Technical Report

TR-06-17

Update of a thermodynamic database for radionuclides to assist solubility limits calculation for performance assessment

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December 2006

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Abstract

This report presents and documents the thermodynamic database used in the assessment of the radionuclide solubility limits within the SR-Can Exercise. It is a supporting report to the solubility assessment.

Thermodynamic data are reviewed for 20 radioelements from Groups A and B, lanthanides and actinides.

The development of this database is partially based on the one prepared by PSI and NAGRA (NAGRA-PSI 01/01 database, /Hummel et al. 2002/). Several changes, updates and checks for internal consistency and completeness to the reference NAGRA-PSI 01/01 database have been conducted when needed. These modifications are mainly related to the information from the various experimental programmes and scientific literature available until the end of 2003. Some of the discussions also refer to a previous database selection conducted by Enviros Spain on behalf of ANDRA /Bruno et al. 2001/, where the reader can find additional information.

When possible, in order to optimize the robustness of the database, the description of the solubility of the different radionuclides calculated by using the reported thermodynamic database is tested in front of experimental data available in the open scientific literature.

When necessary, different procedures to estimate gaps in the database have been followed, especially accounting for temperature corrections.

All the methodologies followed are discussed in the main text.

Sammanfattning

Den här rapporten presenterar och dokumenterar den termodynamiska databas som har används för att bedöma löslighetsgränser för radionuklider i SR-Can analysen. Rapporten skall ses som en underlagsrapport till löslighetsanalysen.

Termodynamiska data för 20 radioelement från grupp A och B, lantanider och aktinider, har granskats.

Utvecklingen av den här databasen är delvis baserat på den som togs fram av PSI och NAGRA (NAGRA-PSI 01/01 Database, /Hummel et al. 2002/). Ett antal förändringar, uppdateringar, kontroller av den interna överensstämmelsen och fullständigheten av den ursprungliga NAGRA-PSI 01/01 Databasen har gjorts där det funnits nödvändigt. Dessa förändringar är i huvudsak relaterade till information från ett antal experimentella program och vetenskaplig litteratur som funnits tillgäng fram till slutet av 2003. En del diskussioner refererar också till en tidigare databas genomgång som genomförts av Enviros för ANDRA /Bruno et al. 2001/, där läsaren kan hitta ytterligare information.

För att optimera robustheten hos databasen har beskrivningen av lösligheten av de olika radionukliderna jämförts mot experimentella från den öppna vetenskapliga litteraturen.

När det har funnits nödvändigt har olika procedurer använts för att fylla brister in databasen. Detta gäller särskilt för temperaturkorrektioner.

Contents

1 Introduction

Thermodynamic databases are a substantial part of the models used in the Performance Assessment of Nuclear Waste repositories. They are mainly used in determining the solubility and speciation of various radionuclides in the various compartments of the repository system and to a lesser extent in the evaluation of the chemical and geochemical evolution of the repository. The assessment of concentration limits for radionuclides in the near and far-field of a HLNW repository is an issue of the utmost relevance for the safety assessment of the repository.

In this context, during the SR-97 exercise a large effort was devoted to the assessment of solubility limits. The result of the assessment was published as a SKB Technical Report /Bruno et al. 1997/.

Later, a SKI report /SKI 2000/ summarized the results of a review of selected geochemical aspects of SR 97. Regarding to the assessment of the solubility limits some issues were raised concerning the consistency of the the thermodynamic data base used to perform the calculations presented in SKB TR 97-33.The original thermodynamic database used in this report was taken from the NTB91-17 and 91-18. This database was combined with additional data compilations prepared by SKB for U, Pu, Tc, REE and Np. Several additions to and modifications of these primary data sources are described in the report and incorporated in the database used there.

The aim of this work is thus to modify and/or update as well as to complete, if considered appropriate, the NAGRA-PSI 01/01 TDB /Hummel et al. 2002/, which will be used as a basic thermodynamic database in the assessment of the solubility limits. SKB therefore has considered the convenience to ensure the consistency and completeness of the thermodynamic database to be used in the new assessment of concentration limits for radionuclides.

The update and check for consistency and completeness of the database to be used will be conducted with available information from the various experimental programmes and scientific literature.

Special attention will be put to the internal consistency of the data included in the TDB, as well as on formation and reaction enthalpy data for the temperature corrections, given that the reference temperature for the SR-Can project is 15°C.

Therefore, the objective of this project is to assure the use of a consistent and quality thermodynamic database to support the geochemical calculations for the performance assessment purposes.

The thermodynamic data to use in this work, as we have already mentioned, is based on the detailed compilation performed /Hummel et al. 2002/, the NAGRA-PSI 01/01 TDB, and refer to standard state conditions. Many of the discussions presented in this report are related to a previous database selection conducted by Enviros Spain on behalf of ANDRA /Bruno et al. 2001/ and the reader is directed to this work when necessary.

The latest updates of the NEA-TDB project on Se and Ni /Olin et al. 2005, Gamsjäger et al. 2005/ have appeared once the literature review process of the present work was already closed. Therefore, we have not included the NEA selection for these elements in this report. This should constitute a part of further work in the process of thermodynamic database continuous update.

In most of the cases, the reference database does neither include enthalpies nor entropies. Given that solubility limits of interest for SKB must be assessed at temperatures that differ from 25°C, we have conducted an extensive literature search to fill in the gaps and some data estimation procedures have been followed when no other possibility was available. Besides considering the chemical analogy existing between lanthanides and trivalent actinides, the methodology proposed in /Sverjensky et al. 1997/ to estimate entropies of formation have been followed in some cases. In addition, we have considered the chemical analogies and where estimates have been included, we have ensured the internal consistency of the database. The uncertainty associated to the entropies estimated by using the equations reported in /Sverjensky et al. 1997/ is 20.9 J/mole·K as proposed by the authors.

The selected thermodynamic database is presented in the following chapters for the elements listed in Table 1-1.

Table 1-1. List of elements included in this TDB review.

Elements groups A
Caesium
Strontium
Radium
Tin
Selenium
Elements groups B
Zirconium
Niobium
Technetium
Nickel
Palladium
Silver
Lanthanides
Samarium
Holmium
Actinides
Americium
Curium
Thorium
Protactinium
Uranium
Neptunium
Plutonium

2 Caesium

The reference database NAGRA-PSI 01/01 TDB /Hummel et al. 2002/, does not include data for this element. We have created a new thermodynamic database for caesium by considering, for most of the species included, the updated NEA TDB /Guillaumont et al. 2003/ and the NBS tables /Wagman et al. 1982/. In case data are not available in the mentioned sources, we have included estimations on Cs stability species conducted by /Shock et al. 1997/ and /Sverjensky et al. 1997/.

The data selection is presented in the following sub-sections.

2.1 Elemental caesium

Elemental caesium is included in the database given that its formation properties are needed for the calculation of certain thermodynamic reaction magnitudes of other Cs species. The entropy of formation, the stability constant and the reaction enthalpy for the reference state, Cs(s), have been calculated from formation data reported in /Guillaumont et al. 2003/. The selected values are presented in Table 2-1.

Table 2-1. Thermodynamic data for elemental caesium.

Reaction	$\log K^0$	$\Delta_r H^0$ (kJ/mole)	$S_f^0{}_{Cs(s)}$ (J/mole·K)
$Cs^+ + e^- = Cs(s)$	–51.06±0.09	258.000±0.500	85.2±0.4

2.2 Simple aqua ions

Caesium is present in solution as the monovalent cation Cs^+. As in the case of elemental caesium, formation data for this species have been taken from /Guillaumont et al. 2003/:

$\Delta_f G^0_{Cs+} = –291.456±0.535$ kJ/mole

$\Delta_f H^0_{Cs+} = –258.000±0.500$ kJ/mole

$S_f^0{}_{Cs+} = 132.1±0.5$ J/mole K

2.3 Oxygen compounds

2.3.1 Aqueous hydroxide complexes

Only evidences of the formation of the first hydrolysis complex, CsOH(aq), have been found in the literature. Its stability constant has been calculated from formation data ($\Delta_f G^0$ and S_f^0) reported in /Bard et al. 1985/ and it is shown in Table 2-2.

Table 2-2. Thermodynamic data for aqueous caesium hydroxide.

Reaction	$\log {}^*\beta^0$
$Cs^+ + H_2O = Cs(OH)(aq) + H^+$	–15.64

No uncertainty associated to this constant can be calculated given that standard deviation for $\Delta_f G^0$ and S_f^0 are not reported in the original source.

The enthalpy of reaction for CsOH(aq) has been calculated from the corresponding formation enthalpies of the species involved in its formation reaction.

$\Delta_r H^0{}_{Cs(OH)(aq)} = 65.736$ kJ/mole

2.3.2 Solid oxides

Only one solid oxide, $Cs_2O(s)$, has been included in this database. We have calculated the formation constant for this solid from the ΔG_f^0 value reported in the NBS tables /Wagman et al. 2003/. We have calculated the error associated by considering that the uncertainty lays within the last digit in the original source.

The enthalpy of reaction has been obtained from the formation enthalpy which has been calculated internally with the Gibbs-Helmholtz equation: $\Delta_r G_i^0 = \Delta_r H_i^0 - T\Delta_r S_i^0$. Formation free energy and entropy have been directly taken from the NBS tables. Uncertainties associated to these values are assigned by considering that the uncertainty in the NBS tables is in the last digit (see Table 2-3).

Table 2-3. Thermodynamic data for Cs_2O.

Reaction	$-\log{}^*K_s^0$	$\Delta_r H^0$ (kJ/mole)
$2Cs^+ + H_2O = Cs_2O(s) + 2H^+$	–89.68±0.19	456.100±1.029

2.4 Group 14

2.4.1 Carbonate compounds

Aqueous complexes.

We have not included any Cs aqueous carbonate in the database. Stability estimations can be found in /Brown and Wanner 1987/. Even by assuming very high carbonate concentrations, this species does not appear to be important which, in combination with the fact that this type of estimations do not produce very good results for monovalent cations, has led us to disregard its inclusion in the database.

Solid phases

Only one solid carbonate has been considered in this revision, $Cs_2CO_3(s)$. Its stability has been calculated from the formation Gibbs energy reported in the NBS tables.

The enthalpy of reaction for the formation of $Cs_2CO_3(s)$ has been calculated from $\Delta_f G^0$ and S_f^0 values reported in the NBS compilation (Table 2-4).

Table 2-4. Thermodynamic data for solid Caesium carbonate.

Reaction	$-\log K_s^0$	$\Delta_r H^0$ (kJ/mol)
$2Cs^+ + CO_3^{2-} = CsCO_3(s)$	–9.90±0.20	55.348±1.063

2.5 Group 15

2.5.1 Nitrate compounds

Aqueous complexes

Only the first aqueous nitrate, $CsNO_3$(aq), has been considered in this database. We have found estimations of the formation constant for the second nitrate /Brown and Wanner 1987/ but given that no other reference to its stability has been found, the low influence that this species has on the Cs geochemistry under the conditions of interest and the reasons presented in Section 2.6.1, we have decided not to include $Cs(NO_3)_2^-$ in the thermodynamic database.

The formation constant for $CsNO_3$(aq) has been calculated from the $\Delta_f G^0$ value reported in /Bard et al. 1985/.

The enthalpy of reaction has been obtained from the formation enthalpy included in /Bard et al. 1985/.

Table 2-5. Thermodynamic data for Caesium nitrate.

Reaction	Logβ^0	$\Delta_r H^0$ (kJ/mol)
$Cs^+ + NO_3^- = CsNO_3$(aq)	–1.71	10.450

Solid phases

No data on solid nitrates have been included in this database given the lack of reliable data on these phases in the literature.

2.5.2 Phosphate compounds

No data on phosphates have been included in this database. We have found estimated values in the literature /Brown and Wanner 1987/ referred to aqueous phosphates. When considering these data in fractional and predominance diagrams this type of species appear exclusively at phosphate concentrations over 0.1 mole/dm^3, which are too high for the conditions of interest.

2.6 Group 16

2.6.1 Aqueous complexes

No experimental data on aqueous sulphates have been found in the open literature. Only estimations reported in /Brown and Wanner 1987/ are available. Nevertheless we have given no credit to the those estimations given that when comparing the stability constants estimated in /Brown and Wanner 1987/ for monovalent cations with formation constants obtained from experimental studies no good correlations are found (for details see /Bruno et al. 2001/). Speciation calculations including these estimates in fractional and predominance diagrams show that in case they existed these complexes would appear only at high sulphate concentrations ($[SO_4^{2-}]_{tot} \geq 0.1$mole/dm^3), therefore, the error associated to neglect these species is probably lower than the one associated to their consideration with the stabilities estimated by /Brown and Wanner 1987/.

2.6.2 Solid phases

Only one solid sulphate has been included in the database. The stability constant has been calculated from the formation Gibbs free energy reported in the NBS tables.

As in the case of the oxide $Cs_2O(s)$ the reaction enthalpy has been obtained from the enthalpy of formation. Δ_fH^0 has been calculated internally from the formation Gibbs energy, Δ_fG^0, and the entropy of formation, S^0_f, reported in /Wagman et al. 1982/.

Table 2-6. Thermodynamic data for solid Caesium sulphate.

Reaction	$-\log K_s^0$	Δ_rH^0 (kJ/mol)
$2Cs^+ + SO_4^{2-} = Cs_2SO_4(s)$	–0.58±0.20	–17.756±1.103

2.7 Group 17

2.7.1 Aqueous complexes

We have included four aqueous halides in the database: CsF(aq), CsCl(aq), CsBr(aq) and CsI(aq). The formation constants of these species have been calculated from Δ_fG^0 values reported in the literature. Formation Gibbs free energy for chloride, bromide and iodide have been taken from /Sverjensky et al. 1997/. Given that no values have been proposed in this reference for the aqueous fluoride we have selected those included in the NBS tables.

The enthalpies of reaction have been obtained from formation enthalpies which have been calculated internally by using the Gibbs-Helmholtz equation. The formation Gibbs energies and entropies for the aqueous fluoride have been taken from /Wagman et al. 1982/ while for the other selected halides we have recalculated the Sf^0 by considering the entropies of formation selected for the basic species and by following the methodology proposed by /Sverjensky et al. 1997/. Thus, we ensured the internal consistency of the selection.

2.7.2 Solid phases

We have selected those solids that have been included in the updated NEA database /Guillaumont et al. 2003/: CsCl(cr) and CsBr(cr) with their associated formation Gibbs free energies. Their calculated stability constants are shown in see Table 2-8.

The selected enthalpies of reaction for these solids have been calculated from formation enthalpies given in /Guillaumont et al. 2003/.

Table 2-7. Thermodynamic data for aqueous Caesium halides.

Reaction	$\log\beta^0$	Δ_rH^0 (kJ/mol)
$Cs^+ + F^- = CsF(aq)$	–0.38±0.15	2.446±0.829
$Cs^+ + Cl^- = CsCl(aq)$	–0.09	7.523
$Cs^+ + Br^- = CsBr(aq)$	0.09	5.922
$Cs^+ + I^- = CsI(aq)$	1.05	–0.055

Table 2-8. Thermodynamic data for solid Caesium halides.

Reaction	$-\log K_s^0$	Δ_rH^0 (kJ/mol)
$Cs^+ + Cl^- = CsCl(cr)$	–1.55±0.10	–17.230±0.534
$Cs^+ + Br^- = CsBr(cr)$	–0.72±0.11	–26.190±0.579

3 Strontium and radium

For Strontium and Radium we have taken directly the reference database NAGRA-PSI 01/01 TDB.

4 Tin

The NAGRA-PSI 01/01 TDB reference database on Sn is based on the review conducted by /Lothenbach et al. 1999/.

We have based our selection in the last Sn TDB update conducted by Séby and co-workers /Séby et al. 2001/. Data sources are the same in both works, but some slight differences between data selected in /Lothenbach et al. 1999/ and the ones selected in /Séby et al. 2001/ can be identified. Those differences arise mainly from the different criteria followed for data correction to infinite dilution.

No general compilations of enthalpy data are available. To fill in the enthalpy gaps we have conducted an extensive literature search and for those cases where absolute lack of data was identified, we have followed established estimation procedures.

We present in the following subsections the TDB selection where, in principle, only data differing from those in the NAGRA-PSI 01/01 database are reported.

4.1 Master species and redox states

The master species is the divalent cation Sn^{2+}. Thermodynamic data for this species have been taken from /Grenthe et al. 1992/ (see Table 4-1).

Thermodynamic data for the reference state, Sn(cr), come from /Cox et al. 1989/, the entropy value is 51.2±0.1 J/mole·K and its stability value has been calculated from $\Delta_f G^0$ data (see Table 4-2).

The NAGRA-PSI 01/01 compilation defines two independent master species Sn^{4+} and Sn^{2+}. These two redox states are decoupled in the mentioned database and therefore no equilibrium constant for redox tin reactions are defined. In the light of the discrepant values existing in the literature for the equilibrium constant for this redox process, the selection of a value for this parameter is fraught with difficulties. Nevertheless it is very convenient to couple these two redox states in order to be able to asses the behaviour of tin under different redox conditions.

Therefore, in the database reported in this document we have selected the tetravalent Sn^{4+} as auxiliary species and have defined the redox equilibrium for the oxidation of Sn^{2+} to Sn^{4+}. The reaction constant selected for this process has been calculated from the value of E^0 recommended in /Séby et al. 2001/. The reaction enthalpy has been calculated from the Sn^{4+} formation enthalpy reported in /Jackson and Helgeson 1985/. The resulting values for these data are shown in Table 4-2.

Table 4-1. Thermodynamic data for Sn^{2+}.

$\Delta_f G^0$ (kJ/mole)	$\Delta_f H^0$ (kJ/mole)	S_f^0 (J/mole·K)
–27.624±1.557	–8.900±1.000	–16.7±4.0

Table 4-2. Thermodynamic data for tin redox species.

Reaction	logK^0	$\Delta_r H^0$ (kJ/mole)
$Sn^{2+}+2e^- = Sn(cr)$	–4.84±0.27	8.900±1.000
$Sn^{2+} = Sn^{4+}+2e^-$	–5.08±0.34	39.146±1.044

4.2 Oxygen and hydrogen compounds

4.2.1 Tin (II) hydrolysis complexes

Stability constants of Sn(II) aqueous hydroxo complexes are selected from /Séby et al. 2001/, as in the case of the redox species Sn^{4+}. The values reported in /Lothenbach et al. 1999/ and included in the NAGRA-PSI 01/01 database are identical except for the stability constant of $Sn(OH)_2(aq)$, for which a difference of 0.1 log units appears. The species $Sn_2(OH)_2^{2+}$ is not included in the NAGRA-PSI 01/01 compilation although we have included it in the database. Enthalpies of reaction have been calculated internally by using the entropy data presented below.

The formation entropy for $SnOH^+$ (S_f^0 = 80.3±40.0 J/mole·K) has been taken from /Shock et al. 1997/, the associated uncertainty covers the range of values published in the literature. Formation entropies for $Sn(OH)_2(aq)$ (113.8 J/mole·K) and $Sn(OH)_3^-$ (178.7 J/mole·K) have been taken from the EQ3/6 data0.com database, whose origin are estimations calculated by means of the approach proposed by Helgeson /Helgeson 1969/. Based upon the general discrepancy between estimated and experimental values for other similar species an uncertainty of 10 cal/moleK has been assigned to those values (41.8 J/moleK).

Selected data for Sn(II) hydroxide complexes are shown in Table 4-3.

No values for entropy and enthalpy have been reported in the literature for the formation of $Sn_2(OH)_2^{2+}$ and $Sn_3(OH)_4^{2+}$. Given the difficulty in assessing these parameters for polynuclear species no estimations have been conducted.

Other polymeric tin-hydroxo species $Sn_3(OH)_5^+$, $Sn_4(OH)_4^{4+}$ and $Sn_6(OH)_8^{4+}$ are proposed in the estimation-based compilation conducted by /Brown and Wanner 1987/. The existence of these species is doubtful and their impact in the speciation of Sn in natural waters is expected to be very low. Therefore, we have not included them in this selection.

4.2.2 Tin (IV) hydrolysis complexes

The NAGRA-PSI 01/01 TDB selects the $Sn(OH)_4(aq)$ complex as master species for Sn(IV) given its predominance in the acidic to neutral pH range. The stabilities of $Sn(OH)_5^-$ and $Sn(OH)_6^{2-}$ in the mentioned database have been taken from the works of Amaya and co-workers /Amaya et al. 1997, Oda and Amaya 1998/, in agreement with data selected in /Lothenbach et al. 1999/.

The review conducted by Séby and co-authors /Séby et al. 2001/ does not recommend any value for the hydrolysis constants of tetravalent tin given the lack of agreement on their existence in the literature.

In our work, the following reasoning has been followed to select the Sn(IV) hydrolytic system.

Table 4-3. Selected thermodynamic data for Sn(II) aqueous hydroxo complexes different from NAGRA-PSI 01/01 DTB.

Reaction	log*β^0	Δ_rH^0 (KJ/mole)
$Sn^{2+}+H_2O = Sn(OH)^++H^+$	–3.80±0.20	29.765±12.117
$Sn^{2+}+2H_2O = Sn(OH)_2(aq)+2H^+$	–7.80±0.20	41.721±12.657
$Sn^{2+}+3H_2O = Sn(OH)_3^-+3H^+$	–17.50±0.20	95.570±12.513
$2Sn^{2+}+2H_2O = Sn_2(OH)_2^{2+}+2H^+$	–2.40±0.30	
$3Sn^{2+}+4H_2O = Sn_3(OH)_4^{2+}+4H^+$	–5.60±0.10	

$SnOH^{3+}$, $Sn(OH)_2^{2+}$ and $Sn(OH)_3^+$ stabilities have been taken from the spectrophotometric work of /Nazarenko et al. 1971/ conducted at I = 1 M. No SIT coefficients have been reported for these species in the open literature. Therefore, we have corrected ionic strength effects by using the Debye-Hückel expression.

Sn(IV) hydrolysis reaction entalphies included in this database have been calculated from entropies estimated by the /Langmuir 1978/ algorithm for tetravalent cations. An uncertainty of 10 cal/mole·K is assigned to entropies estimated by this procedure.

Selected data for these complexes are given in Table 4-4.

The formation constant for $Sn(OH)_4(aq)$ has been calculated according to reaction 4-1.

$Sn^{4+} + 4\ H_2O = Sn(OH)_4(aq) + 4\ H^+$ 4-1

Δ_rG has been obtained from the value of Δ_fG ($Sn(OH)_4(aq)$) = 944.181±0.965 kJ/mole calculated by /Lothenbah et al. 1999/ from the following equilibrium reaction for cassiterite:

$Sn(OH)_4(aq) = SnO_2(cr) + 2\ H_2O$ 4-2

The values selected for $Sn(OH)_5^-$ and $Sn(OH)_6^{2-}$ in the NAGRA-PSI 01/01 database have been adopted in our selection. Neither values for entropies nor for enthalpies have been found. Values are reported in Table 4-4.

The fractional diagram of tin(IV) hydrolysis species is shown in Figure 4-1. No influence of the first, second or third hydrolysis products on the speciation of tin under these conditions is observed in the pH range of interest.

4.2.3 Solid phases, oxides and hydroxides

SnO(s) is the only Sn(II) oxide included in the NAGRA-PSI 01/01 TDB. The reasoning behind this selection is, according to the mentioned reference, the limited data available and the poor characterisations of the solids reported in the literature. Therefore, they propose the inclusion of SnO(s) in the database with an uncertainty assigned to its stability that aims at covering all data so far published.

/Garret and Heiks 1941/ and /Djurdjevic et al. 1995/ showed that $Sn(OH)_2(s)$ is readily dehydrated to SnO(s). For solubility calculations purposes, therefore, we agree with the selection included in the NAGRA-PSI 01/01 database.

From the formation entropy reported in CODATA /Cox et al. 1989/, we have calculated the reaction entropy and enthalpy (see Table 4-5).

Two different tin(IV) solid oxides are included in the NAGRA-PSI 01/01 TDB: Cassiterite, i.e., $SnO_2(cr)$ and an amorphous SnO_2. We keep this selection.

Table 4-4. Selected thermodynamic data for Sn(IV) aqueous hydroxo complexes different from NAGRA-PSI 01/01 DTB.

Reaction	log*β^0	Δ_rH^0 (kJ/mole)
$Sn^{4+}+H_2O = Sn(OH)^{3+}+H^+$	1.79±1.00	–62.218±13.938
$Sn^{4+}+2H_2O = Sn(OH)_2^{2+}+2H^+$	2.71±1.00	–52.279±13.938
$Sn^{4+}+3H_2O = Sn(OH)_3^{+}+3H^+$	2.79±1.00	–50.306±13.938
$Sn^{4+}+4H_2O = Sn(OH)_4(aq)+4H^+$	–0.53±0.67	–36.254±12.785
$Sn^{4+}+5H_2O = Sn(OH)_5^{-}+5H^+$	–8.50±1.00	
$Sn^{4+}+6H_2O = Sn(OH)_6^{2-}+6H^+$	–18.93±1.00	

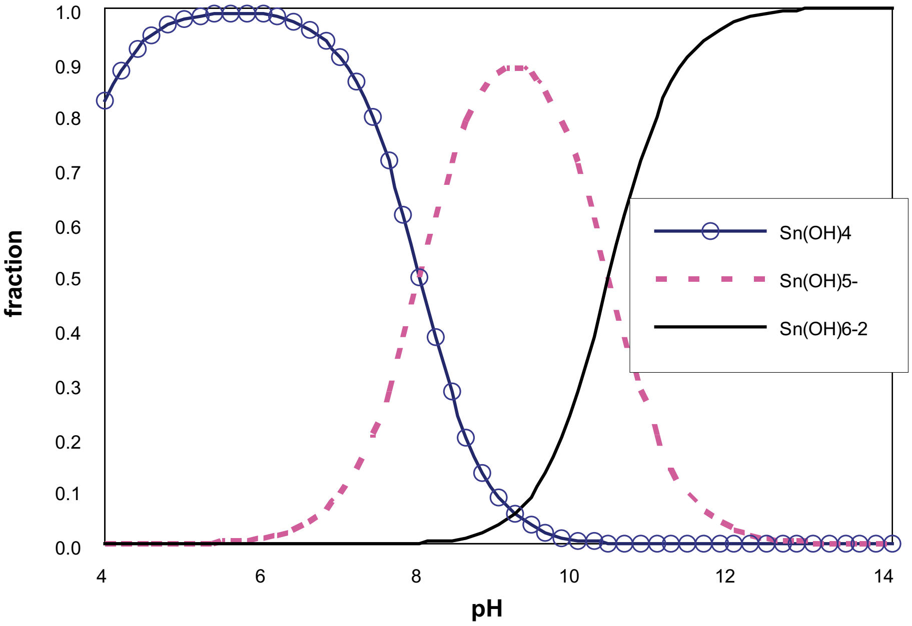

Figure 4-1. *Fraction of tin aqueous complexes, pe=8.5, [Sn^{2+}]=10^{-5}mole·dm^{-3}.*

From the formation enthalpy of SnO_2(cr) reported in /Grenthe et al. 1992/ we have calculated the corresponding reaction enthalpy.

We have included a freshly precipitated amorphous phase that may exhibit a high solubility, $Sn(OH)_4$(am). The selected stability results from data compiled in /Séby and Donart 1999/ and /Séby et al. 2001/ with an assigned uncertainty covering the data range.

From Δ_fH^0 compiled in /Wagman et al. 1982/, Δ_rH^0 has been calculated (see Table 4-5).

/Lothenbach et al. 2000/ identified by X-Ray Diffraction a solid Calcium stannate of stoichiometry, Ca[$(Sn(OH)_6$](s). This solid was found to precipitate from a homogeneous solution of Tin at pH >12 when adding calcium concentrations over 0.001M. In the mentioned reference also solubility measurements of a crystalline Ca[$Sn(OH)_6$](cr) were conducted and a solubility product for this solid was obtained. Different solubilities measured from over and undersaturation experiments were obtained and they were attributed to different cristallinities of the solid phases. Therefore we have included the calcium stannate in this review, and have assigned it an stability and an uncertainty in the logK value corresponding to the difference between the reported stabilities. Selected data are shown in Table 4-5.

Table 4-5. Selected data for Tin oxides and hydroxides solid phases.

Reaction	–log*K_s	Δ_rH^0 (kJ/mole)
$Sn^{2+}+H_2O = SnO(s)+2H^+$	–2.50±0.5	15.439±3.094
$Sn^{4+}+4H_2O = Sn(OH)_4(am)+4H^+$	1.43±0.5	3.074±1.056
$Sn^{4+}+2H_2O = SnO_2(am)+4H^+$	6.77±0.73	
$Sn^{4+}+2H_2O = SnO_2(cr)+4H^+$	7.47±0.73	–35.948±4.871
$Sn^{4+}+6H_2O+Ca^{2+} = Ca[Sn(OH)_6](s)+6H^+$	–8.54±0.74	

4.3 Group 14

No Sn(II) Carbonate species are included in the NAGRA PSI 01/01 TDB.

Neither experimental information on Carbonate complexes of Sn(II) nor of Sn(IV) have been found in the literature. /Brown and Wanner 1987/ report estimated stabilities for $Sn(CO_3)(aq)$ and $Sn(CO_3)_2^{2-}$. In opposition to what occurred with monovalent cations, there is a rather good correlation between experimental data and Brown and Wanner's estimations for divalent cations (see Figure 4-2).

Nevertheless, the hypothetical role of these species in the aqueous Sn speciation in solution is irrelevant even at high carbonate and tin concentrations, and therefore, we have neither included Sn(II) carbonate species in the database.

4.4 Group 15

4.4.1 Nitrate compounds

Nitrate compounds are not selected in the NAGRA PSI 01/01 TDB.

Besides the estimation conducted by /Brown and Wanner 1987/, the only data set on Sn(II) nitrate species comes from the study of /Andreev et al. 1980/ compiled by /Lothenbach et al. 1999/. There are not enough data available as to assign uncertainties. Neither enthalpy nor entropy values are given. Selected data are shown in Table 4-6.

4.4.2 Phosphate compounds

No reliable data are available in the literature on Sn phosphate species.

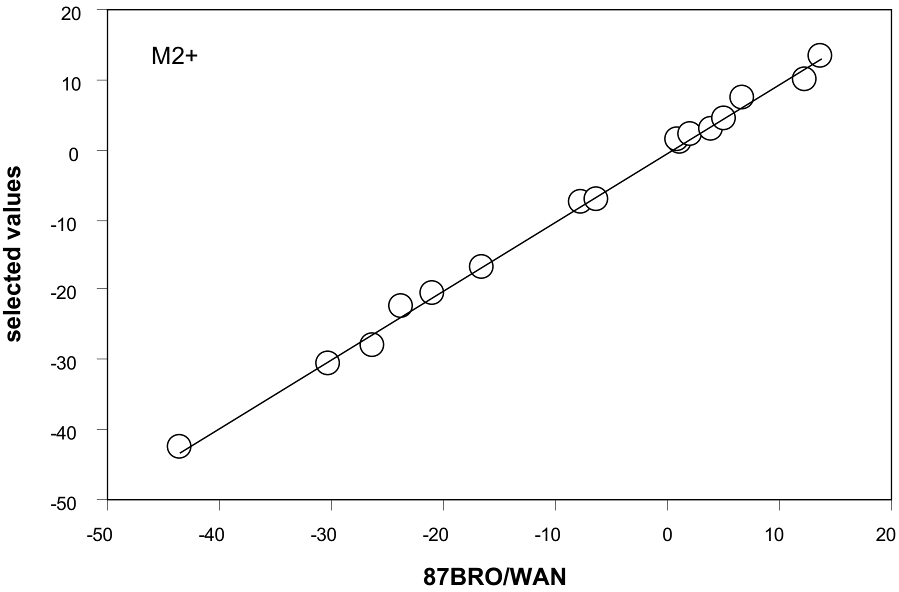

Figure 4-2. Correlation between selected values and estimations of /Brown and Wanner 1987/ for aqueous species of divalent cations (Pb^{2+} and Pd^{2+}).

Table 4-6. Selected thermodynamic data for Tin(II) nitrate complexes different from NAGRA-PSI 01/01 DTB.

Species	Reaction	Logβ⁰
$Sn(NO_3)^+$	$Sn^{2+}+NO_3^- = Sn(NO_3)^+$	1.25
$Sn(NO_3)_2(aq)$	$Sn^{2+}+2NO_3^- = Sn(NO_3)_2(aq)$	1.74
$Sn(NO_3)_3^-$	$Sn^{2+}+3NO_3^- = Sn(NO_3)_3^-$	1.37
$Sn(NO_3)_4^{2-}$	$Sn^{2+}+4NO_3^- = Sn(NO_3)_4^{2-}$	0.30

4.5 Group 16

4.5.1 Tin(II) sulphate and sulphide compounds

In agreement with the NAGRA PSI 01/01 TDB, we only select the first Sn(II) aqueous sulphate species. The second complex is very weak and becomes relevant only in highly concentrated sulphate solutions. Selected data are given in Table 4-7.

Thermodynamic data for the Sn(II) sulphide solid phase has been selected from /Robie and Hemingway 1995/, this selection leads to a logK value of 15.63±0.63 for the reaction:

$$Sn^{2+}+HS^- = SnS\ (s) +H^+ \qquad 4\text{-}3$$

Selected data are shown in Table 4-7.

4.5.2 Tin(IV) sulphate and sulphide compounds

The NAGRA PSI 01/01 database does not report data for these compounds.

In this review, we have taken data selected in /Lothenbach et al. 1999/ for the first sulphate species $Sn(SO_4)^{2+}$, that comes from the original work of /Benson et al. 1980/. For the second sulphate species, $Sn(SO_4)_2(aq)$, the selection reported in Séby and co-authors /Séby et al. 2001/ has been accepted. No entropy or enthalpy data are available for these species. Selected data are shown in Table 4-7.

The solid sulphide, $SnS_2(s)$, has been also included in this database. The formation Gibbs energy reported in /Jackson and Helgeson 1985/ is accepted, although no uncertainties have been assigned (see Table 4-7).

Table 4-7. Selected thermodynamic data for sulphate and sulphide complexes different from NAGRA-PSI 01/01 DTB.

Reaction	logβ⁰	Δ_rH^0 (kJ/mole)
$Sn^{2+}+SO_4^{2-} = Sn(SO_4)(aq)$	2.91	
$Sn^{4+}+SO_4^{2-} = SnSO_4^{2+}$	–3.22±0.86	
$Sn^{4+}+2SO_4^{2-} = Sn(SO_4)_2(aq)$	–0.85	
Reaction	**–logK$_s$**	**Δ_rH^0 (kJ/mole)**
$Sn^{4+}+2HS^- = SnS_2(s)+2H^+$	30.00	–151.199
$Sn^{2+}+HS^- = SnS(s)+H^+$	15.63±0.53	–81.020±2.642

4.6 Group 17

4.6.1 Tin(II) compounds

We have included the stabilities of Sn(II) halide complexes as recommended in /Séby et al. 2001/. When no data was available in /Séby et al. 2001/, we have used the selection of /Lothenbach et al. 1999/ (see Table 4-8).

Formation enthalpies for some of the species are reported in /Wagman et al. 1982/, from these we have calculated reaction enthalpies. Given that no information on the original source is given in the mentioned reference we recommend caution when using the Δ_rH^0 values shown in Table 4-8.

4.6.2 Tin(IV) compounds

Only one source of data for Sn(IV) chloride species stability is available in the literature /Fatoulos et al. 1978/. /Lothenbach et al. 1999/ quote this work although they do not select the reported values. We have included the formation of Sn(IV) chlorides in the database after correcting the values given at I = 5 M to infinite dilution by means of the Debye-Hückel approach due to the absolute lack of data on interaction coefficients to apply the SIT theory. Selected data are presented in Table 4-9.

Table 4-8. Selected thermodynamic data for Tin(II) halide complexes different from NAGRA-PSI 01/01 TDB.

Reaction	**logβ^0**	**Δ_rH^0 (kJ/mole)**
$Sn^{2+}+F^- = SnF+$	5.22±0.01	
$Sn^{2+}+2F^- = SnF_2(aq)$	8.90±0.05	
$Sn^{2+}+3F^- = SnF_3^-$	12.90±0.10	
$Sn^{2+}+Cl^- = SnCl^+$	1.54±0.02	11.18
$Sn^{2+}+2Cl^- = SnCl_2(aq)$	2.30±0.10	13.36
$Sn^{2+}+3Cl^- = SnCl_3^-$	1.97±0.05	23.14
$Sn^{2+}+Br^- = SnBr^+$	1.07±06	5.61
$Sn^{2+}+2Br^- = SnBr_2(aq)$	1.88±0.07	5.72
$Sn^{2+}+3Br^- = SnBr_3^-$	1.50±0.10	–1.77
$Sn^{2+}+I^- = SnI^+$	1.72±0.50	
$Sn^{2+}+2I^- = SnI_2(aq)$	2.66±0.07	
$Sn^{2+}+Cl^-+H_2O = SnOHCl+H^+(aq)$	–2.27±0.10	8.31
Reaction	**–logK_s**	**Δ_rH^0 (kJ/mole)**
$Sn^{2+}+Cl^-+H_2O = SnOHCl(s)+H^+$	2.42±0.15	

Table 4-9. Selected thermodynamic data for Tin(IV) chloride complexes different from NAGRA-PSI 01/01 TDB.

Reaction	**logβ^0**
$Sn^{4+}+Cl^- = SnCl^{3+}$	5.80±0.03
$Sn^{4+}+2Cl^- = SnCl_2^{2+}$	10.12±0.02
$Sn^{4+}+3Cl^- = SnCl_3^+$	13.49±0.02
$Sn^{4+}+4Cl^- = SnCl_4(aq)$	12.62±0.09
$Sn^{4+}+5Cl^- = SnCl_5^-$	16.46±0.06
$Sn^{4+}+6Cl^- = SnCl_6^{2-}$	17.11±0.05

5 Selenium

Thermodynamic data on selenium species are important to understand and to explain the behaviour of selenium under different environmental conditions. Most of the consulted compilations report thermodynamic data for redox species and acid-base equilibria while nothing is reported on solid phases. Reported thermodynamic data agree quite well with the one reported as auxiliary data in the NEA compilations.

The thermodynamics of selenium is one of the topics of the Phase II of the OECD NEA Thermodynamic Database project. The NEA review has been published this year /Olin et al. 2005/, after the closing date of the literature review conducted within this work. Therefore, NEA selected data have not been included in the present report. This database selection has, thus, been based on the review work carried out by /Séby et al. 2001b/. These authors evaluated the accuracy of the thermodynamic data available in the literature based on both the experimental control and the calculation methodology. Some of the data have been selected from the work of /Elrashidi et al. 1987/. These authors reviewed the thermodynamic data available for this element, although no discussion on the source of the values or the way they were obtained is given in their work.

5.1 Master species and redox states

The oxoanion selenate (SeO_4^{2-}) is the master species selected for this compilation. Some of the formation data have been calculated fom thermodynamic parameters reported in /Grenthe et al. 1992/ and stability constants reported in /Séby et al. 2001b/ as indicated below.

/Grenthe et al. 1992/ select $\Delta_f G^0(H_2SeO_3(aq)) = -425.5 \pm 0.6$ kJ/mole, which has been calculated from CODATA values for the species appearing in the following reaction:

$H_2SeO_3(aq)+4\ I^-+4\ H^+ = Se^0+2\ I_2(aq)+3\ H_2O$ 5-1

with $\Delta_r G^0$ calculated from experimental determination of $\log K^0$.

When combining the value of $\Delta_f G^0(H_2SeO_3(aq))$ in /Grenthe et al. 1992/ with the reaction Gibbs free energy for the equilibrium from /Séby et al. 2001b/:

$H_2SeO_3(aq) +2\ H^+ = SeO_3^{2-}$ 5-2

we obtain: $\Delta_f G^0(SeO_3^{2-}) = (-361.342 \pm 0.721)$ kJ/mole.

And, by combining this value with $\Delta_r G^0 = -156.913$ kJ/mole /Séby et al. 2001b/ for the following equilibrium:

$SeO_4^{2-}+2\ H^++2\ e^- = SeO_3^{2-}+H_2O$ 5-3

we obtain $\Delta_f G^0\ (SeO_4^{2-}) = -441.569$ kJ/mole, by applying an uncertainty to this $\Delta_f G^0$ covering all the reported data. This value is in fair agreement with the data in SUPCRT92, $\Delta_f G^0\ (SeO_4^{2-}) = -441.412$ kJ/mole.

The selected value for $\Delta_f H^0(SeO_4^{2-})$ is –599.149 kJ/mole /Shock and Helgesson 1988/, which is in agreement with the value reported in NBS /Wagman et al. 1982/. No information on the uncertainty was reported in /Shock and Helgesson 1988/ or /Wagman et al. 1982/. An uncertainty of 0.1 kJ/mole has been applied. From this value and the previously selected $\Delta_f G^0(SeO_4^{2-})$, a value of 54.7±3.4 J/mole K has been obtained for $S_f(SeO_4^{2-})$.

Table 5-1. Thermodynamic data for SeO_4^{2-}.

Δ_fG^0 (kJ/mole)	Δ_fH^0 (kJ/mole)	S_f^0 (J/mole·K)
–441.569±1.020	–599.149±0.100	54.7±3.4

Auxiliary data accounting for the different redox states of selenium are given in Table 5-2. In general all reaction data have been taken from the review conducted by /Séby et al. 2001b/. However, some internal calculations have been done to report thermodynamic values according to the equilibrium reactions given in Table 5-2.

In the review of /Séby et al. 2001b/ a value of Δ_fG^0 ($H_2Se(aq)$) = 22.200 kJ/mole is given**.** This value is taken from /Wagman et al. 1982/ and an uncertainty of 0.1kJ/mole has been assigned. From this value and by considering the selected equilibrium constant for the reaction Equation 5-4 according to /Séby et al. 2001b/, that is $\Delta_rG^0 = –101.602±5.708$ kJ/mole,

$$Se^{2-}+2\ H^+ = H_2Se(aq) \qquad 5\text{-}4$$

we obtain $\Delta_fG^0(Se^{2-}) = 123.802±5.709$ kJ/mole.

/Séby et al. 2001b/ give a value of $\Delta_rG^0 = –79.912±5.708$ kJ/mole for the reaction:

$$Se^{2-}+H^+ = HSe^- \qquad 5\text{-}5$$

From this value, a value of $\Delta_fG^0(HSe^-) = 43.890±8.073$ kJ/mole can be obtained. The selected $\Delta_fH^0(HSe^-)$ value comes from /Shock and Helgesson 1988/, which is in agreement with the value reported in the NBS tables /Wagman et al. 1982/. No information on the uncertainty of this parameter is given in any of those two sources. Therefore, an uncertainty of 0.1 kJ/mole is considered.

Taking into account the value of $\Delta_rG^0 = –382.222$ kJ/mole for the reaction:

$$SeO_4^{2-}+8\ H^++8\ e^- = Se^{2-}+4H_2O \qquad 5\text{-}6$$

given by /Séby et al. 2001b/, a value of $\Delta_rG^0 = –462.234$ kJ/mole has been obtained for the reaction:

$$SeO_4^{2-}+9\ H^++8\ e^- = HSe^-+4H_2O \qquad 5\text{-}7$$

The $\Delta_fG^0(SeO_3^{2-})$ has been obtained from data of /Grenthe et al. 1992/ and /Séby et al. 2001b/ as explained previously. The selected value of $\Delta_fH^0(SeO_3^{2-})$ is that of /Shoch and Helgesson 1988/ which is in agreement with the value reported in the NBS tables /Wagman et al. 1982/ with an uncertainty of 0.1kJ/mole.

Se(s) is the reference state for selenium, for this reason, both Δ_fG^0 and Δ_fH^0 have a value of 0.0 kJ/mole /Grenthe et al. 1992/. The value for the entropy is 42.27±0.1 J/mole K from /Grenthe et al. 1992/. The entropy of this compound is necessary to calculate the Δ_fH^0 for those selenium species with only information on S_f^0 and Δ_fG^0. The value of Δ_rG^0 is selected from /Grenthe et al. 1992/ and the Δ_rH^0 and Δ_rS^0 are calculated from formation data.

Table 5-2. Thermodynamic data on different redox states of Se.

Species	Reaction	logK⁰	Δ_rH^0 (kJ/mole)
HSe^-	$SeO_4^{2-}+9H^++8e^- = HSe^-+4H_2O$	81.13±1.43	–528.272±0.214
SeO_3^{2-}	$SeO_4^{2-}+2H^++2e^- = SeO_3^{2-}+H_2O$	27.49±0.22	–195.874±0.147
Se(cr)	$HSe^- = Se(cr)+H^++2e^-$	7.69±1.41	–15.899±0.100

5.2 Acid-base equilibria

5.2.1 Se*(–II)*

Se(–II) presents acid-base properties, in analogy to sulphide. The protonated forms of Se^{2-} are the acids HSe^- and $H_2Se(aq)$. Thermodynamic constants have been selected according to /Séby et al. 2001b/. The selected value of $\Delta_fH^0(Se^{2-})$ comes from /Naumov et al. 1974/, while in the case of the species H_2Se, the only value found in the literature for the enthalpy of formation comes from /Wagman et al. 1982/. No uncertainties are given for $\Delta_fH^0(Se^{2-})$ and $\Delta_fH^0(H_2Se(aq))$. However, an uncertainty of 0.1kJ/mole is assigned to the value selected from /Wagman et al. 1982/. With these values, we have calculated the enthalpies of reaction. Selected data are shown in Table 5-3.

There is one polynuclear species of Se(–II) reported in the literature, the Se_4^{2-}. The analysis of sensibility has shown that this species may be important at basic pH and reducing conditions (Figure 5-1). However, no data on protonation of this species exist and, therefore, the calculations obtained by including it predict its predominance under pH values where it has been proven not to exits. For this reason we have not included Se_4^{2-} in the database.

Table 5-3. Thermodynamic data for protonated and de-protonated forms of HSe^-.

Species	Reaction	logK°	Δ_rH^0 (kJ/mole)
Se^{2-}	$HSe^-=Se^{2-}+H^+$	–14.00±1.00	48.116
$H_2Se(aq)$	$HSe^-+H^+=H_2Se(aq)$	3.80±1.41	3.301±0.141

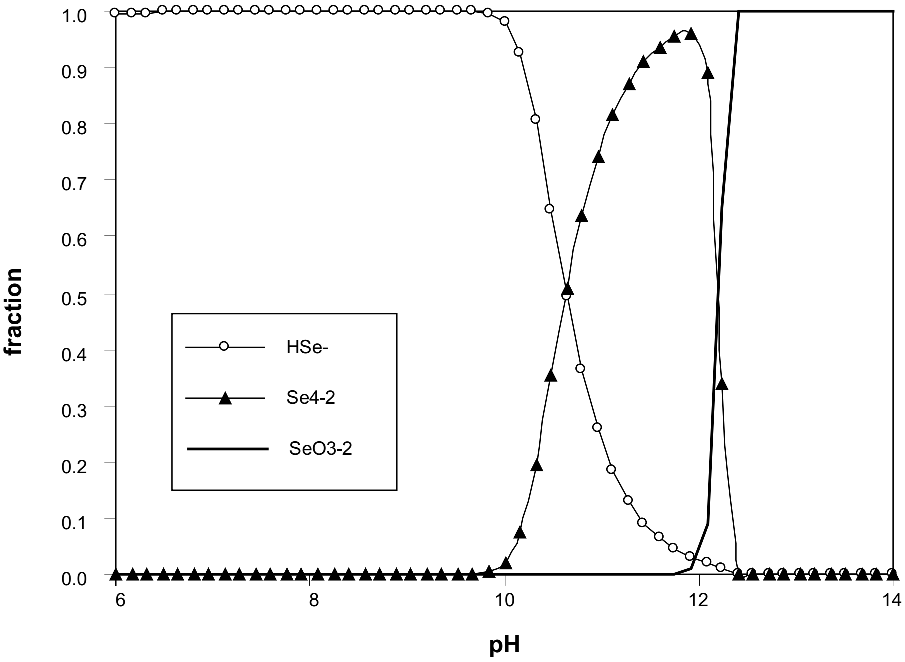

***Figure 5-1.** a) Fraction diagram for selenium at Eh=–0.3 V as a function of pH. [Se]total=10^{-7} M.*

5.2.2 Se*(IV)*

The anion SeO_3^{2-} protonates to form $HSeO_3^-$ and $H_2SeO_3(aq)$. Thermodynamic constants have been selected according to the recommended values of /Séby et al. 2001b/. The enthalpy of reaction for $HSeO_3^-$ according to the equilibrium given in Table 5-4 has been taken from /Grenthe et al. 1992/.

The enthalpy of formation for $H_2SeO_3(aq)$ has been calculated from the Δ_rH^0 reported in /Grenthe et al. 1992/ for the reaction:

$HSeO_3^- + H^+ = H_2SeO_3(aq)$ 5-8

which in combination with the reaction for $HSeO_3^-$ results in the following reaction:

$SeO_3^{2-} + 2H^+ = H_2SeO_3(aq)$ 5-9

with a $\Delta_rH^0 = 12.090 \pm 0.707$ kJ/mole.

Those data are presented in Table 5-4.

5.2.3 Se*(VI)*

The anion SeO_4^{2-} protonates to form $HSeO_4^-$ and $H_2SeO_4(aq)$. Acid-base equilibrium constants have been selected from /Séby et al. 2001b/. The enthalpy of reaction for $HSeO_4^-$ according to the equilibrium given in Table Se5 has been taken from /Grenthe et al. 1992/.

The selected Δ_fH^o for $H_2SeO_4(aq)$ comes from /Wagman et al. 1982/ ($\Delta_fH^0 = -587.000$ kJ/mole) which is the only value that can be found in the literature. No information on the uncertainty of this parameter can be found in /Wagman et al. 1982/, therefore, an uncertainty of 0.1kJ/mole is applied. The entalphy of reaction has been calculated internally. Selected data are presented in Table 5-5.

Table 5-4. Thermodynamic data on protonated Se(IV) species.

Species	Reaction	logK°	Δ_rH^0 (kJ/mole)
$HSeO_3^-$	$SeO_3^{2-}+H^+ = HSeO_3^-$	8.54±0.04	5.020±0.500
$H_2SeO_3(aq)$	$SeO_3^{2-}+2H^+ = H_2SeO_3(aq)$	11.24±0.07	12.090±0.707

Table 5-5. Thermodynamic data on protonated species of Se(VI).

Species	Reaction	logK°	ΔrH (kJ/mole)
$HSeO_4^-$	$SeO_4^{2-}+H^+ = HSeO_4^-$	1.80±0.10	23.800±5.000
$H_2SeO_4(aq)$	$SeO_4^{2-}+2H^+ = H_2SeO_4(aq)$	–0.21±0.12	12.149±0.141

5.3 Aqueous complexes and solid phases

5.3.1 Se*(–II)*

Se(–II) forms solids and aqueous complexes with a variety of metal ions. Experimental data on the solubility of these solid phases is very scarce, and most of the data relies on estimations. We have based our selection in the compilation conducted by /Séby et al. 2001b/, who for alkaline and alkaline-earths elements mainly quote /Elrashidi et al. 1987/. In those cases where /Elrashidi et al. 1987/ have calculated logK from data of /Wagman et al. 1982/ we have selected original data of /Wagman et al. 1982/ instead of data reported in /Elrashidi et al. 1987/. The data selected are shown in Table 5-6, references are also included in this table for the sake of clarify. Stability constant for $FeSe_2$(s) has been taken from /Baeyens and McKinley 1989/.

The free energy and the enthalpy of formation for K_2Se(s) and MgSe(cr) have been selected from /Mills 1974/, because it is the only source of data available for these phases. Reaction data have been calculated from formation data.

All the formation parameters of α-USe_2, β-USe_2 and USe_3(s) are those selected in /Grenthe et al. 1992/. So, reaction data have been calculated internally.

The enthalpies of formation of the solids $FeSe_2$(s), MnSe(s), CuSe(s) and CdSe(s) are selected from /Mills 1974/, which is the only source available. From these values, Δ_rH^0 can be calculated.

The selected enthalpies of formation for Na_2Se(cr), KHSe(aq), NH_4HSe(aq), CaSe(s), SrSe(s), BaSe(s), FeSe(s), NiSe(s), Cu_2Se(s), Ag_2Se(s), PbSe(s) are those reported in /Wagman et al. 1982/, although no information on the original source of these values or their uncertainty are given. An uncertainty of 0.1 kJ/mole is applied in those cases. The values of Δ_rH^0 for each species are calculated internally.

The enthalpies of formation of the species K_2Se(aq) and $(NH_4)_2Se$(aq) have been calculated by selecting the entropy of the equivalent sulphides as they appear in /Wagman et al. 1982/. Reaction data on enthalpies have been calculated internally from formation data.

Finally, the enthalpies of formation of ZnSe(s) and HgSe(s) have been selected from /Vaughan and Craig 1978/, while the Δ_fH^0(SnSe(s)) has been selected from /Kubaschewski and Alcock 1979/.

Table 5-6. Thermodynamic data for aqueous complexes and solid phases of selenides.

Species	Reaction	$\log K^o$	Reference	$\Delta_r H^0$ (kJ/mole)	Reference
$K_2Se(aq)$	$2K^+ + HSe^- = K_2Se + H^+(aq)$	–14.70±1.42	/Wagman et al. 1982/	56.777±0.247	See text
$KHSe(aq)$	$K^+ + HSe^- = KHSe(aq)$	0.12±1.41	/Wagman et al. 1982/	–0.159±0.162	/Wagman et al. 1982/
$Na_2Se(aq)$	$2Na^+ + HSe^- = Na_2Se + H^+(aq)$	–14.96±1.41	/Wagman et al. 1982/		
$NH_4HSe(aq)$	$NH_3 + H^+ + HSe^- = NH_4HSe(aq)$	9.24±1.42	/Wagman et al. 1982/	–23.549±11.423	/Wagman et al. 1982/
$(NH_4)_2Se(aq)$	$2NH_3 + H^+ + HSe^- = (NH_4)_2Se(aq)$	3.44±1.42	/Wagman et al. 1982/	–45.002±0.668	See text
Species	**Reaction**	**$-\log K_s$**	**Reference**	**$\Delta_r H^0$ (kJ/mole)**	**Reference**
$Ag_2Se(s)$	$2Ag^+ + HSe^- = Ag_2Se(s) + H^+$	48.20±1.80	/Séby et al. 2001b/	–265.479±1.020	/Wagman et al. 1982/
$BaSe(s)$	$Ba^{2+} + HSe^- = BaSe(s) + H^+$	–35.86	/Elrashidi et al. 1987/	146.901±2.694	/Wagman et al. 1982/
$CaSe(s)$	$Ca^{2+} + HSe^- = CaSe(s) + H^+$	–25.53±1.43	/Wagman et al. 1982/	158.901±1.010	/Wagman et al. 1982/
$CdSe(s)$	$Cd^{2+} + HSe^- = CdSe(s) + H^+$	17.47±3.86	/Séby et al. 2001b/	–84.746±2.179	/Mills 1974/
$Cu_2Se(s)$	$2Cu^+ + HSe^- = Cu_2Se(s) + H^+$	46.80	/Séby et al. 2001b/	–218.639±0.143	/Wagman et al. 1982/
$CuSe(s)$	$Cu^{2+} + HSe^- = CuSe(s) + H^+$	35.00	/Séby et al. 2001b/	–122.639±4.303	/Mills 1974/
$FeSe(s)$	$Fe^{2+} + HSe^- = FeSe(s) + H^+$	8.00±4.00	/Séby et al. 2001b/	–1.199±0.520	/Wagman et al. 1982/
$FeSe_2(s)$	$Fe^{2+} + 2HSe^- = FeSe_2(s) + 2H^+ + 2e^-$	16.83	/Baeyens and McKinley 1989/	–46.398±12.562	/Mills 1974/
$HgSe(s)$	$Hg^{2+} + HSe^- = HgSe(s) + H^+$	43.30±1.22	/Séby et al. 2001b/	–229.623	/Vaughan and Craig 1978/
$K_2Se(s)$	$2K^+ + HSe^- = K_2Se(s) + H^+$	–26.27±7.49	/Mills 1974/	103.453±41.840	/Mills 1974/
$MgSe(s)$	$Mg^{2+} + HSe^- = MgSe(s) + H^+$	–21.41±7.48	/Mills 1974/	158.221±41.844	/Mills 1974/
$MnSe(s)$	$Mn^{2+} + HSe^- = MnSe(s) + H^+$	–2.50	/Séby et al. 2001b/	50.043±12.562	/Mills 1974/
$Na_2Se(s)$	$2Na^+ + HSe^- = Na_2Se(s) + H^+$	–23.00	/Elrashidi et al. 1987/	123.381±0.185	/Wagman et al. 1982/
$NiSe(s)$	$Ni^{2+} + HSe^- = NiSe(s) + H^+$	18.70	/Séby et al. 2001b/	–20.799±2.694	/Wagman et al. 1982/
$PbSe(s)$	$Pb^{2+} + HSe^- = PbSe(s) + H^+$	24.00±0.30	/Séby et al. 2001b/	–119.719±0.287	/Wagman et al. 1982/
$PdSe(s)$	$Pd^{2+} + HSe^- = PdSe(s) + H^+$	59.40	/Séby et al. 2001b/		
$SnSe(s)$	$Sn^{2+} + HSe^- = SnSe(s) + H^+$	24.40	/Séby et al. 2001b/	–95.700	/Kubaschewski and Alcock 1979/
$SrSe(s)$	$Sr^{2+} + HSe^- = SrSe(s) + H^+$	–32.41	/Elrashidi et al. 1987/	149.201±0.520	/Wagman et al. 1982/
$\alpha\text{-}USe_2$	$U^{4+} + 2HSe^- = \alpha\text{-}USe_2 + 2H^+$	–2.63±7.89	/Grenthe et al. 1992/	132.402±42.130	/Grenthe et al. 1992/
$\beta\text{-}USe_2$	$U^{4+} + 2HSe^- = \beta\text{-}USe_2 + 2H^+$	–2.47±7.92	/Grenthe et al. 1992/	132.402±42.130	/Grenthe et al. 1992/
$USe_3(s)$	$UO_2^{2+} + 3HSe^- + H^+ = USe_3(s) + 2H_2O$	18.46±7.60	/Grenthe et al. 1992/	–52.358±42.028	/Grenthe et al. 1992/
$ZnSe(s)$	$Zn^{2+} + HSe^- = ZnSe(s) + H^+$	15.37±1.91	/Séby et al. 2001b/	–21.501	/Vaughan and Craig 1978/

5.3.2 Se*(IV)*

We have based our selection mainly in /Séby et al. 2001b/ and /Elrashidi et al. 1987/. As in the previous case, when those authors present a logK calculated from /Wagman et al. 1982/ we have selected the original formation data of /Wagman et al. 1982/. In those cases reaction parameters have been calculated internally. When possible, experimental data have been selected. In some cases we have selected a mean value of the stability constants reported in the quoted reference. The logK value of $CuSeO_3{\cdot}2H_2O$ has been selected from /Smith and Martell 1976/. /Essington 1988/ conducted estimations of the formation parameters of some selenites. However, in agreement with the comments in /Séby et al. 2001b/, we have disregarded those values given that they result in general overestimations of the stability of these solids.

The selected enthalpies of formation for all the species that data is reported come from /Wagman et al. 1982/ with one exception, the entalphy of formation of $(UO_2)SeO_3$(cr) coming from /Grenthe et al. 1992/. There is no information to obtain $\Delta_f H^0$ for the rest of the species. Although it seems that we can use the entropy values of the equivalent sulphites to calculate the enthalpy of formation of these selenites, the lack of information on the entropies of the equivalent sulphites, makes it impossible.

Other solids of Se(IV) included are the oxides: SeO_2(s), Se_2O_5(s), and $SeCl_4$(s). The free energy and the enthalpy of formation we have selected come from the compilation of /Mills 1974/. The selected enthalpies of formation for SeO_2(cr) and $SeCl_4$(cr) are the values selected in /Grenthe et al. 1992/.

Data selected are presented in Table 5-7 (aqueous complexes) and Table 5-8 (solid phases). As in the previous case, references are also included in the table for the sake of clarify.

Table 5-7. Thermodynamic data for aqueous complexes of selenites and selenium(IV) oxides.

Species	Reaction	Logβ⁰	Reference	$\Delta_r H^0$ kJ/mole	Reference
$Ag(SeO_3)_2^{3-}$	$Ag^+ + 2SeO_3^{2-} = Ag(SeO_3)_2^{3-}$	3.76±0.05	/Séby et al. 2001b/		
$Ag_2SeO_3(aq)$	$2Ag^+ + SeO_3^{2-} = Ag_2SeO_3(aq)$	1.45±0.14	/Wagman et al. 1982/	–0.287±0.214	/Wagman et al. 1982/
$AgSeO_3^-$	$Ag^+ + SeO_3^{2-} = Ag(SeO_3)^-$	3.23±0.12	/Séby et al. 2001b/		
$CaSeO_3(aq)$	$Ca^{2+} + SeO_3^{2-} = CaSeO_3(aq)$	3.17	/Séby et al. 2001b/		
$CdSeO_3(aq)$	$Cd^{2+} + SeO_3^{2-} = CdSeO_3(aq)$	1.42±0.18	/Wagman et al. 1982/	0.213±0.616	/Wagman et al. 1982/
$Cd(SeO_3)_2^{2-}$	$Cd^{2+} + 2SeO_3^{2-} = Cd(SeO_3)_2^{2-}$	6.78	/Séby et al. 2001b/		
$CuSeO_3(aq)$	$Cu^{2+} + SeO_3^{2-} = CuSeO_3(aq)$	1.37±0.30	/Wagman et al. 1982/		
$FeHSeO_3^{2+}$	$Fe^{3+} + SeO_3^{2-} + H^+ = Fe(HSeO_3)^{2+}$	11.57±0.22	/Séby et al. 2001b/		
$FeSeO_3^+$	$Fe^{3+} + SeO_3^{2-} = FeSeO_3^+$	11.15±0.11	/Séby et al. 2001b/		
$Hg(SeO_3)_2^{2-}$	$Hg^{2+} + 2SeO_3^{2-} = Hg(SeO_3)_2^{2-}$	14.11	/Séby et al. 2001b/		
$K_2SeO_3(aq)$	$2K^+ + SeO_3^{2-} = K_2SeO_3(aq)$	1.74±0.13	/Wagman et al. 1982/	–0.327±0.214	/Wagman et al. 1982/
$MgSeO_3(aq)$	$Mg^{2+} + SeO_3^{2-} = MgSeO_3(aq)$	2.87	/Séby et al. 2001b/		
$Na_2SeO_3(aq)$	$2Na^+ + SeO_3^{2-} = Na_2SeO_3(aq)$	1.48±0.13	/Wagman et al. 1982/	0.373±0.185	/Wagman et al. 1982/
$NaHSeO_3(aq)$	$Na^+ + H^+ + SeO_3^{2-} = NaHSeO_3(aq)$	8.77±0.13	/Wagman et al. 1982/	–5.137±0.117	/Wagman et al. 1982/
$(NH_4)_2SeO_3(aq)$	$2NH_3 + SeO_3^{2-} + 2H^+ = (NH_4)_2SeO_3(aq)$	19.89±0.17	/Wagman et al. 1982/	–102.467±1.319	/Wagman et al. 1982/
$NH_4HSeO_3(aq)$	$NH_3 + SeO_3^{2-} + 2H^+ = NH_4HSeO_3(aq)$	18.00±0.14	/Wagman et al. 1982/	–56.697±1.102	/Wagman et al. 1982/
$PbSeO_3(aq)$	$Pb^{2+} + SeO_3^{2-} = PbSeO_3(aq)$	5.41	/Séby et al. 2001b/		
$ZnSeO_3(aq)$	$Zn^{2+} + SeO_3^{2-} = ZnSeO_3(aq)$	1.43±0.14	/Wagman et al. 1982/	–0.617±0.245	/Wagman et al. 1982/

Table 5-8. Thermodynamic data on solid phases of selenites and selenium(IV) oxides and chlorides.

Species	Reaction	$-\log K_s$	Reference	$\Delta_r H^0$ kJ/mole	Reference
$Ag_2SeO_3(s)$	$2Ag^+ + SeO_3^{2-} = Ag_2SeO_3(s)$	15.15±0.41	/Séby et al. 2001b/	–67.687±0.214	/Wagman et al. 1982/
$BaSeO_3(s)$	$Ba^{2+} + SeO_3^{2-} = BaSeO_3(s)\cdot$	6.57	/Séby et al. 2001b/	3.393±2.504	/Wagman et al. 1982/
$Ca(SeO_3)\cdot 2H_2O(cr)$	$Ca^{2+} + SeO_3^{2-} + 2H_2O = CaSeO_3\cdot 2H_2O(cr)$	7.06±0.22	/Wagman et al. 1982/		
$CaSeO_3\cdot H_2O(s)$	$Ca^{2+} + SeO_3^{2-} + H_2O = CaSeO_3\cdot H_2O(s)$	7.76±0.18	/Séby et al. 2001b/		
$CdSeO_3(s)$	$Cd^{2+} + SeO_3^{2-} = CdSeO_3(s)$	10.29±0.18	/Wagman et al. 1982/	9.813±0.616	/Wagman et al. 1982/
$CuSeO_3(s)$	$Cu^{2+} + SeO_3^{2-} = CuSeO_3(s)$	8.42	/Séby et al. 2001b/		
$CuSeO_3\cdot 2H_2O(s)$	$Cu^{2+} + SeO_3^{2-} + 2H_2O = CuSeO_3\cdot 2H_2O(s)$	7.78	/Smith and Martell 1976/		
$Fe_2(SeO_3)_3\cdot 6H_2O(s)$	$2Fe^{3+} + 3SeO_3^{2-} + 6H_2O = Fe_2(SeO_3)_3\cdot 6H_2O(s)$	41.58±0.11	/Séby et al. 2001b/		
$Hg_2SeO_3(s)$	$Hg_2^{2+} + SeO_3^{2-} = Hg_2SeO_3(s)$	15.70±0.16	/Wagman et al. 1982/		
$HgSeO_3(s)$	$Hg^{2+} + SeO_3^{2-} = HgSeO_3(s)$	15.39±0.14	/Wagman et al. 1982/		
$MgSeO_3\cdot 6H_2O$	$Mg^{2+} + SeO_3^{2-} + 6H_2O = MgSeO_3\cdot 6H_2O$	5.36	/Séby et al. 2001b/	–15.877±0.654	/Wagman et al. 1982/
$MgSeO_3(cr)$	$Mg^{2+} + SeO_3^{2-} = MgSeO_3(cr)$	7.56±0.40	/Séby et al. 2001b/	76.003±0.608	/Wagman et al. 1982/
$MnSeO_3(cr)$	$Mn^{2+} + SeO_3^{2-} = MnSeO_3(cr)$	7.11±0.31	/Séby et al. 2001b/		
$NiSeO_3(cr)$	$Ni^{2+} + SeO_3^{2-} = NiSeO_3(cr)$	5.15±0.15	/Séby et al. 2001b/		
$PbSeO_3(s)$	$Pb^{2+} + SeO_3^{2-} = PbSeO_3(s)$	12.12±0.62	/Elrashidi et al. 1987/	–29.327±0.287	/Wagman et al. 1982/
$Se_2O_5(cr)$	$SeO_3^{2-} + SeO_4^{2-} + 4H^+ = Se_2O_5(cr) + 2H_2O$	–8.05	/Mills 1974/	123.302	/Mills 1974/
$SeO_2(cr)$	$SeO_3^{2-} + 2H^+ = SeO_2(cr) + H_2O$	8.24±0.38	/Mills 1974/	–1.736±2.095	/Mills 1974/
$SeCl_4(cr)$	$SeO_3^{2-} + 4Cl^- + 6H^+ = SeCl_4(cr) + 3H_2O$	–12.91	/Mills 1974/	131.324	/Mills 1974/
$SrSeO_3(cr)$	$Sr^{2+} + SeO_3^{2-} = SrSeO_3(cr)$	6.10±1.00	/Elrashidi et al. 1987/	12.393±0.520	/Wagman et al. 1982/
$Th(SeO_3)_2(s)$	$Th^{4+} + 2SeO_3^{2-} = Th(SeO_3)_2(s)$	19.87	/Séby et al. 2001b/		
$UO_2SeO_3(cr)$	$UO_2^{2+} + SeO_3^{2-} = UO_2SeO_3(cr)$	10.42	/Séby et al. 2001b/	6.193±2.748	/Grenthe et al. 1992/
$ZnSeO_3\cdot H_2O(s)$	$Zn^{2+} + SeO_3^{2-} + H_2O = ZnSeO_3\cdot H_2O(s)$	7.70±0.24	/Séby et al. 2001b/	17.513±0.248	/Wagman et al. 1982/

5.3.3 Se*(VI)*

As selenite, there is a variety of selenates reported in the literature. We have based our selection, as in the other selenium species, on the compilation of /Séby et al. 2001b/. As in the case of selenites and selenides, for some of the data the original reference quoted is /Wagman et al. 1982/ when reporting $\log K_r^0$ when, data in the NBS tables are of formation and not of reaction. In those cases, we have selected the original data of /Wagman et al. 1982/. The solely stability constant taken from another source has been the one of $ZnSeO_4(s)$ /Sillén and Mertell 1964/.

The selected enthalpies of formation for the species $NaHSeO_4(aq)$, $Na_2SeO_4(aq)$, $Na_2SeO_4(cr)$, $K_2SeO_4(aq)$, $KHSeO_4(aq)$, $K_2SeO_4(cr)$, $MgSeO_4{\cdot}6H_2O(s)$, $CaSeO_4{\cdot}2H_2O(s)$, $SrSeO_4(aq)$, $BaSeO_4(aq)$, $Ag_2SeO_4(aq)$, $Ag_2SeO_4(cr)$, $ZnSeO_4(aq)$, $ZnSeO_4(cr)$, $CdSeO_4(aq)$, $UO_2SeO_4(aq)$ and $PbSeO_4(s)$ come from /Wagman et al. 1982/.

There is no information to obtain $\Delta_f H^o$ for the rest of the species. However, the very good correlation between the entropies of selenates and of the equivalent sulphates (Figure 5-2), makes it possible to estimate an entropy value for those selenates for which there is no entropy value available. Enthalpies have been calculated internally by means of entropies and Gibbs free energies values.

The equation obtained with this correlation (equation Se1) allows us to approximate an entropy value for the species $MgSeO_4(aq)$, $CaSeO_4(aq)$, $FeSeO_4(aq)$, $NiSeO_4(aq)$ and $NiSeO_4{\cdot}6H_2O$, using the entropy of formation of their equivalent sulphates.

S_f^0(Selenate) = $(1.04\pm0.07)\cdot S_f^0$(Sulphate)+(16.5 ± 13.8) J/(K mole)equation Se1.

For the NH_4^+ selenates we have selected entropy data of /Wagman et al. 1984/.

There is another solid included in this compilation, the Se(IV) oxide (SeO_3 s). The free energy and the enthalpy of formation for this oxide come from the compilation of /Mills 1974/, which is the only available source of data for this species.

Selected data are shown in Table 5-9 (aqueous complexes) and Table 5-10 (solid phases).

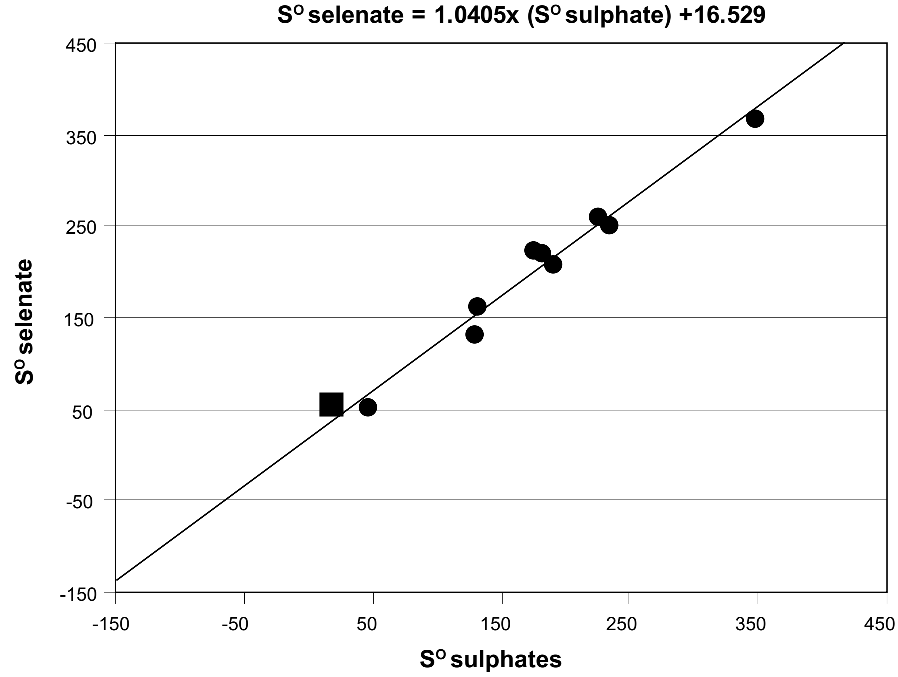

Figure 5-2. *Correlation between the selected entropies for sulphates and entropies for the equivalent selenates. The square represents the* $S_f^0(SO_4^{2-})/S_f^0(SeO_4^{2-})$.

Table 5-9. Thermodynamic data for aqueous complexes of selenates.

Species	Reaction	logβ⁰	Reference	Δ_rH^0 (kJ/mole)	Reference
$Ag_2SeO_4(aq)$	$2Ag^{+}+SeO_4^{2-} = Ag_2SeO_4(aq)$	–0.07±0.19	/Wagman et al. 1982/	–0.331±0.214	/Wagman et al. 1982/
$CaSeO_4(aq)$	$Ca^{2+}+SeO_4^{2-} = CaSeO_4(aq)$	2.00	/Séby et al. 2001b/	–16.314	See text
$CdSeO_4(aq)$	$Cd^{2+}+SeO_4^{2-} = CdSeO_4(aq)$	–0.09±0.22	/Wagman et al. 1982/	0.169±0.616	/Wagman et al. 1982/
$FeSeO_4(aq)$	$Fe^{2+}+SeO_4^{2-} = FeSeO_4(aq)$	2.71	/Séby et al. 2001b/	4.762	See text
$K_2SeO_4(aq)$	$2K^{+}+SeO_4^{2-} = K_2SeO_4(aq)$	0.23±0.18	/Wagman et al. 1982/	–0.271±0.214	/Wagman et al. 1982/
$KHSeO_4(aq)$	$K^{+}+H^{+}+SeO_4^{2-} = KHSeO_4(aq)$	2.00±0.18	/Wagman et al. 1982/	17.389±0.162	/Wagman et al. 1982/
$MgSeO_4(aq)$	$Mg^{2+}+SeO_4^{2-} = MgSeO_4(aq)$	2.20	/Séby et al. 2001b/	–19.692	See text
$MnSeO_4(aq)$	$Mn^{2+}+SeO_4^{2-} = MnSeO_4(aq)$	2.43±0.01	/Séby et al. 2001b/		
$Na_2SeO_4(aq)$	$2Na^{+}+SeO_4^{2-} = Na_2SeO_4(aq)$	–0.05±0.18	/Wagman et al. 1982/	0.329±0.185	/Wagman et al. 1982/
$NaHSeO_4(aq)$	$Na^{+}+H^{+}+SeO_4^{2-} = NaHSeO_4(aq)$	1.85±0.18	/Wagman et al. 1982/	17.789±0.154	/Wagman et al. 1982/
$NH_4HSeO_4(aq)$	$NH_3+SeO_4^{2-}+2H^{+} = NH_4HSeO_4(aq)$	11.10±0.19	/Wagman et al. 1982/	–33.832±0.357	See text
$(NH_4)_2SeO_4(aq)$	$2NH_3+SeO_4^{2-}+2H^{+} = (NH_4)_2SeO_4(aq)$	18.38±0.21	/Wagman et al. 1982/	–102.533±0.668	See text
$NiSeO_4(aq)$	$Ni^{2+}+SeO_4^{2-} = NiSeO_4(aq)$	2.67±0.03	/Séby et al. 2001b/	–21.624±4.877	See text
$UO_2SeO_4(aq)$	$UO_2^{2+}+SeO_4^{2-} = UO_2SeO_4(aq)$	2.64±0.01	/Séby et al. 2001b/	19.949±1.503	/Wagman et al. 1982/
$Zn(SeO_4)_2^{2-}$	$Zn^{2+}+2SeO_4^{2-} = Zn(SeO_4)_2^{2-}$	3.01	/Séby et al. 2001b/		
$ZnSeO_4(aq)$	$Zn^{2+}+SeO_4^{2-} = ZnSeO_4(aq)$	2.39±0.20	/Séby et al. 2001b/	–0.561±0.245	/Wagman et al. 1982/

Table 5-10. Solid phases of selenates and selenium(VI) oxides.

Species	Reaction	$-\log K_s^0$	Reference	$\Delta_r H^0$ kJ/mole	Reference
$Ag_2SeO_4(s)$	$2Ag^+ + SeO_4^{2-} = Ag_2SeO_4(s)$	8.91±1.66	/Séby et al. 2001b/	–32.931±0.214	/Wagman et al. 1982/
$BaSeO_4(cr)$	$Ba^{2+} + SeO_4^{2-} = BaSeO_4(cr)$	7.38±0.08	/Séby et al. 2001b/	–12.451±2.504	/Wagman et al. 1982/
$CaSeO_4 \cdot 2\ H_2O$	$Ca^{2+} + SeO_4^{2-} + 2H_2O = CaSeO_4 \cdot 2H_2O$	3.09	/Séby et al. 2001b/	7.109±1.013	/Wagman et al. 1982/
$K_2SeO_4(cr)$	$2K^+ + SeO_4^{2-} = K_2SeO_4(cr)$	–0.66±0.18	/Wagman et al. 1982/	–6.591±0.189	/Wagman et al. 1982/
$MgSeO_4 \cdot 6H_2O$	$Mg^{2+} + SeO_4^{2-} + 6H_2O = MgSeO_4 \cdot 6H_2O$	1.13	/Séby et al. 2001b/	2.129±0.662	/Wagman et al. 1982/
$Na_2SeO_4(cr)$	$2Na^+ + SeO_4^{2-} = Na_2SeO_4(cr)$	0.89	/Elrashidi et al. 1987/	10.829±0.185	/Wagman et al. 1982/
$NiSeO_4 \cdot 6H_2O$	$Ni^{2+} + SeO_4^{2-} + 6H_2O = NiSeO_4 \cdot 6H_2O$	1.49	/Séby et al. 2001b/	–2.491	See text
$PbSeO_4(s)$	$Pb^{2+} + SeO_4^{2-} = PbSeO_4(s)$	6.84	/Séby et al. 2001b/	–10.971±0.287	/Wagman et al. 1982/
$SeO_3(cr)$	$SeO_4^{2-} + 2H^+ = SeO_3(cr) + H_2O$	–19.24	/Mills 1974/	143.030	/Mills 1974/
$SrSeO_4(s)$	$Sr^{2+} + SeO_4^{2-} = SrSeO_4(s)$	4.40	/Séby et al. 2001b/	7.349±0.520	/Wagman et al. 1982/
$ZnSeO_4(s)$	$Zn^{2+} + SeO_4^{2-} = ZnSeO_4(s)$	13.40	/Sillén and Martell 1964/	88.139±0.245	/Wagman et al. 1982/

6 Zirconium

Thermodynamic data of free ion Zr^{4+} and elemental Zr as well as thermodynamic data of aqueous hydroxides, are deduced from solubility data of Zr oxides and hydroxides. The NAGRA-PSI 01/01 database /Hummel et al. 2002/ takes into account the solubility results of different studies. They consider data of /Bilinski et al. 1966/, but discarded them because the experiments involved colloid precipitation. /Hummel et al. 2002/ relied on data of /Sheka and Pevzner 1960/, /Kovalenko and Bagdasarov 1961/ and /Pouchon et al. 2001/ (data also included in /Curti and Degueldre 2002/). They accepted the hydrolysis system presented by /Baes and Mesmer 1976/, where only the species $Zr(OH)^{3+}$, $Zr(OH)_4(aq)$, $Zr(OH)_5^-$ and ZrO(cr) were considered, because it was able to reproduce the experimental results (Figure 6-1).

However, there are more studies related to the solubility of Zr oxides and hydroxides /Larsen and Gammill 1950/, /Thomason and Williams 1992/ and /Källvenius et al. 2002/. As occurred with /Bilinski et al. 1966/, data from /Larsen and Gammill 1950/ are affected by colloid precipitation. When taking into account data of /Thomason and Williams 1992/ and /Källvenius et al. 2002/, the hydrolysis system selected by /Hummel et al. 2002/ and coming from /Baes and Mesmer 1976/ does not fit the experimental results (Figure 6-2).

Thus, it is evident that a new and more complete analysis of the hydrolysis system of Zr should be done. We have conducted an analysis of these data and the results are published in an ANDRA internal report /Domènech et al. 2004/. The selected hydrolysis system includes the species $Zr(OH)^{3+}$, $Zr(OH)_4(aq)$, $Zr(OH)_5^-$ and $Zr(OH)_6^{2-}$ and considers the precipitation of two different amorphous Zr hydroxides: $Zr(OH)_4(am)$ and $Zr(OH)_4(s)$ as solubility limiting phases. This system reproduces the available solubility data (Figure 6-3).

In addition the crystalline Zirconium oxide has been included in the database, although it will not be used in the solubility calculations, given the unlikely precipitation of this solid versus the readiness of precipitation of more amorphous phases.

All values included in the database are those presented in /Domènech et al. 2004/ and in Table 6-1.

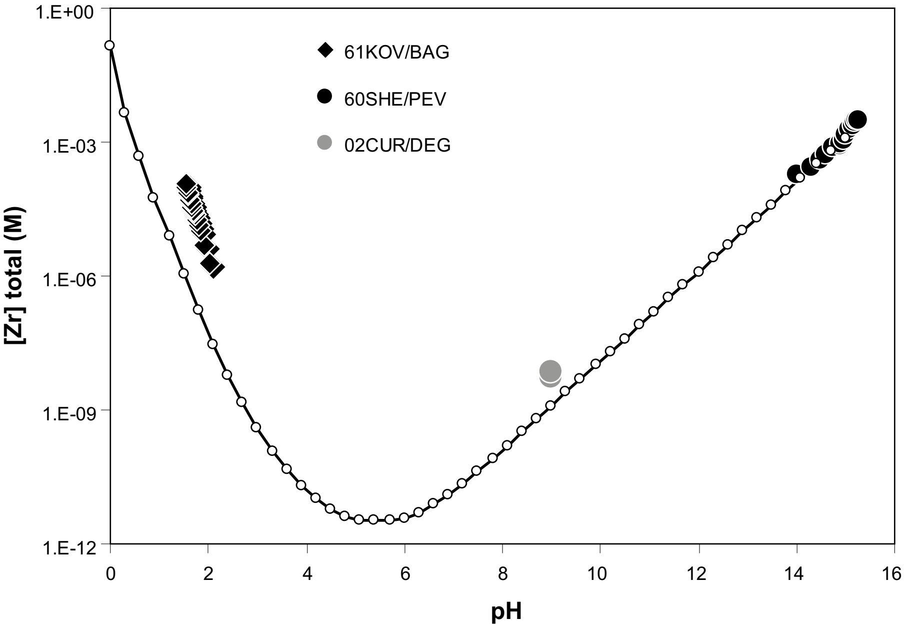

Figure 6-1. *Solubility curve of ZrO_2 using the constants of /Baes and Mesmer 1976/.*

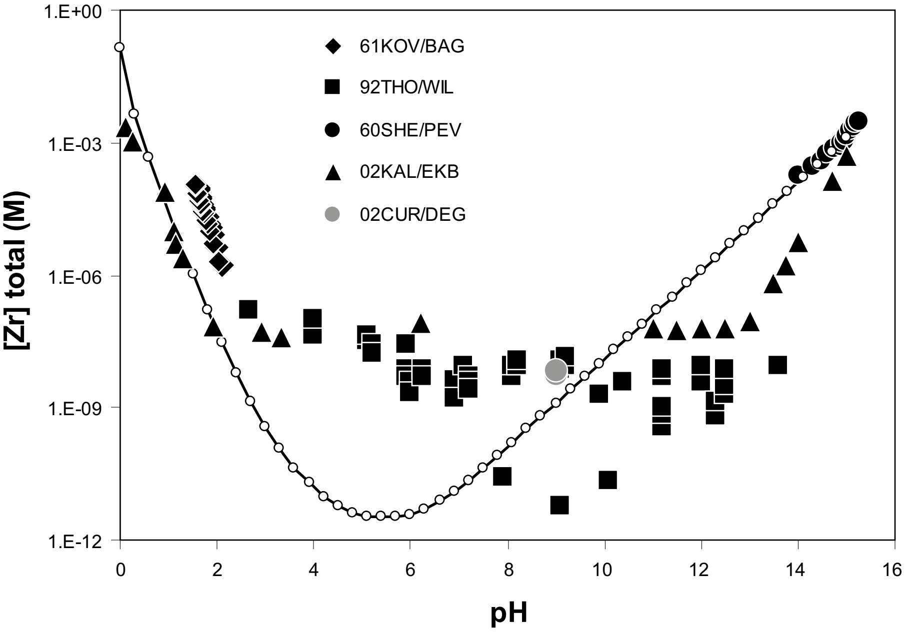

Figure 6-2. *Solubility curve of* $ZrO_2(c)$ *using the constants of /Baes and Mesmer 1976/.*

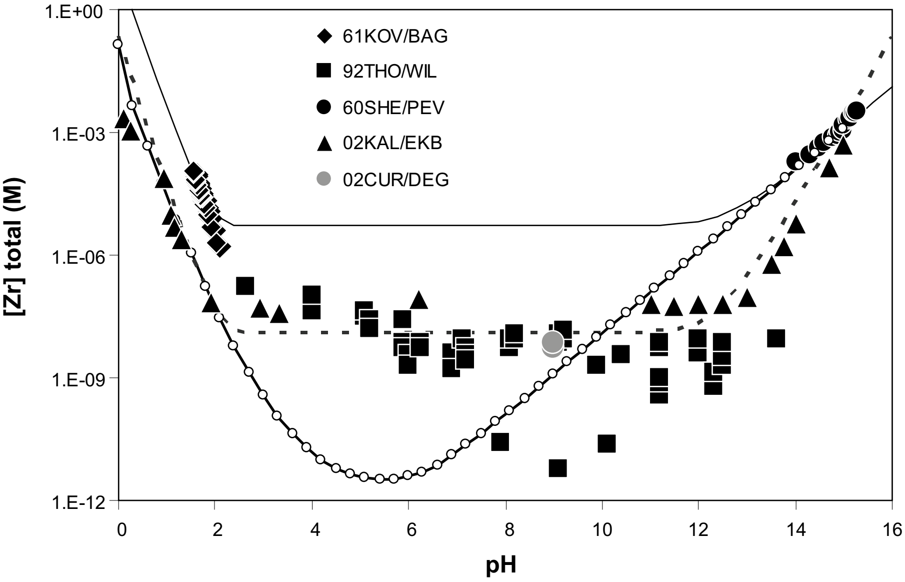

Figure 6-3. *Continuous line: solubility curve of* $Zr(OH)_4(am)$ *obtained by using the constants selected in /Domènech et al. 2004/. Dashed line: solubility curve of* $Zr(OH)_4(s)$ *using the constants selected in /Domènech et al. 2004/. Line+open circles pattern: Solubility curve of* $ZrO_2(c)$ *obtained by using the constants of Baes and /Mesmer 1976/.*

Table 6-1. Selected data for the Zr hydrolysis scheme.

Reaction	**log·β⁰**
$Zr^{4+}+H_2O = Zr(OH)^{3+}+H^+$	0.27±0.13
$Zr^{4+}+2H_2O = Zr(OH)_2^{2+}+2H^+$	≤2.7
$Zr^{4+}+3H_2O = Zr(OH)^{3+}+3H^+$	≤–4.5
$Zr^{4+}+4H_2O = Zr(OH)_4(aq)+4H^+$	–5.13±0.36
$Zr^{4+}+5H_2O = Zr(OH)_5^-+5H^+$	–17.97±0.15
$Zr^{4+}+6H_2O = Zr(OH)_6^{2-}+6H^+$	–31.96±0.35
$4Zr^{4+}+15H_2O = Zr_4(OH)_{15}^++15H^+$	0.04±0.52
$4Zr^{4+}+16H_2O = Zr_4(OH)_{16}+16H^+$	–4.36±0.61
Reaction	**–log·K_s**
$Zr^{4+}+4H_2O = Zr(OH)_4(am)+4H^+$	0.14±0.13
$Zr^{4+}+4H_2O = Zr(OH)_4(s)+4H^+$	2.77±0.13
$Zr^{4+}+2H_2O = ZrO_2(c)+4H^+$	7.54

7 Niobium

Niobium data included in the NAGRA-PSI 01/01 /Hummel et al. 2002/ thermodynamic database are selected. No uncertainties on those data are reported in the mentioned compilation.

The master species is the Nb(V) species NbO_3^-.

Data for niobium hydrolysis species, $Nb(OH)_4^+$ and $Nb(OH)_5(aq)$, and the solid oxides, $Nb_2O_5(s)$ and $NbO_2(s)$, are based on formation parameters compiled in the NBS table /Wagman et al. 1982/.

No uncertainties are reported in the NBS compilation and therefore we have assigned the uncertainties associated to the formation data by assuming that errors arise in the last significant digit.

Note that all formation data referred to NbO_3^-, $Nb(OH)_4^+$ and $Nb(OH)_5(aq)$ included in the NBS tables apply to I = 1.0 mol/dm^3. The stability constants included in the NAGRA-PSI 01/01 database for $Nb_2O_5(s)$ and $NbO_2(s)$ have been obtained from their respective Gibbs energies of formation and the formation data selected for NbO_3^- (which are referred to I = 1.0 mol/dm^3).

The selected stabilities for Nb aqueous and solid species are presented in Table 7-1.

Neither enthalpies nor entropies are published in the open literature.

Table 7-1. Thermodynamic data selected for Nb species.

Species	**$\Delta_f G^0$ (kJ/mole)**	**Reaction**	**$\log\beta^0$**
NbO_3^-	–932.100±0.100 (I = 1M)		–
$Nb(OH)_4^+$	–1208.6±0.100 (I = 1M)	$NbO_3^-+H_2O+2H^+ = Nb(OH)_4^+$	6.90±0.03(I = 1M)
$Nb(OH)_5(aq)$	–1448.3±0.100 (I = 1M)	$NbO_3^-+2H_2O+H^+ = Nb(OH)_5(aq)$	7.34±0.03(I = 1M)
Species	**$\Delta_f G^0$ (kJ/mole)**	**Reaction**	**$-\log{}^*K_s$**
$Nb_2O_5(s)$	–1766.0±0.100	$2NbO_3^-+2H^+ = Nb_2O_5(s)+H_2O$	24.34±0.04
$NbO_2(s)$	–740.5±0.100	$NbO_3^-+2H^++e^- = NbO_2(s)+H_2O$	7.98±0.03

8 Technetium

Thermodynamic data of inorganic compounds and complexes of technetium reported in the NAGRA-PSI 01/01 database /Hummel et al. 2002/ are taken from NEA selection of /Rard et al. 1999/. No changes have been introduced to the selected data.

We have additionally considered other species from the /Rard et al. 1999/ review that were not included in the NAGRA-PSI 01/01 database on the basis of their irrelevance in environments of interest for underground repositories of nuclear waste. The inclusion of these data, though, provides a more complete database and it is the reasoning behind our decision of including them.

These complexes are the aqueous TcO_4^{2-}, and the solids TcO_2(cr), Tc_2O_7(cr), $Tc_2O_7 \cdot H_2O$(cr), $KTcO_4$(cr) and $NaTcO_4 \cdot 4H_2O$(cr). The selected equilibrium constants and selected Δ_rH^0 for the different reactions are listed in Table 8-1.

Table 8-1. New thermodynamic data for Technetium complexes from /Rard et al. 1999/ introduced in the database.

Reaction	**logK^0**	**Δ_rH^0 (kJ mol–1)**
TcO_4^-+e$^-$ = TcO_4^{2-}	–10.80±0.80	Not available
Reaction	**–log*K$_s$**	**Δ_rH^0 (kJ mol–1)**
2 TcO_4^-+2H$^+$ = Tc_2O_7(cr)+H_2O	–15.31±3.82	46.470±21.285
2 TcO_4^-+2H$^+$ = $Tc_2O_7 \cdot H_2O$(cr)	–14.11±3.81	44.654±21.288
Reaction	**–logK$_s$**	**Δ_rH^0 (kJ mol–1)**
$TcO(OH)_2$ = TcO_2(cr)+H_2O	12.39±2.58	Not available
TcO_4^-+ K$^+$ = $KTcO_4$(cr)	2.28±1.28	–53.560±10.748
TcO_4^-+ Na$^+$+4 H_2O = $NaTcO_4 \cdot 4H_2O$(cr)	–0.79±0.04	Not available

9 Nickel

The thermodynamics of nickel is one of the topics of the Phase II of the OECD NEA Thermodynamic Database. This review has appeared after the closing date of the literature review here reported /Gamsjäger et al. 2005/ and, therefore, has not been included in the present review. The NAGRA-PSI 01/01 TDB has postponed a detailed discussion of nickel data, although evaluates some topics in detail; i.e. nickel hydrolysis, carbonate and sulphide compounds and nickel amine complexation. This compilation takes the rest of nickel data from the previous one /Pearson et al. 1992/ with no further analysis. The reference database used for nickel in the current work is the NAGRA-PSI 01/01 TDB, although some of the changes included are discussed below.

9.1 Master species

The master species is the divalent cation Ni^{2+}. Thermodynamic data for Ni^{2+} species have been selected from /Plyasunova et al. 1998/ in agreement with the NAGRA-PSI 01/01 TDB, values are given in Table 9-1.

The absolute entropy of nickel metal is taken from CODATA, as reported in /Plyasunova et al. 1998/ with a value of 29.87±0.21 J/mole·K, reaction parameters have been calculated internally from formation parameters. Thermodynamic data are reported in Table 9-2.

9.2 Hydrolysis of nickel, aqueous complexes and solid compounds

Selected thermodynamic data for aqueous nickel hydroxide complexes as well as for the solid nickel(II) hydroxide are in agreement with the NAGRA-PSI 01/01 TDB. Stability constants as well as enthalpies of reaction have been selected from the work of /Plyasunova et al. 1998/. Reaction enthalpies of $Ni(OH)_2(aq)$, $Ni(OH)_3^-$ and $Ni(OH)_2(s)$ have been calculated internally by using formation data from the same reference. The only value taken from a different source is the entropy of the complex $Ni(OH)_4^{2-}$, which is based on an estimation of /Beverskog and Puigdomènech 1997/ (S_f^0 = 252 J/mole·K). Reported values are given in Table 9-3.

Table 9-1. Thermodynamic data for Ni^{2+}.

Δ_fG^0 (kJ/mole)	Δ_fH^0 (kJ/mole)	S^0_f (J/mole·K)
–45.500±3.400	–54.100±2.500	–130.3±3.0

Table 9-2. Thermodynamic data for metallic nickel different from NAGRA-PSI 01/01 TDB.

Species	Reaction	logK⁰	Δ_rH^0 (kJ/mole)
Ni(m)	$Ni^{2+}+2e^- = Ni(m)$	–7.97±0.60	54.100±2.500

Table 9-3. Thermodynamic data for Ni^{2+} hydrolysis complexes different from NAGRA-PSI 01/01 TDB.

Reaction	$\log{}^*\beta^0$	Δ_rH^0 (kJ/mole)
$Ni^{2+}+H_2O = NiOH^{+}+H^{+}$	–9.50±0.36	50.000±21.000
$Ni^{2+}+2H_2O = Ni(OH)_2(aq)+2H^{+}$	–18.00±1.00	85.760±13.238
$Ni^{2+}+3H_2O = Ni(OH)_3^{-}+3H^{+}$	–29.70±1.50	120.590±18.173
$Ni^{2+}+4H_2O = Ni(OH)_4^{2-}+4H^{+}$	–44.90±0.60	136.391
$2Ni^{2+}+H_2O = Ni_2OH_3^{+}+H^{+}$	–9.80±1.20	35.000±17.000
$4Ni^{2+}+4H_2O = Ni_4(OH)_4^{4+}+4H^{+}$	–27.90±1.00	170.000±17.000
Reaction	**$-\log{}^*K_s$**	**Δ_rH^0 (kJ/mole)**
$Ni^{2+}+2H_2O = Ni(OH)_2(s)+2H^{+}$	–10.50±0.50	78.837±4.223

No other solid phases are reported in the recent NAGRA-PSI 01/01 compilation the reason being mainly the questionable quality of thermodynamic data. Nevertheless, we prefer to include a preliminary selection of the data reported in the literature in the actual compilation taking into account that these thermodynamic parameters will need a further revision in the next future in agreement with the publication of the NEA review team. In the meantime, it will be necessary to take these parameters carefully. Reaction parameters for the solid phases reported in Table 9-4 have been calculated from formation parameters tabulated in different compilations. ΔG_f^0 for bunsenite and trevorite have been taken from /Holmes et al. 1986/ and /Wagman et al. 1969/ respectively while S_f^0 have been both taken from /Robie and Hemingway 1978/. Formation parameters for Ni_2O_3 and Ni_3O_4 solid phases have been taken from the NBS compilations /Wagman et al. 1969/. Reaction parameters are reported in Table 9-4.

The calculated solubilities of the nickel solid oxides in function of pH are shown in Figure 9-1. Left-hand side figure corresponds to calculations conducted in deionised water and under oxidant conditions (pe = 8.5) and the right-hand side picture shows the calculation conducted at fixed pH (8) as a function of pe. In this figure we may compare the stability of the different solid phases selected.

Table 9-4. Thermodynamic data for nickel pure and mixed oxides different from NAGRA-PSI 01/01 TDB.

Reaction	$-\log{}^*K_s^0$	Δ_rH^0 (kJ/mole)
$Ni^{2+}+H_2O = NiO(s)(Bunsenite)+2H^{+}$	–12.41±0.61	100.012± 3.588
$Ni^{2+}+2Fe^{3+}+4H_2O = Fe_2NiO_4(Trevorite)+ 8H^{+}$	–9.40±0.73	214.413±6.253
$2Ni^{2+}+3H_2O = Ni_2O_3(s)+6H^{+}+2e^{-}$	–58.29	414.839
$3Ni^{2+}+4H_2O = Ni_3O_4(s)+8H^{+}+2e^{-}$	–65.36	486.888

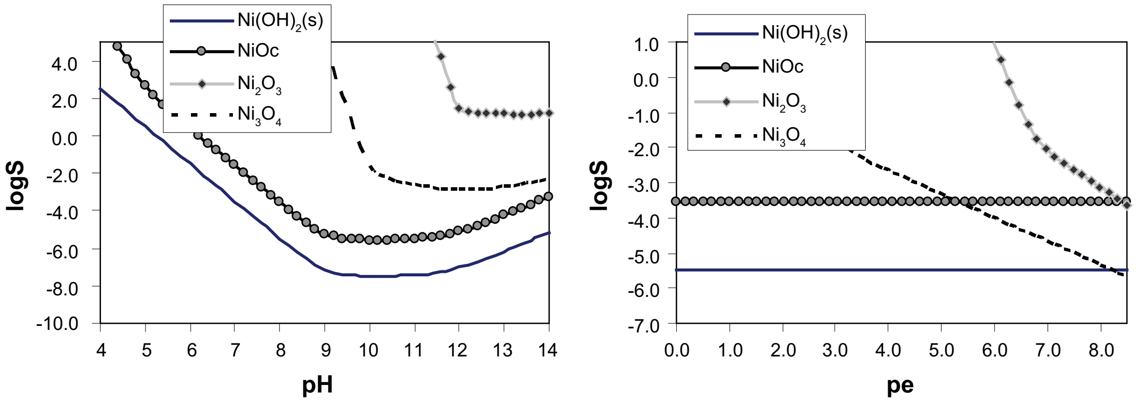

Figure 9-1. *Solubility of several nickel oxide, in deionised water. As a function of pH (pe=–2), left hand and as function of pe (pH=8), right hand. S in mole/dm^3.*

9.3 Group 14

9.3.1 Carbonate compounds

The nickel carbonate selection is based on the NAGRA-PSI 01/01 TDB. The reported values are shown in Table 9-5.

$NiCO_3$(aq) reaction enthalpy is based on the estimation of the reaction entropy according to the /Sverjensky et al. 1997/ approach. The selected thermodynamic parameter is Δ_rH^0 = 4.687±6.491 KJ/mole.

9.3.2 Silicate solid phases

Two silicate solid phases are included in this compilation: pyroxene and olivine. These phases are the pure end-members of different solid solution series. They are not included in the NAGRA PSI 01/01 TDB on the basis of the fact that these pure members that have been never observed in nature. Nevertheless one must bear in mind that the calculation of the stability of a solid solution of a given composition between olivine and pyroxene and other silicates needs of the stability of the pure end-members and therefore we have included them in the database. Reaction parameters are reported in Table 9-6.

Thermochemical data are reported in /Baeyens and McKinley 1989/ for pyroxene while data in /Robie and Hemingway 1995/ have been taken for olivine.

Table 9-5. Thermodynamic data for nickel carbonate complexes.

Reaction	logβ^0
$Ni^{2+}+CO_3^{2-} = NiCO_3(aq)$	4.00±0.30
$Ni^{2+}+2CO_3^{2-} = Ni(CO_3)_2^{2-}$	<6
$Ni^{2+}+CO_3^{2-}+H^+ = NiHCO_3^+$	11.33
Reaction	**–logK$_s$**
$Ni^{2+}+CO_3^{2-} = NiCO_3(cr)$	11.20±0.30

Table 9-6. Thermodynamic data for Ni silicates different from NAGRA-PSI 01/01 TDB.

Reaction	$-\log K_s^0$	$\Delta_r H^0$ (kJ/mole)
$Ni^{2+}+H_4SiO_4 = NiSiO_3(Pyroxene)+2H^++H_2O$	2.09	
$2Ni^{2+}+H_4SiO_4 = Ni_2SiO_4(Olivine)+4H^+$	–19.24±1.32	168.906±8.433

9.4 Group 15

9.4.1 Nitrogen compounds

Aqueous nickel nitrate complexes have been selected in agreement with the NAGRA-PSI 01/01 TDB. Stability constants are shown in Table 9-7. Neither enthalpy nor entropy values are given.

9.4.2 Phosphate compounds

Stability constants of the complexes $NiH_2PO_4^+$, $NiHPO_4(aq)$, $NiPO_4^-$ are the ones reported in /Pearson et al. 1992/, without further evaluation in the update of the NAGRA-PSI 01/01 database. In addition new complexes and solid phases are included in this selection based on formation parameters found in the literature. Reaction parameters for pyrophosphates and solid compounds are calculated from formation parameters reported in /Baeyens and McKinley 1989/. Thermodynamic parameters for the two hydroxyl phosphates reported in the next table are selected from the work of /Ziemniak et al. 1989/. Compiled data for phosphorus compounds are shown in Table 9-8.

Table 9-7. Thermodynamic data for Nickel nitrate.

Reaction	$\log\beta^0$
$Ni^{2+}+NO_3^- = NiNO_3^+$	0.40
$Ni^{2+}+2NO_3^- = Ni(NO_3)_2(aq)$	–0.60

Table 9-8. Thermodynamic data for Nickel phosphorus compounds.

Reaction	$\log\beta^0$	$\Delta_r H^0$ (kJ/mole)
$Ni^{2+}+H_2PO_4^- = NiH_2PO_4^+$	1.54	
$Ni^{2+}+H_2PO_4^- = NiHPO_4(aq)+H^+$	–4.28	
$Ni^{2+}+H_2PO_4^- = NiPO_4^-+2H^+$	–11.19	
$Ni^{2+}+H_2PO_4^-+2H_2O = Ni(OH)_2HPO_4^{2-}+3H^+$	–22.59±3.07	64.698±13.714
$Ni^{2+}+H_2PO_4^-+3H_2O = Ni(OH)_3H_2PO_4^{2-}+3H^+$	–25.24±2.81	85.727±20.608
$Ni^{2+}+2\ H_2PO_4^-– = NiHP_2O_7^-+H^++H_2O$	–7.54±0.81	
$Ni^{2+}+2\ H_2PO_4^-– = NiP_2O_7^{2-}+2H^++H_2O$	–13.71±0.81	30.870±3.907
$2Ni^{2+}+2H_2PO_4^- = Ni_2P_2O_7(aq)+2H^++H_2O$	–7.89±1.31	
Reaction	**$-\log K_s$**	**$\Delta_r H^0$ (kJ/mole)**
$3Ni^{2+}+2H_2PO_4^- = Ni_3(PO_4)_2(cr)+4H^+$	–10.11	185.500

9.5 Group 16

9.5.1 Aqueous complexes

The review of thermodynamic data concerning nickel sulphate and sulphide complexes agree with the values compiled in the NAGRA PSI 01/01 TDB. In addition, we have taken the enthalpy of reaction for the formation of the first aqueous sulphate complex from /Katayama 1973/, to account for its stability dependence on temperature.

An additional aqueous complex, the nickel thiosulphate has been included in the actual selection. Selected data for this species come from the /Sillén and Martell 1964/ compilation (see Table 9-9).

9.5.2 Solid phases

Sulphide and sulphate solid phases are not included in the NAGRA-PSI 01/01. The authors agree with /Thoenen 2002/ on the fact that no reliable data for nickel sulphides have been published so far. Sulphates are very soluble salts not expected to be relevant under environmental conditions.

Nevertheless, we prefer to give the modellers the opportunity to decide about existence, possibility of occurrence, etc., of a given solid phase under the experimental conditions of interest for their work. Therefore, several sulphate and sulphide solid phases have been included in Table 9-9. Formation parameters compiled in different publications have been selected and reaction parameters have been accordingly calculated. Formation parameters are taken from /Robie and Hemingway 1995/ for nickel sulphates. Nickel sulphides have been selected from several sources; mainly /Baeyens and McKinley 1989/ and /Hummel et al. 2002/ for the aqueous species and from /Robie and Hemingway 1979/ for Ni_3S_2, from /Baeyens and McKinley 1989/ for NiS_2 and Ni_3S_4 and from /DeKock 1982/ for $FeNi_2S_4$.

Table 9-9. Thermodynamic data for Nickel sulphur compounds.

Reaction	logβ⁰	Δ_rH^0 (kJ/mole)
$Ni^{2+}+S_2O_3^{2-} = NiS_2O_3(aq)$	2.06	
$Ni^{2+}+SO_4^{2-} = NiSO_4(aq)$	2.2731	5.290
$Ni^{2+}+2SO_4^{2-} = Ni(SO_4)_2^{2-}$	3.20	
$Ni^{2+}+HS^- = NiHS^+$	5.50±0.20	
$Ni^{2+}+2HS^- = Ni(HS)_2(aq)$	11.10±0.10	
Reaction	**–logK$_s$**	**Δ_rH^0 (kJ/mole)**
$Ni^{2+}+SO_4^{2-}+6H_2O = NiSO_4\cdot 6H_2O$	2.23±0.61	–5.015±2.592
$Ni^{2+}+SO_4^{2-}+7H_2O = NiSO_4\cdot 7H_2O$	2.18±0.61	–12.293±2.596
$Ni^{2+}+SO_4^{2-} = NiSO_4(cr)$	–4.70±0.63	90.148±2.722
$Ni^{2+}+HS^- = NiS(s)+H^+$	9.27±1.37	–14.468±5.100
$Ni^{2+}+2HS^- = NiS_2(s)+2e^-+2H^+$	18.43	–47.300
$3Ni^{2+}+2HS^-+2e^- = Ni_3S_2(s)+2H^+$	14.90±1.94	–8.020±8.139
$3Ni^{2+}+4HS^- = Ni_3S_4(s)+2e^-+4H^+$	39.41	–98.900
$2Ni^{2+}+Fe^{2+}+4HS^- = FeNi_2S_4+4H^++2e^-$	37.39	

9.6 Group 17

9.6.1 Aqueous complexes

A wide range of stability constants reported at different ionic strengths, different media and measured mainly by spectophotometric, potentiometric and calorimetric techniques are reported in the literature on aqueus nickel halides. Most of the available data refers to three aqueous complexes: NiF^+, $NiCl^+$ and $NiCl_2(aq)$. The extrapolation to zero ionic strength of the few published data is shown in the following figure for the three complexes reported. The stability constants extrapolated to infinite dilution are: $\log\beta^0(NiCl^+) = 1.01 \pm 0.50$, $\log\beta^0(NiCl_2(aq)) = 1.82 \pm 0.46$ and $\log\beta^0(NiF^+) = 0.90 \pm 0.18$. However, these values must to be considered with caution given the data dispersion.

Entalphies are not included in this selection given the scarcity and dispersion of the different values reported in the literature for the 1:1 aqueous halide complexes.

Selected data are shown in Table 9-10.

9.6.2 Solid phases

As in the case of sulphur compounds, there is no selection for solid phases in the NAGRA-PSI 01/01 database given that these solids are very highly soluble salts. However based on the same reasoning as previously exposed, we include a selection of solid phases compiled from different publications. Reaction parameters are calculated from formation parameters in all cases and they are given in Table 9-10. Formation parameters are taken from /Baeyens and McKinley 1989/ for all solid phases with one exception, $NiCl_2(s)$, whose thermodynamic data have been taken from /Robie and Hemingway 1995/.

Table 9-10. Thermodynamic data for Nickel halide aqueous complexes and solid phases.

Reaction	**$\log\beta^0$**	**Δ_rH^0 (kJ/mole)**
$Ni^{2+}+F^- = NiF^+$	1.00±0.20	
$Ni^{2+}+Cl^- = NiCl^+$	1.00±0.50	
$Ni^{2+}+2Cl^- = NiCl_2(aq)$	0.90±0.50	
Reaction	**$-\log K_s$**	**Δ_rH^0 (kJ/mole)**
$Ni^{2+}+2F^-+4H_2O = NiF_2{\cdot}4H_2O$	4.19±0.67	
$Ni^{2+}+2F^- = NiF_2(s)$	0.17	67.900
$Ni^{2+}+2Cl^-+2H_2O = NiCl_2{\cdot}2H_2O$	–3.87±0.60	37.720±2.511
$Ni^{2+}+2Cl^-+4H_2O = NiCl_2{\cdot}4H_2O$	–3.78±0.60	14.880±2.515
$Ni^{2+}+2Cl^-+6H_2O = NiCl_2{\cdot}6H_2O$	–3.08±0.60	0.040±2.519
$Ni^{2+}+2Cl^- = NiCl_2(s)$	–8.61±0.69	83.321±3.208
$Ni^{2+}+2Br^- = NiBr_2(s)$	–9.60	84.820
$Ni^{2+}+2I^- = NiI_2(s)$	–11.97	89.460

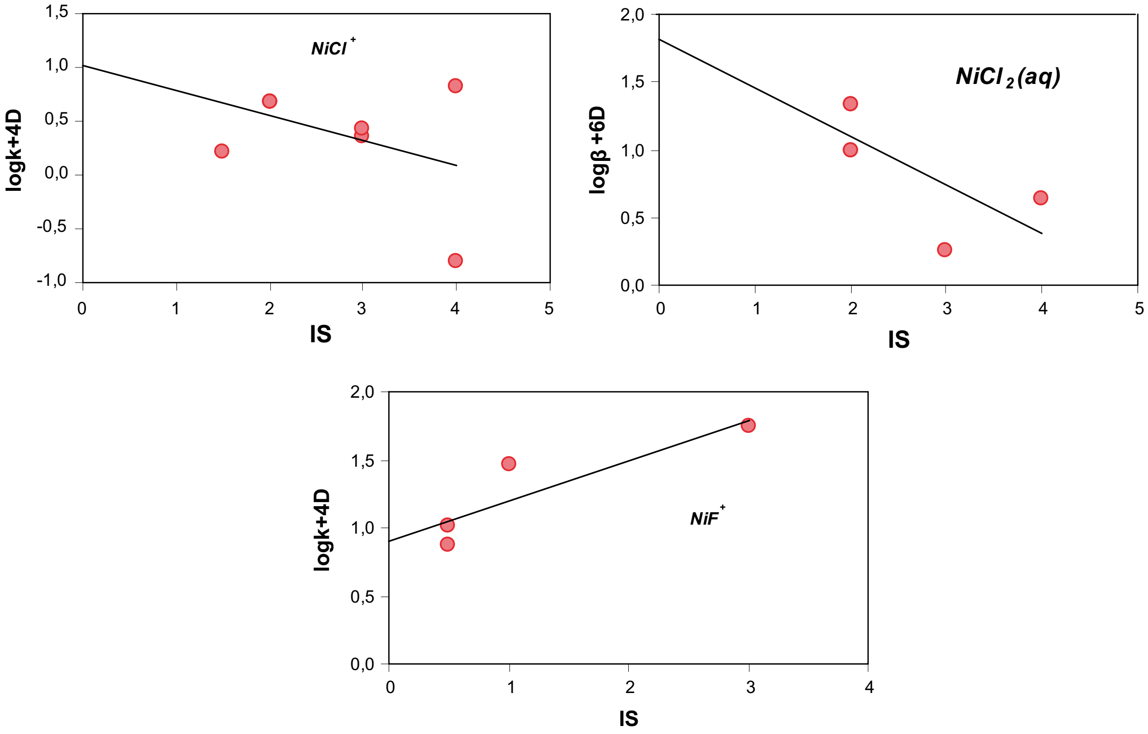

Figure 9-2. *Extrapolation to zero ionic strength of the stability constants of the complexes: $NiCl^+$, $NiCl_2(aq)$ and NiF^+. Stability constants taken from /Sillén and Martell 1964, Grimald and Liberti 1964, Halloff and Vannerberg 1970, Bond and Hefter 1972, Blokhin et al. 1974, Aruga 1974, Kulvinova et al. 1976, Solomon et al. 1983/.*

10 Palladium

Thermodynamic data of inorganic compounds and complexes of palladium reported in the NAGRA-PSI 01/01 database /Hummel et al. 2002/ were taken from the previous NAGRA database /Pearson et al. 1992/ although some modifications regarding Pd(cr) and Pd hydroxides were introduced given the information published in the recent years.

New values included in this reviewed database are based on the work developed for ANDRA published in /Duro et al. 2002/.

We present in the following subsections the TDB selection and only data differing from data in the NAGRA-PSI 01/01 database /Hummel et al. 2002/ are reported.

10.1 Elemental palladium

/Hummel et al. 2002/ propose an $\varepsilon(Pd^{2+}, ClO_4^-)$ and a logK for reaction 10-1 derived from a re-evaluation of the standard potentials of the redox pair $Pd^{2+}/Pd(cr)$ obtained from different sources.

$Pd^{2+}+2e^- = Pd(cr)$ 10-1

Nevertheless the $\varepsilon(Pd^{2+}, ClO_4^-)$ obtained by /Hummel et al. 2002/ is considerably higher than the interaction coefficients of other divalent cations. Thus, we have preferred to estimate the $\varepsilon(Pd^{2+}, ClO_4^-)$ equal to $\varepsilon(Co^{2+}, ClO_4^-) = 0.340\pm0.030$ and obtain the value of logK at $I = 0$ from data of /Templeton et al. 1943/ resulting in $LogK = 33.03\pm0.54$. More details of this selection are presented in /Duro et al. 2002/.

The reaction enthalpy has been calculated internally after the selection of the S^0_f of Pd(cr). Instead of the value given by /Hummel et al. 2002/ we have selected the value in /Wagman et al. 1982/ with its associated uncertainty.

ΔH^0_r (Equation 10-1) = -189.883 ± 3.097 kJ mole^{-1}

10.2 Simple aquo ions

As discussed in /Duro et al. 2002/, we have used the formation entropy of Pd^{2+} reported in /Wagman et al. 1982/ instead of the S^0_f selected in /Hummel et al. 2002/ because it is an experimental value. Thus, thermodynamic data for Pd^{2+}have been modified accordingly.

10.3 Oxygen and hydrogen compounds

/Hummel et al. 2002/ estimated the palladium hydrolysis from the study of /Middlesworth and Wood 1999/. However, a posterior study /Byrne and Yao 2000/ indicated that the solid used by /Middlesworth and Wood 1999/ was not pure $Pd(OH)_2(s)$ but contained Cl^- in its structure, thus leading to erroneous stabilities for the hydrolysis species.

10.3.1 Aqueous palladium hydroxide complexes

We have taken into account the considerations of /Byrne and Yao 2000/ and we have not selected data in /Hummel et al. 2002/. As reported in /Duro et al. 2002/, we have selected the data reported in /Pearson et al. 1992/.

Given that /Hummel et al. 2002/ do not select any value for the enthalpies of reactions, we have estimated the formation entropies of the aqueous hydroxide complexes by applying the /Shock et al. 1997/ methodology, and have calculated the enthalpy values accordingly.

Selected data are shown in Table 10-1.

10.3.2 Solid palladium oxides and hydroxides

For the reasons reported in /Byrne and Yao 2000/ we have not selected the thermodynamic data reported in /Hummel et al. 2002/ for $Pd(OH)_2(s)$. We have selected the data reported in /Pearson et al. 1992/ which are:

$Pd^{2+}+2H_2O = Pd(OH)_2(s)+2H^+$ $-\log{}^*K_s = 1.61$ 10-2

/Hummel et al. 2002/ do not include thermochemical data for PdO(cr). Although this phase is not expected to control the solubility of Pd, we have calculated a log K for reaction in Equation 10-3 from the Gibbs free energy of formation of /Lothenbach et al. 1999/. More details can be found in /Duro et al. 2002/.

$Pd^{2+}+H_2O = PdO(cr)+2H^+$ $-\log{}^*K_s = 6.02$ 10-3

Given that /Hummel et al. 2002/ do not select any value for the enthalpies of solids oxides and hydroxides, we have calculated the correspondent enthalpies for reactions from the formation enthalpy values reported in /Wagman et al. 1982/. More details can be found in /Duro et al. 2002/.

Δ_rH^0 (Equation 10-2) = -13.223 ± 3.099 kJ mole^{-1}

Δ_rH^0 (Equation 10-3) = 10.547 ± 3.099 kJ mole^{-1}

10.4 Group 14

10.4.1 Carbonate compounds

Aqueous complexes

In /Hummel et al. 2002/ is stated that no thermodynamic data have been reported concerning palladium carbonate complexes.

However, due to the good correlation obtained between experimental and estimated values by using the approach of /Brown and Wanner 1987/ for divalent cations (see Figure 4-2), we have selected data for the first and second carbonato complex.

$Pd^{2+}+CO_3^{2-} = PdCO_3(aq)$ $\log \beta^0 = 6.83$ 10-4

$Pd^{2+}+2CO_3^{2-} = Pd(CO_3)_2^{2-}$ $\log \beta^0 = 12.53$ 10-5

Table 10-1. Thermodynamic data for Pd^{2+} different from NAGRA-PSI 01/01 TDB.

Reaction	$\log{}^*\beta^0$	Δ_rH^0 (kJ/mol)
$Pd^{2+}+H_2O = Pd(OH)^++H^+$	–1.86	11.900
$Pd^{2+}+2H_2O = Pd(OH)_2(aq)+2H^+$	–3.79	15.293
$Pd^{2+}+3H_2O = Pd(OH)_3^-+3H^+$	–15.93	54.863
$Pd^{2+}+4H_2O = Pd(OH)_4^{2-}+4H^+$	–29.36	118.563

10.5 Group 15

10.5.1 Nitrate and phosphate aqueous complexes

/Hummel et al. 2002/ do not select any value for nitrate and phosphate compounds and complexes because they may not be relevant for the modelling of environmental systems. We agree with this argument.

10.6 Group 16

10.6.1 Solid sulphides

/Hummel et al. 2002/ consider that the low temperature solubility studies of PdS(s) are inconclusive or unreliable. Thus, they do not select any values for this solid.

However, as discussed in /Duro et al. 2002/, we have included the solubility constant as well as the reaction enthalpy for PdS(s) from the formation values given by /Mills 1974/ (see Table 10-2).

10.6.2 Aqueous sulphate complexes

/Hummel et al. 2002/ do not select any value for sulphate aqueous complexes. However, as discussed in /Duro et al. 2002/, we have considered the stability constant estimated by /Brown and Wanner 1987/ for the complex $PdSO_4(aq)$, while in the case of $Pd(SO_4)_2^{2-}$ we have extrapolated to zero ionic strength the data of /Högfeldt 1982/. No enthalpy data are available.

10.7 Group 17

Pd^{2+} forms weak complexes with fluoride but strong complexes with chloride, bromide and iodide. Hence, no data for palladium fluoride complexes or compounds have been reported.

Table 10-2. Thermodynamic data of PdS(s), different from NAGRA-PSI 01/01 TDB.

Reaction	$-\log K_s$	$\Delta_r H^0$ (kJ/mol)
$Pd^{2+} + HS^- = PdS(s) + H^+$	46.86±1.32	–244.293±7.157

Table 10-3. Thermodynamic data for Palladium aqueous sulphates, different from NAGRA-PSI 01/01 TDB.

Reaction	$\log\beta^0$
$Pd^{2+} + SO_4^{2-} = PdSO_4(aq)$	2.91
$Pd^{2+} + 2SO_4^{2-} = Pd(SO_4)_2^{2-}$	4.17

10.7.1 Aqueous halide complexes

Chloride complexes

/Hummel et al. 2002/ selected the stability values of /Elding 1972/ extrapolated to zero ionic strength by /Lothenbach et al. 1999/. We agree with this selection.

Reaction enthalpies have been calculated from formation entropies calculated according to the method in /Sverjensky et al. 1997/ (Table 10-4).

In the case of the hydroxy-chloride complex ($PdCl_3OH^{2-}$) we have selected the formation constant coming from the experimental work of /Byrne and Yao 2000/, according to the reasons reported in /Duro et al. 2002/:

$Pd^{2+}+3Cl^-+H_2O = PdCl_3OH^{2-}+H^+$ $\log\beta^0 = 2.31$ 10-6

Bromide complexes

/Hummel et al. 2002/ consider that bromide complexes are not relevant for geochemical modelling, thus no stability constants for these species are included in the NAGRA-PSI 01/01 TDB.

Nevertheless, given the good consistency of data of /Elding 1972/, we have extrapolated those data to zero ionic strength by using the SIT methodology and have considered them in the thermodynamic database.

The reaction enthalpy of aqueous bromide palladium species have been calculated, as for the other halide species, by using the formation entropy values estimated with the approach in /Sverjensky et al. 1997/ (seeTable 10-5).

Table 10-4. Reaction enthalpies for Palladium chlorides calculated according to /Sverjensky et al. 1997/.

Reaction	Δ_rH^0 (kJ mole^{-1})
$Pd^{2+}+Cl^- = PdCl^+$	–24.542±6.372
$Pd^{2+}+2Cl^- = PdCl_2(aq)$	–47.297±6.372
$Pd^{2+}+3Cl^- = PdCl_3^-$	–77.344±6.374
$Pd^{2+}+4Cl^- = PdCl_4^{2-}$	–112.469±6.376

Table 10-5. Thermodynamic data for Pd^{2+} aqueous bromides, different from NAGRA-PSI 01/01 TDB.

Reaction	$\log\beta^0$	Δ_rH^0 (kJ/mol)
$Pd^{2+}+Br^- = PdBr^+$	5.77±0.02	–30.140±7.639
$Pd^{2+}+2Br^- = PdBr_2(aq)$	10.06±0.04	–57.708±7.652
$Pd^{2+}+3Br^- = PdBr_3^-$	13.75±0.06	–92.385±7.021
$Pd^{2+}+4Br^- = PdBr_4^{2-}$	15.11±0.08	–126.683±7.703

Iodide complexes

As said previously, /Hummel et al. 2002/ consider that iodide complexes are not relevant for geochemical modelling. Because of that, they do not include these species in their selection.

As presented in /Duro et al. 2002/, we have selected formation constants for the first and fourth iodide complex. No data are available for the second and third iodide species. For the first complex, stability is taken from /Grinberg et al. 1967/, corrected to zero ionic strength by /Pearson et al. 1992/. For the fourth species, the stability constant has been calculated from formation data reported in /Wagman et al. 1982/.

As in the previous cases, the reaction enthalpy of these complexes have been calculated from estimations of the formation entropies (see Table 10-6).

10.7.2 Solid phases

Chloride compounds

As /Hummel et al. 2002/ do not select any value for the solid $PdCl_2(s)$, we have calculated the logK from the formation data of /Baeyens and McKinley 1989/. The reaction enthalpy has been calculated from the $\Delta_f H^0$ of $PdCl_2(cr)$ reported in /Wagman et al. 1982/ (see Table 10-7).

Bromide compounds

/Hummel et al. 2002/ do not select any bromide compounds given that the total concentration of bromine in pore waters is so low that bromide compounds of palladium are not though to be of relevance for geochemical modelling.

However, we have preferred to introduce the solid $PdBr_2(cr)$ with an associated logK equal to that reported in /Baeyens and McKinley 1989/, in agreement with the reasoning presented in /Duro et al. 2002/. From the enthalpy of formation of $PdBr_2(cr)$ in /Baeyens and McKinley 1989/, the enthalpy of reaction has been calculated (see Table 10-8).

Table 10-6. Thermodynamic data for Pd^{2+} aqueous iodides, different from NAGRA-PSI 01/01 TDB.

Reaction	$\log\beta^0$	$\Delta_r H^0$ (kJ/mol)
$Pd^{2+}+I^- = PdI^+$	10.4	–58.201
$Pd^{2+}+4I^- = PdI_4^{2-}$	24.64±0.55	–190.052±7.009

Table 10-7. Thermodynamic data for $PdCl_2(cr)$, different from NAGRA-PSI 01/01 TDB.

Reaction	$-\log K_s$	$\Delta_r H^0$ (kJ/mol)
$Pd^{2+}+2Cl^- = PdCl_2(cr)$	9.20	–54.423±3.105

Table 10-8. Thermodynamic data for $PdBr_2$(cr), different from NAGRA-PSI 01/01 TDB.

Reaction	–logK_s	$\Delta_r H^0$ (kJ/mol)
Pd^{2+}+$2Br^-$ = $PdBr_2$(cr)	13.31	–51.263±3.113

Iodide compounds

/Hummel et al. 2002/ do not select any iodide compounds given that the total concentration of iodine in pore waters is so low that iodide compounds of palladium are not though to be of relevance for geochemical modelling.

Nevertheless, we have introduced the solid palladium iodide phase with an associated equilibrium constant calculated from formation data in /Baeyens and McKinley 1989/. The enthalpy of reaction has been calculated from the formation values of /Baeyens and McKinley 1989/ (see Table 10-9).

Table 10-9. Thermodynamic data for PdI_2(cr), different from NAGRA-PSI 01/01 TDB.

Reaction	–logK_s	$\Delta_r H^0$ (kJ/mol)
Pd^{2+}+$2I^-$ = PdI_2(cr)	25.87	–139.923

11 Silver

The reference database NAGRA-PSI 01/01 TDB does not include data for this element. The selection shown here relies on data reported in the open scientific literature and in other published thermodynamic compilations.

11.1 Master species

The basic species for Silver is the free cation Ag^+. Thermodynamic data for this species is taken from the NEA compilation /Silva et al. 1995/, as shown in Table 11-1.

Thermodynamic data for the reference state, Ag^0, have been also selected from /Silva et al. 1995/, the formation entropy value is 42.6±0.2 J/mole·K, and the formation Gibbs free Energy has been internally calculated. Thermodynamic data are reported in Table 11-2.

11.2 Silver hydrolysis

Stability constants for the two first hydrolysis complexes as well as the solubility constant for the solid hydroxide are taken from /Baes and Mesmer 1976/. Formation entropy data for aqueous species have been estimated by using the methodology suggested in /Shock et al. 1997/ and values for enthalpy have been subsequently calculated.

Relevant data for solubility calculations are shown in Table 11-2.

Table 11-1. Thermodynamic data for Ag^+.

$\Delta_f G^0$ (kJ/mole)	$\Delta_f H^0$ (kJ/mole)	S_f^0 (J/mole·K)
77.096±0.156	105.790±0.080	73.5±0.4

Table 11-2. Thermodynamic data for silver hydroxides.

Reaction	logK°	$\Delta_r H^0$ (kJ/mole)
$Ag^+ + e^- = Ag(s)$	13.51±0.03	–105.790±0.08
Reaction	**log*β⁰**	**$\Delta_r H^0$ (kJ/mole)**
$Ag^+ + H_2O = AgOH(aq) + H^+$	–12.00±0.3	47.178±6.492
$Ag^+ + 2H_2O = Ag(OH)_2^- + 2H^+$	–24.00±0.1	111.634±6.288
Reaction	**$-\log {}^*K_s$**	**$\Delta_r H^0$ (kJ/mole)**
$Ag^+ + H_2O = AgOH(s) + H^+$	–6.30±0.05	

11.3 Group 14

Two aqueous carbonate species and one solid phase have been included in the database. Formation parameters for the solid phase are taken from /Wagman et al. 1982/, from where reaction parameters are calculated. We have considered stabilities and entropy values reported in Sverjensky and co-workers /Sverjensky et al. 1997/ for aqueous carbonate complexes. Enthalpies have been internally calculated. Selected data are shown in Table 11-3.

11.4 Group 15

Two aqueous nitrogen complexes, with associated data reported in the Wagman compilation /Wagman et al. 1968/ are included in the database (see Table 11-4).

The only reliable data on silver phosphates is reported by /Smith and Martell 1976/ and refers to the solid $Ag_3(PO_4)(s)$ (see Table 11-4).

11.5 Group 16

For AgHS(aq) and $Ag(HS)_2^-$ we have selected data from /Naumov et al. 1974/, that is reported in /Ball and Nordstrom 1991/. /Renders and Seward 1989/ re-calculates experimental results from /Schwarzenbach and Widmer 1966/ at zero ionic strength and obtain stability data for AgHS and $Ag(HS)_2^-$ that are in agreement with /Naumov et al. 1974/.

Reaction entropy for the formation of AgHS(aq) has been estimated by applying the approach recommended in /Sverjensky et al. 1997/, and the same procedure has been followed for the formation entropy of $Ag(HS)_2^-$.

Data compiled in /Smith and Martell 1976/ are included in the database for aqueous and solid silver sulphates. Entropy data for these species have been taken from the NBS tables /Wagman et al. 1982/.

Table 11-3. Thermodynamic data for silver carbonates.

Reaction	$\log\beta^0$	Δ_rH^0 (kJ/mole)
$Ag^++CO_3^{2-} = AgCO_3^-$	2.69±0.3	–22.832±6.491
$Ag^++2CO_3^{2-} = Ag(CO_3)_2^{3-}$	2.16±0.3	–28.044±6.520
Reaction	**$-\log K_s$**	**Δ_rH^0 (kJ/mole)**
$2Ag^++CO_3^{2-} = Ag_2CO_3(s)$	11.05±0.09	–42.073±0.339

Table 11-4. Thermodynamic data for nitrogen compounds and the silver phosphate solid phase.

Reaction	$\log\beta^0$	Δ_rH^0 (kJ/mole)
$Ag^++NO_3^- = AgNO_3(aq)$	–0.29	–0.740±0.408
$Ag^++2NO_3^-+4e^-+4H^+ = Ag(NO_2)_2^-+2H_2O$	57.78	
Reaction	**$-\log K_s$**	**Δ_rH^0 (kJ/mole)**
$3Ag^++H_2PO_4^- = Ag_3PO_4(s)+2H^+$	–2.01	

Two aqueous thiosulphates and one sulphite complex are included in this selection with formation data coming from the NBS tables /Wagman et al. 1982/. Enthalpies of reaction have been calculated when possible.

Selected data are shown in Table 11-5.

11.6 Group 17

Thermodynamic data for aqueous chloride and bromide species are taken from /Ball and Nordstrom 1991/. Formation entropies have been estimated by following the /Sverjensky et al. 1997/ approach.

Formation data for solid silver chlorides are reported in /Grenthe et al. 1992/, while for the solid silver bromide formation data in /Wagman et al. 1982/ have been considered.

Aqueous silver iodide data have been selected from the Smith and Martell compilation /Smith and Martell 1976/ with the exception of the 1:3 complex, for which reaction parameters have been calculated from the Gibbs free energies of formation tabulated in /Wagman et al. 1982/. Reaction entropy data are estimated by the /Sverjensky et al. 1997/ method.

Data for the solid silver iodide are taken from the NBS compilation /Wagman et al. 1982/, and reaction parameters have been calculated accordingly.

Selected data are shown in Table 11-6.

Table 11-5. Thermodynamic data for sulphur species.

Reaction	$\log\beta^0$	$\Delta_r H^0$ (kJ/mole)
$Ag^+ + HS^- = AgHS(aq)$	14.05	–78.826
$Ag^+ + 2HS^- = Ag(HS)_2^-$	18.45	–105.805
$Ag^+ + SO_3^{2-} = AgSO_3^-$	5.21±0.71	
$Ag^+ + SO_4^{2-} = AgSO_4^-$	1.38±0.08	4.646±0.520
$Ag^+ + S_2O_3^{2-} = AgS_2O^{3-}$	9.23	–58.994
$Ag^+ + 2S_2O_3^{2-} = Ag(S_2O_3)_2^{3-}$	13.64	–94.450±0.128
Reaction	**$-\log K_s$**	**$\Delta_r H^0$ (kJ/mole)**
$2Ag^+ + HS^- = Ag_2S(s) + H^+$	36.07±0.37	–224.768±1.514
$2Ag^+ + SO_4^{2-} = Ag_2SO_4(s)$	5.01±0.09	–18.162±0.449

Table 11-6. Thermodynamic data for silver halide compounds.

Reaction	$\log\beta^0$	Δ_rH^0 (kJ/mole)
$Ag^++Cl^- = AgCl(aq)$	3.27	–17.105
$Ag^++2Cl^- = AgCl^{2-}$	5.27	–28.766
$Ag^++3Cl^- = AgCl_3^{2-}$	5.29	–29.172
$Ag^++4Cl^- = AgCl_4^{3-}$	5.51	–26.102
$Ag^++Br^- = AgBr(aq)$	4.24	–23.153
$Ag^++2Br^- = AgBr^{2-}$	7.28	–45.338
$Ag^++3Br^- = AgBr_3^{2-}$	8.71	–66.795
$Ag^++I^- = AgI(aq)$	6.58	–36.981
$Ag^++2I^- = AgI^{2-}$	11.70	–76.578
$Ag^++3I^- = AgI_3^{2-}$	13.28±0.07	–114.911±6.280
Reaction	**$-\log K_s$**	**Δ_rH^0 (kJ/mole)**
$Ag^++Cl^- = AgCl(s)$	9.75±0.04	–65.720±0.137
$Ag^++Br^- = AgBr(s)$	12.29±0.04	–84.725±0.188
$Ag^++I^- = AgI(s)$	16.04±0.03	–110.764±0.124

12 Samarium and holmium

Samarium and holmium are not included in the reference thermodynamic database of NAGRA-PSI 01/01 /Hummel et al. 2002/.

Given the chemical analogy existing between both elements, the thermodynamic data selection is presented under the same chapter in this document.

The main source of data is the compilation conducted by Spahiu and Bruno /Spahiu and Bruno 1995/ which contains a review of the previous existing TDB on lanthanides. When necessary we have included some new species from other original sources in order to obtain the most complete and updated thermodynamic database. In those cases, we have ensured the internal consistency of the database. Some data originated from estimations based on linear free energy relationships with other lanthanides and trivalent actinides are also included.

No uncertainty analyses has been conducted on the stabilities reported by /Spahiu and Bruno 1995/. The associated error covers the range of data reported in /Spahiu and Bruno 1995/.

We have assigned an uncertainty of 20.9 J/mol·K to all the formation entropies given that we have estimated these values by using the /Sverjensky et al. 1997/ methodology.

Formation data from the NBS tables /Wagman et al. 1982/ have been used in reaction data calculations. Nevertheless, as no uncertainties are given in the mentioned tables, we have considered that the uncertainties arise in the last digit of the selected figures.

A discussion of the data selection procedure follows.

12.1 Elemental samarium and holmium

Reference states are Sm(c) and Ho(c).

The entropy of formation of elemental samarium has been taken from /Robie and Hemingway 1979/ while for Ho(c) we have considered the value reported in /Wagman et al. 1982/.

Formation entropies have been used to calculate $\Delta_f S^0$ and $\Delta_r S^0$. Those values, combined with $\Delta_r G^0$ obtained from $\Delta_f G^0$ have allowed the calculation of $\Delta_r H^0$ (see Table 12-1).

Table 12-1. Thermodynamic data selected for the reference states, Sm(c) and Ho(c).

Species	S_f^0 (J/mole·K)	Reaction	logK^0	$\Delta_r H^0$ (kJ/mole)
Sm(s)	69.5±2.1	$Sm^{3+}+3e^- = Sm(s)$	–116.62±7.99	691.199±2.138
Ho(s)	75.3±0.1	$Ho^{3+}+3e^- = Ho(s)$	–118.31±1.71	707.042±0.384

12.2 Simple samarium and holmium aqua ions

The basic species selected for these elements are the free trivalent cations, Sm^{3+} and Ho^{3+}.

Formation data for the basic species have been taken from the SUPCRT database /Johnson et al. 1992/. Uncertainties are assigned to cover different data reported in /Bard et al. 1985/.

The selected formation properties for Sm^{3+} and Ho^{3+} are presented in Table 12-2.

12.3 Oxygen and hydrogen compounds

12.3.1 Aqueous hydroxide complexes

Four Ln(III) aqueous hydroxides, $Ln(OH)^{2+}$, $Ln(OH)_2^+$, $Ln(OH)_3(aq)$ and $Ln(OH)_4^-$ are included in the database.

All their stabilities except that of $Ho(OH)_4^-$ are taken from the /Spahiu and Bruno 1995/ compilation.

The stability of $Ho(OH)_4^-$ has been taken from /Turner et al. 1981/. This value is consistent with the other selected stabilities. An uncertainty of 0.20 log units has been assigned to its stability constant, in agreement with the maximum uncertainty on holmium hydroxides stabilities included in the database.

The enthalpies of reaction for these complexes have been obtained calculated by the Gibbs-Helmholtz equation.

We have calculated Δ_rG^0 values from the selected formation constants. The formation entropies have been estimated by using the /Shock et al. 1997/ approach and reaction entropies have been calculated accordingly.

Selected data are presented in Table 12-3.

Table 12-2. Thermodynamic data selected for the basic species, Sm^{3+} and Ho^{3+}.

Species	Δ_fG^0 (kJ/mole)	Δ_fH^0 (kJ/mole)	S_f^0 (J/mole·K)
Sm^{3+}	–665.674±1.400	–691.199±2.138	–212.1±5.0
Ho^{3+}	–675.298±0.300	–707.042±0.384	–227.2±0.8

Table 12-3. Stability constants and reaction enthalpies selected for Ln(III) aqueous hydroxides.

Reaction	Sm log*β⁰	 Δ_rH^0(KJ/mole)	Ho log*β⁰	 Δ_rH^0(KJ/mole)
$Ln^{3+}+H_2O = Ln(OH)^{2+}+H^+$	–7.90±0.10	81.304±6.438	–7.90±0.20	79.900±6.345
$Ln^{3+}+2\ H_2O = Ln(OH)_2^{+}+2\ H^+$	–16.50±0.20	150.264±6.514	–16.10±0.10	146.130±6.268
$Ln^{3+}+3\ H_2O = Ln(OH)_3(aq)+ 3\ H^+$	–25.90±1.00	226.683±8.585	–24.50±0.10	216.364±6.268
$Ln^{3+}+4\ H_2O = Ln(OH)_4^{-}+ 4\ H^+$	–36.90±1.00	276.904±8.585	–33.40±0.20	254.153±6.345

12.3.2 Solid oxides and hydroxides

One solid oxide, Ln_2O_3(s), and two solid hydroxides, $Ln(OH)_3$(s) and $Ln(OH)_3$(am), are included in the database.

Ln_2O_3(s). The stability constants for both solid oxides, Sm_2O_3(s) and Ho_2O_3(s), have been obtained from the reaction Gibbs energies calculated from formation Gibbs energies reported in /Robie and Hemingway 1979/.

The enthalpies of reaction have been obtained from the enthalpies of formation which have been calculated internally by using the Gibbs-Helmholtz equation. Δ_fG^0 and S_f^0 values needed have been adopted from /Robie and Hemingway 1979/.

$Ln(OH)_3$(s) and $Ln(OH)_3$(am). The stability constants considered for these solid phases have been taken from the /Spahiu and Bruno 1995/ compilation.

No enthalpies of reaction have been included for the solid hydroxides included in the database given that the lack of experimental data and of sufficiently well-tested estimation procedures.

The stabilities selected for the oxides and the solid hydroxides are shown in Table 12-4.

12.4 Group 14

12.4.1 Aqueous complexes

Two aqueous carbonates species, $LnCO_3^+$ and $Ln(CO_3)_2^-$, and one aqueous bicarbonate, $LnHCO_3^{2+}$, for each lanthanide have been included in the database. The stabilities considered are those reported in /Spahiu and Bruno 1995/.

As far as the authors of this report are aware neither enthalpy nor entropy data of carbonate lanthanide species are available in the literature.

According to /Hass et al. 1995/ we have been able to estimate S_f^0 for $LnCO_3^+$ and $LnHCO_3^{2+}$. From the mentioned information it is possible to calculate Δ_rS^0 which, in combination with Δ_rG^0 calculated from selected $\log\beta^0$ data permits the calculation of Δ_rH^0 (see Table 12-5).

Table 12-4. Solubility constants selected for the Ln(III) solid oxides and hydroxides.

Reaction	Sm –log*K_s	Δ_rH^0(kJ/mole)	Ho –log*K_s	Δ_rH^0(kJ/mole)
Ln^{3+}+3 H_2O = $Ln(OH)_3$(s)+3 H^+	–16.50±1.00		–15.40	
Ln^{3+}+3 H_2O = $Ln(OH)_3$(am)+3 H^+	–18.60±1.00		–17.80	
2Ln^{3+}+3 H_2O = Ln_2O_3(s)+6 H^+	–43.11±0.61	355.039±5.051	–47.41±0.88	390.718±5.061

Table 12-5. Data included in the TDB for the aqueous Ln-carbonates.

Species	Sm $\log\beta^0$	Δ_rH^0 (kJ/mole)	Ho $\log\beta^0$	Δ_rH^0 (kJ/mole)
Ln^{3+}+CO_3^{2-} = $LnCO_3^+$	7.80±0.50	163.392±6.859	8.00±0.40	168.562±6.636
Ln^{3+}+2CO_3^{2-} = $Ln(CO_3)_2^-$	12.80±0.60		13.30±0.60	
Ln^{3+}+CO_3^{2-}+H^+ = $LnHCO_3^{2+}$	12.43±0.50		12.50±0.50	

12.4.2 Solid phases

Three solid carbonates are considered in this database: $Sm_2(CO_3)_3(s)$, $SmOHCO_3(s)$ and $Ho_2(CO_3)_3(s)$.

$Ln_2(CO_3)_3(s)$. The stabilities selected for these solids have been taken from the /Spahiu and Bruno 1995/ compilation.

$SmOHCO_3(s)$. As explained in the review conducted by /Spahiu and Bruno 1995/, only for the light lanthanides (La to Eu) the mixed hydroxocarbonate solids are formed. However, no formation constant for the mixed hydroxo-carbonate of samarium has been selected in the mentioned REE's database /Spahiu and Bruno 1995/. In the light of the existing analogies along the lanthanide series and by considering that only stabilities for the equivalent solids of Nd (logK = 7.50) and Eu (logK = 7.80) are available, we can estimate a stability constant of $SmOHCO_3(s)$ (see Table 12-6).

No enthalpies of reaction have been obtained for these solid phases.

Table 12-6. Formation constants selected for the solid carbonates.

Reaction	$-\log K_s$
$2Sm^{3+}+3CO_3^{2-} = Sm_2(CO_3)_3(s)$	34.50±2.00
$2Ho^{3+}+3CO_3^{2-} = Ho_2(CO_3)_3(s)$	33.80±1.00
Reaction	**$-\log {}^*K_s$**
$Sm^{3+}+CO_3^{2-}+H_2O = SmOHCO_3(s)+H^+$	7.70

12.5 Group 15

12.5.1 Aqueous nitrate complexes

We have included the first aqueous nitrates, $SmNO_3^{2+}$ and $HoNO_3^{2+}$, in the database. The stabilities have been taken from the /Spahiu and Bruno 1995/ compilation.

12.5.2 Aqueous phosphate complexes

We have considered the same set of aqueous phosphate species included the /Spahiu and Bruno 1995/ compilation as well as their associated stability constants .

Selected data are shown in Table 12-8.

Table 12-7. Data selected for aqueous nitrates $LnNO_3^{2+}$.

Reaction	$\log\beta^0$
$Sm^{3+}+NO_3^- = SmNO_3^{2+}$	0.90±0.20
$Ho^{3+}+NO_3^- = HoNO_3^{2+}$	0.50±0.30

Table 12-8. Formation constants selected for the aqueous phosphates.

Reaction	Sm $\log\beta^0$	Ho $\log\beta^0$
$Ln^{3+}+H_2PO_4^- = LnH_2PO_4^{2+}$	2.35±0.20	2.30±0.10
$Ln^{3+}+H_2PO_4^- = LnHPO_4^+H^+$	–1.61±0.50	–1.41±0.20
$Ln^{3+}+2H_2PO_4^- = Ln(HPO_4)_2^-+2H^+$	–5.02±0.50	–4.52±0.30
$Ln^{3+}+H_2PO_4^- = LnPO_4(aq)+2H^+$	–7.46	–6.96
$Ln^{3+}+2H_2PO_4^- = Ln(PO_4)_2^{3-}+4H^+$	–18.72	–17.82

12.5.3 Solid phosphate phases

Only one solid phosphate, $LnPO_4 \cdot xH_2O$, is reported in the /Spahiu and Bruno 1995/ compilation. In order to reflect the different solid phases identified in the literature we have complemented our database with the anhydrous solid phosphate, $LnPO_4(s)$, described in /Liu and Byrne 1997/. Those authors conducted solubility studies on synthetic trivalent lanthanides solid phosphates. The original data have been corrected to infinite dilution by the Debye-Hückel equation. Selected data are shown in Table 12-9.

Neither data for enthalpy nor for entropy have been found in the literature for these solid phosphates.

12.6 Group 16

12.6.1 Aqueous complexes

The first and the second sulphate are included for both, Sm and Ho: $LnSO_4^+$ and $Ln(SO_4)_2^-$.

Aqueous sulphates stabilities have been taken from the /Spahiu and Bruno 1995/ compilation. No uncertainty can be assigned to the stability of $Ho(SO_4)_2^-$ given that there is only one datum available and no error is assigned in the original source.

Reaction enthalpies have been obtained from the selected Δ_rG^0 and Δ_rS^0 values by using the Gibbs-Helmholtz equation. Δ_rG^0 values have been calculated from the selected stabilities. Reaction entropies have been calculated from formation entropies taken from the NBS tables /Wagman et al. 1982/. Selected data are shown in Table 12-10.

Table 12-9. Formation constants selected for the solid phosphates.

Reaction	$-\log K_s$ Sm	 Ho
$Ln^{3+}+H_2PO_4^-+xH_2O = LnPO_4 \cdot xH_2O+2H^+$	4.94	4.64
$Ln^{3+}+H_2PO_4^- = LnPO_4(s)+2H^+$	6.67±0.03	5.56±0.13

Table 12-10. Thermodynamic data selected for the aqueous sulphates $Ln(SO_4)_n^{3-2n}$.

Reaction	$\log\beta^0$	Δ_rH^0 (kJ/mole)
$Sm^{3+}+SO_4^{2-} = SmSO_4^+$	3.50±0.20	16.575±1.916
$Sm^{3+}+2\ SO_4^{2-} = Sm(SO_4)_2^-$	5.20±0.10	24.910±1.641
$Ho^{3+}+SO_4^{2-} = HoSO_4^+$	3.40±0.30	15.387±2.302
$Ho^{3+}+2\ SO_4^{2-} = Ho(SO_4)_2^-$	4.90	23.670

12.6.2 Solid phases

In spite of the high solubility of $Sm_2(SO_4)_3(s)$ that would a priori prevent its inclusion in the database, we have included it for the sake of completeness. The stability of this solid phase has been taken from the /Spahiu and Bruno 1995/ compilation. The selected formation constant for this species is 9.80.

We have calculated the enthalpy of reaction from the enthalpy of formation reported in the NBS tables /Wagman et al. 1982/. The calculated enthalpy of reaction for $Sm_2(SO_4)_3(s)$ is 211.318±4.442 KJ/mole.

No holmium solid sulphates have been included in the database given the lack of data and the low relevance that this type of solids will have on the assessment of the solubility of lanthanides.

12.7 Group 17

12.7.1 Aqueous complexes

Fluoride complexes

Only the first aqueous fluorides, SmF^{2+} and HoF^{2+}, have been included in the database. The formation constants have been taken from the /Spahiu and Bruno 1995/ compilation.

Reaction enthalpies have been calculated internally by using the Gibbs-Helmholtz equation. We have obtained Δ_rG^0 values from the selected formation constants and Δ_rS^0 from the respective S_f^0 values in /Hass et al. 1995/.

The selected formation constants and enthalpies of reaction for LnF^{2+} are presented in Table 12-11.

Chloride complexes

Only data for the firs samarium chloride complex have been found in the literature, while for holmium data are available for the first two aqueous chlorides, $HoCl^{2+}$ and $HoCl_2^+$. Given the low relevance that these complexes will have under the conditions of interest, we have not conducted any estimation of the stability of the hypothetical $SmCl_2^+$ complex.

$SmCl^{2+}$. The formation constant selected for this species have been taken from the /Spahiu and Bruno 1995/ compilation.

$HoCl_2^+$. The formation constant for this complex has been taken from /Turner et al. 1981/. Although no uncertainty is assigned to this datum in the original reference, we have assigned a value of 0.5 log units by analogy to the first aqueous chloride.

The enthalpies of reaction have been calculated internally by means of the Gibbs-Helmholtz equation. We have calculated ΔrG^0 values from the selected formation constants while ΔrS^0 values have been obtained from the Sf^0 taken from /Sverjensky et al. 1997/.

The data selected for these species are presented in Table 12-12.

Table 12-11. Data selected for the aqueous LnF^{2+}.

Reaction	$\log\beta^0$	Δ_rH^0 (kJ/mole)
$Sm^{3+}+F^- = SmF^{2+}$	3.80±0.30	26.520±6.290
$Ho^{3+}+F^- = HoF^{2+}$	4.30±0.30	25.932±6.462

Table 12-12. Thermodynamic data selected for the aqueous chlorides.

Reaction	$\log\beta^0$	Δ_rH^0 (kJ/mole)
$Sm^{3+}+Cl^- = SmCl^{2+}$	0.40±0.10	24.103±6.079
$Ho^{3+}+Cl^- = HoCl^{2+}$	0.30±0.50	24.525±6.854
$Ho^{3+}+2\ Cl^- = HoCl_2^+$	–0.29±0.50	36.300±6.859

Bromide complexes

We have included only the first aqueous bromide of samarium, $SmBr^{2+}$, in the database. Its stability constant has been taken from the compilation /Falck et al. 1996/ where no uncertainty is assigned to the reported value. The enthalpy of reaction has been calculated internally by using the Gibbs-Helmholtz equation. The Δ_rG^0 has been obtained from the selected formation constant. We have estimated the Δ_rS^0 for this complex by following the /Sverjensky et al. 1997/ methodology.

The selected formation constant and enthalpy of reaction for this complex are shown in Table 12-13.

Table 12-13. Thermodynamic data for $SmBr^{2+}$.

Reaction	$\text{Log}\beta^0$	Δ_rH^0 (kJ/mole)
$Sm^{3+}+Br^- = SmBr^{2+}$	0.23	17.023

12.7.2 Solid phases

Solid fluorides

Although solid fluorides are expected to be very soluble, for the sake of completeness we have included two solid fluorides, $SmF_3{\cdot}0.5H_2O$ and $HoF_3{\cdot}0.5H_2O$ in the database.

The formation constants for both solid phases have been taken from the compilation conducted by /Spahiu and Bruno 1995/.

We have neither included enthalpies nor entropies in the database for $SmF_3{\cdot}0.5H_2O$ given that no values have been included in the literature. However, data for enthalpy of formation for $HoF_3{\cdot}0.5H_2O$ has been published in the NBS tables /Wagman et al. 1982/. We have calculated the enthalpy of reaction for this solid from the selected enthalpy of formation

Selected data are presented below:

Table 12-14. Thermodynamic data selected for solid fluorides.

Reaction	$-\log K_s$	Δ_rH^0 (kJ/mole)
$Sm^{3+}+3\ F^-+0.5\ H_2O = SmF_3{\cdot}0.5H_2O$	17.50±1.80	
$Ho^{3+}+3\ F^-+0.5\ H_2O = HoF_3{\cdot}0.5H_2O$	16.40	149.007±2.628

Solid chlorides

We have included two solid chlorides, $SmCl_3{\cdot}6H_2O$ and $HoCl_3{\cdot}6H_2O$, in the database. The stabilities selected for both solid phases have been taken from the Chemval database /Falck et al. 1996/ where no uncertainties are indicated.

Reaction enthalpies have been calculated by applying the Gibbs-Helmholtz equation. We have calculated Δ_rG^0 values from the selected stabilities for both solids. Δ_rS^0 values have been calculated from the respective entropies of formation, taken from the NBS tables /Wagman et al. 1982/.

Selected formation constants and reaction enthalpies are shown in Table 12-15.

Table 12-15. Thermodynamic data selected for the solid chlorides $LnCl_3{\cdot}6H_2O$.

Reaction	–logK$_s$	Δ_rH^0 (kJ/mole)
Sm^{3+}+3 Cl^-+6 H_2O = $SmCl_3{\cdot}6H_2O$	–4.80	38.311
Ho^{3+}+3 Cl^-+6 H_2O = $HoCl_3{\cdot}6H_2O$	–5.39	43.855

13 Americium and curium

Given the chemical analogy existing between americium and curium, we present in this section the database selection for both trivalent actinides. The effective ionic radii for americium (1.106Å) and curium (1.094 Å) are very similar. Therefore, and following the NEA recommendations, the same stabilities and enthalpies of reaction have been selected for their species. The NAGRA-PSI 01/01 thermodynamic database /Hummel et al. 2002/ does not include curium in the selection. We will present here only data for Americium and all data will be applied to Curium.

As with the other elements, the reference database used for americium is the NAGRA-PSI 01/01 TDB. Most data included in the mentioned database comes from the NEA compilation /Silva et al. 1995/. Besides considering the Americium NEA-TDB /Silva et al. 1995/ we have included in the discussion data updated in the NEA-TDB work of /Guillaumont et al. 2003/ where some re-interpretation of data included in the previous review has been conducted.

13.1 Elemental americium

Metallic Americium is included in the NAGRA-PSI 01/01 database only for computational purposes. The entropy of formation for this species has been taken from the NEA compilations /Silva et al. 1995/, /Guillaumont et al. 2003/.

The selected entropies of formation, stabilities and enthalpies of reaction for the reference state are presented in Table 13-1.

13.2 Simple aquo ions

Dissolved americium species are mainly in the trivalent oxidation state. Therefore, the basic species selected for this element is the free trivalent cation, Am^{3+}.

Data for the americium basic species, Am^{3+}, have been taken from the NAGRA-PSI 01/01 database, where the NEA compilation /Silva et al. 1995/ is quoted as original selected source. The selected properties of formation for the basic species are reported in Table 13-2.

As proposed in the NAGRA-PSI 01/01 TDB no other oxidation states for Am (and by chemical analogy for Cm) have been included given that they are only stable in the presence of very strong ligands and/or more oxidising conditions than expected in the Forsmark site.

Table 13-1. Thermodynamic data selected for the reference states, Am(s).

Species	S_f^0 (J/mole·K)	Reaction	logK⁰	Δ_rH^0 (kJ/mole)
Am(s)	55.4±2.0	$Am^{3+}+3e^- = Am(s)$	–104.89±0.83	616.700±1.500

Table 13-2. Formation properties for the basic species Am^{3+}.

Species	Δ_fG^0 (kJ/mole)	Δ_fH^0 (kJ/mole)	S_f^0 (J/mole·K)
Am^{3+}	–598.698±4.755	–616.700±1.500	–201.0±15.0

13.3 Oxygen and hydrogen compounds

13.3.1 Aqueous hydroxide complexes

The authors of the NAGRA-PSI 01/01 database differ from the initial Americium NEA review given that, in /Silva et al. 1995/, only experimental data referred to Am have been considered. Experimental data obtained from Am and Cm species have been integrated in the NAGRA-PSI 01/01 database obtaining stability constants for aqueous Am(III) hydroxides that differ in less than 0.5 logarithmic units to the ones selected in /Silva et al. 1995/. We agree with the NAGRA-PSI 01/01 re-interpretation of data concerning trivalent actinides. However, in order to obtain a more complete and consistent thermodynamic database, we have considered the updated NEA-TDB /Guillaumont et al. 2003/ where more recent Am and Cm experimental studies /Stadler and Kim 1988/, /Runde and Kim 1994/, /Edelstein et al. 1983/, /Caceci and Choppin 1983/, /Wimmer et al. 1992/ and /Fanghänel et al. 1994/ than the ones reported in the NAGRA-PSI 01/01 database are considered. Consequently, our selection is slightly different than the one presented in NAGRA-PSI 01/01 database. The stabilities proposed by the two thermodynamic databases are shown in Table 13-3 for the sake of comparison.

Neither the NAGRA-PSI 01/01 database nor the NEA compilation /Guillaumont et al. 2003/ include enthalpy selections for Am(III) hydroxides. No experimental enthalpy values are available for these species as far as we are aware.

Therefore, an estimation methodology has been followed to fill in these gaps. S_f^0 for the first, the second and the third An hydroxides has been estimated by using the /Shock et al. 1997/ equations where entropy for $An(OH)_x^y$ is a function of the entropy of An^{3+}.

The estimated entropies in combination with formation energies of the basic components in the formation reactions and with the values of Gibbs free energy of reaction yield the values of Δ_rH^0 shown in Table 13-4.

Table 13-3. Formation constant for the aqueous hydroxides of Am and Cm proposed by the updated NEA TDB and the NAGRA-PSI 01/01 TDB.

Reaction	Log*β⁰ /Guillaumont et al. 2003/	Log*β⁰ NAGRA-PSI 01/01 TDB
$An^{3+}+H_2O = An(OH)^{2+}+H^+$	–7.20±0.50	–7.30±0.30
$An^{3+}+2\ H_2O = An(OH)_2^{+}+2\ H^+$	–15.10±0.70	–15.20±0.60
$An^{3+}+3\ H_2O = An(OH)_3(aq)+3\ H^+$	–26.20±0.50	–25.70±0.50

Table 13-4. Enthalpies of reaction for the aqueous hydroxides of americium.

Reaction	Δ_rH^0 (kJ/mol·K) Am (and Cm)
$An^{3+}+H_2O = An(OH)^{2+}+H^+$	78.411±8.184
$An^{3+}+2\ H_2O = An(OH)_2^{+}+2\ H^+$	143.704±8.648
$An^{3+}+3\ H_2O = An(OH)_3(aq)+3\ H^+$	230.125±8.184

13.3.2 Solid oxides and hydroxides

Two solid Am(III) hydroxides are included in the NAGRA-PSI 01/01 database, $Am(OH)_3$(cr) and $Am(OH)_3$(am), whose stabilities have been taken from the NEA review /Silva et al. 1995/. After the review of the available literature, we have selected different solubility products for both solids in order to keep the internal consistency of the database.

$An(OH)_3$(am). We have taken into account the updated NEA-TDB /Guillaumont et al. 2003/ where data compiled in /Silva et al. 1995/ have been re-interpreted. These thermodynamic data are combined with the stabilities selected for the An(III) hydrolysis products. The experimental data and the solubility calculations for the amorphous solid conducted with the sets of formation constants selected in /Silva et al. 1995/, /Hummel et al. 2002/ and /Guillaumont et al. 2003/ are shown in Figure 13-1.

The selected formation constant for $An(OH)_3$(am) is -16.90 ± 0.80.

$An(OH)_3$(cr). As in the case of the amorphous solid hydroxide we have considered the updated NEA-TDB where data reported in the NEA review /Silva et al. 1995/ have been re-interpreted. There are no important differences when comparing solubilities in equilibrium with $An(OH)_3$(cr) obtained with the two sets of selected formation constants (see Figure 13-2). Nevertheless, for the sake of the internal consistency of the database we have preferred to include in the revised database the selection conducted by the NEA update.

The stability selected for the crystalline hydroxide, $An(OH)_3$(cr), is -15.60 ± 0.60.

The enthalpy of reaction for $An(OH)_3$(cr) has been calculated internally by using the Gibbs-Helmholtz equation. Δ_fG^0 has been obtained from the stability selected for this solid and the Δ_fG^0 included for the basic species while Δ_fS^0 has been calculated from the S_f^0 included in the NEA-TDB update.

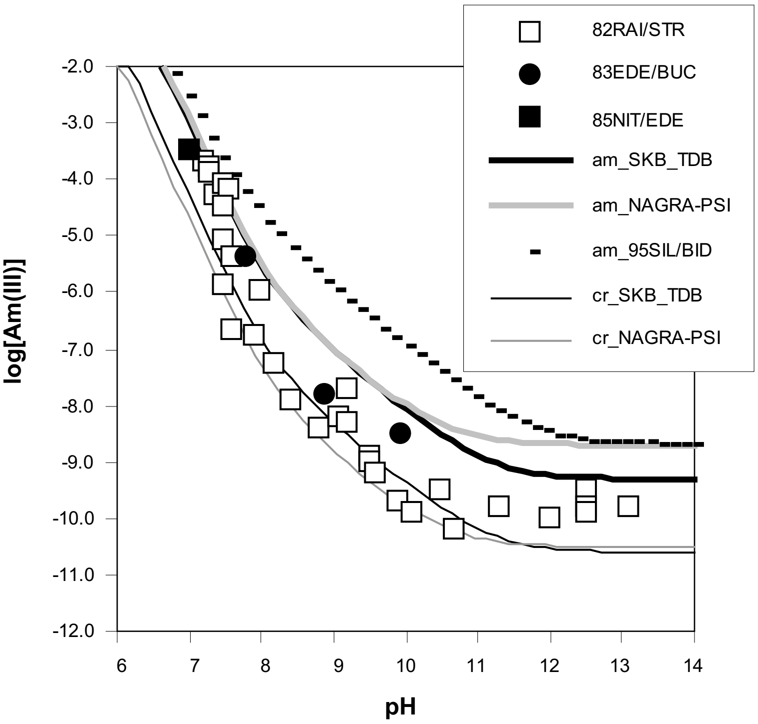

Figure 13-1. Description of the experimental data on $Am(OH)_3$(s) solubility (symbols) obtained by using the different selections of thermodynamic data and solid stability (curves).

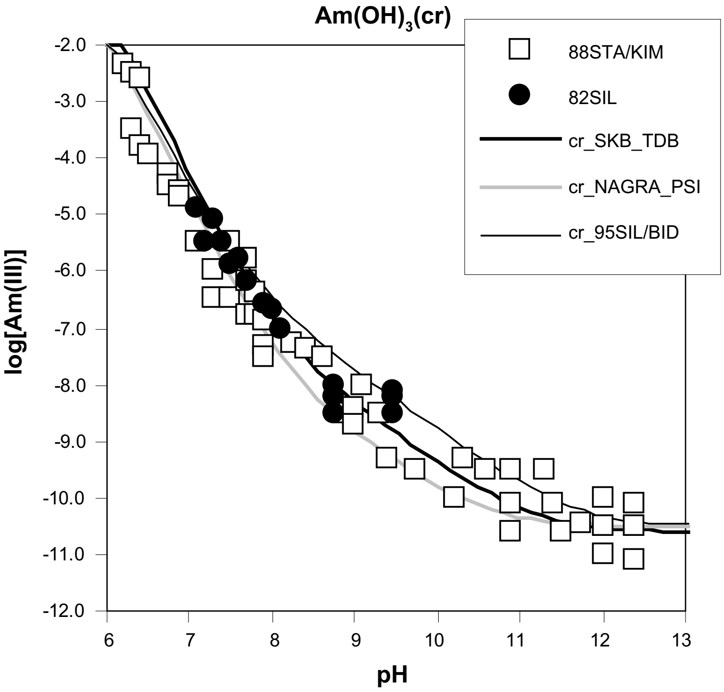

Figure 13-2. *Comparison between experimental data on Am(OH)$_3$(cr) solubility and calculated values obtained by using the different sets of stability constants proposed.*

Even though no other oxides have been considered in the NAGRA-PSI 01/01 TDB, we have included those Am(III) and Am(IV) oxides considered in the NEA compilation /Silva et al. 1995/ that present well characterised thermodynamic properties (Am_2O_3 and AmO_2).

An_2O_3(s). From the values of Δ_fH^0 and the S_f^0 values reported in the literature, the formation Gibbs free energy can be calculated. For Am_2O_3(s) we have taken the enthalpy and the entropy of formation included in the updated NEA-TDB. The selected formation constant for An_2O_3(s) is presented in Table 13-5.

The enthalpy of reaction for An_2O_3(s) has been calculated from the respective formation enthalpies included in /Silva et al. 1995/ (for Am).

Table 13-5. Solubility constants selected for An_2O_3(s).

Reaction	–log*K_s^0
$An^{3+}+3H_2O = An_2O_3(s)+6H^+$	–53.15±2.21

13.4 Group 14

13.4.1 Carbonate compounds

Aqueous An(III) complexes

Three aqueous carbonates of An(III) have been included in the NAGRA-PSI 01/01 database with associated stability data selected by the NEA compilation /Silva et al. 1995/. We have taken into account the updated NEA-TDB where more recent experimental data are included. New data are mainly based on spectroscopic determinations of An(III) carbonates /Fanghänel et al. 1999, Fanghänel et al. 1998b, Wruck et al 1997, Kim et al. 1994, Meinrath and Kim 1991, Nitsche et al. 1989/ and on results from solvent extraction techniques /Runde and Kim 1994, Giffaut 1994, Meinrath and Kim 1991, Felmy et al. 1990, Robouch 1989/. Data obtained in literature have been corrected at zero ionic strength by following the SIT methodology.

The selected formation constants for the aqueous carbonates compiled in /Guillaumont et al. 2003/ are reported below:

$\text{Log}\beta_{1:1}{}^{0} = 8.00\pm0.40$

$\text{Log}\beta_{1:2}{}^{0} = 12.90\pm0.60$

$\text{Log}\beta_{1:3}{}^{0} = 15.00\pm1.00$

$\text{Log}\beta_{1:5}{}^{0} = -5.10\pm1.35$

Neither Am(IV) nor Am(V) carbonates have been included in the NAGRA-PSI 01/01 database. We agree with this decision given that these species are not expected to appear under the conditions of interest for the SKB studies.

No enthalpies are included in the NAGRA-PSI 01/01 database. Our selection includes only enthalpy of reaction for $AnCO_3^+$. Reaction enthalpies have been calculated by using the 3rd principle of thermodynamics where the Gibbs free energy (ΔG^0) can be calculated from enthalpy (ΔH^0) and entropy (ΔS^0) by using the Gibbs-Helmholtz equation. The Gibbs free energies of reaction have been calculated from the selected $\log\beta^0$ values. The entropies of reaction have been obtained from the respective entropies of formation which have been estimated by using the /Sverjensky et al. 1997/ methodology. The enthalpies of reaction selected for $AnCO_3^+$ are reported in Table 13-6.

Table 13-6. Enthalpies of reaction selected for the aqueous $AnCO_3^+$ complexes.

Reaction	Δ_rH^0 (kJ/mole)
$An^{3+}+CO_3^{2-} = AnCO_3^+$	157.585±7.996

Aqueous An(III) hydrogenocarbonates complexes

No An(III) hydrogenocarbonates have been included in the NAGRA-PSI 01/01 database. These complexes have been neither selected in the NEA compilation /Silva et al. 1995/ given that there are no experimental evidences of their existence. The updated NEA-TDB reviews more recent experimental studies /Fanghänel et al. 1998/ where evidences for the formation of bicarbonate species of Cm(III) have been reported. The formation constant obtained by /Fanghänel et al. 1998/ for $CmHCO_3^{2+}$ have been corrected to zero ionic strength an accepted for the analogous Am(III) complex. The selected formation constant for $AnHCO_3^{2+}$, as a function of CO_3^{2-}, is 13.43±0.55.

No enthalpy of reaction have been included in the database for this complex given the lack of experimental data and well-established estimation procedures to obtain entropies or enthalpies for this complex.

Solid An(III) carbonates

The NAGRA-PSI 01/01 database includes those solid carbonates selected in the NEA review /Silva et al. 1995/, $AmCO_3OH$(cr) and $Am_2(CO_3)_3$(s). As included in the NEA TDB update we have considered the solid phase $NaAm(CO_3)_2{\cdot}5H_2O$ in this database. In this case, we must consider that the analogue $NaCm(CO_3)_2{\cdot}5H_2O$ is not included in the database given the lack of evidence of its existence.

$AnCO_3OH$ (cr). Data from /Silva et al. 1995/ are included in the NAGRA-PSI 01/01 database. The selected formation constant for this solid phase is 6.20±1.00 (in terms of CO_3^{2-}) from the /Guillaumont et al. 2003/ compilation.

$NaAm(CO_3)_2{\cdot}5H_2O$. This solid has not been included in the NAGRA-PSI 01/01 TDB given that no thermodynamic data was recommended in the NEA compilation of /Silva et al. 1995/. In agreement with the NEA TDB update /Guillaumont et al. 2003/, we have considered the formation constants obtained from data in /Runde and Kim 1994/ and /Neck et al. 1998/, corrected to zero ionic strength by using the SIT methodology. The selected stability for this solid, in terms of CO_3^{2-}, is 21.00±0.50. This solid is considered only for Am, not for Cm.

$An_2(CO_3)_3$(s). We agree with the NAGRA-PSI 01/01 database about the stability of this solid phase. The formation constant included, 33.4±2.2, has been taken from /Silva et al. 1995/.

No enthalpies have been included in the database for $AnCO_3OH$(cr), $An_2(CO_3)_3$(cr) and $NaAm(CO_3)_2{\cdot}5H_2O$ given the lack of experimental data and well-established estimation procedures.

13.4.2 Silicon compounds

Despite no silicon species are included in the NEA review /Silva et al. 1995/, we agree with the NAGRA-PSI 01/01 database where the aqueous silicate $AmOSi(OH)_3^{2+}$ has been included. As indicated in the updated NEA-TDB /Guillaumont et al. 2003/, thermodynamic data for this complex have been taken from two experimental studies: /Wadsak et al. 2000/ and /Steinle et al. 1997/. In /Wadsak et al. 2000/, the authors studied the interaction between silicate and americium by means of solvent extraction techniques. The interaction between monosilicic acid and Cm(III) has been studied by /Steinle et al. 1997/. The selected formation constant, in terms of H_4SiO_4, is –1.68±0.18.

No enthalpy datum is included given that neither values for entropy nor for enthalpy have been found in the literature for this species.

13.5 Group 15

13.5.1 Nitrate compounds

We agree with the NAGRA-PSI 01/01 selection where the first nitrate complex has been included. The thermodynamic properties for this complex have been taken from the NEA compilation /Silva et al. 1995/.

The selected stability is shown in Table 13-7.

No reaction enthalpy has been found in the literature.

13.5.2 Phosphate compounds

Aqueous complexes

Only one aqueous Am(III) phosphate is included in the NAGRA-PSI 01/01 database, $Am(H_2PO_4)^{2+}$, whose thermodynamic data are taken from the NEA review /Silva et al. 1995/. We have estimated the stabilities of the first and the second phosphates and hydrogenphosphates of Am by taking into account the analogies between trivalent actinides and lanthanides. The formation constant have been obtained by linear free energy relationships based on ionic radii. We have taken data in /Millero 1992/ for the $M(PO_4)_n^{3-3n}$ complexes and data from /Spahiu and Bruno 1995/ for the $M(HPO_4)_n^{3-2n}$ species.

The selected stabilities, as a function of An^{3+} and $H_2PO_4^-$, for the aqueous phosphates are presented in Table 13-8.

No enthalpies have been reported in the NAGRA-PSI 01/01 database. Our selection does neither include enthalpies given the lack of experimental data and well-established procedures to estimate enthalpies or entropies.

Solid phases

No solid phosphates are included in the NAGRA-PSI 01/01 database given that the solubility constant reported in the NEA compilation /Silva et al. 1995/ has been derived at pH<3.0 and the exact stoichiometry of the solid phase used in the experimental study is unknown. Despite of the NAGRA considerations we have decided to include this solid in our database given that the solubility reported in /Silva et al. 1995/ is in agreement with the solubility data on REE phosphates.

The selected formation constants for the solid phosphates of An (as a function of $H_2PO_4^-$) are reported in Table 13-9.

No reaction enthalpy has been selected for this solid phase due to the lack of experimental data and well-established estimation procedures to obtain enthalpies or entropies.

Table 13-7. Thermodynamic data of An aqueous nitrates, different from NAGRA-PSI 01/01 TDB.

Reaction	$Log\beta^0$
$An^{3+}+NO_3^- = AnNO_3^{2+}$	1.33±0.20

Table 13-8. Formation constants for the aqueous phosphates of An, different from NAGRA-PSI 01/01 TDB.

Reaction	logβ^0
$An^{3+}+H_2PO_4^- = AnPO_4(aq)+2H^+$	–7.76±0.61
$An^{3+}+2H_2PO_4^- = An(PO_4)_2^{3-}+4H^+$	–19.43±1.01
$An^{3+}+H_2PO_4^- = AnHPO_4^++H^+$	–1.74±0.67
$An^{3+}+2H_2PO_4^- = An(HPO_4)_2^-+2H^+$	–5.31±1.01
$An^{3+}+H_2PO_4^- = AnH_2PO_4^{2+}$	3.00±0.50

Table 13-9. Thermodynamic data of Am (and Cm) solid phosphate species.

Reaction	–logK$_s$
$An^{3+}+H_2PO_4^-+xH_2O = AnPO_4{\cdot}xH_2O+2H^+$	5.23±0.60 (from /Silva et al. 1995/)

13.6 Group 16

13.6.1 Sulphide compounds

No Am(III) sulphides have been selected in the NAGRA-PSI 01/01 database given that the stabilities and the enthalpies reported in the NEA review /Silva et al. 1995/ are based on estimates and no experimental studies involving thermodynamic properties of these species are available. We agree with the NAGRA selection given that these compounds are not expected to appear under the conditions of interest for SKB.

13.6.2 Sulphate compounds

No solid Am(III) sulphates are included in the NAGRA-PSI 01/01 database given that no well-established experiment studies on these compounds are reported in the NEA compilation /Silva et al. 1995/.

Two aqueous Am(III) sulphate complexes, $AmSO_4^+$ and $Am(SO_4)_2^-$, are included in the NAGRA-PSI 01/01 database, in agreement with the selection reported in the NEA compilation /Silva et al. 1995/. We have taken advantage of the updated NEA-TDB where more recent experimental studies concerning Cm-SO_4 species are included. As proposed in /Guillaumont et al. 2003/ we have included the mean values of the formation constants calculated from /Paviet et al. 1996/ and /Neck et al. 1998/ for the Am (and Cm) sulphates. These authors have investigated the sulphate complexation equilibria of Cm(III) by using TRLFS (Time-Resolved Laser-induced Fluorescence Spectroscopy). The selected formation constants for the aqueous $An(SO_4)_n^{3-2n}$ are presented in Table 13-10

No enthalpies have been reported in the NAGRA-PSI 01/01 database. Given the lack of experimental data on this subject, we have estimated these magnitudes by means of correlations with reported thermodynamic data for Ln(III)-sulphates included in the NBS compilation /Wagman et al. 1982/. The validity of these estimates has been tested in front of the reported Δ_fG^0 values for the Am complexes in /Silva et al. 1995/. The enthalpies of reaction have been calculated from the estimated formation enthalpies, the resulting values are shown in Table 13-11.

Table 13-10. Thermodynamic data selected for the aqueous $An(SO_4)_n^{3-2n}$ complexes, different from NAGRA-PSI 01/01 TDB.

Reaction	Logβ^0
$An^{3+}+SO_4^{2-} = AnSO_4^+$	3.30±0.15
$An^{3+}+2SO_4^{2-} = An(SO_4)_2^-$	3.70±0.15

Table 13-11. Enthalpies of reaction selected for the aqueous $An(SO_4)_n^{3-2n}$ complexes.

Reaction	Δ_rH^0 (kJ/mole)
$An^{3+}+SO_4^{2-} = AnSO_4^+$	15.493±2.159
$An3^++2SO_4^{2-} = An(SO_4)_2^-$	20.927±2.046

13.7 Group 17

13.7.1 Aqueous complexes

Aqueous fluorides

The NAGRA-PSI 01/01 database includes those aqueous Am(III) fluorides selected in /Silva et al. 1995/. We agree with this selection where the first and the second aqueous fluorides are considered but we have also included the third fluoride given that this species, AmF_3(aq), is expected to appear under the conditions of interest for SKB. AmF_3(aq) has been reported in /Aziz and Lyle 1969/, /Feay 1954/ and in the JNC database /Rai et al. 1999b/. The formation constant selected in /Aziz and Lyle 1969/ corrected to I = 0 by using the SIT methodology is in good agreement with data reported in /Feay 1954/ and /Rai et al. 1999b/. No uncertainty can be obtained for the stability of this complex.

No uncertainties can be assigned for the formation constants of the third aqueous fluorides. The stabilities selected for aqueous AnF_n^{3-n} are reported in Table 13-12.

Enthalpies for fluoride species are neither included in the NAGRA-PSI 01/01 TDB nor in the NEA compilation /Silva et al. 1995/. Δ_rH^0 values have been calculated by using the Gibbs-Helmholtz equation, the Gibbs free energies of reaction have been calculated from the selected $\log b^o$ values. The entropies of reaction have been obtained from the respective entropies of formation, which have been estimated by using the /Sverjensky et al. 1997/ methodology. The enthalpies of reaction selected are reported in Table 13-12.

Aqueous chlorides

The NAGRA-PSI 01/01 database includes the first Am(III) aqueous chloride which is selected in the NEA review /Silva et al. 1995/. We have updated this selection with the updated NEA-TDB, where more recent studies are included. The formation constant selected in /Silva et al. 1995/ for $AmCl^{2+}$ has been rejected in the updated NEA TDB. The value recommended in the previous review does not agree with the experimental results of /Fanghänel et al. 1995/ and /Könnecke et al. 1997/. These authors have demonstrated that these inner-sphere complexes are formed only at very high chloride concentrations. The values from /Könnecke et al. 1997/ are selected given that they have been considered by the NEA as the best estimates for the first and the second aqueous complexes. The selected formation constants for the aqueous $AnCl_n^{3-}$ are presented in Table 13-13.

Table 13-12. Formation constants selected for AnF_n^{3-n}(aq), different from NAGRA-PSI 01/01 TDB.

Reaction	Logβ⁰	Δ_rH^0 (kJ/mole)
$An^{3+}+F^- = AnF^{2+}$	3.40±0.40	27.134±4.889
$An^{3+}+2F^- = AnF_2^+$	5.80±0.20	22.320±7.769
$An^{3+}+3F^- = AnF_3$(aq)	10.82	–12.119

As in the case of the fluoride species, enthalpies for chloride species are neither included in the NAGRA-PSI 01/01 TDB nor in the NEA compilation /Silva et al. 1995/. Δ_rH^0 values have been calculated by using the Gibbs-Helmholtz equation, the Gibbs free energies of reaction have been calculated from the selected logb^o values. The entropies of reaction have been obtained from the respective entropies of formation, which have been estimated by using the /Sverjensky et al. 1997/ methodology. The enthalpies of reaction selected are reported in Table 13-13.

Aqueous bromides and iodides

No data for An(III) bromides and iodides are included in the NAGRA-PSI 01/01 database, the reason being the difficulty in differentiating between complexation and activity effects in highly concentrated media. No data for these species are, therefore, included in the database.

13.7.2 Solid phases

No data for solid An(III) halides have been selected in the NAGRA-PSI 01/01 database. The stabilities selected in the NEA compilation /Silva et al. 1995/ have been calculated from estimated enthalpies and entropies and this selection cannot be confirmed with solubility experimental data. In this case, we agree with the discussion in the NAGRA-PSI 01/01 database, given that these solids are not expected to appear under the geochemical conditions of interest for SKB.

Table 13-13. Thermodynamic data selected for the aqueous $AnCl_n^{3-}$ complexes, different from NAGRA-PSI 01/01 TDB.

Reaction	Logβ^0	Δ_rH^0 (kJ/mole)
$An^{3+}+Cl^- = AnCl_2^+$	0.24±0.03	25.106±4.327
$An^{3+}+2Cl^- = AnCl_2^+$	–0.74±0.05	40.568±7.676

14 Thorium

In the following subsections we present the TDB selection for thorium. Since thorium is used frequently as an analogue for other actinide (IV) elements, we have extensively reviewed the thermodynamic database for this element. Given that some complexes have not been reviewed in the NAGRA-PSI 01/01 database we have proceeded to review all the speciation for this element, by including some new references not considered there. For this reason the selection performed in the case of thorium is rather different than the selection reported in the NAGRA-PSI 01/01 database.

14.1 Reference states and basic species

For Th the reference state is the metallic species; Th(cr), and we have taken the stability given by NAGRA-PSI 01/01 database, which comes from /Rard et al. 1999/. Standard $\Delta_f G^o$ and $\Delta_f H^o$ values for Th^{4+} have been taken directly from the NAGRA-PSI 01/01 database as well, where are referred to the work of /Fuger and Oetting 1976/, and S^o_f has been internally calculated.

14.1.1 Oxides and hydroxides

The solubility of thorium oxide and hydroxide and the crystallinity of these solids may vary importantly due to the tendency that this element has to form colloids under near neutral pH values. This fact has lead to the different solubility values recommended in the literature for the solubility of $Th(OH)_4(s)$. This issue has received special attention during the last years and several publications have dealt with the determination of a solubility product able to explain the concentrations of this element in equilibrium with the solid hydroxide in the whole range of pH, what has resulted in very discrepant values.

According to the revision in the NAGRA-PSI 01/01 database there are several authors /Ryan and Rai 1987/, /Moon 1989/, /Felmy et al. 1991/, /Serne et al. 1996/, /Wierczinski et al. 1998/ confirming that the solubility of thorium is well described by using a solubility product constant $\log K^o_{s,4} = -8.5$ /Neck and Kim 2001/.

$ThO_2(s) + 2H_2O \Leftrightarrow Th(OH)_4(aq)$ $\log K^o_{s,4} = -8.5$ 14-1

In the present work we agree with the value selected in the NAGRA-PSI 01/01 update for $\log K^o_{s,4}$. The total solubility is described by the sum of Th^{4+} plus $Th(OH)_4(aq)$ (see below). The update presented in the NAGRA-PSI 01/01 database provides a carefully and wide revision of all the publications dealing with the appropriate dataset describing this system.

$ThO_2(s) + 4H^+ \Leftrightarrow Th^{4+} + 2H_2O$ $\log{}^*K_{s,o}$ 14-2

$Th^{4+} + 4H_2O \Leftrightarrow Th(OH)_4(aq) + 4H^+$ $\log{}^*\beta_{1,4}$ 14-3

As a matter of fact, the NAGRA-PSI 01/01 update does not make any attempt to review equilibrium constants for the second and the third hydrolysis neither for the polymeric hydrolysis products, but only for the equilibrium constants for the first hydrolysis and fourth equilibria defined by the former reactions.

In the present work we have taken into consideration all the revision undertaken in the NAGRA-PSI 01/01 database together with recent publications which were not available during the NAGRA-PSI 01/01 update. Furthermore, we have introduced in the thermodynamic database for thorium, a selection for those hydrolysis constants not selected in the NAGRA-PSI 01/01 update with the aim to obtain a more detailed thermodynamic dataset for this element.

In order to be coherent within the selection for all the hydrolysis species as well as for the solubility product constant we have selected the thermodynamic dataset proposed in /Neck et al. 2002/, which, in turn, agree with the logK$^{o}_{s,4}$ selected in the NAGRA-PSI 01/01 database. The selection made for the hydrolysis of thorium include polynuclear species, that can be important at relatively high concentrations of the actinide. As recommended in /Neck et al. 2002/, we have disregarded the species $Th_6(OH)_{15}^{9+}$, since it is of minor importance at $[Th]<10^{-2}$ mol/l and because of the widely discrepant formation values reported.

No data were available for enthalpy neither for entropy. Given that for the solubility assessment that SKB must conduct on radionuclides the reference water temperature is 15°C, it is important to provide formation and reaction enthalpy data for the system. For this reason, we made estimations of the formation entropy by using the approach proposed by Langmuir /Langmuir 1978/.

From the estimated values of S_f for each thorium species and S_f values selected in the NAGRA-PSI 01/01 database for Th^{4+} and H_2O, we were able to calculate a Δ_rS^o for each reaction. On the other hand, once the logK was selected for each reaction we could calculate the Δ_rG^o describing each process and, therefore, from Δ_rS^o and Δ_rG^o it is possible to calculate the reaction enthalpy data.

In the case of the polynuclear species, neither enthalpies nor entropies values are reported in the open literature. Values for enthalpies and entropies are found only in one work /Baes and Mesmer 1976/, but they are at I = 1 m and are not compatible with the log K selected in this work. Table 14-1 summarizes the enthalpy reaction data selected, from estimated values, for some of the thorium species.

Table 14-1. Selected constants for Thorium oxides and hydroxides species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	log*β	Reference
$Th(OH)^{3+}$	$Th^{4+}+H_2O = Th(OH)^{3+}+H^+$	–2.20±0.20	/Neck and Kim 2001/, /Neck et al. 2002/
$Th(OH)_2^{2+}$	$Th^{4+}+2H_2O = Th(OH)_2^{2+}+2H^+$	–6.00±0.60	/Neck and Kim 2001/, /Neck et al. 2002/
$Th(OH)_3^{+}$	$Th^{4+}+3H_2O = Th(OH)_3^{+}+3H^+$	–11.00±1.00	/Neck and Kim 2001/, /Neck et al. 2002/
$Th(OH)_4(aq)$	$Th^{4+}+4H_2O = Th(OH)_4(aq) +4H^+$	–17.50±0.50	/Neck and Kim 2001/, /Neck et al. 2002/
$Th_2(OH)_2^{6+}$	$2Th^{4+}+2H_2O = Th_2(OH)_2^{6+}+2H^+$	–5.7	/Neck et al. 2002/
$Th_4(OH)_8^{8+}$	$4Th^{4+}+8H_2O = Th_4(OH)_8^{8+}+8H^+$	–20.4	/Neck et al. 2002/
$Th_4(OH)_{12}^{4+}$	$4Th^{4+}+12H_2O = Th_4(OH)_{12}^{4+}+12H^+$	–26.7	/Neck et al. 2002/
Species	**Reaction**	**–log*K$_s$**	**Reference**
$ThO_2(cr)$	$Th^{4+}+2H_2O = ThO_2(cr)+4H^+$	1.80±1.30	/Neck and Kim 2001/
$ThO_2{\cdot}2H_2O(am)$	$Th^{4+}+4H_2O = ThO_2{\cdot}2H_2O(am)+4H^+$	–9.00±1.00	/Neck and Kim 2001/, /Neck et al. 2002/

Table 14-2. Selected enthalpy reaction data for Thorium oxides and hydroxides species.

Species	Reaction	Δ_rH^0 (kJ/mol)	Reference
$Th(OH)^{3+}$	$Th^{4+}+H_2O = Th(OH)^{3+}+H^+$	53.67±10.49	calc.
$Th(OH)_2^{2+}$	$Th^{4+}+2H_2O = Th(OH)_2^{2+}+2H^+$	90.56±10.98	calc.
$Th(OH)_3^{+}$	$Th^{4+}+3H_2O = Th(OH)_3^{+}+3H^+$	121.52±11.89	calc.
$Th(OH)_4(aq)$	$Th^{4+}+4H_2O = Th(OH)_4(aq)+4H^+$	153.74±10.81	calc.

14.2 Group 14

There are few studies giving information on the formation of thorium carbonates. NAGRA-PSI 01/01 database consider all the information available in the literature on the formation of Th carbonates but do not take into consideration a publication /Riglet-Martial and Capdevila 1999/ which perform an accurate reinterpretation of the studies and data previously reported in the literature. This reinterpretation of the carbonate thorium data assigns uncertainty covering the different values reported.

/LaFlamme and Murray 1987/ indicated the presence of mixed hidroxo-carbonato thorium complexes from sorption data.

Later on, /Östhols et al. 1994/ determined the stability of the species $Th(OH)_3CO_3^-$ and Rai and co-authors /Rai et al. 1995/, /Felmy et al. 1997/, also indicated the existence of this type of complexes.

A later work /Riglet-Martial and Capdevila 1999/ made an important effort trying to reconcile the experimental data generated by /Östhols et al. 1994/ and those of Rai and co-authors. /Riglet-Martial and Capdevila 1999/ used different complexation schemes to explain those data and concluded that the best results were obtained when assuming the formation of the species $Th(OH)_3CO_3^-$ and $Th(OH)_2(CO_3)_3^{4-}$. The speciation scheme and associated stability data selected in that work were able to reproduce the experimental data both from /Östhols et al. 1994/ and from Rai and co-authors.

The agreement of the solubility calculated with the speciation scheme and stability constants shown in Table 14-3 and the experimental solubility data on $ThO_2(s)$ is shown in Figure 14-1.

No enthalpy data are available in the literature and no estimations have been conducted in this regard.

New experimental and modelling data have been published during the first months of 2005 /Altmaier et al. 2005/. Although they will not be discussed within this report, these studies should be taken into account for further reviews.

Table 14-3. Selected reaction constants for Thorium carbonate complexes, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	logβ⁰ selected	Reference
$Th(CO_3)_4^{4-}$	$Th^{4+}+4CO_3^{2-} = Th(CO_3)_4^{4-}$	31.60±2.00	/Riglet-Martial and Capdevila 1999/
$Th(CO_3)_5^{6-}$	$Th^{4+}+5CO_3^{2-} = Th(CO_3)_5^{6-}$	28.60±2.00	/Riglet-Martial and Capdevila 1999/
Species	**Reaction**	**log*β⁰ selected**	**Reference**
$Th(OH)_3(CO_3)^-$	$Th^{4+}+CO_3^{2-}+3H_2O = Th(OH)_3(CO_3)^-+3H^+$	–1.90±1.00	/Östhols et al. 1994/, /Riglet-Martial and Capdevila 1999/
$Th(OH)_2(CO_3)_3^{4-}$	$Th^{4+}+3CO_3^{2-}+2H_2O = Th(OH)_2(CO_3)_3^{4-}+2H^+$	10.20	/Riglet-Martial and Capdevila 1999/

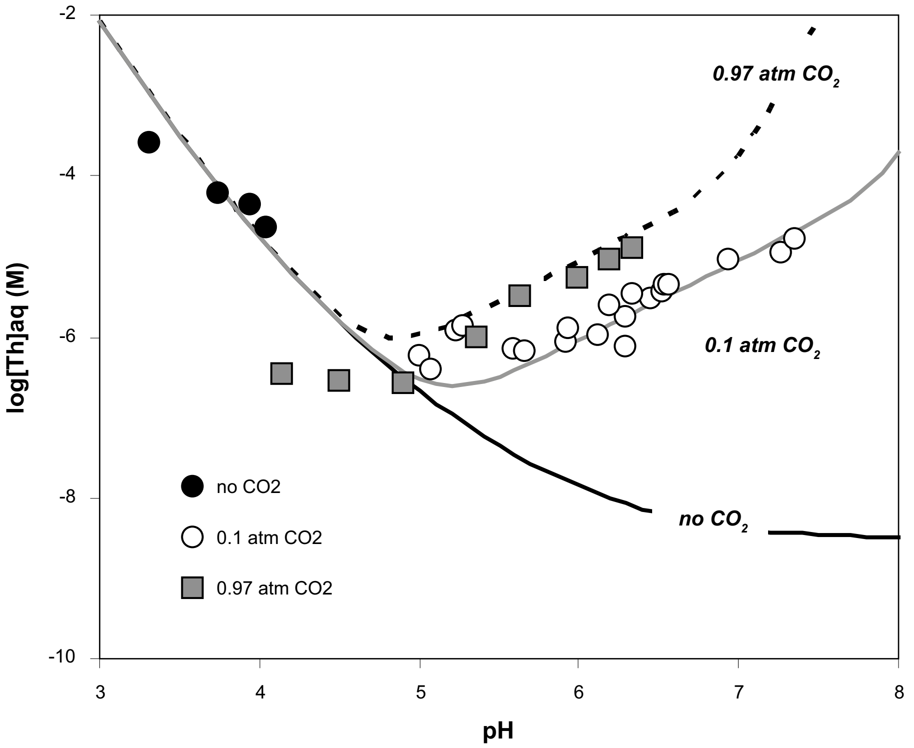

Figure 14-1. Comparison between calculated solubility of $ThO_2 \cdot 2H_2O(am)$ and experimental thorium concentration in equilibrium with this solid phase at different experimental conditions.

14.3 Group 15

14.3.1 Nitrate compounds

NAGRA-PSI 01/01 database does not consider nitrate complexation in this first update step given the low relevance of this species on the geochemical behaviour of Th under the conditions of interest for SKB. In general, nitrate complexation is weak, but by taking into consideration the NEA selection for other IV-actinides, we can credit the formation of $Th(NO_3)^{3+}$ with an estimated stability based on An (IV) ionic radii correlations.

We have not included nitrate species with more than one NO_3^- unit given that no experimental evidences have been reported.

Table 14-4. Selected reaction constants for Thorium nitrate complexes, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	logβ⁰ selected	Reference
$Th(NO_3)^{3+}$	$Th^{4+}+NO_3^- = Th(NO_3)^{3+}$	0.80±0.20	Estimated from An(IV) correlations

14.3.2 Phosphate compounds

The NAGRA-PSI 01/0 update does not consider appropriate the inclusion of aqueous thorium phosphate species in the database, given the questionable quality of the existing data.

However, they include the formation of $ThHPO_4^{2+}$ (data coming from /Moaskovin et al. 1967/ and corrected by SIT to I = 0) as being potentially the most relevant complex, letting the decision to the database user to include it or not in the calculations.

The precipitation of $Th(HPO_4)_2{\cdot}4H_2O(s)$ is excluded, although according to the re-interpretation of the data from /Moskvin et al. 1967/ conducted by the NEA review /Lemire et al. 2001/ for Np and Pu, there are indications that the aqueous phosphate complexes can be eliminated from the databases and that only solid phases of formula $An(HPO_4)_2{\cdot}nH_2O$ are formed.

Data for this type of solids are available for Pu and U, while corresponding data for Th is lacking. Therefore, we have conducted estimations based on linear correlations on the ionic radii of the central cation. The uncertainty for the solubility of this complex has been assigned by analogy to the uncertainty in the Pu solid. Summarizing, we have not included aqueous phosphate complexes of thorium in the database but we included the solid phase, as it is stated for the Pu and Np NEA selection /Lemire et al. 2001/.

No enthalpy data are available in the literature for group(V) thorium species.

14.4 Group 16

Thorium sulphate complexes are accurately evaluated in the NAGRA-PSI 01/01 database /Hummel et al. 2002/. For a comprehensive description of the revision undertaken there the reader is referred to the detailed discussion in /Hummel et al. 2002/. Data selected in the older NAGRA database /Pearson et al. 1992/ are based on the recommendation given in /Langmuir and Herman 1980/. As it is outlined by the authors of the NAGRA-PSI 01/01, the quality of the ionic strength corrections in the work of /Langmuir and Herman 1980/ is unclear since no details of the procedure are given. /Felmy and Rai 1992/ re-evaluated the thermodynamics of Th sulphate complexation including additional data and using a Pitzer approach, although a $\beta_{(1)}(Th^{4+}/SO_4^{2-})$-parameter of zero proposed by the authors is not consistent with the expected ranges for this Pitzer-parameter /Grenthe and Puigdomènech 1997/, as it is explained in the NAGRA-PSI 01/01 update. For this reason the decision taken in the NAGRA-PSI 01/01 update is to recalculate the second and the third thorium sulphate complexes from the tabulated μ^o/RT-values in /Felmy and Rai 1992/. Once they recalculated these two constants they made an estimation of the first sulphate thorium complex. Although we agree with the accurate revision of the NAGRA-PSI 01/01 database, it seems that there is one inconsistency in that procedure, as it is explained below.

Tabulated μ^o/RT-value in /Felmy and Rai 1992/ for Th^{4+} comes from /Fuger and Oetting 1976/, which is exactly the selected value in the NAGRA-PSI 01/01 database. However, in the case of SO_4^{2-} the value reported in /Felmy and Rai 1992/, which comes from /Harvie et al. 1984/, is not the same value selected for this species in the NAGRA-PSI 01/01 database, which comes from /Rard et al. 1999/. Therefore, if we make a re-calculation of the thorium sulphate constants according to the same procedure as followed in /Hummel et al. 2002/, we obtain a set of constants slightly different. In Table 14-6 we compare the constants reported in /Hummel et al. 2002/ with those constants re-calculated by following the same procedure as in /Hummel et al. 2002/ but considering the values selected in the NAGRA-PSI 01/01 database for the SO_4^{2-} species.

Therefore, the constants selected in this work for thorium sulphate species are those re-calculated from selection given in /Hummel et al. 2002/, by taking into consideration their own selection for the sulphate species.

No enthalpy data are available in the literature.

Table 14-5. Selected reaction constants for Thorium phosphate species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	$-\log K_s$ selected	Reference
$Th(HPO_4)_2(s)$	$Th^{4+}+2H_2PO_4^- = Th(HPO_4)_2(s)+2H^+$	15.98±0.50	Estimated from An(IV) correlations

Table 14-6. Selected reaction constants for Thorium sulphate species.

Species	Reaction	logβ⁰ selected in /Hummel et al. 2002/	Logβ⁰ selected in this work (recalculated)
$Th(SO_4)^{2+}$	$Th^{4+}+SO_4^{2-} = Th(SO_4)^{2+}$	7.6	7.9
$Th(SO_4)_2(aq)$	$Th^{4+}+2SO_4^{2-} = Th(SO_4)_2(aq)$	11.6	11.8
$Th(SO_4)_3^{2-}$	$Th^{4+}+3SO_4^{2-} = Th(SO_4)_3^{2-}$	12.4	12.7

14.5 Group 17

Fluoride thorium complexes selected in the NAGRA-PSI 01/01 database /Hummel et al. 2002/ come from the database compiled by /Langmuir and Herman 1980/, which take data from /Wagman et al. 1977/ for those complexes. /Hummel et al. 2002/ do not change the recommendation of Langmuir and Herman to use data from /Wagman et al. 1977/ and NAGRA-PSI 01/01 database contains thorium fluoride constants calculated from Δ_fG data summarized in /Langmuir and Herman 1980/ and coming from /Wagman et al. 1977/. However, instead of using the fluoride Δ_fG values selected in /Hummel et al. 2002/, the authors used the Δ_fG value reported in /Langmuir and Herman 1980/ for this species leading to an inconsistency similar to that reported for the sulphate species.

On the other hand, and related to the recommendation to use data coming from Wagman et al. there is a more recent publication from these authors /Wagman et al. 1982/ with slightly different Δ_fG values for those complexes. Therefore, if we take the recommendation given in the NAGRA-PSI 01/01 database to use values coming from these authors, we consider more appropriate to use values from the more recent publication /Wagman et al. 1982/. If we assume Δ_fG values for thorium fluoride complexes in *this* compilation /Wagman et al. 1982/ together with Δ_fG values selected for Th^{4+} and F^- in /Hummel et al. 2002/ there is a decrease on the formation constants for those complexes, as we can see in Table 14-7.

Although chloride species are not considered in the NAGRA-PSI 01/01 database, we have included a selection for the formation constant of the first thorium chloride, which comes from the same source as the fluoride species. This is entirely consistent with the selection conducted for the other tetravalent actinides (IV), where only the first chloride is selected (according to the NEA selection /Grenthe et al. 1992/, /Lemire et al. 2001/.

From the S_f values for each thorium halide species /Wagman et al. 1982/ and the S_f values selected in the NAGRA-PSI 01/01 database for Th^{4+} and H_2O, we have calculated Δ_rS^o for each reaction and, subsequently reaction enthalpy. A summary of the enthalpy reaction data calculated for each halide species is shown in Table 14-8.

Table 14-7. Selected reaction constants for Thorium halide species.

Species	Reaction	Logβ⁰ selected in /Hummel et al. 2002/	Logβ⁰ selected in this work (recalculated)	Reference
ThF^{3+}	$Th^{4+}+F^- = ThF^{3+}$	8.0	7.64	From /Wagman et al. 1982/
ThF_2^{2+}	$Th^{4+}+2F^- = ThF_2^{2+}$	14.2	13.36	From /Wagman et al. 1982/
ThF_3^+	$Th^{4+}+3F^- = ThF_3^+$	18.9	17.54	From /Wagman et al. 1982/
$ThF_4(aq)$	$Th^{4+}+4F^- = ThF_4(aq)$	22.3	20.41	From /Wagman et al. 1982/
$ThCl^{3+}$	$Th^{4+}+Cl^- = ThCl^{3+}$	1.13	1.21	From /Wagman et al. 1982/

Table 14-8. Selected enthalpy reaction data for Thorium halide species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	$\Delta_r H^0$ (kJ/mol)	Reference
ThF^{3+}	$Th^{4+}+F^- = ThF^{3+}$	–2.01	From /Wagman et al. 1982/
ThF_2^{2+}	$Th^{4+}+2F^- = ThF_2^{2+}$	–2.25	From /Wagman et al. 1982/
ThF_3^+	$Th^{4+}+3F^- = ThF_3^+$	–3.23	From /Wagman et al. 1982/
$ThF_4(aq)$	$Th^{4+}+4F^- = ThF_4(aq)$	–4.46	From /Wagman et al. 1982/
$ThCl^{3+}$	$Th^{4+}+Cl^- = ThCl^{3+}$	0.87	From /Wagman et al. 1982/

15 Protactinium

The reference database NAGRA-PSI 01/01 TDB /Hummel et al. 2002/, does not include data for protactinium. We have created a new thermodynamic database for this element mainly based on data compiled in /Baes and Mesmer 1976/ and /Bard et al. 1985/. Experimental data on Pa complexes and compounds is very scarce, thus, the thermodynamic properties found in literature rely mainly on estimates.

Neither enthalpies nor entropies have been included in the database, except for Pa^{4+} and Pa(c), given that no information for other species has been found in the literature.

15.1 Elemental protactinium

The entropy of formation, the stability constant and the reaction enthalpy for the reference state, Pa(c), have been calculated from formation data reported in /Bard et al. 1985/. The selected values are presented below:

$S^0_{f\,,\,Pa(c)}$ = 51.9±1.7 J/mole·K

$\mathrm{Log}\beta^0_{Pa(c)}$ = –98.75±4.06

$\Delta_rH^0_{Pa(c)}$ = 620.000±13.000 kJ/mole

15.2 Simple aqua ions

Aqueous Pa can exist in two oxidation states: Pa(IV) and Pa(V).

The basic species selected for this element is the free cation Pa^{4+}.

As in the case of the elemental protactinium, formation data for this species come from /Bard et al. 1985/ in an attempt to ensure the internal consistency of the database. Basic data for this tetravalent cation are shown below:

$\Delta_fG^0_{Pa^{4+}}$ = –563.665±23.174 kJ/mole

$\Delta_fH^0_{Pa^{4+}}$ = –620.000±13.000 kJ/mole

$S^0_{f\,,\,Pa^{4+}}$ = –397.6±48.7 J/mole K

The master species for Pa(V) is PaO_2^+ whose formation constant has been adopted from /Bard et al. 1985/:

$\mathrm{Log}\beta^0$ = 4.22±1.70

15.3 Aqueous hydroxides and solid oxides

/Baes and Mesmer 1976/ compiled existing data on Pa hydrolysis. No consistent set of Pa data have been produced from then on. Therefore, all data included in the database have been taken from /Baes and Mesmer 1976/ and shown in the following tables.

Table 15-1. Thermodynamic data selected for Pa(IV) hydroxides and oxides species.

Reaction	$\log{}^*\beta^0$
$Pa^{4+}+H_2O = PaOH^{3+}+H^+$	0.84±0.10
$Pa^{4+}+2H_2O = Pa(OH)_2^{2+}+2H^+$	–0.02±0.20
$Pa^{4+}+3H_2O = Pa(OH)_3^{+}+3H^+$	–1.50±0.30
Reaction	$-\log{}^*K_s$
$Pa^{4+}+2H_2O = PaO_2(s)+2H^+$	–0.60±1.00

Table 15-2. Thermodynamic data selected for Pa(V) hydroxides and oxides species.

Reaction	$\log{}^*\beta^0$
$PaO_2^{+}+H^+ = PaOOH^{2+}$	–0.50±0.10
$PaO_2^{+}+H_2O = PaO_2OH(aq)+H^+$	–4.50±0.20
Reaction	$-\log{}^*K_s$
$PaO_2^{+}+2H_2O = Pa_2O_5(s)+2H^+$	4.00

16 Uranium

Most data for Uranium included in the NAGRA-PSI 01/01 TDB comes from the NEA compilation /Grenthe et al. 1992/. In cases that the reference database does not include enthalpy values we have conducted a literature search and estimations to fill in the gaps when no other possibility was available, given that solubility calculations must be conducted at temperatures that differ from 25°C.

We present in the following subsections the TDB selection where a priori only data differing from those in the NAGRA-PSI 01/01 database and mostly coming from /Guillaumont et al. 2003/ are reported.

16.1 Simple aquo ions

Data for U^{3+}, U^{4+}, UO_2^+ and UO_2^{2+} have been taken directly from the NAGRA-PSI 01/01 database, where are referred to the NEA review /Grenthe et al. 1992/.

16.2 Oxygen and hydrogen compounds

16.2.1 Aqueous uranium hydroxide complexes

Given the relevance of the hydrolysis scheme of uranium, a special attention has been devoted to its description in this sub-section.

U(VI) complexes

Mononuclear U(VI) complexes

All data for aqueous U(VI) hydrolysis species in the NAGRA-PSI 01/01 database, except $UO_2(OH)_2(aq)$, come from the NEA compilation /Grenthe et al. 1992/.

For UO_2OH^+, we select the value in /Guillaumont et al. 2003/, the last NEA update.

The authors of the NAGRA-PSI 01/01 database differ from the initial Uranium NEA review given that in /Grenthe et al. 1992/ the selection of the stability for $UO_2(OH)_2(aq)$ was based on calorimetric data instead than on solubility results.

The discussion on the selection of the stability of this species is based on experimental data from /Chopin and Mathur 1991/ for uranium and on correlations with the stability of $PuO_2(OH)_2(aq)$ determined by /Pashalidis et al. 1995/.

Previous to the selection made in the NAGRA-PSI 01/01 database on this species, the NEA issued the review of data for Americium, including some update of thermodynamic data for uranium /Silva et al. 1995/, where it was suggested that the value of the stability constant for $UO_2(OH)_2(aq)$ in /Grenthe et al. 1992/ should be updated to consider a decrease in the Gibbs energy of formation of approximately 8 kJ/mol. This correction provided an upper limit of $\log{}^*\beta_2^0 = -11.7$.

The value selected in the NAGRA-PSI 01/01 database ($\log{}^*\beta_2^0 = -12.0$) is in agreement with the experimental determination of /Chopin and Mathur 1991/ ($\log{}^*\beta_2^0 = -12.15$), nevertheless, in order to ensure the consistency of the database, we must select the value for $\log\beta_1^0$ obtained by the same source /Chopin and Mathur 1991/ which differs in 0.4 log units from the one initially recommended in /Grenthe et al. 1992/, and is the one selected in /Guillaumont et al. 2003/. For this reason we select log$^*\beta_1^0$ and log$^*\beta_2^0$ from /Chopin and Mathur 1991/.

The stability of $UO_2(OH)_3^-$ in NAGRA-PSI 01/01 also comes from the NEA compilation /Grenthe et al. 1992/, where the value obtained by /Sandino 1991/ is quoted. At the time that the NEA literature review for the selection in /Grenthe et al. 1992/ was closed, the publication of /Sandino and Bruno 1992/ had not yet appeared. In the mentioned publication, the stability of $UO_2(OH)_3^-$ recommended is 0.9 log units lower than in /Grenthe et al. 1992/, therefore we have selected a value in agreement with the log$^*\beta_3^0 = -20.19$ as reported in /Sandino and Bruno 1992/, but re-calculated by the last NEA update to log$^*\beta_3^0 = -20.25$.

In the NAGRA-PSI 01/01 compilation the stability of $UO_2(OH)_4^{2-}$ from the /Grenthe et al. 1992/ estimate is selected. The authors comment on the more recent study by /Yamamura et al. 1998/ where a value of –32.4 for log$^*\beta_4^0$ is obtained. However, as in the mentioned work the stability used for $UO_2(OH)_3^-$ used is –20, versus –19.2 selected from the NEA review, they decided to disesteem the value of –32.4 and to keep the estimate of –33.

In our case, given that the value selected for log$^*\beta_3^0 = -20.25$ is closer to the one used by /Yamamura et al. 1998/, we have decided to select log$^*\beta_4^0 = -32.4$, for the sake of consistency of the whole hydrolysis system and giving more weigh to experimental determinations than to estimates, and in agreement with /Guillaumont et al. 2003/.

The NAGRA-PSI 01/01 database does not contain enthalpy values for the mononuclear U(VI) hydroxide species. Given that SKB wants to include temperature in the calculations, we have made an effort to select reaction enthalpies. The selection is detailed below.

UO_2OH^+. In the NEA review /Grenthe et al. 1992/, the selected S_f^0 for this species is 17±50 J/Kmol which, in combination with the Δ_rG^0 calculated from the former selected stability gives a value for the first hydrolysis reaction of UO_2^{2+} of:
Δ_rH^0 (1,1) = 43.5±14.9 kJ/mol

$UO_2(OH)_2(aq)$. The compilation /Wagman et al. 1982/ provides a value for ΔH_f^0 = 1,479.5 kJ/mol of this species. This value, combined with the selected logK gives:
Δ_rH^0 (1,2) = 111.16 kJ/mol

$UO_2(OH)_3^-$ and $UO_2(OH)_4^{2-}$. There are no data available on enthalpy for the third hydrolysis of uranyl. In /Lemire and Garisto 1989/, a value of S_f^0 = 85 J/mol·K for the fourth hydrolysis species is reported. This value, in combination with the Δ_rG^0 calculated from the selected stability produces:
Δ_rH^0 (1,4) = 156.1 kJ/mol

When analysing the ΔH_f^0 for the three hydrolysis species $UO_2(OH)^+$, $UO_2(OH)_2(aq)$ and $UO_2(OH)_4^{2-}$, it appears that the addition of one water molecule produces a linear increase in Δ_fH^0 of 250 kJ/mol. By interpolating a value for Δ_fH^0 of the species $UO_2(OH)_3^-$, we obtain:
Δ_rH^0 (1,3) = 148.06 kJ/mol

Polynuclear U(VI) complexes

All data in the NAGRA-PSI 01/01 compilation comes from the NEA review /Grenthe et al. 1992/. We agree with this selection except for the case of $(UO_2)_3(OH)_7^-$. In this case we select the stability reported by /Sandino and Bruno 1992/ for the sake of consistency with the previously reported selection, but re-calculated by the last NEA update to log$^*\beta^0 = -32.2$. The stability recommended by the NEA review and adopted in the NAGRA-PSI 01/01 TDB for this type of complexes is in rather good agreement with later experimental determinations of the stabilities for these species.

No values for enthalpy are available in the NAGRA-PSI 01/01 compilation for polynuclear U(VI) hydroxides. /Grenthe et al. 1992/ provide S_f^0 values for $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^+$.

For the remaining polynuclear hydrolysis species we select the recommended values for S_f^0 in /Lemire and Garisto 1989/, from where values for Δ_rH^0 can be calculated.

U(IV) hydroxide complexes

The hydrolysis of tetravalent uranium included in the NAGRA-PSI 01/01 database considers only those species selected in /Grenthe et al. 1992/.

In our case we have taken advantage of the review on the hydrolysis of tetravalent actinides conducted by Neck and co-workers /Neck and Kim 2001/ as well as on the new NEA TDB compilation /Guillaumont et al. 2003/. These authors have expressed the solubility of tetravalent actinide oxides by defining a hydrolysis scheme that includes four hydrolysis products, from $U(OH)^{3+}$ to $U(OH)_4(aq)$. The solubility of $UO_2(s)$ calculated by assuming the aforementioned scheme is in very good agreement with experimental solubilities measured by different authors. The existing correlation among the stability of the hydrolysis species for the different tetravalent actinides adds confidence to the description of the system recommended by /Neck and Kim 2001/.

We agree with the NAGRA-PSI 01/01 selection in eliminating the species $U(OH)_5^-$ whose existence was suggested due to the increase in the solubility of UO_2–type solid phases at high pH values. According to the dependence of the uranium speciation with pH and redox potential, it is not necessary to invoke the existence of this complex to explain the increase in solubility obtained at high pH values given that the oxidation of U(IV) to U(VI) occurs at lower redox potential when increasing pH and, therefore, such solubility increase can be due to the oxidation of tetra to hexavalent uranium with the subsequent appearance of uranyl hydrolysis complexes in solution. This can be observed in Figure 16-1, where we have disregarded the formation of $U(OH)_5^-$ but still an important increase in the $UO_2(s)$ solubility is observed for pH values above 11 due to the appearance of $UO_2(OH)_3^-$ and $UO_2(OH)_4^{2-}$ in solution.

The selected stabilities are reported in Table 16-1.

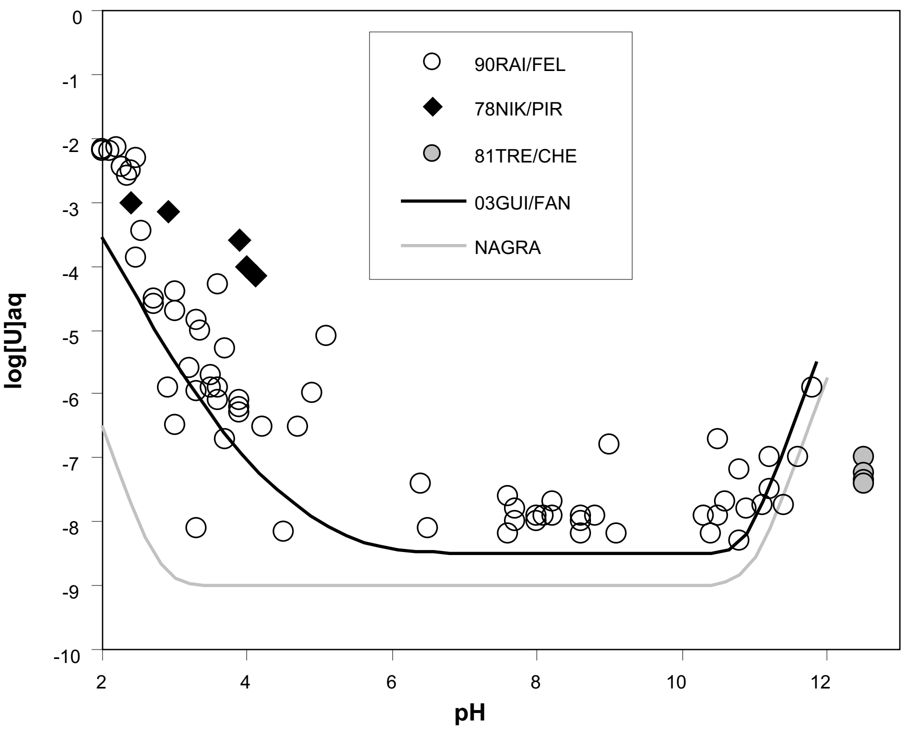

Figure 16-1. *Comparison between the experimental $UO_2(s)$ solubility and the calculated values when using the NAGRA-PSI 01/01 or the /Guillaumont et al. 2003/ database.*

This scheme is combined with a solubility product for UO_2(am) of log*K_s^0 = 1.5, what produces a solubility of [U(IV)] = $10^{-8.5}$ M in the neutral pH value where $U(OH)_4$(aq) is the dominating species in solution. The description of the solubility of UO_2(s) achieved by using the NAGRA-PSI 01/01 database in comparison with the one obtained by using the hydrolysis scheme recommended in /Guillaumont et al. 2003/ is shown in Figure 16-1.

According to the previous comparison, the assumption of only two hydrolysis species to interpret solubility data of UO_2(s) provides a rather good description of the solubility in the circum-neutral pH range, but fails to reproduce the values obtained for pH below 6. On the other hand, the solubility calculated in the plateau where $U(OH)_4$(aq) dominates the aqueous speciation when using the NAGRA-PSI 01/01 database is slightly lower than most experimental determinations.

The NAGRA-PSI 01/01 database contains enthalpy selection only for the first hydrolysis species of U(IV). In this case the value has been taken from the NEA compilation /Grenthe et al. 1992/.

Given the relevance that the hydrolysis of tetravalent uranium has on the results of the solubility calculations required to introduce in a Performance Assessment exercise, we have conducted an extensive literature search in order to assess the influence that temperature has on the stability of this system. Nevertheless, our efforts have not yield the desired results and we have solved this problem by following good established estimation methodologies.

In this case we have taken advantage of the study conducted by /Langmuir 1978/ who identified that the formation entropy of aqueous uranium species is a function of the electrical charge of the species of interest. The adequacy of this methodology can be only tested if comparison with experimental data is possible. The only experimental data available for such comparison come from the NEA selection, where values for S_f^0 of $U(OH)_3^+$, $U(OH)_4$(aq) and $U(OH)_5^-$ are given. In Figure 16-2 we present the comparison between the entropies of formation in the /Grenthe et al. 1992/ selection and the ones calculated from the /Langmuir 1978/ equation (for the sake of comparison we have included in this analyses also the entropy of the hypothetical $U(OH)_5^-$ species, although we do not credit its formation).

The estimated entropies in combination with formation energies of the components in the formation reactions and with the values of Gibbs free energy of reaction yield the following values of $\Delta_r H^0$ for the hydrolysis reactions of U^{4+} to form $U(OH)_n^{4-n}$:

$\Delta_r H^0$ ($U(OH)^{3+}$) = 46.91±9 kJ/mol·K

$\Delta_r H^0$ ($U(OH)_2^{2+}$) = 59.97±9.71 kJ/mol·K

$\Delta_r H^0$ ($U(OH)_3^+$) = 82.94±11.25 kJ/mol·K

$\Delta_r H^0$ ($U(OH)_4$(aq)) = 109.88±11.69 kJ/mol·K

Table 16-1. Selected stabilities for U^{4+} aqueous hydroxides species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	log*β⁰	Reference
$U(OH)^{3+}$	$U^{4+}+H_2O = U(OH)^{3+}+H^+$	–0.54±0.06	/Grenthe et al. 1992/
$U(OH)_2^{2+}$	$U^{4+}+2H_2O = U(OH)_2^{2+}+2H^+$	–1.10±0.1	/Neck and Kim 2001/
$U(OH)_3^+$	$U^{4+}+3H_2O = U(OH)_3^++3H^+$	–4.70±1.00	/Neck and Kim 2001/
$U(OH)_4$(aq)	$U^{4+}+4H_2O = U(OH)_4(aq)+4H^+$	–10.00±1.40	/Guillaumont et al. 2003/

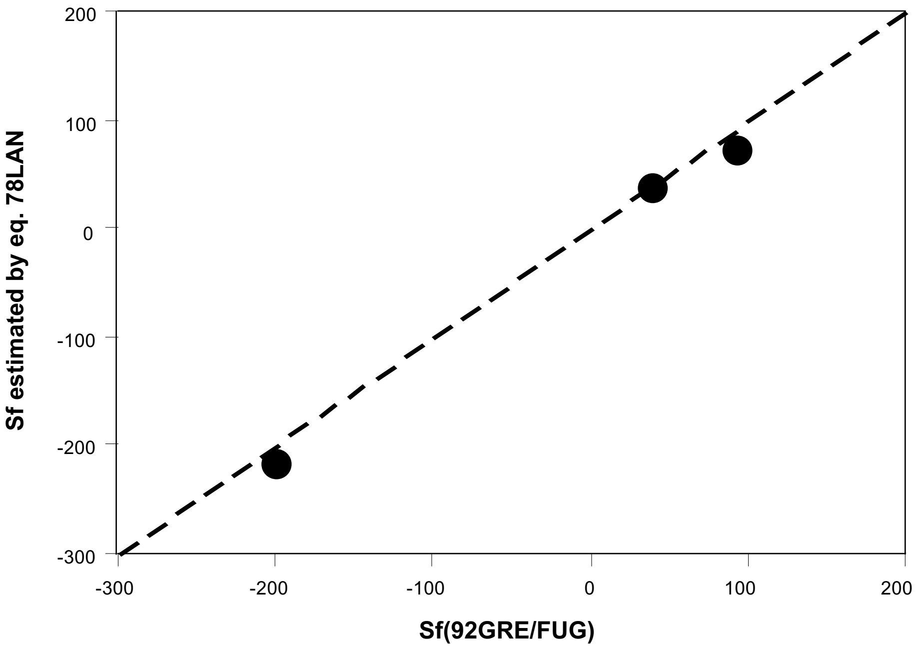

Figure 16-2. *Comparison between the values of S_f^0 for $U(OH)^{3+}$, $U(OH)_4(aq)$ and $U(OH)_5^-$ selected by /Grenthe et al. 1992/ and the ones estimated by applying equation in /Langmuir 1978/.*

Solid oxides and hydroxides

In the NAGRA-PSI 01/01 database one U(IV) solid oxide and one U(VI) solid oxide are included. We have also included in the database those oxides from the /Grenthe et al. 1992/ and /Guillaumont et al. 2003/ reviews that present well characterised thermodynamic properties. Although the use of some of these solids for the calculation of concentration limits used for performance assessment is not recommended, they give completeness to the database and allow to estimate thermodynamic properties that may be necessary in cases of filling in data gaps.

The solid oxides included in the NAGRA-PSI 01/01 database are UO_2(s) and $UO_3\cdot 2H_2O$(cr). The references quoted for the stability of these two solids are in-house NAGRA-PSI 01/01 stability in the case of UO_2(s) and /Bruno and Sandino 1989/ for the stability of schoepite ($UO_3\cdot 2H_2O$(cr)).

In the review of the database we have included the following solid phases:

α and β-UO_3(s) with thermodynamic magnitudes as in /Grenthe et al. 1992/

β-$UO_2(OH)_2$ with thermodynamic magnitudes as in /Grenthe et al. 1992/

$UO_3\cdot 0.9H_2O$(s) with thermodynamic magnitudes as in /Grenthe et al. 1992/

$UO_3\cdot 2H_2O$(cr) whose stability has been selected from the publication /Bruno and Sandino 1989/, in order to be consistent with the hydrolysis scheme selected for U(VI). In this sense we must indicate that the selection of the NAGRA-PSI 01/01 database is not entirely consistent, given that the stabilities selected for the different U(VI) hydrolysis species do not proceed from the same source than the stability selected for $UO_3\cdot 2H_2O$.

Regarding to U(IV) solid oxides, we have selected the stability of UO_2(s) proposed in /Guillaumont et al. 2003/, which is in agreement with the aqueous hydrolysis scheme of U(IV).

In the NAGRA-PSI 01/01 database no mixed valence oxides are included. The reasoning for excluding these solid phases is to avoid errors in the solubility calculations, given that under reducing conditions, for example, U_4O_9 is predicted to be the most stable solid phase, over UO_2(s), when it is not the case in reality. Nevertheless, we try to develop a thermodynamic database useful not only in assessment of solubility under specific near-field conditions, but also able to reproduce data from other sources, as is the case of Natural Analogue studies. Given that the studies of Natural Analogue projects in some cases indicate the adequacy of UO_{2+x} solid phases to explain the measured concentrations of uranium in groundwater, we have included in the database three mixed valence oxides:

U_4O_9(s), that is: $UO_{2.25}$

U_3O_7(s), that is: $UO_{2.33}$

U_3O_8(s), that is: $UO_{2.66}$

The thermodynamic properties included in the database for these oxides are taken from /Grenthe et al. 1992/ and /Guillaumont et al. 2003/.

Solid Uranates

Two solid uranates are selected in the database: $CaUO_4$(s) and Becquerelite. The solid $CaUO_4$(s) is not selected in the NAGRA-PSI 01/01 database by quoting a personal communication of Tits and Wieland, according to whom the dissolved concentrations predicted by using the solubility constant of $CaUO_4$(c) suggested in /Grenthe et al. 1992/ are orders of magnitude lower than the actual measurements. We have included the value in /Grenthe et al. 1992/ for the stability of this solid phase given that the solubilities calculated under cement groundwater compositions are in the order of 10^{-4}M, which are not very low. This value will be re-assessed if the data from Tits and Wieland to which the NAGRA-PSI 01/01 database refers to is made available for us.

The other solid, Becquerelite, is a mixed U(VI)-Ca oxide. The stoichiometric formula is: $Ca(UO_2)_6O_4(OH)_6{\cdot}8H_2O$. The stability of this solid has been determined by different authors. In this review we keep the value determined by /Casas et al. 1997/, given that it corresponds to a natural Becquerelite. Nevertheless, the value of synthetic becquerelite selected by the NEA review, which is an average from /Rai et al. 2002/ and /Sandino and Grambow 1994/, is also kept.

16.3 Group 14

16.3.1 Carbonate compounds

Two *U(IV) carbonate aqueous species* are included in the NAGRA-PSI 01/01 database. Data come from the compilation in /Grenthe et al. 1992/. We have corrected these data with updates in /Silva et al. 1995/ and in /Guillaumont et al. 2003/ and a value for the enthalpy of reaction of $U(CO_3)_5^{6-}$ has been included from the same NEA source.

Summarising, the following changes have been implemented in the database.

Data for U(VI) carbonate aqueous species included in the NAGRA-PSI 01/01 database come from
the /Grenthe et al. 1992/ compilation. We have included stability data in the newest NEA compilation /Guillaumont et al. 2003/, while enthalpy data remains unchanged from /Grenthe et al. 1992/ (Table 16-3).

Table 16-2. Changes implemented in the database concerning U(IV) carbonates species.

Reaction	logβ⁰ (NAGRA-PSI 01/01 TDB)	logβ⁰ (This report)	Δ_rH^0 (kJ/mol)
$U^{4+}+4CO_3^{2-} = U(CO_3)_4^{4-}$	35.22±1.03	35.12±0.93	
$U^{4+}+5CO_3^{2-} = U(CO_3)_5^{6-}$	34.1±1	34.0±0.9	–20±4

Table 16-3. NAGRA-PSI 01/01 and /Guillaumont et al. 2003/ data of aqueous uranium carbonates species.

Reaction	logβ⁰ (NAGRA-PSI 01/01)	logβ⁰ /Guillaumont et al. 2003/
$UO_2^{2+}+CO_3^{2-} = UO_2(CO_3)(aq)$	9.67±0.05	9.94±0.03
$UO_2^{2+}+2CO_3^{2-} = UO_2(CO_3)_2^{2-}$	16.9±0.12	16.61±0.09
$UO_2^{2+}+3CO_3^{2-} = UO_2)(CO_3)_3^{4-}$	21.6±0.05	21.84±0.04
$3UO_2^{2+}+6\ CO_3^{2-} = UO_2)_3(CO_3)_6^{6-}$	54±1	No change
Reaction	**log*β⁰ (NAGRA-PSI 01/01)**	**log*β⁰ /Guillaumont et al. 2003/**
$2UO_2^{2+}+CO_3^{2-}+3\ H_2O = (UO_2)_2(OH)_3CO_3^{-}+3\ H^+$	–0.86±0.5	No change
$3UO_2^{2+}+CO_3^{2-}+3\ H_2O = (UO_2)_3(OH)_3CO_3^{+}+3\ H^+$	0.66±0.5	No change

One solid U(VI) carbonate, rutherfordine, $UO_2CO_3(s)$ is included in the NAGRA-PSI 01/01 database, where the NEA review data has been considered. As in the previous cases, we have introduced data in the 2003 review /Guillaumont et al. 2003/ (see Table 16-4).

Enthalpy for the former reaction has been calculated from S_f^0 selected in /Grenthe et al. 1992/.

Table 16-4. Thermodynamic data comparison for rutherfordine.

Reaction	–logK$_s$ (NAGRA-PSI 01/01)	–logK$_s$ /Guillaumont et al. 2003/
$UO_2^{2+}+CO_3^{2-} = UO_2(CO_3)(s)$	14.49±0.04	14.76±0.02

16.3.2 Silicate compounds

In the NAGRA-PSI 01/01 database no aqueous uranium silicates are included. The reasoning is the discrepant stability obtained by different authors for U(VI) silicate species.

However, given the relevance of *solid silicates* on the uranium geochemistry, it is advisable to include the aqueous silicate species. In fact, in the recent NEA update /Guillaumont et al. 2003/ the species $UO_2SiO(OH)_3^+$ is included and we have also included it in the database, with the recommended stability:

$UO_2^{2+}+H_4SiO_4(aq) = UO_2SiO(OH)_3^{+}+H^+$, $\log\beta^0 = -1.84\pm0.1$ 16-1

Neither entropy nor enthalpy data have been included given the absolute lack of information on the subject.

In the NAGRA-PSI 01/01 database no U(VI) silicate solids are included. It is adduced in this regard that the only known compound is soddyite $(UO_2)_2SiO_4{\cdot}2H_2O$ and that no thermodynamic data are reported for this solid. From different natural analogue studies and laboratory studies intended to find a solution to the problem of the assessment of the solubility of uranium in natural systems, the relevance of two different U(VI) silicates: Soddyite ($(UO_2)_2SiO_4{\cdot}2H_2O$) and Uranophane ($Ca(UO_2)_2(SiO_3OH)_2{\cdot}5H_2O$), has been highlighted.

Stability data for soddyite has been obtained by different authors.

/Nuguyen et al. 1992/ conducted solubility studies of synthetic soddyite at pH = 3 and T = 25°C starting from undersaturated conditions. The experiments were kept under Ar atmosphere in order to avoid CO_2 contamination. These authors observed that solid/solution equilibrium was attached within 60 hours of the starting of the experiments. From the experimental values once reached equilibrium the solubility constant obtained for the reaction:

$\text{Soddyite}+4\ H^+ = 2\ UO_2^{2+}+SiO_2(aq)+4\ H_2O(aq)$ 16-2

was of $\log K_s^0 = 5.74\pm0.21$

Later work of /Pérez et al. 1997/ focused on determining the solubility of synthetic soddyite working also from undersaturated conditions. Different compositions of the contacting water were used in order to determine the influence of the concentration of carbonate in the system, given the strength of the uranyl-carbonate complexes and the ubiquitous presence of carbonate in natural groundwaters. From the experimental results, a value of $\log K_s^0 = 3.9 \pm 0.7$ was obtained for Equation 16-2.

This value is one order of magnitude larger than the solubility of soddyite determined by /Cera 1996/. In /Cera 1996/ the solubility of a natural uranophane sample was determined. The final product of the alteration of uranophane was characterised as soddyite and from the alteration process uranophane → soddyite a $\log K_s^0 = 2.98 \pm 0.29$ was obtained for Equation 16-2.

Considering the different nature of the soddyite samples used in those two later studies, it is somewhat astonishing that the difference in the solubility constant is only of 1 order of magnitude. This analyses shows that the determination of the solubility of soddyite is rather complicated and depends on the crystallinity of the solid phase.

In any case, the inclusion of the solubility constant determined by Nguyen would result in an overestimation of the solubility control exerted by this solid phase. We have followed in this case the NEA guidelines and have taken the average between the experimental data point of Nguyen and that of /Moll et al. 1996/, that is: $\log K_s = 6.2 \pm 1$.

Nevertheless, taking into account that the mentioned constants were obtained from a very limited set of experimental data (pH from 3 to 4.5), while the solubility constants obtained either by /Pérez et al. 1997/ or /Cera 1996/ were determined under a wider range of experimental conditions, we have included also the solubility constant determined by /Pérez et al. 1997/ in the database given that it corresponds to a perfectly defined soddyite. In the /Pérez et al. 1997/ work the aqueous silicate species $UO_2SiO(OH)_3^+$ was not included, nevertheless, under the experimental conditions used its inclusion does not vary the value of the solubility constant obtained by that author, as it can be seen in Figure 16-3.

The solubility of Uranophane ($Ca(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O$) is in agreement with uranium concentrations found in some natural analogues where the existence of this mineral has been reported (see /Bruno et al. 2000/). The stability of Uranophane determined in /Nuguyen et al. 1992/ has been selected.

Coffinite, $USiO_4(s)$, is the only reported U(IV) silicate. Solubility data for this solid is scarce, as acknowledged in the NAGRA-PSI 01/01 database. The NEA guidelines propose to use the approach recommended by Langmuir /Langmuir 1978/ as a guide for the estimation of the stability of this solid, although no stability is selected. This approach is also followed in the NAGRA-PSI 01/01 database. Langmuir, based on three analyses of coffinite-bearing groundwaters proposes a logK = 0.5 for the following equilibrium:

$$USiO_4(s) + 4\,H^+ = U^{4+} + H_4SiO_4(aq) \qquad 16\text{-}3$$

when using logK for $U(OH)_4(aq)$ of –12.0, that is, 2 log units lower than the one we are selecting in this review. Therefore, for the former equation, in order to be consistent with our database, we will have a logK = –1.5, which is the data included in the database.

This value, though, must be taken with caution, given that it has been obtained from three points under very specific conditions.

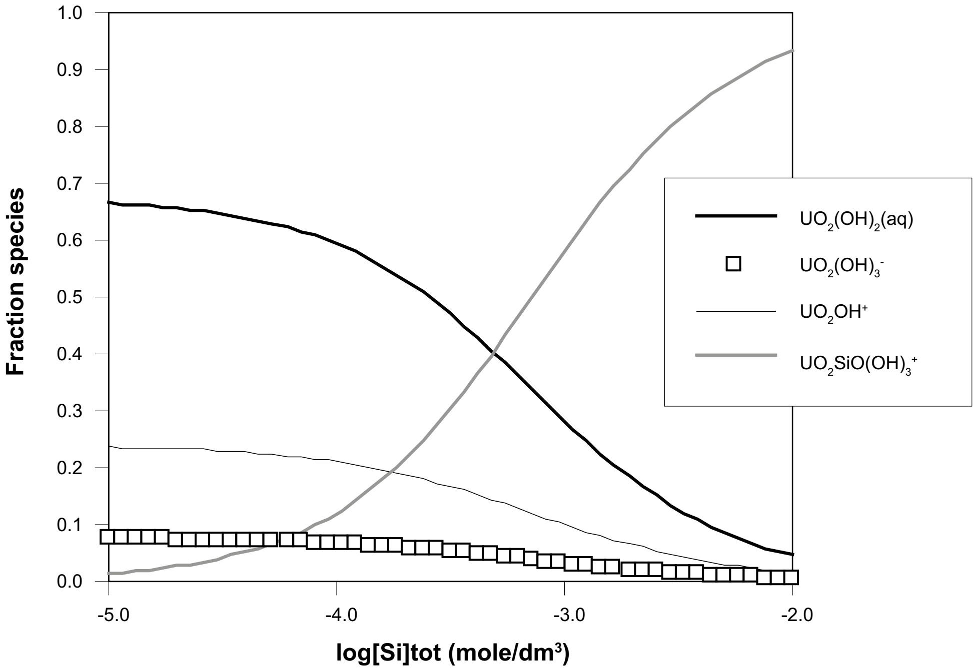

Figure 16-3. *Fractional diagram of uranium species in solution as a function of the total silica concentration. The species $UO_2SiO_2(OH)_3^+$ does not become dominant until $log[Si]_{tot}$=–3.2*

16.4 Group 15

16.4.1 Nitrate compounds

The NAGRA-PSI 01/01 database includes one uranyl nitrate aqueous complex whose stability is selected by /Grenthe et al. 1992/.

The same source is quoted for the tetravalent uranium nitrates included in the database: UNO_3^{3+} and $U(NO_3)_2^{2+}$.

16.4.2 Phosphate compounds

The selected *aqueous uranium(VI) phosphates* species included in the NAGRA-PSI 01/01 database are:

$UO_2(PO_4)^-$

$UO_2(HPO_4(aq)$

$UO_2(H_2PO_4)^+$

$UO_2(H_2PO_4)_2$

$UO_2(H_3PO_4)^{2+}$

$UO_2(H_2PO_4)(H_3PO_4)^+$

The original selection for the stability of the previous species is taken from the /Grenthe et al. 1992/ compilation. Neither enthalpy nor entropy data are selected in the NAGRA-PSI 01/01 database, although for the phosphate species $UO_2(PO_4)^-$ a value for S^0_f is reported, which, in combination with Gibbs delta energy of formation allows the calculation of Δ_rH^0.

In this work we have estimated entropy values for hydrogenphosphate and dihydrogenphosphate species by using the /Langmuir 1978/ equation. The value of S_f^0 in combination with Gibbs free energy allows the calculation of Δ_rH^0.

Summarising, data included in the database are shown in Table 16-5.

Although the existing data on *solid U(VI) phosphates* is not included in the NAGRA-PSI 01/01 database, underlying reasoning being the low quality of the solubility determination of these solid phases, we have preferred to introduce this type of solids given the relevance that uranium phosphates may have in the control of the uranium concentrations in natural systems.

Indeed, phosphate solids, such as autunite, are rather common secondary uranium phases found in natural environments, and therefore, their inclusion in the database may in many cases provide hints for assessing the relevance of phosphates on the geochemical behaviour of uranium.

Data reported in /Grenthe et al. 1992/ regarding U(VI) solid phosphates refer to the following solids: $(UO_2)_3(PO_4)_2(cr)$, $(UO_2)_3(PO_4)_2\cdot4H_2O$, $(UO_2)_3(PO_4)_2\cdot6H_2O$, $UO_2HPO_4\cdot4H_2O$. The solubility for these solid phases has been mainly determined under acidic conditions and, as acknowledged in the NAGRA-PSI 01/01 database, the only work extending up to pH 9 is the one of /Sandino and Bruno 1992/. The solubility of the solid phase $(UO_2)_3(PO_4)_2\cdot4H_2O$ determined by those authors with a well characterised solid is 4 orders of magnitude lower than the solubility selected in /Grenthe et al. 1992/. According to the NEA review the reason for this discrepancy is the different solid crystallinity as well as the differences in the ionic strength. /Grenthe et al. 1992/ prefers to select a solubility product obtained at lower ionic strength rather than the one obtained by /Sandino and Bruno 1992/ at 0.5 M $NaClO_4$.

In opposition to this reasoning, we rather rely on a well characterised solid phase studied throughout a wide pH range of relevance for geochemical studies and therefore we have included in the database the solubility determined by /Sandino and Bruno 1992/ what, on another hand, is the same source selected for the stability of the aqueous U(VI) phosphate species, obtaining a clear and consistent picture of the hexavalent uranium phosphate system. The value of the solubility constant for $(UO_2)_3(PO_4)_2\cdot4H_2O$ is $\log K_s^0 = -14.15\pm0.14$ (when the reaction is written with $H_2PO_4^-$).

The NAGRA-PSI 01/01 database does not include any U(IV)-phosphate species, given that the only selection in /Grenthe et al. 1992/ relates to the solubility of $U(HPO_4)_2\cdot4H_2O$ but is not accompanied by any aqueous U(IV) species, what may lead to large errors in the understanding of this system. We agree with this decision.

Table 16-5. Thermodynamic data of uranium phosphate species included in the database.

Reaction	$\log\beta^0$	Δ_rH^0 (kJ/mol)	Comments
$UO_2^{2+}+H_2PO_4^- = UO_2(H_2PO_4)^+$	3.26±0.07	–15.34±2.68	S_f^0 from /Langmuir 1978/
$UO_2^{2+}+2H_2PO_4^- = UO_2(H_2PO_4)_2(aq)$	4.92±0.13	–51.87±23.79	S_f^0 from /Langmuir 1978/
$UO_2^{2+}+H_2PO_4^- = UO_2(PO_4)^-+2H^+$	–6.33±0.42	No data	
$UO_2^{2+}+H_2PO_4^- = UO_2(HPO_4)+H^+$	0.03±0.47	2.79±3.98	S_f^0 from /Langmuir 1978/
$UO_2^{2+}+H_2PO_4^-+H^+ = UO_2(H_3PO_4)^{2+}$	2.90±0.15	No data	
$UO_2^{2+}+2H_2PO_4^-+H^+ = UO_2(H_2PO_4)(H_3PO_4)^+$	5.93±0.11	No data	

16.5 Group 16

16.5.1 Aqueous complexes

U(IV) species: Data for U(IV) sulphates in the NAGRA-PSI 01/01 database come from /Grenthe et al. 1992/. Two aqueous species USO_4^{2+} and $U(SO_4)_2$ are included.

U(VI) species: In addition to the two uranyl-sulphate species included in the NAGRA-PSI 01/01 database: $UO_2SO_4(aq)$ and $UO_2(SO_4)_2^{2-}$, whose thermodynamic properties come from the /Grenthe et al. 1992/ compilation and we have updated with /Guillaumont et al. 2003/ ($\log\beta_1^0 = 3.15\pm0.02$ and $\log\beta_2^0 = 4.14\pm0.07$), we have included the third sulphate complex $UO_2(SO_4)_3^{4-}$ quoted in /Guillaumont et al. 2003/ ($\log\beta^0 = 3.02\pm0.38$).

The U(VI) thiosulphate $UO_2S_2O_3(aq)$ with stability reported in /Grenthe et al. 1992/ is also included in the present selection.

16.5.2 Solid phases

In the NAGRA-PSI 01/01 database only one hydroxo-sulphate of U(IV), $U(OH)_2SO_4(cr)$, with stability reported in /Grenthe et al. 1992/, is included.

In addition to the former solid, we have included solid U(IV) sulphates reported in /Grenthe et al. 1992/ that vary in the crystallization water molecules:

$USO_4(cr)$

$USO_4{\cdot}4H_2O$

$USO_4{\cdot}8H_2O$

Thermodynamic data for the former species come from /Grenthe et al. 1992/. These solid phases are not included in the NAGRA-PSI 01/01 given that they form only at very acidic conditions ($pH<3$) and, therefore, they are not expected to be of relevance for geochemical modelling of interest for PA. We have preferred to include them for the sake of completeness of the database.

The same reasoning applies to the inclusion of the hexavalent uranium solid sulphates, although in the NAGRA-PSI 01/01 database these solids are not included, we prefer to consider them for the sake of completeness of the database. These solids are:

$UO_2SO_4(cr)$

$UO_2(SO_4){\cdot}2.5H_2O$

$UO_2(SO_4){\cdot}3H_2O$

$UO_2(SO_4){\cdot}3.5H_2O$

With stabilities calculated from enthalpy and entropy values reported in /Grenthe et al. 1992/.

16.6 Group 17

16.6.1 Aqueous complexes

U(VI) fluorides: in the NAGRA-PSI 01/01 database, the four U(VI) fluorides: $UO_2F_n^{2-n}$ with n = 1 to 4 are included, with data source /Grenthe et al. 1992/. We agree with the selection although the stability of the species is slightly varied in order to account for further developments of the database in /Guillaumont et al. 2003/. Differences of less than 0.3 log units are found between the selection in NAGRA-PSI 01/01 and the selection used here.

The enthalpies are as well in coincidence with those in the NAGRA-PSI 01/01 database, where the /Grenthe et al. 1992/ compilation is quoted for the selection.

U(VI) chlorides: The selection as in the NAGRA-PSI 01/01 database, coming from /Grenthe et al. 1992/ is kept here.

U(VI) bromides: Although in the NAGRA-PSI 01/01 database no aqueous U(VI) bromides are included, we have selected the value in /Grenthe et al. 1992/ for the stability of UO_2Br^+.

U(IV) fluorides and chlorides: The selection as in the NAGRA-PSI 01/01 database, coming from /Grenthe et al. 1992/ is updated with data selected in /Guillaumont et al. 2003/.

U(IV) bromides and iodides: Although in the NAGRA-PSI 01/01 database no aqueous U(IV) bromides are included, we have include in our selection the datum in /Grenthe et al. 1992/ for UBr^{3+}, and the same applies for UI^{3+}.

16.6.2 Solid phases

We agree with the discussion on the selection of $UF_4 \cdot 2.5H_2O$ in the NAGRA-PSI 01/01 database.

Table 16-6. Thermodynamic data for UO_2^{2+} aqueous fluorides species.

Species	Reaction	logβ⁰ (NAGRA-PSI 01/01)	logβ⁰ selected
UO_2F^+	$UO_2^{2+}+F^- = UO_2F^+$	5.09±0.13	5.16±0.06
$UO_2F_2(aq)$	$UO_2^{2+}+2F^- = UO_2F_2(aq)$	8.62±0.04	8.83±0.08
$UO_2F_3^-$	$UO_2^{2+}+3F^- = UO_2F_3^-$	10.9±0.4	10.9±0.4
$UO_2F_4^{2-}$	$UO_2^{2+}+4F^- = UO_2F_4^{2-}$	11±7 0.7	11.84±0.11

17 Neptunium

Thermodynamic database for neptunium has been taken mainly from the NAGRA-PSI 01/01 review /Hummel et al. 2002/, which take most of the information from the Np and Pu OECD NEA's book /Lemire et al. 2001/ and restrict the recommended values to data relevant for radioactive waste management or environmental modelling. We have kept the thermodynamic constants selected by the NAGRA reviewers /Hummel et al. 2002/ and we have reported any change and/or modification as well as those new data incorporated to the NAGRA-PSI 01/01 selection in the following sections.

17.1 Reference states and basic species

Neptunium reference and basic species selected for NAGRA-PSI 01/01 database come from the NEA selection /Lemire et al. 2001/ and it is complete in terms of logK and enthalpy reaction data. We have not made any modification of this selection.

17.2 Oxides and hydroxides

Trivalent Np aqueous species are only stable in the presence of strong reductants but they are easily oxidised by air. In consequence, experimental studies to determine the stability of trivalent aqueous complexes are really scarce. Data for the first hydrolysis product has been taken from the selection of the NEA team /Lemire et al. 2001/. Higher hydrolysis complexes have not been included in the NAGRA-PSI 01/01 database. Under mildly reducing conditions common to deep granitic groundwaters Np(IV) is expected to be the predominant oxidation state. However, when moving to highly reducing conditions, which can be produced due to the anaerobic corrosion of iron as expected in the frame of a repository system, Np(III) solid phases as well as the aqueous chemistry for the trivalent actinide could play a significant role on determining neptunium concentrations. For this reason, we have selected values for the subsequent hydrolysis species from /Allard et al. 1980/.

Concerning tetravalent neptunium oxides and hydroxides, we have selected data reported in the update of the NEA team /Guillaumont et al. 2003/ that bases the selection in a more recent publication /Neck and Kim 2001/, where the authors critically review and select a set of thermodynamic constants for tetravalent actinides. In that work, hydrolysis constants are selected preferentially from experimental studies and when this is no possible, unknown formation constants are estimated with a semi-empirical electrostatic model and an empirical correlation with the known constants of other actinide ions. For the solid phase, we have added the selection of the NEA update team as well /Guillaumont et al. 2003/.

Table 17-1. Selected reaction constants for Neptunium(III) hydroxides species, different from NAGRA-PSI 01/01 TDB.

Reaction	$\log{}^*\beta^0$	Reference
$Np^{3+}+H_2O = Np(OH)^{2+}+H^+$	–6.80±0.30	/Lemire et al. 2001/
$Np^{3+}+2H_2O = Np(OH)_2^{+}+2H^+$	–17.00±1.00	/Allard et al. 1980/
$Np^{3+}+3H_2O = Np(OH)_3(aq)+3H^+$	–27.00±2.00	/Allard et al. 1980/
Reaction	**$-\log{}^*K_s$**	**Reference**
$Np^{3+}+3H_2O = Np(OH)_3(s)+3H^+$	–18.00±2.00	/Allard et al. 1980/

Table 17-2. Selected reaction constants for Neptunium (IV) oxides and hydroxides species, different from NAGRA-PSI 01/01 TDB.

Reaction	$\log{}^*\beta^0$	Reference
$Np^{4+}+H_2O = Np(OH)^{3+}+H^+$	0.55±0.20	/Guillaumont et al. 2003/
$Np^{4+}+2H_2O = Np(OH)_2^{2+}+2H^+$	0.35±0.30	/Guillaumont et al. 2003/
$Np^{4+}+3H_2O = Np(OH)_3^{+}+3H^+$	–2.80±1.00	According to the NEA TDB guidelines /Neck and Kim 2001/
$Np^{4+}+4H_2O = Np(OH)_4(aq)+4H^+$	–8.30±1.10	/Guillaumont et al. 2003/
Reaction	**$-\log{}^*K_s$**	**Reference**
$Np^{4+}+2H_2O = NpO_2(am)+4H^+$	0.70±0.50	/Guillaumont et al. 2003/
$Np^{4+}+2H_2O = NpO_2(s)+4H^+$	9.75±1.07	Calculated from. ΔH_f and S_f /Lemire et al. 2001/

Data for the neptunium (V) aqueous hydroxides and for aged and fresh solids $NpO_2(OH)$ are selected in the NAGRA-PSI 01/01 database from /Lemire et al. 2001/ and we have kept that selection in our system. In addition, we have introduced $Np_2O_5(cr)$ selected in the NEA database (see Table 17-3).

In the case of Np (VI) oxides and hydroxides, only the first hydroxide species and the polymeric species 2:2 and 5:3 have been selected in /Lemire et al. 2001/. The NAGRA-PSI 01/01 database include these species with values proposed in the NEA selection as well as an upper value for the third and fourth hydrolysis species. For the second hydrolysis species no value has been proposed although it is recognized that such species may well exist. For this reason we made an estimation of the stability for the species $NpO_2(OH)_2(aq)$ by means of linear correlations based on ionic radii and we have included that value in the database as well.

When NAGRA-PSI 01/01 database gives enthalpy reaction data for the selected species we keep them. For those hydroxide neptunium species discussed and selected in this work we have selected when possible the enthalpy data as well, that are summarized in Table 17-5. In some cases, it has been possible to calculate enthalpy reaction from reported thermodynamic values and from the selected reaction constant. For tetravalent neptunium, where no data were available for enthalpy neither for entropy, estimations of the formation entropy were conducted by using the approach of Langmuir /Langmuir 1978/.

In general, we have taken values for entropy when needed from the NEA reviews and in case that no information were available we have adopted other values included in /Lemire 1984/, who used different approaches to estimate the entropies of formation of the different species of actinides. In the following table, we summarize the enthalpy reaction data proposed.

Table 17-3. Thermodynamic data of Np_2O_5(cr).

Reaction	–log*K_s	Reference
$2NpO_2^{+}+H_2O = Np_2O_5(cr)+2H^{+}$	–3.70±2.78	/Lemire et al. 2001/

Table 17-4. Selected reaction constants for Neptunium (VI) oxides and hydroxides species.

Reaction	–log*β^0	Reference
$NpO_2^{2+}+2H_2O = NpO_2(OH)_2(aq)+2H^{+}$	–12.21±1.50	estimated by correlation

Table 17-5. Selected enthalpies for Neptunium oxides and hydroxides species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction (aqueous complexes)	Δ_rH^0	Reference
$Np(OH)^{2+}$	$Np^{3+}+H_2O = Np(OH)^{2+}+H^{+}$	77.09±8.84	Calculated from logK and S_f estimated as described in /Shock et al. 1997/
$Np(OH)_2^{+}$	$Np^{3+}+2H_2O = Np(OH)_2^{+}+2H^{+}$	155.53±10.39	Calculated from logK /Allard et al. 1980/ and estimated S_f as described in /Sverjensky et al. 1997/
$Np(OH)_3$(aq)	$Np^{3+}+3H_2O = Np(OH)_3+3H^{+}$(aq)	235.824±14.34	Calculated from logK Allard et al. 1980/ and estimated S_f as described in Sverjensky et al. 1997/
$Np(OH)^{3+}$	$Np^{4+}+H_2O = Np(OH)^{3+}+H^{+}$	38.19±9.74	Calculated from. logK and S_f estimated as /Langmuir 1978/
$Np(OH)_2^{2+}$	$Np^{4+}+2H_2O = Np(OH)_2^{2+}+2H^{+}$	54.53±9.83	Calculated from. logK and S_f estimated as /Langmuir 1978/
$Np(OH)_3^{+}$	$Np^{4+}+3H_2O = Np(OH)_3^{+}+3H^{+}$	74.93±11.24	Calculated from. logK and S_f estimated as /Langmuir 1978/
$Np(OH)_4$(aq)	$Np^{4+}+4H_2O = Np(OH)_4(aq) +4H^{+}$	101.44±11.54	Calculated from. logK and S_f estimated as /Langmuir 1978/
NpO_2OH(aq)	$NpO_2^{+}+H_2O = NpO_2OH(aq) +H^{+}$	64.78±18.61	Calculated from LogK and S_f from /Lemire et al. 2001/
$NpO_2(OH)_2^{-}$	$NpO_2^{+}+2H_2O = NpO_2(OH)_2^{-}+2H^{+}$	118.61±5.22	Calculated from LogK and S_f from /Lemire et al. 2001/
$NpO_2(OH)^{+}$	$NpO_2^{2+}+H_2O = NpO_2(OH)^{+}+H^{+}$	42.96±15.40	Calculated from logK and S_f from /Lemire 1984/
$(NpO_2)_2(OH)_2^{2+}$	$2NpO_2^{2+}+2H_2O = (NpO_2)_2(OH)_2^{2+}+2H^{+}$	45.00±16.20	Calculated from logK and S_f from /Lemire 1984/
$(NpO_2)_3(OH)_5^{+}$	$3NpO_2^{2+}+5H_2O = (NpO_2)_3(OH)_5^{+}+5H^{+}$	110.67±17.65	Calculated from logK and S_f from /Lemire 1984/
Species	**Reaction (solid phases)**	**Δ_rH^0**	**Reference**
NpO_2(am, hyd)	$Np^{4+}+2H_2O = NpO_2\cdot(am)+4H^{+}$	81.16±8.79	Calculated from logK and S_f from /Lemire 1984/
NpO_2(s)	$Np^{4+}+2H_2O = NpO_2(s)+4H^{+}$	53.68±4.88	Calculated from Δ_fH and S_f from /Lemire et al. 2001/
NpO_2OH(am, aged)	$NpO_2^{+}+H_2O = NpO_2OH(am, aged)+H^{+}$	41.11±7.19	Calculated from LogK and Δ_fH from /Lemire et al. 2001/
NpO_2OH(am, fresh)	$NpO_2^{+}+H_2O = NpO_2OH(am, fresh)+H^{+}$	41.11±7.19	Calculated from LogK and Δ_fH from /Lemire et al. 2001/
Np_2O_5(cr)	$2NpO_2^{+}+H_2O = Np_2O_5(cr)+2H^{+}$	79.49±13.26	Calculated from Δ_fH and S_f from /Lemire et al. 2001/
$NpO_3\cdot H_2O$ cr	$NpO_2^{2+}+2H_2O = NpO_3\cdot H_2O(cr)+2H^{+}$	52.24±7.11	Calculated from logK and S_f from /Lemire 1984/

17.3 Group 14

As it is explained in the NAGRA-PSI 01/01 update, Np^{3+}, as in the case of Am^{3+} is expected to be complexed by carbonate in near neutral or basic solutions. In these conditions Np (III) is usually oxidised to the (IV) oxidation state. For this reason, there are not experimental studies dealing with neptunium (III) carbonates and there is not a selection in /Lemire et al. 2001/ neither in the NAGRA-PSI 01/01 database. Given the lack of data for these complexes and the recommendation of the NAGRA-PSI 01/01 database to use Am(III) or Lanthanide (III) as chemical analogues, we have estimated the log K of the first and second carbonate of Np(III). This estimation has been based in the linear free energy relationship with the z/r ratio, where z is the charge and r the radii of the cation. Data used in the estimations come from /Shannon 1976/ and /Neck et al. 1998/ and for $Np(CO_3)_3^{3-}$ we have selected data reported in /Lemire et al. 2001/.

$AnOHCO_3(s)$ may be one solid compound of trivalent actinides with significant importance to waste repository, according to several authors /Puigdomènech and Bruno 1991/, /Rai et al. 1999/. The existence of carbonate aqueous species raises the question whether a mixed hydroxo-carbonate solid phase Np(III) may play any role in controlling the solubility of these actinides under extreme reducing conditions. This is the reason why solubility data is selected for this solid phase although this selection is based on estimates on the analogy with Ln(III) due to the lack of experimental data.

Concerning Np(IV) carbonate complexes, NAGRA-PSI 01/01 database select those values reported in /Lemire et al. 2001/ for the carbonate species $Np(CO_3)_4^{4-}$ and $Np(CO_3)_5^{6-}$, which are probably formed in concentrated carbonate media. However, although the authors point out to the relative importance of the formation of mixed hydroxide-carbonate complexes of Np(IV) in environmental modelling, they do not propose thermodynamic values for those complexes because of the lack of experimental studies. Many efforts have been devoted in the last years to establish both, the existence and the stability of these mixed hydroxo-carbonate complexes. Eriksen and co-authors /Eriksen et al. 1993/ suggested the species $Np(OH)_3CO_3^-$, of equal stoichiometry to that of Thorium, and the species $Np(OH)_2(CO_3)_2^{2-}$, while Rai and co-workers /Rai et al. 1999/ conclude with the formation of $Np(OH)_4CO_3^{2-}$. We propose to add these species to the database. Finally, we totally agree with the selection of the NAGRA-PSI 01/01 database for the rest of neptunium carbonated and hydroxo-carbonated species.

Table 17-7 summarizes the additional enthalpy data both calculated and estimated to complete the database to be used in our calculations. In some cases, no values of entropies nor enthalpies have been found, as it is the case of $NpOHCO_3$ (s).

Table 17-6. Selected formation constants for Neptunium (III) and (IV) carbonates and hydroxo-carbonates species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	logβ⁰ selected	Reference
$Np(CO_3)^+$	$Np^{3+}+CO_3^{2-} = Np(CO_3)^+$	7.67±0.86	Estimated by correlation with An(III)
$Np(CO_3)_2^-$	$Np^{3+}+2CO_3^{2-} = Np(CO_3)_2^-$	12.60±0.85	Estimated by correlation with An(III)
$Np(CO_3)_3^{3-}$	$Np^{3+}+3CO_3^{2-} = Np(CO_3)_3^{3-}$	15.66±2.51	/Lemire et al. 2001/
Species	**Reaction**	**$-\log{}^*K_s$ selected**	**Reference**
$Np(CO_3)(OH)(s)$	$Np^{3+}+CO_3^{2-}+H_2O = Np(OH)(CO_3)(s)+H^+$	6.06	Estimated by correlation with An(III)/Ln(III)
Species	**Reaction**	**$\log{}^*\beta^0$ selected**	**Reference**
$Np(OH)_3(CO_3)^-$	$Np^{4+}+CO_3^{2-}+3H_2O = Np(OH)_3(CO_3)^-+3H^+$	3.82±1.13	/Eriksen et al. 1993/
$Np(OH)_4(CO_3)^{2-}$	$Np^{4+}+CO_3^{2-}+4H_2O = Np(OH)_4(CO_3)^{2-}+4H^+$	–6.83±1.13	/Eriksen et al. 1993/
$Np(OH)_2(CO_3)_2^{2-}$	$Np^{4+}+2CO_3^{2-}+2H_2O = Np(OH)_2(CO_3)_2^{2-}+2H^+$	15.17± 1.50	/Rai et al. 1999/

Table 17-7. Selected enthalpies for Neptunium carbonates and hydroxo-carbonates species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction (aqueous complex)	Δ_rH^0	Reference
$Np(CO_3)^+$	$Np^{3+}+CO_3^{2-} = Np(CO_3)^+$	156.37±5.13	Estimated from equation described in /Sverjensky et al. 1997/
$Np(CO_3)_5^{6-}$	$Np^{4+}+5CO_3^{2-} = Np(CO_3)_5^{6-}$	–1.61±6.80	Calculated from logK and S_f /Lemire and Garisto 1989/
$NpO_2CO_3^-$	$NpO_2^++CO_3^{2-} = NpO_2CO_3^-$	59.90±59.72	Calculated from logK and S_f /Lemire and Garisto 1989/
$NpO_2(CO_3)_2^{3-}$	$NpO_2^++2CO_3^{2-} = NpO_2(CO_3)_2^{3-}$	39.03±59.72	Calculated from logK and S_f /Lemire and Garisto 1989/
Species	**Reaction (solid phases)**	**Δ_rH^0**	**Reference**
$NaNpO_2(CO_3)3.5H_2O$	$NpO_2^++CO_3^{2-}+ Na^++3.5H_2O = NaNpO_2(CO_3)3.5H_2O$	–30.99±15.31	Calculated from logK and S_f /Lemire and Garisto 1989/

17.4 Group 15

17.4.1 Nitrate compounds

NAGRA-PSI 01/01 database gives a value for the first nitrate Np(IV) species, which is reported in /Lemire et al. 2001/ as well. Concerning pentavalent neptunium nitrates, the authors confirm the absence of these Np(V) complexes. In the NEA compilations only data on nitrates of hexavalent actinides are selected for uranium. However, according to their recommendations the same data can be taken by analogy for Np and Pu and we have proceeded in this way.

Given that data for Np nitrate stability is taken by analogy, we have no information on enthalpy data.

17.4.2 Phosphate compounds

As it is explained in the NAGRA-PSI 01/01 database and in the NEA selection, there are no experimental data for the Np(III) phosphate system. There is only one quantitative work reported by /Moskovin 1971/ for the Pu (III), Am (III) and Cm(III) phosphate system, and the NEA review team /Lemire et al. 2001/ rejects this study because of possible experimental shortcomings with the solubility measurements. Thus, the values estimated for the $Np(H_2PO_4)_n^{3-n}$ complexes from that experimental work are rejected by the NEA review team. We have then proceeded to estimate logK values based on the analogy with lanthanides for $Np(HPO_4)_n^{3-2n}$ and $Np(PO_4)_n^{3-3n}$ complexes using data of /Millero 1992/ and /Spahiu and Bruno 1995/, which are summarized in Table 17-9.

Table 17-8. Selected formation constants for Neptunium nitrate species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	$\log\beta^0$ selected	Reference
$NpO_2(NO_3)^+$	$NpO_2^{2+}+NO_3^- = NpO_2NO_3^+$	0.30±0.15	Analogy to $UO_2NO_3^+$, according to NEA recommendation

Table 17-9. Selected formation constants for Neptunium phosphate species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	$\log\beta^0$ selected	Reference
$NpPO_4(aq)$	$Np^{3+}+H_2PO_4^- = NpPO_4(aq)+2H^+$	–7.83±0.61	Estimated from correlation with An(III)
$Np(PO_4)_2^{3-}$	$Np^{3+}+2H_2PO_4^- = Np(PO_4)_2^{3-}+4H^+$	–19.57±1.01	Estimated from correlation with An(III)
$NpHPO_4^+$	$Np^{3+}+H_2PO_4^- = NpHPO_4^++H^+$	–1.78±0.67	Estimated from correlation with An(III)
$Np(HPO_4)_2^-$	$Np^{+3}+2H_2PO_4^- = Np(HPO_4)_2^-+2H^+$	–5.38±1.01	Estimated from correlation with An(III)
Species	**Reaction**	**$-\log K_s$ selected**	**Reference**
$Np(HPO_4)_2(s)$	$Np^{4+}+2H_2PO_4^- = Np(HPO_4)_2(s)+2H^+$	16.06±0.51	Estimated by correlation with An(IV)

The NEA team /Lemire et al. 2001/ provides indications that the neptunium (IV) phosphate aqueous complexes can be eliminated from the databases and that only the solid $Np(HPO_4)_2{\cdot}nH_2O$ is formed. Data for that solid is missed and we have conducted estimations for An(IV) based on linear correlations on the ionic radii of the central cation.

In the case of the Np(V) and Np(VI) phosphate complexes the selection of the NEA database is kept in the NAGRA-PSI 01/01 database although in some cases uncertainty limits have substantially increased.

No information on the enthalpies is provided and we have calculated the enthalpy reaction in those cases that we had enough information. (see Table 17-10).

17.5 Group 16

No experimental evidence for the stability of the neptunium (III) sulphate complexes is found. However, we have given estimates for the logK values based on analogies with Pu, Am and lanthanides.

In the case of $Np(SO_4)^+$, the entropy has been estimated by means of /Sverjensky et al. 1997/ equation and the corresponding enthalpy value has been calculated internally.

Table 17-10. Selected reaction enthalpies for Neptunium phosphate species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	Δ_rH^0	Reference
$NpO_2(HPO_4)(aq)$	$NpO_2^{2+}+H_2PO_4^- = NpO_2(HPO_4)(aq)+H^+$	92.21	Calculated from logK and S_f /Lemire and Garisto 1989/

Table 17-11. Selected formation constants for Neptunium sulphate species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	$\log\beta^0$ selected	Reference
$Np(SO_4)^+$	$Np^{3+}+SO_4^{2-} = Np(SO_4)^+$	3.86±0.66	Estimated from correlation with An(III)
$Np(SO_4)_2^-$	$Np^{3+}+2SO_4^{2-} = Np(SO_4)_2^-$	5.56±0.91	Estimated from correlation with An(III)

Table 17-12. Selected enthalpies for Neptunium sulphate species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	Δ_rH^0	Reference
$Np(SO_4)^+$	$Np^{3+}+SO_4^{2-} = Np(SO_4)^+$	17.89±4.05	Calculated from estimated logK and calculated S_f

17.6 Group 17

Neptunium fluoride complexation has been selected for the NEA database and kept for the NAGRA-PSI 01/01 database. The NEA team /Lemire et al. 2001/ does not select neptunium bromide species because the weak basis of the available experimental information while there is a selection for the iodide species not included in the NAGRA-PSI 01/01 database. We have included the constant reported for the first neptunium (IV) iodide, which is also selected in the NEA database /Lemire et al. 2001/ and estimated a value for $NpBr^{3+}$ from correlations with other actinides.

We totally agree with the selection of the other halide complexes at other oxidation states.

Only in the case of NpF^{3+} a value of enthalpy is reported in the NAGRA-PSI 01/01 database. We have included calculated values for the enthalpy reaction when possible for those halide complexes reported in order to have enough data for temperature corrections.

Table 17-13. Selected formation constants for Neptunium halide species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	$\log\beta^0$ selected	Reference
$NpBr^{3+}$	$Np^{4+}+Br^- = NpBr^{3+}$	1.55±0.40	Estimated from correlations with An (IV)
NpI^{3+}	$Np^{4+}+I^- = NpI^{3+}$	1.50±0.40	/Lemire et al. 2001/

Table 17-14. Selected reaction enthalpies for Neptunium halide species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	Δ_rH^0	Reference
NpF_2^{2+}	$Np^{4+}+2F^- = NpF_2^{2+}$	15.93±30.10	Calculated from logK and S_f /Lemire 1984/
$NpO_2F(aq)$	$NpO_2^++F^- = NpO_2F(aq)$	40.77±30.04	Calculated from logK and S_f /Lemire 1984/
NpO_2F^+	$NpO_2^{2+}+F^- = NpO_2F^+$	1.40±24.06	Calculated from logK and S_f /Lemire 1984/
NpO_2F_2	$NpO_2^{2+}+2F^- = NpO_2F_2$	4.32±24.06	Calculated from logK and S_f /Lemire 1984/
$NpCl^{3+}$	$Np^{4+}+Cl^- = NpCl^{3+}$	24.17±44.91	Calculated from logK and S_f /Lemire 1984/
NpO_2Cl^+	$NpO_2^{2+}+Cl^- = NpO_2Cl^+$	8.39±44.84	Calculated from logK and S_f /Lemire 1984/

18 Plutonium

Plutonium data selected to be used in calculations have been taken from the NAGRA/PSI 01/01 database /Hummel et al. 2002/, which is mainly referred to the NEA database selection /Lemire et al. 2001/. We have kept thermodynamic constants selected by the NAGRA reviewers /Hummel et al. 2002/ and reported any change and/or modification as well as those new data incorporated to the NAGRA-PSI 01/01 selection in the following sections.

18.1 Reference states and basic species

Plutonium reference and basic species selected for NAGRA-PSI 01/01 database come form the NEA selection /Lemire et al. 2001/. Data of log K as well as enthalpy reaction data are provided in the selection.

18.2 Oxides and hydroxides

As in the case of the neptunium , under mildly reducing conditions common to deep granitic groundwaters Pu(IV) is expected to be the predominant oxidation state. Nevertheless, under high reducing conditions as can be found due to the anaerobic corrosion of iron, Pu(III) solid phases as well as the aqueous chemistry for the trivalent actinide could be important and consequently determine the aqueous actinide concentrations. Only the first hydrolysis species and the hydroxide solid phase for plutonium in the III oxidation state have been reported and data come from the selection of the NEA team /Lemire et al. 2001/. However, data for the higher hydrolysis species have not been reported in the NAGRA-PSI 01/01 database. As we have explained, the aqueous chemistry of plutonium (III) can play an important role on determining the actinide concentrations under highly reducing conditions and is for this reason that we have included in the database the second and the third hydrolysis species for trivalent plutonium taken from /Allard et al. 1980/.

We have selected tetravalent plutonium oxides and hydroxides from data reported in the update of the NEA selection /Guillaumont et al. 2003/ and thus we have updated the selection of the NAGRA-PSI 01/01 database that selected data from the NEA team /Lemire et al. 2001/.

Table 18-1. Selected reaction constants for Plutonium (III) hydroxide species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	log*β⁰	Reference
$Pu(OH)_2^+$	$Pu^{3+}+2H_2O = Pu(OH)_2^++2H^+$	–15.90±1.00	/Allard et al. 1980/
$Pu(OH)_3$	$Pu^{3+}+3H_2O = Pu(OH)_3+3H^+$	–25.30±1.50	/Allard et al. 1980/

Table 18-2. Selected reaction constants for Plutonium (IV) oxides and hydroxides species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	log*β⁰	Reference
$Pu(OH)^{3+}$	$Pu^{4+}+H_2O = Pu(OH)^{3+}+H^+$	0.60±0.20	/Guillaumont et al. 2003/
$Pu(OH)_2^{2+}$	$Pu^{4+}+2H_2O = Pu(OH)_2^{2+}+2H^+$	0.60±0.30	/Guillaumont et al. 2003/
$Pu(OH)_3^+$	$Pu^{4+}+3H_2O = Pu(OH)_3^++3H^+$	–2.30±0.30	/Guillaumont et al. 2003/
$Pu(OH)_4(aq)$	$Pu^{4+}+4H_2O = Pu(OH)_4(aq)+4H^+$	–8.50±0.50	/Guillaumont et al. 2003/
Species	**Reaction**	**–log*Ks**	**Reference**
PuO_2(am, hyd)	$Pu^{4+}+2H_2O = PuO_2$(am, hyd)$+4H^+$	2.37±0.60	/Guillaumont et al. 2003/
$Pu(OH)_4$(am)	$Pu^{4+}+4H_2O = Pu(OH)_4(am)+4H^+$	0.80±1.30	/Lemire and Garisto 1989/

When looking at the solid phase selected by those authors, PuO_2(am, hyd) /Guillaumont et al. 2003/, we can see (Figure 18-1) that calculated solubility of this solid is in fair agreement with experimental data in the literature although fall slightly below the experimental measurements. After a more detailed analyses of data in the literature we have incorporated data from /Ewart et al. 1985/ obtained as a function of pH in cement pore water where Eh = –300 mV and T = 28°C /Felmy et al. 1989/. According to the authors it seems that initial solid was trivalent $Pu(OH)_3$(s) at –300 mV although the final solid was likely to be a tetravalent hydrous oxide. The solubility constant reported by Lemire and Garisto in /Lemire and Garisto 1989/ reproduces the same trend in the data and slightly overestimates experimental data points (Figure 18-1). For this reason, and in order to constrain the experimental data between two extreme values, we have included an additional $Pu(OH)_4$(am) solid with the stability selected in /Lemire and Garisto 1989/.

Data for the plutonium (V) and (VI) aqueous hydroxides and for the corresponding solids are selected in the NAGRA-PSI 01/01 database from /Lemire et al. 2001/ and we have kept that selection in our system.

As we proceeded with other actinides, for those hydroxide plutonium species discussed and selected in this work in addition to the NAGRA-PSI 01/01 selection we have selected when possible the enthalpy data as well, that are summarized in Table 18-3. In some cases, it has been possible to calculate enthalpy reaction from reported thermodynamic values and from the selected reaction constant.

Formation entropies for plutonium (III) species have been estimated by using approaches in /Baes and Mesmer 1976/ and /Sverjensky et al. 1997/ for the first and the subsequent hydrolysis products respectively.

For tetravalent plutonium, where no data were available for enthalpy neither for entropy, estimations of the formation entropy were conducted by using the approach of Langmuir /Langmuir 1978/. In addition, values selected for the enthalpy reaction of the first hydrolysis of Pu(IV) has been rejected as it is stated in the update undertaken by the NEA team /Guillaumont et al. 2003/.

On the other hand, when needed values for entropy have been taken when available from the NEA reviews and in case that no information were available we have adopted other values included in /Lemire 1984/, who used different approaches to estimate the entropies of formation of the different species of actinides. In the following table, we summarize the enthalpy reaction data proposed. From values of S_f and ΔG_f values we have been able to calculate most thermodynamic data for these species.

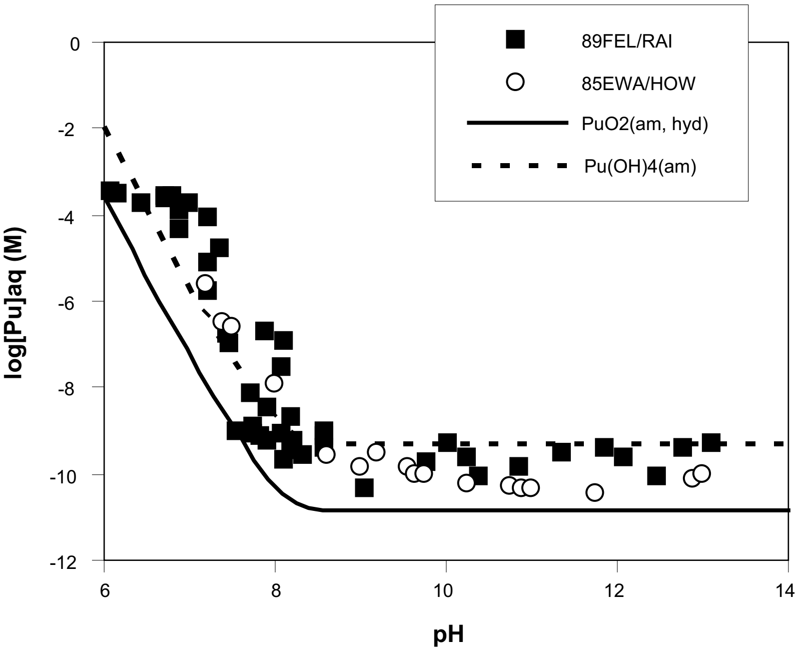

Figure 18-1. Comparison between experimental data on $PuO_2(am)$ solubility experiments and solubility calculated by using the set of data selected in this work.

Table 18-3. Selected enthalpy reaction data for Plutonium oxides and hydroxides species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction (aqueous complex)	$\Delta_r H^0$	Reference
$Pu(OH)^{2+}$	$Pu^{3+}+H_2O = Pu(OH)^{2+}+H^+$	78.27±6.72	Calculated from logK and S_f estimated as described in /Shock et al. 1997/
$Pu(OH)_2^+$	$Pu^{3+}+2H_2O = Pu(OH)_2^++2H^+$	150.342±8.65	Calculated from logK /Allard et al. 1980/ and estimated S_f as described in /Shock et al. 1997/
$Pu(OH)_3(aq)$	$Pu^{3+}+3H_2O = Pu(OH)_3(aq)+3H^+$	227.54±10.75	Calculated from logK /Allard et al. 1980/ and estimated S_f as described in /Shock et al. 1997/
$Pu(OH)_2^{2+}$	$Pu^{4+}+2H_2O = Pu(OH)_2^{2+}+2H^+$	49.57±9.60	Calculated from logK and S_f estimated as /Langmuir 1978/
$Pu(OH)_3^+$	$Pu^{4+}+3H_2O = Pu(OH)_3^++3H^+$	68.54±9.60	Calculated from logK and S_f estimated as /Langmuir 1978/
$Pu(OH)_4(aq)$	$Pu^{4+}+4H_2O = Pu(OH)_4(aq)+4H^+$	99.05±9.87	Calculated from logK and S_f estimated as /Langmuir 1978/
$PuO_2OH(aq)$	$PuO_2^++H_2O = PuO_2OH(aq)+H^+$	71.83±60.90	Calculated from logK and S_f from /Lemire and Tremaine 1980/
$PuO_2(OH)^+$	$PuO_2^{2+}+H_2O = PuO_2OH^++H^+$	28.00±15.00	Lemire et al. 2001/
$(PuO_2)_2(OH)_2^{2+}$	$2PuO_2^{2+}+2H_2O = (PuO_2)_2(OH)_2^{2+}+2H^+$	43.58±27.85	Calculated from logK and S_f from /Lemire 1984/
Species	**Reaction (solid phases)**	**$\Delta_r H^0$**	**Reference**
$Pu_2O_3(s)$	$2Pu^{+3}+3H_2O = Pu_2O_3(s)+6H^+$	385.07±10.74	Calculated from formation data /Lemire et al. 2001/
$PuO_2(am, hyd)$	$Pu^{4+}+2H_2O = PuO_2(am, hyd)+4H^+$	58.55±7.76	Calculated from logK and S_f from /Lemire 1984/
$PuO_2(OH)_2{\cdot}H_2O(s)$	$PuO_2^{2+}+3H_2O = PuO_2(OH)_2{\cdot}H_2O(s)+2H^+$	46.72±15.04	Calculated from logK and S_f /Lemire et al. 2001/

18.3 Group 14

As it is explained in the NAGRA-PSI 01/01 database the readiness of Pu(III) to oxidise to Pu(IV) in alkaline solutions and consequently the lack of experimental studies to determine the identity of these complexes lead up to the lack of experimental studies with respect to the identity and stability of Pu(III) carbonate. For this reason /Lemire et al. 2001/ do not select any values for Pu(III) carbonate complexes.

As we have already mentioned in previous sections, it is expected to have reducing conditions, common the deep groundwaters, which can move to highly reducing conditions due to the anaerobic corrosion of iron, as expected in the frame of a repository system. $Pu(OH)_4(s)$ is expected to control the solubility of Pu and no experimental evidences on the formation of Pu(III)-carbonate species have been found in the literature. Nevertheless, none of the publications we have considered denies the existence of this type of complexes. In general, data for these complexes are based on chemical analogies with other trivalent elements, mainly lanthanides. According to some authors /Bruno et al. 1997/ the stability of the $PuCO_3^+$ species has an important effect on the solubility of $Pu(OH)_4(am)$. The NAGRA-PSI 01/01 database /Hummel et al. 2002/ suggests the use of Am data as chemical analogue in model calculations. In addition, when moving to highly reducing conditions Pu(III) solid phases could play a critical role on determining plutonium solubilities. Both $Pu(OH)_3(s)$ and $Pu(OH)CO_3(s)$ could be stable under the chemical conditions expected to occur at bentonite/canister interface.

In the case of aqueous Pu(III) carbonates we have estimated logK for these species by correlations with Ln(III) and An(III).We have included formation of $Pu(CO_3)_3^{3-}$ but this species could become predominant increasing pH and at higher carbonate concentrations than those in equilibrium with calcite, what may have important implications in the near field solubilities under bentonite interacted groundwater /Bruno and Arcos 1999/.

Since the publication of the NEA update /Guillaumont et al. 2003/ is a later publication than the NAGRA-PSI 01/01 database and accept and select new values for plutonium (IV) carbonates, we decided to replace values for these species for those selected for the update of the NEA team /Guillaumont et al. 2003/. Concerning the mixed hydroxo-carbonato complexes, we agree with the decision of the NAGRA-PSI 01/01 database authors who prefer not to select a value for these species. As they say, these species, if exist, are not dominant and experiments that have lead to assuming mixed hydroxide carbonate complexes can be explained by the independent formation of hydrolysis products and carbonate complexes.

Data for aqueous Pu(V) carbonate complexes are included in the NAGRA-PSI 01/01 database with the exception of the second carbonate because of the lack of experimental evidence for the existence of $PuO_2(CO_3)_2^{3-}$, which may result from disproportionation of this species indicating a very small field for this species, as it is explained in the NEA database. Finally, for plutonium (VI) carbonate species we have included and when necessary we have replaced values selected in the NAGRA-PSI 01/01 database for those values revised and updated in the NEA update Guillaumont et al. 2003/. All these values are summarized in Table 18-4.

In addition to the enthalpy reaction data reported for plutonium carbonate species, we report in Table 18-5 enthalpy data calculated to complete the database to be used in our calculations. In some cases, when no enthalpy reaction data is given in the NAGRA-PSI 01/01 database and no values of entropies nor enthalpies have been found in the literature no enthalpy reaction data is given.

Table 18-4. Selected thermodynamic data for Plutonium carbonates species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	$\log\beta^0$	Reference
$PuCO_3^+$	$Pu^{3+}+CO_3^{2-} = PuCO_3^+$	7.64±0.86	estimated by correlation with An(III)/Ln(III
$Pu(CO_3)_2^-$	$Pu^{3+}+2CO_3^{2-} = Pu(CO_3)_2^-$	12.54±0.86	estimated by correlation with An(III)/Ln(III
$Pu(CO_3)_3^{3-}$	$Pu^{3+}+3CO_3^{2-} = Pu(CO_3)_3^{3-}$	16.40	estimated by correlation with An(III)/Ln(III
$Pu(CO_3)_4^{4-}$	$Pu^{4+}+4CO_3^{2-} = Pu(CO_3)_4^{4-}$	37.00±1.10	/Guillaumont et al. 2003/
$Pu(CO_3)_5^{6-}$	$Pu^{4+}+5CO_3^{2-} = Pu(CO_3)_5^{6-}$	35.65±1.13	/Guillaumont et al. 2003/
$PuO_2CO_3^-$	$PuO_2^++CO_3^{2-} = PuO_2CO_3^-$	5.12±0.14	/Lemire et al. 2001/
$PuO_2(CO_3)_3^{5-}$	$PuO_2^++3CO_3^{2-} = PuO_2(CO_3)_3^{5-}$	5.03±0.92	/Lemire et al. 2001/
$PuO_2CO_3(aq)$	$PuO_2^{2+}+CO_3^{2-} = PuO_2CO_3(aq)$	9.50±0.50	/Guillaumont et al. 2003/
$PuO_2(CO_3)_2^{2-}$	$PuO_2^{2+}+2CO_3^{2-} = PuO_2(CO_3)_2^{2-}$	14.70±0.50	/Guillaumont et al. 2003/
$PuO_2(CO_3)_3^{4-}$	$PuO_2^{2+}+3CO_3^{2-} = PuO_2(CO_3)_3^{4-}$	18.00±0.50	/Guillaumont et al. 2003/
$(PuO_2)_3(CO_3)_6^{6-}$	$3PuO_2^{2+}+ 6CO_3^{2-} = (PuO_2)_3(CO_3)_6^{6-}$	46.02±2.50	/Lemire et al. 2001/
Species	**Reaction**	**$-\log{}^*K_s$**	**Reference**
$PuCO_3OH(s)$	$Pu^{3+}+CO_3^{2-}+H_2O = PuOHCO_3(s)+H^+$	5.74	estimated by correlation with An(III)/Ln(III)
Species	**Reaction**	**$-\log K_s$**	**Reference**
$PuO_2(CO_3)_6(UO_2)_2^{6-}$	$PuO_2^{2+}+6CO_3^{2-}+2UO_2^{2+} = PuO_2(CO_3)_6(UO_2)_2^{6-}$	53.48±1.60	Recalculated from new selection /Guillaumont et al. 2003/
$PuO_2CO_3(s)$	$PuO_2^{2+}+CO_3^{2-} = PuO_2CO_3(s)$	14.65±0.47	/Guillaumont et al. 2003/

Table 18-5. Selected enthalpies for Plutonium carbonates species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	Δ_rH^0	Reference
$PuCO_3^+$	$Pu^{3+}+CO_3^{2-} = Pu(CO_3)^+$	152.76±7.24	Calculated from logK and S_f estimated as described in /Sverjensky et al. 1997/
$PuO_2CO_3^-$	$PuO_2^++CO_3^{2-} = PuO_2CO_3^-$	44.87	Calculated from logK and S_f from /Lemire and Garisto 1989/

18.4 Group 15

18.4.1 Nitrate compounds

Nitrate complexation is in general weak and very few data are reported for the trivalent actinides. We have introduced the species $PuNO_3^{2+}$ with a logK value selected for Am /Silva et al. 1995/ in agreement with the NEA recommendation. In addition we have included a value for the plutonium (VI) nitrate according to the NEA recommendations by analogy with the uranium complex, as in the case of neptunium.

No enthalpy values are given.

Table 18-6. Selected formation constants for Plutonium nitrate species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	logβ⁰ selected	Reference
$PuNO_3^{2+}$	$Pu^{3+}+NO_3^- = PuNO_3^{2+}$	1.33±0.20	/Silva et al. 1995/
$PuO_2(NO_3)^+$	$PuO_2^{2+}+NO_3^- = PuO_2NO_3^+$	0.30±0.15	Analogy to $UO_2NO_3^+$, according to NEA recommendation

18.4.2 Phosphate compounds

For the plutonium (III) phosphate system, there is only one quantitative work reported by /Moskovin 1971/. The NEA review team /Lemire et al. 2001/ rejects this study because of possible experimental shortcomings with the solubility measurements. In consequence, due to the lack of thermodynamic data for this system, the same estimates as the ones given for Np are applied. The NEA review /Lemire et al. 2001/ selects only one solubility constant for the $PuPO_4{\cdot}xH_2O$ solid, which is reported in the NAGRA-PSI 01/01 database as well. In the case of Pu(V), only data for one aqueous phosphate has been reported in /Moskvin and Poznyakov 1979/. Since the experiment was gatered using a sorption-coprecipitation of Pu(V) on Fe(III) hydroxide study, the NEA team as well as the NAGRA team do not select this species since there is no confirmation on it and no more conventional experimental method is available. We have included this species within the database, since it seems that there is no reason to deny its existence. The estimated or reported data for Pu phosphate complexes added to the NAGRA-PSI 01/01 database are given in Table 18-7.

In general no enthalpy values are given for the plutonium phosphate system. Only in the case of the solid we have been able to calculate the enthalpy reaction data.

18.5 Group 16

We agree with the selection undertaken for the stability of the plutonium sulphate species in the NAGRA-PSI 01/01 database.

We have only added enthalpy reaction data when possible in order to have a more complete database when temperature corrections are needed (see Table 18-9).

Table 18-7. Selected formation constants for Plutonium phosphate species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	log*β⁰ selected	Reference
$PuPO_4(aq)$	$Pu^{3+}+H_2PO_4^- = PuPO_4(aq)+2H^+$	–7.92±0.61	Estimated from correlation with An(III)
$Pu(PO_4)_2^{3-}$	$Pu^{3+}+2H_2PO_4^- = Pu(PO_4)_2^{3-}+4H^+$	–19.73±1.03	Estimated from correlation with An(III)
$PuHPO_4^+$	$Pu^{3+}+H_2PO_4^- = PuHPO^{4+}+H^+$	–1.82±0.67	Estimated from correlation with An(III)
$Pu(HPO_4)_2^-$	$Pu^{3+}+2H_2PO_4^- = Pu(HPO_4)_2^-+2H^+$	–5.46±1.02	Estimated from correlation with An(III)
$PuO_2HPO_4^-$	$PuO_2^+ +H_2PO_4^- = PuO_2HPO_4^-+H^+$	–4.86±0.05	/Moskvin and Poznyakov 1979/

Table 18-8. Selected reaction enthalpies for Plutonium phosphates species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	Δ_rH^0	Reference
$Pu(HPO_4)_2$(am,hyd)	$Pu^{4+}+2H_2PO_4^- = Pu(HPO_4)_2(am, hyd)+2H^+$	32.72±4.915	Calculated from logK and S_f /Lemire and Tremaine 1980/

Table 18-9. Selected reaction enthalpies for Plutonium sulphate species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	Δ_rH^0	Reference
$PuSO_4^{2+}$	$Pu^{4+}+SO_4^{2-} = PuSO_4^{2+}$	13.75±9.63	Calculated from logK and S_f /Lemire and Tremaine 1980/
$Pu(SO_4)_2$(aq)	$Pu^{4+}+2SO_4^{2-} = Pu(SO_4)_2$(aq)	43.91±15.58	Calculated from logK and S_f /Lemire and Tremaine 1980/

18.6 Group 17

Plutonium fluoride complexes included in the NAGRA-PSI 01/01 database come from the selection of the NEA team /Lemire et al. 2001/. We have added to this selection the species PuO_2F(aq) in analogy to the NpO_2F(aq) as the NEA recommendation.

As it is explained in the NEA update /Guillaumont et al. 2003/ the logK value selected for the formation of $PuCl^{2+}$ seems to be overestimated and therefore the NEA team reject that value. For this reason we have eliminated from the NAGRA-PSI 01/01 database this species, since it was selected from the older NEA database /Lemire et al. 2001/. Pu(VI) chloride complexes have been carefully revised in the update of the NEA selection /Guillaumont et al. 2003/, where the authors decide to select Pu(VI) chloride complexes from absorption spectroscopy and EXAFS measurements /Runde et al. 1997/, /Runde et al. 1999/ that are close to the values selected by /Grenthe et al. 1992/ for the analogous U(VI) chloride complexes.

We have included in the NAGRA-PSI 01/01 database the NEA selected data /Lemire et al. 2001/ for $PuBr^{3+}$ and PuI^{2+} as well. To complete halide database and to be similar to the other actinide ions we have made an estimation of the constant of PuI^{3+}.

We have only added enthalpy reaction data when possible in order to have a more complete database when temperature corrections are needed (see Table 18-11).

Table 18-10. Selected formation constants for Plutonium halide species, different from NAGRA-PSI 01/01 TDB.

Species	Reaction	$\log\beta^0$ selected	Reference
PuO_2F(aq)	$PuO_2^++F^- = PuO_2F$(aq)	1.20±0.30	In analogy to NEA recommendations
PuO_2Cl^+	$PuO_2^{2+}+Cl^- = PuO_2Cl^+$	0.23±0.03	/Guillaumont et al. 2003/
PuO_2Cl_2(aq)	$PuO_2^{2+}+2Cl^- = PuO_2Cl_2$(aq)	–1.15±0.30	/Guillaumont et al. 2003/
PuI^{2+}	$Pu^{3+}+I^- = PuI^{2+}$	1.10±0.40	/Lemire et al. 2001/
PuI^{3+}	$Pu^{4+}+I^- = PuI^{3+}$	1.62±0.30	Estimated from correlation with An(IV)
$PuBr^{3+}$	$Pu^{4+}+Br^- = PuBr^{3+}$	1.60±0.30	/Lemire et al. 2001/

Table 18-11. Selected reaction enthalpies for Plutonium halides species.

Species	Reaction	Δ_rH^0	Reference
PuO_2F^+	$PuO_2^{2+}+F^- = PuO_2F^+$	–3.65±24.77	Calculated from logK and S_f /Lemire and Tremaine 1980/
$PuO_2F_2(aq)$	$PuO_2^{2+}+2F^- = PuO_2F_2(aq)$	1.21±24.88	Calculated from logK and S_f /Lemire and Tremaine 1980/
$PuCl^{3+}$	$Pu^{4+}+Cl^- = PuCl^{3+}$	19.82±38.92	Calculated from logK and S_f /Lemire and Tremaine 1980/
PuO_2Cl^+	$PuO_2^{2+}+Cl^- = PuO_2Cl^+$	4.19±39.32	Calculated from logK and S_f /Lemire and Tremaine 1980/

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ISSN 1404-0344
CM Digitaltryck AB, Bromma, 2007