

Thermodynamic Reference Database

Gesellschaft für Anlagen-
und Reaktorsicherheit (GRS)



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Chemie



HZDR

Helmholtz-Zentrum Dresden-
Rossendorf, Institute for
Resource Ecology (HZDR-
IRE)

Karlsruhe Institute of
Technology, Institut für
Nukleare Entsorgung (KIT-
INE)

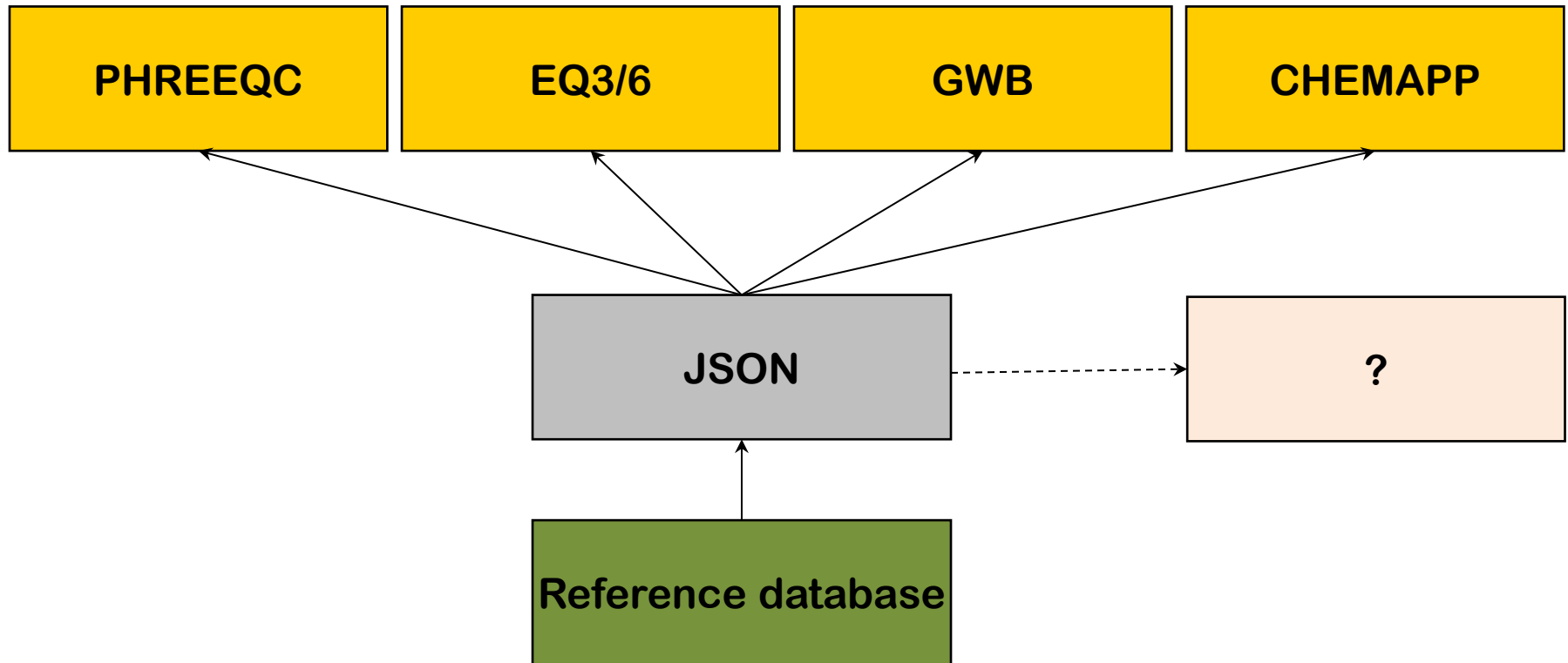


AF-Consult Switzerland Ltd.

Helge C. Moog, Frank Bok

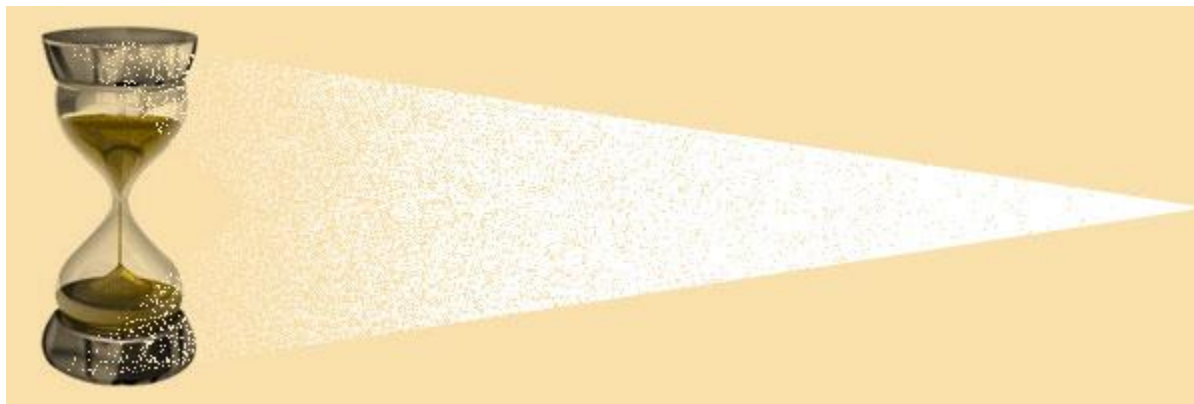
Basic idea

Thermodynamic calculations of various institutions become comparable, by creating parameter files from a common database.

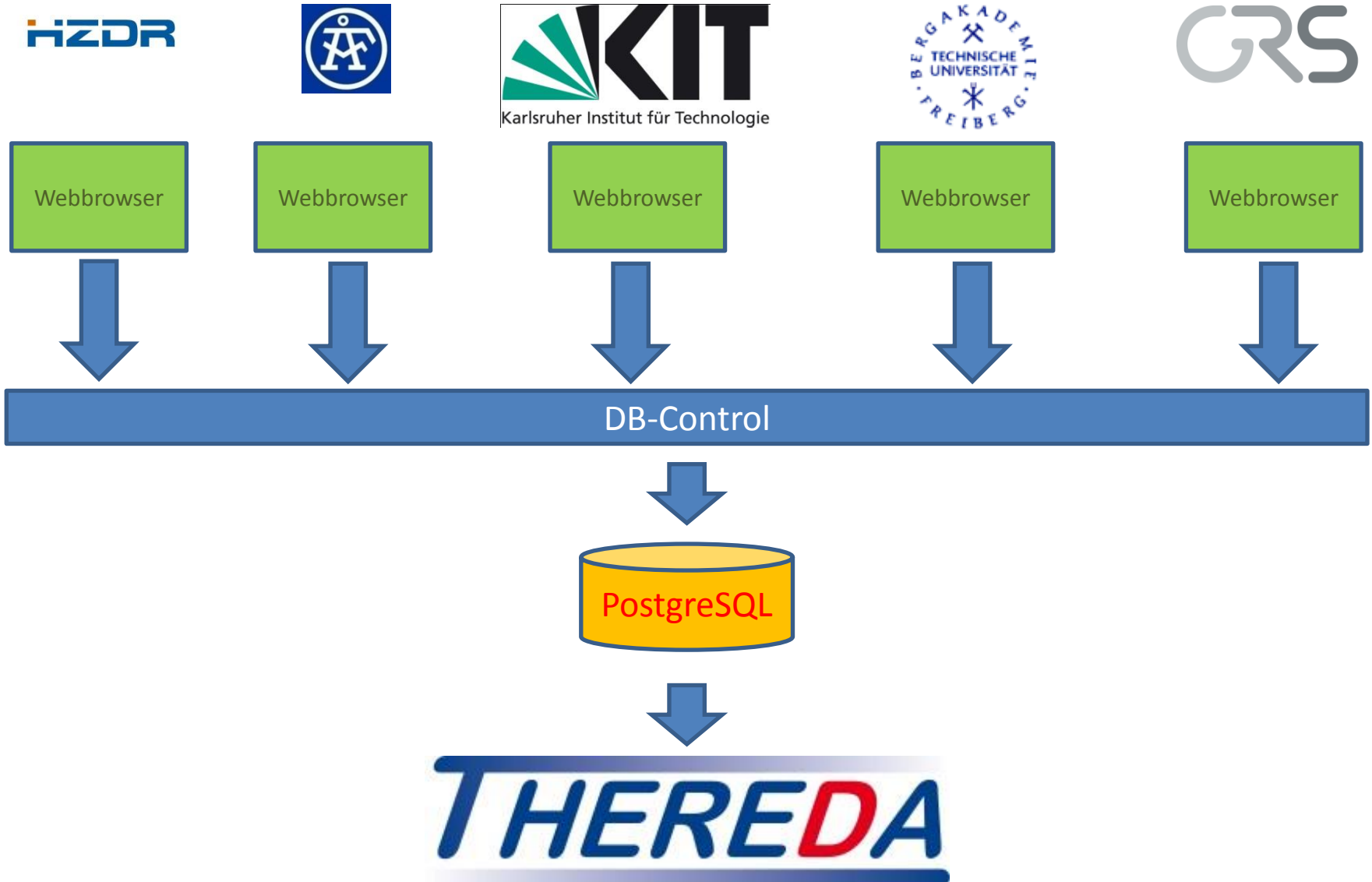


Long-term useability

- Usage of open-source programs
 - JOOMLA!, PostgreSQL, web-browser to manipulate data
- Low degree of abstraction of the data model
- Documentation of databank structure
- Flexible databank structure
 - Various interaction models for gas- and aqueous phase and solid phases
- Backups in ASCII-format (SQL-scripts)
- Joint project of five research institutions



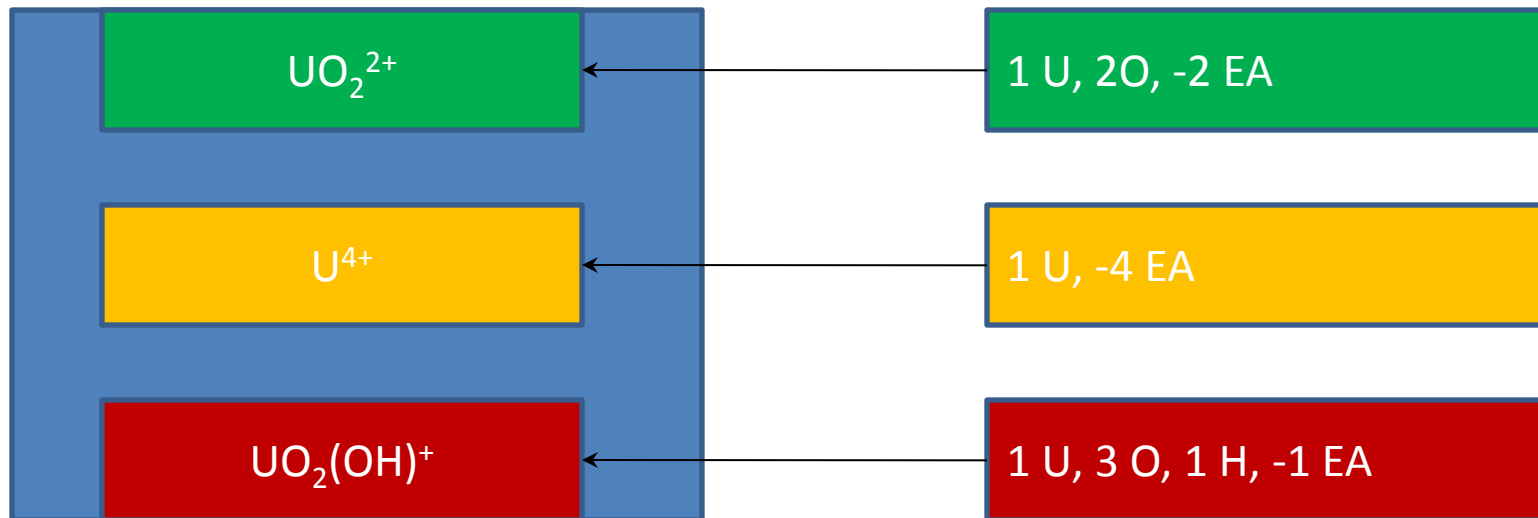
Operation of THEREDA



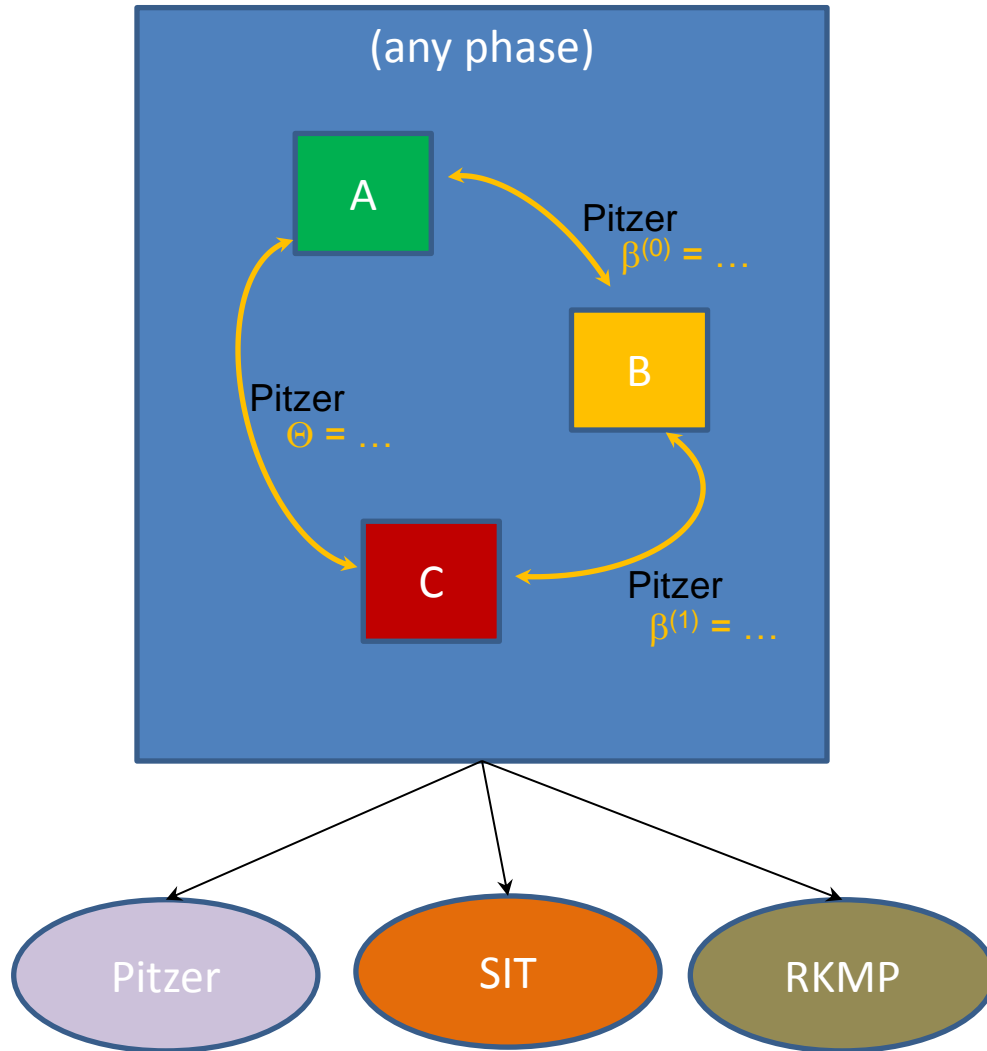
Data structure: Phases and Phase constituents

Phase Phase Constituent

Elements



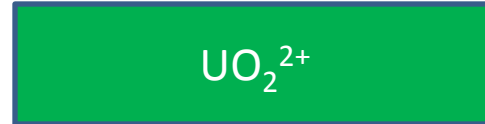
Data structure: non-ideal interactions



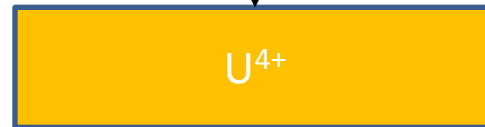
- Declaration of interaction models (Pitzer, SIT, RKMP, etc.)
- Assignment of interaction model to phase
 - Pitzer \leftrightarrow aq
 - RKMP \leftrightarrow (any solid mixed phase)
- Declaration of interacting phase constituents in conjunctions with a particular interaction model
- Assignment of interaction coefficients

Data structure: Phase constituent types and Reactions

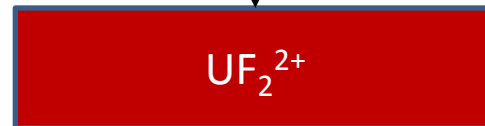
Primary Master



Secondary Master



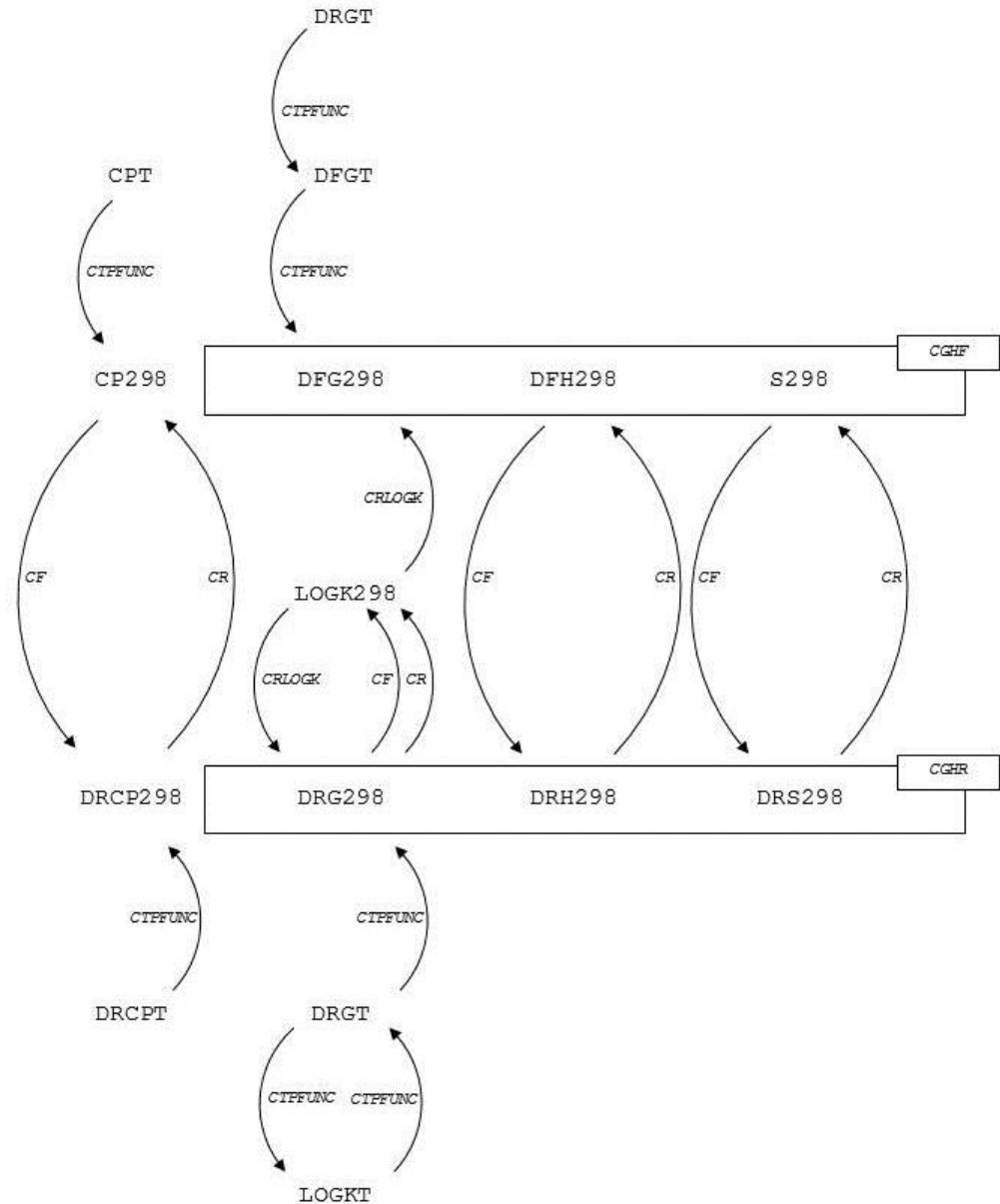
Products



Reactant	Coefficient
UF2<2+>	+1
U<4+>	-1
F<->	-2

Internal calculation scheme

- A technical framework which ensures that dependent and independent data are stored in a manner which ensures internal consistency when independent data are modified
- Editor determines, which data have to be calculated and how
- Internally, calculations are executed by SQL scripts
- Only those data are recalculated which are affected by a change



Benefit of THEREDA

- The scientist can focus on scientific issues.
- Peripheral programs assist in debugging, surveying, converting, and exporting data into ready-to-use parameter files.

Test calculations

- To be performed with parameter files created from the databank
- Demonstrate that calculational results match with lab data or expert judgment
- Make sure that results are the same with several codes (or give reasons why they cannot because of shortcomings of the code)
- Is a means of control for the user to check the accurateness of the downloaded parameter file

Test calculations released so far

- R01: **Polythermal** solubilities in selected ternary solutions with regard to the **system of oceanic salts**
- R02:
 - **Am(III), Cm(III), Nd(III)** in MgCl_2 and CaCl_2 solutions at 298.15K
 - **Am(III), Cm(III), Nd(III)** in NaCl solutions at 298.15K
- R03: Solubility in selected ternary salt solutions with regard to the system of oceanic salts in presence of **CO₂ and carbonates**
- R04: Solubility and hydrolysis of **Np(V)** in NaCl solutions at 298.15K
- R05: Activities and solubilities in solutions of **Cs**, Na, K, Mg, Ca, Cl and SO_4 at 298.15 K
- R06: Solubilities and activities in solutions of metastable and stable **cement phase assemblages**
- R07: **Th(IV), Np(IV) and Pu(IV)** solubility in NaCl, CaCl_2 , Na_2CO_3 and KHCO_3 solutions

These parameterfiles are ready for download to anyone interested!

Test calculations in preparation

- (Am, Cm, Nd) – (SO₄, CO₃) – H₂O
- Na, K – PO₄ – Cl, SO₄ – H₂O
- U(+IV/+VI) solubility in Na, K, Mg, Ca – Cl, SO₄, CO₃ – Si/Al – H₂O
- Generally: solubilities of Si/Al-bearing phases at elevated temperatures
- Fe(II) – Na, K, Mg, Ca – Cl – H₂O for 25°C

Using THEREDA (1)

- Select Single Data Query
→ get equilibrium constants, Pitzer parameters
- Export as CSV or MS Excel[©] possible
- Select Tailored databases
→ download parameter files for
 - PHREEQC
 - EQ3/6
 - GWB
 - CHEMAPP

■ Please visit: www.thereda.de

The screenshot displays the 'SINGLE DATA QUERY' page on the THEREDA website. The left sidebar contains a navigation menu with options like 'Home', 'THEREDA Project', 'THEREDA Partners', 'THEREDA Data Query', 'Downloads', 'Forum', 'FAQ', 'News', 'Links', 'Sitemap', 'Search', 'Job Opportunities', 'Contact', and 'DBControl'. The main content area provides instructions on how to use the query tool, including a note that registration is required. It guides the user through selecting an element (Hydrogen H, oxygen O, and electron E⁻ are pre-selected), choosing a data category (thermodynamic or interaction), and defining a temperature range. A periodic table is shown with the 'O' element selected. Below the table, the 'Thermodynamic data' radio button is selected, and the 'aqueous species' and 'solid phase' checkboxes are checked. The temperature range is set to 25.00 °C. The 'PITZER' interaction model is selected. A 'Continue' button is at the bottom.

Using THEREDA (2): JSON

- Export data in a general standard
- “JavaScript Object Notation” designed for human-readable data interchange
- Principal end primary



Thermodynamic Reference Database

JSON formatted generic database structure

This format can be downloaded for everyone interested to feed other geochemical codes!




es"

rray

rray: "Bibliography"

rray

ct closing

Current activities / Outlook (1)

- THEREDA has been extended to hold **surface complexation data**. Further activities will include the implementation in DB-Control.
- Implementation of a model for **non-ideal gases**
- Extension of some data-sets to **higher temperatures**
- Possibly addition of **another supported code**

Current activities / Outlook (2) – Surface Complexation Data

- Intensive literature search & critical assessment of Surface Complexation data → {RES3T} → Generation of “Recommended Values” → THEREDA
- Consistent with Extended-Debye-Hückel data
- Mineral specific information:
 - Specific Surface Area [m^2/g]
 - Surface Site Density [nm^{-2}]
 - Capacitance values [F/m^2]
- Mineral-Ligand-combinations data - Surface Protolysis ($\text{p}K$) & Surface Complex Formation constants ($\log K$) for:
 - Diffuse Double-Layer Model
 - Constant Capacitance Model
 - Non-electrostatic Model
 - 1pK-Basic Stern Model
- Test calculations including comparisons with measured values from literature
- Data releases with “ready-to-use” parameter files for SCM-supporting geochemical codes
- Currently Surface complexation Modeling data will be collected for 298.15 K only, but adaptation to temperature-dependent functions is possible.

Conclusion

- THEREDA offers a web-based, thermodynamic reference database **for high-saline aqueous systems** in equilibrium with **nuclear waste** forms in Germany
- **Joint-project** of five research institutions
- Access to **code-specific parameter files**

Acknowledgements



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Special thanks are extended to all members of the THEREDA team, for dedication, perseverance, and for the readiness to collaboratively work for a common goal.

Thank you very much for your attention!