

# ***THEREDA***

## **Thermodynamic Reference Database**

**Final Report Part KIT-INE**

**Database for Radionuclides**

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## Zusammenfassung

Das THEREDA-Vorhaben, eine Datenbank thermodynamischer Daten zur Modellierung von Radionuklidlöslichkeiten in sämtlichen relevanten Wirtsgesteinsformationen, lief in den Jahren 2009 bis 2013 in der zweiten Phase. Fokus der Arbeiten lag auf der Analyse und Bereitstellung von thermodynamischen Daten im Kontext des Pitzer Modells. Dieses Wechselwirkungsmodell ist insbesondere geeignet zur Beschreibung von aquatischen Systemen mittlerer und hoher Ionenstärken, wie sie in norddeutschen Tonformationen auftreten oder bei Zutritt von Wasser in ein Endlager im Salzgestein generiert werden können. Die Arbeiten konzentrierten sich einerseits darauf, die technische Plattform von THEREDA zur Dateneingabe, Verwaltung und Ausgabe für externe Nutzer zu prüfen und weiter zu entwickeln, und andererseits die verschiedenen Daten und Wechselwirkungsparameter nach dem Pitzer-Modell zusammenzustellen, zu bewerten und zu selektieren. Hierzu wurden im Rahmen des THEREDA-Datenbank-Vorhabens von KIT - Institut für Nukleare Entsorgung, die thermodynamischen Daten und Pitzer-Parameter zu den Reaktionen und Festphasen der Actiniden und zweier langlebiger Spaltprodukten (Tc, Sm) in wässrigen Lösungen zusammengetragen, bewertet und ausgewählt. Die neuen Datensätze, Komplexbildungs- und Löslichkeitskonstanten sowie Wechselwirkungsparameter, sind konsistent zu den Daten aus der ersten THEREDA-Vorhabensphase. Bevor die Daten in kleinen Einheiten für den externen Benutzer freigegeben wurden, wurden sie im Rahmen einer detaillierten Qualitätssicherung, in Testrechnungen mit den verschiedenen Codes – EQ3/6, Phreeqc, Geochemists Workbench, ChemApp – eingehend überprüft. Als Testsysteme wurden gut definierte Elektrolytsysteme unter jeweils verschiedenen chemischen Bedingungen verwendet. Die Rechenergebnisse der einzelnen Codes wurden jeweils untereinander sowie mit belastbaren experimentellen Daten verglichen und in über die THEREDA Website ([www.thereda.de](http://www.thereda.de)) öffentlich zugänglichen Berichten dokumentiert. Zusätzlich wurde für jede Datenfreigabe ein Audit-Prozess eingeführt, der einem internen Review-Prozess entspricht. Hierzu wurden von ausgewählten Personen der beteiligten Forschungsinstitutionen, die nicht an dem entsprechenden Daten-Release direkt involviert waren, die Daten selbst sowie die dazugehörigen Dokumente nochmals unabhängig überprüft.

Von KIT-INE wurden für die Actiniden Protactinium, Thorium, Neptunium, Plutonium, Americium, Curium und die Spaltprodukte Neodym und Samarium konsistente Datensätze ausgegeben. Für externe Nutzer wurden innerhalb von THEREDA insgesamt die folgenden Datensätze freigegeben, die als Parameterfiles für vier Codes von der THEREDA-Webseite heruntergeladen werden können. Die Releases von KIT-INE sind hervorgehoben:

1. Release: System Na, K, Mg, Ca – Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> - H<sub>2</sub>O(l)
- 2. Release: System Na, Mg, Ca - Cl<sup>-</sup> - Am(III), Nd(III), Cm(III) - H<sub>2</sub>O(l)**
3. Release: System Na, K, Mg, Ca - Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> - HCO<sub>3</sub><sup>-</sup>/CO<sub>2</sub>(g) - H<sub>2</sub>O(l)
- 4. Release: System Na – Cl<sup>-</sup> - Np(V)**
5. Release: System Na, K, Mg, Ca - Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> - Cs - HCO<sub>3</sub><sup>-</sup>/CO<sub>2</sub>(g) - H<sub>2</sub>O(l)

6. Release: System Zement-Phasen (Si, Al) - Na, Mg, Ca, K - Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> - H<sub>2</sub>O(l) (25°C)

**7. Release: System Na - K - Ca - Cl<sup>-</sup> - Th(IV) - Np(IV) - Pu(IV) - C (25°C)**

**8. Release: System Na, Mg, Ca - Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup> - Am(III), Cm(III) - H<sub>2</sub>O(l) (25°C)**

Basierend auf dem vorhandenen Datensatz kann eine Vielzahl von Elektrolytsysteme, die für die Endlagersicherheit radioaktiver Abfälle in Tonformationen und salinaren Systemen relevant sind, auf Basis des Pitzer Formalismus und entsprechender thermodynamischer Daten, belastbar und nachvollziehbar modelliert werden.

Alle Daten sowie die dazugehörigen relevanten Informationen können über die Webseite des THEREDA-Vorhabens – [www.thereda.de](http://www.thereda.de) – abgefragt werden. Einzelheiten zur Datenzusammenstellung unserer Datenauswahl finden sich in diesem Abschlussbericht des Vorhabens.

## Summary

The THEREDA project, a project to derive a thermodynamic database covering all potential host-rocks for a nuclear waste repository in Germany, has completed its second project phase from 2009 to 2013. Focus of activities was put on thermodynamic data and model parameters derived within the Pitzer approach, relevant for the description of aqueous systems at intermediate to highly saline ionic strength, as can be expected in the case of North-German clay formations or water intrusion in a salt-based repository. In this project phase, the testing and development of the technical platform for data input, management and data output for external users was advanced. Furthermore, work was continued in order to collect, evaluate and select the thermodynamic data with their corresponding interaction parameters according to the Pitzer approach. The Institute for Nuclear Waste Disposal (INE) at KIT has evaluated and supplied thermodynamic data for the reactions and solid phases of actinides and selected fission products relevant in aqueous solutions. The data set of complex formation and solubility constants and interaction parameters are internally consistent with the data from the first THEREDA phase. Prior to the official release of data for external users, the data were validated in test calculations by using various codes like EQ3/6, Phreeqc, Geochemists Workbench, and ChemApp. For that, well-defined electrolyte systems were selected as test systems under varying chemical conditions. The test systems were modelled with the above mentioned codes and the results of the calculations compared between the codes. Furthermore, all modelling results were compared with experimental data reported in the literature. Each test calculation was documented in specific reports available via the THEREDA website ([www.thereda.de](http://www.thereda.de)). Additionally, for each release an audit process has been launched to check again the data and the documents, thus serving as an internal peer-review process. The audit was performed by selected specialists of the partners involved in the THEREDA project without participating in the corresponding release.

Within THEREDA, KIT-INE has provided a consistent dataset for the actinides protactinium, thorium, neptunium, plutonium, americium, curium, and the long-lived fission products neodymium and samarium. For external users data of THEREDA the following total number of systems have been addressed, with data available for download at the THEREDA webpage as parameter files for the above mentioned codes. The releases by KIT-INE are marked:

1. Release: system Na, K, Mg, Ca – Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> - H<sub>2</sub>O(l)
- 2. Release: system Na, Mg, Ca – Cl<sup>-</sup> - Am(III), Nd(III), Cm(III) - H<sub>2</sub>O(l)**
3. Release: system Na, K, Mg, Ca – Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> - HCO<sub>3</sub><sup>-</sup>/CO<sub>2</sub>(g) - H<sub>2</sub>O(l)
- 4. Release: system Na – Cl<sup>-</sup> - Np(V)**
5. Release: system Na, K, Mg, Ca – Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> - Cs - HCO<sub>3</sub><sup>-</sup>/CO<sub>2</sub>(g) - H<sub>2</sub>O(l)
6. Release: system cement phases (Si, Al) - Na, Mg, Ca, K – Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> - H<sub>2</sub>O(l) (25°C)
- 7. Release: system Na - K - Ca - Cl<sup>-</sup> - Th(IV) - Np(IV) - Pu(IV) - C (25°C)**
- 8. Release: system Na, Mg, Ca, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup> - Am(III), Cm(III) - H<sub>2</sub>O(l) (25°C)**

With this data set provided by THEREDA, several electrolyte systems at intermediate to high ionic strength can be modelled using the Pitzer Approach, that are relevant for the safety analysis of final disposals for radioactive waste in North-German clay formations and saline systems.

All data and more corresponding relevant information can be obtained from the THEREDA website – [www.thereda.de](http://www.thereda.de). Details on the data selections provided by KIT-INE can be found in the present project report.

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This work was performed by KIT-INE with several colleagues contributing to data evaluation, implementation and writing of the present report.

Christian Marquardt contributed to: Sm, Np(V) and data implementation

Xavier Gaona contributed to: Th(IV), Pa, Np(IV), Pu and data implementation

Christiane Bube contributed to: geochemical modelling and data implementation

# 1 Development of DBControl, an user-interface for data entry

One technical part of the second phase of THEREDA was to develop an interface for the data entry into the THEREDA databank. This interface should also automatically control and assist the actions of the users to avoid errors during the data input. The concept of this interface was elaborated by the THEREDA partner and the technical implementation realized by the software company LINEAS. KIT has sub-contracted LINEAS, as part of the financial support received by the BMWi within the THEREDA Phase II project. After one year the interface was finished and then, extensively tested by the members of THEREDA, to improve the tools to control the data input and to calculate internal transformations of thermodynamic data. As a result of these test, many details were changed in the first version of DBControl by LINEAS.

The screenshot displays the THEREDA Thermodynamic Data interface. At the top, the THEREDA logo and 'Thermodynamic Data' title are visible. Below the navigation bar, the 'Phase Constituent Information' section shows the following details:

- Phase Constituent: AmCl<sub>2</sub><sup>+</sup>
- Phase(s): aq
- Reaction: 1.00 AmCl<sub>3</sub> +> + 1.00 Cl<sup>-</sup> -> 1.00 AmCl<sub>2</sub><sup>+</sup>
- Pcon Type: Product
- Molarmass [g/mol]: 278.513
- Redox: no
- Equilibrium Constraint: Complete equilibrium
- Charge: 2
- Editor: Marquardt

Below this information, there are tabs for 'Data Standard Pitzer', 'Data Standard SIT', 'Data Standard EDH', and 'Data Variable Pitzer'. The 'Data Standard Pitzer' tab is active, showing a table with the following columns: Data Type, Catego, Value, Positive Unc, Calc Mode, Reference1, Dataclass, Ds Data Source, Data Quality, Editor, Db Datetime, and Note For Editor.

| Data Type | Catego | Value         | Positive Unc | Calc Mode        | Reference1            | Dataclass                              | Ds Data Source                           | Data Quality               | Editor    | Db Datetime | Note For Editor |
|-----------|--------|---------------|--------------|------------------|-----------------------|--|--|----------------------------|-----------|-------------|-----------------|
| CP298     | NA     |               |              | NotYetDetermined | NotYetDetermined,     | 6, Data class not yet entered (to ...  | 6, Data source not yet entered (to b...  | 6, Data quality not yet... | Marquardt | 12/15/2011  |                 |
| DFG298    | R      | -731286.00036 | 4759         | CRLODGK          | InternallyCalculated, | -1, Internally calculated with Calc... | -1, Internally calculated                | -1, Internally calculated  | Marquardt | 12/12/2012  |                 |
| DFH298    | NA     |               |              | NotYetDetermined | NotYetDetermined,     | 6, Data class not yet entered (to ...  | 6, Data source not yet entered (to b...  | 6, Data quality not yet... | Marquardt | 12/15/2011  |                 |
| DRCP298   | NA     |               |              | NotYetDetermined | NotYetDetermined,     | 6, Data class not yet entered (to ...  | 6, Data source not yet entered (to b...  | 6, Data quality not yet... | Marquardt | 12/15/2011  |                 |
| DRG298    | R      | -1369.0284397 | 171          | CRLODGK          | InternallyCalculated, | -1, Internally calculated with Calc... | -1, Internally calculated                | -1, Internally calculated  | Marquardt | 12/12/2012  |                 |
| DRH298    | NA     |               |              | NotYetDetermined | NotYetDetermined,     | 6, Data class not yet entered (to ...  | 6, Data source not yet entered (to b...  | 6, Data quality not yet... | Marquardt | 12/15/2011  |                 |
| DRS298    | NA     |               |              | NotYetDetermined | NotYetDetermined,     | 6, Data class not yet entered (to ...  | 6, Data source not yet entered (to b...  | 6, Data quality not yet... | Marquardt | 12/15/2011  |                 |
| LOGP298   | R      | 0.24          | 0.03         | Entered          | GUL/PAN2003, LPD...   | 1, Value based upon experimenta...     | 1, Value taken from an international ... | -1, Internally calculated  | Marquardt | 12/15/2011  |                 |
| S298      | NA     |               |              | NotYetDetermined | NotYetDetermined,     | 6, Data class not yet entered (to ...  | 6, Data source not yet entered (to b...  | 6, Data quality not yet... | Marquardt | 12/15/2011  |                 |
| V298      | NA     |               |              | Entered          | NotYetDetermined,     | 6, Data class not yet entered (to ...  | 6, Data source not yet entered (to b...  | 6, Data quality not yet... | Marquardt | 10/22/2012  |                 |

Figure 1: Screenshot of the DBControl interface for data input in the THEREDA data base. The data and information of the AmCl<sup>+</sup> complex are shown as an example. Beside the Thermodynamic data flag for the thermodynamic data screen, eleven other flags corresponding to specific tools are available for data input and control.

In Figure 1, the screenshot for the thermodynamic data of the AmCl<sup>+</sup> complex is shown as a typical example. The figure demonstrates that the interface is composed of several specific tools labelled by the different flags on the screen. The basis for the development of the interface was a specification document written by the THEREDA members detailing all demands on such an interface [THEREDA2012]. These demands were implemented by LINEAS. Until the end of the THEREDA Phase II, the interface is

now considerably matured, functions very well and can now be extensively used for data input and control.

## **2 Technical fundamentals of database**

The technical fundamentals of the database like the DBControl or the data output in form of parameter files for specific modelling codes, have been tested extensively among others by all members of THEREDA. The technical implementation of these tools was mainly performed by the GRS Braunschweig and the Helmholtz Center Dresden-Rossendorf. Therefore, the KIT-INE part of the present final report does not address these technical aspects of THEREDA. The interested reader can obtain information on the technical implementation in the final reports of the other partners (GRS; HZDR).

## **3 Documentation of data selection**

In the THEREDA project, KIT is responsible for the data selection of radionuclides relevant to the final disposal of radioactive waste in Germany. It was decided that the long-lived actinides thorium, protactinium, neptunium, plutonium, americium and curium as well as the fission products technetium and samarium have the first priority in THEREDA phase I and II. In the following chapters the data selection concerning these radionuclides is documented. Because the chemistry of the radionuclides governs the mobility or retention of radionuclides and because this behavior is often related to the oxidation state of the element, the chapters of the documentation are indexed according to the oxidation state of the radionuclides. This means that chapters are arranged in trivalent, tetravalent, pentavalent, hexavalent, and heptavalent radionuclides referring to the possible oxidation state.

### **3.1.1 Samarium, Sm(III): Sm<sup>3+</sup>**

It was decided to take the thermodynamic data of neodymium, curium and americium as chemical analogue values for samarium. This approach is justified in view of the close chemical analogy between these elements and specific uncertainties related to the reported samarium data. In the next chapters, the literature data of samarium are

compared with the selected data of the analogue elements to support that the decision is reasonable within the experimental uncertainties.

### 3.1.1.1 Sm<sup>3+</sup> - aquo ion

For the aquo ion of samarium (Sm<sup>3+</sup>), reliable data for the standard molar enthalpy of formation  $\Delta_f H_m^\circ$ , standard molar Gibbs free energy of formation  $\Delta_f G_m^\circ$  and the standard molar entropy  $S_m^\circ$  exceptionally exist. The  $\Delta_f H_m^\circ$ ,  $\Delta_f G_m^\circ$ , and  $S_m^\circ$  for Sm<sup>3+</sup> were selected from the NBS tables [WAG/EVA1982], instead of taking the values of the chemical analogues.

Table 1: Thermodynamic formation data of Sm<sup>3+</sup> selected for THEREDA.

|               | $\Delta_f H_m^\circ$ (KJ mol <sup>-1</sup> ) | $S_m^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> ) | $\Delta_f G_m^\circ$ (KJ mol <sup>-1</sup> ) | $C_p$ |
|---------------|--|--|--|-------|
| [WAG/EVA1982] | -691.6                                       | -211.7   | -666.6                                       | -21   |

#### 3.1.1.1.1 Pitzer parameter for Sm(III) aquo ion

There are no Pitzer parameters available for the samarium aquo ion Sm<sup>3+</sup>. Therefore, the parameter set of Nd(III) (with data often derived from Cm(III)) as an analogue element for Sm(III) is chosen. The differences for the trace activity coefficients are very small among ions with same charge, symmetry, and similar ionic radius. The experimental uncertainties are in any case larger. [NEC/ALT2009] developed a comprehensive thermodynamic model, including Pitzer parameter sets for the hydrolysis reaction in chloride and perchlorate solutions. The bases and the criteria for data selection are discussed in [NEC/ALT2009] and are summarized in Table 2.

Table 2: Pitzer parameter for the system Sm(V) – H<sub>2</sub>O – Cl<sup>-</sup> - ClO<sub>4</sub><sup>-</sup> - Na<sup>+</sup> - K<sup>+</sup> - Mg<sup>2+</sup>  
Sm(III) aquo ion Sm<sup>3+</sup> at 25°C.

| <b>Binäre Pitzer -Parameter</b>              |                    |                  |               |               |  |            |            |                  |
|--|--------------------|------------------|---------------|---------------|--|------------|------------|------------------|
| <b>c</b>                                     | <b>a</b>           | $\beta^{(0)}$    | $\beta^{(1)}$ | $\beta^{(2)}$ | <b>C<sup>ϕ</sup></b>                         | $\alpha_1$ | $\alpha_2$ | <b>Reference</b> |
| <b>(Analog)</b>                              | <b>(Analog)</b>    |                  |               |               |  |            |            |                  |
| <b>Sm&lt;3+&gt;</b>                          |                    |                  |               |               |  |            |            |                  |
| (Nd<3+>) <sup>°</sup>                        | Cl<->              | 0.5856           | 5.6           | 0             | -0.016*                                      | 2          | 0          | NEC/ALT2009      |
| (Nd<3+>) <sup>°</sup>                        | ClO4<->            | 0.754            | 6.533         | 0             | 0.0075                                       | 2          | 0          | NEC/FAN1998      |
| (Lu<3+>)                                     | SO4<2->            | 1.792            | 15.044        | 0             | -0.6   | 2          | 0          | ALT/BRE2004      |
| <b>Ternary Pitzer parameter</b>              |                    |                  |               |               |  |            |            |                  |
| <b>c</b>                                     | <b>c'</b>          | <b>a</b>         | $\theta(cc')$ | $\psi(cc'a)$  | <b>Reference for <math>\psi(cc'a)</math></b> |            |            |                  |
| <b>(Analogue)</b>                            | <b>(Analogue)</b>  | <b>(Analog.)</b> | <b>(HMW)</b>  |               |  |            |            |                  |
| (Nd<3+>)                                     | Na<+>              | Cl<->            | 0.1           | 0             | NEC/ALT2009                                  |            |            |                  |
| (Nd<3+>)                                     | K<+><br>(Na<+>)    | Cl<->            | 0.1           | 0             | ALT/BRE2004                                  |            |            |                  |
| (Nd<3+>)                                     | Ca<2+>             | Cl<->            | 0.2           | 0             | NEC/ALT2009                                  |            |            |                  |
| (Nd<3+>)                                     | Mg<2+><br>(Ca<2+>) | Cl<->            | 0.2           | 0             | NEC/ALT2009                                  |            |            |                  |
| * calculated from Cm(III) data [KOE/FAN1997] |                    |                  |               |               |  |            |            |                  |
| ° Original data from [PIT1991]               |                    |                  |               |               |  |            |            |                  |

### 3.1.1.2 Hydrolysis of Sm<sup>3+</sup>

[SPA/BRU1995] have made a review of all lanthanide data available in the literature. However, only a few thermodynamic data for samarium exist in the literature. Because neodymium is close to samarium in terms of solution chemistry and thermodynamics, and because more reliable data exist for the Nd(III) species than for other lanthanides, the data of neodymium selected in THEREDA have been taken as analogue data for samarium. The data for samarium are listed in Table 3: Hydrolysis constants for Sm(III) at ionic strength I = 0 selected in THEREDA. Because of lack of appropriate experimental data, Nd(III) data from THEREDA has been chosen as analogue values for Sm(III).

Polynuclear complexes are discussed in [KRA/DEC1979] to explain their experimental results. They suggest  $\text{Sm}_3(\text{OH})_4^{5+}$  as the most dominant species. Within the THEREDA review it was decided not to use these polynuclear species in the chemical model for samarium, because of uncertainties in the reported model.

Table 3: Hydrolysis constants for Sm(III) at ionic strength  $I = 0$  selected in THEREDA. Because of lack of appropriate experimental data, Nd(III) data from THEREDA has been chosen as analogue values for Sm(III).

|   | $\log\beta_n^0$ | Comment                | Reference   |
|---|-----------------|------------------------|-------------|
| <b>Dissolved species</b>  |                 |                        |             |
| $\text{Sm}^{3+} + \text{H}_2\text{O} = \text{SmOH}^{2+} + \text{H}^+$                   |                 | $n = 1$                |             |
| $\text{SmOH}^{2+}$  | $-7.4 \pm 0.4$  | Analogue value (Nd)    | NEC/ALT2009 |
| $\text{Sm}^{3+} + 2\text{H}_2\text{O} = \text{Sm}(\text{OH})_2^+ + 2\text{H}^+$         |                 | $n = 2$                |             |
| $\text{Sm}(\text{OH})_2^+$  | $-15.7 \pm 0.7$ | Analogue value (Nd)    | NEC/ALT2009 |
| $\text{Sm}^{3+} + 3\text{H}_2\text{O} = \text{Sm}(\text{OH})_3 + 3\text{H}^+$           |                 | $n = 3$                |             |
| $\text{Sm}(\text{OH})_3$  | $-26.2 \pm 0.5$ | Analogue value (Am/Cm) | NEC/ALT2009 |
| $\text{Sm}^{3+} + 4\text{H}_2\text{O} = \text{Sm}(\text{OH})_4^- + 4\text{H}^+$         |                 | $n = 4$                |             |
| $\text{Sm}(\text{OH})_4^-$  | $-40.7 \pm 0.7$ | Analogue value (Am)    | NEC/ALT2009 |
| <b>Solid components</b>   |                 |                        |             |
| $\text{Sm}^{3+} + 3\text{H}_2\text{O} = \text{Sm}(\text{OH})_3(\text{s}) + 3\text{H}^+$ |                 |                        |             |
| $\text{Sm}(\text{OH})_3(\text{am})$   | $-17.2 \pm 0.4$ | Analogue value (Nd)    | NEC/ALT2009 |
| $\text{Sm}(\text{OH})_3(\text{s})$  | $-16.0 \pm 0.4$ |                        |             |

### 3.1.1.2.1 Pitzer parameters for hydrolysis species

All Pitzer parameter for Sm hydrolysis species are adopted from experiments with Nd(III) as analogue element. The experimental uncertainty is higher than the discrepancy in the interaction coefficients between Sm(III) and Nd(III). For that, the interaction coefficients are set to be identical.

Table 4: Pitzer parameter for hydrolysis species of Sm(III) in the system of the oceanic salts: Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>. (Lit.: 1: THEREDA, 2: [NEC/ALT2009])

| <b>Pitzer, binary</b>               |                                    | $\beta^{(0)}$    | $\beta^{(1)}$    | $\beta^{(2)}$    | $C^\ominus$     | $\alpha$        | <b>Lit.</b> |  |
|-------------------------------------|------------------------------------|------------------|------------------|------------------|-----------------|-----------------|-------------|--|
| Sm/Nd(OH) <sup>2+</sup>             | Cl <sup>-</sup>                    | 0.055            | 1.81             | 0                | 0               | 2               | 1, 2        |  |
| Sm/Nd(OH) <sub>2</sub> <sup>+</sup> | Cl <sup>-</sup>                    | -0.13            | 0                | 0                | 0               | 2               | 1, 2        |  |
| Sm/Nd(OH) <sub>4</sub> <sup>-</sup> | Na <sup>+</sup>                    | 0                | 0                | 0                | 0               | 2               | 1, 2        |  |
|                                     | K <sup>+</sup>                     | 0                | 0                | 0                | 0               | 2               | 1, 2        |  |
|                                     | Mg <sup>2+</sup>                   | 0                | 0                | 0                | 0               | 2               | 1, 2        |  |
| <b>Pitzer, ternary</b>              |                                    | $\Theta$         |                  |                  |                 |                 |             |  |
|                                     | Na <sup>+</sup>                    | Ca <sup>2+</sup> | Mg <sup>2+</sup> | Cl <sup>-</sup>  | OH <sup>-</sup> |                 |             |  |
| Sm/Nd(OH) <sup>2+</sup>             | 0                                  | 0                | 0                |                  |                 |                 | 1, 2        |  |
| Sm/Nd(OH) <sub>2</sub> <sup>+</sup> | 0                                  | 0.29             | 0.29             |                  |                 |                 | 1, 2        |  |
| Sm/Nd(OH) <sub>4</sub> <sup>-</sup> |                                    |                  |                  | 0                | 0               |                 |             |  |
|                                     |                                    | $\Psi$           |                  |                  |                 |                 |             |  |
|                                     |                                    | Cl <sup>-</sup>  | OH <sup>-</sup>  |                  |                 |                 |             |  |
| Sm/Nd(OH) <sup>2+</sup>             | Na <sup>+</sup>                    | 0                |                  |                  |                 |                 | 1, 2        |  |
|                                     | Ca <sup>2+</sup>                   | 0.04             |                  |                  |                 |                 | 1, 2        |  |
|                                     | Mg <sup>2+</sup>                   | 0.04             |                  |                  |                 |                 | 1, 2        |  |
| Sm/Nd(OH) <sub>2</sub> <sup>+</sup> | Na <sup>+</sup>                    | 0                |                  |                  |                 |                 | 1, 2        |  |
|                                     | Ca <sup>2+</sup>                   | 0.07             |                  |                  |                 |                 | 1, 2        |  |
|                                     | Mg <sup>2+</sup>                   | 0.07             |                  |                  |                 |                 | 1, 2        |  |
| Sm/Nd(OH) <sub>4</sub> <sup>-</sup> | Na <sup>+</sup> /K <sup>+</sup>    | 0                | 0                |                  |                 |                 | 1, 2        |  |
|                                     | Ca <sup>2+</sup> /Mg <sup>2+</sup> | 0                |                  |                  |                 |                 | 1, 2        |  |
| <b>Neutral species</b>              |                                    | $\Lambda$        |                  |                  |                 |                 |             |  |
|                                     | Na <sup>+</sup>                    | K <sup>+</sup>   | Ca <sup>2+</sup> | Mg <sup>2+</sup> | Cl <sup>-</sup> | OH <sup>-</sup> |             |  |
| Sm/Nd(OH) <sub>3</sub> (aq)         | -0.2                               | 0                | 0                | 0                | 0               | 0               | 1, 2        |  |



### 3.1.1.3 Sm(III) chloride complexes

Samarium forms only weak chloride complexes in chloride solutions, either outer sphere or inner sphere complexes. As described in the final report of the THEREDA phase one, several studies on the chloride complexation of lanthanides exist. However, no spectroscopic studies have been performed to characterise lanthanide chloride complexes. One exemption for trivalent cations is the work by Könnecke et al [KON/FAN1997] who investigated the Cm(III) chloride complexation with TRLFS. Therefore, the formation constant from this work has been chosen for THEREDA, because outer sphere complexes can only be differentiated from inner sphere complexation by spectroscopy. The values of 0.24 and -0.74 for the first and second chloride complex are consistent with the Pitzer parameters given below in this chapter.

Table 5: Formation constants for the Sm(III) chloride complexation

|  | $\log\beta_n^0$                    | Comment                                 | Reference                                 |
|--|------------------------------------|---|---|
| $M^{3+} + Cl^- = MCl^{2+}$             | $n = 1$                            |   |   |
| SmCl <sup>2+</sup>                     | 0.4                                |   | DUR/GRI2006<br>SPA/BRU1995                |
| AnCl <sup>2+</sup> (Am/Cm)             | $0.24 \pm 0.03$                    | Spectroscopy                            | GUI/FAN2003<br>KON/FAN1997<br>NEC/ALT2009 |
| NdCl <sup>2+</sup>                     | $0.24 \pm 0.03$                    | Cm(III) analogue value                  | NEC/ALT2009                               |
|  | $0.28 \pm 0.16$                    | regarded as non-reliable<br>MIG/WIL2002 | MIG/WIL2002                               |
| <b>Selected value</b>                  | <b><math>0.24 \pm 0.03</math></b>  | <b>Cm(III) analogue value</b>           | <b>THEREDA</b>                            |
| $M^{3+} + 2 Cl^- = MCl_2^+$            | $n = 2$                            |   |   |
| AnCl <sub>2</sub> <sup>+</sup> (Am/Cm) | $-0.74 \pm 0.05$                   |   | GUI/FAN2003<br>KON/FAN1997<br>NEC/ALT2009 |
| <b>Selected value</b>                  | <b><math>-0.74 \pm 0.05</math></b> | <b>Cm(III) analogue value</b>           | <b>THEREDA</b>                            |

Table 6: Pitzer parameter for Sm(III) chloride ions at 25°C.

| <b>Binäre Pitzer -Parameter</b> |                  |                  |               |               |  |            |            |                  |
|---------------------------------|------------------|------------------|---------------|---------------|--|------------|------------|------------------|
| <b>c</b>                        | <b>A</b>         | $\beta^{(0)}$    | $\beta^{(1)}$ | $\beta^{(2)}$ | $C^\phi$                                     | $\alpha_1$ | $\alpha_2$ | <b>Reference</b> |
| <b>(Analog Nd<sup>3+</sup>)</b> |                  |                  |               |               |  |            |            |                  |
| Sm <sup>3+</sup>                | Cl <sup>-</sup>  | 0.5856           | 5.60          | 0             | -0.016*                                      | 2          | 0          | NEC/ALT2009      |
| SmCl <sup>2+</sup>              | Cl <sup>-</sup>  | 0.593            | 3.15          | 0             | -0.006                                       | 2          | 0          | NEC/ALT2009      |
| SmCl <sub>2</sub> <sup>+</sup>  | Cl <sup>-</sup>  | 0.516            | 1.75          | 0             | 0.010  | 2          | 0          | NEC/ALT2009      |
| <b>Ternary Pitzer parameter</b> |                  |                  |               |               |  |            |            |                  |
| <b>c</b>                        | <b>c'</b>        | <b>a</b>         | $\theta(cc')$ | $\psi(cc'a)$  | <b>Reference for <math>\psi(cc'a)</math></b> |            |            |                  |
| <b>(Analog)</b>                 | <b>(Analog)</b>  | <b>(Analog.)</b> | <b>(HMW)</b>  |               |  |            |            |                  |
| Sm <sup>3+</sup>                | Na <sup>+</sup>  | Cl <sup>-</sup>  | 0.1           | 0             | NEC/ALT2009                                  |            |            |                  |
| Sm <sup>3+</sup>                | K <sup>+</sup>   | Cl <sup>-</sup>  | 0.1           | 0             | ALT/BRE2004                                  |            |            |                  |
| Sm <sup>3+</sup>                | Ca <sup>2+</sup> | Cl <sup>-</sup>  | 0.2           | 0             | NEC/ALT2009                                  |            |            |                  |
| Sm <sup>3+</sup>                | Mg <sup>2+</sup> | Cl <sup>-</sup>  | 0.2           | 0             | NEC/ALT2009                                  |            |            |                  |
| SmCl <sup>2+</sup>              | Na <sup>+</sup>  | Cl <sup>-</sup>  | 0             | 0             | NEC/ALT2009                                  |            |            |                  |
| SmCl <sup>2+</sup>              | Ca <sup>2+</sup> | Cl <sup>-</sup>  | -0.014        | 0             | NEC/ALT2009                                  |            |            |                  |
| SmCl <sup>2+</sup>              | Mg <sup>2+</sup> | Cl <sup>-</sup>  | -0.014        | 0             | NEC/ALT2009                                  |            |            |                  |
| SmCl <sub>2</sub> <sup>+</sup>  | Na <sup>+</sup>  | Cl <sup>-</sup>  | 0             | 0             | NEC/ALT2009                                  |            |            |                  |
| SmCl <sub>2</sub> <sup>+</sup>  | Ca <sup>2+</sup> | Cl <sup>-</sup>  | -0.196        | 0             | NEC/ALT2009                                  |            |            |                  |
| SmCl <sub>2</sub> <sup>+</sup>  | Ca <sup>2+</sup> | Cl <sup>-</sup>  | -0.196        | 0             | NEC/ALT2009                                  |            |            |                  |

\* calculated from Cm(III) data [KON/FAN1997]  
° Original data from [PIT1991]

### 3.1.1.4 Sm(III) carbonate complexation and solid Sm(III) carbonates

The carbonate complexation of Sm(III) is briefly discussed in [SPA/BRU1995], and the values for the complexation constants at  $I = 0$  are summarized in Table 7. Together with the data for Am(III) and Cm(III) from NEA-TDB it is obvious that the difference among all data are smaller than the range of uncertainties. The tricarbonat complex was detected only in the experiments with Am(III) and Cm(III), and it is assumed that Sm(III) will form the same complex under analogous experimental conditions. The tetracarbonat complex was not considered for Sm(III) in THEREDA. This complex was only be observed in experiments for the Cm(III) and not for Am(III) and this complex was also not considered in the selection process by the NEA-TDB for the acti-

nides. Hence, to be consistent with the only set of Pitzer parameters for trivalent actinides and Nd(III), the chemical model and the corresponding values from [GUI/FAN2003] were selected as analogue values for the complexation constants of Sm(III) carbonate complexes (see Table 7 values in bold face).

The hydrogencarbonate complex of the trivalent actinide ions is extremely weak and existent only in a small stability field that is not relevant for natural systems ( $p\text{CO}_2 = 1$  atm, low pH values) or scenarios considered in nuclear waste disposal. The complexation constant for this weak complex is mentioned for completeness.

### **3.1.1.5 Mixed Sm(III) hydroxide carbonate complexes**

Mixed hydroxide carbonate complexes of Eu(III) and Ce(III) are described in literature by Bernkopf [BER1984], Bidoglio [BID1982] and Ferri et al. [FER/GRE1983]. However, their existence in carbonate systems were not proven by experimental work. [NEC/FAN1998] have done an estimation for trivalent actinides Am(III) and Cm(III), whether such complexes could be relevant or not. They concluded that only at pH values higher than 10 and  $\text{CO}_2$  partial pressure below the equilibrium concentrations of atmospheric conditions, mixed hydroxide carbonate complexes could eventually occur. Such systems can be described with a chemical model regarding only binary hydroxide and carbonate complexes. Therefore, the mixed hydroxide carbonate complexes are not considered for Sm(III) in THEREDA.

### **3.1.1.6 Solid Sm(III) carbonate compounds**

According to the trivalent actinides Am(III) and Cm(III) and the lanthanide Nd(III) the solids  $\text{Sm}_2(\text{CO}_3)_3(\text{am})$ ,  $\text{Sm}(\text{OH})\text{CO}_3(\text{am,hyd})$ ,  $\text{Sm}(\text{OH})\text{CO}_3 \times 0.5\text{H}_2\text{O}(\text{cr})$ , and  $\text{NaSm}(\text{CO}_3)_2 \times 5\text{H}_2\text{O}(\text{cr})$  should occur at corresponding chemical conditions. For the  $\text{Sm}_2(\text{CO}_3)_3(\text{am})$  phase, Spahiu and Bruno [SPA/BRU1995] have selected a value of  $\log K^\circ = 34.5$  (formation constant), 34.55 for  $\text{Pm}_2(\text{CO}_3)_3(\text{am})$ , and 34.65 for  $\text{Nd}_2(\text{CO}_3)_3(\text{am})$ , and [GUI/FAN2003] selected a value for the  $\text{Am}_2(\text{CO}_3)_3(\text{am})$  with  $\log K^\circ = 33.4 \pm 1.1$ . If one regards the experimental uncertainty that is higher than the deviation of these values, the given solid formation constants are the same. As preliminary approach, the mean value of all formation constant  $\log K^\circ = 34.3 \pm 1.1$ , and the error from [GUI/FAN2003] have been selected in THEREDA for  $\text{Sm}_2(\text{CO}_3)_3(\text{am})$ .

Table 7: Complexation constants for An(III) and Ln(III) carbonate complexes  $\log\beta_n^0$  (I = 0)

|   | $\log\beta_n^0$                  | Comment                              | Reference                            |
|---|----------------------------------|--------------------------------------|--------------------------------------|
| $\text{Sm}^{3+} + \text{CO}_3^{2-} = \text{SmCO}_3^+$                 | 7.8                              | Correlation                          | DUR/GRI2006<br>SPA/BRU1995           |
|   | $7.93 \pm 0.05$                  | Correlation                          | LEE/BYR1992                          |
|   | 7.88                             | Correlation                          | LEE/BYR1993                          |
|   | 7.30                             | Correlation                          | MIL1992                              |
|   | <b>Selected value</b>            | <b><math>8.00 \pm 0.4</math></b>     | Correlation Am(III)/Cm, spectroscopy |
| $\text{Sm}^{3+} + 2 \text{CO}_3^{2-} = \text{Sm}(\text{CO}_3)_2^-$    | $\log\beta_2^0$                  |                                      |                                      |
|   | 12.8                             | Correlation                          | DUR/GRI2006<br>SPA/BRU1995           |
|   | $13.37 \pm 0.11$                 | Correlation                          | LEE/BYR1992,<br>LEE/BYR1993          |
|   | 12.11                            | Correlation                          | MIL1992                              |
|   | $12.9 \pm 0.6$                   | Correlation Am(III)/Cm, spectroscopy | GUI/FAN2003                          |
| <b>Selected value</b>   | <b><math>12.9 \pm 0.6</math></b> |                                      | <b>THEREDA</b>                       |
| $\text{Sm}^{3+} + 3 \text{CO}_3^{2-} = \text{Sm}(\text{CO}_3)_3^{3-}$ | $\log\beta_3^0$                  |                                      |                                      |
|   | <b>Selected value</b>            | <b><math>15 \pm 1.0</math></b>       | Correlation Am(III)/Cm, spectroscopy |
| $\text{Sm}^{3+} + \text{HCO}_3^- = \text{SmHCO}_3^{2+}$               | $\log\beta_1^0$                  |                                      |                                      |
|   | 2.1                              | Correlation                          | DUR/GRI2006<br>SPA/BRU1995           |
|   | 1.75                             | Correlation                          | MIL1992                              |
|   | $3.1 \pm 0.3$                    | Correlation Am(III)/Cm, spectroscopy | GUI/FAN2003                          |
| <b>Selected value</b>   | <b><math>3.1 \pm 0.3</math></b>  |                                      | <b>THEREDA</b>                       |
| $\text{Sm}^{3+} + \text{CO}_3^- + \text{H}^+ = \text{SmHCO}_3^{2+}$   | <b><math>13.4 \pm 0.3</math></b> | Reaction needed for THEREDA          |                                      |

Table 8: Formation constants of solid carbonate and hydroxide carbonate compounds at ionic strength of I = 0.

|  | logK <sup>0</sup> | Comment     | Reference                     |
|--|-------------------|-------------|-------------------------------|
| 2 Sm <sup>3+</sup> + 3 CO <sub>3</sub> <sup>2-</sup> = Sm <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> (am, hyd)   |                   |             |                               |
| Sm <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> (am, hyd)  | 34.5              |             | DUR/GRI2006<br>SPA/BRU1995    |
|  | 33.4 ± 1.1        | Correlation | GUI/FAN2003                   |
| <b>Selected value</b>  | <b>34.5 ± 1.1</b> |             | <b>THEREDA</b>                |
| Sm <sup>3+</sup> + CO <sub>3</sub> <sup>2-</sup> + OH <sup>-</sup> = SmCO <sub>3</sub> OH(am,hyd)  | 20.2 ± 1.0        | Correlation | GUI/FAN2003                   |
| Sm <sup>3+</sup> + CO <sub>3</sub> <sup>2-</sup> + H <sub>2</sub> O = SmCO <sub>3</sub> OH(am,hyd) + H <sup>+</sup>                                      |                   |             |                               |
| <b>Selected value</b>  | <b>6.20 ± 1.0</b> |             | <b>THEREDA</b>                |
| Sm <sup>3+</sup> + CO <sub>3</sub> <sup>2-</sup> + 0.5H <sub>2</sub> O + OH <sup>-</sup> =<br>SmCO <sub>3</sub> OH x 0.5H <sub>2</sub> O(cr)             | 22.4 ± 0.5        | Correlation | GUI/FAN2003                   |
| Sm <sup>3+</sup> + CO <sub>3</sub> <sup>2-</sup> + 1.5H <sub>2</sub> O = SmCO <sub>3</sub> OH x 0.5H <sub>2</sub> O(cr) + H <sup>+</sup>                 |                   |             |                               |
| <b>Selected Value</b>  | <b>8.4 ± 0.5</b>  |             | <b>THEREDA</b>                |
| Sm <sup>3+</sup> + 2 CO <sub>3</sub> <sup>2-</sup> + 5 H <sub>2</sub> O + Na <sup>+</sup> = NaSm(CO <sub>3</sub> ) <sub>2</sub> x 5H <sub>2</sub> O (cr) |                   |             |                               |
| <b>Selected value</b>  | <b>21.0 ± 0.5</b> | Correlation | <b>THEREDA</b><br>GUI/FAN2003 |

For the solid compound Sm(OH)CO<sub>3</sub> (am, hyd), Sm(OH)CO<sub>3</sub> x 0.5H<sub>2</sub>O(cr), and NaSm(CO<sub>3</sub>)<sub>2</sub>x5H<sub>2</sub>O(cr), the values of the Am(III) compounds have been selected as analogue values without proving the correctness because of lack of experimental data. The values are log K<sup>o</sup> = 20.2 ± 1.0, log K<sup>o</sup> = 22.4 ± 0.5 and log K<sup>o</sup> = 21.0 ± 0.5 , respectively [GUI/FAN2003] and were re-calculated owing to the formulation for the reaction regarding protons instead of the hydroxide anion.

### 3.1.1.6.1 Pitzer parameter for the system Sm(III) / CO<sub>3</sub><sup>2-</sup> / H<sub>2</sub>O / Na<sup>+</sup> / Cl<sup>-</sup>

It can be assumed that the Pitzer parameter of trivalent actinides and lanthanides have very similar values. The experimental error of these values is usual larger than the dif-

ference as a result of different chemical, structural and physical properties of the ions. Therefore, we use the Pitzer parameter of americium and curium as analogue values for the samarium. Experimental results concerning the Pitzer parameters of Sm(III) in the carbonate system do not exist so far.

Table 9: Pitzer parameter for Sm(III) carbonate complexes in chloride solutions.

| <b>Binäre Pitzer -Parameter</b>  |   |               |               |               |  |            |            |                  |
|--|---|---------------|---------------|---------------|--|------------|------------|------------------|
| <b>c</b><br>(Analog<br>Am <sup>3+</sup> /Cm <sup>3+</sup> )                        | <b>a</b>  | $\beta^{(0)}$ | $\beta^{(1)}$ | $\beta^{(2)}$ | <b>C<sup>ϕ</sup></b>                         | $\alpha_1$ | $\alpha_2$ | <b>Reference</b> |
| SmCO <sub>3</sub> <sup>+</sup>   | Cl <sup>-</sup>                                 | -0.072        | 0.403         | 0             | 0.0388                                       | 2          | 0          | ALT/BRE2004      |
| Na <sup>+</sup>  | Sm(CO <sub>3</sub> ) <sub>2</sub> <sup>-</sup>  | -0.24         | 0.224         | 0             | 0.0284                                       | 2          | 0          | ALT/BRE2004      |
| Na <sup>+</sup>  | Sm(CO <sub>3</sub> ) <sub>3</sub> <sup>3-</sup> | 0.125         | 4.73          | 0             | 0.0007                                       | 2          | 0          | ALT/BRE2004      |
| <b>Ternary Pitzer parameter</b>  |   |               |               |               |  |            |            |                  |
| <b>c</b>   | <b>c'</b>                                       | <b>a</b>      | $\theta(cc')$ | $\psi(cc'a)$  | <b>Reference for <math>\psi(cc'a)</math></b> |            |            |                  |
| Ternary Pitzer parameter for Am/Cm/Sm(III) carbonate species are not known so far! |   |               |               |               |  |            |            |                  |

### 3.1.1.7 Sm(III) sulphate compounds

#### 3.1.1.7.1 Sm(III) sulphate complexes

According to [WOO1990] the sulphate complexation is maybe the best studied inorganic complex formation reaction of trivalent lanthanides. However, for Sm(III) no direct experimental data are available from literature. If data are reported, they are estimated values deduced from correlations of the chemical behaviour within the lanthanide series. The values for the first lanthanide sulphate complex LnSO<sub>4</sub><sup>+</sup> found in the literature vary from  $\log \beta_1^0 = 3.26$  to  $3.65$ . The [SPA/BRU1995] selected a complex formation constant - note that it is an estimated value - for SmSO<sub>4</sub><sup>+</sup> of  $\log \beta_1^0 = 3.5$ . This value is slightly higher than an experimental value for CmSO<sub>4</sub><sup>+</sup> with  $\log \beta_1^0 = 3.30 \pm 0.15$ . However, the Sm(III) value relies on experimental data of other lanthanides mainly performed with two-phase equilibrium techniques like ion exchange and solvent extraction. These techniques cannot differentiate between ion-ion interaction and inner-sphere

complexation. As a consequence, changes in the activity coefficient because of background electrolyte ion exchange, outer-sphere complexation or ion pair formation were misinterpreted as complex formation. This misinterpretation results in higher complex formation constants. The problems with experimental results obtained by phase separation methods is clearly described in [GUI/FAN2003] for the trivalent americium sulphate complexation.

For the second sulphate complex, [SPA/BRU1995] selected a complex formation constant of  $\log \beta_2^0 = 5.2$  that is significant higher than the value selected for Am(III) disulphate complex with  $\log \beta_2^0 = 3.70 \pm 0.15$ . The NEA realised in the update review [GUI/FAN2003], that the first selection of the constant with  $\log \beta_2^0 = 5.4$  was chosen without taking into consideration the above discussed problems. Please note that this wrong value is very similar to the value selected by [SPA/BRU1995].

For that, we rely for the Sm(III) sulphate complexes on the formation constant deduced from the spectroscopic studies of the trivalent actinide ions.

#### **3.1.1.7.2 Solid Sm(III) sulphate compounds**

In literature, only the  $\text{Ln}_2(\text{SO}_4)_3(\text{s})$  phases are discussed that potentially can be formed in aqueous solutions. For trivalent actinides this type of solid is never mentioned nor discussed and one can conclude that these component is not relevant for the context of final disposal of radioactive waste. Therefore, in the stage of this report, no efforts have been undertaken to evaluate experimental as well as estimated data to select thermodynamic data for THEREDA. In any case, the formation of pure sulfate solid phases under the expected conditions of nuclear waste repositories are highly unrealistic, given the expected low sulfate concentration.

#### **3.1.1.7.3 Pitzer parameter for the system Sm(III) / $\text{SO}_4^{2-}$ / $\text{H}_2\text{O}$ / $\text{Na}^+$ / $\text{Cl}^-$**

For the Sm(III) sulphate complexes, no Pitzer parameters are available from literature. Therefore, because of the findings that complexes of the same charge and ligands show very similar pitzer parameters, the data set of Am(III) and Cm(III) sulphate complexes as chemical surrogates was selected for Sm(III).

Table 10: Complex formation constants  $\log\beta_n^0$  ( $l = 0$ ) for Sm(III) sulphate complexes available in the literature. The selected value from THEREDA is given in boldface.

|   | $\log\beta_n^0$                   | Comment                | Reference                  |
|---|-----------------------------------|------------------------|----------------------------|
| $\text{Sm}^{3+} + \text{SO}_4^{2-} = \text{SmSO}_4^+$             | $n = 1$                           |                        |                            |
|   | 3.5                               | Correlation            | DUR/GRI2006<br>SPA/BRU1995 |
|   | 3.28                              | Correlation            | MIL1992                    |
|   | 3.65                              | Correlation            | HAA/SHO1995                |
|   | $3.30 \pm 0.15$                   | Correlation Am(III)/Cm | GUI/FAN2003                |
| <b>Selected value</b>   | <b><math>3.30 \pm 0.15</math></b> |                        | <b>THEREDA</b>             |
| $\text{Sm}^{3+} + 2\text{SO}_4^{2-} = \text{Sm}(\text{SO}_4)_2^-$ | $n = 2$                           |                        |                            |
|   | 5.2                               | Correlation            | DUR/GRI2006<br>SPA/BRU1995 |
|   | 5.15                              | Correlation            | WOO1990<br>KIP/POW1974     |
|   | 5.42                              | Correlation            | WOO1990<br>KIP/POW1974     |
|   | $3.70 \pm 0.15$                   | Correlation Am(III)/Cm | GUI/FAN2003                |
| <b>Selected value</b>   | <b><math>3.70 \pm 0.15</math></b> |                        | <b>THEREDA</b>             |

Table 11: Pitzer parameter for the Sm(III) aquo ion in sulphate solutions at 25°C.

| Binäre Pitzer -Parameter                        |                              |               |               |               |          |            |            |                            |
|---|------------------------------|---------------|---------------|---------------|----------|------------|------------|----------------------------|
| c   | a                            | $\beta^{(0)}$ | $\beta^{(1)}$ | $\beta^{(2)}$ | $C^\phi$ | $\alpha_1$ | $\alpha_2$ | Reference                  |
| <b>(Analog Am<sup>3+</sup>/Cm<sup>3+</sup>)</b> |                              |               |               |               |          |            |            |                            |
| $\text{Sm}^{3+}$                                | $\text{SO}_4^{2-}$           | 1.792         | 15.044        | 0             | -0.60    | 2          | 0          | ALT/BRE2004<br>PAV/FAN2010 |
| $\text{SmSO}_4^+$                               | $\text{Cl}^-$                | -0.091        | -0.390        | 0             | 0.048    | 2          | 0          | ALT/BRE2004                |
| $\text{SmSO}_4^+$                               | $\text{SO}_4^{2-}$           | 0*            | 0*            | 0             | 0*       | 2          | 0          | PAV/FAN2010                |
| $\text{Na}^+$                                   | $\text{Sm}(\text{SO}_4)_2^-$ | -0.354        | -0.400        | 0             | 0.051    | 2          | 0          | ALT/BRE2004                |

#### Ternary Pitzer parameter

Ternary Pitzer parameter for Am/Cm/Sm(III) sulfate species are not known so far!

\* parameters are set equal to zero



### 3.1.2 Plutonium, Pu(III): Pu<sup>3+</sup>

#### 3.1.2.1 Aqueous species and solid compounds

Neither stability constants nor Pitzer activity coefficients have been selected for Pu(III) aqueous species and solid compounds. In spite of this, the use of Am(III) analogues is recommended for log  $\beta$  and Pitzer parameters of Pu(III) aqueous species, respectively. Thermodynamic data on Am has been made available through the corresponding releases 2 of THEREDA. Note that it is strongly discouraged to use these analogies to fill in thermodynamic data for the corresponding solid phases of Pu(III).

The thermodynamic data gaps existing for Pu(III) will be tackled at KIT-INE through a new experimental program and is partly performed within a PhD study starting in 2014. The effect of carbonate on the aqueous speciation and solubility of Pu(III) will be also assessed together with studies on solid phase stability.

### 3.1.3 Americium, Am(III): Am<sup>3+</sup>

#### 3.1.3.1 Hydrolysis of Am(III)

##### 3.1.3.1.1 Am<sup>3+</sup> hydroxide complexes

In NaCl and NaClO<sub>4</sub> solutions in the pH range of 5–13, mononuclear hydrolysis species Am(OH)<sub>3</sub><sup>3-n</sup> with n=1-3 dominate the aqueous speciation [NEC/ALT2009]. In THEREDA, the Pitzer model of [NEC/ALT2009] is adopted, which is based on the equilibrium constant data of [GUI/FAN2003]. Only in extremely alkaline solutions with OH<sup>-</sup> concentrations >3 M, an increase of americium concentrations is observed, which can be described by formation of an Am(OH)<sub>4</sub><sup>-</sup>-complex [NEC/ALT2009]. In their TRLFS study in alkaline CaCl<sub>2</sub>-solutions, [RAB/ALT2008] observed the formation of tri-, tetra- and hexahydroxo complexes of the composition Ca<sub>p</sub>[Cm(OH)<sub>n</sub>]<sup>2p+3-n</sup>. [NEC/ALT2009] included these complexes into their solubility model, which was included in the THEREDA database.

The stability constants for the formation of the solids  $\text{Am}(\text{OH})_3(\text{cr})$  and  $\text{Am}(\text{OH})_3(\text{am})$  in the model of [NEC/ALT2009] agree with the selection of [GUI/FAN2003]. Kinetics of formation of the crystalline solid from the amorphous  $\text{Am}(\text{OH})_3(\text{am})$  are not clear so that  $\text{Am}(\text{OH})_3(\text{cr})$  was given the flag „dissolution only“ in the database and thus discouraged for equilibrium modeling. In consequence, only  $\text{Am}(\text{OH})_3(\text{am})$  is exported to the THEREDA parameter files with Am that can be downloaded from the THEREDA webpages (details can be found in the Benchmark-paper of Release 02). The hydrolysis data of Am(III) selected for the THEREDA database is given in Table 12.

Table 12: Thermodynamic data selected for the hydrolysis species of Am(III) in THEREDA

| Reaction   | $\log \beta^\circ / \log K^\circ$ | Reference     |
|--|-----------------------------------|---------------|
| $\text{Am}^{3+} + \text{H}_2\text{O} = \text{Am}(\text{OH})^{2+} + \text{H}^+$           | $-7.2 \pm 0.5$                    | [GUI/FAN2003] |
| $\text{Am}^{3+} + 2\text{H}_2\text{O} = \text{Am}(\text{OH})_2^+ + 2\text{H}^+$          | $-15.1 \pm 0.7$                   | [GUI/FAN2003] |
| $\text{Am}^{3+} + 3\text{H}_2\text{O} = \text{Am}(\text{OH})_3^0 + 3\text{H}^+$          | $-26.2 \pm 0.5$                   | [GUI/FAN2003] |
| $\text{Am}^{3+} + 4\text{H}_2\text{O} = \text{Am}(\text{OH})_4^- + 4\text{H}^+$          | $-40.7 \pm 0.7$                   | [NEC/ALT2009] |
| $\text{Am}^{3+} + 3\text{H}_2\text{O} = \text{Am}(\text{OH})_3(\text{am}) + 3\text{H}^+$ | $-16.9 \pm 0.8$                   | [GUI/FAN2003] |
| $\text{Am}^{3+} + 3\text{H}_2\text{O} = \text{Am}(\text{OH})_3(\text{cr}) + 3\text{H}^+$ | $-15.6 \pm 0.6$                   | [GUI/FAN2003] |

### 3.1.3.1.2 Ternary Ca-Am(III)-hydroxo-complexes

Most of the studies on trivalent americium and curium under high ionic strength conditions had been done with NaCl. The formation of ternary Ca-M-hydroxo complexes had been observed in highly alkaline  $\text{CaCl}_2$ -systems for Zr(IV) and Th(IV). The formation of ternary Ca-Cm(III)-hydroxo-complexes was studied with TRLFS by [RAB/ALT2008] and a comprehensive Pitzer model was derived in [NEC/ALT2009]. Under alkaline condi-

tions, these complexes lead to a solubility increase and thus need to be considered in modeling such systems. The dataset of [NEC/ALT2009] including the formation constants of the ternary complexes for Am(III), in analogy to Cm(III), as well as Pitzer coefficients for the interactions with  $\text{Ca}^{2+}$  and  $\text{Cl}^-$ , are selected for the THEREDA database (see Table 13 and Table 14).

Table 13: Equilibrium constants ( $I=0$ ,  $T=25\text{ °C}$ ) for ternary calcium-Am(III)-hydroxo-complexes (data derived from analogies to Cm(III))

| Reaction<br>(analogue)   | $\log \beta^\circ$ | Reference     |
|--|--------------------|---------------|
| $\text{Am}^{3+} + \text{Ca}^{2+} + 3\text{H}_2\text{O} = \text{Ca}[\text{Am}(\text{OH})_3]^{2+} + 3\text{H}^+$<br>( $\text{Cm}^{3+} + \text{Ca}^{2+} + 3\text{H}_2\text{O} = \text{Ca}[\text{Cm}(\text{OH})_3]^{2+} + 3\text{H}^+$ )       | $-26.3 \pm 0.5$    | [NEC/ALT2009] |
| $\text{Am}^{3+} + 2\text{Ca}^{2+} + 4\text{H}_2\text{O} = \text{Ca}_2[\text{Am}(\text{OH})_4]^{3+} + 4\text{H}^+$<br>( $\text{Cm}^{3+} + 2\text{Ca}^{2+} + 4\text{H}_2\text{O} = \text{Ca}_2[\text{Cm}(\text{OH})_4]^{3+} + 4\text{H}^+$ ) | $-37.2 \pm 0.6$    | [NEC/ALT2009] |
| $\text{Am}^{3+} + 3\text{Ca}^{2+} + 6\text{H}_2\text{O} = \text{Ca}_3[\text{Am}(\text{OH})_6]^{3+} + 6\text{H}^+$<br>( $\text{Cm}^{3+} + 3\text{Ca}^{2+} + 6\text{H}_2\text{O} = \text{Ca}_3[\text{Cm}(\text{OH})_6]^{3+} + 6\text{H}^+$ ) | $-60.7 \pm 0.5$    | [NEC/ALT2009] |

### 3.1.3.1.3 Pitzer parameters for Am(III)-hydroxides

The Pitzer parameters of Neck et al. [NEC/ALT2009] are based on the Cm-data of [KON/FAN1997] for the aquo ion and the two chloride complexes. For the hydrolysis complexes, [NEC/ALT2009] derived a new set of Pitzer parameters except for the binary and ternary interaction of  $\text{An}(\text{OH})^{2+}$  with  $\text{Cl}^-$  and  $\text{Na}^+$ , which was included from [NEC/FAN1998] and the interaction between the neutral species  $\text{An}(\text{OH})_3^0$  with  $\text{Na}^+$ , which was adopted from the data of [KON/FAN1997]. As explained elsewhere, [NEC/ALT2009] also derived Pitzer parameters for the ternary Ca-Am(III)-hydroxo-complexes in analogy to Cm(III). The Pitzer parameters included in the THEREDA database are summarized in Table 14.

Though Pitzer parameters for actinide species and -complexes were originally derived with the Pitzer set of [HAR/MOL1984] for the system of oceanic salts, differences between that parameterization and that of THEREDA are small. Benchmark calculations were done combining the Pitzer parameters for the actinides with the THEREDA model

for the oceanic salts. It was shown that differences are negligible compared to the experimental errors (see Benchmark papers of Release 02 and 04).

Table 14: Pitzer parameters for the system Am(III) – H<sub>2</sub>O – Cl<sup>-</sup> - ClO<sub>4</sub><sup>-</sup> - Na<sup>+</sup> - K<sup>+</sup> - Mg<sup>2+</sup> - Ca<sup>2+</sup> (brackets show if value was derived from chemical analogue)

| Pitzer binary   |                               | $\beta(0)$ | $\beta(1)$ | $\beta(2)$ | $C\Phi$ | $\alpha_1$ $\alpha_2$ | Ref.       |
|---|-------------------------------|------------|------------|------------|---------|-----------------------|------------|
| Am <sup>3+</sup><br>(Nd <sup>3+</sup> /Cm <sup>3+</sup> )   | Cl <sup>-</sup>               | 0.5856     | 5.6        | 0          | -0.016  | 2 0                   | 1, 3, 4    |
| Am <sup>3+</sup><br>(Nd <sup>3+</sup> )   | ClO <sub>4</sub> <sup>-</sup> | 0.754      | 6.533      |            | 0.0075  | 2 0                   | 1, 5       |
| Am(OH) <sup>2+</sup>  | Cl <sup>-</sup>               | 0.055      | 1.81       | 0          | 0       | 2 0                   | 1, 3, 5    |
| Am(OH) <sub>2</sub> <sup>+</sup>  | Cl <sup>-</sup>               | -0.13      | 0          | 0          | 0       | 2 0                   | 1, 3       |
| Am(OH) <sub>4</sub> <sup>-</sup>  | Na <sup>+</sup>               | 0          | 0          | 0          | 0       | 2 0                   | 1, 3       |
|   | K <sup>+</sup>                | 0          | 0          | 0          | 0       | 2 0                   | 1, 3       |
|   | Ca <sup>2+</sup>              | 0          | 0          | 0          | 0       | 2 0                   | 1, 3       |
|   | Mg <sup>2+</sup>              | 0          | 0          | 0          | 0       | 2 0                   | 1, 3       |
| AmCl <sup>2+</sup><br>(CmCl <sup>2+</sup> )   | Cl <sup>-</sup>               | 0.593      | 3.15       | 0          | -0.006  | 2 0                   | 1, 3, 4, 5 |
| AmCl <sub>2</sub> <sup>+</sup><br>(CmCl <sub>2</sub> <sup>+</sup> )   | Cl <sup>-</sup>               | 0.516      | 1.75       | 0          | 0.01    | 2 0                   | 1, 3, 4, 5 |
| Ca[Am(OH) <sub>3</sub> ] <sup>2+</sup><br>(Ca[Cm(OH) <sub>3</sub> ] <sup>2+</sup> )                             | Cl <sup>-</sup>               | 0.21       | 1.6        | 0          | 0       | 2 0                   | 1, 3       |
| Ca <sub>2</sub> [Am(OH) <sub>4</sub> ] <sup>3+</sup><br>(Ca <sub>2</sub> [Cm(OH) <sub>4</sub> ] <sup>3+</sup> ) | Cl <sup>-</sup>               | 0.7        | 4.3        | 0          | 0       | 2 0                   | 1, 3       |
| Ca <sub>3</sub> [Am(OH) <sub>6</sub> ] <sup>3+</sup><br>(Ca <sub>3</sub> [Cm(OH) <sub>6</sub> ] <sup>3+</sup> ) | Cl <sup>-</sup>               | 0.37       | 4.3        | 0          | 0       | 2 0                   | 1, 3       |

Table 14 cont.: ternary pitzer parameter  $\Theta$ 

| Pitzer ternary  | $\Theta$        |  |                  |                               |                 |                 |            |
|---|-----------------|--|------------------|-------------------------------|-----------------|-----------------|------------|
|   | Na <sup>+</sup> | K <sup>+</sup>                           | Ca <sup>2+</sup> | Mg <sup>2+</sup>              | Cl <sup>-</sup> | OH <sup>-</sup> |            |
| Am <sup>3+</sup><br>(Nd <sup>3+</sup> )   | 0.1             | 0.1 <sup>(6)</sup><br>(Na <sup>+</sup> ) | 0.2              | 0.2<br>(Ca <sup>2+</sup> )    |                 |                 | 1, 3, 4, 5 |
| Am(OH) <sup>2+</sup>  | 0               |  | 0                | 0<br>(Ca <sup>2+</sup> )      |                 |                 | 1, 3, 4, 5 |
| Am(OH) <sub>2</sub> <sup>+</sup>  | 0               |  | 0.29             | 0.29<br>(Ca <sup>2+</sup> )   |                 |                 | 1, 3       |
| Am(OH) <sub>4</sub> <sup>-</sup>  |                 |  |                  |                               | 0               | 0               | 1, 3       |
| AmCl <sup>2+</sup><br>(CmCl <sup>2+</sup> )   | 0               |  | -0.014           | -0.014<br>(Ca <sup>2+</sup> ) |                 |                 | 1, 3, 4, 5 |
| AmCl <sub>2</sub> <sup>+</sup><br>(CmCl <sub>2</sub> <sup>+</sup> )   | 0               |  | -0.196           | -0.196<br>(Ca <sup>2+</sup> ) |                 |                 | 1, 3, 4, 5 |
| Ca[Am(OH) <sub>3</sub> ] <sup>2+</sup><br>(Ca[Cm(OH) <sub>3</sub> ] <sup>2+</sup> )                             |                 |  | 0                |                               |                 |                 | 1, 3       |
| Ca <sub>2</sub> [Am(OH) <sub>4</sub> ] <sup>3+</sup><br>(Ca <sub>2</sub> [Cm(OH) <sub>4</sub> ] <sup>3+</sup> ) |                 |  | 0                |                               |                 |                 | 1, 3       |
| Ca <sub>3</sub> [Am(OH) <sub>6</sub> ] <sup>3+</sup><br>(Ca <sub>3</sub> [Cm(OH) <sub>6</sub> ] <sup>3+</sup> ) |                 |  | 0                |                               |                 |                 | 1, 3       |

Table 14 cont.: ternary pitzer parameter  $\Psi$ 

| Pitzer, ternary   | $\Psi$          |                 |                         |                  |                             |            |
|---|-----------------|-----------------|-------------------------|------------------|-----------------------------|------------|
|   |                 | Na <sup>+</sup> | K <sup>+</sup>          | Ca <sup>2+</sup> | Mg <sup>2+</sup>            |            |
| Am <sup>3+</sup><br>(Nd <sup>3+</sup> )   | Cl <sup>-</sup> | 0               | 0<br>(Na <sup>+</sup> ) | 0                | 0<br>(Ca <sup>2+</sup> )    | 1, 3, 4, 5 |
| Am(OH) <sup>2+</sup>  | Cl <sup>-</sup> | 0               | 0                       | 0.04             | 0.04<br>(Ca <sup>2+</sup> ) | 1, 3, 4, 5 |
| Am(OH) <sub>2</sub> <sup>+</sup>  | Cl <sup>-</sup> | 0               |                         | 0.07             | 0.07<br>(Ca <sup>2+</sup> ) | 1, 3       |
| Am(OH) <sub>4</sub> <sup>-</sup>  | Cl <sup>-</sup> | 0               | 0                       | 0                | 0                           | 1, 3       |
| Am(OH) <sub>4</sub> <sup>-</sup>  | OH <sup>-</sup> | 0               | 0                       |                  |                             | 1, 3       |
| AmCl <sup>2+</sup><br>(CmCl <sup>2+</sup> )   | Cl <sup>-</sup> | 0               |                         | 0                | 0<br>(Ca <sup>2+</sup> )    | 1, 3, 4, 5 |
| AmCl <sub>2</sub> <sup>+</sup><br>(CmCl <sub>2</sub> <sup>+</sup> )   | Cl <sup>-</sup> | 0               |                         | 0                | 0<br>(Ca <sup>2+</sup> )    | 1, 3, 4, 5 |
| Ca[Am(OH) <sub>3</sub> ] <sup>2+</sup><br>(Ca[Cm(OH) <sub>3</sub> ] <sup>2+</sup> )                             | Cl <sup>-</sup> |                 |                         | 0                |                             | 1, 3       |
| Ca <sub>2</sub> [Am(OH) <sub>4</sub> ] <sup>3+</sup><br>(Ca <sub>2</sub> [Cm(OH) <sub>4</sub> ] <sup>3+</sup> ) | Cl <sup>-</sup> |                 |                         | 0                |                             | 1, 3       |
| Ca <sub>3</sub> [Am(OH) <sub>6</sub> ] <sup>3+</sup><br>(Ca <sub>3</sub> [Cm(OH) <sub>6</sub> ] <sup>3+</sup> ) | Cl <sup>-</sup> |                 |                         | 0                |                             | 1, 3       |

Table 14 cont.: pitzer parameter  $\lambda$  for neutral species

| neutral species                  | $\lambda$                           |                |                  |                  |                 |                 |         |
|----------------------------------|-------------------------------------|----------------|------------------|------------------|-----------------|-----------------|---------|
|                                  | Na <sup>+</sup>                     | K <sup>+</sup> | Ca <sup>2+</sup> | Mg <sup>2+</sup> | Cl <sup>-</sup> | OH <sup>-</sup> |         |
| Am(OH) <sub>3</sub> <sup>0</sup> | -0.2                                | 0              | 0                | 0                | 0               | 0               | 1, 3, 4 |
|                                  | (Cm(OH) <sub>3</sub> ) <sup>0</sup> |                |                  |                  |                 |                 |         |
| 1 THEREDA                        | 5 NEC/FAN1998                       |                |                  |                  |                 |                 |         |
| 2 GUI/FAN2003                    | 6 ALT/BRE2004                       |                |                  |                  |                 |                 |         |
| 3 NEC/ALT2009                    |                                     |                |                  |                  |                 |                 |         |
| 4 KON/FAN1997                    |                                     |                |                  |                  |                 |                 |         |

### 3.1.3.2 Am(III) chloride complexes

The thermodynamic data and Pitzer parameters for Am(III) chloride complexes of [NEC/ALT2009], based on TRLFS studies with Cm(III) [KON/FAN1997], [FAN/KIM1995], are included in the THEREDA.

Table 15: Thermodynamic data selected for the chloride complexes of Am(III) in THEREDA

| Reaction  | log $\beta^\circ$ /logK <sup>o</sup> | Reference     |
|---|--------------------------------------|---------------|
| Am <sup>3+</sup> + Cl <sup>-</sup> = AmCl <sup>2+</sup><br>(Cm <sup>3+</sup> + Cl <sup>-</sup> = CmCl <sup>2+</sup> )                           | 0.24±0.03                            | [GUI/FAN2003] |
| Am <sup>3+</sup> + 2Cl <sup>-</sup> = AmCl <sub>2</sub> <sup>+</sup><br>(Cm <sup>3+</sup> + 2Cl <sup>-</sup> = CmCl <sub>2</sub> <sup>+</sup> ) | -0.74±0.05                           | [GUI/FAN2003] |

### 3.1.3.3 Am(III) carbonates

#### 3.1.3.3.1 Aqueous Am(III)-carbonate complexes

Complexation of Am(III) with carbonate ions was studied under different boundary conditions. An overview of the results has been given by [NEC/FAN1998], [SIL/BID1995] and [GUI/FAN2003].

Carbonate complexation can be described by a relatively simple model using only the mono-, di- and trivalent carbonate complexes,  $\text{Am}(\text{CO}_3)_n^{3-2n}$  with  $n = 1-3$ . While several authors find evidence for the formation of a  $\text{Cm}(\text{CO}_3)_4^{5-}$  or  $\text{Ln}(\text{CO}_3)_4^{5-}$  complex, such a tetracarbonato complex has not been identified for Am(III). Minor differences in the ionic radii of Cm and Am may cause this different behavior regarding the formation of the highly-coordinated complex [GUI/FAN2003]. In the NEA review [GUI/FAN2003] it was shown that most experimental data can be described without considering an An(III)-hydroxo-carbonate complex. Fanghänel et al. [FAN/WEG1998], [FAN/KON1999] explain that this complex will only form under very high partial pressures of  $\text{CO}_2$  ( $p\text{CO}_2 \geq 500$  mbar) and pH-values lower than 6.5. In the Pitzer model of [NEC/FAN1998], the hydroxo-carbonato-complex is not included so that the consistency with this model remains to be demonstrated. For this reason, we exclude this complex from being exported to the parameter files by unchecking the “enable” field.

The  $\log K^\circ$ -values of [GUI/FAN2003] are within the given uncertainties equal to the values given by [NEC/FAN1998]. Although the Pitzer parameters of [NEC/FAN1998] were derived in combination with the formation data and are, therefore, a consistent parameter set, we decided to select the NEA values [GUI/FAN2003] for the formation constants together with the Pitzer parameter set from [NEC/FAN1998]. Within the experimental uncertainties, this leads to negligible deviations.

Table 16: Equilibrium constants ( $I = 0$ ,  $25^\circ\text{C}$ ) for Am(III)-carbonate complexes according to different sources

|                                 | <b><math>\log \beta^\circ</math></b><br>[GUI/FAN2003]<br>SIT | <b><math>\log \beta^\circ</math></b><br>[NEC/FAN1998,<br>FAN/KON1999]<br>Pitzer | <b><math>\log \beta^\circ</math></b><br>THEREDA<br>Pitzer/SIT |
|---------------------------------|--|---|---|
| $\text{AmCO}_3^+$               | $8.0 \pm 0.4$  | $8.1 \pm 0.3$   | $8.0 \pm 0.4$   |
| $\text{Am}(\text{CO}_3)_2^-$    | $12.9 \pm 0.6$   | $13.0 \pm 0.5$  | $12.9 \pm 0.6$  |
| $\text{Am}(\text{CO}_3)_3^{3-}$ | $15.0 \pm 1.0$   | $15.2 \pm 0.4$  | $15.0 \pm 1.0$  |

Since the Am(III) hydroxo-carbonate species was not considered in the Pitzer model of [FAN/KON1999] and its consistency has not been proven yet, the “enabled” box is unchecked, which prevents its export to the THEREDA parameter files.

Table 17: Equilibrium constants for aqueous Am(III)-carbonate- and hydroxo-carbonate complexes (I = 0, 25 °C)

| Reaction   | log $\beta^\circ$            | Reference                       |
|--|------------------------------|---------------------------------|
| $\text{AnCO}_3^+ + \text{H}^+ = \text{An}^{3+} + \text{HCO}_3^-$                 | $8.0 \pm 0.4$                | [GUI/FAN2003]                   |
| $\text{An}(\text{CO}_3)_2^- + 2\text{H}^+ = \text{An}^{3+} + 2\text{HCO}_3^-$    | $12.9 \pm 0.6$               | [GUI/FAN2003]                   |
| $\text{An}(\text{CO}_3)_3^{3-} + 3\text{H}^+ = \text{An}^{3+} + 3\text{HCO}_3^-$ | $15.0 \pm 1.0$               | [GUI/FAN2003]                   |
| $\text{Cm}(\text{CO}_3)_4^{5-} + 4\text{H}^+ = \text{Cm}^{3+} + 4\text{HCO}_3^-$ | $13.0 \pm 0.5^{\text{a}}$    | [FAN/KON1999],<br>[NEC/FAN1998] |
| $\text{AnHCO}_3^{2+} = \text{An}^{3+} + \text{HCO}_3^-$                          | $13.428 \pm 0.30^{\text{b}}$ | [GUI/FAN2003]                   |

<sup>a)</sup> existence of  $\text{Am}(\text{CO}_3)_4^{5-}$  could not be verified spectroscopically,

<sup>b)</sup> excluded from the export to the parameter files because consistency with the current Pitzer model has not been proven yet

### 3.1.3.3.2 Solid Am(III)-carbonates

The thermodynamic data – formation constant of the solid - of the Am(III)-carbonate solids were taken from the NEA-TDB data selection [GUI/FAN2003] and they were regarded as reliable and consistent with the THEREDA database. The solids and the corresponding reaction and formation constants are shown in Table 18.

The solid  $\text{Am}_2(\text{CO}_3)_3(\text{am,hyd})$  was considered to be metastable over the range of relevant natural conditions in the report of [NEC/FAN1998] and is therefore marked in the THEREDA database with the equilibrium constraint “dissociation”. The flag “dissociation” causes the phase to be included only in the comments section of the parameter files that are released from the THEREDA database. It was shown that even at low  $\text{Na}^+$ -concentrations (0.1 m) the formation of  $\text{NaAm}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}(\text{cr})$  is favoured over  $\text{Am}_2(\text{CO}_3)(\text{s})$  [NEC/FAN1998]. In dilute solutions, mixed hydroxo carbonates, e.g.  $\text{Am}(\text{CO}_3)(\text{OH})_{\text{hyd}}(\text{am})$  and  $\text{Am}(\text{CO}_3)(\text{OH}) \cdot 0.5\text{H}_2\text{O}(\text{cr})$  will be the solubility-controlling solids.



Table 18: Formation constants  $\log K_{s,0}$  of solid Am(III) carbonate compounds from [GUI/FAN2003] and if necessary, the re-calculation to meet the demands of THEREDA

|   |  |
|---|--|
| <p><b>AmCO<sub>3</sub>OH(am,hyd) (<math>\cong</math> Am(CO<sub>3</sub>)(OH)_hyd(am))</b><br/> <math>\text{Am}^{3+} + \text{CO}_3^{2-} + \text{OH}^- \rightleftharpoons \text{AmCO}_3\text{OH}(\text{am,hyd})</math><br/> <math>\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-</math></p>  | <p><math>\log K_{s,0} = 20.2 \pm 1.0^{\text{a)}</math><br/> <math>\log K^\circ = -14.001</math></p>  |
| <p><math>\text{Am}^{3+} + \text{CO}_3^{2-} + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{AmCO}_3\text{OH}(\text{am,hyd}) + \text{H}^+</math></p>  | <p><math>\log K_{s,0} = 6.199 \pm 1.0</math></p>   |
| <p><b>AmCO<sub>3</sub>OH·0.5H<sub>2</sub>O(cr) (<math>\cong</math> Am(CO<sub>3</sub>)(OH):0.5H<sub>2</sub>O(cr))</b><br/> <math>\text{Am}^{3+} + \text{CO}_3^{2-} + \text{OH}^- + 0,5\text{H}_2\text{O} \rightleftharpoons \text{AmCO}_3\text{OH}\cdot 0.5\text{H}_2\text{O}(\text{cr})</math><br/> <math>\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-</math></p> | <p><math>\log K_{s,0} = 22.40 \pm 0.5^{\text{a)}</math><br/> <math>\log K^\circ = -14.001</math></p> |
| <p><math>\text{Am}^{3+} + \text{CO}_3^{2-} + 1.5\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{AmCO}_3\text{OH}\cdot 0.5\text{H}_2\text{O}(\text{cr}) + \text{H}^+</math></p>  | <p><math>\log K_{s,0} = 8.399 \pm 0.5</math></p>   |
| <p><b>NaAm(CO<sub>3</sub>)<sub>2</sub>·5 H<sub>2</sub>O(cr)</b></p>   |  |
| <p><math>\text{Am}^{3+} + 2\text{CO}_3^{2-} + 5\text{H}_2\text{O}(\text{l}) + \text{Na}^+ \rightleftharpoons \text{NaAm}(\text{CO}_3)_2\cdot 5\text{H}_2\text{O}(\text{cr})</math></p>  | <p><math>\log K_{s,0} = 21.0 \pm 0.5^{\text{a)}</math></p>   |

a) GUI/FAN2003

### 3.1.3.3.3 Pitzer parameters for the Am(III) carbonate system

Fanghänel et al. [FAN/KON1999]) and Neck et al. [NEC/FAN1998] have established a Pitzer parameter set for the carbonate species of Am(III) in sodium chloride as back electrolyte (s. Table 19). Details about the deduction of the Pitzer parameters can be found in the two publications above mentioned.

### 3.1.3.3.4 Modelling of Am(III) hydrolysis and comparison with experimental data

This chapter illustrates the agreement between experimental data and thermodynamic calculation using the thermodynamic data selected within THEREDA. Although there are some small differences between the experimental data and the modelled curves, the agreement is quite good (s. Figure 2 Figure 4). Nevertheless, some improvements are advised in the chemical model at low ionic strengths for the Am(III) in the carbonate system.

Table 19: Pitzer parameters for the Am(III) carbonate system (theta and psi cannot be separated from the binary parameters and are therefore set equal to 0 [FAN/KON1999])

| Pitzer binary   |                                    | $\beta(0)$                         | $\beta(1)$       | $\beta(2)$       | $C\Phi$          | $\alpha_1 \alpha_2$ | Ref.    |
|---|------------------------------------|------------------------------------|------------------|------------------|------------------|---------------------|---------|
| Am(CO <sub>3</sub> ) <sup>+</sup><br>(Cm(CO <sub>3</sub> ) <sup>+</sup> )                             | Cl <sup>-</sup>                    | -0.072                             | 0.403            | 0                | 0.0388           | 2 0                 | 1, 2, 3 |
| Am(CO <sub>3</sub> ) <sub>2</sub> <sup>-</sup><br>(Cm(CO <sub>3</sub> ) <sub>2</sub> <sup>-</sup> )   | Na <sup>+</sup>                    | -0.240                             | 0.224            | 0                | 0.0284           | 2 0                 | 1, 2, 3 |
| Am(CO <sub>3</sub> ) <sub>3</sub> <sup>3-</sup><br>(Cm(CO <sub>3</sub> ) <sub>3</sub> <sup>3-</sup> ) | Na <sup>+</sup>                    | 0.125                              | 4.730            | 0                | 0.0007           | 2 0                 | 1, 2, 3 |
| Cm(CO <sub>3</sub> ) <sub>4</sub> <sup>5-</sup>   | Na <sup>+</sup>                    | 2.022                              | 19.22            | 0                | -0.305           | 2 0                 | 1, 2, 3 |
| <b>Pitzer ternary</b>   |                                    |                                    |                  |                  |                  |                     |         |
| <b>Θ</b>  |                                    |                                    |                  |                  |                  |                     |         |
| Am(CO <sub>3</sub> ) <sup>+</sup><br>(Cm(CO <sub>3</sub> ) <sup>+</sup> )                             | Na <sup>+</sup><br>0 <sup>a)</sup> | K <sup>+</sup>                     | Ca <sup>2+</sup> | Mg <sup>2+</sup> | Cl <sup>-</sup>  | OH <sup>-</sup>     | 1, 2, 3 |
| Am(CO <sub>3</sub> ) <sub>2</sub> <sup>-</sup><br>(Cm(CO <sub>3</sub> ) <sub>2</sub> <sup>-</sup> )   |                                    |                                    |                  |                  | 0 <sup>a)</sup>  |                     | 1, 2, 3 |
| Am(CO <sub>3</sub> ) <sub>3</sub> <sup>3-</sup><br>(Cm(CO <sub>3</sub> ) <sub>3</sub> <sup>3-</sup> ) |                                    |                                    |                  |                  | 0 <sup>a)</sup>  |                     | 1, 2, 3 |
| Cm(CO <sub>3</sub> ) <sub>4</sub> <sup>5-</sup>   |                                    |                                    |                  |                  | 0 <sup>a)</sup>  |                     | 1, 2, 3 |
| <b>Ψ</b>  |                                    |                                    |                  |                  |                  |                     |         |
| Am(CO <sub>3</sub> ) <sup>+</sup><br>(Cm(CO <sub>3</sub> ) <sup>+</sup> )                             | Cl <sup>-</sup>                    | Na <sup>+</sup><br>0 <sup>a)</sup> | K <sup>+</sup>   | Ca <sup>2+</sup> | Mg <sup>2+</sup> |                     | 1, 2, 3 |
| Am(CO <sub>3</sub> ) <sub>2</sub> <sup>-</sup><br>(Cm(CO <sub>3</sub> ) <sub>2</sub> <sup>-</sup> )   | Cl <sup>-</sup>                    | 0 <sup>a)</sup>                    |                  |                  |                  |                     | 1, 2, 3 |
| Am(CO <sub>3</sub> ) <sub>3</sub> <sup>3-</sup><br>(Cm(CO <sub>3</sub> ) <sub>3</sub> <sup>3-</sup> ) | Cl <sup>-</sup>                    | 0 <sup>a)</sup>                    |                  |                  |                  |                     | 1, 2, 3 |
| Cm(CO <sub>3</sub> ) <sub>4</sub> <sup>5-</sup>   | Cl <sup>-</sup>                    | 0 <sup>a)</sup>                    |                  |                  |                  |                     | 1, 2, 3 |
| 1 THEREDA<br>2 FAN/KON1999<br>3 NEC/FAN1998   |                                    |                                    |                  |                  |                  |                     |         |

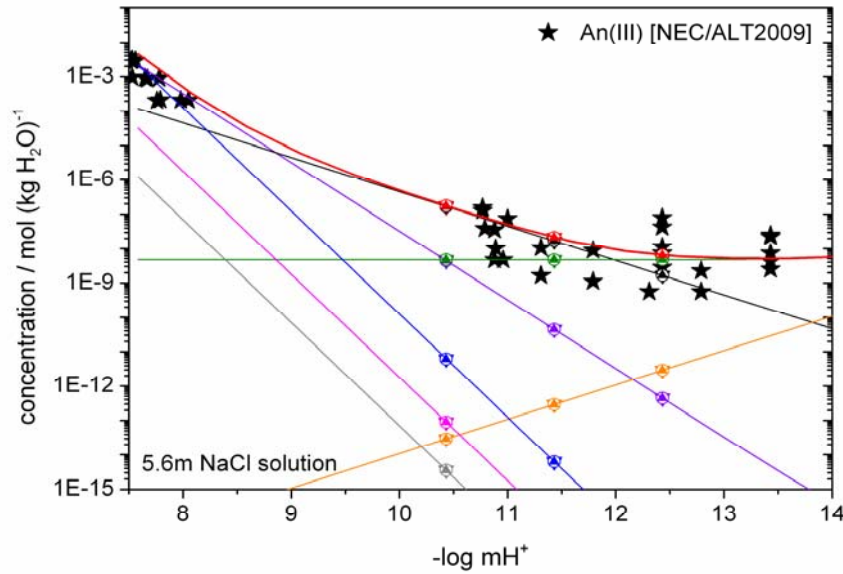


Figure 2: Solubility of  $\text{Am}(\text{OH})_3(\text{am})$  in 5.6 m NaCl solution. Black stars: experimental data of [NEC/ALT2009] (solubility of analogon  $\text{Nd}(\text{OH})_3(\text{am})$ ); lines: Phreeqc results; open circles, down- and upward triangles: results by using ChemApp, EQ3/6, and GWB.

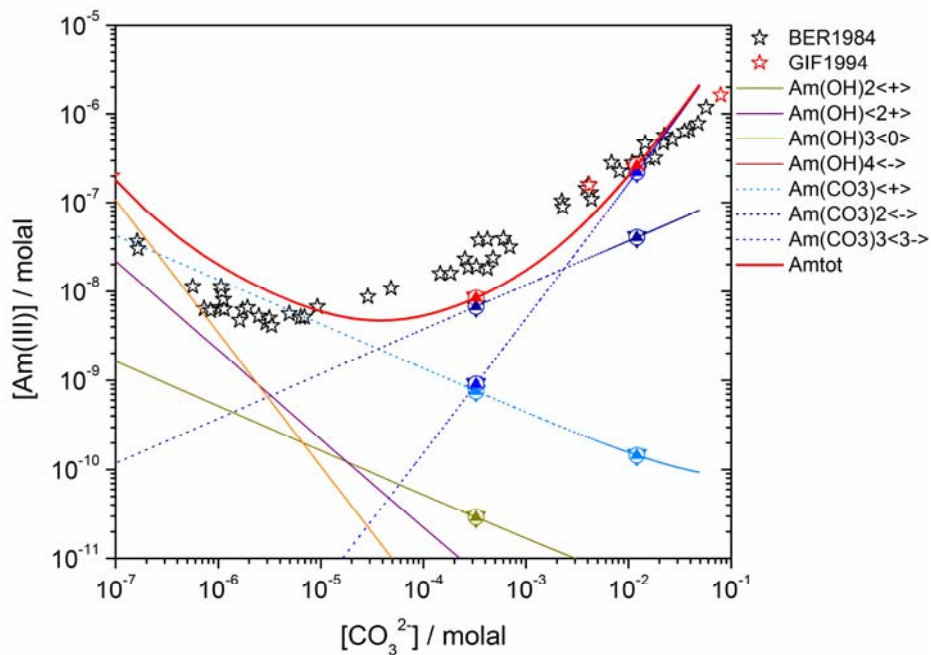


Figure 3: Solubility of  $\text{Am}(\text{CO}_3)(\text{OH}) \cdot 0.5\text{H}_2\text{O}(\text{cr})$  at  $I=0.1$  m and  $p\text{CO}_2=10^{-3.5}$  atm. Black and red stars: experimental data of [BER1984] (solubility in 0.1 m  $\text{NaClO}_4$  solution) and [GIF1994] (solubility in 0.1 m NaCl solution,  $p\text{CO}_2=10^{-3.9}$ - $10^{-3.3}$  atm); lines: GWB results; open circles, down- and upward triangles: results by using ChemApp, Phreeqc and EQ3/6.

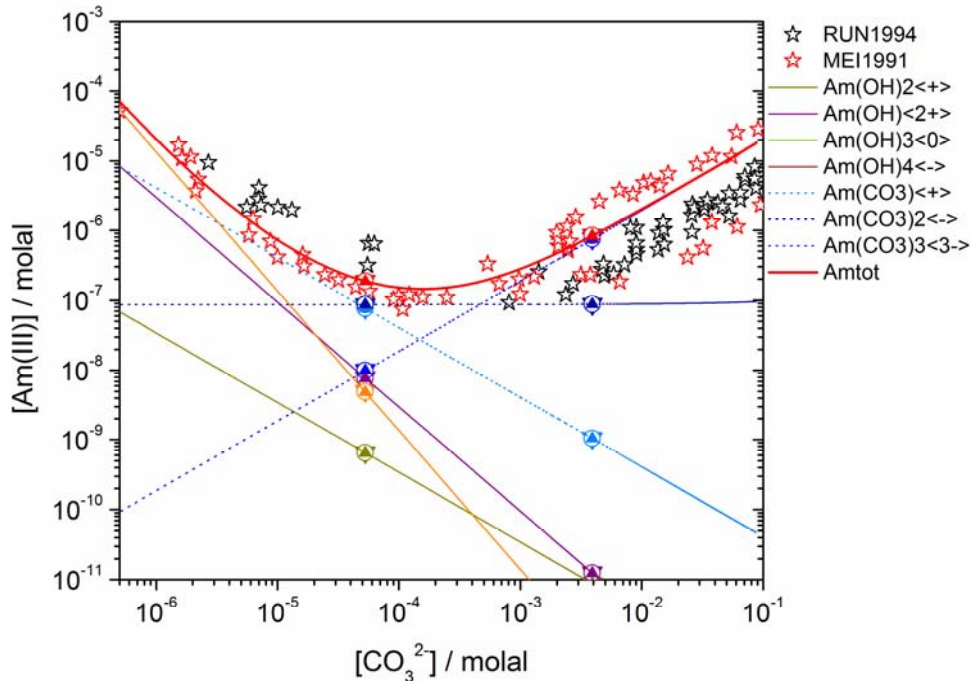


Figure 4: Solubility of  $\text{NaAm}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}(\text{cr})$  in 5.6 m NaCl solution at  $p\text{CO}_2 = 10^{-2.0}$  atm. Black and red stars: experimental data of [RUN1994] and [MEI1991]; lines: GWB results; open circles, down- and upward triangles: results by using ChemApp, Phreeqc and EQ3/6.

### 3.2 Tetravalent radionuclides: actinides, technetium and zirconium

#### 3.2.1 Thorium, Th(IV): $\text{Th}^{4+}$

Thorium only exists in the tetravalent oxidation state in aqueous solutions relevant for final disposal in deep geologic formation. No redox reactions involving Th have been accordingly considered in THEREDA database.  $\text{Th}^{4+}$  has been defined as a primary master species in the database.

Thermodynamic data of thorium and its aqueous species were evaluated by OECD/NEA and recently published in the eleventh volume of the OECD/NEA series “Chemical Thermodynamics” [RAN/FUG2008]. The NEA–TDB data selection does not consider Pitzer for the correction of ionic strength effects and therefore has been disregarded as main source of thermodynamic data in the selection of Th in THEREDA. Instead, a number of publications from the research groups of Rai, Felmy and co-workers

and Neck, Altmaier and co-workers have been chosen as main source of data. As discussed in the following sections, these studies allow a selection of thermodynamic data for Th hydrolysis, solubility and carbonate complexation within the Pitzer approach, although at the cost of relevant shortcomings (mostly in terms of hydrolysis species and Th–CO<sub>3</sub> complexes at low carbonate concentrations) which will need to be addressed in the future.

### 3.2.2 Th aqueous species and solid compounds

The following aqueous species and solid compounds have been included in the current selection of THEREDA for Th(IV), and are discussed in the following sections:

- Aquo Ion: Th<sup>4+</sup>
- Hydrolysis species, Ca ternary species and oxo-hydroxide compounds: Th(OH)<sub>4</sub>(aq), Ca<sub>4</sub>[Th(OH)<sub>8</sub>]<sup>4+</sup>, Th(OH)<sub>4</sub>(am, aged)
- Carbonate complexes: Th(OH)<sub>3</sub>CO<sub>3</sub><sup>-</sup>, Th(CO<sub>3</sub>)<sub>5</sub><sup>6-</sup>
- Chloride complexes: no species selected. Effect of chloride included in the Pitzer ion interaction parameters.
- Fluoride complexes: no species selected.
- Sulphate complexes: no species selected.
- Phosphate complexes: no species selected.

Pitzer ion interaction parameters reported in the original experimental studies have been selected for all the species included in THEREDA except for Th(OH)<sub>3</sub>CO<sub>3</sub><sup>-</sup>, for which estimated values reported in [ALT/BRE2004] have been considered.

#### 3.2.2.1 Hydrolysis, complexes with Ca and oxy-hydroxide compounds

Th(IV) has a very complex hydrolysis scheme, as indicated in very many publications available in the literature and accordingly selected in the NEA–TDB review [RAN/FUG2008]. The latter selects up to 9 hydrolysis species, namely Th(OH)<sup>3+</sup>, Th(OH)<sub>2</sub><sup>2+</sup>, Th(OH)<sub>4</sub>(aq), Th<sub>2</sub>(OH)<sub>2</sub><sup>6+</sup>, Th<sub>2</sub>(OH)<sub>3</sub><sup>5+</sup>, Th<sub>4</sub>(OH)<sub>8</sub><sup>8+</sup>, Th<sub>4</sub>(OH)<sub>12</sub><sup>4+</sup>, Th<sub>6</sub>(OH)<sub>14</sub><sup>10+</sup> and Th<sub>6</sub>(OH)<sub>15</sub><sup>9+</sup>. This selection is characterized by the large number of oligomers with

very high charges (up to +10), which makes these species very sensitive to changes in ionic strength.

In contrast to the large number of experimental studies dealing with Th(IV) solubility and hydrolysis in diluted systems, studies covering highly saline conditions are rather scarce. Based on their systematic experimental work in dilute to concentrated NaCl solutions, Rai, Felmy and co-workers [RYA/RAI1987, FEL/RAI1991, FEL/RAI1992, ROY/VOG1992, RAI/FEL1997, FEL/RAI1999, RAI/MOO2000] proposed a simplified hydrolysis scheme including  $\text{Th}^{4+}$  and  $\text{Th}(\text{OH})_4(\text{aq})$  aqueous species in equilibrium with an amorphous solid  $\text{ThO}_2(\text{am, hyd})$ . This scheme has been retained in the current selection of THEREDA, mostly due to the lack of additional chemical models coupled with the Pitzer formalism. Although stability constants reported by Rai and co-workers have been disregarded in this selection (see discussion below), Pitzer ion interaction coefficients reported by these authors have been included in THEREDA. Note that the activity model originally derived by the authors was complemented in [RAI/FEL1997] with the ternary parameters  $\varphi_{\text{Na}^+, \text{Th}^{4+}}$  and  $\psi_{\text{Na}^+, \text{Th}^{4+}, \text{Cl}^-}$ . This activity model explains properly the trend of Th(IV) solubility observed up to 6.0 m NaCl within the pH range 3–5 [RAI/FEL1997].

The comprehensive solubility studies with  $\text{Th}(\text{OH})_4(\text{am})$  conducted by Altmaier, Neck, Fellhauer and co-workers in dilute to concentrated  $\text{CaCl}_2$  solutions [ALT/NEC2008, FEL/NEC2010] have been used as anchoring point in defining the solubility-controlling solid phase selected for Th(IV). These authors considered the aged amorphous phase  $\text{Th}(\text{OH})_4(\text{am, aged})$  selected in the NEA–TDB ( $\log K_{\text{s},0}^\circ = -47.5 \pm 0.9$ ) for the development of their thermodynamic model. Based on a chemical model including the formation of the species  $\text{Ca}_4[\text{An}(\text{OH})_8]^{4+}$  in concentrated  $\text{CaCl}_2$  solutions, the authors determined a  $\log K_{\text{s},(4,1,8)}^\circ$  and accordingly calculated  $\log \beta_{(4,1,8)}^\circ$ . This value has been included without further modifications in THEREDA. Values of  $\beta^{(0)}$ ,  $\beta^{(1)}$  and  $C^\phi$  selected in [FEL/NEC2010] for  $\text{Ca}_4[\text{An}(\text{OH})_8]^{4+}$  have been also selected in the THEREDA database.

Probably the most relevant hydrolysis reaction of Th(IV) (and also of U(IV), Np(IV) and Pu(IV)) is the formation of  $\text{Th}(\text{OH})_4(\text{aq})$ . This species controls the aqueous chemistry of

Th(IV) within  $6 \leq \text{pH}_c \leq 14$ , except in concentrated  $\text{CaCl}_2$  brines where  $\text{Ca}_4[\text{An}(\text{OH})_8]^{4+}$  forms above  $\text{pH}_c \sim 11$ . The solubility reaction  $\text{Th}(\text{OH})_4(\text{am}) \Leftrightarrow \text{Th}(\text{OH})_4(\text{aq})$  defines the concentration limits calculated within this pH range, and it is thus responsible for the source term of Th(IV) under a large variety of repository-relevant conditions. Although there is a general agreement that  $\log K_{s,(1,4)}^\circ$  lays between  $-8$  and  $-9$ , the value of  $\log \beta_{(1,4)}^\circ$  is fully dependent on the  $\log K_{s,0}^\circ$  selected in the thermodynamic model.  $\log \beta_{(1,4)}^\circ = -17.4 \pm 0.7$  has been selected in agreement with the NEA–TDB, thus maintaining the consistency with the selected  $\log K_{s,0}^\circ$  as well as retaining a realistic  $\log K_{s,(1,4)}^\circ = -8.9$ . Note that, although similar  $\log K_{s,(1,4)}^\circ$  results from the data selection by Rai, Felmy and co-workers, very different  $\log \beta_{(1,4)}^\circ$  ( $\leq -19.7$ ) and  $\log K_{s,0}^\circ$  (between  $-44.8$  and  $-45.5$ ) are proposed by the authors.

Table 20, Table 21 and Table 22 summarize the thermodynamic data ( $\log K$  and Pitzer binary and ternary parameters) available for Th(IV) hydrolysis species, ternary complexes with Ca and oxy-hydroxide compounds. Data highlighted in bold correspond to the final selection considered in THEREDA. Although disregarded in the present selection, thermodynamic data for  $\text{ThOH}^{3+}$ ,  $\text{Th}(\text{OH})_2^{2+}$  and  $\text{Th}(\text{OH})_3^+$  species reported in the reviews by Neck and co-workers [NEC/MÜL2002] as well as in the NEA–TDB [RAN/FUG2008] have been appended in the table for comparison purposes.

Table 20: Log  $K^\circ$  values available in the literature from experimental studies for the formation of  $\text{Th}(\text{OH})_4(\text{aq})$ ,  $\text{Th}(\text{OH})_4(\text{am})$  and  $\text{Ca}_4[\text{Th}(\text{OH})_8]^{4+}$ . Bold-marked data corresponding to the current THEREDA selection. Log  $K$  values reported in [NEC/MÜL2002] and [RAN/FUG2008] for the formation of  $\text{ThOH}^{3+}$ ,  $\text{Th}(\text{OH})_2^{2+}$  and  $\text{Th}(\text{OH})_3^+$  species (not selected in THEREDA) are included for comparison. Thermodynamic data available for  $\text{ThO}_2(\text{cr})$  and polynuclear species of Th(IV) not considered in the comparison.

| Reaction   | log $K^\circ$                     | Reference                     |
|--|-----------------------------------|-------------------------------|
| $\text{Th}(\text{OH})_4(\text{am}) \Leftrightarrow \text{Th}^{4+} + 4 \text{OH}^-$   | -44.8                             |                               |
|  | -45.5                             | [RYA/RAI1987]                 |
|  | -45.5                             | [FEL/RAI1991]                 |
|  | $-44.9 \pm 0.5$                   | [RAI/FEL1997]                 |
|  | $-47.8 \pm 0.3$                   | [RAI/MOO2000]                 |
|  | $-46.7 \pm 0.9$                   | [NEC/MÜL2002]                 |
|  | (fresh)                           | [RAN/FUG2008]                 |
|  | $-47.5 \pm 0.9$                   | [RAN/FUG2008]                 |
| (aged)   | <b>THEREDA [p.w.]</b>             |                               |
|  | <b><math>-47.5 \pm 0.9</math></b> |                               |
| $\text{Th}^{4+} + \text{H}_2\text{O} \Leftrightarrow \text{ThOH}^{3+} + \text{H}^+$  | $-2.2 \pm 0.2^{\text{a}}$         | [NEC/MÜL2002]                 |
|  | $-2.5 \pm 0.5$                    | [RAN/FUG2008]                 |
| $\text{Th}^{4+} + 2 \text{H}_2\text{O} \Leftrightarrow \text{Th}(\text{OH})_2^{2+} + 2 \text{H}^+$                                 | $-6.0 \pm 0.6^{\text{a}}$         | [NEC/MÜL2002]                 |
|  | $-6.2 \pm 0.5$                    | [RAN/FUG2008]                 |
| $\text{Th}^{4+} + 3 \text{H}_2\text{O} \Leftrightarrow \text{Th}(\text{OH})_3^+ + 3 \text{H}^+$                                    | $-11.0 \pm 1.0^{\text{a}}$        | [NEC/MÜL2002]                 |
| $\text{Th}^{4+} + 4 \text{H}_2\text{O} \Leftrightarrow \text{Th}(\text{OH})_4(\text{aq}) + 4 \text{H}^+$                           | $\leq -19.7$                      | [RYA/RAI1987]                 |
|  | $-17.5 \pm 1.0^{\text{a}}$        | [NEC/MÜL2002]                 |
|  | $-17.4 \pm 0.7$                   | [RAN/FUG2008]                 |
|  | <b><math>-17.4 \pm 0.7</math></b> | <b>THEREDA [p.w.]</b>         |
| $4 \text{Ca}^{2+} + \text{Th}^{4+} + 8 \text{H}_2\text{O} \Leftrightarrow \text{Ca}_4[\text{Th}(\text{OH})_8]^{4+} + 8 \text{H}^+$ | $-63.5 \pm 1.0$                   | [ALT/NEC2008,<br>FEL/NEC2010] |
|  | <b><math>-63.5 \pm 1.0</math></b> | <b>THEREDA [p.w.]</b>         |

a. review of available experimental data



Table 21: Binary Pitzer parameters available in the literature for  $\text{Th}^{4+}$ ,  $\text{Th}(\text{OH})_4(\text{aq})$  and  $\text{Ca}_4[\text{Th}(\text{OH})_8]^{4+}$ . Bold-marked data corresponding to the current THEREDA selection.

| Species                                    | $\beta^{(0)}$<br>( $\text{kg}\cdot\text{mol}^{-1}$ ) | $\beta^{(1)}$<br>( $\text{kg}\cdot\text{mol}^{-1}$ ) | $\beta^{(2)}$<br>( $\text{kg}\cdot\text{mol}^{-1}$ ) | $\mathbf{C}^\phi$<br>( $\text{kg}^2\cdot\text{mol}^{-2}$ ) | $\alpha_1$ | $\alpha_2$ | Reference                     |
|--|--|--|--|--|------------|------------|-------------------------------|
| $\text{Th}^{4+}$                           | 1.014  | 13.3   | -200   | -0.103   | 2.0        |            | [FEL/RAI1991]                 |
|  | 1.014  | 13.3   | -200   | -0.103   | 2.0        |            | [FEL/RAI1992]                 |
|  | 1.092  | 13.7   | -160   | -0.112   | 2.0        | 12         | [ROY/VOG1992]                 |
|  | 1.092  | 13.7   | -160   | -0.112   | 2.0        | 12         | [RAI/FEL1997]                 |
|  | 1.092  | 13.7   | -160   | -0.112   | 2.0        | 12         | [FEL/RAI1999]                 |
|  | 1.092  | 13.7   | -160   | -0.112   | 2.0        | 12         | [RAI/MOO2000]                 |
|  | <b>1.092</b>   | <b>13.7</b>  | <b>-160</b>  | <b>-0.112</b>  | <b>2.0</b> | <b>12</b>  | <b>THEREDA [p.w.]</b>         |
| $\text{Th}(\text{OH})_4(\text{aq})$        | $\lambda = 0$  |  |  |  |            |            | per definition                |
| $\text{Ca}_4[\text{Th}(\text{OH})_8]^{4+}$ | 0.58   | 8.9  |  | 0.07   |            |            | [ALT/NEC2008,<br>FEL/NEC2010] |
|  | <b>0.58</b>  | <b>8.9</b>   |  | <b>0.07</b>  |            |            | <b>THEREDA [p.w.]</b>         |

Table 22: Ternary Pitzer parameters available in the literature for  $\text{Th}^{4+}$ . Bold-marked data corresponding to the current THEREDA selection.

| Species ( <i>i</i> ) | <i>J</i>      | <i>k</i>      | ${}^s\theta_{i,k}$ | $\Psi_{i,j,k}$ | Reference             |
|----------------------|---------------|---------------|--------------------|----------------|-----------------------|
| $\text{Th}^{4+}$     | $\text{Cl}^-$ | $\text{H}^+$  | 0.60               | 0.37           | [ROY/VOG1992]         |
|                      |               |               | 0.60               | 0.08           | [FEL/RAI1992]         |
|                      |               |               | 0.60               | 0.08           | [FEL/RAI1999]         |
|                      |               |               | 0.60               | 0.08           | [RAI/MOO2000]         |
|                      |               |               | <b>0.60</b>        | <b>0.08</b>    | <b>THEREDA [p.w.]</b> |
| $\text{Th}^{4+}$     | $\text{Cl}^-$ | $\text{Na}^+$ | 0.420              | 0.210          | [RAI/FEL1997]         |
|                      |               |               | 0.420              | 0.210          | [FEL/RAI1999]         |
|                      |               |               | 0.420              | 0.210          | [RAI/MOO2000]         |
|                      |               |               | <b>0.420</b>       | <b>0.210</b>   | <b>THEREDA [p.w.]</b> |

A series of test calculations have been conducted with GWB, Phreeqc, EQ3/6 and Chemapp based on the thermodynamic data selection for Th(IV) in THEREDA. The results are summarized in detail in the document "Benchmark R07: Th(IV), Np(IV) and

Pu(IV) solubility in NaCl, CaCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub> and KHCO<sub>3</sub> solutions”. The comparison of these test calculations with experimental solubility data in 4.0 m NaCl [RAI/FEL1997] and 5.26 m CaCl<sub>2</sub> [ALT/NEC2008] is provided in Figure 5 and Figure 6, respectively.

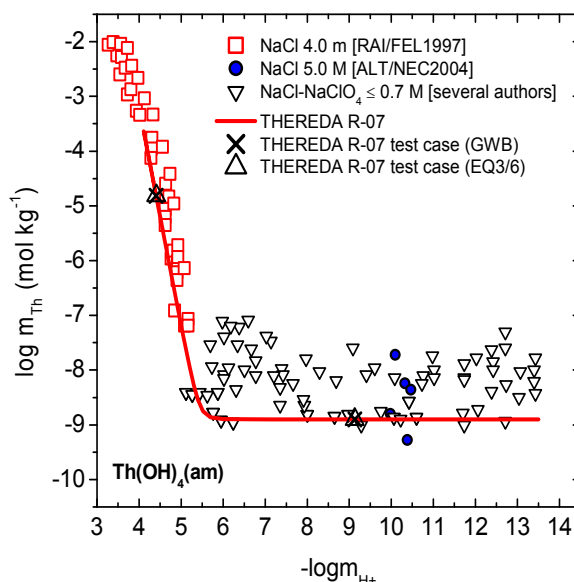


Figure 5: Solubility of Th(OH)<sub>4</sub>(am). Red squares: solubility data in 4.0 m NaCl reported in [RAI/FEL1997]; blue circles: solubility data in 5.0 M NaCl reported in [04ALT/NEC]; inverted triangles: solubility data in NaCl and NaClO<sub>4</sub> ≤ 0.7 M reported by several authors; solid line: solubility in 4.0 m NaCl calculated with THEREDA TDB; black triangles and crosses: benchmark calculations with GWB and EQ3/6 using THEREDA TDB.

Figure 5 shows that Th(IV) solubility calculated with THEREDA TDB is lower than experimental data reported by Felmy and co-workers in 4.0 m NaCl. This is due to the selection in THEREDA of a log  $K_{s,0}^{\circ}$  significantly lower than the value reported in [RAI/FEL1997]. Note that large uncertainties affect the experimentally determined solubility products of Th(IV) (uncertainty ±0.9 log-units considered in NEA–TDB), mostly because of the large impact of particle size on the solubility. In their solubility experiments with ThO<sub>2</sub>(cr) and ThO<sub>2</sub>(mcr), Neck and co-workers reported a clear change in the solid phase controlling the solubility when shifting pH towards more alkaline conditions. Th(OH)<sub>4</sub>(am) was finally the solid phase controlling the solubility above pH ~4 [NEC/ALT2003]. The underestimation of experimental data in [RAI/FEL1997] is also related with the lack of hydrolysis species other than (1,4) in the current THEREDA se-

lection. Although conceptually correct, this approach is not fully consistent with the selection of a  $\log K_{s,0}^\circ$  originally provided in connection with (1,1) and (1,2) hydrolysis species [RAN/FUG2008].

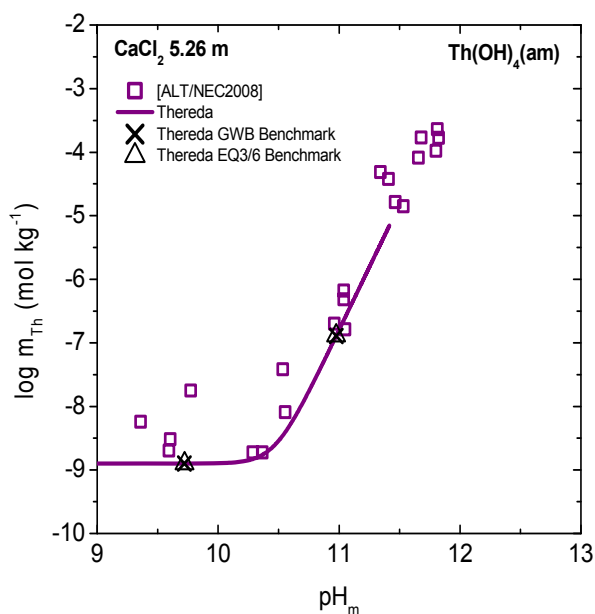


Figure 6: Solubility of  $\text{Th}(\text{OH})_4(\text{am})$  in 5.26 m  $\text{CaCl}_2$ . Purple squares: experimental data reported in [ALT/NEC2008]; solid line: solubility calculated with THEREDA TDB; black triangles and crosses: test calculations with GWB and EQ3/6 using THEREDA TDB.

Experimental Th(IV) solubility in concentrated  $\text{CaCl}_2$  solutions is properly explained by the current THEREDA database (Figure 6). This is consistent with the selection of  $\log K_{s,0}^\circ$  and  $\log \beta_{(4,1,8)}^*$  analogous to the data reported in [ALT/NEC2008, FEL/NEC2010].

Thermodynamic calculations in the pH-region where the species  $\text{Th}(\text{OH})_4(\text{aq})$  prevails (both in Figure 5 and Figure 6) slightly underestimate the available experimental data. This minor deviation arises from the selection of a  $\log K_{s,0}^\circ$  corresponding to an aged amorphous phase (see discussion above).

### 3.2.2.2 Complexes with carbonate

A very limited number of experimental studies are available in the literature dealing with the complexation of Th(IV) with carbonate under high ionic strength conditions [OST/BRU1994, FEL/RAI1997, ALT/NEC2005, ALT/NEC2006]. Given the known formation of highly charged carbonato species, the availability of accurate activity models results of the utmost relevance when assessing the system Th(IV)–CO<sub>3</sub> at elevated ionic strengths. From the abovementioned experimental studies, only Felmy and co-workers provided a thermodynamic model coupled to a Pitzer-based activity model [FEL/RAI1997]. This study focussed in concentrated NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> and thus, the chemical model derived (including only Th(CO<sub>3</sub>)<sub>5</sub><sup>6-</sup> and Th(OH)<sub>3</sub>CO<sub>3</sub><sup>-</sup> species) appears incomplete when dealing with diluted (repository-relevant) carbonate systems. On the other hand, Altmaier and co-workers studied the solubility of Th(IV) in the presence of lower carbonate concentrations and up to 4.0 M NaCl. The chemical and thermodynamic models derived by these authors clearly indicated the predominance of ThOH(CO<sub>3</sub>)<sub>4</sub><sup>5-</sup> and Th(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup> (in addition to the formation of other ternary species, see Table 23), although only a SIT model was provided for the correction of ionic strength. Mostly based on the work by Altmaier and co-workers, the NEA–TDB recently included the species ThOH(CO<sub>3</sub>)<sub>4</sub><sup>5-</sup>, Th(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup>, Th(OH)<sub>4</sub>CO<sub>3</sub><sup>2-</sup> and Th(CO<sub>3</sub>)<sub>5</sub><sup>6-</sup> in the thermodynamic data selection of Th [RAN/FUG2008].

Given the limited availability of experimental data, the current thermodynamic selection in THEREDA is based on the single work by Felmy and co-workers [FEL/RAI1997]. Note that as a solubility study, the stability constants experimentally determined in this work correspond to the equilibrium between a solid phase (Th(OH)<sub>4</sub>(am)) and the Th(IV)–CO<sub>3</sub> species. The resulting log  $K_{s,(1,x,y)}^{\circ}$  values (see Table 23) have been combined with log  $K_{s,0}^{\circ}$  selected in THEREDA TDB in order to calculate log  $\beta_{(1,x,y)}^{\circ}$ , so that internal consistency has been maintained whilst adequately explaining experimental solubility data in [FEL/RAI1997] (see Figure 7). At low carbonate concentrations, the solubility of Th(IV) in this study tends to  $\sim 10^{-8}$  M, and thus can be properly explained by the log  $K_{s,(1,4)}^{\circ}$  calculated with THEREDA TDB for the reaction Th(OH)<sub>4</sub>(am)  $\leftrightarrow$  Th(OH)<sub>4</sub>(aq) (see Figure 7). This further supports the use of log  $K_{s,0}^{\circ}$  selected in THEREDA and the approach considered to calculate log  $\beta_{(1,x,y)}^{\circ}$ .

Pitzer coefficients selected in THEREDA for the carbonato species of Th(IV) are summarized in Table 23 and

Table 24, together with the original source reporting these values. Note that no such coefficients were provided for the species  $\text{Th}(\text{OH})_3\text{CO}_3^-$  in [FEL/RAI1997]. The binary Pitzer parameters selected for this species correspond to estimates provided in [ALT/BRE2004] based on the available SIT parameters.

Table 23: Log  $K_{s,(1,x,y)}^\circ$  values available in the literature from experimental solubility studies for the formation of Th(IV)–OH–CO<sub>3</sub> aqueous species. Only studies with data available at elevated ionic strength are summarized in the table. Bold-marked data corresponding to the current THEREDA selection.

| Reaction  | log $K_{s,(1,x,y)}^\circ$               | Reference   |
|---|---|---|
| $\text{Th}(\text{OH})_4(\text{am}) + 5 \text{CO}_3^{2-} \Leftrightarrow \text{Th}(\text{CO}_3)_5^{6-} + 4 \text{OH}^-$              | -18.4<br>< -16.6<br><b>-18.4</b>        | [FEL/RAI1997]<br>[ALT/NEC2005]<br><b>THEREDA [p.w.]</b> |
| $\text{Th}(\text{OH})_4(\text{am}) + 4 \text{CO}_3^{2-} \Leftrightarrow \text{ThOH}(\text{CO}_3)_4^{5-} + 3 \text{OH}^-$            | $-12.0 \pm 0.2$                         | [ALT/NEC2005]   |
| $\text{Th}(\text{OH})_4(\text{am}) + \text{CO}_3^{2-} \Leftrightarrow \text{Th}(\text{OH})_2\text{CO}_3(\text{aq}) + 2 \text{OH}^-$ | $-17.1 \pm 0.3$                         | [ALT/NEC2005]   |
| $\text{Th}(\text{OH})_4(\text{am}) + 2 \text{CO}_3^{2-} \Leftrightarrow \text{Th}(\text{OH})_2(\text{CO}_3)_2^{2-} + 2 \text{OH}^-$ | $-10.8 \pm 0.2$                         | [ALT/NEC2005]   |
| $\text{Th}(\text{OH})_4(\text{am}) + \text{CO}_3^{2-} \Leftrightarrow \text{Th}(\text{OH})_3\text{CO}_3^- + \text{OH}^-$            | -7.22<br>$-9.3 \pm 0.5$<br><b>-7.22</b> | [FEL/RAI1997]<br>[ALT/NEC2005]<br><b>THEREDA [p.w.]</b> |
| $\text{Th}(\text{OH})_4(\text{am}) + \text{CO}_3^{2-} \Leftrightarrow \text{Th}(\text{OH})_4\text{CO}_3^{2-}$                       | $-7.2 \pm 0.3$                          | [ALT/NEC2005]   |

Table 24: Binary Pitzer parameters available in the literature for Th(IV)–carbonate species. Bold-marked data corresponding to the current THEREDA selection.

| Species                               | $\beta^{(0)}$<br>(kg·mol <sup>-1</sup> ) | $\beta^{(1)}$<br>(kg·mol <sup>-1</sup> ) | $\beta^{(2)}$<br>(kg·mol <sup>-1</sup> ) | $C^\phi$<br>(kg <sup>2</sup> ·mol <sup>-2</sup> ) | $\alpha_1$    | $\alpha_2$    | Reference                              |
|---------------------------------------|--|--|--|---|---------------|---------------|--|
| $\text{Th}(\text{CO}_3)_5^{6-}$       | 1.31<br><b>1.31</b>                      | 30.0<br><b>30.0</b>                      | 0<br><b>0</b>                            | 0<br><b>0</b>                                     | 2<br><b>2</b> | 0<br><b>0</b> | [FEL/RAI1997]<br><b>THEREDA [p.w.]</b> |
| $\text{Th}(\text{OH})_3\text{CO}_3^-$ | 0<br><b>0</b>                            | 0.2<br><b>0.2</b>                        | 0<br><b>0</b>                            | 0<br><b>0</b>                                     | 2<br><b>2</b> | 0<br><b>0</b> | [ALT/BRE2004]<br><b>THEREDA [p.w.]</b> |

Table 25: Ternary Pitzer parameters available in the literature for Th(IV)–carbonate species. Bold-marked data corresponding to the current THEREDA selection.

| Species ( <i>i</i> )                            | <i>j</i>        | <i>K</i>        | $\beta^s \Theta_{i,k}$ | $\Psi_{i,j,k}$ | Reference                  |
|---|-----------------|-----------------|------------------------|----------------|----------------------------|
| Th(CO <sub>3</sub> ) <sub>5</sub> <sup>6-</sup> | Cl <sup>-</sup> | Na <sup>+</sup> | 1.8                    | 0.3            | [FEL/RAI1999] <sup>a</sup> |
|   |                 |                 | <b>1.8</b>             | <b>0.3</b>     | <b>THEREDA [p.w.]</b>      |

a. estimated by correlation with ternary parameters in NaClO<sub>4</sub> determined in [FEL/RAI1997]

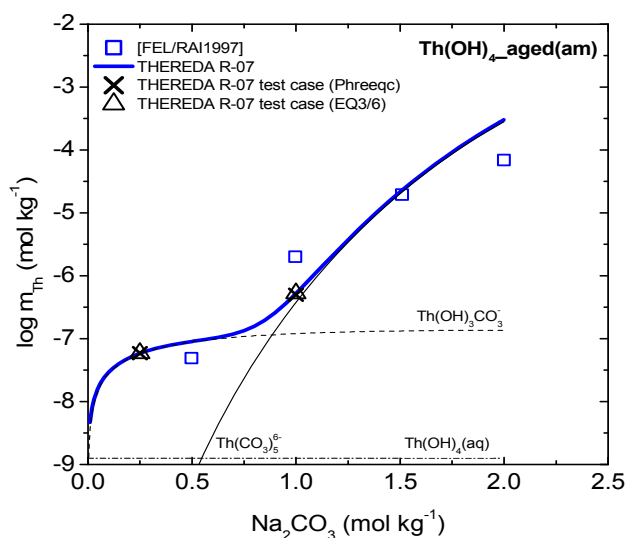


Figure 7: Solubility of Th(OH)<sub>4\_aged(am)</sub> in 0.1 M NaOH (initial condition) and increasing Na<sub>2</sub>CO<sub>3</sub> concentration. Blue squares: experimental data reported in [FEL/RAI1997]; solid line: solubility calculated with THEREDA TDB; black triangles and crosses: test calculations with Phreeqc and EQ3/6 using THEREDA TDB. Thin black lines indicate Th aqueous speciation underlying solubility of Th(OH)<sub>4\_aged(am)</sub>.

### 3.2.2.3 Complexes with chloride

The possible complexation of chloride with Th(IV) (up to 6 m Cl<sup>-</sup>) has been implicitly included in the Pitzer ion-interaction parameters between Th<sup>4+</sup> and Cl<sup>-</sup>. This is especially reflected in the selection of a large negative value for  $\beta^{(2)}$  [RAI/FEL1997].

### 3.2.3 Limitations of the current data selection for Th(IV)

The main limitations of the current thermodynamic data selection in THEREDA are summarized below:

- The selected value for  $\log K_{s,0}^{\circ}$  is not fully consistent with the simplified hydrolysis scheme proposed by Felmy and co-workers and adapted in this work. This results in a underestimation of the solubility of Th(IV) in the pH range 3 to 5. Although this pH range is not relevant for disposal conditions, a combined assessment of the available solubility data could help in addressing this problem.
- Th(IV)–CO<sub>3</sub> species currently selected in THEREDA are only relevant at high carbonate concentrations. Within the context of the joint project EDUKEM, it is planned to fit the data reported in [ALT/NEC2005, ALT/NEC2006] according with the Pitzer formulism. This will allow including in the chemical model species not currently considered and more relevant under repository conditions.
- No ion interaction parameters with Mg<sup>2+</sup> are currently included in THEREDA. Although Rai and co-workers reported three series of Th(IV) solubility data in MgCl<sub>2</sub> (1 m, 1.8 m and 3 m), these data have been disregarded in the present selection due to the very short equilibration times (8 days for two of the series) and the clear overestimation of the solubility data with the model. Long-term systematic solubility experiments in MgCl<sub>2</sub> are foreseen within the framework of EDUKEM.

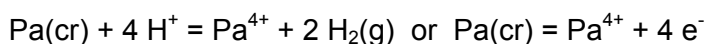
### 3.2.4 Protactinium, Pa(IV): Pa<sup>4+</sup>

In aqueous solution with reducing properties like in natural aquifers in deep geological formations, protactinium can exist in the tetravalent oxidation state. The main oxidation state under air conditions is the pentavalent protactinium. Therefore, most investigations of the chemical properties of protactinium have been performed on the pentavalent one. There are only a limited number of papers dealing with the tetravalent Pa, mainly concerning extraction properties or work of theoretical nature. Experimental studies to determine thermodynamic data for the tetravalent protactinium are still missing in the literature, even for dilute aquatic systems.

The tetravalent Pa should show very similar chemical properties like the other tetravalent actinides (Th<sup>4+</sup>, U<sup>4+</sup>, Np<sup>4+</sup> und Pu<sup>4+</sup>). Therefore, the principle of chemical analogy can be used to estimate thermodynamic data like complex formation constants, solubilities as well as interaction parameters. Because the Pa<sup>4+</sup> aquo ion is well defined and occurs in very acidic solution – in contrast to the pentavalent oxidation state of protactinium Pa(V) (see chapter 3.3.1) – THEREDA decided to define the Pa<sup>4+</sup> as the primary master species for protactinium.

### 3.2.4.1 The aquo ion of Pa(IV): Pa<sup>4+</sup>

The standard molar enthalpy of formation  $\Delta_f H_m^\circ$  of Pa<sup>4+</sup> is given in [WAG/EVA1982] at various ionic strengths of HCl with values from -606 to -668 kJ mol<sup>-1</sup>. The origin of these values are not discussed in [WAG/EVA1982] and hence, cannot be assessed here. The  $\Delta_f H_m^\circ$  and the standard molar entropy  $S_m^\circ$  values from [FUG/OET1976] seem to be more reliable with values of  $\Delta_f H_m^\circ = -619.7 \pm 13$  kJ mol<sup>-1</sup> and  $S_m^\circ = -397.5 \pm 42$  JK<sup>-1</sup>mol<sup>-1</sup> in 1 M HCl. The standard molar Gibbs energy of formation  $\Delta_f G^\circ$  is calculated from the molar formation entropy  $\Delta_f S_m^\circ$  that is derived from the following reaction:



with

$$\begin{aligned} \Delta_f S_m^\circ(\text{Pa}^{4+}) &= S^\circ(\text{Pa}^{4+}) + 2 S^\circ(\text{H}_2(\text{g})) - S^\circ(\text{Pa}(\text{cr})) - 4 S^\circ(\text{H}^+) \\ &= S^\circ(\text{Pa}^{4+}) + 4 S^\circ(\text{e}^-) - S^\circ(\text{Pa}(\text{cr})) \end{aligned}$$

$$\text{with } S^\circ(\text{H}_2(\text{g})) = 130.68 \pm 0.003 \text{ J K}^{-1}\text{mol}^{-1}$$

$$S^\circ(\text{H}^+) = 0$$

$$\text{or } S^\circ(\text{e}^-) = 65.34 \pm 0.0015 \text{ J K}^{-1}\text{mol}^{-1}$$

$$= -397.5 + 2 \times 130.68 - 51.9 - 0 = -188.(04) \pm 42$$

$$\Delta_f S_m^\circ(\text{Pa}^{4+}) = -397.5 + 4 \times 65.34 - 51.9 = -188.(04) \pm 42.$$

With  $\Delta_f H_m^\circ(\text{Pa}^{4+}) = -619700 \pm 13000$  J mol<sup>-1</sup> the value for

$$\Delta_f G_m^\circ(\text{Pa}^{4+}) = (-619700 \pm 13000) - 298.15 \times (-188.04 \pm 42) \text{ is calculated to be}$$

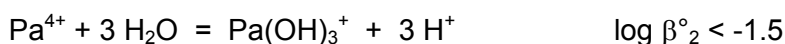
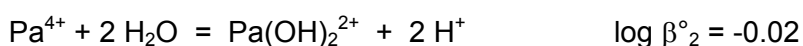
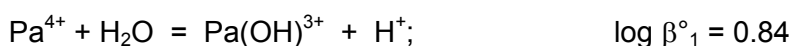
$$\Delta_f G_m^\circ(\text{Pa}^{4+}) = -563636 \pm 18050 \text{ J mol}^{-1} \text{ is}$$



[FUG/OET1976] gives a value of  $-564840 \pm 16736 \text{ J mol}^{-1}$  in 1.0 M HCl that is within the uncertainties equivalent.

### 3.2.4.2 The hydrolysis of $\text{Pa}^{4+}$

Guillaumont [GUI1968] and Lundqvist [LUN1974] have studied the hydrolysis of Pa(IV) in perchlorate medium by TTA and acetylacetone solvent extraction. Some difficulties have emerged because of co-extraction of the perchlorate anion resulting in biasing a higher degree of hydrolysis. However, the  $\text{ClO}_4^-$  effect is negligible at conditions where the first two hydrolysis species are formed. The  $\text{Pa}^{4+}$  is formed above 1 M acid and the estimate of  $K_1$  and  $K_2$  is seriously affected in 3 M (Li)ClO<sub>4</sub>. Baes and Messmer [BAE/MES1976] derived the following formation constants that are based on the experiments from Guillaumont [GUI1968, DUP/GUI1977]



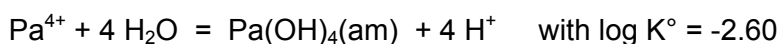
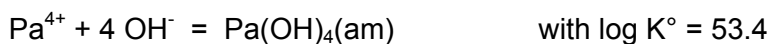
Studying the hydrolysis of  $\text{Pa}^{4+}$ , the experiments are faced with some difficulties because of the strong tendency of protactinium(IV) to polymerise as well as to sorb onto surface. As a result, the formation constants of the hydroxide complexes as well as the solubility of the  $\text{Pa}(\text{OH})_4(\text{cr})$  cannot easily be evaluated. The quantification of the polymerization of Pa(IV) is hardly possible so far. Therefore, Tarapcik et al. [TAR/FOU2005] tried to estimate the formation constants with various estimation methods, like the electrostatic model (HSE), the Brown-Wanner theory (BWT) and the hydrolysis correlation method (CSC). A detailed description of these methods is given elsewhere (see reference list in [TAR/FOU2005]).

The Brown-Wanner theory results in values very close to the experimental data from Guillaumont for the first and second hydrolysis constant (s. Table 26, Figure 8) and the constants selected by THEREDA. However, Tarapcik et al. give experimental values for the third and fourth hydrolysis constants that are much higher and do not fit in the

usual trend. As reference of these experimental data [DUP/GUI1977] is cited. This paper does not give any hint or information about the third and fourth hydrolysis constant, but it deals only with the first and second hydrolysis constant of Np(IV) with comparison to constants of Th(IV), Pa(IV), U(IV), and Pu(IV). In this paper Duplessis and Guillaumont refer to [GUI1968] as source of the experiment and its hydrolysis constants. The origin of these two values cannot be followed so far and they were regarded as not consistent with the first two hydrolysis constants. THEREDA relies on the data from the Brown-Wanner prediction confirmed also by comparison with the data for the tetravalent neptunium and plutonium. It seems that enhanced polynuclear or other side reactions of the Pa(IV) disturb the interpretation of the experiment. However, to get a more precise result more experimental efforts are needed for Pa(IV) hydrolysis.

### 3.2.4.3 Solid Pa(IV) hydrolysis compounds

Similar to the tetravalent actinides U(IV), Np(IV), and Pu(IV), the tetrahydroxide compound is discussed as the main solid protactinium compound ( $\text{Pa}(\text{OH})_4(\text{s})$ ). And as similar to other tetravalent hydrolysis products, the strong tendency to polymerise and to be sorbed impedes the clear evaluation of solubility products. Consequently, the solubility product of Muxart and Guillaumont [TAR/FOU2005, MUX/GUI1974] of  $\log K^\circ_{\text{sp}} = -53.4$  corresponding to the following reaction



has to be taken with cautions. Tarapcik et al. compared this value with predicted values of other tetravalent actinides obtained by estimation theories based on experimental data, like the electrostatic model (HSE), the Brown-Wanner theory (BWT) and the method according to Neck and Kim. A detailed description of these methods is given elsewhere (see reference list in [TAR/FOU2005]). The comparison showed that the BWT gives values for all tetravalent actinides that are significant lower than all other values and hence, they were not regarded for some estimation purposes. All values of the formation constants of the tetravalent actinides, whether estimated or deduced from experimental data, show the same trend. The formation constant  $\log K^\circ$  increases linearly with increasing atomic number of the actinides (s. Figure 9).

Table 26: Hydrolysis constants (formation constants for Pa(IV) hydroxide complexes) and comparison with Np(IV) and Pu(IV) data. Values in boldface were selected by THEREDA.

| Reaction   | $\log \beta^\circ$  | Reference   |
|--|---|---|
| $\text{Pa}^{4+} + \text{H}_2\text{O} \Leftrightarrow \text{PaOH}^{3+} + \text{H}^+$                      | 0.84 <sup>a</sup><br>0.8 <sup>a</sup><br>0.1 ± 1.5 <sup>b</sup><br><b>0.8 ± 1.5<sup>a</sup></b> | [DUP/GUI1977]<br>[TAR/FOU2005]<br>[TAR/FOU2005]<br><b>THEREDA</b> |
| $\text{Np}^{4+} + \text{H}_2\text{O} \Leftrightarrow \text{NpOH}^{3+} + \text{H}^+$                      | 0.55 ± 0.2  | THEREDA   |
| $\text{Pu}^{4+} + \text{H}_2\text{O} \Leftrightarrow \text{PuOH}^{3+} + \text{H}^+$                      | 0.6 ± 0.2   | THEREDA   |
| $\text{Pa}^{4+} + 2 \text{H}_2\text{O} \Leftrightarrow \text{Pa}(\text{OH})_2^{2+} + 2 \text{H}^+$       | -0.02 <sup>a</sup><br>0 <sup>a</sup><br>-0.5 ± 1.5 <sup>b</sup><br><b>0 ± 1.5<sup>a</sup></b>   | [DUP/GUI1977]<br>[TAR/FOU2005]<br>[TAR/FOU2005]<br><b>THEREDA</b> |
| $\text{Np}^{4+} + 2 \text{H}_2\text{O} \Leftrightarrow \text{Np}(\text{OH})_2^{2+} + 2 \text{H}^+$       | 0.35 ± 0.3  | THEREDA   |
| $\text{Pu}^{4+} + 2 \text{H}_2\text{O} \Leftrightarrow \text{Pu}(\text{OH})_2^{2+} + 2 \text{H}^+$       | 0.6 ± 0.3   | THEREDA   |
| $\text{Pa}^{4+} + 3 \text{H}_2\text{O} \Leftrightarrow \text{Pa}(\text{OH})_3^+ + 3 \text{H}^+$          | -1.5 <sup>a</sup><br>-3 ± 3 <sup>b</sup><br><b>-3 ± 3<sup>b</sup></b>                           | [TAR/FOU2005]<br>[TAR/FOU2005]<br><b>THEREDA</b>                  |
| $\text{Np}^{4+} + 3 \text{H}_2\text{O} \Leftrightarrow \text{Np}(\text{OH})_3^+ + 3 \text{H}^+$          | -2.8 ± 1.0  | THEREDA   |
| $\text{Pu}^{4+} + 3 \text{H}_2\text{O} \Leftrightarrow \text{Pu}(\text{OH})_3^+ + 3 \text{H}^+$          | -2.3 ± 0.4  | THEREDA   |
| $\text{Pa}^{4+} + 4 \text{H}_2\text{O} \Leftrightarrow \text{Pa}(\text{OH})_4(\text{aq}) + 4 \text{H}^+$ | -4.6 <sup>a</sup><br>-8 ± 3 <sup>b</sup><br><b>-8 ± 3<sup>b</sup></b>                           | [TAR/FOU2005]<br>[TAR/FOU2005]<br><b>THEREDA</b>                  |
| $\text{Np}^{4+} + 4 \text{H}_2\text{O} \Leftrightarrow \text{Np}(\text{OH})_4(\text{aq}) + 4 \text{H}^+$ | -8.3 ± 1.1  | THEREDA   |
| $\text{Pu}^{4+} + 4 \text{H}_2\text{O} \Leftrightarrow \text{Pu}(\text{OH})_4(\text{aq}) + 4 \text{H}^+$ | -8.5 ± 0.5  | THEREDA   |

a: data from experiment; b: data predicted from the Brown-Wanner theory [TAR/FOU2005].

Each of these methods yield in a linear relationship with a slope that differs from each other, resulting in big differences at atomic number 90 and 94. However, the smallest deviation is obtained at atomic number 91, the protactinium. Hence, we used all experimental, predicted and interpolated values for Pa(IV) to calculate a mean value for the

formation constants, that is  $53.7 \pm 1.2$ . This value is very near to the only existing experimental value of 53.4 from Muxart and Guillaumont [MUX/GUI1974]. On the base of these findings, this experimental value was selected as formation constants of amorphous protactinium(IV) tetrahydroxide (s. Table 27):

Table 27: Formation constants of amorphous protactinium(IV) tetrahydroxide. Value in boldface was selected by THEREDA.

| Reaction  | $\log K^\circ$ | Reference      |
|---|----------------|----------------|
| $\text{Pa}^{4+} + 4 \text{OH}^- = \text{Pa}(\text{OH})_4(\text{am})$                                    | 53.4           | [MUX/GUI1974]  |
| $\text{Pa}^{4+} + 4\text{H}_2\text{O} \Leftrightarrow \text{Pa}(\text{OH})_4(\text{am}) + 4 \text{H}^+$ | <b>-2.6</b>    | <b>THEREDA</b> |

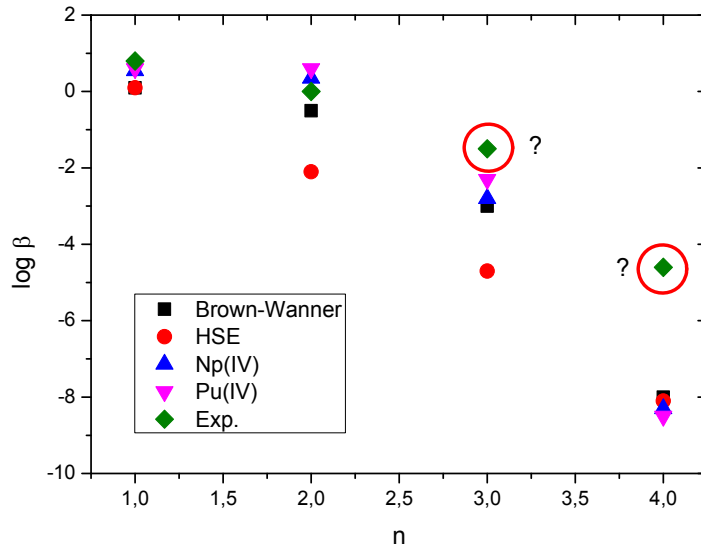


Figure 8: Formation constants  $\log \beta_n$ ,  $n = 1, 2, 3, 4$ , for hydroxide complexes of tetra-valent actinides Pa(IV), Np(IV), and Pu(IV). The figure comprises formation constants evaluated from experimental data (Np(IV), Pu(IV), and Pa(IV)) and derived from theoretical models (Pa(IV)), the Brown-Wanner theory and the electrostatic model [TAR/FOU2005]. Np(IV) and Pu(IV) from THEREDA, Pa(IV) from [TAR/FOU2005].

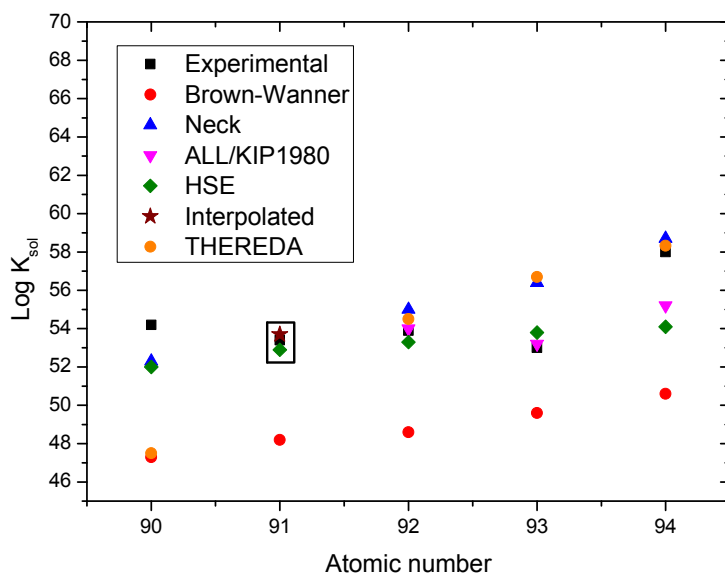


Figure 9: Experimental and predicted or interpolated formation constants of amorphous tetravalent actinide hydroxides. Data are from [TAR/FOU2005] and THEREDA.

### 3.2.5 Neptunium, Np(IV): Np<sup>4+</sup>

The following aqueous species and solid compounds have been included in the current selection of THEREDA for Np(IV), and are discussed in the following sections:

- Aquo Ion: Np<sup>4+</sup>
- Hydrolysis species, Ca ternary species and oxo-hydroxide compounds: NpOH<sup>3+</sup>, Np(OH)<sub>2</sub><sup>2+</sup>, Np(OH)<sub>3</sub><sup>+</sup>, Np(OH)<sub>4</sub>(aq), Ca<sub>4</sub>[Np(OH)<sub>8</sub>]<sup>4+</sup>, Np(OH)<sub>4</sub>(am)
- Carbonate complexes: Np(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup>, Np(CO<sub>3</sub>)<sub>5</sub><sup>6-</sup>
- Chloride complexes: NpCl<sup>3+</sup>
- Fluoride complexes: no species selected.
- Sulphate complexes: no species selected.
- Phosphate complexes: no species selected.

Only a very limited number of Pitzer ion interaction parameters for Np(IV) species are available from experimental studies (i.e. Ca<sub>4</sub>[Np(OH)<sub>8</sub>]<sup>4+</sup> and Np(CO<sub>3</sub>)<sub>5</sub><sup>6-</sup>). The remain-

ing Pitzer parameters selected in THEREDA were estimated in [ALT/BRE2004] by analogy with other aqueous species.

### 3.2.5.1 Hydrolysis, complexes with Ca and oxy-hydroxide compounds

The NEA–TDB selects a Np(IV) hydrolysis scheme including  $\text{Np(OH)}^{3+}$ ,  $\text{Np(OH)}_2^{2+}$  and  $\text{Np(OH)}_4(\text{aq})$  species. Due to the lack of additional experimental studies providing Pitzer ion interaction parameters for Np(IV) hydrolysis species, the NEA–TDB selection has been directly transferred to THEREDA. In agreement with [ALT/BRE2004], this selection has been extended with the third hydrolysis species of Np(IV),  $\text{Np(OH)}_3^+$ , as estimated in [NEC/KIM2001]. The complete lack of Pitzer ion interaction parameters for these species has been overcome by considering the estimates provided in [ALT/BRE2004] from analogue aqueous species.

The comprehensive solubility study with  $\text{Np(OH)}_4(\text{am})$  conducted by Fellhauer, Neck, Altmaier and co-workers in dilute to concentrated  $\text{CaCl}_2$  solutions [FEL/NEC2010] has been considered for the selection of  $\log^* \beta_{(4,1,8)}$  for the formation of the species  $\text{Ca}_4[\text{Np(OH)}_8]^{4+}$  (as  $4 \text{Ca}^{2+} + \text{Np}^{4+} + 8 \text{H}_2\text{O} \Leftrightarrow \text{Ca}_4[\text{Np(OH)}_8]^{4+} + 8 \text{H}^+$ ). Provided the use by [FEL/NEC2010] of the same  $\log^* K_{s,0}^\circ$  ( $\text{Np(OH)}_4(\text{am}) + 4 \text{H}^+ \Leftrightarrow \text{Np}^{4+} + 4 \text{H}_2\text{O}$ ) for the solid phase  $\text{Np(OH)}_4(\text{am})$  as such selected in the NEA–TDB and THEREDA, the value of  $\log^* \beta_{(4,1,8)}$  can be directly gained by combining the experimentally determined  $\log^* K_{s,(4,1,8)}^\circ$  ( $\text{Np(OH)}_4(\text{am}) + 4 \text{Ca}^{2+} + 4 \text{H}_2\text{O} \Leftrightarrow \text{Ca}_4[\text{Np(OH)}_8]^{4+} + 4 \text{H}^+$ ) and  $\log^* K_{s,0}^\circ$  without leading to any internal inconsistency. The values of  $\beta^{(0)}$ ,  $\beta^{(1)}$  and  $C^\phi$  selected in [FEL/NEC2010] for  $\text{Ca}_4[\text{Np(OH)}_8]^{4+}$  have been also selected in the THEREDA database.

Table 28 and Table 29 summarize the thermodynamic data ( $\log K$  and Pitzer binary parameters) available for Np(IV) hydrolysis species, ternary complexes with Ca and oxy-hydroxide compounds as selected in THEREDA database. Note that, in contrast to  $\text{Th}^{4+}$ , no ternary Pitzer parameters are available for  $\text{Np}^{4+}$ .

Table 28: Log  $K^\circ$  values available in the literature (experimental and review work) for the formation of  $\text{NpOH}^{3+}$ ,  $\text{Np(OH)}_2^{2+}$ ,  $\text{Np(OH)}_3^+$ ,  $\text{Np(OH)}_4(\text{aq})$ ,  $\text{Np(OH)}_4(\text{am})$  and  $\text{Ca}_4[\text{Np(OH)}_8]^{4+}$ . Bold-marked data corresponding to the current THEREDA selection.

| Reaction  | log $K^\circ$                     | Reference             |
|---|-----------------------------------|-----------------------|
| $\text{Np(OH)}_4(\text{am}) \Leftrightarrow \text{Np}^{4+} + 4 \text{OH}^-$   | -54.9                             | [RAI/SWA1987]         |
|   | -54.5                             | [LEM/FUG2001]         |
|   | $-56.7 \pm 0.5$                   | [GUI/FAN2003]         |
|   | $-56.7 \pm 0.5$                   | [ALT/BRE2004]         |
|   | $-56.7 \pm 0.5$                   | [FEL/NEC2010]         |
|   | <b><math>-56.7 \pm 0.5</math></b> | <b>THEREDA [p.w.]</b> |
| $\text{Np}^{4+} + \text{H}_2\text{O} \Leftrightarrow \text{NpOH}^{3+} + \text{H}^+$   | $0.55 \pm 0.2$                    | [GUI/FAN2003]         |
|   | <b><math>0.55 \pm 0.2</math></b>  | <b>THEREDA [p.w.]</b> |
| $\text{Np}^{4+} + 2 \text{H}_2\text{O} \Leftrightarrow \text{Np(OH)}_2^{2+} + 2 \text{H}^+$                                 | $0.35 \pm 0.3$                    | [GUI/FAN2003]         |
|   | <b><math>0.35 \pm 0.3</math></b>  | <b>THEREDA [p.w.]</b> |
| $\text{Np}^{4+} + 3 \text{H}_2\text{O} \Leftrightarrow \text{Np(OH)}_3^+ + 3 \text{H}^+$                                    | $-2.8 \pm 1.0$                    | [ALT/BRE2004]         |
|   | <b><math>-2.8 \pm 1.0</math></b>  | <b>THEREDA [p.w.]</b> |
| $\text{Np}^{4+} + 4 \text{H}_2\text{O} \Leftrightarrow \text{Np(OH)}_4(\text{aq}) + 4 \text{H}^+$                           | $-8.3 \pm 1.1$                    | [GUI/FAN2003]         |
|   | <b><math>-8.3 \pm 1.1</math></b>  | <b>THEREDA [p.w.]</b> |
| $4 \text{Ca}^{2+} + \text{Np}^{4+} + 8 \text{H}_2\text{O} \Leftrightarrow \text{Ca}_4[\text{Np(OH)}_8]^{4+} + 8 \text{H}^+$ | $-56.9 \pm 0.6$                   | [FEL/NEC2010]         |
|   | <b><math>-56.9 \pm 0.6</math></b> | <b>THEREDA [p.w.]</b> |

Table 29: Binary Pitzer parameters available in the literature for  $\text{Np}^{4+}$ ,  $\text{NpOH}^{3+}$ ,  $\text{Np(OH)}_2^{2+}$ ,  $\text{Np(OH)}_3^+$ ,  $\text{Np(OH)}_4(\text{aq})$ ,  $\text{Np(OH)}_4(\text{am})$  and  $\text{Ca}_4[\text{Np(OH)}_8]^{4+}$ . Bold-marked data corresponding to the current THEREDA selection.

| Species                             | $\beta^{(0)}$<br>( $\text{kg}\cdot\text{mol}^{-1}$ ) | $\beta^{(1)}$<br>( $\text{kg}\cdot\text{mol}^{-1}$ ) | $\beta^{(2)}$<br>( $\text{kg}\cdot\text{mol}^{-1}$ ) | $\mathbf{C}^\phi$<br>( $\text{kg}^2\cdot\text{mol}^{-2}$ ) | $\alpha_1$ | $\alpha_2$ | Reference             |
|-------------------------------------|--|--|--|--|------------|------------|-----------------------|
| $\text{Np}^{4+}$                    | 1.32   | 13.5   | 0  | 0  | 2.0        | 0          | [ALT/BRE2004]         |
|                                     | <b>1.32</b>  | <b>13.5</b>  | <b>0</b>   | <b>0</b>   | <b>2.0</b> | <b>0</b>   | <b>THEREDA [p.w.]</b> |
| $\text{NpOH}^{3+}$                  | 0.6  | 5.9  | 0  | 0  | 2.0        | 0          | [ALT/BRE2004]         |
|                                     | <b>0.6</b>   | <b>5.9</b>   | <b>0</b>   | <b>0</b>   | <b>2.0</b> | <b>0</b>   | <b>THEREDA [p.w.]</b> |
| $\text{Np(OH)}_2^{2+}$              | 0.23   | 1.9  | 0  | 0  | 2.0        | 0          | [ALT/BRE2004]         |
|                                     | <b>0.23</b>  | <b>1.9</b>   | <b>0</b>   | <b>0</b>   | <b>2.0</b> | <b>0</b>   | <b>THEREDA [p.w.]</b> |
| $\text{Np(OH)}_3^+$                 | 0.1  | 0.4  | 0  | 0  | 2.0        | 0          | [ALT/BRE2004]         |
|                                     | <b>0.1</b>   | <b>0.4</b>   | <b>0</b>   | <b>0</b>   | <b>2.0</b> | <b>0</b>   | <b>THEREDA [p.w.]</b> |
| $\text{Np(OH)}_4(\text{aq})$        | $\lambda = 0$  |  |  |  |            |            | per definition        |
| $\text{Ca}_4[\text{Np(OH)}_8]^{4+}$ | 0.58   | 8.9  |  | 0.07   |            |            | [FEL/NEC2010]         |
|                                     | <b>0.58</b>  | <b>8.9</b>   |  | <b>0.07</b>  |            |            | <b>THEREDA [p.w.]</b> |

Test calculations with the system Np(IV)–carbonate have been conducted with GWB, Phreeqc, EQ3/6 and Chemapp based on the thermodynamic data selection for Np(IV) in THEREDA. The results are summarized in detail in the document “Benchmark R07: Th(IV), Np(IV) and Pu(IV) solubility in NaCl, CaCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub> and KHCO<sub>3</sub> solutions”. The comparison of these test calculations with experimental solubility data in 5.26 m CaCl<sub>2</sub> [FEL/NEC2010] is provided in Figure 10. As shown in the figure, experimental Np(IV) solubility in concentrated CaCl<sub>2</sub> solutions is properly explained by the current THEREDA database. This is consistent with the selection of  $\log^* K_{s,0}^\circ$  and  $\log^* \beta_{(4,1,8)}^\circ$  analogous to the data reported in [FEL/NEC2010].



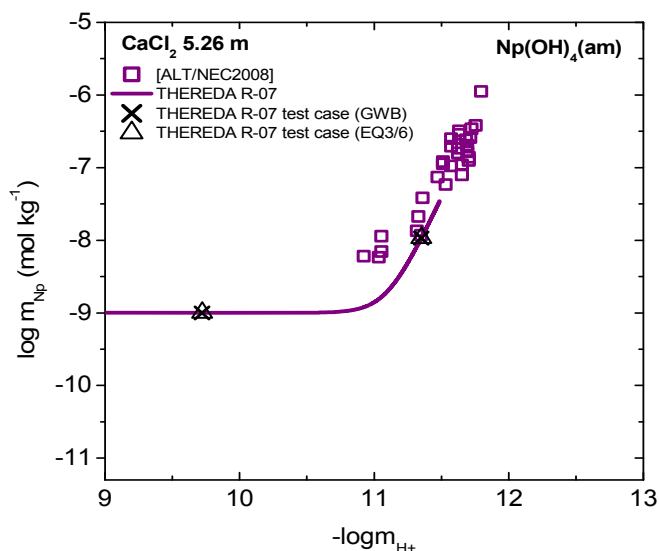


Figure 10: Solubility of  $\text{Np(OH)}_4(\text{am})$  in 5.26 m  $\text{CaCl}_2$ . Purple squares: experimental data reported in [FEL/NEC2010]; solid line: solubility calculated with THEREDA TDB; black triangles and crosses: benchmark calculations with GWB and EQ3/6 using THEREDA TDB.

### 3.2.5.2 Complexes with carbonate

There is one single reference in the literature dealing with the complexation of carbonate with Np(IV) at elevated ionic strengths (up to 6.4 m  $\text{K}_2\text{CO}_3$ ), and providing the corresponding chemical, thermodynamic and Pitzer activity models [RAI/HES1999a]. Rai and co-workers proposed the only formation of the species  $\text{Np(OH)}_2(\text{CO}_3)_2^{2-}$  and  $\text{Np(CO}_3)_5^{6-}$  to explain their solubility observations in  $\text{KHCO}_3$  and  $\text{K}_2\text{CO}_3$  solutions under alkaline to hyperalkaline conditions. Although acknowledging the potential relevance of mixed  $\text{Np}^{\text{IV}}(\text{OH})_x(\text{CO}_3)_y^{4-x-2y}$  species, the NEA–TDB did only select the species  $\text{Np(CO}_3)_4^{4-}$  and  $\text{Np(CO}_3)_5^{6-}$ . In addition to the tetra- and penta-carbonato species, Altmaier and co-workers [ALT/BRE2004] selected three further ternary species, namely  $\text{Np(OH)}_2(\text{CO}_3)_2^{2-}$ ,  $\text{Np(OH)}_4\text{CO}_3^{2-}$  and  $\text{Np(OH)}_4(\text{CO}_3)_2^{4-}$ , based upon the solubility data reported in [RAI/HES1999a] and [KIT/KOH2001].

Consistently with the case of Th(IV), this review has favoured the selection of the chemical and thermodynamic models generated within an experimental study conducted from diluted to concentrated solutions, namely [RAI/HES1999a] (Table 30). The species  $\text{Np(CO}_3)_4^{4-}$ ,  $\text{Np(OH)}_4\text{CO}_3^{2-}$  and  $\text{Np(OH)}_4(\text{CO}_3)_2^{4-}$  selected in [GUI/FAN2003] and [ALT/BRE2004] have been disregarded in the final selection of THEREDA. Pitzer parameters determined in [RAI/HES1999a] for  $\text{Np(CO}_3)_5^{6-}$  and

estimated in [ALT/BRE2004] for  $\text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-}$  have been also included in THEREDA (Table 31).

Note that, in addition to the differences in the speciation scheme proposed by [RAI/HES1999a] and selected in the NEA–TDB [LEM/FUG2001, GUI/FAN2003], differences greater than two log-units arise between  $\log K_{s,(1,0,5)}^\circ$  reported in both sources (Table 30). Lemire and co-workers [LEM/FUG2001] state in their review that “*these differences probably result, at least in part, from the different assumptions used for extrapolation to  $I = 0$* ”. Provided the focus in SIT of the NEA–TDB reviews, and the Pitzer approach favoured in THEREDA,  $\log K_{s,(1,0,5)}^\circ$  values originally reported in [RAI/HES1999] have been included in THEREDA. A similar reasoning was followed in [ALT/BRE2004] for the selection of  $\log K_{s,(1,0,5)}^\circ$  and  $\log \beta_{1,0,5}^\circ$ .

The existing discrepancies in terms of speciation scheme and magnitude of the stability of the limiting carbonato-complex,  $\text{Np}(\text{CO}_3)_5^{6-}$ , clearly indicate the need of further experimental investigations to properly assess the behaviour of Np(IV) in carbonate-rich systems at elevated ionic strengths. This is especially true considering the complex speciation scheme reported for the system Th(IV)–carbonate, where a number of ternary Th–OH–CO<sub>3</sub> species have been confirmed and properly characterized in recent publications [ALT/NEC2005, ALT/NEC2006]. It is also relevant mentioning the more accurate description provided by Pitzer of systems including highly charged species (i.e.  $\text{Np}(\text{CO}_3)_5^{6-}$ ), not only at elevated ionic strengths, but also in the extrapolation of these data at  $I = 0$ . A dedicated PhD study focusing on this topic is under planning at KIT-INE.

Figure 11 shows the comparison of the experimental  $\text{Np}(\text{OH})_4(\text{am})$  solubility data under increasing  $\text{KHCO}_3$  concentrations as reported in [RAI/HES1999a] and calculated with the current THEREDA thermodynamic selection. The figure shows a moderate agreement between calculations and experimental data, with the predominance of the ternary species  $\text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-}$  up to 0.2 m  $\text{KHCO}_3$ , and the subsequent prevalence of the limiting carbonato complex  $\text{Np}(\text{CO}_3)_5^{6-}$ . It is also noteworthy that experimental data at low carbonate concentration approaches well the solubility limit reported for Np(IV) in alkaline conditions in the absence of complexing ligands, i.e.  $\sim 10^{-9}$  M, dominated by the pH-independent solubility reaction  $\text{Np}(\text{OH})_4(\text{am}) \Leftrightarrow \text{Np}(\text{OH})_4(\text{aq})$ .

Table 30: Log  $K_{s,(1,x,y)}^{\circ}$  values available in the literature from experimental and review studies for the formation of Np(IV)–CO<sub>3</sub> species. Bold-marked data corresponding to the current THEREDA selection.

| Reaction   | log $K_{s,(1,x,y)}^{\circ}$ | Reference             |
|--|-----------------------------|-----------------------|
| Np(OH) <sub>4</sub> (am) + 4 CO <sub>3</sub> <sup>2-</sup> ⇌ Np(CO <sub>3</sub> ) <sub>4</sub> <sup>4-</sup> + 4 OH <sup>-</sup>                   | -17.79                      | [LEM/FUG2001]         |
|  | -17.79                      | [GUI/FAN2003]         |
|  | -20.02                      | [ALT/BRE2004]         |
| Np(OH) <sub>4</sub> (am) + 5 CO <sub>3</sub> <sup>2-</sup> ⇌ Np(CO <sub>3</sub> ) <sub>5</sub> <sup>6-</sup> + 4 OH <sup>-</sup>                   | -21.15                      | [RAI/HES1999]         |
|  | -18.86                      | [GUI/FAN2003]         |
|  | -21.09                      | [ALT/BRE2004]         |
|  | <b>-21.09</b>               | <b>THEREDA [p.w.]</b> |
| Np(OH) <sub>4</sub> (am) + 2 CO <sub>3</sub> <sup>2-</sup> ⇌ Np(OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup> + 2 OH <sup>-</sup> | -11.78                      | [RAI/HES1999]         |
|  | -11.75                      | [ALT/BRE2004]         |
|  | <b>-11.75</b>               | <b>THEREDA [p.w.]</b> |
| Np(OH) <sub>4</sub> (am) + CO <sub>3</sub> <sup>2-</sup> ⇌ Np(OH) <sub>4</sub> CO <sub>3</sub> <sup>2-</sup>                                       | -6.9                        | [ALT/BRE2004]         |
| Np(OH) <sub>4</sub> (am) + 2 CO <sub>3</sub> <sup>2-</sup> ⇌ Np(OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>                     | -6.5                        | [ALT/BRE2004]         |

Table 31: Binary Pitzer parameters available in the literature for Np(IV)–CO<sub>3</sub> species. Bold-marked data corresponding to the current THEREDA selection.

| Species   | $\beta^{(0)}$<br>(kg·mol <sup>-1</sup> ) | $\beta^{(1)}$<br>(kg·mol <sup>-1</sup> ) | $\beta^{(2)}$<br>(kg·mol <sup>-1</sup> ) | $C^{\phi}$<br>(kg <sup>2</sup> ·mol <sup>-2</sup> ) | $\alpha_1$ | $\alpha_2$ | Reference             |
|---|--|--|--|---|------------|------------|-----------------------|
| Np(CO <sub>3</sub> ) <sub>5</sub> <sup>6-</sup> – Na <sup>+</sup> /K <sup>+</sup>                   | 1.5                                      | 31.3                                     | 0  | 0   | 2          | 0          | [RAI/HES1999]         |
|   | <b>1.5</b>                               | <b>31.3</b>                              | <b>0</b>                                 | <b>0</b>  | <b>2</b>   | <b>0</b>   | <b>THEREDA [p.w.]</b> |
| Np(OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup> – Na <sup>+</sup> /K <sup>+</sup> | 0  | 2  | 0  | 0   | 2          | 0          | [ALT/BRE2004]         |
|   | <b>0</b>                                 | <b>2</b>                                 | <b>0</b>                                 | <b>0</b>  | <b>2</b>   | <b>0</b>   | <b>THEREDA [p.w.]</b> |

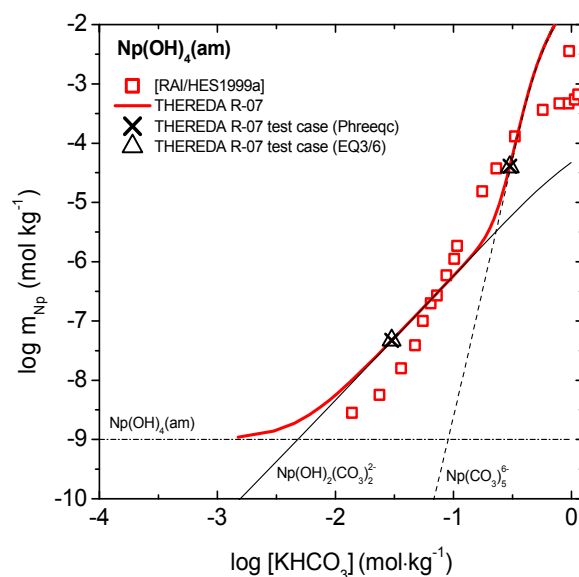


Figure 11: Solubility of  $\text{Np(OH)}_4(\text{am})$  under increasing  $\text{KHCO}_3$  concentrations. Red squares: experimental data reported in [RAI/HES1999a]; solid line: solubility calculated with THEREDA TDB; black triangles and crosses: test calculations with Phreeqc and EQ3/6 using THEREDA TDB. Thin black lines indicate Np aqueous speciation underlying solubility of  $\text{Np(OH)}_4(\text{am})$ .

### 3.2.5.3 Complexes with chloride

In contrast to Th(IV), the first chloride complex of Np(IV) ( $\text{NpCl}^{3+}$ ) has been included in the thermodynamic data selection of THEREDA, in agreement with the selection proposed in [GUI/FAN2003] and [ALT/BRE2004] (Table 32). However, neither SIT nor Pitzer parameters for the interaction of  $\text{NpCl}^{3+}$  with chloride were provided in any of these publications. This data gap has been retained in the current THEREDA data selection. The lack of these ion interaction parameters has no effect on calculations performed under repository-relevant pH conditions (near-neutral to alkaline), but reflects some of the limitations of the current THEREDA data selection for Np(IV) (see next section).

Table 32: Log  $K^\circ$  values available in the literature for the formation of Np(IV)–Cl species. Bold-marked data corresponding to the current THEREDA selection.

| Reaction   | log $K^\circ$                                    | Reference                              |
|--|--|--|
| $\text{Np}^{4+} + \text{Cl}^- \rightleftharpoons \text{NpCl}^{3+}$ | $1.5 \pm 0.3$<br><b><math>1.5 \pm 0.3</math></b> | [GUI/FAN2003]<br><b>THEREDA [p.w.]</b> |

### 3.2.5.4 Limitations of the current data selection for Np(IV)

The main limitations affecting the current Np(IV) thermodynamic data selection in THEREDA are summarized below:

- There are no dedicated experimental studies investigating the solubility/hydrolysis of  $\text{Np}^{4+}$  under acidic conditions and elevated ionic strength. All Pitzer parameters selected for hydrolysis species are estimates, thus impacting the quality of thermodynamic calculations under these particular conditions. In this concern, the Np(IV) selection is not consistent with the approach followed for Th(IV), where the effect of ionic strength (i.e.  $[\text{Cl}^-]$ ) was only taken into Pitzer ion interaction parameters and the definition of Th–Cl species was disregarded.
- The current THEREDA selection for the system Np(IV)– $\text{CO}_3$  includes only two species and is, likely, an oversimplification not representative of all repository-relevant conditions. Further ternary Np(IV)–OH– $\text{CO}_3$  species as those described for Th(IV) [ALT/NEC2005, ALT/NEC2006] are to be expected under alkaline conditions and lower carbonate concentrations. Given the high charge of some of these ternary species (i.e.  $\text{ThOH}(\text{CO}_3)_4^{5-}$ ), a strong stabilization with respect to less-charged species is to be expected at elevated ionic strength. Plutonium, Pu(IV):  $\text{Pu}^{4+}$

The following aqueous species and solid compounds have been included in the current selection of THEREDA for Pu(IV), and are discussed in the following sections:

- Aquo Ion:  $\text{Pu}^{4+}$
- Hydrolysis species, Ca ternary species and oxo-hydroxide compounds:  $\text{PuOH}^{3+}$ ,  $\text{Pu}(\text{OH})_2^{2+}$ ,  $\text{Pu}(\text{OH})_3^+$ ,  $\text{Pu}(\text{OH})_4(\text{aq})$ ,  $\text{Ca}_4[\text{Pu}(\text{OH})_8]^{4+}$ ,  $\text{Pu}(\text{OH})_4(\text{am})$
- Carbonate complexes:  $\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$ ,  $\text{Pu}(\text{CO}_3)_4^{4-}$ ,  $\text{Pu}(\text{CO}_3)_5^{6-}$
- Chloride complexes:  $\text{PuCl}^{3+}$
- Fluoride complexes: no species selected.
- Sulphate complexes: no species selected.
- Phosphate complexes: no species selected.

Only a very limited number of Pitzer ion interaction parameters for Pu(IV) species are available from experimental studies (i.e.  $\text{Ca}_4[\text{Pu}(\text{OH})_8]^{4+}$  and  $\text{Pu}(\text{CO}_3)_5^{6-}$ ). The rest of Pitzer parameters selected in THEREDA were estimated in [ALT/BRE2004] by analogy with other aqueous species.

### 3.2.5.5 Hydrolysis, complexes with Ca and oxy-hydroxide compounds

The NEA–TDB selects a Pu(IV) hydrolysis scheme including  $\text{Pu}(\text{OH})^{3+}$ ,  $\text{Pu}(\text{OH})_2^{2+}$ ,  $\text{Pu}(\text{OH})_3^+$  and  $\text{Pu}(\text{OH})_4(\text{aq})$  species. Due to the lack of additional experimental studies providing Pitzer ion interaction parameters for Pu(IV) hydrolysis species, the NEA–TDB selection has been included in THEREDA. The complete lack of Pitzer ion interaction parameters for these species have been overcome by considering the estimates provided in [ALT/BRE2004] from analogue aqueous species.

As for Th(IV) and Np(IV), the comprehensive solubility study with  $\text{Pu}(\text{OH})_4(\text{am})$  conducted by Fellhauer, Neck, Altmaier and co-workers in dilute to concentrated  $\text{CaCl}_2$  solutions [FEL/NEC2010] has been considered for the selection of  $\log {}^*\beta_{(4,1,8)}^\circ$  for the formation of the species  $\text{Ca}_4[\text{Pu}(\text{OH})_8]^{4+}$ . The values of  $\beta^{(0)}$ ,  $\beta^{(1)}$  and  $C^\phi$  selected in [FEL/NEC2010] for  $\text{Ca}_4[\text{Pu}(\text{OH})_8]^{4+}$  have been directly transferred to THEREDA. Table 33 and

Table 34 summarize the thermodynamic data ( $\log K$  and Pitzer binary parameters) available for Pu(IV) hydrolysis species, ternary complexes with Ca and oxy-hydroxide compounds as selected in THEREDA database.

Test calculations with the system Pu(IV) in NaCl,  $\text{CaCl}_2$  solutions and  $\text{KHCO}_3$  solutions have been conducted with GWB, Phreeqc, EQ3/6 and Chemapp based on the thermodynamic data selection for Np(IV) in THEREDA. The results are summarized in detail in the document “Benchmark R07: Th(IV), Np(IV) and Pu(IV) solubility in NaCl,  $\text{CaCl}_2$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{KHCO}_3$  solutions”. The comparison of these test calculations with experimental solubility data in 5.26 m  $\text{CaCl}_2$  [ALT/NEC2008, FEL/NEC2010] is provided in Figure 12. As shown in the figure, experimental Pu(IV) solubility in concentrated  $\text{CaCl}_2$  solutions is properly explained by the current THEREDA database. This is consistent with the selection of the same  $\log {}^*K_{s,0}^\circ$  and  $\log {}^*\beta_{(4,1,8)}^\circ$  as reported in [FEL/NEC2010].

Table 33: Log  $K^\circ$  values available in the literature (experimental and review work) for the formation of  $\text{PuOH}^{3+}$ ,  $\text{Pu(OH)}_2^{2+}$ ,  $\text{Pu(OH)}_3^+$ ,  $\text{Pu(OH)}_4(\text{aq})$ ,  $\text{Pu(OH)}_4(\text{am})$  and  $\text{Ca}_4[\text{Pu(OH)}_8]^{4+}$ . Bold-marked data corresponding to the current THEREDA selection.

| Reaction  | log $K^\circ$        | Reference             |
|---|----------------------|-----------------------|
| $\text{Pu(OH)}_4(\text{am}) \Leftrightarrow \text{Pu}^{4+} + 4 \text{OH}^-$   | -56.85               | [RAI1984]             |
|   | -58.33 ± 0.52        | [GUI/FAN2003]         |
|   | -58.33 ± 0.52        | [ALT/BRE2004]         |
|   | -58.3 ± 0.5          | [FEL/NEC2010]         |
|   | <b>-58.33 ± 0.52</b> | <b>THEREDA [p.w.]</b> |
| $\text{Pu}^{4+} + \text{H}_2\text{O} \Leftrightarrow \text{PuOH}^{3+} + \text{H}^+$   | 0.6 ± 0.2            | [GUI/FAN2003]         |
|   | <b>0.6 ± 0.2</b>     | <b>THEREDA [p.w.]</b> |
| $\text{Pu}^{4+} + 2 \text{H}_2\text{O} \Leftrightarrow \text{Pu(OH)}_2^{2+} + 2 \text{H}^+$                                 | 0.6 ± 0.3            | [GUI/FAN2003]         |
|   | <b>0.6 ± 0.3</b>     | <b>THEREDA [p.w.]</b> |
| $\text{Pu}^{4+} + 3 \text{H}_2\text{O} \Leftrightarrow \text{Pu(OH)}_3^+ + 3 \text{H}^+$                                    | -2.3 ± 0.4           | [ALT/BRE2004]         |
|   | -2.3 ± 0.4           | <b>THEREDA [p.w.]</b> |
| $\text{Pu}^{4+} + 4 \text{H}_2\text{O} \Leftrightarrow \text{Pu(OH)}_4(\text{aq}) + 4 \text{H}^+$                           | -8.5 ± 0.5           | [GUI/FAN2003]         |
|   | <b>-8.5 ± 0.5</b>    | <b>THEREDA [p.w.]</b> |
| $4 \text{Ca}^{2+} + \text{Np}^{4+} + 8 \text{H}_2\text{O} \Leftrightarrow \text{Ca}_4[\text{Np(OH)}_8]^{4+} + 8 \text{H}^+$ | -57.0 ± 0.6          | [FEL/NEC2010]         |
|   | <b>-57.0 ± 0.6</b>   | <b>THEREDA [p.w.]</b> |

Table 34: Binary Pitzer parameters available in the literature for  $\text{Pu}^{4+}$ ,  $\text{PuOH}^{3+}$ ,  $\text{Pu(OH)}_2^{2+}$ ,  $\text{Pu(OH)}_3^+$ ,  $\text{Pu(OH)}_4(\text{aq})$ ,  $\text{Pu(OH)}_4(\text{am})$  and  $\text{Ca}_4[\text{Pu(OH)}_8]^{4+}$ . Bold-marked data corresponding to the current THEREDA selection.

| Species                             | $\beta^{(0)}$<br>(kg·mol <sup>-1</sup> ) | $\beta^{(1)}$<br>(kg·mol <sup>-1</sup> ) | $\beta^{(2)}$<br>(kg·mol <sup>-1</sup> ) | $C^\phi$<br>(kg <sup>2</sup> ·mol <sup>-2</sup> ) | $\alpha_1$ | $\alpha_2$ | Reference             |
|-------------------------------------|--|--|--|---|------------|------------|-----------------------|
| $\text{Pu}^{4+}$                    | 1.32                                     | 13.5                                     | 0  | 0   | 2.0        | 0          | [ALT/BRE2004]         |
|                                     | <b>1.32</b>                              | <b>13.5</b>                              | <b>0</b>                                 | <b>0</b>  | <b>2.0</b> | <b>0</b>   | <b>THEREDA [p.w.]</b> |
| $\text{PuOH}^{3+}$                  | 0.6                                      | 5.9                                      | 0  | 0   | 2.0        | 0          | [ALT/BRE2004]         |
|                                     | <b>0.6</b>                               | <b>5.9</b>                               | <b>0</b>                                 | <b>0</b>  | <b>2.0</b> | <b>0</b>   | <b>THEREDA [p.w.]</b> |
| $\text{Pu(OH)}_2^{2+}$              | 0.23                                     | 1.9                                      | 0  | 0   | 2.0        | 0          | [ALT/BRE2004]         |
|                                     | <b>0.23</b>                              | <b>1.9</b>                               | <b>0</b>                                 | <b>0</b>  | <b>2.0</b> | <b>0</b>   | <b>THEREDA [p.w.]</b> |
| $\text{Pu(OH)}_3^+$                 | 0.1                                      | 0.4                                      | 0  | 0   | 2.0        | 0          | [ALT/BRE2004]         |
|                                     | <b>0.1</b>                               | <b>0.4</b>                               | <b>0</b>                                 | <b>0</b>  | <b>2.0</b> | <b>0</b>   | <b>THEREDA [p.w.]</b> |
| $\text{Pu(OH)}_4(\text{aq})$        | $\lambda = 0$                            |  |  |   |            |            | per definition        |
| $\text{Pu}_4[\text{Np(OH)}_8]^{4+}$ | 0.58                                     | 8.9                                      |  | 0.07  |            |            | [FEL/NEC2010]         |
|                                     | <b>0.58</b>                              | <b>8.9</b>                               |  | <b>0.07</b>                                       |            |            | <b>THEREDA [p.w.]</b> |

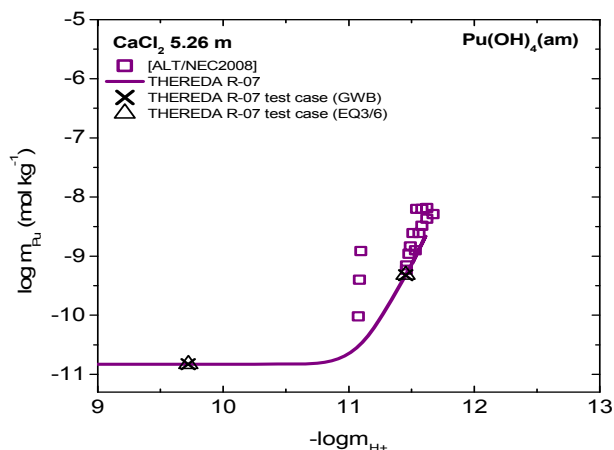


Figure 12: Solubility of  $\text{Pu(OH)}_4(\text{am})$  in 5.26 m  $\text{CaCl}_2$ . Purple squares: experimental data reported in [ALT/NEC2008, FEL/NEC2010]; solid line: solubility calculated with THEREDA TDB; black triangles and crosses: test calculations with GWB and EQ3/6 using THEREDA TDB.

The selection of the later species was based upon solubility data reported by Yamaguchi and co-workers [YAM/SAK1994] at low ionic strength. The final scheme selected for THEREDA relies upon all experimental sources dealing with the system  $\text{Pu(IV)-CO}_3$  at elevated ionic strengths, thus including the species  $\text{Pu(CO}_3)_4^{4-}$ ,  $\text{Pu(CO}_3)_5^{6-}$  and  $\text{Pu(OH)}_2(\text{CO}_3)_2^{2-}$  (Table 35). Pitzer ion interaction coefficients reported in [RAI/HES1999b] for  $\text{Pu(CO}_3)_5^{6-}$  and estimates reported in [ALT/BRE2004] for  $\text{Pu(CO}_3)_4^{4-}$  and  $\text{Pu(OH)}_2(\text{CO}_3)_2^{2-}$  have been selected in THEREDA (Table 36).

Figure 13 shows the comparison of the experimental  $\text{Pu(OH)}_4(\text{am})$  solubility data under increasing  $\text{KHCO}_3$  concentrations as reported in [RAI/HES1999b] and calculated with the current THEREDA thermodynamic selection. The figure shows a good agreement between calculations and experimental data, with the predominance of the ternary species  $\text{Pu(OH)}_2(\text{CO}_3)_2^{2-}$  up to 0.2 m  $\text{KHCO}_3$ , and the subsequent prevalence of the limiting carbonato complex  $\text{Pu(CO}_3)_5^{6-}$ . Note that in the conditions of this solubility study, the presence of the species  $\text{Pu(CO}_3)_4^{4-}$  is always minor compared to  $\text{Pu(CO}_3)_5^{6-}$  and  $\text{Np(OH)}_2(\text{CO}_3)_2^{2-}$ .



Table 35: Log  $K^\circ$  values available in the literature from experimental spectroscopic and solubility studies for the formation of Pu(IV)–CO<sub>3</sub> aqueous species. Bold-marked data corresponding to the current THEREDA selection.

| Reaction  | log $K^\circ$  | Reference   |
|---|--|---|
| $\text{Pu}(\text{CO}_3)_4^{4-} + \text{CO}_3^{2-} \leftrightarrow \text{Pu}(\text{CO}_3)_5^{6-}$                                    | -1.36 <sup>a</sup><br>-1.35<br>-1.35<br><b>-1.35</b> | [96CAP/VIT]<br>[GUI/FAN2003]<br>[ALT/BRE2004]<br><b>THEREDA [p.w.]</b>    |
| $\text{Pu}(\text{OH})_4(\text{am}) + 5 \text{CO}_3^{2-} \leftrightarrow \text{Pu}(\text{CO}_3)_5^{6-} + 4 \text{OH}^-$              | -22.68<br>-22.68<br>-22.68<br><b>-22.68</b>          | [RAI/HES1999b]<br>[GUI/FAN2003]<br>[ALT/BRE2004]<br><b>THEREDA [p.w.]</b> |
| $\text{Pu}(\text{OH})_4(\text{am}) + 2 \text{CO}_3^{2-} \leftrightarrow \text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-} + 2 \text{OH}^-$ | -12.12<br>-12.09<br><b>-12.09</b>                    | [RAI/HES1999b]<br>[ALT/BRE2004]<br><b>THEREDA [p.w.]</b>                  |
| $\text{Pu}(\text{OH})_4(\text{am}) + \text{CO}_3^{2-} \leftrightarrow \text{Pu}(\text{OH})_4\text{CO}_3^{2-}$                       | -7.4   | [ALT/BRE2004]   |
| $\text{Pu}(\text{OH})_4(\text{am}) + 2 \text{CO}_3^{2-} \leftrightarrow \text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$                 | -6.0   | [ALT/BRE2004]   |

<sup>a</sup> Original spectroscopic data reported as step-wise formation of  $\text{Pu}(\text{CO}_3)_5^{6-}$

Table 36: Binary Pitzer parameters available in the literature for Pu(IV)–carbonate species. Bold-marked data corresponding to the current THEREDA selection.

| Species   | $\beta^{(0)}$<br>(kg·mol <sup>-1</sup> ) | $\beta^{(1)}$<br>(kg·mol <sup>-1</sup> ) | $\beta^{(2)}$<br>(kg·mol <sup>-1</sup> ) | $C^\dagger$<br>(kg <sup>2</sup> ·mol <sup>-2</sup> ) | $\alpha_1$    | $\alpha_2$    | Reference                               |
|---|--|--|--|--|---------------|---------------|---|
| $\text{Np}(\text{CO}_3)_4^{4-} - \text{Na}^+/\text{K}^+$              | 1<br><b>1</b>                            | 13<br><b>13</b>                          | 0<br><b>0</b>                            | 0<br><b>0</b>  | 2<br><b>2</b> | 0<br><b>0</b> | [RAI/HES1999b]<br><b>THEREDA [p.w.]</b> |
| $\text{Np}(\text{CO}_3)_5^{6-} - \text{Na}^+/\text{K}^+$              | 1.5<br><b>1.5</b>                        | 31.3<br><b>31.3</b>                      | 0<br><b>0</b>                            | 0<br><b>0</b>  | 2<br><b>2</b> | 0<br><b>0</b> | [RAI/HES1999]<br><b>THEREDA [p.w.]</b>  |
| $\text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-} - \text{Na}^+/\text{K}^+$ | –<br>0<br><b>0</b>                       | 2<br><b>2</b>                            | 0<br><b>0</b>                            | 0<br><b>0</b>  | 2<br><b>2</b> | 0<br><b>0</b> | [ALT/BRE2004]<br><b>THEREDA [p.w.]</b>  |

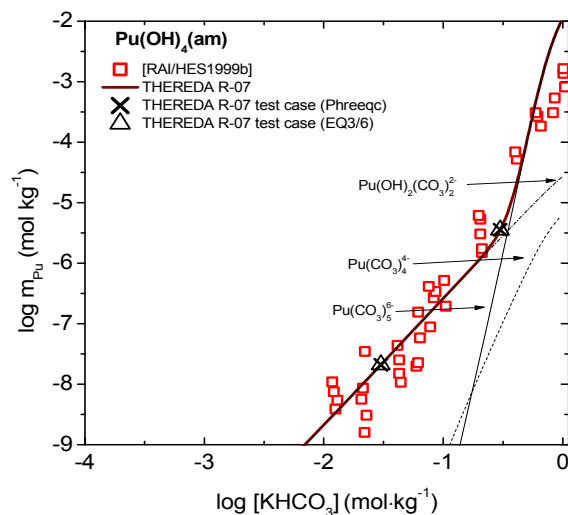


Figure 13: Solubility of  $\text{Pu}(\text{OH})_4(\text{am})$  under increasing  $\text{KHCO}_3$  concentrations. Red squares: experimental data reported in [RAI/HES1999b]; solid line: solubility calculated with THEREDA TDB; black triangles and crosses: test calculations with Phreeqc and EQ3/6 using THEREDA TDB. Thin black lines indicate Pu aqueous speciation underlying solubility of  $\text{Pu}(\text{OH})_4(\text{am})$ .

### 3.2.5.6 Complexes with chloride

As for Np(IV), the first chloride complex of Pu(IV) ( $\text{PuCl}^{3+}$ ) has been included in the thermodynamic data selection of THEREDA, in agreement with the selection proposed in [GUI/FAN2003] and [ALT/BRE2004] (Table 37). Neither SIT nor Pitzer parameters for the interaction of  $\text{PuCl}^{3+}$  with chloride were provided in [GUI/FAN2003] and [ALT/BRE2004]. This data gap has been retained in the current THEREDA data selection. The lack of these ion interaction parameters has no effect on calculations performed under repository-relevant pH conditions (near-neutral to alkaline), but reflects one of the several limitations of the current THEREDA data selection for Pu(IV) (see next section).

Table 37: Log  $K^\circ$  values available in the literature for the formation of Pu(IV)–Cl species. Bold-marked data corresponding to the current THEREDA selection.

| Reaction  | log $K^\circ$    | Reference             |
|---|------------------|-----------------------|
| $\text{Pu}^{4+} + \text{Cl}^- \leftrightarrow \text{PuCl}^{3+}$ | 1.8 ± 0.3        | [GUI/FAN2003]         |
|   | <b>1.8 ± 0.3</b> | <b>THEREDA [p.w.]</b> |

### 3.2.5.7 Limitations of the current data selection for Pu(IV)

The main limitations of the current thermodynamic data selection in THEREDA are summarized below:

- There are no dedicated experimental studies investigating the behavior of  $\text{Pu}^{4+}$  under acidic conditions and elevated ionic strength. This impacts the quality of the Pitzer activity model for the hydrolysis species, and thus the quality of thermodynamic calculations using THEREDA under these particular conditions. As for Np(IV), the Pu(IV) selection is not consistent with the approach followed for Th(IV), where the effect of ionic strength (as  $[\text{Cl}^-]$ ) was put into Pitzer ion interaction parameters whilst avoiding the definition of Th–Cl species, as done for Np(IV) and Pu(IV).
- Only one ternary Pu(IV)–OH– $\text{CO}_3$  species is currently defined in the Pu– $\text{CO}_3$  system. Analogous ternary species as those described for Th(IV) [ALT/NEC2005, ALT/NEC2006] are likely expected under alkaline conditions and lower carbonate concentrations. Given the high charge of some of these ternary species (i.e.  $\text{ThOH}(\text{CO}_3)_4^{5-}$ ), a strong stabilization against less-charged species is to be expected at elevated ionic strength.

### 3.2.6 Technetium(IV): $\text{Tc}^{4+}$

As agreed with the Project Management Agency Karlsruhe (PTKA), the thermodynamic data for Tc(VII) and Tc(IV) aqueous species and solid compounds will only be incorporated to THEREDA database after the completion of the project VESPA (BMW). In the framework of WP1 of this project, a PhD thesis on the redox behaviour and solubility of Tc under reducing conditions is underway at KIT-INE (by Ezgi

Yalcintas). This PhD thesis (which will be completed in 2015) tackles the following topics:

- Tc(VII)/Tc(IV) redox chemistry in dilute to concentrated NaCl and MgCl<sub>2</sub> solutions
- Solubility of Tc(IV) in dilute to concentrated NaCl solutions
- Solubility of Tc(IV) in dilute to concentrated MgCl<sub>2</sub> solutions
- Solubility of Tc(IV) in dilute to concentrated CaCl<sub>2</sub> solutions

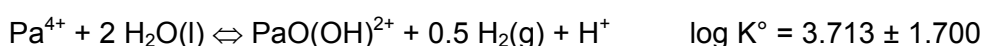
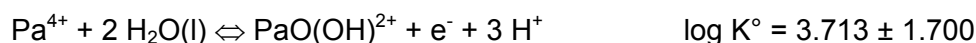
The outcome of this work will be a comprehensive thermodynamic model including Pitzer parameters for the system Tc<sup>4+</sup>-Na<sup>+</sup>-Mg<sup>2+</sup>-Ca<sup>2+</sup>-H<sup>+</sup>-TcO<sub>4</sub><sup>-</sup>-Cl<sup>-</sup>. The experimental and modelling work will be published in international peer reviewed journals, and then incorporated into THEREDA database after the mandatory test calculations.

### **3.3 Pentavalent radionuclides: the actinides Pa(V), Np(V), Pu(V), and Am(V)**

The pentavalent actinides U(V), Np(V), Pu(V), and Am(V) occur in water as dioxo cations AnO<sub>2</sub><sup>2+</sup> and because of their same structure and charge they show very similar chemical properties. In contrast to these actinides, the structure of the unhydrolysed pentavalent protactinium is still being under discussion, and no clear evidence exists from experience what kind of species occurs in solution. DFT calculations showed that the PaO<sub>2</sub><sup>+</sup> is unstable in aqueous solution, but that the PaO<sup>3+</sup> can be stabilized in solution with complexing ligands like the sulphate anion. However, the PaO<sup>3+</sup> react very strong with water and hydrolyse even in acidic solutions to PaO(OH)<sup>2+</sup>, a species that was also confirmed by theoretical DFT calculations. This cation has a different structure compared to the dioxo cations and hence, shows different chemical properties. For protactinium, no chemical analogue actinide exists and therefore no analogue values can be taken in case of missing thermodynamic data. However, Vitorge and coworkers suggest [VIT/PHY2007] using pentavalent niobium as analogue element, because its chemical behavior is quite similar. In contrast to the Pa(V), analogue values are possible for the dioxo cations of the other actinides, e.g. reliable Np(V) data can be taken for the Pu(V) or Am(V) and vice versus.

### 3.3.1 Protactinium, Pa(V): PaO(OH)<sup>2+</sup>

The pentavalent protactinium ion Pa<sup>5+</sup> is a very reactive ion that reacts very strong with water, even in very acidic solutions and does not occur in aqueous solutions as an aquo cation with the charge +5. It is assumed that the Pa(V) exist as PaO<sup>3+</sup>, although it could not be proved from the experiments. However, also this ion reacts very strong with water already in acidic solution. From the experiment it is quite certain that the hydrolysis product species PaO(OH)<sup>2+</sup> occurs in solution. From these observations KIT-INE selected the PaO(OH)<sup>2+</sup> as the secondary master species in THEREDA, formed from the primary master species Pa<sup>4+</sup> according to the following reaction:



The redox reaction between Pa(IV) and Pa(V) was defined via the hydrogen reaction H<sup>+</sup>/H<sub>2</sub>(g) in THEREDA database. The equilibrium constant for the redox reaction was calculated from the redox potential E(Pa(V)/(IV)) = -0.1 ± 0.1 V in 1 M HCl and corrected to ionic strength zero by the SIT approach. The calculation is as followed:

E (Pa(IV)/Pa(V) in 1 M HCl) = -0.1 ± 0.1 V [FUG/OET1976] (pe = -1.690)



for 1 M HCl applies:

$$\frac{[\text{PaO}(\text{OH})^{2+}]}{[\text{Pa}^{4+}]} = 1 \quad \text{at } pe = -1.690$$

$$\Rightarrow \log K' = \log \frac{[\text{PaO}(\text{OH})^{2+}]}{[\text{Pa}^{4+}]} + 3 \log [\text{H}^+] - pe$$

$$= \log (1) + 3 \log (1) - (-1.690 \pm 1.690) = 1.690 \pm 1.690$$

On the molal scale applies: 1 M HCl = 1.0222 m HCl

$$\Rightarrow \log K' = (1.690 \pm 1.690) + 3 \log (1.0222) = 1.719 \pm 1.690$$

The formation constant can be corrected to ionic strength zero with:

$$\log K^\circ = \log K' - \Delta z^2 D + \Delta \varepsilon I_m$$

$$= 1.719 + 9 \times (0.2045) + (0.15 \pm 0.18) \times 1.0222$$

$$\log K^\circ = 3.713 \pm 1.700$$

with

$$\Delta z^2 = -9 ; \Delta \varepsilon = 0.15 \pm 0.18 \text{ kg/mol}$$

$$\varepsilon(\text{H}^{<+>}, \text{Cl}^{<->}) = 0.12 \pm 0.01 \text{ [GUI/FAN2003]}$$

$$\varepsilon(\text{PaO}(\text{OH})^{<2+>}, \text{Cl}^{<->}) = 0.09 \pm 0.09,$$

estimated from charge analogies:  $\text{UO}_2^{2+}$  ( $0.21 \pm 0.02$ ) ,  $\text{Am}(\text{OH})^{2+}$  ( $-0.04 \pm 0.07$ ) and  $\text{Al}(\text{OH})^{2+}$  ( $0.09$ ) (see also chapter 3.3.1.1 *Interaction parameters*)

$$\varepsilon(\text{Pa}^{<4+>}, \text{Cl}^{<->}) = 0.3 \pm 0.1$$

estimated from charge analogies:  $\text{An}^{<4+>}$ .

### 3.3.1.1 The hydrolysis of Pa(V)

#### 3.3.1.1.1 The hydroxide complexes of Pa(V)

The hydrolysis reaction has been studied by a few groups with extraction methods. A short overview is given in [MYA/KIR2006]. Earlier studies are from [GUI1966] and [BOU1971]. The most reliable data concerning the hydrolysis are from [TRU/LEN2002, TRU/LEN2003 and LEN/TRU2003]. These studies, as well as the older ones, have been performed with solvent extraction using TTA as extractant at tracer concentrations of Pa. This method implies some difficulties like side reactions of the TTA and other unwanted side reactions and sorption of Pa(V) on the vessels. This problem was also exposed in studies with other actinide elements [RAN/FUG2008]. Therefore, [VIT/PHY2007] has reviewed and re-estimated the data of the “Trubert group”. They considered only data at high ionic strength and low TTA concentration to avoid inconsistent results because of ternary TTA complexes. As a result, only data with the lowest systematic error and the smallest contribution from side reactions are regarded for deducing the complex formation constant. The suppression of inconsistency results in higher uncertainty of the measurements. Additionally, they suggest that the hydrolysis behaviour of Nb(V) seems to be similar to Pa(V), because of the more d-elemental-like chemical behaviour of Pa(V). They re-estimated a data set of Nb(V) for comparison reasons with the Pa(V) values. The new values are given in Table 38 for three hydrolysis reactions that were discussed so far, including the values for Nb(V) hydrolysis.

Table 38: Stepwise formation constants  $\log K_n^\circ$  for the Pa(V) hydrolysis reaction at ionic strength  $I = 0$ .

| Reaction  | $\log K^\circ$   |   |
|---|--|---|
| $\text{PaO}^{3+} + \text{H}_2\text{O} = \text{PaO}(\text{OH})^{2+} + \text{H}^+$  | $\log K_1^\circ = -0.04 \pm 0.36$<br>$\geq -0.75$ (Nb(V))  | VIT/PHR2007   |
| $\text{PaO}(\text{OH})^{2+} + \text{H}_2\text{O} = \text{PaO}(\text{OH})_2^+ + \text{H}^+$  | $\log K_2^\circ = -1.44 \pm 0.71$<br>$-1.24 \pm 0.02$<br>$-1.26 \pm 0.15$<br>$-1.61 \pm 0.15$<br>$-1.65 \pm 0.2$ (Nb(V)) | VIT/PHR2007<br>TRU/LEN2003<br>TRU/LEN2002<br>FOU/PER2007<br>VIT/PHR2007 |
| $\text{PaO}(\text{OH})_2^+ + 2\text{H}_2\text{O} = \text{Pa}(\text{OH})_5$  | $\log K_3^\circ \leq -3.6$<br>$-7.03 \pm 0.15$<br>$-7.15 \pm 0.4$<br>$-6.96 \pm 0.4$<br>$-4.95 \pm 0.2$ (Nb(V))          | VIT/PHR2007<br>TRU/LEN2003<br>TRU/LEN2002<br>FOU/PER2007<br>VIT/PHR2007 |
| $\text{Pa}(\text{OH})_5 + \text{H}_2\text{O} = \text{Pa}(\text{OH})_6^- + \text{H}^+$ or<br>$\text{PaO}_2(\text{OH}) + \text{H}_2\text{O} = \text{PaO}_2(\text{OH})_2^- + \text{H}^+$ | $\log K_4^\circ = -9.13 \pm 0.1$   | FOU/PER2007   |

The formation of the  $\text{PaO}^{3+}$  is not proposed by the group of Trubert because this species has never been observed from experiments and its existence has still to be proved. The species  $\text{PaOOH}^{2+}$  and  $\text{PaO}(\text{OH})_2^+$  could be confirmed by classical slope analysis of the raw data in the pH range between 0 and 4. Unfortunately, there was no clear evidence for a neutral species, because of the scattering of the data. This can be due to a reaction with ionized deprotonated TTA forming a mixed complex. However, the  $\text{Pa}(\text{OH})_5$ , written also as  $\text{PaO}(\text{OH})_3$  or  $\text{PaOOH}(\text{OH})_2$ , is certainly formed. Vitorge et al. do not rely on the values for the third stepwise hydrolysis constant  $\log K_3^\circ = -7.15 \pm 0.4$  and  $-7.03 \pm 0.15$ , because the corresponding hydrolysis constant could not be detected in their experiment. At pH lower than 4, a hydrolysis constant lower than about -4 cannot be fitted from the experimental data. Therefore, an upper limit of  $\log K_3^\circ \leq -3.6$  was estimated. The value of Nb(V) ( $K_3^\circ = -4.95 \pm 0.2$ ) can also be considered as a rough estimate value, only. At the same time, Fourest et al. published a work on

the hydrolysis of Pa(V) by capillary diffusion in perchlorate medium from pH 0 to pH 13. They tested this method with  $\text{Eu}^{3+}$  and compared the results with the Pa(V) experiment. The evaluation of the experimental results confirmed the hydrolysis constants from [TRU/LEN2002] and suggested a further negative hydrolysis species at higher pH values ( $\text{pH} > 10$ ):  $\text{Pa}(\text{OH})_6^-$  or  $\text{PaO}_2(\text{OH})_2^-$ .

DFT calculations from [SIB/MAR2008] hint that the  $\text{PaO}_2^+$  ion is instable in water because of the short apical-bonded H-atom and a highly negative charge on the O-yl. For the solvated species they showed that  $\text{PaO}^{3+}$  can exist in the form of a complex, like with e.g. sulphate.  $\text{PaOOH}^{2+}$  is confirmed to be the Pa(V) aqueous di-cation for the pH below  $1.4 \pm 0.7$ . The stability of the mono-cation  $\text{PaO}(\text{OH})_2^+$  is still under discussion. Siboulet et al. claim that  $\text{PaO}(\text{OH})_2^+$  is at least as unstable as the  $\text{PaO}_2^+$  species. So neither the  $\text{PaO}_2^+$  nor the  $\text{PaO}(\text{OH})_2^+$  could be the mono-cation that was observed from the experiments. A tri-cation has never been observed although from theory the  $\text{PaO}^{3+}$  in sulphate solutions and the  $\text{Pa}(\text{OH})_2^{3+}$  in general can be stable in aqueous solutions [SIB/MAR2008].

Table 39: Selected values for the Pa(V) hydrolysis reactions expressed as cumulative (or overall) formation constants  $\log \beta^\circ$  at ionic strength  $I = 0$ .

| Reaction  | $\log \beta^\circ$                     |             |
|---|--|-------------|
| $\text{PaO}(\text{OH})^{2+} + \text{H}_2\text{O} = \text{PaO}(\text{OH})_2^+ + \text{H}^+$  | $\log \beta_2^\circ = -1.26 \pm 0.15$  | TRU/LEN2002 |
| $\text{PaO}(\text{OH})^{2+} + 3\text{H}_2\text{O} = \text{Pa}(\text{OH})_5 + 2\text{H}^+$   | $\log \beta_3^\circ = -8.41 \pm 0.42$  | TRU/LEN2002 |
| $\text{PaO}(\text{OH})^{2+} + 4\text{H}_2\text{O} = \text{Pa}(\text{OH})_6^- + 3\text{H}^+$ | $\log \beta_4^\circ = -17.54 \pm 0.44$ | FOU/PER2007 |

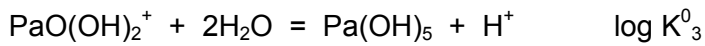
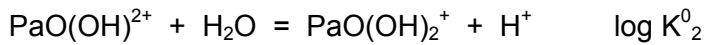
In THEREDA, as a first approach, the chemical model for Pa(V) according to Trubert and coworkers was adopted [TRU/LEN2002]. The overall formation constants  $\log \beta^\circ$  are given in Table 39. The first equilibrium to form the  $\text{PaO}(\text{OH})^{2+}$  ion with  $\log K_1^\circ$  was not selected because the existence of  $\text{PaO}^{3+}$  species was not proved and, even if it exists, this species would occur at conditions not relevant for waste disposal in geological formations. For that, in THEREDA the  $\text{PaO}(\text{OH})^{2+}$  was selected as a secondary master species formed by oxidation of  $\text{Pa}^{4+}$  (primary master species, s. page 59). The fourth hydrolysis equilibrium was considered for THEREDA for the sake of completeness. However, it must be emphasized that all values are rough estimations



at the moment and have to be adapted in the future based upon more complete experimental data. Polymerization reactions of Pa(V) are not considered in the THEREDA database, because these reactions cannot be quantified on basis of the present data.

### *Ion interaction parameters*

Ion interaction parameters have been deduced from the experimental data for the SIT approach, the specific interaction coefficient  $\epsilon(i,j)$ . The Pitzer model could not be applied on the experimental data, because of the lack of data. However, because of a linear relationship between the SIT and the Pitzer equation, the Pitzer parameter  $\beta^{(0)}$  and  $\beta^{(1)}$  can be derived from the  $\epsilon(i,j)$  of the SIT approach. Trubert et al. gives the following SIT parameter for the  $\text{PaO}(\text{OH})^{2+}/\text{ClO}_4^-$  and  $\text{PaO}(\text{OH})_2^+/\text{ClO}_4^-$  interaction, according to the following two reactions:



and using the basic SIT equations [GRE/PUI1997] to extrapolate to  $I = 0$ :

$$\log K_2 + 2D = \log K_2^0 - \Delta\epsilon_2 I_m \quad \text{and} \quad \log K_3 = \log K_3^0 - \Delta\epsilon_3 I_m$$

$$\Delta\epsilon_2 = \epsilon[\text{PaO}(\text{OH})_2^+, \text{ClO}_4^-] + \epsilon(\text{H}^+, \text{ClO}_4^-) - \epsilon[\text{PaO}(\text{OH})^{2+}, \text{ClO}_4^-] = -0.06 \pm 0.01$$

$$\Delta\epsilon_3 = \epsilon(\text{H}^+, \text{ClO}_4^-) - \epsilon[\text{PaO}(\text{OH})_2^+, \text{ClO}_4^-] = -0.37 \pm 0.08$$

With  $\epsilon(\text{H}^+, \text{ClO}_4^-) = 0.14 \pm 0.02 \text{ kg mol}^{-1}$  at 25°C and 1 bar pressure from [GRE/PUI1997], the specific interaction coefficient can be derived from  $\Delta\epsilon_1$  and  $\Delta\epsilon_2$ :

$$\epsilon[\text{PaO}(\text{OH})^{2+}, \text{ClO}_4^-] = -0.03 \pm 0.02 \text{ kg mol}^{-1} \quad \text{and}$$

$$\epsilon[\text{PaO}(\text{OH})_2^+, \text{ClO}_4^-] = -0.23 \pm 0.02 \text{ kg mol}^{-1}.$$

For the chloride system the SIT parameter  $\varepsilon(\text{PaO}(\text{OH})^{2+}, \text{Cl}^-)$  was estimated from charge analogies between  $\text{UO}_2^{2+}$  ( $0.21 \pm 0.02$ ),  $\text{Am}(\text{OH})^{2+}$  ( $-0.04 \pm 0.07$ ) and  $\text{Al}(\text{OH})^{2+}$  ( $0.09$ ). The mean value of  $\varepsilon(\text{PaO}(\text{OH})^{2+}, \text{Cl}^-) = 0.09 \pm 0.09$  is obtained. By comparison with the  $\varepsilon[\text{PaO}(\text{OH})^{2+}, \text{ClO}_4^-] = -0.03$ , the value in the chloride system is larger than the latter one. This observation is in contrast to a comparison of SIT parameters between species in the chloride and perchlorate system listed in the NEA-TDB. The  $\varepsilon(\text{PaO}(\text{OH})_2^+, \text{Cl}^-)$  was estimated from charge analogies between  $\text{Th}(\text{OH})_3^+$  ( $0.06 \pm 0.05$ ),  $\text{UF}_3^+$  ( $0.1 \pm 0.1$ ),  $\text{NpO}_2^+$  ( $0.09 \pm 0.05$ ),  $\text{AmCO}_3^+$  ( $0.01 \pm 0.05$ ),  $\text{ZnHCO}_3^+$  ( $0.2$ ), and  $\text{Am}(\text{OH})_2^+$  ( $-0.27 \pm 0.2$ ). The mean value  $\varepsilon(\text{PaO}(\text{OH})_2^+, \text{Cl}^-) = 0.03 \pm 0.2$  is obtained.

The Pitzer parameter  $\beta^{(0)}$  and  $\beta^{(1)}$  have been deduced according to the Pitzer model approach [GRE/PUI1997] by Trubert et al. and Jaussaud [TRU/LEN2002, JAU2003] for the perchlorate system and by THEREDA for the chloride system. The values are listed in Table 40 and more details are also given in chapter 3.3.1.3.

It must be emphasized that the Pitzer interaction parameters  $\beta^{(0)}$  and  $\beta^{(1)}$  are very rough estimates and are also only valid at ionic strengths below 4 mol/L.

Table 40: The Pitzer parameter for Pa(V) hydrolysis species at 25°C.

| Binary Pitzer Parameter        |                  | $\beta^{(0)}$ | $\beta^{(1)}$ | $\beta^{(2)}$ | $C^\phi$ | $\alpha_1$ | $\alpha_2$ | Reference |
|--------------------------------|------------------|---------------|---------------|---------------|----------|------------|------------|-----------|
| c                              | a                |               |               |               |          |            |            |           |
| $\text{PaO}(\text{OH})^{2+}$ , | $\text{ClO}_4^-$ | 0.076         | 1.30          |               |          |            |            | 1         |
|                                | $\text{ClO}_4^-$ | 0.12          | 1.30          | 0             | 0        | 2          | 0          | 2         |
|                                | $\text{Cl}^-$    | 0.25          | 1.6           |               |          |            |            | 3         |
| $\text{PaO}(\text{OH})_2^+$    | $\text{ClO}_4^-$ | 0.027         | 0.35          |               |          |            |            | 1         |
|                                | $\text{ClO}_4^-$ | 0.10          | 0.35          | 0             | 0        | 2          | 0          | 2         |
|                                | $\text{Cl}^-$    | 0.14          | 0.3           |               |          |            |            | 3         |

1: TRU/LEN2002; 2: JAU2003; 3: THEREDA

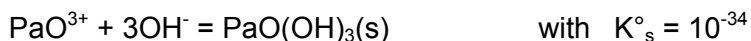
### 3.3.1.1.2 Solubilities of Pa(V) oxides and hydroxide

The discussion of the solubility of Pa(V) is faced with the same difficulties like discussed in the former chapters related to this element. Hence, the uncertainty affecting the aqueous species involved in the solubility reaction is high. The  $\text{PaO}(\text{OH})^{2+}$  is again the only species that is regarded as the stable one.

Solubility studies of Pa(V) are very seldom in the literature. Also the IUPAC-NIST Solubility data series mention only two studies [HAL/MIY2007]. The only value for a solubility of Pa(V) was given from Starik et al. [STA/SHE1959]. In this paper the reaction considered was

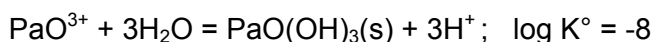


At Pa concentration of  $10^{-12} \text{ mol L}^{-1}$  and pH 5 at ionic strength of  $I = 0$  a solubility product of  $K_s = 10^{-55} \text{ mol}^6 \text{ L}^{-6}$  is suggested. Neither the solid nor the solved species were characterized. In [TAR/FOU2005] this value was adapted to the reaction of:



or as formation constant  $\log K^\circ = 34$ .

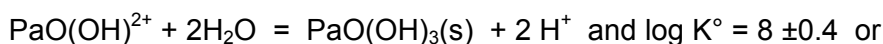
Changing the reaction to the reaction with water, one gets the following reaction

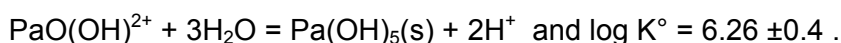


As mentioned before, the  $\text{PaO}^{3+}$  species is not regarded in the THEREDA base and consequently, the reaction has to be adapted to the species  $\text{PaO}(\text{OH})^{2+}$ . For this, the hydrolysis reaction according to [VIT/PHR2007] can be taken into consideration



with a first estimate of the formation constant to be  $\log K^\circ = -0.04 \pm 0.36$ . It must be emphasised that this approach must be regarded as an estimation, because we use two different sources that are not sufficiently consistent. After rearranging, the reaction can be written in the form





The latter reaction with its formation constants can be used for THEREDA, but it must again be emphasized that the value is a rough estimated value. However, considering that solubility control under repository conditions by a pure protactinium phase is extremely unlikely, owing to the low abundance and very high tendency towards sorption on surfaces, the approach to derive thermodynamic data within THEREDA seems justified.

### 3.3.1.2 Chloride complexation of Pa(V)

The chloride complexation of Pa(V) was investigated by Guillaumont and by LeNour et al. [LEN/DIG2009] at 3 M NaCl and acid concentration of 0.5, 1.0 and 3 M  $[\text{H}^+]$ . They evaluated a complex formation constants of  $\log \beta_1(I = 3 \text{ M NaCl}) = 1.20$  and  $1.09 \pm 0.05$ , respectively, without taking into consideration the hydrolysis and based on the reaction



Both values of the formation constant are very similar and it can be concluded that the chloride complexation is rather weak. As a consequence, the influence of the hydrolysis reaction will compensate the chloride complexation effect at higher pH values. The chloride complexation effect can be described by the interaction parameters only without explicit formulation of complexes. No complex formation constant for the chloride complexation of Pa(V) was selected for the THEREDA database.

### 3.3.1.3 Reaction of Pa(V) with sulphate anions

The sulphate complexation of Pa(V) was investigated by Le Naour et al. [LEN/DIG2009] at tracer concentration of protactinium. Even in sulphate and chloride solutions at rather high concentrations (4 M HCl or  $\text{H}_2\text{SO}_4$ ) the polymerisation of higher concentration of Pa(V) cannot be avoided [MUX/GUI1974]. To get rid of these problems, the studies have been performed at tracer concentration Pa-233 ( $<10^{-10}$  M). However, investigations at such low concentration suffer in lacking of structural information about the species involved in the complexation process. Nevertheless,

using extraction methods, the complexation constants can be deduced from the different behavior of the species in the organic and aqueous phase. By varying the ligand concentration the variation in the distribution coefficient gives information about the complexation of Pa(V). Le Naour et al. [LEN/DIG2009] and Di Giandomenico [DIG2007] could also deduce interaction coefficients according to the SIT approach by variation of the ionic strength between 0.78 and 2.90 mol kg<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>/HClO<sub>4</sub>. The complex formation constants are given in Table 41. Le Naour and coworkers [LEN/TRU2005] could show in a XAFS investigation that the mono-oxo bond in the Pa(V) species is still present in the tri-sulphate complex. Therefore, the sulphate complexation equilibria are written by considering the third hydrolysis species of Pa(V), PaO(OH)<sup>2+</sup>.

Table 41: Complex formation constants log β<sub>i</sub><sup>o</sup> for the Pa(V) sulphate complexation at 25 °C [LEN/DIG2009, DIG2007].

| Reaction   | log β <sup>o</sup>              |           |
|--|---------------------------------|-----------|
| $\text{PaO(OH)}^{2+} + \text{SO}_4^{2-} + \text{H}^+ = \text{PaO(SO}_4\text{)}^+ + \text{H}_2\text{O}$       | log β <sub>1</sub> <sup>o</sup> | 3.9 ± 0.2 |
| $\text{PaO(OH)}^{2+} + 2\text{SO}_4^{2-} + \text{H}^+ = \text{PaO(SO}_4\text{)}_2^- + \text{H}_2\text{O}$    | log β <sub>2</sub> <sup>o</sup> | 7.0 ± 0.2 |
| $\text{PaO(OH)}^{2+} + 3\text{SO}_4^{2-} + \text{H}^+ = \text{PaO(SO}_4\text{)}_3^{3-} + \text{H}_2\text{O}$ | log β <sub>3</sub> <sup>o</sup> | 8.6 ± 0.2 |

These studies confirm again the difference between the pentavalent neptunium and protactinium. Np(V) seemingly forms only one sulphate complex (NpO<sub>2</sub>SO<sub>4</sub><sup>-</sup>) in contrast to Pa(V) and its formation constants is about one order of magnitude lower than of Pa(V).

The interaction coefficients for the sulphate complexation reaction were deduced by Di Giandomenico and Le Nour with the SIT approach according to the recommendation given in the NEA guidelines. These interaction parameters are therefore consistent with NEA-TDB thermodynamic data set. The values are listed in Table 43. However, for THEREDA the interaction coefficients according to the Pitzer model have to be used. For that, an estimate method proposed by Grenthe et al. [GRE/PLY1997] can be

performed to convert the  $\varepsilon(j,k)$  into the Pitzer parameters  $\beta^{(0)}$  and  $\beta^{(1)}$  by a simple relationship. The  $\beta^{(1)}$  values for a  $(M^+, X^-)$  and  $(M^+, X^{3-})$  electrolyte are tabulated in [GRE/PLY1997] and the  $\beta^{(0)}$  is calculated with the relationship

$$A = (\beta^{(0)} - \varepsilon_\gamma \cdot 0.5)$$

The A values are also tabulated in [GRE/PLY1997] for a  $(M^+, X^-)$  and  $(M^+, X^{3-})$  electrolyte. The relationship between  $\varepsilon_\gamma$  and  $\varepsilon$  is  $\varepsilon(j,k) = \varepsilon_\gamma(j,k) / \ln(10)$ . The values of both, A and  $\beta^{(1)}$  used for the estimation of the Pitzer data in this work are given Table 42.

Table 42: Parameter A and  $\beta^{(1)}$  for the estimation of the Pitzer parameter  $\beta^{(0)}$  from the SIT parameter  $\varepsilon(i,j)$  according to [GRE/PLY1997].

| Ion combination | A     | $\beta^{(1)}$ |
|-----------------|-------|---------------|
| $(M^+, X^-)$    | 0.035 | 0.3           |
| $(M^{2+}, X^-)$ | 0.150 | 1.6           |
| $(M^+, X^{3-})$ | 0.366 | 4.3           |

Table 43: SIT and Pitzer interaction parameter for the Pa(V) sulphate complexes at 25 °C. These interaction parameters are only valid at ionic strengths between 0 and 4 mol/kg.

| Ion j                       | Ion k                            | SIT<br>$\varepsilon(j,k)$ (kg/mol) | Pitzer<br>$\beta^{(0)}$ | Pitzer<br>$\beta^{(1)}$ |
|-----------------------------|----------------------------------|------------------------------------|-------------------------|-------------------------|
| $\text{PaO}(\text{SO}_4)^+$ | $\text{ClO}_4^-$                 | $0.8 \pm 0.2$                      | $0.96 \pm 0.2$          | 0.3                     |
| $\text{Na}^+$               | $\text{PaO}(\text{SO}_4)_2^-$    | $0.4 \pm 0.1$                      | $0.50 \pm 0.1$          | 0.3                     |
| $\text{Na}^+$               | $\text{PaO}(\text{SO}_4)_3^{3-}$ | $0.2 \pm 0.1$                      | $0.60 \pm 0.1$          | 4.3                     |

### 3.3.2 Uranium, U(V): $\text{UO}_2^+$

The thermodynamic data of the pentavalent uranium U(V) have been collected and evaluated by the Helmholtz Centre Dresden-Rossendorf within the THEREDA project. Information about the selection can be found in their final report.

### 3.3.3 Neptunium, Np(V): $\text{NpO}_2^+$

#### 3.3.3.1 Hydrolysis and (hydr)oxide compounds of $\text{NpO}_2^+$

The relevant equilibrium reactions of the neptunyl cation ( $\text{NpO}_2^+$ ) with water for the assessment of geochemical processes in alkaline media are summarized in Table 44. The hydrolysis of  $\text{NpO}_2^+$  is quite weak due to the single positive charge and starts at about pH 9. The formation of the first and second (binary) hydrolysis complex,  $\text{NpO}_2\text{OH}(\text{aq})$  and  $\text{NpO}_2(\text{OH})_2^-$ , have been described for NaCl and  $\text{NaClO}_4$  systems up to  $[\text{OH}]^- = 1 \text{ M}$ . Neck et al. observed in their experiments [NEC/KIM1992] a green amorphous solid ( $\text{NpO}_2\text{OH}(\text{am}, \text{fresh})$ ) by exceeding the solubility of Np(V) that changed under certain conditions with time into a white solid ( $\text{NpO}_2\text{OH}(\text{am}, \text{aged})$ ). The solubility of the latter is lower by 0.6 log-units. The formation constants of all four hydrolysis species and solid compounds were reviewed by [LEM/FUG2001, GUI/FAN2003] and are listed in Table 44. This set of data has been deduced by using the SIT approach for correction of the ionic strength to infinite dilution. However, for the reaction between  $\text{NpO}_2^+$  and water, a set of formation constants and Pitzer parameters (set 1) was evaluated by Neck et al. [FAN/NEC1995, NEC/FAN1995, NEC1997] and another set of formation constants and Pitzer parameter set (set 2) was deduced by Runde et al. [RUN/NEU1996] (see Table 46). Based on Pitzer parameter set 1 and the NEA data, a new set of data consistent to the data from the NEA [GUI/FAN2003] within the experimental uncertainties has been developed [ALT/BRE2004]. These data have been adopted by THEREDA. The values are collected in Table 44, 45 and 46.

Table 44: Formation equilibria and thermodynamic constants from NEA (derived with SIT) for binary Np(V) hydrolysis species and (hydr)oxide solid compounds

| Reaction   |                                   | log * $\beta^\circ$ or log * $K^\circ$ |
|--|-----------------------------------|--|
| $\text{NpO}_2^+ + \text{H}_2\text{O} = \text{NpO}_2\text{OH}(\text{aq}) + \text{H}^+$        | log * $\beta^\circ_1$             | <b>-11.30 ± 0.7</b>                    |
| $\text{NpO}_2^+ + 2\text{H}_2\text{O} = \text{NpO}_2(\text{OH})_2^- + \text{H}^+$            | log * $\beta^\circ_2$             | <b>-23.6 ± 0.5</b>                     |
| $\text{NpO}_2^+ + \text{H}_2\text{O} = \text{NpO}_2\text{OH}(\text{am, fresh}) + \text{H}^+$ | log * $K^\circ_{(\text{fresh})}$  | <b>-5.30 ± 0.2</b>                     |
| $\text{NpO}_2^+ + \text{H}_2\text{O} = \text{NpO}_2\text{OH}(\text{am, aged}) + \text{H}^+$  | log * $K^\circ_{(\text{aged})}$   | <b>-4.70 ± 0.5</b>                     |
| $2 \text{NpO}_2^+ + \text{H}_2\text{O} = \text{Np}_2\text{O}_5(\text{cr}) + 2 \text{H}^+$    | log * $K^\circ_{(\text{cr},2,5)}$ | <b>-3.6 ± 0.8*</b>                     |

\*value internally estimated ; not selected by the NEA.

There is another binary Np(V) solid compound,  $\text{Np}_2\text{O}_5(\text{cr})$ , that is discussed in the literature. Its formation in solution is questionable. The formation from the under-saturation and over-saturation was measured by [EFU/RUN1998]. The greenish brown precipitates were interpreted as poorly crystallized hydrated  $\text{Np}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ . The information about the structure was obtained from diffuse and rather inconclusive X-ray powder diffraction pattern. The authors derived a solubility constant of  $\log *K^\circ_s = 2.6 \pm 0.4$  for the reaction  $0.5 \text{Np}_2\text{O}_5(\text{cr}) + \text{H}^+ = \text{NpO}_2^+ + 0.5 \text{H}_2\text{O}(\text{l})$  (original:  $\log *K^\circ_s = 5.2 \pm 0.8$  for the reaction  $\text{Np}_2\text{O}_5(\text{cr}) + 2\text{H}^+ = 2\text{NpO}_2^+ + \text{H}_2\text{O}(\text{l})$ ).

[PAN/CAM1995,1998] reports a solubility product of  $\log K^\circ_{\text{sp}} = -10.08 \pm 0.2$  for the reaction  $0.5 \text{Np}_2\text{O}_5(\text{cr}) + 0.5 \text{H}_2\text{O} = \text{NpO}_2^+ + \text{OH}^-$ . By re-calculation of this value to account for the equilibrium reaction with water,  $\log *K^\circ_s = 3.92 \pm 0.2$  is obtained. This value is more than one order of magnitude higher than the solubility constant from Efurud et al. discussed above.

In thermochemical studies, the enthalpy and entropy of  $\text{Np}_2\text{O}_5(\text{cr})$  formation was determined (see discussion in [GUI/FAN2003, MER/FUG1994, BEL/SMI1979])

Table 45). The NEA-TDB has shown that the formation constants, the molar enthalpy of formation as well as the molar entropy obtained by the different reported ways are inconsistent. They also question that  $\text{Np}_2\text{O}_5(\text{cr})$  forms in solution with regard to equilibrium chemistry. On the basis of these arguments, the NEA-TDB has not selected any formation constant for  $\text{Np}_2\text{O}_5(\text{cr})$ .



In ALT/BRE2004, the solid  $\text{Np}_2\text{O}_5$  or  $\text{NpO}_{2.5}(\text{hyd},\text{s})$  is also reported as a species required for modelling aquatic systems. Because THEREDA relies on equilibrium experiments in solution rather than on thermochemical experiments and in view of the discussions summarized above, the data from [EFU/RUN1998] and [PAN/CAM1995,1998] are considered in THEREDA. We introduced the mean value of both formation constants ( $-2.60 \pm 0.8$  and  $-3.92 \pm 0.2$ ) with an estimated uncertainty yielding in  $\log K^\circ = -3.3 \pm 1.0$  (s. Table 47).

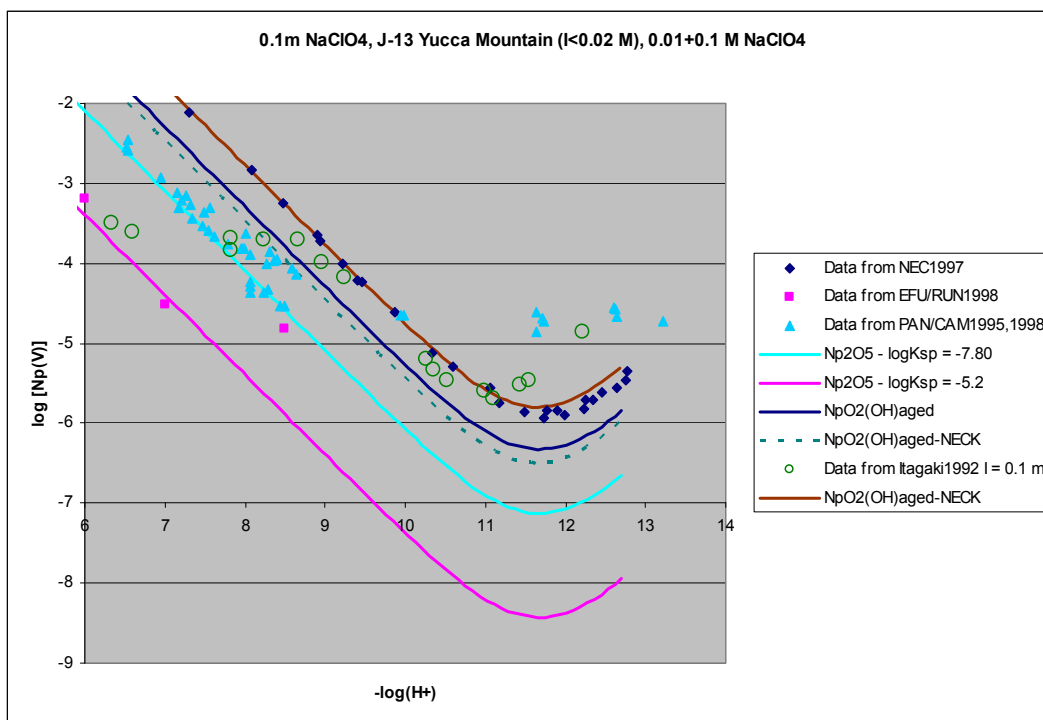


Figure 14: Comparison between modelling of the  $\text{Np}(\text{V})$  solubility in 0.1 M  $\text{NaClO}_4$  with data from THEREDA and experimental data from literature ([NEC1997, EFU/RAN1998, PAN/CAM1995,1998, ITA/NAK1992])

Although the solid species  $\text{NpO}_{2.5}(\text{hyd},\text{s})$  is found in THEREDA, it must be cautioned against its incorporation in the modelling as the  $\text{NpO}_{2.5}(\text{hyd},\text{s})$  may not be in equilibrium with the system analysed. It consequently may be removed by the user from the parameter file generated by THEREDA.

Table 45: Thermodynamic data from literature for the solubility of  $\text{Np}_2\text{O}_5(\text{cr})$  according to the reaction:  $0.5 \text{Np}_2\text{O}_5(\text{cr}) + \text{H}^+ = \text{NpO}_2^+ + 0.5 \text{H}_2\text{O}(\text{l})$  (or  $\text{NpO}_{2.5}(\text{cr}) + \text{H}^+ = \text{NpO}_2^+ + 0.5 \text{H}_2\text{O}$ ). The data are critically discussed in [LEM/FUG2001] and [GUI/FAN2003].

|             | $\Delta_f H^\circ_m$ (KJ mol <sup>-1</sup> ) | $S^\circ_m$ (J K <sup>-1</sup> mol <sup>-1</sup> ) | $\Delta_f G^\circ_m$ (KJ mol <sup>-1</sup> ) | log Ksp     |
|-------------|--|--|--|-------------|
| LEM/FUG2001 | -2162 ± 9.5                                  | 174 ± 20   | -2031.6 ± 11.2                               | 3.90 ± 0.02 |
| MER/FUG1994 | -2162.7 ± 9.5                                | 186 ± 15   |  | 2.75 ± 1.9  |
| BEL/SMI1979 | -2142 ± 13                                   |  |  |             |
| PAN/CAM1995 |  | 95 ± 46  | -2008 ± 11                                   | 3.90 ± 0.02 |
| VIT/CAP2003 |  |  |  | 3.70        |
| LEM1984     |  | 163 ± 23   |  | 9.50        |
| EFU/RUN1998 |  |  |  | 2.6 ± 0.4   |

Table 46: Values for the formation constants of the Np(V) hydrolysis species. The values in boldface are selected for THEREDA and they are regarded as consistent with the SIT and Pitzer approach within the experimental uncertainties. The formation constants correspond to the reactions in Table 44.

|                              | Pitzer consistent according (A) (set 2) | Pitzer consistent according (B) (set 1) | THEREDA (C) Pitzer consistent (set 1) |
|------------------------------|---|---|---------------------------------------|
| log $*K_{\text{fresh}}(I=0)$ | -                                       | -5.22 ± 0.05                            | <b>-5.30 ± 0.2</b>                    |
| log $*K_{\text{aged}}(I=0)$  | -4.49 ± 0.18                            | -4.52 ± 0.07                            | <b>-4.70 ± 0.5</b>                    |
| log $*\beta_1 (I=0)$         | -11.42 ± 0.27                           | -11.31 ± 0.13                           | <b>-11.30 ± 0.7</b>                   |
| log $*\beta_2 (I=0)$         | -23.58 ± 0.19                           | -23.54 ± 0.06                           | <b>-23.6 ± 0.5</b>                    |

(A): RUN/NEU1996; (B) NEC1997, NEC/FAN1995, FAN/NEC1995; (C) ALT/BRE2004, GUI/FAN2003

Table 47: Formation constants  $\log K^{\circ}_{(s,hyd)}$  or solubility products  $\log K^{\circ}_{sp}$  of the formation/dissolution of  $Np_2O_5(s,hyd)$  from the literature and the selected THEREDA value.

| Reaction  | $\log K^{\circ}_{(s,hyd)}$       | Reference         |
|---|----------------------------------|-------------------|
| $Np_2O_5 \cdot xH_2O + 2H^+ = 2NpO_2^+ + (x+1)H_2O$ | $5.2 \pm 0.8^a$                  | EFU/RUN1998       |
|   | $5.5 \pm 1.9^{a,b}$              | EFU/RUN1998       |
| $Np_2O_5(cr) + 2H^+ = 2NpO_2^+ + H_2O$              | $9.5 \pm 2.6^c$                  | PAN/CAM1995, 1998 |
| $0.5 Np_2O_5(cr) + 0.5 H_2O = NpO_2^+ + OH^-$       | $-9.25 \pm 1.3^{c,d}$            | PAN/CAM1995, 1998 |
| $0.5 Np_2O_5(cr) + 0.5 H_2O = NpO_2^+ + OH^-$       | $-10.08 \pm 0.2^d$               | PAN/CAM1995, 1998 |
| $H^+ + OH^- = H_2O$                                 | 14.001                           |                   |
| $0.5 Np_2O_5(cr) + H^+ = NpO_2^+ + 0.5 H_2O$        | $3.92 \pm 0.2$                   |                   |
| Selected values by THEREDA:                         |                                  |                   |
| $NpO_2^+ + 0.5 H_2O = 0.5Np_2O_5(s, hyd) + H^+$     | $-2.60 \pm 0.8^a$                | PAN/CAM1995, 1998 |
|   | $-3.92 \pm 0.2$                  | EFU/RUN1998       |
| $0.5 Np_2O_5(cr) + 0.5 H_2O = NpO_2^+ + OH^-$       | $-10.7 \pm 1.0^e$                | ALT/BRE2004       |
| $NpO_2^+ + 0.5 H_2O = 0.5Np_2O_5(s, hyd) + H^+$     | <b><math>-3.3 \pm 1.0</math></b> | <b>THEREDA</b>    |

<sup>a</sup>from  $K_{sp} = [NpO_2^+]^2 / [H^+]^2$ ; <sup>b</sup> thermochemical data from MER/FUG1994; <sup>c</sup> thermochemical data of LEM1984; <sup>d</sup>  $\log K^{\circ}_{sp} = [NpO_2^+][OH^-]/[H_2O]^{0.5}$ ; <sup>e</sup> mean value of PAN/CAM1998 and EFU/RUN1998: -10.08 and -11.4

Another solid compound that may control the solubility of Np(V) at  $pH_c > 11.5$  is still up for debate. [PET/GAO2011] presented some new data demonstrating that a solid phase transition from a green solid ( $NpO_2OH$ (fresh), over a white to a pink solid ( $Na_2NpO_2(OH)_2$ ) occur in 1, 3 and 5 M NaCl solutions (s. Figure 15).

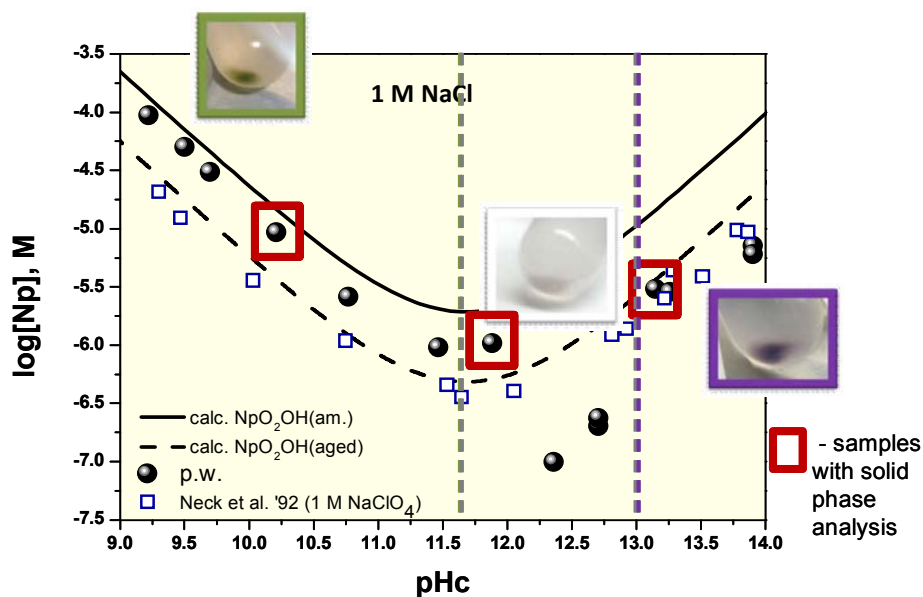


Figure 15: Experimental data of Np(V) in 1 M NaCl solution as a function of  $\text{pH}_c$ . Red rectangle means that the solid was characterised by solid phase analysis (SEM, XRD, XAFS). Graph from [PET/GAO2011].

This type of solid was not considered relevant in solubility studies under these conditions so far and the concept of solubility control by the binary solid Np(V) hydroxides discussed above may need to be scrutinized. However, the work by Petrov et al. clearly showed that calculations with thermodynamic values from the NEA-TDB selection can provide robust upper limit concentrations for Np(V) from dilute to concentrated (5 M) NaCl solution.

### 3.3.3.1.1 Pitzer parameters for hydrolysis species

Neck et al. developed a set of Pitzer parameters for the hydrolysis reaction in chloride and perchlorate solutions. The basis and the criteria for data selection are discussed in [NEC1997] and are briefly summarized in the following paragraphs. The data are summarized in Table 48.

From experimental data in  $\text{NaClO}_4$  and  $\text{NaCl}$  solutions, Novak and Roberts [NOV/ROB1995], Neck et al. [NEC/FAN1995, FAN/NEC1995] and Runde et al. [RUN/NEU1996] have parameterized Np(V) species to describe solubilities and complexation reactions with the Pitzer model.

Table 48: Pitzer parameters for the Np(V) aquo ion and its hydrolysis species at 25°C.

| <b>Binary Pitzer Parameter</b> |   |               |               |               |          |            |            |                  |
|--------------------------------|---|---------------|---------------|---------------|----------|------------|------------|------------------|
| <b>c</b>                       | <b>a</b>  | $\beta^{(0)}$ | $\beta^{(1)}$ | $\beta^{(2)}$ | $C^\phi$ | $\alpha_1$ | $\alpha_2$ | <b>Reference</b> |
| NpO <sub>2</sub> <sup>+</sup>  | Cl <sup>-</sup>                                 | 0.1415        | 0.281         | 0             | 0        | 2          | 0          | 1, 3, 4, 8       |
| NpO <sub>2</sub> <sup>+</sup>  | ClO <sub>4</sub> <sup>-</sup>                   | 0.257         | 0.180         | 0             | 0.0081   | 2          | 0          | 1, 3             |
| Na <sup>+</sup>                | NpO <sub>2</sub> (OH) <sub>2</sub> <sup>-</sup> | 0             | 0             | 0             | 0        | 2          | 0          | 1, 3, 8, 9       |
| K <sup>+</sup>                 | NpO <sub>2</sub> (OH) <sub>2</sub> <sup>-</sup> | 0             | 0             | 0             | 0        | 2          | 0          | 8, 9             |
| Mg <sup>2+</sup>               | NpO <sub>2</sub> (OH) <sub>2</sub> <sup>-</sup> | 0             | 0             | 0             | 0        | 2          | 0          | 8, 9             |

| <b>Ternary Pitzer parameter</b>                 |                                 |                               |                        |              |  |
|---|---------------------------------|-------------------------------|------------------------|--------------|--|
| <b>c</b>  | <b>c'</b>                       | <b>A</b>                      | $\theta(cc')$<br>(HMW) | $\psi(cc'a)$ | <b>Reference for<br/><math>\psi(cc'a)</math></b> |
| NpO <sub>2</sub> <sup>+</sup>                   | Na <sup>+</sup> /K <sup>+</sup> | Cl <sup>-</sup>               | 0                      | 0            | 1, 3, 4, 9                                       |
| NpO <sub>2</sub> <sup>+</sup>                   | Mg <sup>2+</sup>                | Cl <sup>-</sup>               | 0.05                   | 0            | 1, 3, 4, 9                                       |
| NpO <sub>2</sub> (OH) <sub>2</sub> <sup>-</sup> | Na <sup>+</sup> /K <sup>+</sup> | Cl <sup>-</sup>               | -0.24                  | 0            | 1, 3, 9  |
| NpO <sub>2</sub> (OH) <sub>2</sub> <sup>-</sup> | Na <sup>+</sup>                 | ClO <sub>4</sub> <sup>-</sup> | 0                      | 0            | 1, 3, 9  |
| NpO <sub>2</sub> (OH) <sub>2</sub> <sup>-</sup> | Mg <sup>2+</sup>                | Cl <sup>-</sup>               | 0                      | 0            | 9  |

| <b>Neutral species</b>              |                               | $\lambda$ |
|-------------------------------------|-------------------------------|-----------|
| NpO <sub>2</sub> (OH) <sub>aq</sub> | Na <sup>+</sup>               | 0         |
| NpO <sub>2</sub> (OH) <sub>aq</sub> | Cl <sup>-</sup>               | -0.19     |
| NpO <sub>2</sub> (OH) <sub>aq</sub> | ClO <sub>4</sub> <sup>-</sup> | 0         |

|               |               |
|---------------|---------------|
| 1 THEREDA     | 6 NOV/ALM1997 |
| 2 GUI/FAN2003 | 7 NOV/ROB1995 |
| 3 FAN/NEC1995 | 8 WAL/WAL2006 |
| 4 FEL/RAI1999 | 9 NEC1997     |
| 5 NEC/FAN1995 |               |

By using the parameters from [NOV/ROB1995], a description of experimental data showed deviations up to one order of magnitude. This was a result of using the parameter set from [HAR/MOL1984] for the matrix system Na-OH-CO<sub>3</sub>-Cl-H<sub>2</sub>O as well as Na-OH-CO<sub>3</sub>-ClO<sub>4</sub> from [PIT1992], even perchlorate solution was not subject of this publication. Many data necessary are unidentified for the NaCl / NaClO<sub>4</sub> solutions and were disregarded in the calculations.

Neck et al. and Runde et al. assembled a comprehensive set of Pitzer parameter that offered a significantly improved description of the experimental data. The parameterization of the electrolyte system Np(V)-Na-OH-CO<sub>3</sub>-Cl or ClO<sub>4</sub>-H<sub>2</sub>O has been performed in two steps:

First, the interaction parameter of NpO<sub>2</sub><sup>+</sup> was calculated from known activity coefficients of NpO<sub>2</sub>ClO<sub>4</sub> and NpO<sub>2</sub>Cl in NaClO<sub>4</sub> and NaCl solutions, respectively. The weak interaction between Np(V) and Cl<sup>-</sup> is described by strong ion-ion interaction and not by a complexation reaction. As a consequence, significant lower tracer activity coefficients of NpO<sub>2</sub><sup>+</sup> in concentrated NaCl solution are reported compared to the NaClO<sub>4</sub> system of same ionic strength.

Second, the interaction parameters for the hydrolysis species (or carbonate species) of Np(V) were deduced from the experimentally determined conditional stability constants log β' at various NaClO<sub>4</sub> or NaCl concentrations:

$$\log \beta'_{1n0} = \log \beta^{\circ}_{1n0} + \log \gamma(\text{NpO}_2^+) + n \log \gamma(\text{OH}^-) - \log \gamma(\text{NpO}_2(\text{OH})_n^{1-n})$$

$$\log \beta'_{10n} = \log \beta^{\circ}_{10n} + \log \gamma(\text{NpO}_2^+) + n \log \gamma(\text{CO}_3^{2-}) - \log \gamma(\text{NpO}_2(\text{CO}_3)_n^{1-2n})$$

Due to the limited input data and their limited precision a lot of assumptions or simplifications had to be introduced. Interactions among different Np(V) species can be disregarded, because they are present only at trace concentrations. The same assumption is valid for interactions between Np(V) species and the ions H<sup>+</sup>, OH<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>, as long as their concentrations are not higher than 0.1 m. Data for the binary Np(V) systems are not available, only the ternary systems Np(V)-Na-ClO<sub>4</sub> and Np(V)-Na-Cl are reported. Therefore, in each set one of the following parameters has to be fixed to be zero (0)

a)  $\beta^{(0)}(\text{NpO}_2^+/\text{ClO}_4^-)$  or  $\beta^{(0)}(\text{NpO}_2^+/\text{Cl}^-)$  and  $\theta(\text{NpO}_2^+/\text{Na}^+)$

b)  $\beta^{(0)}(\text{Np-complex}^{n-}/\text{Na}^+)$  and  $\theta(\text{Np-complex}^{n-}/\text{ClO}_4^-)$  or  $\theta(\text{Np-complex}^{n-}/\text{Cl}^-)$

c)  $\lambda(\text{NpO}_2\text{OH}^0/\text{Na}^+)$  and  $\lambda(\text{NpO}_2\text{OH}^0/\text{ClO}_4^-)$  or  $\lambda(\text{NpO}_2\text{OH}^0/\text{Cl}^-)$

With the available experimental data, no precise values for the parameters C<sup>Φ</sup> and Ψ<sub>ijk</sub> that describe the triple interaction of Np(V) species can be derived. Again, they are

fixed to be zero (0). Lack of experimental data at low ionic strengths and scattering of data requires fixing of additional parameters.

As a consequence, every Pitzer parameter in the THEREDA data set that has to be fixed to zero value according to the above discussed requirements are notified by the quality label “tentative value for unknown interaction coefficient, which cannot be estimated”. They have additionally the notification “set to be zero” in the remark field.

The different  $\log K^\circ$  values between [GUI/FAN2003] and [FAN/NEC1995, NEC1997] are equal within the experimental uncertainties. THEREDA selects the NEA values for the formation constants together with the Pitzer parameters from [FAN/NEC1995, NEC1997]. They are both consistent within the experimental uncertainties (see next chapter).

[WAL/WAL2006] reports binary interaction parameters for  $Mg^{2+}$  that are fixed to be zero. They have also the notification: “tentative value for unknown interaction coefficient, which cannot be estimated”.

### **3.3.3.1.2 Modeling of Np(V) hydrolysis and comparison with experimental data**

This section gives a comparison between experimental and numerical results. In Figure 16, the solubilities of  $NpO_2(OH)_{fresh}(am)$  (upper part) and of  $NpO_2(OH)_{aged}(s)$  (lower part) are calculated with Geochemists Workbench using the THEREDA data set. Additionally, a few calculations were done with the Codes EQ3/6, Chem App and Phreeqc. It is obvious that the experimental data can well be described by the theoretical curves and that all experimental data are encompassed within the uncertainties.

It must be emphasized that in the automatically generated parameter files from the THEREDA platform, the solid  $NpO_2(OH)_{aged}(s)$  is commented out by default. In some experiments, however, the solid  $NpO_2(OH)_{aged}(s)$  has to be regarded. This is demonstrated in Figure 16 (lower part), where the data of [RUN/KIM1994] are better described involving the solid  $NpO_2(OH)_{aged}(s)$ . If the user wants to calculate solubilities in equilibrium with  $NpO_2(OH)_{aged}(s)$ , he needs to manually include this

phase into the “mineral” section of the parameter file. The figure shows that similar results are achieved with the different geochemical codes. Kinetics of transformation are not certainly known, therefore  $\text{NpO}_2(\text{OH})_{\text{fresh}}(\text{am})$  is used to calculate the upper limit  $\text{Np}(\text{V})$  concentration. In the THEREDA database, this solid is given as equilibrium phase to be exported to the minerals section of the parameter files for the different geochemical codes, while  $\text{NpO}_2(\text{OH})_{\text{aged}}(\text{s})$  is set to “dissociation only” so that it will only be written into a comments section at the end of the parameter files.

### 3.3.3.2 $\text{Np}(\text{V})$ chloride complexes

Several experimental investigation of the chloride complexation of  $\text{Np}(\text{V})$  have been performed with contrary results. Only at very high chloride concentrations ( $I > 3\text{M}$ ) formation of neptunyl chloride complex was observed. In view of the limited experimental data, any extrapolation to  $I=0$  is dominated by large uncertainties. No formation constants were selected by the NEA.

For very weak complexes like the formation of neptunyl-chloride complexes, Neck et al. and Novak and Robert demonstrated another approach for the thermodynamic description. The weak interaction between  $\text{NpO}_2^+$  and  $\text{Cl}^-$  is not described with formation reactions of weak chloride complex, but rather by a strong ion-ion interaction with Pitzer or SIT interaction parameters. For the Pitzer formalism, Neck et al. have developed Pitzer coefficients in the  $\text{NaCl}$  system up to 5 M  $\text{NaCl}$ . Figure 17 demonstrates, that the chemical behaviour of  $\text{NpO}_2^+$  in  $\text{NaCl}$  (and  $\text{NaClO}_4$ ) solutions can be described by a Pitzer ion-interaction model without taking into account any formation of chloride complexes. Detailed work on the chloride complexation of the actinyl cation  $\text{NpO}_2^+$  is available in [FAN/NEC1995, NEC/FAN1995, NEC1999, LEM/FUG2001].

THEREDA adopts the thermodynamic model suggested by Neck et al. and hence, no formation constants were selected or estimated for any neptunyl chloride complexes. Instead, only Pitzer parameters for the interaction between neptunyl species with chloride are given in the Table 49.



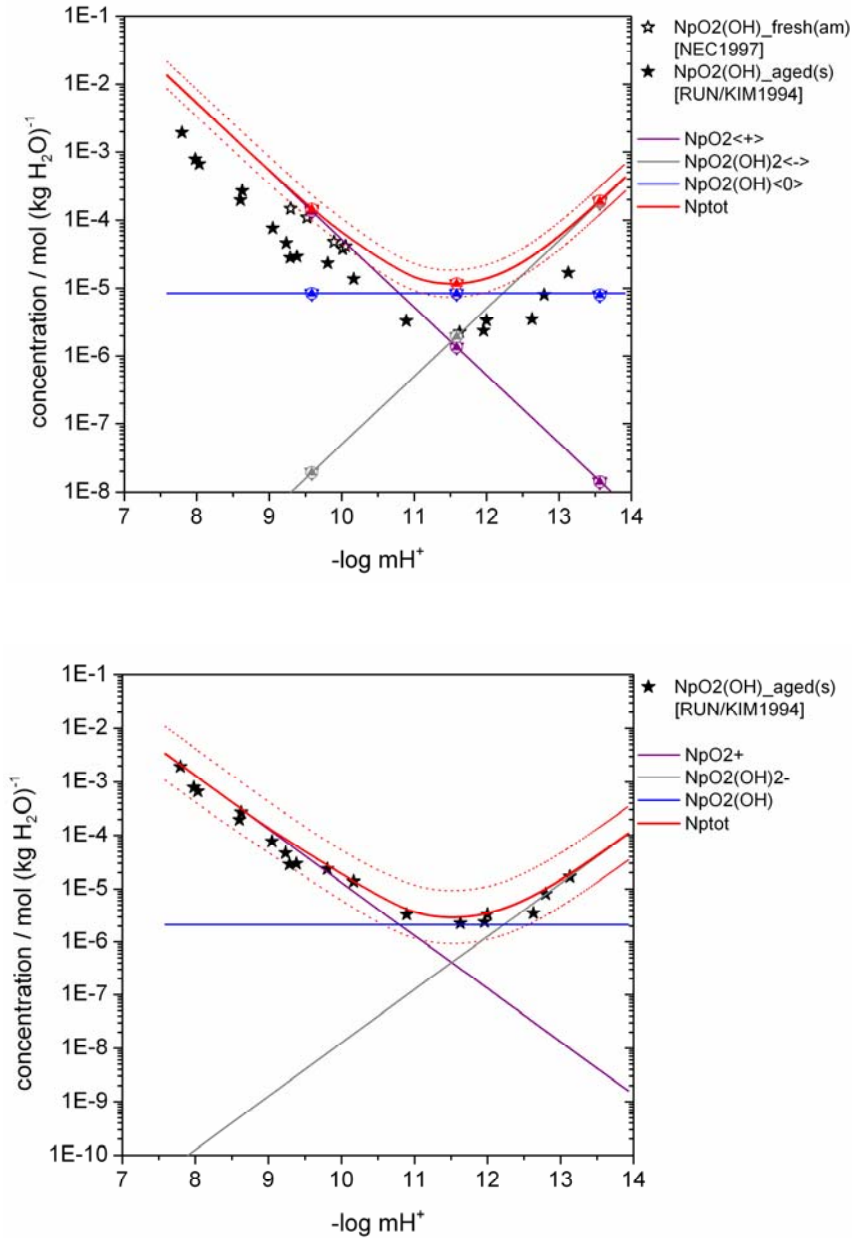


Figure 16: Calculation of the solubility of NpO<sub>2</sub>(OH)<sub>fresh(am)</sub> and speciation (upper part), NpO<sub>2</sub>(OH)<sub>aged(s)</sub> and speciation (lower part), both in 5.6 m NaCl solution with logmH<sup>+</sup>. Experimental solubility data is marked by stars, open stars for data of [NEC1997] with NpO<sub>2</sub>(OH)<sub>fresh(am)</sub> and filled stars for data of [RUN/KIM1994] with NpO<sub>2</sub>(OH)<sub>aged(s)</sub>. Solid lines represent GWB results, open circles, down- and upward triangles denote results with ChemApp, Phreeqc and EQ3/6, total concentration of Np(V) in solution is marked with red line and symbols. The error range of the logK-value is shown as dotted lines.

Table 49: Pitzer parameter for Np(V) aquo ion and its hydrolysis species at 25°C.

| <b>Binary Pitzer Parameter</b> |                 |               |               |               |                      |            |            |                  |
|--------------------------------|-----------------|---------------|---------------|---------------|----------------------|------------|------------|------------------|
| <b>c</b>                       | <b>A</b>        | $\beta^{(0)}$ | $\beta^{(1)}$ | $\beta^{(2)}$ | <b>C<sup>ϕ</sup></b> | $\alpha_1$ | $\alpha_2$ | <b>Reference</b> |
| NpO <sub>2</sub> <sup>+</sup>  | Cl <sup>-</sup> | 0.1415        | 0.281         | 0             | 0                    | 2          | 0          | 6, 7, <b>10</b>  |
| NpO <sub>2</sub> <sup>+</sup>  | Cl <sup>-</sup> | 0.1467        | 0.2010        | 0             | 0                    | 2          | 0          | 8                |
| Na <sup>+</sup>                | Cl <sup>-</sup> | 0.0765        | 0.2664        | 0             | 0.00127              | 2          | 0          | 1 - 8            |
| Na <sup>+</sup>                | Cl <sup>-</sup> | 0.07528       | 0.27692       | 0             | 0.00141              | 2          | 0          | <b>10</b>        |

| <b>Ternary Pitzer parameter</b> |                  |                 |               |              |  |
|---------------------------------|------------------|-----------------|---------------|--------------|--|
| <b>c</b>                        | <b>c'</b>        | <b>A</b>        | $\theta(cc')$ | $\psi(cc'a)$ | <b>Reference for <math>\psi(cc'a)</math></b> |
| Na <sup>+</sup>                 | H <sup>+</sup>   | Cl <sup>-</sup> | 0.036         | -0.004       | 1, 3, 6 - 8                                  |
| Na <sup>+</sup>                 | H <sup>+</sup>   | Cl <sup>-</sup> | 0.03454       | -0.00251     | <b>10</b>                                    |
| Na <sup>+</sup>                 | K <sup>+</sup>   | Cl <sup>-</sup> | 0.012         | -0.0018      | 9, <b>10</b>                                 |
| Na <sup>+</sup>                 | Mg <sup>2+</sup> | Cl <sup>-</sup> | 0.07          | -0.012       | 9, <b>10</b>                                 |
| Na <sup>+</sup>                 | Ca <sup>2+</sup> | Cl <sup>-</sup> | 0.05813       | -0.0011      | 9, <b>10</b>                                 |
| <b>a</b>                        | <b>a'</b>        | <b>C</b>        | $\theta(cc')$ | $\psi(cc'a)$ | <b>Reference for <math>\psi(cc'a)</math></b> |
| OH <sup>-</sup>                 | Cl <sup>-</sup>  | Na <sup>+</sup> | -0.050        | -0.006       | 1, 3, 6 - 8                                  |
|                                 |                  |                 | -0.05507      | -            | 9, <b>10</b>                                 |
|                                 |                  |                 |               | 0.004273     |  |

| <b>Neutral species</b>              |  | $\lambda$ |
|-------------------------------------|--|-----------|
| NpO <sub>2</sub> (OH) <sub>aq</sub> | <b>Cl<sup>-</sup></b>                              | -0.19     |
| 1 PIT1973                           | 6 NEC1997  |           |
| 2 PIT/MAY1973                       | 7 FAN/NEC1995                                      |           |
| 3 PIT/KIM1974                       | 8 RUN/NEU1996                                      |           |
| 4 PIT1991                           | 9 not checked with NpO <sub>2</sub> <sup>+</sup> . |           |
| 5 HAR/MOL1984                       | <b>10 THEREDA</b>                                  |           |

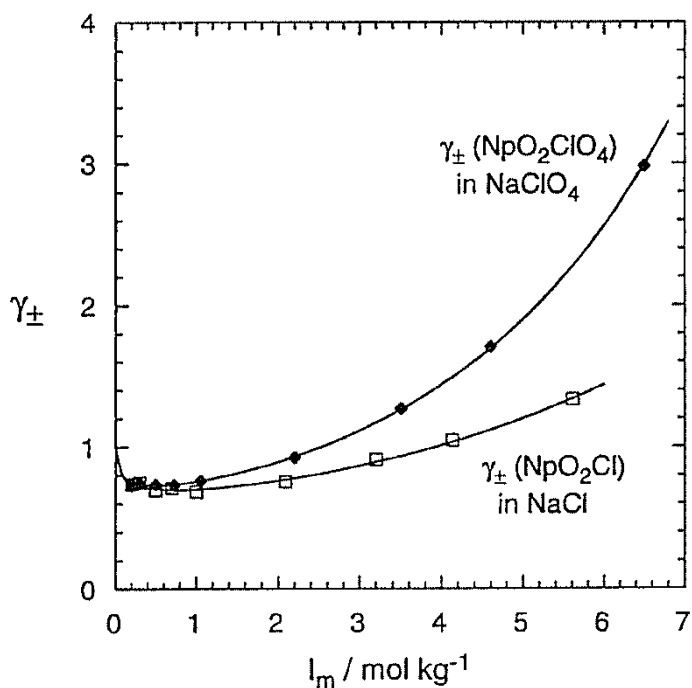


Figure 17: Modelling of the mean activity coefficients of the  $\text{NpO}_2\text{Cl}$  and the  $\text{NpO}_2\text{ClO}_4$  by the Pitzer approach (Graph from [NEC/FAN1995]).

### 3.3.3.3 Np(V) carbonate complexation and solid Np(V) carbonates

The following aqueous carbonate complexes and solid phases are considered:  $\text{NpO}_2\text{CO}_3^-$ ,  $\text{NpO}_2(\text{CO}_3)_2^{3-}$ ,  $\text{NpO}_2(\text{CO}_3)_3^{5-}$ ,  $\text{NpO}_2(\text{CO}_3)_2\text{OH}^{4-}$ ,  $\text{NaNpO}_2(\text{CO}_3) \cdot 3.5\text{H}_2\text{O}(\text{s})$ ,  $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ ,  $\text{NaNpO}_2(\text{CO}_3)(\text{s})$ ,  $\text{K}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ ,  $\text{NpO}_2(\text{OH})_2\text{CO}_3^{3-}$  (not selected by NEA, but recommended as a guideline value). The formation reaction and the corresponding formation constants  $\log \beta^\circ$  are shown in Table 50.

The formation of the carbonate complexes are spectroscopically identified and characterized by several authors and can be regarded as confirmed. Complexes with four and more carbonate ligands were not identified. The complex with  $\text{HCO}_3^-$  as ligand similarly be excluded, because this complex is very weak and not relevant under conditions relevant for waste disposal.

Spectroscopic investigations in solutions with high pH values ( $[\text{OH}^-] > 0.1 \text{ mol/L}$ ) and carbonate concentrations above 0.01 M showed that mixed hydroxo carbonate species are formed beside the pure hydrolysis and carbonate complexes. The thermodynamic

stability field of the mixed hydroxo carbonate complexes is restricted to carbonate concentrations and pH values as can be found in alkaline cement leachates.

Table 50: Np(V) carbonate species selected in the NEA-TDB [GUI/FAN2003].

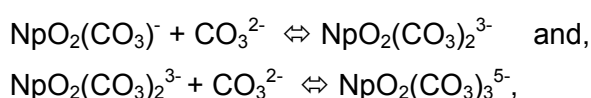
| Reaction   | log $\beta^\circ$       |              |
|--|-------------------------|--------------|
| $\text{NpO}_2^+ + \text{CO}_3^{2-} \Leftrightarrow \text{NpO}_2(\text{CO}_3)^-$  | log $\beta^\circ_{11}$  | 4.96 ± 0.06  |
| $\text{NpO}_2^+ + 2 \text{CO}_3^{2-} \Leftrightarrow \text{NpO}_2(\text{CO}_3)_2^{3-}$   | log $\beta^\circ_{12}$  | 6.53 ± 0.10  |
| $\text{NpO}_2^+ + 3 \text{CO}_3^{2-} \Leftrightarrow \text{NpO}_2(\text{CO}_3)_3^{5-}$   | log $\beta^\circ_{13}$  | 5.50 ± 0.15  |
| $\text{NpO}_2^+ + 2 \text{CO}_3^{2-} + \text{H}_2\text{O} \Leftrightarrow \text{NpO}_2(\text{CO}_3)_2\text{OH}^{4-} + \text{H}^+$                            | log $\beta^\circ_{121}$ | -5.31 ± 1.17 |
| $\text{NpO}_2^+ + \text{CO}_3^{2-} + 2 \text{H}_2\text{O} \Leftrightarrow \text{NpO}_2(\text{CO}_3)(\text{OH})_2^{3-} + 2 \text{H}^+$                        | log $\beta^\circ_{112}$ | -            |
| $\text{Na}^+ + \text{NpO}_2^+ + \text{CO}_3^{2-} + 3.5 \text{H}_2\text{O} \Leftrightarrow \text{NaNpO}_2(\text{CO}_3) \cdot 3.5\text{H}_2\text{O}(\text{s})$ | log $K^\circ_{(111)}$   | 11.00 ± 0.24 |
| $\text{K}^+ + \text{NpO}_2^+ + \text{CO}_3^{2-} \Leftrightarrow \text{KNpO}_2(\text{CO}_3)(\text{s})$  | log $K^\circ_{(111)}$   | 13.15 ± 0.19 |
| $3 \text{Na}^+ + \text{NpO}_2^+ + 2 \text{CO}_3^{2-} \Leftrightarrow \text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$                                       | log $K^\circ_{(312)}$   | 14.22 ± 0.50 |
| $3 \text{K}^+ + \text{NpO}_2^+ + 2 \text{CO}_3^{2-} \Leftrightarrow \text{K}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$   | log $K^\circ_{(312)}$   | 15.46 ± 0.16 |

The NEA selected only complex formation constants for the  $\text{NpO}_2(\text{CO}_3)_2\text{OH}^{4-}$ , and disregarded the other mixed complexes described in literature ( $\text{NpO}_2(\text{CO}_3)(\text{OH})_2^{3-}$ ,  $\text{NpO}_2(\text{OH})_2\text{CO}_3^{3-}$ ,  $\text{NpO}_2(\text{CO}_3)_2(\text{OH})_2^{5-}$  [NEC/FAN1997, VIT/CAP1998, RIG1990]. The existence of these complexes are not unambiguously proven, and even the NEA review suggest to use the formation constant for the complex  $\text{NpO}_2(\text{CO}_3)(\text{OH})_2^{3-}$  as a guideline value. The value of the formation constant has been given only for an ionic strength of 3 M  $\text{NaClO}_4$  and needs certainly to be corrected to ionic strength zero.

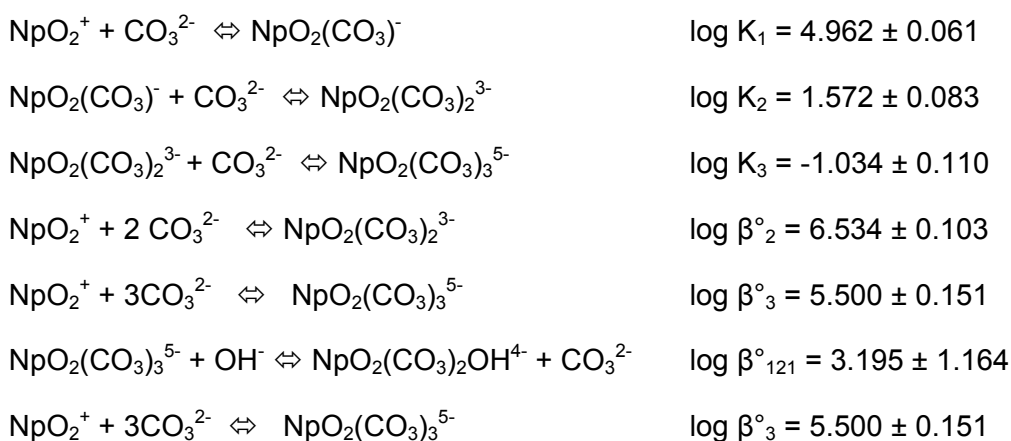
Table 51: Formation constants of Np(V) carbonate species selected by the NEA-TDB [GUI/FAN2003] and THEREDA for 25 °C and I = 0. The values from the NEA are derived with the SIT, whereas the values from Neck et al. are consistent with the SIT and Pitzer approach. However, the selected THEREDA value corresponds to the NEA and are also consistent with both approaches, SIT and Pitzer, within the range of uncertainties.

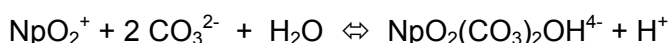
| Complex                                       | log $\beta_{(l,j)}$  |                              |                         |
|---|----------------------|------------------------------|-------------------------|
|   | GUI/FAN2003<br>(SIT) | NEC1997, FAN/NEC1995         | THEREDA<br>(Pitzer/SIT) |
| $\text{NpO}_2(\text{CO}_3)^-$                 | $4.962 \pm 0.061$    | $5.03 \pm 0.06$              | $4.96 \pm 0.06$         |
| $\text{NpO}_2(\text{CO}_3)_2^{3-}$            | $6.534 \pm 0.103$    | $6.47 \pm 0.14$              | $6.53 \pm 0.10$         |
| $\text{NpO}_2(\text{CO}_3)_3^{5-}$            | $5.500 \pm 0.151$    | $5.37 \pm 0.36$              | $5.50 \pm 0.15$         |
| $\text{NpO}_2(\text{CO}_3)_2\text{OH}^{4-}$   | $-5.306 \pm 1.17$    | $-4.14 \pm 0.11$             | $-5.31 \pm 1.17$        |
| $\text{NpO}_2(\text{CO}_3)(\text{OH})_2^{3-}$ |                      | $-18.836 \pm 0.15$ (I = 3 M) |                         |

In [GUI/FAN2003], the formation reaction of the second and the third carbonate complex is defined as



and have to be reformulated for THEREDA.





$$\log \beta_{121}^\circ = -5.306 \pm 1.174$$

### 3.3.3.3.1 Pitzer parameter for the Np(V) carbonate system

Neck et al. [NEC1997, FAN/NEC1995] determined a Pitzer parameter set for neptunyl cation and its complexes in carbonate containing NaCl and NaClO<sub>4</sub> solutions, which were regarded as reliable and extended to Mg<sup>2+</sup> system by [WAL/WAL2006].

The Pitzer parameter of the basic carbonate system in THEREDA are taken from [HAR/MOL1984] (HMW). Contrary to that, the Pitzer parameter of the neptunyl-carbonate system was deduced with the Pitzer parameter set of the basic carbonate system from [PIT1991] and [PEI/PIT1992]. However, both parameter sets are essentially equal within the experimental uncertainties. Hence, the HMW-Pitzer parameter set is also consistent with the neptunyl-carbonate parameter set within the experimental uncertainties. For Na-HCO<sub>3</sub> and Na-CO<sub>3</sub>, respectively, values from [PIT1991] and [PEI/PIT1992] are:  $\beta(0)$ : 0.028, 0.0362;  $\beta(1)$  0.044, 1.510;  $C^\phi$ : 0, 0.0052. The values according to HMW parameter set are:  $\beta(0)$ : 0.0277, 0.0399;  $\beta(1)$  0.0411, 1.389;  $C^\phi$ : 0, 0.0044. The differences in the calculation of trace activity coefficients of Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> or H<sub>2</sub>CO<sub>3</sub> dissociation constants in NaClO<sub>4</sub> and NaCl solutions are small.

A few Pitzer parameter for Mg<sup>2+</sup> and neptunyl complex anions are estimated values from [WAL/WAL2006]. Here, we should refer to a comment in [ALM/NOV1998]: “We can approximate the ion interaction parameters for Mg<sup>2+</sup> and the neptunyl carbonate ions as the average of the parameter values for Na<sup>+</sup> and K<sup>+</sup>, that is,  $\beta^\circ(\text{Mg}/\text{NpO}_2\text{CO}_3^-) = 0.10$ ,  $\beta^1(\text{Mg}/\text{NpO}_2\text{CO}_3^-) = 0.34$ ,  $\{\beta^\circ(\text{Mg}/\text{NpO}_2(\text{CO}_3)_2^{2-}) = 0.48$ ,  $\beta^1(\text{Mg}/\text{NpO}_2(\text{CO}_3)_2^{2-}) = 4.4$ ,  $\beta^\circ(\text{MgX}) = 2.07$ ,  $\beta^1(\text{MgX}) = 22.7$ ,  $\beta^2(\text{MgX}) = -48$ , and  $C^\phi(\text{MgX}) = -0.11$ . This is a reasonable although arbitrary first approximation and no attempt was made to correlate between monovalent and divalent ions. Using these assignments, the data base predictions provide a remarkably good estimate of  $\log(m_{\text{NP(V)}}) = -5.3$  to  $-6.6$  for the 7.8 mol kg<sup>-1</sup> ionic strength brine. A graphical comparison can be found in [6].“ The reference [6] in the comment refers to [ALM/NOV1997].

For the Pitzer data set, the coefficient  $\alpha_1$  was usually set to 2.0 and  $\alpha_2$  to 0. Only for interactions between 5-1 electrolytes where  $\beta^{(2)}$  was introduced,  $\alpha_1$  was set to 1.4 and  $\alpha_2$  to 12 by Pitzer [PIT1991].

Table 52: Binary Pitzer parameter for the Np(V) carbonate species

| Binary Pitzer Parameters                                       |                               |           |                |           |          |                   |
|--|-------------------------------|-----------|----------------|-----------|----------|-------------------|
| c  | A                             | $\beta^0$ | $\beta^1$      | $\beta^2$ | $C^\phi$ | Ref.              |
| NpO <sub>2</sub> <sup>+</sup>                                  | Cl <sup>-</sup>               | 0.1415    | 0.281          | 0         | 0        | 1, 3, 4, 5, 8, 11 |
| NpO <sub>2</sub> <sup>+</sup>                                  | ClO <sub>4</sub> <sup>-</sup> | 0.257     | 0.180          | 0         | 0.0081   | 1, 3, 5, 8, 11    |
| NpO <sub>2</sub> CO <sub>3</sub> <sup>-</sup>                  | Na <sup>+</sup>               | 0.10      | 0.34           | 0         | 0        | 1, 3, 4, 8, 11    |
| NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>3-</sup> | Na <sup>+</sup>               | 0.48      | 4.4            | 0         | 0        | 1, 3, 4, 8, 11    |
| NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>5-</sup> | Na <sup>+</sup>               | 1.80      | 22.7           | 0         | 0        | 1, 3, 4, 8, 11    |
| NpO <sub>2</sub> CO <sub>3</sub> <sup>-</sup>                  | K <sup>+</sup>                | 0.10      | 0.34           | 0         | 0        | 1, 6, 8, 11       |
| NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>3-</sup> | K <sup>+</sup>                | 0.48      | 4.4            | 0         | 0        | 1, 6, 8, 11       |
| NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>5-</sup> | K <sup>+</sup>                | 1.8       | 22.7           | -95.1     | -0.219   | 1, 6, 11          |
|  |                               | 2.34      | 22.7           | -96       | -0.22    | 6, 8              |
| NpO <sub>2</sub> CO <sub>3</sub> <sup>-</sup>                  | Mg <sup>2+</sup>              | 0.4       | 1.7            | 0         | 0        | 1, 11             |
|  |                               | 0.10      | 0.34           | 0         | 0        | 6, 8, 9           |
| NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>3-</sup> | Mg <sup>2+</sup>              | 0.48      | 4.4            | 0         | 0        | 1, 6, 8, 9        |
| NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>5-</sup> | Mg <sup>2+</sup>              | 2.07      | 22.7           | -48       | -0.11    | 1, 6, 8, 9        |
| 1 THEREDA  | 6 NOV/ALM1997                 |           | 11 ALT/BRE2004 |           |          |                   |
| 2 GUI/FAN2003  | 7 NOV/ROB1995                 |           |                |           |          |                   |
| 3 FAN/NEC1995  | 8 WAL/WAL2006                 |           |                |           |          |                   |
| 4 FEL/RAI1999  | 9 ALM/NOV1998                 |           |                |           |          |                   |
| 5 NEC/FAN1995  | 10 RUN/NEU1996                |           |                |           |          |                   |

### 3.3.3.4 Sulphate complexes

After the evaluation of Np(V) sulphate complexation data, two new studies have been described in the literature. Xia and coworkers [XIA/FRI2006] used a solvent extraction method with HDEHP as extractant to deduce complexation constants from the distribution of Np(V) between the aqueous and organic phase. Surprisingly and in contrast to all other publications, they claim to found not only the 1:1 Np-sulphate complex, but also the 1:2 complex. For the complex formation constant at 25 °C they give a value of  $\log K^\circ = 0.49 \pm 0.31$  at an ionic strength of 1 M NaClO<sub>4</sub>.

The second work has been described in [TOP/AUP2009], a new approach to deduce complex formation constants from ionic mobility measurements in an electric field using capillary electrophoresis. They measured the sulphate complexation at four different ionic strengths (0.36 to 1.62 M NaClO<sub>4</sub>) and calculated a conditional complex formation constants of log K° = 0.66 to 0.31, respectively. The conditional formation constants of all studies concerning the neptunyl sulphate complexation are listed in Table 54.

Table 53: Ternary Pitzer parameter of the Np(V) hydrolysis species at 25 °C.

| Pitzer. ternär   | Θ               |                 |                               |             |
|--|-----------------|-----------------|-------------------------------|-------------|
|  | Na <sup>+</sup> | Cl <sup>-</sup> | CO <sub>3</sub> <sup>2-</sup> |             |
| NpO <sub>2</sub> <sup>+</sup>                                  | 0               |                 |                               |             |
| NpO <sub>2</sub> CO <sub>3</sub> <sup>-</sup>                  |                 | -0.21           |                               | 1, 3, 4, 11 |
| NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>3-</sup> |                 | -0.26           |                               | 1, 3, 4, 11 |
| NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>5-</sup> |                 | -0.26           | -0.83                         | 1,3,4,6,11  |
|  |                 |                 | -1.9                          | 6           |
| Ψ  |                 |                 |                               |             |
|  |                 | Cl <sup>-</sup> | ClO <sub>4</sub> <sup>-</sup> |             |
| NpO <sub>2</sub> <sup>+</sup>                                  | Na <sup>+</sup> | 0               | 0                             | 1, 3        |
| NpO <sub>2</sub> CO <sub>3</sub> <sup>-</sup>                  | Na <sup>+</sup> | 0               | 0                             | 1, 3        |
| NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>3-</sup> | Na <sup>+</sup> | 0               | 0                             | 1, 3        |
| NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>5-</sup> | Na <sup>+</sup> | 0               | 0                             | 1, 3        |
| Neutral species  | λ no species    |                 |                               |             |
| 1 THEREDA  | 6 NOV/ALM1997   |                 | 11 ALT/BRE2004                |             |
| 2 GUI/FAN2003  | 7 NOV/ROB1995   |                 | 12 NOV/ALM1997                |             |
| 3 FAN/NEC1995  | 8 WAL/WAL2006   |                 |                               |             |
| 4 FEL/RAI1999  | 9 ALM/NOV1998   |                 |                               |             |
| 5 NEC/FAN1995  | 10 RUN/NEU1996  |                 |                               |             |



Table 54: Conditional formation constants of the Np(V) sulphate complex extracted from TOP/AUP2009 and XIA/FRI2006 and the sulphate complexation constant at  $I = 0$  selected from the NEA-TDB [GUI/FAN2003].

| Method  | $I$ (m)                          | Electrolyte        | Log $\beta_{11}$   | $[\text{SO}_4]^{2-}$ (M) | Reference   |
|---------|----------------------------------|--------------------|--|--------------------------|-------------|
| Dis.    | 1 M                              | NaClO <sub>4</sub> | $0.49 \pm 0.31$  | 0 – 0.21                 | XIA/FRI2006 |
| Elec.   | 0.357<br>0.725<br>1.051<br>1.617 | NaClO <sub>4</sub> | $0.66 \pm 0.11$<br>$0.54 \pm 0.12$<br>$0.40 \pm 0.11$<br>$0.31 \pm 0.11$ | 0 – 0.15                 | TOP/AUP2009 |
| Dis.    | 2 M                              | NaClO <sub>4</sub> | $0.44 \pm 0.09$  |                          | RAO/GUD1979 |
| Coprec. | 1.5 M                            | NH <sub>4</sub> Cl | $1.04 \pm 0.4$   |                          | MOS/POZ1979 |
| Dis.    | 8.5 M                            | NaClO <sub>4</sub> | 0.45   |                          | PAT/RAM1981 |
| Dis.    | 0.52<br>1.05<br>2.2              | NaClO <sub>4</sub> | $-0.1 \pm 0.08$<br>$0.06 \pm 0.04$<br>$0.19 \pm 0.08$                    |                          | HAL/OLI1983 |
|         | 1 M                              | NaClO <sub>4</sub> | $0.76 \pm 0.27$  |                          | INO/TOC1985 |
| Review  | 0                                |                    | $0.44 \pm 0.27$  |                          | GUI/FAN2003 |

The conditional formation constants are illustrated in Figure 18 as a function of the ionic strength. The figure shows clearly that there is no clear trend with the ionic strength, beside the data deduced from the electrophoretic experiment [TOP/AUP2009] when they are separately considered. It is clear from all these data that the sulphate complexation is weak like the chloride complexation. No Pitzer parameter are known for this interaction couple so far.

Note that from the view of likely waste disposal scenarios in Germany, the interaction parameters for  $\text{NpO}_2^+$  with  $\text{SO}_4^{2-}$  can be neglected, because this ion will likely occur only in relative low concentrations in the brine solutions. The corresponding parameter in the Pitzer equations are then multiplied by small molality factors and have therefore only limited impact on the activity coefficient of the Np(V) species.

For cases where higher sulphate concentrations are expected no convincing description is available at present.

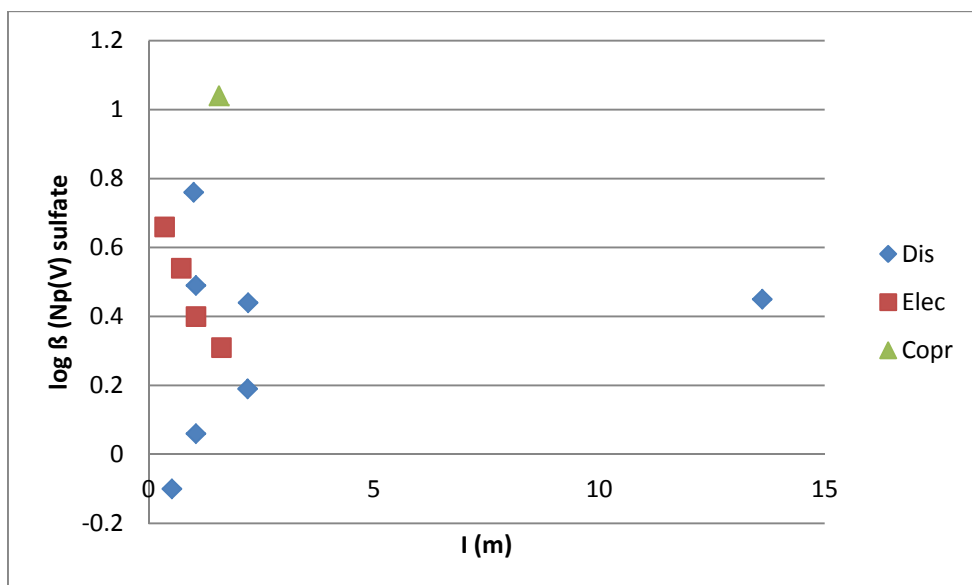


Figure 18: Np(V) sulphate complex formation constants as a function of the ionic strength  $I$  in the molal scale. Data from Table 54.

### 3.3.4 Plutonium, Pu(V): $\text{PuO}_2^+$

#### 3.3.4.1 Aqueous species and solid compounds

Neither stability constants nor Pitzer activity coefficients have been selected for Pu(V) aqueous species and solid compounds. In spite of this, the use of Np(V) analogues is recommended for  $\log \beta$  and Pitzer parameters of Pu(V) aqueous species. Thermodynamic data on Np has been made available through the corresponding release 4 of THEREDA. Note that it is strongly discouraged to use these analogies to fill in thermodynamic data for the corresponding solid phases of Pu(V).

### 3.3.5 Americium, Am(V) : $\text{AmO}_2^+$

THEREDA selects thermodynamic data for modelling scenarios in the frame of disposal of radioactive waste in deep geological formations. However, in a long term development of the repository, reducing conditions occur and oxidation of the stable oxidation state of Am(III) to Am(V) is not expected. Especially in the far field and under

normal air atmosphere conditions Am(V) is not considered as a relevant species. Am(V) can may be formed by radiolysis at the surface of the fuel that is in contact with water. But the very strong reducing conditions generated by the container corrosion will stabilize the trivalent oxidation state of americium. Because of these circumstances, Am(V) is neglected in the frame of THEREDA so far, until a scenario is derived that necessitates a specific Am(V) model.

### **3.4 Hexavalent radionuclides : the actinides U(VI), Np(VI), and Pu(VI)**

#### **3.4.1 Uranium, U(VI) : $\text{UO}_2^{2+}$**

The U(VI) and its species in the system of the oceanic salts were edited by the Helmholtz Center Dresden-Rossendorf. For information on this system refer to final report of HZDR.

#### **3.4.2 Neptunium, Np(VI): $\text{NpO}_2^{2+}$**

The hexavalent neptunium is not implemented in THEREDA, because from view of redox conditions in deep underground repositories at high ionic strength, it has no proven relevance. Although oxidative conditions may occur at the spent fuel because of radiolysis effects, the spatial range of these oxidative conditions is limited at the surface of the spent fuel. The iron corrosion of the iron of the container material compensates the oxidative impact and establishes a reductive barrier where Np(VI) is reduced to lower oxidation states.

#### **3.4.3 Plutonium, Pu(VI): $\text{PuO}_2^{2+}$**

The hexavalent plutonium is not implemented in THEREDA, because from view of redox conditions in deep underground repository and presence of high ionic strength conditions, it has very minor relevance. See discussion on Np(VI) above.

### **3.5 Heptavalent radionuclides: technetium**

#### **3.5.1 Technetium, Tc(VII): $\text{TcO}_4^-$**

The heptavalent technetium species are not regarded within this phase of THEREDA. For more explanation on the present and future activities on Tc(VII) concerning THEREDA we refer to chapter 3.2.6.

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