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# M4SF-21LL010301052-SUPCRTNE Thermodynamic Database Engine

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## 1. Introduction

This progress report (Level 4 Milestone Number M4SF-21LL010301052) summarizes research conducted at Lawrence Livermore National Laboratory (LLNL) within the Argillite Activity Number SF-21LL01030105. LLNL is leading efforts in the development of thermodynamic databases in support of the Spent Fuel and Waste Science Technology (SFWST) program. Thermodynamic models provide the basis for understanding the stability of solid phases and speciation of aqueous species and modeling the evolution of repository conditions. The LLNL effort is being performed in coordination with other US database development efforts. The effort includes a review of available thermochemical databases and a path forward for database integration. International coordination with the NEA-TDB is supported through crystalline international work package.

## 2. Background

The present effort follows the vision of H. C. Helgeson and students beginning in the 1970s to create an internally consistent thermodynamic database that would allow calculations of interactions of aqueous species and minerals over a wide range of geologically relevant temperatures and pressures. This was a major step forward as many early geochemistry-focused databases only addressed conditions of 25°C (298.15K) and atmospheric pressure, with little attention to internal consistency. Early efforts by the Helgeson school addressed the thermodynamic properties of water (Helgeson and Kirkham, 1974ab), aqueous species (Helgeson and Kirkham, 1976; Helgeson et al., 1981), and minerals (Helgeson et al., 1978).

This early work was associated with the development of a computer code called SUPCRT (see historical description by Johnson et al., 1992), which could be used to calculate thermodynamic properties of water, aqueous species, minerals, and chemical reactions over a wide range of temperature and pressure. The treatment of water was notable for the use of an equation of state (Keenan et al., 1969). The treatment of aqueous (solute) species was notable for the development of the "HKF equation of state," a model that allowed extrapolation of 25°C data to elevated temperature and pressures. The treatment of minerals was based on a groundbreaking analysis of published experimental studies of mineral equilibria at various temperatures and pressures. This work inspired a series of other, independent works (too numerous to list here) to develop "internally consistent" thermodynamic databases for minerals. The most recent of these is that of Holland and Powell (2011).

Subsequent development in the Helgeson school led to the creation of the computer code SUPCRT92 (Johnson et al., 1992), which incorporated various improvements over the earlier software. The water equation of state was replaced by that of Haar et al. (1984) and, near the critical point, that of Levelt Sengers et al. (1983), extending the range of application. SUPCRT92 was widely distributed and became a tool used by many members of the geochemistry community. Like the earlier SUPCRT, SUPCRT92 has its own thermodynamic database, consisting of 25°C data and other data necessary to

extrapolate to high temperatures and pressures. A number of such databases were created, incorporating various improvements including data for additional chemical species. The most notable of which was slop98.dat, which was an important starting point for work by others.

In the early days of the Yucca Mountain Project at Lawrence Livermore, the functionality of SUPCRT92 was incorporated into software called GEMBOCHS (Johnson and Lundeen, 1994ab). GEMBOCHS used a relational database to contain thermodynamic data (of the sort found in SUPCRT92 databases). This software could directly produce data files for geochemical modeling codes such as EQ3/6 (see for example Wolery, 1992), whereas SUPCRT92 output had to be integrated into such data files manually or by running scripts. A number of such data files were produced (see Johnson and Lundeen, 1994b). GEMBOCHS utilized costly proprietary relational database software. This had the effect of making the system inaccessible to other would-be users, which in turn made the system non-transparent. GEMBOCHS was also insufficiently documented. Today no copies of GEMBOCHS, or any pieces thereof, are known to exist. Also, the need for a relational database for this purpose now seems absurd owing to advances in computer technology.

In subsequent work on the Yucca Mountain Project (see Wolery and Jove-Colon, 2007, and references cited therein), the decision was made to use SUPCRT92 (with a partially updated form of slop98.dat representing basically the same set of chemical species) in combination with newly developed spreadsheet tools. Data for additional species were processed using the spreadsheet tools. This allowed multiple investigators to develop the data for new species that they required for their subsequent analyses. The output from SUPCRT92 and the spreadsheet tools were assembled by hand into a data file called data0.ymp, of which several versions were produced. Many NEA data (starting with Grenthe, 1992) were included. This later Yucca Mountain work was done under NQA-1 level quality assurance. The data0.ymp databases were used in analyses of interaction of aqueous solutions with both natural and engineering materials. Many of these analyses were included in the Yucca Mountain License Application.

## 3. Earlier Work Under the UFD and SFWST Campaigns

In 2011 the Used Fuel Disposition (UFD) Campaign was initiated to study disposal of spent fuel and other high level waste (U.S. Dept. of Energy, 2011). UFD was chartered to examine various possible disposal scenarios, including geologic disposal in a variety of geologic settings, under conditions different from those at Yucca Mountain. Work on thermodynamic database development began in 2015, reuniting two of the principal investigators (T. Wolery and C.F. Jove-Colon) who were involved in producing the Yucca Mountain thermodynamic database. In 2017, the UFD Campaign was replaced by the Spent Fuel and Waste Science and Technology (SFWST) Campaign (see Swift, 2017).

The first product under the UFD Campaign was an extensive and detailed examination of key thermodynamic data (Wolery and Jové Colón, 2017). Key data are data used to derive data for other species, using data for chemical reactions (as for solublities and phase equilibria). For example, considering quartz ($SiO_2$) as a key species,

thermodynamic data for aqueous silica ($SiO_2$(aq)) can be obtained from quartz solubility data representing the reaction quartz ($SiO_2$) = $SiO_2$(aq) . Key data species include:

- Chemical elements in their standard reference forms
- Water and simple aqueous solute species such as $Na^+$ and $Cl^-$, as well as some more complex species such as $HCO_3^-$ and $H_2PO_4^{2-}$
- Simple solids, such as quartz ($SiO_2$) and corundum ($Al_2O_3$)
- Simple gases such as $O_2$

A minimum of one key species is needed to represent a chemical element in each of its oxidation states. Apart from the chemical element reference forms (zero oxidation state), different choices of key species are possible. Considering $Al^{3+}$ and corundum ($Al_2O_3$), only one is required as the key species representing Al(III). However, as long as the relationship between two such species is strongly established, both can be used in practice (one primary key species and one or more secondary key species).

Wolery and Jové Colón (2017) reviewed decades' worth of thermodynamic data for commonly used key species and noted a number of trends and specific instances of errors. One purpose of this review was to serve as a guide to which key data should be used in developing a new internally consistent database (more or less in the form of a SUPCRT database). The other purpose was to provide a means of correcting data for non-key species to account for differences in key data. Thus, data from a significant body of historical sources (see Wolery and Jové Colón, 2017, covering all the major data efforts by U.S. and other programs over the years, including CODATA, NBS/NIST, the U.S. Geological Survey, NEA, and other organizations and entities) can be considered in the new database without introducing thermodynamic inconsistencies.

Although the intent of the Helgeson school was to produce accurate and internally consistent databases for SUPCRT and later SUPCRT92, cracks developed over the years. When the work began, the preferred source of key thermodynamic data was CODATA (Committee on Thermodynamic Data), an international organization. If needed key data were not available, they were taken from NBS (later NIST) reports. Unfortunately, when the Helgeson school was developing SUPCRT, both CODATA and NBS/NIST were periodically issuing updated values for key data (see Wolery and Jové Colón, 2017). Various data might require revision if key data values used to derive them were changed, for example by a revision in CODATA-recommended values. There seems to have been no dedicated, ongoing effort at such revision, other than replacing old values of key data by new ones in the database. Other affected (non-key) data would be left as-is, unless someone pointed that there was a problem. There were also accuracy concerns. In particular, Helgeson et al. (1978) made two notably unfortunate choices, one concerning the data for aqueous silica ($SiO_2$(aq)), the other for the data for kaolinite (see Wolery and Jové Colón, 2017, and pertinent references cited therein). The silica problem was recognized and corrected in the Yucca Mountain work described earlier, but the kaolinite problem was appreciated only later.

# 4. Updating SUPCRT92 in support of the Spent Fuel and Waste Science and Technology Program

## *4.1. General Approach*

GEMBOCHS (Johnson and Lundeen, 1994ab) is no longer supported. SUPCRT92 (Johnson et al., 1992) is still promising as a tool in continuing development, but only if the software is updated and otherwise improved, and if a new, updated and improved database is created for it. That is essentially our current approach. We note that the ability of SUPCRT92 to calculate thermodynamic data to high temperatures and pressures is critical to the application of geochemical and reactive transport modeling of the majority of actual and potential scenarios for the disposal of high-level nuclear waste. The Yucca Mountain thermodynamic database development was largely limited to relatively low temperatures and pressures.

Strong points of SUPCRT92 include representation of the body of work of the Helgeson school in the associated databases, open-source software (written in Fortran), the use of an equation of state to calculate the thermodynamic properties of water, the inclusion of the "HKF equation of state" model for aqueous solute species, the ability to specify reactions for which data are to be calculated, the ability to specify temperatures and pressures for which data are desired, long-term acceptance by the geochemical community (see for example Anderson, 2005; Walther, 2009)., and a quality assurance history from use on the Yucca Mountain Project. The only obvious open-source potential alternative is CHNOSZ (Dick, 2019), which was developed by one of Helgeson's later students (Jeffrey M. Dick). It has a strong focus on organics, is written in the R programming language, and at this point is more of a pure research code.

The weak points of SUPCRT92 include the use of a combination of obsolete equation of state models for water, the inclusion of obsolete "add-on" models for some additional water properties (discussed below), the use of obsolete coding practices that were concessions to the limitations of computers in the 1970s when SUPCRT was first created, a limitation of no more than 50 reactions on an input (.rxn) file, and output formats that are not optimal for building a thermodynamic data file intended directly support geochemical modeling and reactive transport codes. In addition, SUPCRT92 and its data files continue to use the obsolete calorie unit, instead of the modern accepted Joule. It is probably fair to say that the continued use of the calorie in geochemical studies is largely due to SUPCRT92. Another problem is that for solids and gases, SUPCRT92 and its databases use a three-term Maier-Kelley for the heat capacity of minerals and gases, while a four-term form is more appropriate (see for example Holland and Powell, 2011). This has been corrected in SUPCRTBL (Zimmer et al., 2016).

Our long-term plan is to revise the SUPCRT92 software to address the above deficiencies, to develop a series of internally consistent data files to support it, and to create a new suite of data files to directly support geochemical modeling and reactive transport codes, providing for various required formats for popular codes (e.g., EQ3/6, GWB, PHREEQC).

Our analysis of key thermodynamic data (Wolery and Jové Colón, 2017) represented a first step. After completion of that work, we began analysis and revision of SUPCRT92, dubbing the new product SUPCRTNE. This work is still ongoing. We have previously addressed the issues of conversion from calorie to Joule units, including writing a code to convert existing SUPCRT92 data files to Joule units. We also eliminated the "no more than 50 reactions at a time" limit. We then focused on replacing the part of the software dealing with the properties of water. This consists of a number of subroutines and functions contained in the "H2O92D" module, which comprises a large part of the SUPCRT92 source code.

The International Association for the Properties of Water and Steam (IAPWS, see iapws.org) is an international entity that sanctions models for the calculation of water properties. The equation of state model of Haar et al. (1984) used in SUPCRT92 is a second-generation IAPWS standard (IAPS-84). It does not extend to the critical point of water (647.096K and 22.064 MPa). Near the critical point, SUPCRT92 uses equation of state model of Levelt Sengers et al. (1983), which is unsanctioned. The present sanctioned model is that of Wagner and Pruss (2002), known as IAPWS-95. The model is valid across a wide range of temperature (273.16K-1273K) and pressure (0-1000 MPa), including at and near the critical point (647.9906K and 22.064 MPa). It is thus technically superior in addition to merely being the current sanctioned model.

Both IAPS-84 and IAPWS-95 are *general and scientific* models. They (and also the earlier model of Keenan et al. 1969) use temperature and density instead of temperature and pressure as the independent variables. Evaluating such models for specified temperature and pressure requires iteration to adjust the density to yield the desired pressure. A similar but more complex iteration is required to calculate results for a specified temperature on the liquid-vapor equilibrium curve (the saturation curve), or to calculate results for a specified pressure on that curve. Because in the past such iteration was considered overly onerous for engineering calculations, for each *general and scientific* model there is a corresponding *industrial formulation*, which is a model fit to the general and scientific model using temperature and pressure as the primary variables. Although that is advantageous in avoiding iteration for typical problems, it is not as accurate as the original models, and accuracy is critical for the thermochemical usage which is of interest here. There is additional complexity in the industrial formulation in the form of different equations for different regions of temperature-pressure space. The industrial formulation corresponding to IAPWS-95 is IAPWS-IF97 (Wagner et al., 2000).

### *4.2. H2OI95 v. 1.0: Software for Dealing with the IAPWS-95 Model (FY19)*

Since the IAPWS-95 model has been around for some years, we first looked for an open source implementation (preferably in Fortran) that had no proprietary strings attached. None was located, so we began writing the requisite software from scratch. It was decided to first develop this as a stand-alone code, in order to facilitate testing. The code was dubbed H2OI95. H2OI95 was written in "simple" Fortran, with explicit variable

typing, all passing of variables done through calling sequences, extensive commenting, straightforward flow in the coding, and no dependencies on external libraries.

In late 2018 we completed version 1.0 of H2OI95 (Wolery, 2018), which implements the IAPWS-95 model described by Wagner and Pruss (2002) and IAPWS (2016). H2OI95 includes calculation of thermochemical properties of water using the key thermodynamic data of CODATA (Cox et al., 1989). This is not a part of the IAPWS-95 model, and is not a common feature of IAPWS-95 calculators.

The report, "H2OI95: A Stand-Alone Fortran Code for Evaluating the IAPWS-95 Equation-of-State Model for Water" (Wolery, 2018) was released by LLNL on December 12, 2018 as document LLNL-TR-761227. This document describes the implementation of the model, extensive convergence testing and numerical examination, and results of computer verification testing. Convergence testing was necessary to assure that starting values for density would converge rapidly to physically meaningful results. Neither Wagner and Pruss (2002) nor IAPWS (2016) speak to the issue of starting values. Testing of various schemes for defining starting estimates was required to find ones that would lead rapidly to physically valid results. It was found that, depending on starting values, convergence could lead to results that are non-physical, as shown by negative absolute entropy or some other non-physical condition. The report also describes results of computer verification tests specified by Wagner and Pruss (2002) and IAPWS (2016). These tests are high precision, at the level of eight or nine significant figures. The term "verification" here is that used by Wagner and Pruss (2002) and IAPWS (2016); it is equivalent in meaning to "validation" as used on the Yucca Mountain Project.

The H2OI95 software was released under an open source BSD-3 license and placed as a complete package (Windows executable, source code, report, associated text files, and a test case library of input and output files) in February 2019 on GitHub (https://github.com/llnl/h2oi95). Github is now the favored repository for LLNL open-source software. Our intent has been to also make the code available for download on the EQ3/6 website hosted at LLNL (https://www-gs.llnl.gov/energy-cyber-and-infrastructure/geochemistry) or on another LLNL institutional web site whose creation is presently under consideration. The reason for needing another web site is that GitHub is a product for software developers to use in the development process, not something intended as a repository for finished software products. It can be used that way, but the web pages cannot be set up in a way that is oriented toward geochemists.

### *4.3. H2OI95 v. 1.1: Calculation of Additional Water Properties (FY20)*

After the release of H2OI95 version 1.0, we returned to SUPCRTNE to determine how best to link in the new EOS model for water properties. We had previously made other functional changes to SUPCRT92, including eliminating the inconvenient and obsolete direct access data file, and converting the code from obsolete calorie units to Joule units. We had also written a small code to convert SUPCRT92 data files from calorie units to Joule units.

Resuming work on SUPCRTNE, we found code in the H2O92D module for calculating additional properties that are not part of the IAPWS-95 model. These include the dynamic viscosity, thermal conductivity, surface tension, and dielectric constant, along with Born functions calculated from the dielectric constant. Examination of SUPCRT92 showed that coding used to calculate these properties is always executed when water properties are calculated. However, except for the four Born functions, these additional property values are not used in subsequent calculations, nor are they are written to any output. The Born functions are used in evaluating the HKF "equation of state" model (Helgeson and Kirkham, 1976; Helgeson et al., 1981) for calculating the thermodynamic properties of aqueous ions at elevated temperature and pressure.

The dielectric constant model can also be used to compute Debye-Hückel parameters (see Fernández et al., 1997), which we need to develop working data files to support geochemical modeling and reactive transport codes. These additional properties (especially the dielectric constant and derivative parameters) were a focus of attention in the early development of thermodynamic data and models for water and aqueous (solute) species by H. C. Helgeson and colleagues (see Helgeson and Kirkham, 1974a, 1974b, 1976; Helgeson et al., 1981). This makes current IAPWS-sanctioned models of additional water properties significant to ongoing and future thermodynamic database development (the models in SUPCRT92 being obsolete). The current IAPWS-sanctioned additional properties models are consistent with IAPWS-95. We decided to address additional properties in an extended version of H2OI95 (version 1.1). Full documentation of this work is given in Wolery (2020). The values of the new properties calculated by H2OI95 are output on a new comma-separated-variable (.csv) file called xtab.csv.

There are three "additional" thermodynamic properties of interest that can be obtained from the IAPWS-95 model itself but for which the requisite formulas were not given by Wagner and Pruss (2002) or IAPWS (2016). Consequently, most IAPWS-95 software does not provide them. These are the isothermal compressibility, the thermal expansivity, and the dimensionless isothermal compressibility. The requisite formulas were derived and coded into H2OI95, and values are reported on the xtab.csv output file. For details, see Wolery (2020).

IAWPS (2008) describes the IAPWS-sanctioned model for the dynamic viscosity of water. The model is developed in the corresponding paper by Huber et al. (2009). The model requires the isothermal compressibility function noted earlier, which is obtained from the IAPWS-95 model. During verification of the implementation of the dynamic viscosity model, a coding error was found involving the IAPWS-95 model's $55^{th}$ and $56^{th}$ terms, which are highly complex. This error notably affected "higher order" properties including the isothermal compressibility and the dimensionless isothermal compressibility in a small region close to the critical point. It also affected the calculated pressure and the pressure derivative with respect to density, but only slightly. Correction of the error was verified by comparison with results given by Huber et al. (2009).

In retrospect, the verification tests for IAPWS-95 implementation given by Wagner and Pruss (2002) and IAPWS (2016) appear to be insufficient. For example, the uncorrected code produced results that matched values in the steam tables (Table 13.2) of Wagner and Pruss (2002) to the precision used in those tables (four to five significant figures), except for very slight differences at a single pressure and temperature close to the critical point. See Wolery (2020) for more detailed discussion. Additional opportunities for verification close to the critical point are based on plots for "higher-order" water properties given by Wagner and Pruss (2002) and Kiselev and Friend (1999). Comparison of these plots with results for the corrected H2OI95 are only graphical, but still helpful.

IAPWS (2011a) describes the IAPWS-sanctioned model for the thermal conductivity of water. The model is developed in the corresponding paper by Huber et al. (2012). Like the above noted viscosity model, this model also has a dependency on the dimensionless isothermal compressibility.

The above described models for the viscosity (IAPWS, 2008) and thermal conductivity (IAPWS, 2011a) have temperature ranges of validity partially defined in terms of the melting temperature as a function of pressure. The model for the melting temperature is taken from IAPWS (2011b), which in turn is based on the paper of Wagner et al. (2011). This model describes the melting pressure as a function of temperature. To obtain the melting temperature as a function of pressure, it is necessary to invert the model. In H2OI95, the inversion is accomplished using secant method iteration. For further details, see Wolery (2020, Section 5.2.6).

IAPWS (2014) describes the IAPWS-sanctioned model for the surface tension of water. The model is based on the work of Vargaftik et al. (1983). The model describes to the surface tension between coexisting vapor and liquid as a function of temperature.

IAPWS (1997) describes the IAPWS-sanctioned model for the dielectric constant of water. The model is developed in the corresponding paper by Fernández et al. (1997). The dielectric constant is one of the most important properties of water, as it in turn is needed to calculate both Born functions (Helgeson and Kirkham, 1974ab) and Debye-Hückel parameters (Helgeson and Kirkham, 1974ab; Fernández et al., 1997).

IAPWS (2014) does not address partial derivatives (with respect to temperature and pressure) of the dielectric constant and various derivative properties, such as Debye-Hückel parameters and Born functions. However, the source paper by Fernández et al. (1997) addresses the first-order partial derivatives and the Debye-Hückel "A" (or limiting law) parameters. These partial derivatives are included on the xtab.csv output file.

IAPWS itself is silent on Debye-Hückel parameters. However, these parameters can be obtained from the dielectric constant model (IAPWS, 2014, Fernández et al., 1997). The discussion here is abbreviated. For a full discussion, see Wolery 2020, Section 5.2.5)

The Debye-Hückel parameters include the "A" or "limiting law" parameters and "B" or "extended" parameters. The primary A and B parameters (commonly given as $A_\gamma$ and $B_\gamma$)

are used in some form of the basic Debye-Hückel model for describing the activity coefficient of an aqueous electrolyte or ion in dilute solution, or as part of some more elaborate model for more concentrated solutions (such as Pitzer's 1973 equations). For an extended discussion of aqueous activity coefficient models, see Section 3 of Wolery, 1992 or any other pertinent review of the subject. Aqueous geochemistry texts such as Anderson (2005) and Walther (2009) include discussions of such models. Helgeson and Kirkham (1974b) provide a wide-ranging discussion of Debye-Hückel parameters and Born functions.

The Debye-Hückel "A" and "B" parameters are dependent on the dielectric constant, which depends on temperature and pressure. In addition to the constants noted above, there are others associated with related thermodynamic properties, for example $A_V$ (with apparent molar volume), $A_H$ (with apparent molar enthalpy), $A_K$ (with apparent molar compressibility), and $A_C$ (with apparent molar heat capacity). These are discussed by Fernández et al. (1997) and Helgeson and Kirkham (1974b). Helgeson and Kirkham also discuss the corresponding "B" parameters, which Fernández et al. (1977) does not.

The Born functions Z, Q, Y, and X used in SUPCRT92 were not included in H2OI95 v. 1.1 pending resolution of questions concerning their usage in SUPCRT92. They will be included in the next version (v. 1.2).

The report, "H2OI95: A Stand-Alone Fortran Code for Evaluating the IAPWS-95 Equation-of-State Model for Water (Rev. 1)" (Wolery, 2020) was released by LLNL on May 18, 2020 as document LLNL-TR-805304. This document (the report for H2OI95 v. 1.1) is an extended and revised version of the report for H2OI95 v. 1.0, documenting all the new material. The report documents the extensive testing and verification activities.

The H2OI95 v. 1.1 software was released on June 3, 2020 under an open source BSD-3 license. A complete package (Windows executable, source code, report, associated text files, and a test case library of input and output files) was completed on June 6, 2020. It was placed on GitHub on July 30, 2020, where the v. 1.0 package is also still available for download. We anticipate that v. 1.1 will also be made available on an LLNL institutional web site. The reason for needing an alternative web site is that GitHub is a product mainly intended for software developers to use in the development process. It can be is used utilized as a repository for finished software products. However, the GitHub web pages cannot be customized in a way that is oriented toward geochemists.

### *4.4. SUPCRTNE v 1.0 and H2OI95 v. 1.2 (FY21)*

Work is presently focused on connecting SUPCRTNE (under development) with H2OI95. SUPCRT v. 1.0 will be the first working version of SUPCRTNE. It will use the "modularized" version of H2OI95 (v. 1.2). to in place of the existing H2O92d module from SUPCRT92 (Johnson et al., 1992). The existing H2O92d module uses the older IAPS-84 (Haar et al., 1984) equation-of-state model in conjunction with the Levelt Sengers et al. (1983) model near the critical point. Current intent is to retain this

alongside the H2OI95 model for some time to allow comparative studies of how much change the IAPWS-95 (IAPWS, 2016; Wagner and Pruss, 2002) model introduces to SUPCRTNE calculations.

H2OI95 v. 1.2 introduces two major changes from v. 1.1. The code is being "modularized" by breaking up the existing main program into a shorter main program that just reads the H2OI95 input file and a lead subroutine H2O95E that can be called by other programs, including SUPCRTNE. Also, the Born functions Z, Q, Y, and X are being added. These will be calculated using the Fernandez et al. (1997) model for the dielectric constant. Actually X will not, because it requires the second partial derivative of the dielectric constant with respect to temperature. This is presently not available from the Fernandez et al. (1997) model.

The formula in the Fernandez et al. (1997) model for the first partial derivative is already quite complex, and Fernandez et al. have questioned whether the usefulness of the second partial derivative as obtained from their model. X appears to be needed in SUPCRT92 only to compute the heat capacity of aqueous ions, a result that is written on the main output file but appears otherwise unused. It does not appear to be needed for anything critical, for example computing Gibbs energies as a function of temperature and pressure.

Because of this and the importance of the other Born functions generally in computing the thermodynamic properties of aqueous species at elevated temperature and pressure, it was decided to "import" the Johnson and Norton (1991) model for the dielectric constant from SUPCRT92 and use it in parallel with the Fernandez et al. (1997) model. The Johnson and Norton model includes the formula for computing the second order partial derivative needed to compute the Born function X. Comparative studies will then be conducted.

At this writing, H2OI95 v. 1.2 is nearly complete. Testing of the modularized version with SUPCRTNE will be made to assess satisfactory completeness. SUPCRTNE will then contain the latest IAPWS-sanctioned models for water properties. The new version of H2OI95 (as both stand-alone code and as a module) will be placed on GitHub along with the previous versions.

## 5. Planned FY22 Efforts

SUPCRTNE (starting with v. 1.0) will be the primary engine for future thermodynamic database development. It will replace SUPCRT92 and GEMBOCHS. In addition to melding H2OI95 into SUPCRNE, other improvements will be made. The other parts of the source code will be cleaned up for transparency and to eliminate coding aspects that were originally adopted (going back to the 1970s) to accommodate now obsolete computer limitations. We note that one of the worst of these, the direct-access data file, has been previously eliminated. The data file is now a text file, which is easier to examine and modify. We have also replaced the usage of the obsolete calorie unit with the Joule.

We will modify the code output to better support incorporation in data files that will support geochemical modeling and reactive transport codes. We will fold in the functionality of another modified SUPCRT92, the SUPCRTBL of Zimmer et al., 2016, which can use the mineral thermodynamic model of Holland and Powell (2011). This involves the addition of a fourth term to the existing three-term treatment of heat capacity of minerals and other solids, with provision for a corresponding additional constant on the SUPCRTNE data file. Completion of H2OI95 v. 1.2 is expected before the end of FY21. Completion of SUPCRTNE v. 1.0 is expected to extend into FY22. .

Once SUPCRTNE is complete, we will return to a focus on thermodynamic data development. The logical place to begin is modifying the SUPCRT data file (slop98.dat or something more recent) to update key thermodynamic data, following on our earlier review of the subject (Wolery and Jové Colón 2017). We will start by adopting of values from CODATA (Cox et al., 1989). Other key data will be taken mostly from NEA volumes (e.g., Grenthe et al., 1992, and other volumes too numerous to list here). NEA, has followed key data from CODATA for many years, but is now preparing its own Ancillary Data volume. Some data from CODATA may be superseded. Otherwise, we will take key data from other sources tabulated by Wolery and Jové Colón (2017) or more recent pertinent sources, should any exist. We will then revise other data in the SUPCRT data file for consistency with the new key data.

The new data file will likely include at least some of the Helgeson et al. (1978) mineral data (with potential corrections). However, we are intending to replace most of that with the mineral data of Holland and Powell (2011), which is overall more extensive and which draws on more recent experimental literature. As noted previously, the Holland and Powell data utilize a four-term isobaric heat capacity equation, which is superior to the older three-term form used by Helgeson et al. (1978). We will also include some mineral data that is founded on estimation techniques, as we did for a number of clay mineral compositions for the Yucca Mountain database.

As part of this follow-on effort, we anticipate preparing a second paper, “Chemical Thermodynamic Data. II. Water in SUPCRT92 and Similar Codes: Thermochemical Properties in Relation to Equations of State,” by Wolery and Jové-Colón. We had put that off until completing H2OI95. We will be watching for potentially impactful developments by others, including the new paper by Miron et al. (2017) in addition to the forthcoming NEA Ancillary Data volume. Integration of LLNL’s databases with NEA-TDB will be pursued in coordination with the international work packages.

The thermochemical data for some key species including the aqueous species $Ca^{2+}$ and $Mg^{2+}$ may be changed from the CODATA values owing to recent developments, and if so, some of the NEA recommended data may have to be adjusted to conform from newly chosen values (unless NEA itself makes such adjustments). This is important to maintain consistency between data for natural minerals on the one hand and substances containing radionuclide elements (granted that the two groups overlap). Our effort at database development will begin with a simple, nearly “sequential” derivation aimed at elucidating differences resulting from alternative values for certain of the key thermochemical data.

Such derivations are useful in showing the structure associated with data dependencies. They are also useful in identifying key issues and those input data that should be rejected before performing a more general "optimization" process to obtain a higher-level database.

As noted earlier, we will develop a project web page with ancillary web pages on which our products can be downloaded. This will provide an alternative to GitHub that will be more geochemist friendly, although we will still use GitHub. The project web page will expand on the current LLNL web page that provides download of EQ3/6 and its existing thermodynamic databases. All codes and data files will be available for download as open source products. Historical and new versions of thermochemical databases will be made available in several formats for use by the SFWST-relevant codes (PFlotran, PhreeqC, Geochemists WorkBench, etc.).

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