

THEREDA Database Project: Data Selections for Actinides

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The project

- Design of waste repositories requires reliable thermodynamic data to predict the geochemical behaviour of contaminants
- Need:** aqueous speciation, solubility limiting solid phases and ion-interaction parameters
- Challenges:** Incomplete sets of major and trace elements, inconsistencies between species considered and corresponding formation constants / activity models, restricted variation ranges of parameters (temperature, density, pressure, ionic strength)
- Main objective:** a centrally administrated and maintained database of verified thermodynamic parameters for environmental applications in general and radiochemical issues in particular

The partners

- Gesellschaft für Anlagen- und Reaktorsicherheit mbH, Braunschweig (Coordinator)
- Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology
- Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal
- TU Bergakademie Freiberg, Institute of Inorganic Chemistry
- AF-Consult Switzerland AG, Baden (Switzerland).

The chemistry

- Actinides, Fission and Activation Products:
 - Pa, Th, U, Np, Pu, Am, Cm
 - Rb, Sr, Tc, Cs, Sm, Nd, Ra
- Matrix:
 - System of oceanic salts: Na⁺, K⁺, H⁺, OH⁻, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻, CO₃²⁻ / HCO₃⁻ / CO₂(aq) – H₂O
 - Hydrated cement phases (including Al, Si)
- Ion-Ion-Interactions:
 - Pitzer approach
 - (SIT & extended Debye-Hückel)

Data releases

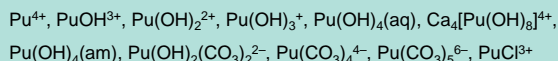
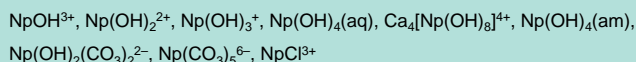
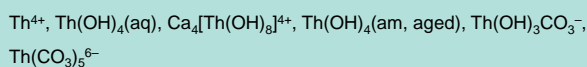
Nine official releases so far, all based on Pitzer:

- Na, K, Mg, Ca – Cl⁻, SO₄²⁻ – H₂O(l)
- Na, Mg, Ca – Cl – **Am(III), Nd(III), Cm(III)** – H₂O(l) (date of release: 2011-11-23)
- Na, K, Mg, Ca – Cl⁻, SO₄²⁻ – HCO₃⁻/CO₂(g) – H₂O(l) (2012-02-21)
- Na – Cl – **Np(V)** – H₂O(l) (2012-11-30)
- Na, Mg, Ca, K – Cl⁻, SO₄²⁻ – HCO₃⁻/CO₂(g) – Cs – H₂O(l) (2013-01-28)
- Na, K, Mg, Ca – Cl⁻, SO₄²⁻ – HCO₃⁻/CO₂(g) – Si, Al – H₂O(l) (2013-07-04)
- Na, K, Ca – Cl⁻, HCO₃⁻/CO₂(g) – **Th(IV), Np(IV), Pu(IV)** – H₂O(l) (2013-08-04)
- Na, Mg, Ca – Cl⁻, SO₄²⁻, HCO₃⁻/CO₂(g) – **Am(III), Cm(III)** – H₂O(l). (2013-10-21)
- Na, Mg, Ca, K – Cl⁻, SO₄²⁻, CO₃²⁻, HCO₃⁻; Si – **U(IV/VI)** – H₂O(l). (2014-07-14)

Example: tetravalent actinides: Th(IV), Np(IV), Pu(IV)

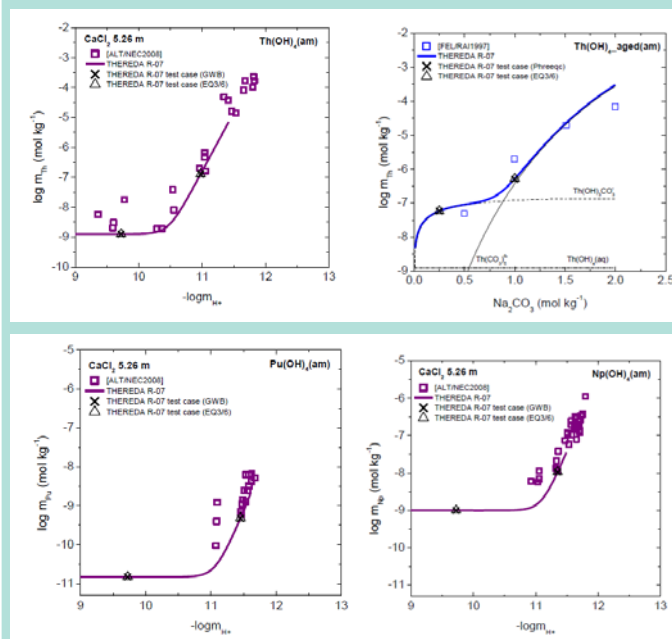
Publications from the research groups of Rai, Felmy and co-workers and Neck, Altmaier and co-workers have been chosen as main source of data.

Species considered:



Example: hydrolysis of tetravalent actinides

THEREDA selected data can properly describe the experimental data of Th(IV), Np(IV), and Pu(IV) in NaCl/CaCl₂ solutions and in presence of CO₃²⁻. Calculations with Geochemists Workbench and experimental data are shown in the figures:



Reaction	log K°	Reference
Th(OH) ₄ (aq) ⇌ Th ⁴⁺ + 4 OH ⁻	-44.8	[RYARA1987]
	-45.5	[FELRA1991]
	-44.8 ± 0.5	[RAIFEL1997]
	-47.8 ± 0.3	[RAIMOC2000]
	-46.7 ± 0.9	[NECMUL2002]
	-47.5 ± 0.9	[RANFUG2006]
	-47.5 ± 0.9	[RANFUG2006]
	-47.5 ± 0.9	[RANFUG2006]
Th ⁴⁺ + H ₂ O ⇌ ThOH ³⁺ + H ⁺	-2.2 ± 0.2 ^a	[NECMUL2002]
	-2.5 ± 0.5	[RANFUG2006]
Th ⁴⁺ + 2 H ₂ O ⇌ Th(OH) ₂ ²⁺ + 2 H ⁺	-6.0 ± 0.9 ^a	[NECMUL2002]
	-4.2 ± 0.5	[RANFUG2006]
Th ⁴⁺ + 3 H ₂ O ⇌ Th(OH) ₃ ⁺ + 3 H ⁺	-11.0 ± 1.0 ^a	[NECMUL2002]
Th ⁴⁺ + 4 H ₂ O ⇌ Th(OH) ₄ (aq) + 4 H ⁺	5. - 19.7	[RYARA1987]
	-17.5 ± 1.0 ^a	[NECMUL2002]
	-17.4 ± 0.7	[RANFUG2006]
	-17.4 ± 0.7	THEREDA [a.m.]
4 Ca ²⁺ + Th ⁴⁺ + 8 H ₂ O ⇌ Ca ₄ [Th(OH) ₈] ⁴⁺ + 8 H ⁺	-63.5 ± 1.0	[ALTNEC2008]
	-63.5 ± 1.0	FELNEC2010]
	-63.5 ± 1.0	THEREDA [a.m.]

Species	μ ⁰ (kJ mol ⁻¹)	μ ⁰ (kJ mol ⁻¹)	μ ⁰ (kJ mol ⁻¹)	μ ⁰ (kJ mol ⁻¹)	μ ⁰ (kJ mol ⁻¹)	μ ⁰ (kJ mol ⁻¹)	μ ⁰ (kJ mol ⁻¹)	μ ⁰ (kJ mol ⁻¹)	μ ⁰ (kJ mol ⁻¹)	Reference
Th ⁴⁺	1.014	10.3	-205	-1.123	2.0					[FELRA1991]
	1.014	10.3	-205	-1.123	2.0					[FELRA1992]
	1.014	10.3	-205	-1.123	2.0					[ROFFVGG1992]
	1.014	10.3	-205	-1.123	2.0					[RAIFEL1997]
	1.014	10.3	-205	-1.123	2.0					[RANFUG1999]
	1.014	10.3	-205	-1.123	2.0					[RANFUG2000]
	1.014	10.3	-205	-1.123	2.0					[RANFUG2006]
	1.014	10.3	-205	-1.123	2.0					THEREDA [a.m.]
Th(OH) ₄ (aq)	1.014	10.3	-205	-1.123	2.0					[ALTNEC2008]
	1.014	10.3	-205	-1.123	2.0					[FELNEC2010]
	1.014	10.3	-205	-1.123	2.0					THEREDA [a.m.]

Selection of data

The data for Th(IV) hydrolysis is exemplary shown on the left:

- Species formation constants,
- Binary/ternary Pitzer Parameter

Quality assurance

- Test calculations and integration of auditing scheme
- Monitor of data selections
- Automatic logging system storing all data changes in separate files
- Extension of the internal calculation scheme for mutually dependent thermodynamic data to check for data consistency and plausibility.

Data access

Download as separate files (www.thereda.de) in five formats: generic ASCII type and specific to geochemical speciation codes (PhreeQC, EQ3/6, ChemApp, Geochemist's Workbench – GWB).

Acknowledgement

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