M4SF-19LL010302082-International Thermodynamics Activities

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June 19, 2019

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M4SF-19LL010302082-International Thermodynamics Activities

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Contents

1. Introduction

This progress report (Level 4 Milestone Number M4SF-19LL010302082) summarizes research conducted at Lawrence Livermore National Laboratory (LLNL) within the Crystalline International Collaborations Activity Number SF-19LL010302081. The activity is focused on our long-term commitment of engaging our partners in international nuclear waste repository research. This includes participation in the Nuclear Energy Agency Thermochemical Database (NEA TDB) Project (Cindy Atkins-Duffin) and development of methodologies for integrating US and international thermodynamic databases for use in SFWST Generic Disposal System Assessment (GDSA) efforts.

LLNL is supporting the overall objectives of the Disposal Research (DR) Crystalline International Collaborations Research and Development (R&D) control account. The objective of this control account is to advance our understanding of long-term disposal of spent fuel in crystalline rocks (including both granitic and metamorphic rocks) and to develop necessary experimental and computational capabilities to evaluate various disposal concepts in such media. LLNL efforts in the Crystalline International Collaborations work package are focused on the following:

- Continued engagement with the NEA TDB project through the support of Dr. Atkins-Duffin as the SFWST representative for international thermodynamic database development effort. This effort ensures that US GDSA model efforts are aligned with internationally accepted practices for repository performance assessment calculations.
- Coordinating and integrating LLNL thermodynamic database efforts (Argillite DR workscope) with international efforts to ensure that GDSA model efforts are performed using internationally accepted thermochemical data.

A particular focus for FY19 efforts has been to develop mechanisms for integration of NEA-TDB thermochemical data (new electronic database made available in 2018) with LLNL's thermodynamic databases that support GDSA. This effort is coordinated with the Argillite work package database development efforts. The goal is to provide a downloadable database that will be hosted on LLNL's thermodynamics website which incorporates NEA-TDB data into the LLNL database where appropriate. This M4 is focused developing a path forward for integration of international thermochemical databases (where appropriate) with LLNL database development efforts. The M4 to be delivered on 3/27/20 will include such a database that is based on LLNL's foundational database and enhanced by the additional data supplied by the NEA-TDB effort for use in GDSA. This activity will be conducted towards a basic, "minimal" process model development for GDSA to support a 2020 repository performance assessment schedule.

2. Nuclear Energy Agency Thermochemical Database Program

2.1 History of Project

The Nuclear Energy Agency (NEA) Thermochemical Database Program was conceived of and initiated with the goal to: 1) make available a comprehensive, internally consistent, internationally recognized database of selected chemical elements; 2) meet the specialized modeling requirements for safety assessments of radioactive waste and; 3) prioritize the critical review of relevant data for inorganic compounds and complexes containing actinides. Data from other elements present in radioactive waste are also critically reviewed as well as compounds and complexes of the previously considered elements with selected organic ligands.

The objective of the Program is to produce a database that contains data for all the elements of interest in radioactive waste disposal systems; document why and how the data are selected; give recommendations based on original experimental data, rather than compilation and estimates; document the sources of experimental data; provide an internally consistent thermodynamic parameters, and treat solids and aqueous species of the elements of interest for nuclear storage performance assessment calculations.

The qualification of existing data is conducted using documented Guidelines which include several components. A Technical Review is conducted by subject matter experts who critically review experimentally-determined literature data; reanalyze the data as necessary; and select data for inclusion in the database. Upon completion of the Technical Review, a Peer Review is undertaken. A second, independent panel of reviewers ensure that the technical reviewers followed the review Guidelines. A Comment Resolution component ensures that the Technical Reviewers address the comments made by the Peer Reviewers. At this time the volume is readied for final publication.

2.2 History of Phases and New Phase 6 Efforts

Phase I of the NEA-TDB program was conducted between 1984 and 1998. Initial review volumes included Uranium, Americium, Technetium, Neptunium/Plutonium.

Phase II of the NEA-TDB program updated all the actinide volumes. The update is contained in a single volume. Added in this phase were Nickel, Selenium, Zirconium, and the compounds and complexes of the reviewed elements with selected organic ligands - EDTA, ISA, oxalate, and citrate. The Program also conducted a workshop, "The Use of Thermodynamics Databases in Performance Assessment." The phase ran from 1998-2003.

Phase III of the NEA-TDB program saw the introduction of a second product, State-of-the-Art reports. The first such report covered solid solutions of interest to nuclear waste

management. Thorium, Iron (part I), and Tin volumes were added to the published collection.

Phase IV of the NEA-TDB program, conducted from 2008-2014, started the second portion of the Iron review; review of Molybdenum, and; review of Auxiliary Data which includes species and compounds necessary to describe aqueous chemistry of Aluminum and Silicon, data on inorganic species and compounds of elements such as Iodine, Boron, Magnesium, Calcium, Strontium, and Barium.

Phase 5 of the NEA-TDB program, conducted from 2014-2019 took on a second update to actinide and fission product volumes, and two State-of-the-Art reviews - Cement Minerals and High Ionic Strength Aqueous Systems. The design and development of a new TDB electronic database that is compatible with PHREEQC was undertaken.

Phases 6 of the NEA-TDB program was officially started in February 2019 with all participating member parties having signed the Framework Agreement. The First Meeting of the Management Board (MB) and the Executive Group (EG) were held at the NEA in Paris February 19-20, 2019. Lena Evins (Sweden-SKB) was elected Chair of the MB and Stephane Brassinnes (ONDRAF/NIRAS- Belgium) Vice Chair. Canada and the Netherlands joined the Programme for this Phase. Elected to the Executive Group were Chair Marcus Altmaier (INE-Germany), Cindy Atkins-Duffin (DOE/LLNL-USA), Benoit Made (ANDRA-France), Pascal Reiller (CEA Saclay – France), and Kastriot Spahiu (SKB (retired)-Sweden. In process projects from Phase 5 were brought forward to Phase 6.

The current status of the Phase 5 program and the associated reviews are:
- **Iron, part 2** - The Peer Review process was finalized in December 2018 and reviewers are now working on the requested modifications. Publication of the volume is expected in the second half of 2019.
- **Molybdenum** - The Technical Review team required restructuring and reassignment of tasks. Even with this restructuring the project is not progressing at a satisfactory pace. A face-to-face meeting with the Review Team Chairs and the NEA has been scheduled. The option of cancelling this project is under consideration.
- **Ancillary Data** – A full Peer Review draft has been put together by the NEA. The NEA and the Review Team are now going through the third round of corrections together, after which, the draft will be sent to peer reviewers. The volume is expected to become available in the second half of 2019.
- **Second update of Actinides** - A full draft volume has been put together by the NEA and the Review Team are now making their final corrections. The NEA, in parallel, is conducting consistency checks on the selected data and is identifying issues. The volume is expected to become available in the second quarter of 2019.
- **State-of-the-Art report on Cement Materials** – The authors' individual drafts are still in progress. A progress videoconference took place in February 2019. Two more have been scheduled for July and September. The authors expect to

finalize their individual tasks by the end of 2019, after which, a meeting in person will be scheduled. Publication of the report in anticipated in 2020.
- **State-of-the-Art report on High-Ionic Strength Solutions** – The authors' individual drafts are still in progress. A progress meeting of the team is tentatively scheduled for June 2019. Publication of the report is anticipated in 2020.
- **Electronic Database** – The database was released to external users in July 2018 and the PHREEQC-formatted database became available in November 2018. An article describing the database has been submitted to Applied Geochemistry for consideration.
- **TDB course/workshop** – The 3rd edition of the course will be offered in Kyoto, in conjunction with Migration 2019. A 4 year plan for future course offerings was presented to the MB by Don Reed (DOE-LANL-WIPP).

The workscope for Phase 6 will include the following review volumes:
- **Update of the Organic ligand review**
- **Lanthanides**
- **Weak Complexes**
- **State-of-the-Art report on High Temperature data**.

At the Management Board meeting in February, possible Leads for the new Review Teams were identified and the NEA is reaching out to the identified scientists to determine their availability to lead a Review.

3. An Interactive SUPCRT Data Tool for Adding New Species and Outputting New Data Files For Reactive Transport Codes

3.1 Introduction

Currently, there exist many thermodynamic data compilations collected for various purposes. Once compiled, the data files are subsequently added to or edited as new data become available in order to satisfy the needs of users. Over time, the data files evolve, with little accountability or accessibility of the modified files to other users.

New data are logistically somewhat difficult to add to these compilations, and in particular, data are often added that are not internally consistent with the existing data. What is needed is a tool to carry out these modifications in a defensible manner, with documentation, and to make the resulting data files available to other users.

The goal of this task is to create software to help manage this problem in such a way to ensure users adding data to databases do so in way that is correct, convenient, consistent with existing data, and moreover that the results are available to other users.

Our task consists of two main efforts:

1. Method to add thermodynamic data for new species, or replace thermodynamic data for existing species to the existing database
2. Produce a new user-defined data file for the user-specified reaction path code (e.g. PHREEQC, EQ3/6, GWB etc.) that contains the new or modified data formatted for the code of choice.

We choose for this version of the software to work from the SUPCRT data base developed by Helgeson and others at UC Berkeley (Helgeson et al., 1974, 1976, 1981). Our starting file is the SUPCRT version that has been augmented with additional data by Chen Zhu and co-workers at Indiana University and referred to as SUPCRTBL (Zimmer et al., 2016). The Bloomington data compilation has become a standard for many workers modeling fate and transport issues in the near-surface environment. Note that the code produced in this effort could be easily modified to use other data files as the core repository of data, instead of SUPCRT. In particular, this code will be applied to the modified SUPCRT code (the revised SUPCRT92 with incorporated H2OI95) under development in the Argillite work package and led by T. Wolery for use in the US SFWST Generic Disposal System Assessment (GDSA) efforts.

We have chosen to use the scripting language Tcl/Tk to create the software. Tcl can be used with all major platforms and Tk provides easy creation of a graphical interface for convenient and fool-proof user input.

3.2 Methods and Algorithms

The scenario we envision for typical use of this software is that of a user needing to add additional species to the data file for a reaction path computer model. For example, the user has thermodynamic data for several new neptunium complexes and wants to use them to model neptunium transport near a waste storage site. The user needs to add these species to the data file used by their preferred reaction path code.

One way to do this is to simply edit the data file and add the new species. This is currently what most users are forced to do. And it is not as simple as it seems. Most reaction path codes have strict rules as to how reactions are written, and have previously chosen a set of "basis species" that identify one particular species as the basis species for each element. The log K must be written in terms of those species in the form consistent with other reactions in the file.

For example, a user wants to add $NpO_2(CO_3)_2^{--}$ to their data file, and the log K provided by the user is for the reaction:

$$NpO_2(CO_3)_2^{--} + 2\ H^+ = 2\ HCO_3^- + NpO_2^{++} \qquad\qquad (1)$$
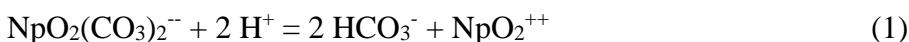
The user must ensure that NpO_2^{++} is the basis species for neptunium (vs. Np^{++++} or Np^{+++}), and that HCO_3^- (vs. CO_3^{--} or $CO_2(aq)$) is the basis species for carbonate. If not, the reaction must be revised using the appropriate reaction equilibria in the database. For

example, if Np^{++++} and not NpO_2^{++} is the basis species for neptunium, the reaction should be rewritten as:

$$NpO_2(CO_3)_2^{--} + 4\ H^+ = 2\ HCO_3^- + 0.5\ O_2(aq) + H_2O + Np^{++++} \qquad (2)$$

and log K adjusted before it can be entered into the data file. One goal of this task is to make this addition easy and less prone to error.

User supplied log K data

The new data entered by a user may be one of two types: (1) log K data for reactions, or (2) free energy, enthalpy, entropy (G-H-S) data. The two options are handled differently by our code.

Assume the user has a log K for a reaction involving a species not currently in the database (the species of interest that is to be added). The user supplies to the code the formula of the new species, and the formulas for other species in the reaction for the log K provided, and the elemental components (O, H, C, Np etc.) of each species. This is done using a GUI. Note that the user does not need to re-write the reaction in terms of basis species. Our code will do that. At this point the code checks mass and charge balance for the reaction to make sure it is correctly balanced. Note that the user must also specify the temperature for the log K, generally 25 °C.

For log K data, the code must convert the log K for the reaction to a free energy for the new species. This is because the SUPCRT data file consists of G-H-S data (free energy, enthalpy, entropy) for each individual species and not log Ks for reactions. The G-H-S data in SUPCRT are combined to derive log K values for reactions.

Reaction path codes generally use log K data. Producing the log K data from the G-H-S data is described below. The net result here is that for the new species, the reaction provided by the user will be re-written (if necessary) in terms of the basis species in a form consistent for the reactive transport code selected by the user. The data for the new species will remain in SUPCRT and be available for incorporation in other reactive transport data files as well.

Using the reaction supplied, the code searches for each of the species in the reaction (except for the new species) in the SUPCRT database and collects their G-H-S data. The free energy of the new species is then calculated using these data and the relationship:

$$RTlnK = \Delta G_r = \Sigma\ nG_i \qquad (3)$$

For example, the free energy (ΔG) for $NpO_2(CO_3)_2^{--}$ in eqn (1) is given by:

$$\Delta G_{NpO2(CO3)2--} = 2 \times \Delta G_{HCO3-} + \Delta G_{NpO2++} - 2 \times \Delta G_{H+} - RTlnK \qquad (4)$$

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The code then generates a data block in SUPCRT for the new species. The block contains the species' elemental composition and free energy.   This is sufficient to output a new version of a data file including the new species. This method also insures that the free energy of the new species is calculated correctly relative to the key thermodynamic values used in SUCPRT, as long as the species in the user-supplied reaction are present in SUPCRT with G-H-S data correctly derived from the accepted source (e.g. CODATA).

Note that if the user provides only a log K value for a new species, this limits what can be added to the SUPCRT data block for the new species. There is no information in the log K alone on temperature dependence of the species with respect to other species (such as would be possible if enthalpy or entropy were available, or the log K provided at two or more temperatures). The user will be warned that the new data file is good only at the temperature for which the log K was provided.

User supplied G-H-S data

The user may also supply data for a new species in terms of G-H-S data. These data can be directly input into the SUPCRT data block for the new species. The code accepts the data using the GUI, and places it into the appropriate locations in the SUPCRT data block (see below for example of data in SUPCRT). The user also must supply the elemental composition of the species as this is needed to write reactions in step 2, and the temperature for which the free energy data is associated.

If only the Gibbs Energy is supplied, the log K data are limited to the temperature of the input data. It cannot be extrapolated to higher or lower temperatures. If enthalpy is also provided, the data can be extrapolated, although for a limited range. If the entropy is also provided the data can be extrapolated with better accuracy.   For species native to the SUPCRT file, there are associated equation of state parameters that are meant to allow extrapolation to very high temperatures and pressures. These determinations of the validity of extrapolation vary widely and it will be left up to the user to decide the appropriate use of the new information. The code will simply provide the appropriate warning message for each case.

Example of SUPCPRT data block for Al+++ ion

```
        SUPCRT data block (aqueous species)
        Al+3 (NAME)          Al+3 (FORMULA)
        Al+3 (ALT NAME)      Al(1)+(3) (ELEMENTAL COMP AND
        CHARGE)
        TS01 (REF)             14.Au (DATE)
        -487.478(G)   -538.761 (H)  -339.753 (S)
        -14.2189   -67.2741    50.5005    -8.8462   ES
        parameters
        60.3730   -37.0380    11.4654    3.
```

Generation of files for reactive transport codes

Now that the new data has been entered into SUPCRT and a data block is present for each new species, the revised SUPCRT data file can be used to generate a database file for the chosen reactive transport or other code that uses reaction data (log Ks) to compute chemical equilibrium. Before generating the file, the user can choose to either produce a comprehensive data file containing all species present in SUPCRT, or can request a subset of the database. Reducing the size of the data file and types of species present can be useful in order to simplify some aspects of running reaction path codes.

The following options will be available:

- Produce data blocks for the new species provided by the user
- Produce a file containing all species sharing the elements in the new species (e.g. all Np species)
- Produce a file containing a user-specified set of elements (e.g. Na-Cl-Np-C would produce a file containing all species containing at least one of the elements sodium, chlorine, neptunium, and carbon)
- Produce a file containing all species present in SUPCRT

In order to write the reactions and produce a data file that can be read by the desired reaction path code, we need to know the set of basis species used by that code, and the way reactions are written. This is provided by a file that we will generate for each code of interest.   The file is simply list of the elements followed by the basis species for each element. For example, in GWB, the file would contain the following list of species, one for each element:

Table 1. Basis species in GWB data file "thermo.com.V8.R6+.dat"

H2O	Co++	HPO4--	MoO4--	ReO4-	Ti(OH)4(aq)
Ag+	CrO4--	He(aq)	NH3(aq)	Rn(aq)	Tl+
Al+++	Cs+	Hf++++	Na+	RuO4--	Tm+++
Am+++	Cu++	Hg++	Nd+++	SO4--	UO2++
Ar(aq)	Dy+++	Ho+++	Ne(aq)	Sb(OH)3(aq)	VO++
Au+	Er+++	I-	Ni++	Sc+++	WO4--
B(OH)3(aq)	Eu+++	In+++	Np++++	SeO3--	Xe(aq)
Ba++	F-	K+	Pb++	SiO2(aq)	Y+++
Be++	Fe++	Kr(aq)	Pd++	Sm+++	Yb+++
Br-	Ga+++	La+++	Pm+++	Sn++	Zn++
Ca++	Gd+++	Li+	Pr+++	Sr++	Zr(OH)2++
Cd++	H+	Lu+++	Pu++++	Tb+++	O2(aq)
Ce+++	H2AsO4-	Mg++	Ra++	TcO4-	
Cl-	HCO3-	Mn++	Rb+	Th++++	

The reactions must all be written in terms of these species. Note redox equilibria are balanced in GWB using the species O_2(aq).

An algorithm exists using matrix algebra that allows convenient balancing of reactions (Table 2). It needs as input the elemental composition of the species of interest and the basis species for each element. An example is shown for the species $NpO_2(CO_3)_2^{--}$ below. The goal is to write a balanced reaction for $NpO_2(CO_3)_2^{--}$ in terms of the specified basis species.

The orange matrix shows in the far left column the basis species that are to be used to write the reaction. That choice is determined by the reaction path code, such as Table 1 above showing basis species used by GWB. On the far right and across the top is a list of the elements needed to write the reaction. The element list includes all the elements in the new species (Np-O-C) and also any additional species that exist in the basis species (for example using HCO_3^- for C means H must also be in the elements list). This matrix will always be square.

The blue matrix is the inverse of the orange matrix computed using a standard linear algebra package. It is fairly obvious that the answer, which is a list of the stoichiometric coefficients for the balanced reaction, is computed by multiplying a scalar containing the elemental composition of $NpO_2(CO_3)_2^{--}$ (light blue box) by the inverted matrix. The gray box at the bottom is the result. The order of stoichiometric coefficients corresponds to the order in the far left column of the initial matrix (orange box).

This process is repeated for each non-basis species in the SUPCRT file in order to produce a data file of reactions and log K values for reactions. The log K values are similarly computed from the stoichiometric coefficients using the free energies for the species in the reaction present in the SUPCRT file.

Table 2. Process for formatting a balanced reaction based on specified basis species.

NpO2(CO3)2--

	Np	C	O	H	charge	
Np++++	1	0	0	0	4	Np
HCO3-	0	1	3	1	-1	C
H2O	0	0	1	2	0	O
H+	0	0	0	1	1	H
O2(aq)	0	0	2	0	0	charge
	1	0	2	-4	-1	
	0	1	-1	1	-1	
	0	0	0	0	0.5	
	0	0	0.5	0	-0.25	
	0	0	-0.5	1	0.25	
NpO2(CO3)2--	1	2	8	0	-2	
-1	1	2	1	-4	0.5	
NpO2(CO3)2--	Np++++	HCO3-	H2O	H+	O2(aq)	

Balanced reaction -> NpO2(CO3)2-- + 4 H+ = Np++++ + 2HCO3- + H2O + 0.5 O2

The final task is to take the list of balanced chemical reactions and log K data and re-write it in the format of the desired reactive transport code. This work has not yet been started, but is not expected to involve anything other than providing the correct output format for each code. No additional data manipulation should be needed.

3.3 Summary

Work is in progress to produce a software tool to add new species and to produce enhanced data files for reactive transport codes relevant to the SFWST Generic Disposal System Assessment (GDSA) efforts. The tool is built around the SUPCRT data base as amended by Chen Zhu and co-workers (SUPCRTBL). The code is meant to be used by someone wanting to add new data to SUPCRT and ensure that it is internally consistent with the existing data. The code will produce a new version of the data file needed to run any of several reactive transport codes. Currently we plan to produce files for PHREEQC, EQ3/6, and GWB. Additional file configurations can be readily added to support the GDSA efforts. Furthermore, our code can readily be modified to use data files other than SUCPRT as the starting database. In particular, this code will be applicable to the modified SUPCRT code under development in the Argillite work package and led by T. Wolery for use in the US SFWST Generic Disposal System Assessment (GDSA) efforts. A key goal is to facilitate the integration of US SFWST thermodynamic database

development with international thermodynamic database compilations (e.g. the NEA-TDB radiochemical thermodynamic data).

5. Planned FY19/FY20 Efforts

A continuing focus for FY19/FY20 efforts will be to support the US participation in the NEA-TDB effort and developing mechanisms for integration of NEA-TDB thermochemical data (new electronic database made available in 2018) with LLNL's thermodynamic databases that support the SFWST GDSA activities. This effort is coordinated with the Argillite work package database development efforts. The goal is to provide a downloadable database that will be hosted on LLNL's thermodynamics website which incorporates NEA-TDB data into the LLNL database where appropriate. The M4 to be delivered on 3/27/20 will include a database that is based on LLNL's foundational database (updated SUPCRT92) and enhanced by the additional data supplied by the NEA-TDB effort for use in GDSA. Updating thermodynamic databases and enhancement of our database integration code to ensure that SFWST GDSA efforts are based on current and internationally accepted thermodynamic data will be a key focus in the next fiscal year.

6. Acknowledgments

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