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M4FT-16LL080302052-Update to Thermodynamic Database Development and Sorption Database Integration

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August 16, 2016

M4FT-16LL080302052-Update to Thermodynamic Database Development and Sorption Database Integration

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1. Introduction

This progress report (Level 4 Milestone Number M4FT-16LL080302052) summarizes research conducted at Lawrence Livermore National Laboratory (LLNL) within the Argillite Disposal R&D Work Package Number FT-16LL08030205. The focus of this research is the thermodynamic modeling of Engineered Barrier System (EBS) materials and properties and development of thermodynamic databases and models to evaluate the stability of EBS materials and their interactions with fluids at various physico-chemical conditions relevant to subsurface repository environments. The development and implementation of equilibrium thermodynamic models are intended to describe chemical and physical processes such as solubility, sorption, and diffusion. The scope of the effort included the following:

- Illustrating the concepts developed by Wolery and Jove-Colon (FY15 effort) and applying them to mineralogic components of greatest interest to UFD research
- Testing the PhreeqcRM-PEST framework for surface complexation modeling as part of sorption database development.
- Supporting the involvement of the Used Fuel Disposition campaign in the Nuclear Energy Agency Thermodynamic Database Development (supported through the International Work Package Number FT-16LL08030306)

The thermodynamic database development effort is a longterm investment by the Used Fuel Disposition (UFD) program. It includes reviewing and revising previously developed thermodynamic databases and expanding them to cover the needs of the repository types currently under consideration by the UFD program (i.e. clay, granite, deep borehole). The effort is a collaboration between LLNL and SNL.

Two manuscripts have been prepared as a result of the recent effort. In FY16, LLNL prepared a follow-on manuscript to that of Wolery and Jove-Colon's FY15 manuscript, creating a modified SUPCRT92 code data file, and producing a modified version of a water model consistent with the CODATA recommendations. This will provide a core for additional database development. As much as possible, the efforts of the NEA TDB effort and other investigators were leveraged. Information contained in the two manuscripts is described in the following section.

The second effort involves development of surface complexation and cation exchange databases for use in PA models. This effort is a continuation of FY15 work, in collaboration with Dr. V. Brendler (HZDR) and the RES^{3}T database development team. The goal of this effort is to develop a path forward for future sorption database development. The effort builds upon the RES^{3}T database effort by assembling digitized data collected from references contained in RES^{3}T and providing a modeling framework for fitting the digitized data to a self-consistent surface complexation model and associated database.

A third effort involves participation of Cynthia Atkins-Duffin (LLNL) in the Nuclear Energy Agency (NEA) Thermochemical Database (TDB) project. Dr. Atkins-Duffin is the UFD representative for thermodynamic database development efforts at the NEA in support of international nuclear waste repository research. This effort was supported through the International Work Package. However, a short summary is provided in this document.

2. Thermodynamic Database Development

The paper “Chemical Thermodynamic Data. I. The Concept of Links to the Chemical Elements and the Historical Development of Key Thermodynamic Data” by Thomas J. Wolery (LLNL) and Carlos F. Jové-Colón (SNL) was submitted to *Geochimica et Cosmochimica Acta* in December, 2015. Editorial decision (likely acceptance upon responding to reviewers’ comments) was received in March, 2016). A significant part of this fiscal year’s effort has been spent into responding to the comments of the Associate Editor and four reviewers, including shortening the paper from 99 to 70 pages. As of this writing (8/16/16), the paper is ready for resubmission. The current abstract from this paper is:

> Chemical thermodynamic data remain a keystone for geochemical modeling and reactive transport simulation as applied to an increasing number of applications in the earth sciences, as well as applications in other areas including metallurgy, material science, and industrial process design. The last century has seen the development of a large body of thermodynamic data and a number of major compilations. The past several decades have seen the development of thermodynamic databases in digital form designed to support computer calculations. However, some problems with thermodynamic data appear to be persistent. One problem pertains to the use of inconsistent primary key reference data. Such data pertain to elemental reference forms and key, stoichiometrically simple chemical species including metal oxides, CO_2, water, and aqueous species such as Na^+ and Cl^-. A consistent set of primary key data (standard Gibbs energies, standard enthalpies, and standard entropies for key chemical species) for 298.15K and 1 bar pressure is essential. Thermochemical convention is to define the standard Gibbs energy and the standard enthalpy of an individual chemical species in terms of formation from the reference forms of the constituent chemical elements. We propose a formal concept of “links” to the elemental reference forms, as thermochemical convention. This concept involves a documented understanding of all reactions and calculations leading to values for a formation property (Gibbs energy or enthalpy). A valid link consists of two parts: (a) the path of reactions and corrections and (b) the associated data, which are key data. Such a link differs from a bare “key” or “reference” datum in that it requires additional information. Some or perhaps all of its associated data may also be key data. In evaluating a reported thermodynamic datum, one should identify the links to the chemical elements, a process which can be time-consuming and which may lead to a dead end (an incomplete link). The use of two or more inconsistent links to the same elemental reference form in a thermodynamic database will necessarily result in an inconsistency in the database. Thus, in constructing a database, it is important to establish a set of reliable links (generally resulting in a set of primary reference data) and then correct all data adopted subsequently for consistency with that set. Recommended values of key data have not been constant through history. We review some of this history through the lens of major compilations and other influential reports, and note a number of problem areas. Finally, we illustrate the concepts developed in this paper by applying them to some key species of geochemical interest, including liquid water, quartz and aqueous silica, and gibbsite, corundum, and the aqueous aluminum ion.

This paper describes a methodology for evaluating consistency in thermodynamic data and building thermodynamically consistent databases. It reviews nearly a century of thermodynamic data. It then applies the methodology to key data for (1) water, (2) quartz and aqueous silica, and (3) gibbsite, corundum, and the aluminum ion. Follow-on efforts will focus on further illustrating these concepts and applying them to mineralogic components of greatest interest to the UFD program.

A second manuscript, “Chemical Thermodynamic Data. II. Water in SUPCRT92 and Similar Codes: Thermochemical Properties in Relation to Equations of State” was recently prepared for submission to *Computers & Geosciences*. The abstract is

> The properties of liquid water and steam are central to the thermodynamics of aqueous systems and phase relations among water and minerals. SUPCRT92 (Johnson et al., 1992) has been a useful tool for generating thermodynamic data to support geochemical modeling and reactive transport calculations. The code uses standard thermodynamic models for which the relevant data are mostly provided on the code’s own thermodynamic data base. However, the thermodynamic properties of water are hard-coded. They are calculated in part from a two-phase, single-component fluid equation of state (EOS) model. SUPCRT92 uses the EOS developed by Haar et al. (1984) and, near the critical point, that of Levelt Sengers et al. (1983). These models account for the temperature and pressure dependence of the usual thermochemical properties (e.g., the standard Gibbs energy, enthalpy, and entropy). However, they use non-thermochemical reference conditions of u (specific internal energy, kJ kg-1) = 0 and s (specific entropy, kJ kg-1 K-1) = 0 at the triple point of water (273.16K and ~ 0.00611 bar). Results from these models must be translated to accord with thermochemical reference values for the standard enthalpy and entropy at 298.15K and 1 bar. In SUPCRT92, this is accomplished by the use of a “translation function” derived by Helgeson and Kirkham (1974a), which was built into earlier versions of the software and retained unchanged. This function presumes standard thermochemical data from Wagman et al. (1968), which are obsolete. The data for the original translation are comprised of compound constants that were further calculated using the older Keenan et al. (1969) EOS. Here we update the translation function for consistency with the standard thermochemical data recommended by CODATA (Cox et al., 1989). We do this for both the Haar et al. (1984) EOS and the more recent IAPWS-95 EOS (Wagner and Pruss, 2002). The IAPWS-95 EOS is analogously used to compute the thermochemical properties of water in two other codes, CHNOSZ (Dick, 2008; this also offers the Haar et al., 1984, EOS) and Cantera (Moffat and Jóve Colón, 2015). We calculated the “ideal gas” properties for both the Haar et al. (1984) EOS and the IAPWS-95 EOS. Results for the former basically confirm data given by other standard references (see for example Cox et al., 1989; and Chase, 1998). Results for the latter differ somewhat. The “H2O,g” model in SUPCRT92 for treating metastable vapor is not consistent with these results and should be discarded. Future database development should emphasize the use of the IAPWS-95 EOS, which is the current international standard, the EOS of Haar et al. (1984) being the previous standard). The gas-only EOS model given by Wagner and Pruss (2002) in their Section 3.1 should also be considered for dealing with metastable vapor.

This paper describes how to update the thermochemical data for water in SUPCRT92 for consistency with CODATA (Cox et al., 1989) and the equation of state (Haar et al., 1984, also known as IAPS-84) for water that is currently in SUPCRT92. The original SUPCRT implementation for calculating water properties as a function of temperature and pressure used an older equation of state and obsolete thermochemical data from NBS 270-3 (Wagman et al., 1968). That linkage (“translation function”) was implemented in a nontransparent wat, with the thermochemical data being combined with data from the equation of state and the results stored as constants in a DATA statement. The paper addresses the needed update for two water equations of state, the IAPS84 currently in SUPCRT92 and the more recent IAPWS-95 one that is currently in two other pieces of software, CHNOSZ (Dick, 2008) and Cantera code suite (Moffat and Jove Colon, 2009). A simpler method for linking thermochemical data with a single-component fluid equation of state is also presented. The manuscript is presently being shortened, and submission to the journal is expected by the end of August, 2016.

We have made some other modifications to SUPCRT92, notably eliminating the obsolete direct access data file, creation of a SUPCRT data file converter (that converts from obsolete calorie units to Joule units), and changes to SUPCRT92 itself to do everything in Joule units. We will be comparing these modifications with SUPCRTBL (Zimmer et al., 2016), which is a SUPCRT92 modification that also uses Joule units and has been developed to use the Holland and Powell (2011) thermodynamic data for minerals. FY17 is expected to see a merge of these modified versions of SUPCRT92.

3. Surface Complexation and Ion Exchange Model and Database Development

The need to develop self-consistent surface complexation/ion exchange models, in concert with thermodynamic models, for nuclear waste repository performance assessment was identified many years ago (Bradbury and Baeyens, 1993). This issue was expressly identified in the recent NEA Sorption project reports (Davis et al., 2005; Ochs et al., 2012). However, significant progress on this issue has been made only recently in various international nuclear waste repository programs (e.g. (Bradbury and Baeyens, 2009), (Dresden-Rossendorf, 2013), (Geckeis et al., 2013)). Hybrid approaches have also been attempted (Bradbury et al., 2010). The best path forward for developing such databases remains an open question (Geckeis et al., 2013), particularly in cases where generic repositories are being investigated resulting in a need to model radionuclide behavior over a very broad range of solution and mineralogic conditions.

The RES^{3}T project is a recent effort by HZDR to develop a digital open source thermodynamic sorption database. It includes mineral-specific surface complexation constants that can be used in additive models of more complex solid phases such as rocks or soils. It includes an integrated user interface to access selected mineral and sorption data and export data into formats suitable for other modeling software. Data records comprise mineral properties, specific surface areas, characteristics of surface binding sites and their protolysis constants, sorption ligand information, and surface complexation reactions (SC models include the Non-Electrostatic, Diffuse Double Layer, Constant Capacitance, Triple Layer, Basic Stern, and the 1-pK Model as extended to CD-MUSIC). The database also includes a comprehensive list of publications that are the primary sources of the surface complexation data. In total, the database includes over 130 minerals, 5000 surface complexation reaction constants, and 2800 references. The database provides a comprehensive list of reaction constants reported in the literature for a very large number of radionuclide-mineral reaction pairs. However, this database project does not provide recommended values. It also does not capture the primary sorption data or provide information on the aqueous speciation constants used in determining those surface complexation constants. As a result, the RES^{3}T project provides a foundation for developing a comprehensive surface complexation database but does not go so far as to provide one.

Three key issues prevent the application of the RES^{3}T database in performance assessment and other radionuclide transport/risk assessment models. They are:

- An inability to integrate disparate data sets and surface complexation model constructs into single unified model and associated set of reaction constants
- An inability to produce self-consistent reaction constants based on a common set of aqueous speciation constants and surface properties.

- The absence of error propagation in the sorption data and/or database constants needed to assess model uncertainties.

To address these limitations, the inclusion of primary sorption data in the RES^{3}T database is needed. This would allow for integration of all available literature data, error propagation, and database updating and ensure self-consistency between aqueous speciation, mineral solubility, and surface complexation databases.

In our FY14 progress report, we developed a test-case for U(VI) sorption to quartz and demonstrated how a self-consistent set of surface complexation constants could be produced from ~400 batch sorption data digitized from the published literature (10 publications in total). The minimization routine was performed using the FIT4FD software developed at LLNL (Zavarin et al., 2004) and based on the FITEQL software (Herbelin and Westall, 1994). However, this approach did not provide the flexibility needed to easily evaluate and test various surface complexation models. This LLNL software could only be used for a non-electrostatic model of the U(VI)-quartz system. One promising new approach identified in FY15 was the use of a recently released PhreeqC module, PreeqcRM (Charlton and Parkhurst, 2011; Parkhurst and Wissmeier, 2015). The module was developed to facilitate operator splitting approaches to reactive transport modeling. However, it was believed that the same code could be used in performing equilibrium calculations on individual batch sorption data. When linked to a parameter estimation software (e.g. PEST (Doherty, 2003)), the PhreeqcRM module could provide a framework for testing various surface complexation models on large sets of sorption data in a comprehensive manner.

This new approach was tested in FY16 on a small set of U(VI)-quartz sorption data. For the test-case, only one U(VI)-quartz dataset was used ((Arnold et al., 2000) identified as azbn00 using the reference formatting in RES^{3}T); the code PhreeqC rather than PhreeqcRM was used in this case. The following describes the scheme used to run the fitting routine:

1. U(VI) and quartz were chosen as the test case
2. RES^{3}T “Data assembly and formatting” query was run for Quartz and UO2<2+>
    a. Surface area, site density, and pKa’s for each reference were collected
    b. All references and associated DOI’s were collected
3. References and DOI’s were used to access a digital copy of EACH original reference
4. Datathief software used to digitize data included in EACH original reference
5. PhreeqC input file was written such that each digitized sorption datapoint constituted a separate condition in the input file[1], including
    a. Solution composition
    b. Surface complexation reactive site density
    c. Mineral surface area
    d. Mineral concentration
6. PhreeqC output file was set to output total aqueous U(VI) concentration
7. PhreeqC thermodynamic database was set to thermo.com.V8.R6.230 file that is included in PhreeqC package
8. Surface complexation reactions were added to thermo.com.V8.R6.230 with estimated reaction constants
9. PEST control.pst file included all variables that will be fit during the minimization routine and all observational data (equilibrium U(VI) aqueous concentration) digitized from EACH original reference.

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[1] In this case, only the data from one reference were used.

10. PEST template file was used to identify location of surface complexation variables in the thermodynamic databased used by PhreeqC
11. PEST instruction file was used to identify location of the PhreeqC output data that are used in the minimization routine (along with the observational data)
12. PEST was run to optimize surface complexation reactions for the U(VI)-quartz system.

The resulting fits to the data using the non-electrostatic model are comparable to the fits produced using LLNL's FIT4FD software (Figure 1). Thus, it appears that the approach developed in FY16 can provide a robust path forward for surface complexation database development. Importantly, the approach provides a unique opportunity to develop surface complexation modeling databases that can

1. Provide self-consistent fitted reaction constants based on large assemblies of data available in the literature.
2. Account for data uncertainty and goodness-of-fit to the overall uncertainty in model parameters.
3. Allow for updating the fitted surface complexation reaction constants as thermodynamic speciation and solubility databases evolve.
4. Provide a platform for testing various surface complexation models and assess their ability to capture observed sorption data reported in the literature in a comprehensive manner.

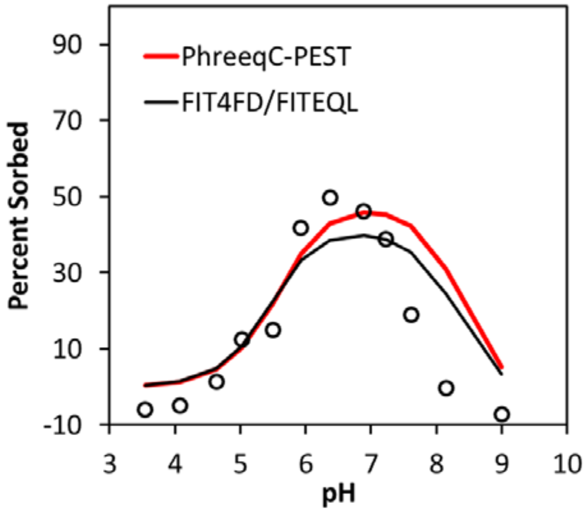

Figure 1. PhreeqC and FIT4FD non-electrostatic models fits to the data of (Arnold et al., 2000). The U(VI)-quartz sorption data were collected using 12.5 g/L quartz with a 0.2 m^2/g surface area and 4.8 sites/nm^2 estimates reactive site density. The total U(VI) concentration in all samples was 10^{-6} M.

4. Nuclear Energy Agency Thermodynamic Database Development

In FY16, Dr. Cindy Atkins-Duffin continued her participation in the Organization of Economic Cooperation and Development (OECD) Nuclear Energy Agency (NEA) Thermochemical Database (TDB) Project. Dr. Atkins-Duffin serves the United States representative to the Project's Management Board and is an elected member of the Board's Executive Group. The principal product of this activity is to make available a comprehensive, internally consistent, quality-assured and internationally recognized chemical thermodynamic database of selected chemical elements in order to meet the specialized modelling requirements for safety assessments of radioactive waste disposal systems. The Management Board and its Executive Group meet periodically to assess progress on the Project's approved plan of work and to suggest and approve technical contributors for both the conduct of the reviews and as peer reviewers of the work. The United States joins Belgium, Canada, Czech Republic, Finland, France, Germany, Japan, Spain, Sweden, Switzerland, and United Kingdom in the TDB Project.

The objective of the TDB Project is to produce a database that:

- contains data for all the elements of interest in radioactive waste disposal systems;
- documents why and how the data were selected;
- gives recommendations based on original experimental data, rather than compilations and estimates;
- documents the sources of experimental data used;
- is internally consistent;
- treats all solids and aqueous species of the elements of interest for nuclear waste storage performance assessment calculations.

In 2014, the Project entered its fifth phase (2014-2018) of activities which include:

- Completion of the review of Ancillary Data (commonly used data required for use in calculations by all authors in reviews)
- Completion of second volume of Iron Data (thermochemical data of Iron is extensive. The review of Iron data was divided into two volumes. The first volume was completed in the fourth phase of the TDB.)
- Completion of the review of Molybdenum data.
- Initiate and complete an update of the Actinide data review.
- Initiate and complete a State-of-the-Art review of Cement chemistry and suggest options for including these findings in safety case efforts.
- Initiate and complete a State-of-the-Art review of High Ionic Strength thermochemical data and suggest options for including these findings in safety case efforts.

At the recent Executive Group meeting held in Paris on April 4-5, 2016, Maria-Eleni Ragoussi presented the status of all ongoing activities of the NEA-TDB project (Table 1). SOAR documents listed in Table 1 are "State of the Art Reports". In general, these reports assess the means by which various repository programs deal with non stoichiometric moieties/processes in performance assessment/safety cases. They are intended to provide users with an assessment of options. However, no recommendations are made about data or methods. In general these documents, while written under the NEA Guidelines, do not carry the same pedigree as the selected data in the more traditional NEA-TDB Volumes. A draft manuscript entitled "Fundamentals of the NEA Thermochemical Database and its influence over national nuclear programs on the performance assessment of deep geological repositories" by Maria-Eleni Ragoussi and David Costa was recently prepared for submission to the Journal and Environmental Radioactivity. The manuscript summarizes the 30 year effort by the NEA to develop comprehensive databases for use by the international nuclear waste repository science community and includes insights into how these and similar efforts may be more broadly applicable to environmental science research.

Table 1. Status of NEA-TDB Activities

Activity	Status	Final milestone

Ancillary Data Review	Most sections completed and currently under edition	Book to peer review summer 2016. Publication in 2017.
Fe – Part II Review	Most sections completed and currently under edition	Book to peer-review summer 2016. Publication in 2017.
Mo Review	Big part of single contributions concluded Completion expected during summer 2016	Book to peer-review end 2016. Publication in 2017.
SOAR Cements	Ongoing (initiated beginning 2014)	Completion of 1st draft mid 2018. Publication in 2019.
SOAR Pitzer	Ongoing (Initiated beginning 2015)	Completion of 1st draft end 2017. Publication in 2018.
Update Actinides	Ongoing (Initiated beginning 2015)	Completion of 1st draft end of 2016. Publication in 2017.

5. Planned FY17 Efforts

In FY17, we plan to continue our efforts in the development of thermodynamic databases in support of the UFD program. These include

- Illustrating the concepts developed by Wolery and Jove-Colon (Parts 1 and 2) and applying them to mineralogic components of greatest interest to UFD research, starting with a Part 3 paper re-analyzing the mineral data model of Helgeson et al. (1978).
- Testing the PhreeqC-PEST fitting routine using various surface complexation models (non-electrostatic, diffuse double layer, etc.) and applying the method to larger sets of sorption data (all U(VI)-quartz data available in the literature) in a comprehensive manner.
- Continued engagement with the NEA TDB project through the support of Dr. Atkins-Duffin as the UFD representative for international thermodynamic database development effort.

In addition to re-analyzing the mineral data of Helgeson et al., (1978), a Part 3 manuscript will be prepared and will update the thermochemical data for aqueous species and make comparisons with the mineral data of Holland and Powell (2011). We will create a modified SUPCRT92 data file, and produce a modified version of SUPCRT92 that contains key reference data based on the CODATA (Cox et al., 1989) values or updated values known to be better. We expect to merge the improvements with others made in SUPCRTBL (Zimmer et al., 2016). This will provide a core for additional database development. As much as possible, we will leverage the efforts of the NEA TDB effort and other investigators. The Part 1 paper is now expected to be published in FY17. In FY17, we will also publish the Part 2 paper. We will be working on the Part 3 paper, with expected publication in early FY18.

6. Acknowledgments

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