

THEREDA - The Thermodynamic Reference Database for Nuclear Waste Disposal in Germany - 9187

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ABSTRACT

Part of the process to ensure the safety of radioactive waste disposal is the predictive modeling of the solubility of certain toxic components in a complex aqueous solution. To ensure the reliability of thermodynamic equilibrium modeling as well as to facilitate the comparison of such calculations done by different institutions it is necessary to create a mutually accepted thermodynamic reference database. To meet this demand several institutions in Germany joined efforts and created THEREDA. THEREDA is a relational databank whose structure was designed in a way that facilitates internal consistency of thermodynamic data entered. It serves as backend to a variety of peripheral programs which allow for adding, editing, and extracting subsets of data. Data considered cover the needs for Gibbs Energy Minimizers and Law-of-Mass-Action-programs alike. Interaction parameters for an arbitrary number of mixed phases and p,T-functions of thermodynamic data may also entered. To enhance public use THEREDA is accessible via internet.

INTRODUCTION

Part of performance assessment for repositories for radioactive or chemical-toxic waste alike is an assessment of the maximum likely solubility of contaminants in an aqueous solution of relevant composition. Those calculations are based on finding a global thermodynamic equilibrium between all constituents in all phases of a given system. There exist two major strategies to accomplish this: minimizing the global Gibbs energy of the system under consideration (GEM-approach) or solving a system of equations which represent individual equilibrium reactions (LAM-approach). While the two major strategies are different numerically, thermodynamic data underlying them - of course - are the same. Both approaches are linked by the following relation:

$$\Delta_f G_{i \neq j}^0 = -RT \ln K - \sum_{j \neq i} \nu_j \Delta_f G_j^0 \quad [1]$$

where $\Delta_f G_j^0$ = standard Gibbs energy of formation, R = general gas constant, T = absolute temperature, and K = equilibrium constant for the formation of phase constituent j .

For a complete description of thermodynamic equilibrium Gibbs Energies of Formation or the formation constant for all relevant constituents need to be known. For calculations in non-ideal solutions (aqueous or solid), interaction parameters may be necessary.

There exist a number of different programs to calculate thermodynamic equilibrium. The following figure shows some details.

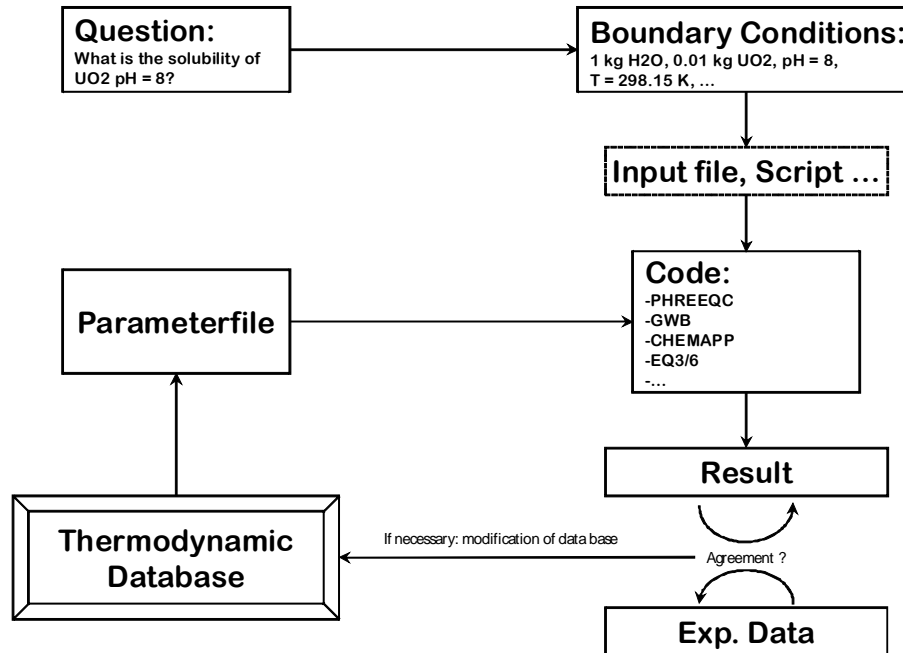


Fig. 1: Work flow for thermodynamic equilibrium modeling

Any calculation of thermodynamic equilibrium begins with a specific question, e. g. as to how much UO_2 might be soluble in pure water. Such a question must be expressed in terms of boundary conditions. These are the input for the code applied to perform the calculation. Where a graphical user interface exists they are entered in some forms. Other programs need the boundary conditions in a code-specific format written in ASCII-files (input files, scripts...).

From the thermodynamic database, in what ever form this is maintained, a so called parameter files needs to be extracted. This is again code-specific and delivers the thermodynamic data which are used by the code to calculate the equilibrium.

Input file and parameter file are the prerequisites for the code to perform the calculation. Results are compared with experimental data to refine the database. After refinement a new set of data needs to be exported into a parameter file. The step of producing a parameter file may be time consuming and tedious, depending on the data modified and relationships with other data, which must be accounted for. It is common practise to exchange parameter files via e-mail or download them from the web und to adapt them to own requirement afterwards. If this is done and certain rules of internal consistency are not obeyed, the new parameter file will give rise to erroneous results. It is therefore important to create a functional link between the database and the (code-specific) parameter file, which is both reliable and time-saving for the scientist.

The importance of reliable thermodynamic data for the use in long-term safety analyses of geological repositories has been acknowledged internationally since decades. For selected actinides (U, Np, Pu, Am) and fission products (Tc, Zr, Ni, Se) a thermodynamic database from the Nuclear Energy Agency of the Organisation for Economic Cooperation and Development (NEA/OECD) is available [1], being permanently updated and extended. However, as a result of high demands for quality this database is rather restrictive and therefore incomplete for extensive modeling calculations. E.g., there are 197 solids in the NEA uranium database, but only five uranium minerals out of about 250 natural occurring ones made their way into the recommended data set. This has been pointed out (but unfortunately not corrected for) also by the Nagra/PSI data base [2]. The use of further established databases (NBS tables [3], CODATA [4]) is limited, especially when dealing with solutions of high ionic strength. Moreover, they lack data on many relevant radionuclides and other toxic metals.

Other thermodynamic databases were assembled in the context of specific final repository projects in the USA and in Switzerland and have been adapted to the respective projects [5]. Therefore, a direct adaptation of already existing databases proved to be not sensible, especially when taking into account that Germany will have further requirements not relevant in other countries. First, the selection of a specific deep geological repository for high level radioactive waste (HLRW) is still an open question in Germany. Therefore, different types of host rock formations (salt and clay) are still conceivable, which implies varying solution compositions and ionic strengths. Second, the time frame for intermediate storage of the nuclear waste is not fixed yet, thus there are also concepts to be discussed coping with temperatures as high as 150 °C. Third, as there is not clear yet whether a German repository will be used for HLW, ILW and LLW simultaneously or not (then implying more than one deposit) the composition of the waste may vary considerably, too, again with effects on the temperatures to be dealt with. For all reasons mentioned it was decided that it is necessary to set up a new thermodynamic reference database for German concerns.

REQUIREMENTS AND DECISIONS

Already in 2002 the five leading institutions in the field of safety research for the final disposal of radioactive waste in Germany set up a task group to find a mutual agreement upon requirements the new database should meet, on the technical frame work and on work-sharing within the joint-project to come.

Internal Consistency

There is to be distinguished between different levels of consistency.

Data Consistency

Thermodynamic data within the database should be mutually convertible following the usual thermodynamic relations. In fact this requirement entails:

A technical framework which enforces internal consistency by automatically triggered internal calculations;

A clear distinction between “entered” data, which are not subject to internal calculations, and “internally calculated” data;

For each datum to be calculated internally a clear specification as to by which thermodynamic relation this shall be done (or has been done, respectively). This information implies which other data the specific datum is dependent on.

Algorithm Consistency

Two different cases can be counted to this category of consistency. First, conditional equilibrium constants should be extrapolated to $I = 0$ applying the same model for activity coefficients. Equilibrium

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constants exist which were derived from conditional constants at different ionic strengths, extrapolated applying SIT-parameters, while others were derived applying the Pitzer model. Those equilibrium constants must not be combined in a single calculation of thermodynamic equilibrium. Second, also SIT- or Pitzer-parameters for the calculation of activity coefficients may be derived using slightly different formulas, superficially being assigned to SIT- or Pitzer-theory. Therefore, all equations used for parameter optimization (including such inconspicuous numbers like the Debye Hückel limiting slope at various temperatures) must be agreed upon and held stringently throughout the work. In addition, such conventions are to be documented for those who apply the database.

Correlation Consistency

While it is obvious for some data that they are interrelated (e. g. those contained in the Gibbs-Helmholtz-relation), for others it is not. E. g. some Pitzer parameters might had been determined by assuming a certain solubility constant for a specific solid phase. Leaving the Pitzer parameters at their original values but changing the solubility constant for the solid phase involved in their determination, will lead to erroneous results in future calculations with the modified database. Such data have therefore to be combined in a set and appropriate warning messages have to be issued when an editor tries to modify parts of the set individually.

Traceability

In order to enhance confidence in the compiled data, it was agreed that all data are back-traceable to publicly available references. This does not imply, however, that each individual datum can be related to original, primary experimental data. This might be the case for some data and others not. Thus, the scope of THEREDA is to be distinguished from a database as it is generated by THERMOML, which represents a system, where primary experimental results are compiled together with derived thermodynamic data [6].

Preference of solubility-calculation

It was common sense within the task group that the thermodynamic data compiled should be first of all properly suited to calculate solubilities of contaminants properly. This decision has a profound impact on the selection of thermodynamic data. For several solid phases such as some anhydrous oxides of actinides precisely determined data of purely thermochemical origin exist, nevertheless leading to calculated actinide solubilities orders of magnitude too low. This is because the phase actually governing the solubility is a secondary, hydrous, in some cases meta-stable phase which covers the surface of the anhydrous oxide. Bearing this in mind, all thermodynamic data compiled in THEREDA are assigned a mark, which classifies their origin, whether it originates from thermochemical measurements or determinations of the solubility of a specific phase. In case of doubt preference is given to solubility-related data.

IMPLEMENTATION OF THE PROJECT

Formally, work on the database began 2006-07 as a joint project of

- Forschungszentrum Dresden-Rossendorf, Institute of Radiochemistry (FZD-IRC);
- Forschungszentrum Karlsruhe, Institute for Nuclear Waste Disposal (FZK-INE);
- Gesellschaft für Anlagen- und Reaktorsicherheit mbH (GRS);
- TU Bergakademie Freiberg, Institute of Inorganic Chemistry (TU-BAF);

- AF-Colenco Ltd, Groundwater Protection and Waste Disposal (Switzerland).

The project is jointly financed by the Federal Ministry of Economics and Technology, the Federal Ministry for the Environment, Nature Conservation and Nuclear Safety, and the Federal Ministry of Education and Research. The present (first) phase of the project will be completed by 2009-06. A second phase running from 2009-07 to 2012-06 is envisaged, which will be dedicated to further data capture, support of more thermodynamic codes, and the implementation of sorption processes. After 2012-06 the database will be further maintained in the long term. THEREDA is envisaged as the compulsory thermodynamic reference database for issues concerning the long-term disposal of radioactive and chemical-toxic waste in Germany.

The thermodynamic reference database will be operative as of 2009-06.

TECHNICAL APPROACH

Generally spoken THEREDA can be regarded as a set of mutually harmonized programs designed to facilitate the generation of internally consistent parameter files in order to calculate solubilities of contaminants properly. The core of THEREDA is PostgreSQL, an object-relational system for the administration of databanks. The predecessor called POSTGRES was developed at the University of California in Berkeley. PostgreSQL is open source and features up-to-date capabilities such as foreign keys, referential integrity, and propagative editing of data sets. What makes PostgreSQL even more interesting for our purpose is its capability to be extended by the user with functions and scripts in a number of procedural languages.

In the running start-up phase of the project, data are imported in large numbers using a popular spreadsheet program. This task will be taken over step by step by a system of PHP-Scripts, designed to aid in data import, to trigger internal calculations and to export sub sets into parameter files. PHP is a widely-used general-purpose scripting language that is especially suited for web development and can be embedded into HTML. It generally runs on a web server, taking PHP code as its input and creating web pages as output. It can be deployed on most web servers and on almost every operating system and platform free of charge. PHP is installed on more than 20 million websites and 1 million web servers. The most recent major release of PHP was version 5.2.6 on May 1, 2008.

To ensure operability in the long term, it was decided to use open-source software wherever possible. To promote readability by humans all identifiers within the databank (technically serving as primary key to data sets) and to the extent it was feasible were designed as plain text rather than index numbers. Ideally, a human reader should be able to draw all information from the data bank by simply looking at the datasets.

At the time being the databank includes 56 relations (table), containing more than 370 attributes (columns) connected by more than 120 relationships. However, not all relationships necessary to render a thermodynamic database fully consistent internally can be imposed by databank-logic alone; the mentioned PHP-scripts allow for a very detailed control of recorded data and assist editors.

The data model allows for the entry of an arbitrary number of phases, of which aqueous and gaseous phase are just two. Phases are built up by phase constituents which in turn consist of elements. Phase constituents are assigned thermodynamic data. For any phase declared and defined in terms of phase constituents, interaction models may be declared which allow for the calculation of excess Gibbs energies of mixing. Thus, interaction coefficients for the aqueous phase (like Pitzer- or SIT-parameters) and those for the gaseous phase or solid solutions are stored within the same structure.

To assist the editor in managing and exporting large subsets of data, an arbitrary number of these may be grouped into so called sets. Sets of data may be mutually exclusive (such as aqueous species defined in chloride-rich brines vs. other speciation models for groundwater-type solutions) or internally inclusive (such as equilibrium constants and Pitzer parameters which must not be altered independently). For any individual datum as well as for whole sets of data an arbitrary number of constraints can be entered which

mark their limits of applicability. Other measures allow for a fairly fine-grained classification of data in terms of quality, kind of its derivation and the source it was adapted from.

COMPREHENSIVENESS

So far, no decision has been made in Germany as to the type of host rock, a future disposal site for radioactive waste will be situated in. The database has therefore to provide datasets for both brine- and groundwater-type solutions. For some particular cases this means that different strings of species, e. g. complexes, are maintained which are valid depending on the ionic strength in solution.

Persistent data gaps are closed via data of higher uncertainty or estimated values. The identification of such gaps can also aid toward decisions about the targets and priorities of future experimental programs. The provision of uncertain or estimated data (which are, of course, marked accordingly) is important. It is our conviction that a comprehensive thermodynamic equilibrium calculation with estimated – but as such: documented! – data is better than an incomprehensive parameter file, which will inevitably lead potential users into temptation to add missing data on their own account.

The following elements are covered in running project phase, usually both for brine- or groundwater-type solutions, including interaction parameters with aqueous species of the oceanic system of salts.

- Na, K, Mg, Ca, Cl, SO₄ for temperatures up to 393 K
- The above system with CO₂/CO₃ at 298.15 K; an extension to higher temperatures is planned for the second project phase
- Radionuclides (actinides and fission products): U, Np, Pu, Am, Cm, Pa, Th, Tc, Cs, Sm, I, Se, Sr, Ni, Ra
- Toxic elements: Zn, Cr, Co, Cu, Cd, Hg, Pb, and As.
- Matrix elements: Si, Al (including a thermodynamic model for cementitious materials)

For solutions of ionic strengths higher than 0.5, which cannot be treated with extended Debye-Hückel or Davies, SIT- and Pitzer parameters are provided. In the first project phase no solid solutions will be present in the database, even though this would be possible technically.

Parameter files will be ready for download as of 2008-07 for the following codes: PHREEQC, Geochemist's Workbench, and CHEMAPP.

QUALITY MANAGEMENT

We seek to compile data of high quality, internal consistency and traceability, mainly from existing databases, and to complement this basis particularly with datasets for high saline systems (Pitzer and SIT parameters) and systems at elevated temperatures.

For any phase constituent it is stored whether the appending set of data is consistent with SIT- or Pitzer-formalism. Further, information is mandatory whether a possible formation reaction is usually at equilibrium or not. Of course, this information is first of all crucial for constituents of solid phases.

Each datum assigned to a phase constituent is classified as follows:

- Calculation mode: a datum may be entered directly or calculated using other data. Which other data have to be used follows from the entered calculation mode. E. g., direct entry of $\Delta_f G_j^0$ is not permitted; it must be calculated internally from reaction data or with the Gibbs-Helmholtz-equation. If a datum was calculated from a p,T-function, this is also indicated here.
- Uncertainty
- Data class: this field gives note as to whether the datum originates from thermochemical or solubility measurements, whether it was derived using chemical analogues, whether it was estimated or internally calculated.
- Data quality: this delivers a ranking scheme for the quality of the datum. Reliable data get a lower number than data which were deemed questionable.

- Data source: a similar ranking scheme relating to the trustworthiness. International peer-reviewed mark the lower end while values based on internal sources (but nevertheless accessible to members of THEREDA) receive higher (worse) grades.
- Reference: the source where the datum was adopted from, internally classified by the field data source.

A similar ranking scheme is applied to interaction coefficients.

For a proper classification according to the above-mentioned schemes THEREDA-members agreed to guidelines, which for a large part go back to those from NEA, but which were extended significantly for the assessment of interaction coefficients and for procedures for the estimation of missing data.

CONCLUSIONS

The data compiled and evaluated in THEREDA can be utilized for all final repository systems discussed in Germany. In contrast to existing databases, internal consistency in THEREDA will be permanently ensured. Host rock related subsets of data, extracted from the database and converted to various parameter file formats required by geochemical codes (such as PHREEQC, GWB, or ChemApp), allow a widespread use in the fields of storage of radioactive waste or chemo-toxic substances.

It is hoped that THEREDA will contribute to a reliable, comparable and traceable widespread use of thermodynamic equilibrium modeling, especially in conjunction with long-term safety analyses for radioactive waste disposal sites.

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