

# Data compilation and evaluation of U(IV) and U(VI) for the Thermodynamic Reference Database THEREDA

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## 1 Introduction

For geochemical modelling of scenarios for the disposal of radioactive and (chemo-) toxic waste, comprehensive and internally consistent thermodynamic data and sorption data for the surrounding host rocks are required. The use of different databases makes it difficult to compare the results of geochemical modelling directly. This is due to the incompleteness of existing data bases, conflicting data, different validity and model constraints in the composition of the solution (ionic strength), and not least the lack of sorption data.

THEREDA (Thermodynamic Reference Database) is a collaborative project, which has been addressed this challenge. The partners are Helmholtz-Zentrum Dresden-Rossendorf, Karlsruhe Institute of Technology (KIT-INE), Gesellschaft für Anlagen- und Reaktorsicherheit Braunschweig mbH (GRS), TU Bergakademie Freiberg (TUBAF) and AF-Consult Switzerland AG (Baden, Switzerland). The aim of the project is the establishment of a consistent and quality assured database for all safety relevant elements, temperature and pressure ranges, with its focus on saline systems. This implied the use of the Pitzer approach [PIT1991] to compute activity coefficients suitable for such conditions. Data access is possible via commonly available internet browsers under the address <http://www.thereda.de>.

One part of the project – the data collection and evaluation for uranium – was a task of the Helmholtz-Zentrum Dresden-Rossendorf. The aquatic chemistry and thermodynamics of U(VI) and U(IV) is of great importance for geochemical modelling in repository-relevant systems. The OECD/NEA Thermochemical Database (NEA TDB) compilation [GRE/FUG1992, GUI/FAN2003] is the major source for thermodynamic data of the aqueous and solid uranium species, even though this data selection does not utilize the Pitzer model for the ionic strength effect correction. However, data without relevance for final repository conditions in salt rocks and the geochemical modelling of radionuclides in aquatic systems were not adopted from the NEA TDB. This concerns, for example, data for gases such as  $UF_6$ , data for complexes with ligands such as bromide or iodide, high temperature phases, and data for highly soluble solid phases such as chlorides and nitrates.

To be able to utilize the Pitzer approach, recently published paper and partially unpublished works from the research group of Neck, Altmaier and co-workers (KIT-INE) are considered. Their work (i.e. [NEC/FAN2001]) is also the primary source of the Pitzer ion-ion interaction parameters for uranium with the system of oceanic salts con-

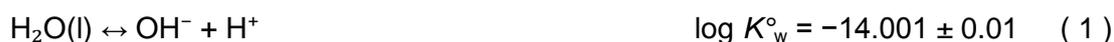
taining the elements Na, K, Mg, Ca, Cl, S, C. With the exception of relevant solid phases and unless otherwise commented, only data with available Pitzer ion-ion interaction parameters for the system of oceanic salts are accessible currently and released with the respective parameter files for the users in THEREDA, even though the database is more comprehensive.

As a result of the very stringent quality demands, NEA TDB is rather restrictive and therefore incomplete for extensive modelling calculations of real systems. Only 5 minerals of about 250 described by mineralogists found their way into the recommended data set. Therefore, the THEREDA compilation includes additional thermodynamic data of solid secondary phases formed in the waste material, the backfill and the host rock, though falling into quality assessment (QA) categories of lower accuracy. Compared to solubility constants calculated from thermochemical data for well-crystalline solid phases, the equilibrium constants determined from solubility measurements reflect the actual behavior of solid phases in contact with water. The directly measured solubility of a solid phase in contact with water is almost always much larger. In principle, these solid phases are thermodynamically instable (metastable) compared to ideally crystallized phases but nevertheless they control in many cases the solubility. Therefore, the data review process prefers  $\log K^\circ$  values from solubility experiments (if available) to those calculated from thermochemical data.

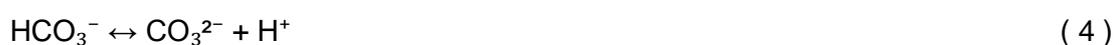
## 2 General remarks

To generate parameter files for geochemical speciation codes such as EQ3/6, GWB, PHREEQC, CHEMAPP, all formation reactions in THEREDA are transformed in such a way that all educts comprise only the phase constituents provided in the database (primary and secondary master species). In some cases, the reactions in [GUI/FAN2003] (Table 3-2, p. 64 ff.) deviate from this convention. From this it follows that a transformation of these reaction equations and a recalculation of the  $\log K^\circ$  values (and the respective uncertainties) became necessary. As it is an unequivocal and straightforward algorithm, the reference [GUI/FAN2003] was kept. This rephrasing is described in [ALT/BRE2011] in detail. For the sake of completeness, the original transformed reactions and  $\log^\circ K$  values are retained in the respective tables as comments.

The temperature dependent  $K_w$  function according to Harvey-Møller-Weare yields a  $\log K_w^\circ = -14.001$  at 25 °C. All reaction equations in [GUI/FAN2003] with  $\text{OH}^-$  as an educt were transformed including



The equilibria between  $\text{CO}_2(\text{aq})$  -  $\text{CO}_2(\text{g})$  -  $\text{HCO}_3^-$  -  $\text{CO}_3^{2-}$  are the basis for the formulation of the formation reactions of the uranyl carbonate species based on the primary master species  $\text{CO}_3^{2-}$ :



The new chosen  $\log K^\circ$  for the formation of  $\text{CO}_2(\text{aq})$ ,  $\text{HCO}_3^-$  and  $\text{CO}_2(\text{g})$  [DEV/VAN2012] (this is explained in detail in the report of the THEREDA partner TUBAF [VOI/SUK2014]) yields to the following entry changes in THEREDA compared to [GUI/FAN2003] in [ALT/BRE2011]:

Table 1 Reactions and respective equilibrium constants  $\log K^\circ \pm 2\sigma$  for carbonate equilibria

Reaction equation	[GUI/FAN2003]	NEW: [DEV/VAN2012]
$\text{CO}_3^{2-} + 2\text{H}^+ \leftrightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	$18.155 \pm 0.035$	$18.156 \pm 0.04$
$\text{CO}_3^{2-} + 2\text{H}^+ \leftrightarrow \text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$	$16.683 \pm 0.028$	$16.675 \pm 0.03$
$\text{CO}_3^{2-} + \text{H}^+ \leftrightarrow \text{HCO}_3^-$	$10.329 \pm 0.020$	$10.328 \pm 0.02$

This change has negligible consequences for recalculated  $\log K^\circ$  in transformed reaction equations and for modelling results.

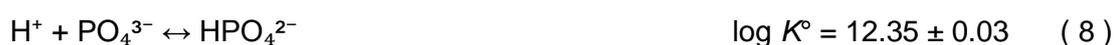
Phase constituents with phosphorus (P) are currently still excluded from the released data block because they will be subject to a future release. Nevertheless relevant solid phases were selected, where the data entry in THEREDA requires the transformation of the reaction and additional recalculation of the  $\log K^\circ$ . In [GUI/FAN2003], the master species for the element P is  $\text{HPO}_4^{2-}$ , composed as follows:



This leads to formation reactions of  $\text{H}_2\text{PO}_4^-$  and  $\text{H}_3\text{PO}_4(\text{aq})$  as given below:



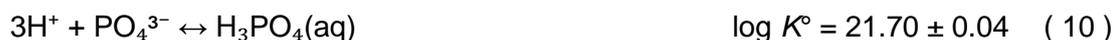
In THEREDA,  $\text{PO}_4^{3-}$  is defined as primary master species, resulting in the following transformed reaction equations and recalculated  $\log K^\circ \pm 2\sigma$ :



The outcome of this is the reaction and  $\log K^\circ$  of  $\text{H}_2\text{PO}_4^-$



and for  $\text{H}_3\text{PO}_4(\text{aq})$



In THEREDA, the hexavalent uranium ( $\text{UO}_2^{2+}$ ) is defined as master species for U, so the redox reaction for the creation of tetravalent U has to be involved. The following fundamental convention for redox reactions arises from the definitions and conventions for the dissolved hydronium ion ( $\text{H}^+$ ) and gaseous  $\text{H}_2(\text{g})$  (basis species for the electron):



From this the following formation equation and respective equilibrium constant [GUI/FAN2003] of the secondary master species  $U^{4+}$



was transformed into:



In the following chapters, the selected  $\log K^\circ$  values for the formation of aquatic and solid U(IV) species as well as the respective Pitzer parameters for the aquatic species are summarized in tables. Please note that here only the thermodynamic data with the interaction model Pitzer are published and discussed which are relevant for the system of oceanic salts (apart from solids without Pitzer parameters per se and species which are shown separately). The number of data entries in THEREDA is much higher.

As mentioned above, the major source for thermodynamic data is the NEA TDB-compilation [GRE/FUG1992, GUI/FAN2003]. The selection of data derived from this review will not be discussed again. In the respective chapters, the selection of data differing from those in [GRE/FUG1992, GUI/FAN2003] for reasons of consistency and of additionally recorded aqueous and solid species are discussed.

### 3 Compilation and discussion of selected thermodynamic data of U(IV)

#### 3.1 Aquatic U(IV) species

The selected log  $K^\circ$  values for the formation of aquatic U(IV) species are summarized in the following table.

Table 2 Selected log  $K^\circ$  values for the formation of aquatic U(IV) species (original reactions and log  $K^\circ$  in italics)

Species	Formation reaction	log $K^\circ$	Reference
$U^{4+}$	$UO_2^{2+} + H_2(g) + 2H^+ \leftrightarrow U^{4+} + 2H_2O(l)$ <i><math>UO_2^{2+} + 4H^+ + 2e^- \leftrightarrow U^{4+} + 2H_2O(l)</math></i>	$9.38 \pm 0.41$ <i><math>9.38 \pm 0.41</math></i>	[GUI/FAN2003]
$U(OH)^{3+}$	$U^{4+} + H_2O(l) \leftrightarrow U(OH)^{3+} + H^+$	$-0.54 \pm 0.06$	[GUI/FAN2003]
$U(OH)_2^{2+}$	$U^{4+} + 2H_2O(l) \leftrightarrow U(OH)_2^{2+} + 2H^+$	$-1.1 \pm 1.0$	[NEC/FAN2001]
$U(OH)_3^+$	$U^{4+} + 3H_2O(l) \leftrightarrow U(OH)_3^+ + 3H^+$	$-4.7 \pm 1.0$	[NEC/FAN2001]
$U(OH)_4(aq)$	$U^{4+} + 4H_2O(l) \leftrightarrow U(OH)_4(aq) + 4H^+$ <i><math>U^{4+} + 4OH^- \leftrightarrow U(OH)_4(aq)</math></i>	$-10.00 \pm 1.40$ <i><math>46.00 \pm 1.40</math></i>	[GUI/FAN2003]
$U(CO_3)_4^{4-}$	$4CO_3^{2-} + U^{4+} \leftrightarrow U(CO_3)_4^{4-}$ <i><math>U(CO_3)_5^{6-} \leftrightarrow CO_3^{2-} + U(CO_3)_4^{4-}</math></i>	$35.12 \pm 0.93$ <i><math>1.12 \pm 0.25</math></i>	[GUI/FAN2003]
$U(CO_3)_5^{6-}$	$U^{4+} + 5CO_3^{2-} \leftrightarrow U(CO_3)_5^{6-}$ <i><math>UO_2(am) + 5CO_3^{2-} + 4H^+ \leftrightarrow U(CO_3)_5^{6-} + 2H_2O(l)</math></i>	$32.3 \pm 1.4$ <i><math>33.8</math></i>	[RAI/FEL1998]
$U(OH)_2(CO_3)_2^{2-}$	$U^{4+} + 2H_2O(l) + 2CO_3^{2-} \leftrightarrow U(OH)_2(CO_3)_2^{2-} + 2H^+$ <i><math>UO_2(am) + 2HCO_3^- \leftrightarrow U(OH)_2(CO_3)_2^{2-} + 2H_2O(l)</math></i>	$14.36 \pm 2.0$ <i><math>-4.8</math></i>	[NEC/FAN2001] <sup>a)</sup>
$U(SO_4)^{2+}$	$U^{4+} + SO_4^{2-} \leftrightarrow U(SO_4)^{2+}$	9	[RAI/RAO1999]
$U(SO_4)_2(aq)$	$U^{4+} + 2SO_4^{2-} \leftrightarrow U(SO_4)_2(aq)$	11.7	[RAI/RAO1999]

<sup>a)</sup> Original value from [RAI/FEL1998], discussed and took in their database with the uncertainty of 2 from [NEC/FAN2001].

As mentioned, the major source of thermodynamic data for THEREDA is [GRE/FUG1992,GUI/FAN2003]. But some of data which were not selected are very important for the modelling nevertheless. These values are taken from the detailed and systematic review [NEC/FAN2001]:

#### $U(OH)_2^{2+}$



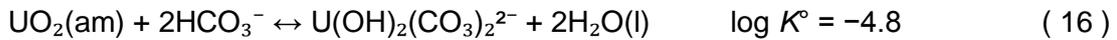
The log  $K^\circ$  is a well-founded estimation based on the method described by [NEC/KIM2001].

**$U(OH)_3^+$** 

The  $\log K^\circ$  is a well-founded estimation based on the method described by [NEC/KIM2001].

 **$U(OH)_2(CO_3)_2^{2-}$** 

Despite of deficiencies in the experiments of [RAI/FEL1998] (no evidence of postulated formation, ionic strength, pH value, carbonate concentration or  $CO_2$  partial pressure not constant in the experiments), [NEC/FAN2001] included the equilibrium constant in their database because no other data for ternary complexes are available. [RAI/FEL1998] determined the constant



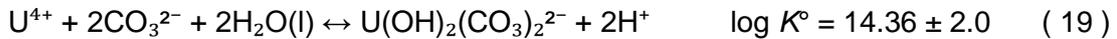
The combination of



and



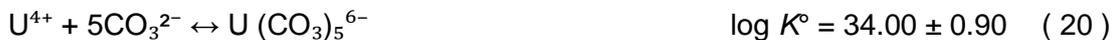
implies



By reason that [RAI/FEL1998] do not give an error estimation and no information relating to the calculation of activity coefficients, [NEC/FAN2001] assume a relatively large uncertainty  $\pm 2$ .

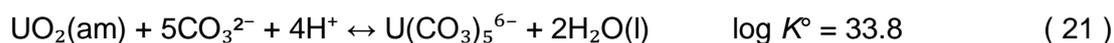
 **$U(CO_3)_5^{6-}$** 

For the formation of the species  $U(CO_3)_5^{6-}$ , the following reaction and  $\log K^\circ$  is given in [GUI/FAN2003]:

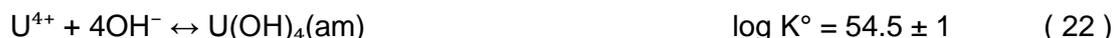


[GUI/FAN2003] remark, that the data of [RAI/FEL1998] have a high quality and the chemical model proposed gives a reasonable representation of them. Nevertheless they did not select the value because of doubts in correctness of the model and the lack of an analysis of the uncertainty.

For modelling in solutions with high ionic strength and for consistency reasons, [NEC/FAN2001] took the Pitzer parameters determined by [RAI/FEL1998] together with the associated equilibrium constants.



This value, combined with the  $\log K^\circ$  of formation of  $\text{U}(\text{OH})_4(\text{am})$  from [GUI/FAN2003]



and



provides a  $\log K^\circ$  for the reaction



This value was selected for THEREDA together with the value for the uncertainty given by [GUI/FAN2003] of 1.4.

### ***USO<sub>4</sub><sup>2-</sup> and U(SO<sub>4</sub>)<sub>2</sub>(aq)***

[GUI/FAN2003] select the  $\log K^\circ$  for the formation of the species  $\text{U}(\text{SO}_4)(\text{aq})$  and  $\text{U}(\text{SO}_4)_2^{2-}$ :



To be consistent with the selected Pitzer parameters of [RAI/RAO1999] (see chapter 3.3), the following  $\log K^\circ$  of [RAI/RAO1999] are selected in THEREDA:



These values are assumed to be identical with value for the corresponding Np(IV)-species. Note that the suitability for modelling or correctness is not yet determined.

### 3.2 Solid U(IV) phases

The following table summarizes the selected  $\log K^\circ$  values for the formation of solid U(IV) phases.

Table 3 Selected  $\log K^\circ$  values for the formation of solid U(IV) phases (original reactions and  $\log K^\circ$  in italics)

Solid phase	Formation reaction	$\log K^\circ$	Reference
<b>UO<sub>2</sub>(cr)<sup>a</sup></b> <b>Uraninite</b>	$U^{4+} + 4H_2O(l) \leftrightarrow UO_2(cr) + 4H^+$	4.85	[GUI/FAN2003]
<b>U(OH)<sub>4</sub>(am)</b>	$U^{4+} + 4H_2O(l) \leftrightarrow U(OH)_4(am) + 4H^+$ <i><math>U^{4+} + 4OH^- \leftrightarrow U(OH)_4(am)</math></i>	-1.5±1.0 <i>54.5±1.0</i>	[GUI/FAN2003]
<b>U(OH)<sub>2</sub>(SO<sub>4</sub>)(cr)</b>	$SO_4^{2-} + U^{4+} + 2H_2O(l) \leftrightarrow U(OH)_2SO_4(cr) + 2H^+$ <i><math>SO_4^{2-} + U^{4+} + 2OH^- \leftrightarrow U(OH)_2SO_4(cr)</math></i>	3.17±0.50 <i>31.17±0.50</i>	[GUI/FAN2003]
<b>U(SiO<sub>4</sub>)(cr)</b> <b>Coffinite</b>	$U^{4+} + Si(OH)_4(aq) \leftrightarrow U(SiO_4)(cr) + 4H^+$	7.81 <sup>b</sup>	New calc. in [THEREDA]
<b>CaU(PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O(cr)</b> <b>Ningoyite</b>	$U^{4+} + Ca^{2+} + 2PO_4^{3-} + 2H_2O(l) \leftrightarrow$ CaU(PO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O(cr) $U^{4+} + Ca^{2+} + 2H_3PO_4(aq) + 2H_2O(l) \leftrightarrow$ CaU(PO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O(cr)+6H <sup>+</sup>	55.92±1.67 <i>12.52±1.67</i>	[MUT1965]
<b>U(HPO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O(cr)</b>	$U^{4+} + 4H_2O(l) + 2H^+ + 2PO_4^{3-} \leftrightarrow$ U(HPO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O(cr) <i><math>U^{4+} + 4H_2O(l) + 2H_3PO_4(aq) \leftrightarrow 4H^+ +</math></i> <i>U(HPO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O(cr)</i>	55.19±0.17 <i>11.79±0.15</i>	[GUI/FAN2003]

<sup>a</sup>) Equilibrium constraint "Dissociation", not suitable for solution predictions in geochemical modelling

<sup>b</sup>)  $\log K^\circ$  calculated from thermochemical data of [GUI/FAN2003]

#### **Uraninite UO<sub>2</sub>(cr)**

Internally calculated from thermochemical data [GRE/FUG1992, GUI/FAN2003]



[NEC/FAN2001] showed that the solubility in neutral and basic solution is not determined by UO<sub>2</sub>(cr) but by an amorphous surface layer. This value is not suitable for solution predictions in geochemical modelling because it is too low compared to experimental solubility measurements. In THEREDA it is accessed with the equilibrium constraint "Dissociation".

#### **U(OH)<sub>4</sub>(am)**

As mentioned above, the solubility in natural aquatic systems is determined by U(OH)<sub>4</sub>(am) instead of the hardly soluble UO<sub>2</sub>(cr) as explained and demonstrated extensively by [NEC/FAN2001]. So THEREDA selects the value from [GUI/FAN2003].



### ***Coffinite USiO<sub>4</sub>(cr)***

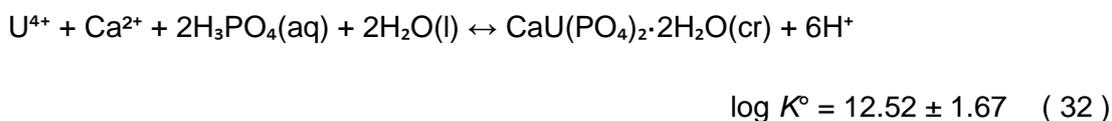
Coffinite is the single U(IV)silicate with thermodynamic data approved in the NEA review [GUI/FAN2003]. Calculated from the Gibbs standard formation enthalpy of coffinite ( $\Delta_f G^\circ = -1883.6 \pm 4$  kJ/mol) [NEC/FAN2001] and [ALT/BRE2004] arrive at  $\log K^\circ = -8.06 \pm 0.77$  for the reaction



With the new data for the standard formation enthalpy for the aqueous silica species  $Si(OH)_4(aq)$   $\Delta_f G^\circ = -1309.183 \pm 1.156$  kJ/mol [GUN/ARN2000]) instead of  $\Delta_f G^\circ = -1307.735 \pm 1.156$  kJ/mol [GUI/FAN2003], in THEREDA a  $\log K^\circ$  of  $-7.81$  is calculated.

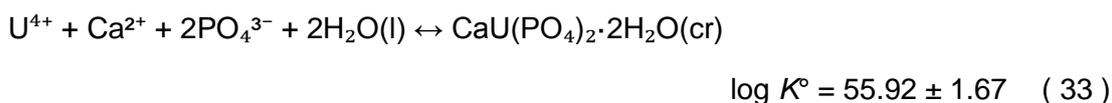
### ***Ningoyite CaU(PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O(s)***

[MUT1965] measured the solubility of synthetic ningoyite mainly at 25 °C and 100 °C by immersing it in water with pH ranging from 0 to 6. Equilibrium constant of the dissolution reaction of the mineral was obtained by estimating activities of the concerning ions with the aid of the Debye-Hückel limiting law from the uranium concentrations and the pH values of the solutions.



The mean  $\log K^\circ$  is based on 4 values (12.97/13.59/11.57/11.96).

The following  $\log K^\circ$  of ningoyite results from the transformed reaction



According to [LAN1978], the value for the formation entropy based on the temperature function of [MUT1965] (150.6 J/mol K) is too low, we selected the value of [LAN1978] (293 J/mol K).

**Attention: Phase constituents with P are currently still excluded from the released data block because they will be subject to a future release.**

### 3.3 Pitzer parameters for U(IV) species

Table 4 summarizes the respective Pitzer parameters for the aquatic species.

Table 4 Selected binary Pitzer parameters for U(IV) species

Cation i	Anion k	$z_i$	$z_k$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\Phi$	Reference
$U^{4+}$	$Cl^-$	4	-1	1.27	13.5	0	0	[NEC/FAN2001] <sup>a)</sup>
$UOH^{3+}$	$Cl^-$	3	-1	0.6	5.9	0	0	[NEC/FAN2001] <sup>a)</sup>
$U(OH)_2^{2+}$	$Cl^-$	2	-1	0.23	1.93	0	0	[NEC/FAN2001] <sup>a)</sup>
$U(OH)_3^+$	$Cl^-$	1	-1	0.08	0.39	0	0	[NEC/FAN2001] <sup>a)</sup>
$U(OH)_4(aq)$	$Cl^-$	0	-1	$\lambda = 0 \pm 0.1$				[NEC/FAN2001] <sup>b)</sup>
$Na^+$	$U(OH)_4(aq)$	1	0	$\lambda = 0 \pm 0.1$				[NEC/FAN2001] <sup>b)</sup>
$K^+$	$U(OH)_4(aq)$	1	0	$\lambda = 0 \pm 0.1$				[NEC/FAN2001] <sup>b)</sup>
$Mg^{2+}$	$U(OH)_4(aq)$	2	0	$\lambda = 0 \pm 0.1$				[NEC/FAN2001] <sup>b)</sup>
$Na^+$	$U(CO_3)_4^{4-}$	1	-4	1	13	0	0	[NEC/FAN2001] <sup>b)</sup>
$K^+$	$U(CO_3)_4^{4-}$	1	-4	1	13	0	0	[NEC/FAN2001] <sup>b)</sup>
$Na^+$	$U(CO_3)_5^{6-}$	1	-6	1.5	31.3	0	0	[NEC/FAN2001] <sup>c)</sup>
$K^+$	$U(CO_3)_5^{6-}$	1	-6	1.5	31.3	0	0	[NEC/FAN2001] <sup>c)</sup>
$Na^+$	$U(OH)_2(CO_3)_2^{2-}$	1	-2	0	2	0	0	[NEC/FAN2001] <sup>b)</sup>
$K^+$	$U(OH)_2(CO_3)_2^{2-}$	1	-2	0	2	0	0	[NEC/FAN2001] <sup>b))</sup>
$USO_4^{2+}$	$Cl^-$	2	-1	1.64	0	0	-0.2635	[RAI/RAO1999]
$U(SO_4)_2(aq)$	$Cl^-$	0	-1	$\lambda = 0 \pm 0.1$				[RAI/RAO1999]

a) Based on conversion of SIT coefficients: better correlation of activity coefficients calculated with SIT and Pitzer parameters by simultaneous fit of  $\beta^{(0)}_{ik}$  and  $\beta^{(1)}_{ik}$  than by methods of [PLY/FAN1998],  $C^\Phi$  and ternary parameters unknown (set to be zero); may lead to wrong activity coefficients with increasing ionic strength: parameter set is suitable only for chloride concentration <0.5 M

b) Estimated according to Pitzer parameters of analogous species

c) Originally published in [RAI/FEL1998], selected in [NEC/FAN2001] by consistency reasons with the respective equilibrium constants and not own from SIT coefficients calculated values ( $\beta^{(0)}=2.36$ ,  $\beta^{(1)}=45.6$ ), value based on solubility data of  $UO_2(am)$  in bicarbonate and carbonate solutions without NaCl or  $NaClO_4$  addition (no ternary interactions), value not transferable to mixed carbonate-chloride-solutions!

The modelling of U species in concentrated salt solutions requires a set of Pitzer parameters for the interactions with the ions of the hexary system Na-K-Mg-Ca-Cl-SO<sub>4</sub>-H<sub>2</sub>O (25 °C). Unfortunately, as a result of the absence of experimental data in NaCl and MgCl<sub>2</sub> solution, no interaction coefficients exist, on which the activity coefficients of the aquatic U(IV) species in concentrated chloride solutions can be calculated or predicted reliably. The binary parameters have to be determined using various methods (conversion of SIT coefficients, conclusions by analogy). The fundamental basis was established by the KIT-INE [NEC/FAN2001]. Additionally, recently published data are comprised. In most cases, these data apply for systems not exceeding middle salinity.

The consistency and compatibility with the respective equilibrium constants for the formation of the aqueous species has to be regarded. The ternary parameters  $\Theta$  and  $\Psi$  of U(IV) species are not assessable.

The Pitzer parameters of the interaction of  $U^{4+} / UOH^{3+} / U(OH)_2^{2+} / U(OH)_3^+$  with Cl<sup>-</sup> were determined by [NEC/FAN2001] based on the conversion of SIT coefficients. A better correlation of activity coefficients calculated with SIT and Pitzer parameters is accomplished by simultaneous fit of  $\beta_{ik}^{(0)}$  and  $\beta_{ik}^{(1)}$  than by methods of [PLY/FAN1998].  $C^\phi$  and ternary parameters are unknown (set to be zero). This may lead to wrong activity coefficients with increasing ionic strength: [NEC/FAN2001] emphasize that the parameter set is suitable only for a chloride concentration <0.5 mol/L.

For the neutral species  $U(OH)_4(aq)$ , no Pitzer parameters are published. According to SIT, [NEC/FAN2001] set the interaction parameters of the electrically neutral species to be zero. An influence of the NaCl/KCl/MgCl<sub>2</sub> concentration on the solubility of  $U(OH)_4(am)$  in neutral and basic solution is not expected, according to [NEC/FAN2001] this assumption is not confirmed experimentally.

The Pitzer parameters for  $U(CO_3)_4^{4-}$  are estimated by [NEC/FAN2001] according to Pitzer parameters of analogous species. Rai and Felmy are the single authors who determined experimental data for all tetravalent actinides (Th, Np, U, Pu). From reasons of consistency, [NEC/FAN2001] selected the Pitzer parameters for the complex  $U(CO_3)_5^{6-}$  from [RAI/FEL1998] and not the own values ( $\beta^{(0)}=2.36$ ,  $\beta^{(1)}=45.6$ ) which were calculated from SIT coefficients. [NEC/FAN2001] point out that the values are based on solubility data of  $UO_2(am)$  in highly concentrated bicarbonate and carbonate solutions without NaCl or NaClO<sub>4</sub> addition (no ternary interactions), so that the value is not transferable to mixed carbonate-chloride-solutions. These values are selected for THEREDA together with the respective equilibrium constants of [RAI/FEL1998].

As no Pitzer parameters for the mixed hydroxy-carbonato species of U(IV) are found in the literature, [NEC/FAN2001] estimated the binary parameters according their valence type on the basis of comparative values of other actinide complexes. This ensures the calculation of reasonable activity coefficients at least in the range of low ionic strengths. However, an extrapolation to high NaCl concentrations is combined with a high uncertainty.

Table 5 Pitzer parameters for mixed hydroxo-carbonato species of U(IV) [NEC/FAN2001]

Cation i	Anion k	$z_i$	$z_k$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\Phi$
Na <sup>+</sup>	U(OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>	1	-2	0	2	0	0
K <sup>+</sup>	U(OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>	1	-2	0	2	0	0
Na <sup>+</sup>	U(OH) <sub>4</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>	1	-2	0	2	0	0
K <sup>+</sup>	U(OH) <sub>4</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>	1	-2	0	2	0	0
Na <sup>+</sup>	U(OH) <sub>3</sub> (CO <sub>3</sub> ) <sup>-</sup>	1	-1	0	0.2	0	0
K <sup>+</sup>	U(OH) <sub>3</sub> (CO <sub>3</sub> ) <sup>-</sup>	1	-1	0	0.2	0	0
Na <sup>+</sup>	U(OH) <sub>4</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>4-</sup>	1	-4	1	13	0	0
K <sup>+</sup>	U(OH) <sub>4</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>4-</sup>	1	-4	1	13	0	0

As no equilibrium constants for the formation of the 141-, 131- and 142-species are available, only the Pitzer parameters of the 122-species U(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup> are selected for THEREDA.

Only [RAI/RAO1999] give parameters for the interaction between U<sup>4+</sup> and SO<sub>4</sub><sup>2-</sup>. They were selected assuming to be identical with the values for the corresponding Np(IV) species, which were fitted simultaneously with the equilibrium constants for the Th(IV)-sulphate-complexes. In THEREDA, these Pitzer parameters for the interactions of USO<sub>4</sub><sup>2+</sup> and U(SO<sub>4</sub>)<sub>2</sub>(aq) respectively with Cl<sup>-</sup> were selected. The suitability for modeling or correctness is not yet determined.

[NEC/FAN2001] emphasize that the carbonate- and hydroxy-carbonate-complexes are irrelevant in brines containing MgCl<sub>2</sub>. The same applies to solution saturated with respect to calcite. Setting the Pitzer parameters to zero may yield to total unrealistic activity coefficients and overestimation of the concentration of these – in MgCl<sub>2</sub> not relevant – species. To avoid this, notional values should be taken, typically for the valence type. Because no comparative values are known for the valence type 2:4 or 2:6 (e.g., interaction parameters between Mg<sup>2+</sup> and U(CO<sub>3</sub>)<sub>4</sub><sup>4-</sup> and U(CO<sub>3</sub>)<sub>5</sub><sup>6-</sup>, respectively), these species should be disabled.

Attention: The weak chloride complexation is included in the Pitzer coefficients of the ion-ion-interaction between U<sup>4+</sup> and Cl<sup>-</sup>, it must not be incorporated as chloro-complexes in model calculations additionally.

## 4 Compilation and discussion of selected thermodynamic data of U(VI)

### 4.1 Aquatic U(VI) species

The following table shows the selected  $\log K^\circ$  values for the formation of aquatic U(VI) species.

Table 6 Selected  $\log K^\circ$  values for the formation of aquatic U(VI) species (original reactions and  $\log K^\circ$  in italics)

Species	Formation reaction	$\log K^\circ$	Reference
$\text{UO}_2^{2+}$			[GUI/FAN2003]
$\text{UO}_2(\text{OH})^+$	$\text{UO}_2^{2+} + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{UO}_2(\text{OH})^+ + \text{H}^+$	$-5.25 \pm 0.24$	[GUI/FAN2003]
$\text{UO}_2(\text{OH})_2(\text{aq})$	$\text{UO}_2^{2+} + 2\text{H}_2\text{O}(\text{l}) \leftrightarrow \text{UO}_2(\text{OH})_2(\text{aq}) + 2\text{H}^+$	$-12.15 \pm 0.07$	[GUI/FAN2003]
$\text{UO}_2(\text{OH})_3^-$	$\text{UO}_2^{2+} + 3\text{H}_2\text{O}(\text{l}) \leftrightarrow \text{UO}_2(\text{OH})_3^- + 3\text{H}^+$	$-20.25 \pm 0.42$	[GUI/FAN2003]
$\text{UO}_2(\text{OH})_4^{2-}$	$\text{UO}_2^{2+} + 4\text{H}_2\text{O}(\text{l}) \leftrightarrow \text{UO}_2(\text{OH})_4^{2-} + 4\text{H}^+$	$-31.92 \pm 0.33$	[ALT/BRE2004]]
$(\text{UO}_2)_2(\text{OH})_2^{2+}$	$2\text{UO}_2^{2+} + 2\text{H}_2\text{O}(\text{l}) \leftrightarrow (\text{UO}_2)_2(\text{OH})_2^{2+} + 2\text{H}^+$	$-5.62 \pm 0.04$	[GUI/FAN2003]
$(\text{UO}_2)_3(\text{OH})_4^{2+}$	$3\text{UO}_2^{2+} + 4\text{H}_2\text{O}(\text{l}) \leftrightarrow (\text{UO}_2)_3(\text{OH})_4^{2+} + 4\text{H}^+$	$-11.90 \pm 0.30$	[GUI/FAN2003]
$(\text{UO}_2)_3(\text{OH})_5^+$	$3\text{UO}_2^{2+} + 5\text{H}_2\text{O}(\text{l}) \leftrightarrow (\text{UO}_2)_3(\text{OH})_5^+ + 5\text{H}^+$	$-15.55 \pm 0.12$	[GUI/FAN2003]
$(\text{UO}_2)_3(\text{OH})_7^-$	$3\text{UO}_2^{2+} + 7\text{H}_2\text{O}(\text{l}) \leftrightarrow (\text{UO}_2)_3(\text{OH})_7^- + 7\text{H}^+$	$-32.20 \pm 0.80$	[GUI/FAN2003]
$(\text{UO}_2)_4(\text{OH})_7^+$	$4\text{UO}_2^{2+} + 7\text{H}_2\text{O}(\text{l}) \leftrightarrow (\text{UO}_2)_4(\text{OH})_7^+ + 7\text{H}^+$	$-21.90 \pm 1.00$	[GUI/FAN2003]
$\text{UO}_2(\text{CO}_3)(\text{aq})$	$\text{UO}_2^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{UO}_2(\text{CO}_3)(\text{aq})$	$9.94 \pm 0.03$	[GUI/FAN2003]
$\text{UO}_2(\text{CO}_3)_2^{2-}$	$\text{UO}_2^{2+} + 2\text{CO}_3^{2-} \leftrightarrow \text{UO}_2(\text{CO}_3)_2^{2-}$	$16.61 \pm 0.09$	[GUI/FAN2003]
$\text{UO}_2(\text{CO}_3)_3^{4-}$	$\text{UO}_2^{2+} + 3\text{CO}_3^{2-} \leftrightarrow \text{UO}_2(\text{CO}_3)_3^{4-}$	$21.84 \pm 0.04$	[GUI/FAN2003]
$(\text{UO}_2)_2(\text{CO}_3)(\text{OH})_3^-$ <sup>a)</sup>	$2\text{UO}_2^{2+} + \text{CO}_3^{2-} \leftrightarrow (\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ $2\text{UO}_2^{2+} + \text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l}) \leftrightarrow (\text{UO}_2)_2(\text{CO}_3)_3(\text{OH})_3^- + 5\text{H}^+$	$-0.855 \pm 0.50$ $-19.01 \pm 0.50$	[GUI/FAN2003]
$(\text{UO}_2)_3\text{O}(\text{OH})_2(\text{HCO}_3)^+$ <sup>a)</sup>	$3\text{UO}_2^{2+} + \text{CO}_3^{2-} + 3\text{H}_2\text{O}(\text{l}) \leftrightarrow 3\text{H}^+ + (\text{UO}_2)_3\text{O}(\text{OH})_2(\text{HCO}_3)^+$ $\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l}) + 3\text{UO}_2^{2+} \leftrightarrow 5\text{H}^+ +$	$0.655 \pm 0.50$ $-17.50 \pm 0.50$	[GUI/FAN2003]

Species	Formation reaction	log K°	Reference
	$(\text{UO}_2)_3\text{CO}_3(\text{OH})_3^-$		
$(\text{UO}_2)_{11}(\text{CO}_3)_6(\text{OH})_{12}^{2-}$ a)	$11\text{UO}_2^{2+} + 12\text{H}_2\text{O}(\text{l}) + 6\text{CO}_3^{2-} \leftrightarrow (\text{UO}_2)_{11}(\text{CO}_3)_6(\text{OH})_{12}^{2-} + 12\text{H}^+$ $11\text{UO}_2^{2+} + 6\text{CO}_2(\text{g}) + 18\text{H}_2\text{O}(\text{l}) \leftrightarrow 24\text{H}^+ + (\text{UO}_2)_{11}(\text{CO}_3)_6(\text{OH})_{12}^{2-}$	$36.42 \pm 2.00$ $-72.50 \pm 2.00$	[GUI/FAN2003]
$\text{UO}_2(\text{SO}_4)(\text{aq})$	$\text{UO}_2^{2+} + \text{SO}_4^{2-} \leftrightarrow \text{UO}_2(\text{SO}_4)(\text{aq})^-$	$3.15 \pm 0.02$	[GUI/FAN2003]
$\text{UO}_2(\text{SO}_4)_2^{2-}$	$\text{UO}_2^{2+} + 2\text{SO}_4^{2-} \leftrightarrow \text{UO}_2(\text{SO}_4)_2^{2-}$	$4.14 \pm 0.07$	[GUI/FAN2003]
$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ a)	$2\text{Ca}^{2+} + \text{UO}_2^{2+} + 3\text{CO}_3^{2-} \leftrightarrow \text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$	$30.60 \pm 0.09$	This report
$\text{CaUO}_2(\text{CO}_3)_3^{2-}$ a)	$\text{Ca}^{2+} + \text{UO}_2^{2+} + 3\text{CO}_3^{2-} \leftrightarrow \text{CaUO}_2(\text{CO}_3)_3^{2-}$	$27.18 \pm 0.06$	[DON/BRO2006]
$\text{MgUO}_2(\text{CO}_3)_3^{2-}$ a)	$\text{Mg}^{2+} + \text{UO}_2^{2+} + 3\text{CO}_3^{2-} \leftrightarrow \text{MgUO}_2(\text{CO}_3)_3^{2-}$	$26.13 \pm 0.08$	This report
$\text{UO}_2\text{SiO}(\text{OH})_3^+$	$\text{UO}_2^{2+} + \text{Si}(\text{OH})_4(\text{aq}) \leftrightarrow \text{UO}_2\text{SiO}(\text{OH})_3^+ + \text{H}^+$	$-1.84 \pm 0.1$	[GUI/FAN2003]

a) This species was selected in the data\_standard\_pitzer tables with restrictions (admission in the user's sole discretion).

Most of the data for aquatic species selected for THEREDA are evaluated in the NEA compilation [GRE/FUG1992,GUI/FAN2003]. Differences and additional values which are very important for the modelling are discussed in the following. Some species which were not considered or not enabled for the modelling but can be admitted in the user's sole discretion, respectively, are discussed briefly, too.

#### $\text{UO}_2(\text{OH})_4^{2-}$

This value is selected by [ALT/BRE2004] and was derived from solubility data (metaschoepite  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  and clarkeite  $\text{Na}[(\text{UO}_2)\text{O}(\text{OH})](\text{cr})$  in 5M NaCl and up to 4.5M  $\text{MgCl}_2$  solution) the collaborative partner KIT-INE ([NEC/ALT2003]).



From consistency reasons, this value is different from the value of [GUI/FAN2003] ( $-32.00 \pm 0.68$ ).

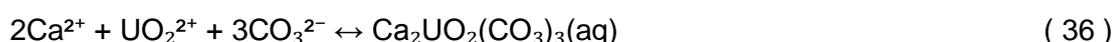
Also from consistency reasons, the species  $(\text{UO}_2)_2(\text{OH})^{3+}$  in [GUI/FAN2003] was **not selected**.



**$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ ,  $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ ,  $\text{MgUO}_2(\text{CO}_3)_3^{2-}$** 

Ternary aqueous complexes between alkaline earth metals, uranium(VI) and carbonate were reported by Bernhard et al. [BER/GEI1996] for the first time, with respect to  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ . Later, the originally reported stability constant of this species was updated based on new experiments [BER/GEI2001], and later GEI/AMA2008 this value changed again. They took into account the revised stability constant for the  $\text{UO}_2(\text{CO}_3)_3^{4-}$  complex that changed from  $21.60 \pm 0.05$  in [GRE/FUG1992] to  $21.84 \pm 0.04$  in [GUI/FAN2003]. Simultaneously, independent proofs for the  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$  (and related) species were provided by [KAL/CHO2000] and [DON/BRO2006]. [GUI/FAN2003] discussed the values in [BER/GEI2001] and [KAL/CHO2000]. They revealed some contradictions, which eventually prevented the  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$  and  $\text{CaUO}_2(\text{CO}_3)_3^{2-}$  species from being incorporated in the tables for recommended values, whereas the mere existence of these species was clearly acknowledged.

**$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ :** The available primary experimental data given in [BER/GEI2001], [KAL/CHO2000] and [DON/BRO2006] are revisited to obtain robust  $\log K^\circ$  values for the reaction



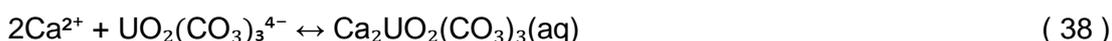
Before starting the data evaluation, a few words are necessary about extrapolating experimental thermodynamic values to infinite dilution applying the Davies equation for activity coefficient correction:

$$-\log f_i = Az_i^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - bI \right) \quad (37)$$

where  $f_i$  is the single ion activity coefficient,  $A$  is the Debye-Hückel parameter (and depends on temperature and pressure, see [MOO2011]),  $z_i$  the charge of the ion,  $I$  denotes the ionic strength and  $b$  is an empirical factor.

Though in widespread use, this approach is, unfortunately, an ambiguous one. Whereas the original paper by Davies [DAV1938] sets  $b$  to 0.2, in [DAV1962]  $b$  is changed to 0.3. To make things worse, the Davies equation is implemented in various codes differently: EQ3/6 uses  $b = 0.2$ , whereas FITEQL, MINTQA2 and PHREEQC use  $b = 0.3$ . So depending on the code extrapolations will deliver different activity coefficients despite formally following the same procedure.

Concerning the value published in [KAL/CHO2000] the shift of the formation constant for  $\text{UO}_2(\text{CO}_3)_3^{4-}$  has to be considered, this yields  $\log \beta_{213} = 30.04 \pm 0.70$ . The value from [DON/BRO2006] is retained, whereas its unrealistically low uncertainty is increased from 0.05 to 0.1. For [BER/GEI2001] the procedure becomes more complicated. Their experiments belong to two series, the five separately determined conditional  $\log K$  values ( $I = 0.1 \text{ M}$ ) for the reaction

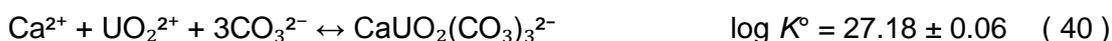


are listed in their Table 4. Applying the statistical methodology taking the uncertainty into account as recommended by the NEA TDB (Appendix C4 in all volumes), a weighted average  $\log K^\circ = 6.30 \pm 0.19$  is obtained. The correction to infinite dilution with a Davies factor of 0.3 leads to  $\log K^\circ = 8.87 \pm 0.19$ . Adding the  $\log K^\circ$  for the formation of  $\text{UO}_2(\text{CO}_3)_3^{4-}$  yields  $\log K^\circ = 30.71 \pm 0.19$  for the formation of  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ . Averaging then all three values finally delivers a recommended value of  $\log K^\circ = 30.60 \pm 0.09$  for reaction (36).

**$\text{CaUO}_2(\text{CO}_3)_3^{2-}$** : The formation constant of  $\text{CaUO}_2(\text{CO}_3)_3^{2-}$  ( $\log K^\circ = 25.4 \pm 0.25$ ) published in [BER/GEI2001] for the reaction



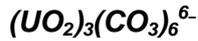
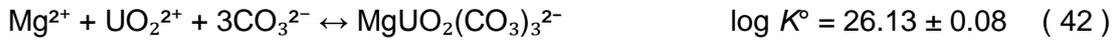
was comprehensibly criticized in [GUI/FAN2003] and consequently shifted in [GEI/AMA2008] to  $\log K^\circ = 26.93 \pm 0.25$ , but without any explanations how this new value was derived. Therefore, here only the value published in [DON/BRO2006] is recommended: with  $\log K^\circ = 27.18 \pm 0.06$  for the reaction



**$\text{MgUO}_2(\text{CO}_3)_3^{2-}$** : In case of the Mg analogues to the above discussed Ca complexes, so far there is only evidence for the  $\text{MgUO}_2(\text{CO}_3)_3^{2-}$  species, where stability constants were reported by both [DON/BRO2006] and GEI/AMA2008. The latter had a flaw in their ionic strength corrections in so far that they reported a correction value of 1.795. This, however, is not the right value for  $b = 0.3$  (as stated in their paper) but would refer to  $b = 0.2$ . Setting  $b = 0.3$  in Eq. (37) yields an ionic strength correction of only 1.713 for the reaction



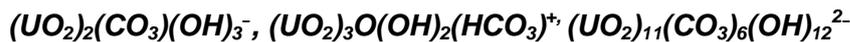
Consequently, the stability constant based on [GEI/AMA2008] changes to  $26.16 \pm 0.13$ . When increasing the uncertainty reported by [DON/BRO2006] to 0.10, the averaging of their value with the adjusted result from [GEI/AMA2008] leads to  $26.13 \pm 0.08$  for the reaction



[NEC/FAN2001] point out that solubility experiments with  $\text{UO}_2\text{CO}_3(\text{cr})$  as solid phase provided no evidence for this complex being relevant in the solid-liquid equilibrium. Furthermore, it is not possible to estimate reasonable Pitzer coefficients. Therefore the value in [GUI/FAN2003]



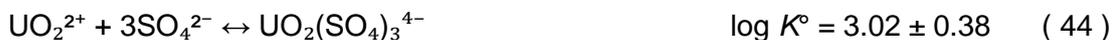
was **not selected** for THEREDA.



The values in [GUI/FAN2003] were derived from potentiometric titrations in solutions containing carbonate. These complexes dominate the speciation only at higher concentration near the visible precipitation or in supersaturated solution. According to [NEC/FAN2001], the stoichiometry and the formation constants of these complexes do not appear to be confirmed. Therefore and because no Pitzer parameters are available, the data are entered in the data\_standard\_pitzer tables of THEREDA, but with the label "Not enabled". An admission is possible in the user's sole discretion.



The formation of this species is not relevant under the discussed saline conditions, and no Pitzer parameters are available. So this species was not considered with the thermodynamic data given in [GUI/FAN2003].



For this species, no Pitzer parameters are available currently. Nevertheless, the species is important and necessary for modelling, so the data are entered in the data\_standard\_pitzer tables of THEREDA with the data quality label 3 (questionable value but nevertheless suitable and necessary for the description of experimental data in the system of interest).

## 4.2 Solid U(VI) phases

Table 7 shows the selected log  $K^\circ$  values for the formation of solid U(VI) phases.

Table 7 Selected log  $K^\circ$  values for the formation of solid U(VI) phases (original reactions and log  $K^\circ$  values in italics)

Solid phase	Formation reaction	log $K^\circ$	Reference
<b>Oxides</b>			
UO <sub>3</sub> ·2H <sub>2</sub> O(cr) Metaschoepite	UO <sub>2</sub> <sup>2+</sup> + 3H <sub>2</sub> O(l) ↔ UO <sub>3</sub> ·2H <sub>2</sub> O(cr) + 2H <sup>+</sup> <i>UO<sub>2</sub><sup>2+</sup> + 2OH<sup>-</sup> + H<sub>2</sub>O(l) ↔ UO<sub>3</sub>·2H<sub>2</sub>O(cr)</i>	-5.35 ± 0.13  <i>22.65 ± 0.13</i>	[ALT/BRE2004]
Ca(UO <sub>2</sub> )O <sub>4</sub> (OH) <sub>6</sub> ·8H <sub>2</sub> O(cr) Becquerelite	6UO <sub>2</sub> <sup>2+</sup> + Ca <sup>2+</sup> + 18H <sub>2</sub> O(l) ↔ Ca(UO <sub>2</sub> ) <sub>6</sub> O <sub>4</sub> (OH) <sub>6</sub> ·8H <sub>2</sub> O(cr) + 14H <sup>+</sup>	-40.5 ± 1.6	[GUI/FAN2003]
Na(UO <sub>2</sub> )O(OH)(cr) (=0.5Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub> ·H <sub>2</sub> O(cr)) Clarkeite	UO <sub>2</sub> <sup>2+</sup> + Na <sup>+</sup> + 2H <sub>2</sub> O(l) ↔ Na[(UO <sub>2</sub> )O(OH)](cr) + 3H <sup>+</sup> <i>UO<sub>2</sub><sup>2+</sup> + Na<sup>+</sup> + 3OH<sup>-</sup> ↔ Na[(UO<sub>2</sub>)O(OH)](cr) + H<sub>2</sub>O(l)</i>	-12.2 ± 0.2  <i>29.8 ± 0.2</i>	[ALT/BRE2004]
K <sub>2</sub> (UO <sub>2</sub> ) <sub>6</sub> O <sub>4</sub> (OH) <sub>6</sub> ·7H <sub>2</sub> O(cr) Compreignacite	6UO <sub>2</sub> <sup>2+</sup> + 2K <sup>+</sup> + 17H <sub>2</sub> O(l) ↔ K <sub>2</sub> (UO <sub>2</sub> ) <sub>6</sub> O <sub>4</sub> (OH) <sub>6</sub> ·7H <sub>2</sub> O(cr) + 14H <sup>+</sup>	-35.8 <i>+1.0/ -0.6</i>	[GOR/FEI2008]
Na <sub>2</sub> (UO <sub>2</sub> ) <sub>6</sub> O <sub>4</sub> (OH) <sub>6</sub> ·7H <sub>2</sub> O(cr) Na-Compreignacite	6UO <sub>2</sub> <sup>2+</sup> + 2Na <sup>+</sup> + 17H <sub>2</sub> O(l) ↔ Na <sub>2</sub> (UO <sub>2</sub> ) <sub>6</sub> O <sub>4</sub> (OH) <sub>6</sub> ·7H <sub>2</sub> O(cr) + 14H <sup>+</sup>	-39.4 <i>+2.2/ -1.4</i>	[GOR/FEI2008]
CaU <sub>2</sub> O <sub>7</sub> ·3H <sub>2</sub> O(cr)	2UO <sub>2</sub> <sup>2+</sup> + Ca <sup>2+</sup> + 6H <sub>2</sub> O(l) ↔ CaU <sub>2</sub> O <sub>7</sub> ·3H <sub>2</sub> O(cr) + 6H <sup>+</sup>	-23.4 ± 1.0	[ALT/NEC2006]
<b>Carbonates</b>			
Na <sub>4</sub> UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> (cr) Cejkaite	4Na <sup>+</sup> + 3CO <sub>3</sub> <sup>2-</sup> + UO <sub>2</sub> <sup>2+</sup> ↔ Na <sub>4</sub> UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> (cr) <i>4 Na<sup>+</sup> + UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup> ↔ Na<sub>4</sub>UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>(cr)</i>	27.18 ± 0.17  <i>-5.34 ± 0.16</i>	[GUI/FAN2003]
UO <sub>2</sub> (CO <sub>3</sub> )(cr) Rutherfordine	UO <sub>2</sub> <sup>2+</sup> + CO <sub>3</sub> <sup>2-</sup> ↔ UO <sub>2</sub> (CO <sub>3</sub> )(cr)	14.76 ± 0.02	[GUI/FAN2003]
<b>Silicates</b>			
KUO <sub>2</sub> (SiO <sub>3</sub> OH)(UO <sub>2</sub> )·H <sub>2</sub> O(cr) Boltwoodite	UO <sub>2</sub> <sup>2+</sup> + K <sup>+</sup> + Si(OH) <sub>4</sub> (aq) + H <sub>2</sub> O(l) ↔ KUO <sub>2</sub> (SiO <sub>3</sub> OH)·H <sub>2</sub> O(cr) + 3H <sup>+</sup>	-4.12 <i>+0.48/ -0.30</i>	[SHV/MAZ2011]
NaUO <sub>2</sub> (SiO <sub>3</sub> OH)(UO <sub>2</sub> )·H <sub>2</sub> O(cr) Na-Boltwoodite	UO <sub>2</sub> <sup>2+</sup> + Na <sup>+</sup> + Si(OH) <sub>4</sub> (aq) + H <sub>2</sub> O(l) ↔ NaUO <sub>2</sub> (SiO <sub>3</sub> OH)·H <sub>2</sub> O(cr) + 3H <sup>+</sup>	-6.07 <i>+0.16/ -0.26</i>	[SHV/MAZ2011]
(UO <sub>2</sub> ) <sub>2</sub> (SiO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O(cr) Soddyite	Si(OH) <sub>4</sub> (aq) + 2H <sub>2</sub> O(l) + 2UO <sub>2</sub> <sup>2+</sup> ↔ 4H <sup>+</sup> + (UO <sub>2</sub> ) <sub>2</sub> (SiO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O(cr)	-6.2 ± 1.0	[GUI/FAN2003]

Solid phase	Formation reaction	log $K^\circ$	Reference
Ca(UO <sub>2</sub> ) <sub>2</sub> (SiO <sub>3</sub> OH) <sub>2</sub> ·5H <sub>2</sub> O(cr) Uranophane	2Si(OH) <sub>4</sub> (aq) + 5H <sub>2</sub> O(l) + Ca <sup>2+</sup> + 2UO <sub>2</sub> <sup>2+</sup> ↔ Ca[(UO <sub>2</sub> ) <sub>2</sub> (SiO <sub>3</sub> OH) <sub>2</sub> ]·5H <sub>2</sub> O cr) + 6H <sup>+</sup>	-10.82 +0.62/ -0.29	[SHV/MAZ2011]
K <sub>2</sub> (UO <sub>2</sub> ) <sub>2</sub> (Si <sub>2</sub> O <sub>5</sub> ) <sub>3</sub> ·4H <sub>2</sub> O(cr) Weeksite	2K <sup>+</sup> + 2UO <sub>2</sub> <sup>2+</sup> + 6Si(OH) <sub>4</sub> (aq) ↔ 5H <sub>2</sub> O(l) + 6H <sup>+</sup> + K <sub>2</sub> [(UO <sub>2</sub> ) <sub>2</sub> (Si <sub>2</sub> O <sub>5</sub> ) <sub>3</sub> ]·4H <sub>2</sub> O(cr)	-16.91 <sup>b)</sup>	[HEM1982]
Na <sub>2</sub> (UO <sub>2</sub> ) <sub>2</sub> (Si <sub>2</sub> O <sub>5</sub> ) <sub>3</sub> ·4H <sub>2</sub> O(cr) Na-Weeksite	2Na <sup>+</sup> + 2UO <sub>2</sub> <sup>2+</sup> + 6Si(OH) <sub>4</sub> (aq) ↔ 5H <sub>2</sub> O(l) + Na <sub>2</sub> [(UO <sub>2</sub> ) <sub>2</sub> (Si <sub>2</sub> O <sub>5</sub> ) <sub>3</sub> ]·4H <sub>2</sub> O(cr) + 6H <sup>+</sup>	-1.5 ± 0.08	[GUI/FAN2003] <sup>a)</sup>
Mg(UO <sub>2</sub> ) <sub>2</sub> (SiO <sub>3</sub> OH) <sub>2</sub> ·6H <sub>2</sub> O(cr) Sklodowskite	Mg <sup>2+</sup> + 6H <sub>2</sub> O(l) + 2UO <sub>2</sub> <sup>2+</sup> + 2Si(OH) <sub>4</sub> (aq) ↔ 6H <sup>+</sup> + Mg[(UO <sub>2</sub> ) <sub>2</sub> (SiO <sub>3</sub> OH) <sub>2</sub> ]·6H <sub>2</sub> O (cr)	-14.48 <sup>b)</sup>	[HEM1982]
Ca(UO <sub>2</sub> ) <sub>2</sub> (Si <sub>2</sub> O <sub>5</sub> ) <sub>3</sub> ·5H <sub>2</sub> O(cr) Haiweeite	Ca <sup>2+</sup> + 2UO <sub>2</sub> <sup>2+</sup> + 6Si(OH) <sub>4</sub> (aq) ↔ 6H <sup>+</sup> + 4H <sub>2</sub> O(l) + Ca[(UO <sub>2</sub> ) <sub>2</sub> (Si <sub>2</sub> O <sub>5</sub> ) <sub>3</sub> ]·5H <sub>2</sub> O(cr)	5.52 <sup>b)</sup>	[HEM1982]
<b>Sulphates</b>			
UO <sub>2</sub> SO <sub>4</sub> ·2.5H <sub>2</sub> O(cr)	UO <sub>2</sub> <sup>2+</sup> + 2.5H <sub>2</sub> O(l) + SO <sub>4</sub> <sup>2-</sup> ↔ UO <sub>2</sub> (SO <sub>4</sub> )·2.5H <sub>2</sub> O(cr)	1.59 ± 0.02	[GUI/FAN2003]
UO <sub>2</sub> SO <sub>4</sub> ·3H <sub>2</sub> O(cr)	3H <sub>2</sub> O(l) + SO <sub>4</sub> <sup>2-</sup> + UO <sub>2</sub> <sup>2+</sup> ↔ UO <sub>2</sub> (SO <sub>4</sub> )·3H <sub>2</sub> O(cr) UO <sub>2</sub> SO <sub>4</sub> ·3.5H <sub>2</sub> O(cr) ↔ 0.5H <sub>2</sub> O(g) + UO <sub>2</sub> SO <sub>4</sub> ·3H <sub>2</sub> O(cr)	1.50 ± 0.03  0.83 ± 0.02	[GUI/FAN2003]
UO <sub>2</sub> SO <sub>4</sub> ·3.5H <sub>2</sub> O(cr)	UO <sub>2</sub> <sup>2+</sup> + 3.5H <sub>2</sub> O(l) + SO <sub>4</sub> <sup>2-</sup> ↔ UO <sub>2</sub> (SO <sub>4</sub> )·3.5H <sub>2</sub> O(cr)	1.59 ± 0.02	[GUI/FAN2003]
<b>Phosphates<sup>c)</sup></b>			
Ca(UO <sub>2</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> ·3(H <sub>2</sub> O)(cr) Autunite	2PO <sub>4</sub> <sup>3-</sup> + 3H <sub>2</sub> O(l) + Ca <sup>2+</sup> + 2UO <sub>2</sub> <sup>2+</sup> ↔ Ca(UO <sub>2</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O(cr)	48.36 ± 0.03	[GOR/SHV2009]
Mg(UO <sub>2</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> (cr) Saleeite	2UO <sub>2</sub> <sup>2+</sup> + Mg <sup>2+</sup> + 2PO <sub>4</sub> <sup>3-</sup> ↔ Mg[(UO <sub>2</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> ](cr) Mg <sup>2+</sup> + 2UO <sub>2</sub> OH <sup>-</sup> + 2H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> + 8 H <sub>2</sub> O(l) ↔ Mg(UO <sub>2</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> ·10H <sub>2</sub> O(cr) + 2H <sup>+</sup>	46.32  17.7	[MUT/HIR1968]
UO <sub>2</sub> (HPO <sub>4</sub> )·4H <sub>2</sub> O(cr) Chernikovite (H-Autunite)	H <sup>+</sup> + UO <sub>2</sub> <sup>2+</sup> + PO <sub>4</sub> <sup>3-</sup> + 4H <sub>2</sub> O(l) ↔ UO <sub>2</sub> (HPO <sub>4</sub> )·4H <sub>2</sub> O(cr) 4H <sub>2</sub> O(l) + H <sub>3</sub> PO <sub>4</sub> (aq) + UO <sub>2</sub> <sup>2+</sup> ↔ 2H <sup>+</sup> + UO <sub>2</sub> (HPO <sub>4</sub> )·4H <sub>2</sub> O(cr)	24.20 ± 0.10  2.50 ± 0.09	[GUI/FAN2003]
(UO <sub>2</sub> ) <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O(cr)	4H <sub>2</sub> O(l) + 2PO <sub>4</sub> <sup>3-</sup> + 3UO <sub>2</sub> <sup>2+</sup> ↔ (UO <sub>2</sub> ) <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O(cr)	49.36 ± 0.31	[GUI/FAN2003]

Solid phase	Formation reaction	log $K^\circ$	Reference
	$4\text{H}_2\text{O}(l) + 2\text{H}_3\text{PO}_4(aq) + 3\text{UO}_2^{2+} \leftrightarrow 6\text{H}^+ + (\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}(cr),$	$5.96 \pm 0.30$	
$(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}(cr)$	$6\text{H}_2\text{O}(l) + 3\text{UO}_2^{2+} + 2\text{PO}_4^{3-} \leftrightarrow (\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}(cr)$ $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}(cr) + 2\text{H}_2\text{O}(g) \leftrightarrow (\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}(cr),$	49.91  <3.54	[GUI/FAN2003]
$\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}(cr)$	$2\text{PO}_4^{3-} + 4\text{H}^+ + \text{UO}_2^{2+} + 3\text{H}_2\text{O}(l) \leftrightarrow \text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}(cr)$ $\text{UO}_2^{2+} + 2\text{H}_3\text{PO}_4(aq) + 3\text{H}_2\text{O}(l) \leftrightarrow \text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}(cr) + 2\text{H}^+$	45.1  1.7	[GRE/FUG1992]

a) Value not recommended but given as a guidance value for scoping calculations

b) log  $K^\circ$  calculated from thermochemical data

c) Attention: The solid phosphates are currently excluded from the data block because they will be subject to a future release

### **Metaschoepite $\text{UO}_3 \cdot 2\text{H}_2\text{O}(cr)$**

The name schoepite is commonly applied to a mineral or synthetic preparation with a formula close to  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ . In compliance with [GUI/FAN2003] it should be named metaschoepite [FIN/HAW1998]. Throughout the review [GUI/FAN2003] the name “schoepite”, commonly used by chemists, was however retained. THEREDA uses the name “metaschoepite” for the mineral with the formula  $\text{UO}_3 \cdot 2\text{H}_2\text{O}(cr)$ .

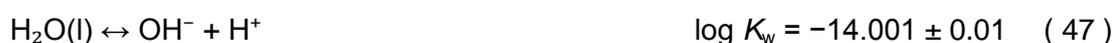


The log  $K^\circ$  was calculated from thermochemical data based on calorimetric measures with dried well defined solids [GUI/FAN2003]. However, this log  $K^\circ$  is not suitable to predict solubilities in geochemical calculations because the measured solubility of the solid phase in contact with water is a magnitude order higher. This was acknowledged by [HUM/BER2002] who selected the value log  $K^\circ = 5.97 \pm 0.14$  [SAN/BRU1992] from solubility studies.

From solubility experiments of metaschoepite, stable in dilute to concentrated NaCl solution at pH<7, [ALT/BRE2004] calculated a log  $K^\circ$  which is more suitable for geochemical calculations.



From this and



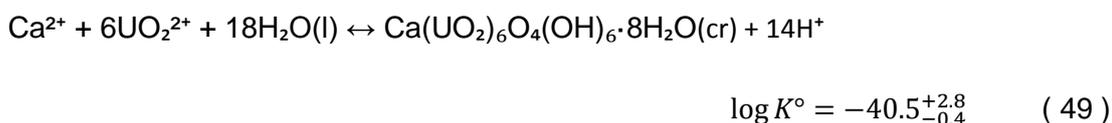
it follows that



***Becquerelite*  $\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 8\text{H}_2\text{O}(\text{cr})$**

Solubility measurements of the solid phase becquerelite  $\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 8\text{H}_2\text{O}(\text{cr})$  were performed by [SAN/GRA1994] at 298.15 K in 1 molal  $\text{CaCl}_2$  at several pH values, following the equilibrium. [GUI/FAN2003] calculated a  $\log K^\circ$  of  $39.5 \pm 1.0$  using SIT. This infinite dilution constant disagrees for unknown reasons substantially from those tabulated by [SAN/GRA1994]. [RAI/FEL2002] have made a very careful study of the solubility product of a synthetic becquerelite in  $2 \cdot 10^{-2}$ , 0.1 and 0.5 M  $\text{CaCl}_2$  at  $(296 \pm 2)$  K. In the pH range 4.4 to 9, the data refined using hydrolysis data for U(VI) selected by [GRE/FUG1992] and a Pitzer approach give a  $\log K^\circ$  of  $41.4 \pm 0.2$  (uncertainty was increased by [GUI/FAN2003] to 1.2). The selected value of [GUI/FAN2003] is the average of both values ( $\log K^\circ = 40.5 \pm 1.6$ ).

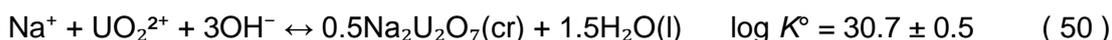
[GOR/FEI2008] performed solubility measurements from both undersaturation and supersaturation under controlled-pH conditions. The calculated  $\log K^\circ$  for becquerelite is lower than that of most previous measurements for synthetic becquerelite ([RAI/FEL2002, VOC/HAV1990]). However, because their experiments were reversed and the run products were well characterized, the value is more rigorously constrained than those from previous studies (uncertainty  $2\sigma$ ).



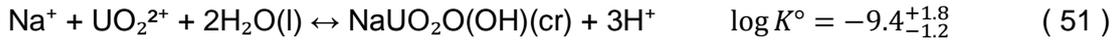
This value confirms the suggested mean value of [GUI/FAN2003] perfectly, so we keep the value of  $40.5 \pm 1.6$  in THEREDA.

***Clarkeite*  $\text{Na}[(\text{UO}_2)\text{O}(\text{OH})](\text{cr}) = 0.5 \text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$**

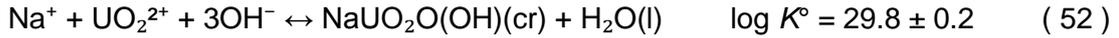
From thermochemical data [GUI/FAN2003] calculated an equilibrium constant for a crystalline anhydrous phase  $\text{Na}_2\text{U}_2\text{O}_7$



[GOR/FEI2008] performed solubility experiments of synthesized clarkeite under controlled-pH conditions, starting from undersaturation as well as supersaturation. The calculated solubility product with respective uncertainty resulting a  $\log K^\circ \pm 2\sigma$  (authors give  $1\sigma$ ) for the reaction:



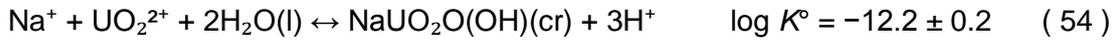
[ALT/BRE2004] published a value which was derived with Pitzer parameters from U(VI) hydrolysis solubility experiments. After preliminary studies (see [FAN/NEC2002]), extensive investigations were performed, including a correct determination of crystal water and in various matrix electrolyte solutions, were made. This value is consistent with the Pitzer parameters in THEREDA and the hydrolysis model in THEREDA. Though not published in a peer-reviewed journal, this value was selected for THEREDA.



From this and



it follows that

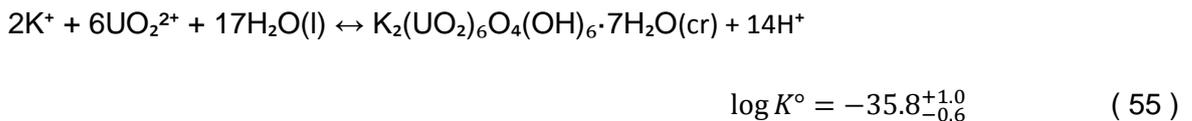


A comparable value of  $\log K^\circ = -29.45 \pm 1.04$  for  $\text{Na}_2\text{U}_2\text{O}_7(\text{cr,hyd})$  derived from solubility experiments in [YAM/KIT1998] is discussed in [GUI/FAN2003].

#### **Compreignacite $\text{K}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 7\text{H}_2\text{O}(\text{cr})$**

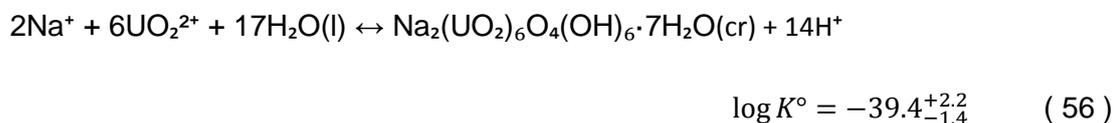
Solubility measurements of compreignacite,  $\text{K}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 8\text{H}_2\text{O}(\text{cr})$  were performed by Sandino and Grambow [SAN/GRA1994] at 298.15 K in 1 molal KCl at several pH values by allowing metaschoepite to convert to compreignacite and also by measuring the solubility of compreignacite directly. No experiment was conducted from supersaturation. [GUI/FAN2003] calculated the  $\log K^\circ$  of  $37.1 \pm 0.54$  using SIT. This infinite dilution constant disagrees for unknown reasons substantially from those tabulated by [SAN/GRA1994], but [GUI/FAN2003] retained the recalculated solubility products.

[GOR/FEI2008] obtained a  $\log K^\circ$  from supersaturation and undersaturation experiments, which is in agreement with the conversion experiment value of [SAN/GRA1994]. Therefore, this new value was selected (uncertainty  $2\sigma$ ).

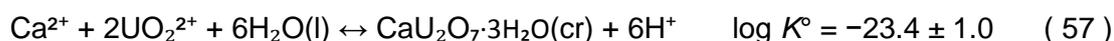


**Na-Compreignacite  $\text{Na}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 7\text{H}_2\text{O}(\text{cr})$** 

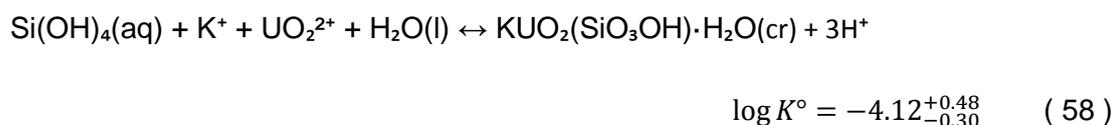
The only Na-compreignacite solubility experiments were performed by [GOR/FEI2008]. The substitution of sodium for potassium in compreignacite appears to increase its solubility product by approximately 3.5 orders of magnitude (uncertainty  $2\sigma$ ).

 **$\text{CaU}_2\text{O}_7 \cdot 3\text{H}_2\text{O}(\text{cr})$** 

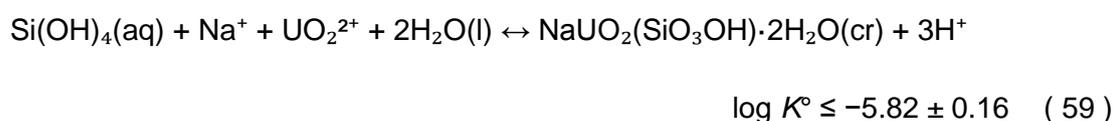
Calculated solubility curves of metaschoepite and becquerelite in  $\text{CaCl}_2$  solution differ strongly from the experimental data of [RAI/FEL2002] at  $\text{pH} > 8$  (0.02 – 0.5 M  $\text{CaCl}_2$ ). The solubility at  $\text{pH} > 8$  is much lower than expected for becquerelite. [RAI/FEL2002] determined a solid phase ratio Ca:U  $\approx$  1:2 (not 1:6 for becquerelite). [ALT/NEC2006] investigated the solubility of metaschoepite in 0.1 – 4.5M  $\text{CaCl}_2$  at  $\text{pH}$  9 – 12 and proved the evidence of calcium diuranate  $\text{CaU}_2\text{O}_7 \cdot 3\text{H}_2\text{O}(\text{cr})$  with XRD. The slow formation of this phase was reproducible. Based on the experimental data and SIT calculations the  $\log K^\circ$  for the reaction could be calculated:

**Boltwoodite  $\text{KUO}_2(\text{SiO}_3\text{OH}) \cdot \text{H}_2\text{O}(\text{cr})$** 

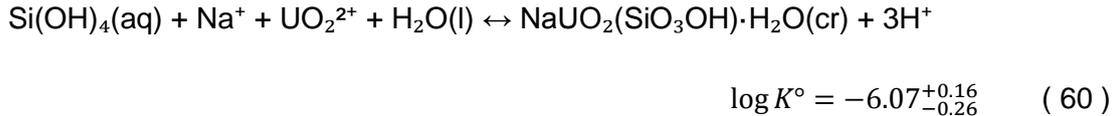
[SHV/MAZ2011] measured the formation enthalpy of synthetic boltwoodite by high temperature oxide melt solution chemistry. They also studied the aqueous solubility of these phase from both saturated and undersaturated conditions at a variety of  $\text{pH}$ , which was the first reported solubility measurement of boltwoodite.

**Na-Boltwoodite  $\text{NaUO}_2(\text{SiO}_3\text{OH}) \cdot \text{H}_2\text{O}(\text{cr})$** 

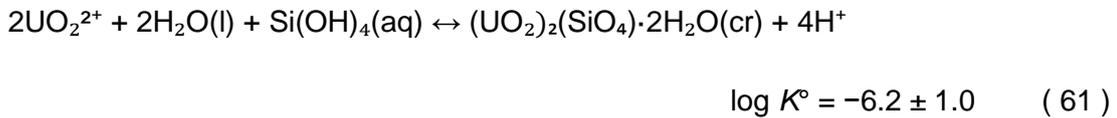
[NGU/SIL1992] determined the solubility of synthetic Na-boltwoodite in water under inert conditions. For reasons of purity of the phases and calculations and the probable supersaturation in terms of silica, [GUI/FAN2003] does not choose these values as recommended values, but suggested them for scoping calculations.



[SHV/MAZ2011] measured the formation enthalpy of synthetic Na-boltwoodite by high temperature oxide melt solution chemistry. They also studied the aqueous solubility of these phase from both saturated and undersaturated conditions at a variety of pH. The difference of  $\log K^\circ$  between boltwoodite and Na-boltwoodite explain [SHV/MAZ2011] with the influence of interlayer cations to the solubility (behaviour similar to compregnacite and Na-compregnacite, cf. [GOR/FEI2008]). We selected this value for THEREDA.



**Soddyite  $(\text{UO}_2)_2(\text{SiO}_4) \cdot 2\text{H}_2\text{O}(\text{cr})$**

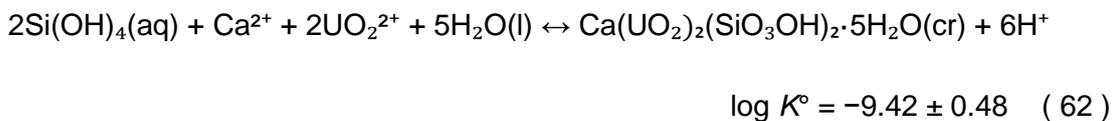


In view of non-concordant solubility constants, [GUI/FAN2003] does not recommend a value, but suggest, that the average value from NGU/SIL1992 and [MOL/GEI1996] ( $-6.7 \pm 0.5 / -5.74 \pm 0.21$ ) with increased uncertainty may be used as a guideline.

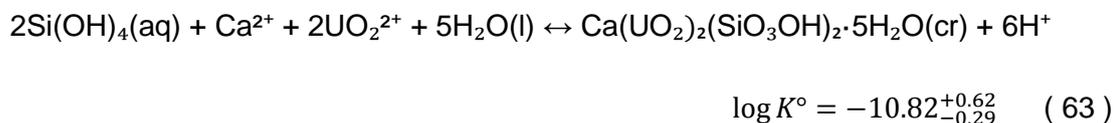
[GOR/MAZ2007] performed solubility measurements from both undersaturation and super-saturation and calorimetric measurements. The solubility measurements rigorously constrain the value of the solubility product of synthetic soddyite, and consequently its standard-state Gibbs free energy of formation. The equilibrium constant with its error ( $1\sigma$ ) is given with  $-6.43 +0.37/-0.2$ . This value confirms the suggested value of [GUI/FAN2003] very well, THEREDA keeps the value suggested by [GUI/FAN2003].

**Uranophane  $\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2 \cdot 5\text{H}_2\text{O}(\text{cr})$**

[NGU/SIL1992] determined the solubility of synthetic uranophane  $\text{Ca}(\text{H}_3\text{O})_2(\text{UO}_2)_2(\text{SiO}_4)_2 \cdot 3\text{H}_2\text{O}(\text{cr})$  (which is equivalent to  $\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2 \cdot 5\text{H}_2\text{O}(\text{cr})$ ) in water under inert conditions. For reasons of purity of the phases and calculations and the probable supersaturation in terms of silica, [GUI/FAN2003] does not choose these values as recommended values, but recommended it for scoping calculations.

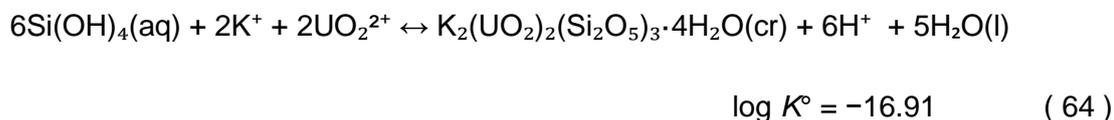


[SHV/MAZ2011] measured the formation enthalpy of synthetic uranophane by high temperature oxide melt solution chemistry. They also studied the aqueous solubility of these phase from both saturated and undersaturated conditions at a variety of pH. This value was selected for THEREDA.



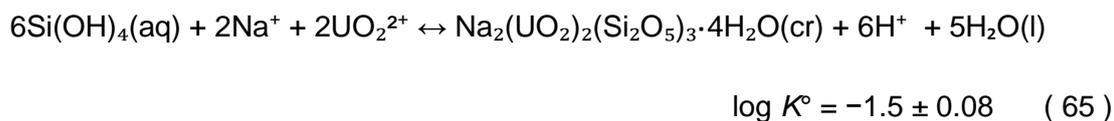
**Weeksite  $\text{K}_2(\text{UO}_2)_2(\text{Si}_2\text{O}_5)_3 \cdot 4\text{H}_2\text{O}(\text{cr})$**

[HEM1982] estimated a value for  $\Delta_f G^\circ = -9043 \pm 25$  kJ/mol. There are no log  $K$  values from solubility experiments available, the entered log  $K^\circ$  value in THEREDA is calculated from thermochemical data! Hence, the log  $K^\circ$  value should be used with reservation.



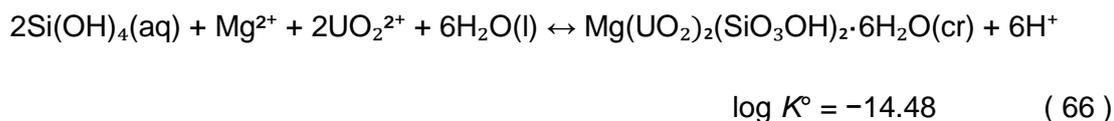
**Na-Weeksite  $\text{Na}_2(\text{UO}_2)_2(\text{Si}_2\text{O}_5)_3 \cdot 4\text{H}_2\text{O}(\text{cr})$**

NGU/SIL1992 determined the solubility of synthetic Na-weeksite in water under inert conditions. For reasons of purity of the phases and calculations and the probable supersaturation in terms of silica, [GUI/FAN2003] does not choose this value as recommended value, but it can be used in scoping calculations.



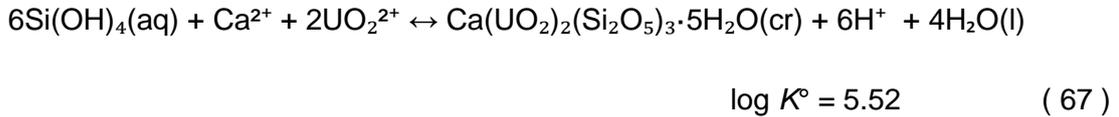
**Sklodowskite  $\text{Mg}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2 \cdot 6\text{H}_2\text{O}(\text{cr})$**

[HEM1982] estimated a value for  $\Delta_f G^\circ = -6319 \pm 25$  kJ/mol. There are no log  $K^\circ$  values from solubility experiments available, the entered log  $K^\circ$  value in THEREDA is calculated from thermochemical data! Hence, the log  $K^\circ$  value should be used with reservation.



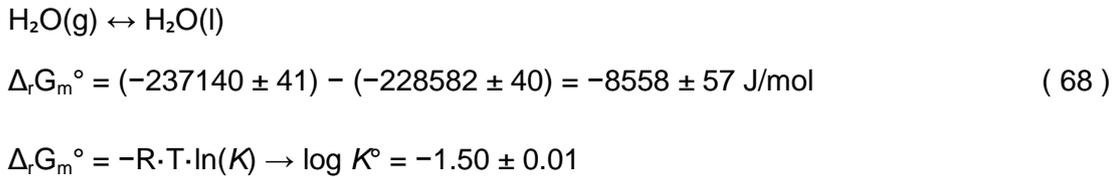
**Haiweeite  $\text{Ca}(\text{UO}_2)_2(\text{Si}_2\text{O}_5)_3 \cdot 5\text{H}_2\text{O}(\text{cr})$**

[HEM1982] estimated a value for  $\Delta_f G^\circ = -9396 \pm 25$  kJ/mol. There are no  $\log K^\circ$  values from solubility experiments available, the entered  $\log K^\circ$  value in THEREDA is calculated from thermochemical data! Hence, the  $\log K^\circ$  value should be used with reservation.

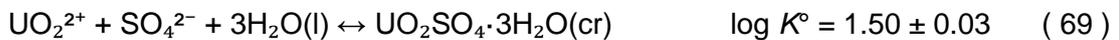


**$\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}(\text{cr})$**

With  $\text{H}_2\text{O}(\text{l})$  as primary master species for the element O, the formation reaction of  $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}(\text{cr})$  was transformed using the  $\log K^\circ$ , which is internally calculated in THEREDA:



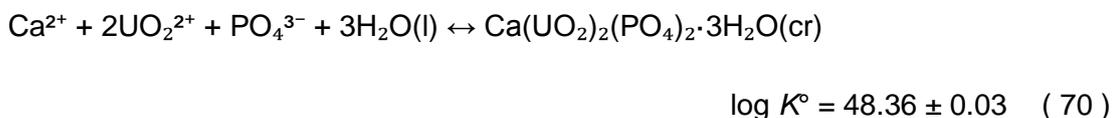
This leads to the transformed formation reaction and the respective  $\log K^\circ$ :



**Attention:** The following phosphate phases are currently excluded from the data block of the uranium release because they will be subject to a future release.

**Autunite  $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 3(\text{H}_2\text{O})(\text{cr})$**

[GOR/SHV2009] determined thermodynamic properties of the uranyl phosphates autunite  $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6(\text{H}_2\text{O})(\text{cr})$ , uranyl hydrogen phosphate  $\text{UO}_2(\text{HPO}_4) \cdot 3\text{H}_2\text{O}(\text{cr})$ , and uranyl orthophosphate  $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}(\text{cr})$  using solubility and (in the case of the two last) calorimetry measurements. The solubility experiments were made from both undersaturation and supersaturation. The minerals were characterized by XRD and FTIR.

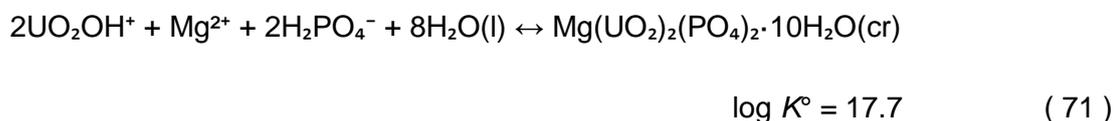


[GUI/FAN2003] did not select a  $\log K^\circ$  value because the composition of the mineral in [MUT1965] was not well established.

The  $\log K^\circ$  for  $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}(\text{cr})$  of  $49.36 + 0.04/-0.02$  is in excellent agreement with the value of [GUI/FAN2003] and has therefore been retained. The  $\log K^\circ$  for  $\text{UO}_2(\text{HPO}_4) \cdot 3\text{H}_2\text{O}(\text{cr})$  of 25.52 was not selected because of other water content, the value of [GUI/FAN2003] for  $\text{UO}_2(\text{HPO}_4) \cdot 4\text{H}_2\text{O}(\text{cr})$  24.202 (with basis species  $\text{PO}_4^{3-}$ ) was retained.

***Saleeite*  $\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}(\text{cr})$**

[MUT/HIR1968] performed solubility experiments, synthesis and exchange reactions among the H, Na, K, Mg, Ca, Sr, Ba, Fe, Cu and Pb autunites. The so calculated  $\log K^\circ$  should be used with reservation.



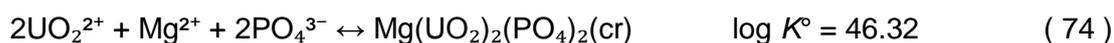
With



and



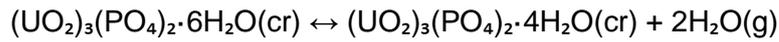
the  $\log K^\circ$  for the following reaction equation can be calculated



[LAN1978] gives values for the formation constants ( $\Delta_f G^\circ = -1111$  kcal/mol (-4648.4 kJ/mol) and estimated the  $\Delta_f H^\circ = -1189$  kcal/mol (-4974.8 kJ/mol) and  $S^\circ = 82$  cal/mol·K (343.1 J/mol·K)). In the absence of experimental published data [LAN1978] estimated the  $\Delta_f G^\circ$  values for the autunites with the least assumptions from the metal cation exchange free energies vs. H-autunite. He also estimated values for S and  $\Delta_f H$ . But erroneously he shows no water content of the uranyl phosphates with the statement that they are often poorly known and unnecessarily complicate the calculations.

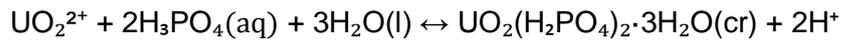
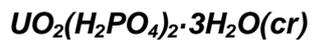
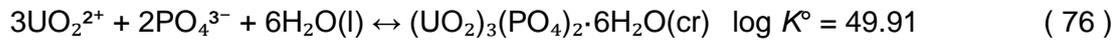
***(UO<sub>2</sub>)<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O(cr)***

[GUI/FAN2003] reworked the calculation of [GRE/FUG1992] and replaced the suggested  $\log K^\circ = \text{ca. } -3.54$  for the reaction



$$\log K^\circ \geq -3.54 \quad (75)$$

The transformation of the equation and recalculation of the  $\log K^\circ$  values additively leads to



$$\log K^\circ = 1.7 \quad (77)$$

This estimated value (without uncertainty) was not selected by [GRE/FUG1992] but given as a guideline. Transformation of the equation and recalculation of  $\log K^\circ$  leads to



$$\log K^\circ = 45.1 \quad (78)$$

### 4.3 Pitzer parameters for U(VI) species

In the following table, the respective Pitzer parameters for the aquatic species are summarized.

Table 8 Selected binary Pitzer parameters for U(VI) species

Cation i	Anion k	$z_i$	$z_k$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\Phi$	Reference
$UO_2^{2+}$	$Cl^-$	2	-1	0.42735	1.644	0	-0.03686	[NEC/FAN2001] <sup>(a)</sup>
$UO_2^{2+}$	$SO_4^{2-}$	2	-2	0.322	1.827		-0.0176	[NEC/FAN2001] <sup>(b)</sup>
$UO_2(OH)^+$	$Cl^-$	1	-1	0.15	0.3	0	0	[ALT/BRE2004] <sup>(c)</sup>
$(UO_2)_2(OH)_2^{2+}$	$Cl^-$	2	-1	0.5	1.6	0	0	[ALT/BRE2004] <sup>(c)</sup>
$(UO_2)_3(OH)_4^{2+}$	$Cl^-$	2	-1	0.07	1.6	0	0	[ALT/BRE2004] <sup>(c)</sup>
$(UO_2)_3(OH)_5^+$	$Cl^-$	1	-1	0.31	0.3	0	0	[ALT/BRE2004] <sup>(c)</sup>
$(UO_2)_4(OH)_7^+$	$Cl^-$	1	-1	0.23	0.3	0	0	[ALT/BRE2004] <sup>(c)</sup>
$Na^+$	$UO_2(OH)_2(aq)$	1	0	$\lambda = 0 \pm 0.1$				[NEC/FAN2001] <sup>(d)</sup>
$K^+$	$UO_2(OH)_2(aq)$	1	0	$\lambda = 0 \pm 0.1$				[NEC/FAN2001] <sup>(d)</sup>
$Mg^{2+}$	$UO_2(OH)_2(aq)$	2	0	$\lambda = 0 \pm 0.1$				[NEC/FAN2001]
$Ca^{2+}$	$UO_2(OH)_2(aq)$	2	0	$\lambda = 0 \pm 0.1$				[NEC/FAN2001]
$UO_2(OH)_2(aq)$	$Cl^-$	0	-1	$\lambda = 0 \pm 0.1$				[NEC/FAN2001] <sup>(d)</sup>
$UO_2(OH)_2(aq)$	$SO_4^{2-}$	0	-2	$\lambda = 0 \pm 0.1$				[NEC/FAN2001] <sup>(d)</sup>
$Na^+$	$UO_2(OH)_3^-$	1	-1	-0.24	0.3	0	0	[ALT/BRE2004] <sup>(c)</sup>
$Mg^+$	$UO_2(OH)_3^-$	2	-1	0.2	1.6	0	0	[ALT/BRE2004] <sup>(c)</sup>
$Na^+$	$UO_2(OH)_4^{2-}$	1	-2	0.16	1.6	0	0	[ALT/BRE2004] <sup>(c)</sup>
$Mg^{2+}$	$UO_2(OH)_4^{2-}$	2	-2	0	3	-40	0	[ALT/BRE2004] <sup>(c)</sup>
$Na^+$	$(UO_2)_3(OH)_7^-$	1	-1	-0.24	0.3	0	0	[ALT/BRE2004] <sup>(c)</sup>
$Mg^{2+}$	$(UO_2)_3(OH)_7^-$	2	-1	0.2	1.6	0	0	[ALT/BRE2004] <sup>(c)</sup>
$UO_2(CO_3)(aq)$	$Cl^-$	0	-1	$\lambda = -0.25 \pm 0.1$				[NEC/FAN2001] <sup>(d)</sup>
$UO_2(CO_3)(aq)$	$SO_4^{2-}$	0	-2	$\lambda = 0 \pm 0.1$				[NEC/FAN2001] <sup>(e)</sup>
$Na^+$	$UO_2(CO_3)(aq)$	1	0	$\lambda = 0.05$				[NEC/FAN2001] <sup>(f)</sup>
$Mg^{2+}$	$UO_2(CO_3)(aq)$	2	0	$\lambda = 0 \pm 0.1$				[NEC/FAN2001] <sup>(e)</sup>
$Na^+$	$UO_2(CO_3)_2^{2-}$	1	-2	0.212	2.5	0	0	[NEC/FAN2001] <sup>(g)</sup>
$Na^+$	$UO_2(CO_3)_3^{4-}$	1	-4	1.25	11.6	0	0	[NEC/FAN2001] <sup>(g)</sup>
$Na^+$	$UO_2(SO_4)_2^{2-}$	1	-2	$0.30 \pm 0.16$	1.9	0	0	[PLY/FAN1998] <sup>(h)</sup>
$UO_2(SO_4)(aq)$	$Cl^-$	0	-1	$\lambda=0$				[NEC/FAN2001]
$UO_2(SO_4)(aq)$	$SO_4^{2-}$	0	-2	$\lambda=0$				[NEC/FAN2001]
$Na^+$	$UO_2(SO_4)(aq)$	1	0	$\lambda=0$				[NEC/FAN2001]
$K^+$	$UO_2(SO_4)(aq)$	1	0	$\lambda=0$				[NEC/FAN2001]
$Mg^{2+}$	$UO_2(SO_4)(aq)$	2	0	$\lambda=0$				[NEC/FAN2001]

Cation i	Anion k	z <sub>i</sub>	z <sub>k</sub>	β <sup>(0)</sup>	β <sup>(1)</sup>	β <sup>(2)</sup>	C <sup>ϕ</sup>	Reference
Ca <sup>2+</sup>	UO <sub>2</sub> (SO <sub>4</sub> )(aq)	2	0	λ = 0				[NEC/FAN2001]

- a) Originally published in [PIT/MAY1973]
- b) Originally published in [PIT/MAY1974]
- c) Not published yet in a journal, preliminary results; derived by using a correlation of SIT and Pitzer coefficients [PLY/FAN1998], valence type MX: β<sup>(1)</sup><sub>MX</sub> = 0.3; β<sup>(0)</sup><sub>MX</sub> = 0.035 + ε<sub>MX</sub> \* (ln10)/2, valence type M<sub>2</sub>X or MX<sub>2</sub>: β<sup>(1)</sup><sub>MX</sub> = 1.6; β<sup>(0)</sup><sub>MX</sub> = 0.15 + ε<sub>MX</sub> \* (ln10)/2, experimental validation for ionic strength up to 5 M NaCl and 4.5 M MgCl<sub>2</sub>, respectively
- d) Originally published in [PAS/CZE1997], Estimated value assuming that Θ<sub>a/Cl</sub> = -0.25 ± 0.1 for a=Np(V)-carbonato complex NpO<sub>2</sub>(CO<sub>3</sub>)<sub>n</sub><sup>1-2n</sup> with n = 1 – 3 (in [FAN/NEC1995, RUN/NEU1996]), valid only for low ionic strength (<0.5 – 1m)
- e) Estimated value according to SIT with ε<sub>ik</sub> = 0 for neutral species
- f) Originally published in [PAS/CZE1997]
- g) Pitzer equation parameterized on the basis of the literature data
- h) Estimation of binary Pitzer parameters β<sup>(0)</sup><sub>ik</sub> and β<sup>(1)</sup><sub>ik</sub>, based on semi-empirical correlation of SIT coefficient ε<sub>ik</sub> and Pitzer parameters β<sup>(0)</sup><sub>ik</sub> and β<sup>(1)</sup><sub>ik</sub>, fitted parameter β<sup>(1)</sup><sub>ik</sub>

Table 9 Selected ternary Pitzer parameters for U(VI)

Cation i	Cation j	Θ <sub>ij</sub>	Ψ <sub>ijCl</sub>	Ψ <sub>ijClO4</sub>	Reference
UO <sub>2</sub> <sup>2+</sup>	Na <sup>+</sup>	0	0		[ALT/BRE2004] <sup>a)</sup>
(UO <sub>2</sub> ) <sub>3</sub> (OH) <sub>4</sub> <sup>2+</sup>	Na <sup>+</sup>	0.05	0		[ALT/BRE2004] <sup>a)b)</sup>
(UO <sub>2</sub> ) <sub>3</sub> (OH) <sub>5</sub> <sup>+</sup>	Mg <sup>2+</sup>	0	-0.08		[ALT/BRE2004] <sup>a)b)</sup>
Anion i	Anion j	Θ <sub>ij</sub>	Ψ <sub>ijCl</sub>	Ψ <sub>ijClO4</sub>	Reference
UO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>	Cl <sup>-</sup>	0.25 ± 0.1			[NEC/FAN2001] <sup>c)</sup>
UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>4-</sup>	Cl <sup>-</sup>	0.25 ± 0.1			[NEC/FAN2001] <sup>c)</sup>

- a) Not published yet in a journal, preliminary results
- b) Fit to solubility data of metaschoepite in concentrated NaCl and MgCl<sub>2</sub>
- c) Estimated value based on analogous value of Np(V)-species assuming that Θ<sub>a/Cl</sub> = -0.25 ± 0.1 for a=Np(V)-carbonato complex NpO<sub>2</sub>(CO<sub>3</sub>)<sub>n</sub><sup>1-2n</sup> with n = 1 – 3 (in [FAN/NEC1995, RUN/NEU1996])

Only few Pitzer parameters for the U(VI) species can be found in the literature derived from experimental data directly. [NEC/FAN2001] list the essential and available Pitzer parameters to describe the activity coefficients of aquatic U(VI) species in highly-concentrated brine solutions of the system Na-K-Mg-Ca-Cl-SO<sub>4</sub>-H<sub>2</sub>O. The authors describe the data situation, validity and constraints in detail. Based on own experiments and on estimations, in [ALT/BRE2004] and [ALT/NEC2006] some more parameters are given. In terms of the consistent data set for the hydrolysis species in [ALT/BRE2004], [ALT/NEC2006] want to emphasize the preliminary character of the values. Basis is the hydrolysis schema of [GUI/FAN2003] (with one exception: UO<sub>2</sub>(OH)<sub>4</sub><sup>2-</sup>), the data are experimentally validated for the whole ionic strength range up to 5 M NaCl and 4.5 M

MgCl<sub>2</sub> (inclusive of precipitates). Nevertheless, experimental results after these works showed the need to revise the data set which will result in partially different values.

Attention: The effect of weak chloride complexation is already included in the binary parameters between UO<sub>2</sub><sup>2+</sup> and Cl<sup>-</sup>. So the formulation of additional chloride complexes has to be omitted.

## 5 Data evaluation of U(IV) and U(VI)

### 5.1 Categories

To evaluate the data, three different categories have been used [ALT/BRE2011]:

- Data source
- Data class
- Data quality

For every category a numerical flag is used to describe the grading in steps from 1 to 6. The higher this numerical flag, the lower is the rating of the datum's reliability.

The flag "0" (zero) is used for values that are definitions or convention fixed values, data types produced by an internal calculation procedure have been flagged "-1".

#### Data source

The category "Data source" is used to describe the rating of a datum in terms of their origin.

Table 10 Data source flags and their definitions

Symbol	Description
-1	Internally calculated
0	By definition / convention fixed value
1	Value taken from an international review (e. g. CODATA, NEA TDB) or from an internationally acknowledged review article
2	Value taken from an institutional review
3	Value is based upon a number of publicly accessible publications (paper, report)
4	Value is based upon a single publicly accessible publication (paper, report)
5	Value is based upon internal sources not available to the public, but available to editors of THEREDA
6	Data source not yet entered (to be done)

#### Data class

The category "Data class" is used to describe the rating of a datum in terms of their determination. The assessment distinguishes between experimental values, chemical analogies, estimates and values of unknown origin. A distinction is made between experimental values (e.g. from solubility experiments) and thermochemically determined values. This is indicated by the category flag R and F, respectively.

Table 11 Data class flags and their definitions

Symbol	Category	Description
-1	F	Internally calculated with CalcMode CF, CGHF or CTPFUNC
-1	R	Internally calculated with CalcMode CR, CGHR or CRLOG
0	F	By definition / convention fixed value
0	R	By definition / convention fixed value
1	F	Value based upon experimental thermochemical data
1	R	Value based upon experimental equilibrium data in aqueous solution
2	F	Chemical analogue value, based upon thermochemical data
2	R	Chemical analogue value, based upon experimental equilibrium data in aqueous solution
3	F	Estimated value, based upon founded correlations and models for formation data
3	R	Estimated value, based upon founded correlations and models for reaction data
4	NA	Origin of value not reported; data class cannot be determined
5	NA	Not consistent with other data in THEREDA
6	NA	Data class not yet entered (to be done)

### Data quality

The category "Data quality" is used to describe the rating of a datum's quality.

Table 12 Data quality flags and their definitions

Symbol	Description
-1	Internally calculated
0	By definition / convention fixed value
1	Reliable datum
2	Datum is reliable within the given range of error, but error is relatively high (because of experimental problems, errors in utilized auxiliary data, or uncertainties due to inappropriate analogy-data or methods of estimation)
3	Questionable value (uncertain model for speciation, uncertain auxiliary data), but nevertheless suitable and necessary for the description of experimental data in the system of interest
4	Suitability for modelling or correctness not yet determined
5	Scrutinized and deemed inapplicable for modelling (due to experimental shortcomings or inadequate assumptions in the course of processing experimental data or inadequate estimation procedures)
6	Data quality not yet entered (to be done)

## 5.2 Data evaluation

In the following tables, the data evaluation flags (Data Class, Data Source und Data Quality) are assembled for the equilibrium constants  $\log K^\circ$  of the aquatic species and solid phases and for the Pitzer interaction parameters.

Table 13 Data evaluation of the solid U(IV) and U(VI) species (only for the  $\log K^\circ$ )

Phase	Data Class	Data Source	Data Quality	Comment
UO <sub>2</sub> (cr)	-1F	-1	-1	Internally calculated from thermochemical data, equilibrium constraint "Dissociation"
U(OH) <sub>4</sub> (am)	1R	1	1	
U(OH) <sub>2</sub> (SO <sub>4</sub> )(cr)	1R	1	1	
U(SiO <sub>4</sub> )(cr) Coffinite	-1F	-1	-1	
CaU(PO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O(cr) Ningoyite	1R	4	3	
U(HPO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O(cr)	1R	1	1	
UO <sub>3</sub> ·2H <sub>2</sub> O(cr) Metaschoepite	1R	4	1	
Ca(UO <sub>2</sub> )O <sub>4</sub> (OH) <sub>6</sub> ·8H <sub>2</sub> O(cr) Becquerelite	1R	1	1	
Na(UO <sub>2</sub> )O(OH)(cr) Clarkeite	1R	4	2	
K <sub>2</sub> (UO <sub>2</sub> ) <sub>6</sub> O <sub>4</sub> (OH) <sub>6</sub> ·7H <sub>2</sub> O(cr) Compreignacite	1R	4	2	
Na <sub>2</sub> (UO <sub>2</sub> ) <sub>6</sub> O <sub>4</sub> (OH) <sub>6</sub> ·7H <sub>2</sub> O(cr) Na-Compreignacite	1R	4	2	
CaU <sub>2</sub> O <sub>7</sub> ·3H <sub>2</sub> O(cr)	1R	5	2	
Na <sub>4</sub> UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> (cr) Cejkaite	1R	1	1	
UO <sub>2</sub> (CO <sub>3</sub> )(cr) Rutherfordine	1R	1	1	
KUO <sub>2</sub> (SiO <sub>3</sub> OH)(UO <sub>2</sub> )·H <sub>2</sub> O(cr) Boltwoodite	1R	4	2	
NaUO <sub>2</sub> (SiO <sub>3</sub> OH)(UO <sub>2</sub> )·H <sub>2</sub> O(cr) Na-Boltwoodite	1R	4	2	
(UO <sub>2</sub> ) <sub>2</sub> (SiO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O(cr) Soddyite	1R	1	2	
Ca(UO <sub>2</sub> ) <sub>2</sub> (SiO <sub>3</sub> OH) <sub>2</sub> ·5H <sub>2</sub> O(cr) Uranophane	1R	4	2	
K <sub>2</sub> (UO <sub>2</sub> ) <sub>2</sub> (Si <sub>2</sub> O <sub>5</sub> ) <sub>3</sub> ·4H <sub>2</sub> O(cr) Weeksite	3F	4	3	Based on thermochemical data of [HEM1982], $\log K^\circ$ calculated from DFG
Na <sub>2</sub> (UO <sub>2</sub> ) <sub>2</sub> (Si <sub>2</sub> O <sub>5</sub> ) <sub>3</sub> ·4H <sub>2</sub> O(cr)	1R	1	2	

Phase	Data Class	Data Source	Data Quality	Comment
Na-Weeksite				
Mg(UO <sub>2</sub> ) <sub>2</sub> (SiO <sub>3</sub> OH) <sub>2</sub> ·6H <sub>2</sub> O(cr) Sklodowskite	3F	4	3	Based on thermochemical data of [HEM1982], log K° calculated from DFG
Ca(UO <sub>2</sub> ) <sub>2</sub> (SiO <sub>2</sub> ) <sub>3</sub> ·5H <sub>2</sub> O(cr) Haiweeite	3F	4	3	Based on thermochemical data of [HEM1982], log K° calculated from DFG
UO <sub>2</sub> SO <sub>4</sub> ·2.5H <sub>2</sub> O(cr)	-1R	-1	-1	Internally calculated from DFG [GUI/FAN2003]
UO <sub>2</sub> SO <sub>4</sub> ·3H <sub>2</sub> O(cr)	1R	1	1	
UO <sub>2</sub> SO <sub>4</sub> ·3.5H <sub>2</sub> O(cr)	-1R	-1	-1	Internally calculated from DFG [GUI/FAN2003]
Ca(UO <sub>2</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> ·3(H <sub>2</sub> O)(cr) Autunite	1R	4	4	
Mg(UO <sub>2</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> (cr) Saleeite	1R	4	4	
(UO <sub>2</sub> )(HPO <sub>4</sub> )·4H <sub>2</sub> O(cr) Chernikovite (H-Autunite)	1R	1	1	
(UO <sub>2</sub> ) <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O(cr)	1R	1	1	
(UO <sub>2</sub> ) <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O(cr)	1R	1	2	
UO <sub>2</sub> (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O(cr)	3R	1	3	

Table 14 Data evaluation of the aqueous U(IV) and U(VI) species (only for log K°)

Phase	Data Class	Data Source	Data Quality	Comment
U <sup>4+</sup>	1R	1	1	
U(OH) <sup>3+</sup>	1R	1	1	
U(OH) <sub>2</sub> <sup>2+</sup>	3R	2	2	
U(OH) <sub>3</sub> <sup>+</sup>	3R	2	2	
U(OH) <sub>4</sub> (aq)	1R	1	3	
U(CO <sub>3</sub> ) <sub>4</sub> <sup>4-</sup>	1R	1	1	
U(CO <sub>3</sub> ) <sub>5</sub> <sup>6-</sup>	1R	4	3	
U(OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>	1R	2	3	
U(SO <sub>4</sub> ) <sup>2+</sup>	2R	2	4	
U(SO <sub>4</sub> ) <sub>2</sub> (aq)	2R	2	4	
UO <sub>2</sub> <sup>2+</sup>				Primary species, no log K°
UO <sub>2</sub> (OH) <sup>+</sup>	1R	1	1	
UO <sub>2</sub> (OH) <sub>2</sub> (aq)	1R	1	1	
UO <sub>2</sub> (OH) <sub>3</sub> <sup>-</sup>	1R	1	1	

Phase	Data Class	Data Source	Data Quality	Comment
$\text{UO}_2(\text{OH})_4^{2-}$	1R	4	2	
$(\text{UO}_2)_2(\text{OH})_2^{2+}$	1R	1	1	
$(\text{UO}_2)_3(\text{OH})_4^{2+}$	1R	1	1	
$(\text{UO}_2)_3(\text{OH})_5^+$	1R	1	1	
$(\text{UO}_2)_3(\text{OH})_7^-$	1R	1	1	
$(\text{UO}_2)_4(\text{OH})_7^+$	1R	1	1	
$\text{UO}_2(\text{CO}_3)(\text{aq})$	1R	1	1	
$\text{UO}_2(\text{CO}_3)_2^{2-}$	1R	1	1	
$\text{UO}_2(\text{CO}_3)_3^{4-}$	1R	1	1	
$(\text{UO}_2)_2(\text{CO}_3)(\text{OH})_3^{-\text{a}}$	1R	1	4	No Pitzer parameters available
$(\text{UO}_2)_3\text{O}(\text{OH})_2(\text{HCO}_3)^{+\text{a}}$	1R	1	4	No Pitzer parameters available
$(\text{UO}_2)_{11}(\text{CO}_3)_6(\text{OH})_{12}^{2-\text{a}}$	1R	1	4	No Pitzer parameters available
$\text{UO}_2(\text{SO}_4)(\text{aq})$	1R	1	1	
$\text{UO}_2(\text{SO}_4)_2^{2-}$	1R	1	1	
$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})^{\text{a}}$	1R	3	1	No Pitzer parameters available
$\text{CaUO}_2(\text{CO}_3)_3^{2-\text{a}}$	1R	4	1	No Pitzer parameters available
$\text{MgUO}_2(\text{CO}_3)_3^{2-\text{a}}$	1R	3	1	No Pitzer parameters available
$\text{UO}_2\text{SiO}(\text{OH})_3^+$	1R	1	3	No Pitzer parameters available

a) This species was selected with restrictions, see text in the chapter 4.1.

Table 15 Data evaluation of U interaction parameters

Interaction parameter	Interaction type	Data Class	Data Source	Data Quality	Comment
$\text{U}^{4+}:\text{Cl}^-$	Pitzer binary	3	2	2	
$\text{UOH}^{3+}:\text{Cl}^-$	Pitzer binary	3	2	2	
$\text{U}(\text{OH})_2^{2+}:\text{Cl}^-$	Pitzer binary	3	2	2	
$\text{U}(\text{OH})_3^+:\text{Cl}^-$	Pitzer binary	3	2	2	
$\text{U}(\text{OH})_4(\text{aq}):\text{Na}^+$	Pitzer lambda	2	2	2	
$\text{U}(\text{OH})_4(\text{aq}):\text{K}^+$	Pitzer lambda	2	2	2	
$\text{U}(\text{OH})_4(\text{aq}):\text{Mg}^{2+}$	Pitzer lambda	2	2	2	
$\text{U}(\text{OH})_4(\text{aq}):\text{Cl}^-$	Pitzer lambda	2	2	2	
$\text{U}(\text{CO}_3)_4^{4-}:\text{Na}^+$	Pitzer binary	2	2	2	
$\text{U}(\text{CO}_3)_4^{4-}:\text{K}^+$	Pitzer binary	2	2	2	
$\text{U}(\text{CO}_3)_5^{6-}:\text{Na}^+$	Pitzer binary	1	2	3	
$\text{U}(\text{CO}_3)_5^{6-}:\text{Na}^+$	Pitzer binary	1	2	3	
$\text{U}(\text{OH})_2(\text{CO}_3)_2^{2-}:\text{Na}^+$	Pitzer binary	2	2	2	

Interaction parameter	Interaction type	Data Class	Data Source	Data Quality	Comment
$U(OH)_2(CO_3)_2^{2-}:Na^+$	Pitzer binary	2	2	2	
$USO_4^{2+}:Cl^-$	Pitzer binary	2	2	4	
$U(SO_4)_2(aq):Cl^-$	Pitzer binary	2	2	4	
$UO_2^{2+}:Cl^-$	Pitzer binary	1	2	1	
$UO_2^{2+}:SO_4^{2-}$	Pitzer binary	1	2	4	
$UO_2(OH)^+:Cl^-$	Pitzer binary	3	4	1	Preliminary value
$(UO_2)_2(OH)_2^{2+}:Cl^-$	Pitzer binary	3	4	1	Preliminary value
$(UO_2)_3(OH)_4^{2+}:Cl^-$	Pitzer binary	3	4	1	Preliminary value
$(UO_2)_3(OH)_5^+:Cl^-$	Pitzer binary	3	4	1	Preliminary value
$(UO_2)_4(OH)_7^+:Cl^-$	Pitzer binary	3	4	1	Preliminary value
$UO_2(OH)_2(aq):Na^+$	Pitzer lambda	3	2	1	
$UO_2(OH)_2(aq):K^+$	Pitzer lambda	3	2	1	
$UO_2(OH)_2(aq):Mg^{2+}$	Pitzer lambda	3	2	1	
$UO_2(OH)_2(aq):Cl^-$	Pitzer lambda	3	2	1	
$UO_2(OH)_2(aq):SO_4^{2-}$	Pitzer lambda	3	2	1	
$UO_2(OH)_3^-:Na^+$	Pitzer binary	3	4	1	Preliminary value
$UO_2(OH)_3^-:Mg^{2+}$	Pitzer binary	3	4	1	Preliminary value
$UO_2(OH)_4^{2-}:Na^+$	Pitzer binary	3	4	1	Preliminary value
$UO_2(OH)_4^{2-}:Mg^{2+}$	Pitzer binary	3	4	1	Preliminary value
$(UO_2)_3(OH)_7^-:Na^+$	Pitzer binary	3	4	1	Preliminary value
$(UO_2)_3(OH)_7^-:Mg^{2+}$	Pitzer binary	3	4	1	Preliminary value
$UO_2(CO_3)(aq):Cl^-$	Pitzer lambda	2	2	1	
$UO_2(CO_3)(aq):SO_4^{2-}$	Pitzer lambda	3	2	4	
$UO_2(CO_3)(aq):Na^+$	Pitzer lambda	1	2	1	
$UO_2(CO_3)(aq):Mg^{2+}$	Pitzer lambda	3	2	1	
$UO_2(CO_3)_2^{2-}:Na^+$	Pitzer binary	1	2	1	
$UO_2(CO_3)_3^{4-}:Na^+$	Pitzer binary	1	2	1	
$UO_2(SO_4)_2^{2-}:Na^+$	Pitzer binary	3	4	4	Preliminary value
$UO_2(SO_4)(aq):Cl^-$	Pitzer lambda	3	2	4	
$UO_2(SO_4)(aq):SO_4^{2-}$	Pitzer lambda	3	2	4	
$UO_2(SO_4)(aq):Na^+$	Pitzer lambda	3	2	4	
$UO_2(SO_4)(aq):K^+$	Pitzer lambda	3	2	4	
$UO_2(SO_4)(aq):Mg^{2+}$	Pitzer lambda	3	2	4	
$UO_2(SO_4)(aq):Ca^{2+}$	Pitzer lambda	3	2	4	
$UO_2^{2+}:Na^+$	Pitzer theta	3	4	1	Preliminary value
$UO_2^{2+}:Na^+:Cl^-$	Pitzer psi	3	4	1	Preliminary value

Interaction parameter	Interaction type	Data Class	Data Source	Data Quality	Comment
$(\text{UO}_2)_3(\text{OH})_4^{2+}:\text{Na}^+$	Pitzer theta	3	4	1	Preliminary value
$(\text{UO}_2)_3(\text{OH})_4^{2+}:\text{Na}^+:\text{Cl}^-$	Pitzer psi	3	4	1	Preliminary value
$(\text{UO}_2)_3(\text{OH})_5^+:\text{Mg}^{2+}$	Pitzer theta	3	4	1	Preliminary value
$(\text{UO}_2)_3(\text{OH})_5^+:\text{Mg}^{2+}:\text{Cl}^-$	Pitzer psi	3	4	1	Preliminary value
$\text{UO}_2(\text{CO}_3)_2^{2-}:\text{Cl}^-$	Pitzer theta	2	2	1	
$\text{UO}_2(\text{CO}_3)_3^{4-}:\text{Cl}^-$	Pitzer theta	2	2	1	

## 6 Comparing numerical and experimental results

A number of U(IV) / U(VI) solubility calculations have been performed to demonstrate the possibilities of the compiled data set. The calculated chemical scenarios are taken from literature references with the corresponding solubility experiments of various uranium phases in high saline solutions:

- Solubility of  $U(OH)_4(am)$  in  $\leq 1$  M  $NaHCO_3$  solution [RAI/FEL1995],
- Solubility of  $U(OH)_4(am)$  in  $\leq 5$  M  $K_2CO_3$  solution with 0.01 M NaOH [RAI/FEL1995],
- Solubility of  $U(OH)_4(am)$  in 1 m NaCl [NEC/KIM2001],
- Solubility of Becquerelite in 1 m  $CaCl_2$  [SAN/GRA1994],
- Solubility of Compreignacite in 1 m KCl, [SAN/GRA1994],
- Solubility of Metaschoepite/Clarkeite in 0.5 m NaCl, from [FAN/NEC2002],
- Solubility of Metaschoepite in 5 m NaCl, [DIA/GRA1998]

The following graphics compare the numerical results of the test case calculations using Geochemist's Workbench® (Modul React Release 10.0.7) with measured values from the literature. The nomenclature of the axis labels is adopted from the original literature reference where the experimental were taken from.

## 6.1 Test calculations for U(IV) solubilities

### Case 1:

The solubility of fresh precipitated  $U(OH)_4(am)$  in  $\leq 1$  M  $NaHCO_3$  solution was calculated according to the experimental conditions given in [RAI/FEL1995] (Fig. 6-1).

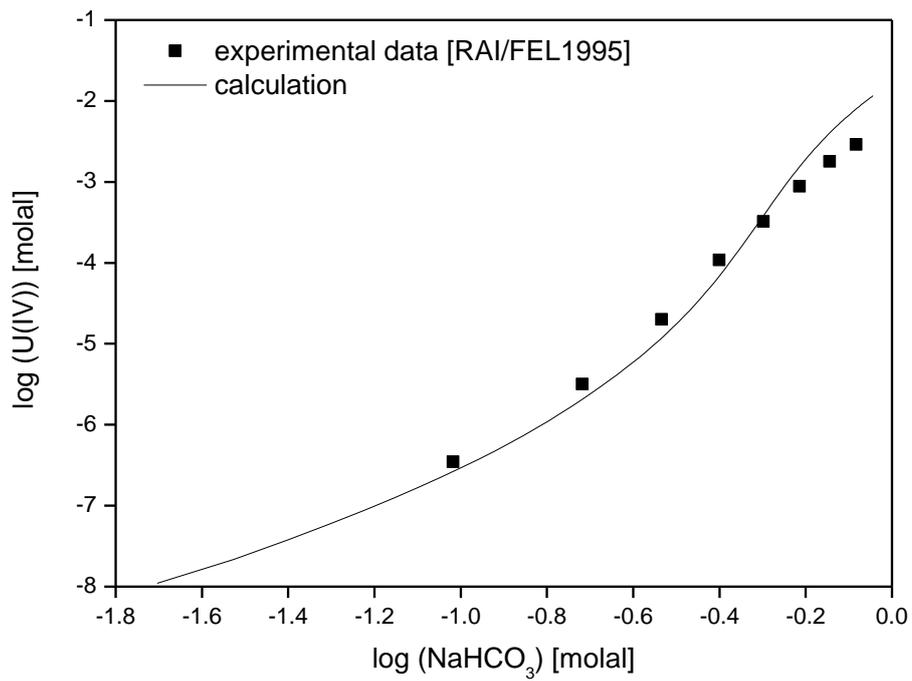


Fig. 6-1: Solubility of  $U(OH)_4(am)$  in  $\leq 1$  M  $NaHCO_3$  solution, measured values taken from [RAI/FEL1995].

**Case 2:**

The solubility of fresh precipitated  $U(OH)_4(am)$  in  $\leq 5$  M  $K_2CO_3$  solution was calculated according to the experimental conditions given in [RAI/FEL1995] (Fig. 6-2).

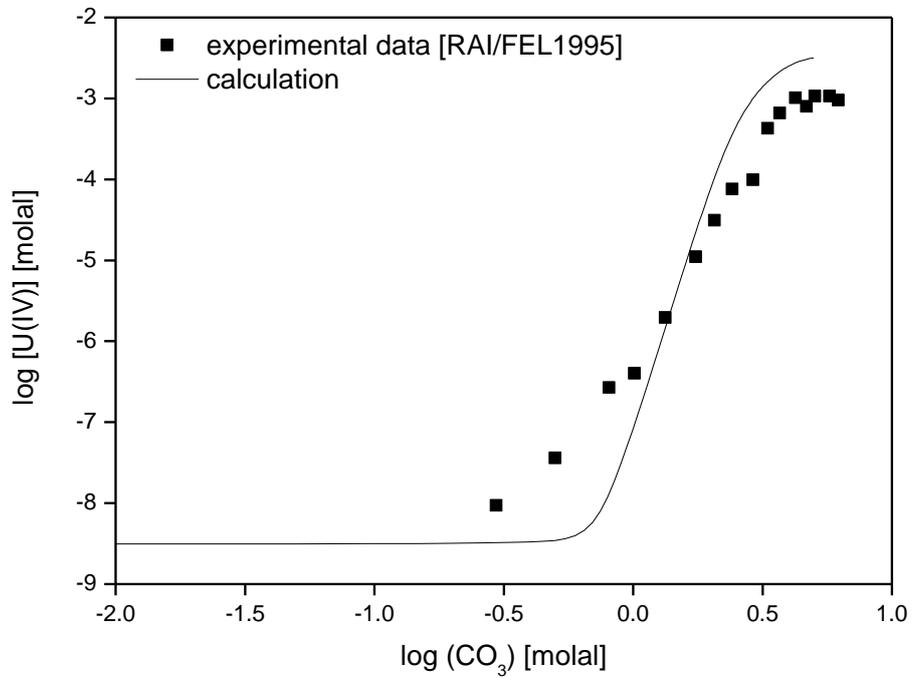


Fig. 6-2: Solubility of  $U(OH)_4(am)$  in  $\leq 5$  M  $K_2CO_3$  solution with 0.01 M NaOH [RAI/FEL1995].

**Case 3:**

The solubility of fresh precipitated  $U(OH)_4(am)$  in 1 M NaCl solution was calculated according to the experimental conditions given in [NEC/KIM2001] (Fig. 6-3).

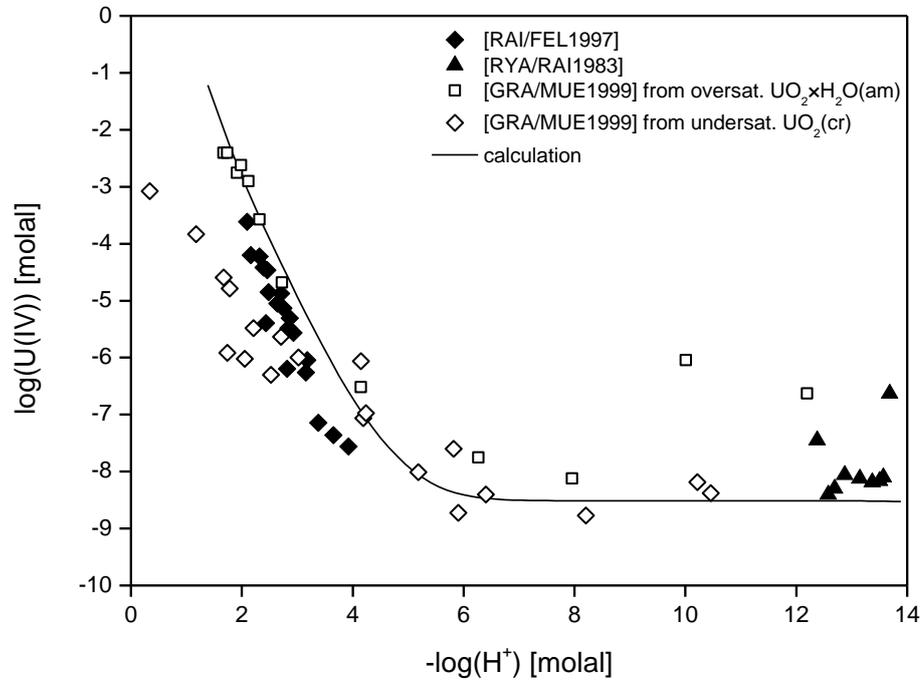


Fig. 6-3: Solubility of  $U(OH)_4(am)$  in 1 m NaCl solution [NEC/KIM2001].

## 6.2 Test calculations for U(VI) solubilities

### Case 4:

The solubility of Becquerelite in 1 m  $\text{CaCl}_2$  solution was calculated according to the experimental conditions given in [SAN/GRA1994] (Fig. 6-4).

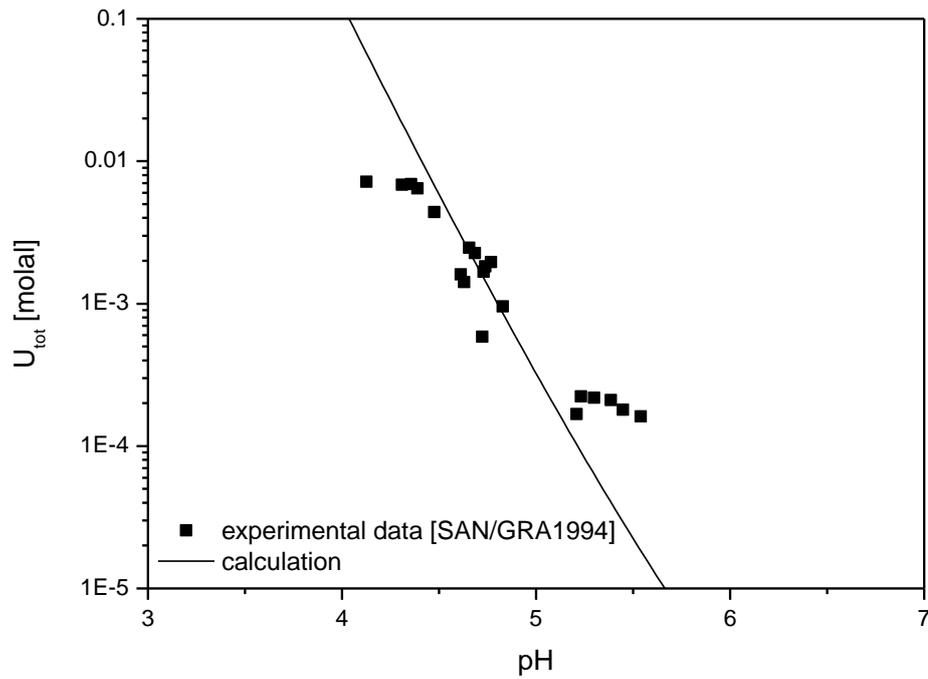


Fig. 6-4: Solubility of Becquerelite in 1 m  $\text{CaCl}_2$  solution [SAN/GRA1994].

**Case 5:**

The solubility of Compréignacite in 1 m KCl solution was calculated according to the experimental conditions given in [SAN/GRA1994] (Fig. 6-5).

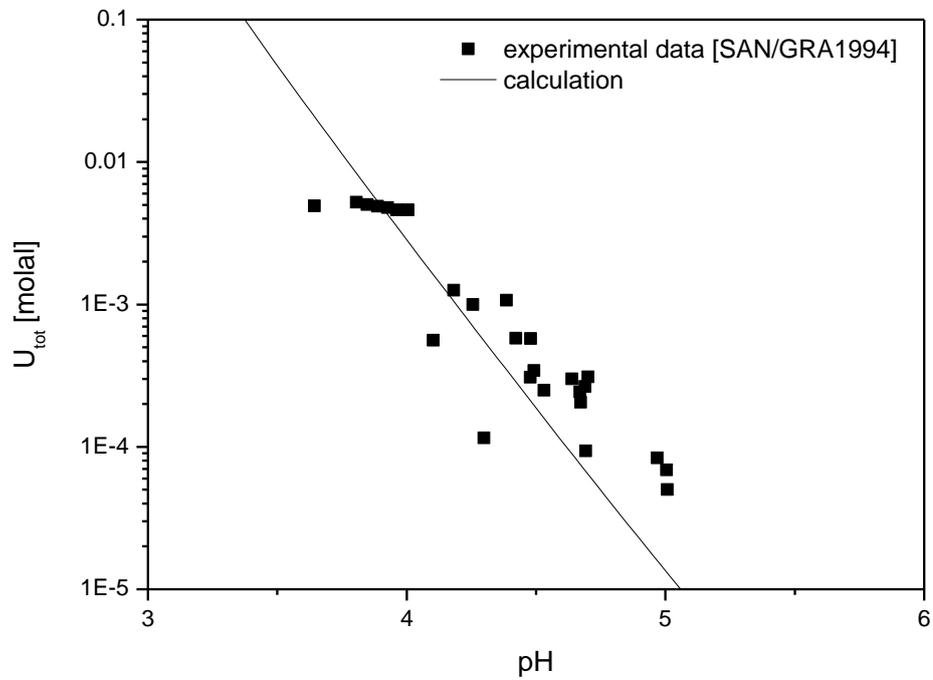


Fig. 6-5: Solubility of Compréignacite in 1 m KCl solution [SAN/GRA1994].

**Case 6:**

The solubility of Metaschoepite/Clarkeite in 0.5 m NaCl solution was calculated according to the experimental conditions given in [FAN/NEC2002] (Fig. 6-6).

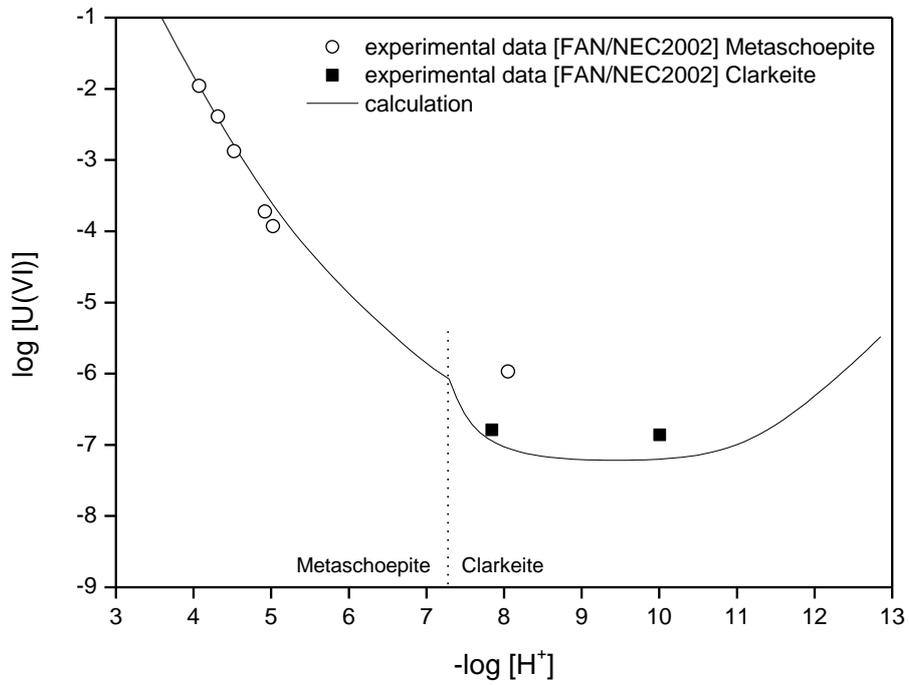


Fig. 6-6: Solubility of Metaschoepite/Clarkeite in 0.5 m NaCl solution [FAN/NEC2002].

**Case 7:**

The solubility of Metaschoepite in 5 m NaCl solution was calculated according to the experimental conditions given in [DIA/GRA1998] (Fig. 6-7).

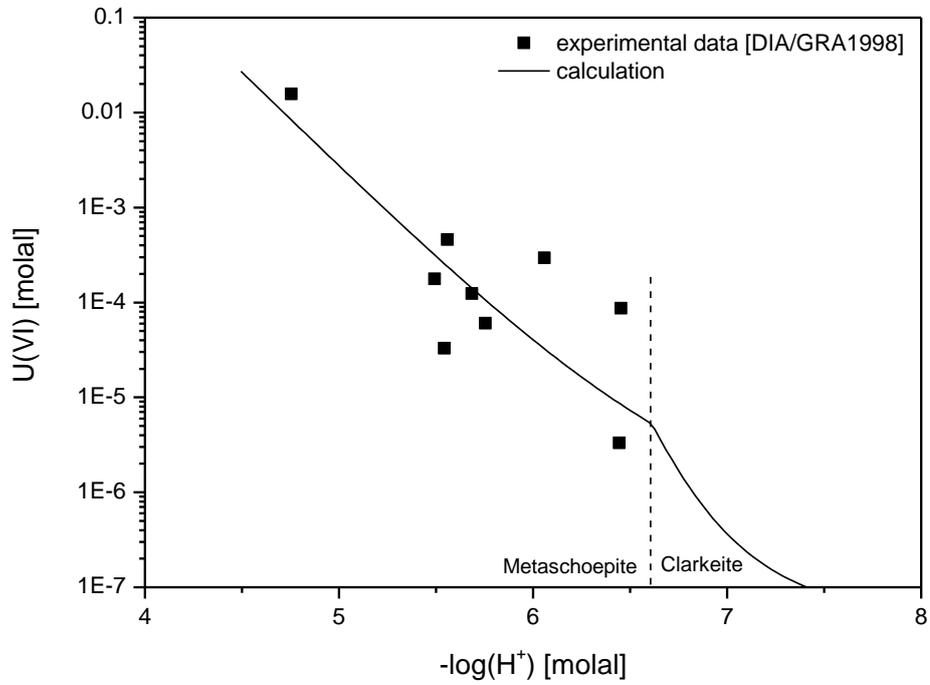


Fig. 6-7: Solubility of Metaschoepite 5 m NaCl solution [DIA/GRA1998].

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## List of abbreviations and symbols

<b>A</b>	Debye-Hückel parameter
<b>(am)</b>	Annex to the solid phase name to identify the amorphous state
<b>(aq)</b>	Label for neutrally charged aquatic species
<b>b</b>	Empirical factor in the Davies equation
<b>(cr)</b>	Annex to the solid phase name to identify the crystalline state
$f_i$	Single ion activity coefficient
<b>(g)</b>	Annex to the species to identify the gaseous state
<b>I</b>	Ionic strength
$K_w$	Ionization constant of water
<b>(l)</b>	Annex to the species name to identify the liquid state
<b>log <math>K^\circ</math></b>	Thermodynamic equilibrium constant at standard state (logarithm thereof)
<b>NAGRA-PSI database</b>	Chemical thermodynamic database of Nagra/PSI TDB 01/01 [HUM/BER2002]
<b>NEA TDB</b>	Nuclear Energy Agency Thermochemical Database
<b>OECD/NEA</b>	Organisation for Economic Co-operation and Development - Nuclear Energy Agency
<b>SIT</b>	Specific Interaction Theory
<b>THEREDA</b>	Thermodynamic Reference Database
$z_i$	Charge of the ion
$\Delta_F G^\circ$	Standard molar Gibbs energy of formation from constituting elements in their standard state
$\Delta_R G^\circ$	Standard molar Gibbs energy of reaction
$\beta^{(0)}, \beta^{(1)}, \beta^{(2)}, C^\Phi, \lambda$	Binary Pitzer coefficients
$\Theta_{ij}, \Psi_{ijCr}, \Psi_{ijClO_4}$	Ternary Pitzer coefficients
$\epsilon_{ik}$	SIT coefficient
$^\circ$	Superscript for standard state