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M4FT-15LL0806062-LLNL Thermodynamic and Sorption Data FY15 Progress Report

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Contents

1. Introduction

This progress report (Milestone Number M4FT-15LL0806062) summarizes research conducted at Lawrence Livermore National Laboratory (LLNL) within Work Package Number FT-15LL080606. 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:

1. Develop thermodynamic databases and models to evaluate the stability of barrier materials and their interactions with fluids at various physico-chemical conditions relevant to subsurface repository environments (in collaboration with Sandia National Laboratory (SNL)).
2. Evaluate sorption processes such as surface complexation (SC) and cation exchange (CE). Develop a methodology to test various SC models using global approaches to digitized data available in the literature. The ultimate goals are 1) the integration of all available sorption data with updated thermodynamic speciation databases 2) development and testing of surface complexation modeling formulations, and 3) the development of a flexible and comprehensive methodology for determining K_ds and associated uncertainties for use in Performance Assessment (PA) models.
3. Enhance international collaborations with other groups on the development of thermodynamic data and benchmarks to evaluate and perform quality assessments and model testing that is key to the geochemical evaluation of repository performance. SC methodologies will be coordinated with international effort headed by Helmholtz Zentrum Dresden Rossendorf (HZDR).
4. Integrate with the crystalline control account for the evaluation of experiments on uranium and neptunium sorption/diffusion onto clay and related modeling efforts.

The thermodynamic database development effort is a continuation of FY14 work. It includes reviewing and revising the previously developed thermodynamic databases and expanding them to cover the needs of the repository types currently under consideration by the Used Fuel Disposition (UFD) program (i.e. clay, granite, deep borehole). The effort is a collaboration between LLNL and SNL. A draft manuscript summarizing this effort was prepared for submission later this fiscal year; we include only a short summary of that effort here.

A second effort involves development of surface complexation and cation exchange models and databases for use in PA models. This effort is also a continuation of FY14 work, in collaboration with Dr. V. Brendler (HZDR).

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.

A fourth effort is integrated with the crystalline control account and focused on the study of radionuclide sorption and diffusion through clay. This has relevance to both clay/bentonite barrier systems in crystalline repository scenarios and clay rock in argillite repository scenarios. This fourth effort was recently summarized in the progress report (M4FT-15LL0807052) as part of the LLNL crystalline repository effort within the UFD program (FT-15LL080705). It will not be described herein.

2. Thermodynamic Database Development

The following abstract was prepared as part of the manuscript in preparation and authored by Thomas J. Wolery (LLNL) and Carlos F. Jové-Colón (SNL). The manuscript, entitled "Chemical Thermodynamic Data. I. The Concept of Links to the Chemical Elements and the Historical Development of Key Thermodynamic Data" will be submitted for publication later this fiscal year.

> Chemical thermodynamic data remain a keystone for geochemical modeling and reactive transport simulation as applied to an increasing number of applications including geologic disposal of nuclear waste, carbon sequestration, climate change, and environmental analysis and remediation, as well as applications outside the earth sciences such as metallurgy, material science, and industrial process design. The last century has seen the development of large quantities of thermodynamic data and numerous compilations of such. In addition, the past several decades have seen the development of thermodynamic databases in digital form designed to support computer calculations. Nevertheless, problems with thermodynamic data appear to be persistent. Here we examine some of these problems and argue that many of them arise from a "data value" focused perspective that fails to account for the full origin of resulting values. As a partial solution to this problem as it pertains to Gibbs energies and enthalpies of formation at 298.15K and 1 bar pressure (reference temperature and pressure), we propose a formal concept of "links" to the chemical elements in their reference forms. 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. Such a link differs from a bare "key" or "reference" datum in that it requires additional information, although some or perhaps all of its associated data may also be considered key data. In evaluating a reported thermodynamic datum, one should identify the links to the elements, a process which can be time-consuming and which may lead to a dead end (and hence an unsupported hence invalid 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 first establish a set of reliable links and then correct all data adopted subsequently for consistency with that set. Key reference data of concern include atomic weights, entropies of the elements in their reference forms at reference temperature and pressure, and formation properties at reference temperature and pressure of various key species including simple oxides and principal aqueous ions. Recommended values have not been constant through history, and data derived from such values have apparently been passed on in a number of compilations and databases without consistent correction to a single set of preferred reference data values. In this paper, we review some of this history 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. These species include 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.

We illustrate the process with an example from the paper. We want to use CODATA (Cox et al., 1989) key reference data as much as possible, especially in that this will maintain consistency with the NEA-TDB works. Aluminum is a key component of both natural geochemical systems and EBS materials such as aluminosilicates including clays and zeolites. In the case of the aqueous ion Al^{3+} we found newer and more reliable data in the work of Tagirov and Schott (2001), who made a comprehensive study of the solubility of gibbsite ($Al(OH)_{3(c)}$) over a wide range of temperature. In contrast, the CODATA development for the aluminum ion focuses on low temperature data, is rather complex, and averages various reported results where culling might have been more appropriate. The CODATA report does not give recommended data for gibbsite, although data for it are used in part in its development of recommended data for Al^{3+}. For gibbsite, we chose the enthalpy (calorimetrically determined) and entropy from Robie et al. (1978). However, we recalculated the corresponding Gibbs energy from these data using the CODATA recommendations for the entropies of the requisite standard elemental reference forms, resulting in a slight correction to the value given by Robie et al. (1978) (Table 1). Although in this case the Gibbs energy correction is only -0.004 kJ/mol, this illustrates the practice that must be employed to maintain consistency with chosen key reference data.

Table 1. G-H-S data for $Al(OH)_3$ (Gibbsite) at 298.15K, 1 bar. Data from Robie et al. (1978) *a*re shown, along with corrections (affecting only the Gibbs energies of formation) for consistency with other data from *CODATA*.

		$Al(OH)_3$ (Gibbsite)		
Source	**Year of Publication**	**ΔG°$_f$ kJ/mol**	**ΔH°$_f$ kJ/mol**	**S° J/mol-K**
Robie et al. (1978)	1978	-1154.889	-1293.128	68.440
Robie et al. (1978), corrected	this work	-1154.903	-1293.128	68.440

Tagirov and Schott (2001) obtained the corresponding data for the aluminum ion by fitting the “HKF equation of state” model to solubility data over a wide range of temperature, consistent with the reaction $Al(OH)_{3(c)} + 3\ H^{+} = Al^{3+} + 3\ H_2O$. They first determined the Gibbs energy and entropy of reaction. Using data for the other species in the reaction, they obtained the Gibbs energy and entropy of the aluminum ion. With some elemental reference form data, the enthalpy for the aluminum ion was obtained from the Gibbs energy and the entropy. We recalculated their results to be consistent with our corrected data for gibbsite (Table 1), the CODATA recommendations for liquid water, and the CODATA recommendations for the requisite elemental entropies. No correction is associated with the aqueous hydrogen ion, as the requisite values for it are zero by convention. The results, which preserve the Tagirov and Schott values for the Gibbs energy and entropy of the reaction, are shown in Table 2.

Table 2. G-H-S data for Al^{3+} at 298.15K, 1 bar. Data from Tagirov and Schott (2001) are shown along with corrections for consistency with other data from *CODATA.*

		Al^{3+}		
Source	**Year of Publication**	**ΔG°$_f$ kJ/mol**	**ΔH°$_f$ kJ/mol**	**S° J/mol-K**
Tagirov and Schott (2001)	2001	-487.478	-538.769	-339.753
Tagirov and Schott (2001), corrected	this work	-487.621	-538.937	-339.834

The corrections in this case are larger. A notable cause is that Tagirov and Schott (2001) developed their model for use with the SUPCRT92 code (Johnson et al., 1992), which contains a hard-coded model for the thermodynamic properties of water that is affected by a small but significant error (1 atm data were used as 1 bar data). Implementing the CODATA recommended values for water in SUPCRT92 will be explained in the Part II paper.

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 100 minerals, 4000 surface complexation reaction constants, and 2000 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 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. Thus, an alternative approaches have been investigated. One promising approach that has become available is 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. The module may also be ideal for performing equilibrium calculations on individual batch sorption data. When linked to a parameter estimation software (e.g. PEST (Doherty, 2003)), the PhreeqcRM module may provide a framework for testing various surface complexation models on large sets of sorption data in a comprehensive manner. This new approach will be tested in the following months.

4. NEA Thermodynamic database development

Dr. Atkins-Duffin is the UFD representative for thermodynamic database development efforts at the NEA in support of international nuclear waste repository research. In the following table (Table 3), we provide a summary of the ongoing efforts by the NEA TDB project and the upcoming releases of new data compilations. A history of NEA TDB activities was recently published and summarizes the accomplishment of the project since its inception in 1984 (Ragoussi and Brassinnes, 2015).

The Ancillary Data Review (Table 3) may be useful for comparison with the thermodynamic database efforts of Wolery and Jove-Colon described in Section 2. All draft content for aqueous species, with the exception of the phosphate data, was sent to the NEA in March 2015. These sections are being reviewed by the Chairman of the activity. A completed draft for solids should have been sent to the NEA by the end of June 2015 and all synopses for Appendix A should be received at the NEA by July 2015. A complete peer-review draft is planned to be readied by the end of the summer 2015. The document will be provided to UFD as soon as it becomes available.

Table 3. Summary of NEA TDB Activities.

Activity	Status	Final milestone
Fe – Part II Review	Most single contributions concluded All first drafts expected to be ready by end of summer 2015	Book to peer-review in beginning 2016.
Mo Review	Big part of single contributions concluded All first drafts expected to be ready by end of 2015	Book to peer-review in 2016.
Ancillary Data Review	Aqueous drafts completed. Solids drafts expected by June 2015 Synopses expected by July 2015	Book to peer review end 2015
State-of-the Arts Report Cements	Ongoing	Completion of 1st draft in mid-2017
State-of-the Arts Report Pitzer	Just initiated	Completion of 1st draft end of 2016
Update Actinides	Just initiated	Completion of 1st draft end of 2016

5. Planned FY16 Efforts

In FY16, 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 and applying them to mineralogic components of greatest interest to UFD research
- Testing the PhreeqcRM-PEST framework for testing various surface complexation models on large sets of sorption data 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.

A second paper, "Chemical Thermodynamic Data. II. Analysis and Revision of the Mineral Thermodynamic Dataset of Helgeson et al. (1978)" is in preparation and will be completed FY16. The objective of this paper is to examine the key thermodynamic data used in the original work and to revise the original dataset for consistency with a more appropriate set of key thermodynamic data, much of it taken from CODATA (Cox et al., 1989). The revised results, along with some corresponding revisions to aqueous species data, will be incorporated into a new database for the SUPCRT92 program. A methodology for revising the built-in model of water properties for consistency with CODATA will be described and applied. Although the original development of Helgeson and co-workers is known to have a number of flaws, it is less well known that the original development incorporates a number of ties to key reference data for aqueous species. This likely gives it an advantage (specifically when the known flaws are corrected) in modeling mineral-aqueous solution interactions at relative low temperatures (less than 300°C). Other more recent models that have obtained thermodynamic data from mineral phase equilibria at high temperature and pressure, such as that of Holland and Powell (2011), have done so without making ties to key reference data for aqueous species, other than water itself. However, these models do have features that allow them to extend accurately to significantly higher temperature and pressure, and such models will be considered in the future. The main issue is whether or not these models can be accurately applied to mineral-aqueous solution interactions at relatively low temperature and pressure. To meaningfully compare such models, it is necessary to put them on the same footing with regard to key reference data. The benefit can be maximized by linking, as much as possible, to the key reference data associated with the NEA-TDB project.

In FY16 we will complete and publish the Part II paper, create a modified SUPCRT92 data file, and produce a modified version of SUPCRT92 that contains a modified water model consistent with the CODATA (Cox et al., 1989) recommendations. 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.

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