{2,2,2}°(298.15\ K) = -(0.64 \pm 0.01)$$

$$\varepsilon((UO_2)_2(OH)_2(SO_4)_2^{2-}, Na+) = -(0.14 \pm 0.22)\ kg \cdot mol^{-1}$$

$$3\ UO_2^{2+} + 4\ H_2O(l) + 3\ SO_4^{2-} \Leftrightarrow (UO_2)_3(OH)_4(SO_4)_3^{4-} + 4\ H^+$$

$$\log_{10}{}^*\beta_{3,4,3}°(298.15\ K) = -(5.9 \pm 0.2)$$

$$\varepsilon((UO_2)_3(OH)_4(SO_4)_3^{4-}, Na+) = (0.6 \pm 0.6)\ kg \cdot mol^{-1}$$

$$4\ UO_2^{2+} + 7\ H_2O(l) + 4\ SO_4^{2-} \Leftrightarrow (UO_2)_4(OH)_7(SO_4)_4^{7-} + 7\ H^+$$

$$\log_{10}{}^*\beta_{4,7,4}°(298.15\ K) = -(18.9 \pm 0.2)$$

$$\varepsilon((UO_2)_4(OH)_7(SO_4)_4^{7-}, Na+) = (2.8 \pm 0.7)\ kg \cdot mol^{-1}$$

$$5\ UO_2^{2+} + 8\ H_2O(l) + 4\ SO_4^{2-} \Leftrightarrow (UO_2)_5(OH)_8(SO_4)_4^{6-} + 8\ H^+$$

$$\log_{10}{}^*\beta_{5,8,4}°(298.15\ K) = -(18.7 \pm 0.1)$$

$$\varepsilon((UO_2)_5(OH)_8(SO_4)_4^{6-}, Na+) = (1.1 \pm 0.5)\ kg\cdot mol^{-1}$$

Note that due to an oversight, these data were not included in our database.

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 $mol\cdot kg^{-1}$ 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 recognized 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 behavior of the zippeites in aqueous solutions" (Grenthe et al. 1992).

When uranium(IV) sulphate solutions are hydrolyzed, 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 to the reaction

$$U(OH)_2SO_4(cr) \Leftrightarrow U^{4+} + 2\ OH^- + SO_4^{2-}$$

$$\log_{10}K_{s,0}^\circ = -(31.17 \pm 0.50)$$

For inclusion in our database, this equilibrium is expressed in terms of H^+ instead of OH^-. Hence

$$U(OH)_2SO_4(cr) + 2\ H^+ \Leftrightarrow U^{4+} + SO_4^{2-} + 2\ H_2O(l)$$

$$\log_{10}{}^*K_{s,0}^\circ = -(3.17 \pm 0.50)$$

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 modeling and thus, thermochemical data of $U(SO_4)_2\cdot nH_2O$(cr) are not considered further.

11.6.1.4 Uranium thiosulphates

Grenthe et al. (1992) accepted a tentative equilibrium constant for the 1:1 uranium(VI) thiosulphate complex $UO_2S_2O_3$(aq). 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.

11.6.2 Selenium compounds

Based on thermochemical measurements, Grenthe et al. (1992) selected data for α-USe_2(cr), β-USe_2(cr), USe_3(cr), U_2Se_3(cr), U_3Se_4(cr), U_3Se_5(cr). No solubility data are available for these selenide solids and they are therefore not included in our database. For the selenite UO_2SeO_3(cr) and the selenate UO_2SeO_4(cr), Grenthe et al. (1992) selected only standard molar enthalpies of formation, which are also not included in our database

11.6.3 Tellurium compounds

Grenthe et al. (1992) selected a standard entropy value for a uranium telluride solid, UOTe(cr), and Guillaumont et al. (2003) standard enthalpy values for the uranium tellurite schmitterite, UO_2TeO_3(cr) or $UTeO_5$(cr), and for a uranium polytellurite UTe_3O_9(cr). None of these solids is included in our database.

No experimental information is available on tellurium complexes with uranium.

11.7 Group 15 compounds and complexes

11.7.1 Nitrogen compounds and complexes

11.7.1.1 Uranium nitrides

Grenthe et al. (1992) selected thermochemical data for the binary uranium nitride solids UN(cr), β-$UN_{1.466}$(cr), α-$UN_{1.59}$(cr), α-$UN_{1.606}$(cr), α-$UN_{1.674}$(cr), and α-$UN_{1.73}$(cr). However, binary uranium nitrides are not relevant under environmental conditions and are not included in our database.

11.7.1.2 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.

11.7.1.3 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

$$UO_2^{2+} + NO_3^- \Leftrightarrow UO_2NO_3^+$$

$$\log_{10}\beta^\circ(298.15\ K) = (0.30 \pm 0.15)$$

and considered that there is no reliable information on higher U(VI) nitrato complexes. Conditional stability constants were extrapolated to zero ionic strength by Grenthe et al. (1992) using the estimate

$$\varepsilon(UO_2NO_3^+, ClO_4^-) \approx \varepsilon(UO_2Cl^+, ClO_4^-) = (0.33 \pm 0.04)\ kg\cdot mol^{-1}$$

For chloride media, we estimated

$$\varepsilon(UO_2NO_3^+, Cl^-) = (0.05 \pm 0.10)\ kg\cdot mol^{-1}$$

based on charge correlations (see Appendix A).

Aqueous U(IV) nitrates: The uranium(IV) nitrate system was studied by several investigators using spectrophotometry, distribution measurements and potentiometry. Using data from two studies carried out in $H(ClO_4, NO_3)$ Grenthe et al. (1992) evaluated equilibrium constants for the reactions

$$U^{4+} + n\,NO_3^- \Leftrightarrow U(NO_3)_n^{(4-n)}$$

with n =1 and n = 2. Their SIT regression resulted in.

$$U^{4+} + NO_3^- \Leftrightarrow UNO_3^{3+}$$

$$\log_{10}\beta_1°(n = 1, 298.15\text{ K}) = (1.47 \pm 0.13)$$

$$U^{4+} + 2\,NO_3^- \Leftrightarrow U(NO_3)_2^{2+}$$

$$\log_{10}\beta_2°(n = 2, 298.15\text{ K}) = (2.30 \pm 0.35)$$

with $\Delta\varepsilon(n = 1) = -(0.21 \pm 0.05)$ kg·mol^{-1} and $\Delta\varepsilon(n = 2) = -(0.41 \pm 0.13)$. From these values, the selected $\varepsilon(U^{4+}, ClO_4^-) = (0.76 \pm 0.06)$ kg·mol^{-1}, and the estimate $\varepsilon(NO_3^-, H^+) \approx \varepsilon(NO_3^-, Li^+) = (0.08 \pm 0.01)$ kg·mol^{-1} they derived

$$\varepsilon(UNO_3^{3+}, ClO_4^-) = (0.62 \pm 0.08)\text{ kg·mol}^{-1}$$

$$\varepsilon(U(NO_3)_2^{2+}, ClO_4^-) = (0.49 \pm 0.14)\text{ kg·mol}^{-1}$$

For chloride media, we estimated

$$\varepsilon(UNO_3^{3+}, Cl^-) = (0.25 \pm 0.10)\text{ kg·mol}^{-1}$$

$$\varepsilon(U(NO_3)_2^{2+}, Cl^-) = (0.15 \pm 0.10)\text{ kg·mol}^{-1}$$

based on charge correlations (see Appendix A).

Solid uranium nitrates: Thermochemical data have been selected by Grenthe et al. (1992) for a series of U(VI) nitrate solids, $UO_2(NO_3)_2$(cr), $UO_2(NO_3)_2·H_2O$(cr), $UO_2(NO_3)_2·2H_2O$(cr), $UO_2(NO_3)_2·3H_2O$(cr), and $UO_2(NO_3)_2·6H_2O$(cr). The calculated Gibbs energies suggest that all these compounds are highly soluble salts. 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 $UO_2(NO_3)_2·6H_2O$(cr) it states "hygroscopic". Hence, none of these highly soluble salts is included in our database.

11.7.2 Phosphorous compounds and complexes

11.7.2.1 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 $(UO_2)_3(PO_4)_2·4H_2O$(cr) was measured in the range $6 < pH < 9$.

Complex formation in the U(VI)-H_3PO_4 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:

$$UO_2^{2+} + H_3PO_4(aq) \Leftrightarrow UO_2H_2PO_4^+ + H^+$$

$$\log_{10}\beta°(298.15 \text{ K}) = (1.12 \pm 0.06)$$

$$UO_2^{2+} + H_3PO_4(aq) \Leftrightarrow UO_2H_3PO_4^{2+}$$

$$\log_{10}\beta°(298.15 \text{ K}) = (0.76 \pm 0.15)$$

$$UO_2^{2+} + 2\ H_3PO_4(aq) \Leftrightarrow UO_2(H_2PO_4)_2(aq) + 2\ H^+$$

$$\log_{10}\beta°(298.15 \text{ K}) = (0.64 \pm 0.11)$$

$$UO_2^{2+} + 2\ H_3PO_4(aq) \Leftrightarrow UO_2(H_2PO_4)(H_3PO_4)^+ + H^+$$

$$\log_{10}\beta°(298.15 \text{ K}) = (1.65 \pm 0.11)$$

Grenthe et al. (1992) did not explain how they extrapolated the conditional stability constants of these complexes to $I = 0$ and did not select any ion interaction coefficients. Therefore, we estimated the missing coefficients based on charge correlations (see Appendix A):

$$\varepsilon(UO_2H_2PO_4^+, Cl^-) = (0.05 \pm 0.10) \text{ kg·mol}^{-1}$$

$$\varepsilon(UO_2H_2PO_4^+, ClO_4^-) = (0.2 \pm 0.1) \text{ kg·mol}^{-1}$$

$$\varepsilon(UO_2H_3PO_4^{2+}, Cl^-) = (0.15 \pm 0.10) \text{ kg·mol}^{-1}$$

$$\varepsilon(UO_2H_3PO_4^{2+}, ClO_4^-) = (0.4 \pm 0.1) \text{ kg·mol}^{-1}$$

$$\varepsilon(UO_2H_2PO_4H_3PO_4^+, Cl^-) = (0.05 \pm 0.10) \text{ kg·mol}^{-1}$$

$$\varepsilon(UO_2H_2PO_4H_3PO_4^+, ClO_4^-) = (0.2 \pm 0.1) \text{ kg·mol}^{-1}$$

In neutral to basic solutions, a solubility study of $(UO_2)_3(PO_4)_2\cdot4H_2O(cr)$ 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 11.4.1.1. Grenthe et al. (1992) accepted Sandino's formation constants for $UO_2PO_4^-$ and $UO_2HPO_4(aq)$, according to the reactions

$$UO_2^{2+} + PO_4^{3-} \Leftrightarrow UO_2PO_4^-$$

$$\log_{10}\beta_1°(298.15 \text{ K}) = (13.23 \pm 0.15)$$

$$UO_2^{2+} + HPO_4^{2-} \Leftrightarrow UO_2HPO_4(aq)$$

$$\log_{10}\beta_1°(298.15 \text{ K}) = (7.24 \pm 0.26)$$

but increased the uncertainties from two to three standard deviations. Sandino (1991) used the estimate

$$\varepsilon(UO_2PO_4^-, Na^+) \approx \varepsilon(UO_2(OH)_3^-, Na^+) = -(0.09 \pm 0.05) \text{ kg·mol}^{-1}$$

for recalculating the conditional stability constant to $I = 0$. This value is included in our database, although Grenthe et al. (1992) apparently did not select it.

In view of the importance of the phosphate system for the modeling 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. Only a few additional data were reviewed by Guillaumont et al. (2003) which did not change the selections made by Grenthe et al. (1992).

Solubility equilibria in the U(VI)-H_3PO_4 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:

$$UO_2HPO_4 \cdot 4H_2O(cr) + 2\,H^+ \Leftrightarrow UO_2^{2+} + H_3PO_4(aq) + 4\,H_2O(l)$$

$$\log_{10}{}^*K_{s,0}^\circ(298.15\text{ K}) = -(2.50 \pm 0.09)$$

$$(UO_2)_3(PO_4)_2 \cdot 4H_2O(cr) + 6\,H^+ \Leftrightarrow 3\,UO_2^{2+} + 2\,H_3PO_4(aq) + 4\,H_2O(l)$$

$$\log_{10}{}^*K_{s,0}^\circ(298.15\text{ K}) = -(5.96 \pm 0.30)$$

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: $H_2(UO_2)_2(PO_4)_2 \cdot xH_2O(cr)$ (x = 0, 2, 4, 8, 10). Hence, the solubility of $UO_2HPO_4 \cdot 4H_2O(cr)$ may represent that 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:

$$U(HPO_4)_2 \cdot 4H_2O(cr) + 4\,H^+ \Leftrightarrow U^{4+} + 2\,H_3PO_4(aq) + 4\,H_2O(l)$$

$$\log_{10}{}^*K_{s,0}^\circ(298.15\text{ K}) = -(11.79 \pm 0.15)$$

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 and Guillaumont et al. (2003) did not discuss new quantitative data. 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.

11.7.2.2 Solid uranium phosphorous compounds

Uranium phosphides: Thermochemical data have been selected by Grenthe et al. (1992) for the binary uranium phosphide solids UP(cr), UP_2(cr), and U_3P_4(cr). 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 Section 11.7.2.1). 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 a value for $\Delta_f G_m°$ of the hexahydrate, which is erroneous and was corrected by Guillaumont et al. (2003). 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 the uranium pyrophosphate solids UPO_5(cr) or 1/2 $U_2O_3P_2O_7$(cr), UP_2O_7(cr), and $(UO_2)_2P_2O_7$(cr). 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 Section 11.7.2.1). In summary, none of these compounds is included in our database.

Other uranium phosphorous compounds: The only other 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 11.7.2.1.

11.7.3 Arsenic compounds and complexes

Thermochemical data for the uranium arsenide solids UAs(cr), UAs_2(cr), U_3As_4(cr), UAsS(cr), UAsSe(cr), and UAsTe(cr), for the arsenate solids $UO_2(AsO_3)_2$(cr), $(UO_2)_2As_2O_7$(cr), and $(UO_2)_3(AsO_4)_2$(cr), and for $UAsO_5$(cr) 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.

Guillaumont et al. (2003) selected formation constants for the complexation of U(VI) with $HAsO_4^{2-}$ and H_3AsO_4(aq), based on a fluorescence spectroscopical study that identified the species UO_2HAsO_4(aq), $UO_2H_2AsO_4^+$, and $UO_2(H_2AsO_4)_2$(aq) in 0.1 M $NaClO_4$:

$$UO_2^{2+} + HAsO_4^{2-} \Leftrightarrow UO_2HAsO_4(aq)$$

$$\log_{10}K°(298.15 \text{ K}) = (7.16 \pm 0.37)$$

$$UO_2^{2+} + H_3AsO_4(aq) \Leftrightarrow UO_2H_2AsO_4^+ + H^+$$

$$\log_{10}{}^*K°(298.15 \text{ K}) = (1.34 \pm 0.42)$$

$$UO_2^{2+} + 2\ H_3AsO_4(aq) \Leftrightarrow UO_2(H_2AsO_4)_2(aq) + 2\ H^+$$

$$\log_{10}K°(298.15\ \mathrm{K}) = (0.29 \pm 0.53)$$

These values were calculated from those of the conditional stability constants using the Davies equation. Guillaumont et al. (2003) made no attempt to recalculate them, remarking that they are not significantly different when the SIT model is used. In the absence of ion interaction coefficients, we used the method based on charge correlations (see Appendix A) to estimate

$$\varepsilon(\mathrm{UO_2H_2AsO_4^+, Cl^-}) = (0.05 \pm 0.10)\ \mathrm{kg \cdot mol^{-1}}$$

$$\varepsilon(\mathrm{UO_2H_2AsO_4^+, ClO_4^-}) = (0.2 \pm 0.1)\ \mathrm{kg \cdot mol^{-1}}$$

11.7.4 Antimony compounds

Thermochemical data for the binary uranium antimonide solids USb(cr), USb_2(cr), U_4Sb_3(cr), and U_3Sb_4(cr) 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.

11.8 Group 14 compounds and complexes

11.8.1 Carbon compounds and complexes

11.8.1.1 Uranium carbides

Thermochemical data for the binary uranium carbide solids UC(cr), α-$UC_{1.94}$(cr), and U_2C_3(cr) have been selected by Grenthe et al. (1992). However, carbides are not relevant under environmental conditions and are not included in our database.

11.8.1.2 Uranium carbonates

Grenthe et al. (1995) rejected the ion interaction coefficients of CO_3^{2-} and HCO_3^- with Na^+ selected by Grenthe et al. (1992) and instead selected the values

$$\varepsilon(\mathrm{CO_3^{2-}, Na^+}) = -(0.08 \pm 0.03)\ \mathrm{kg \cdot mol^{-1}}$$

$$\varepsilon(\mathrm{HCO_3^-, Na^+}) = (0.00 \pm 0.02)\ \mathrm{kg \cdot mol^{-1}}$$

determined by Ciavatta (1980). Due to this change, Grenthe et al. (1995) reevaluated the data selected by Grenthe et al. (1992) for uranium carbonate/bicarbonate complexes and uranium carbonate solids leading to modifications of the following ion interaction coefficients: $\varepsilon(\mathrm{U(CO_3)_5^{6-}, Na^+})$, $\varepsilon(\mathrm{UO_2(CO_3)_3^{5-}, Na^+})$, $\varepsilon(\mathrm{UO_2(CO_3)_2^{2-}, Na^+})$, $\varepsilon(\mathrm{UO_2(CO_3)_3^{4-}, Na^+})$, and $\varepsilon(\mathrm{(UO_2)_3(CO_3)_6^{6-}, Na^+})$. In addition, the stability constants of UO_2CO_3(aq), UO_2CO_3(cr), $U(CO_3)_5^{6-}$, $(UO_2)_2(PuO_2)(CO_3)_6^{6-}$, and $(UO_2)_2(NpO_2)(CO_3)_6^{6-}$ also needed a revision.

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 $(UO_2)_3(CO_3)_6^{6-}$.

Grenthe et al. (1992) derived stability constants for

$$\mathrm{UO_2^{2+} + n\,CO_3^{2-} \Leftrightarrow UO_2(CO_3)_n^{(2-2n)}}$$

with n = 1 to 3 from the available experimental data (mainly in 0.03 M to 3 M $NaClO_4$) by using SIT. Note a somewhat enigmatic inconsistency in the argumentation of Grenthe et al. (1992) regarding their procedures to evaluate $\log_{10}\beta°$ 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 $\Delta\varepsilon$ calculated from the selected values for $\varepsilon(UO_2^{2+}, ClO_4^-)$ and $\varepsilon(CO_3^{2-}, Na^+)$) 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 $\log_{10}\beta°$. 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 to be zero. The above described procedure disguises this inconsistency.

From the experimental data for $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$, Grenthe et al. (1992) derived $\Delta\varepsilon(n = 2) = -(0.32 \pm 0.06)$ kg·mol^{-1} and $\Delta\varepsilon(n = 3) = -(0.23 \pm 0.05)$ kg·mol^{-1}, respectively. From these values for $\Delta\varepsilon$ and the selected $\varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$ kg·mol^{-1} and $\varepsilon(CO_3^{2-}, Na^+) = -(0.08 \pm 0.03)$ kg·mol^{-1} (as revised by Grenthe et al. 1995) then follow $\varepsilon(UO_2(CO_3)_2^{2-}, Na^+) = -(0.02 \pm 0.09)$ kg·mol^{-1} and $\varepsilon(UO_2(CO_3)_3^{4-}, Na^+) = -(0.01 \pm 0.11)$ kg·mol^{-1}.

Guillaumont et al. (2003) considered additional experimental data (in 0.1 M $NaClO_4$) and Appraising the available experimental data evaluated the following values using linear SIT regressions for all three complexes

$$UO_2^{2+} + CO_3^{2-} \Leftrightarrow UO_2CO_3(aq)$$

$$\log_{10}\beta_1°(n = 1, 298.15\text{ K}) = (9.94 \pm 0.03)$$

$$UO_2^{2+} + 2\,CO_3^{2-} \Leftrightarrow UO_2(CO_3)_2^{2-}$$

$$\log_{10}\beta_2°(n = 2, 298.15\text{ K}) = (16.61 \pm 0.09)$$

$$UO_2^{2+} + 3\,CO_3^{2-} \Leftrightarrow UO_2(CO_3)_3^{4-}$$

$$\log_{10}\beta_3°(n = 3, 298.15\text{ K}) = (21.84 \pm 0.04)$$

with $\Delta\varepsilon(n = 1) = -(0.232 \pm 0.027)$ kg·mol^{-1}, $\Delta\varepsilon(n = 2) = -(0.454 \pm 0.052)$ kg·mol^{-1}, and $\Delta\varepsilon(n = 3) = -(0.233 \pm 0.046)$ kg·mol^{-1}. They recommended their new values for $\log_{10}\beta_1°$, $\log_{10}\beta_2°$, and $\log_{10}\beta_3°$ (they are also included in our database) but decided to retain the values for $\varepsilon(UO_2(CO_3)_2^{2-}, Na^+)$ and $\varepsilon(UO_2(CO_3)_3^{4-}, Na^+)$ as revised by Grenthe et al. (1995). They explained this somewhat cryptically:

"The addition of new experimental data at *I* = 0.1 M results in a change in most of the values given in [92GRE/FUG]. As judged by the estimated uncertainty in the average values these deviations are significant; however, considering the largest uncertainty in the individual experimental determinations, the difference in the two averages is acceptable. It is clear that the uncertainty estimates must be looked upon with caution as discussed in the introduction in Appendix C. The uncertainty reported is a measure of the precision of an experiment, not its accuracy. The values of $\Delta\Sigma$ for the various reactions are in fair agreement with the tabulated values for the individual reactants/products as seen above[25]. In view of the uncertainty in these parameters this review has not considered a revision of the individual ε values."

Is it possible that Guillaumont et al. (2003) shied away from using $\Delta\varepsilon(n = 2)$ and $\Delta\varepsilon(n = 3)$ for revising the values for $\varepsilon(UO_2(CO_3)_2^{2-}, Na^+)$ and $\varepsilon(UO_2(CO_3)_3^{4-}, Na^+)$ because they wanted to avoid a discussion of $\Delta\varepsilon(n = 1)$, which points to a non-zero interaction coefficient of the neutral

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[25] From $\varepsilon(UO_2^{2+}, ClO_4^-)$ and the values for $\varepsilon(CO_3^{2-}, Na^+)$, $\varepsilon(UO_2(CO_3)_2^{2-}, Na^+)$ and $\varepsilon(UO_2(CO_3)_3^{4-}, Na^+)$ revised by Grenthe et al. (1995), Guillaumont et al. (2003) calculated $\Delta\varepsilon(n = 1) = -(0.38 \pm 0.06)$ kg·mol^{-1}, $\Delta\varepsilon(n = 2) = -(0.32 \pm 0.15)$ kg·mol^{-1}, and $\Delta\varepsilon(n = 3) = -(0.24 \pm 0.18)$ kg·mol^{-1}.

species $UO_2CO_3(aq)$? In fact, one obtains from $\Delta\varepsilon(n = 1)$ and the values for $\varepsilon(UO_2^{2+}, ClO_4^-)$ and $\varepsilon(CO_3^{2-}, Na^+)$ discussed above

$$\varepsilon(UO_2CO_3(aq), Na^+ + ClO_4^-) = (0.15 \pm 0.06)\ kg\cdot mol^{-1}$$

As in the case of $\varepsilon(UO_2F_2(aq), Na^+ + ClO_4^-) = (0.13 \pm 0.05)\ kg\cdot mol^{-1}$, we decided to include this interaction coefficient in our database, since it is too large to be assumed to be equal to zero and since ion interaction coefficients for neutral species have also been selected in the NEA-reviews by Gamsjäger et al. (2005) and Hummel et al. (2005). From $\Delta\varepsilon(n = 2)$ similarly follows

$$\varepsilon(UO_2(CO_3)_2^{2-}, Na^+) = -(0.15 \pm 0.08)\ kg\cdot mol^{-1}$$

which is included in our database, and from $\Delta\varepsilon(n = 3)$

$$\varepsilon(UO_2(CO_3)_3^{4-}, Na^+) = -(0.01 \pm 0.11)\ kg\cdot mol^{-1}$$

which is identical to the value revised by Grenthe et al. (1995) and is also included in our database.

Enthalpy of reaction data were selected by Grenthe et al. (1992) as follows:

$$\Delta_r H_m°(n = 1, 298.15\ K) = (5 \pm 2)\ kJ\cdot mol^{-1}$$

$$\Delta_r H_m°(n = 2, 298.15\ K) = (18.5 \pm 4.0)\ kJ\cdot mol^{-1}$$

$$\Delta_r H_m°(n = 3, 298.15\ K) = -(39.2 \pm 4.1)\ kJ\cdot mol^{-1}$$

As reported by Grenthe et al. (1992), the trinuclear complex is characterized by the following well established constants which were retained by Guillaumont et al. (2003):

$$3\ UO_2^{2+} + 6\ CO_3^{2-} \Leftrightarrow (UO_2)_3(CO_3)_6^{6-}$$

$$\log_{10}\beta_{6,3}°(298.15\ K) = (54.0 \pm 1.0)$$

$$\Delta_r H_m°(298.15\ K) = -(62.7 \pm 2.4)\ kJ\cdot mol^{-1}$$

The value of $(0.55 \pm 0.11)\ kg\cdot mol^{-1}$ for $\varepsilon((UO_2)_3(CO_3)_6^{6-}, Na^+)$ determined by Grenthe et al. (1992) from $\Delta\varepsilon$ was modified by Grenthe et al. (1995) to account for the revised $\varepsilon(CO_3^{2-}, Na^+) = -(0.08 \pm 0.03)\ kg\cdot mol^{-1}$ leading to

$$\varepsilon((UO_2)_3(CO_3)_6^{6-}, Na^+) = (0.37 \pm 0.11)\ kg\cdot mol^{-1}$$

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) concluded 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

$$\log_{10}{}^*K\ (298.15\ K) = -(72.5 \pm 2.0)$$

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) proposed the following constant, corrected to $I = 0$:

$$\log_{10}{}^*K°(298.15\ K) = -(17.5 \pm 0.5)$$

For the extrapolation from 3 M $NaClO_4$ to $I = 0$, Grenthe et al. (1992) used the estimate $\varepsilon((UO_2)_3O(OH)_2HCO_3^+, ClO_4^-) = (0.0 \pm 0.1)$ kg·mol^{-1} but did not explain what this estimate is based on. It does not appear in their list of ion interaction coefficients. For chloride media, we estimated

$$\varepsilon((UO_2)_3O(OH)_2HCO_3^+, Cl^-) = (0.05 \pm 0.10)\ kg \cdot mol^{-1}$$

based on charge correlations (see Appendix A). Both estimates are included in our database.

Using the carbonate equilibrium constants[26] selected in our database, (see Hummel et al. 2002, Chapter 4, Core Data) relating $CO_2(g)$ with CO_3^{2-} we converted the above value for inclusion in our database to

$$3\ UO_2^{2+} + CO_3^{2-} + 3\ H_2O(l) \Leftrightarrow (UO_2)_3O(OH)_2(HCO_3)^+ + 3\ H^+$$

$$\log_{10}{}^*K°(298.15\ K) = (0.66 \pm 0.50)$$

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

$$\log_{10}{}^*K°(298.15\ K) = -(19.01 \pm 0.50)$$

which they extrapolated to $I = 0$ from the experimental value for 0.5 m $NaClO_4$ using the estimate

$$\varepsilon((UO_2)_2CO_3(OH)_3^-, Na^+) = (0.00 \pm 0.05)\ kg \cdot mol^{-1}$$

for which they gave no explanations. As above, we expressed the stability constant in terms of CO_3^{2-} instead of $CO_2(g)$ and included

$$2\ UO_2^{2+} + CO_3^{2-} + 3\ H_2O(l) \Leftrightarrow (UO_2)_2CO_3(OH)_3^- + 3\ H^+$$

$$\log_{10}{}^*K°(298.15\ K) = -(0.86 \pm 0.50)$$

in our database, together with the estimated ion interaction coefficient.

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.

Ternary U(VI) fluoride carbonate complexes: In a single experimental study, the formation of ternary fluoride carbonate complexes was investigated in 1.00 M $NaClO_4$ at 298.15 K according to

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[26] $\log_{10}{}^*K°(HCO_3^- + H^+ \Leftrightarrow CO_2(g) + H_2O(l), 298.15\ K) = 7.82$
$\log_{10}{}^*K°(CO_3^{2-} + H^+ \Leftrightarrow HCO_3^-, 298.15\ K) = 10.329$

$$UO_2^{2+} + p\,CO_3^{2-} + q\,F^- \Leftrightarrow UO_2(CO_3)_pF_q^{(2-2p-q)}$$

Guillaumont et al. (2003) recalculated the conditional formation constants to $I = 0$ with SIT and obtained the following selected values which are also included in our database

$$UO_2^{2+} + CO_3^{2-} + F^- \Leftrightarrow UO_2CO_3F^-$$

$$\log_{10}\beta^\circ_{1,1,1}(p = 1, q = 1, 298.15\text{ K}) = (13.75 \pm 0.09)$$

$$UO_2^{2+} + CO_3^{2-} + 2\,F^- \Leftrightarrow UO_2CO_3F_2^{2-}$$

$$\log_{10}\beta^\circ_{1,1,2}(p = 1, q = 2, 298.15\text{ K}) = (15.57 \pm 0.14)$$

$$UO_2^{2+} + CO_3^{2-} + 3\,F^- \Leftrightarrow UO_2CO_3F_3^{3-}$$

$$\log_{10}\beta^\circ_{1,1,3}(p = 1, q = 3, 298.15\text{ K}) = (16.38 \pm 0.11)$$

For the extrapolation of the experimental data to $I = 0$, Guillaumont et al. (2003) calculated the corresponding values for $\Delta\varepsilon$ from the selected $\varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$ kg·mol^{-1}, $\varepsilon(CO_3^{2-}, Na^+) = -(0.08 \pm 0.03)$ kg·mol^{-1}, $\varepsilon(F^-, Na^+) = (0.02 \pm 0.02)$ kg·mol^{-1}, and the estimated

$$\varepsilon(UO_2CO_3F^-, Na^+) = (0.00 \pm 0.05)\text{ kg·mol}^{-1}$$

$$\varepsilon(UO_2CO_3F_2^{2-}, Na^+) = -(0.02 \pm 0.09)\text{ kg·mol}^{-1}$$

$$\varepsilon(UO_2CO_3F_3^{3-}, Na^+) = -(0.25 \pm 0.05)\text{ kg·mol}^{-1}$$

Guillaumont et al. (2003) did not explain how these estimates were found and neither do they appear in the list of selected ion interaction coefficients. Nonetheless, they are included in our database.

Ternary alkaline earth U(VI) carbonate complexes: Alkaline earth cations may form ternary complexes with uranyl and carbonate according to the reaction

$$p\,Ca^{2+} + UO_2^{2+} + 3\,CO_3^{2-} \Leftrightarrow Ca_pUO_2(CO)_3(aq)$$

for p = 1 and 2 with formation constants $\log_{10}\beta^\circ_{p,1,3}$.

The formation of such ternary complexes was first described by Bernhard et al. (1996) in a study concerning the speciation of U(VI) in seepage waters from uranium mine and mill tailing piles in Saxony and Thuringia. The seepage waters are characterized by relatively high concentrations of carbonate, sulfate, calcium and magnesium with a uranium content of 2.6 mg/l. TRFLS investigations of original and synthetic seepage waters revealed the existence of the ternary calcium U(VI) carbonate complex $Ca_2UO_2(CO_3)_3(aq)$. From their spectroscopic data at $I = 0.1$ M and 25°C , Bernhard et al. (1996) derived $\log_{10}K(298.15\text{ K}, I = 0.1\text{ M}) = (5.0 \pm 0.7)$ for the reaction $2\,Ca^{2+} + UO_2(CO_3)_3^{4-} \Leftrightarrow Ca_2UO_2(CO_3)_3(aq)$. With $\log_{10}\beta_3(298.15\text{ K}, I = 0.1\text{ M}) = (21.8 \pm 1)$ for $UO_2(CO_3)_3^{4-}$ this corresponds to $\log_{10}\beta_{2,1,3}(298.15\text{ K } I = 0.1\text{ M}) = (26.8 \pm 0.7)$ for the reaction $2\,Ca^{2+} + UO_2^{2+} + 3\,CO_3^{2-} \Leftrightarrow Ca_2UO_2(CO_3)_3(aq)$.

In a follow-up study, Bernhard et al. (2001) validated the stoichiometry of $Ca_2UO_2(CO_3)_3(aq)$ and determined its formation constant by means of two independent analytical approaches with TRLFS. In a first experiment, a non-fluorescent uranyl tricarbonate complex solution was titrated with Ca^{2+} and the formation of fluorescent $Ca_2UO_2(CO_3)_3(aq)$ was detected with TRLFS. In the second experiment, the concentration of Ca^{2+} available for the formation of $Ca_2UO_2(CO_3)_3(aq)$ was reduced by competitive calcium complexation with EDTA^{4-}. The concentration ratios R of uranium with and without complexed calcium were determined from the measured fluorescence intensities.

Table 11.1: Stability constants for ternary alkaline earth U(VI) carbonate complexes.

$Mg^{2+} + UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow MgUO_2(CO_3)_3^{2-}$

Medium	T(°C)	$\log_{10}\beta_{1,1,3}$	$\log_{10}\beta^\circ_{1,1,3}$	Reference
0.1 M $NaNO_3$	25		(26.11 ± 0.04)[a]	Dong & Brooks (2006)
0.101 - 0.509 m $NaNO_3$	25		(25.8 ± 0.5)[a]	Dong & Brooks (2008)
0.101 - 0.509 m $NaNO_3$	25		(25.02 ± 0.08)[b]	Dong & Brooks (2008)
0.1 M $(Na,H)ClO_4$	room temperature		(26.24 ± 0.13)[a]	Geipel et al. (2008)

$Ca^{2+} + UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow CaUO_2(CO_3)_3^{2-}$

Medium	T(°C)	$\log_{10}\beta_{1,1,3}$	$\log_{10}\beta^\circ_{1,1,3}$	Reference
0.1 M $(Na,H)ClO_4$	room temperature		(25.4 ± 0.25)[a]	Bernhard et al. (2001)
0.1 M $NaNO_3$	25		(27.18 ± 0.06)[a]	Dong & Brooks (2006)
0.1 M $(Na,H)ClO_4$	room temperature		(27.27 ± 0.14)[b]	Lee & Yun (2013)

$2\ Ca^{2+} + UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow Ca_2UO_2(CO_3)_3(aq)$

Medium	T(°C)	$\log_{10}\beta_{2,1,3}$	$\log_{10}\beta^\circ_{2,1,3}$	Reference
0.1 M $(Na,H)ClO_4$	room temperature	26.8 ± 0.7	-	Bernhard et al. (1996)
0.1 - 3.0 m $NaClO_4$	25.0 ± 0.5		(29.8 ± 0.7)[b]	Kalmykow & Choppin (2000)
0.1 M $(Na,H)ClO_4$	room temperature		(30.55 ± 0.25)[a]	Bernhard et al. (2001)
0.1 M $NaNO_3$	25		(30.7 ± 0.05)[a]	Dong & Brooks (2006)
0.1 M $(Na,H)ClO_4$	room temperature		(29.81 ± 0.19)[b]	Lee & Yun (2013)

$Sr^{2+} + UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow SrUO_2(CO_3)_3^{2-}$

Medium	T(°C)	$\log_{10}\beta_{1,1,3}$	$\log_{10}\beta^\circ_{1,1,3}$	Reference
0.1 M $NaNO_3$	25		(26.86 ± 0.04)[a]	Dong & Brooks (2006)
0.1 M $(Na,H)ClO_4$	room temperature		(26.07 ± 0.13)[a]	Geipel et al. (2008)

$2\ Sr^{2+} + UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow Sr_2UO_2(CO_3)_3(aq)$

Medium	T(°C)	$\log_{10}\beta_{2,1,3}$	$\log_{10}\beta^\circ_{2,1,3}$	Reference
0.1 M $(Na,H)ClO_4$	room temperature		(29.73 ± 0.47)[a]	Geipel et al. (2008)

$Ba^{2+} + UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow BaUO_2(CO_3)_3^{2-}$

Medium	T(°C)	$\log_{10}\beta_{1,1,3}$	$\log_{10}\beta^\circ_{1,1,3}$	Reference
0.1 M $NaNO_3$	25		(26.68 ± 0.04)[a]	Dong & Brooks (2006)
0.1 M $(Na,H)ClO_4$	room temperature		(26.16 ± 0.32)[a]	Geipel et al. (2008)

$2\ Ba^{2+} + UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow Ba_2UO_2(CO_3)_3(aq)$

Medium	T(°C)	$\log_{10}\beta_{2,1,3}$	$\log_{10}\beta^\circ_{2,1,3}$	Reference
0.1 M $NaNO_3$	25		(29.75 ± 0.07)[a]	Dong & Brooks (2006)
0.1 M $(Na,H)ClO_4$	room temperature		(29.76 ± 0.75)[a]	Geipel et al. (2008)

[a] Extrapolated to $I = 0$ using the Davies equation

[b] Extrapolated to $I = 0$ using SIT

Data of $\log_{10}R$ plotted as a function of $\log_{10}[Ca^{2+}]$ were fitted by a linear equation, where the slope provided the number of Ca^{2+} ions in the calcium uranyl carbonate complex. The formation constants obtained at $I = 0.1$ M were extrapolated to infinite dilution using the Davies equation, resulting in $\log_{10}\beta^{\circ}_{2,1,3}$(298.15 K) = (30.45 ± 0.35) for the first and in $\log_{10}\beta^{\circ}_{2,1,3}$(298.15 K) = (30.77 ± 0.25) for the second method. The average of both values is $\log_{10}\beta^{\circ}_{2,1,3}$(298.15 K) = (30.55 ± 0.25). Bernhard et al. (2001) also reported that at low calcium concentrations there is good evidence for the formation of the $CaUO_2(CO_3)_3^{2-}$ complex, with $\log_{10}\beta^{\circ}_{1,1,3}$(298.15 K) = (25.4 ± 0.25). Guillaumont et al. (2003) remarked that these constants are not precise since the slope analyses by Bernhard et al. (2001) resulted in non-integral values, indicating large experimental errors or insufficient resolution of the fluorescence spectra into different components. In addition, Guillaumont et al. (2003) noted that with these values for $\log_{10}\beta^{\circ}_{1,1,3}$(298.15 K) and $\log_{10}\beta^{\circ}_{2,1,3}$(298.15 K), the binding constant of Ca^{2+} to $CaUO_2(CO_3)_3^{2-}$ is much larger than that of Ca^{2+} to $UO_2(CO_3)_3^{4-}$, which is not very likely.

Kalmykow & Choppin (2000) used fluorescence spectroscopy to study the formation of the ternary calcium uranyl carbonate complexes. Fluorescence titrations with Ca^{2+} were carried out in 0.1, 0.3, 0.7, 1.0, and 3.0 m $NaClO_4$ solutions at pH 8. SIT was used to extrapolate the conditional stability constants of $Ca_2UO_2(CO_3)_3$(aq) to $I = 0$, and these authors obtained $\log_{10}\beta^{\circ}_{2,1,3}$(298.15 K) = (29.8 ± 0.7)[27] stating that this value must be used with caution due to the relatively small number of data. Guillaumont et al. (2003) noticed that the equilibrium constant for $2\ Ca^{2+} + UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow Ca_2UO_2(CO)_3(aq)$ is nearly independent of I in the range 0.1 to 1 M and that $\Delta\varepsilon$ for this reaction has a large positive value of 2.67 $kg{\cdot}mol^{-1}$ as estimated from Fig. 3 in Kalmykow & Choppin (2000), resulting in $\varepsilon(Ca_2UO_2(CO)_3(aq), NaCl) \approx 3.3\ kg{\cdot}mol^{-1}$, which is very high for an uncharged complex. Guillaumont et al. (2003) proposed an alternative interpretation of the experimental data by suggesting that the strong interaction between Ca^{2+} and $UO_2(CO_3)_3^{4-}$ might be accompanied by a similar but weaker interaction between Na^+ and $UO_2(CO_3)_3^{4-}$ and that the actual reaction studied by Kalmykow & Choppin (2000) is

$$Na_4UO_2(CO)_3(aq) + 2\ Ca^{2+} \Leftrightarrow Ca_2UO_2(CO)_3(aq) + 4\ Na^+$$

A reanalysis of the experimental data in terms of this reaction resulted in a SIT plot that is approximately linear over the experimental range of I. The value of $\Delta\varepsilon$ for this reaction indicates that the difference between the ε values for the uncharged complexes is at most 0.06 $kg{\cdot}mol^{-1}$ which is reasonable.

Dong & Brooks (2006) measured the formation constants of ternary complexes of the alkaline earth elements Mg, Ca, Sr and Ba with uranyl and carbonate using an anion exchange method. Metal concentrations at pH 8.1 and under atmospheric CO_2 were varied from 0.1 to 5 mmol/l. Ionic strength was kept constant at 0.1 M $NaNO_3$ and the total concentration of U(VI) at 50 µmol/l. The conditional stability constants were extrapolated to $I = 0$ using the Davies equation. Dong & Brooks (2006) obtained $\log_{10}\beta^{\circ}_{1,1,3}$(298.15 K) = (26.11 ± 0.04), (27.18 ± 0.06), (26.86 ± 0.04) and (26.68 ± 0.04) for Mg, Ca, Sr, and Ba, respectively. For Ca and Ba they also obtained $\log_{10}\beta^{\circ}_{2,1,3}$(298.15 K) = (30.7 ± 0.05) and (29.75 ± 0.07), respectively. They noted that in the case of Mg, the experimental results were equivocal with respect to the formation of $Mg_2UO_2(CO)_3$(aq) in addition to $MgUO_2(CO)_3^{2-}$.

In order to resolve this uncertainty, Dong & Brooks (2008) carried out additional experiments with higher Mg concentrations, which varied from 5 to 20 mmol/l at constant ionic strength (I = 0.101, 0.202, 0.304, 0.406, and 0.509 mol/kg $NaNO_3$), pH = 8.1, atmospheric CO_2 and a total concentration of U(VI) of 10.4 µmol/l. Even with these higher concentrations of Mg there was

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[27] Value given by Kalmykow & Choppin (2000) in the abstract. In the text the uncertainty is given as ± 0.6.

no evidence for the formation of $Mg_2UO_2(CO)_3(aq)$. For $MgUO_2(CO)_3^{2-}$, Dong & Brooks (2008) obtained $\log_{10}\beta°_{1,1,3}(298.15\ K) = (25.8 \pm 0.5)$ if the Davies equation was used, and $\log_{10}\beta°_{1,1,3}(298.15\ K) = (25.02 \pm 0.06)$ if SIT was used.

Geipel et al. (2008) studied the formation of ternary complexes of Mg, Sr, and Ba with uranyl and carbonate with TRLFS using a similar procedure as Bernhard et al. (2001). As in the studies by Dong & Brooks (2006) and (2008), there was no evidence for the formation of $Mg_2UO_2(CO)_3(aq)$. The experiments were performed in 0.1 M $(Na,H)ClO_4$ and the stability constants were extrapolated to zero ionic strength using the Davies equation resulting in $\log_{10}\beta°_{1,1,3}(298.15\ K) = (26.24 \pm 0.13)$, (26.07 ± 0.13), and (26.16 ± 0.32) for Mg, Sr, and Ba, resp., and in $\log_{10}\beta°_{2,1,3}(298.15\ K) = (29.73 \pm 0.47)$ and (29.76 ± 0.75) for Sr and Ba, respectively.

Lee & Yun (2013) determined the stability constants of $CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3(aq)$ in neutral to weakly alkaline solutions at constant ionic strength maintained by 0.1 M $(Na, H)ClO_4$ using TRLFS and EDTA complexation. Using SIT for the extrapolation of the formation constants to $I = 0$, Lee & Yun (2013) obtained $\log_{10}\beta°_{1,1,3}(298.15\ K) = (27.27 \pm 0.14)$ and $\log_{10}\beta°_{2,1,3}(298.15\ K) = (29.81 \pm 0.19)$.

As an interesting aside, the formation of ternary $Ca\text{-}UO_2\text{-}CO_3$ complexes appears to have consequences on bacterial U(VI) reduction and on the toxicity of groundwaters. Brooks et al. (2003) monitored the bacterial reduction of U(VI) by anaerobic bacteria in the presence and absence of Ca and found a significant decrease in the rate and extent of bacterial reduction in the presence of Ca. The results were consistent with the hypothesis that U is energetically less favorable to accept electrons when $Ca\text{-}UO_2\text{-}CO_3$ complexes are present, but there was no direct evidence for the formation of such complexes. EXAFS studies by Kelly et al. (2005) of such microbial reduction systems indicated the presence of $Ca\text{-}UO_2\text{-}CO_3$ complexes. Prat et al. (2009) studied the speciation of drinking waters from drilled wells in Southern Finland with exceptionally high concentrations of natural uranium ranging from 6–3400 µg/l. Despite the high concentrations, no clear clinical symptoms are observed among the exposed population. The EXAFS measurements and the geochemical modeling performed by Prat et al. (2009) are both consistent with the predominance of $CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3(aq)$ in these drinking waters which may explain their low toxicity.

Guillaumont et al. (2003) based their discussion of the ternary complexes on Bernhard et al. (1996), Bernhard et al. (2001), four short communications in annual reports by these authors appearing in 1997 and 1998, and Kalmykow & Choppin (2000).

When we selected the stability constants for the ternary alkaline earth U(VI) carbonate complexes, we had the data discussed by Guillaumont et al. (2003) at hand, as well as the data by Dong & Brooks (2006). Considering the critical discussion by Guillaumont et al. (2003), who recommended no data, and the fact that these ternary complexes were not yet firmly established, we chose to include them as supplemental data serving as placeholders for scoping calculations or qualitative modeling. For $Ca_2UO_2(CO)_3(aq)$, we selected the value by Kalmykow & Choppin (2000), as reported by Guillaumont et al. (2003)

$$2\,Ca^{2+} + UO_2^{2+} + 3\,CO_3^{2-} \Leftrightarrow Ca_2UO_2(CO)_3(aq)$$

$$\log_{10}\beta°_{2,1,3}(298.15\ K) = (29.22 \pm 0.25)$$

It was only during the preparation of this documentation of our database that we noticed that the actual value for $\log_{10}\beta°_{2,1,3}$ reported by Kalmykow & Choppin (2000) is (29.8 ± 0.7) and not (29.22 ± 0.25), but we cannot explain this discrepancy.

For the remaining ternary complexes we selected the stability constants by Dong & Brooks (2006) as supplemental data and increased the uncertainties to ± 0.5. Thus

$$Mg^{2+} + UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow MgUO_2(CO_3)_3^{2-}$$

$$\log_{10}\beta^\circ_{1,1,3}(298.15\ K) = (26.11 \pm 0.50)$$

$$Ca^{2+} + UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow CaUO_2(CO_3)_3^{2-}$$

$$\log_{10}\beta^\circ_{1,1,3}(298.15\ K) = (27.18 \pm 0.50)$$

$$Sr^{2+} + UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow SrUO_2(CO_3)_3^{2-}$$

$$\log_{10}\beta^\circ_{1,1,3}(298.15\ K) = (26.86 \pm 0.50)$$

$$Ba^{2+} + UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow BaUO_2(CO_3)_3^{2-}$$

$$\log_{10}\beta^\circ_{1,1,3}(298.15\ K) = (26.68 \pm 0.50)$$

$$2\ Ba^{2+} + UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow Ba_2UO_2(CO_3)_3(aq)$$

$$\log_{10}\beta^\circ_{2,1,3}(298.15\ K) = (29.75 \pm 0.50)$$

Because Dong & Brooks (2006) used the Davies equation for ionic strength corrections we estimated

$$\varepsilon(MgUO_2(CO_3)_3^{2-}, Na^+) = -(0.10 \pm 0.10)\ kg{\cdot}mol^{-1}$$

$$\varepsilon(CaUO_2(CO_3)_3^{2-}, Na^+) = -(0.10 \pm 0.10)\ kg{\cdot}mol^{-1}$$

$$\varepsilon(SrUO_2(CO_3)_3^{2-}, Na^+) = -(0.10 \pm 0.10)\ kg{\cdot}mol^{-1}$$

$$\varepsilon(BaUO_2(CO_3)_3^{2-}, Na^+) = -(0.10 \pm 0.10)\ kg{\cdot}mol^{-1}$$

based on charge correlations (see Appendix A).

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 Guillaumont et al. (2003) selected the stability constant reported by Capdevila & Vitorge (1999). Capdevila & Vitorge (1999) based the value for $\log_{10}\beta_3°$ on their measurements of the redox potential for

$$UO_2(CO_3)_3^{4-} + e^- \Leftrightarrow UO_2(CO_3)_3^{5-}$$

in Na_2CO_3 media (I = 0.9 to 4.5 M), which resulted in $E°(298.15\ K) = -(779 \pm 10)$ mV/SHE, corresponding to $\log_{10}K°(298.15\ K) = -(13.17 \pm 0.17)$, and $\Delta\varepsilon = -(0.91 \pm 0.10)\ kg{\cdot}mol^{-1}$[28]. Combining this $\log_{10}K°$ with $\log_{10}K°(298.15\ K) = -(1.484 \pm 0.22)$ (Grenthe et al. 1992) for

$$UO_2^{+} \Leftrightarrow UO_2^{2+} + e^-$$

and with $\log_{10}\beta_3°(UO_2(CO_3)_3^{4-}, 298.15\ K) = (21.60 \pm 0.05)$ (Grenthe et al. 1992) for

$$UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow UO_2(CO_3)_3^{4-}$$

Capdevila & Vitorge (1999) obtained $\log_{10}\beta_3°(298.15\ K) = (6.95 \pm 0.18)$ for the reaction $UO_2^{+} + 3\ CO_3^{2-} \Leftrightarrow UO_2(CO_3)_3^{5-}$. Guillaumont et al. (2003) adopted this value, but doubled the uncertainty and selected $\log_{10}\beta_3°(UO_2(CO_3)_3^{5-}, 298.15\ K) = (6.95 \pm 0.36)$.

Unfortunately, Guillaumont et al. (2003) overlooked that they had themselves replaced the value of (21.60 ± 0.05) by Grenthe et al. (1992) for $\log_{10}\beta_3°(UO_2(CO_3)_3^{4-}, 298.15\ K)$ with (21.84 ± 0.04) and that $\log_{10}\beta_3°(UO_2(CO_3)_3^{5-}, 298.15\ K)$ should be therefore recalculated, thus leading to

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[28] Guillaumont et al. (2003) reported this value as $-(0.97 \pm 0.20)\ kg{\cdot}mol^{-1}$. 0.97 instead of 0.91 is most likely a typographical error, while the uncertainty was probably doubled on purpose.

$$UO_2^+ + 3\ CO_3^{2-} \Leftrightarrow UO_2(CO_3)_3^{5-}$$

$$\log_{10}\beta_3°(298.15\ K) = (7.19 \pm 0.36)$$

which is included in our database[30].

From $\Delta\varepsilon$ = -(0.91 ± 0.20) kg·mol^{-1}, the value reported by Capdevila & Vitorge (1999) for $UO_2(CO_3)_3^{4-} + e^- \Leftrightarrow UO_2(CO_3)_3^{5-}$ with doubled uncertainties, and the selected $\varepsilon(UO_2(CO_3)_3^{4-}, Na^+)$ = -(0.01 ± 0.11) kg·mol^{-1} follows

$$\varepsilon(UO_2(CO_3)_3^{5-}, Na^+) = -(0.92 \pm 0.23)\ kg{\cdot}mol^{-1}$$

This value is also included in our database. Note that for unknown reasons, Guillaumont et al. (2003) retained the value -(0.62 ± 0.15) kg·mol^{-1} selected by Grenthe et al. (1995).

$UO_2(CO_3)_3^{5-}$ 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 have only been 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 Section 11.3) and β_3 for the formation of $UO_2(CO_3)_3^{4-}$, Grenthe et al. (1992) calculated the equilibrium constant for the reaction

$$U^{4+} + 5\ CO_3^{2-} \Leftrightarrow U(CO_3)_5^{6-}$$

and obtained $\log_{10}\beta_5°$(298.15 K) = (34.0 ± 0.9). Grenthe et al. (1995) revised this value (due to the changed value for $\varepsilon(CO_3^{2-}, Na^+)$, see above) and selected

$$\log_{10}\beta_5°(298.15\ K) = (33.9 \pm 1.0)$$

Guillaumont et al. (2003) discussed new data for this reaction, but did not accept them. Probably by accident, the $\log_{10}\beta_5°$ value listed in their Table 3-2 of selected uranium data is that originally selected by Grenthe et al. (1992) and not the revised value by Grenthe et al. (1995). Unfortunately, the value selected by Hummel et al. (2002), $\log_{10}\beta_5°$(298.15 K) = (34.1 ± 1.0), supposedly based on Grenthe et al. (1992), corresponds to neither of these (but is only slightly different). This error has now been corrected and $\log_{10}\beta_5°$(298.15 K) = (33.9 ± 1.0) is included in our database[31].

The enthalpy of the formation reaction of $U(CO_3)_5^{6-}$ has been determined experimentally as

$$\Delta_r H_m°(298.15\ K) = -(20 \pm 4)\ kJ{\cdot}mol^{-1}$$

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[30] Note that Thoenen (2012) and the electronic versions of TDB 12/07 for PHREEQC and GEMS-PSI released before December 2014 contain the incorrect $\log_{10}\beta_3°(UO_2(CO_3)_3^{5-}$, 298.15 K) = (6.95 ± 0.36) instead of (7.19 ± 0.36).

[31] Note that Thoenen (2012) and the electronic versions of TDB 12/07 for PHREEQC and GEMS-PSI released before December 2014 contain the incorrect $\log_{10}\beta_5°(U(CO_3)_5^{6-}$, 298.15 K) = (34.1 ± 1.0) instead of (33.9 ± 1.0).

and is included in our database. The dissociation of the limiting complex $U(CO_3)_5^{6-}$ to $U(CO_3)_4^{4-}$ was studied in CO_2/HCO_3^- solutions of varying ionic strength (0.5–3.0 m $NaClO_4$) and an SIT regression of the data resulted in

$$U(CO_3)_4^{4-} + CO_3^{2-} \Leftrightarrow U(CO_3)_5^{6-}$$

$$\log_{10}K_5°(298.15\ K) = -(1.12 \pm 0.25)$$

with $\Delta\varepsilon = -(0.13 \pm 0.11)$. Grenthe et al. (1992) estimated

$$\varepsilon(U(CO_3)_4^{4-}, Na^+) = -(0.09 \pm 0.10)\ kg \cdot mol^{-1}$$

but gave no details on this estimate and accidentally omitted the minus sign. From $\Delta\varepsilon$, the estimate, and the selected $\varepsilon(CO_3^{2-}, Na^+) = -(0.08 \pm 0.03)$[32] $kg \cdot mol^{-1}$ follows

$$\varepsilon(U(CO_3)_5^{6-}, Na^+) = -(0.30 \pm 0.15)\ kg \cdot mol^{-1}$$

According to a footnote to their Table B.3, Lemire et al. (2001) calculated the selected

$$\varepsilon(U(CO_3)_5^{6-}, K^+) = -(0.70 \pm 0.31)\ kg \cdot mol^{-1}$$

from published Pitzer-coefficients, but neither this value nor any reference to it appears elsewhere in Lemire et al. (2001).

Combining $\log_{10}\beta_5°(298.15\ K)$ with $\log_{10}K_5°(298.15\ K)$ results in the selected overall formation constant

$$U^{4+} + 4\ CO_3^{2-} \Leftrightarrow U(CO_3)_4^{4-}$$

$$\log_{10}\beta_4°(298.15\ K) = (35.22 \pm 1.03)$$

which is also included in our database, as well as the mentioned ion interaction coefficients for $U(CO_3)_4^{4-}$ and $U(CO_3)_5^{6-}$. 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).

Ternary U(IV) hydroxide carbonate complexes: There appear to be very little experimental data on ternary U(IV) hydroxide carbonate species. However, scoping calculations (Hummel & Berner 2002) showed that such complexes can be of importance in environmental modeling. Hummel & Berner (2002) estimated maximum feasible values for ternary hydroxide-carbonate complexes of U(IV), Np(IV), and Pu(IV) at low bicarbonate concentrations. They assumed that $AnCO_3(OH)_3^-$ is the dominant mixed hydroxide-carbonate complex and adjusted the formation constants to the maximal feasible values that are still consistent with the available experimental solubility data. In the case of $UCO_3(OH)_3^-$ they obtained

$$U^{4+} + CO_3^{2-} + 3\ H_2O(l) \Leftrightarrow UCO_3(OH)_3^- + 3\ H^+$$

$$\log_{10}{}^*K°(298.15\ K) = 4$$

This value is included in our database as supplemental data as well as the estimate

$$\varepsilon(UCO_3(OH)_3^-, Na^+) = -(0.05 \pm 0.10)\ kg \cdot mol^{-1}$$

based on charge correlations (see Appendix A).

Guillaumont et al. (2003) discussed the experimental study by Rai et al. (1998) which proposed the formation of the ternary complex $U(CO_3)_2(OH)_2^{2-}$. Guillaumont et al. (2003) remarked that

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[32] Value selected by Grenthe et al. (1995), replacing the value $\varepsilon(CO_3^{2-}, Na^+) = -(0.05 \pm 0.03)$ selected by Grenthe et al. (1992).

the experimental method applied by Rai et al. (1998) does not allow to determine the number of coordinated carbonate ions and suggested that the proposed stability constant be used as a phenomenological parameter to describe the solubility at high carbonate and hydroxide concentrations. We suggest to do this with our constant for $UCO_3(OH)_3^-$.

$UO_2(CO_3)$(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. Ten reliable values of the equilibrium constant for reaction

$$UO_2(CO_3)(cr) \Leftrightarrow UO_2^{2+} + CO_3^{2-}$$

were considered by Guillaumont et al. (2003). From the weighted average of the values extrapolated to $I = 0$ by SIT they obtained:

$$\log_{10}K_{s,0}°(298.15 \text{ K}) = -(14.76 \pm 0.02)$$

Guillaumont et al. (2003) noticed that most of the additional values they considered (all experiments were performed in 0.1 M $NaClO_4$) are systematically somewhat lower than those obtained from previous investigations. Guillaumont et al. (2003) had no explanation for this discrepancy, but reasoned that it may be due to differences in the degree of crystallinity of the solids, since the stability constants for complexes deduced from these solubility experiments are in good agreement with data from other sources. The entropy and heat capacity of $UO_2(CO_3)$(cr) were determined experimentally and Grenthe et al. (1992) selected the following values, which were confirmed by Guillaumont et al. (2003):

$$S_m°(UO_2(CO_3), \text{cr}, 298.15 \text{ K}) = (144.2 \pm 0.3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$C_{p,m}°(UO_2(CO_3), \text{cr}, 298.15 \text{ K}) = (120.1 \pm 0.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

Other uranium carbonates: Thermodynamic data exist for $Na_4UO_2(CO_3)_3$(cr), and for the minerals $Ca_2UO_2(CO_3)_3\cdot10H_2O$(cr) (liebigite), $CaMgUO_2(CO_3)_3\cdot12H_2O$(cr) (swartzite), $Mg_2UO_2(CO_3)_3\cdot10H_2O$(cr) (bayleyite), $CaNa_2UO_2(CO_3)_3\cdot6H_2O$(cr) (andersonite) (Grenthe et al. 1992), $Ca_3NaUO_2(CO_3)_3FSO_4\cdot10H_2O$(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)

$$\log_{10}K_{s,3}°(298.15 \text{ K}) = -(5.34 \pm 0.16)$$

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, $UO_3\cdot2H_2O$(s), and rutherfordine, $UO_2(CO_3)$(cr). As a consequence, $Na_4UO_2(CO_3)_3$(cr), is not known as a naturally occurring mineral. Hence, $Na_4UO_2(CO_3)_3$(cr) is not relevant under environmental conditions and is not included in our database.

Neither Grenthe et al. (1992) nor Guillaumont et al. (2003) selected any thermodynamic data for liebigite, swartzite, bayleyite, andersonite, schröckingerite and grimselite, as the quality of the experimental data was regarded as not adequate enough 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.

11.8.2 Uranium thiocyanate complexes

Uranium(VI) thiocyanate complexes: Grenthe et al. (1992) selected equilibrium constants for the formation of U(VI) thiocyanate complexes

$$UO_2^{2+} + n\,SCN^- \Leftrightarrow UO_2(SCN)_n^{(2-n)}$$

with n = 1, 2 and 3, which are also selected for our database:

$$UO_2^{2+} + SCN^- \Leftrightarrow UO_2SCN^+$$

$$\log_{10}\beta_1°(298.15\ K) = (1.40 \pm 0.23)$$

$$UO_2^{2+} + 2\,SCN^- \Leftrightarrow UO_2(SCN)_2(aq)$$

$$\log_{10}\beta_2°(298.15\ K) = (1.24 \pm 0.55)$$

$$UO_2^{2+} + 3\,SCN^- \Leftrightarrow UO_2(SCN)_3^-$$

$$\log_{10}\beta_3°(298.15\ K) = (2.1 \pm 0.5)$$

These equilibrium constants are based on conditional constants measured in 1 M $NaClO_4$, in 1 M $HClO_4$, in 2.5 M $NaNO_3$, and in 0.1 and 0.33 M KNO_3. Grenthe et al. (1992) extrapolated these constants to $I = 0$ with estimated values for $\Delta\varepsilon$ but reported details of the procedure only for perchlorate media. For UO_2SCN^+, they adopted $\Delta\varepsilon(n = 1) = -(0.25 \pm 0.02)\ kg\cdot mol^{-1}$ from the corresponding reaction with Cl^-. From this value and the selected $\varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)\ kg\cdot mol^{-1}$ and $\varepsilon(SCN^-, Na^+) = (0.05 \pm 0.01)\ kg\cdot mol^{-1}$ one obtains

$$\varepsilon(UO_2SCN^+, ClO_4^-) = (0.26 \pm 0.04)\ kg\cdot mol^{-1}$$

which is included in our database. The value $(0.22 \pm 0.04)\ kg\cdot mol^{-1}$ selected by Grenthe et al. (1992) is obviously incorrect. For chloride media, we estimated

$$\varepsilon(UO_2SCN^+, Cl^-) = (0.05 \pm 0.10)\ kg\cdot mol^{-1}$$

based on charge correlations (see Appendix A). For estimating $\Delta\varepsilon(n = 2)$, Grenthe et al. (1992) assumed (in line with the SIT) that ion interaction coefficients of neutral species are zero. For calculating $\Delta\varepsilon(n = 3)$, Grenthe et al. (1992) used the estimate

$$\varepsilon(UO_2(SCN)_3^-, Na^+) \approx \varepsilon(UO_2F_3^-, Na^+) = (0.00 \pm 0.05)\ kg\cdot mol^{-1}$$

which is included in our database, although this value is not listed in the table of selected ion interaction coefficients by Grenthe et al. (1992).

The standard reaction enthalpies

$$\Delta_rH_m°(n = 1, 298.15\ K) = (3.22 \pm 0.06)\ kJ\cdot mol^{-1}$$

$$\Delta_rH_m°(n = 2, 298.15\ K) = (8.9 \pm 0.6)\ kJ\cdot mol^{-1}$$

$$\Delta_rH_m°(n = 3, 298.15\ K) = (6.0 \pm 1.2)\ kJ\cdot mol^{-1}$$

selected by Grenthe et al. (1992) and included in our database are based on calorimetric measurements carried out in 1 M $NaClO_4$. Grenthe et al. (1992) assumed that the values determined in 1 M $NaClO_4$ are also valid at $I = 0$ and accounted for this assumption by doubling the uncertainties.

Uranium(IV) thiocyanate complexes: Grenthe et al. (1992) also selected equilibrium constants and standard enthalpies of reaction for the formation of U(IV) thiocyanate complexes

$$U^{4+} + n\,SCN^- \Leftrightarrow U(SCN)_n^{(4-n)}$$

with n = 1 and 2. They accepted the conditional stability constants measured by Ahrland & Larsson (1954) in a mixture of 0.6 M $HClO_4$ and 0.4 M $NaClO_4$ at 20°C and by Day et al. (1955) in 1.00 M $NaClO_4$ at 10, 25, and 40°C. Grenthe et al. (1992) extrapolated the conditional formation constants of $USCN^{3+}$ to $I = 0$ by assuming that $\Delta\varepsilon(n=1)$ is equal to the corresponding reaction with Cl^- in $NaClO_4$ and chose $\Delta\varepsilon(n = 1) = -(0.13 \pm 0.05)$ kg·mol^{-1}. With this value, they obtained $\log_{10}\beta_1°(298.15\text{ K}) = (2.97 \pm 0.06)$ from $\log_{10}\beta_1(298.15\text{ K}) = (1.49 \pm 0.03)$ by Ahrland & Larsson (1954), and $\log_{10}\beta_1°(298.15\text{ K}) = (2.97 \pm 0.21)$ from $\log_{10}\beta_1(298.15\text{ K}) = (1.49 \pm 0.20)$ by Day et al. (1955), and selected $\log_{10}\beta_1°(298.15\text{ K}) = (2.97 \pm 0.06)$. Unfortunately, the value of -(0.13 ± 0.05) kg·mol^{-1} for $\Delta\varepsilon(U^{4+} + Cl^- \Leftrightarrow UCl^+)$ is incorrect since Grenthe et al. (1992) themselves derived (on p. 199) a value of -(0.29 ± 0.08) kg·mol^{-1}. We recalculated the conditional stability constants with this value and obtained $\log_{10}\beta_1°(298.15\text{ K}) = (2.83 \pm 0.09)$ from the data by Ahrland & Larsson (1954) and $\log_{10}\beta_1°(298.15\text{ K}) = (2.83 \pm 0.22)$ from the data by Day et al. (1955) and selected the mean

$$U^{4+} + SCN^- \Leftrightarrow USCN^{3+}$$

$$\log_{10}\beta_1°(298.15\text{ K}) = (2.83 \pm 0.15)$$

for our database[33]. From $\Delta\varepsilon(n = 1) = -(0.29 \pm 0.08)$ kg·mol^{-1} and the selected $\varepsilon(U^{4+}, ClO_4^-) = (0.76 \pm 0.06)$ kg·mol^{-1} and $\varepsilon(SCN^-, Na^+) = (0.05 \pm 0.01)$ follows

$$\varepsilon(USCN^{3+}, ClO_4^-) = (0.52 \pm 0.10)\text{ kg·mol}^{-1}$$

which is also included in our database. Note that Grenthe et al. (1992) did not select any ε values for U(IV) thiocyanate complexes.

For $U(SCN)_2^{2+}$, Grenthe et al. (1992) selected

$$U^{4+} + 2\ SCN^- \Leftrightarrow U(SCN)_2^{2+}$$

$$\log_{10}\beta_2°(298.15\text{ K}) = (4.26 \pm 0.18)$$

which is the weighted average of the stability constants by Ahrland & Larsson (1954) and Day et al. (1955) extrapolated by Grenthe et al. (1992) to $I = 0$ with $\Delta\varepsilon(n = 2) = -(0.56 \pm 0.14)$ kg·mol^{-1}. They derived this value from the selected $\varepsilon(U^{4+}, ClO_4^-)$ and $\varepsilon(SCN^-, Na^+) = (0.05 \pm 0.01)$, and from the estimate

$$\varepsilon(U(SCN)_2^{2+}, ClO_4^-) \approx \varepsilon(UF_2^{2+}, ClO_4^-) = (0.3 \pm 0.1)\text{ kg·mol}^{-1}$$

These data for $U(SCN)_2^{2+}$ are included in our database, as well as

$$\varepsilon(USCN^{3+}, Cl^-) = (0.25 \pm 0.10)\text{ kg·mol}^{-1}$$

$$\varepsilon(U(SCN)_2^{2+}, Cl^-) = (0.15 \pm 0.10)\text{ kg·mol}^{-1}$$

estimated based on charge correlations (see Appendix A).

The reaction enthalpies

$$\Delta_r H_m°(n=1, 298.15\text{ K}) = -(27 \pm 8)\text{ kJ·mol}^{-1}$$

$$\Delta_r H_m°(n=2, 298.15\text{ K}) = -(18 \pm 4)\text{ kJ·mol}^{-1}$$

selected by Grenthe et al. (1992) and also included in our database were determined by Day et al. (1955) from the temperature dependence of the corresponding equilibrium constants. Grenthe et al. (1992) assumed that these enthalpies are also valid at $I = 0$.

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[33] Note that Thoenen (2012) and the electronic versions of the PSI/Nagra TDB 12/07 released before December 2014 contain the incorrect value $\log_{10}\beta_1°$ (298.15 K) = (2.97 ± 0.06) selected by Grenthe et al. (1992) instead of (2.83 ± 0.15).

11.8.3 Silicon compounds and complexes

Uranium silicon compounds and complexes are discussed in Chapter 8.

11.9 Alkali and alkaline-earth compounds

Thermochemical data have been selected by Grenthe et al. (1992) and Guillaumont et al. (2003) for the entire series of alkali[36] and alkaline-earth[37] 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 extent any of these compounds might be stable in high pH aqueous systems. Scoping calculations using $\Delta_f G_m°$ 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 Section 11.4.1.3) and the mixed valence oxides (see Section 11.4.2.2). Hence, the mentioned alkali and alkaline-earth uranates are presently not included in our database.

Guillaumont et al. (2003) selected solubility product constants for $CaU_6O_{19}\cdot 11H_2O$(cr), becquerelite, and for $K_2U_6O_{19}\cdot 11H_2O$(cr), compreignacite. For becquerelite, Guillaumont et al. (2003) accepted solubility data from two studies, one performed at 298.15 K in 1 m $CaCl_2$ (pH = 4.16, 4.46 and 5.85) and the other at (296 ± 2) K in 0.02, 0.1 and 0.5 M $CaCl_2$, at a pH range of about 4 to 11. Guillaumont et al. (2003) extrapolated the mean of the conditional solubility products of the former study to $I = 0$ using SIT and obtained $\log_{10}{}^*K_{s,0}° = (39.5 \pm 1.0)$. The authors of the latter study extrapolated their data using the Pitzer approach and obtained $\log_{10}{}^*K_{s,0}° = (41.4 \pm 0.2)$, for which Guillaumont et al. (2003) increased the uncertainty to ± 1.2. They selected the mean of both solubility products

$$CaU_6O_{19}\cdot 11H_2O(cr) + 14\ H^+ \Leftrightarrow Ca^{2+} + 6\ UO_2^{2+} + 18\ H_2O(l)$$

$$\log_{10}{}^*K_{s,0}°(298.15\ K) = (40.5 \pm 1.6)$$

The solubility of compreignacite was investigated by one study in 1 m KCl at 298.15 K (pH = 3.12, 4.46, and 5.83). Guillaumont et al. (2003) extrapolated the mean of the conditional solubility products to $I = 0$ using SIT and obtained

$$K_2U_6O_{19}\cdot 11H_2O(cr) + 14H^+ \Leftrightarrow 2K^+ + 6\ UO_2^{2+} + 18\ H_2O(l)$$

$$\log_{10}{}^*K_{s,0}°(298.15\ K) = (37.1 \pm 0.5)$$

Both becquerelite and compreignacite are included in our database.

Guillaumont et al. (2003) also reported the results of solubility measurements for $Na_2U_2O_7\cdot xH_2O$(cr) and $Na_2U_6O_{19}\cdot 12H_2O$(cr) but did not select their solubility products.

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[37] $Be_{13}U$(cr), α-$Mg_{0.17}UO_{2.95}$(cr), $MgUO_4$(cr), MgU_3O_{10}(cr), β-$CaUO_4$, $CaUO_4$(cr), Ca_3UO_6(cr), $SrUO_3$(cr), α-$SrUO_4$, β-$SrUO_4$, $Sr_2UO_{4.5}$(cr), Sr_2UO_5(cr), Sr_3UO_6(cr), $Sr_3U_2O_9$(cr), $Sr_2U_3O_{11}$(cr), SrU_4O_{13}(cr), $Sr_5U_3O_{14}$(cr), $Sr_3U_{11}O_{36}$(cr), $BaUO_3$(cr), $BaUO_4$(cr), Ba_3UO_6(cr), BaU_2O_7(cr), $Ba_2U_2O_7$(cr), Ba_2MgUO_6(cr), Ba_2CaUO_6(cr), Ba_2SrUO_6(cr)

[37] $Be_{13}U$(cr), α-$Mg_{0.17}UO_{2.95}$(cr), $MgUO_4$(cr), MgU_3O_{10}(cr), β-$CaUO_4$, $CaUO_4$(cr), Ca_3UO_6(cr), $SrUO_3$(cr), α-$SrUO_4$, β-$SrUO_4$, $Sr_2UO_{4.5}$(cr), Sr_2UO_5(cr), Sr_3UO_6(cr), $Sr_3U_2O_9$(cr), $Sr_2U_3O_{11}$(cr), SrU_4O_{13}(cr), $Sr_5U_3O_{14}$(cr), $Sr_3U_{11}O_{36}$(cr), $BaUO_3$(cr), $BaUO_4$(cr), Ba_3UO_6(cr), BaU_2O_7(cr), $Ba_2U_2O_7$(cr), Ba_2MgUO_6(cr), Ba_2CaUO_6(cr), Ba_2SrUO_6(cr)

11.10 Uranium compounds with elements from other groups

Guillaumont et al. (2003) selected heat capacity data for $Tl_2U_4O_{11}$(cr) and a standard molar enthalpy of formation for $Zn_{0.12}UO_{2.95}$(cr). Since Tl is not considered in our database and solubilities are not known for both solids, they are not included in our database.

11.11 Uranium compounds and uranium minerals

A final remark on uranium compounds and uranium minerals: Guillaumont et al. (2003) selected thermodynamic data for 223 uranium solids (see their Table 3-1). A comparably large number, 242, of naturally occurring uranium minerals have been “officially” recognized (Mineral Database 1997). However, the set of uranium minerals for which thermodynamic data have been selected is surprisingly small: 7 (!), i.e. "uraninite" UO_2(am, hyd), metaschoepite $UO_3 \cdot 2H_2O$(cr), chernikovite $UO_2HPO_4 \cdot 4H_2O$(cr), rutherfordine UO_2CO_3(cr), becquerelite $CaU_6O_{19} \cdot 11H_2O$(cr), compreignacite $K_2U_6O_{19} \cdot 11H_2O$(cr), and coffinite $USiO_4$(cr) (for coffinite see Chapter 8). All these minerals are included in our database. In addition, solubility products of three synthetic solid phases have been included in our database which are thought to be of some relevance for environmental modeling: $UF_4 \cdot 2.5H_2O$(cr), $U(OH)_2SO_4$(cr) and $(UO_2)_3(PO_4)_2 \cdot 4H_2O$(cr).

Table 11.2: Uranium data selected by NEA (Grenthe et al. 1992 and Guillaumont et al. 2003) but not included in TDB Version 12/07. For explanations see text.

Gases	$U(g)$ [a], $UO(g)$ [a], $UO_2(g)$ [a], $UO_3(g)$ [a], $UF(g)$ [a], $UF_2(g)$ [a], $UF_3(g)$ [a], $UF_4(g)$ [ad], $UF_5(g)$ [ad], $UF_6(g)$ [ad], $U_2F_{10}(g)$ [bd], $UOF_4(g)$ [a], $UO_2F_2(g)$ [ad], $UCl(g)$ [a], $UCl_2(g)$ [a], $UCl_3(g)$ [a], $UCl_4(g)$ [ad], $UCl_5(g)$ [a], $UCl_6(g)$ [ad], $U_2Cl_{10}(g)$ [bd], $UO_2Cl_2(g)$ [a], $UBr(g)$ [a], $UBr_2(g)$ [a], $UBr_3(g)$ [a], $UBr_4(g)$ [ad], $UBr_5(g)$ [ad], $UI(g)$ [a], $UI_2(g)$ [a], $UI_3(g)$ [a], $UI_4(g)$ [ad]
Solids	$UO_2(cr)$ [a], $\beta\text{-}UO_{2.25}(cr)$ [a], $UO_{2.25}(cr)$ [a], $\alpha\text{-}UO_{2.3333}(cr)$ [b], $\beta\text{-}UO_{2.3333}(cr)$ [a], $UO_{2.6667}(cr)$ [ad], $UO_{2.86}\cdot 0.5H_2O(cr)$ [b], $UO_{2.86}\cdot 1.5H_2O(cr)$ [b], $\alpha\text{-}UO_{2.95}(cr)$ [bd], $\alpha\text{-}UO_3(cr)$ [a], $\beta\text{-}UO_3(cr)$ [a], $\gamma\text{-}UO_3(cr)$ [ad], $\delta\text{-}UO_3(cr)$ [bd], $\varepsilon\text{-}UO_3(cr)$ [b], $\beta\text{-}UH_3(cr)$ [a], $UO_3\cdot 0.393H_2O(cr)$ [b], $UO_3\cdot 0.648H_2O(cr)$ [b], $\alpha\text{-}UO_3\cdot 0.85H_2O\ (cr)$ [b], $\alpha\text{-}UO_3\cdot 0.9H_2O(cr)$ [a], $\delta\text{-}UO_3H_{0.83}(cr)$ [bd], $\beta\text{-}UO_2(OH)_2$ [a], $\gamma\text{-}UO_2(OH)_2$ [b], $UO_4\cdot 2H_2O(cr)$ [b], $UO_4\cdot 4H_2O(cr)$ [b], $UF_3(cr)$ [a], $UF_4(cr)$ [ad], $\alpha\text{-}UF_5(cr)$ [a], $\beta\text{-}UF_5(cr)$ [a], $UF_6(cr)$ [ad], $U_2F_9(cr)$ [a], $U_4F_{17}(cr)$ [a], $UOF_2(cr)$ [a], $UOF_4(cr)$ [a d], $UO_2F_2(cr)$ [ad], $U_2O_3F_6(cr)$ [ad], $U_3O_5F_8(cr)$ [ad], $H_3OUF_6(cr)$ [bd], $UOFOH(cr)$ [a], $UOFOH\cdot 0.5H_2O(cr)$ [a], $UOF_2\cdot H_2O(cr)$ [a], $UF_4\cdot 2.5H_2O(cr)$ [a], $UO_2FOH\cdot H_2O(cr)$ [ac], $UO_2FOH\cdot 2H_2O(cr)$ [ac], $UO_2F_2\cdot 3H_2O(cr)$ [ad], $UCl_3(cr)$ [a], $UCl_4(cr)$ [ad], $UCl_5(cr)$ [a], $UCl_6(cr)$ [ad], $UOCl(cr)$ [a], $UOCl_2(cr)$ [a], $UOCl_3(cr)$ [a], $UO_2Cl(cr)$ [a], $UO_2Cl_2(cr)$ [a], $U_2O_2Cl_5(cr)$ [a], $(UO_2)_2Cl_3(cr)$ [a], $U_5O_{12}Cl(cr)$ [a], $UO_2Cl_2\cdot H_2O(cr)$ [a], $UO_2ClOH\cdot 2H_2O(cr)$ [a], $UO_2Cl_2\cdot 3H_2O(cr)$ [a], $UCl_3F(cr)$ [a], $UCl_2F_2(cr)$ [a], $UClF_3(cr)$ [a], $UBr_3(cr)$ [a], $UBr_4(cr)$ [a d], $UBr_5(cr)$ [a], $UOBr_2(cr)$ [a], $UOBr_3(cr)$ [a], $UO_2Br_2(cr)$ [a], $UO_2Br_2\cdot H_2O(cr)$ [a], $UO_2BrOH\cdot 2H_2O(cr)$ [a], $UO_2Br_2\cdot 3H_2O(cr)$ [a], $UBr_2Cl(cr)$ [a], $UBr_3Cl(cr)$ [a], $UBrCl_2(cr)$ [a], $UBr_2Cl_2(cr)$ [a], $UBrCl_3(cr)$ [a], $UI_3(cr)$ [a], $UI_4(cr)$ [ad], $UO_2(IO_3)_2(cr)$ [ac], $UClI_3(cr)$ [a], $UCl_2I_2(cr)$ [a], $UCl_3I(cr)$ [a], $UBrI_3(cr)$ [b], $UBr_2I_2(cr)$ [b], $UBr_3I(cr)$ [b], $US(cr)$ [a], $US_{1.90}(cr)$ [a], $US_2(cr)$ [a], $US_3(cr)$ [a], $U_2S_3(cr)$ [a], $U_2S_5(cr)$ [b], $U_3S_5(cr)$ [a], $UO_2SO_3(cr)$ [a], $UO_2SO_4(cr)$ [a], $U(SO_3)_2(cr)$ [a], $U(SO_4)_2(cr)$ [a], $UO_2SO_4\cdot 2.5H_2O(cr)$ [ac], $UO_2SO_4\cdot 3H_2O(cr)$ [ac], $UO_2SO_4\cdot 3.5H_2O(cr)$ [ac], $U(SO_4)_2\cdot 4H_2O(cr)$ [a], $U(SO_4)_2\cdot 8H_2O(cr)$ [a], $USe(cr)$ [a], $\alpha\text{-}USe_2(cr)$ [a], $\beta\text{-}USe_2(cr)$ [a], $USe_3(cr)$ [a], $U_2Se_3(cr)$ [a],$U_3Se_4(cr)$ [a], $U_3Se_5(cr)$ [a], $UO_2SeO_3(cr)$ [b], $UO_2SeO_4(cr)$ [b], $UOTe(cr)$ [b], $UTeO_5(cr)$ [b], $UTe_3O_9(cr)$ [b], $UN(cr)$ [a], $\beta\text{-}UN_{1.466}(cr)$ [b], $\alpha\text{-}UN_{1.59}(cr)$ [a], $\alpha\text{-}UN_{1.606}(cr)$ [b], $\alpha\text{-}UN_{1.674}(cr)$ [b], $\alpha\text{-}UN_{1.73}(cr)$ [a], $UO_2(NO_3)_2(cr)$ [a], $UO_2(NO_3)_2\cdot H_2O(cr)$ [a], $UO_2(NO_3)_2\cdot 2H_2O(cr)$ [a], $UO_2(NO_3)_2\cdot 3H_2O(cr)$ [a], $UO_2(NO_3)_2\cdot 6H_2O(cr)$ [a], $UP(cr)$ [a], $UP_2(cr)$ [a], $U_3P_4(cr)$ [a], $UPO_5(cr)$ [a], $UP_2O_7(cr)$ [a], $(UO_2)_2P_2O_7(cr)$ [a], $U(HPO_4)_2\cdot 4H_2O(cr)$ [a c], $(UO_2)_3(PO_4)_2\cdot 6H_2O(cr)$ [a], $UAs(cr)$ [a], $UAs_2(cr)$ [a], $U_3As_4(cr)$ [a], $UAsO_5(cr)$ [b], $UO_2(AsO_3)_2(cr)$ [a], $(UO_2)_2As_2O_7(cr)$ [a], $(UO_2)_3(AsO_4)_2(cr)$ [a], $UAsS(cr)$ [b], $UAsSe(cr)$ [b], $UAsTe(cr)$ [b], $USb(cr)$ [a], $USb_2(cr)$ [a], $U_4Sb_3(cr)$ [b], $U_3Sb_4(cr)$ [a], $UC(cr)$ [a], $\alpha\text{-}UC_{1.94}(cr)$ [a], $U_2C_3(cr)$ [a], $Tl_2U_4O_{11}(cr)$ [b], $Zn_{0.12}UO_{2.95}(cr)$ [b], $Be_{13}U(cr)$ [a], $\alpha\text{-}Mg_{0.17}UO_{2.95}(cr)$ [b], $MgUO_4(cr)$ [a], $MgU_3O_{10}(cr)$ [b], $\beta\text{-}CaUO_4$ [b], $CaUO_4(cr)$ [a], $Ca_3UO_6(cr)$ [b], $SrUO_3(cr)$ [b], $\alpha\text{-}SrUO_4(cr)$ [a], $\beta\text{-}SrUO_4(cr)$ [b], $Sr_2UO_{4.5}(cr)$ [b], $Sr_2UO_5(cr)$ [b], $Sr_3UO_6(cr)$ [b], $Sr_3U_2O_9(cr)$ [b], $Sr_2U_3O_{11}(cr)$ [b], $SrU_4O_{13}(cr)$ [b], $Sr_5U_3O_{14}(cr)$ [b], $Sr_3U_{11}O_{36}(cr)$ [b], $BaUO_3(cr)$ [b], $BaUO_4(cr)$ [a], $Ba_3UO_6(cr)$ [a], $BaU_2O_7(cr)$ [a], $Ba_2U_2O_7(cr)$ [a], $Ba_2MgUO_6(cr)$ [b], $Ba_2CaUO_6(cr)$ [b], $Ba_2SrUO_6(cr)$ [b], $Li_{0.12}UO_{2.95}(cr)$ [bd], $\gamma\text{-}Li_{0.55}UO_3(cr)$ [bd], $\delta\text{-}Li_{0.69}UO_3(cr)$ [bd], $LiUO_3(cr)$ [bd], $Li_2UO_4(cr)$ [a], $Li_4UO_5(cr)$ [b], $Li_2U_2O_7(cr)$ [b], $Li_{0.19}U_3O_8(cr)$ [bd], $Li_{0.88}U_3O_8(cr)$ [bd], $Li_2U_3O_{10}(cr)$ [b], $Na_{0.12}UO_{2.95}(cr)$ [bd], $\alpha\text{-}Na_{0.14}UO_3(cr)$ [bd], $\delta\text{-}Na_{0.54}UO_3(cr)$ [bd], $NaUO_3(cr)$ [ad], $\alpha\text{-}Na_2UO_4(cr)$ [a], $\beta\text{-}Na_2UO_4(cr)$ [b], $Na_3UO_4(cr)$ [a], $Na_4UO_5(cr)$ [b], $Na_2U_2O_7(cr)$ [a], $Na_{0.20}U_3O_8(cr)$ [bd], $Na_6U_7O_{24}(cr)$ [b], $Na_4UO_2(CO_3)_3(cr)$ [ac], $KUO_3(cr)$ [b], $K_2UO_4(cr)$ [a], $K_2U_2O_7(cr)$ [b], $K_2U_4O_{13}(cr)$ [b], $RbUO_3(cr)$ [b], $Rb_2UO_4(cr)$ [a], $Rb_2U_2O_7(cr)$ [b], $Rb_2U_4O_{11}(cr)$ [b], $Rb_2U_4O_{13}(cr)$ [b], $Rb_2U(SO_4)_3(cr)$ [b], $Cs_2UO_4(cr)$ [a], $Cs_2U_2O_7(cr)$ [a], $Cs_2U_4O_{12}(cr)$ [a], $Cs_4U_5O_{17}(cr)$ [b]
Aqueous species	U^{3+} [ac], $UO_2ClO_3^{+}$ [ac], UBr^{3+} [ac], UO_2Br^{+} [ac], $UO_2BrO_3^{+}$ [ac], $UO_2SO_3(aq)$ [ac], $UO_2S_2O_3(aq)$ [ac], $UO_2N_3^{+}$ [ac], $UO_2(N_3)_2(aq)$ [ac], $UO_2(N_3)_3^{-}$ [ac], $UO_2(N_3)_4^{2-}$ [ac], $(UO_2)_{11}(CO_3)_6(OH)_{12}^{2-}$ [ac]

[a] Single species data including $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}$
[b] Single species data excluding $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}$
[c] Reaction data including $\log_{10}K^{\circ}$
[d] Reaction data excluding $\log_{10}K^{\circ}$

Table 11.3: Selected uranium data. All data included in TDB Version 12/07 are taken from Grenthe et al. (1992), Grenthe et al. (1995), and Guillaumont et al. (2003), except where marked with an asterisk (*). Core data are bold and supplemental data are in italics. New or changed data with respect to TDB Version 01/01 (Hummel et al., 2002) are shaded.

		TDB Version 01/01				**TDB Version 12/07**				
Name	**Redox**	$\Delta_f G_m°$ [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}]	$\Delta_f G_m°$ [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}]	**Species**
U(cr)	0	0.0	0.0	50.2 ± 0.20	27.66 ± 0.05	0.0	0.0	50.2 ± 0.20	27.66 ± 0.05	U(cr)
U+4	IV	-529.9 ± 1.8	-591.2 ± 3.3	(-416.9 ± 12.6)[a]	-48 ± 15	-529.9 ± 1.8	-591.2 ± 3.3	(-416.9 ± 12.6)[a]	-220 ± 50	U^{4+}
UO2+	V	-961.0 ± 1.8	(-1025.1 ± 3.0)[a]	-25 ± 8	-	-961.0 ± 1.8	-(1025.1 ± 3.0)[a]	-25 ± 8	-	UO_2^+
UO2+2	VI	**(-952.55 ± 1.75)**[a]	**-1019.0 ± 1.5**	**-98.2 ± 3.0**	**42.4 ± 3.0**	**(-952.55 ± 1.75)**[a]	**-1019.0 ± 1.5**	**-98.2 ± 3.0**	**42.4 ± 3.0**	UO_2^{2+}

[a] Calculated value

		TDB Version 01/01				**TDB Version 12/07**				
Name	**Redox**	$\log_{10}\beta°$	$\Delta_r H_m°$ [kJ·mol^{-1}]	$\Delta_r S_m°$ [J·K^{-1}·mol^{-1}]	$S_m°$	$\log_{10}\beta°$	$\Delta_r H_m°$ [kJ·mol^{-1}]	$\Delta_r S_m°$ [J·K^{-1}·mol^{-1}]	$S_m°$	**Reaction**
UO2OH+	VI	-5.2 ± 0.3	-	-	17 ± 50	-5.25 ± 0.24	-	-	17 ± 50	$UO_2^{2+} + H_2O(l) \Leftrightarrow UO_2OH^+ + H^+$
UO2(OH)2	VI	-12.0 ± 0.5	-	-	-	-12.15 ± 0.07	-	-	-	$UO_2^{2+} + 2\ H_2O(l) \Leftrightarrow UO_2(OH)_2(aq) + 2\ H^+$
UO2(OH)3-	VI	-19.2 ± 0.4	-	-	-	-20.25 ± 0.42	-	-	-	$UO_2^{2+} + 3\ H_2O(l) \Leftrightarrow UO_2(OH)_3^- + 3\ H^+$
UO2(OH)4-2	VI	-33 ± 2	-	-	-	-32.40 ± 0.68	-	-	-	$UO_2^{2+} + 4\ H_2O(l) \Leftrightarrow UO_2(OH)_4^{2-} + 4\ H^+$
(UO2)2OH+3	VI	-2.7 ± 1.0	-	-	-	-2.7 ± 1.0	-	-	-	$2\ UO_2^{2+} + H_2O(l) \Leftrightarrow (UO_2)_2OH^{3+} + H^+$
(UO2)2(OH)2+2	VI	-5.62 ± 0.04	-	-	-38 ± 15	-5.62 ± 0.04	-	-	-38 ± 15	$2\ UO_2^{2+} + 2\ H_2O(l) \Leftrightarrow (UO_2)_2(OH)_2^{2+} + 2\ H^+$
(UO2)3(OH)4+2	VI	-11.9 ± 0.3	-	-	-	-11.9 ± 0.3	-	-	-	$3\ UO_2^{2+} + 4\ H_2O(l) \Leftrightarrow (UO_2)_3(OH)_4^{2+} + 4\ H^+$
(UO2)3(OH)5+	VI	-15.55 ± 0.12	-	-	83 ± 30	-15.55 ± 0.12	-	-	83 ± 30	$3\ UO_2^{2+} + 5\ H_2O(l) \Leftrightarrow (UO_2)_3(OH)_5^+ + 5\ H^+$
(UO2)3(OH)7-	VI	-31 ± 2	-	-	-	-32.2 ± 0.8	-	-	-	$3\ UO_2^{2+} + 7\ H_2O(l) \Leftrightarrow (UO_2)_3(OH)_7^- + 7\ H^+$
(UO2)4(OH)7+	VI	-21.9 ± 1.0	-	-	-	-21.9 ± 1.0	-	-	-	$4\ UO_2^{2+} + 7\ H_2O(l) \Leftrightarrow (UO_2)_4(OH)_7^+ + 7\ H^+$
UO2F+	VI	5.09 ± 0.13	1.70 ± 0.08	-	-	5.16 ± 0.06	1.70 ± 0.08	-	-	$UO_2^{2+} + F^- \Leftrightarrow UO_2F^+$
UO2F2	VI	8.62 ± 0.04	2.10 ± 0.19	-	-	8.83 ± 0.08	2.10 ± 0.19	-	-	$UO_2^{2+} + 2\ F^- \Leftrightarrow UO_2F_2(aq)$
UO2F3-	VI	10.9 ± 0.4	2.35 ± 0.31	-	-	10.90 ± 0.10	2.35 ± 0.31	-	-	$UO_2^{2+} + 3\ F^- \Leftrightarrow UO_2F_3^-$

		TDB Version 01/01				TDB Version 12/07				
Name	**Redox**	**$\log_{10}\beta°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**$\Delta_rS_m°$** [J·K^{-1}·mol^{-1}]	**$S_m°$**	**$\log_{10}\beta°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**$\Delta_rS_m°$** [J·K^{-1}·mol^{-1}]	**$S_m°$**	**Reaction**
UO2F4-2	VI	11.7 ± 0.7	0.29 ± 0.47	-	-	11.84 ± 0.11	0.29 ± 0.47	-	-	$UO_2^{2+} + 4\ F^- \Leftrightarrow UO_2F_4^{2-}$
UO2Cl+	VI	0.17 ± 0.02	8 ± 2	-	-	0.17 ± 0.02	8 ± 2	-	-	$UO_2^{2+} + Cl^- \Leftrightarrow UO_2Cl^+$
UO2Cl2	VI	-1.1 ± 0.4	15 ± 6	-	-	-1.1 ± 0.4	15 ± 6	-	-	$UO_2^{2+} + 2\ Cl^- \Leftrightarrow UO_2Cl_2(aq)$
UO2IO3+	VI	-	-	-	-	2.00 ± 0.02	-	-	-	$UO_2^{2+} + IO_3^- \Leftrightarrow UO_2IO_3^+$
UO2(IO3)2	VI	-	-	-	-	3.59 ± 0.15	-	-	-	$UO_2^{2+} + 2\ IO_3^- \Leftrightarrow UO_2(IO_3)_2(aq)$
UO2SO4	VI	3.15 ± 0.02	19.5 ± 1.6	-	-	3.15 ± 0.02	19.5 ± 1.6	-	-	$UO_2^{2+} + SO_4^{2-} \Leftrightarrow UO_2SO_4(aq)$
UO2(SO4)2-2	VI	4.14 ± 0.07	35.1 ± 1.0	-	-	4.14 ± 0.07	35.1 ± 1.0	-	-	$UO_2^{2+} + 2\ SO_4^{2-} \Leftrightarrow UO_2(SO_4)_2^{2-}$
UO2(SO4)3-4	VI	-	-	-	-	3.02 ± 0.38	-	-	-	$UO_2^{2+} + 3\ SO_4^{2-} \Leftrightarrow UO_2(SO_4)_3^{4-}$
UO2NO3+	VI	0.30 ± 0.15	-	-	-	0.30 ± 0.15	-	-	-	$UO_2^{2+} + NO_3^- \Leftrightarrow UO_2NO_3^+$
UO2PO4-	VI	13.23 ± 0.15	-	-	-	13.23 ± 0.15	-	-	-	$UO_2^{2+} + PO_4^{3-} \Leftrightarrow UO_2PO_4^-$
UO2HPO4	VI	7.24 ± 0.26	-	-	-	7.24 ± 0.26	-	-	-	$UO_2^{2+} + HPO_4^{2-} \Leftrightarrow UO_2HPO_4(aq)$
UO2H2PO4+	VI	1.12 ± 0.06	-	-	-	1.12 ± 0.06	-	-	-	$UO_2^{2+} + H_3PO_4(aq) \Leftrightarrow UO_2H_2PO_4^+ + H^+$
UO2H3PO4+2	VI	0.76 ± 0.15	-	-	-	0.76 ± 0.15	-	-	-	$UO_2^{2+} + H_3PO_4(aq) \Leftrightarrow UO_2H_3PO_4^{2+}$
UO2(H2PO4)2	VI	0.64 ± 0.11	-	-	-	0.64 ± 0.11	-	-	-	$UO_2^{2+} + 2\ H_3PO_4(aq) \Leftrightarrow UO_2(H_2PO_4)_2(aq) + 2\ H^+$
UO2H2PO4H3PO4+	VI	1.65 ± 0.11	-	-	-	1.65 ± 0.11	-	-	-	$UO_2^{2+} + 2\ H_3PO_4(aq) \Leftrightarrow UO_2(H_2PO_4)(H_3PO_4)^+ + H^+$
UO2HAsO4	VI	-	-	-	-	7.16 ± 0.37	-	-	-	$UO_2^{2+} + HAsO_4^{2-} \Leftrightarrow UO_2HAsO_4(aq)$
UO2H2AsO4+	VI	-	-	-	-	1.34 ± 0.42	-	-	-	$UO_2^{2+} + H_3AsO_4(aq) \Leftrightarrow UO_2H_2AsO_4^+ + H^+$
UO2(H2AsO4)2	VI	-	-	-	-	0.29 ± 0.53	-	-	-	$UO_2^{2+} + 2\ H_3AsO_4(aq) \Leftrightarrow UO_2(H_2AsO_4)_2(aq) + 2\ H^+$
UO2CO3	VI	9.67 ± 0.05	5 ± 2	-	-	9.94 ± 0.03	5 ± 2	-	-	$UO_2^{2+} + CO_3^{2-} \Leftrightarrow UO_2CO_3(aq)$
UO2(CO3)2-2	VI	16.94 ± 0.12	18.5 ± 4.0	-	-	16.61 ± 0.09	18.5 ± 4.0	-	-	$UO_2^{2+} + 2\ CO_3^{2-} \Leftrightarrow UO_2(CO_3)_2^{2-}$
UO2(CO3)3-4	VI	21.60 ± 0.05	-39.2 ± 4.1	-	-	21.84 ± 0.04	-39.2 ± 4.1	-	-	$UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow UO_2(CO_3)_3^{4-}$
(UO2)3(CO3)6-6	VI	54.0 ± 1.0	-62.7 ± 2.4	-	-	54.0 ± 1.0	-62.7 ± 2.4	-	-	$3\ UO_2^{2+} + 6\ CO_3^{2-} \Leftrightarrow (UO_2)_3(CO_3)_6^{6-}$
(UO2)2CO3(OH)3-	VI	-0.86 ± 0.50	-	-	-	-0.86 ± 0.50	-	-	-	$2\ UO_2^{2+} + CO_3^{2-} + 3\ H_2O(l) \Leftrightarrow (UO_2)_2CO_3(OH)_3^- + 3\ H^+$

		TDB Version 01/01				TDB Version 12/07				
Name	**Redox**	**$\log_{10}\beta°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**$\Delta_r S_m°$** [J·K^{-1}·mol^{-1}]	**$S_m°$**	**$\log_{10}\beta°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**$\Delta_r S_m°$** [J·K^{-1}·mol^{-1}]	**$S_m°$**	**Reaction**
(UO2)3O(OH)2HCO3+	VI	0.66 ± 0.50	-	-	-	0.66 ± 0.50	-	-	-	$3UO_2^{2+} + CO_3^{2-} + 3H_2O(l)$ $\Leftrightarrow (UO_2)_3O(OH)_2(HCO_3)^+ + 3H^+$
UO2CO3F-	VI	-	-	-	-	13.75 ± 0.09	-	-	-	$UO_2^{2+} + CO_3^{2-} + F^- \Leftrightarrow UO_2CO_3F^-$
UO2CO3F2-2	VI	-	-	-	-	15.57 ± 0.14	-	-	-	$UO_2^{2+} + CO_3^{2-} + 2\ F^- \Leftrightarrow UO_2CO_3F_2^{2-}$
UO2CO3F3-3	VI	-	-	-	-	16.38 ± 0.11	-	-	-	$UO_2^{2+} + CO_3^{2-} + 3\ F^- \Leftrightarrow UO_2CO_3F_3^{3-}$
MgUO2(CO3)3-2	VI	-	-	-	-	(26.11 ± 0.50)*	-	-	-	$Mg^{2+} + UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow MgUO_2(CO_3)_3^{2-}$
CaUO2(CO3)3-2	VI	-	-	-	-	(27.18 ± 0.50)*	-	-	-	$Ca^{2+} + UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow CaUO_2(CO_3)_3^{2-}$
Ca2UO2(CO3)3	VI	-	-	-	-	(29.22 ± 0.25)*[b]	-	-	-	$2\ Ca^{2+} + UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow Ca_2UO_2(CO_3)_3(aq)$
SrUO2(CO3)3-2	VI	-	-	-	-	(26.86 ± 0.50)*	-	-	-	$Sr^{2+} + UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow SrUO_2(CO_3)_3^{2-}$
BaUO2(CO3)3-2	VI	-	-	-	-	(26.68 ± 0.50)*	-	-	-	$Ba^{2+} + UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow BaUO_2(CO_3)_3^{2-}$
Ba2UO2(CO3)3	VI	-	-	-	-	(29.75 ± 0.50)*	-	-	-	$2\ Ba^{2+} + UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow Ba_2UO_2(CO_3)_3(aq)$
UO2SCN+	VI	-	-	-	-	1.40 ± 0.23	3.22 ± 0.06	-	-	$UO_2^{2+} + SCN^- \Leftrightarrow UO_2SCN^+$
UO2(SCN)2	VI	-	-	-	-	1.24 ± 0.55	8.9 ± 0.6	-	-	$UO_2^{2+} + 2\ SCN^- \Leftrightarrow UO_2(SCN)_2(aq)$
UO2(SCN)3-	VI	-	-	-	-	2.1 ± 0.5	6.0 ± 1.2	-	-	$UO_2^{2+} + 3\ SCN^- \Leftrightarrow UO_2(SCN)_3^-$
UO2+	VI/V	1.484 ± 0.022	-	-	-	1.484 ± 0.022	-	-	-	$UO_2^{2+} + e^- \Leftrightarrow UO_2^+$
UO2(CO3)3-5	V	7.41 ± 0.27	-	-	-	(7.19 ± 0.36)*[c]	-	-	-	$UO_2^+ + 3\ CO_3^{2-} \Leftrightarrow UO_2(CO_3)_3^{5-}$
U+4	VI/IV	9.038 ± 0.041	-	-	-	9.038 ± 0.041	-	-	-	$UO_2^{2+} + 4H^+ + 2e^- \Leftrightarrow U^{4+} + 2H_2O(l)$
UOH+3	IV	-0.54 ± 0.06	(46.91)[a]	147 ± 30	-	-0.54 ± 0.06	(46.91)[a]	147 ± 30	-	$U^{4+} + H_2O(l) \Leftrightarrow UOH^{3+} + H^+$
U(OH)2+2	IV	-	-	-	-	(-1.1 ± 1.0)*	-	-	-	$U^{4+} + 2\ H_2O(l) \Leftrightarrow U(OH)_2^{2+} + 2\ H^+$
U(OH)3+	IV	-	-	-	-	(-4.7 ± 1.0)*	-	-	-	$U^{4+} + 3\ H_2O(l) \Leftrightarrow U(OH)_3^+ + 3\ H^+$
U(OH)4	IV	-9 ± 2	-	-	-	-10.0 ± 1.4	-	-	-	$U^{4+} + 4\ H_2O(l) \Leftrightarrow U(OH)_4(aq) + 4\ H^+$
UF+3	IV	9.28 ± 0.09	-5.6 ± 0.5	-	-	9.42 ± 0.51	-5.6 ± 0.5	-	-	$U^{4+} + F^- \Leftrightarrow UF^{3+}$
UF2+2	IV	16.23 ± 0.15	-3.5 ± 0.6	-	-	16.56 ± 0.71	-3.5 ± 0.6	-	-	$U^{4+} + 2\ F^- \Leftrightarrow UF_2^{2+}$

		TDB Version 01/01				**TDB Version 12/07**				
Name	**Redox**	**$\log_{10}\beta°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**$\Delta_r S_m°$** [J·K^{-1}·mol^{-1}]	**$S_m°$**	**$\log_{10}\beta°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**$\Delta_r S_m°$** [J·K^{-1}·mol^{-1}]	**$S_m°$**	**Reaction**
UF3+	IV	21.6 ± 1.0	0.5 ± 4.0	-	-	21.89 ± 0.83	0.5 ± 4.0	-	-	$U^{4+} + 3 F^- \Leftrightarrow UF_3^+$
UF4	IV	25.6 ± 1.0	(-4.206)[a]	476 ± 17	-	26.34 ± 0.96	-	476 ± 17	-	$U^{4+} + 4 F^- \Leftrightarrow UF_4(aq)$
UF5-	IV	27.01 ± 0.30	-	-	-	27.73 ± 0.74	-	-	-	$U^{4+} + 5 F^- \Leftrightarrow UF_5^-$
UF6-2	IV	29.08 ± 0.18	-	-	-	29.80 ± 0.70	-	-	-	$U^{4+} + 6 F^- \Leftrightarrow UF_6^{2-}$
UCl+3	IV	1.72 ± 0.13	-19 ± 9	-	-	1.72 ± 0.13	-19 ± 9	-	-	$U^{4+} + Cl^- \Leftrightarrow UCl^{3+}$
UI+3	IV	-	-	-	-	1.25 ± 0.30	-	-	-	$U^{4+} + I^- \Leftrightarrow UI^{3+}$
USO4+2	IV	6.58 ± 0.19	8.0 ± 2.7	-	-	6.58 ± 0.19	8.0 ± 2.7	-	-	$U^{4+} + SO_4^{2-} \Leftrightarrow USO_4^{2+}$
U(SO4)2	IV	10.51 ± 0.20	32.7 ± 2.8	-	-	10.51 ± 0.20	32.7 ± 2.8	-	-	$U^{4+} + 2 SO_4^{2-} \Leftrightarrow U(SO_4)_2(aq)$
UNO3+3	IV	1.47 ± 0.13	-	-	-	1.47 ± 0.13	-	-	-	$U^{4+} + NO_3^- \Leftrightarrow UNO_3^{3+}$
U(NO3)2+2	IV	2.30 ± 0.35	-	-	-	2.30 ± 0.35	-	-	-	$U^{4+} + 2 NO_3^- \Leftrightarrow U(NO_3)_2^{2+}$
U(CO3)4-4	IV	35.22 ± 1.03	-	-	-	35.22 ± 1.03	-	-	-	$U^{4+} + 4 CO_3^{2-} \Leftrightarrow U(CO_3)_4^{4-}$
U(CO3)5-6	IV	(34.1 ± 1.0)[d]	-20 ± 4	-	-	(33.9 ± 1.0)[e]	-20 ± 4	-	-	$U^{4+} + 5 CO_3^{2-} \Leftrightarrow U(CO_3)_5^{6-}$
UCO3(OH)3-	IV	-	-	-	-	(4)*	-	-	-	$U^{4+} + CO_3^{2-} + 3 H_2O(l) \Leftrightarrow UCO_3(OH)_3^- + 3 H^+$
USCN+3	IV	-	-	-	-	(2.83 ± 0.15)*[f]	-27 ± 8	-	-	$U^{4+} + SCN^- \Leftrightarrow USCN^{3+}$
U(SCN)2+2	IV	-	-	-	-	4.26 ± 0.18	-18 ± 4			$U^{4+} + 2 SCN^- \Leftrightarrow U(SCN)_2^{2+}$

[a] Calculated value

[b] Value not selected but supplied by Guillaumont et al. (2003) for guidance or for scoping calculations

[c] This work, the value selected by Guillaumont et al. (2003) is incorrect, see text for discussion (note that Thoenen , 2012, and the electronic versions of TDB 12/07 released before December 2014 contain the incorrect $\log_{10}\beta_3°(UO_2(CO_3)_3^{5-}$, 298.15 K) = 6.95 ± 0.36 by Guillaumont et al., 2003)

[d] This value should have been (33.9 ± 1.0), see text for discussion

[e] Note that Thoenen , 2012, and the electronic versions of TDB 12/07 for PHREEQC and GEMS-PSI released before December 2014 contain the incorrect value of 34.1 ± 1.0

[f] The value (2.97 ± 0.06) selected by Grenthe et al. (1992) is incorrect, see text for discussion (note that Thoenen, 2012, and the electronic versions of the PSI/Nagra TDB 12/07 released before December 2014 contain the incorrect value)

		TDB Version 01/01			**TDB Version 12/07**			
Name	**Redox**	**$\log_{10}K_{s,0}^\circ$**	**S_m°** [$J \cdot K^{-1} \cdot mol^{-1}$]	**$C_{p,m}^\circ$** [$J \cdot K^{-1} \cdot mol^{-1}$]	**$\log_{10}K_{s,0}^\circ$**	**S_m°** [$J \cdot K^{-1} \cdot mol^{-1}$]	**$C_{p,m}^\circ$** [$J \cdot K^{-1} \cdot mol^{-1}$]	**Reaction**
UO2(s)	IV	0 ± 2	77.03 ± 0.20	63.60 ± 0.08	-	-	-	$UO_2(s) + 4 H^+ \Leftrightarrow U^{4+} + 2 H_2O(l)$
UO2(am, hyd)	IV	-	-	-	1.5 ± 1.0	-	-	$UO_2(am, hyd) + 4 H^+ \Leftrightarrow U^{4+} + 2 H_2O(l)$
Metaschoepite[a]	VI	5.96 ± 0.18	188.54 ± 0.38	172.07 ± 0.34	(5.96 ± 0.18)*	188.54 ± 0.38	172.07 ± 0.34	$UO_3 \cdot 2H_2O(cr) + 2 H^+ \Leftrightarrow UO_2^{2+} + 3 H_2O(l)$
UF4:2.5H2O(cr)	IV	-29.38 ± 0.19	263.5 ± 15.0	263.7 ± 15.0	(-30.12 ± 0.70)*	263.5 ± 15.0	263.7 ± 15.0	$UF_4 \cdot 2.5H_2O(cr) \Leftrightarrow U^{4+} + 4 F^- + 2.5 H_2O(l)$
U(OH)2SO4(cr)	IV	-3.17 ± 0.50	-	-	-3.17 ± 0.50	-	-	$U(OH)_2SO_4(cr) + 2 H^+ \Leftrightarrow U^{4+} + SO_4^{2-} + 2 H_2O(l)$
Rutherfordine	VI	-14.49 ± 0.04	144.2 ± 0.3	20.1 ± 0.1	-14.76 ± 0.02	144.2 ± 0.3	20.1 ± 0.1	$UO_2CO_3(cr) \Leftrightarrow UO_2^{2+} + CO_3^{2-}$
(UO2)3(PO4)2:4H2O(cr)	VI	-5.96 ± 0.30	-	-	-5.96 ± 0.30	-	-	$(UO_2)_3(PO_4)_2 \cdot 4H_2O(cr) + 6H^+ \Leftrightarrow 3UO_2^{2+} + 2H_3PO_4(aq) + 4H_2O(l)$
Chernikovite	VI	-2.50 ± 0.09	-	-	-2.50 ± 0.09	-	-	$UO_2HPO_4 \cdot 4H_2O(cr) + 2H^+ \Leftrightarrow UO_2^{2+} + H_3PO_4(aq) + 4H_2O(l)$
Becquerelite	VI	-	-	-	40.5 ± 1.6	-	-	$CaU_6O_{19} \cdot 11H_2O(cr) + 14H^+ \Leftrightarrow Ca^{2+} + 6UO_2^{2+} + 18H_2O(l)$
Compreignacite	VI	-	-	-	37.1 ± 0.5	-	-	$K_2U_6O_{19} \cdot 11H_2O(cr) + 14H^+ \Leftrightarrow 2K^+ + 6UO_2^{2+} + 18H_2O(l)$

[a] Previously referred to as schoepite by Grenthe et al. (1992) and Hummel et al. (2002)

Table 11.4: Selected SIT ion interaction coefficients $\varepsilon_{j,k}$ [kg·mol^{-1}] for uranium species. All data included in TDB Version 12/07 are taken from Grenthe et al. (1992), Grenthe et al. (1995), and Guillaumont et al. (2003) unless indicated otherwise. Own data estimates based on charge correlations (see Appendix A) are shaded. Supplemental data are in italics.

j k→	Cl^-	ClO_4^-	NO_3^-	Li^+	Na^+	K^+
↓	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$
UO2+2	(0.21 ± 0.02)[a]	0.46 ± 0.03	(0.24 ± 0.03)[a]	0	0	0
UO2OH+	0.05 ± 0.10	-0.06 ± 0.40	0.51 ± 1.40	0	0	0
UO2(OH)2	0	0	0	0	0	0
UO2(OH)3-	0	0	0	-	-0.09 ± 0.05	-
UO2(OH)4-2	0	0	0	-	-0.10 ± 0.10	-
(UO2)2OH+3	0.25 ± 0.10	0.6 ± 0.1	-	0	0	0
(UO2)2(OH)2+2	0.69 ± 0.07	0.57 ± 0.07	0.49 ± 0.09	0	0	0
(UO2)3(OH)4+2	0.50 ± 0.18	0.89 ± 0.23	0.72 ± 1.00	0	0	0
(UO2)3(OH)5+	0.81 ± 0.17	0.45 ± 0.15	0.41 ± 0.22	0	0	0
(UO2)3(OH)7-	0	0	0	-	-0.05 ± 0.10	-
(UO2)4(OH)7+	0.05 ± 0.10	0.2 ± 0.1	-	0	0	0
UO2F+	(0.05 ± 0.10)[b]	0.28 ± 0.04	-	0	0	0
UO2F2	0	0	0	0	0	0
UO2F3-	0	0	0	-	-0.14 ± 0.05	-
UO2F4-2	0	0	0	-	-0.30 ± 0.06	-
UO2Cl+	(0.33 ± 0.04)[c]	0.33 ± 0.04	-	0	0	0
UO2Cl2	0	0	0	0	0	0
UO2IO3+	0.05 ± 0.10	0.33 ± 0.04	-	0	0	0
UO2(IO3)2	0	0	0	0	0	0
UO2SO4	0	0	0	0	0	0
UO2(SO4)2-2	0	0	0	-	-0.12 ± 0.06	-
UO2(SO4)3-4	0	0	0	-	(-0.26 ± 0.05)[d]	-
UO2NO3+	0.05 ± 0.10	0.33 ± 0.04	-	0	0	0
UO2PO4-	0	0	0	-	(-0.09 ± 0.05)[e]	-
UO2HPO4	0	0	0	0	0	0
UO2H2PO4+	0.05 ± 0.10	0.2 ± 0.1	-	0	0	0
UO2H3PO4+2	0.15 ± 0.10	0.4 ± 0.1	-	0	0	0
UO2(H2PO4)2	0	0	0	0	0	0
UO2H2PO4H3PO4+	0.05 ± 0.10	0.2 ± 0.1	-	0	0	0
UO2HAsO4	0	0	0	0	0	0
UO2H2AsO4+	0.05 ± 0.10	0.2 ± 0.1	-	0	0	0
UO2(H2AsO4)2	0	0	0	0	0	0
UO2(CO3)2-2	0	0	0	-	(-0.15 ± 0.08)[f]	-
UO2(CO3)3-4	0	0	0	-	-0.01 ± 0.11	-
(UO2)3(CO3)6-6	0	0	0	-	0.37 ± 0.11	-
(UO2)2CO3(OH)3-	0	0	0	-	0.00 ± 0.05	-
(UO2)3O(OH)2HCO3+	0.05 ± 0.10	(0.0 ± 0.1)[g]	-	0	0	0
UO2CO3F-	0	0	0	-	(0.00 ± 0.05)[h]	-
UO2CO3F2-2	0	0	0	-	(-0.02 ± 0.09)[h]	-
UO2CO3F3-3	0	0	0	-	(-0.25 ± 0.05)[h]	-

MgUO2(CO3)3-2	*0*	*0*	*0*	-	*-0.10 ± 0.10*	-
CaUO2(CO3)3-2	*0*	*0*	*0*	-	*-0.10 ± 0.10*	-
Ca2UO2(CO3)3	*0*	*0*	*0*	*0*	*0*	*0*
SrUO2(CO3)3-2	*0*	*0*	*0*	-	*-0.10 ± 0.10*	-
BaUO2(CO3)3-2	*0*	*0*	*0*	-	*-0.10 ± 0.10*	-
Ba2UO2(CO3)3	*0*	*0*	*0*	*0*	*0*	*0*
UO2SCN+	0.05 ± 0.10	(0.26 ± 0.04)[i]	-	0	0	0
UO2(SCN)2	0	0	0	0	0	0
UO2(SCN)3-	0	0	0	-	(0.00 ± 0.05)[j]	-
UO2+	0.05 ± 0.10	0.26 ± 0.03	-	0	0	0
UO2(CO3)3-5	0	0	0	-	(-0.92 ± 0.23)[k]	-
U+4	0.35 ± 0.10	0.76 ± 0.06	-	0	0	0
UOH+3	0.25 ± 0.10	0.48 ± 0.08	-	0	0	0
U(OH)2+2	*0.15 ± 0.10*	*0.4 ± 0.1*	-	*0*	*0*	*0*
U(OH)3+	*0.05 ± 0.10*	*0.2 ± 0.1*	-	*0*	*0*	*0*
U(OH)4	0	0	0	0	0	0
UF+3	0.25 ± 0.10	0.48 ± 0.08	-	0	0	0
UF2+2	(0.3 ± 0.1)[l]	0.3 ± 0.1	-	0	0	0
UF3+	0.1 ± 0.1	0.1 ± 0.1	-	0	0	0
UF4	0	0	0	0	0	0
UF5-	0	0	0	-	-0.05 ± 0.10	-
UF6-2	0	0	0	-	-0.10 ± 0.10	-
UCl+3	(0.59 ± 0.10)[p]	(0.59 ± 0.10)[m]	-	0	0	0
UI+3	0.25 ± 0.10	0.55 ± 0.10	-	0	0	0
USO4+2	0.15 ± 0.10	0.3 ± 0.1	-	0	0	0
U(SO4)2	0	0	0	0	0	0
UNO3+3	0.25 ± 0.10	0.62 ± 0.08	-	0	0	0
U(NO3)2+2	0.15 ± 0.10	0.49 ± 0.14	-	0	0	0
U(CO3)4-4	0	0	0	-	-0.09 ± 0.10	-
U(CO3)5-6	0	0	0	-	-0.30 ± 0.15	-0.70 ± 0.31
UCO3(OH)3-	*0*	*0*	*0*	-	*-0.05 ± 0.10*	-
USCN+3	0.25 ± 0.10	(0.52± 0.10)[n]	-	0	0	0
U(SCN)2+2	0.15 ± 0.10	(0.3 ± 0.1)[o]	-	0	0	0

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[a] This value by Ciavatta (1980) was not used by Grenthe et al. (1992), since Ciavatta (1980) did not explicitly consider the formation of complexes of the metal cations with the background electrolyte anions. Grenthe et al. (1992) did explicitly consider the weak complexation of UO_2^{2+} with chloride and nitrate (if these anions were part of the background electrolyte), using $\varepsilon(UO_2^{2+}, Cl^-) = \varepsilon(UO_2^{2+}, NO_3^-) = \varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$ kg·mol^{-1}.

[b] Instead of the value (0.04 ± 0.07) kg·mol^{-1} by Grenthe et al. (1992), whose origins are unknown (see text for discussion).

[c] This work, in combination with $\varepsilon(UO_2^{2+}, Cl^-) = \varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$ kg·mol^{-1}.

[d] Neither Grenthe et al. (1992) nor Guillaumont et al. (2003) selected a value. This value is estimated from $\varepsilon(P_2O_7^{4-}, Na^+) = -(0.26 \pm 0.05)$ kg·mol^{-1}, see text for discussion.

[e] Sandino (1991).

[f] This work.

[g] Not included by Grenthe et al. (1992) in their list of selected ion interactions coefficients, but used by them (see their p. 646).

[h] Not included by Guillaumont et al. (2003) in their list of selected ion interaction coefficients, but used by them (see their p. 568).

[i] The value (0.22 ± 0.04) kg·mol^{-1} selected by Grenthe et al. (1992) is incorrect, see text for discussion.

[j] Not included by Grenthe et al. (1992) in their list of selected ion interactions coefficients, but used by them (see their p. 331).

[k] This work, instead of -(0.62 ± 0.15) kg·mol^{-1} selected by Grenthe et al. (1995) and retained by Guillaumont et al. (2003), see text.

[l] Not included by Grenthe et al. (1992) in their list of selected ion interaction coefficients, but used by them (see their p. 630).

[m] This value by Grenthe et al. (1992) was replaced by Guillaumont et al. (2003) by (0.50 ± 0.10) kg·mol^{-1}. For reasons discussed in the text, we retained the value by Grenthe et al. (1992).

[n] This work.

[o] Not included by Grenthe et al. (1992) in their list of selected ion interaction coefficients, but used by them (see their p. 332).

[p] This work, in combination with $\varepsilon(U^{4+}, Cl^-) = \varepsilon(U^{4+}, ClO_4^-) = (0.76 \pm 0.06)$ kg·mol^{-1}.

Table 11.5: Selected SIT ion interaction coefficients $\varepsilon_{j,k}$ [kg·mol^{-1}] for neutral uranium species. All data were derived in this work.

j k → **↓**	**$Na^+ + ClO_4^-$** **$\varepsilon_{j,k}$**
UO2F2	0.13 ± 0.05
UO2CO3	0.15 ± 0.06

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12 Zirconium

12.1 Introduction

The data compiled for Zr in Hummel et al. (2002) were based on the in-house review carried out by Curti (2001). In the meantime, newer literature on zirconium has been evaluated in OECD NEA's review "Chemical Thermodynamics of Zirconium" by Brown et al. (2005). The present report very closely follows the review by Brown et al. (2005) and all of the data on zirconium contained in the PSI/Nagra Chemical Thermodynamic Database 12/07 (in the following referred to as "our database") originate from Brown et al. (2005) with the exception of the data for ternary calcium zirconium hydroxide complexes, which were taken from Altmaier et al. (2008), and some estimates of SIT ion interaction coefficients. The selected data are compiled in Tables 12.2–12.4.

Not all data recommended by Brown et al. (2005) are included in our database since the NEA reviews (unlike our database) are not restricted to data relevant for radioactive waste management or even environmental modeling in general. We tried to exclude from our database all phases and aqueous species which most probably will never be relevant in low temperature ($T <$ about 150°C) environmental systems. The omitted solids, liquids and gases are listed in Table 12.1, while all aqueous species were accepted.

The NEA review volumes provide tables with selected SIT coefficients for the interaction of cations with Cl^-, ClO_4^-, and NO_3^-, and of anions with Li^+, Na^+, and K^+. Since numerous ion interaction coefficients are not known, we used an estimation method based on charge correlations to fill the gaps (see Appendix A).

The notation of formulae and symbols used in this text follows the NEA recommendations.

12.2 Elemental zirconium

Zirconium metal, liquid and gas are not relevant under environmental conditions. Therefore, the thermodynamic data selected by Brown et al. (2005) for Zr(β), Zr(ω), Zr(l), and Zr(g) are not included in our database. However, the absolute entropy and heat capacity of Zr(α), in our database referred to as Zr(cr), are included as they are used for the calculation of certain thermodynamic reaction properties. The values selected by Brown et al. (2005)

$$S_m°(\text{Zr, cr, 298.15 K}) = (39.08 \pm 0.10)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

$$C_{p,m}°(\text{Zr, cr, 298.15 K}) = (26.08 \pm 0.05)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

were derived from calorimetric heat capacity measurements.

12.3 Zirconium aqua ions

Zirconium exists in aqueous solution only in the +4 oxidation state. In earlier times (until the middle of the last century) it was believed that the solution chemistry of zirconium was dominated by the zirconyl ion ZrO^{2+}. Crystal structure determinations, however, of so-called zirconyl chloride and bromide octahydrates by Clearfield & Vaughan (1956) disproved the existence of a zirconyl ionic structure. No zirconium halogen bonds were found and the central moiety of the solid zirconium halogen "complexes" turned out to be $[Zr_4(OH)_8\cdot16H_2O]^{8+}$. Hence, the formula for "zirconyl chloride octahydrate" "$ZrOCl_2\cdot8H_2O$(cr)" should rather be understood as $Zr(OH)_2(H_2O)_7Cl_2$(cr). X-ray diffraction results by Muha & Vaughan (1960) for 0.5–2 m aqueous solutions of "$MOX_2\cdot8H_2O$" (with M = Zr and Hf, and X = Cl and Br) could be explained by the existence of aqueous complexes of the type $M_4(OH)_8(H_2O)_{16}X_8$, with a structure very similar to that found in the solids. According to Brown et al. (2005), there has never been found any unequivocal evidence for the zirconyl ion, neither in solids, nor in aqueous solution.

The free aqua ion Zr^{4+} is only stable under very acidic conditions due to its strong tendency for hydrolysis and polymerization. Brown et al. (2005) stressed that the thermodynamic data they selected for Zr^{4+} strongly relies on the overall fit of the hydrolysis data (discussed in Section 12.4.1 below). The standard molar Gibbs free energy of formation for Zr^{4+} selected by Brown et al. (2005)

$$\Delta_f G_m°(Zr^{4+}, 298.15\ K) = -(528.5 \pm 9.2)\ kJ\cdot mol^{-1}$$

was calculated from the selected equilibrium constant $\log_{10}K_{s,0}° = -(7.0 \pm 1.6)$ (see Section 12.4.3 below), equivalent to $\Delta_r G_m° = (40.0 \pm 9.1)\ kJ\cdot mol^{-1}$, for the reaction

$$ZrO_2(cr) + 4\ H^+ \Leftrightarrow Zr^{4+} + 2\ H_2O(l)$$

and from the selected $\Delta_f G_m°(ZrO_2, cr, 298.15\ K) = -(1042.6 \pm 0.7)\ kJ\cdot mol^{-1}$ (see Section 12.4.3 below) and $\Delta_f G_m°(H_2O, l, 298.15\ K) = -(237.140 \pm 0.041)\ kJ\cdot mol^{-1}$. The standard molar enthalpy of formation selected by Brown et al. (2005)

$$\Delta_f H_m°(Zr^{4+}, 298.15\ K) = -(608.5 \pm 5.0)\ kJ\cdot mol^{-1}$$

is based on calorimetrically determined enthalpies of dissolution for $ZrCl_4$(cr) and $ZrBr_4$(cr) in $HClO_4$, HNO_3, and HCl, corrected by Brown et al. (2005) for the formation of polynuclear complexes at high concentrations of Zr. $\Delta_f S_m°(Zr^{4+}, 298.15\ K)$ was calculated by Brown et al. (2005) from $\Delta_f G_m°(Zr^{4+}, 298.15\ K)$ and $\Delta_f H_m°(Zr^{4+}, 298.15\ K)$ by means of G = H - TS. Using the selected values $S_m°(Zr, cr, 298.15\ K) = (39.08 \pm 0.10)\ J\cdot K^{-1}\cdot mol^{-1}$ and $S_m°(H_2, g, 298.15\ K) = (130.680 \pm 0.003)\ J\cdot K^{-1}\cdot mol^{-1}$, Brown et al. (2005) obtained

$$S_m°(Zr^{4+}, 298.15\ K) = -(491.0 \pm 35.2)\ J\cdot K^{-1}\cdot mol^{-1}$$

The values of $\Delta_f G_m°$, $\Delta_f H_m°$, and $S_m°$ selected by Brown et al. (2005) for Zr^{4+} are included in our database.

The SIT interaction coefficient of Zr^{4+} with ClO_4^- was obtained by Brown et al. (2005) from an SIT analysis of experimental data for the reaction $Zr^{4+} + HF(aq) \Leftrightarrow ZrF^{3+} + H^+$ (see Section 12.5.1.1 below), resulting in

$$\varepsilon(Zr^{4+}, ClO_4^-) = (0.89 \pm 0.10)\ kg\cdot mol^{-1}$$

The interaction coefficients of Zr^{4+} with Cl^- and NO_3^- could not be derived from experimental data and Brown et al. (2005) had to take recourse to estimation methods. From an empirical linear relation between the values of interaction coefficients of simple cations in perchlorate media and the ratios of their charge with the square root of their radius, Brown et al. (2005) estimated

$$\varepsilon(Zr^{4+}, Cl^-) = (0.33 \pm 0.09)\ kg\cdot mol^{-1}$$

For the interaction with NO_3^-, Brown et al. (2005) used Th^{4+} as a substitute for Zr^{4+}, assuming that homovalent pairs of ions have similar ion interaction coefficients. Hence,

$$\varepsilon(Zr^{4+}, NO_3^-) \approx \varepsilon(Th^{4+}, NO_3^-) = (0.33 \pm 0.35)\ kg\cdot mol^{-1}$$

The ion interaction coefficients selected by Brown et al. (2005) for Zr^{4+} are also included in our database.

12.4 Zirconium hydrogen and oxygen compounds and complexes

12.4.1 Aqueous zirconium hydroxide complexes

There is a large number of experimental data on the stoichiometry and stability of aqueous zirconium hydroxide complexes. Brown et al. (2005) noted, however, that the hydrolysis constants reported in the literature are highly contradictory. For a given ionic strength, e.g., the reported stability constants for $Zr(OH)_2^{2+}$ and for $Zr(OH)_3^-$ vary over four orders of magnitude, those for $Zr(OH)_4(aq)$ over five orders of magnitude, and those for $Zr_4(OH)_8^{8+}$ over ten orders of magnitude (in this case the ionic strength varies between 1 and 2 m). In addition, many investigators based their interpretations of experimental data on untested or on inconsistent hypotheses, especially with respect to the nature and predominance of monomeric species under experimental conditions where polymers might be favored. By direct SIT-regression of published results, Brown et al. (2005) were only able to derive standard stability constants for $ZrOH^{3+}$ and $Zr_3(OH)_4^{8+}$. The stability constants for all other zirconium hydroxide complexes needed a global reinterpretation of the experimental data using common and consistent hypotheses for all data.

The main points of the reinterpretation by Brown et al. (2005) are as follows: There is clear evidence that polynuclear hydroxide complexes are formed even in extremely acid solutions, i.e., they become dominant at a pH as low as about 0.5 for zirconium concentrations around 10^{-4} m. Polymerization increases with increasing pH and Zr concentration. Structural studies of highly concentrated Zr solutions and of the solids precipitated from these solutions reveal that tetrameric hydroxide complexes are the dominant stable polynuclear solution species over a wide range of pH. Higher degrees of polymerization are sometimes observed and the degree of polymerization increases with time, suggesting that such highly polymerized species are metastable intermediates at the onset of precipitation. Thus, the maximum degree of polymerization in the hydrolysis model is four. At high pH, there appears to be a region where a negatively charged monomer becomes dominant.

Based on these observations, Brown et al. (2005) concluded that many zirconium hydrolysis models in the literature are erroneous, but that their basic experimental data can still be taken advantage of in a global reevaluation. For this purpose, Brown et al. (2005) used the following procedure: In a first step, the stability constants and ion interaction coefficients for $ZrOH^{3+}$ and for $Zr_3(OH)_4^{8+}$ were obtained from selected sets of data by standard SIT-regression. In a second step, the equilibrium constants and ion interaction parameters for all other species in the hydrolysis model were obtained by a global least-squares-type fit (minimizing an objective function that is composed of the squares of the deviations of the calculated from the experimental quantities) to the complete set of experimental data, keeping the stability constants and ion interaction coefficients for $ZrOH^{3+}$ and for $Zr_3(OH)_4^{8+}$ fixed at the values derived in the first step. The global fit was based on a preselection of the dominant species, which always included $Zr(OH)_4(aq)$, $Zr_4(OH)_8^{8+}$, $Zr_4(OH)_{15}^+$, and $Zr_4(OH)_{16}(aq)$. Various other mono-, di-, tri-, and tetrameric species were added to improve the fit (although with hardly an objective base for their selection). If the fitted results were found to be insensitive to the stability constant of a given species, the species was removed from the list of considered species. The set of species resulting in the lowest overall objective function was considered as best fit and was used as hydrolysis model. In this way, Brown et al. (2005) obtained their zirconium hydrolysis model, which consists of stability constants and ion interaction coefficients for $ZrOH^{3+}$, $Zr(OH)_2^{2+}$, $Zr(OH)_4(aq)$, $Zr(OH)_6^{2-}$, $Zr_3(OH)_4^{8+}$, $Zr_3(OH)_9^{3+}$, $Zr_4(OH)_8^{8+}$, $Zr_4(OH)_{15}^+$, and $Zr_4(OH)_{16}(aq)$.

Monomeric hydrolysis species: The stability constant selected by Brown et al. (2005) for $ZrOH^{3+}$ is based on two studies in mixed $HClO_4/NaClO_4$ solutions (1 and 4 M) using potentiometry, spectrophotometry, and liquid ion exchange. SIT analysis of three data points resulted in

$$Zr^{4+} + H_2O(l) \Leftrightarrow ZrOH^{3+} + H^+$$

$$\log_{10}{}^*\beta_{1,1}^\circ(298.15) = (0.32 \pm 0.22)$$

with $\Delta\varepsilon = -(0.18 \pm 0.08)$ kg·mol^{-1} and

$$\varepsilon(ZrOH^{3+}, ClO_4^-) = (0.57 \pm 0.13) \text{ kg·mol}^{-1}$$

following from the value of $\Delta\varepsilon$ and from the selected $\varepsilon(Zr^{4+}, ClO_4^-) = (0.89 \pm 0.10)$ kg·mol^{-1} and $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$ kg·mol^{-1}.

The stability constant and SIT coefficient for $Zr(OH)_2^{2+}$ were obtained by Brown et al. (2005) from the global fit to the hydrolysis data:

$$Zr^{4+} + 2\ H_2O(l) \Leftrightarrow Zr(OH)_2^{2+} + 2\ H^+$$

$$\log_{10}{}^*\beta_{2,1}^\circ(298.15) = (0.98 \pm 1.06)$$

$$\varepsilon(Zr(OH)_2^{2+}, ClO_4^-) = (0.62 \pm 0.39) \text{ kg·mol}^{-1}$$

Brown et al. (2005) did not select any stability constant for $Zr(OH)_3^+$. Due to the apparently small stability field of this species, the global fit to the available hydrolysis data did not fully constrain its stability constant, i.e., the resulting uncertainty was too large to justify the selection of a value.

In the case of $Zr(OH)_4(aq)$, the global fit to the available hydrolysis data resulted in

$$Zr^{4+} + 4\ H_2O(l) \Leftrightarrow Zr(OH)_4(aq) + 4\ H^+$$

$$\log_{10}{}^*\beta_{4,1}^\circ(298.15) = -(2.19 \pm 1.70)$$

The formation of $Zr(OH)_5^-$ was proposed on the basis of an experimental observation that, at high pH, the solubility of zirconium hydroxide increases with pH. A later experiment suggested, however, that the observed solubility increase was rather due to a contamination with carbon dioxide leading to the formation of Zr carbonate complexes. For this reason, Brown et al. (2005) did not consider any stability constant for $Zr(OH)_5^-$.

Solubility experiments of Zr hydroxides in alkaline media showed that Zr solubility increases with increasing pH, which is compatible with the formation of the zirconate ion, ZrO_3^{2-}, or of $Zr(OH)_6^{2-}$. Since there is no evidence from the solubility experiments as to the true stoichiometry of this divalent anion, Brown et al. (2005) assumed it to be $Zr(OH)_6^{2-}$, based on the absence of discrete zirconate ions in crystalline so-called zirconate phases. The solubility data were included by Brown et al. (2005) in the global fit, leading to

$$Zr^{4+} + 6\ H_2O(l) \Leftrightarrow Zr(OH)_6^{2-} + 6\ H^+$$

$$\log_{10}{}^*\beta_{6,1}^\circ(298.15) = -(29.0 \pm 0.70)$$

The ion interaction coefficient

$$\varepsilon(Zr(OH)_6^{2-}, Na^+) = -(0.10 \pm 0.10) \text{ kg·mol}^{-1}$$

was estimated by Brown et al. (2005) from the NEA-selected interaction coefficients of fourteen twofold negative charged species.

Dimeric hydrolysis species: The presence of $Zr_2(OH)_7^+$ was reported in a study based on potentiometric and solubility data. Brown et al. (2005), however, found the overall hydrolysis model applied in this study as incompatible with the presence of dimeric species and suggested that the proposed dimer is more likely the tetramer $Zr_4(OH)_{15}^+$.

Trimeric hydrolysis species: In very acid media, $Zr_3(OH)_4^{8+}$ becomes dominant. Brown et al. (2005) reanalyzed experimental data from five studies that applied solvent extraction, spectroscopy, and potentiometry in chloride and perchlorate media. The SIT-regression lines for perchlorate and chloride media intersected at infinite dilution, supporting the experimental data, and Brown et al. (2005) obtained

$$3\ Zr^{4+} + 4\ H_2O(l) \Leftrightarrow Zr_3(OH)_4^{8+} + 4\ H^+$$

$$\log_{10}{}^*\beta_{4,3}°(298.15) = (0.4 \pm 0.3)$$

with $\Delta\varepsilon_{4,3}(HClO_4)$ = -(0.22 ± 0.05) kg·mol^{-1} and $\Delta\varepsilon_{4,3}(HCl)$ = -(0.18 ± 0.06) kg·mol^{-1}. From these values for $\Delta\varepsilon$ and the selected $\varepsilon(Zr^{4+}, Cl^-)$ = (0.33 ± 0.09) kg·mol^{-1}, $\varepsilon(H^+, Cl^-)$ = (0.12 ± 0.01) kg·mol^{-1}, $\varepsilon(Zr^{4+}, ClO_4^-)$ = (0.89 ± 0.10) kg·mol^{-1}, and $\varepsilon(H^+, ClO_4^-)$ = (0.14 ± 0.02) kg·mol^{-1}, Brown et al. (2005) calculated

$$\varepsilon(Zr_3(OH)_4^{8+}, Cl^-) = (0.33 \pm 0.28)\ kg{\cdot}mol^{-1}$$

$$\varepsilon(Zr_3(OH)_4^{8+}, ClO_4^-) = (1.89 \pm 0.31)\ kg{\cdot}mol^{-1}$$

The ion interaction coefficient

$$\varepsilon(Zr_3(OH)_4^{8+}, NO_3^-) = (2.28 \pm 0.35)\ kg{\cdot}mol^{-1}$$

resulted from the global fit to the hydrolysis data.

The standard molar enthalpy of formation for $Zr_3(OH)_4^{8+}$

$$\Delta_f H_m°(Zr_3(OH)_4^{8+}, 298.15\ K) = -(2970.8 \pm 10.0)\ kJ{\cdot}mol^{-1}$$

selected by Brown et al. (2005) is based on a reevaluation of measured enthalpies of dissolution of $ZrCl_4(cr)$ in perchloric, hydrochloric, and nitric acid.

The trimer $Zr_3(OH)_9^{3+}$ was introduced by Brown et al. (2005)—without any experimental evidence—just to improve the quality of the global fit to the experimental data. They obtained

$$3\ Zr^{4+} + 9\ H_2O(l) \Leftrightarrow Zr_3(OH)_9^{3+} + 9\ H^+$$

$$\log_{10}{}^*\beta_{9,3}°(298.15) = (12.19 \pm 0.08)$$

and

$$\varepsilon(Zr_3(OH)_9^{3+}, ClO_4^-) = (0.93 \pm 0.35)\ kg{\cdot}mol^{-1}$$

from the global fit but stressed that this species has not yet been identified or proposed in the experimental literature and that additional experiments are needed to confirm its existence and its field of stability.

Tetrameric hydrolysis species: The stability constants and ion interaction coefficients for the tetramers $Zr_4(OH)_8^{8+}$, $Zr_4(OH)_{15}^{+}$, and $Zr_4(OH)_{16}(aq)$ were all derived from the global fit to the available hydrolysis data, leading to

$$4\ Zr^{4+} + 8\ H_2O(l) \Leftrightarrow Zr_4(OH)_8^{8+} + 8\ H^+$$

$$\log_{10}{}^*\beta_{8,4}°(298.15) = (6.52 \pm 0.65)$$

$$\varepsilon(Zr_4(OH)_8^{8+}, ClO_4^-) = (3.61 \pm 1.02)\ kg{\cdot}mol^{-1}$$

$$4\ Zr^{4+} + 15\ H_2O(l) \Leftrightarrow Zr_4(OH)_{15}^{+} + 15\ H^+$$

$$\log_{10}{}^*\beta_{15,4}°(298.15) = (12.58 \pm 0.24)$$

$$\varepsilon(Zr_4(OH)_{15}^{+}, ClO_4^-) = (0.09 \pm 0.92)\ kg{\cdot}mol^{-1}$$

$$\varepsilon(\mathrm{Zr_4(OH)_{15}^{+}, NO_3^{-}}) = -(0.02 \pm 1.46)\ \mathrm{kg{\cdot}mol^{-1}}$$

$$4\ \mathrm{Zr^{4+}} + 16\ \mathrm{H_2O(l)} \Leftrightarrow \mathrm{Zr_4(OH)_{16}(aq)} + 16\ \mathrm{H^+}$$

$$\log_{10}{}^*\beta_{16,4}^{\circ}(298.15) = (8.39 \pm 0.80)$$

The standard molar enthalpy of formation for $Zr_4(OH)_{16}(aq)$ was derived by Brown et al. (2005) from a heat of solution measurement of $ZrCl_4(cr)$ in aqueous solution. Their selected value is

$$\Delta_f H_m^{\circ}(\mathrm{Zr_4(OH)_{16}, aq, 298.15\ K}) = -(6706.16 \pm 7.20)\ \mathrm{kJ{\cdot}mol^{-1}}$$

Since several ion interaction coefficients of zirconium hydrolysis species with Cl^- are missing, we estimated

$$\varepsilon(\mathrm{ZrOH^{3+}, Cl^{-}}) = (0.25 \pm 0.10)\ \mathrm{kg{\cdot}mol^{-1}}$$

$$\varepsilon(\mathrm{Zr(OH)_2^{2+}, Cl^{-}}) = (0.15 \pm 0.10)\ \mathrm{kg{\cdot}mol^{-1}}$$

$$\varepsilon(\mathrm{Zr_3(OH)_9^{3+}, Cl^{-}}) = (0.25 \pm 0.10)\ \mathrm{kg{\cdot}mol^{-1}}$$

$$\varepsilon(\mathrm{Zr_4(OH)_8^{8+}, Cl^{-}}) = (0.75 \pm 0.50)\ \mathrm{kg{\cdot}mol^{-1}}$$

$$\varepsilon(\mathrm{Zr_4(OH)_{15}^{+}, Cl^{-}}) = (0.05 \pm 0.10)\ \mathrm{kg{\cdot}mol^{-1}}$$

based on charge correlations (see Appendix A).

In a study that was carried out after the publication of Brown et al. (2005), Walther et al. (2007) investigated the speciation of Zr in acidic solutions (pH_c=0–3) at total Zr concentrations between 1.5 x 10^{-3} and 10^{-2} M, with time-of-flight electrospray mass spectrometry (ESI-MS) and X-ray absorption spectroscopy (XANES, XAFS). The solutions were prepared by dissolving "zirconyl chloride hydrate" ("$ZrOCl_2{\cdot}xH_2O(cr)$", which rather corresponds to $Zr(OH)_2(H_2O)_{x-1}Cl_2$, see discussion in Section 12.3 above) in hydrochloric acid of appropriate concentration.

The ESI-MS measurements were conducted using mild injection conditions (low flow rate and low electrostatic potential) to avoid the splitting of the (nanometric) droplets and other secondary effects. The good agreement of the obtained data with the EXAFS results and with independent published data is a convincing argument in favor of the non-invasiveness of the method. The authors conclude that the observed mass distributions faithfully reflect the complexes present in the solution.

Because of the large number of stable isotopes in natural Zr, it was possible to resolve unequivocally the very complex mass spectra and to assign to each peak an unambiguous stoichiometry. Typically, the measured masses consisted of polymeric Zr-hydroxo species with chloride ions and up to 20–25 water molecules in the solvation shell. The main results from this study can be summarized as follows:

1. At these relatively high Zr concentrations (1.5 x 10^{-3}–10^{-2} M) and low pH the Zr hydroxo species are dominantly polymeric; nevertheless also monomers were detected.
2. A large number of polymeric species was identified. In general, the degree of polymerization was found to increase with increasing pH and the mean charge of the hydroxo species approached to -2 towards the solubility limit of amorphous $Zr(OH)_4$.
3. Overall, tetramers, pentamers and octamers (with a variable number of hydroxyls) are the dominating species.
4. No evidence was found for the presence of trimeric species. Hence, the existence of $Zr_3(OH)_4^{8+}$ and $Zr_3(OH)_9^{3+}$, two complexes proposed and selected by Brown et al. (2005) is not confirmed by the ESI-MS data.

The X-ray spectroscopic data generally agree with the ESI-MS data. In particular, the Fourier transforms of solutions dominated by polymeric species ([Zr]= 10 mM) could only be fitted by splitting the first oxygen shell in two distances (4 O at 2.12 and 4 O at 2.26 A), in agreement with the structural parameters for the tetrameric units of "$ZrOCl_2 \cdot 8H_2O$". In addition, the fitting of Zr-Zr backscattering peaks could be fitted assuming CN ~ 1–2, as expected from the polymer structures. The broadening and in some cases disappearance of the Zr-Zr contribution was explained by the simultaneous presence of many different Zr species in the intermediate pH range (0.6–1.5) as indicated by the ESI-MS data (see Fig. 7 in original paper).

In summary, the work of Walther et al. (2007) provides valuable insight into the process of Zr polymerization at low pH and high Zr concentrations. The results disprove the existence of $Zr_3(OH)_4^{8+}$ and $Zr_3(OH)_9^{3+}$ and indicate the formation of a large variety of Zr hydroxo polymers (note, however, that the solubilities measured by Altmaier et al. (2008) of aged $Zr(OH)_4$ precipitates at pH < 3 in $CaCl_2$ and in NaCl solutions are consistent with the formation of $Zr_3(OH)_9^{3+}$, see Section 12.4.2 below). On the other hand, a thermodynamic model including all the species detected by ESI-MS would be highly impractical and not credible, due to the large number of unconstrained model parameters.

Despite the fact that $Zr_3(OH)_4^{8+}$ and $Zr_3(OH)_9^{3+}$ were not identified by Walther et al. (2007) we have decided to adopt the hydrolysis model by Brown et al. (2005), as presented in this Section, for our database. Brown et al. (2005) state in the preface of their review: *"The contribution of Bernd Grambow warrants a special mention. As is clear from the review, data on the hydrolysis of zirconium reported in the literature is highly contradictory. For example, the variation in a stability constant, at a particular ionic strength, may be as great as ten orders of magnitude. To overcome this difficulty, the original experimental data was reinterpreted in the present review to obtain a consistent hydrolysis model with common hypotheses. This model was critical in the interpretation and re-interpretation of the thermochemical data in all other sections of the book".* Thus, for the sake of consistency with all the other zirconium data, the hydrolysis model by Brown et al. (2005) cannot be disposed of. Brown et al. (2005) continue in the preface: *"To our knowledge, this is the first time that a reevaluation has been undertaken in this way. Due to the complexity and contradictory nature of currently available hydrolysis data, we nevertheless feel that, at least in the low pH-region, the data selected in this review will be susceptible to amendments in the future".* It is very important to keep this in mind when using these data.

12.4.2 Aqueous calcium zirconium hydroxide complexes

Altmaier et al. (2008) studied the solubility of Zr(IV), Th(IV), and U(IV) oxyhydroxide precipitates, which can be described as $MO_2 \cdot xH_2O(pr)$ or as $M(OH)_4(pr)$, in 0.1–4.5 M $CaCl_2$ solutions. In the case of Zr, solubilities decrease at pH 1 to 3 with a slope consistent with the formation of $Zr_3(OH)_9^{3+}$. At pH 3 to 9, Zr concentrations remain constant, due to the formation of neutral $Zr(OH)_4(aq)$, or a multiple thereof. At pH > 9 solubilities increase, which, unlike the solubility increase observed in NaCl and $NaClO_4$ solutions at pH > 12, cannot be explained by the formation of $Zr(OH)_6^{2-}$. The data could best be interpreted by Altmaier et al. (2008) with the ternary calcium zirconium hydroxide complexes $Ca_2Zr(OH)_6^{2+}$ and $Ca_3Zr(OH)_6^{4+}$. The latter complex was identified by Brendebach et al. (2007) in an EXAFS study. From an SIT regression of the solubility data, Altmaier et al. (2008) obtained $\log_{10}K_{s,(2,1,6)}°(298.15 \text{ K}) = (1.1 \pm 0.2)$ for $Zr(OH)_4(pr) + 2\ OH^- + 2\ Ca^{2+} \Leftrightarrow Ca_2Zr(OH)_6^{2+}$ and $\log_{10}K_{s,(3,1,6)}°(298.15 \text{ K}) = (0.5 \pm 0.2)$ for $Zr(OH)_4(pr) + 2\ OH^- + 3\ Ca^{2+} \Leftrightarrow Ca_3Zr(OH)_6^{4+}$ and $\log_{10}K_{s,(0,1,6)}°(298.15 \text{ K}) = -(5.5 \pm 0.2)$ for $Zr(OH)_4(pr) + 2\ OH^- \Leftrightarrow Zr(OH)_6^{2-}$ in the Ca-free system. From their solubility product $\log_{10}K_{s,0}°(298.15 \text{ K}) = -(60.3 \pm 0.2)$ for $Zr(OH)_4(pr) \Leftrightarrow Zr^{4+} + 4\ OH^-$ then follow $\log_{10}\beta_{2,1,6}°(298.15 \text{ K}) = (61.4 \pm 0.3)$ for the reaction $2\ Ca^{2+} + Zr^{4+} + 6\ OH^- \Leftrightarrow Ca_2Zr(OH)_6^{2+}$, $\log_{10}\beta_{3,1,6}°(298.15 \text{ K}) = (60.8 \pm 0.3)$ for the reaction $3\ Ca^{2+} + Zr^{4+} + 6\ OH^- \Leftrightarrow Ca_3Zr(OH)_6^{4+}$ and $\log_{10}\beta_{0,1,6}°(298.15 \text{ K}) = (54.8 \pm 0.3)$ for the reaction $Zr^{4+} + 6\ OH^- \Leftrightarrow Zr(OH)_6^{2-}$ (note that the value for $\log_{10}\beta_{0,1,6}°(298.15 \text{ K})$ selected by Brown et al. 2005 and included in our database is 55.0 ± 0.7). For inclusion in our database, we used the dissociation constant of water to express the reactions in terms of $H_2O(l)$ and H^+ instead of OH^-. Thus

$$2\ Ca^{2+} + Zr^{4+} + 6\ H_2O(l) \Leftrightarrow Ca_2Zr(OH)_6^{2+} + 6\ H^+$$

$$\log_{10}{}^*\beta_{2,1,6}°(298.15 \text{ K}) = -(22.6 \pm 0.3)$$

$$3\ Ca^{2+} + Zr^{4+} + 6\ H_2O(l) \Leftrightarrow Ca_3Zr(OH)_6^{4+} + 6\ H^+$$

$$\log_{10}{}^*\beta_{3,1,6}°(298.15 \text{ K}) = -(23.2 \pm 0.3)$$

From the Δε values of their SIT regressions, Altmaier et al. (2008) obtained

$$\varepsilon\varepsilon(Ca_2Zr(OH)_6^{2+}, Cl^-) = (0.1 \pm 0.1) \text{ kg·mol}^{-1}$$

$$\varepsilon(Ca_3Zr(OH)_6^{4+}, Cl^-) = (0.40 \pm 0.07) \text{ kg·mol}^{-1}$$

by using their experimentally determined $\varepsilon(OH^-, Ca^{2+}) = -(0.45 \pm 0.03)$ kg·mol^{-1} and $\varepsilon(Ca^{2+}, Cl^-) = (0.12 \pm 0.01)$ kg·mol^{-1} selected by NEA (e.g., Brown et al. 2005). Altmaier et al. (2008) also measured the solubility of $Zr(OH)_4(pr)$ in $Ca(ClO_4)_2$ solutions. The value

$$\varepsilon(Ca_3Zr(OH)_6^{4+}, ClO_4^-) = (0.89 \pm 0.12) \text{ kg·mol}^{-1}$$

was derived by Altmaier et al. (2008) from these experiments, while they estimated

$$\varepsilon(Ca_2Zr(OH)_6^{2+}, ClO_4^-) = (0.3 \pm 0.1) \text{ kg·mol}^{-1}$$

by analogy from known SIT coefficients for ions with the same charge. These interaction coefficients of $Ca_2Zr(OH)_6^{2+}$ and $Ca_3Zr(OH)_6^{4+}$ with Cl^- and ClO_4^- are included in our database, as well as $\varepsilon(OH^-, Ca^{2+})$.

For estimating the stability constant of $CaZr(OH)_6(aq)$, which is negligible at Ca concentrations lager than 0.1 M, Altmaier et al. (2008) proceeded as follows (for this discussion, we neglect the uncertainties and keep in mind that the equilibrium constants refer to 298.15 K): From $\log_{10}\beta_{2,1,6}° = 61.4$ and $\log_{10}\beta_{3,1,6}° = 60.8$ follows $\log_{10}K_3° = -0.6$ for the reaction $Ca_2Zr(OH)_6^{2+} + Ca^{2+} \Leftrightarrow Ca_3Zr(OH)_6^{4+}$. Furthermore, from $\log_{10}\beta_{0,1,6}° = 54.8$ and $\log_{10}\beta_{2,1,6}° = 61.4$ follows $\log_{10}\beta_2° = 6.6$ for the reaction $Zr(OH)_6^{2-} + 2\ Ca^{2+} \Leftrightarrow Ca_2Zr(OH)_6^{2+}$. Altmaier et al. (2008) assumed a linear decrease of $\log_{10}K_n°$ for the stepwise association of Ca^{2+} to $Zr(OH)_6^{2-}$

$$Ca_{n-1}Zr(OH)_6^{2n-4} + Ca^{2+} \Leftrightarrow Ca_nZr(OH)_6^{2n-2}$$

Thus,

$$\log_{10}K_1° - \log_{10}K_2° = \log_{10}K_2° - \log_{10}K_3° = \log_{10}K_2° + 0.6$$

In addition

$$\log_{10}\beta_2° = \log_{10}K_1° + \log_{10}K_2° = 6.6$$

From these two equations then follows that $\log_{10}K_1°(298.15\ K) = 4.6$ and $\log_{10}K_2°(298.15\ K) = 2.0$. Combining $\log_{10}K_1°(298.15\ K)$ with $\log_{10}\beta_{0,1,6}°(298.15\ K) = (54.8 \pm 0.3)$ leads to the estimate by Altmaier et al. (2008) for

$$Ca^{2+} + Zr^{4+} + 6\ OH^- \Leftrightarrow CaZr(OH)_6(aq)$$

$$\log_{10}\beta_{1,1,6}°(298.15\ K) = 59.4 \pm 0.3$$

We include this estimate in the supplemental data of our database, rewriting the equilibrium in terms of H^+ and $H_2O(l)$ instead of OH^-. Hence

$$Ca^{2+} + Zr^{4+} + 6\ H_2O(l) \Leftrightarrow CaZr(OH)_6(aq) + 6\ H^+$$

$$\log_{10}{}^*\beta_{1,1,6}°(298.15\ K) = -(24.6 \pm 0.3)$$[38]

12.4.3 Crystalline and amorphous zirconium oxides and dioxides

The most stable zirconium oxide solid is ZrO_2 and its monoclinic low-temperature (T < 1147°C) polymorph is the mineral baddeleyite, which appears to be the solubility-limiting phase in low-temperature natural waters. Brown et al. (2005) accepted data from a solubility study of amorphous and of well-crystallized ZrO_2. Since the measured solubilities were very similar, datasets of both phases were included in the overall fit procedure for the hydrolysis model, from which Brown et al. (2005) obtained

$$ZrO_2(\text{baddeleyite}) + 4\ H^+ \Leftrightarrow Zr^{4+} + 2\ H_2O(l)$$

$$\log_{10}K_{s,0}°(298.15\ K) = -(7.0 \pm 1.6)$$

The value for the formation enthalpy of baddeleyite selected by Brown et al. (2005)

$$\Delta_f H_m°(\text{baddeleyite, 298.15 K}) = -(1100.6 \pm 1.3)\ kJ\cdot mol^{-1}$$

is the weighted average of two values that were determined by oxygen bomb calorimetry. Brown et al. (2005) reevaluated data from two studies of the low-temperature heat capacity of baddeleyite. They fitted data in the temperature range from 50 to 301 K by least squares analysis and calculated the standard molar heat capacity for baddeleyite

$$C_{p,m}°(\text{baddeleyite, 298.15 K}) = (55.96 \pm 0.79)\ J\cdot K^{-1}\cdot mol^{-1}$$

from the regression equation.

In the initial phase of precipitation from Zr solutions, the solids formed are often amorphous and gelatinous oxyhydroxides. Brown et al. (2005) referred to those as $Zr(OH)_4$(am, fresh), but they remarked that this is rather a name than a real composition. They included datasets from three solubility studies in the overall fit procedure for the hydrolysis model and selected the average of the two largest solubility constants[39]. Hence

$$Zr(OH)_4(\text{am, fresh}) + 4\ H^+ \Leftrightarrow Zr^{4+} + 4\ H_2O(l)$$

$$\log_{10}K_{s,0}°(298.15\ K) = -(3.24 \pm 0.10)$$

All these data for baddeleyite and $Zr(OH)_4$(am, fresh) are included in our database. The solubility product measured by Altmaier et al. (2008) for $Zr(OH)_4(s)$, $\log_{10}K_{s,0}°(298.15\ K)$

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[38] Note that the uncertainty was not reported in Thoenen (2012).

[39] Note that the explanations by Brown et al. (2005) made it not entirely clear to us, how the solubility constants for different experimental datasets were extracted individually.

= -(4.3 ± 0.2) is typical for an aged precipitate and lies in between the selected values for $Zr(OH)_4$(am, fresh) and ZrO_2(baddeleyite).

12.4.4 Gaseous zirconium oxides and dioxides

The thermodynamic data selected by Brown et al. (2005) for ZrO(g) and ZrO_2(g) are not included in our database since these gases are not relevant in natural environments.

12.4.5 Zirconium hydride

Brown et al. (2005) calculated standard molar Gibbs free energies of formation for ZrH(cr) and $ZrH_2(\varepsilon)$ from calorimetric measurements. These synthetic solids are not found in natural environments and are therefore not considered in our database.

12.5 Zirconium halogen compounds and complexes

12.5.1 Fluorine compounds and complexes

12.5.1.1 Aqueous zirconium fluoride complexes

There are several experimental studies on the formation of zirconium fluoride complexes. Brown et al. (2005) accepted data from eight of these studies, some equilibrium constants, however, were recalculated using least squares techniques. Complexation was measured using solvent extraction, cation exchange resins, or potentiometry in either perchloric acid, perchloric acid/sodium perchlorate, or ammonium perchlorate at concentrations of 0.5, 1, 2, or 4 M. The equilibrium constants were reported for the stepwise formation of fluoride complexes according to

$$ZrF_{p-1}^{5-p} + HF(aq) \Leftrightarrow ZrF_p^{4-p} + H^+$$

with p ranging from one to six.

From an SIT regression of four data points concerning the formation of ZrF_4(aq) in 0.5, 1, and 4 M perchlorate, Brown et al. (2005) obtained

$$ZrF_3^+ + HF(aq) \Leftrightarrow ZrF_4(aq) + H^+$$

$$\log_{10}{}^*K_4^\circ(p = 4, 298.15\ K) = (2.18 \pm 0.12)$$

with $\Delta\varepsilon = -(0.06 \pm 0.06)\ kg\cdot mol^{-1}$. Using this $\Delta\varepsilon$ and the selected $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)\ kg\cdot mol^{-1}$, Brown et al. (2005) found

$$\varepsilon(ZrF_3^+, ClO_4^-) = (0.20 \pm 0.06)\ kg\cdot mol^{-1}$$

For the formation of ZrF_3^+, Brown et al. (2005) considered four data points in 0.5, 2, and 4 M perchlorate, the SIT regression gave

$$ZrF_2^{2+} + HF(aq) \Leftrightarrow ZrF_3^+ + H^+$$

$$\log_{10}{}^*K_3^\circ(p = 3, 298.15\ K) = (2.99 \pm 0.22)$$

with $\Delta\varepsilon = -(0.13 \pm 0.05)\ kg\cdot mol^{-1}$. From $\Delta\varepsilon$ and the selected values for $\varepsilon(ZrF_3^+, ClO_4^-)$ and $\varepsilon(H^+, ClO_4^-)$ then follows

$$\varepsilon(ZrF_2^{2+}, ClO_4^-) = (0.47 \pm 0.08)\ kg\cdot mol^{-1}$$

Seven data points were accepted by Brown et al. (2005) for the formation of ZrF_2^{2+} in 1, 2, and 4 M perchlorate, the SIT regression resulted in

$$ZrF^{3+} + HF(aq) \Leftrightarrow ZrF_2^{2+} + H^+$$

$$\log_{10}{}^*K_2°(p = 2, 298.15 \text{ K}) = (5.29 \pm 0.30)$$

with $\Delta\varepsilon = -(0.02 \pm 0.06)$ kg·mol^{-1}. Combining this value for $\Delta\varepsilon$ with those selected for $\varepsilon(ZrF_2^{2+}, ClO_4^-)$ and $\varepsilon(H^+, ClO_4^-)$ leads to

$$\varepsilon(ZrF^{3+}, ClO_4^-) = (0.63 \pm 0.10) \text{ kg·mol}^{-1}$$

Six data points for ZrF^{3+} in 1, 2, and 4 M perchlorate were included in the SIT regression, and Brown et al. (2005) reported

$$Zr^{4+} + HF(aq) \Leftrightarrow ZrF^{3+} + H^+$$

$$\log_{10}{}^*K_1°(p = 1, 298.15 \text{ K}) = (6.94 \pm 0.07)$$

with $\Delta\varepsilon = -(0.12 \pm 0.01)$ kg·mol^{-1}, which leads to

$$\varepsilon(Zr^{4+}, ClO_4^-) = (0.89 \pm 0.10) \text{ kg·mol}^{-1}$$

by using the selected values for $\varepsilon(ZrF^{3+}, ClO_4^-)$ and $\varepsilon(H^+, ClO_4^-)$.

The stability constant for ZrF_5^- was determined by Brown et al. (2005) from four data points in 0.5, 1, and 4 M perchlorate. According to the SIT regression

$$ZrF_4(aq) + HF(aq) \Leftrightarrow ZrF_5^- + H^+$$

$$\log_{10}{}^*K_5°(p = 5, 298.15 \text{ K}) = (1.31 \pm 0.12)$$

with $\Delta\varepsilon = -(0.00 \pm 0.02)$ kg·mol^{-1}. Combining this value for $\Delta\varepsilon$ with that selected for $\varepsilon(H^+, ClO_4^-)$ results in

$$\varepsilon(ZrF_5^-, Na^+) = -(0.14 \pm 0.03) \text{ kg·mol}^{-1}$$

For ZrF_6^{2-}, finally, Brown et al. (2005) considered four data points in 0.5, 1, and 4 M perchlorate, their SIT analysis gave

$$ZrF_5^- + HF(aq) \Leftrightarrow ZrF_6^{2-} + H^+$$

$$\log_{10}{}^*K_6°(p = 6, 298.15 \text{ K}) = (0.31 \pm 0.08)$$

with

$$\Delta\varepsilon = -(0.13 \pm 0.05) \text{ kg·mol}^{-1}$$

and

$$\varepsilon(ZrF_6^{-2}, Na^+) = -(0.15 \pm 0.06) \text{ kg·mol}^{-1}$$

following from this $\Delta\varepsilon$ and the selected $\varepsilon(ZrF_5^-, Na^+)$ and $\varepsilon(H^+, ClO_4^-)$.

For our database, we converted these stepwise stability constants of reactions expressed in terms of HF(aq) to overall stability constants of reactions of type $Zr^{4+} + q\ F^- \Leftrightarrow ZrF_q^{4-q}$ by using the selected $\log_{10}\beta°(H^+ + F^- \Leftrightarrow HF(aq), 298.15 \text{ K}) = (3.18 \pm 0.02)$ (Grenthe et al. 1992, Hummel et al. 2002), resulting in:

$$Zr^{4+} + F^- \Leftrightarrow ZrF^{3+}$$

$$\log_{10}\beta_1°(q = 1, 298.15 \text{ K}) = (10.12 \pm 0.07)$$

$$Zr^{4+} + 2\ F^- \Leftrightarrow ZrF_2^{2+}$$

$$\log_{10}\beta_2°(q = 2, 298.15 \text{ K}) = (18.55 \pm 0.31)$$

$$Zr^{4+} + 3 F^- \Leftrightarrow ZrF_3^+$$

$$\log_{10}\beta_3°(q = 3, 298.15 \text{ K}) = (24.72 \pm 0.38)$$

$$Zr^{4+} + 4 F^- \Leftrightarrow ZrF_4(aq)$$

$$\log_{10}\beta_4°(q = 4, 298.15 \text{ K}) = (30.11 \pm 0.40)$$

$$Zr^{4+} + 5 F^- \Leftrightarrow ZrF_5^-$$

$$\log_{10}\beta_5°(q = 5, 298.15 \text{ K}) = (34.60 \pm 0.42)$$

$$Zr^{4+} + 6 F^- \Leftrightarrow ZrF_6^{2-}$$

$$\log_{10}\beta_6°(q = 6, 298.15 \text{ K}) = (38.11 \pm 0.43)$$

In addition to the values of $\varepsilon(Zr^{4+}, ClO_4^-)$, $\varepsilon(ZrF^{3+}, ClO_4^-)$, $\varepsilon(ZrF_2^{2+}, ClO_4^-)$, (ZrF_3^+, ClO_4^-), $\varepsilon(ZrF_5^-, Na^+)$, and $\varepsilon(ZrF_6^{-2}, Na^+)$ reported above, we also selected

$$\varepsilon(ZrF^{3+}, Cl^-) = (0.25 \pm 0.10) \text{ kg·mol}^{-1}$$

$$\varepsilon(ZrF_2^{2+}, Cl^-) = (0.15 \pm 0.10) \text{ kg·mol}^{-1}$$

$$\varepsilon(ZrF_3^+, Cl^-) = (0.05 \pm 0.10) \text{ kg·mol}^{-1}$$

for our database by taking advantage of an estimation method based on charge correlations (see Appendix A).

There is one study that used calorimetry to determine the standard molar enthalpies of formation of zirconium fluoride complexes at 25°C in 4.0 M $HClO_4$. The measured enthalpy changes for reactions of the type $ZrF_{p-1}^{5-p} + HF(aq) \Leftrightarrow ZrF_p^{4-p} + H^+$ are

$$\Delta_r H_m°(p = 1, 298.15 \text{ K}) = -(17.5 \pm 0.7) \text{ kJ·mol}^{-1}$$

$$\Delta_r H_m°(p = 2, 298.15 \text{ K}) = -(16.8 \pm 1.0) \text{ kJ·mol}^{-1}$$

$$\Delta_r H_m°(p = 3, 298.15 \text{ K}) = -(11.2 \pm 2.1) \text{ kJ·mol}^{-1}$$

$$\Delta_r H_m°(p = 4, 298.15 \text{ K}) = -(22.0 \pm 2.7) \text{ kJ·mol}^{-1}$$

The associated uncertainties were increased by Brown et al. (2005) to account for the assumption that these enthalpy values are also valid at zero ionic strength[40]. For inclusion into our database, we expressed them in terms of reactions of type $Zr^{4+} + q F^- \Leftrightarrow ZrF_q^{4-q}$ by using the selected $\Delta_r H_m°(H^+ + F^- \Leftrightarrow HF(aq), 298.15 \text{ K}) = (12.2 \pm 0.3) \text{ kJ·mol}^{-1}$. Hence

$$\Delta_r H_m°(q = 1, 298.15 \text{ K}) = -(5.3 \pm 0.8) \text{ kJ·mol}^{-1}$$

$$\Delta_r H_m°(q = 2, 298.15 \text{ K}) = -(9.9 \pm 1.3) \text{ kJ·mol}^{-1}$$

$$\Delta_r H_m°(q = 3, 298.15 \text{ K}) = -(8.9 \pm 2.1) \text{ kJ·mol}^{-1}$$

$$\Delta_r H_m°(q = 4, 298.15 \text{ K}) = -(18.7 \pm 3.4) \text{ kJ·mol}^{-1}$$

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[40] Note that in the list of selected zirconium data (Table III-2 in Brown et al. 2005) these reaction enthalpies were erroneously attributed to reactions of form $Zr^{4+} + q F^- \Leftrightarrow ZrF_q^{4-q}$, therefore, the reaction entropies listed in the same table are also incorrect. Moreover, the reaction enthalpies for $ZrF_{p-1}^{5-p} + HF(aq) \Leftrightarrow ZrF_p^{4-p} + H^+$ in Hummel et al. (2002) have a wrong sign. As a consequence, the reaction enthalpies for reactions written in terms of F^- calculated by Hummel et al. (2002) are also incorrect.

12.5.1.2 Solid, liquid and gaseous zirconium fluorides

The synthetic solid $ZrF_4(\beta)$ is highly soluble and liquid $ZrF_4(l)$, as well as gaseous $ZrF_4(g)$, $ZrF_3(g)$, $ZrF_2(g)$, and ZrF(g) are not relevant under low-temperature environmental conditions. Therefore, the corresponding data selected by Brown et al. (2005) are not considered in our database.

12.5.2 Chlorine compounds and complexes

12.5.2.1 Aqueous zirconium chloride complexes

Brown et al. (2005) examined five experimental studies dealing with zirconium chloride complexation in mixtures of perchloric and hydrochloric acid (2, 4, and 6.54 M) and re-interpreted all data using least-squares analysis. The data are consistent with the formation of $ZrCl^{3+}$, $ZrCl_2^{2+}$, $ZrCl_3^{+}$, and $ZrCl_4(aq)$. The mixed hydroxo-chloride complex $ZrOHCl^{2+}$ proposed in one study was considered to be very unlikely and was not accepted by Brown et al. (2005). From their SIT analysis of four data points concerning the formation of $ZrCl^{3+}$ at all three ionic strengths follows

$$Zr^{4+} + Cl^- \Leftrightarrow ZrCl^{3+}$$

$$\log_{10}\beta_1°(298.15 \text{ K}) = (1.59 \pm 0.06)$$

and $\Delta\varepsilon = -(0.14 \pm 0.02)$ kg·mol^{-1}. With the selected $\varepsilon(Zr^{4+}, ClO_4^-) = (0.89 \pm 0.10)$ kg·mol^{-1}, and $\varepsilon(Cl^-, H^+) = (0.12 \pm 0.01)$ kg·mol^{-1} this value for $\Delta\varepsilon$ leads to

$$\varepsilon(ZrCl^{3+}, ClO_4^-) = (0.87 \pm 0.10) \text{ kg·mol}^{-1}$$

These data for $ZrCl^{3+}$ are included in our database.

In the case of $ZrCl_2^{2+}$, the SIT analysis of four data points at all three ionic strengths led Brown et al. (2005) to

$$Zr^{4+} + 2\,Cl^- \Leftrightarrow ZrCl_2^{2+}$$

$$\log_{10}\beta_2°(298.15 \text{ K}) = (2.17 \pm 0.24)$$

with $\Delta\varepsilon = -(0.29 \pm 0.04)$ kg·mol^{-1}. From this value and those selected for $\varepsilon(Zr^{4+}, ClO_4^-)$ and $\varepsilon(Cl^-, H^+)$ follows

$$\varepsilon(ZrCl_2^{2+}, ClO_4^-) = (0.84 \pm 0.11) \text{ kg·mol}^{-1}$$

These data for $ZrCl_2^{2+}$ are also included in our database.

Following the discussion by Hummel et al. (2005) in their Chapter V.4 on weak complexes versus strong specific ion interaction, we used the value of $\varepsilon(ZrCl^{3+}, ClO_4^-)$ for

$$\varepsilon(ZrCl^{3+}, Cl^-) = \varepsilon(ZrCl^{3+}, ClO_4^-) = (0.87 \pm 0.10) \text{ kg·mol}^{-1}$$

and the value of $\varepsilon(ZrCl_2^{2+}, ClO_4^-)$ for

$$\varepsilon(ZrCl_2^{2+}, Cl^-) = \varepsilon(ZrCl_2^{2+}, ClO_4^-) = (0.84 \pm 0.11) \text{ kg·mol}^{-1}$$

It is important to keep in mind that in order to be consistent, these values for $\varepsilon(ZrCl^{3+}, Cl^-)$ and $\varepsilon(ZrCl_2^{2+}, Cl^-)$ should only be used in combination with $\varepsilon(Zr^{4+}, Cl^-) = \varepsilon(Zr^{4+}, ClO_4^-) = (0.89 \pm 0.10)$ kg·mol^{-1}.

Brown et al. (2005) did not recommend any stability constants for $ZrCl_3^+$ and $ZrCl_4(aq)$ because of insufficient data for extrapolating the conditional constants to zero ionic strength.

12.5.2.2 Solid and gaseous zirconium chlorides

The data selected by Brown et al. (2005) for the synthetic zirconium chloride solids $ZrCl_4$(cr), $ZrCl_3$(cr), $ZrCl_2$(cr), and ZrCl(cr) are not included in our database. $ZrCl_4$(cr) is highly soluble. $ZrCl_3$(cr), $ZrCl_2$(cr), and ZrCl(cr) are not relevant in aqueous environments because zirconium exists only in the +4 oxidation state.

The gaseous zirconium chlorides $ZrCl_4$(g), $ZrCl_3$(g), $ZrCl_2$(g), and ZrCl(g) are not relevant under low-temperature environmental conditions. The data selected by Brown et al. (2005) are therefore not considered in our database.

12.5.3 Bromine compounds

The data selected by Brown et al. (2005) for the synthetic zirconium bromide solids $ZrBr_4$(cr), $ZrBr_3$(cr), $ZrBr_2$(cr), and ZrBr(cr) are not included in our database. $ZrBr_4$(cr) is highly soluble. $ZrBr_3$(cr), $ZrBr_2$(cr), and ZrBr(cr) are not relevant in aqueous environments because zirconium exists only in the +4 oxidation state.

The data selected by Brown et al. (2005) for the gaseous zirconium bromides $ZrBr_4$(g), $ZrBr_3$(g), $ZrBr_2$(g), and ZrBr(g) are not included in our database, because these gases are not relevant under low-temperature environmental conditions.

12.5.4 Iodine compounds

Brown et al. (2005) selected thermodynamic data for the synthetic zirconium iodide solids ZrI_4(cr), ZrI_3(cr), ZrI_2(cr), and ZrI(cr). None of these solids occur naturally. In aqueous solutions, zirconium exists only in the +4 oxidation state. Therefore, ZrI_3(cr), ZrI_2(cr), ZrI(cr) are not relevant in aqueous environments and are not considered in our database. ZrI_4(cr) is hygroscopic and highly soluble and is also not considered.

Brown et al. (2005) also selected thermodynamic data for the gaseous zirconium iodides ZrI_4(g), ZrI_3(g), ZrI_2(g), and ZrI(g). Since these gases are not relevant under low-temperature environmental conditions they are not part of our database.

12.6 Zirconium chalcogen compounds and complexes

12.6.1 Sulphur compounds and complexes

12.6.1.1 Zirconium sulphide compounds

Values for the Gibbs free energy of formation for the synthetic high-temperature zirconium sulphides ZrS_3(cr) , ZrS_2(cr), and $ZrS_{1.5}$(cr) were calculated by Brown et al. (2005) using thermochemically measured enthalpies of formation and estimated entropies. These high-temperature solids are not considered in our database.

12.6.1.2 Zirconium sulphite compounds

Brown et al. (2005) calculated a value for the standard molar Gibbs free energy of formation for the synthetic solid $Zr(SO_3)_2$(cr), which is not found in natural environments. This value is based on estimates for the standard molar enthalpy of formation and for the standard molar entropy and is not included in our database.

12.6.1.3 Zirconium sulphate compounds and complexes

12.6.1.3.1 Zirconium sulphate complexes

Solvent extraction and ion exchange techniques were employed in five experimental studies of zirconium sulphate complexes in perchloric acid media at three different ionic strengths (2, 2.33, and 4 M). The experimental data were reevaluated by Brown et al. (2005) with least squares analysis providing stability constants for $ZrSO_4^{2+}$, $Zr(SO_4)_2(aq)$, and $Zr(SO_4)_3^{2-}$. SIT regression of the conditional constants (five data points) for the formation of $ZrSO_4^{2+}$ resulted in

$$Zr^{4+} + HSO_4^- \Leftrightarrow ZrSO_4^{2+} + H^+$$

$$\log_{10}{}^*\beta_1°(298.15 \text{ K}) = (5.06 \pm 0.08)$$

with $\Delta\varepsilon = -(0.19 \pm 0. 02)$ kg·mol^{-1}. Brown et al. (2005) obtained

$$\varepsilon(ZrSO_4^{2+}, ClO_4^-) = (0.39 \pm 0.13) \text{ kg·mol}^{-1}$$

from $\Delta\varepsilon$ and the selected $\varepsilon(Zr^{4+}, ClO_4^-) = (0.89 \pm 0.10)$ kg·mol^{-1}, $\varepsilon(HSO_4^-, H^+) = -(0.17 \pm 0.05)$ kg·mol^{-1} (see below), and $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$ kg·mol^{-1}. Note that this value for $\varepsilon(ZrSO_4^{2+}, ClO_4^-)$ is, probably by oversight, not listed in the NEA compilation of selected ion interaction coefficients (Brown et al. 2005, Table B-4). Nevertheless, it is included in our database. For $Zr(SO_4)_2(aq)$, the SIT regression (five data points) by Brown et al. (2005) gave

$$Zr^{4+} + 2\ HSO_4^- \Leftrightarrow Zr(SO_4)_2(aq) + 2\ H^+$$

$$\log_{10}{}^*\beta_2°(298.15 \text{ K}) = (7.58 \pm 0.20)$$

with $\Delta\varepsilon = -(0.26 \pm 0.02)$ kg·mol^{-1}. Brown et al. (2005) made use of this $\Delta\varepsilon$ together with the selected $\varepsilon(Zr^{4+}, ClO_4^-)$ and $\varepsilon(H^+, ClO_4^-)$ to derive $\varepsilon(HSO_4^-, H^+) = -(0.17 \pm 0.05)$ kg·mol^{-1}, assuming that there is no interaction of the neutral $Zr(SO_4)_2(aq)$ with any ion. From three data points for $Zr(SO_4)_3^{2-}$, finally, Brown et al. (2005) obtained

$$Zr^{4+} + 3\ HSO_4^- \Leftrightarrow Zr(SO_4)_3^{2-} + 3\ H^+$$

$$\log_{10}{}^*\beta_3°(298.15 \text{ K}) = (8.4 \pm 0.5)$$

with $\Delta\varepsilon = (0.02 \pm 0.12)$ kg·mol^{-1}. With the value just derived for $\varepsilon(HSO_4^-, H^+)$ and those selected for $\varepsilon(Zr^{4+}, ClO_4)$ and $\varepsilon(H^+, ClO_4^-)$, this $\Delta\varepsilon$ leads to $\varepsilon(Zr(SO_4)_3^{2-}, H^+) = -(0.05 \pm 0.22)$ kg·mol^{-1}.

For inclusion in our database, the formation reactions of the Zr sulphate complexes were expressed in terms of SO_4^{2-} instead of HSO_4^-, and the stability constants derived above were converted by means of $\log_{10}{}^*\beta°(H^+ + SO_4^{2-} \Leftrightarrow HSO_4^-, 298.15 \text{ K}) = (1.98 \pm 0.09)$ leading to

$$Zr^{4+} + SO_4^{2-} \Leftrightarrow ZrSO_4^{2+}$$

$$\log_{10}\beta_1°(298.15 \text{ K}) = (7.04 \pm 0.09)$$

$$Zr^{4+} + 2\ SO_4^{2-} \Leftrightarrow Zr(SO_4)_2(aq)$$

$$\log_{10}\beta_2°(298.15 \text{ K}) = (11.54 \pm 0.21)$$

$$Zr^{4+} + 3\ SO_4^{2-} \Leftrightarrow Zr(SO_4)_3^{2-}$$

$$\log_{10}\beta_3°(298.15 \text{ K}) = (14.3 \pm 0.5)$$

As the values for $\varepsilon(ZrSO_4^{2+}, Cl^-)$ and $\varepsilon(Zr(SO_4)_3^{2-}, Na^+)$ cannot be obtained from experiments in perchloric acid media, we estimated them based on charge correlations (see Appendix A). The estimates

$$\varepsilon(Zr(SO_4)_3^{2-}, Na^+) = -(0.10 \pm 0.10)\ kg\cdot mol^{-1}$$

$$\varepsilon(ZrSO_4^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg\cdot mol^{-1}$$

are included in our database.

Brown et al. (2005) derived the standard molar enthalpies of formation for $ZrSO_4^{2+}$ and $Zr(SO_4)_2(aq)$ as follows: An experimental determination of the enthalpies of complexation of zirconium by sulphate in 2 M perchloric acid resulted in

$$\Delta_r H_m°(Zr^{4+} + HSO_4^- \Leftrightarrow ZrSO_4^{2+} + H^+, 298.15\ K) = (13.0 \pm 0.5)\ kJ\cdot mol^{-1}$$

and

$$\Delta_r H_m°(ZrSO_4^{2+} + HSO_4^- \Leftrightarrow Zr(SO_4)_2(aq) + H^+, 298.15\ K) = (8 \pm 1)\ kJ\cdot mol^{-1}$$

Assuming that the enthalpies of reaction at zero ionic strength are within the error intervals of the enthalpies measured in 2 M $HClO_4$, Brown et al. (2005) employed these measured values together with the selected $\Delta_f H_m°(Zr^{4+}, 298.15\ K) = -(608.5 \pm 5.0)\ kJ\cdot mol^{-1}$ and $\Delta_f H_m°(HSO_4^-, 298.15\ K) = -(886.9 \pm 1.0)\ kJ\cdot mol^{-1}$ (the standard molar enthalpy of formation for H^+ is by definition zero) to get

$$\Delta_f H_m°(ZrSO_4^{2+}, 298.15\ K) = -(1480.9 \pm 5.1)\ kJ\cdot mol^{-1}$$

$$\Delta_f H_m°(Zr(SO_4)_2, aq, 298.15\ K) = -(2359.8 \pm 5.2)\ kJ\cdot mol^{-1}$$

These values are also included in our database.

12.6.1.3.2 Zirconium sulphate solids

Brown et al. (2005) calculated standard molar Gibbs free energies of formation for the synthetic solid $Zr(SO_4)_2(cr)$, and for the mineral $Zr(SO_4)_2\cdot 4H_2O(cr)$ (zircosulphate) from standard molar enthalpies of formation and standard molar entropies. Since these phases are extremely soluble in water, they are not included in our database.

12.6.2 Selenium and tellurium compounds

$Zr(SeO_3)_2(cr)$: Brown et al. (2005) selected only a value for the standard molar enthalpy of formation of this synthetic solid, which is therefore not considered in our database.

Zircon tellurium compounds: Brown et al. (2005) selected thermodynamic data for the synthetic solids $ZrTe_{1.843}(cr)$, $ZrTe_2(cr)$, $Zr_5Te_4(cr)$, and $ZrTe_3O_8(cr)$. As Te is not part of our database, these phases are omitted.

12.7 Group 15 compounds and complexes

12.7.1 Zirconium nitrogen compounds and complexes

12.7.1.1 Zirconium nitride compounds

Thermodynamic data for the synthetic phase ZrN(cr), which does not occur in natural environments, were selected by Brown et al. (2005) based on calorimetric measurements. It is doubtful, whether this phase forms at low temperatures and it is therefore omitted from our database.

12.7.1.2 Zirconium nitrate complexes

Experimental data on zirconium nitrate complexation are limited and only available at two different ionic strengths (2 and 4 M mixed nitrate/perchlorate solutions). The nitrate complexes appear to be weak. The best constrained stability constant is that for $ZrNO_3^{3+}$. The experimental data were re-analyzed by Brown et al. (2005) using least squares techniques to provide conditional stability constants. In the case of $ZrNO_3^{3+}$, SIT analysis by Brown et al. (2005) of three such constants, obtained by cation exchange resin, and liquid ion exchange methods, resulted in

$$Zr^{4+} + NO_3^- \Leftrightarrow ZrNO_3^{3+}$$

$$\log_{10}\beta_1°(298.15\ K) = (1.59 \pm 0.08)$$

with $\Delta\varepsilon = -(0.08 \pm 0.04)$ kg·mol^{-1}. From this $\Delta\varepsilon$ and the selected $\varepsilon(Zr^{4+}, ClO_4^-) = (0.89 \pm 0.10)$ kg·mol^{-1} and $\varepsilon(NO_3^-, H^+) = (0.07 \pm 0.01)$ kg·mol^{-1} Brown et al. (2005) calculated

$$\varepsilon(ZrNO_3^{3+}, ClO_4^-) = (0.88 \pm 0.11)\ kg{\cdot}mol^{-1}$$

These data for $ZrNO_3^{3+}$ are included in our database, as well as

$$\varepsilon(ZrNO_3^{3+}, Cl^-) = (0.25 \pm 0.10)\ kg{\cdot}mol^{-1}$$

which we estimated based on charge correlations (see Appendix A).

For the stability constant of $Zr(NO_3)_2^{2+}$, Brown et al. (2005) relied on a liquid ion exchange, and a cation exchange resin experiment in 2 M mixed nitrate/perchlorate solutions. They extrapolated the average of the conditional constants for

$$Zr^{4+} + 2\ NO_3^- \Leftrightarrow Zr(NO_3)_2^{2+}$$

to zero ionic strength with a value for $\Delta\varepsilon$ calculated from the selected values for $\varepsilon(Zr^{4+}, ClO_4^-)$ and $\varepsilon(NO_3^-, H^+)$ and from the estimate

$$\varepsilon(Zr(NO_3)_2^{2+}, ClO_4^-) \approx \varepsilon(ZrCl_2^{2+}, ClO_4^-) = (0.84 \pm 0.11)\ kg{\cdot}mol^{-1}$$

and selected the resulting

$$\log_{10}\beta_2°(298.15\ K) = (2.64 \pm 0.17)$$

These values for $\log_{10}\beta_2°$ and $\varepsilon(ZrCl_2^{2+}, ClO_4^-)$ are also included in our database accompanied by

$$\varepsilon(Zr(NO_3)_2^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg{\cdot}mol^{-1}$$

which we estimated on the basis of charge correlations (see Appendix A).

Stability constants for $Zr(NO_3)_3^+$ and $Zr(NO_3)_4(aq)$ were not recommended by Brown et al. (2005), because the conditional constants could not be reliably extrapolated to zero ionic strength.

12.7.2 Zirconium phosphorous compounds

$Zr(HPO_4)_2{\cdot}H_2O(cr)$: The solubility of zirconium phosphate was measured by Hevesy & Kimura (1925) in hydrochloric acid solutions (6.01 and 10.00 m HCl). The composition of the solid used in the experiments was found to be $ZrH_4P_2O_9$, which the authors interpreted as $ZrO(H_2PO_4)_2$ resulting from the reaction of zirconyl ions, ZrO^{2+}, with phosphate ions. Since it was later shown that zirconyl ions do not exist in solution, the solid used in the experiments was more likely $Zr(HPO_4)_2{\cdot}H_2O(cr)$. Using the SIT, Brown et al. (2005), obtained from the solubility data

$$Zr(HPO_4)_2\cdot H_2O(cr) + 4\ H^+ \Leftrightarrow Zr^{4+} + 2\ H_3PO_4(aq) + H_2O(l)$$

$$\log_{10}K_{s,0}°(298.15\ K) = -(22.8 \pm 3.1)$$

The value

$$\Delta_f H_m°(Zr(HPO_4)_2\cdot H_2O,\ cr,\ 298.15\ K) = -(3466.1 \pm 1.6)\ kJ\cdot mol^{-1}$$

selected by Brown et al. (2005) is the average of data obtained by adiabatic calorimetry. For the following reasons, the data selected by Brown et al. (2005) for $Zr(HPO_4)_2\cdot H_2O(cr)$ are included in our database as supplemental data only, serving as placeholders: $Zr(HPO_4)_2\cdot H_2O(cr)$ is a synthetic phase and does not occur in natural environments. The solubilities were only measured by dissolution of the solid. As Brown et al. (2005) mention, the applicability of the SIT at such high concentrations of HCl may be questionable.

$Zr(HPO_4)_2(\alpha)$: The data selected by Brown et al. (2005) for this synthetic solid, which is not found in natural environments, are based on thermochemical measurements. Since it is unclear whether this solid forms in low-temperature environments we did not include it in our database.

$Zr(HPO_4)_2(\beta)$: Since Brown et al. (2005) selected only a value for the enthalpy of formation for this synthetic phase, it is not considered in our database.

$Zr(HPO_4)_2\cdot 2H_2O(cr)$: Since Brown et al. (2005) selected only a value for the enthalpy of formation for this synthetic phase, it is not considered in our database.

$ZrP_2O_7(cr)$: Brown et al. (2005) selected only values for the heat capacity and entropy for this synthetic solid, which is therefore not included in our database.

$NaZr_2P_3O_{12}(cr)$: The data selected by Brown et al. (2005) for this synthetic solid, which does not occur in natural environments, are based on calorimetry. Since it is unlikely that this phase is formed in low-temperature environments it is not considered in our database.

12.7.3 Zirconium arsenic compounds

Brown et al. (2005) selected only standard molar formation enthalpies for $Zr(HAsO_4)_2(\alpha)$, $Zr(HAsO_4)_2(\beta)$, and $Zr(HAsO_4)_2\cdot H_2O(cr)$. Therefore, these phases are omitted from our database.

12.8 Group 14 compounds and complexes

12.8.1 Carbon compounds and complexes

12.8.1.1 Zirconium carbides

The thermodynamic data for ZrC(cr) selected by Brown et al. (2005) are based on thermochemical data. Carbides are formed neither at low temperatures nor in aqueous environments. For these reasons, ZrC(cr) is not included in our database.

12.8.1.2 Zirconium carbonate complexes

There are only a few experimental studies dealing with Zr-carbonate complexes and Brown et al. (2005) were able to derive reliable thermodynamic constants only for $Zr(CO_3)_4^{4-}$. This species appears to be dominant when carbonate concentrations exceed the concentration of dissolved Zr. Based on the experimental data, Brown et al. (2005) identified $Zr(CO_3)_2(aq)$, $Zr(CO_3)_3^{2-}$, and $ZrOH(CO_3)_3^{3-}$ as other probable carbonate complexes and remarked that considering only $Zr(CO_3)_4^{4-}$ as Zr carbonate complex may not be sufficient to describe the complexity of the Zr carbonate complexation, especially in dilute solutions.

A conditional constant for the reaction

$$Zr^{4+} + 4\ CO_3^{2-} \Leftrightarrow Zr(CO_3)_4^{4-}$$

was derived by Brown et al. (2005) from a re-evaluation of solubility data of amorphous $Zr(OH)_4$ in NH_4NO_3 (I = 1 M) at 20°C by taking into account the new hydrolysis model (discussed in Section 12.4.1 above). Since the solubility was measured at a single ionic strength, the usual linear SIT extrapolation procedure was not possible. Instead, Brown et al. (2005) calculated a value for

$$\Delta\varepsilon = \varepsilon(Zr(CO_3)_4^{4-}, NH_4^+) - \varepsilon(Zr^{4+}, NO_3^-) - 4\ \varepsilon(CO_3^{2-}, NH_4^+)$$

estimating the unknown interaction parameters by analogy with homovalent pairs of ions:

$$\varepsilon(Zr(CO_3)_4^{4-}, NH_4^+) \approx \varepsilon(U(CO_3)_4^{4-}, Na^+) = -(0.09 \pm 0.20)\ kg\cdot mol^{-1}$$

$$\varepsilon(Zr^{4+}, NO_3^-) \approx \varepsilon(Th^{4+}, NO_3^-) = (0.33 \pm 0.35)^{41}\ kg\cdot mol^{-1}$$

$$\varepsilon(CO_3^{2-}, NH_4^+) \approx \varepsilon(CO_3^{2-}, K^+) = (0.02 \pm 0.10)\ kg\cdot mol^{-1}$$

Using the resulting Δε, Brown et al. (2005) obtained the thermodynamic constant at infinite dilution and at 20°C, which they assumed to be valid also at 25°C. Thus, they selected

$$\log_{10}\beta_4°(298.15\ K) = (42.9 \pm 1.0)$$

which is also selected for our database.

Note that $\varepsilon(Zr(CO_3)_4^{4-}, NH_4^+) \approx \varepsilon(U(CO_3)_4^{4-}, Na^+) = -(0.09 \pm 0.20)\ kg\cdot mol^{-1}$ was erroneously listed by Brown et al. (2005) in their Table B-5 as $\varepsilon(Zr(CO_3)_4^{4-}, Na^+)$, which is also a reasonable estimate, since all three pairs of ions are homovalent. We therefore included

$$\varepsilon(Zr(CO_3)_4^{4-}, Na^+) = -(0.09 \pm 0.20)\ kg\cdot mol^{-1}$$

in our database.

12.8.2 Silicon compounds

$ZrSiO_4$(cr), zircon: Brown et al. (2005) selected thermodynamic data for zircon from various thermochemical measurements. Since zircon is a high-temperature mineral mainly formed in igneous rocks, these data are not included in our database.

Calcium zirconium silicate compounds: Based on thermochemical measurements (enthalpies of formation and heat capacities), Brown et al. (2005) selected thermodynamic data for $Ca_2ZrSi_3O_{12}$(cr) and $Ca_3ZrSi_2O_9$(cr). Since it is not known whether these synthetic solids (they are not found in natural environments) form at low temperatures they are not included in our database.

Strontium zirconium silicate compounds: Brown et al. (2005) selected a value for the standard molar formation enthalpy of $Sr_6ZrSi_5O_{18}$(cr). As no other data were given, this solid (not found in natural environments) is not included in our database. Brown et al. (2005) also calculated a value for $\Delta_fG_m°(SrZrSi_2O_7, cr, 298.15\ K)$ from calorimetric data (heat capacity, entropy, enthalpy of formation). Since nothing is known about the formation of this synthetic solid (not found in natural environments) at low temperatures it is not included in our database.

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[41] Note that the value selected in a later NEA review by Rand et al. (2008) and included in our database is slightly different: $\varepsilon(Th^{4+}, NO_3^-) = (0.31 \pm 0.12)\ kg\cdot mol^{-1}$.

Sodium zirconium silicate compounds: The $\Delta_f G_m°$ values selected by Brown et al. (2005) for Na_2ZrSiO_5(cr), $Na_2ZrSi_2O_7$(cr) (parakeldyshite), and $Na_4Zr_2Si_3O_{12}$(cr), were calculated from thermochemical data. It is unlikely that these solids are formed under low-temperature conditions, therefore they are not included in our database. The $\Delta_f G_m°$ values for the minerals, $Na_2ZrSi_3O_9·2H_2O$(cr) (catapleiite), $Na_2ZrSi_4O_{11}$(cr) (vlasovite), and $Na_2ZrSi_6O_{15}·3H_2O$(cr) (elpidite) selected by Brown et al. (2005) were derived from dissolution experiments at 50°C by Aja et al. (1995 and 1997) that could not be reversed. Baussy et al. (1974) synthesized these minerals from amorphous silica, amorphous ZrO_2 gels, and from hydrated Na_2CO_3 under hydrothermal conditions at a constant pressure of 700 bars. Formation temperatures were 340–450°C for catapleiite, 350–500°C for elpidite, and > 500°C for vlasovite. Thus, it is very unlikely that these minerals are formed under low-temperature conditions and they are therefore excluded from our database.

Cesium zirconium silicate compounds: Brown et al. (2005) selected a calorimetrically determined value for the formation enthalpy of $Cs_2ZrSi_2O_7$(cr). No other data were given, therefore, $Cs_2ZrSi_2O_7$(cr) is not considered in our database.

Table 12.1: Zirconium data selected by NEA (Brown et al. 2005) but not included in TDB Version 12/07. For explanations see text.

Gases	Zr(g) [a], ZrO(g) [ad], ZrO_2(g) [ad], ZrF_4(g) [bd], ZrF_3(g) [a], ZrF_2(g) [a], ZrF(g) [a], $ZrCl_4$(g) [ad], $ZrCl_3$(g) [ad], $ZrCl_2$(g) [ad], ZrCl(g) [a], $ZrBr_4$(g) [ad], $ZrBr_3$(g) [b], $ZrBr_2$(g) [b], ZrBr(g) [b], ZrI_4(g) [ac], ZrI_3(g) [a], ZrI_2(g) [a], ZrI(g) [a]
Solids	Zr(β) [b], Zr(ω) [b], ZrH(cr) [a], ZrH_2(ε) [a], ZrF_4(β) [ad], $ZrCl_4$(cr) [ad], $ZrCl_3$(cr) [a], $ZrCl_2$(cr) [a], ZrCl(cr) [a], $ZrBr_4$(cr) [bd], $ZrBr_3$(cr) [b], $ZrBr_2$(cr) [b], ZrBr(cr) [b], ZrI_4(cr) [ac], ZrI_3(cr) [a], ZrI_2(cr) [a], ZrI(cr) [a], ZrS_3(cr) [a], ZrS_2(cr) [a], $ZrS_{1.5}$(cr) [a], $Zr(SO_3)_2$(cr) [a], $Zr(SO_4)_2$(cr) [a], $Zr(SO_4)_2·4H_2O$(cr) [a], $Zr(SeO_3)_2$(cr) [b], $ZrTe_{1.843}$(cr) [a], $ZrTe_2$(cr) [a], Zr_5Te_4(cr) [a], $ZrTe_3O_8$(cr) [b], ZrN(cr) [ad], $Zr(HPO_4)_2$(α) [a], $Zr(HPO_4)_2$(β) [b], $Zr(HPO_4)_2·2H_2O$(cr) [b], ZrP_2O_7(cr) [b], $NaZr_2P_3O_{12}$(cr) [a], $Zr(HAsO_4)_2$(α) [b], $Zr(HAsO_4)_2$(β) [b], $Zr(HAsO_4)_2·H_2O$(cr) [b], ZrC(cr) [a], $ZrSiO_4$(cr) [a], $Ca_2ZrSi_3O_{12}$(cr) [a], $Ca_3ZrSi_2O_9$(cr) [a], $SrZrSi_2O_7$(cr) [a], $Sr_6ZrSi_5O_{18}$(cr) [b], Na_2ZrSiO_5(cr) [a], $Na_2ZrSi_2O_7$(cr) [a], $Na_2ZrSi_3O_9·2H_2O$(cr) [a], $Na_2ZrSi_4O_{11}$(cr) [a], $Na_2ZrSi_6O_{15}·3H_2O$(cr) [a], $Na_4Zr_2Si_3O_{12}$(cr) [a], $Cs_2ZrSi_2O_7$(cr) [b]
Liquids	Zr(l) [b], ZrF_4(l) [bd]
Aq. species	All included

[a] Single species data including $\Delta_f G_m°$

[b] Single species data excluding $\Delta_f G_m°$

[c] Reaction data including $\log_{10}K°$

[d] Reaction data excluding $\log_{10}K°$

Table 12.2: Selected zirconium data. All data included in TDB Version 12/07 are taken from Brown et al. (2005) with the exception of those marked with an asterisk (*). Supplemental data are in italics. New or changed data with respect to TDB Version 01/01 (Hummel et al. 2002) are shaded.

		TDB Version 01/01				**TDB Version 12/07**				
Name	**Redox**	$\Delta_f G_m°$ [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}]	$\Delta_f G_m°$ [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}]	**Species**
Zr(cr)	0	0.0	0.0	39.0	-	0.0	0.0	39.08 ± 0.10	26.08 ± 0.05	Zr(cr)
Zr+4	IV	-557.7 ± 10.8	-	-	-	-528.5 ± 9.2	-608.5 ± 5.0	-491.0 ± 35.2	-	Zr^{4+}

		TDB Version 01/01		**TDB Version 12/07**			
Name	**Redox**	$\log_{10}\beta°$	$\Delta_r H_m°$ [kJ·mol^{-1}]	$\log_{10}\beta°$	$\Delta_r H_m°$ [kJ·mol^{-1}]	$\Delta_f H_m°$ [kJ·mol^{-1}]	**Reaction**
ZrOH+3	IV	0.3	-	0.32 ± 0.22	-	-	$Zr^{4+} + H_2O(l) \Leftrightarrow ZrOH^{3+} + H^+$
Zr(OH)2+2	IV	-	-	0.98 ± 1.06	-	-	$Zr^{4+} + 2\ H_2O(l) \Leftrightarrow Zr(OH)_2^{2+} + 2\ H^+$
Zr(OH)4	IV	-9.7	-	-2.19 ± 1.70	-	-	$Zr^{4+} + 4\ H_2O(l) \Leftrightarrow Zr(OH)_4(aq) + 4\ H^+$
Zr(OH)5-	IV	-16	-	-	-	-	$Zr^{4+} + 5\ H_2O(l) \Leftrightarrow Zr(OH)_5^- + 5\ H^+$
Zr(OH)6-2	IV	-	-	-29.0 ± 0.7	-	-	$Zr^{4+} + 6\ H_2O(l) \Leftrightarrow Zr(OH)_6^{2-} + 6\ H^+$
Zr3(OH)4+8	IV	-	-	0.4 ± 0.3	-	-2970.8 ± 10.0	$3\ Zr^{4+} + 4\ H_2O(l) \Leftrightarrow Zr_3(OH)_4^{8+} + 4\ H^+$
Zr3(OH)9+3	IV	-	-	12.19 ± 0.08	-	-	$3\ Zr^{4+} + 9\ H_2O(l) \Leftrightarrow Zr_3(OH)_9^{3+} + 9\ H^+$
Zr4(OH)8+8	IV	-	-	6.52 ± 0.65	-	-	$4\ Zr^{4+} + 8\ H_2O(l) \Leftrightarrow Zr_4(OH)_8^{8+} + 8\ H^+$
Zr4(OH)15+	IV	-	-	12.58 ± 0.24	-	-	$4\ Zr^{4+} + 15\ H_2O(l) \Leftrightarrow Zr_4(OH)_{15}^+ + 15\ H^+$
Zr4(OH)16	IV	-	-	8.39 ± 0.80	-	-6706.16 ± 7.20	$4\ Zr^{4+} + 16\ H_2O(l) \Leftrightarrow Zr_4(OH)_{16}(aq) + 16\ H^+$
CaZr(OH)6	IV	-	-	*(-24.6 ± 0.3)** [a]	-	-	$Ca^{2+} + Zr^{4+} + 6\ H_2O(l) \Leftrightarrow CaZr(OH)_6(aq) + 6\ H^+$
Ca2Zr(OH)6+2	IV	-	-	(-22.6 ± 0.3)*	-	-	$2\ Ca^{2+} + Zr^{4+} + 6\ H_2O(l) \Leftrightarrow Ca_2Zr(OH)_6^{2+} + 6\ H^+$
Ca3Zr(OH)6+4	IV	-	-	(-23.2 ± 0.3)*	-	-	$3\ Ca^{2+} + Zr^{4+} + 6\ H_2O(l) \Leftrightarrow Ca_3Zr(OH)_6^{4+} + 6\ H^+$

		TDB Version 01/01		TDB Version 12/07			
Name	**Redox**	**$\log_{10}\beta°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**$\log_{10}\beta°$**	**$\Delta_rH_m°$** [kJ·mol^{-1}]	**$\Delta_fH_m°$** [kJ·mol^{-1}]	**Reaction**
ZrF+3	IV	10.2 ± 0.1	(-5.3)[b]	10.12 ± 0.07	(-5.3 ± 0.8)[c]	-	$Zr^{4+} + F^- \Leftrightarrow ZrF^{3+}$
ZrF2+2	IV	18.5 ± 0.2	(-9.9)[b]	18.55 ± 0.31	(-9.9 ± 1.3)[c]	-	$Zr^{4+} + 2\ F^- \Leftrightarrow ZrF_2^{2+}$
ZrF3+	IV	24.7 ± 0.3	(-8.9)[b]	24.72 ± 0.38	(-8.9 ± 2.1)[c]	-	$Zr^{4+} + 3\ F^- \Leftrightarrow ZrF_3^{+}$
ZrF4	IV	30.1 ± 0.8	(-19)[b]	30.11 ± 0.40	(-18.7 ± 3.4)[c]	-	$Zr^{4+} + 4\ F^- \Leftrightarrow ZrF_4(aq)$
ZrF5-	IV	34.7 ± 1.1	-	34.60 ± 0.42	-	-	$Zr^{4+} + 5\ F^- \Leftrightarrow ZrF_5^{-}$
ZrF6-2	IV	38.4 ± 1.5	-	38.11 ± 0.43	-	-	$Zr^{4+} + 6\ F^- \Leftrightarrow ZrF_6^{2-}$
ZrCl+3	IV	1.5 ± 0.3	-	1.59 ± 0.06	-	-	$Zr^{4+} + Cl^- \Leftrightarrow ZrCl^{3+}$
ZrCl2+2	IV	-	-	2.17 ± 0.24	-	-	$Zr^{4+} + 2\ Cl^- \Leftrightarrow ZrCl_2^{2+}$
ZrSO4+2	IV	7.0 ± 0.1	-	7.04 ± 0.09	-	-1480.9 ± 5.1	$Zr^{4+} + SO_4^{2-} \Leftrightarrow ZrSO_4^{2+}$
Zr(SO4)2	IV	-	-	11.54 ± 0.21	-	-2359.8 ± 5.2	$Zr^{4+} + 2\ SO_4^{2-} \Leftrightarrow Zr(SO_4)_2(aq)$
Zr(SO4)3-2	IV	-	-	14.3 ± 0.5	-	-	$Zr^{4+} + 3\ SO_4^{2-} \Leftrightarrow Zr(SO_4)_3^{2-}$
ZrNO3+3	IV	-	-	1.59 ± 0.08	-	-	$Zr^{4+} + NO_3^- \Leftrightarrow ZrNO_3^{3+}$
Zr(NO3)2+2	IV	-	-	2.64 ± 0.17	-	-	$Zr^{4+} + 2\ NO_3^- \Leftrightarrow Zr(NO_3)_2^{2+}$
Zr(CO3)4-4	IV	-	-	42.9 ± 1.0	-	-	$Zr^{4+} + 4\ CO_3^{2-} \Leftrightarrow Zr(CO_3)_4^{4-}$

[a] Note that the uncertainty was not reported in Thoenen (2012)

[b] Corrected values, the original values given by Hummel et al. (2002) are incorrect (see text for discussion)

[c] Note that the values reported in Table III-2 by Brown et al. (2005) are incorrect (see text for discussion)

		TDB Version 01/01			TDB Version 12/07			
Name	**Redox**	**$\log_{10}K_{s,0}°$**	**$\Delta_f H_m°$** [kJ·mol^{-1}]	**$C_{p,m}°$** [J·K^{-1}·mol^{-1}]	**$\log_{10}K_{s,0}°$**	**$\Delta_f H_m°$** [kJ·mol^{-1}]	**$C_{p,m}°$** [J·K^{-1}·mol^{-1}]	**Reaction**
Baddeleyite	IV	-1.9	-	-	-7.0 ± 1.6	-1100.6 ± 1.3	55.96 ± 0.79	$ZrO_2(cr) + 4 H^+ \Leftrightarrow Zr^{4+} + 2 H_2O(l)$
Zr(OH)4(am)(fr)	IV	-	-	-	-3.24 ± 0.10	-	-	$Zr(OH)_4(am, fr) + 4 H^+ \Leftrightarrow Zr^{4+} + 4 H_2O(l)$
Zr(HPO4)2:H2O(cr)	*IV*	-	-	-	*-22.8 ± 3.1*	*-3466.1 ± 1.6*	-	$Zr(HPO_4)_2 \cdot H_2O(cr) + 4 H^+ \Leftrightarrow Zr^{4+} + 2 H_3PO_4(aq) + H_2O(l)$

Table 12.3: Selected SIT ion interaction coefficients $\varepsilon_{j,k}$ [kg·mol^{-1}] for zirconium species. All data included in TDB Version 12/07 are taken from Brown et al. (2005) unless indicated otherwise. Own data estimates based on charge correlations (see Appendix A) are shaded. Supplemental data are in italics.

j k→ **↓**	Cl^- $\varepsilon_{j,k}$	ClO_4^- $\varepsilon_{j,k}$	NO_3^- $\varepsilon_{j,k}$	Li^+ $\varepsilon_{j,k}$	Na^+ $\varepsilon_{j,k}$	K^+ $\varepsilon_{j,k}$
Zr+4	0.33 ± 0.09	0.89 ± 0.10	0.33 ± 0.35	0	0	0
ZrOH+3	0.25 ± 0.10	0.57 ± 0.13	-	0	0	0
Zr(OH)2+2	0.15 ± 0.10	0.62 ± 0.39	-	0	0	0
Zr(OH)4	0	0	0	0	0	0
Zr(OH)6-2	0	0	0	-	-0.10 ± 0.10	-
Zr3(OH)4+8	0.33 ± 0.28	1.89 ± 0.31	2.28 ± 0.35	0	0	0
Zr3(OH)9+3	0.25 ± 0.10	0.93 ± 0.35	-	0	0	0
Zr4(OH)8+8	0.75 ± 0.50	3.61 ± 1.02	-	0	0	0
Zr4(OH)15+	0.05 ± 0.10	0.09 ± 0.92	-0.02 ± 1.46	0	0	0
Zr4(OH)16	0	0	0	0	0	0
CaZr(OH)6	*0*	*0*	*0*	*0*	*0*	*0*
Ca2Zr(OH)6+2	(0.1 ± 0.1)[a]	(0.3 ± 0.1)[a]	-	0	0	0
Ca3Zr(OH)6+4	(0.40 ± 0.07)[a]	(0.89 ± 0.12)[a]	-	0	0	0
ZrF+3	0.25 ± 0.10	0.63 ± 0.10	-	0	0	0
ZrF2+2	0.15 ± 0.10	0.47 ± 0.08	-	0	0	0
ZrF3+	0.05 ± 0.10	0.20 ± 0.06	-	0	0	0
ZrF4	0	0	0	0	0	0
ZrF5-	0	0	0	-	-0.14 ± 0.03	-
ZrF6-2	0	0	0	-	-0.15 ± 0.06	-
ZrCl+3	(0.87 ± 0.10)[b]	0.87 ± 0.10	-	0	0	0
ZrCl2+2	(0.84 ± 0.11)[b]	0.84 ± 0.11		0	0	0
ZrSO4+2	0.15 ± 0.10	(0.39 ± 0.13)[c]	-	0	0	0
Zr(SO4)2	0	0	0	0	0	0
Zr(SO4)3-2	0	0	0	-	-0.10 ± 0.10	-
ZrNO3+3	0.25 ± 0.10	0.88 ± 0.11	-	0	0	0
Zr(NO3)2+2	0.15 ± 0.10	0.84 ± 0.11	-	0	0	0
Zr(CO3)4-4	0	0	0	-	-0.09 ± 0.20	-

[a] Altmaier et al. (2008)

[b] This work, to be used in combination with $\varepsilon(Zr^{4+}, Cl^-) = \varepsilon(Zr^{4+}, ClO_4^-) = (0.89 \pm 0.10)$ kg·mol^{-1}

[c] Data given by Brown et al. (2005) in text but not in Table B-4

Table 12.4: Selected SIT ion interaction coefficients $\varepsilon_{j,k}$ [kg·mol^{-1}] for auxiliary species needed to derive data for zirconium.

j k→ **↓**	OH^- $\varepsilon_{j,k}$
Ca^{2+}	(-0.45 ± 0.03)[a]

[a] Altmaier et al. (2008)

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13 Updated Auxiliary Data

13.1 Introduction

The Nagra/PSI TDB 01/01 (Hummel et al. 2002) did not consider any complexes with iodate, cyanide, thiocyanate, and pyrophosphate. Since such complexes are included in our update, several auxiliary data are needed. Their selection is discussed below.

13.2 Iodine

For the Nagra/PSI TDB 01/01 (Hummel et al. 2002) we selected

$$2\ \mathrm{I}^- \Leftrightarrow \mathrm{I_2(aq)} + 2\ \mathrm{e}^-$$

$$\log_{10}K°(298.15\ \mathrm{K}) = -20.95$$

Unfortunately, we entered this value with a reversed sign (as +20.95) into the electronic versions of the Nagra/PSI TDB 01/01 for PMATCHC and PHREEQC. As a consequence, the values for $\Delta_f G_m°(\mathrm{I_2}$, aq, 298.15 K) and $\Delta_f G_m°(\mathrm{I_3^-}$, 298.15 K) entered into the GEMS-version of the Nagra/PSI TDB 01/01 were also incorrect. These errors have been corrected. From the corrected $\log_{10}K°$(298.15 K) = -20.95 and the selected $\Delta_f G_m°(\mathrm{I^-}$, 298.15 K) = -(51.724 ± 0.112) kJ·mol^{-1} (Grenthe et al. 1992 and Hummel et al. 2002, from CODATA by Wagman et al. 1982) follows $\Delta_f G_m°(\mathrm{I_2}$, aq, 298.15 K) = (16.135) kJ·mol^{-1}, by virtue of $\Delta_r G_m° = -\mathrm{RT}\ln K°$, or $\Delta_r G_m° = -5.70804 \log_{10}K°$, if T = 298.15 K and $\Delta_r G_m°$ is in kJ·mol^{-1}.

Iodate: The thermodynamic quantities for iodate, $\mathrm{IO_3^-}$, included in our database

$$\Delta_f G_m°(\mathrm{IO_3^-}, 298.15\ \mathrm{K}) = -(126.34 \pm 0.78)\ \mathrm{kJ{\cdot}mol^{-1}}$$

$$\Delta_f H_m°(\mathrm{IO_3^-}, 298.15\ \mathrm{K}) = -(219.7 \pm 0.5)\ \mathrm{kJ{\cdot}mol^{-1}}$$

$$S_m°(\mathrm{IO_3^-}, 298.15\ \mathrm{K}) = (118 \pm 2)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$\varepsilon(\mathrm{IO_3^-}, \mathrm{Na^+}) = -(0.06 \pm 0.02)\ \mathrm{kg{\cdot}mol^{-1}}$$

were selected by Grenthe et al. (1992). The values for $\Delta_f H_m°(\mathrm{IO_3^-}$, 298.15 K) and $S_m°(\mathrm{IO_3^-}$, 298.15 K) are based on calorimetric data and were used to calculate $\Delta_f G_m°(\mathrm{IO_3^-}$, 298.15 K). The specific ion interaction coefficient was estimated by Grenthe et al. (1992), assuming it to be equal to the value of $\varepsilon(\mathrm{BrO_3^-}, \mathrm{Na^+})$ determined by Ciavatta (1980) from isopiestic mean activity coefficient data.

The stability constant for the redox reaction linking I(0) with I(V)

$$0.5\ \mathrm{I_2(aq)} + 3\ \mathrm{H_2O(l)} \Leftrightarrow \mathrm{IO_3^-} + 6\ \mathrm{H^+} + 5\ \mathrm{e^-}$$

$$\log_{10}K°(298.15\ \mathrm{K}) = -101.09$$

was calculated from the selected values for $\Delta_f G_m°(\mathrm{IO_3^-}$, 298.15 K) and $\Delta_f G_m°(\mathrm{I_2}$, aq, 298.15 K) discussed above and from $\Delta_f G_m°(\mathrm{H_2O}$, l, 298.15 K) = -(237.140 ± 0.041) kJ·mol^{-1} (selected by Grenthe et al. 1992 and Hummel et al. 2002), using $\Delta_r G_m° = -\mathrm{RT}\ln K°$, or $\log_{10}K° = -\Delta_r G_m°/5.70804$ if T = 298.15 K and $\Delta_r G_m°$ is in kJ·mol^{-1}.

The protonation constant of iodate to form iodic acid, $\mathrm{HIO_3(aq)}$, included in our database

$$\mathrm{IO_3^-} + \mathrm{H^+} \Leftrightarrow \mathrm{HIO_3(aq)}$$

$$\log_{10}K°(298.15\ \mathrm{K}) = (0.788 \pm 0.029)$$

was selected by Grenthe et al. (1992).

13.3 Cyanide and thiocyanate

Cyanide: Olin et al. (2005) selected the following thermodynamic quantities for HCN(aq)

$$\Delta_f G_m°(\text{HCN, aq, 298.15 K}) = (114.37 \pm 2.52)\ \text{kJ·mol}^{-1}$$

$$\Delta_f H_m°(\text{HCN, aq, 298.15 K}) = (103.75 \pm 3.54)\ \text{kJ·mol}^{-1}$$

$$S_m°(\text{HCN, aq, 298.15 K}) = (131.3 \pm 8.4)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

which are also included in our database. Combining the value for $\Delta_f G_m°$(HCN, aq, 298.15 K) with $\Delta_f G_m°(CO_3^{2-}$, 298.15 K) = -(527.917 ± 0.39) kJ·mol^{-1}, $\Delta_f G_m°(NO_3^-$, 298.15 K) = -(110.794 ± 0.417) kJ·mol^{-1} and $\Delta_f G_m°(H_2O$, l, 298.15 K) = -(237.140 ± 0.041) kJ·mol^{-1}, all selected by Hummel et al. (2002), one obtains $\Delta_r G_m°$(298.15 K) = -(669.759 ± 2.596) kJ·mol^{-1} for the reaction

$$13\ \text{H}^+ + \text{CO}_3^{2-} + \text{NO}_3^- + 10\ \text{e}^- \Leftrightarrow \text{HCN(aq)} + 6\ \text{H}_2\text{O(l)}$$

which corresponds to

$$\log_{10}K°(298.15\ \text{K}) = (117.34 \pm 0.45)$$

since $\Delta_r G_m° = -RT\ln K°$, or $\log_{10}K° = -\Delta_r G_m°/5.70804$ for T = 298.15 K and $\Delta_r G_m°$ in kJ·mol^{-1}. The standard deprotonation constant of HCN and the corresponding standard molar enthalpy of reaction included in our database

$$\text{HCN(aq)} \Leftrightarrow \text{CN}^- + \text{H}^+$$

$$\log_{10}K°(298.15\ \text{K}) = -(9.21 \pm 0.02)$$

$$\Delta_r H_m°(298.15\ \text{K}) = (43.60 \pm 0.20)\ \text{kJ·mol}^{-1}$$

were selected by Olin et al. (2005). The former is based on a IUPAC-review by Beck (1987) and the latter on calorimetric measurements. The ion interaction coefficient

$$\varepsilon(\text{CN}^-, \text{Na}^+) = (0.07 \pm 0.03)\ \text{kg·mol}^{-1}$$

selected by Gamsjäger et al. (2005) and included in our database was reported by Bányai et al. (1992).

Thiocyanate: Grenthe et al. (1992) selected the standard Gibbs free energy and the standard enthalpy of formation for SCN^- from Wagman et al. (1982) and calculated the standard entropy from these values. Thus

$$\Delta_f G_m°(\text{SCN}^-, 298.15\ \text{K}) = (92.7 \pm 4.0)\ \text{kJ·mol}^{-1}$$

$$\Delta_f H_m°(\text{SCN}^-, 298.15\ \text{K}) = (76.4 \pm 4.0)\ \text{kJ·mol}^{-1}$$

$$S_m°(\text{SCN}^-, 298.15\ \text{K}) = (144.27 \pm 18.97)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

The equilibrium constant for the redox reaction linking HCN(aq) and HS^- with SCN^- can be calculated as follows: From $\Delta_f G_m°$(HCN, aq, 298.15 K) = (114.37 ± 2.52) kJ·mol^{-1} discussed above, and $\Delta_f G_m°(HS^-$, 298.15 K) = (12.243 ± 2.115) kJ·mol^{-1} and $\Delta_f G_m°(SCN^-$, 298.15 K) = (92.7 ± 4.0) kJ·mol^{-1}, both selected by Grenthe et al. (1992), follows $\Delta_r G_m°$(298.15 K) = -(33.913 ± 7.137) kJ·mol^{-1} for

$$\text{HCN(aq)} + \text{HS}^- \Leftrightarrow \text{SCN}^- + 2\ \text{H}^+ + 2\text{e}^-$$

which corresponds to

$$\log_{10}K°(298.15\ \text{K}) = (5.94 \pm 1.25)$$

The ion interaction coefficients for SCN^-

$$\varepsilon(\mathrm{SCN^-, Na^+}) = (0.05 \pm 0.01)\ \mathrm{kg\cdot mol^{-1}}$$

$$\varepsilon(\mathrm{SCN^-, K^+}) = -(0.01 \pm 0.01)\ \mathrm{kg\cdot mol^{-1}}$$

included in our database were selected by Grenthe et al. (1992), based on Ciavatta (1980), who obtained them from isopiestic mean activity coefficient data.

13.4 Pyrophosphate

The standard formation constants (from HPO_4^{2-}) for $P_2O_7^{4-}$ and $HP_2O_7^{3-}$ included in our database were calculated from $\Delta_fG_m°(HPO_4^{2-}$, 298.15 K) = -(1095.985 ± 1.567) kJ·mol^{-1}, $\Delta_fG_m°(H_2O$, l, 298.15 K) = -(237.140 ± 0.041) kJ·mol^{-1}, $\Delta_fG_m°(P_2O_7^{4-}$, 298.15 K) = -(1935.503 ± 4.563) kJ·mol^{-1}, and $\Delta_fG_m°(HP_2O_7^{3-}$, 298.15 K) = -(1989.158 ± 4.482) kJ·mol^{-1}, all selected by Grenthe et al. (1992). As above, the resulting $\Delta_rG_m°(2\ HPO_4^{2-} \Leftrightarrow P_2O_7^{4-} + H_2O(l)$, 298.15 K) = (19.327 ± 5.536) kJ·mol^{-1} and $\Delta_rG_m°(2\ HPO_4^{2-} + H^+ \Leftrightarrow HP_2O_7^{3-} + H_2O(l)$, 298.15) = -(34.328 ± 5.469) kJ·mol^{-1} were transformed into the corresponding stability constants, leading to the selected

$$2\ \mathrm{HPO_4^{2-}} \Leftrightarrow \mathrm{P_2O_7^{4-}} + \mathrm{H_2O(l)}$$

$$\log_{10}K°(298.15\ \mathrm{K}) = -(3.39 \pm 0.97)$$

$$2\ \mathrm{HPO_4^{2-}} + \mathrm{H^+} \Leftrightarrow \mathrm{HP_2O_7^{3-}} + \mathrm{H_2O(l)}$$

$$\log_{10}K°(298.15\ \mathrm{K}) = (6.01 \pm 0.96)$$

The ion interaction coefficients

$$\varepsilon(\mathrm{P_2O_7^{4-}, Na^+}) = -(0.26 \pm 0.05)\ \mathrm{kg\cdot mol^{-1}}$$

$$\varepsilon(\mathrm{P_2O_7^{4-}, K^+}) = -(0.15 \pm 0.05)\ \mathrm{kg\cdot mol^{-1}}$$

included in our database were selected by Grenthe et al. (1992), based on Ciavatta (1980), who derived them from isopiestic mean activity coefficient data, while we estimated

$$\varepsilon(\mathrm{HP_2O_7^{3-}, Na^+}) = -(0.15 \pm 0.20)\ \mathrm{kg\cdot mol^{-1}}$$

based on charge correlations (see Appendix A).

Table 13.1: New or updated auxiliary data. New or changed data with respect to TDB Version 01/01 (Hummel et al., 2002) are shaded.

	TDB Version 01/01				**TDB Version 12/07**				
Name	$\Delta_f G_m°$ [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}]	$\Delta_f G_m°$ [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}]	**Species**
IO3-	-	-	-	-	-126.34 ± 0.78	-219.7 ± 0.5	118 ± 2	-	IO_3^-
HCN	-	-	-	-	114.37 ± 2.52	103.75 ± 3.54	131.3 ± 8.4	-	HCN(aq)
SCN-	-	-	-	-	92.7 ± 4.0	76.4 ± 4.0	144.27 ± 18.97	-	SCN^-

	TDB Version 01/01		**TDB Version 12/07**		
Name	$\log_{10}\beta°$	$\Delta_r H_m°$ [kJ·mol^{-1}]	$\log_{10}\beta°$	$\Delta_r H_m°$ [kJ·mol^{-1}]	**Reaction**
I2	(-20.95)[a]	-	-20.95	-	$2\,I^- \Leftrightarrow I_2(aq) + 2\,e^-$
IO3-	-	-	-101.09	-	$0.5\,I_2(aq) + 3\,H_2O(l) \Leftrightarrow IO_3^- + 6\,H^+ + 5\,e^-$
HIO3	-	-	0.788 ± 0.029	-	$IO_3^- + H^+ \Leftrightarrow HIO_3(aq)$
HCN	-	-	(117.34 ± 0.45)[b]	-	$13\,H^+ + CO_3^{2-} + NO_3^- + 10\,e^- \Leftrightarrow HCN(aq) + 6\,H_2O(l)$
CN-	-	-	-9.21 ± 0.02	43.60 ± 0.20	$HCN(aq) \Leftrightarrow CN^- + H^+$
SCN-	-	-	(5.94 ± 1.25)[b]	-	$HCN(aq) + HS^- \Leftrightarrow SCN^- + 2\,H^+ + 2e^-$
P2O7-4	-	-	-3.39 ± 0.97	-	$2\,HPO_4^{2-} \Leftrightarrow P_2O_7^{4-} + H_2O(l)$
HP2O7-3	-	-	6.01 ± 0.96	-	$2\,HPO_4^{2-} + H^+ \Leftrightarrow HP_2O_7^{3-} + H_2O(l)$

[a] This value was erroneously entered with a reversed sign (as +20.95) into the PMATCHC- and PHREEQC-version of the Nagra/PSI TDB 01/01. As a consequence, the values for $\Delta_f G_m°(I_2, aq)$ and $\Delta_f G_m°(I_3^-)$ entered into the GEMS-version of the Nagra/PSI TDB 01/01 were also incorrect.

[b] Note that compared to Thoenen (2012), this value is rounded to hundredths. In addition, Thoenen (2012) reported no uncertainty.

Table 13.2: Selected SIT ion interaction coefficients $\varepsilon_{j,k}$ [kg·mol^{-1}] for updated auxiliary data. The data included in TDB Version 12/07 are taken from Rand et al. (2008). Data estimated according to charge correlations (see Appendix A) are shaded.

j *k*→ ↓	**Cl^-** $\varepsilon_{j,k}$	**ClO_4^-** $\varepsilon_{j,k}$	**NO_3^-** $\varepsilon_{j,k}$	**Li^+** $\varepsilon_{j,k}$	**Na^+** $\varepsilon_{j,k}$	**K^+** $\varepsilon_{j,k}$
I2	0	0	0	0	0	0
IO3-	0	0	0	-	-0.06 ± 0.02	-
HIO3	0	0	0	0	0	0
HCN	0	0	0	0	0	0
CN-	0	0	0	-	0.07 ± 0.03	-
SCN-	0	0	0	-	0.05 ± 0.01	-0.01 ± 0.01
P2O7-4	0	0	0	-	-0.26 ± 0.05	-0.15 ± 0.05
HP2O7-3	0	0	0	-	-0.15 ± 0.20	-

13.5 References

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Appendix A: Ionic strength corrections and estimation of SIT ion interaction coefficients

A.1 Ionic strength corrections

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 historically most "popular" media were $NaClO_4$ and KNO_3 at high concentrations. Both are of no relevance for environmental modelling. Nowadays, also NaCl is used as ionic medium.

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 different 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 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.

A.1.1 The Debye-Hückel limiting law

The classical Debye-Hückel limiting law takes into account only long-range electrostatic interactions between ions of opposite charge which are 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 0.509 $kg^{1/2} \cdot mol^{-1/2}$ 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

$$I_m = 1/2 \, \Sigma \, m_i \cdot z_i^2$$

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.

A.1.2 The extended Debye-Hückel equation

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

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

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 $å_i$ is know as the ion-size parameter or the 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 PSI/Nagra TDB for use with the extended Debye-Hückel equation which is implemented in PHREEQC and GEMS.

A.1.3 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, EQ3/6 and GEMS 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 PSI/Nagra 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 and GEMS the **B-dot equation** of Helgeson (1969) is used (Wolery et al. 1990):

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

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 $B \cdot å_i = 1$ $kg^{1/2} \cdot mol^{-1/2}$ 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 and GEMS 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.

A.1.4 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)

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

where the term $B \cdot å_j = 1.5\ kg^{1/2} \cdot mol^{-1/2}$ is assumed to be a constant, and $\varepsilon(j,k)$ is an aqueous species interaction coefficient which describes the specific short-range interactions between aqueous species j 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

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

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 $\varepsilon(j,k)$ coefficients were taken from Rand et al. (2008), or were derived from $\log_{10}K$ data at varying ionic strength whenever possible.

A.1.5 Ion association versus ion interaction

The various extended Debye-Hückel equations discussed in A.1.2 and A.1.3 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.

$$Na^+ + HCO_3^- \Leftrightarrow NaHCO_3(aq)$$

which are described by equilibrium constants.

In contrast to these ion association models, ion interaction models like SIT and the Pitzer formalism account for individual characteristics of electrolytes by different interaction coefficients $\varepsilon(j,k)$, i.e. $\varepsilon(HCO_3^-, Na^+) \neq \varepsilon(HCO_3^-, K^+)$, and a weak complex like $NaHCO_3(aq)$ 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. The present version of the PSI/Nagra TDB is not yet internally consistent with respect to the treatment of weak complexes. Note that no unambiguous procedure exists for discriminating weak complexes versus strong ion interactions. There is no agreement where to set the borderline between weak and strong complexes, which would be different for SIT and the Pitzer formalism. In addition, weak complexes at room temperature may become strong complexes at high temperatures.

A.1.6 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 (A.1.1), the extended Debye-Hückel equation (A.1.2) and the Davies equation (A.1.3) 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 (A.1.3) a term proportional to the ionic strength remains for neutral species:

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

In PHREEQC $b_i = 0.1$ is used as default expression for all neutral species at all temperatures. In all MINEQL-type codes $b_i = 0$ is used. In GEMS individual values of b_i are used, wherever provided, or the user can set a common b_i parameter for all neutral species. This may lead to (small) differences comparing otherwise identical speciation calculations done with PHREEQC, MINEQL and GEMS.

In EQ3/6, following Helgeson (1969), the activity coefficients for all neutral species are taken as equal to those of dissolved CO2. 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.

For the SIT equation the case of neutral species is less clear. Whereas in SIT the ion interaction coefficients are assumed to be zero for ions of the same charge sign, e.g. $\varepsilon(\text{Al(OH)}_4^-,\text{Cl}^-) = 0$ there is no conceptual problem with including possible interactions between uncharged and ionic species in the SIT model (Grenthe et al. 1997), e.g.

$$\log_{10}\gamma(\text{H}_2\text{S(aq)}) = \varepsilon(\text{H}_2\text{S(aq)},\text{Na}^+) \cdot m(\text{Na}^+) + \varepsilon(\text{H}_2\text{S(aq)},\text{Cl}^-) \cdot m(\text{Cl}^-) =$$

$$\varepsilon(\text{H}_2\text{S(aq)},\text{Na}^+ + \text{Cl}^-) \cdot m(\text{NaCl})$$

where we assume $\varepsilon(\text{H}_2\text{S(aq)},\text{Na}^+) = \varepsilon(\text{H}_2\text{S(aq)},\text{Cl}^-)$, and $m(\text{Na}^+) = m(\text{Cl}^-)$ in pure NaCl medium.

However, for the sake of simplicity, the guidelines for NEA reviews (Grenthe et al. 1992) assumed that the SIT interaction coefficients for uncharged species were zero. We generally followed these guidelines, as did the NEA reviewers, but for a growing number of cases in the NEA reviews (see Table B-7 in Rand et al. 2008), as well as for H_2S(aq) and $Si(OH)_4$(aq) from our in-house reviews it can be shown that ε(j,k) is not zero.

In all these cases extrapolations of experimental data to $I = 0$ with $\varepsilon(j,k) = 0$ or $\varepsilon(j,k) \neq 0$ lead to slightly different $\log_{10}K°$ values. Furthermore, deriving consistent sets of ε(j,k) for aqueous sulphide and aqueous silicate species from reaction data depend on this decision. At present, most data in our TDB ultimately are based on the assumption $\varepsilon(j,k) = 0$ for uncharged species.

The formally correct treatment of non-zero SIT ion interaction coefficients for uncharged species is implemented in GEMS.

A.2 Estimation of SIT ion interaction coefficients

A.2.1 Estimation from mean activity coefficient data

Most of the currently used SIT ion interaction coefficients for simple ions were originally derived by Ciavatta (1980) from mean activity coefficient data, $\gamma_\pm$, published by Robinson & Stokes (1959). These mean activity data in turn were derived from osmotic coefficient data mainly coming from isopiestic measurements. Robinson & Stokes (1959) critically reviewed the available experimental data and published the results as smoothed values in tabular form. It is believed that the values in these tables are reliable and nobody ever went back beyond these tables in order to re-review the original experimental data.

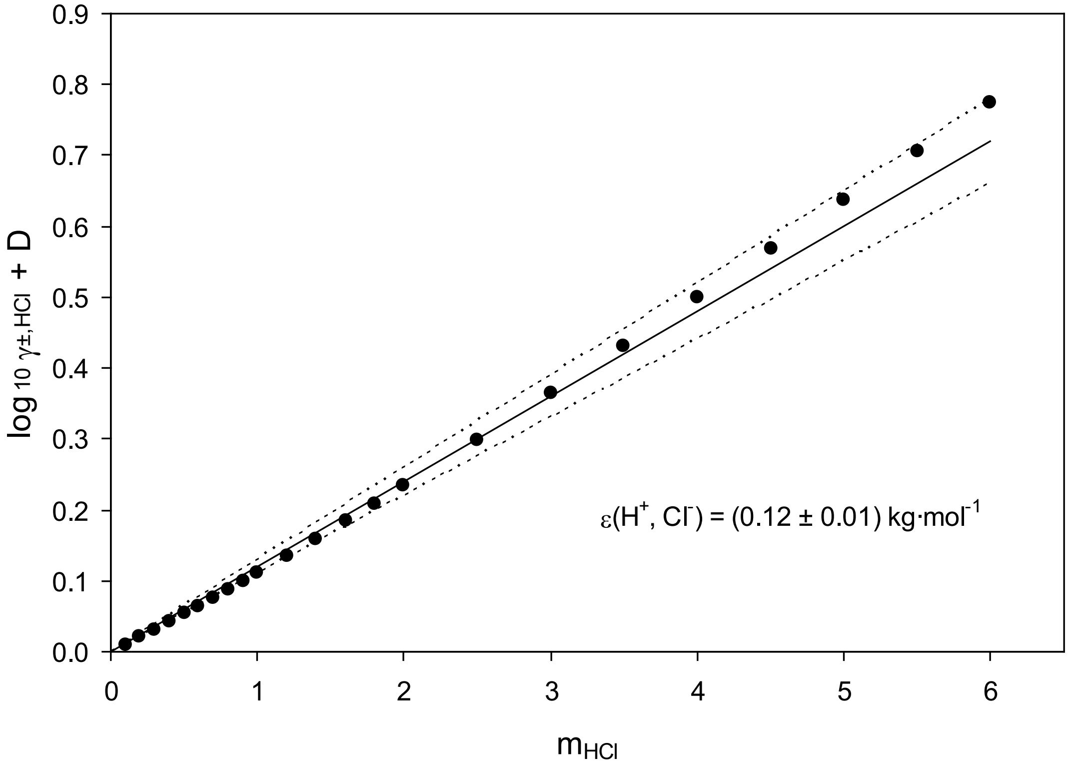

Fig. A.1: Mean activity coefficient data of HCl plotted versus the molal concentration of HCl. Data (black circles) taken from Table 9 in Appendix 8.10 of Robinson & Stokes (1959). The slope (solid line) and its uncertainty range, back propagated from zero to high concentration (dotted lines) represent the value $\varepsilon(H^+,Cl^-) = (0.12 \pm 0.01)$ kg·mol^{-1} evaluated by Ciavatta (1980).

As an example, the ion interaction coefficient $\varepsilon(H^+,Cl^-)$ can be obtained from published values of $\gamma_\pm(HCl)$ versus m(HCl):

$$2\log_{10}\gamma_\pm(\mathrm{HCl}) = \log_{10}\gamma(\mathrm{H}^+) + \log_{10}\gamma(\mathrm{Cl}^-)$$

$$2\log_{10}\gamma_\pm(\mathrm{HCl}) = -D + \varepsilon(\mathrm{H}^+,\mathrm{Cl}^-)\cdot m(\mathrm{Cl}^-) - D + \varepsilon(\mathrm{Cl}^-,\mathrm{H}^+)\cdot m(\mathrm{H}^+)$$

where $D = A \cdot z_i^2 \cdot \sqrt{I_m} / (1 + 1.5 \cdot \sqrt{I_m})$. Considering the symmetry $\varepsilon(H^+,Cl^-) = \varepsilon(Cl^-,H^+)$ and assuming that HCl is completely dissociated into H^+ and Cl^- over the entire concentration range of pure aqueous HCl solution, i.e. $m(Cl^-) = m(H^+) = m(HCl)$, we obtain

$$\log_{10}\gamma_{\pm}(\mathrm{HCl}) + D = \varepsilon(\mathrm{H^+,Cl^-}) \cdot m(\mathrm{HCl})$$

By plotting ($\log_{10}\gamma_{\pm}$(HCl) + D) versus m(HCl) a straight line through the origin with a slope $\varepsilon(\mathrm{H^+,Cl^-})$ should result (Fig. A.1). The degree of linearity should itself indicate the range of validity of the specific ion interaction approach. Actually, none of the plots involving mean activity data result in exactly straight lines. The above plot of HCl data exhibits one of the smallest curvatures and thus is not a "typical example" but belongs to the class of "very good examples".

Ciavatta (1980) calculated ε(j,k) for every single data point given in the tables of Robinson & Stokes (1959) and obtained the final results "as the weighed (sic!) average, $\Sigma I\cdot\varepsilon(j,k) / \Sigma I$, when a trend not exceeding 0.03 was observed in the I range from 0.5 to 3.5 mol/kg".

The decision to inspect this ionic strength range may have been guided by the fact that reliable experimental complexation studies should be carried out in 0.5 to 3.5 $\mathrm{mol\cdot kg^{-1}}$ background electrolyte. The same decision may be the origin of the often repeated statement that SIT works only up to $I_m = 3.5$ molal. By contrast, the value $\varepsilon(\mathrm{H^+,Cl^-}) = (0.12 \pm 0.01)\ \mathrm{kg\cdot mol^{-1}}$ chosen by Ciavatta (1980) encloses the entire data range up to the maximum concentration of 6 molal HCl in Fig. A.1.

In his original publication Ciavatta (1980) did not report uncertainties for SIT interaction parameters. These were provided later as "private communication" for the NEA TDB project (reference [88CIA] in Grenthe et al. 1992).

In some cases of strong deviations from linearity, e.g. for sulphate and phosphate salts, Ciavatta (1980) proposed an alternative SIT equation with two adjustable SIT interaction parameters. In these cases, the data were fitted with the linear function $\varepsilon(j,k) = \varepsilon(1,j,k) + \varepsilon(2,j,k) \cdot \log_{10}I_m$.

These parameters are tabulated (e.g. Table B-6 in Rand et al. 2008) but there is no consistent use of them in NEA reviews and they are not included in the current implementation of SIT in GEMS. The main reason for not using this linear function is that it is ill-behaved at low ionic strengths. If I_m approaches zero the term $\varepsilon(2,j,k) \cdot \log_{10}I_m$ approaches minus infinity.

Note that the same mean activity coefficient data published by Robinson & Stokes (1959) have been used to derive the basic set of Pitzer parameters for simple ions (Pitzer & Mayorga 1973). The Pitzer formalism involves more adjustable parameters and hence perfectly describes the generally non-linear behavior of mean activity coefficient data.

A.2.2 Estimations based on experimental values of equilibrium constants at different ionic strengths

Starting from a set of basic SIT interaction parameters for simple ions, derived from mean activity coefficient data as described above, experimental values of equilibrium constants at different ionic strengths have been used to estimate SIT interaction parameters for complexes.

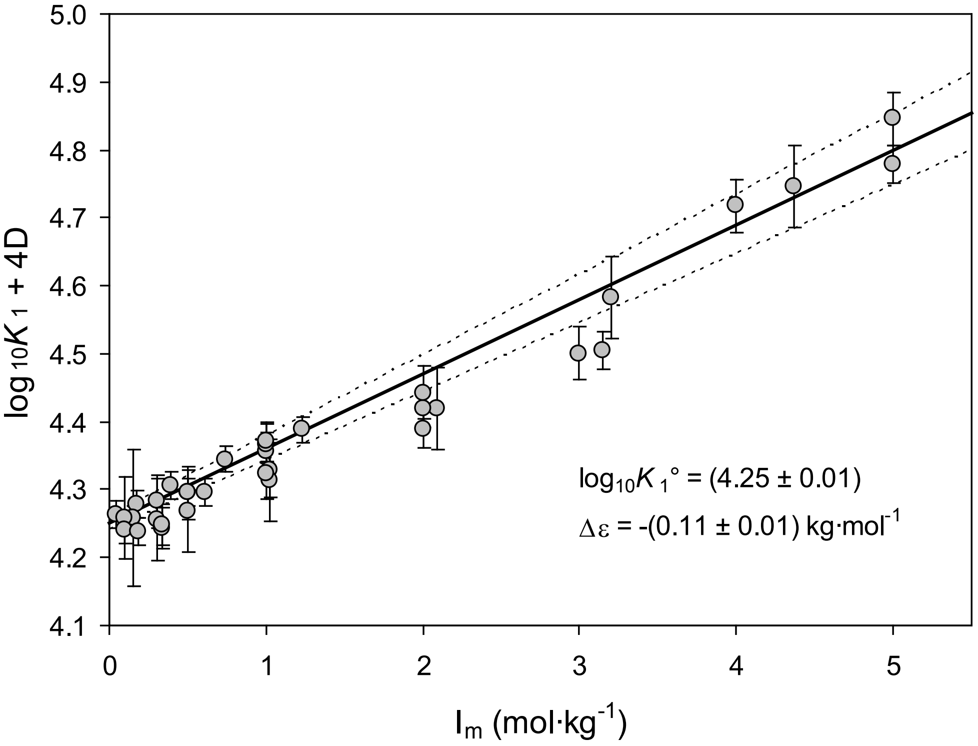

Fig. A.2: Plot of $\log_{10}K_1 + 4D$ versus I_m for reaction $ox^{2-} + H^+ \Leftrightarrow Hox^-$, in NaCl at 25°C and 1 bar. The solid straight line shows the result of a weighted linear regression, and the dotted lines represent the uncertainty range obtained by propagating the resulting uncertainties at $I_m = 0$ back to 5 molal. Data taken from Hummel et al. (2005).

As an example, we consider the reaction $ox^{2-} + H^+ \Leftrightarrow Hox^-$. The abbreviation ox stands for oxalate, and the above reaction represents the first protonation step of the oxalate anion, ox^{2-}, to Hox^-. The second protonation step, $Hox^- + H^+ \Leftrightarrow H_2ox(aq)$, leads to dissolved oxalic acid.

The formation constant of Hox^-, K_1, in the ionic medium NaCl of the ionic strength I_m, is related to the corresponding value at zero ionic strength, $K_1°$, by the following equation:

$$\log_{10}K_1 = \log_{10}K_1° + \log_{10}\gamma(ox^{2-}) + \log_{10}\gamma(H^+) - \log_{10}\gamma(Hox^-)$$

Substituting the $\log_{10}\gamma(j)$ values with the corresponding SIT equations and rearranging leads to:

$$\log_{10}K_1 - \Delta z^2 \cdot D = \log_{10}K_1° - \Delta\varepsilon \cdot I_m$$

where $\Delta z^2 = 1^2 - 1^2 - 2^2 = -4$, and $\Delta\varepsilon = \varepsilon(Hox^-,Na^+) - \varepsilon(ox^{2-},Na^+) - \varepsilon(H^+,Cl^-)$.

A weighted linear regression as described in Appendix C of Rand et al. (2008) using data taken from Hummel et al. (2005) yields the following results (Fig. A.2):

$$\log_{10}K_1° = (4.25 \pm 0.01) \text{ and } \Delta\varepsilon = -(0.11 \pm 0.01) \text{ kg·mol}^{-1}.$$

From the result of the linear regression, $\Delta\varepsilon$, and the value $\varepsilon(H^+,Cl^-) = (0.12 \pm 0.01)$ kg·mol^{-1} determined from mean activity coefficient data, we obtain:

$$\varepsilon(Hox^-,Na^+) - \varepsilon(ox^{2-},Na^+) = \Delta\varepsilon + \varepsilon(H^+,Cl^-) = (0.01 \pm 0.01) \text{ kg·mol}^{-1}$$

Hence, the result of the SIT regression analysis (Fig. A.2) is the difference between two unknown SIT interaction parameters, $\varepsilon(Hox^-,Na^+) - \varepsilon(ox^{2-},Na^+)$. In an analogous way, the SIT regression analysis of the second protonation step, $Hox^- + H^+ \Leftrightarrow H_2ox(aq)$, leads to another difference of two unknown SIT parameters, $\varepsilon(H_2ox(aq),NaCl) - \varepsilon(Hox^-,Na^+) = (0.07 \pm 0.01)$ $kg \cdot mol^{-1}$ (Hummel et al. 2005). There are no experimental data to determine the value of $\varepsilon(H_2ox(aq),NaCl)$.

Hummel et al. (2005) decided to assume $\varepsilon(H_2ox(aq),NaCl) = 0$ and hence calculated, based on this assumption, $\varepsilon(Hox^-,Na^+) = -(0.07 \pm 0.01)\ kg \cdot mol^{-1}$ and $\varepsilon(ox^{2-},Na^+) = -(0.08 \pm 0.01)$ $kg \cdot mol^{-1}$.

Most SIT interaction coefficient values for complexes depend on such assumed zero values for neutral species. Note that the situation would not improve if all the above analyses would have been done using the Pitzer formalism. In the absence of experimental data for neutral species, the same kind of assumptions are necessary to derive Pitzer parameters for aqueous complexes.

A.2.3 Estimations based on correlations involving SIT parameters

If experimental data as described in Sections A.2.1 and A.2.2 are not available, or not sufficiently reliable for SIT analyses, SIT interaction parameters sometimes have to be estimated in order to obtain a reasonably complete data base.

The simplest and most often used estimation procedure is based on assumptions concerning **chemical analogy**.

The similar ionic radii of the actinide series are often used to justify assumptions like $\varepsilon(UO_2^{2+},ClO_4^-) \approx \varepsilon(NpO_2^{2+},ClO_4^-) \approx \varepsilon(PuO_2^{2+},ClO_4^-)$. In this series only $\varepsilon(UO_2^{2+},ClO_4^-)$ has been derived from mean activity data as described in A.2.1, and the values for NpO_2^{2+} and PuO_2^{2+} were assumed to be the same as for UO_2^{2+}.

The similar values for Na and K forms of SIT interaction coefficients are used as an argument for analogies like $\varepsilon(Mg(ox)_2^{2-},Na^+) \approx \varepsilon(Mg(ox)_2^{2-},K^+)$. Likewise, the similar values for Ca and Mg forms of SIT interaction coefficients may justify $\varepsilon(Mg(ox)_2^{2-},Na^+) \approx \varepsilon(Ca(ox)_2^{2-},Na^+)$. In these cases only $\varepsilon(Mg(ox)_2^{2-},Na^+)$ has been derived from experimental values of equilibrium constants at different ionic strengths as described in A.2.2.

Sometimes only charge considerations serve as plausibility argument, e.g. $\varepsilon(Np(SCN)_3^+,ClO_4) \approx \varepsilon(AmF_2^+,ClO_4^-)$. In this example the actinides do not have the same charge and the complexes have different stoichiometries, only the resulting charge of the complex is the same.

All the above examples were taken from Appendix B in Rand et al. (2008).

There are no formal criteria for estimating SIT interaction parameters by chemical analogy. They are all expert judgments, mostly introduced ad hoc when the need arose in the TDB review procedure.

An estimation method based on statistics is the correlation of SIT parameters in different media. As an example, the **linear correlation of SIT interaction parameters** for non-complexed cations in perchlorate and chloride media is shown in Fig. A.3 (see also Neck et al. 2006).

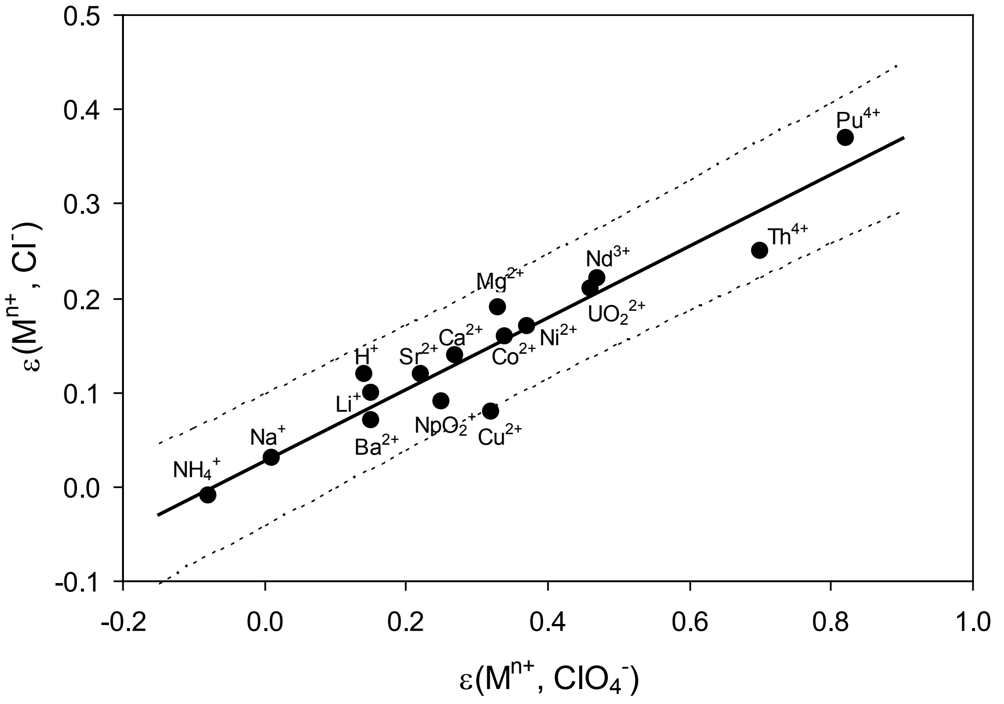

Fig. A.3: Linear correlation of SIT interaction parameters in perchlorate and chloride media. Data (black circles) taken from Rand et al. (2008). The solid straight line is the result of an unweighted linear regression, $\varepsilon(M^{n+},Cl^-) = 0.028 + 0.38 \cdot \varepsilon(M^{n+},ClO_4^-)$ $kg \cdot mol^{-1}$. The bent dotted lines indicate the 95% confidence interval for estimating $\varepsilon(M^{n+},Cl^-)$ from a given value $\varepsilon(M^{n+},ClO_4^-)$. The confidence interval ranges from ± 0.07 $kg \cdot mol^{-1}$ in the centre of the regression region to ± 0.08 $kg \cdot mol^{-1}$ at its lower and upper limits.

A similar linear correlation exists for SIT interaction parameters in perchlorate and nitrate media (Grenthe et al. 1997, Neck et al. 2006).

Linear correlations are also found between SIT interaction parameters and the ion potential Z/r (Z and r stand for the charge and crystallographic ion radius, respectively). For examples of such correlations see Grenthe et al. (1997) and Neck et al. (2006).

These correlations are rarely used to actually estimate new SIT parameters. Their main application is to discuss and possibly confirm the reliability of new experimentally determined SIT interaction parameters. An example of such applications of linear correlations of SIT parameters in different media and between SIT parameters and ionic radius is given by Neck et al. (2006) concerning the values of $\varepsilon(Th^{4+},ClO_4^-)$, $\varepsilon(Th^{4+},NO_3^-)$ and $\varepsilon(Pu^{4+},Cl^-)$.

A.2.4 Estimations of SIT parameters by charge considerations only

In the past SIT was solely used to extrapolate experimental values of equilibrium constants to zero ionic strength as part of TDB review procedures. For this purpose the above described estimation methods were sufficient to fill the gaps in the SIT interaction coefficient matrix and to obtain an internally consistent set of recommended thermodynamic data.

However, when SIT is applied in environmental modelling, the formally correct implementation of SIT in a speciation code like GEMS is not sufficient. The remaining gaps in the SIT interaction coefficient matrix have to be filled with reasonably justified "default values" in all cases where the above described estimation procedures cannot be applied due to a lack of specific data.

In the current version of our TDB we decided to restrict the application of SIT to environmental systems where the salinity is governed by NaCl.

In addition, laboratory systems can be modelled for NaCl and $NaClO_4$ media. The nowadays rarely used background medium KNO_3 was not considered.

The method to estimate "default" SIT values was a thorough statistical analysis of all published SIT interaction coefficients for NaCl and $NaClO_4$ media.

SIT ε(j,k) values were taken from Tables B-4, B-5 and B-7 in Rand et al. (2008). Uncertainties of individual ε(j,k) smaller than ± 0.05 $kg \cdot mol^{-1}$ have been increased to ± 0.05 $kg \cdot mol^{-1}$.

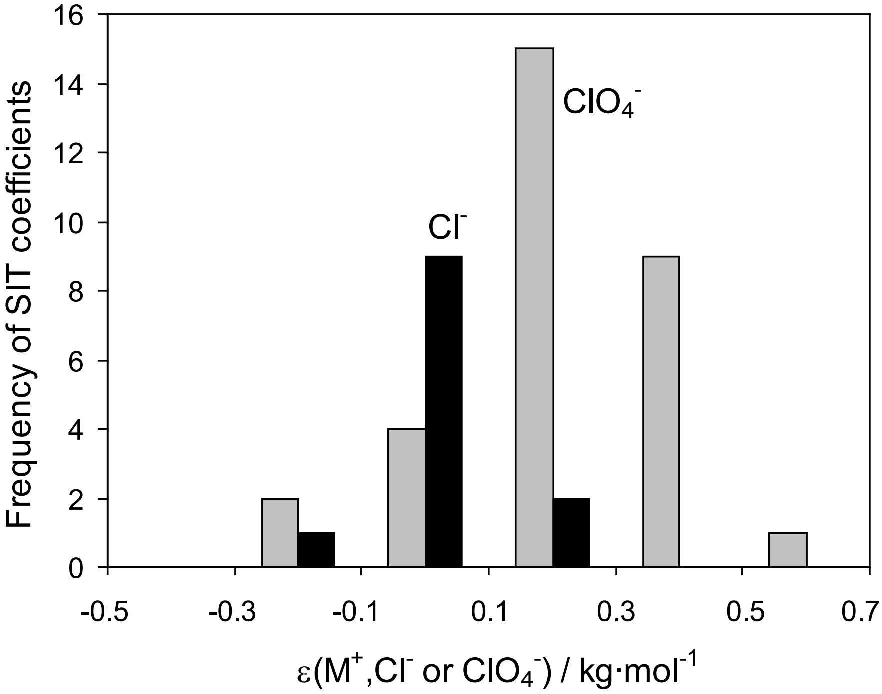

Fig. A.4: Frequency of SIT interaction parameters $\varepsilon(M^+,Cl^-)$ (black bars) and $\varepsilon(M^+,ClO_4^-)$ (grey bars). The histogram is produced with data taken from Rand et al. (2008). Statistical analyses of these data resulted in $\varepsilon(M^+,Cl^-)$ = (0.02 ± 0.08) $kg \cdot mol^{-1}$ (unweighted mean) or (0.04 ± 0.02) $kg \cdot mol^{-1}$ (weighted mean); and $\varepsilon(M^+,ClO_4^-)$ = (0.22 ± 0.07) $kg \cdot mol^{-1}$ (unweighted mean) or (0.20 ± 0.01) $kg \cdot mol^{-1}$ (weighted mean). All uncertainties refer to the 95% confidence level.

Data estimated by correlation methods as described in Section A.2.3 were removed from the data set for statistical analyses. Furthermore, three other data were excluded from statistical analyses:

The values for $\varepsilon((UO_2)_3(OH)_5^+,Cl^-)$ and $\varepsilon((UO_2)_2(OH)_2^{2+},Cl^-)$ were each derived based on one experimentally determined equilibrium constant only (Grenthe et al. 1992). The results are total outliers compared with values derived for the same species in perchlorate and nitrate media.

The value reported for ε($NiHS^+$,Cl^-) by Gamsjäger et al. (2005) is dubious. In Table B-4 of Gamsjäger et al. (2005) the value is given in the perchlorate column, but in the corresponding text the discussion is about equilibrium constants determined in sea water. The calculation of ε($NiHS^+$,Cl^-) from Δε is unclear, i.e. the value used for ε(HS^-,Na^+) is not given.

To this data set, taken from Rand et al. (2008), the values ε(H_2S(aq),NaCl) = (0.06 ± 0.05) kg·mol^{-1} and ε($Si(OH)_4$(aq),NaCl) = (0.10 ± 0.05) kg·mol^{-1} from our in-house reviews were added.

Table A.1: SIT interaction parameter estimations based on charge considerations only. For each charge type and medium the number of data used for statistical analysis, the unweighted mean, the weighted mean and the finally selected "default value" is given. In addition, for chloride medium the value calculated with the linear correlation (Fig. A.3) is given, based on the selected "default" value for perchlorate medium.

Charge	ε(M^{n+},ClO_4^-)				ε(M^{n+},Cl^-)				
	No.	Unweighted mean	Weighted mean	Selec ted	No.	Unweighted mean	Weighted mean	Selec ted	Correlation
1	31	0.22 ± 0.07	0.20 ± 0.01	0.2	12	0.02 ± 0.08	0.04 ± 0.02	0.05	0.10 ± 0.07
2	23	0.37 ± 0.07	0.33 ± 0.01	0.4	15	0.17 ± 0.07	0.16 ± 0.01	0.15	0.18 ± 0.07
3	15	0.58 ± 0.06	0.55 ± 0.02	0.6	5	0.27 ± 0.07	0.27 ± 0.02	0.25	0.26 ± 0.07
4	9	0.79 ± 0.11	0.81 ± 0.02	0.8	5	0.34 ± 0.11	0.34 ± 0.03	0.35	0.33 ± 0.08

Table A.2: SIT interaction parameter estimations based on charge considerations only. For each charge type the number of data used for statistical analysis, the unweighted mean, the weighted mean and the finally selected "default value" is given.

Charge	ε(MX, NaCl or $NaClO_4$)			
	No.	Unweighted mean	Weighted mean	Selected
0	11	−0.01 ± 0.11	0.03 ± 0.02	0.0
	ε(X^{n-}, Na^+)			
−1	37	−0.03 ± 0.06	−0.02 ± 0.01	−0.05
−2	23	−0.10 ± 0.05	−0.11 ± 0.01	−0.10
−3	8	−0.10 ± 0.19	−0.15 ± 0.03	−0.15

Table A.3: SIT interaction parameter estimations based on charge considerations only. The results of linear regression analyses, based on weighted means given in Tabs. A.1 and A.2 and Fig. A.5, and the finally selected "default values" are given.

SIT coefficient	linear regression of weighted mean values			selected	
	charge range	constant	slope	constant	slope
$\varepsilon(M^{n+},Cl^-)$	1 … 5	-0.049 ± 0.016	0.100 ± 0.005	-0.05	0.10
$\varepsilon(M^{n+},ClO_4^-)$	0 … 4	0.00 ± 0.03	0.191 ± 0.014	0.00	0.20
$\varepsilon(X^{n-},Na^+)$	-1 … -4	0.01 ± 0.03	0.049 ± 0.013	0.00	0.05

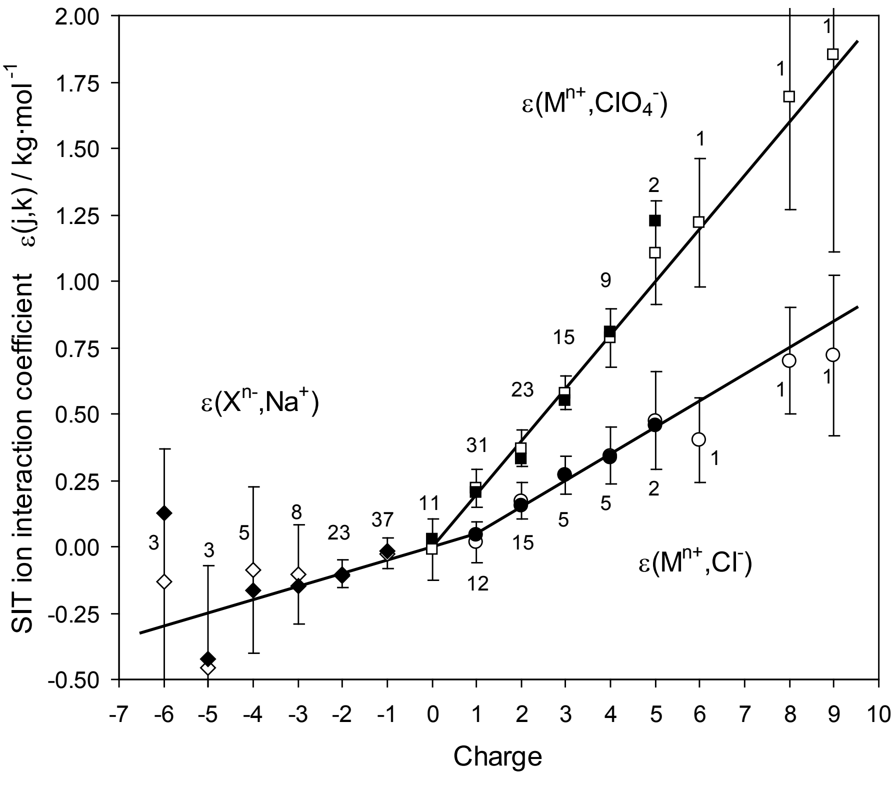

Fig. A.5: Correlation of SIT interaction parameters with charge only. White symbols with error bars represent unweighted means where the uncertainty is based on the dispersion of the data points. Black symbols represent weighted means, their uncertainties are always ±0.02 or less, i.e. in the size of the black symbols. The number of data points used to calculate the means are given in the figure. In the case of just one data point the estimated uncertainty of the SIT parameter is shown. In all cases the uncertainty is estimated on the 95% confidence level. Black solid lines visualise the finally selected "default values" of SIT interaction parameters.

The statistical analyses comprised the following procedures:

1. Calculation of the unweighted mean, $\langle X\rangle \pm t \cdot s / \sqrt{n}$, for each charge type and medium, where $\langle X\rangle = \Sigma\varepsilon(j,k) / n$, $s = \sqrt{[\Sigma(\varepsilon(j,k) - \langle X\rangle)^2 / (n - 1)]}$ is the standard deviation, n is the number of $\varepsilon(j,k)$ values, and t is the Student t factor accounting for the number of data points used (for $n \rightarrow \infty$ $t = 1.96$). The uncertainty, $\pm t \cdot s / \sqrt{n}$, represents the dispersion of the data points at the 95% confidence level. Results are given in Tables A.1 and A.2 and Fig. A.5.
2. Calculation of the weighted mean, $\langle X\rangle \pm \sigma_{\langle X\rangle}$, for each charge type and medium, where $\langle X\rangle = \Sigma[\varepsilon(j,k) / \sigma(j,k)] / \Sigma[1 / \sigma(j,k)^2]$, $\sigma_{\langle X\rangle} = \Sigma[1 / \Sigma\{1 / \sigma(j,k)^2\}]$ and $\sigma(j,k)$ is the individual uncertainty assigned to each $\varepsilon(j,k)$ value at the 95% confidence level. Hence, the uncertainty of the weighted mean, $\pm \sigma_{\langle X\rangle}$, is based on the individual uncertainties $\sigma(j,k)$ only, and is independent of the dispersion of the data points. Results are given in Tables A.1, A.2 and Fig. A.5.
3. Calculation of linear regressions based on the weighted means. Results are given in Table A.3.

The finally selected “default values” given in Tables A.1 to A.3 and visualised in Fig. A.5 are based on these statistical results. However, they are expert choices which were guided by the idea to provide numbers as simple as possible which are still compatible with the statistical results.

The recommended “default values” are summarised in Table A.4 with estimated uncertainties. As uncertainty estimates in the charge range -3 to +4 the uncertainties of the unweighted means were taken (Tables A.1 and A.2, rounded to one significant digit), i.e. the uncertainty estimate is based on the dispersion of the data points. Uncertainties outside this charge range are mere guesses following the uncertainty trends revealed in Fig. A.5. The “default values” can also be calculated using the following equations:

$$\varepsilon(M^{n+},ClO_4^-) = \text{charge} \times 0.2$$

$$\varepsilon(M^{n+},Cl^-) = -0.05 + \text{charge} \times 0.1$$

$$\varepsilon(X^{n-},Na^+) = \text{charge} \times 0.05$$

Table A.4: SIT interaction parameter estimations based on charge considerations only. These values are recommended as "default values", i.e. in the absence of any specific SIT parameters.

Charge	$\varepsilon(M^{n+},ClO_4^-)$	$\varepsilon(M^{n+},Cl^-)$	ε(MX,NaCl)	$\varepsilon(X^{n-},Na^+)$	Uncertainty ±
9	1.8	0.85			0.7
8	1.6	0.75			0.5
7	1.4	0.65			0.4
6	1.2	0.55			0.3
5	1.0	0.45			0.2
4	0.8	0.35			0.1
3	0.6	0.25			0.1
2	0.4	0.15			0.1
1	0.2	0.05			0.1
0			0.0		0.1
-1				-0.05	0.1
-2				-0.10	0.1
-3				-0.15	0.2
-4				-0.20	0.3
-5				-0.25	0.4
-6				-0.30	0.5

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Appendix B: Tables of selected thermodynamic data

All tables of selected thermodynamic data were created with PMATCHC, Version 1.1 for Win32, (see Hummel et al. 2002), with only minor manual editing. Derived thermodynamic properties calculated by PMATCHC from "primary" thermodynamic properties are followed by an asterisk (*).

The standard state data refer to 25°C and 1 bar.

Three types of data are distinguished (see Section 1.2):

1. **Core data are set in bold.**
2. Recommended application data are set in regular font.
3. *Supplemental data are set in italics.*

Explanations to Table B1: Properties of formation from the elements and absolute properties

$\Delta_f G_m°$	Standard molar Gibbs free energy of formation from the elements	$kJ \cdot mol^{-1}$
$\Delta_f H_m°$	Standard molar enthalpy of formation from the elements	$kJ \cdot mol^{-1}$
$\Delta_f S_m°$	Standard molar entropy of formation from the elements	$J \cdot mol^{-1} \cdot K^{-1}$
$S_m°$	Standard molar entropy	$J \cdot mol^{-1} \cdot K^{-1}$
$C_{p,m}°$	Standard molar isobaric heat capacity	$J \cdot mol^{-1} \cdot K^{-1}$

Explanations to Table B2: Reaction properties

$\log_{10}K°$	Equilibrium constant	
$\Delta_r G_m°$	Standard molar Gibbs free energy of reaction	$kJ \cdot mol^{-1}$
$\Delta_r H_m°$	Standard molar enthalpy of reaction	$kJ \cdot mol^{-1}$
$\Delta_r S_m°$	Standard molar entropy of reaction	$J \cdot mol^{-1} \cdot K^{-1}$
$\Delta_r C_{p,m}°$	Standard molar isobaric heat capacity of reaction	$J \cdot mol^{-1} \cdot K^{-1}$

Values of $\log_{10}K°$ followed by a double dagger (‡) were calculated from $\Delta_r G_m°$ and—due to a bug in PMATCHC—had to be entered manually into the table.

Table B1: Properties of formation from the elements and absolute properties.

Name	**$\Delta_f G_m$°** **kJ·mol^{-1}**	**$\Delta_f H_m$°** **kJ·mol^{-1}**	**$\Delta_f S_m$°** **J·mol^{-1}·K^{-1}**	**S_m°** **J·mol^{-1}·K^{-1}**	**$C_{p,m}$°** **J·mol^{-1}·K^{-1}**
ELEMENTS					
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**
Cm	0.000	0.000	0.000	70.800	
Cs	0.000	0.000	0.000	85.230	32.210
e	0.000	0.000	0.000	**0.000**	**0.000**
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	**95.805**	**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**	26.070
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	42.090	25.090
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	52.640	26.230
U	0.000	0.000	0.000	50.200	27.660
Zr	0.000	0.000	0.000	39.080	26.080
MASTER SPECIES					
Al+3	-487.740	-538.424	-169.995*	-337.710	-133.070
Am+3	-598.700	-616.700	-60.372*	-201.000	
B(OH)3	**-969.268**	**-1072.800**	**-347.248***	**162.400**	
Ba+2	**-557.656**	**-534.800**	**76.659***	**8.400**	
Br-	**-103.850**	**-121.410**	**-58.897***	**82.550**	
Ca+2	**-552.806**	**-543.000**	**32.889***	**-56.200**	
Cl-	**-131.217**	**-167.080**	**-120.285***	**56.600**	
Cm+3	-595.388*	-615.000	-65.780*	-191.000	
Cs+	-291.456	-258.000	112.212*	132.100	
e-	**0.000**	**0.000**	**0.000***	**65.340**	**14.418**
Eu+3	-555.100	-586.000	-103.639*	-222.000	
F-	**-281.523**	**-335.350**	**-180.537***	**-13.800**	
Fe+2	-78.900	-89.100	-34.211*	-137.700	
H+	**0.000**	**0.000**	**0.000***	**0.000**	**0.000**
H2O	**-237.140**	**-285.830**	**-163.307***	**69.950**	**75.351**
HAsO4-2	**-714.592**	**-906.340**	**-643.126***	**-1.700**	
HCO3-	**-586.875**	**-690.215**	**-346.604***	**98.400**	
HPO4-2	**-1095.985**	**-1299.000**	**-680.916***	**-33.500**	
I-	**-51.724**	**-56.780**	**-16.958***	**106.450**	
K+	**-282.510**	**-252.140**	**101.861***	**101.200**	
Li+	**-292.918**	**-278.470**	**48.459***	**12.240**	
Mg+2	**-455.375**	**-467.000**	**-38.990***	**-137.000**	
Mn+2	-228.100	-220.750	24.652*	-73.600	50.000
MoO4-2	-836.300	-997.900	-542.009*	27.200	
Na+	**-261.953**	**-240.340**	**72.490***	**58.450**	
NbO3-	-932.100				
Ni+2	-45.770	-55.010	-30.991*	-131.800	-46.100
NO3-	**-110.794**	**-206.850**	**-322.173***	**146.700**	
NpO2+2	-795.900	-860.700	-217.340*	-92.400	
Pd+2	175.800	177.200	4.696*	-88.300	
PuO2+2	-762.400	-822.000	-199.899*	-71.200	
Ra+2	-561.500	-527.600	113.701*	54.000	
SeO3-2	-362.390	-507.200	-485.695*	5.100	
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	
SO4-2	**-744.004**	**-909.340**	**-554.540***	**18.500**	
Sr+2	**-563.864**	**-550.900**	**43.481***	**-31.500**	
TcO4-	-637.400	-729.400	-308.570*	199.600	-15.000
Th+4	-704.783	-768.700	-214.379*	-423.100	-224.000
UO2+2	-952.551	-1019.000	-222.871*	-98.200	42.400
Zr+4	-528.500	-608.500	-268.321*	-491.000	

Table B2: Reaction properties**.**

Name	**Reaction**					$\log_{10}K^{\circ}$	$\Delta_{r}G_{m}^{\circ}$ $kJ\cdot mol^{-1}$	$\Delta_{r}H_{m}^{\circ}$ $kJ\cdot mol^{-1}$	$\Delta_{r}S_{m}^{\circ}$ $J\cdot mol^{-1}\cdot K^{-1}$	$\Delta_{r}C_{p,m}^{\circ}$ $J\cdot mol^{-1}\cdot K^{-1}$
AQUEOUS SPECIES										
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
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
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*	
AlF2+	+1.0 Al+3	+2.0 F-			= AlF2+	12.730	-72.663*	8.100	270.882*	
AlF3	+1.0 Al+3	+3.0 F-			= AlF3	16.780	-95.781*	8.900	351.102*	
AlF4-	+1.0 Al+3	+4.0 F-			= AlF4-	19.290	-110.108*	10.100	403.180*	
AlF5-2	+1.0 Al+3	+5.0 F-			= AlF5-2	20.300	-115.873*	7.000	412.119*	
AlF6-3	+1.0 Al+3	+6.0 F-			= AlF6-3	20.300	-115.873*	0.500	390.318*	
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*	41.000	279.187*	
AlSiO3(OH)4-3	*+1.0 Al(OH)4-*	*+1.0 SiO2(OH)2-2*	*-1.0 H2O*		*= AlSiO3(OH)4-3*	*0.530*	*-3.025**			
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-	12.900	-73.634*			
Am(CO3)3-3	+1.0 Am+3	+3.0 CO3-2			= Am(CO3)3-3	15.000	-85.621*			
Am(OH)2+	+1.0 Am+3	+2.0 H2O	-2.0 H+		= Am(OH)2+	-15.100	86.191*			
Am(OH)3	+1.0 Am+3	+3.0 H2O	-3.0 H+		= Am(OH)3	-26.200	149.551*			
Am(SO4)2-	+1.0 Am+3	+2.0 SO4-2			= Am(SO4)2-	3.700	-21.120*			
AmCl+2	+1.0 Am+3	+1.0 Cl-			= AmCl+2	0.240	-1.370*			
AmCl2+	+1.0 Am+3	+2.0 Cl-			= AmCl2+	-0.740	4.224*			
AmCO3+	+1.0 Am+3	+1.0 CO3-2			= AmCO3+	8.000	-45.664*			
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*			
AmHCO3+2	+1.0 Am+3	+1.0 HCO3-			= AmHCO3+2	3.100	-17.695*			
AmNO3+2	+1.0 Am+3	+1.0 NO3-			= AmNO3+2	1.330	-7.592*			
AmO2(CO3)2-3	+1.0 AmO2+	+2.0 CO3-2			= AmO2(CO3)2-3	6.700	-38.244*			
AmO2(CO3)3-5	+1.0 AmO2+	+3.0 CO3-2			= AmO2(CO3)3-5	5.100	-29.111*			
AmO2(OH)2-	+1.0 AmO2+	+2.0 H2O	-2.0 H+		= AmO2(OH)2-	-23.600	134.710*			
AmO2+	+1.0 Am+3	+2.0 H2O	-4.0 H+	-2.0 e-	= AmO2+	-59.700	340.580*	384.100	145.833*	
AmO2CO3-	+1.0 AmO2+	+1.0 CO3-2			= AmO2CO3-	5.100	-29.111*			
AmO2OH	+1.0 AmO2+	+1.0 H2O	-1.0 H+		= AmO2OH	-11.300	64.501*			
AmOH+2	+1.0 Am+3	+1.0 H2O	-1.0 H+		= AmOH+2	-7.200	41.098*			
AmSCN+2	+1.0 Am+3	+1.0 SCN-			= AmSCN+2	1.300	-7.420*			
AmSiO(OH)3+2	+1.0 Am+3	+1.0 SiO(OH)3-			= AmSiO(OH)3+2	8.100	-46.235*	15.000	205.384*	
AmSO4+	+1.0 Am+3	+1.0 SO4-2			= AmSO4+	3.300	-18.837*			
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***
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*	
AsO4-3	+1.0 HAsO4-2	-1.0 H+			= AsO4-3	-11.603	66.232*	18.200*	-161.100*	
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***
Ba2UO2(CO3)3	*+2.0 Ba+2*	*+1.0 UO2+2*	*+3.0 CO3-2*		*= Ba2UO2(CO3)3*	*29.750*	*-169.814**			
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***			
BaUO2(CO3)3-2	*+1.0 Ba+2*	*+1.0 UO2+2*	*+3.0 CO3-2*		*= BaUO2(CO3)3-2*	*26.680*	*-152.291**			
Ca2Am(OH)4+3	*+2.0 Ca+2*	*+1.0 Am+3*	*+4.0 H2O*	*-4.0 H+*	*= Ca2Am(OH)4+3*	*-37.200*	*212.339**			
Ca2Cm(OH)4+3	*+2.0 Ca+2*	*+1.0 Cm+3*	*+4.0 H2O*	*-4.0 H+*	*= Ca2Cm(OH)4+3*	*-37.200*	*212.339**			
Ca2UO2(CO3)3	*+2.0 Ca+2*	*+1.0 UO2+2*	*+3.0 CO3-2*		*= Ca2UO2(CO3)3*	*29.220*	*-166.789**			
Ca2Zr(OH)6+2	+2.0 Ca+2	+1.0 Zr+4	+6.0 H2O	-6.0 H+	= Ca2Zr(OH)6+2	-22.600	129.002*			
Ca3Am(OH)6+3	*+3.0 Ca+2*	*+1.0 Am+3*	*+6.0 H2O*	*-6.0 H+*	*= Ca3Am(OH)6+3*	*-60.700*	*346.478**			
Ca3Cm(OH)6+3	*+3.0 Ca+2*	*+1.0 Cm+3*	*+6.0 H2O*	*-6.0 H+*	*= Ca3Cm(OH)6+3*	*-60.700*	*346.478**			
Ca3Zr(OH)6+4	+3.0 Ca+2	+1.0 Zr+4	+6.0 H2O	-6.0 H+	= Ca3Zr(OH)6+4	-23.200	132.427*			
Ca4Pu(OH)8+4	*+4.0 Ca+2*	*+1.0 Pu+4*	*+8.0 H2O*	*-8.0 H+*	*= Ca4Pu(OH)8+4*	*-55.700*	*317.938**			
Ca4Th(OH)8+4	+4.0 Ca+2	+1.0 Th+4	+8.0 H2O	-8.0 H+	= Ca4Th(OH)8+4	-62.400	356.182*			
CaAm(OH)3+2	*+1.0 Ca+2*	*+1.0 Am+3*	*+3.0 H2O*	*-3.0 H+*	*= CaAm(OH)3+2*	*-26.300*	*150.122**			
CaCm(OH)3+2	*+1.0 Ca+2*	*+1.0 Cm+3*	*+3.0 H2O*	*-3.0 H+*	*= CaCm(OH)3+2*	*-26.300*	*150.122**			
CaCO3	**+1.0 Ca+2**	**-1.0 H+**	**+1.0 HCO3-**		**= CaCO3**	**-7.105***	**40.554***	**29.733***	**-36.292***	**330.347***
CaF+	**+1.0 Ca+2**	**+1.0 F-**			**= CaF+**	**0.940**	**-5.366***	**17.238**	**75.813***	
CaHCO3+	**+1.0 Ca+2**	**+1.0 HCO3-**			**= CaHCO3+**	**1.106***	**-6.311***	**11.263***	**58.945***	**-408.288***

Table B2: Reaction properties continued.

Name	**Reaction**					**$\log_{10}K^\circ$**	**$\Delta_r G_m^\circ$ kJ·mol^{-1}**	**$\Delta_r H_m^\circ$ kJ·mol^{-1}**	**$\Delta_r S_m^\circ$ J·mol^{-1}·K^{-1}**	**$\Delta_r C_{p,m}^\circ$ J·mol^{-1}·K^{-1}**
CaOH+	**+1.0 Ca+2**	**+1.0 H2O**	**-1.0 H+**		**= CaOH+**	**-12.780**	**72.949***			
CaSeO4	+1.0 Ca+2	+1.0 SeO4-2			= CaSeO4	2.000	-11.416*			
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***	
CaUO2(CO3)3-2	*+1.0 Ca+2*	*+1.0 UO2+2*	*+3.0 CO3-2*		*= CaUO2(CO3)3-2*	*27.180*	*-155.145**			
CaZr(OH)6	*+1.0 Ca+2*	*+1.0 Zr+4*	*+6.0 H2O*	*-6.0 H+*	*= CaZr(OH)6*	*-24.600*	*140.418**			
CH4	**+1.0 HCO3-**	**+9.0 H+**	**+8.0 e-**	**-3.0 H2O**	**= CH4**	**27.849***	**-158.961***	**-255.882***	**-325.075***	**429.061***
Cm(CO3)2-	+1.0 Cm+3	+2.0 CO3-2			= Cm(CO3)2-	12.900	-73.634*			
Cm(CO3)3-3	+1.0 Cm+3	+3.0 CO3-2			= Cm(CO3)3-3	15.000	-85.621*			
Cm(OH)2+	+1.0 Cm+3	+2.0 H2O	-2.0 H+		= Cm(OH)2+	-15.100	86.191*			
Cm(OH)3	+1.0 Cm+3	+3.0 H2O	-3.0 H+		= Cm(OH)3	-26.200	149.551*			
Cm(SO4)2-	+1.0 Cm+3	+2.0 SO4-2			= Cm(SO4)2-	3.700	-21.120*			
CmCl+2	+1.0 Cm+3	+1.0 Cl-			= CmCl+2	0.240	-1.370*			
CmCl2+	+1.0 Cm+3	+2.0 Cl-			= CmCl2+	-0.740	4.224*			
CmCO3+	+1.0 Cm+3	+1.0 CO3-2			= CmCO3+	8.000	-45.664*			
CmF+2	+1.0 Cm+3	+1.0 F-			= CmF+2	3.400	-19.407*			
CmF2+	+1.0 Cm+3	+2.0 F-			= CmF2+	5.800	-33.107*			
CmH2PO4+2	+1.0 Cm+3	+1.0 H2PO4-			= CmH2PO4+2	3.000	-17.124*			
CmHCO3+2	+1.0 Cm+3	+1.0 HCO3-			= CmHCO3+2	3.100	-17.695*			
CmNO3+2	+1.0 Cm+3	+1.0 NO3-			= CmNO3+2	1.330	-7.592*			
CmOH+2	+1.0 Cm+3	+1.0 H2O	-1.0 H+		= CmOH+2	-7.200	41.098*			
CmSCN+2	+1.0 Cm+3	+1.0 SCN-			= CmSCN+2	1.300	-7.420*			
CmSiO(OH)3+2	+1.0 Cm+3	+1.0 SiO(OH)3-			= CmSiO(OH)3+2	8.100	-46.235*	15.800	208.067*	
CmSO4+	+1.0 Cm+3	+1.0 SO4-2			= CmSO4+	3.300	-18.837*			
CN-	+1.0 HCN	-1.0 H+			= CN-	-9.210	52.571*	43.600	-30.089*	
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(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(SO4)2-	+1.0 Eu+3	+2.0 SO4-2			= Eu(SO4)2-	5.700	-32.536*			
Eu+2	+1.0 Eu+3	+1.0 e-			= Eu+2	-5.920	33.800*	78.100*	148.583*	
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	8.100	-46.235*	14.500	203.707*	
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*	71.547	131.420*	
Fe(OH)3	+3.0 H2O	-3.0 H+	+1.0 Fe+3		= Fe(OH)3	-12.560	71.693*	103.764	107.568*	
Fe(OH)4-	+4.0 H2O	-4.0 H+	+1.0 Fe+3		= Fe(OH)4-	-21.600	123.294*	133.471	34.134*	
Fe(SO4)2-	+2.0 SO4-2	+1.0 Fe+3			= Fe(SO4)2-	5.380	-30.709*	19.247	167.556*	
Fe+3	+1.0 Fe+2	-1.0 e-			= Fe+3	-13.020	74.319*	40.500	-113.428*	
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*	
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*	
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*	23.431	106.924*	
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*	
FeF2+	+2.0 F-	+1.0 Fe+3			= FeF2+	10.800	-61.647*	20.084	274.127*	
FeF3	+3.0 F-	+1.0 Fe+3			= FeF3	14.000	-79.913*	22.595	343.812*	
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*	
FeOH+2	+1.0 H2O	-1.0 H+	+1.0 Fe+3		= FeOH+2	-2.190	12.501*	43.515	104.022*	

Table B2: Reaction properties continued.

Name	**Reaction**						$\log_{10}K^{\circ}$	$\Delta_{r}G_{m}^{\circ}$ kJ·mol^{-1}	$\Delta_{r}H_{m}^{\circ}$ kJ·mol^{-1}	$\Delta_{r}S_{m}^{\circ}$ J·mol^{-}1·K^{-1}	$\Delta_{r}C_{p,m}^{\circ}$ J·mol^{-}1·K^{-1}
FeSeO3+	+1.0 Fe+3	+1.0 SeO3-2				= FeSeO3+	11.150	-63.645*			
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*	
FeSO4+	+1.0 SO4-2	+1.0 Fe+3				= FeSO4+	4.040	-23.060*	16.360	132.217*	
H2	**+2.0 H+**	**+2.0 e-**				**= H2**	**-3.105***	**17.726***	**-4.039***	**-73.000***	**144.187***
H2AsO4-	+1.0 HAsO4-2	+1.0 H+				= H2AsO4-	6.764‡	-38.611*	-3.220*	118.702*	
H2PO4-	**+1.0 HPO4-2**	**+1.0 H+**				**= H2PO4-**	**7.212**	**-41.166***	**-3.600**	**125.998***	
H2S	+1.0 HS-	+1.0 H+				= H2S	6.990	-39.899*	-22.300	59.028*	
H2Se	+1.0 SeO3-2	+8.0 H+	+6.0 e-	-3.0 H2O		= H2Se	57.400	-327.530*	-335.990*	-28.375*	
H2SeO3	+1.0 HSeO3-	+1.0 H+				= H2SeO3	2.640	-15.069*	7.000	74.021*	
H3AsO4	+1.0 HAsO4-2	+2.0 H+				= H3AsO4	9.027‡	-51.527*	3.840*	185.702*	
H3PO4	**+1.0 HPO4-2**	**+2.0 H+**				**= H3PO4**	**9.352**	**-53.382***	**4.880**	**195.410***	
HCN	+13.0 H+	+1.0 CO3-2	+1.0 NO3-	+10.0 e-	-6.0 H2O	= HCN	117.336	-669.759*	-729.066*	-198.918*	
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***
HIO3	+1.0 H+	+1.0 IO3-				= HIO3	0.788	-4.498*			
HP2O7-3	+2.0 HPO4-2	+1.0 H+	-1.0 H2O			= HP2O7-3	6.010	-34.305*			
HS-	**+1.0 SO4-2**	**+9.0 H+**	**+8.0 e-**	**-4.0 H2O**		**= HS-**	**33.690**	**-192.313***	**-250.280**	**-194.422***	
HSe-	+1.0 H2Se	-1.0 H+				= HSe-	-3.850	21.976*			
HSeO3-	+1.0 SeO3-2	+1.0 H+				= HSeO3-	8.360	-47.719*	-5.100	142.946*	
HSeO4-	+1.0 SeO3-2	+1.0 H2O	-1.0 H+	-2.0 e-		= HSeO4-	-26.300	150.030*	210.330*	202.247*	
HSO3-	+1.0 H+	+1.0 SO3-2				= HSO3-	7.220‡	-41.212*	120.950*	543.894*	
HSO4-	**+1.0 H+**	**+1.0 SO4-2**				**= HSO4-**	**1.988***	**-11.346***	**16.128***	**92.149***	**239.237***
I2	+2.0 I-	-2.0 e-				= I2	-20.950	119.583*			
I3-	+1.0 I-	+1.0 I2				= I3-	2.870	-16.382*			
IO3-	+0.5 I2	+3.0 H2O	-6.0 H+	-5.0 e-		= IO3-	-101.090	577.012*			
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***	
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***	
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***			
MgSeO4	*+1.0 Mg+2*	*+1.0 SeO4-2*				*= MgSeO4*	*2.200*	*-12.558**			
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***	
MgUO2(CO3)3-2	*+1.0 Mg+2*	*+1.0 UO2+2*	*+3.0 CO3-2*			*= MgUO2(CO3)3-2*	*26.110*	*-149.037**			
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*	
MnSeO4	+1.0 Mn+2	+1.0 SeO4-2				= MnSeO4	2.430	-13.871*			
MnSO4	+1.0 Mn+2	+1.0 SO4-2				= MnSO4	2.250	-12.843*	14.100	90.368*	
N2	+2.0 NO3-	+12.0 H+	+10.0 e-	-6.0 H2O		= N2	207.263*	-1183.064*	-1311.717*	-431.504*	689.398*
NaCO3-	**+1.0 Na+**	**-1.0 H+**	**+1.0 HCO3-**			**= NaCO3-**	**-9.059**	**51.709***	**52.180**	**1.579***	
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**	**29.118***	
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*			
NH3	**+1.0 NH4+**	**-1.0 H+**				**= NH3**	**-9.237**	**52.725***	**52.090**	**-2.130***	
NH4+	**+1.0 NO3-**	**+10.0 H+**	**+8.0 e-**	**-3.0 H2O**		**= NH4+**	**119.134***	**-680.024***	**-783.900***	**-348.402***	**277.178***
Ni(CN)4-2	+1.0 Ni+2	+4.0 CN-				= Ni(CN)4-2	30.200	-172.383*	-180.700	-27.896*	
Ni(CN)5-3	+1.0 Ni+2	+5.0 CN-				= Ni(CN)5-3	28.500	-162.679*	-191.100	-95.324*	
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*			

Table B2: Reaction properties continued.

Name	Reaction					$\log_{10}K°$	$\Delta_r G_m°$ kJ·mol^{-1}	$\Delta_r H_m°$ kJ·mol^{-1}	$\Delta_r S_m°$ J·mol^{-}1·K^{-1}	$\Delta_r C_{p,m}°$ J·mol^{-}1·K^{-1}
_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(OH)2_	_+1.0 Ni+2_	_+2.0 H2O_	_-2.0 H+_		_= Ni(OH)2_	_-18.000_	_102.745*_	_90.000_	_-42.746*_	
Ni(OH)3-	+1.0 Ni+2	+3.0 H2O	-3.0 H+		= Ni(OH)3-	-29.200	166.675*	121.200	-152.523*	
Ni(SCN)2	+1.0 Ni+2	+2.0 SCN-			= Ni(SCN)2	2.690	-15.355*	-21.000	-18.935*	
Ni(SCN)3-	+1.0 Ni+2	+3.0 SCN-			= Ni(SCN)3-	3.020	-17.238*	-29.000	-39.449*	
Ni(SeCN)2	+1.0 Ni+2	+2.0 SeCN-			= Ni(SeCN)2	2.240	-12.786*	-25.000	-40.966*	
Ni2OH+3	+2.0 Ni+2	+1.0 H2O	-1.0 H+		= Ni2OH+3	-10.600	60.505*	45.900	-48.986*	
Ni4(OH)4+4	+4.0 Ni+2	+4.0 H2O	-4.0 H+		= Ni4(OH)4+4	-27.520	157.085*	190.000	110.396*	
NiCl+	+1.0 Ni+2	+1.0 Cl-			= NiCl+	0.080	-0.457*			
NiCO3	+1.0 Ni+2	+1.0 CO3-2			= NiCO3	4.200	-23.974*			
NiF+	+1.0 Ni+2	+1.0 F-			= NiF+	1.430	-8.163*	9.500	59.240*	
NiHAsO4	+1.0 Ni+2	+1.0 HAsO4-2			= NiHAsO4	2.900	-16.553*			
NiHCO3+	_+1.0 Ni+2_	_+1.0 HCO3-_			_= NiHCO3+_	_1.000_	_-5.708*_			
NiHP2O7-	+1.0 Ni+2	+1.0 HP2O7-3			= NiHP2O7-	5.140	-29.339*	47.900	259.062*	
NiHPO4	+1.0 Ni+2	+1.0 HPO4-2			= NiHPO4	3.050	-17.410*			
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+	0.500	-2.854*			
NiOH+	+1.0 Ni+2	+1.0 H2O	-1.0 H+		= NiOH+	-9.540	54.455*	53.800	-2.196*	
NiP2O7-2	+1.0 Ni+2	+1.0 P2O7-4			= NiP2O7-2	8.730	-49.831*	30.600	269.768*	
NiSCN+	+1.0 Ni+2	+1.0 SCN-			= NiSCN+	1.810	-10.332*	-11.800	-4.925*	
NiSeCN+	+1.0 Ni+2	+1.0 SeCN-			= NiSeCN+	1.770	-10.103*	-12.800	-9.045*	
NiSeO4	+1.0 Ni+2	+1.0 SeO4-2			= NiSeO4	2.670	-15.240*			
NiSiO(OH)3+	_+1.0 Ni+2_	_+1.0 SiO(OH)3-_			_= NiSiO(OH)3+_	_6.300_	_-35.961*_			
NiSO4	+1.0 Ni+2	+1.0 SO4-2			= NiSO4	2.350	-13.414*	5.660	63.974*	
_Np(CO3)2-_	_+1.0 Np+3_	_+2.0 CO3-2_			_= Np(CO3)2-_	_12.900_	_-73.634*_			
_Np(CO3)3-3_	_+1.0 Np+3_	_+3.0 CO3-2_			_= Np(CO3)3-3_	_15.000_	_-85.621*_			
Np(CO3)4-4	+1.0 Np+4	+4.0 CO3-2			= Np(CO3)4-4	38.900	-222.043*			
Np(CO3)5-6	+1.0 Np+4	+5.0 CO3-2			= Np(CO3)5-6	37.800	-215.764*			
_Np(OH)2+_	_+1.0 Np+3_	_+2.0 H2O_	_-2.0 H+_		_= Np(OH)2+_	_-14.700_	_83.908*_			
Np(OH)2+2	+1.0 Np+4	+2.0 H2O	-2.0 H+		= Np(OH)2+2	0.350	-1.998*			
_Np(OH)3_	_+1.0 Np+3_	_+3.0 H2O_	_-3.0 H+_		_= Np(OH)3_	_-25.800_	_147.267*_			
_Np(OH)3+_	_+1.0 Np+4_	_+3.0 H2O_	_-3.0 H+_		_= Np(OH)3+_	_-2.800_	_15.983*_			
Np(OH)4	+1.0 Np+4	+4.0 H2O	-4.0 H+		= Np(OH)4	-8.300	47.377*			
Np(SCN)2+2	+1.0 Np+4	+2.0 SCN-			= Np(SCN)2+2	4.100	-23.403*	-9.000	48.308*	
Np(SCN)3+	+1.0 Np+4	+3.0 SCN-			= Np(SCN)3+	4.800	-27.399*	-13.000	48.293*	
Np(SO4)2	+1.0 Np+4	+2.0 SO4-2			= Np(SO4)2	11.050	-63.074*	55.400	397.363*	
_Np(SO4)2-_	_+1.0 Np+3_	_+2.0 SO4-2_			_= Np(SO4)2-_	_3.700_	_-21.120*_			
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*	
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*	
NpCl+2	_+1.0 Np+3_	_+1.0 Cl-_			_= NpCl+2_	_0.240_	_-1.370*_			
NpCl+3	+1.0 Np+4	+1.0 Cl-			= NpCl+3	1.500	-8.562*			
NpCl2+	_+1.0 Np+3_	_+2.0 Cl-_			_= NpCl2+_	_-0.740_	_4.224*_			
NpCO3(OH)3-	_+1.0 Np+4_	_+1.0 CO3-2_	_+3.0 H2O_	_-3.0 H+_	_= NpCO3(OH)3-_	_2.000_	_-11.416*_			
NpCO3+	_+1.0 Np+3_	_+1.0 CO3-2_			_= NpCO3+_	_8.000_	_-45.664*_			
NpF+2	_+1.0 Np+3_	_+1.0 F-_			_= NpF+2_	_3.400_	_-19.407*_			
NpF+3	+1.0 Np+4	+1.0 F-			= NpF+3	8.960	-51.144*	1.500	176.569*	
NpF2+	_+1.0 Np+3_	_+2.0 F-_			_= NpF2+_	_5.800_	_-33.107*_			
NpF2+2	+1.0 Np+4	+2.0 F-			= NpF2+2	15.700	-89.616*			
NpI+3	+1.0 Np+4	+1.0 I-			= NpI+3	1.500	-8.562*			
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*	
NpO2(CO3)3-5	+1.0 NpO2+	+3.0 CO3-2			= NpO2(CO3)3-5	5.500	-31.394*	-13.300	60.688*	
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*			

Table B2: Reaction properties continued.

Name	**Reaction**					**log$_{10}$K°**	**$\Delta_r G_m$° kJ·mol^{-1}**	**$\Delta_r H_m$° kJ·mol^{-1}**	**$\Delta_r S_m$° J·mol^{-}1·K^{-1}**	**$\Delta_r C_{p,m}$° J·mol^{-}1·K^{-1}**
NpO2(OH)3-	_+1.0 NpO2+2_	_+3.0 H2O_	_-3.0 H+_		_= NpO2(OH)3-_	_-20.000_	_114.161*_			
NpO2(OH)4-2	_+1.0 NpO2+2_	_+4.0 H2O_	_-4.0 H+_		_= NpO2(OH)4-2_	_-32.000_	_182.657*_			
NpO2(SO4)2-2	+1.0 NpO2+2	+2.0 SO4-2			= NpO2(SO4)2-2	4.700	-26.828*	26.000	177.185*	
NpO2+	+1.0 NpO2+2	+1.0 e-			= NpO2+	19.590	-111.900*	-117.500*	-18.782*	
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*			
NpO2IO3	+1.0 NpO2+	+1.0 IO3-			= NpO2IO3	0.500	-2.854*			
NpO2IO3+	+1.0 NpO2+2	+1.0 IO3-			= NpO2IO3+	1.200	-6.850*			
NpO2OH+	+1.0 NpO2+2	+1.0 H2O	-1.0 H+		= NpO2OH+	-5.100	29.111*			
NpO2SCN	_+1.0 NpO2+_	_+1.0 SCN-_			_= NpO2SCN_	_0.080_	_-0.457*_			
NpO2SiO(OH)3	_+1.0 NpO2+_	_+1.0 SiO(OH)3-_			_= NpO2SiO(OH)3_	_7.000_	_-39.956*_			
NpO2SiO(OH)3+	_+1.0 NpO2+2_	_+1.0 SiO(OH)3-_			_= NpO2SiO(OH)3+_	_7.200_	_-41.098*_			
NpO2SiO2(OH)2	_+1.0 NpO2+2_	_+1.0 SiO2(OH)2-2_			_= NpO2SiO2(OH)2_	_16.500_	_-94.183*_			
NpO2SO4	+1.0 NpO2+2	+1.0 SO4-2			= NpO2SO4	3.280	-18.722*	16.700	118.807*	
NpO2SO4-	+1.0 NpO2+	+1.0 SO4-2			= NpO2SO4-	0.440	-2.512*	23.200	86.237*	
(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*			
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	0.550	-3.139*			
NpSCN+3	+1.0 Np+4	+1.0 SCN-			= NpSCN+3	3.000	-17.124*	-7.000	33.956*	
NpSiO(OH)3+2	_+1.0 Np+3_	_+1.0 SiO(OH)3-_			_= NpSiO(OH)3+2_	_8.100_	_-46.235*_	_15.000_	_205.384*_	
NpSiO(OH)3+3	_+1.0 Np+4_	_+1.0 SiO(OH)3-_			_= NpSiO(OH)3+3_	_11.200_	_-63.930*_			
NpSO4+	_+1.0 Np+3_	_+1.0 SO4-2_			_= NpSO4+_	_3.300_	_-18.837*_			
NpSO4+2	+1.0 Np+4	+1.0 SO4-2			= NpSO4+2	6.850	-39.100*	29.800	231.092*	
__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*__
P2O7-4	+2.0 HPO4-2	-1.0 H2O			= P2O7-4	-3.390	19.350*			
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*			
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*			
__PO4-3__	__+1.0 HPO4-2__	__-1.0 H+__			__= PO4-3__	__-12.350__	__70.494*__	__14.600__	__-187.470*__	
_Pu(CO3)2-_	_+1.0 Pu+3_	_+2.0 CO3-2_			_= Pu(CO3)2-_	_12.900_	_-73.634*_			
_Pu(CO3)3-3_	_+1.0 Pu+3_	_+3.0 CO3-2_			_= Pu(CO3)3-3_	_15.000_	_-85.621*_			
Pu(CO3)4-4	+1.0 Pu+4	+4.0 CO3-2			= Pu(CO3)4-4	37.000	-211.198*			
Pu(CO3)5-6	+1.0 Pu+4	+5.0 CO3-2			= Pu(CO3)5-6	35.650	-203.492*			
_Pu(OH)2+_	_+1.0 Pu+3_	_+2.0 H2O_	_-2.0 H+_		_= Pu(OH)2+_	_-14.800_	_84.479*_			
Pu(OH)2+2	+1.0 Pu+4	+2.0 H2O	-2.0 H+		= Pu(OH)2+2	-1.200	6.850*			
_Pu(OH)3_	_+1.0 Pu+3_	_+3.0 H2O_	_-3.0 H+_		_= Pu(OH)3_	_-25.900_	_147.838*_			
Pu(OH)3+	+1.0 Pu+4	+3.0 H2O	-3.0 H+		= Pu(OH)3+	-3.100	17.695*			
Pu(OH)4	+1.0 Pu+4	+4.0 H2O	-4.0 H+		= Pu(OH)4	-9.300	53.085*			
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*	
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*	
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*	
PuCl+2	_+1.0 Pu+3_	_+1.0 Cl-_			_= PuCl+2_	_1.200_	_-6.850*_			

Table B2: Reaction properties continued.

Name	**Reaction**						**log$_{10}$K°**	**Δ$_r$G$_m$°** kJ·mol^{-1}	**Δ$_r$H$_m$°** kJ·mol^{-1}	**Δ$_r$S$_m$°** J·mol^{-}1·K^{-1}	**Δ$_r$C$_{p,m}$°** J·mol^{-}1·K^{-1}
PuCl+3	+1.0 Pu+4	+1.0 Cl-				= PuCl+3	1.800	-10.274*			
PuCO3(OH)3-	_+1.0 Pu+4_	_+1.0 CO3-2_	_+3.0 H2O_	_-3.0 H+_		_= PuCO3(OH)3-_	_6.000_	_-34.248*_			
PuCO3+	_+1.0 Pu+3_	_+1.0 CO3-2_				_= PuCO3+_	_8.000_	_-45.664*_			
PuF+2	_+1.0 Pu+3_	_+1.0 F-_				_= PuF+2_	_3.400_	_-19.407*_			
PuF+3	+1.0 Pu+4	+1.0 F-				= PuF+3	8.840	-50.459*	9.100	199.762*	
PuF2+	_+1.0 Pu+3_	_+2.0 F-_				_= PuF2+_	_5.800_	_-33.107*_			
PuF2+2	+1.0 Pu+4	+2.0 F-				= PuF2+2	15.700	-89.616*	11.000	337.469*	
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	14.700	-83.908*	-27.000	190.871*	
PuO2(CO3)3-4	+1.0 PuO2+2	+3.0 CO3-2				= PuO2(CO3)3-4	18.000	-102.745*	-38.600	215.143*	
PuO2(CO3)3-5	+1.0 PuO2+	+3.0 CO3-2				= PuO2(CO3)3-5	5.030	-28.711*	-19.110	32.203*	
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*	
PuO2+	+1.0 PuO2+2	+1.0 e-				= PuO2+	15.820	-90.200*	-88.100*	7.043*	
PuO2Cl+	+1.0 PuO2+2	+1.0 Cl-				= PuO2Cl+	0.230	-1.313*			
PuO2Cl2	+1.0 PuO2+2	+2.0 Cl-				= PuO2Cl2	-1.150	6.564*			
PuO2CO3	+1.0 PuO2+2	+1.0 CO3-2				= PuO2CO3	9.500	-54.226*			
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*	
PuO2SiO(OH)3+	_+1.0 PuO2+2_	_+1.0 SiO(OH)3-_				_= PuO2SiO(OH)3+_	_6.000_	_-34.248*_			
PuO2SiO2(OH)2	_+1.0 PuO2+2_	_+1.0 SiO2(OH)2-2_				_= PuO2SiO2(OH)2_	_12.600_	_-71.921*_			
PuO2SO4	+1.0 PuO2+2	+1.0 SO4-2				= PuO2SO4	3.380	-19.293*	16.100	118.709*	
(PuO2)2(OH)2+2	+2.0 PuO2+2	+2.0 H2O	-2.0 H+			= (PuO2)2(OH)2+2	-7.500	42.810*			
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	0.000	-0.000*			
PuSCN+2	+1.0 Pu+3	+1.0 SCN-				= PuSCN+2	1.300	-7.420*			
PuSiO(OH)3+2	_+1.0 Pu+3_	_+1.0 SiO(OH)3-_				_= PuSiO(OH)3+2_	_8.100_	_-46.235*_	_15.000_	_205.384*_	
PuSiO(OH)3+3	_+1.0 Pu+4_	_+1.0 SiO(OH)3-_				_= PuSiO(OH)3+3_	_11.800_	_-67.355*_			
PuSO4+	+1.0 Pu+3	+1.0 SO4-2				= PuSO4+	3.900	-22.261*	17.200	132.354*	
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*	
RaCO3	+1.0 Ra+2	+1.0 CO3-2				= RaCO3	2.500	-14.270*	4.480	62.888*	
RaOH+	+1.0 Ra+2	+1.0 OH-				= RaOH+	0.500	-2.854*	4.600	25.001*	
RaSO4	+1.0 Ra+2	+1.0 SO4-2				= RaSO4	2.750	-15.697*	5.400	70.760*	
S-2	+1.0 HS-	-1.0 H+				= S-2	-19.000	108.453*			
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*	
SCN-	+1.0 HCN	+1.0 HS-	-2.0 e-	-2.0 H+		= SCN-	5.941	-33.913*	-11.050*	76.683*	
Se-2	+1.0 HSe-	-1.0 H+				= Se-2	-14.910	85.107*			
Se2-2	+2.0 Se-2	-2.0 e-				= Se2-2	25.320	-144.528*			
Se3-2	+3.0 Se-2	-4.0 e-				= Se3-2	49.970	-285.231*			
Se4-2	+4.0 Se-2	-6.0 e-				= Se4-2	73.020	-416.801*			
SeCN-	+1.0 HCN	+1.0 SeO3-2	+5.0 H+	+4.0 e-	-3.0 H2O	= SeCN-	57.300	-327.071*			
SeO4-2	+1.0 HSeO4-	-1.0 H+				= SeO4-2	-1.750	9.989*	-20.800	-103.267*	
Si4O8(OH)4-4	+4.0 Si(OH)4	-4.0 H+	-4.0 H2O			= Si4O8(OH)4-4	-36.300	207.202*			
SiO(OH)3-	+1.0 Si(OH)4	-1.0 H+				= SiO(OH)3-	-9.810	55.996*	25.600	-101.948*	
SiO2(OH)2-2	+1.0 Si(OH)4	-2.0 H+				= SiO2(OH)2-2	-23.140	132.084*	75.000	-191.461*	
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*			
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*	

Table B2: Reaction properties continued.

Name	**Reaction**					$\log_{10}K^\circ$	$\Delta_r G_m^\circ$ $\mathrm{kJ\cdot mol^{-1}}$	$\Delta_r H_m^\circ$ $\mathrm{kJ\cdot mol^{-1}}$	$\Delta_r S_m^\circ$ $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$	$\Delta_r C_{p,m}^\circ$ $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$
__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__	__73.032*__	
SrUO2(CO3)3-2	_+1.0 Sr+2_	_+1.0 UO2+2_	_+3.0 CO3-2_		_= SrUO2(CO3)3-2_	_26.860_	_-153.318*_			
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)2	+1.0 TcO4-	+4.0 H+	+3.0 e-	-1.0 H2O	= TcO(OH)2	29.400	-167.816*			
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*			
Th(CO3)5-6	+1.0 Th+4	+5.0 CO3-2			= Th(CO3)5-6	31.000	-176.949*			
Th(H2PO4)2+2	+1.0 Th+4	+2.0 H3PO4	-2.0 H+		= Th(H2PO4)2+2	6.200	-35.390*			
Th(H3PO4)(H2PO4)+3	+1.0 Th+4	+2.0 H3PO4	-1.0 H+		= Th(H3PO4)(H2PO4)+3	5.420	-30.938*			
Th(IO3)2+2	+1.0 Th+4	+2.0 IO3-			= Th(IO3)2+2	6.970	-39.785*			
Th(IO3)3+	+1.0 Th+4	+3.0 IO3-			= Th(IO3)3+	9.870	-56.338*			
Th(NO3)2+2	+1.0 Th+4	+2.0 NO3-			= Th(NO3)2+2	2.300	-13.128*			
Th(OH)2(CO3)2-2	+1.0 Th+4	+2.0 OH-	+2.0 CO3-2		= Th(OH)2(CO3)2-2	36.800	-210.056*			
Th(OH)2+2	+1.0 Th+4	+2.0 H2O	-2.0 H+		= Th(OH)2+2	-6.200	35.390*	85.700	168.741*	
_Th(OH)2CO3_	_+1.0 Th+4_	_+2.0 OH-_	_+1.0 CO3-2_		_= Th(OH)2CO3_	_30.500_	_-174.095*_			
Th(OH)3(SiO(OH)3)3-2	_+1.0 Th+4_	_+3.0 Si(OH)4_	_+3.0 H2O_	_-6.0 H+_	_= Th(OH)3(SiO(OH)3)3-2_	_-27.800_	_158.684*_			
_Th(OH)3CO3-_	_+1.0 Th+4_	_+3.0 OH-_	_+1.0 CO3-2_		_= Th(OH)3CO3-_	_38.300_	_-218.618*_			
Th(OH)4	+1.0 Th+4	+4.0 H2O	-4.0 H+		= Th(OH)4	-17.400	99.320*			
Th(OH)4CO3-2	+1.0 Th+4	+4.0 OH-	+1.0 CO3-2		= Th(OH)4CO3-2	40.400	-230.605*			
Th(SCN)2+2	+1.0 Th+4	+2.0 SCN-			= Th(SCN)2+2	3.400	-19.407*			
Th(SO4)2	+1.0 Th+4	+2.0 SO4-2			= Th(SO4)2	9.690	-55.311*	40.380	320.949*	
Th(SO4)3-2	+1.0 Th+4	+3.0 SO4-2			= Th(SO4)3-2	10.748	-61.350*			
Th2(OH)2+6	+2.0 Th+4	+2.0 H2O	-2.0 H+		= Th2(OH)2+6	-5.900	33.677*	58.300	82.584*	
Th2(OH)3+5	+2.0 Th+4	+3.0 H2O	-3.0 H+		= Th2(OH)3+5	-6.800	38.815*			
Th4(OH)12+4	+4.0 Th+4	+12.0 H2O	-12.0 H+		= Th4(OH)12+4	-26.600	151.834*			
Th4(OH)8+8	+4.0 Th+4	+8.0 H2O	-8.0 H+		= Th4(OH)8+8	-20.400	116.444*	243.000	424.471*	
Th6(OH)14+10	+6.0 Th+4	+14.0 H2O	-14.0 H+		= Th6(OH)14+10	-36.800	210.056*			
Th6(OH)15+9	+6.0 Th+4	+15.0 H2O	-15.0 H+		= Th6(OH)15+9	-36.800	210.056*	472.800	881.248*	
ThCl+3	+1.0 Th+4	+1.0 Cl-			= ThCl+3	1.700	-9.704*			
ThF+3	+1.0 Th+4	+1.0 F-			= ThF+3	8.870	-50.630*	-0.400	168.473*	
ThF2+2	+1.0 Th+4	+2.0 F-			= ThF2+2	15.630	-89.217*	-3.300	288.166*	
ThF3+	+1.0 Th+4	+3.0 F-			= ThF3+	20.670	-117.985*			
ThF4	+1.0 Th+4	+4.0 F-			= ThF4	25.580	-146.012*			
ThF6-2	_+1.0 Th+4_	_+6.0 F-_			_= ThF6-2_	_29.230_	_-166.846*_			
ThH2PO4+3	+1.0 Th+4	+1.0 H3PO4	-1.0 H+		= ThH2PO4+3	3.450	-19.693*			
ThH3PO4+4	+1.0 Th+4	+1.0 H3PO4			= ThH3PO4+4	1.890	-10.788*			
ThIO3+3	+1.0 Th+4	+1.0 IO3-			= ThIO3+3	4.140	-23.631*			
ThNO3+3	+1.0 Th+4	+1.0 NO3-			= ThNO3+3	1.300	-7.420*			
ThOH(CO3)4-5	+1.0 Th+4	+1.0 OH-	+4.0 CO3-2		= ThOH(CO3)4-5	35.600	-203.206*			
ThOH+3	+1.0 Th+4	+1.0 H2O	-1.0 H+		= ThOH+3	-2.500	14.270*	44.200	100.385*	
ThSCN+3	+1.0 Th+4	+1.0 SCN-			= ThSCN+3	2.000	-11.416*			
ThSO4+2	+1.0 Th+4	+1.0 SO4-2			= ThSO4+2	6.170	-35.219*	20.920	188.290*	
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	33.900	-193.503*	-20.000	581.931*	
U(NO3)2+2	+1.0 U+4	+2.0 NO3-			= U(NO3)2+2	2.300	-13.128*			
_U(OH)2+2_	_+1.0 U+4_	_+2.0 H2O_	_-2.0 H+_		_= U(OH)2+2_	_-1.100_	_6.279*_			
_U(OH)3+_	_+1.0 U+4_	_+3.0 H2O_	_-3.0 H+_		_= U(OH)3+_	_-4.700_	_26.828*_			
U(OH)4	+1.0 U+4	+4.0 H2O	-4.0 H+		= U(OH)4	-10.000	57.080*			
U(SCN)2+2	+1.0 U+4	+2.0 SCN-			= U(SCN)2+2	4.260	-24.316*	-18.000	21.185*	
U(SO4)2	+1.0 U+4	+2.0 SO4-2			= U(SO4)2	10.510	-59.992*	32.700	310.889*	
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*	
UCl+3	+1.0 U+4	+1.0 Cl-			= UCl+3	1.720	-9.818*	-19.000	-30.797*	
UCO3(OH)3-	_+1.0 U+4_	_+1.0 CO3-2_	_+3.0 H2O_	_-3.0 H+_	_= UCO3(OH)3-_	_4.000_	_-22.832*_			
UF+3	+1.0 U+4	+1.0 F-			= UF+3	9.420	-53.770*	-5.600	161.562*	
UF2+2	+1.0 U+4	+2.0 F-			= UF2+2	16.560	-94.525*	-3.500	305.300*	
UF3+	+1.0 U+4	+3.0 F-			= UF3+	21.890	-124.949*	0.500	420.758*	
UF4	+1.0 U+4	+4.0 F-			= UF4	26.340	-150.350*	-8.430*	476.000	
UF5-	+1.0 U+4	+5.0 F-			= UF5-	27.730	-158.284*			

Table B2: Reaction properties continued.

Name	**Reaction**					$\log_{10}K^\circ$	$\Delta_r G_m^\circ$ kJ·mol^{-1}	$\Delta_r H_m^\circ$ kJ·mol^{-1}	$\Delta_r S_m^\circ$ J·mol^{-1}·K^{-1}	$\Delta_r C_{p,m}^\circ$ J·mol^{-1}·K^{-1}
UF6-2	+1.0 U+4	+6.0 F-			= UF6-2	29.800	-170.100*			
UI+3	+1.0 U+4	+1.0 I-			= UI+3	1.250	-7.135*			
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	16.610	-94.811*	18.500	380.046*	
UO2(CO3)3-4	+1.0 UO2+2	+3.0 CO3-2			= UO2(CO3)3-4	21.840	-124.664*	-39.200	286.646*	
UO2(CO3)3-5	+1.0 UO2+	+3.0 CO3-2			= UO2(CO3)3-5	7.190	-41.041*			
UO2(H2AsO4)2	+1.0 UO2+2	+2.0 H3AsO4	-2.0 H+		= UO2(H2AsO4)2	0.290	-1.655*			
UO2(H2PO4)2	+1.0 UO2+2	+2.0 H3PO4	-2.0 H+		= UO2(H2PO4)2	0.640	-3.653*			
UO2(IO3)2	+1.0 UO2+2	+2.0 IO3-			= UO2(IO3)2	3.590	-20.492*			
UO2(OH)2	+1.0 UO2+2	+2.0 H2O	-2.0 H+		= UO2(OH)2	-12.150	69.353*			
UO2(OH)3-	+1.0 UO2+2	+3.0 H2O	-3.0 H+		= UO2(OH)3-	-20.250	115.588*			
UO2(OH)4-2	+1.0 UO2+2	+4.0 H2O	-4.0 H+		= UO2(OH)4-2	-32.400	184.941*			
UO2(SCN)2	+1.0 UO2+2	+2.0 SCN-			= UO2(SCN)2	1.240	-7.078*	8.900	53.590*	
UO2(SCN)3-	+1.0 UO2+2	+3.0 SCN-			= UO2(SCN)3-	2.100	-11.987*	6.000	60.328*	
UO2(SeO4)2-2	*+1.0 UO2+2*	*+2.0 SeO4-2*			*= UO2(SeO4)2-2*	*3.100*	*-17.695**			
UO2(SO4)2-2	+1.0 UO2+2	+2.0 SO4-2			= UO2(SO4)2-2	4.140	-23.631*	35.100	196.986*	
UO2(SO4)3-4	+1.0 UO2+2	+3.0 SO4-2			= UO2(SO4)3-4	3.020	-17.238*			
UO2+	+1.0 UO2+2	+1.0 e-			= UO2+	1.484	-8.471*	-6.127*	7.861*	
UO2Cl+	+1.0 UO2+2	+1.0 Cl-			= UO2Cl+	0.170	-0.970*	8.000	30.087*	
UO2Cl2	+1.0 UO2+2	+2.0 Cl-			= UO2Cl2	-1.100	6.279*	15.000	29.251*	
UO2CO3	+1.0 UO2+2	+1.0 CO3-2			= UO2CO3	9.940	-56.738*	5.000	207.070*	
UO2CO3F-	+1.0 UO2+2	+1.0 CO3-2	+1.0 F-		= UO2CO3F-	13.750	-78.486*			
UO2CO3F2-2	+1.0 UO2+2	+1.0 CO3-2	+2.0 F-		= UO2CO3F2-2	15.570	-88.874*			
UO2CO3F3-3	+1.0 UO2+2	+1.0 CO3-2	+3.0 F-		= UO2CO3F3-3	16.380	-93.498*			
UO2F+	+1.0 UO2+2	+1.0 F-			= UO2F+	5.160	-29.453*	1.700	104.489*	
UO2F2	+1.0 UO2+2	+2.0 F-			= UO2F2	8.830	-50.402*	2.100	176.093*	
UO2F3-	+1.0 UO2+2	+3.0 F-			= UO2F3-	10.900	-62.218*	2.350	216.561*	
UO2F4-2	+1.0 UO2+2	+4.0 F-			= UO2F4-2	11.840	-67.583*	0.290	227.648*	
UO2H2AsO4+	+1.0 UO2+2	+1.0 H3AsO4	-1.0 H+		= UO2H2AsO4+	1.340	-7.649*			
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*			
UO2HAsO4	+1.0 UO2+2	+1.0 HAsO4-2			= UO2HAsO4	7.160	-40.870*			
UO2HPO4	+1.0 UO2+2	+1.0 HPO4-2			= UO2HPO4	7.240	-41.326*			
UO2IO3+	+1.0 UO2+2	+1.0 IO3-			= UO2IO3+	2.000	-11.416*			
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+	-5.250	29.967*			
UO2PO4-	+1.0 UO2+2	+1.0 PO4-3			= UO2PO4-	13.230	-75.517*			
UO2SCN+	+1.0 UO2+2	+1.0 SCN-			= UO2SCN+	1.400	-7.991*	3.220	37.603*	
UO2SeO4	+1.0 UO2+2	+1.0 SeO4-2			= UO2SeO4	2.740	-15.640*			
UO2SiO(OH)3+	+1.0 UO2+2	+1.0 SiO(OH)3-			= UO2SiO(OH)3+	7.800	-44.523*	8.300	177.168*	
UO2SO4	+1.0 UO2+2	+1.0 SO4-2			= UO2SO4	3.150	-17.980*	19.500	125.710*	
(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	53.500	-305.380*			
(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*	
(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-	-32.200	183.799*			
(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*			
UOH+3	+1.0 U+4	+1.0 H2O	-1.0 H+		= UOH+3	-0.540	3.082*	46.910	147.000	
USCN+3	+1.0 U+4	+1.0 SCN-			= USCN+3	2.830	-16.154*	-27.000	-36.378*	
USO4+2	+1.0 U+4	+1.0 SO4-2			= USO4+2	6.580	-37.559*	8.000	152.805*	
Zr(CO3)4-4	+1.0 Zr+4	+4.0 CO3-2			= Zr(CO3)4-4	42.900	-244.875*			
Zr(NO3)2+2	+1.0 Zr+4	+2.0 NO3-			= Zr(NO3)2+2	2.640	-15.069*			
Zr(OH)2+2	+1.0 Zr+4	+2.0 H2O	-2.0 H+		= Zr(OH)2+2	0.980	-5.594*			
Zr(OH)4	+1.0 Zr+4	+4.0 H2O	-4.0 H+		= Zr(OH)4	-2.190	12.501*			
Zr(OH)6-2	+1.0 Zr+4	+6.0 H2O	-6.0 H+		= Zr(OH)6-2	-29.000	165.533*			
Zr(SO4)2	+1.0 Zr+4	+2.0 SO4-2			= Zr(SO4)2	11.540	-65.871*	67.380*	446.925*	
Zr(SO4)3-2	+1.0 Zr+4	+3.0 SO4-2			= Zr(SO4)3-2	14.300	-81.625*			

Table B2: Reaction properties continued.

Name	**Reaction**						**$\log_{10}K^\circ$**	**$\Delta_r G_m^\circ$** kJ·mol^{-1}	**$\Delta_r H_m^\circ$** kJ·mol^{-1}	**$\Delta_r S_m^\circ$** J·mol^{-1}·K^{-1}	**$\Delta_r C_{p,m}^\circ$** J·mol^{-1}·K^{-1}
Zr3(OH)4+8	+3.0 Zr+4	+4.0 H2O	-4.0 H+			= Zr3(OH)4+8	0.400	-2.283*	-1.980*	1.017*	
Zr3(OH)9+3	+3.0 Zr+4	+9.0 H2O	-9.0 H+			= Zr3(OH)9+3	12.190	-69.581*			
Zr4(OH)15+	+4.0 Zr+4	+15.0 H2O	-15.0 H+			= Zr4(OH)15+	12.580	-71.807*			
Zr4(OH)16	+4.0 Zr+4	+16.0 H2O	-16.0 H+			= Zr4(OH)16	8.390	-47.890*	301.120*	1170.587*	
Zr4(OH)8+8	+4.0 Zr+4	+8.0 H2O	-8.0 H+			= Zr4(OH)8+8	6.520	-37.216*			
ZrCl+3	+1.0 Zr+4	+1.0 Cl-				= ZrCl+3	1.590	-9.076*			
ZrCl2+2	+1.0 Zr+4	+2.0 Cl-				= ZrCl2+2	2.170	-12.386*			
ZrF+3	+1.0 Zr+4	+1.0 F-				= ZrF+3	10.120	-57.765*	-5.300	175.970*	
ZrF2+2	+1.0 Zr+4	+2.0 F-				= ZrF2+2	18.550	-105.884*	-9.900	321.933*	
ZrF3+	+1.0 Zr+4	+3.0 F-				= ZrF3+	24.720	-141.103*	-8.900	443.410*	
ZrF4	+1.0 Zr+4	+4.0 F-				= ZrF4	30.110	-171.869*	-18.700	513.732*	
ZrF5-	+1.0 Zr+4	+5.0 F-				= ZrF5-	34.600	-197.498*			
ZrF6-2	+1.0 Zr+4	+6.0 F-				= ZrF6-2	38.110	-217.533*			
ZrNO3+3	+1.0 Zr+4	+1.0 NO3-				= ZrNO3+3	1.590	-9.076*			
ZrOH+3	+1.0 Zr+4	+1.0 H2O	-1.0 H+			= ZrOH+3	0.320	-1.827*			
ZrSO4+2	+1.0 Zr+4	+1.0 SO4-2				= ZrSO4+2	7.040	-40.185*	36.940*	258.677*	
MINERALS											
Am(CO3)1.5(am,hyd)	+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	-16.900	96.466*			
Am(OH)3(cr)	+1.0 Am+3	+3.0 H2O	-3.0 H+			= Am(OH)3	-15.600	89.045*			
AmO2OH(am)	+1.0 AmO2+	+1.0 H2O	-1.0 H+			= AmO2OH	-5.300	30.253*			
AmOHCO3:0.5H2O(cr)	+1.0 Am+3	+1.0 OH-	+1.0 CO3-2	+0.5 H2O		= AmOHCO3:0.5H2O	22.400	-127.860*			
AmOHCO3(am,hyd)	+1.0 Am+3	+1.0 OH-	+1.0 CO3-2			= AmOHCO3	20.200	-115.302*			
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***	
Baddeleyite	+1.0 Zr+4	+2.0 H2O	-4.0 H+			= ZrO2	7.000	-39.956*	79.560*	400.860*	
Barite	**+1.0 Ba+2**	**+1.0 SO4-2**				**= BaSO4**	**9.970***	**-56.911***	**-26.575***	**101.749***	**404.044***
BaSeO3(cr)	+1.0 Ba+2	+1.0 SeO3-2				= BaSeO3	6.500	-37.102*	5.300*	142.218*	
BaSeO4(cr)	+1.0 Ba+2	+1.0 SeO4-2				= BaSeO4	7.560	-43.153*	-5.700*	125.617*	
Becquerelite	+1.0 Ca+2	+6.0 UO2+2	+18.0 H2O	-14.0 H+		= CaU6O19:11H2O	-40.500	231.176*			
Brucite	**+1.0 Mg+2**	**+2.0 H2O**	**-2.0 H+**			**= Mg(OH)2**	**-16.840**	**96.123***	**113.386**	**57.900***	
Calcite	**+1.0 Ca+2**	**-1.0 H+**	**+1.0 HCO3-**			**= CaCO3**	**-1.849***	**10.554***	**24.510***	**46.808***	**4.584***
CaSeO3:H2O(cr)	+1.0 Ca+2	+1.0 SeO3-2	+1.0 H2O			= CaSeO3:H2O	6.400	-36.531*			
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*			
Cm(OH)3(am,coll)	*+1.0 Cm+3*	*+3.0 H2O*	*-3.0 H+*			*= Cm(OH)3*	*-17.200*	*98.178**			
Compreignacite	+2.0 K+	+6.0 UO2+2	+18.0 H2O	-14.0 H+		= K2U6O19:11H2O	-37.100	211.768*			
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***	
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***	
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*	
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*	
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***	
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-		= MnMn2O4	-61.030	348.362*	421.078	243.891*	
Hematite	+3.0 H2O	-6.0 H+	+2.0 Fe+3			= Fe2O3	-1.120	6.393*			
K3NpO2(CO3)2(s)	+3.0 K+	+1.0 NpO2+	+2.0 CO3-2			= K3NpO2(CO3)2	15.460	-88.246*			
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*	
KNpO2CO3(s)	+1.0 K+	+1.0 NpO2+	+1.0 CO3-2			= KNpO2CO3	13.150	-75.061*			

Table B2: Reaction properties continued.

Name	**Reaction**						$\log_{10}K^\circ$	$\Delta_r G_m^\circ$ $\mathrm{kJ\cdot mol^{-1}}$	$\Delta_r H_m^\circ$ $\mathrm{kJ\cdot mol^{-1}}$	$\Delta_r S_m^\circ$ $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$	$\Delta_r C_{p,m}^\circ$ $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$
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		= FeFe2O4	-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*
Metaschoepite	+1.0 UO2+2	+3.0 H2O	-2.0 H+			= UO3:2H2O	-5.960	34.020*			
MgSeO3:6H2O(cr)	+1.0 Mg+2	+1.0 SeO3-2	+6.0 H2O			= MgSeO3:6H2O	5.820	-33.221*	-13.030*	67.720*	
MnSeO3:2H2O(cr)	+1.0 Mn+2	+1.0 SeO3-2	+2.0 H2O			= MnSeO3:2H2O	7.600	-43.381*			
Mo(cr)	+1.0 MoO4-2	+8.0 H+	+6.0 e-	-4.0 H2O		= Mo	19.667‡	-112.260*	-145.420*	-111.219*	
Molybdite	+1.0 MoO4-2	+2.0 H+	-1.0 H2O			= MoO3	12.055‡	-68.810*	-33.020*	120.040*	
Na-Boltwoodite	_+1.0 Na+_	_+1.0 UO2+2_	_+1.0 Si(OH)4_	_+2.0 H2O_	_-3.0 H+_	_= Na(H3O)UO2SiO4:H2O_	_-5.800_	_33.107*_			
Na-Weeksite	_+2.0 Na+_	_+2.0 UO2+2_	_+6.0 Si(OH)4_	_-6.0 H+_	_-5.0 H2O_	_= Na2(UO2)2(Si2O5)3:4H2O_	_-1.500_	_8.562*_			
Na3NpO2(CO3)2(cr)	+3.0 Na+	+1.0 NpO2+	+2.0 CO3-2			= Na3NpO2(CO3)2	14.220	-81.168*			
Na6Th(CO3)5:12H2O(cr)	+6.0 Na+	+1.0 Th+4	+5.0 CO3-2	+12.0 H2O		= Na6Th(CO3)5:12H2O	42.200	-240.879*			
NaAm(CO3)2:5H2O(cr)	+1.0 Na+	+1.0 Am+3	+2.0 CO3-2	+5.0 H2O		= NaAm(CO3)2:5H2O	21.000	-119.869*			
NaAmO2CO3(s)	+1.0 Na+	+1.0 AmO2+	+1.0 CO3-2			= NaAmO2CO3	10.900	-62.218*			
NaNpO2CO3:3.5H2O(cr)	+1.0 Na+	+1.0 NpO2+	+1.0 CO3-2	+3.5 H2O		= NaNpO2CO3:3.5H2O	11.000	-62.788*			
Nb2O5(cr)	+2.0 NbO3-	+2.0 H+	-1.0 H2O			= Nb2O5	24.341‡	-138.940*			
NbO2(cr)	+1.0 NbO3-	+2.0 H+	+1.0 e-	-1.0 H2O		= NbO2	7.978‡	-45.540*			
(NH4)4NpO2(CO3)3(s)	+4.0 NH4+	+1.0 NpO2+2	+3.0 CO3-2			= (NH4)4NpO2(CO3)3	26.810	-153.033*			
Ni(OH)2(cr, beta)	+1.0 Ni+2	+2.0 H2O	-2.0 H+			= Ni(OH)2	-11.020	62.903*	84.340*	71.900	
Ni3(AsO4)2:8H2O(s)	+3.0 Ni+2	+2.0 AsO4-3	+8.0 H2O			= Ni3(AsO4)2:8H2O	28.100	-160.396*			
NiCO3:5.5H2O(s)	+1.0 Ni+2	+1.0 CO3-2	+5.5 H2O			= NiCO3:5.5H2O	7.530	-42.982*			
NiCO3(cr)	+1.0 Ni+2	+1.0 CO3-2				= NiCO3	11.000	-62.788*			
NiO(cr)	+1.0 Ni+2	+1.0 H2O	-2.0 H+			= NiO	-12.480	71.236*			
NiSeO3:2H2O(cr)	+1.0 Ni+2	+1.0 SeO3-2	+2.0 H2O			= NiSeO3:2H2O	5.800	-33.107*			
NpO2(am,hyd)	+1.0 Np+4	+2.0 H2O	-4.0 H+			= NpO2	0.700	-3.996*			
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*	
NpO2OH(am,fr)	+1.0 NpO2+	+1.0 H2O	-1.0 H+			= NpO2OH	-5.300	30.253*	41.100	36.382*	
NpO3:H2O(cr)	+1.0 NpO2+2	+2.0 H2O	-2.0 H+			= NpO3:H2O	-5.470	31.223*			
Pd(cr)	+1.0 Pd+2	+2.0 e-				= Pd	30.800	-175.800*	-177.200	-4.696*	
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*__	
Pu(HPO4)2(am,hyd)	+1.0 Pu+4	+2.0 HPO4-2				= Pu(HPO4)2	30.450	-173.810*			
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	2.330	-13.300*			
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	14.650	-83.623*			
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-		= FeSS	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*	
Quartz	+1.0 Si(OH)4	-2.0 H2O				= SiO2	3.746	-21.384*	-20.637	2.505*	
RaCO3(cr)	+1.0 Ra+2	+1.0 CO3-2				= RaCO3	8.300	-47.377*	-11.700	119.660*	
RaSO4(cr)	+1.0 Ra+2	+1.0 SO4-2				= RaSO4	10.260	-58.565*	-39.300	64.613*	
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	14.760	-84.251*			
__S(rhomb)__	__+1.0 HS-__	__-1.0 H+__	__-2.0 e-__			__= S__	__2.144__	__-12.243*__	__16.300__	__95.734*__	
Se(cr)	+1.0 SeO3-2	+6.0 H+	+4.0 e-	-3.0 H2O		= Se	61.150	-349.030*	-350.290*	-4.226*	
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*	
Sn(cr)	+1.0 Sn+2	+2.0 e-				= Sn	-4.630	26.430*	7.700*	-62.821*	
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*			
Soddyite	_+2.0 UO2+2_	_+1.0 Si(OH)4_	_+2.0 H2O_	_-4.0 H+_		_= (UO2)2SiO4:2H2O_	_-6.200_	_35.390*_			
SrSeO3(cr)	+1.0 Sr+2	+1.0 SeO3-2				= SrSeO3	6.300	-35.961*	6.200*	141.408*	
__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				= TcO2:1.6H2O	8.400	-47.948*			
_Th3(PO4)4(s)_	_+3.0 Th+4_	_+4.0 PO4-3_				_= Th3(PO4)4_	_112.000_	_-639.301*_			

Table B2: Reaction properties continued.

Name	**Reaction**						**log$_{10}$*K*°**	**Δ$_r$*G*$_m$°** **kJ·mol^{-1}**	**Δ$_r$*H*$_m$°** **kJ·mol^{-1}**	**Δ$_r$*S*$_m$°** **J·mol¯1·K^{-1}**	**Δ$_r$*C*$_{p,m}$°** **J·mol¯1·K^{-1}**
ThF4(cr,hyd)	+1.0 Th+4	+4.0 F-				= ThF4	31.800	-181.516*			
ThO2(am,hyd,ag)	+1.0 Th+4	+2.0 H2O	-4.0 H+			= ThO2	-8.500	48.518*			
ThO2(am,hyd,fr)	+1.0 Th+4	+2.0 H2O	-4.0 H+			= ThO2	-9.300	53.085*			
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*	
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	30.120	-171.926*			
UO2(am,hyd)	+1.0 U+4	+2.0 H2O	-4.0 H+			= UO2	-1.500	8.562*			
(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*			
Uranophane	_+1.0 Ca+2_	_+2.0 UO2+2_	_+2.0 Si(OH)4_	_+5.0 H2O_	_-6.0 H+_	_= Ca(H3O)2(UO2)2(SiO4)2:3H2O_	_-9.400_	_53.656*_			
USiO4(s)	_+1.0 U+4_	_+1.0 Si(OH)4_	_-4.0 H+_			_= USiO4_	_1.500_	_-8.562*_			
__Witherite__	__+1.0 Ba+2__	__-1.0 H+__	__+1.0 HCO3-__			__= BaCO3__	__-1.767*__	__10.087*__	__11.961*__	__6.285*__	__293.360*__
Zr(HPO4)2:H2O(cr)	_+1.0 Zr+4_	_+2.0 H3PO4_	_+1.0 H2O_	_-4.0 H+_		_= Zr(HPO4)2:H2O_	_22.800_	_-130.143*_			
Zr(OH)4(am,fr)	+1.0 Zr+4	+4.0 H2O	-4.0 H+			= Zr(OH)4	3.240	-18.494*			
GASES											
__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*__
H2S(g)	+1.0 HS-	+1.0 H+				= H2S	8.010	-45.721*	-4.300	138.928*	
H2Se(g)	+1.0 H2Se					= H2Se	1.100	-6.279*	-29.000*	-76.207*	
__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*__

B.1 References

Hummel, W., Berner, U., Curti, E., Pearson, F.J. & Thoenen, T. (2002): Nagra/PSI Chemical Thermodynamic Data Base 01/01. Nagra NTB 02-16, Nagra, Wettingen, Switzerland. Also published by Universal Publishers/upublish.com, Parkland, USA, 565 pp.

Appendix C: Changes with respect to previous documentation

Several small changes to selected data have been made since Thoenen (2012). They are summarized in Table C1. These changes are not included in the electronic versions of TDB 12/07 for PHREEQC and GEMS-PSI released before December 2014.

Table C1: Changes of $\log_{10}\beta°$ values with respect to Thoenen (2012).

Reaction	**$\log_{10}\beta°$ Thoenen (2012)**	**$\log_{10}\beta°$ This work**	**Comments**
$2\ UO_2^{2+} + PuO_2^{2+} + 6\ CO_3^{2-} \Leftrightarrow (UO_2)_2(PuO_2)(CO_3)_6^{6-}$	52.7 ± 1.6	53.5 ± 1.4	see p. 150
$UO_2^{+} + 3\ CO_3^{2-} \Leftrightarrow UO_2(CO_3)_3^{5-}$	6.95 ± 0.36	7.19 ± 0.36	see p. 333
$U^{4+} + 5\ CO_3^{2-} \Leftrightarrow U(CO_3)_5^{6-}$	34.1 ± 1.0	33.9 ± 1.0	see p. 333
$U^{4+} + SCN^{-} \Leftrightarrow USCN^{3+}$	2.97 ± 0.06	2.83 ± 0.15	see p. 337

C.1 References

Thoenen, T. (2012): The PSI/Nagra Chemical Thermodynamic Data Base 12/07: Compilation of updated and new data with respect to the Nagra/PSI Chemical Thermodynamic Data Base 01/01. PSI Technical Report TM-44-12-06, Paul Scherrer Institut, Villigen.

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