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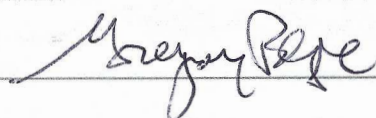
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M4SF-20LL010301042: Updated Thermodynamic Database for Use in Generic Disposal System Assessment

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1. Introduction

This progress report (Level 4 Milestone Number M4SF-20LL010301042) summarizes research conducted at Lawrence Livermore National Laboratory (LLNL) within the Argillite Activity Number SF-20LL010301041. 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. The Yucca Mountain Project was defunded in 2011.

3. Previous 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 solubilities and

phase equilibria). For example, considering quartz (SiO_2) as a key species, thermodynamic data for aqueous silica ($\text{SiO}_2(\text{aq})$) can be obtained from quartz solubility data representing the reaction $\text{quartz} (\text{SiO}_2) = \text{SiO}_2(\text{aq})$. 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 $\text{H}_2\text{PO}_4^{2-}$
- 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 ($\text{SiO}_2(\text{aq})$), 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 out of the picture. SUPCRT92 (Johnson et al., 1992) is still promising as a tool in continuing development, but only if both 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.

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

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

4.3.1. General

After the release of H2OI95 version 1.0, we returned to SUPCRTNE to figure out 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.

While 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. It seems likely that these routines carried over from previous versions of SUPCRT. Examination of SUPCRT92 showed that coding used to calculate these properties is always executed when water properties are calculated. However, these additional property values are not used in any subsequent calculations, nor are they written to any output.

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). It is noted that the current IAPWS-sanctioned additional properties models are consistent with IAPWS-95. We decided to address additional properties in an extended version of H2OI95 (which was dubbed version 1.1). Full documentation of this work is given in Wolery (2020). What follows is a shortened summary. The values of the new properties calculated by H2OI95 are output on a new comma-separated-variable (.csv) file called xtab.csv.

4.3.2. Compressibility and Expansivity

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 (κ_T), the thermal expansivity (α_p), and the dimensionless isothermal compressibility (ζ_T). The requisite formulas were derived and coded into H2OI95. As will be discussed later, the dimensionless isothermal compressibility is required as an input to the IAPWS-sanctioned models for viscosity and thermal conductivity.

The isothermal compressibility is defined by

$$\kappa_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T \quad (1)$$

where v is volume, p is pressure, and T is the absolute temperature. This property has dimensions of inverse pressure. An equivalent formula in terms of density (ρ) is:

$$\kappa_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_T \quad (2)$$

It can be shown that

$$\kappa_T = 1 / \delta \left(\frac{\partial p}{\partial \delta} \right)_T \quad (3)$$

where δ is the reduced density (ρ/ρ_{cr} , where ρ_{cr} is the critical density), and the partial derivative is obtained from the IAPWS-95 model. The same partial derivative is used in Newton-Raphson iteration to find the density corresponding to a specified pressure. The compressibility was actually included in version 1.0 of H2OI95, although the value output was consistent with units of kPa^{-1} , not the intended MPa^{-1} .

The isobaric thermal expansivity is defined by:

$$\alpha_p = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p \quad (4)$$

This property has dimensions of inverse temperature. It can be shown that this is equivalent to

$$\alpha_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p \quad (5)$$

Obtaining an expression for obtaining the expansivity directly from the equation-of-state model is more complicated than obtaining the one for the compressibility. There is a useful relation between the two properties (Helgeson and Kirkham, 1974a, equation (26)):

$$\left(\frac{\delta p}{\delta T} \right)_\rho = \alpha_p / \kappa_T \quad (6)$$

This is a kind of Maxwell relation, meaning that it ultimately relates to the equivalence of second order derivatives, regardless of order of differentiation.

It can then be shown that:

$$\alpha_p = -\left(\frac{\tau}{T} \right) \kappa_T \left(\frac{\partial p}{\partial \tau} \right)_\delta \quad (7)$$

where τ is the inverse reduced temperature (T_{cr}/T), where T_{cr} is the critical temperature. The derivative here is analogous to the one needed to obtain the compressibility. The pressure is obtained from Wagner and Pruss, 2002

$$p = \rho RT(1 + \delta \phi_\delta^r) \quad (8)$$

where R is the gas constant and ϕ_δ^r is one of the “phi” functions calculated in the IAPWS-95 model (see Wagner and Pruss, 2002, or IAPWS, 2016). Therefore

$$\frac{\partial p}{\partial \tau} = -\frac{p}{\tau} + \frac{p\delta\phi_{\delta\tau}^r}{(1 + \delta\phi_{\delta}^r)} \quad (9)$$

and $\phi_{\delta\tau}^r$ is another “phi” function. The dimensionless isothermal compressibility is defined as

$$\zeta_T = \left(\frac{\partial \bar{p}}{\partial \bar{p}}\right)_T \quad (10)$$

(See Huber et al., 2009, and IAPWS, 2008, describing the IAPWS-sanctioned model for dynamic viscosity). Here $\bar{\rho} = \rho/\rho_{cr}$ and $\bar{p} = p/p_{cr}$. These are both dimensionless. Here $\bar{\rho} = \delta$ in the symbology of the IAPWS-95 model (Wagner and Pruss, 2002; IAPWS, 2016). It follows that

$$\zeta_T = p_{cr} \left(\frac{\partial \delta}{\partial p}\right)_T \quad (11)$$

and hence

$$\zeta_T = p_{cr} \left/\left(\frac{\partial p}{\partial \delta}\right)_T\right. \quad (12)$$

where the partial derivative is the same one used to obtain the compressibility κ_T . The two kinds of compressibility are related by

$$\zeta_T = p_{cr}\delta\kappa_T \quad (13)$$

No independent tables of isothermal compressibility, thermal expansivity, or dimensionless isothermal compressibility consistent with IAPWS-95 were found that could be used. For strict computer verification, the implementation in H2OI95 was instead verified by comparing expansivity results with Table 7 of Helgeson and Kirkham (1974a) and compressibility results with Table 8 from the same source. These tables present property values over a wide range of temperature (up to 900°C) and pressure (up to 8 kb, or 800 MPa). They were constructed using different models, but the comparison is reasonably good. H2OI95 calculations were made using test case VCalx, which is included in the version 1.1 test case package. No comparable tables could be found for the dimensionless isothermal compressibility. However, some useful data were found in connection with examination of the IAPWS (2008) model for the dynamic viscosity (discussed below).

4.3.3. Viscosity and Discovery of a Coding Error

IAPWS (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). In the model, the viscosity μ is given by

$$\mu = \mu^* \times \bar{\mu} \quad (14)$$

where $\mu^* = 1.00 \times 10^{-6}$ Pa-s. The dimensionless viscosity $\bar{\mu}$ is represented by:

$$\bar{\mu} = \bar{\mu}_0(\bar{T}) \times \bar{\mu}_1(\bar{T}, \bar{\rho}) \times \bar{\mu}_2(\bar{T}, \bar{\rho}) \quad (15)$$

where $\bar{T} = T/T_{cr} = 1/\tau$ and $\bar{\rho} = \rho/\rho_{cr} = \delta$. The factor $\bar{\mu}_0$ is represented by a direct function of \bar{T} , and $\bar{\mu}_1$ is represented by a direct function of \bar{T} and $\bar{\rho}$. (see IAPWS, 2008). The third factor, $\bar{\mu}_2$, is called the critical enhancement. A computed non-unit value is necessary in a small region around the critical point.

The factor $\bar{\mu}_2$ is a function of \bar{T} , $\bar{\rho}$, and the isothermal compressibility function ζ_T presented earlier. The need for a ζ_T input defines an interface between the viscosity model and the IAPWS-95 equation-of-state model. According to IAPWS (2008), the viscosity model may be used with the corresponding industrial formulation (IAPWS-IF97). It is suggested that when using the industrial formulation that the critical enhancement can be neglected (setting $\bar{\mu}_2$ to unity) for the sake of greater computational speed.

IAPWS (2008) provides data at sample points for computer verification. Table 5 provides such data for verifying calculation of the critical enhancement factor. All points are for 647.35K (near the critical temperature of 647.096K) and densities ranging from 122-422 kg-m³. For a density of 322 kg-m³ (which matches the critical density), the critical enhancement factor is given a value of 1.09190440. H2OI95 initially gave a value of 1.0. Comparing intermediate results from H2OI95 with corresponding results from a Russian on-line calculator at <http://twf.mpei.ac.ru/mcs/worksheets/iapws/wspsDVRT.xmcd> showed that the problem lay in the calculation of the dimensionless isothermal compressibility ζ_T (at the specified temperature, ζ_T values at the reference temperature being essentially identical). The difference is most pronounced for the case with a density of 322 kg-m³, which matches the critical density.

A re-examination of the relevant coding in H2OI95 revealed a coding error dealing with the IAPWS-95 model's 55th and 56th terms, which are more complex than any of the other terms. These terms are calculated in several pieces. The pieces appeared to have been coded correctly, but the results incorrectly assembled. The affected IAPWS-95 "phi" functions were ϕ^r , ϕ_δ^r , and $\phi_{\delta\delta}^r$. This error notably affects "higher order" properties including the isothermal compressibility and the dimensionless isothermal compressibility. It also affects the calculated pressure and the pressure derivative with respect to density, but only slightly.

Table 1 shows values of the dimensionless isothermal compressibility calculated from H2OI95 v. 1.0, the Russian online calculator, and the corrected H2OI95. Results from the latter two agree to high precision.

Table 1. Values of ζ_T for IAPWS (2008, Table 5) cases for computer-program verification in the region near the critical point.

ρ (kg-m ⁻³)	H2OI95 (version 1.0)	RNC Calculator*	H2OI95 (corrected)
122	1.172364336	1.172359572993	1.172359573
222	12.13628693	12.022617478793	12.02261748
272	85.00038494	103.349971362412	103.3499714
322	0.0000009589589725**	831.608570294227	831.6085703
372	56.57653032	85.372413655772	85.37241366
422	9.250662168	8.93479199275	8.934791993

*RNC IAWPS-95 on-line calculator: <http://twf.mpei.ac.ru/mcs/worksheets/iapws/wspsDVRT.xmcd>.

**This value is effectively zero. It is obtained by resetting δ to a value just slightly different from unity in order to avoid a calculational singularity.

Table 2 shows the effect of the correction on the calculated critical enhancement factor. The IAPWS (2008) Table 5 values are now exactly reproduced. Also shown are H2OI95 outputs in which the dimensionless compressibility at the reference temperature of 970.644K is approximated using a fitted polynomial, as opposed to a using an IAPWS-95 computation. These results are not exact, but excellent.

Table 2. Values of the critical enhancement ($\bar{\mu}_2$) from IAPWS (2008, Table 5), compared with results obtained from the corrected version of H2OI95.

ρ (kg-m ⁻³)	IAPWS (2008, Table 5)	H2OI95 (corrected)*	H2OI95 (corrected)**
122	1.00000289	1.00000289	1.00000289
222	1.00375120	1.00375120	1.00375121
272	1.03416789	1.03416789	1.03416789
322	1.09190440	1.09190440	1.09190440
372	1.03665871	1.03665871	1.03665873
422	1.00596332	1.00596332	1.00596307

*Using ζ_{T_R} calculated from the IAPWS-95 model.

**Using ζ_{T_R} values calculated from fitted polynomials (function GZTTBR).

The nature of the code correction is further illustrated by comparing ζ_T as a function of δ at 647.35K, as calculated by the uncorrected and corrected code. Figure 1 (left) shows the result obtained from the uncorrected code. Figure 1 (right) shows the result obtained from the corrected code. The curve in the corrected case gives the expected value of 831.6085703 at $\delta = 1$ (density of 322 kg-m⁻³).

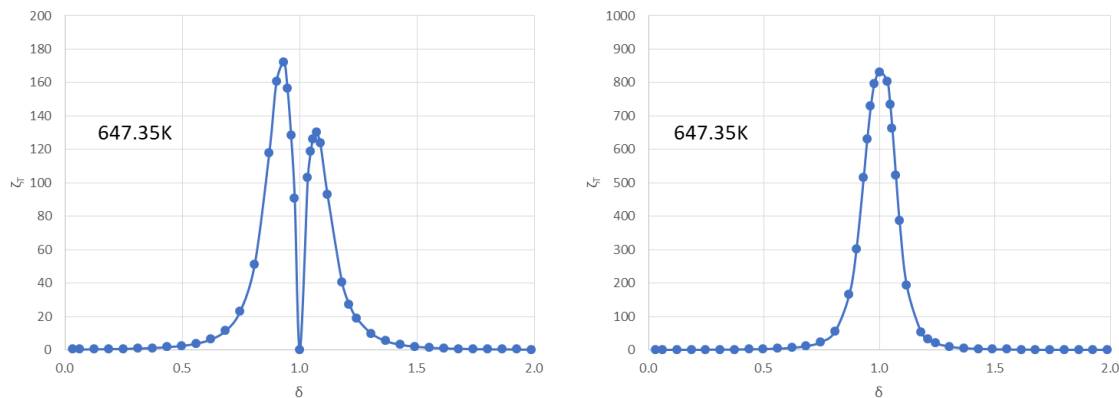


Figure 1. ζ_T as a function of δ at 647.35K, calculated using the uncorrected H2OI95 (left) and the corrected H2OI95 (right). Note the change in scale on the vertical axis.

With the coding corrected, H2OI95 produces values of dynamic viscosity that exactly match the verification test values given by IAPWS (2008), except for the case of a density of 422 kg-m⁻³m where there is a difference of unity in the last (eighth) digit (Table 3). This can be attributed to differences in rounding. Also shown in Table 3 are results obtained from the MEPI RNC Calculator. H2OI95 matches these perfectly.

Table 3. Values of the dynamic viscosity (μ Pa-s) from IAPWS (2008, Table 5), compared with results obtained from the MPEI RNC Calculator and the corrected version of H2OI95. The temperature in all cases is 647.35K.

ρ (kg-m ⁻³)	IAPWS (2008, Table 5)	MPEI RNC Calculator	H2OI95 (Version 1.1)*
122	25.520677	25.520677	25.520677
222	31.337589	31.337589	31.337589
272	36.228143	36.228143	36.228143
322	42.961579	42.961579	42.961579
372	45.688204	45.688204	45.688204
422	49.436257	49.436256	49.436256

*Using ζ_{T_R} calculated from the IAPWS-95 model.

In retrospect, the tests for computer verification given by Wagner and Pruss (2002) and IAPWS (2016) appear to be insufficient for complete verification. To be fair, IAPWS (2016) in their Table 6 test did not include the second part of the Table 6.6 test of Wagner and Pruss (2002). Both parts address “phi” functions to high precision (nine significant figures). The first part addresses phi functions for 500K and density of 838.025 kg m⁻³. Results from both the uncorrected and corrected code exactly match the test values. The second part (not included by IAPWS, 2016) is a like test for 647K and density of 358 kg m⁻³. The corrected code exactly produces the specified test values, whereas the uncorrected code produced somewhat different values. Since IAPWS (2016) was silent about why they did not include the second part, it gave the impression that there might have been some issue with the values given by Wagner and Pruss (2002). As the temperature and density for the second part are close to the critical point where some

property values become quasi-infinite, the differences found with the uncorrected code might seem to be attributable to numerical effects. However, the corrected H2OI95 matched the test values exactly, indicating that this was not the case.

In testing of H2OI95, other tests were also made (Wagner and Pruss, 2002, Tables 6.7 and 6.8; reproduced as IAPWS (2016) Tables 7 and 8, respectively). Those high precision tests showed no differences with test values. The steam tables of Wagner and Pruss (2002) were also examined for indications of a problem. However, the tabulated values are only given to about four to five significant figures, the set of properties tabulated is limited, and temperature and pressure values are not finely spaced about the critical point. Comparing H2OI95 v. 1.0 results with Wagner and Pruss (2002) Table 13.1 (saturation curve), one can note small differences in values of the isobaric heat capacity (c_p) for temperatures just below the critical temperature. As this heat capacity becomes quasi-infinite approaching the critical point, it would not be unreasonable to assume such differences might be due to numerical issues. A similar comparison with Wagner and Pruss (2002 Table 13.2 (various temperatures and pressures, a pressure of 22.5 MPa being closest to the critical pressure of 22.064 MPa, no differences were found.

In discussing the behavior of IAPWS-95 near the critical point, Wagner and Pruss (2002) reference a paper by Kiselev and Friend (1999). Those authors present an alternative equation-of-state model and a possible modification to IAPWS-95 to obtain improved results near the critical point. Wagner and Pruss (2002) chose not to implement that modification in their model due to its additional complexity. However, Kiselev and Friend (1999) present plots of heat capacity functions close to the critical point. These plots address IAPWS-95, their proposed modification, and their own equation-of-state model. These plots are useful in providing additional verification (though graphical) of the proper implementation of IAPWS-95 in H2OI95.

Figure 8 of Kiselev and Friend (1999) shows the isobaric heat capacity (c_p) at 647.5K as a function of density. The corresponding result obtained using H2OI95 (corrected) is shown below in Figure 2. This closely recreates the IAPWS-95 curve from Figure 8 of Kiselev and Friend (1999). Wagner and Pruss (2002) give similar plots in their Figures 6.11 and 6.12. Those plots could also be used as a basis of verification for conditions near the critical point.

The implementation of the IAPWS (2008) viscosity model was helpful in uncovering a coding error in H2OI95. The consequences of the error mainly limited to higher-order functions (such as c_p , κ_T , and ζ_T), and then mainly close to the critical point. A substantial number of verification test cases (“VC” series tests) were used in testing H2OI95 version 1.0, and those did not clearly reveal problems as noted earlier. In some additional test problems run with the corrected code, small differences from previous results were apparent near the critical point, as expected. In tests involving convergence ranges for initial density values, the range boundaries changed slightly in some cases.

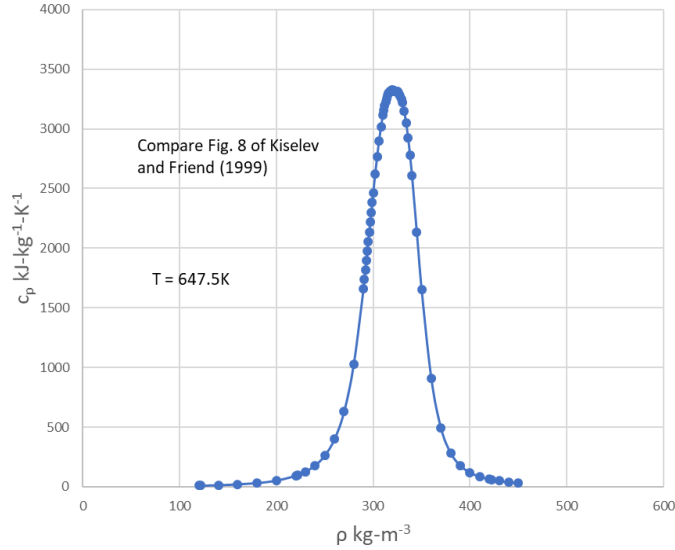


Figure 2. Re-creation of Kiselev and Friend (1999) Figure 8 IAPWS-95 result using the corrected H2OI95.

4.3.4. Thermal Conductivity

IAPWS (2011a) describes the IAPWS-sanctioned model for the thermal conductivity of water, represented by λ ($\text{W}\cdot\text{K}^{-1}\cdot\text{m}^{-1}$). The model is developed in the corresponding paper by Huber et al. (2012). The mathematical form of the thermal conductivity model somewhat follows that of the viscosity model described above. It is not closely analogous despite having its own critical enhancement. The thermal conductivity model will not be presented in detail here. For a full description, see Wolery (2020, Section 5.2.2) or the relevant original works (IAPWS, 2011a; Huber et al., 2012).

We will here focus only on computer verification of the implementation in H2OI95 v. 1.1. Table 4 shows that H2OI95 v. 1.1 produces thermal conductivity results that exactly match the verification test values given by IAPWS (2011a, Table 5). Also shown are matching results obtained from the MPEI RNS Calculator for thermal conductivity (<http://twf.mpei.ac.ru/mcs/worksheets/iapws/wspsTCRT.xmcd>).

Table 4. Values of thermal conductivity ($\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) from IAPWS (2011a, Table 5), compared with results obtained from the MPEI RNC Calculator and the corrected version of H2OI95. The temperature in all cases is 647.35K.

ρ ($\text{kg}\cdot\text{m}^{-3}$)	IAPWS (2011a, Table 5)	MPEI RNC Calculator*	H2OI95 (Version 1.1)**
1	51.9298924	51.9298924	51.9298924
122	130.922885	130.922885	130.922885
222	367.787459	367.787459	367.787459
272	757.959776	757.959776	757.959776

ρ (kg·m ⁻³)	IAPWS (2011a, Table 5)	MPEI RNC Calculator*	H2OI95 (Version 1.1)**
322	1443.75556	1443.75556	1443.75556
372	650.319402	650.319402	650.319402
422	448.883487	448.883487	448.883487
750	600.961346	600.961346	600.961346

*MPEI RNC IAWPS-95 on-line thermal conductivity calculator:

<http://twf.mpei.ac.ru/mcs/worksheets/iapws/wspstCRT.xmcd>.

**Using ζ_{T_R} calculated from the IAPWS-95 model.

4.3.5. Surface Tension

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. The surface tension (σ) is treated as a simple function of temperature, covering the range from the triple-point temperature (273.16K) to the critical temperature (647.096K). The surface tension model will not be presented in detail here. For a full description, see Wolery (2020, Section 5.2.3) or the relevant original works (IAPWS, 2014; Vargaftik et al., 1983).

Here we will again present results of computer verification. Table 5 compares selected values of surface tension from IAPWS (2014, Table 1) with values calculated by H2OI95 v. 1.1. The H2OI95 values match to the precision given by IAPWS (2014, Table 1).

Table 5. Selected values of surface tension (mN·m⁻¹) from IAPWS (2014, Table 1), compared with results obtained from H2OI95.

Temp. °C	Temp. K	IAPWS (2014, Table 1)	H2OI95
0.01	273.16	75.65	75.65
25	298.15	71.97	71.97
50	323.15	67.94	67.94
75	348.15	63.58	63.58
100	373.15	58.91	58.91
125	398.15	53.96	53.96
150	423.15	48.74	48.74
175	448.15	43.30	43.30
200	473.15	37.67	37.67
225	498.15	31.90	31.90
250	523.15	26.04	26.04
275	548.15	20.16	20.16
300	573.15	14.36	14.36

Temp. °C	Temp. K	IAPWS (2014, Table 1)	H2OI95
325	598.15	8.77	8.77
350	623.15	3.67	3.67
370	643.15	0.39	0.39
373.946	647.096	-----	0.00

4.3.6. Dielectric Constant

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 Born functions and Debye-Hückel parameters (Helgeson and Kirkham, 1974ab; Fernández et al., 1997). The IAPWS (1997) model treats the dielectric constant (ϵ) as a function of temperature and density. The relevant equations and constants for the model are given in the source document and the paper by Fernández et al. (1997) and will not be repeated here. It is noted that ρ in these documents refers to density mostly in units of $\text{mol}\cdot\text{m}^{-3}$, not the usual $\text{kg}\cdot\text{m}^{-3}$. In the model equations, density is referred to in units of $\text{mol}\cdot\text{m}^{-3}$.

The dielectric constant, or relative permittivity (permittivity divided by the permittivity of free space), is dimensionless. Permittivity itself has dimensions of $\text{C}^2\cdot\text{J}^{-1}\cdot\text{m}^{-1}$ (C referring to Coulombs). In the model, the permittivity of free space is given by an expression rather than a simple constant. For a full description of the dielectric constant model, see Wolery (2020, Section 5.2.4) or the relevant original works (IAPWS, 1997; Fernández et al., 1997).

Values of the dielectric constant from IAPWS (1997, Table 4) intended for code verification are compared in Table 5.11 with corresponding results from H2OI95. Corresponding values match to the precision shown.

Table 6. Values of the dielectric constant (ϵ) from IAPWS (1997, Table 4), compared with results obtained from H2OI95.

p (MPa)	T (K)	IAPWS (1997)	H2OI95
0.101325	240	104.34982	104.34982
0.101325	300	77.74735	77.74735
10	300	78.11269	78.11269
1000	300	103.69632	103.69632
10	650	1.26715	1.26715
100	650	17.71733	17.71733
500	650	26.62132	26.62132

p (MPa)	T (K)	IAPWS (1997)	H2OI95
10	870	1.12721	1.12721
100	870	4.98281	4.98281
500	870	15.09746	15.09746

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. We will not directly address the partial derivatives here, but they are addressed in detail in Wolery, 2020, Section 5.2.4).

4.3.7. Debye-Hückel Parameters

IAPWS itself is silent on Debye-Hückel parameters. However, they 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_γ and B_γ) 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 (which are also related to the partial derivatives of the dielectric constant).

The basic Debye-Hückel model can be written as:

$$\log \gamma_i = \frac{-A_{\gamma,10} z_i^2 \sqrt{I}}{1 + \hat{a}_i B_\gamma \sqrt{I}} \quad (16)$$

where γ_i is the activity coefficient of the i -th ion, z_i is the charge number of that ion, \hat{a}_i is the ion’s diameter (commonly the “ion size”), I is the ionic strength, $A_{\gamma,10}$ is explicitly the “ A_γ ” parameter for calculating the base ten logarithm of the activity coefficient, and B_γ is the relevant Debye-Hückel “B” parameter. There is also an “ A_γ ” consistent with the use of natural logarithms, which can be represented as $A_{\gamma,e}$.

Pitzer’s (1973) equations use a different model for the limiting law that employs a different “A” parameter denoted as A_ϕ . It is related to the A_γ forms by:

$$A_{\phi} = \frac{A_{\gamma,e}}{3} = \frac{\ln(10) A_{\gamma,10}}{3} \quad (17)$$

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.

For H2OI95 version 1.1, the calculated Debye-Hückel parameters include A_{ϕ} , $A_{\gamma,e}$, $A_{\gamma,10}$, A_V , A_H , B_V , B_V , and B_H . A_H is tabulated as A_H/RT , and B_H as B_H/RT . The “A” and “B” parameters associated with compressibility and heat capacity are not currently treated. These would require higher order partial derivative functions than are normally provided. Fernández et al. (1997) suggest that if higher-order functions such as A_K and A_C are desired, one might utilize numerical differentiation. They include examples of this approach. Although they do not explicitly say this, their tone seems to suggest that a better model for the dielectric constant might be desirable if one were to seriously address such higher-order parameters.

Table 7 compares values of A_{ϕ} ($\text{kg}^{1/2} \text{mol}^{-1/2}$) from Fernández et al. (1977, Table 17) with values calculated using H2OI95. Results match to the precision given by Fernández et al. Similar closeness would be attained for $A_{\gamma,e}$ and $A_{\gamma,10}$, hence no comparisons for those parameters are presented here.

Table 7. Values of the Debye-Hückel limiting law parameter A_{ϕ} ($\text{kg}^{1/2} \text{mol}^{-1/2}$) from Fernández et al. (1997, Table 17), compared with results obtained from H2OI95.

T (K)	10 MPa		100 MPa		1000 MPa	
	Fernández et al. (1997)	H2OI95	Fernández et al. (1997)	H2OI95	Fernández et al. (1997)	H2OI95
300	0.39062	0.39062	0.37505	0.37505	0.28396	0.28396
350	0.43196	0.43196	0.41139	0.41139	0.30807	0.30807
400	0.48972	0.48972	0.45996	0.45996	0.33202	0.33202
450	0.56654	0.56654	0.52081	0.52081	0.35814	0.35814
500	0.67109	0.67109	0.59528	0.59528	0.38630	0.38630
550	0.83030	0.83030	0.68741	0.68741	0.41568	0.41568
600			0.80562	0.80562	0.44557	0.44557
650			0.96577	0.96577	0.47552	0.47552
700			1.1969	1.1969	0.50527	0.50527
750			1.5472	1.5472	0.53474	0.53474
800			2.0669	2.0669	0.56392	0.56392

Table 8 compares values of A_V ($\text{cm}^3 \text{kg}^{1/2} \text{mol}^{-3/2}$) from Fernández et al. (1977, Table 17) with values calculated using H2OI95. Results match closely to the precision given by Fernández et al. Some minor differences at the “last significant figure” level are apparent, but there is no trend in differences, suggesting that these differences are not significant. Most differences are probably due to differences in rounding procedure.

Table 8. Values of the Debye-Hückel parameter A_V ($\text{cm}^3 \text{kg}^{1/2} \text{mol}^{-3/2}$) from Fernández et al. (1997, Table 17), compared with results obtained from H2OI95.

T (K)	10 MPa		100 MPa		1000 MPa	
	Fernández et al. (1997)	H2OI95	Fernández et al. (1997)	H2OI95	Fernández et al. (1997)	H2OI95
300	1.8857	1.8857	1.5854	1.5854	0.70218	0.70217
350	3.0191	3.0191	2.3625	2.3624	0.86445	0.86444
400	5.2234	5.2234	3.7522	3.7521	1.1319	1.1319
450	9.6718	9.6716	6.1132	6.1131	1.4923	1.4923
500	20.023	20.022	10.230	10.229	1.9331	1.9330
550	52.399	52.398	17.800	17.800	2.4520	2.4519
600			32.686	32.686	3.0526	3.0526
650			64.214	64.213	3.7421	3.7420
700			135.69	135.69	4.5293	4.5292
750			299.47	299.47	5.4244	5.4243
800			616.62	616.61	6.4374	6.4373

Table 9 compares values of A_H/RT ($\text{kg}^{1/2} \text{mol}^{-1/2}$) from Fernández et al. (1977, Table 17) with values calculated using H2OI95. Here the results match to the precision given by Fernández et al. (1997)

Table 9. Values of the Debye-Hückel parameter A_H/RT ($\text{kg}^{1/2} \text{mol}^{-1/2}$) from Fernández et al. (1997, Table 17), compared with results obtained from H2OI95.

T (K)	10 MPa		100 MPa		1000 MPa	
	Fernández et al. (1997)	H2OI95	Fernández et al. (1997)	H2OI95	Fernández et al. (1997)	H2OI95
300	0.80315	0.80315	0.72666	0.72666	0.60001	0.60001
350	1.3821	1.3821	1.1891	1.1891	0.65507	0.65507
400	2.1291	2.1291	1.7485	1.7485	0.79737	0.79737

T (K)	10 MPa		100 MPa		1000 MPa	
	Fernández et al. (1997)	H2OI95	Fernández et al. (1997)	H2OI95	Fernández et al. (1997)	H2OI95
450	3.1823	3.1823	2.4212	2.4212	0.98133	0.98133
500	4.9811	4.9811	3.2934	3.2934	1.1563	1.1563
550	9.1593	9.1593	4.5447	4.5447	1.3084	1.3084
600			6.5128	6.5128	1.4388	1.4388
650			9.8437	9.8437	1.5534	1.5534
700			15.739	15.739	1.6584	1.6584
750			25.776	25.776	1.7591	1.7591
800			38.835	38.835	1.8592	1.8592

Fernández et al. (1977) did not address the “B” parameters. There is no set of test values known to be consistent with IAPWS-95 and the IAPWS (2014) dielectric constant model. There is only comparison, which is expected to be approximate, from results obtained from other models. Table 10 compares values for B_γ ($\text{\AA}^{-1} \text{kg}^{1/2} \text{mol}^{-1/2}$) reported by Helgeson and Kirkham (1974b) (hereafter HK74b in the following tables) with results obtained from H2OI95. The comparison is generally good. Again, Helgeson and Kirkham used different models to obtain their results.

Table 10. Values of the Debye-Hückel parameter B_γ ($\text{\AA}^{-1} \text{kg}^{1/2} \text{mol}^{-1/2}$) from Helgeson and Kirkham (1974b) [HK74b], compared with results obtained from H2OI95.

T (C)	Saturation Curve		100 MPa (1 kbar)		500 MPa (5 kbar)	
	HK74b, Table 2	H2OI95	HK74b, Table 2	H2OI95	HK74b, Table 2	H2OI95
25	0.3283	0.3284	0.3281	0.3279	0.3280	0.3236
50	0.3325	0.3326	0.3317	0.3315	0.3304	0.3267
75	0.3371	0.3371	0.3358	0.3355	0.3334	0.3299
100	0.3422	0.3420	0.3402	0.3399	0.3366	0.3333
150	0.3533	0.3528	0.3496	0.3493	0.3435	0.3405
200	0.3655	0.3647	0.3592	0.3594	0.3503	0.3480
250	0.3792	0.3782	0.3686	0.3698	0.3567	0.3553
300	0.3965	0.3950	0.3780	0.3807	0.3629	0.3623
350	0.4256	0.4229	0.3882	0.3925	0.3694	0.3688
400			0.4004	0.4057	0.3766	0.3749
450			0.4154	0.4213	0.3843	0.3805

T (C)	Saturation Curve		100 MPa (1 kbar)		500 MPa (5 kbar)	
	HK74b, Table 2	H2OI95	HK74b, Table 2	H2OI95	HK74b, Table 2	H2OI95
500			0.4321	0.4392	0.3912	0.3858
550			0.4454	0.4569	0.3934	0.3907
600			0.4428	0.4703	0.3842	0.3954

Similar comparisons were made for the parameters B_V ($\text{cm}^3 \text{kg}^{1/2} \text{mol}^{-3/2} \text{\AA}^{-1}$) and B_H/RT ($\text{kg}^{1/2} \text{mol}^{-1/2} \text{\AA}^{-1}$). The comparisons are again quite good. These are not shown here (see Wolery, 2020, Section 5.2.5). The set of Debye-Hückel parameters addressed here in H2OI95 should be sufficient for most problems likely to be encountered in aqueous geochemistry. Indeed, the present set exceeds what is found on most thermodynamic databases that directly support existing geochemical modeling and reactive transport modeling codes.

4.3.8. Melting Pressure and Melting Temperature

The previously described models for the viscosity (IAPWS, 2008) and thermal conductivity (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 a secant method iteration. For further details, see Wolery (2020, Section 5.2.6).

4.3.9. Status of H2OI95 v. 1.1

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 H2OI95 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. This will be placed on GitHub, where the v. 1.0 package is available for download. The actual upload of the v. 1.1 package has been delayed due some GitHub issues. 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 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 customized in a way that is oriented toward geochemists.

5. Summary and FY21 Activities

The H2OI95 code to evaluate the IAPWS-95 equation of state has been revised to calculate additional water properties, most of them described by IAPWS-sanctioned supplementary models. Adding the viscosity model uncovered an error in the IAPWS-95 implementation, which manifested in the calculation of “higher order” properties including compressibility and isobaric heat capacity near the critical point of water. This was corrected, and additional computer verification was carried out. The revised code is version 1.1. A revised code report (Wolery, 2020) has been completed, and the revised software has been released as open-source. Version 1.1 is anticipated to be the last stand-alone version of the code. H2OI95 is now being modified to replace the H2O92d module of SUPCRT92. The plan is to produce a new version of SUPCRT92 called SUPCRTNE, for which other work has been carried out previously. Thus, SUPCRTNE will contain the latest IAPWS-sanctioned models for water properties.

Our plan is to make SUPCRTNE 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 will modify the code output to better support incorporation in data files that will support geochemical modeling and reactive transport codes. We may leave the older equation of state model for water in the SUPCRTNE as an option, at least for some time. 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 SUPCRTNE is expected in mid-FY21.

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). We are aware that NEA, which has followed key data from CODATA for many years, is now preparing its own Ancillary Data volume. Otherwise, we will take key data from other sources tabulated by Wolery and Jové Colón (2017) or more recent pertinent sources, should any be found to exist. We will then revise other data in the SUPCRT data file for consistency with the new key data. This will likely include at least some of the Helgeson

et al., 1978) mineral data. We are intending, however, 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. 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).

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 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 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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