

THEREDA

Thermodynamic Reference Database

Final Report

(Short version)

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Table of Contents

	Zusammenfassung	1
	Abstract.....	7
1	Documentation	11
1.1	Calculation mode	11
1.2	Category.....	12
1.3	Class	13
1.4	Source.....	13
1.5	Quality	13
1.6	Interaction model.....	13
1.7	Sets	13
1.8	Validities.....	14
1.9	Technical papers.....	14
1.10	Other information	14
2	Quality assurance	15
3	Manual.....	17
4	Database	19
5	WWW Interface	21
5.1	Software installed.....	21
5.2	Public Access.....	21
5.2.1	Single Data Query.....	22
5.2.2	Tailored Databases	22
5.2.3	Complex Systems	23
5.2.4	Literature References.....	23
5.3	User Administration.....	23

6	Oceanic salt systems	25
7	Cesium	29
8	Rubidium	31
9	Strontium	33
10	Cement phases and corrosion products	35
11	Radium	39
12	Arsenic	41
13	Uranium	43
14	Thorium	45
14.1	SIT interaction coefficients	46
14.2	Interaction coefficients according to Pitzer model	46
15	Transuranic elements	47
15.1	Neptunium	47
15.2	Plutonium	47
15.3	Americium	48
15.4	Curium.....	49
15.5	SIT interaction coefficients	50
15.6	Interaction coefficients according to the Pitzer model	51
15.6.1	Americium	51
15.6.2	Curium.....	52
16	Technetium	53
16.1	SIT interaction parameter for Tc species	53
16.2	Interaction coefficients according to Pitzer model	53
17	Samarium and Protactinium	55

17.1	Samarium.....	55
17.2	Protactinium.....	56
18	Conclusion.....	57
	References.....	59

Zusammenfassung

In einem Langzeitsicherheitsnachweis muss man belegen, dass alle wesentlichen Prozesse, die in einem Endlager für radioaktive Abfälle ablaufen und dessen Sicherheit positiv aber auch negativ beeinflussen können, verstanden worden sind. Für den Fall eines Lösungszutritts zu den Abfallgebinden ist daher zu zeigen, dass die dabei ablaufenden chemischen Reaktionen nicht zu einer unzulässigen Freisetzung von Radionukliden in die Biosphäre führen. Ausgangspunkt hierfür stellen Abschätzungen der Löslichkeit von Schadstoffen in jenen Lösungen dar, die mit dem endgelagerten Abfall in Kontakt kommen. Diese Beurteilungen werden entweder auf der Basis möglichst realitätsnah ermittelter Daten oder aber durch thermodynamische Modellrechnungen vorgenommen.

Grundlage für thermodynamische Modellrechnungen ist eine sogenannte „thermodynamische Datenbasis“, die auf experimentellen Daten basiert. In Deutschland arbeitet eine Reihe von Forschungseinrichtungen an der Verbesserung der thermodynamischen Datenbasis. Diese Arbeit umfasst die Bestimmung grundlegender Daten, wie etwa Dampfdrücke oder Löslichkeiten, sowie die Anwendung hochentwickelter analytischer und spektroskopischer Methoden, die Einblick in die Speziation der Elemente in wässriger Lösung und in Strukturen von Oberflächenkomplexen als Grundlage für wirklichkeitsnahe chemische und thermodynamische Modelle geben.

Die Erfahrung zeigt, dass thermodynamische Gleichgewichtsrechnungen, die von unterschiedlichen Experten durchgeführt werden, schnell schwierig vergleichbar und schwer verständlich werden. Dies liegt nur zum Teil an ungenügend definierten und dokumentierten Randbedingungen für die Berechnungen, sondern ist oft auf unterschiedliche thermodynamische Daten oder unterschiedliche Modellannahmen zurückzuführen. Weitere Schwierigkeiten resultieren aus der Tatsache, dass viele thermodynamische Daten, die für die Rechnungen verwendet wurden, in Wahrheit zueinander in Beziehung stehen; die Änderung einzelner Daten und das Bestehenlassen anderer führt zu „inkonsistenten“ Daten. Wendet man solche inkonsistenten Datensätze in einer Rechnung an, kann dies zu falschen Ergebnissen führen, oftmals unbemerkt durch den Anwender.

Auf diese Weise entsteht die Situation, dass in verschiedenen Institutionen unterschiedliche Datenbasen bestehen, von denen jede für spezifische Aufgabenstellungen

geeignet ist. Werden solche Datenbasen auf eine identische Fragestellung angewendet, kann es aber passieren, dass unterschiedliche Ergebnisse erhalten werden. Diese Ausgangslage ist inakzeptabel, sowohl in wissenschaftlicher Hinsicht als auch im Hinblick auf die besondere Aufmerksamkeit der Öffentlichkeit für Fragen der Endlagerung radioaktiver Abfälle.

Im Jahr 2002 schlossen sich fünf Institutionen mit dem Ziel, eine gemeinsame thermodynamische Datenbasis für die Belange der Endlagerung radioaktiver Abfälle in tiefen geologischen Formationen zu schaffen, zusammen. Die gemeinsame Datenbasis wurde THEREDA genannt: **Thermodynamische Referenzdatenbasis**. Folgende Fachorganisationen sind im „Arbeitskreis THEREDA“ tätig:

- Helmholtz-Zentrum Dresden-Rossendorf, Institut für Radiochemie (HZDR-IRC), hieß bis zum 31.12.2010 Forschungszentrum Dresden-Rossendorf, Institut für Radiochemie (FZD-IRC),
- Karlsruher Institut für Technologie, Institut für Nukleare Entsorgung (KIT-INE),
- Technische Universität Bergakademie Freiberg, Fakultät für Chemie und Physik, Institut für Anorganische Chemie (TU-BAF),
- AF-Colenco AG, Baden (CH), Geschäftsbereich Grundwasserschutz und Entsorgung,
- Gesellschaft für Anlagen- und Reaktorsicherheit, Braunschweig, Abteilung Prozessanalyse (GRS).

Es wurde vereinbart, dass die neue Datenbasis von allen Mitgliedern des Verbunds gemeinsam betrieben werden soll. Zukünftig soll die Verwendung von Daten aus THEREDA obligatorisch für Fragen der Endlagerung radioaktiver Abfälle in Deutschland werden. Es wurde ferner vereinbart, dass die neu zu schaffende Datenbasis sich an den folgenden Leitlinien orientieren soll:

Langfristige Anwendbarkeit: Die Entsorgung radio- und chemotoxischer Stoffe ist eine Jahrzehnte umfassende Aufgabe. THEREDA soll über lange Zeiträume hinweg operativ bleiben. Dies hat weitreichende Auswirkungen auf die Datenstruktur, die Detailtiefe der Dokumentation und die Auswahl verwendeter Programme. THEREDA ist an aktuelle Erfordernisse und Rechencodes angepasst, erlaubt aber Entwicklungsmöglichkeiten für weiter gehende Ansprüche in der Zukunft.

Freier und einfacher Zugang: Die Datenbasis soll kostenfrei über das Internet zugänglich sein.

Anwendbarkeit: Um die Anwendung der in THEREDA zusammengestellten Daten zu fördern, werden gebrauchsfertige, automatisch generierte Parameterdateien für die gebräuchlichsten geochemischen Rechenprogramme zur Verfügung gestellt. Derzeit sind dies: PHREEQC, EQ3/6, Geochemist's Workbench und CHEMAPP.

Interne Datenkonsistenz: Es wird zwischen unabhängigen und intern berechneten Daten unterschieden. Zur Wahrung der internen Datenkonsistenz werden die thermodynamischen Daten so strukturiert und gespeichert, dass bei der Änderung unabhängiger Daten von diesen abhängige Daten automatisch neu berechnet werden.

Hinreichender Umfang: Die in THEREDA gespeicherten Daten sollen so umfassend sein, dass die Datenbasis für die Belange der Endlagerung gefährlicher Stoffen auch tatsächlich eingesetzt werden kann, ohne dass für den Anwender die Notwendigkeit besteht, eigene Daten hinzuzufügen. Da die bestehenden thermodynamischen Daten in der Literatur derzeit nicht umfassend sind und verschiedene geochemische Systeme noch nicht untersucht wurden, werden in THEREDA Daten aus chemischen Analogiebeziehungen und Schätzwerte gespeichert, solange diese im Rahmen einer vernünftigen Unsicherheit liegen. THEREDA liefert somit einen thermodynamischen Datensatz für geochemische Modellierungen. Die Qualität der Daten wird dabei aber stets dokumentiert. Somit kann die Datenbasis auch dazu genutzt werden, Kenntnislücken zu identifizieren und zukünftige Forschungsaktivitäten zu steuern.

Dokumentation: Alle Daten werden hinsichtlich ihrer Qualität und ihrer Herkunft klassifiziert. Selbst wenn Daten geringerer Qualität oder sogar Schätzwerte eingegeben werden, wird der Anwender somit auf diesen Umstand hingewiesen. Ferner werden alle Daten dergestalt klassifiziert, dass erkennbar wird, durch welche Art von Experiment sie bestimmt wurden.

Die im Berichtszeitraum 2006 - 07 bis 2010 - 06 durchgeführten Arbeiten decken ein weites Spektrum ab. So musste zunächst ein Datenmodell erstellt werden, das eine Speicherung thermodynamischer Daten einerseits, sowie den beabsichtigten Export in code-spezifische Parameterdateien andererseits erlaubt. Bei dem Design des Datenmodells wurde auf Zukunftssicherheit geachtet, d. h., es wurde eine Abstraktionstiefe gewählt, die über die heutigen Erfordernisse hinausgeht und eine Erweiterung für zu-

künftige Anforderungen ermöglicht. Die Datenbank wurde technisch auf einem Webserver implementiert. Es wurden Programme erstellt, die lesenden und schreibenden Zugriff gewähren. Ferner wurden Internet-Seiten erstellt, die Programme aufrufen, welche vom Anwender zu spezifizierende Parameterdateien generieren und zum Herunterladen anbieten.

Somit kann man sich THEREDA als eine Datenbank in Verbindung mit einer Reihe von Hilfsprogrammen vorstellen, die darauf abzielen, thermodynamische Daten zu administrieren, weiter zu verarbeiten und zu exportieren. Der Export zielt dabei auf Programme ab, die thermodynamische Gleichgewichte in wässrigen Lösungen für Temperaturen berechnen sollen, die für hydrogeologische Systeme im allgemeinen und für Lösungen im Kontakt mit gefährlichen Abfällen radioaktiver wie auch chemotoxischer Art im speziellen relevant sind. Insofern ist THEREDA weder dafür gedacht, primäre Labordaten zu speichern, noch Daten mit Bezug zu Systemen, die andere Flüssigkeiten als wässrige Lösung enthalten, wie etwa Schmelzen oder andere Substanzen, die unter Bedingungen existieren, unter denen wässrige Lösungen nicht mehr stabil sind. Das Hauptaugenmerk liegt auf der korrekten Berechnung von experimentell bestimmten Lösungsgleichgewichten und der Speziation in wässriger Lösung.

Begleitend zu den oben beschriebenen Aktivitäten wurden Richtlinien erstellt, die bei der Selektion und Bewertung von Daten einzuhalten sind. Ein System qualitätssichernder Maßnahmen wurde erstellt. Dieses umfasst einerseits technische Aspekte auf Datenbankebene, andererseits Kriterien, nach denen Daten vor ihrer Freigabe nach außen verbundintern geprüft werden (Audit). Als verbundsexterne Maßnahme zur Qualitätssicherung und um Fragen und Anforderungen von Anwendern aus der Praxis in die eigene Arbeit einfließen zu lassen, wurde ein Internet-Forum eingerichtet. Ferner soll ein Handbuch Anwendern den Umgang mit THEREDA erleichtern (zurzeit nur auf Deutsch).

Schließlich wurden thermodynamische Daten eingegeben. Diese umfassen sowohl das System der ozeanischen Salze als auch eine Reihe von radiotoxischen bzw. chemotoxischen Elementen. Diese Arbeiten schreiten kontinuierlich voran. Zum Zeitpunkt der Erstellung dieses Berichts wurden 215 Festphasen sowie 310 Konstituenten der wässrigen und der gasförmigen Phase erfasst. Es existieren 827 Pitzer-konsistente und 821 SIT-konsistente Datensätze. Insgesamt 746 nicht-ideale Wechselwirkungen wurden erfasst, 70 davon auf einer polythermen Basis. Derzeit befinden sich Benchmark-

Rechnungen in Vorbereitung. Die erste Freigabe von Daten wird die Elemente des Systems der ozeanischen Salze (außer C) umfassen.

Abstract

A long term safety assessment of a repository for radioactive waste requires evidence, that all relevant processes are known and understood, which might have a significant positive or negative impact on its safety. In case of brine intrusion into the disposal area, it has to be demonstrated, that the initiated chemical reactions don't lead to an undue release of radionuclides into the biosphere. One key parameter to assess the propagation of a radionuclide is its solubility in solutions interacting with the waste. Solubility estimations can either be based on experimental data determined at conditions close to those in the repository or on thermodynamic calculations.

A so called "thermodynamic database" created from experimental data is the basis for thermodynamic model calculations. Several research institutions in Germany are working on an improvement of such a thermodynamic database. This work comprises investigations into fundamental thermodynamic data (such as vapour pressures or solubilities) as well as the application of sophisticated analytical or spectroscopic tools, which allow insight into aqueous speciation or structural details of surface complexes as basis for correct chemical and thermodynamic models.

On the strength of past experiences, thermodynamic equilibrium calculations performed by different experts readily become difficult to compare and evaluate. This is only in part due to ill-defined (and -documented!) boundary conditions imposed on the calculations, but is frequently related to the use of different thermodynamic data or different conceptual models underlying them. Further difficulties arise by the fact that thermodynamic data used for a calculation actually are strongly interrelated; modification of an individual value without adapting the dependent values leads to "inconsistent" data. Applying such data may lead to erroneous results, often unnoticed by the user.

As a result, in different institutions various databases exist that are appropriate for specific tasks. However, they might lead to different results when they are applied to the same problem. This situation is unacceptable, both from a scientific point of view and considering the special public awareness for the final disposal of radioactive waste.

In 2002, a working group of five institutions was established to create a common thermodynamic database for nuclear waste disposal in deep geological formations. The

common database was named THEREDA: **Th**ermodynamic **R**eference **D**atabase. The following institutions are members of the working group:

- Helmholtz-Zentrum Dresden-Rossendorf, Institute of Radiochemistry, Dresden, Germany (HZDR-IRC), before January 1, 2011 officially called Forschungszentrum Dresden-Rossendorf., Institute of Radiochemistry (FZD-IRC),
- Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, Karlsruhe, Germany (KIT-INE),
- Technische Universität Bergakademie Freiberg, Institute of Inorganic Chemistry, Freiberg, Germany,
- AF-Colenco AG, Baden, Switzerland, Department of Groundwater Protection and Waste Disposal,
- Gesellschaft für Anlagen- und Reaktorsicherheit, Braunschweig, Department of Process Analysis, Germany.

It was agreed that the newly created database should jointly be operated by all members of the working group. For the future it is intended that its usage becomes mandatory for geochemical model calculations for nuclear waste disposal in Germany. Furthermore, it was agreed that the new database should be established in accordance with the following guidelines:

Long-term usability: The disposal of radioactive waste is a task encompassing decades. The database is projected to operate on a long-term basis. This has influenced the choice of software (which is open source), the documentation and the data structure. THEREDA is adapted to the present-day necessities and computational codes but also leaves many degrees of freedom for varying demands in the future.

Easy access: The database is accessible via the World Wide Web for free.

Applicability: To promote the usage of the database in a wide community, THEREDA is providing ready-to-use parameter files for the most common codes. These are at present: PHREEQC, EQ3/6, Geochemist's Workbench, and CHEMAPP.

Internal consistency: It is distinguished between dependent and independent data. To ensure the required internal consistency of THEREDA, the thermodynamic data are

structured and stored in a way that upon modification of independent data the dependent data are recalculated automatically.

Comprehensiveness: The thermodynamic database in THEREDA will be as comprehensive as necessary for thermodynamic equilibrium calculations in the frame of radioactive waste disposal without compelling the user to supplement the database with own data. As the currently available thermodynamic data reported in literature are far from being comprehensive and various systems have not even been investigated at all, THEREDA is using values from chemical analogues and estimated values to fill data gaps wherever this is possible within a reasonable uncertainty. THEREDA is thus providing a set of thermodynamic data for geochemical calculations and it documents the quality of the data at any time. The database can thus be used to identify gaps in knowledge and as tool to control future research activities.

Documentation: All data entered are classified as to their origin and quality. Thus, even when data of less quality or estimated data are entered, the user is always alerted to this fact. In addition, all data are classified according to the type of experiment, they were derived from.

Activities within the time for which this report is valid cover a wide range of aspects. At first, a data model had to be designed from scratch which allows for the storage of thermodynamic data, at the same time facilitating export into code-specific parameter files. Creating the data model emphasis was laid upon its long term usage. Thus, a degree of abstraction was chosen which exceeds today's necessities and allows for future extensions. Technically the databank is implemented on a web server. Programs were created, which permit reading and writing access to the data. From the created webpages programs can be called that produce code specific parameter files ready for download upon specific request by the user.

THEREDA can thus be thought of as a databank in conjunction with a suite of peripheral programs, which aims at administrating, processing and extracting data. The data export is intended for the use in programs that calculate thermodynamic equilibria in aqueous solutions at temperatures which are of potential interest for hydro-geochemical systems in general and solutions containing hazardous contaminants like radionuclides or heavy metals in particular. As such, THEREDA is not designed to hold primary experimental data, neither data concerning any liquid other than aqueous solution, e. g. melts or other substances which are stable under conditions beyond those

where aqueous solutions may exist. Emphasis is laid on the correct calculation of experimentally determined solubilities and aqueous speciation.

Accompanying the above mentioned activities the working group agreed upon guidelines which are to be followed upon selection and assessment of data. A system of quality assuring measure was set up; this comprises technical aspects relating to the databank as well as criteria determining how data are to be internally reviewed prior to release (auditing). As an external measure of quality assurance an internet forum was established to feedback questions and requirements from realistic problems into the project. A handbook was written to guide users in the handling of THEREDA (for the time being in german only).

Finally, thermodynamic data were entered. They comprise the system of oceanic salts as well as species and solid phase of a variety of radio-toxic and chemo-toxic elements. This piece of work is on-going. At the time of writing this report a total of 215 solid phases and 310 aqueous and gaseous phase constituents are covered. Altogether 827 Pitzer-consistent and 821 SIT-consistent datasets exist. 746 non-ideal interactions were entered, including 70 on a polythermal base. At present, benchmark calculations are prepared. The first release of data will cover the system of oceanic salts (apart from C).

1 Documentation

All data entered in THEREDA are subject to comprehensive documentation. In part this documentation is attached to specific data, and in part it consists of separate documents.

1.1 Calculation mode

Data may be entered directly (“independent data”) or calculated internally (“dependent data”). In the latter case, information is given, how the datum was calculated. For example. Gibbs Free Energies of formation $\Delta_f G^\circ_m$ may be calculated internally from enthalpy of formation $\Delta_f H^\circ_m$ and standard entropy S°_m applying the Gibbs-Helmholtz equation. Similarly, $\Delta_f G^\circ_m$ may be calculated from the equilibrium constant for the formation of the respective compound and the Gibbs Free Energies of formation of the other reactants.

The following figure gives an impression on how data are linked within THEREDA. Each arrow represents a calculational path. A full calculation of all dependent data usually involves several cycles where chains of dependent data are calculated successively.

For a more comprehensive description please refer to the handbook, chapter 2.9 (see chapter 3).

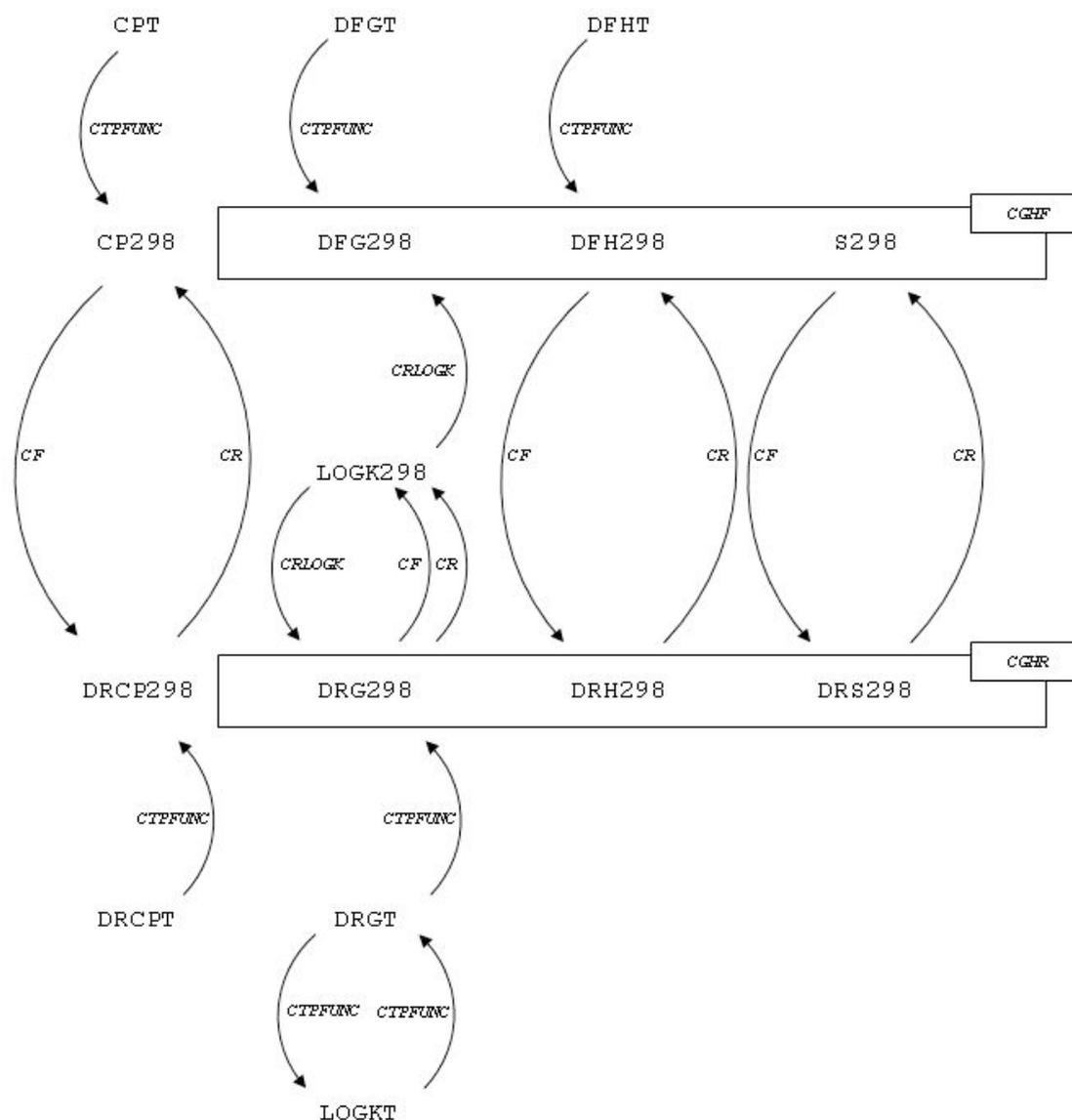


Fig. 1.1 Scheme of internal calculations in THEREDA

1.2 Category

Thermodynamic data are derived from reaction or formation data. The former are usually derived from experiments in aqueous solution where thermodynamic equilibrium was attained. The latter are usually based on calorimetric measurements. As a matter of fact, calculated solubilities based on solubility constants which were calculated from enthalpy of formation $\Delta_f H_m^\circ$ and standard entropy S_m° tend to be orders of magnitude too low.

Wherever possible, in THEREDA preference is given to data derived from experiments in aqueous solution.

1.3 Class

The class describes whether the datum has been derived experimentally or is based on analogies or estimations. In other words, the class gives a measure on the degree of experimental foundation.

1.4 Source

The source describes from which kind of publication the datum was adopted. The ranking ranges from international reviews down to internal, publicly not available reports (even though these must have been peer reviewed by THEREDA members).

1.5 Quality

The quality provides a ranking for the overall reliability of the datum.

1.6 Interaction model

Within THEREDA actually three kinds of databases are held separately, depending on which kind of model for the calculation of aqueous phase constituent activity coefficients the data are consistent with. Three models are distinguished: Pitzer, Specific Ion Interaction Theory (SIT), and Extended Debye Hückel (EDH). While data are also compiled for SIT and EDH, only Pitzer-consistent data are considered in the present release of data.

1.7 Sets

Thermodynamic data may be grouped into sets. Sets of data are interrelated in ways beyond the scope of pure thermodynamics. Examples are equilibrium constants and Pitzer parameters which were derived simultaneously and hence must not be modified independently. Other examples are sets of data which are mutually excluding and which must not be exported into the same parameter file.

1.8 Validities

All p,T-functions of data are assigned fields of validity in terms of temperature and pressure. Other validities may be defined by the editor, either to individual data or sets of data. Information as to the consistency with a given interaction model (see above) are implicitly given by the structure of the databank.

1.9 Technical papers

Issues and data of general importance are usually covered in so called “Technical Papers”. At the time being the following issues are available or in preparation:

- Dielectric constant, vapour pressure, and density of water and the calculation of Debye-Hückel parameters A_{DH} , B_{DH} , and A^ϕ for water
- Temperature and pressure dependence of the ionization constant of water
- Procedure for the internal review of data (in german only so far, Title: “Elemente und Kriterien zur Qualitätssicherung bei der Datenerfassung und -bewertung”)
- Technical documentation for the databank underlying THEREDA
- Guideline for the creation of identifiers of phase constituents and phases

1.10 Other information

In addition to the possibilities for documentation given above, the editor may decide to comment on the experimental results, usually given in publicly available literature, which were adopted to derive some data. For this purpose, documents are prepared which are attached to data or sets of data and which can be downloaded by the user.

2 Quality assurance

Quality assurance (QA) in THEREDA is based on a tiered approach derived from quality objectives that are defined in respective guideline documents.

The first level comprises a critical data selection and assessment („Data Collection“) following a comprehensive literature survey. The whole process, including averaging (if applicable) and the derivation of uncertainties, is documented in a transparent way. In cases where no published data could be retrieved, approximations are derived. Their applicability is checked externally.

Within the second QA level („Data Assessment“) a series of quality labels is assigned to each datum. These markers cover data class (experimental/theoretical origin), data quality (categories of uncertainty) and data source (where was it published, which external peer-review was passed).

The third stage („Data Submission“ & „Internal Calculations“) involves data evaluations by the editor and internal plausibility and consistency checks provided directly by the data input tool or within the database management system (DBMS).

Then an automatically (by the DBMS) triggered audit process has to be passed. It is only after this auditing process has been successfully passed that the edited/newly introduced data sets can be subject of benchmark calculations. This audit is done by another editor, optionally in collaboration with an administrator. The criteria to be applied by the auditor are described in a separate document (issued as Technical Paper).

A fifth QA level to be passed before a data set is made publicly accessible (“released”) is the execution of benchmark tests. Respective pre-defined packages are provided for many typical application scenarios, together with the „expected“ result. These benchmarks are available for various geochemical speciation codes simultaneously.

A sixth and last instance of QA is the user itself – or rather his/her application of data sets obtained from THEREDA. By frequenting the www-based user forum (with sub-categories for many topics and respective qualified persons from the project team) user feedback can be collected and processed. Of course also the classic email can be used to contact the THEREDA team.

The interaction of the different QA elements is illustrated in Fig. 2.1 below.

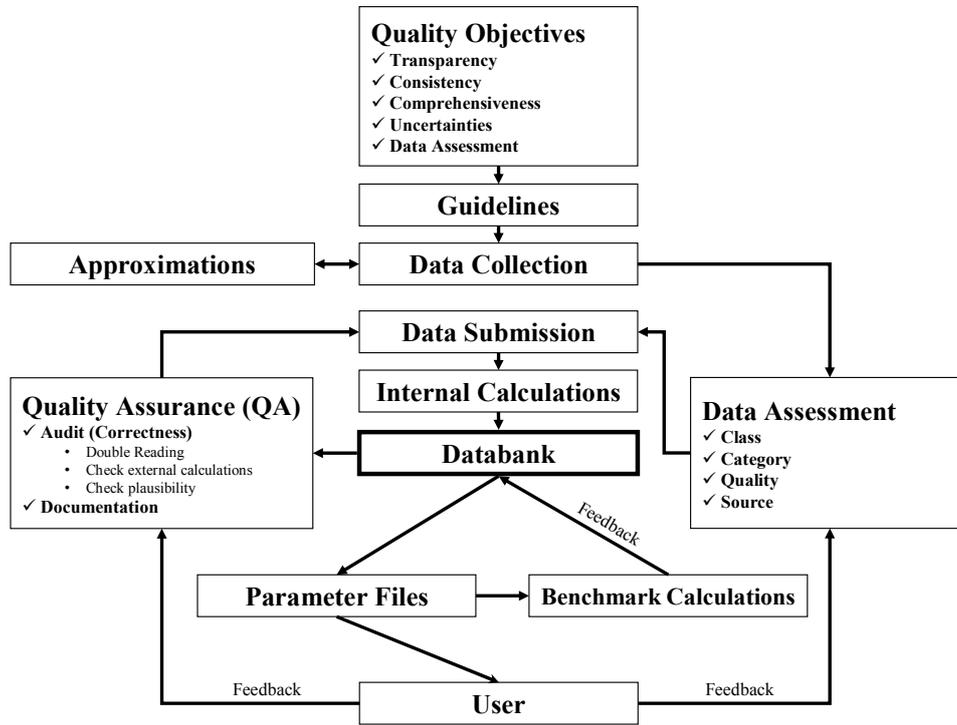


Fig. 2.1 QA elements and their relationships in THEREDA

3 Manual

Detailed documentation is an important part of the THEREDA project. Besides several other and more specific documents, THEREDA encompasses a general manual. This manual goes beyond the reliable description of the database and the user interface. It contains information regarding the background and initiation of the THEREDA project as well as technical information such as quality guidelines, consistency requirements, approximation methods, and data traceability.

Target groups of the manual are the database users as well as those persons who compile, assess and enter data into the database, i. e., data editors and administrators. The latter is important in so far as the continuance of the database and its usability shall be ensured for a long time beyond the initial phase of the THEREDA project, possibly with reduced material resources and partially or completely replaced staffing. Therefore, the general structure of the database and the project workflow are explained in detail. Furthermore, the manual contains the guidelines for the data selection and the procedural steps regarding the entry and maintenance of the data.

The documentation is presented in seven chapters, each as a separate file and it is supported by a glossary

1. THEREDA – Background
2. Basic conventions and structures
3. Guidelines for data selection
4. Quality assurance
5. Technical base of the database
6. Data entry
7. Data retrieval and output
8. A - Glossary

Chapter 1 describes the reasons that led to the origin of THEREDA. The characteristics and the aim of the database as well as the project structure are explained. Chapter 2 contains the information about the fundamental conventions and structures of the data-

base. Therefore, this chapter deals with the elements and phases under consideration and the corresponding data types for the description of chemical reactions. The concepts of supporting datasets, physical and chemical boundary conditions are explained too. Within chapter 3, the THEREDA specific guidelines for the selection of appropriate thermodynamic data and interaction coefficients are presented.

Chapter 4 contains the guidelines for the quality assurance and therefore addresses the data editors and administrators as well as the users. With this guideline, the description and the classification of the data concerning type, data source and quality is regulated. Additional comments provide specific information as the used sources, error range, validity limits and other information, e. g. analogues or estimation methods used.

The technical base is principally described in chapter 5. Data entry is described in chapters 6 and the retrieval of data is described chapter 7. Finally, the glossary shall help to clarify the different technical phrases and abbreviations used.

The manual is available at www.thereda.de. Each chapter as well as the glossary can be downloaded separately in a PDF format. At present, only a German version exists. An English translation is planned within phase II of THEREDA.

4 Database

THEREDA is organized as a so called relational database¹. Its content is structured in tables (“relations”), consisting of columns (“attributes”) and rows (“tuples”). All fields belonging to an attribute are assigned a specific data type, such as “char” for denotational information, or “numeric” for numerical information. Designing the structure for THEREDA efforts were undertaken to ensure internal consistency on the database level. The selected database management system (DBMS) allows enforcing referential integrity between different tables sharing information (single attributes or even groups of attributes). Two fields of information being linked in this way can be considered as “parent” (as the information to which is referred) and “child” (as the information which refers to its parent). As a consequence a specific piece of information can only be entered after another one has been entered elsewhere. The database can be accessed through SQL (Structured Query Language) which itself is implemented in nearly all higher-level programming languages. SQL relies on ASCII (pure alpha-numeric) information, is thus readable by humans and can be processed by a huge variety of external codes. It is thus a major point in guaranteeing a long-time availability of THEREDA.

PostgreSQL was chosen as DBMS for several reasons: It is open source software (implying independence from proprietary business models and allowing to operate on low budgets), it is backed-up by a large community devoted to the product since more than 15 years, it is a powerful tool providing all features to ensure a safe, efficient and transparent operation (proven by many large industrial applications), and it runs on all major operating systems, including Linux, various commercial UNIX implementations, (among them AIX, BSD, HP-UX, SGI IRIX, Mac OS X, Solaris, Tru64), and Windows.

However, requirements necessary to render a set of data strictly consistent in terms of thermodynamics are much more complicated than may be realized exclusively by means of the internal database logic. Furthermore, the databank itself does not offer convenient means of editing, displaying, and exporting data. Therefore, the DBMS is

¹ Two technical terms are standing side-by-side in the literature. While the German „Datenbasis“ clearly means something different than the German „Datenbank“, in English language „database“ and „databank“ are commonly used interchangeably. In view of its more common use, we decided for the English report to adopt the term „database“ for the technical implementation, while in German we use “Datenbank”.

coupled to a suite of tools (mainly programmed in Java and PHP) that provide storage, administration and interactions of thermodynamic data. Also a multi-level back-up/recovery methodology is implemented. Further measures to ensure physical integrity of the database are a detailed user hierarchy combined with distinct data access permissions and password-secured access, whereas the signing of specific databases with MD5 hash codes allows detecting a-posteriori data manipulations. A full logging of all data editing allows also the back-tracking and (if required) reversal of all data changes. All communication with the server is encrypted via SSL (Secure Sockets Layer).

The more than 90 tables representing the content of THEREDA can roughly be grouped into five categories: Basic information (elements, species, and phases), thermodynamic data, interaction data, bibliographic information, and auxiliary information (quality categories, models, users, math operators,). Their internal relationships can be illustrated by entity-relationship diagrams. For respective examples but also a more detailed description of the database structure please refer to the Technical Paper "Database structure of THEREDA".

THEREDA is currently hosted on a dedicated server, with Suse Linux 11.1 as operating system and an Apache web server version 2.2.10. PHP 5.2.11 and a Tomcat Application Server (for Java) are installed, too. The DBMS PostgreSQL is available in version 8.3.8.

The database is by default accessed via the World Wide Web using conventional browser software. This is described in more detail in the chapter "Web-Interface".

5 WWW Interface

5.1 Software installed

THEREDA is accessible through common internet browsers under the URL <http://www.thereda.de>, which is also aliased from <http://www.thereda.eu> and <http://www.thereda.com>. This web presence is based on the Content Management System (CMS) Joomla! in version 1.5, which in turn relies on a MySQL database (version 5.0.67). The following Joomla! components and modules are installed:

- DocMan as document administration tool (Version 1.4.0)
 - Module Notify to issue emails informing about newly uploaded documents
 - Module DocLink to put direct links to documents in articles
 - Module Search DocMan as a search extension
- JoomFish for support of multiple languages (version 2.0.3) with extension for DocMan
- JoomlaStats for website statistics (Version 3.0.0)
- XMap for a site map (Version 1.2.2)
- Weblinks for link lists organized in categories (Version 1.5.0)
- Joomla Content Editor (JCE) as universal editor (Version 1.5.7)
- Jnews to show news that can be grouped into categories
- Kunena implements a user forum to interact with the project team and also to exchange ideas within the user community
- Contacts providing a flexible contact form
- The module called “thereda” is an extension specifically programmed for the data access by external users.

5.2 Public Access

The web site offers a public area where general information about the project (including FAQs), news, public documents and contact forms are hosted. This area is accessible

to all visitors without any previous authentication. However, the proper data content is not retrievable. To do so a registration is required which then gives access to some restricted areas namely offering various types of data access. The following possibilities are offered for data access.

5.2.1 Single Data Query

Here, the user can query for specific data, with selection criteria defined interactively. First, one has to select an element. Hydrogen H, oxygen O, and the electron EA (for redox reactions) are implicitly added. Next, the user has to decide which data category is wanted:

Thermodynamic data; then up to three phase types can be specified: gas, aqueous species, solid phases.

Interaction coefficients; so far only models for interactions between ions in aqueous solution can be selected.

The final decisions to be made are the definition of a temperature range and the selection of a model for ion-ion interactions in aqueous solution.

The result of this query is a list of all relevant species. The user now can further reduce the species list based on phase type or oxidation state. This finally leads to a table with all data stored in THEREDA that satisfy the user selection criteria. This data set can be exported, but does not constitute an internally consistent and complete data base ready for use in any geochemical speciation code. If this is required please refer to the "Complex Systems" navigation menu item.

5.2.2 Tailored Databases

THEREDA will issue ready-to-use parameter files which are fixed ("frozen") and will not be changed later. They are polythermal and come in different shapes, specific for an ion interaction model (extended Debye-Hückel according to Davies, SIT or Pitzer). The different databases can be exported (downloaded) in various formats to suit the needs of a variety of geochemical speciation codes. In addition, a generic ASCII format (JSON) can be selected. Each database generated will be stored – with date stamp

and hash code – within the THEREDA archive, allowing the retrieval of old database versions.

However, at the time being, focus is laid on creating Pitzer-consistent parameter files. Other parameter files consistent with the SIT- or Debye-Hückel theory are envisaged for the future.

5.2.3 Complex Systems

For complex systems, it is planned, that users can define complex systems (H, O, and many more elements) for which the database will be queried. The construction of the query is done stepwise. First, all wanted elements must be marked. Implicitly, H, O and the electron (for redox reactions) will be added. Then the user defines the temperature range of interest and the ion-ion-interaction model to be applied. The database will deliver an internally complete and consistent database. At the moment, the query result will be presented as an ASCII file (JSON format) or formatted specifically as input for the selected code and offered for download.

5.2.4 Literature References

This menu item allows the user to obtain all data related to a selected bibliographic reference. The values will be presented in tabulated form. The search term is looked for as part of author, title or mnemonic short code.

5.3 User Administration

Project partners can become members of the Joomla! user group „editors“. This status allows the active manipulation of the site content (upload and edit articles etc.). Thus the THEREDA web site can also be (and is) used as intranet for the project management. Primarily this involves the exchange and collaborative work on documents such as meeting minutes, talks and other presentation, reports, manuals, and technical documentations. Furthermore the intranet facilitates the testing of database queries.

The user administration is part of the Joomla! backend and managed by a separate administrator. But in any case the manipulation of the data within the THEREDA database is not possible.

In addition, the WWW can also be used for active data manipulations through the phpPgAdmin tool. Here, however, separate user accounts and passwords are required that are managed on the server rather than within the Joomla! CMS.

6 Oceanic salt systems

The system of oceanic salts Na^+ , K^+ , H^+ , OH^- , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , $\text{CO}_3^{2-}/\text{HCO}_3^-/\text{CO}_2(\text{aq}) - \text{H}_2\text{O}$ containing the elements Na, K, Mg, Ca, Cl, S, C – is the matrix system in the THEREDA database. At present a Pitzer equation [PIT1991] based on polythermal model is available valid in a temperature range from 273 K to 383 K except for the carbonate species. For $T = 298.15$ K the database is nearly identical with the Harvie, Möller, Weare (1984) [HAR/MOL1984] model, except a very few modifications including new data (for example solubility of CaSO_4 in solutions of MgSO_4).

To describe the temperature dependence of the standard Gibbs energy of formation, solubility constants, the ionization constant of water, the coefficients in the Pitzer equation β , C^ϕ , θ and ψ the following equations were used:

$$\Delta_f G^\circ(\text{salt}); \Delta_f G^\circ(\text{water}) = A + BT + CT \ln T + DT^2 + ET^3 + \frac{F}{T} \quad (6.1)$$

$$\beta^u, \beta^1, \beta^2, C^\phi, \theta, \psi = \frac{A}{T} + B + C \ln T + DT + ET^2 + \frac{F}{T^2} \quad (6.2)$$

Model parameters were selected systematically, beginning with the solubility in binary systems, then extending to triple, and up to multi-component systems. For binary systems available data of the temperature coefficients of the Pitzer equation and solubility constants of minerals were used as starting points.

The binary systems $\text{NaCl}-\text{H}_2\text{O}$, $\text{KCl}-\text{H}_2\text{O}$, and $\text{CaCl}_2-\text{H}_2\text{O}$ are well studied by potentiometric and isopiestic measurements between 0.01 mol/kg and saturation. The Pitzer parameters and the solubility constants of NaCl and KCl received from [GRE/MOL1989] are classified as reliable. Pitzer parameters for the system $\text{MgCl}_2-\text{H}_2\text{O}$ were obtained after calculating the osmotic coefficients based on the models of [HOL/MES1996] and [VAL/URU1988]. For CaCl_2 the validity range of Pitzer parameters is restricted to maximum concentrations of about 4.5 mol/kg H_2O .

For the systems $\text{Na}_2\text{SO}_4-\text{H}_2\text{O}$ and $\text{MgSO}_4-\text{H}_2\text{O}$ temperature functions given in the work [PAB/PIT1987] were refined. Pitzer parameters for the system K_2SO_4 were refined from the calculation of osmotic coefficients and mean activity coefficients in the model of

[HOL/MES1996]. The solubility constant of arcanite was calculated on the basis of solubility data in the range 0 – 200 °C. Literature data for binary parameters of CaSO₄ were fitted against solubility data in binary and ternary CaCl₂-CaSO₄-H₂O, Na₂SO₄-CaSO₄-H₂O systems.

Parameters for the binary hydroxide systems NaOH-H₂O, KOH-H₂O were evaluated from [CHR/MOL2004a] and compared with osmotic and activity data measurements for the range 0 – 150 °C and up to 8 mol/kg. The formation of hydrates MOH·nH₂O within the concentrations higher than 10 mol/kg is not considered in this work.

The solubility in the binary system Mg(OH)₂-H₂O is described using only the stability constant of the MgOH⁺ ion pair taken from [PAL/WES1997] and the solubility product of Mg(OH)₂. The model was compared with the IUPAC solubility compilation for Mg(OH)₂ showing excellent agreement. Binary parameters for Ca(OH)₂ were estimated by re-fitting the equations given by [CHR/MOL2004b] to the form of eq. (6.1) and (6.2).

The same is valid for the binary parameters for HCl-H₂O and H₂SO₄-H₂O. Christov and Møller proposed as well to consider H-HSO₄ parameters for the description of H₂SO₄-H₂O system [CHR/MOL2004b]. The final model agrees well with osmotic and activity data measurements.

For the ternary systems with common chloride anion [NaCl-KCl-H₂O (840) NaCl-MgCl₂-H₂O (300) KCl-MgCl₂-H₂O (360) NaCl-CaCl₂-H₂O (280) KCl-CaCl₂-H₂O (360) MgCl₂-CaCl₂-H₂O (250)] the parameters θ (M₁⁺-M₂⁺) and Ψ (M₁⁺-M₂⁺-Cl) were evaluated from the considerably large amount of solubility data (the number of experimental points is given in brackets) in the corresponding systems with temperature range from 0 to 250 °C. Isopiestic data are also available at 25 °C.

For the ternary systems with sulphate as common anion [Na₂SO₄-K₂SO₄-H₂O (300) Na₂SO₄-MgSO₄-H₂O (700) K₂SO₄-MgSO₄-H₂O (600) Na₂SO₄-CaSO₄-H₂O (460) K₂SO₄-CaSO₄-H₂O (220) MgSO₄-CaSO₄-H₂O (~110)] (number of experimental solubility points given in brackets) the parameters θ (M₁⁺-M₂⁺) were taken from the similar chloride system and adjusted if necessary (for θ (Na-Ca)). Parameters Ψ (M₁⁺-M₂⁺-SO₄) were adjusted simultaneously with the solubility constant (expressed as lnK) of the double salts (Na₂SO₄·MgSO₄·4H₂O, 3K₂SO₄·Na₂SO₄, Na₂SO₄·CaSO₄, K₂SO₄·5CaSO₄·H₂O, K₂SO₄·2MgSO₄ etc.). Due to a lack of data in the system MgSO₄-CaSO₄-H₂O for the

temperatures higher than 50 °C, our own measurements were used for parameterisation [WOL/VOI2008], [WOL/VOI2010].

In the systems with common cation [NaCl-Na₂SO₄-H₂O (700), KCl-K₂SO₄-H₂O (200), MgCl₂-MgSO₄-H₂O (240), CaCl₂-CaSO₄-H₂O (110)] parameters $\theta(\text{Cl}^-, \text{SO}_4^{2-})$ and $\Psi(\text{M}^+, \text{Cl}^-, \text{SO}_4^{2-})$ were evaluated from solubility data (number given in brackets). Parameter ψ (Ca-Cl-SO₄) is taken from Greenberg et al. [GRE/MOL1989] without change. Parameter ψ (Mg²⁺, Cl⁻, SO₄²⁻) was possible to adjust only after consideration of higher order Na⁺, Mg²⁺//Cl⁻, SO₄²⁻ and K⁺, Mg²⁺//Cl⁻, SO₄²⁻ reciprocal systems.

Ternary hydroxide systems are much less studied. Systems NaOH-NaCl-H₂O, KOH-KCl-H₂O, NaOH-Na₂SO₄-H₂O seems to be the only ones which meet all the requirements for the temperature and concentration range of interest. The systems Ca(OH)₂-NaOH-H₂O, Ca(OH)₂-KOH-H₂O, Ca(OH)₂-CaCl₂-H₂O, KOH-K₂SO₄-H₂O clearly lack experimental data for high temperatures and concentrations. The system Mg(OH)₂-MgCl₂-H₂O is studied only at 25 °C. Parameters in the system NaOH-KOH-H₂O are studied indirectly by considering the higher order Na-K-OH-Cl-H₂O system at 100 °C.

The ternary salt systems considered in this work are as follows: HCl-NaCl-H₂O, HCl-KCl-H₂O, HCl-MgCl₂-H₂O, H₂SO₄-Na₂SO₄-H₂O, H₂SO₄-K₂SO₄-H₂O, H₂SO₄-Mg₂SO₄-H₂O. Almost all the parameters are taken from [CHR/MOL2004b] and [HAR/MOL1984] after a refit with the exception of ψ (Mg-H-Cl), $\beta^{(1)}$ (K-HSO₄), and ψ (K-H-HSO₄) which are adjusted in this work. The mixing parameters were fitted simultaneously with the solubility constants of new solid phases (7 salt-acid solid phases) in these systems.

Quaternary systems are well described in temperature range 0 – 100 °C with the model. The most reliable and thoroughly studied systems are the following reciprocal systems: Na⁺, K⁺/Cl⁻, SO₄²⁻//H₂O (600); K⁺, Mg²⁺/Cl⁻, SO₄²⁻//H₂O (> 1000); Na⁺, Mg²⁺/Cl⁻, SO₄²⁻//H₂O (> 3000), with the number of experimental points given in brackets. For the system Na₂SO₄-K₂SO₄-CaSO₄-H₂O no reliable data were found.

Solubility of gypsum in chloride solutions is limited at moderate temperatures and up to the salt saturation concentrations. Data for the solubility of anhydrite in the chloride solutions are sparse, so that calculations generate a larger uncertainty.

The solubility of gypsum, anhydrite und bassanite was studied in HCl und H₂SO₄ solutions for the temperatures up to 80 °C and concentrations up to 7 mol/kg of H₂SO₄ or

HCl. Because parameters for Ca-SO₄ and the CaSO₄⁰ ion pair in our model differ from those in [CHR/MOL2004b] all parameters relevant to these systems have been checked for their ability to describe the solubilities and were modified when necessary.

In reviewing the five-component Na⁺, K⁺, Mg²⁺/Cl⁻, SO₄²⁻//H₂O system with more than 4000 data points the invariant points Q: halite, sylvite, carnallite, kainite; R: halite, carnallite, kainite, kieserite and Z: halite carnallite, bischofite, kieserite were considered. For the paragenesis Q it is clear that the THEREDA model reflects quite well the literature data within the fluctuation of the various papers. An exception is the SO₄ value at temperatures above 55 °C. For the paragenesis Z the SO₄ concentration is in very good agreement with Usdowski [USD1998].

When considering the six-component system the fields of crystallization of CaSO₄ containing minerals are of interest, but due to scattered and uncertain experimental data the stability regions are not as accurate as needed for geochemical applications. The stability regions have been calculated with use of our model and compared with Harvie et al. [HAR/MOL1984] at 25 °C. 22 solid phases are considered in the Na⁺, K⁺, Mg²⁺, Ca²⁺/Cl⁻, SO₄²⁻//H₂O system.

All the CO₂, CO₃²⁻, HCO₃⁻ species at the moment are taken from [HAR/MOL1984] and are valid only for 25 °C. Expansion to higher temperatures and variable pressures are to be done yet.

7 Cesium

Thermodynamic data in particular Pitzer parameters for the interaction of Cs^+ with Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , and SO_4^{2-} were developed in the course of THEREDA. Experimental data including results of solubility, isopiestic, and potentiometric measurements of around 70 papers published between 1904 and 2007 were selected and analysed. In case of positive assessment, the data were used to evaluate Pitzer parameters and the associated equilibrium constants of the occurring solid phases. All data are valid for 25 °C.

For the binary systems $\text{CsCl-H}_2\text{O}$ and $\text{Cs}_2\text{SO}_4\text{-H}_2\text{O}$ several usable data were available. Especially in the last few years, some new potentiometric measurements on the chloride system were published. They could improve the description of diluted solutions till 0.001 mol/kg CsCl . The upper limit for the binary parameter set is 7 mol/kg. By varying the parameter $\alpha^{(1)}$ the water activity of CsCl -solutions could be simulated till saturation. Therefore, also the solubility constant of $\text{CsCl}(\text{cr})$ could be calculated. The parameter set of the sulfate system is reliable till 1 mol/kg Cs_2SO_4 . Beyond that, the experimental values of different authors show significant disagreement. Thus, the determined solubility constant of $\text{Cs}_2\text{SO}_4(\text{cr})$ is questionable but suitable as it can be shown in the ternary systems.

The parameter $\Psi_{\text{Cs-Cl-SO}_4}$ is based on potentiometric and solubility measurements and is classified as reliable. The ternary systems with sodium and potassium were well studied with solubility and isopiestic experiments. The determined ternary parameter sets are reliable over the total concentration range except the CsCl molality has to be below 7 mol/kg. Besides the known solid phases ($\text{CsCl}(\text{cr})$, $\text{Cs}_2\text{SO}_4(\text{cr})$, halite, sylvite, mirabilite, thenardite, and arcanite), the double salt $\text{CsNa}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}(\text{cr})$ and solid solutions occur in the chloride systems. For these phases no thermodynamic data were given in THEREDA. The systems $\text{Cs-Mg-Cl-H}_2\text{O}$ and $\text{Cs-Mg-SO}_4\text{-H}_2\text{O}$ are less well investigated. Thus, the parameter sets have a minor quality label. This also applies for the equilibrium constant of the double salts $\text{CsMgCl}_3 \cdot 6\text{H}_2\text{O}(\text{s})$ and $\text{CsMg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}(\text{s})$.

There is only one publication which describes the interaction with calcium in chloride solutions and none for sulphate solutions. These two systems cannot be modelled with THEREDA.

8 Rubidium

Experimental data of about 50 articles published between 1904 and 2007 containing solubility, potentiometric, and isopiestic measurements were evaluated. In case of positive assessment they were used to develop ion interaction Pitzer parameters and equilibrium constants for Rb^+ in solutions containing Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , and SO_4^{2-} . All data are valid for 25 °C.

The binary system $\text{RbCl-H}_2\text{O}$ is well studied with isopiestic and potentiometric measurements between 0.002 mol/kg and saturation. Thus, a reliable parameter set and solubility constant for $\text{RbCl}(\text{cr})$ could be developed. The few available isopiestic data for the sulfate system differ remarkable of each other. Here, the parameter set as well as the solubility constant of $\text{Rb}_2\text{SO}_4(\text{cr})$ are reliable within a high range of error but suitable in particular for the higher systems.

In case of the ternary systems with sodium, solubility and isopiestic data are available. The phase equilibria in both systems can be well described with the parameter sets given in THEREDA. As solid phases occur only $\text{RbCl}(\text{cr})$ or halite and $\text{Rb}_2\text{SO}_4(\text{cr})$ or mirabilite, respectively. By contrast in the ternary systems with potassium solid phases appear only as solid solutions. For the development of Pitzer parameter, isopiestic data are used. The water activity in these ternary systems can be simulated satisfactorily. The parameter set for the system $\text{Mg-Rb-Cl-H}_2\text{O}$ is based on solubility data. Beside $\text{Rb}_2\text{SO}_4(\text{cr})$ and bischofite the double salt $\text{RbMgCl}_3 \cdot 6\text{H}_2\text{O}$ is observed. The phase equilibrium can be described well with the developed parameters.

For the system $\text{Rb-Cl-SO}_4\text{-H}_2\text{O}$, only one publication with potentiometric data is available. The correctness of the in this way calculated Pitzer parameters cannot be determined. There are no experimental data available for ternary systems with calcium. Also in this case, measurements are necessary to close a gap.

9 Strontium

For THEREDA the thermodynamic data of Sr^{2+} in solutions containing Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , or SO_4^{2-} were developed if possible. Around 40 articles published between 1916 and 2005 with experimental data like solubility, isopiestic, and potentiometric measurements were selected. By positive assessment, the data were used to develop ion interaction Pitzer parameter and equilibrium constants. All data are valid for 25 °C.

The binary system $\text{SrCl}_2\text{-H}_2\text{O}$ is well studied by isopiestic and potentiometric measurements between 0.03 mol/kg and saturation. The resultant Pitzer parameters and the solubility constant of $\text{SrCl}_2\cdot 6\text{H}_2\text{O}(\text{cr})$ are therefore classified as reliable. Also for the ternary chloride systems, $\text{Na-Sr-Cl-H}_2\text{O}$ and $\text{K-Sr-Cl-H}_2\text{O}$, sufficient data are available, so that these solutions can be modelled with the parameters developed for THEREDA.

$\text{SrSO}_4(\text{cr})$, Celestite, is hardly soluble. Hence isopiestic experiments cannot be performed. For the binary system only one publication can be found. The potentiometric data given here are not enough for the development of adequate parameters. Also the ternary systems are rarely investigated. Only for the system $\text{Na-Sr-SO}_4\text{-H}_2\text{O}$ solubility data are available. They were together with the potentiometric of $\text{Sr-SO}_4\text{-H}_2\text{O}$ used to develop binary and ternary parameters at once. The parameters were tested on the quaternary system $\text{Na-Sr-Cl-SO}_4\text{-H}_2\text{O}$ and classified as questionable but nevertheless suitable.

Further experimental data are needed to describe the interaction of strontium with the oceanic system. Due to the low solubility of SrSO_4 there is a lack of data for sulfate systems. Further on the interaction with magnesium and calcium cannot be described at all.

10 Cement phases and corrosion products

The aim of this subproject is the development of a consistent thermodynamic dataset for cement phases at 25 °C and their reaction products (corrosion products). Emphasis is given to the interaction between cement and high saline solutions to respect the existing and planned nuclear waste repositories in salt formations. However, with this dataset systems based on weak saline solutions can be described as well.

As a first step, the relevant cement phases and corrosion products at 25 °C have been identified by a extensive literature search. Afterwards the results of solubility experiments for these phases have been extracted from the literature and evaluated. From the reliable solubility experiments the solubility products have been derived based on the thermodynamic data already available in the THEREDA database. Thus, the consistency with the other data is assured.

The thermodynamic data for the carbonate, Al and Si species as well as their interaction coefficients have not been available when starting the estimation of the solubility products of the cement phases. To keep a maximum of consistency to the established databases, the information on the carbonate species was taken from [HAR/MOL1984] and those for Al and Si species from [REA1992]. Nevertheless, as soon as more actual information on these species is available within THEREDA an update of the cement data base may necessary. This will probably be the case together with the derivation of the polythermal cement dataset intended for phase II of THEREDA. Thus, the dataset derived here is a kind of a preliminary dataset. Following, the principle decisions are listed on which the evaluation of the cement phases and the belonging thermodynamic data are based:

- Thermodynamic data of solids which have been evaluated prior within other sub-projects of THEREDA are adopted. This is the case e. g. for the minerals of the oceanic salt system.
- Because of their variable composition and the incongruent solubility behaviour the C-S-H phases are described by three distinct model phases. This respects that some established geochemical codes cannot deal with solid solutions. The choice of this model phases is based on popular cement literature, e. g. [REV/ADE1997].

- Despite various hints for incongruent solubility the behaviour of the individual minerals of the AFm group² are described by simple logK values.
- The relevance of the AFm group mineral hemisulfoaluminathydrate is not yet clarified and no significant experimental data are available. Therefore, this phase is not included in the actual dataset.
- Solid solutions within the AFm group have been identified but are not considered in the preliminary dataset. This is due to the above mentioned limitations of some geochemical codes.
- Ettringite is the best investigated cement phase besides the C-S-H phases. Although some hints for incongruent solubility behaviour are reported in the literature it is considered by a simple logK value.
- Tricarboante is another mineral of the AFt³ group. It is also described by a simple logK value. Because of the sparse experimental support this value has to be considered as preliminary.
- Thaumassite is a typical low temperature phase (approx. 5 – 15 °C) and thus is not considered for the 25 °C dataset.
- The solid solution between hydrogarnet and Si-Hydrogarnet is described by two distinct endmembers, each with a simple logK, value following [MAT2007].
- In the literature the Mg-Aluminate hydrates are described usually by hydrotalcite and with a simple logK value. This approach is also adopted for the actual dataset.
- The characterization of the M-S-H phases is difficult to perform due to their poor crystallinity and sparse occurrence. Three potentially relevant, weak crystalline M-S-H phases have been identified and for two of them, sepiolite und kerolite, thermodynamic data at 25 °C have been estimated. For the third phase, resembling serpentinite, only data above 39 °C could be gathered. Kerolite seems

² AFm (Al₂O₃-Fe₂O₃-mono) represents a group of calcium aluminate hydrates with the general formula [Ca₂(Al,Fe)(OH)₆]₂·X·nH₂O where X represents a singly charged anion or 'half' a doubly-charged anion. X may be one of many anions; the most important in Portland cement hydration are hydroxyl, sulfate and carbonate.

³ AFt (Al₂O₃-Fe₂O₃-tri) represents another group of calcium aluminate hydrates with the general formula [Ca₃(Al,Fe)(OH)₆·12H₂O]₂·X₃·xH₂O where X represents a doubly-charged anion or, sometimes, two singly-charged anions. Ettringite is the most common and important member of the AFt group (X in this case denoting sulfate).

to correspond reasonably with the observed structure. Sepiolite is kept in the dataset for the compatibility with [REA1992].

- The amorphous SiO_2 phase is described by the simple logK value from [REA1992].
- The logK value for Gibbsite is also taken from [REA1992]. It considers the dependence of gibbsite solubility of its crystallinity.

11 Radium

As the NEA-TDB does not cover thermodynamic data for radium a few publications resulting from a comprehensive literature survey were the major source of information, accomplished by three review reports. Some other review reports lack the bibliography of the original raw data sources. Parameter taken from such compilations consequently did get a low quality label.

Most of the data published for Radium so far focus on the solubility products of either $\text{Ra}(\text{SO}_4)(\text{s})$ or $\text{Ra}(\text{OH})_2(\text{s})$. The respective values have been evaluated and averaged. Values published for $\text{Ra}(\text{s})$, $\text{RaCl}_2(\text{s})$, $\text{RaCl}_2 \cdot 2\text{H}_2\text{O}(\text{s})$ and $\text{Ra}(\text{CO}_3)(\text{s})$ could only be found in reviews without proper citing of the original paper, thus they obtained respective low data quality labels only.

All thermodynamic data published for aqueous Ra species (Ra^{2+} , RaCl^+ , $\text{RaCl}_2(\text{aq})$, $\text{Ra}(\text{OH})^+$, $\text{Ra}(\text{OH})_2(\text{aq})$, $\text{Ra}(\text{CO}_3)(\text{aq})$, $\text{Ra}(\text{SO}_4)(\text{aq})$) are estimates derived from plots of thermodynamic values of earth alkaline (Ca, Sr, Ba) metal complexes and solid phases vs. the cation radius or the charge/radius ratio. This probably is due to the enormous experimental difficulties to work with highly concentrated Ra solutions. With the exception of RaCl^+ and $\text{Ra}(\text{SO}_4)(\text{aq})$, the values of all the other Ra species are at least internally consistent.

All data entered into THEREDA refer to standard conditions ($T = 298.15 \text{ K}$, $p = 0.1 \text{ MPa}$).

A data survey concerning Pitzer parameters for Ra species is currently going on.

12 Arsenic

Thermodynamic data regarding arsenic in THEREDA include on the one hand EDH consistent data taken from the NEA-TDB. This applies to equilibrium constants of aqueous species formed from arsenic and arsenious acid as well as formation constants of As(III)/As(V) oxides, uranium and nickel arsenates. On the other hand Pitzer parameters for the interaction of AsO_4^{3-} with Na^+ , K^+ , Cl^- , and SO_4^{2-} in aqueous solutions are developed based on equilibrium experiments. All data are valid for 25 °C.

Sufficient experimental data in form of solubility and isopiestic measurements are rare in the literature. Only two sources exist for binary systems of sodium and potassium with AsO_4^{3-} , HAsO_4^{2-} and H_2AsO_4^- . One is valid for diluted solutions up to 1.3 mol/kg, the other is not reliable. Parameters based on the former are developed and available via THEREDA. They are classified as reliable but limited to certain concentrations. Thus, resultant equilibrium constants have a questionable quality. In case of ternary systems with Cl^- and SO_4^{2-} the situation is even worse. There are doubtful isopiestic data and a few solubility measurements whose correctness cannot be guaranteed. Ternary parameter sets are developed but their quality is uncertain.

Magnesium and calcium arsenate are hardly soluble. There are no experimental data which describe the interaction of AsO_4^{3-} in Mg or Ca containing solutions. Equilibrium constants of solid phases are investigated by several authors but they are discordant in respect of the phase compositions. Thus, they are not present in THEREDA.

All in all, the thermodynamic data available today, are not sufficient to describe interactions of arsenic species in saline solutions. Exceptions are sodium and potassium containing binary systems where at least simulations of the water activities for a limited concentration range are possible.

13 Uranium

The NEA-TDB ([GRE/FUG1992] and [GUI/FAN2003]) is the major source for data of the aqueous and solid uranium species. Additional sources provide information concerning uranium(IV), coordination chemistry (mixed complexes, complexes at $\text{pH} > 8$ and $T > 25\text{ }^\circ\text{C}$) and saline systems (SIT and Pitzer parameters).

As a result of high demands for quality, the NEA-TDB is rather restrictive and therefore incomplete for extensive modeling calculations. E. g., there are 197 solids in the U-database but only 5 minerals of about 250 found their way into the recommended data set. This has been pointed out but unfortunately not corrected by the NAGRA/PSI database [HUM/BER2002]. However, the really solubility-dominating phases should be gathered in the THEREDA database. Therefore, the data compilation was focused on additional thermodynamic data of solid secondary uranium phases formed in the waste material, too.

The following uranium constituents are recorded: hydrolysis products, sulphates, carbonates, arsenates, silicates, phosphates, nitrates, halogenides, solid uranites. Examples for secondary mineral phases are the uranyl silicates haiweeite, (Na-) weeksite, (Na-) boltwoodite and the uranyl phosphate saleeite.

Data for gaseous species and high temperature solids are not relevant for German requirements. Therefore, they have not been imported in the database. The main parameters are data relating to chemical elements (most stable modification in standard state, formation enthalpy, function of heat capacity), stoichiometry factors and reaction equations, reaction data including phase transitions, parameters of ion interaction models (SIT, Pitzer) and, if available, confidence interval. Additional remarks provide further information (literature reference, validity limits, underlying analogue or method of estimation).

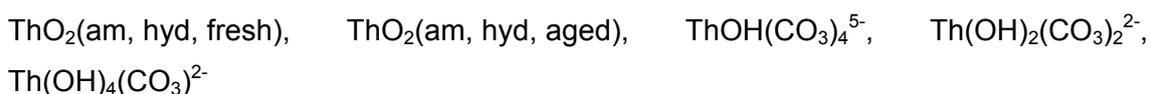
110 uranium species including 37 solid phases (thereof 21 are not covered by the NEA & Nagra/PSI database [HUM/BER2002]) are recorded in the database. Respective to the solid phases, the process of data compilation and evaluation is not completed yet.

14 Thorium

Thermodynamic data of thorium and its aqueous species were evaluated by OECD/NEA and recently published in the eleventh volume of the OECD/NEA series "Chemical Thermodynamics" [RAN/FUG2008]. These data are used for the THEREDA database without additional evaluation, because they can be regarded as reliable data sets. The description of the selection process is not given here or in the extended final report, but can be found in detail in [RAN/FUG2008].

Thorium only exists in the tetravalent oxidation state in aqueous solutions relevant to final disposal in deep geologic formation. Therefore, redox reactions have not to be considered and have not to be paraphrased like for neptunium and plutonium described later. Th^{4+} is defined as a primary master species in THEREDA database.

In the NEA database the formation reactions of thorium hydrolysis species are expressed with the hydroxide ion OH^- . The OH^- is defined as a product species in THEREDA and can therefore not be used for the formation reaction of other product species. Therefore several formation reactions for ionic species and solid phases have to be paraphrased by using the H_2O and H^+ as master species. This is described in detail in the extended final report. For the following species reported equilibrium reactions have been redefined according to THEREDA primary and secondary master species selections and the corresponding equilibrium constants were derived:



Further activities on thorium have not been performed by end 2009. The complete data set for thorium will be achieved in 2012 because of necessary extensive evaluation – regarding consistency of new data with the existing THEREDA database.

Regarding the Pitzer model, the NEA database does not provide any corresponding parameters. The Pitzer parameters for some thorium species have been summarized and evaluated by [NEC2000]. Because this set of parameters is based on equilibrium data different from the NEA database, it cannot be taken without further evaluation of its consistency with the existing THEREDA data set. If the consistency is not fulfilled,

the data have to be re-calculated. The process of evaluation will be performed in the second financed period of THEREDA.

14.1 SIT interaction coefficients

For modeling in aqueous solutions with higher ionic strengths interaction parameters for SIT or the Pitzer model are necessary. The SIT cannot be used for ionic strengths larger than about 3 molal solutions and for that one can only rely on the Pitzer model. SIT parameters are given for a lot of thorium species in the NEA database. The origin, calculation and selection of them are described in detail in [RAN/FUG2008]. These SIT interaction coefficients have fully been taken for THEREDA:

Th^{4+} , $\text{Th}(\text{OH})^{3+}$, $\text{Th}(\text{OH})_2^{2+}$, $\text{Th}(\text{OH})_3^+$, $\text{Th}_4(\text{OH})_{12}^{4+}$, $\text{Th}_2(\text{OH})_3^{5+}$, $\text{Th}_2(\text{OH})_2^{6+}$, $\text{Th}_4(\text{OH})_8^{8+}$, $\text{Th}_6(\text{OH})_{14}^{10+}$, ThCl^{3+} , $\text{Th}(\text{NO}_3)^{3+}$, $\text{Th}(\text{NO}_3)_2^{2+}$, $\text{Th}(\text{NO}_3)_3^+$.

14.2 Interaction coefficients according to Pitzer model

The NEA database does not regard Pitzer parameter. In the last decade Neck has assembled a set of Pitzer parameter for thorium hydrolysis species in chloride, carbonate and perchlorate solutions [NEC2000]. These Pitzer parameters can be used for modeling only with reservation, because they are estimated values deduced from SIT interaction coefficients and possess high uncertainties. Furthermore, the chemical models regarding Th-hydrolysis and carbonate complexation is rather simplistic and does not properly reflect the rather complex Th-speciation scheme. Pitzer parameters for thorium were not selected for THEREDA up to date and have to be re-evaluated in future activities.

15 Transuranic elements

15.1 Neptunium

Neptunium can exist in five oxidation states from +III to +VII: Np^{3+} , Np^{4+} , NpO_2^+ , NpO_2^{2+} , and NpO_3^+ . Np(VII) is only stable at extremely oxidizing conditions and in very alkaline aqueous solutions. Therefore, the Np(VII) is not relevant for safety assessment of a deep geological waste disposal, and is neglected in the THEREDA database. The relevance of Np(III) species is likewise questionable. The other oxidation states distributions depends on the redox conditions in the near and far field with Np(V) and Np(IV) being dominant under most geochemical boundary conditions.

The Np^{4+} ion is defined as the primary master species, Np^{3+} , NpO_2^+ , and NpO_2^{2+} are the secondary master species. The NEA database [GUI/FAN2003] expressed the formation of the secondary master species by redox reactions using the free electron e^- . This is not in accordance with the concept of THEREDA as it was defined to express all redox reactions by using the H_2/H^+ half redox reaction. For that the formation reactions of trivalent, pentavalent, and hexavalent Np ions from Np(IV) have to be re-formulated. They are summarized in detail in the extended final report.

Although many formation constants are being reported for neptunium species in the NEA database, the consistency of this set of data with Pitzer interaction parameters originating from other sources have to be proved in a next step before the data can be selected for THEREDA. The evaluation will be performed in 2011, beginning with the pentavalent neptunium. At the moment, only the data consistent with the parameter set of SIT interaction coefficients have been taken for THEREDA.

15.2 Plutonium

Plutonium can exist in five oxidation states from +III to +VII in aqueous solutions: Pu^{3+} , Pu^{4+} , PuO_2^+ , PuO_2^{2+} and Pu(VII). Pu(VII) is only relevant for exceedingly oxidizing conditions and not relevant for safety assessment of deep geological waste disposal. Therefore Pu(VII) is disregarded in THEREDA database. The other oxidation states are relevant depending on the redox conditions in the near and far field. In the NEA database [GUI/FAN2003] several thermodynamic data were selected that have been taken

for THEREDA. These data are only consistent with a set of SIT interaction coefficient $\epsilon(i,k)$. The data set is not consistent with Pitzer interaction coefficients. Due to the high complexity of plutonium chemistry, a lot of thermodynamic data and especially interaction parameters are missing. Hence, the chemical analogues (Cm(III), Th(IV), Np(V) and U(VI)) are needed to derive missing thermodynamic parameters and activity coefficients. These estimated values will not be deduced in any circumstance, but only if it is reasonable. From that the plutonium data can only be evaluated after the respective analogues have been selected. This will be performed towards the end of the second financed phase of the THEREDA.

The primary master species in the database is the aquo-ion Pu^{4+} , whereas Pu^{3+} , PuO_2^+ , and PuO_2^{2+} are defined as secondary master species. These redox reactions were reformulated from the NEA database into the concept of THEREDA in the same manner as for neptunium. Details of the process are described in the final report. As already mentioned, the release of the plutonium data set will be expected at the end of the second financed period of THEREDA 2013.

15.3 Americium

Americium can principally exist in four oxidation states from trivalent to hexavalent: Am^{3+} , Am^{4+} , AmO_2^+ , and AmO_2^{2+} . Only the trivalent americium occurs under redox conditions relevant to waste disposal in deep geological formations (reducing conditions). Under some circumstances in the near field – oxidative conditions, e. g. due to radiolysis – pentavalent americium can be formed. Tetravalent americium is not very stable and rather poorly characterized and plays an inferior role in solutions with very strong complexing agents. Therefore, only Am(III) is considered in the first release of THEREDA database. For trivalent americium a set of data consistent with a parameter set of the SIT theory as well as for the Pitzer formalism is available for modeling in aqueous solution containing NaCl, MgCl_2 and CaCl_2 up to ionic strengths of about 6 molal. The data are partly selected from NEA database (SIT consistent) and partly from the INE database assembled by Neck (Pitzer consistent). As basis for the Pitzer interaction parameters, the data set of HMW ([HAR/MOL1984], [FEL/WEA1986]), was used.

The selection of the NEA thermodynamic data of Am(III) and further details can be found in [SIL/BID1995], [GUI/FAN2003] and in the extended final report. Am(III) was defined as primary master species.

The following americium species are included in THEREDA data base, consistent with SIT and Pitzer formalism:

Am^{3+} , $\text{Am}(\text{OH})^{2+}$, $\text{Am}(\text{OH})_2^+$, $\text{Am}(\text{OH})_3(\text{aq})$, $\text{Am}(\text{OH})_4^-$, $\text{Am}(\text{OH})_3(\text{cr/aged})$,
 $\text{Am}(\text{OH})_3(\text{am})$, $\text{Ca}[\text{Am}(\text{OH})_3]^{2+}$, $\text{Ca}_2[\text{Am}(\text{OH})_4]^{3+}$, $\text{Ca}_3[\text{Am}(\text{OH})_6]^{3+}$, $\text{Am}(\text{CO}_3)^+$, $\text{Am}(\text{CO}_3)_2^-$,
 $\text{Am}(\text{CO}_3)_3^{3-}$, $\text{Am}(\text{HCO}_3)_2^+$, $\text{Am}_2(\text{CO}_3)_3(\text{am,hyd})$, $\text{AmCO}_3\text{OH}(\text{am,hyd})$,
 $\text{AmCO}_3\text{OH}\cdot 0,5\text{H}_2\text{O}(\text{c})$, $\text{NaAm}(\text{CO}_3)_2\cdot 5\text{H}_2\text{O}(\text{c})$.

Details about the selection of the data can be found in the extended final report.

15.4 Curium

Curium forms only species in the trivalent oxidation state in aqueous solution. The chemical behaviour is very similar to americium(III) and neodymium aquo-ion as a result of similar ionic radius and charge. As the experimental uncertainties underlying thermodynamic data are larger than changes resulting from small differences in ionic radius and effective charge, the data for aqueous species and especially activity coefficients are set to be similar or equal for Am(III), Cm(III), and in most cases Nd(III). This is the same approach as the NEA has followed in their review of Am(III): they considered data for both, Am(III) and Cm(III) and selected mean values valid for both metal species. Thermodynamic data for solid phases of curium are very seldom, and hence, analogue values from the trivalent americium and lanthanides, where a lot of experimental data are available, have been used.

For Curium(III) the same species are selected in THEREDA as for Am(III):

Cm^{3+} , $\text{Cm}(\text{OH})^{2+}$, $\text{Cm}(\text{OH})_2^+$, $\text{Cm}(\text{OH})_3(\text{aq})$, $\text{Cm}(\text{OH})_4^-$, $\text{Cm}(\text{OH})_3(\text{cr/aged})$,
 $\text{Cm}(\text{OH})_3(\text{am})$, $\text{Ca}[\text{Cm}(\text{OH})_3]^{2+}$, $\text{Ca}_2[\text{Cm}(\text{OH})_4]^{3+}$, $\text{Ca}_3[\text{Cm}(\text{OH})_6]^{3+}$, $\text{Cm}(\text{CO}_3)^+$,
 $\text{Cm}(\text{CO}_3)_2^-$, $\text{Cm}(\text{CO}_3)_3^{3-}$, $\text{Cm}(\text{HCO}_3)_2^+$, $\text{Cm}_2(\text{CO}_3)_3(\text{am,hyd})$, $\text{CmCO}_3\text{OH}(\text{am,hyd})$,
 $\text{CmCO}_3\text{OH}\cdot 0,5\text{H}_2\text{O}(\text{c})$, $\text{NaCm}(\text{CO}_3)_2\cdot 5\text{H}_2\text{O}(\text{c})$.

15.5 SIT interaction coefficients

For the actinide elements neptunium, plutonium, and americium SIT interaction coefficients $\epsilon(i,k)$ have been exclusively taken from the NEA-TDB ([RAN/FUG2008], Table B-4 und B-5). The SIT parameters for curium have been set equal to americium parameters. The experimental uncertainties of the equilibrium data are much larger than the differences in $\epsilon(i,k)$ expected from the differences in the ionic radius and effective ionic charge. Beyond that, new SIT interaction coefficients have been selected only for a few americium and curium species. SIT interaction coefficients $\epsilon(i,k)$ of the following species valid for aqueous solutions of NaCl and NaClO₄ are implemented in THEREDA:

Neptunium: Np^{3+} , Np^{4+} , NpO_2^+ , NpO_2^{2+} , NpCl_3^+ , NpO_2Cl^+ , NpOH^{3+} , $(\text{NpO}_2)_2(\text{OH})_2^{2+}$, NpO_2OH^+ , $\text{NpO}_2(\text{OH})_2^-$, $(\text{NpO}_2)_3(\text{OH})_5^+$, $\text{Np}(\text{CO}_3)_3^{3-}$, $\text{Np}(\text{CO}_3)_5^{6-}$, $\text{NpO}_2\text{CO}_3^-$, $\text{NpO}_2(\text{CO}_3)_2^{3-}$, $\text{NpO}_2(\text{CO}_3)_3^{5-}$, $\text{NpO}_2(\text{CO}_3)_2^{2-}$, $\text{NpO}_2(\text{CO}_3)_3^{4-}$, $(\text{NpO}_2)_3(\text{CO}_3)_6^{6-}$, NpSO_4^{2+} , $(\text{NpO}_2)_2\text{CO}_3(\text{OH})_3^-$, $\text{NpO}_2(\text{CO}_3)_2\text{OH}^{4-}$.

Plutonium: Pu^{3+} , Pu^{4+} , PuO_2^+ , PuO_2^{2+} , PuOH^{3+} , PuCl^{2+} , PuCl_3^+ , PuO_2Cl^+ , $\text{PuO}_2\text{CO}_3^-$.

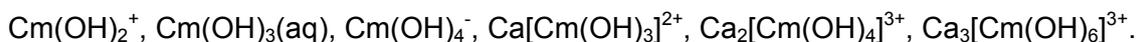
Americium: Am^{3+} , $\text{Am}(\text{OH})^{2+}$, $\text{Am}(\text{OH})_2^+$, AmCl^{2+} , AmCO_3^+ , $\text{Am}(\text{CO}_3)_2^-$, $\text{Am}(\text{CO}_3)_3^{3-}$, AmSO_4^+ , $\text{Am}(\text{SO}_4)_2^-$.

SIT interaction coefficients have been selected for americium species in CaCl₂ and MgCl₂ solutions from a “peer reviewed” article [NEC/ALT2009]. Neck et al. have assembled a new parameter set for the hydrolysis of Am(III), Cm(III) und Nd(III) based on experimental equilibrium data. These SIT parameters are consistent on one hand with the speciation model of the NEA-TDB, and on the other hand consistent with Pitzer interaction coefficients of the same species which were assembled by the same authors [NEC/ALT2009].

Americium: $\text{Am}(\text{OH})_2^+$, $\text{Am}(\text{OH})_3(\text{aq})$, $\text{Am}(\text{OH})_4^-$, $\text{Ca}[\text{Am}(\text{OH})_3]^{2+}$, $\text{Ca}_2[\text{Am}(\text{OH})_4]^{3+}$, $\text{Ca}_3[\text{Am}(\text{OH})_6]^{3+}$.

Curium (analogue to americium): Cm^{3+} , $\text{Cm}(\text{OH})^{2+}$, $\text{Cm}(\text{OH})_2^+$, CmCl^{2+} , CmCO_3^+ , $\text{Cm}(\text{CO}_3)_2^-$, $\text{Cm}(\text{CO}_3)_3^{3-}$, CmSO_4^+ , $\text{Cm}(\text{SO}_4)_2^-$.

Also analogue to americium, SIT parameters of the following curium species valid for aqueous solutions of CaCl_2 and MgCl_2 can be found in THEREDA:



15.6 Interaction coefficients according to the Pitzer model

In contrast to the SIT interaction coefficients, the interaction coefficients according to the Pitzer model were not considered in the NEA database [GUI/FAN2003]. Hence, Pitzer interaction coefficients must be taken from other sources. One of these sources is the INE database [ALT/BRE2004], [NEC1997], [NEC2000], [NEC/FAN1998], [NEC/FAN1999], [NEC/FAN2001], which contains a set of Pitzer parameters mostly consistent with the THEREDA Pitzer data set of the oceanic salts; but several interaction coefficients have not been checked on consistency with the parameter of the oceanic salts. That applies mainly for the elements thorium, neptunium, plutonium and technetium. The consistency of other sources from literature is not known to date. The extensive evaluation of these data will be performed in the second financed period of THEREDA. In the THEREDA database, the following interaction coefficients, experimental and analogue values, are given till end 2009: α_1 , α_2 , $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, C^ϕ , $\theta(\text{cc}')$, $\psi(\text{cc}'a)$, λ_{nc} (explanation of the parameters see in [PIT1991] or [FEL/WEA1986]).

15.6.1 Americium

Based on studies from [RAB/ALT2008], [KOE/FAN1997], [RUN/KIM1994], [FAN/KIM1995], and the review of the data in [NEC/ALT2009] and [ALT/BRE2004], a set of Pitzer interaction coefficients for the following species is given in THEREDA:

Actinide species: Am^{3+} , $\text{Am}(\text{OH})^{2+}$, $\text{Am}(\text{OH})_2^+$, AmO_2^+ , $\text{Am}(\text{OH})_4^-$, $\text{Ca}[\text{Am}(\text{OH})_3]^{2+}$, $\text{Ca}_2[\text{Am}(\text{OH})_4]^{3+}$, $\text{Ca}_3[\text{Am}(\text{OH})_6]^{3+}$, AmCl^{2+} , AmCl_2^+ .

Cations: Na^+ , Ca^{2+} , Mg^{2+} .

Anions: Cl^- , ClO_4^- , SO_4^{2-} .

Several interaction coefficients of americium are analogue values obtained from spectroscopic curium studies. Pitzer parameters have been set equal for americium and curium if no experimental values are available from literature.

15.6.2 Curium

Using the same approach described in the last paragraph for americium, a reliable and consistent set of Pitzer interaction coefficients is given in THEREDA:

Actinide species: Cm^{3+} , $\text{Cm}(\text{OH})^{2+}$, $\text{Cm}(\text{OH})_2^+$, CmO_2^+ , $\text{Cm}(\text{OH})_4^-$, $\text{Ca}[\text{Cm}(\text{OH})_3]^{2+}$, $\text{Ca}_2[\text{Cm}(\text{OH})_4]^{3+}$, $\text{Ca}_3[\text{Cm}(\text{OH})_6]^{3+}$, CmCl^{2+} , CmCl_2^+ .

Cations: Na^+ , Ca^{2+} , Mg^{2+} .

Anions: Cl^- , ClO_4^- , SO_4^{2-} .

This selection is based on studies from [RAB/ALT2008], [KOE/FAN1997], [RUN/KIM1994], [FAN/KIM1995], and a review of [NEC/ALT2009] and [ALT/BRE2004].

16 Technetium

The fission product technetium can form compounds with a wide range of oxidation states ranging up to +VII. The oxidation states in aqueous solutions can be Tc(III), Tc(IV), Tc(V), TcO_4^{2-} and TcO_4^- . Technetium in the heptavalent state (TcO_4^-) is dominating from oxidizing to slightly reducing conditions. At the strongly reducing conditions relevant for deep geological formations Tc(VII) will be reduced to the lower oxidation states down to Tc(IV). The intermediate oxidation states Tc(VI) and Tc(V) are highly unstable and disproportionate almost immediately. The trivalent technetium (Tc^{3+}) is stable only at pH values below 3. Thermodynamic data are available from OECD/NEA project. The selected values are listed in [RAR/RAN1999] together with a very detailed description of the selection process.

For THEREDA the TcO_4^- is selected as primary master species. The thermodynamic formation and reaction data were taken from NEA database [RAR/RAN1999], GUI/FAN2003]. Exceptions are discussed in the final report. Formation data for the secondary master species have to be re-formulate by the H_2/H^+ redox reaction and not by the free electron.

For technetium the following species are considered by THEREDA so far:

TcO_4^- , TcO_4^{2-} , $\text{TcO}(\text{OH})_2(\text{aq})$, TcO^{2+} , $\text{TcCl}_4(\text{am})$, $\text{TcCl}_4(\text{aq})$, TcCl_6^{2-} , $\text{K}_2(\text{TcCl}_6)(\text{cr})$.

16.1 SIT interaction parameter for Tc species

SIT interaction coefficient $\epsilon(i,k)$ are not given in the NEA database and were not considered by THEREDA so far.

16.2 Interaction coefficients according to Pitzer model

The Pitzer interaction coefficients were not considered by THEREDA so far.

17 Samarium and Protactinium

17.1 Samarium

The thermodynamic equilibrium constants of the trivalent lanthanides and actinides show systematic trends regarding the ionic radii of the elements. Comparing the ionic radii of Nd^{3+} , Pu^{3+} , Am^{3+} and Cm^{3+} (111, 112, 110, 109 pm) at coordination number of 8 ([CHO/RIZ1994]) with the ionic radius of Sm^{3+} at the same coordination number (108 pm), the thermodynamic equilibrium constants are expected to be very similar. Looking at the equilibrium constants of the lanthanides from Nd^{3+} to Sm^{3+} within the lanthanide series, the difference between the log K is smaller than 0.2 log units [HAA/SHO1995]. This difference due to the various ionic radii is smaller than the experimental uncertainties. Therefore, data of Nd(III), Eu(III) (ionic radius: 107 pm), and trivalent actinides can be used as analogue or estimated values, when no reliable experimental data are available. For samarium, only few data are available directly from literature. In this report data from [GUI/FAN2003] and [NEC/ALT2009] for the trivalent actinides and Nd(III) were faced to data from [SPA/BRU1995] in the THEREDA review. Data from NEA [GUI/FAN2003] and [NEC/ALT2009] are based mainly on solubility studies and spectroscopic investigations. Spahiu and Bruno published a review over literature data of lanthanides and re-evaluated these data if necessary [SPA/BRU1995]. From this expert review, the data for Sm^{3+} were taken and complemented by other values found in literature. A more detailed comparison, check of consistency and a final evaluation will be conducted.

In this report the following samarium compounds soluble in aqueous solution are compiled including estimated values deduced from analogue elements:

Chloride complexes: SmCl^{2+} , SmCl_2^+ .

Hydroxide complexes: $\text{Sm}(\text{OH})_2^{2+}$, $\text{Sm}(\text{OH})_2^+$, $\text{Sm}(\text{OH})_3(\text{aq})$, $\text{Sm}(\text{OH})_4^-$.

Carbonate complexes: $\text{Sm}(\text{CO}_3)^+$, $\text{Sm}(\text{CO}_3)_2^-$, $\text{Sm}(\text{CO}_3)_3^{3-}$, $\text{Sm}(\text{HCO}_3)_2^{2+}$.

Fluoride complexes: SmF^{2+} , SmF_2^+ , $\text{SmF}_3(\text{aq})$.

Sulfate complexes: $\text{Sm}(\text{SO}_4)^+$, $\text{Sm}(\text{SO}_4)_2^-$.

Phosphate complexes: $\text{Sm}(\text{H}_2\text{PO}_4)^{2+}$, $\text{Sm}(\text{HPO}_4)^+$, $\text{Sm}(\text{HPO}_4)_2^-$, $\text{Sm}(\text{PO}_4)(\text{aq})$, $\text{Sm}(\text{PO}_4)_2^{3-}$.

17.2 Protactinium

Protactinium can exist in the tetravalent or pentavalent oxidation state in aqueous solution depending on the redox potential of the solution. Pentavalent Protactinium (Pa(V)) is the stable form under ambient conditions, whereas tetravalent Protactinium (Pa(IV)) occurs only at reducing conditions and strict exclusion of oxygen. Pa(V) does not form cation like Pa^{5+} in aqueous solution, but it reacts readily with water to form oxo-cations and condensate polymeric species. Pa(V) shows a very complex aqueous chemistry that resembles the chemical behaviour of the elements Niobium and Tantalum. Experimental determination of thermodynamic data for Pa is complicated by the high specific radioactivity and the formation of polymeric species even at low concentrations down to 10^{-8} molar showing very strong sorption on various surfaces. Therefore thermodynamic data are very rare in literature.

Pa(IV) should resemble to other tetravalent actinides regarding their chemical behaviour in aqueous solution. Also for Pa(IV) the number of experiments and therefore the number of publications on thermodynamic data in aqueous solutions is very rare.

In THEREDA Pa^{4+} and $\text{PaO}(\text{OH})^{2+}$ were defined as primary and secondary master species, respectively. Because of the lack of Pa data, thermodynamic data will have to be deduced from the chemical trends drawn from analogues elements. For tetravalent Pa, the trends in the series Th^{4+} , U^{4+} , Np^{4+} , and Pu^{4+} can be used to extrapolate its thermodynamic properties in aqueous solution. The pentavalent Pa is a special case, because there is no analogues cation with similar charge and geometry. Pa(V) is a mono Oxo-cation PaO^{3+} that already hydrolyses even at low pH values like pH 1 forming $\text{PaO}(\text{OH})^{2+}$. Given this peculiarity, the pentavalent NpO_2^+ , PuO_2^+ , AmO_2^+ or VO_2^+ cannot be used as direct surrogates. The estimation of ion interaction parameter for Pa(V) will be done at a later project stage.

In the present report the following species are listed, based on experimental data from [LEN/TRU2003], [TRU/GUZ1998], [TRU/LEN2002], [TRU/LEN2003]: $\text{PaO}(\text{OH})^{2+}$, $\text{Pa}(\text{OH})_5(\text{aq})$. Data on Pa(IV) and Pa(V) species are evaluated in the near future.

18 Conclusion

"THEREDA" represents a web-based system of programs enabling access to thermodynamic reference data for the needs of the final disposal of radioactive and chemical-toxic waste in Germany.

Within the joint project expertises from different research institutions are bundled: obtaining and processing of primary experimental data, development of parameters, and development of database, database design, web design, and thermodynamic modeling.

In 2011 THEREDA will become operative: Code-specific parameter files will be ready for download free of charge. For the sake of quality assurance, release of data will not be for all stored data at once, but in a pre-determined succession of elements mutually agreed upon within the joint project. The first data envisaged for release relate to the system of oceanic salts, Nd, Am, and Cm.

THEREDA will also be a mean of directing future research efforts and for quality assurance for civil agencies, service providers and research institutions. Future extensions of the thermodynamic database in Germany will be networked with THEREDA.

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