PAUL SCHERRER INSTITUT		Registrierung TM-44-14-03
Titel	The PSI/Nagra Chemical Thermodynamic Database 12/07 (Update of the Nagra/PSI TDB 01/01): Data Selection for Uranium	Ersetzt
Autoren	Tres Thoenen and Wolfgang Hummel	Erstellt 05.05.2014

Summary:

This report provides an update of the Nagra/PSI Thermochemical Data Base 01/01 (HUMMEL et al. 2002) with respect to uranium. Most data for uranium in the Nagra/PSI TDB 01/01 were taken from OECD NEA's book "Chemical Thermodynamics of Uranium" by GRENTHE et al. (1992). Newer literature on uranium was reviewed in "Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium" by GUILLAUMONT et al. (2003), which served as a basis for this update of Chapter 5.23 (written by W. Hummel) on uranium in HUMMEL et al. (2002). The updated database will be called PSI/Nagra Chemical Thermodynamic Database 12/07.

This is the 9th of a continuing series of reports concerning the PSI/Nagra Chemical Thermodynamic Database 12/07.

Verteiler	Abt.	Empfänger / Empfängerinnen	Expl.	Abt.	Empfänger / Empfängerinnen	Expl.
	44	B. Baeyens	1	Nagra	V. Cloet	1
		U. Berner	1		L. Johnson	1
		S. Churakov	1		J. Mibus	1
		E. Curti	1		J. Schneider	1
		R. Dähn	1		B. Schwyn	1
		T. Gimmi	1		P. Zuidema	1
		M. Glaus	1			
		W. Hummel	1	NewBern	F.J. Pearson	1
		G. Kosakowski	1			
		D. Kulik	1			
		M. Marques	1			
		W. Pfingsten	1			
		T. Thoenen	1			
		J. Tits	1			
		L. Van Loon	1			
		E. Wieland	1			

	Expl.
Bibliothek	2
Reserve	4
Total	29
Seiten	81
Beilagen	-

Informationsliste

D	1	2	3	4	5	8	9	A

Visum ~~Abt.-/Laborleitung~~:

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 1.2. All data selected for our database are listed in Table 1.3.

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 developed by HUMMEL (2009), 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 1.4 and 1.5.

The notation of formulae and symbols used in this text follows the NEA recommendations and practice.

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 1.2 for computational purposes only.

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

$$\Delta_f H_m\,°(UO_2^{2+}, aq, 298.15\ K) = -(1019.0 \pm 1.5)\ kJ \cdot mol^{-1}$$

has been adopted by GRENTHE et al. (1992). As an expedient to assure maximum CODATA consistency, the CODATA value of the entropy of the UO_2^{2+} ion is recommended by GRENTHE et al. (1992):

$$S_m\,°(UO_2^{2+}, aq, 298.15\ K) = -(98.2 \pm 3.0)\ J \cdot K^{-1} \cdot mol^{-1}$$

The Gibbs energy of formation is obtained from the above values

$$\Delta_f G_m\,°(UO_2^{2+}, aq, 298.15\ K) = -(952.55 \pm 1.75)\ kJ \cdot mol^{-1}$$

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 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 ± 1.8) kJ · 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:

$$\log_{10}K\,°(298.15\ \text{K}) = 1.484 \pm 0.022$$

with

$$\Delta\varepsilon = -(0.20 \pm 0.01)\ \text{kg} \cdot \text{mol}^{-1}$$

resulting in $\varepsilon(UO_2^+, ClO_4^-) = (0.26 \pm 0.03)$ kg · mol^{-1} by using the value for $\varepsilon(UO_2^{2+}, ClO_4^-)$ selected above. Since data for chloride systems are missing, we estimated

$$\varepsilon(UO_2^+, Cl^-) = (0.05 \pm 0.10)\ \text{kg} \cdot \text{mol}^{-1}$$

according to HUMMEL (2009).

In the absence of experimental data, GRENTHE et al. (1992) selected an estimated entropy value

$$S_m\,°(UO_2^+, \text{aq}, 298.15\ \text{K}) = -(25 \pm 8)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

The enthalpy of formation is derived from the selected $\log_{10}K\,° \rightarrow \Delta_f G_m°$ and $S_m°$ values:

$$\Delta_f H_m°(UO_2^+, \text{aq}, 298.15\ \text{K}) = -(1025.1 \pm 3.0)\ \text{kJ} \cdot \text{mol}^{-1}$$

The validity of this estimate is corroborated by the experimental value of -(60 ± 11) J·K^{-1}·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 · 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:

$$\log_{10}K°(298.15\ \text{K}) = 9.038 \pm 0.041$$

From

$$\Delta\varepsilon = -(0.20 \pm 0.01)\ \text{kg} \cdot \text{mol}^{-1}$$

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 · mol^{-1}. Since neither GRENTHE et al. (1992) nor GUILLAUMONT et al. (2003) reported any value for the chloride system, we estimated

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

using the method by HUMMEL (2009).

The enthalpy of formation as selected by GRENTHE et al. (1992) is based on two series of experiments.

$$\Delta_f H_m°(U^{4+}, aq, 298.15\ K) = -(591.2 \pm 3.3)\ kJ \cdot mol^{-1}$$

The entropy is derived from the selected $\log_{10}K° \rightarrow \Delta_f G_m°$ and $\Delta_f H_m°$ values:

$$S_m°(U^{4+}, aq, 298.15\ K) = -(416.9 \pm 12.6)\ J \cdot K^{-1} \cdot mol^{-1}$$

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 $C_{p,m}°(Th^{4+}, aq, 298.15\ K)$

$$C_{p,m}°(U^{4+}, aq, 298.15\ K) = -(220 \pm 50)\ J \cdot K^{-1} \cdot mol^{-1}$$

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.

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.

4.1 Aqueous uranium hydroxide complexes

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 $\Delta\varepsilon$ values:

$$2\ UO_2^{2+} + 2\ H_2O(l) \Leftrightarrow (UO_2)_2(OH)_2^{2+} + 2\ H^+$$

$$\log_{10}{}^*\beta_{2,2}^\circ(m = 2, n = 2, 298.15\ K) = -5.62 \pm 0.04$$

$$\Delta\varepsilon((UO_2)_2(OH)_2^{2+}, Cl^-) = (0.01 \pm 0.03)\ kg \cdot mol^{-1}$$

$$\Delta\varepsilon((UO_2)_2(OH)_2^{2+}, ClO_4^-) = -(0.07 \pm 0.02)\ kg \cdot mol^{-1}$$

$$\Delta\varepsilon((UO_2)_2(OH)_2^{2+}, NO_3^-) = -(0.29 \pm 0.07)\ kg \cdot mol^{-1}$$

$$3\ UO_2^{2+} + 4\ H_2O(l) \Leftrightarrow (UO_2)_3(OH)_4^{2+} + 4\ H^+$$

$$\log_{10}{}^*\beta_{4,3}^\circ(m = 3, n = 4, 298.15\ K) = -11.9 \pm 0.3$$

$$\Delta\varepsilon((UO_2)_3(OH)_4^{2+}, Cl^-) = -(0.40 \pm 0.15)\ kg \cdot mol^{-1}$$

$$\Delta\varepsilon((UO_2)_3(OH)_4^{2+}, ClO_4^-) = (0.1 \pm 0.2)\ kg \cdot mol^{-1}$$

$$\Delta\varepsilon((UO_2)_3(OH)_4^{2+}, NO_3^-) = -(0.4 \pm 1.0)\ kg \cdot mol^{-1}$$

$$3\ UO_2^{2+} + 5\ H_2O(l) \Leftrightarrow (UO_2)_3(OH)_5^{+} + 5\ H^+$$

$$\log_{10}{}^*\beta_{5,3}^\circ(m = 3, n = 5, 298.15\ K) = -15.55 \pm 0.12$$

$$\Delta\varepsilon((UO_2)_3(OH)_5^{+}, Cl^-) = (0.03 \pm 0.13)\ kg \cdot mol^{-1}$$

$$\Delta\varepsilon((UO_2)_3(OH)_5^{+}, ClO_4^-) = -(0.23 \pm 0.07)\ kg \cdot mol^{-1}$$

$$\Delta\varepsilon((UO_2)_3(OH)_5^{+}, NO_3^-) = -(0.6 \pm 0.2)\ kg \cdot mol^{-1}$$

Using these $\Delta\varepsilon$ values together with the selected values $\varepsilon(UO_2^{2+}, Cl^-) = \varepsilon(UO_2^{2+}, NO_3^-) = \varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)\ kg \cdot mol^{-1}$, $\varepsilon(H^+, Cl^-) = (0.12 \pm 0.01)\ kg \cdot mol^{-1}$, $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)\ kg \cdot mol^{-1}$, and $\varepsilon(H^+, NO_3^-) = (0.07 \pm 0.01)\ kg \cdot mol^{-1}$, GRENTHE et al. (1992) derived the following selected ion interaction coefficients

$$\varepsilon((UO_2)_2(OH)_2^{2+}, Cl^-) = (0.69 \pm 0.07)\ kg \cdot mol^{-1}$$

$$\varepsilon((UO_2)_2(OH)_2^{2+}, ClO_4^-) = (0.57 \pm 0.07)\ kg \cdot mol^{-1}$$

$$\varepsilon((UO_2)_2(OH)_2^{2+}, NO_3^-) = (0.49 \pm 0.09)\ kg \cdot mol^{-1}$$

$$\varepsilon((UO_2)_3(OH)_4^{2+}, Cl^-) = (0.50 \pm 0.18)\ kg \cdot mol^{-1}$$

$$\varepsilon((UO_2)_3(OH)_4^{2+}, ClO_4^-) = (0.89 \pm 0.23)\ kg \cdot mol^{-1}$$

$$\varepsilon((UO_2)_3(OH)_4^{2+}, NO_3^-) = (0.72 \pm 1.00)\ kg \cdot mol^{-1}$$

$$\varepsilon((UO_2)_3(OH)_5^+, Cl^-) = (0.81 \pm 0.17)\ kg \cdot mol^{-1}$$

$$\varepsilon((UO_2)_3(OH)_5^+, ClO_4^-) = (0.45 \pm 0.15)\ kg \cdot mol^{-1}$$

$$\varepsilon((UO_2)_3(OH)_5^+, NO_3^-) = (0.41 \pm 0.22)\ kg \cdot mol^{-1}$$

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

$$2\ UO_2^{2+} + H_2O(l) \Leftrightarrow (UO_2)_2OH^{3+} + H^+$$

$$\log_{10}{}^*\beta_{1,2}^\circ(m = 2, n = 1, 298.15\ K) = -2.7 \pm 1.0$$

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 according to the method developed by HUMMEL (2009), 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 values are

$$\varepsilon((UO_2)_2OH^{3+}, Cl^-) = (0.25 \pm 0.10)\ kg \cdot mol^{-1}$$

$$\varepsilon((UO_2)_2OH^{3+}, ClO_4^-) = (0.6 \pm 0.1)\ kg \cdot mol^{-1}$$

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

$$4\ UO_2^{2+} + 7\ H_2O(l) \Leftrightarrow (UO_2)_4(OH)_7^+ + 7\ H^+$$

$$\log_{10}{}^*\beta_{7,4}^\circ(m = 4, n = 7, 298.15\ K) = -21.9 \pm 1.0$$

We estimated

$$\varepsilon((UO_2)_4(OH)_7^+, Cl^-) = (0.05 \pm 0.10)\ kg \cdot mol^{-1}$$

$$\varepsilon((UO_2)_4(OH)_7^+, ClO_4^-) = (0.2 \pm 0.1)\ kg \cdot mol^{-1}$$

according to the estimation method by HUMMEL (2009).

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 revised by GUILLAUMONT et al. (2003) due to a reinterpretation of the original data. The revised value selected by GUILLAUMONT et al. (2003)

$$3\ UO_2^{2+} + 7\ H_2O(l) \Leftrightarrow (UO_2)_3(OH)_7^- + 7\ H^+$$

$$\log_{10}{}^*\beta_{7,3}^\circ(m = 3, n = 7, 298.15\ K) = -32.2 \pm 0.8$$

is included in our database, as well as

$$\varepsilon((UO_2)_3(OH)_7^-, Na^+) = -(0.05 \pm 0.10)\ kg \cdot mol^{-1}$$

which we estimated following HUMMEL (2009).

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 $^*\beta_1^\circ$ 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 $\log_{10}{}^*\beta_1^\circ(298.15\ K) = -5.2 \pm 0.3$ for the reaction

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

with $\Delta\varepsilon(UO_2OH^+, ClO_4^-) = -(0.4 \pm 3.7)\ kg \cdot mol^{-1}$ and $\Delta\varepsilon(UO_2OH^+, NO_3^-) = (0.1 \pm 1.4)\ kg \cdot mol^{-1}$, 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 $\varepsilon(UO_2^{2+}, ClO_4^-) = \varepsilon(UO_2^{2+}, NO_3^-) = (0.46 \pm 0.03)\ kg \cdot mol^{-1}$, GRENTHE et al. (1992) obtained $\varepsilon(UO_2OH^+, ClO_4^-) = -(0.06 \pm 0.40)\ kg \cdot mol^{-1}$ and $\varepsilon(UO_2OH^+, NO_3^-) = (0.51 \pm 1.40)\ kg \cdot mol^{-1}$ (our calculations with these data resulted in $-(0.08 \pm 3.7)$ and $(0.59 \pm 1.40)\ kg \cdot mol^{-1}$, 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,

$$\log_{10}{}^*\beta_1^\circ(298.15\ K) = -5.25 \pm 0.24$$

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).

$$\varepsilon(UO_2OH^+, ClO_4^-) = -(0.06 \pm 0.40)\ kg \cdot mol^{-1}$$

$$\varepsilon(UO_2OH^+, NO_3^-) = (0.51 \pm 1.40)\ kg \cdot mol^{-1}$$

which we adopt for our database, despite the problem with the uncertainty for $\varepsilon(UO_2OH^+, ClO_4^-)$. We also selected

$$\varepsilon(UO_2OH^+, Cl^-) = (0.05 \pm 0.10)\ kg \cdot mol^{-1}$$

as estimated according to HUMMEL (2009).

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 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 4.2.1) as $\log_{10}{}^*K_{s,0}° = 4.8 \pm 0.4$. Thus, a limiting value of $\log_{10}{}^*\beta_2° \le -10.3$ 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 $\log_{10}{}^*\beta_2°$

≤ -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 $\log_{10}{}^*\beta_2^\circ = -12.0 \pm 0.2$. 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 $\log_{10}{}^*\beta_2^\circ = -12.6 \pm 0.4$ 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 $\beta_{1,2}^\circ$ has been done incorrectly in PASHALIDIS et al. (1995), the value of $\log_{10}{}^*\beta_2^\circ$ 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 $\log_{10}{}^*\beta_2^\circ(m = 1, n = 2, 298.15\ K) = -12.0 \pm 0.5$ 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

$$\log_{10}{}^*\beta_2^\circ(m = 1, n = 2, 298.15\ K) = -12.15 \pm 0.07$$

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 $\log_{10}{}^*\beta_3^\circ$ 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)

$$UO_2^{2+} + 3\ H_2O(l) \Leftrightarrow UO_2(OH)_3^- + 3\ H^+$$

$$\log_{10}{}^*\beta_3^\circ(m = 1, n = 3, 298.15\ K) = -20.25 \pm 0.42$$

which is also included in our database. The source of the value for the ion interaction coefficient

$$\varepsilon(UO_2(OH)_3^-, Na^+) = -(0.09 \pm 0.05)\ kg \cdot mol^{-1}$$

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 ± 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 $\varepsilon(UO_2^{2+}, ClO_4^-)$ = 0.46, $\varepsilon(UO_2(OH)_3^-, Na^+)$ = -0.09 and $\varepsilon(H^+, ClO_4^-)$ = 0.14. This extrapolation resulted in $\log_{10}{}^*\beta_3^\circ$ = -(19.18 ± 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 $\Delta\varepsilon(UO_2(OH)_3^-, Na^+)$ = -(0.13 ± 0.08) kg · mol^{-1} and marked it as an estimated value. This value is exactly reproducible by using $\varepsilon(UO_2^{2+}, ClO_4^-)$ = (0.46 ± 0.03) kg · mol^{-1}, $\varepsilon(H^+, ClO_4^-)$ = (0.14 ± 0.02) kg · mol^{-1}, both selected by GRENTHE et al. (1992), and $\varepsilon(UO_2(OH)_3^-, Na^+)$ = -(0.09 ± 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 $\varepsilon(UO_2^{2+}, ClO_4^-)$ = 0.46 ± 0.03, $\varepsilon(HPO_4^{2-}, Na^+)$ = -0.15 ± 0.06, $\varepsilon(PO_4^{3-}, Na^+)$ = -0.25 ± 0.03, $\varepsilon(UO_2PO_4^-, Na^+)$ = $\varepsilon(UO_2(OH)_3^-, Na^+)$ = -0.09 ± 0.05 (GRENTHE and WANNER, 1989)."

Going back to GRENTHE & WANNER (1989), one finds no values whatsoever for $\varepsilon(UO_2PO_4^-, Na^+)$ and $\varepsilon(UO_2(OH)_3^-, Na^+)$ and the source for $\varepsilon(UO_2(OH)_3^-, Na^+)$ = -(0.09 ± 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} calculated according to HUMMEL (2009).

$UO_2(OH)_4^{2-}$: Based on the experimental data by YAMAMURA et al. (1998), GUILLAUMONT et al. (2003) selected

$$UO_2^{2+} + 4\ H_2O(l) \Leftrightarrow UO_2(OH)_4^{2-} + 4\ H^+$$

$$\log_{10}{}^*\beta_4^\circ(m = 1, n = 4, 298.15\ K) = -32.40 \pm 0.68$$

which is included in our database.

Since GUILLAUMONT et al. (2003) did not select any ion interaction coefficients, we estimated

$$\varepsilon(UO_2(OH)_4^{2-}, Na^+) = -(0.10 \pm 0.10)\ kg \cdot mol^{-1}$$

according to HUMMEL (2009).

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:

$$S_m°(UO_2OH^+, aq, 298.15\ K) = (17 \pm 50)\ J \cdot K^{-1} \cdot mol^{-1}$$

$$S_m°((UO_2)_2(OH)_2^{2+}, aq, 298.15\ K) = -(38 \pm 15)\ J \cdot K^{-1} \cdot mol^{-1}$$

$$S_m°((UO_2)_3(OH)_5^+, aq, 298.15\ K) = (83 \pm 30)\ J \cdot K^{-1} \cdot mol^{-1}$$

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.

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 $\Delta\varepsilon = -(0.14 \pm 0.05)\ kg \cdot mol^{-1}$. From this value and the selected $\varepsilon(U^{4+}, ClO_4^-) = (0.76 \pm 0.06)\ kg \cdot mol^{-1}$ and $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)\ kg \cdot mol^{-1}$ follows

$$\varepsilon(UOH^{3+}, ClO_4^-) = (0.48 \pm 0.08)\ kg \cdot mol^{-1}$$

For use in chloride media we estimated

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

according to HUMMEL (2009).

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.

$$\Delta_r H_m°(298.15\ K) = (46.9 \pm 9.0)\ kJ \cdot mol^{-1}$$

$$\Delta_r S_m°(298.15\ K) = (147 \pm 30)\ J \cdot K^{-1} \cdot mol^{-1}$$

$U(OH)_4(aq)$: 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 $log_{10}*\beta_4° = -4.5 \pm 1.4$ based on two solubility studies:

(1) PARKS & POHL (1988) measured the solubility of uraninite (UO_2) at temperatures from 100 to 300°C. They found that the temperature and pH dependence are statistically insignificant in the experimental results for all pH > 4, suggesting the predominance of a single species $U(OH)_4(aq)$, and the dissolution equilibrium

$$UO_2(s) + 2\ H_2O(l) \Leftrightarrow U(OH)_4(aq)$$

for which, at all temperatures from 100 to 300°C, $log_{10}K_{s,4} = -9.47 \pm 0.56$. The solubility product of $UO_2(cr)$ for the reaction

$$UO_2(cr) + 4\ H^+ \Leftrightarrow U^{4+} + 2\ H_2O(l)$$

can be calculated from the selected Gibbs energy of formation ($\Delta_f G_m°(UO_2, cr, 298.15\ K)$, see Section 4.2.2) as $log_{10}*K_{s,0}° = -4.85 \pm 0.36$. A value of $log_{10}*\beta_4° = log_{10}K_{s,4} - log_{10}*K_{s,0}° = -4.6 \pm 0.7$ can be derived from these two numbers.

(2) BRUNO et al. (1987) measured the solubility of a so-called amorphous (actually partially crystalline) form of UO_2 at 25°C. The solubility of this material was $log_{10}K_{s,4} = -4.4 \pm 0.4$, independent of pH between pH values of 5.5 to 10.0. The solubility product for a similarly prepared solid was determined potentiometrically by BRUNO et al. (1986) as $log_{10}*K_{s,0}° = 0.1 \pm 0.7$. A value of $log_{10}*\beta_4° = log_{10}K_{s,4} - log_{10}*K_{s,0}° = -4.5 \pm 0.8$ can be derived from these two numbers.

GRENTHE et al. (1992) stated that the agreement of these values is unexpectedly good, especially considering the difficulties in characterising an amorphous solid as the one used by BRUNO et al. (1987). The uncertainty of the recommended value had been increased "to allow for uncertainties in the nature of the solids and for compatibility with the values for other hydrolysis species". However, the latter aspect prompted GRENTHE et al. (1992) to add a section entitled "A potential inconsistency" (GRENTHE et al. 1992, pp.129-131): The selected values for $log_{10}*\beta_1° = -0.54$ and

$log_{10}*\beta_4° = -4.5$ imply equal concentrations of UOH^{3+} and $U(OH)_4(aq)$ near pH = 1.8 (see solid line in Fig. 1.1), but there has been no experimental evidence that $U(OH)_4(aq)$ occurs in acidic solutions of pH < 3. As a consequence, the stability of the neutral species $U(OH)_4(aq)$ has been overestimated by orders of magnitude. In GRENTHE et al. (1995) one reads: "Although it appears that the stability of $U(OH)_4(aq)$ has been overestimated by orders of magnitude in GRENTHE et al. (1992), the inconsistencies mentioned by GRENTHE et al. (1992) still remain unresolved, and a re-examination of this system is being undertaken simultaneously with the neptunium and plutonium NEA-review." Apparently, this re-examination has been further postponed to the NEA-TDB update of the uranium review which will not be published before 2002.

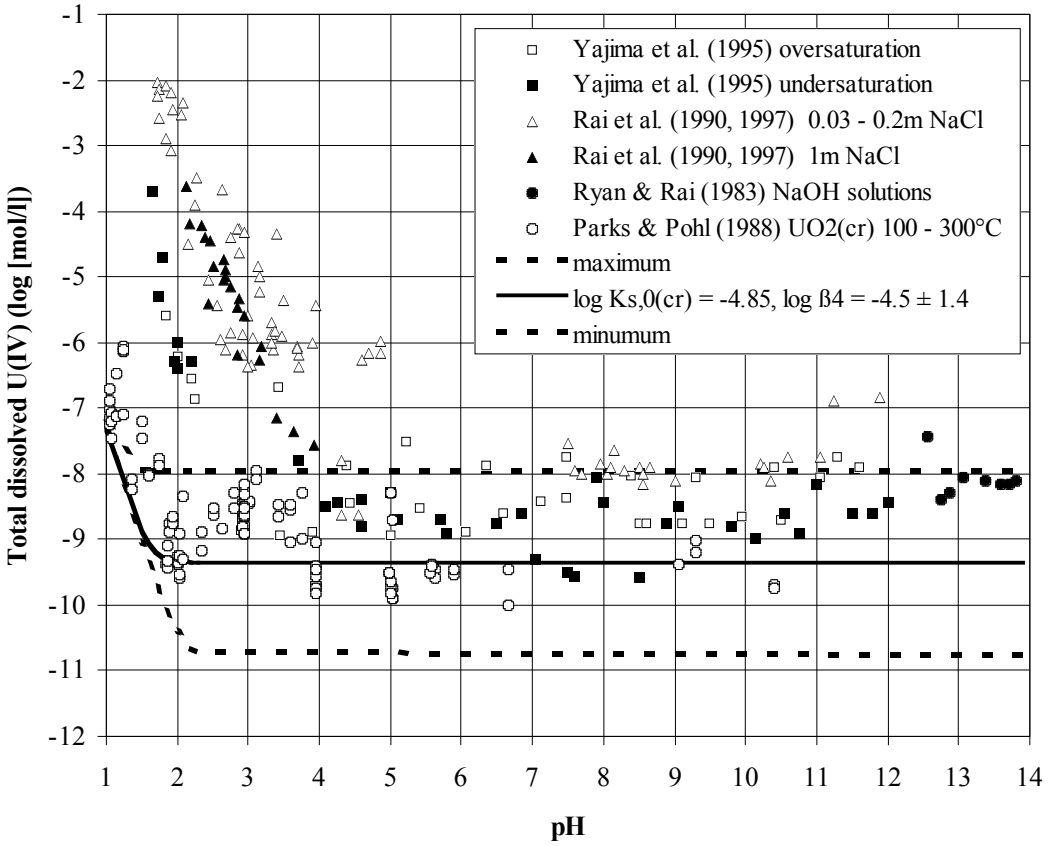

Fig. 1.1: *Solubility data of the system UO_2 - H_2O. The lines have been calculated using thermodynamic constants recommended by GRENTHE et al. (1992).*

This inconsistency and a possible resolution has been discussed in detail by BERNER (1995). As discussed by RAI et al. (1990) and BERNER (1995), BRUNO et al. (1987) were not successful in effectively controlling the oxidation state of uranium and most probably their measurements reflect the solubility of "UO_2" in a partly 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. 1.2). X-ray diffraction patterns of the solids separated from the equilibrated solutions indicated that the precipitates were amorphous UO_2. More recently, YAJIMA et al. (1995) studied the solubility of UO_2 in 0.1 M $NaClO_4$ from oversaturation and undersaturation between pH 2 and 12. At pH > 3 they found constant uranium concentrations (see Fig. 1.2). 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. 1.2). No temperature dependence has been observed between 100 to 300°C and therefore, we do not expect significant temperature effects between 100 and 25°C. However, the surface of the solids controlling the solubility in the hydrothermal experiments of PARKS & POHL (1988) might have been more crystalline than in the 25°C experiments of YAJIMA et al. (1995) and very long term experiments at 25°C might converge to values as found in the hydrothermal experiments. As long as there is no experimental evidence supporting this hypothesis we propose

$$\log_{10}K_{s,4}°(UO_2, s, 298.15\ K) = -9 \pm 1$$

assuming that all dissolved uranium is present as $U(OH)_4(aq)$ and ionic strength effects for this neutral species are much smaller than the uncertainty in solubility data. The thick solid and dotted lines in Fig. 1.2 at pH > 4 represent our choice of $\log_{10}K_{s,4}° = -9$ and its associated uncertainty of ± one order of magnitude.

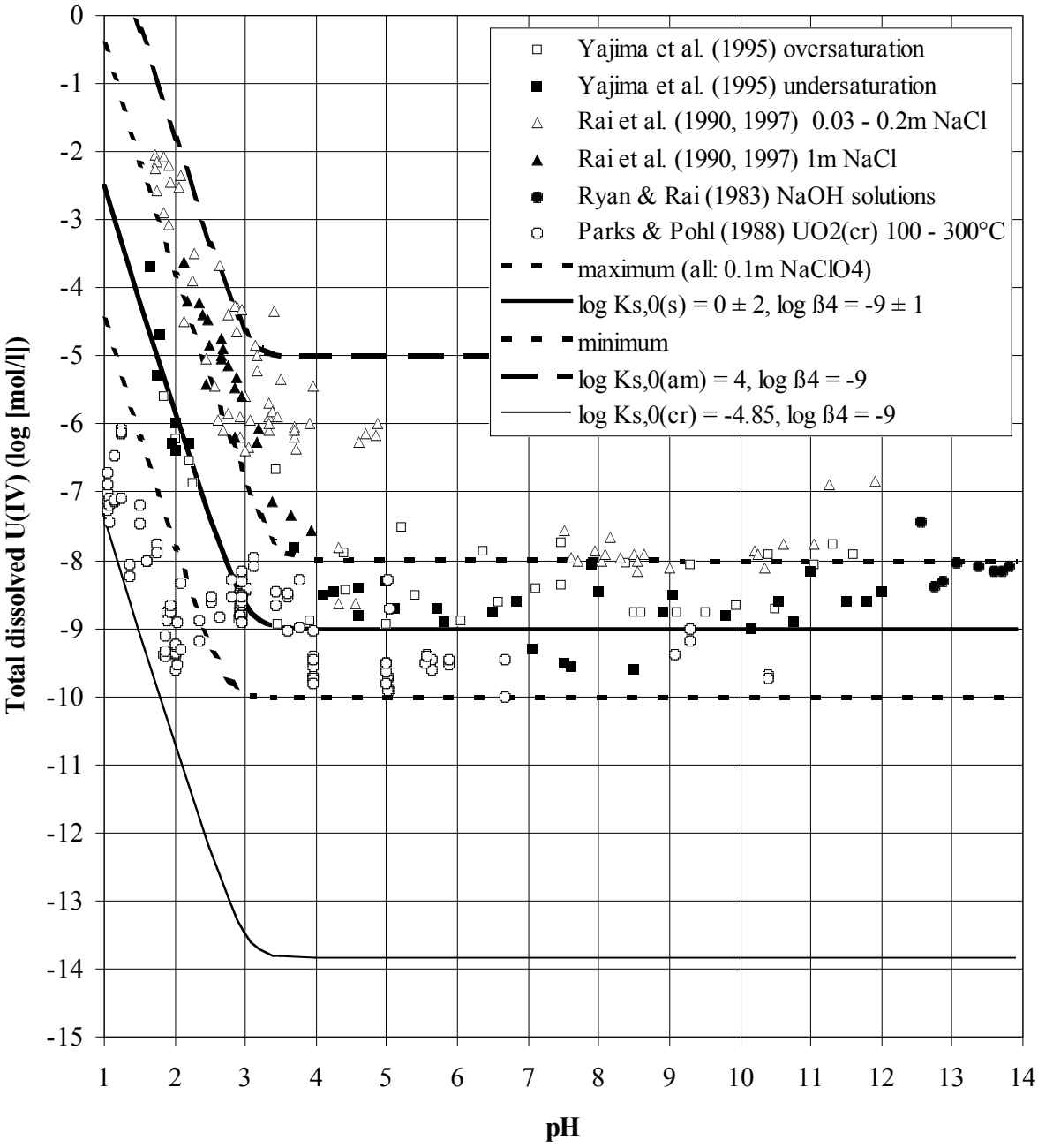

Fig. 1.2: *Solubility data of the system UO_2 - H_2O. The thick solid line is calculated using thermodynamic constants estimated in this review. Dotted lines represent the estimated uncertainty. The dashed line is calculated using $\log_{10}{}^*K_{s,0}{}^\circ$(am) = 4 given by RAI et al. (1990). The 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).*

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. 1.2 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. 1.2 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. 1.2.* 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. 1.2 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. 1.2). 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 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. 1.2 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 *solubility has been observed at pH > 4 which can be represented by* $\log_{10}K_{s,4}^\circ(s) = -9 \pm 1$ *(Fig. 1.2). Both ranges are coupled by the (unknown) constant* $\log_{10}{}^*\beta_4^\circ$*. Obviously, no unique set of constants* $\log_{10}{}^*K_{s,0}^\circ + \log_{10}{}^*\beta_4^\circ = \log_{10}K_{s,4}^\circ$ *can be selected which is compatible with all experimental data.* GRENTHE *et al. (1992) attempted to resolve this dilemma by selecting* $\log_{10}K_{s,4}^\circ(s)$ *compatible with the experimental data of* PARKS *&* POHL *(1988) at pH > 4 and selecting* $\log_{10}{}^*K_{s,0}^\circ(cr)$ *derived from*

$\Delta_f G_m°$ of UO_2(cr). As a consequence, the value of $\log_{10}*\beta_4°$ has been overestimated by orders of magnitude. But what is a "more reasonable" value of $\log_{10}*\beta_4°$?

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 $\log_{10}*\beta_4°$ 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 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 tetra-valent actinides like Th.

Thus, HUMMEL et al. (2002) selected

$$UO_2(s) + 2\ H_2O(l) \Leftrightarrow U(OH)_4(aq)$$

$$\log_{10}K_{s,4}°(298.15\ K) = -9 \pm 1$$

and

$$UO_2(s) + 4\ H^+ \Leftrightarrow U^{4+} + 2\ H_2O(l)$$

$$\log_{10}{}^*K_{s,0}°(298.15\ K) = 0 \pm 2$$

From $\log_{10}K_{s,4}°(298.15\ K)$ and $\log_{10}{}^*K_{s,0}°(298.15\ K)$ follows

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

$$\log_{10}{}^*\beta_4°(298.15\ K) = \log_{10}K_{s,4}°(298.15\ K) - \log_{10}{}^*K_{s,0}°(298.15\ K) = -9 \pm 2$$

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

$$UO_2(s) + 2\ H_2O(l) \Leftrightarrow U(OH)_4(aq)$$

$$\log_{10}K_{s,4}°(298.15\ K) = -8.5 \pm 1$$

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

$$\log_{10}{}^*\beta_4°(298.15\ K) = -10 \pm 1.4$$

From $\log_{10}K_{s,4}°(298.15\ K)$ and $\log_{10}{}^*\beta_4°(298.15\ K)$ then follows

$$UO_2(s) + 4\ H^+ \Leftrightarrow U^{4+} + 2\ H_2O(l)$$

$$\log_{10}{}^*K_{s,0}°(298.15\ K) = 1.5 \pm 1.0$$

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

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

$$\log_{10}{}^*\beta_4°(298.15\ K) = -10 \pm 1.4$$

with

$$UO_2(am, hyd) + 4\ H^+ \Leftrightarrow U^{4+} + 2\ H_2O(l)$$

$$\log_{10}{}^*K_{s,0}°(298.15\ K) = 1.5 \pm 1.0$$

$U(OH)_5^-$: 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 0.01M U(IV) are not relevant for radioactive waste management and this species can safely be ignored in our database.

We expect that other monomeric hydrolysis species would be involved at low uranium concentrations. However, no unambiguous evidence for the formation of species like $U(OH)_2^{2+}$ and $U(OH)_3^+$ in acidic solutions has been reported. From the viewpoint of U(IV) solubility 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

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

$$log_{10}{}^*\beta_2°(298.15\ K) = -1.1 \pm 1.0$$

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

$$log_{10}{}^*\beta_3°(298.15\ K) = -4.7 \pm 1.0$$

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 according to HUMMEL (2009)

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

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

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

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

4.2 Solid uranium oxides and hydroxides

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 $\log_{10}{}^*K_{s,0}^\circ = 4.8 \pm 0.4$. On the other hand, SANDINO (1991) determined the solubility product of $UO_3 \cdot 2H_2O$ and reported $\log_{10}{}^*K_{s,0}^\circ = 5.96 \pm 0.18$. 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 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 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:

$$\Delta_f H_m^\circ(UO_3{\cdot}2H_2O, cr, 298.15\ K) = -(1826.1 \pm 1.7)\ kJ \cdot mol^{-1}$$

Calorimetric data are available for the determination of entropy and heat capacity of $UO_3{\cdot}2H_2O$(cr) (GRENTHE et al. 1992) and the following values have been selected by GRENTHE et al. (1992):

$$S_m^\circ(UO_3{\cdot}2H_2O, cr, 298.15\ K) = (188.54 \pm 0.38)\ J \cdot K^{-1} \cdot mol^{-1}$$

$$C_{p,m}^\circ(UO_3{\cdot}2H_2O, cr, 298.15\ K) = (172.07 \pm 0.34)\ J \cdot K^{-1} \cdot mol^{-1}$$

To be consistent with our arguments for preferring measured solubility products we have to discard either the entropy or the enthalpy recommendation of GRENTHE et al. (1992), or both. For the purpose of estimating the temperature dependence of "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.

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) kJ · 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 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 $\log_{10}{}^*K_{s,0}^\circ(am) = 4.0$ (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 $\log_{10}K_{s,4}^\circ(s) = -8.5 \pm 1$ (Fig. 1.2). Both ranges are coupled by the (unknown) constant $\log_{10}{}^*\beta_4^\circ$. Obviously, no unique set of constants $\log_{10}{}^*K_{s,0}^\circ + \log_{10}{}^*\beta_4^\circ = \log_{10}K_{s,4}^\circ$ can be selected which is compatible with all experimental data. As a pragmatic solution to this dilemma, values for $\log_{10}{}^*\beta_4^\circ$ and $\log_{10}{}^*K_{s,0}^\circ$ 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 4.1.3, the selected solubility product is

$$UO_2(am, hyd) + 4\ H^+ \Leftrightarrow U^{4+} + 2\ H_2O(l)$$

$$\log_{10}{}^*K_{s,0}^\circ = 1.5 \pm 1.0$$

4.2.3 Mixed valence oxides

Values for the enthalpy of formation and entropy of $U_3O_8(cr) \equiv 3 \cdot UO_{2.6667}(cr)$, $\beta\text{-}U_3O_7(cr,) \equiv 3 \cdot \beta\text{-}UO_{2.3333}(cr)$[1] , $U_4O_9(cr) \equiv 4 \cdot UO_{2.25}(cr)$, and $\beta\text{-}U_4O_9(cr) \equiv 4 \cdot \beta\text{-}UO_{2.25}(cr)$ (higher-temperature polymorph) were recommended by GRENTHE et al. (1992). The enthalpy of formation, $\Delta_f H_m^\circ$, of $U_3O_8(cr)$ has been determined from the heat of combustion of uranium metal to U_3O_8, $\Delta_f H_m^\circ$ of $\beta\text{-}U_3O_7(cr)$, $U_4O_9(cr)$ and $\beta\text{-}U_4O_9(cr)$ 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, $\alpha\text{-}UO_{2.95}(cr)$. Again, no solubility measurements are reported.

Combining calculated $\Delta_f G_m^\circ$ 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

---

[1] GRENTHE et al. (1992) also selected values for the heat capacity and entropy of $\alpha\text{-}U_3O_7(cr) \equiv 3 \cdot \alpha\text{-}UO_{2.3333}(cr)$, but none for the enthalpy of formation.

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.

4.3 Uranium hydrides

β-UH_3(cr) is not relevant under environmental conditions, this phase is not included in the database.

5 Halogen compounds and complexes

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

$$UO_2^{2+} + F^- \Leftrightarrow UO_2F^+$$

$$\log_{10}\beta_1^\circ(n = 1, 298.15\ K) = 5.16 \pm 0.06$$

$$UO_2^{2+} + 2\ F^- \Leftrightarrow UO_2F_2(aq)$$

$$\log_{10}\beta_2°(n = 2, 298.15\ K) = 8.83 \pm 0.08$$

$$UO_2^{2+} + 3\ F^- \Leftrightarrow UO_2F_3^-$$

$$\log_{10}\beta_3°(n = 3, 298.15\ K) = 10.90 \pm 0.10$$

$$UO_2^{2+} + 4\ F^- \Leftrightarrow UO_2F_4^{-2}$$

$$\log_{10}\beta_4°(n = 4, 298.15\ K) = 11.84 \pm 0.11$$

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 $(0.04 \pm 0.07)\ kg \cdot mol^{-1}$ 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 $(0.04 \pm 0.07)\ kg \cdot mol^{-1}$ for $\varepsilon(UO_2F^+, Cl^-)$ appears nowhere else in GRENTHE et al. (1992), while on p.639, they make use of the estimate $\varepsilon(UO_2F^+, Cl^-) \approx \varepsilon(UO_2F^+, ClO_4^-) = (0.29 \pm 0.05)\ kg \cdot mol^{-1}$. 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

$$\varepsilon(UO_2F^+, Cl^-) = (0.05 \pm 0.10)\ kg \cdot mol^{-1}$$

according to Hummel (2009), 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.

$$\Delta_r H_m°(n = 1, 298.15\ K) = (1.70 \pm 0.08)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m°(n = 2, 298.15\ K) = (2.10 \pm 0.19)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m°(n = 3, 298.15\ K) = (2.35 \pm 0.31)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m°(n = 4, 298.15\ K) = (0.29 \pm 0.47)\ kJ \cdot mol^{-1}$$

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 $\log_{10}{}^*\beta_n°$ 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: $\Delta\varepsilon = -(0.14 \pm 0.05)\ kg \cdot mol^{-1}$ 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 $\varepsilon(U^{4+}, ClO_4^-) = (0.76 \pm 0.06)\ kg \cdot mol^{-1}$ and $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)\ kg \cdot mol^{-1}$ one then obtains

$$\varepsilon(UF^{3+}, ClO_4^-) = (0.48 \pm 0.08)\ kg \cdot mol^{-1}$$

The ion interaction coefficients for UF_2^{2+} and UF_3^+ were directly estimated according to

$$\varepsilon(UF_2^{2+}, Cl^-)^{2} \approx \varepsilon(M^{2+}, ClO_4^-) = (0.3 \pm 0.1)\ kg \cdot mol^{-1}$$

$$\varepsilon(UF_3^+, Cl^-) \approx \varepsilon(M^+, ClO_4^-) = (0.1 \pm 0.1)\ kg \cdot mol^{-1}$$

(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 selected $\varepsilon(U^{4+},$

---

2 Note that $\varepsilon(UF_2^{2+}, Cl^-) = (0.3 \pm 0.1)\ kg \cdot mol^{-1}$ 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).

ClO_4^-) and $\varepsilon(H^+, ClO_4^-)$ for the calculation of the corresponding $\Delta\varepsilon$. After the extrapolation to zero ionic strength, the resulting values of $\log_{10}{}^*\beta_n^\circ$ were converted to $\log_{10}\beta_n^\circ$ for the reaction

$$U^{4+} + n\ F^- \Leftrightarrow UF_n^{(4-n)}$$

by adding the selected $\log_{10}\beta^\circ = 3.18 \pm 0.02$ for $H^+ + F^- \Leftrightarrow HF(aq)$.

In this way, GUILLAUMONT et al. (2003) obtained the following recommended equilibrium constants:

$$U^{4+} + F^- \Leftrightarrow UF^{3+}$$

$$\log_{10}\beta_1^\circ(n = 1, 298.15\ K) = 9.42 \pm 0.51$$

$$U^{4+} + 2\ F^- \Leftrightarrow UF_2^{2+}$$

$$\log_{10}\beta_2^\circ(n = 2, 298.15\ K) = 16.56 \pm 0.71$$

$$U^{4+} + 3\ F^- \Leftrightarrow UF_3^+$$

$$\log_{10}\beta_3^\circ(n = 3, 298.15\ K) = 21.89 \pm 0.83$$

$$U^{4+} + 4\ F^- \Leftrightarrow UF_4(aq)$$

$$\log_{10}\beta_4^\circ(n = 4, 298.15\ K) = 26.34 \pm 0.96$$

These constants and the ion interaction coefficients mentioned above are included in our database, as well as

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

estimated according to HUMMEL (2009).

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 5.2. Following GRENTHE et al. (1992), the solubility product $\log_{10}K_{s,0}^\circ = -30.12 \pm 0.70$ derived from this study was used by GUILLAUMONT et al. (2003) for the evaluation of $\log_{10}\beta_5^\circ$ and $\log_{10}\beta_6^\circ$ 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 $\Delta_f G_m^\circ(UF_4 \cdot 2.5H_2O, cr, 298.15\ K)$ recommended by GRENTHE et al. (1992) and GUILLAUMONT et al. (2003), which is based on thermochemical data (see Section 5.2). For the formation of UF_5^- and UF_6^{2-}, GUILLAUMONT et al. (2003) selected

$$U^{4+} + 5\ F^- \Leftrightarrow UF_5^-$$

$$\log_{10}\beta_5^\circ(n = 5, 298.15\ K) = 27.73 \pm 0.74$$

$$U^{4+} + 6\ F^- \Leftrightarrow UF_6^{2-}$$

$$\log_{10}\beta_6^\circ(n = 6, 298.15\ K) = 29.80 \pm 0.70$$

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

$$\varepsilon(UF_5^-, Na^+) = -(0.05 \pm 0.10)\ kg \cdot mol^{-1}$$

$$\varepsilon(UF_6^{2-}, Na^+) = -(0.10 \pm 0.10)\ kg \cdot mol^{-1}$$

according to HUMMEL (2009).

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.

$$\Delta_r H_m°(n = 1, 298.15\ K) = -(5.6 \pm 0.5)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m°(n = 2, 298.15\ K) = -(3.5 \pm 0.6)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m°(n = 3, 298.15\ K) = (0.5 \pm 4.0)\ kJ \cdot mol^{-1}$$

No enthalpy of reaction is reported for $UF_4(aq)$. GRENTHE et al. (1992) therefore estimated an entropy of reaction based on experimental data

$$\Delta_r S_m°(n = 4, 298.15\ K) = (476 \pm 17)\ J \cdot K^{-1} \cdot mol^{-1}$$

GRENTHE et al. (1992) concluded that the enthalpies of reaction in the U^{4+}-F^- system are small, hence the corresponding equilibria are not 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

$$UO_2^{2+} + Cl^- \Leftrightarrow UO_2Cl^+$$

$$\log_{10}\beta_1°(n = 1, 298.15\ K) = 0.17 \pm 0.02$$

with $\Delta\varepsilon = -(0.25 \pm 0.02)\ kg \cdot mol^{-1}$ and

$$UO_2^{2+} + 2\ Cl^- \Leftrightarrow UO_2Cl_2(aq)$$

$$\log_{10}\beta_2°(n = 2, 298.15\ K) = -1.1 \pm 0.4$$

with $\Delta\varepsilon = -(0.25 \pm 0.02)$ 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

$$\varepsilon(UO_2Cl^+, ClO_4^-) = (0.33 \pm 0.04)\ kg \cdot mol^{-1}$$

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

$$\varepsilon(UO_2Cl^+, Cl^-) = \varepsilon(UO_2Cl^+, ClO_4^-) = (0.33 \pm 0.04)\ kg \cdot mol^{-1}$$

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.

$$\Delta_r H_m°(n = 1, 298.15\ K) = (8 \pm 2)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m°(n = 2, 298.15\ K) = (15 \pm 6)\ kJ \cdot mol^{-1}$$

U(V) chlorides: No aqueous species of the form $UO_2Cl_n^{(1-n)}$ have been identified.

U(IV) chlorides: There are fairly few studies of chloride complexes of U(IV). For UCl^{3+}, GRENTHE et al. (1992) recommended

$$U^{4+} + Cl^- \Leftrightarrow UCl^{3+}$$

$$\log_{10}\beta_1°(298.15\ K) = 1.72 \pm 0.13^{3}$$

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

$$\varepsilon(UCl^{3+}, ClO_4^-) = (0.59 \pm 0.10)\ kg \cdot mol^{-1}$$

---

[3] 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.

GUILLAUMONT et al. (2003) claimed that this value is erroneous and replaced it with (0.50 ± 0.10) kg · mol^{-1}. Apparently, they used ε(Cl$^-$, Na$^+$) instead of ε(Cl$^-$, H$^+$) in deriving ε(UCl^{3+}, ClO$_4^-$) from Δε. 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 ε(Cl$^-$, H$^+$) than ε(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 ε(UCl^{3+}, Cl$^-$) should only be used in combination with ε(U^{4+}, Cl$^-$) = ε(U^{4+}, ClO$_4^-$) = (0.76 ± 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$_2$ClO$_3^+$ 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 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$_2$Br$^+$, UBr^{3+}, and UO$_2$BrO$_3^+$. 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:

$$U^{4+} + I^- \Leftrightarrow UI^{3+}$$

$$\log_{10}\beta_1°(298.15\ K) = 1.25 \pm 0.30$$

$$UO_2^{2+} + IO_3^- \Leftrightarrow UO_2IO_3^+$$

$$\log_{10}\beta_1°(298.15\ K) = 2.00 \pm 0.02$$

$$UO_2^{2+} + 2\ IO_3^- \Leftrightarrow UO_2(IO_3)_2(aq)$$

$$\log_{10}\beta_2°(298.15\ K) = 3.59 \pm 0.15$$

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

$$\varepsilon(UI^{3+}, ClO_4^-) = (0.55 \pm 0.10)\ kg \cdot mol^{-1}$$

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

$$\varepsilon(UO_2IO_3^+, ClO_4^-) \approx \varepsilon(UO_2Cl^+, ClO_4^-) = (0.33 \pm 0.04)\ kg \cdot mol^{-1}$$

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.

Following HUMMEL (2009), we estimated for chloride media

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

$$\varepsilon(UO_2IO_3^+, Cl^-) = (0.05 \pm 0.10)\ kg \cdot mol^{-1}$$

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.

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 $\log_{10}K°_{s,n}$ for n = 2 - 6. Following GRENTHE et al. (1992), GUILLAUMONT et al. (2003) used the selected values for $\log_{10}\beta_2°$, $\log_{10}\beta_3°$, and $\log_{10}\beta_4°$ with $\log_{10}K°_{s,2}$, $\log_{10}K°_{s,3}$, and $\log_{10}K°_{s,4}$, 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

$$\log_{10}K_{s,0}° = -30.12 \pm 0.70$$

and used this value to derive $\log_{10}\beta_5°$ and $\log_{10}\beta_6°$ for UF_5^- and UF_6^{2-} from $\log_{10}K°_{s,5}$, and $\log_{10}K°_{s,6}$ (see Section 5.1). The selected solubility product differs by 3 orders of magnitude from the value of -33.5 ± 1.2 which can be calculated from $\Delta_f G_m°(UF_4{\cdot}2.5H_2O, cr, 298.15\ K)$ that was 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):
$\Delta_f H_m°(UF_4{\cdot}2.5H_2O, cr, 298.15\ K) = -(2671.5 \pm 4.3)\ kJ \cdot mol^{-1}$
The entropy and the heat capacity as estimated by GRENTHE et al. (1992) are:

$$S_m°(UF_4{\cdot}2.5H_2O, cr, 298.15\ K) = (263.5 \pm 15.0)\ J \cdot K^{-1} \cdot mol^{-1}$$

$$C_{p,m}°(UF_4{\cdot}2.5H_2O, cr, 298.15\ K) = (263.7 \pm 15.0)\ J \cdot K^{-1} \cdot mol^{-1}$$

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, $\Delta_f H_m^\circ$ 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.

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.

6 Chalcogen compounds and complexes

6.1 Sulphur compounds and complexes

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.

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.

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} [4], 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} [5], 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 $\log_{10}K^\circ = 1.98 \pm 0.05$ for $SO_4^{2-} + H^+ \Leftrightarrow HSO_4^-$. By taking the average of all accepted constants, GRENTHE et al. (1992) obtained the selected

$$UO_2^{2+} + SO_4^{2-} \Leftrightarrow UO_2SO_4(aq)$$

$$\log_{10}\beta_1^\circ(n = 1, 298.15\ K) = 3.15 \pm 0.02$$

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

$$UO_2^{2+} + 2\ SO_4^{2-} \Leftrightarrow UO_2(SO_4)_2^{2-}$$

$$\log_{10}\beta_2^\circ(n = 2, 298.15\ K) = 4.14 \pm 0.07$$

These values for $\log_{10}\beta_1^\circ$ and $\log_{10}\beta_2^\circ$ as well as the estimated

$$\varepsilon(UO_2(SO_4)_2^{2-}, Na^+) = -(0.12 \pm 0.06)\ kg \cdot mol^{-1}$$

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

$$UO_2^{2+} + 3\ SO_4^{2-} \Leftrightarrow UO_2(SO_4)_3^{4-}$$

$$\log_{10}\beta_3^\circ(n = 3, 298.15\ K) = 3.02 \pm 0.38$$

but retained $\log_{10}\beta_1^\circ$ and $\log_{10}\beta_2^\circ$ 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

---

[4] Incorrect value of $-(0.33 \pm 0.04)$ kg · mol^{-1} given on p. 244 in GRENTHE et al. (1992). The correct value is given on p. 558 and 638.

[5] Estimated according to $\varepsilon(HSO_4^-, H^+) \approx \varepsilon(HSO_4^-, Na^+) = -(0.01 \pm 0.02)$ kg · mol^{-1}

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,

$$\varepsilon(UO_2(SO_4)_3^{4-}, Na^+) \approx \varepsilon(P_2O_7^{4-}, Na^+) = -(0.26 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1}$$

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:

$$\Delta_r H_m°(n = 1, 298.15 \text{ K}) = (19.5 \pm 1.6) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m°(n = 2, 298.15 \text{ K}) = (35.1 \pm 1.0) \text{ kJ} \cdot \text{mol}^{-1}$$

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

$$\varepsilon(USO_4^{2+}, ClO_4^-) \approx \varepsilon(M^{2+}, ClO_4^-) = (0.3 \pm 0.1) \text{ kg} \cdot \text{mol}^{-1}$$

For chloride media, we estimated

$$\varepsilon(USO_4^{2+}, Cl^-) = (0.15 \pm 0.10) \text{ kg} \cdot \text{mol}^{-1}$$

according to HUMMEL (2009).

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

$$U^{4+} + SO_4^{2-} \Leftrightarrow USO_4^{2+}$$

$$\log_{10}\beta_1°(n = 1, 298.15 \text{ K}) = 6.58 \pm 0.19$$

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

$$\log_{10}\beta_2°(n = 2, 298.15 \text{ K}) = 10.51 \pm 0.20$$

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

$$U(OH)_2SO_4(cr) \Leftrightarrow U^{4+} + 2\ OH^- + SO_4^{2-}$$

$$\log_{10}K_{s,0}° = -31.17 \pm 0.50$$

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.

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.

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

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.

7 Group 15 compounds and complexes

7.1 Nitrogen compounds and complexes

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.

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.

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

$$UO_2^{2+} + NO_3^- \Leftrightarrow UO_2NO_3^+$$

$$\log_{10}\beta^\circ(298.15\ \mathrm{K}) = 0.30 \pm 0.15$$

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

$$\varepsilon(UO_2NO_3^+, ClO_4^-) \approx \varepsilon(UO_2Cl^+, ClO_4^-) = (0.33 \pm 0.04)\ \mathrm{kg \cdot mol^{-1}}$$

For chloride media, we estimated

$$\varepsilon(UO_2NO_3^+, Cl^-) = (0.05 \pm 0.10)\ \mathrm{kg \cdot mol^{-1}}$$

according to HUMMEL (2009).

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.

$$U^{4+} + NO_3^- \Leftrightarrow UNO_3^{3+}$$

$$\log_{10}\beta_1°(n = 1, 298.15\ K) = 1.47 \pm 0.13$$

$$U^{4+} + 2\ NO_3^- \Leftrightarrow U(NO_3)_2^{2+}$$

$$\log_{10}\beta_2°(n = 2, 298.15\ K) = 2.30 \pm 0.35$$

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

$$\varepsilon(UNO_3^{3+}, ClO_4^-) = (0.62 \pm 0.08)\ kg \cdot mol^{-1}$$

$$\varepsilon(U(NO_3)_2^{2+}, ClO_4^-) = (0.49 \pm 0.14)\ kg \cdot mol^{-1}$$

For chloride media, we estimated

$$\varepsilon(UNO_3^{3+}, Cl^-) = (0.25 \pm 0.10)\ kg \cdot mol^{-1}$$

$$\varepsilon(U(NO_3)_2^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg \cdot mol^{-1}$$

according to HUMMEL (2009).

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), $UO_2(NO_3)_2{\cdot}H_2O$(cr), $UO_2(NO_3)_2{\cdot}2H_2O$(cr), $UO_2(NO_3)_2{\cdot}3H_2O$(cr), and $UO_2(NO_3)_2{\cdot}6H_2O$(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 $UO_2(NO_3)_2{\cdot}6H_2O$(cr) it states “hygroscopic”. Hence, none of these highly soluble salts is included in our database.

7.2 Phosphorous compounds and complexes

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 $(UO_2)_3(PO_4)_2{\cdot}4H_2O$(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:

$$UO_2^{2+} + H_3PO_4(aq) \Leftrightarrow UO_2H_2PO_4^+ + H^+$$

$$\log_{10}\beta°(298.15\ K) = 1.12 \pm 0.06$$

$$UO_2^{2+} + H_3PO_4(aq) \Leftrightarrow UO_2H_3PO_4^{2+}$$

$$\log_{10}\beta°(298.15\ K) = 0.76 \pm 0.15$$

$$UO_2^{2+} + 2\ H_3PO_4(aq) \Leftrightarrow UO_2(H_2PO_4)_2(aq) + 2\ H^+$$

$$\log_{10}\beta°(298.15\ K) = 0.64 \pm 0.11$$

$$UO_2^{2+} + 2\ H_3PO_4(aq) \Leftrightarrow UO_2(H_2PO_4)(H_3PO_4)^+ + H^+$$

$$\log_{10}\beta°(298.15\ K) = 1.65 \pm 0.11$$

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 according to HUMMEL (2009).

$$\varepsilon(UO_2H_2PO_4^+, Cl^-) = (0.05 \pm 0.10)\ kg \cdot mol^{-1}$$

$$\varepsilon(UO_2H_2PO_4^+, ClO_4^-) = (0.2 \pm 0.1)\ kg \cdot mol^{-1}$$

$$\varepsilon(UO_2H_3PO_4^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg \cdot mol^{-1}$$

$$\varepsilon(UO_2H_3PO_4^{2+}, ClO_4^-) = (0.4 \pm 0.1)\ kg \cdot mol^{-1}$$

$$\varepsilon(UO_2H_2PO_4H_3PO_4^+, Cl^-) = (0.05 \pm 0.10)\ kg \cdot mol^{-1}$$

$$\varepsilon(UO_2H_2PO_4H_3PO_4^+, ClO_4^-) = (0.2 \pm 0.1)\ kg \cdot mol^{-1}$$

In neutral to basic solutions, a solubility study of $(UO_2)_3(PO_4)_2{\cdot}4H_2O$(cr) in the pH range between 6 and 9 has been published by SANDINO (1991). Equilibrium data were reported for the formation of UO_2HPO_4(aq), $UO_2PO_4^-$ and $UO_2(OH)_3^-$, in addition to the solubility product for the solid phase. The constant reported for $UO_2(OH)_3^-$ is consistent with the value selected in Section 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

$$UO_2^{2+} + PO_4^{3-} \Leftrightarrow UO_2PO_4^-$$

$$\log_{10}\beta_1°(298.15\ K) = 13.23 \pm 0.15$$

$$UO_2^{2+} + HPO_4^{2-} \Leftrightarrow UO_2HPO_4(aq)$$

$$\log_{10}\beta_1°(298.15\ K) = 7.24 \pm 0.26$$

but increased the uncertainties from two to three standard deviations. SANDINO (1991) used the estimate

$$\varepsilon(UO_2PO_4^-, Na^+) \approx \varepsilon(UO_2(OH)_3^-, Na^+) = -(0.09 \pm 0.05)\ kg \cdot mol^{-1}$$

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:

$$UO_2HPO_4 \cdot 4H_2O(cr) + 2\ H^+ \Leftrightarrow UO_2^{2+} + H_3PO_4(aq) + 4\ H_2O(l)$$

$$\log_{10}{}^*K_{s,0}°(298.15\ K) = -2.50 \pm 0.09$$

$$(UO_2)_3(PO_4)_2 \cdot 4H_2O(cr) + 6\ H^+ \Leftrightarrow 3\ UO_2^{2+} + 2\ H_3PO_4(aq) + 4\ H_2O(l)$$

$$\log_{10}{}^*K_{s,0}°(298.15\ K) = -5.96 \pm 0.30$$

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: $H_2(UO_2)_2(PO_4)_2 \cdot x\ H_2O(cr)$ (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:

$$U(HPO_4)_2 \cdot 4H_2O(cr) + 4\ H^+ \Leftrightarrow U^{4+} + 2\ H_3PO_4(aq) + 4\ H_2O(l)$$

$$\log_{10}{}^*K_{s,0}^\circ(298.15\ K) = -11.79 \pm 0.15$$

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.

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 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 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 7.2.1.

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 $NaClO_4$:

$$UO_2^{2+} + HAsO_4^{2-} \Leftrightarrow UO_2HAsO_4(aq)$$

$$\log_{10}K°(298.15\ K) = 7.16 \pm 0.37$$

$$UO_2^{2+} + H_3AsO_4(aq) \Leftrightarrow UO_2H_2AsO_4^+ + H^+$$

$$\log_{10}{}^*K°(298.15\ K) = 1.34 \pm 0.42$$

$$UO_2^{2+} + 2\ H_3AsO_4(aq) \Leftrightarrow UO_2(H_2AsO_4)_2(aq) + 2\ H^+$$

$$\log_{10}K°(298.15\ K) = 0.29 \pm 0.53$$

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 proposed by Hummel (2009) to estimate

$$\varepsilon(UO_2H_2AsO_4^+, Cl^-) = (0.05 \pm 0.10)\ kg \cdot mol^{-1}$$

$$\varepsilon(UO_2H_2AsO_4^+, ClO_4^-) = (0.2 \pm 0.1)\ kg \cdot mol^{-1}$$

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.

8 Group 14 compounds and complexes

8.1 Carbon compounds and complexes

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.

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

$$\varepsilon(CO_3^{2-}, Na^+) = -(0.08 \pm 0.03)\ kg \cdot mol^{-1}$$

$$\varepsilon(HCO_3^-, Na^+) = (0.00 \pm 0.02)\ kg \cdot mol^{-1}$$

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: $\varepsilon(U(CO_3)_5^{6-}, Na^+)$, $\varepsilon(UO_2(CO_3)_3^{5-}, Na^+)$, $\varepsilon(UO_2(CO_3)_2^{2-}, Na^+)$, $\varepsilon(UO_2(CO_3)_3^{4-}, Na^+)$, and $\varepsilon((UO_2)_3(CO_3)_6^{6-}, Na^+)$. 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

$$UO_2^{2+} + n\ CO_3^{2-} \Leftrightarrow UO_2(CO_3)_n^{(2-2n)}$$

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 evaluated the following values using linear SIT regressions for all three complexes

$$UO_2^{2+} + CO_3^{2-} \Leftrightarrow UO_2CO_3(aq)$$

$$\log_{10}\beta_1°(n = 1, 298.15\ K) = 9.94 \pm 0.03$$

$$UO_2^{2+} + 2\ CO_3^{2-} \Leftrightarrow UO_2(CO_3)_2^{2-}$$

$$\log_{10}\beta_2°(n = 2, 298.15\ K) = 16.61 \pm 0.09$$

$$UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow UO_2(CO_3)_3^{4-}$$

$$\log_{10}\beta_3°(n = 3, 298.15\ K) = 21.84 \pm 0.04$$

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 $\Delta\varepsilon$ for the various reactions are in fair agreement with the tabulated values for the individual reactants/products as seen above[6]. 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 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:

---

[6] 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 $\Delta\varepsilon(n = 1) = -(0.38 \pm 0.06)\ kg \cdot mol^{-1}$, $\Delta\varepsilon(n = 2) = -(0.32 \pm 0.15)\ kg \cdot mol^{-1}$, and $\Delta\varepsilon(n = 3) = -(0.24 \pm 0.18)\ kg \cdot mol^{-1}$.

$$\Delta_r H_m°(n = 1, 298.15\ K) = (5 \pm 2)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m°(n = 2, 298.15\ K) = (18.5 \pm 4.0)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m°(n = 3, 298.15\ K) = -(39.2 \pm 4.1)\ kJ \cdot mol^{-1}$$

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

$$\varepsilon((UO_2)_3O(OH)_2HCO_3^+, Cl^-) = (0.05 \pm 0.10) \text{ kg} \cdot \text{mol}^{-1}$$

according to HUMMEL (2009). Both estimates are included in our database.

Using the carbonate equilibrium constants[7] 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

$$3\ UO_2^{2+} + CO_3^{2-} + 3\ H_2O(l) \Leftrightarrow (UO_2)_3O(OH)_2(HCO_3)^+ + 3\ H^+$$

$$\log_{10}{}^*K^\circ(298.15\ K) = 0.66 \pm 0.50$$

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

$$\log_{10}{}^*K^\circ(298.15\ K) = -19.01 \pm 0.50$$

which they extrapolated to I = 0 from the experimental value for 0.5 m $NaClO_4$ using the estimate

$$\varepsilon((UO_2)_2CO_3(OH)_3^-, Na^+) = (0.00 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1}$$

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

$$2\ UO_2^{2+} + CO_3^{2-} + 3\ H_2O(l) \Leftrightarrow (UO_2)_2CO_3(OH)_3^- + 3\ H^+$$

$$\log_{10}{}^*K^\circ(298.15\ K) = -0.86 \pm 0.50$$

in our database, together with the estimated ion interaction coefficient.

---

[7] $\log_{10}{}^*K^\circ(HCO_3^- + H^+ \Leftrightarrow CO_2(g) + H_2O(l), 298.15\ K) = 7.82$
$\log_{10}{}^*K^\circ(CO_3^{2-} + H^+ \Leftrightarrow HCO_3^-, 298.15\ K) = 10.329$

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

$$UO_2^{2+} + p\ CO_3^{2-} + q\ F^- \Leftrightarrow UO_2(CO_3)_pF_q^{(2-2p-q)}$$

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

$$UO_2^{2+} + CO_3^{2-} + F^- \Leftrightarrow UO_2CO_3F^-$$

$$\log_{10}\beta^\circ_{1,1,1}\ (p = 1, q = 1, 298.15\ K) = \ 13.75 \pm 0.09$$

$$UO_2^{2+} + CO_3^{2-} + 2\ F^- \Leftrightarrow UO_2CO_3F_2^{2-}$$

$$\log_{10}\beta^\circ_{1,1,2}\ (p = 1, q = 2, 298.15\ K) = \ 15.57 \pm 0.14$$

$$UO_2^{2+} + CO_3^{2-} + 3\ F^- \Leftrightarrow UO_2CO_3F_3^{3-}$$

$$\log_{10}\beta^\circ_{1,1,3}\ (p = 1, q = 3, 298.15\ K) = \ 16.38 \pm 0.11$$

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

$$\varepsilon(UO_2CO_3F^-, Na^+) = (0.00 \pm 0.05)\ kg \cdot mol^{-1}$$

$$\varepsilon(UO_2CO_3F_2^{2-}, Na^+) = -(0.02 \pm 0.09)\ kg \cdot mol^{-1}$$

$$\varepsilon(UO_2CO_3F_3^{3-}, Na^+) = -(0.25 \pm 0.05)\ kg \cdot mol^{-1}$$

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 K, I = 0.1 M) = 5.0 ± 0.7 for the reaction 2 Ca^{2+} + $UO_2(CO_3)_3^{4-}$ ⇔ $Ca_2UO_2(CO_3)_3(aq)$. With $\log_{10}\beta_3$(298.15 K, I = 0.1 M) = 21.8 ± 1 for $UO_2(CO_3)_3^{4-}$ this corresponds to $\log_{10}\beta_{2,1,3}$(298.15 K I = 0.1 M) = 26.8 ± 0.7 for the reaction 2 Ca^{2+} + UO_2^{2+} + 3 CO_3^{2-} ⇔ $Ca_2UO_2(CO_3)_3(aq)$.

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. Data of log$R$ plotted as a function of log[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.

Table 1.1: 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

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 $\log_{10}\beta^\circ_{2,1,3}(298.15\ K) = 29.8 \pm 0.7$[8] 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 · 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 · 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 · 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 $\log_{10}\beta^\circ_{1,1,3}(298.15\ K) = 26.11 \pm 0.04$, 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 $\log_{10}\beta^\circ_{2,1,3}(298.15\ K) = 30.7 \pm 0.05$ 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 no evidence for the formation of $Mg_2UO_2(CO)_3(aq)$. For $MgUO_2(CO)_3^{2-}$, DONG & BROOKS (2008) obtained $\log_{10}\beta^\circ_{1,1,3}(298.15\ K) = 25.8 \pm 0.5$ if the Davies equation was used, and $\log_{10}\beta^\circ_{1,1,3}(298.15\ K) = 25.02 \pm 0.06$ if SIT was used.

---

[8] Value given by KALMYKOW & CHOPPIN (2000) in the abstract. In the text the uncertainty is given as ± 0.6.

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 $\log_{10}\beta^\circ_{1,1,3}(298.15\ K) = 26.24 \pm 0.13$, 26.07 ± 0.13, and 26.16 ± 0.32 for Mg, Sr, and Ba, resp., and in $\log_{10}\beta^\circ_{2,1,3}(298.15\ K) = 29.73 \pm 0.47$ 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 $\log_{10}\beta^\circ_{1,1,3}(298.15\ K) = 27.27 \pm 0.14$ and $\log_{10}\beta^\circ_{2,1,3}(298.15\ K) = 29.81 \pm 0.19$.

As an interesting aside, the formation of ternary Ca-UO_2-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-UO_2-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-UO_2-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)

$$2\ Ca^{2+} + UO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow Ca_2UO_2(CO)_3(aq)$$

$$\log_{10}\beta^\circ_{2,1,3}(298.15\ K) = 29.22 \pm 0.25$$

It was only during the preparation of this documentation of our database that we noticed that the actual value for $\log_{10}\beta^\circ_{2,1,3}$ 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

$$\varepsilon(MgUO_2(CO_3)_3^{2-}, Na^+) = -(0.10 \pm 0.10)\ kg \cdot mol^{-1}$$

$$\varepsilon(CaUO_2(CO_3)_3^{2-}, Na^+) = -(0.10 \pm 0.10)\ kg \cdot mol^{-1}$$

$$\varepsilon(SrUO_2(CO_3)_3^{2-}, Na^+) = -(0.10 \pm 0.10)\ kg \cdot mol^{-1}$$

$$\varepsilon(BaUO_2(CO_3)_3^{2-}, Na^+) = -(0.10 \pm 0.10)\ kg \cdot mol^{-1}$$

according to HUMMEL (2009).

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 ± 10) mV/SHE, corresponding to $\log_{10}K°$(298.15 K) = -13.17 ± 0.17, and $\Delta\varepsilon$ = -(0.91 ± 0.10) kg · mol^{-1}[9]. Combining this $\log_{10}K°$ with $\log_{10}K°$(298.15 K) = -1.484 ± 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 ± 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

$$UO_2^+ + 3\ CO_3^{2-} \Leftrightarrow UO_2(CO_3)_3^{5-}$$

$$\log_{10}\beta_3°(298.15\ K) = 6.95 \pm 0.36$$

which is also included in our database[10].

From $\Delta\varepsilon$ = -(0.91 ± 0.20) kg · mol^{-1}, the value reported by CAPDEVILA & VITORGE (1999) 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 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).

---

[9] GUILLAUMONT et al. (2003) reported this value as -(0.97 ± 0.20) kg · mol^{-1}. 0.97 instead of 0.91 is most likely a typographical error, while the uncertainty was probably doubled on purpose.

[10] Note added in proof: Unfortunately, GUILLAUMONT et al. (2003) and also we overlooked that this value is based on $\log_{10}\beta_3°(UO_2(CO_3)_3^{4-}, 298.15\ K) = 21.60 \pm 0.05$ by GRENTHE et al. (1992), a value that GUILLAUMONT et al. (2003) themselves replaced in their update with 21.84 ± 0.04. For this reason, $\log_{10}\beta_3°(UO_2(CO_3)_3^{5-}, 298.15\ K)$ should be replaced by the recalculated $\log_{10}\beta_3°(298.15\ K) = 7.19 \pm 0.36$.

$UO_2(CO_3)_3^{5-}$ 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 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 $\log_{10}\beta_5°(298.15\ K) = 34.0 \pm 0.9$. 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), $\log_{10}\beta_5°(298.15\ K) = 34.1 \pm 1.0$, supposedly based on GRENTHE et al. (1992), corresponds to neither of these (but is only slightly different). This error was not recognized during our update procedure and the incorrect value was retained. It will be corrected in the next update.

The enthalpy of the formation reaction of $U(CO_3)_5^{6-}$ has been determined experimentally as

$$\Delta_r H_m°(298.15\ K) = -(20 \pm 4)\ kJ \cdot mol^{-1}$$

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 $\varepsilon(CO_3^{2-}, Na^+) = -(0.08 \pm 0.03)$[11] $kg \cdot mol^{-1}$ 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

$$U^{4+} + CO_3^{2-} + 3\ H_2O(l) \Leftrightarrow UCO_3(OH)_3^- + 3\ H^+$$

---

[11] 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).

$$log_{10}{}^{*}K^{\circ}(298.15\ K) = 4$$

This value is included in our database as supplemental data as well as

$$\varepsilon(UCO_3(OH)_3^-, Na^+) = -(0.05 \pm 0.10)\ kg \cdot mol^{-1}$$

estimated according to HUMMEL (2009).

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 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:

$$\log_{10}K_{s,0}^{\circ}(298.15\ K) = -14.76 \pm 0.02$$

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):

$$S_m^{\circ}(UO_2(CO_3), cr, 298.15\ K) = (144.2 \pm 0.3)\ J \cdot K^{-1} \cdot mol^{-1}$$

$$C_{p,m}^{\circ}(UO_2(CO_3), cr, 298.15\ K) = (120.1 \pm 0.1)\ J \cdot K^{-1} \cdot mol^{-1}$$

Other uranium carbonates: Thermodynamic data exist for $Na_4UO_2(CO_3)_3$(cr), and for the minerals $Ca_2UO_2(CO_3)_3 \cdot 10H_2O$(cr) (liebigite), $CaMgUO_2(CO_3)_3 \cdot 12H_2O$(cr) (swartzite), $Mg_2UO_2(CO_3)_3 \cdot 10H_2O$(cr) (bayleyite), $CaNa_2UO_2(CO_3)_3 \cdot 6H_2O$(cr) (andersonite) (GRENTHE et al. 1992), $Ca_3NaUO_2(CO_3)_3FSO_4 \cdot 10H_2O$(cr) (schröckingerite) and $K_3NaUO_2(CO_3)_3 \cdot H_2O$(cr) (grimselite) (GRENTHE et al. 1995).

The solubility product of $Na_4UO_2(CO_3)_3$(cr) was measured at different ionic strengths and in different media. GRENTHE et al. (1992) used six values reported for $NaClO_4$ media up to I = 3 M for the reaction

$$Na_4UO_2(CO_3)_3(cr) \Leftrightarrow 4\ Na^+ + UO_2(CO_3)_3^{4-}$$

to make an extrapolation to I = 0. The resulting selected solubility constant is (GRENTHE et al. 1992)

$$\log_{10}K_{s,3}°(298.15\ K) = -5.34 \pm 0.16$$

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, $UO_3{\cdot}2H_2O$(s), and rutherfordine, $UO_2(CO_3)$(cr). As a consequence, $Na_4UO_2(CO_3)_3$(cr), is not known as 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.

8.1.3 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 gave details of the procedure only for perchlorate media. For UO_2SCN^+, they adopted $\Delta\varepsilon(n = 1) = -(0.25 \pm 0.02)$ kg · 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 · mol^{-1} and $\varepsilon(SCN^-, Na^+) = (0.05 \pm 0.01)$ kg · mol^{-1} one obtains

$$\varepsilon(UO_2SCN^+, ClO_4^-) = (0.26 \pm 0.04) \text{ kg} \cdot \text{mol}^{-1}$$

which is included in our database. The value (0.22 ± 0.04) kg · mol^{-1} selected by GRENTHE et al. (1992) is obviously incorrect. For chloride media, we estimated

$$\varepsilon(UO_2SCN^+, Cl^-) = (0.05 \pm 0.10) \text{ kg} \cdot \text{mol}^{-1}$$

according to HUMMEL (2009). 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

$$\varepsilon(UO_2(SCN)_3^-, Na^+) \approx \varepsilon(UO_2F_3^-, Na^+) = (0.00 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1}$$

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

$$\Delta_r H_m°(n = 1, 298.15 \text{ K}) = (3.22 \pm 0.06) \text{ kJ·mol}^{-1}$$

$$\Delta_r H_m°(n = 2, 298.15 \text{ K}) = (8.9 \pm 0.6) \text{ kJ·mol}^{-1}$$

$$\Delta_r H_m°(n = 3, 298.15 \text{ K}) = (6.0 \pm 1.2) \text{ kJ·mol}^{-1}$$

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 $\log_{10}\beta_1°(298.15\ K) = 2.97 \pm 0.06$ from $\log_{10}\beta_1(298.15\ K) = 1.49 \pm 0.03$ by AHRLAND & LARSSON (1954) and $\log_{10}\beta_1°(298.15\ K) = 2.97 \pm 0.21$ from $\log_{10}\beta_1(298.15\ K) = 1.49 \pm 0.20$ by DAY et al. (1955) and selected $\log_{10}\beta_1°(298.15\ K) = 2.97 \pm 0.06$. Unfortunately, the value of $-(0.13 \pm 0.05)$ 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 $-(0.29 \pm 0.08)$ kg · mol^{-1}. We recalculated the conditional stability constants with this value and obtained $\log_{10}\beta_1°(298.15\ K) = 2.83 \pm 0.09$ from the data by AHRLAND & LARSSON (1954) and $\log_{10}\beta_1°(298.15\ K) = 2.83 \pm 0.22$ from the data by DAY et al. (1955) and selected the mean

$$U^{4+} + SCN^- \Leftrightarrow USCN^{3+}$$

$$\log_{10}\beta_1°(298.15\ K) = 2.83 \pm 0.15$$

for our database[12]. 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

$$\varepsilon(USCN^{3+}, ClO_4^-) = (0.52 \pm 0.10) \text{ kg} \cdot \text{mol}^{-1}$$

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

$$U^{4+} + 2\ SCN^- \Leftrightarrow U(SCN)_2^{2+}$$

$$\log_{10}\beta_2°(298.15\ K) = 4.26 \pm 0.18$$

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

$$\varepsilon(U(SCN)_2^{2+}, ClO_4^-) \approx \varepsilon(UF_2^{2+}, ClO_4^-) = (0.3 \pm 0.1) \text{ kg} \cdot \text{mol}^{-1}$$

These data for $U(SCN)_2^{2+}$ are included in our database, as well as

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

---

[12] Note that the electronic versions of the PSI/Nagra TDB 12/07 contain the incorrect value $\log_{10}\beta_1°(298.15\ K) = 2.97 \pm 0.06$ selected by GRENTHE et al. (1992).

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

estimated according to HUMMEL (2009).

The reaction enthalpies

$$\Delta_r H_m°(n=1, 298.15\ K) = -(27 \pm 8)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m°(n=2, 298.15\ K) = -(18 \pm 4)\ kJ \cdot mol^{-1}$$

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.

8.2 Silicon compounds and complexes

Uranium silicon compounds and complexes will be discussed in a separate report on silica and silicates.

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[13] and alkaline-earth[14] 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 4.1.3) and the mixed valence oxides (see Section 4.2.2). Hence, the mentioned alkali and alkaline-earth uranates are presently not included in our database.

---

[13] $Li_{0.12}UO_{2.95}$(cr), γ-$Li_{0.55}UO_3$, δ-$Li_{0.69}UO_3$, $LiUO_3$(cr), Li_2UO_4(cr), Li_4UO_5(cr), $Li_2U_2O_7$(cr), $Li_{0.19}U_3O_8$(cr), $Li_{0.88}U_3O_8$(cr), $Li_2U_3O_{10}$(cr), $Na_{0.12}UO_{2.95}$(cr), α-$Na_{0.14}UO_3$, δ-$Na_{0.54}UO_3$, $NaUO_3$(cr), α-Na_2UO_4, β-Na_2UO_4, Na_3UO_4(cr), Na_4UO_5(cr), $Na_2U_2O_7$(cr), $Na_{0.20}U_3O_8$(cr), $Na_6U_7O_{24}$(cr), $Na_4UO_2(CO_3)_3$(cr), KUO_3(cr), K_2UO_4(cr), $K_2U_2O_7$(cr), $K_2U_4O_{13}$(cr), $RbUO_3$(cr), Rb_2UO_4(cr), $Rb_2U_2O_7$(cr), $Rb_2U_4O_{11}$(cr), $Rb_2U_4O_{13}$(cr), $Rb_2U(SO_4)_3$(cr), Cs_2UO_4(cr), $Cs_2U_2O_7$(cr), $Cs_2U_4O_{12}$(cr), $Cs_4U_5O_{17}$(cr)

[14] $Be_{13}U$(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)

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 $\log_{10}{}^*K_{s,0}^\circ = 39.5 \pm 1.0$. The authors of the latter study extrapolated their data using the Pitzer approach and obtained $\log_{10}{}^*K_{s,0}^\circ = 41.4 \pm 0.2$, for which GUILLAUMONT et al. (2003) increased the uncertainty to ± 1.2. They selected the mean of both solubility products

$$CaU_6O_{19} \cdot 11\ H_2O(cr) + 14\ H^+ \Leftrightarrow Ca^{2+} + 6\ UO_2^{2+} + 18\ H_2O(l)$$

$$\log_{10}{}^*K_{s,0}^\circ(298.15\ K) = 40.5 \pm 1.6$$

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

$$K_2U_6O_{19} \cdot 11\ H_2O(cr) + 14H^+ \Leftrightarrow 2K^+ + 6\ UO_2^{2+} + 18\ H_2O(l)$$

$$\log_{10}{}^*K_{s,0}^\circ(298.15\ K) = 37.1 \pm 0.5$$

Both becquerelite and compreignacite are included in our database.

GUILLAUMONT et al. (2003) also reported the results of solubility measurements for $Na_2U_2O_7 \cdot x\ H_2O$(cr) and $Na_2U_6O_{19} \cdot 12\ H_2O$(cr) but did not select their solubility products.

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 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 HUMMEL 2014). 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 1.2: 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	$UO_2(cr)^{a}$, β-$UO_{2.25}(cr)^{a}$, $UO_{2.25}(cr)^{a}$, α-$UO_{2.3333}(cr)^{b}$, β-$UO_{2.3333}(cr)^{a}$, $UO_{2.6667}(cr)^{ad}$, $UO_{2.86} \cdot 0.5H_2O(cr)^{b}$, $UO_{2.86} \cdot 1.5H_2O(cr)^{b}$, α-$UO_{2.95}(cr)^{bd}$, α-$UO_3(cr)^{a}$, β-$UO_3(cr)^{a}$, γ-$UO_3(cr)^{ad}$, δ-$UO_3(cr)^{bd}$, ε-$UO_3(cr)^{b}$, β-$UH_3(cr)^{a}$, $UO_3 \cdot 0.393H_2O(cr)^{b}$, $UO_3 \cdot 0.648H_2O(cr)^{b}$, α-$UO_3 \cdot 0.85H_2O\ (cr)^{b}$, α-$UO_3 \cdot 0.9H_2O\ (cr)^{a}$, δ-$UO_3H_{0.83}(cr)^{bd}$, β-$UO_2(OH)_2{}^{a}$, γ-$UO_2(OH)_2{}^{b}$, $UO_4 \cdot 2H_2O(cr)^{b}$, $UO_4 \cdot 4H_2O(cr)^{b}$, $UF_3(cr)^{a}$, $UF_4(cr)^{ad}$, α-$UF_5(cr)^{a}$, β-$UF_5(cr)^{a}$, $UF_6(cr)^{ad}$, $U_2F_9(cr)^{a}$, $U_4F_{17}(cr)^{a}$, $UOF_2(cr)^{a}$, $UOF_4(cr)^{a\,d}$, $UO_2F_2(cr)^{ad}$, $U_2O_3F_6(cr)^{ad}$, $U_3O_5F_8(cr)^{ad}$, $H_3OUF_6(cr)^{bd}$, $UOFOH(cr)^{a}$, $UOFOH \cdot 0.5H_2O(cr)^{a}$, $UOF_2 \cdot H_2O(cr)^{a}$, $UF_4 \cdot 2.5H_2O(cr)^{a}$, $UO_2FOH \cdot H_2O(cr)^{ac}$, $UO_2FOH \cdot 2H_2O(cr)^{ac}$, $UO_2F_2 \cdot 3H_2O(cr)^{ad}$, $UCl_3(cr)^{a}$, $UCl_4(cr)^{ad}$, $UCl_5(cr)^{a}$, $UCl_6(cr)^{ad}$, $UOCl(cr)^{a}$, $UOCl_2(cr)^{a}$, $UOCl_3(cr)^{a}$, $UO_2Cl(cr)^{a}$, $UO_2Cl_2(cr)^{a}$, $U_2O_2Cl_5(cr)^{a}$, $(UO_2)_2Cl_3(cr)^{a}$, $U_5O_{12}Cl(cr)^{a}$, $UO_2Cl_2 \cdot H_2O(cr)^{a}$, $UO_2ClOH \cdot 2H_2O(cr)^{a}$, $UO_2Cl_2 \cdot 3H_2O(cr)^{a}$, $UCl_3F(cr)^{a}$, $UCl_2F_2(cr)^{a}$, $UClF_3(cr)^{a}$, $UBr_3(cr)^{a}$, $UBr_4(cr)^{a\,d}$, $UBr_5(cr)^{a}$, $UOBr_2(cr)^{a}$, $UOBr_3(cr)^{a}$, $UO_2Br_2(cr)^{a}$, $UO_2Br_2 \cdot H_2O(cr)^{a}$, $UO_2BrOH \cdot 2H_2O(cr)^{a}$, $UO_2Br_2 \cdot 3H_2O(cr)^{a}$, $UBr_2Cl(cr)^{a}$, $UBr_3Cl(cr)^{a}$, $UBrCl_2(cr)^{a}$, $UBr_2Cl_2(cr)^{a}$, $UBrCl_3(cr)^{a}$, $UI_3(cr)^{a}$, $UI_4(cr)^{ad}$, $UO_2(IO_3)_2(cr)^{ac}$, $UClI_3(cr)^{a}$, $UCl_2I_2(cr)^{a}$, $UCl_3I(cr)^{a}$, $UBrI_3(cr)^{b}$, $UBr_2I_2(cr)^{b}$, $UBr_3I(cr)^{b}$, $US(cr)^{a}$, $US_{1.90}(cr)^{a}$, $US_2(cr)^{a}$, $US_3(cr)^{a}$, $U_2S_3(cr)^{a}$, $U_2S_5(cr)^{b}$, $U_3S_5(cr)^{a}$, $UO_2SO_3(cr)^{a}$, $UO_2SO_4(cr)^{a}$, $U(SO_3)_2(cr)^{a}$, $U(SO_4)_2(cr)^{a}$, $UO_2SO_4 \cdot 2.5H_2O(cr)^{ac}$, $UO_2SO_4 \cdot 3H_2O(cr)^{ac}$, $UO_2SO_4 \cdot 3.5H_2O(cr)^{ac}$, $U(SO_4)_2 \cdot 4H_2O(cr)^{a}$, $U(SO_4)_2 \cdot 8H_2O(cr)^{a}$, $USe(cr)^{a}$, α-$USe_2(cr)^{a}$, β-$USe_2(cr)^{a}$, $USe_3(cr)^{a}$, $U_2Se_3(cr)^{a}$, $U_3Se_4(cr)^{a}$, $U_3Se_5(cr)^{a}$, $UO_2SeO_3(cr)^{b}$, $UO_2SeO_4(cr)^{b}$, $UOTe(cr)^{b}$, $UTeO_5(cr)^{b}$, $UTe_3O_9(cr)^{b}$, $UN(cr)^{a}$, β-$UN_{1.466}(cr)^{b}$, α-$UN_{1.59}(cr)^{a}$, α-$UN_{1.606}(cr)^{b}$, α-$UN_{1.674}(cr)^{b}$, α-$UN_{1.73}(cr)^{a}$, $UO_2(NO_3)_2(cr)^{a}$, $UO_2(NO_3)_2 \cdot H_2O(cr)^{a}$, $UO_2(NO_3)_2 \cdot 2H_2O(cr)^{a}$, $UO_2(NO_3)_2 \cdot 3H_2O(cr)^{a}$, $UO_2(NO_3)_2 \cdot 6H_2O(cr)^{a}$, $UP(cr)^{a}$, $UP_2(cr)^{a}$, $U_3P_4(cr)^{a}$, $UPO_5(cr)^{a}$, $UP_2O_7(cr)^{a}$, $(UO_2)_2P_2O_7(cr)^{a}$, $U(HPO_4)_2 \cdot 4H_2O(cr)^{a\,c}$, $(UO_2)_3(PO_4)_2 \cdot 6H_2O(cr)^{a}$, $UAs(cr)^{a}$, $UAs_2(cr)^{a}$, $U_3As_4(cr)^{a}$, $UAsO_5(cr)^{b}$, $UO_2(AsO_3)_2(cr)^{a}$, $(UO_2)_2As_2O_7(cr)^{a}$, $(UO_2)_3(AsO_4)_2(cr)^{a}$, $UAsS(cr)^{b}$, $UAsSe(cr)^{b}$, $UAsTe(cr)^{b}$, $USb(cr)^{a}$, $USb_2(cr)^{a}$, $U_4Sb_3(cr)^{b}$, $U_3Sb_4(cr)^{a}$, $UC(cr)^{a}$, α-$UC_{1.94}(cr)^{a}$, $U_2C_3(cr)^{a}$, $Tl_2U_4O_{11}(cr)^{b}$, $Zn_{0.12}UO_{2.95}(cr)^{b}$, $Be_{13}U(cr)^{a}$, α-$Mg_{0.17}UO_{2.95}(cr)^{b}$, $MgUO_4(cr)^{a}$, $MgU_3O_{10}(cr)^{b}$, β-$CaUO_4{}^{b}$, $CaUO_4(cr)^{a}$,

	$Ca_3UO_6(cr)$[b], $SrUO_3(cr)$[b], α-$SrUO_4(cr)$[a], β-$SrUO_4(cr)$[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], γ-$Li_{0.55}UO_3(cr)$[bd], δ-$Li_{0.69}UO_3(cr)$[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], α-$Na_{0.14}UO_3(cr)$[bd], δ-$Na_{0.54}UO_3(cr)$[bd], $NaUO_3(cr)$[ad], α-$Na_2UO_4(cr)$[a], β-$Na_2UO_4(cr)$[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 $\Delta_f G_m^\circ$
[b] Single species data excluding $\Delta_f G_m^\circ$
[c] Reaction data including $\log_{10} K^\circ$
[d] Reaction data excluding $\log_{10} K^\circ$

Table 1.3: 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}]	**$S_m°$** [J · K^{-1} · mol^{-1}]	**$\log_{10}\beta°$**	**$\Delta_r H_m°$** [kJ · mol^{-1}]	**$\Delta_r S_m°$** [J · K^{-1} · mol^{-1}]	**$S_m°$** [J · K^{-1} · mol^{-1}]	**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	-	-	$UO_2^{2+} + 3\ F^- \Leftrightarrow UO_2F_3^-$
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	-	-	$UO_2^{2+} + Cl^- \Leftrightarrow UO_2Cl^+$

		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**
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	-	-	-	$2\ UO_2^{2+} + CO_3^{2-} + 3\ H_2O(l) \Leftrightarrow (UO_2)_2CO_3(OH)_3^- + 3\ H^+$
(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	-	-	-	$UO_2^{2+} + CO_3^{2-} + 2\ F^- \Leftrightarrow UO_2CO_3F_2^{2-}$

		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**
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	-	-	-	(6.95 ± 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	-	-	$U^{4+} + 2\ F^- \Leftrightarrow UF_2^{2+}$
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	-	-	-	$U^{4+} + I^- \Leftrightarrow UI^{3+}$

		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}]	**$S_m°$** [J · K^{-1} · mol^{-1}]	**$\log_{10}\beta°$**	**$\Delta_r H_m°$** [kJ · mol^{-1}]	**$\Delta_r S_m°$** [J · K^{-1} · mol^{-1}]	**$S_m°$** [J · K^{-1} · mol^{-1}]	**Reaction**
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)[e]	-20 ± 4	-	-	(34.1 ± 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)*[d]	-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 value selected by GUILLAUMONT et al. (2003) is incorrect and should be 7.19 ± 0.36. This will be corrected in the next update, see text for discussion
[d] The value 2.97 ± 0.06 selected by GRENTHE et al. (1992) is incorrect, see text for discussion
[e] This value should be 33.9 ± 1.0 and will be corrected in the next update, see text for discussion

		TDB Version 01/01			TDB Version 12/07			
Name	**Redox**	**$\log_{10}K_{s,0}°$**	**$S_m°$** [J · K^{-1} · mol^{-1}]	**$C_{p,m}°$** [J · K^{-1} · mol^{-1}]	**$\log_{10}K_{s,0}°$**	**$S_m°$** [J · K^{-1} · mol^{-1}]	**$C_{p,m}°$** [J · K^{-1} · 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	-	-	$UO_2HPO_4{\cdot}4H_2O(cr) + 2H^+ \Leftrightarrow UO_2^{2+} + H_3PO_4(aq) + 4H_2O(l)$

		TDB Version 01/01			TDB Version 12/07			
Name	**Redox**	**$\log_{10}K_{s,0}^\circ$**	**S_m°** [J · K^{-1} · mol^{-1}]	**$C_{p,m}^\circ$** [J · K^{-1} · mol^{-1}]	**$\log_{10}K_{s,0}^\circ$**	**S_m°** [J · K^{-1} · mol^{-1}]	**$C_{p,m}^\circ$** [J · K^{-1} · mol^{-1}]	**Reaction**
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 1.4: 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. Data estimated according to HUMMEL (2009) 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^+ $\varepsilon_{j,k}$
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)[c]	(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

[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 for discussion.

[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).

Table 1.5: 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

12 References

AHRLAND, S. & LARSSON, R. (1954): The complexity of uranium(IV) chloride, bromide and thiocyanate. Acta Chemica Scandinavica, 8, 137-150.

AHRLAND, S. & KULLBERG, L. (1971): Thermodynamics of metal complex formation in aqueous solution. I. A potentiometric study of fluoride complexes of hydrogen, uranium(VI), and Vanadium(V). Acta Chemica Scandinavica, 25, 3457-3470.

BERNER, U. (1995): Kristallin-I: Estimates of Solubility Limits for Safety Relevant Radionuclides. PSI-Bericht Nr. 95-07, Paul Scherrer Institute, Villigen, Switzerland, 58 pp.

BERNHARD, G., GEIPEL, G., BRENDLER, V. & NITSCHE H. (1996): Speciation of uranium in seepage waters of a mine tailing pile studied by time-resolved laser-induced fluorescence spectroscopy (TRLFS). Radiochimica Acta, 74, 87-91.

BERNHARD, G., GEIPEL, G., REICH, T., BRENDLER, V., AMAYRI, S. & NITSCHE H. (2001): Uranyl(VI) carbonate complex formation: Validation of the $Ca_2UO_2(CO_3)_3$(aq.) species. Radiochimica Acta, 89, 511-518.

BROOKS, S.C., FREDRICKSON, J.K., CARROLL, S.L., KENNEDY, D.W., ZACHARA. J.M., PLYMALE, A.E., KELLY, S.D., KEMNER, K.M. & FENDORF, S. (2003): Inhibition of bacterial U(VI) reduction by calcium. Environmental Science & Technology, 37, 1850-1858.

BRUGGER, J., MEISSER, N., ETSCHMANN, B., ANSERMET, S. & PRING (2011): Paulscherrerite from the Number 2 Workings, Mount Painter Inlier, Northern Flinders Ranges, South Australia: "Dehydrated schoepite" is a mineral after all. American Mineralogist, 96, 229-240.

BRUNO, J., CASAS, I., LAGERMANN, B. & MUÑOZ, M. (1987): The determination of the solubility of amorphous UO_2(s) and the mononuclear hydrolysis constants of uranium(IV) at 25°C. Mat. Res. Soc. Symp. Proc., 84, 153-160.

BRUNO, J., FERRI, D., GRENTHE, I. & SALVATORE, F. (1986): Studies on metal carbonate equilibria: 13. On the solubility of uranium(IV) dioxide, UO_2(s). Acta Chemica Scandinavica, 40, 428-434.

CAPDEVILA, H. & VITORGE, P. (1999): Redox potentials of M(VI)/M(V) limiting carbonate complexes (M = U or Pu) at different ionic strenght and temperatures. Entropy and heat capacity. Czechoslovak Journal of Physics, 49, Suppl. S1, 603-609.

CHOPPIN, G.R. & MATHUR, J.N. (1991): Hydrolysis of actinyl(VI) cations. Radiochimica Acta, 53/54, 25-28.

CIAVATTA, L. (1980): The specific interaction theory in evaluating ionic equilibria. Annali di Chimica, 70, 551-567.

CIAVATTA, L., DE TOMMASO, G. & IULIANO, M. (2003): On the hydrolysis of the dioxouranium(VI) ion in sulfate solutions. Annali di Chimica, 93, 281-290.

COMARMOND, M.J. & BROWN, P.L. (2000): The hydrolysis of uranium(VI) in sulfate media. Radiochimica Acta, 88, 573-577.

DAY, R.A., WILHITE, R.N. & HAMILTON, F.D. (1955): Stability of complexes of uranium(IV) wiht chloride, sulfate and thiocyanate. Journal of the American Chemical Society, 77, 3180-3182.

DONG, W. & BROOKS, S.C. (2006): Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals (Mg^2+. Ca^{2+}, Sr^{2+}, and Ba^{2+}) using anion exchange method. Environmental Science & Technology, 40, 4689-4695.

DONG, W. & BROOKS, S.C. (2008): Formation of aqueous $MgUO_2(CO_3)_3^{2-}$ complex and uranium anion exchange mechanism onto an exchange resin. Environmental Science & Technology, 42, 1979-1983.

FERRI, D., SALVATORE, F., VASCA, E., GLASER, J. & GRENTHE, I. (1993): Complex formation in the U(VI)-OH^--F^- system. Acta Chemica Scandinavica, 47, 855-861.

GAMSJÄGER, H., BUGAJSKI, J., GAJDA, T., LEMIRE, R.J. & PREIS, W. (2005): Chemical Thermodynamics of Nickel. Elsevier, Amsterdam, 617 pp.

GEIPEL, G., AMAYRI, S. & BERNHARD, G. (2008): Mixed complexes of alkaline earth uranyl carbonates: A laser-induced time-resolved fluorescence spectroscopic study. Spectrochimica Acta Part A, 71, 53-58.

GRENTHE, I. & WANNER, H. (1989): Guidelines for the Extrapolation to Zero Ionic Strength. TDB-2.1, OECD Nuclear Energy Agency (NEA), Gif-sur-Yvette, France, 23 pp.

GRENTHE, I. & LAGERMAN, B. (1993): Ternary metal complexes 2. The U(VI)-SO_4^{2-}-OH^-- system. Radiochimica Acta, 61, 169-176.

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

GRENTHE, I., PUIGDOMÈNECH, I., SANDINO, M.C.A. & RAND, M.H. (1995): Corrections to the Uranium NEA-TDB review. In: SILVA, R.J., BIDOGLIO, G., RAND, M.H., ROBOUCH, P.B., WANNER, H. & PUIGDOMÈNECH, I.: Chemical Thermodynamics of Americium, Elsevier, Amsterdam, Appendix D, 347-374.

GUILLAUMONT, R., FANGHÄNEL, T., FUGER, J., GRENTHE, I., NECK, V., PALMER, D.A. & RAND, M.A. (2003): Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium. Elsevier, Amsterdam, 763 pp.

GUNNARSSON, I. & ARNORSSON, S. (2000): Amorphous silica solubility and the thermodynamic properties of $H_4SiO_4^o$ in the range of 0º to 350ºC at P_{sat}. Geochimica et Cosmochimica Acta, 64, 2295-2307.

HOVEY, J.K. (1997): Thermodynamics of Hydration of a 4+ Aqueous Ion: Partial Molar Heat Capacities and Volumes of aqueous Thorium(IV) from 10 to 55°C. The Journal of Physical Chemistry B, 101, 4321-4334.

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.

HUMMEL, W., ANDEREGG, G., PUIGDOMÈNECH, I., RAO, L. & TOCHIYAMA, O. (2005): Chemical Thermodynamics of Compounds and Complexes of U, Np, Pu, Am, Tc, Se, Ni and Zr with Selected Organic Ligands. Elsevier, Amsterdam, 1088 pp.

HUMMEL, W. (2009): Ionic strength corrections and estimation of SIT ion interaction coefficients. PSI Internal Report, TM-44-09-01, Paul Scherrer Institut, Villigen, Switzerland, 15 pp.

HUMMEL, W. (2014): The PSI/Nagra Chemical Thermodynamic Database 12/07 (Update of the Nagra/PSI TDB 01/01): Data Selection for Silicon. PSI Internal Report, TM-44-12-05, Paul Scherrer Institut, Villigen, Switzerland, 40 pp.

KALMYKOW, S.N. & CHOPPIN, G.R. (2000): Mixed $Ca^{2+}/UO_2^{2+}/CO_3^{2-}$ complex formation at different ionic strengths. Radiochimica Acta, 88, 603-606.

KELLY, S.D., KEMNER, K.M., BROOKS, S.C., FREDRICKSON, J.K., CARROLL, S.L., KENNEDY, D.W., ZACHARA, J.M, PLYMALE, A.E. & FENDORF, S. (2005): $Ca\text{-}UO_2\text{-}CO_3$ complexation - Implications for bioremediation of U(VI), Physica Scripta, T115, 915-917.

LANGMUIR, D. (1978): Uranium solution–mineral equilibria at low temperatures with applications to sedimentary ore deposits. Geochimica et Cosmochimica Acta, 42, 547-569.

LEE, J.-Y. & YUN, J.-I. (2013): Formation of ternary $CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3(aq)$ complexes under neutral to weakly alkaline conditions. Dalton Transactions, 42, 9862-9869.

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

MINERAL DATABASE (1997), Version 97.2 - December 1997, Aleph Enterprises, P.O. Box 213, Livermore, CA 94551-0213, USA.

MOLL, H., REICH, T., HENNIG, C., ROSSBERG, A., SZABÓ, Z. & GRENTHE, I. (2000): Solution coordination chemistry of uranium in the binary UO_2^{2+}-SO_4^{2-} and the ternary UO_2^{2+}-SO_4^{2-}-OH^- system. Radiochimica Acta, 88, 559-566.

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

NIKITIN, A.A., SERGEYEVA, E.I., KHODAKOVSKY, I.L. & NAUMOV, G.B. (1972): Hydrolysis of uranyl in the hydrothermal region. Geokhimiya, 3, 297-307, in Russian.

PARKS, G.A. & POHL, D.C. (1988): Hydrothermal solubility of uraninite. Geochimica et Cosmochimica Acta, 52, 863-875.

PASHALIDIS, I., KIM, J.I., ASHIDA, T. & GRENTHE, I. (1995): Spectroscopic study of the hydrolysis of PuO_2^{2+} in aqueous solution. Radiochimica Acta, 68, 99-104.

PETERSON, A. (1961): Studies on the hydrolysis of metal ions 32. The uranyl ion, UO_2^{2+} in Na_2SO_4 medium. Acta Chemica Scandinavica, 15, 101-120.

PRAT, O., VERCOUTER, T., ANSOBORLO, E., FICHET, P., PERRET, P., KURTTIO, P. & SALONEN L. (2009): Uranium speciation in drinking water from drilled wells in southern Finland and its potential links to health effects. Environmental Science & Technology, 43, 3941-3946.

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

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

RAI, D., FELMY, A.R., HESS, N.J., MOORE, D.A. & YUI, M. (1998): A thermodynamic model for the solubility of UO_2(am) in the aqueous K^+-Na^+-HCO_3^--CO_3^{2-}-OH^--H_2O system. Radiochimica Acta, 82, 17-25.

RIGLET, C., ROBOUCH, P. & VITORGE, P. (1989): Standard potentials of the (MO_2^{2+}/MO_2^+) and (M^{4+}/M^{3+}) redox systems for neptunium and plutonium. Radiochimica Acta, 46, 85-94.

RIMSTIDT, J. D. (1997): Quartz solubility at low temperatures. Geochimica et Cosmochimica Acta, 61, 2553-2558.

ROBINSON, R.A. & STOKES, R.H. (1959): Electrolyte solutions. London, Butterworths, 2nd ed., 559p.

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

SANDINO, A. (1991): Processes affecting the mobility of uranium in natural waters. Ph.D. thesis in inorganic chemistry, The Royal Institute of Technology, Stockholm, Sweden.

SANDINO, A. & BRUNO, J. (1992): The solubility of $(UO_2)_3(PO_4)_2 \cdot 4H_2O$(s) and the formation of U(VI) phosphate complexes: Their influence in uranium speciation in natural waters. Geochimica et Cosmochimica Acta, 56, 4135-4145.

YAJIMA, T., KAWAMURA, Y. & UETA, S. (1995): Uranium(IV) solubility and hydrolysis constants under reduced conditions. Materials Research Society Symposium Proceedings, 353, 1137-1142.

YAMAMURA, T., KITAMURA, A., FUKUI, A., NISHIKAWA, S., YAMAMOTO, T. & MORIYAMA, H. (1998): Solubility of U(VI) in Highly Basic Solutions. Radiochimica Acta, 83, 139-146.