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H2OI95: A Stand-Alone Fortran Code for Evaluating the IAPWS-95 Equation-of-State Model for Water

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This report describes H2OI95, Version 1.0, Build 64.

Abstract

H2OI95 is a stand-alone Fortran code for evaluating the IAPWS-95 equation-of-state model (Wagner and Pruss, 2002) for the thermodynamic properties of water. It further evaluates the corresponding thermochemical properties of water consistent with the CODATA recommendations (Cox et al., 1989). The IAPWS-95 model is based on a model equation for the dimensionless Helmholtz energy for which the primary variables are the *inverse* reduced temperature ($\tau = T_{cr}/T$) and reduced density ($\delta = \rho/\rho_{cr}$). Here T is the absolute temperature (K), ρ is density (kg/m^3), and the subscript “ cr ” refers to the critical point of water (647.096 K and 22.064 MPa pressure in this model, for which ρ_{cr} is $322 \text{ kg}/\text{m}^3$). The code solves four basic types of problems, distinguished by the specified inputs:

1. Temperature (K) and density ($\rho \text{ kg}/\text{m}^3$) or reduced density (δ)
2. Temperature (K) and pressure (MPa).
3. Temperature (K) on the saturation (liquid-vapor equilibrium) curve
4. Pressure (MPa) on the saturation curve

Each type of problem is run using a corresponding input (text) file. All but the first type of problem require iteration. For example, to solve for desired temperature and pressure, the reduced density must be adjusted to give the desired pressure. Iteration is accomplished using the Newton-Raphson method, though the secant method is also used in solving the fourth type of problem. H2OI95 has been used to conduct numerical studies of convergence and the problem of multiple numerical solutions, only some of which correspond to valid results. Obtaining valid results depends mainly on appropriate choice of starting values. The default values in H2OI95 appear to consistently lead to generally desired results. With modification (not addressed here), H2OI95 can be used to support SUPCRT92 (Johnson et al., 1992) and similar codes that compute chemical thermodynamic properties of species and reactions over a wide range of temperature and pressure (273.16-1273K and 0-1000 MPa).

1. Introduction

H2OI95 was written primarily to make the IAPWS-95 model (Wagner and Pruss, 2002; IAPWS, 2016) available in the program SUPCRT92 (Johnson et al., 1992) and other codes that similarly compute chemical thermodynamic properties of species and reactions at various temperatures and pressures. SUPCRT92 (unmodified) uses a combination of two older equation-of-state models, IAPS-84 (Haar et al., 1984) and, near the critical point, the model of Levelt Sengers et al. (1983). IAPWS-95 is recognized by the International Association for the Properties of Water and Steam (IAPWS) is the current standard model, IAPS-84 being the earlier standard. A still earlier equation-of-state model (Keenan et al., 1969) was used in the original SUPCRT program written during 1974 and 1975 (see Johnson et al., 1992). That appears to have represented the first use of an equation-of-state model to calculate the thermochemical properties of water over a wide range of temperature and pressure. The IAPWS-95 model covers a temperature range of 273.16K (the triple point temperature) to 1273K, and a pressure range of 0-1000 MPa. This includes the critical point (647.096 K and 22.064 MPa) and surrounding regions.

IAPWS-95 is the most recent *general and scientific* model adopted by IAPWS. It is not to be confused with IAPWS-IF97 (Wagner et al., 2000), which is the corresponding *industrial formulation*. The industrial formulation is essentially a model fit to the IAPWS-95 model. It was created so that temperature and pressure are the primary variables, instead of temperature and density, which are the primary variables in IAPWS-95. The IAPS-84 and the Keenan et al. (1969) models are analogous in this respect to IAPWS-95, having their own corresponding industrial formulations. The main purpose of the industrial formulations is to avoid the computational burden of iterative calculations required to solve temperature-pressure and similar types of problems using a model based on temperature and density.

Why use IAPWS-95 to compute thermochemical properties instead of using IAPWS-IF97? The former is more accurate (see Wagner and Pruss, 2002; Wagner et al., 2000). Maximum accuracy is desired as minor differences in thermochemical property values may significantly affect the results of thermochemical calculations. The use of the general and scientific model avoids a second issue with its corresponding industrial formulation. The latter uses different mathematical descriptions in different regions of temperature-pressure space, a characteristic that can result in inconsistencies at boundaries or small areas where regions may overlap (see Wagner et al., 2000). The present report does not compare of run times of software implementations of IAPWS-95 and IAPWS-IF97, but it is noted that the run times for problems run in developing and testing H2OI95 were trivial on a modern Windows PC.

H2OI95 is written in Fortran to assist with linking to SUPCRT92. It presently exists as a stand-alone code. The notion is that the main program can be replaced by an appropriate interface routine for incorporation into SUPCRT92 or similar software, using the remaining routines largely as-is, but eliminating much of the associated input/output needed for numerical studies. The FORTRAN used is relatively simple, so that translation into other computer languages should be relatively easy. All variable typing is explicit, and communication of variables among routines is made using only calling sequences.

Prior to developing H2OI95, a search was conducted for existing software for IAPWS-95 that might serve the purpose. Requirements were that the software be in Fortran or something close (such as C or C++), with available source code and no proprietary constraints or other problematic restrictions on usage. No such software was located. Consequently, H2OI95 was written following the model description given by IAPWS (2016). This description is more concise than that given by Wagner and Pruss (

Two existing IAPWS-95 implementations were found that are nonetheless of special interest. One is a part of the NIST on-line Chemistry WebBook entitled “Thermophysical Properties of Fluid Systems” (<http://webbook.nist.gov/chemistry/fluid/>). If the selected species is “water,” this web resource is an IAPWS-95 calculator. Because the user can specify the precision desired in the results, this tool allows high-precision comparison with results from H2OI95 (more so than using printed steam tables). The other implementation of interest is the MATLAB application of Junglas (2008), which includes source code. This will be referenced regarding iterative approach, numerical analysis, and starting values for iterative calculations (but not for comparison of numerical results).

2. The IAPWS-95 Equation-of-State Model

The IAPWS-95 model (Wagner and Pruss, 2002) is based on the following model equation for the dimensionless Helmholtz energy:

$$A = \phi^o(\tau, \delta) + \phi^r(\tau, \delta)$$

This formulation divides the Helmholtz energy into an ideal part (ϕ^o) and a residual part (ϕ^r). Here τ is the *inverse* reduced temperature ($\tau = T_{cr}/T$) and δ is the reduced density ($\delta = \rho/\rho_{cr}$). Here T is the absolute temperature (K), ρ is density (kg/m³), and the subscript “*cr*” refers to the critical point of water (647.096 K and 22.064 MPa pressure in this model). Also in this model, ρ_{cr} is 322 kg/m³. The preceding general and scientific equation-of-state models noted previously also use some form of temperature and

density as the primary variables, though they do not take this exact form. The Helmholtz energy is chosen to define the master equation because equations for all other thermodynamic functions can be obtained by applying various thermodynamic relations to the master equation. In general, these relations involve partial differentiation. A complete description of the relevant equations for the model is given by Wagner and Pruss (2002) and in condensed form by periodic “revised releases” put out by the International Association for the Properties of Water and Steam (IAPWS) on their web site. The most recent of these, IAPWS (2016), was followed in creating H2OI95. Note that IAPWS (2016, Table 1) gives slightly revised values for the constants n_1^o and n_2^o (compare with the original values given in Wagner and Pruss, 2002, Table 6.1).

The basic equations to first deal with in evaluating the model are the set of “ ϕ ” functions. These include ϕ^i and ϕ^r and their first and second order partial derivatives with respect to τ and δ . For the ideal function (ϕ^i) these partial derivatives are $\phi_\delta^i = \frac{\partial \phi^i}{\partial \delta}$, $\phi_{\delta\delta}^i = \frac{\partial^2 \phi^i}{\partial \delta^2}$, $\phi_\tau^i = \frac{\partial \phi^i}{\partial \tau}$, $\phi_{\tau\tau}^i = \frac{\partial^2 \phi^i}{\partial \tau^2}$, and $\phi_{\delta\tau}^i = \frac{\partial^2 \phi^i}{\partial \delta \partial \tau}$. Corresponding partial derivatives apply to the residual function (ϕ^r). See IAPWS (2016, Tables 4 and 5) for the equations to use in evaluating the ϕ functions. These equations are complex and require many constants (see IAPWS, 2016, Tables 1 and 2). The equations and constants are not repeated here.

IAPWS (2016, Table 3) gives equations for the basic thermodynamic functions (pressure, internal energy, entropy, etc.) in terms of the “ ϕ ” functions. For example, the pressure p (MPa) is given by

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

where ρ (kg/m³) and T (K) have been introduced previously, and R is the gas constant (0.46151805 kJ kg⁻¹ K⁻¹ for the IAPWS-95 model). The enthalpy h (kJ kg⁻¹) is given by

$$h = RT(1 + \tau(\phi_\tau^o + \phi_\tau^r) + \delta \phi_\delta^r)$$

and the entropy (kJ kg⁻¹ K⁻¹) by

$$s = R(\tau(\phi_\tau^o + \phi_\tau^r) - (\phi^o + \phi^r))$$

IAPWS (2016, Table 3) gives such formulas for thirteen thermodynamic properties, including the three noted above. It does not give the corresponding equation for the Gibbs energy g (kJ kg⁻¹). However, using the standard relation $g = h - Ts$, one may obtain that

$$g = RT(1 + \phi^o + \phi^r + \delta\phi_\delta^r)$$

It also does not give the corresponding equation for the Helmholtz energy a (kJ kg⁻¹). However, this is given by the following minor modification of the previously noted master equation

$$a = RT(\phi^o + \phi^r)$$

The equations for p , a , and g are of special note here because their partial derivatives with respect to δ are useful in iterative calculations. These derivatives can be obtained from:

$$\frac{\partial p}{\partial \delta} = \frac{p}{\delta} + \rho_{cr}RT\delta(\phi_\delta^r + \delta\phi_{\delta\delta}^r)$$

$$\frac{\partial g}{\partial \delta} = RT(\phi_\delta^o + 2\phi_\delta^r + \delta\phi_{\delta\delta}^r)$$

$$\frac{\partial a}{\partial \delta} = RT(\phi_\delta^o + \phi_\delta^r)$$

Note that no “phi” functions are required other than those in the normally computed set.

3. Types of Problems: Inputs and Outputs

There are four basic types of problems in evaluating an equation-of-state models such as IAPWS-95. All are addressed by H2OI95. These problems are distinguished by the specified inputs:

1. Temperature (K) and density (ρ kg/m³) or reduced density (δ)
2. Temperature (K) and pressure (MPa).
3. Temperature (K) on the saturation (liquid-vapor equilibrium) curve
4. Pressure (MPa) on the saturation curve

These types of problems are also addressed in SUPCRT92 (Johnson et al., 1992) and similar codes .

Problems are specified by text-based input files, examples of which will be noted later. H2OI95 expects an input file named “input”. The code is run simply by entering its name, “h2oi95”. Four pieces of output are produced. The first is screen output. This can be captured to a file using “tee” when running the code. For example, “h2oi95 | tee out” captures the screen output on a file called “out”. The screen output is still written to the screen in the normal fashion. The screen output basically shows how the calculations are progressing. It does not include the full calculated results. Those are written to the “output” file, which is another text-based file. Included on this file are the “thermodynamic” or “thermophysical” results and the corresponding “thermochemical” results. The .csv files can be opened by any common spreadsheet or plotting program. The “thermodynamic” results are those which are native to the equation-of-state model, employing the units used in the model. These are the results that any equation-of-state solver would typically produce. Here for example entropy is on the model scale in which entropy is zero at the triple point and the calculated result is given in units of $\text{kJ kg}^{-1} \text{K}$. The “thermochemical” results are the results translated to standard thermochemical scales and corresponding units (see the Appendix for details). Here entropy is on the absolute or thermochemical scale and the result is given in units of $\text{kJ mol}^{-1} \text{K}$. The “thermodynamic” results are written to a comma-separated-variable (.csv) file called “mtab.csv”, while the corresponding “thermochemical” results are written to another such file called “ctab.csv”.

3.1. Properties as a Function of Temperature and Density

The first type of problem is straightforward, as the inputs match the primary variables of the model. It is simply a matter of evaluating the model equations. In H2OI95, this is done by subroutine EVAI95. More commonly, the model user is interested in results for one of the other three problem types. In these it is necessary to make iterative calculations, adjusting density values so that the problem inputs are satisfied. Calculating properties as a function of temperature and density is generally a step in making such calculations. Calculation of properties from temperature and density can be very useful in numerical studies, as for determining ranges of convergence and analyzing the potential problem of multiple numerical solutions, as will be shown later in this report.

3.2 Calculating Properties as a Function of Temperature and Pressure

The IAPWS-95 model uses temperature and density as its primary variables. This choice facilitates correlation of data (development of an accurate model, as exemplified by IAPWS-95 and many other

equation of state models for fluid substances). However, most model users are interested in thermodynamic properties as a function of temperature and pressure, not temperature and density. To calculate the properties for a given temperature and pressure, it is necessary to assume a starting value for density, calculate the corresponding pressure, and revise values of density and calculated pressure until the desired pressure is found. The most obvious method to apply to this problem is Newton-Raphson iteration (or some related method, such as the secant method). In the case of the Newton-Raphson method, one may write a residual function as

$$\alpha = p - p^*$$

where p is the pressure calculated from a value of δ and p^* is the desired pressure. The Newton-Raphson method generates a corrected value (δ_{i+1} , where i is iteration number) from the formula

$$\delta_{i+1} = \delta_i + c_i$$

where c_i is a correction term obtained from the equation

$$\left(\frac{\partial \alpha}{\partial \delta}\right) c_i = -\alpha_i$$

Here the partial derivative is evaluated using δ_i . This derivative constitutes the Jacobian matrix. Since this problem represents one equation in one unknown, the Jacobian is reduced to a scalar. It is apparent that

$$\frac{\partial \alpha}{\partial \delta} = \frac{\partial p}{\partial \delta}$$

where $\frac{\partial p}{\partial \delta}$ can be obtained as shown previously.

The convergence tolerance is generally placed on the relative error

$$\varepsilon_i = \frac{p_i - p^*}{p^*}$$

For thermochemical calculations, the tolerance itself should be rather tight, say $|\varepsilon_i| \leq 1 \times 10^{-9}$. As will be noted, this is not always achievable, but when it is not, $|\varepsilon_i| \leq 1 \times 10^{-8}$ can generally be achieved.

In H2OI95 this type of calculation is solved by subroutine CALPRE. CALPRE makes successive calls to EVAI95 to evaluate the model equations. There are many ways that one might establish a starting value for δ . This value should be something that will facilitate rapid convergence to the desired solution, which is usually stable fluid satisfying certain constraints (discussed later). The default set of values provided in CALPRE generally appear to assure this. For any calculation for which the temperature is below the critical temperature, it is extremely helpful to know the densities of vapor and liquid on the saturation curve (as discussed later in conjunction with subroutine CALSCT). Thus one may appropriately determine what sort of values are appropriate to vapor-like and liquid-like densities at the desired temperature. It is possible to run CALPRE with user-specified starting density values. This is typically done only in advanced work part of numerical studies. Results may then correspond to other than desired stable fluid (there is a multiple solutions problem), or the calculation may not converge.

The iterative process described above is essentially equivalent to that used in SUPCRT92 (Johnson et al., 1992), which uses for this purpose code borrowed from Haar et al. (1984) for use with the IAPS-84 model. Doubtless most other examples of software for evaluating IAPS-84 or IAPWS-95 also use this. A somewhat different approach is used in the MATLAB application of Junglas (2008), who uses MATLAB's FZERO function to find an iterative solution. FZERO does not use Newton-Raphson, but rather the secant method and related methods that do not require evaluating a formula for a derivative.

The default starting density values provided in CALPRE are somewhat different from the starting values used in SUPCRT92 and Junglas' (2008) MATLAB application (2008). The general problem of starting values and the problems of multiple solutions and non-convergence will be addressed later in this report.

3.3 Calculating Properties on the Saturation Curve

The third and fourth types of problem deal with calculation of properties on the saturation (vapor-liquid equilibrium) curve, which extends from the triple point (273.16K, 0.611657 MPa) up to the critical point (647.096K, 22.064 MPa) (Figure 1). Usually the problem specifies a temperature value. It is then part of the problem to find the corresponding pressure and vapor and liquid densities. Less often, a pressure value is specified in place of one for temperature, in which case the problem includes finding the corresponding temperature.

The saturation curve represents a discontinuity of sort. If a third axis were to be added to represent density, the saturation curve would appear as sort of cliff, with higher values (liquid) above the curve and

lower values (vapor) below it. The difference between the densities of liquid and vapor decreases going from the triple point to the critical point, decreasing rapidly near the critical point (Figure 2). What is shown in Figure 2 is not like a cliff or wall, but a gap. From the surface representing vapor, one could proceed through the gap onto extended vapor surface underlying the liquid surface. Similarly, from the liquid surface, one could step out onto its extension overlying the vapor surface. Very close to the saturation curve, such extended surfaces represent metastable vapor and metastable liquid. The IAPWS-95 and similar models permit this, though most applications developed for the model do not support this. There are two points about this to keep in mind. First, how far these extensions go from the saturation curve is not well known. Second, no data for metastable fluids were used in developing the IAPWS-95 model, so accuracy would be expected to drop off rapidly moving away from the saturation curve.

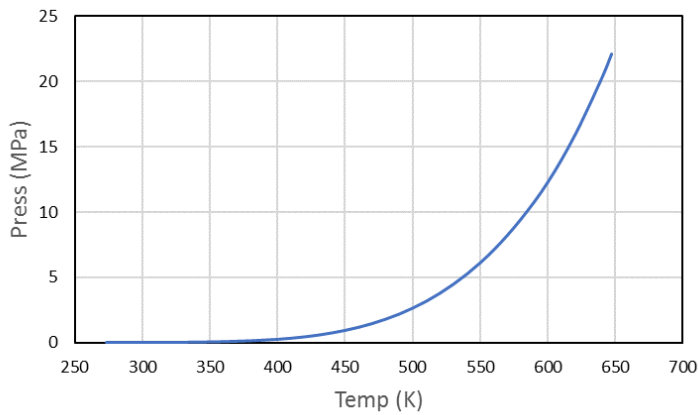


Figure 1. The saturation curve. The triple point is at the lower left end of the curve. The critical point is at the upper right end.

As shown in Figure 2, near the critical temperature (647.096K), the slope of the density versus temperature curve becomes nearly infinite for the vapor curve and nearly negatively infinite for the liquid curve. The saturation curve on the density surface as represented by a three-dimensional plot of density versus temperature and pressure therefore does not resemble a simple tear in the surface at the critical point; if it did, the slopes would approach a common finite value at the critical point. The actual behavior near the critical point is more like a tear combined with a sharp fold; this is associated with extreme behavior of some of the thermodynamic functions (for example, the heat capacity functions c_v and c_p) near the critical point.

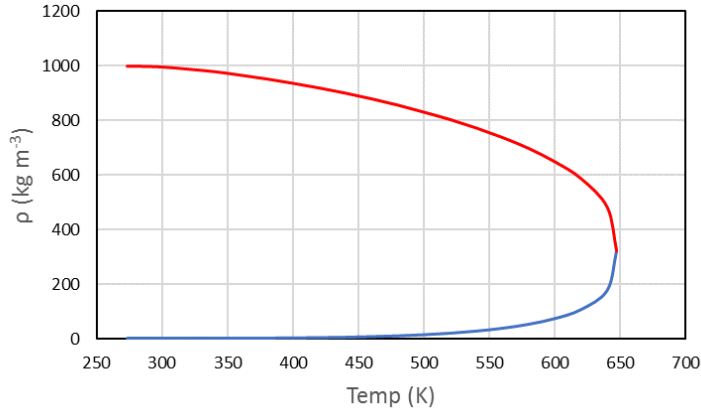


Figure 2. The density of vapor (blue) and liquid (red) on the saturation curve, as a function of temperature.

Wagner and Pruss (2002) cite equations describing the pressure and liquid and vapor densities on the saturation curve (their equations 2.5, 2.6 and 2.7). These equations are formally not part of IAPWS-95. However, they provide an excellent starting point for calculating values consistent with IAPWS-95. They are used for this purpose by Junglas (2008), and very likely by others as well. They will be referred to as the *saturation curve approximation*. An earlier saturation curve approximation also existed for IAPS-84 (Haar et al., 1984). It provided an estimate of the saturation pressure, but not estimates of the vapor and liquid saturation densities.

Consider the problem of finding the thermodynamic properties on the saturation curve where temperature is specified. It is desired to find the saturation pressure (p_S) and the vapor and liquid densities (δ_V and δ_L , respectively). The pressure equation previously introduced can be applied to each of vapor and liquid:

$$p_V = \rho_V RT(1 + \delta_V \phi_\delta^r(\tau, \delta_V))$$

$$p_L = \rho_L RT(1 + \delta_L \phi_\delta^r(\tau, \delta_L))$$

A third equation is required. The vapor and liquid are equilibrium on the saturation curve, therefore

$$g_V = g_L$$

Since these Gibbs energies can be calculated as functions of the respective densities using the Gibbs energy relation previously given, this provides a route to completing the saturation curve calculation. Noting that at saturation $p_V = p_L = p_S$, the right-hand sides of the above pressure equations can be

combined to yield an equation in the densities, matching the dependency in a similar combination for the Gibbs energies. One then has two equations in two unknowns (the densities). Once this system of equations is solved, one can obtain the saturation pressure from either of the pressure equations.

This approach was used by Shi and Mao (2012), who initialize their calculations using the *saturation curve approximation* noted by Wagner and Pruss (2002). This approach appears to work fine in this context. For computational details, see Shi and Mao's (2012) paper. The method is otherwise problematic, as other starting estimates can lead to undesired numerical solutions, such as convergence to the same fluid state for both "liquid" and "vapor." This final fluid state could technically be anywhere in the pressure-temperature field. The equation-of-state model itself only knows "fluid." It does not contain a built-in distinction between vapor and liquid. During the development of H2OI95, this numerical approach was tried and found sometimes to lead to such "single fluid state" results when the *saturation curve approximation* was not used to generate starting values.

To avoid this "single fluid state" issue, one generally uses some form of the so-called Maxwell criterion. This comes in different forms. James Clerk Maxwell's original analysis addresses a model cubic equation of state and deals directly with the notion of work (as in steam engines). A more direct approach for our purposes is to start with the Gibbs energy equality and replace Gibbs energy with Helmholtz energy. Recall that $g = a + pv$. Substituting this for vapor and liquid into the Gibbs energy equality and recognizing that there is only one pressure at saturation leads to:

$$p_M = \frac{(a_L - a_V)}{(v_V - v_L)}$$

where the calculated pressure here is marked as the "Maxwell" pressure. Because the difference of the specific volumes ($v = 1/\rho$) appears in the denominator, an iterative process accounting for this equation cannot converge to a numerical solution in which the "vapor" and "liquid" correspond to the same fluid state. Although including a form of the Maxwell equation is better than omitting it, this still does not eliminate certain other kinds of undesired numerical solutions, for example one where metastable liquid (which is nearly incompressible) is in equilibrium with vapor for some pressure less than the saturation pressure. Thus, it remains important to initialize saturation curve calculations using the *saturation curve approximation*.

The final approach taken in H2OI95 is to define three residual functions in three unknowns (p_S , δ_V , and δ_S). The three functions are

$$\alpha_V = p_V - p_S$$

$$\alpha_L = p_L - p_S$$

$$\alpha_M = p_M - p_S$$

The equations are solved using Newton-Raphson iteration. A 3 x 3 matrix equation is solved for each iteration using Gaussian elimination (formulas for the Jacobian matrix are not given here but can readily be derived or inferred from the H2OI95 source code). Convergence testing is based on the largest magnitude relative error for the three residual functions. The normal convergence tolerance is 1×10^{-9} , the same value used in pressure-temperature calculations. The saturation curve problem for specified temperature is solved by subroutine CALSCT.

As found during testing, there are convergence issues between the triple point temperature (273.16K) and 298.15K and between 647.082K and the critical point temperature (647.096K). In the first instance, the convergence criterion is increased to 1×10^{-8} . In the second instance, the convergence criterion is increased to 1×10^{-7} . In addition, between 647.090K and the critical point temperature, iteration is otherwise stopped after five iterations. These accommodations were found necessary, as at some point further iteration would fail to result in any improvement. This is a characteristic of the equation of state itself in these regions, not something showing a need for an improved numerical method. In the treatment of this kind of problem in SUPCRT92 (which uses the IAPS-84 model), there are similar accommodations. Special accommodations are also made by Junglas (2008) for his treatment of the IAPWS-95 model. In addressing the causes requiring these accommodations, Junglas points to the highly non-cubic form of the model. Further remarks on this subject will be given in the Numerical Studies section of the present report.

Others (Haar et al., 1984; Johnson et al., 1992; Junglas, 2008) use a different numerical approach in which the saturation pressure is first assumed known. The corresponding densities of vapor and liquid are then iteratively determined by applying the pressure equation separately to each phase. This is equivalent to two CALPRE calculations. The saturation pressure value is then adjusted using some form of the Maxwell criterion. Then the densities of the two phases are again determined. This continues until this nested iteration procedure converges. To adjust the saturation pressure value, Junglas (2008) uses the same Helmholtz energy-volume approach previously described. Haar et al. (1984) and Johnson et al.

(1992) [who both address the IAPS-84 model, not IAPWS-95] use a different form based on Gibbs energy and the standard thermodynamic relation $\frac{\partial \Delta G}{\partial p} = -\Delta v$, where the “ Δ ” refers to the vapor-liquid transition.

The saturation curve problem for specified pressure is solved by subroutine CALSCP. The approach is to first estimate the corresponding temperature by inverting the *saturation curve approximation* equation for saturation pressure as a function of temperature. This is another iterative calculation (using the Newton-Raphson method). Once a temperature value is established, the next step is a CALSCT calculation to evaluate the calculated saturation pressure, which is then compared to the specified pressure. The temperature is then corrected using the secant method. This nested approach is less elegant than a direct approach, but it is easy to implement and likely nearly as fast as a direct approach. It avoids the need for certain ϕ functions (higher order derivatives) than are normally obtained. Also, this type of saturation curve problem is usually of less interest than the type in which the temperature is specified.

4. Test Cases

A library of test cases including examples of input files is included with the software. There are three groups of test cases. Those beginning with “VC” are software validation test cases for which results are intended to be compared with mostly high-precision results given by other sources including IAPWS (2016). Those beginning with “TC” include some cases intended for comparison with results of others and additionally some cases addressing performance evaluation. Those beginning with “MC” are more advanced test cases addressing the problem of multiple numerical solutions. One test case beginning with “RC” (RCsar) is included for reference purposes. It calculates results for coexisting vapor and liquid at 298.15K, the thermochemical reference temperature. Results for this temperature are not included in the steam tables of Wagner and Pruss (2002).

Only limited discussion of the full test case library is presented here. Attention here will focus on common examples of the problem type most users would typically address and on more advanced examples of numerical studies, particularly of the issue of multiple numerical solutions for some problems. Some numerical results noted here required several runs over specific density ranges at varying density resolutions. As will be noted, the input files for these runs will not be given in this report, nor are they included in the test case library accompanying the H2OI95 software.

4.1. Common Examples

This section addresses common examples of the type most code users would address. These also include cases addressing software validation. These examples include cases in which any starting values needed for iterative calculations are provided in the code itself. The results obtained correspond to what a user would ordinarily be seeking, data for “stable” fluid such as one would find in steam tables.

4.1.1. The Properties of Liquid Water at 298.15K and 0.1 MPa

The following input file calculates the properties of (liquid) water at 298.15K and 1 bar (0.1 MPa) and at the same temperature and 1 atm (1.01325 bar or 0.101325 MPa). The number of temperature-pressure pairs that can be specified is not limited by the input file format.

```
Input_298
# VC298

# Calculate results for 298.15K and 1 bar pressure.
# The purpose is to validate the thermochemical results
# against the CODATA (Cox et al., 1989) recommendations
# for the thermochemical properties of water. For
# illustrative purposes, results are also obtained for
# 1 atm pressure (1.01325 bar). Pressure must be
# specified in MPa, not bars.

# The following strings are write option switches.

#showphi
#showdetails1
#showdetails2
#showdetails3

    tempk      press (MPa)
298.150      1.000000000d-01
298.150      1.013250000d-01
```

Lines beginning with “#” are treated as comment lines. The input file must begin with a line containing a name, usually the input file name. If the option strings shown in the example are not commented out, they will cause additional information to be written to the code output, which generally consists of screen output and the file named “output”. The next essential line is the header line, here containing the string “tempk press”. The “ (MPa) ” following “press” is optional and is there only as a reminder to input pressure in MPa units. Other potential units cannot be specified here. MPa units are intrinsic to the software. Following the header are lines containing temperature-pressure pairs. Note that temperature must always be given in K.

Partial output (for 298.15K and 0.1 MPa only) is:

```
CALPRE: Temp(K) = 298.1500          tau    = 0.217037062E+01
        press  = 0.100000000E+00 MPa
```

This appears to be liquid.

```
CALPRE: iter= 0, px= 3.169929329E-03, sbetmx= -9.68301E-01
CALPRE: iter= 1, px= 1.000099349E-01, sbetmx= 9.93490E-05
CALPRE: iter= 2, px= 1.000000000E-01, sbetmx= 4.36567E-11
```

```
Temp(K)      press(MPa)
298.1500     0.100000000E+00
```

H2O(liquid)

```
delta      rho(kg/m3)
0.309641938E+01  0.997047039E+03
```

Thermodynamic Results

```
u(kJ/kg)      h(kJ/kg)      s(kJ/kg/K)
0.104818597E+03  0.104918893E+03  0.367199984E+00

a(kJ/kg)      g(kJ/kg)      v(m3/kg)
-0.466207858E+01 -0.456178241E+01  0.100296171E-02

cv(kJ/kg/K)   cp(kJ/kg/K)   w(m/s)
0.413756934E+01  0.418131883E+01  0.149669916E+04

mu(K/MPa)     dt(kJ/kg/MPa)  bs(K/MPa)
-0.221467031E-03  0.926024267E-06  0.184002805E-04

kt(/MPa)
0.452463259E-06
```

Thermochemical Results

```
g(kJ/mol)      h(kJ/mol)      s(J/mol/K)
-237.1403      -285.8300      69.9500

a(kJ/mol)      u(kJ/mol)      v(m3/mol)
-233.4724      -282.1621      1.80686E-05

cv(J/mol/K)    cp(J/mol/K)    dt(kJ/mol/Mpa)
4137.5693      4181.3188      1.66826E-08
```

Here CALPRE is the subroutine that carries out this calculation. As shown, the calculation only required two iterations. The residual betamx is the relative error in the pressure. The normal convergence tolerance is 1×10^{-9} , which is very tight in part to support software validation. The high precision of the results shown is also intended to support validation. The thermochemical results for enthalpy (h (kJ/mol)) and entropy (s (J/mol/K)) exactly match the recommended CODATA (Cox et al.,

1989) values. Here `rho` is density and `delta` (δ) is the reduced density (density divided by the critical point density). The other thermodynamic and thermochemical results shown use standard symbolic representation (e.g., `a` is Helmholtz energy, `g` is Gibbs energy, `cp` is heat capacity at constant pressure). Explanation of all symbols except `kt` (compressibility) is given by Wagner and Pruss (2002) and IAPWS (2016). Some of the thermodynamic and thermochemical values associated with the same symbol are different not only in units, but also tied to different arbitrary conventions. For example, this is true for the Gibbs energies, enthalpies, Helmholtz energies, internal energies (`u`), and entropies.

4.1.2. A Validation Test Case: Calculated “phi” Functions

Another type of input file is illustrated by the following validation test case. Most of the necessary discussion of what this test case is about is included in the input file itself. The basic purpose is to compare with high-precision values for the ϕ functions given by IAPWS (2016). Here the “showphi” option is active. Note that in this example, density (“rho”) is specified instead of pressure. In this mode, density can also be specified as “delta”. This type of calculation is done by subroutine CALDLT, which basically just calls EVAI95 to make a direct (non-iterative) evaluation of the equation-of-state model equations.

```
input_wt6
# VCwt6

# Compare results with Table 6 of IAPWS (2016), "Revised Release
# on the IAPWS Formulation 1995 for the Thermodynamic Properties
# of Ordinary Water Substance for General and Scientific Use".
# This document is available from the iapws.org web site as
# document IAPWS R6-95 (IAPWS95-2016.pdf). The purpose is to
# validate the calculation of the phi functions, for 500K and
# a density of 838.0250 kg/m3. Running the software with
# with "showphi" causes the phi functions to be written on the
# output. Density must be specified in kg/m3, not g/cm3.

# The contents of Table 6 from IAPWS (2016) partially duplicate
# Table 6.6 of Wagner and Pruss (2002). The latter table also
# includes a test at 647K and density of 358 kg/m3. Our results
# for phir, phird, and phirdd not precisely match theirs for
# these conditions. We believe it likely that IAPWS (2016)
# dropped this part of the original test for a reason, though
# they do not give one. This close to the critical point, minor
# differences may result from differences in numerical methods
# and tolerances. Results may also be compared with results
# (for liquid) from Table 13.1 of Wagner and Pruss (2002).
# However, their results are given to less precision.

# For the case at 500K and density of 838.0250 kg/m3, the result
# for phi0 given by Wagner and Pruss (2002) is off by one in the
```

```

# last decimal place from the value given by IAPWS (2016).

# The following strings are write option switches.

showphi
#showdetails1
#showdetails2
#showdetails3

tempk    rho (kg/m3)
500.000  0.8380250d+03
647.000  0.3580000d+03

```

The relevant output (for the 500K case only, for the reasons noted in the input file text) is

```

tempk = 0.500000000E+03    rho = 0.838025000E+03
delta = 0.260256211E+01    tau = 0.129419200E+01

```

phi functions

```

phi0    = 0.204797733E+01    phir   = -0.342693206E+01
phi0d   = 0.384236747E+00    phird  = -0.364366650E+00
phi0dd  = -0.147637878E+00   phirdd = 0.856063701E+00
phi0t   = 0.904611106E+01    phirt  = -0.581403435E+01
phi0tt  = -0.193249185E+01   phirtt = -0.223440737E+01
phi0dt  = 0.000000000E+00    phirdt = -0.112176915E+01

```

4.1.3. Saturation Curve Properties as a Function of Temperature

The main “saturation curve” option (specified temperature or temperatures) is illustrated by the following input file:

```

input_sct
# VCscct

# Calculate results for specified temperatures along the
# saturation curve, using the "psat" option. The purpose
# is to compare results with those given in Table 13.1
# of Wagner and Pruss (2002).

# The following strings are write option switches.

#showphi
#showdetails1
#showdetails2
#showdetails3

tempk    psat
273.160
274.000
280.000

```

300.000
320.000
340.000
360.000
380.000
400.000
420.000
440.000
460.000
480.000
500.000
520.000
540.000
560.000
580.000
600.000
620.000
640.000
647.096

This “psat” option utilizes specified temperature values (the last value is 647.096K, the critical point temperature). The saturation pressure and the properties of both saturated vapor and saturated liquid are calculated. In H2OI95, the iterative calculation here is done by simultaneously solving three equations in three unknowns as described previously.

Convergence is illustrated by the following snippet of standard output:

```
CALSCT: Temp(K) = 400.0000          tau      = 0.161774000E+01

CALSCT: iter= 0, psat= 2.457652635E-01, betamx= 1.25696E-02
CALSCT: iter= 1, psat= 2.457693473E-01, betamx= 6.81047E-08
CALSCT: iter= 2, psat= 2.457693456E-01, betamx= 3.36621E-12

CALSCT key results:

Temp(K)          press (MPa)
400.0000         0.245769346E+00

H2O (vapor)

      delta          rho (kg/m3)
0.425281845E-02  0.136940754E+01

H2O (liquid)

      delta          rho (kg/m3)
0.291144733E+01  0.937486039E+03
```

Here CALSCT is the subroutine that carries out this type of calculation. The final value of psat is the calculated saturation pressure.

As implied in the input file text, one of the purposes of this test case is to calculate results that should match those in Table 13.1 of Wagner and Pruss (2002). The full fluid properties output appears on the output file (not shown here) and the corresponding mtab.csv file (also not shown here).

4.1.4. Saturation Curve Properties as a Function of Pressure

The other saturation curve option is that in which the pressure is specified instead of the temperature. An input file illustrating this is:

```
input_scp
# TCscp

# Calculate the saturation temperature and corresponding
# results for specified pressure values. This is an example
# of the "tsat" option. The purpose is to examine convergence
# behavior and to illustrate this option. Pressure must be
# specified in MPa, not bars.

# The following strings are write option switches.

#showphi
#showdetails1
#showdetails2
#showdetails3

    press (MPa)    tsat
    0.0100
    0.0500
    0.1000
    0.5000
    1.0000
    5.0000
    10.0000
    15.0000
    20.0000
```

This “tsat” option is implemented by making “psat” calculations for putative temperature values, and correcting the putative temperature to produce the specified pressure, using the nested approach described earlier. Correction of the temperature is done using the secant method, as previously noted. An advantage of this nested approach is that the calculation for any putative temperature utilizes coding in subroutine CALSTC that deals with the previously described issues regarding convergence in certain ranges of temperature.

A partial standard output snippet shows that convergence of the secant method is rapid:

```
CALSCP: press = 0.100000000E+00 MPa
```

```
CALSCP: iter= 0, tempk= 372.7559, betamx= 4.27316E-07
CALSCP: iter= 1, tempk= 374.7559, betamx= 7.36995E-02
CALSCP: iter= 2, tempk= 372.7559, betamx= 1.24792E-08
CALSCP: iter= 3, tempk= 372.7559, betamx= 9.99201E-15
```

CALSCP key results:

```
Temp (K)          press (MPa)
372.7559          0.1000000000E+00
```

H2O (vapor)

```
delta            rho (kg/m3)
0.183336640E-02  0.590343980E+00
```

H2O (liquid)

```
delta            rho (kg/m3)
0.297711648E+01  0.958631506E+03
```

Here CALSCP is the subroutine that carries out this type of calculation. Iteration in CALSTC done for each CALSCP iteration is not shown here.

There are other test cases in the library which also address software validation, but those will not be discussed in the present report. Some involve additional software validation tests specified by IAPWS (2016). Others involve comparison with the published steam tables (Wagner and Pruss, 2002) or with high-precision results obtained from the NIST on-line calculator “Thermophysical Properties of Fluid Systems” (<http://webbook.nist.gov/chemistry/fluid/>).

4.2. Numerical Studies

The complexity of the equation-of-state model along with the need for iterative calculations to solve common problem types suggests that there would be some minimum of pertinent literature regarding the numerical aspects of applying IAPWS-95 (or similar models, including the earlier IAPS-84 of Haar et al., 1984, and the even earlier model of Keenan et al., 1969). Such literature would focus on details of numerical methods, convergence properties including requirements on starting estimates of density, and an examination of the uniqueness and significance of numerical solutions. In fact, there is very little documented information of such studies. Haar et al., (1984) included code to evaluate the IAPS-84 model. Some details including starting estimates can be obtained from this. However, there is no discussion of how these values were established. Essentially the same coding is used in SUPCRT92 (Johnson et al., 1992). Junglas (2008) presented original numerical studies on the problem of obtaining saturation curve

properties as a function of temperature but did not address the general case of specified pressure and temperature.

Wagner and Pruss (2002) presented no numerical studies, instead concentrating on how well the IAPWS-95 model reproduced experimental measurements. Clearly, they must have made some numerical studies in creating the software used to develop their model. Prof. Wagner has made code available to academic investigators, but with restricted distribution and apparently no additional software documentation.

Obtaining results for stable fluid from iterative calculations is mainly dependent on the choice of starting values for density, and to a lesser degree on details of the iteration procedure. Precisely what Wagner and Pruss (2002) did in this regard appears to be undocumented. Anyone developing an implementation of IAPWS-95 can do their own numerical studies, as did Junglas (2008) for saturation curve calculations. Some additional numerical studies will be presented here, with a special focus on multiple numerical solutions and how to identify solutions that are non-physical.

4.2.1. Multiple Solutions for Water at 500K and 25 MPa

The following input file was created for finding the properties of water at 500K (226.85°C) and 25 MPa. The temperature is a “mid-range” value in relation to the saturation curve. The pressure is slightly higher than the critical pressure (22.064 MPa). Stable fluid in this region would commonly be referred to as “compressed liquid.” This input file specifies the density values to use as starting estimates. The file was created by making multiple runs, trying various values. The process included finding “boundary” values for obtaining specific numerical solutions.

```
input_clx
# MCclx

# Calculate results for 500K and 25 MPa
# (in the compressed liquid field), specifying
# different starting values for the density
# (rho_g, kg/m3). The purpose is to examine convergence
# behavior and to check for multiple solutions.
# Here three solutions are found, one of which
# is the expected solution for stable compressed liquid.
# The second solution might be thought of as corresponding
# to "compressed metastable vapor," although this represents
# an extrapolation and may not be accurate. It does not
# yield a valid result for the speed of sound. The third
# solution gives a negative absolute (thermochemical)
# entropy. Thus, it is a numerical solution with no
# realistic physical interpretation.
#
# The following strings are write option switches.
```

```

#showphi
#showdetails1
#showdetails2
#showdetails3

      tempk      press (MPa)      rhog (kg/m3)

# High density solution
500.      25.00000000d+00      5000.
500.      25.00000000d+00      2000.
500.      25.00000000d+00      1100.
500.      25.00000000d+00      1000.
500.      25.00000000d+00      900.
500.      25.00000000d+00      800.
500.      25.00000000d+00      710.572

# Mid density solution
500.      25.00000000d+00      710.571
500.      25.00000000d+00      700.
500.      25.00000000d+00      600.
500.      25.00000000d+00      500.
500.      25.00000000d+00      400.
500.      25.00000000d+00      388.429

# No solution
500.      25.00000000d+00      388.428
500.      25.00000000d+00      385.
500.      25.00000000d+00      380.
500.      25.00000000d+00      375.703

# Low density solution
500.      25.00000000d+00      375.702
500.      25.00000000d+00      300.
500.      25.00000000d+00      290.439

# No solution
500.      25.00000000d+00      290.438
500.      25.00000000d+00      200.
500.      25.00000000d+00      100.

```

The pertinent results are that over a range of starting density values from 100 to 5000 kg/m³, three solutions were found, each characterized by a specific range of starting values. Two ranges were also found in which no solution was found. Starting values from 710.572 to 5000 kg/m³ led to a “high density” solution characterized by a final density of 850.558202 kg/m³. Starting values from 388.429 to 710.571 kg/m³ led to a “mid density” solution with a density of 621.049863 kg/m³. Starting values from 290.439 to 375.702 kg/m³ led to a “low density” solution with a density of 331.832991 kg/m³.

When convergence was obtained, it was generally rapid, requiring 4-16 iterations. As would be expected, iteration number increased when starting farther from the obtained solution. Part of the screen output for the starting value of 2000 kg/m³ illustrates convergence behavior:

```
CALPRE: Temp (K) = 500.0000          tau    = 0.129419200E+01
        press  = 0.250000000E+02 MPa

        rhog   = 0.200000000E+04 kg/m3 (starting value)
```

This appears to be compressed liquid.

```
CALPRE: iter= 0, px= 2.238910656E+04, sbetmx= 8.94564E+02
CALPRE: iter= 1, px= 6.488315591E+03, sbetmx= 2.58533E+02
CALPRE: iter= 2, px= 2.008598643E+03, sbetmx= 7.93439E+01
CALPRE: iter= 3, px= 6.061533203E+02, sbetmx= 2.32461E+01
CALPRE: iter= 4, px= 1.729760662E+02, sbetmx= 5.91904E+00
CALPRE: iter= 5, px= 5.224314248E+01, sbetmx= 1.08973E+00
CALPRE: iter= 6, px= 2.690545502E+01, sbetmx= 7.62182E-02
CALPRE: iter= 7, px= 2.501200918E+01, sbetmx= 4.80367E-04
CALPRE: iter= 8, px= 2.500000049E+01, sbetmx= 1.95018E-08
CALPRE: iter= 9, px= 2.500000000E+01, sbetmx= -2.10321E-14
```

```
Temp (K)          press (MPa)
500.0000          0.250000000E+02
```

H2O (compressed liquid)

```
delta          rho (kg/m3)
0.264148510E+01  0.850558202E+03
```

The principal question is, what is the significance of three numerical solutions? The “mid density” solution was accompanied by the following messages:

```
WARNING, PRESSURE DERIVATIVE WITH RESPECT TO
DENSITY IS LESS THAN ZERO. HAVE AN UNSTABLE SOLUTION.
```

```
WARNING -- SPEED OF SOUND VALUE IS NOT POSITIVE.
MAY HAVE A NON-PHYSICAL SOLUTION.
```

A negative value for the derivative of the pressure with respect to the density implies an unstable state (see for example Junglas, 2008). This condition is more often noted in conjunction with numerical solutions for density values that lie between the densities of vapor and liquid on the saturation curve, but it is not uniquely tied to that context. A negative value for this derivative corresponds to a negative value of the compressibility [$\kappa = \delta / (\partial p / \partial \delta)$]. In the IAPWS-95 model, the square of the speed of sound is calculated from the “phi” functions. In this instance, the square had a negative value. Therefore, a valid value for the speed of sound was not obtained. Therefore, the “mid density” solution is non-physical.

The “low density” solution was accompanied by the following message:

```
WARNING -- THERMOCHEMICAL ENTROPY VALUE IS NOT POSITIVE.
MAY HAVE A NON-PHYSICAL SOLUTION.
```

A thermochemical or absolute entropy must have a positive value. Therefore, the “low density” solution is also non-physical. A typical calculator for evaluating IAPWS-95 would not produce a value for the absolute entropy. In this situation, the non-physical nature of the “low density” solution might not be readily apparent if such a solution were to be calculated.

The “high density” solution shows no anomalies. Also, the results for this solution match the corresponding results given in the steam tables (Table 13.2) of Wagner and Pruss (2002). This is the desired solution. The results of this study indicate that a liquid-like density value is required to converge to the desired result. Per Table 13.1 of Wagner and Pruss (2002), the density of liquid on the saturation curve is 831.313 kg/m³, which suggests a minimum value to use in the present case. Thus, when a calculation for the properties of water at any temperature below the critical temperature (647.096K) and any pressure is made, it is very useful in constructing appropriate starting density values to know the density values on the saturation curve. H2OI95 and probably most if not all other calculators for IAPWS-95 and similar equation-of-state models calculate the saturation curve values for this purpose when solving this type of problem. Some may use values obtained from a saturation curve approximation; others, including H2OI95, use refined values starting from such. Either kind seems adequate.

Table 1 summarizes some of the key results from these calculations. In addition to the points already raised, the “low density” solution has a very low value for compressibility and a very high value for the speed of sound. The mid density solution has thermochemical entropy and Gibbs energy values similar to those of the “high density” solution. A key point to raise here is that the Gibbs energy value cannot be used to identify the desired solution. One might expect that the solution with the lowest such value would be the desired one, as this would seem to be the most thermodynamically stable. However, the “low density” solution here has the lowest Gibbs energy value, which appears to be absurdly low.

Table 1. Partial results for water at 500K and 25 MPa. Cells highlighted in orange contain unrealistic results.

| Solution | ρ kg m ⁻³ | κ MPa ⁻¹ | w m s ⁻¹ | S J kg ⁻¹ K ⁻¹ | G kJ mol ⁻¹ |
|--------------|------------------------------|---------------------------------|-------------------------------|---|----------------------------|
| High density | 850.558202 | 0.930558751 x 10 ⁻⁶ | 0.133010698 x 10 ⁴ | 109.1009 | -255.0398 |
| Mid density | 621.049863 | -0.487483957 x 10 ⁻⁶ | NC* | 111.8598 | -254.5668 |
| Low density | 331.832991 | 0.275002785 x 10 ⁻¹⁰ | 0.338667401 x 10 ⁶ | -2.03222 x 10 ⁶ | -4.80574 x 10 ⁴ |

*Not calculated ($w^2 \leq 0$)

An issue is how can one be confident that an IAPWS-95 calculator will consistently produce results for stable fluid from an iterative calculation, particularly when using a proprietary calculator whose details regarding exact iterative procedure and starting values for density are unknown. This concern is largely mitigated if the calculator has been extensively compared with the steam tables of Wagner and Pruss (2002). One would hope that Wagner and Pruss took sufficient care to assure that the development of IAPWS-95 itself was not affected by convergence to any undesired numerical solutions. Although there seems to be no documentation directly addressing this point, the extensive comparison with experimental data in their paper suggests that no problems of this type occurred.

4.2.2. Water at 500K over a Wide Range of Pressure

Another way of analyzing this problem is to calculate the curve of pressure versus density and note how many times the curve is intersected by the horizontal line representing the pressure of interest. Figure 3 shows the calculated curve for 500K over the density range 0 to 1200 kg/m³ and for pressure in the range -400 to 1000 MPa. The full range of calculated pressure cannot be shown without losing necessary detail. The behavior of the curve is highly non-cubic. Calculated pressure can vary over many orders of magnitude, and exhibit both positive and negative values. The pressure curve extends well beyond the boundaries of the figure. The three numerical solutions for 25 MPa (low, mid, and high density solutions) are marked on the diagram. Several runs, each covering a different part of the density range and varying in density resolution, were used to generate this figure. Input files for these runs are not given here, nor are they included in the test case package.

One can see that for higher pressures (up to at least 1000 MPa) and for somewhat lower pressure, there will also be three numerical solutions. For still lower pressures, the associated lines may intersect the portion of the pressure-density curve at lower density values (the part of the curve in the lower left-hand corner of Figure 3). Where that is the case, there may be up to five numerical solutions for a given pressure. It will be shown that, in general, only one solution is physically valid, or two, if the pressure is the saturation pressure for the given temperature.

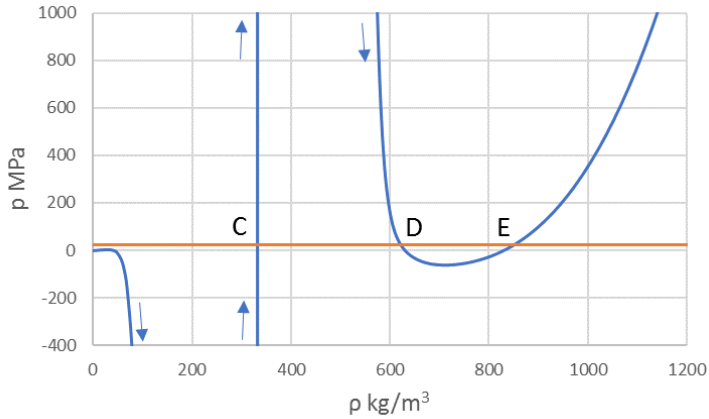


Figure 3. Pressure as a function of density (blue) at 500K. Arrows are shown to indicate curve direction moving outside the field of view. The line for 25 MPa is shown in red. For this pressure, C = low density solution, D = mid density solution, and E = high density solution.

Figure 4 depicts the part of the pressure curve in the bottom left portion of Figure 3. The violet line represents the saturation pressure (2.64 MPa). This is much lower than the 25 MPa shown by the red line in Figure 3. The 25 MPa line is not shown here because the pressure scale in Figure 4 only extends to 10 MPa. At saturation pressure, two numerical solutions are evident in this range. The higher density portion of the pressure curve in Figure 3 extends down past the saturation pressure (past zero pressure, for that matter). Therefore, for the problem of finding solutions for the saturation pressure, there are another three numerical solutions (like C, D, and E in Figure 3, but adjusted to the saturation pressure).

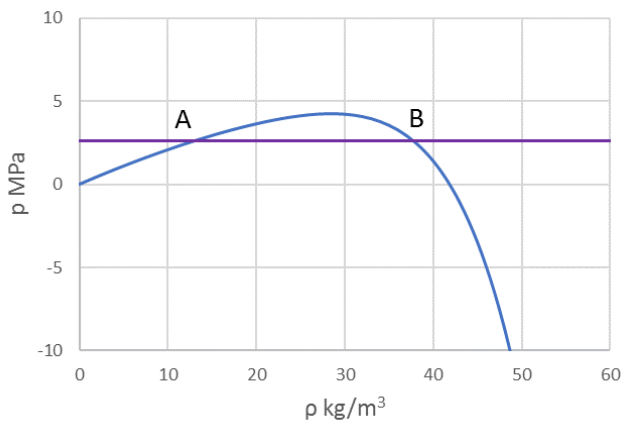


Figure 4. Pressure as a function of density (blue) and the saturation pressure (violet) at 500K. Points A and B mark numerical solutions in this range. Point A marks the physically valid solution for vapor. Point B marks an unstable solution (pressure decreasing with increasing density).

For slightly higher pressure for which the corresponding line would touch the top of the curve shown in Figure 4, there would be four numerical solutions. Above that pressure, there would be three such solutions.

For the case of saturation pressure as exemplified in Figure 4 and implied by Figure 3, one would assume that the solutions for saturated vapor and saturated liquid are the only valid ones. To higher accuracy, the saturation pressure is 2.63919587 MPa. The five numerical solutions were calculated using this more accurate value. Point A represents the stable saturated vapor, while the adjusted (to the saturation pressure) point E represents the stable saturated liquid. Point B and the adjusted point D have negative slope of pressure versus density and are therefore unstable. In addition, point B has a negative value for the heat capacity at constant pressure, while the adjusted point D has a negative value for the square of the speed of sound. The adjusted point C has a negative value for the thermochemical (absolute) entropy. This disqualified solution has the lowest calculated Gibbs energy, again showing that the Gibbs energy cannot be used to identify a valid solution.

Some analysis is required to assure that any calculated numerical solutions have physical meaning. Four methods of disqualifying numerical solutions have been noted. These are (a) the calculated derivative of pressure with respect to density is negative, (b) a speed of sound value cannot be obtained because the calculated square is negative, (c) the calculated thermochemical (absolute) entropy is not positive, and (d) the heat capacity at constant pressure (c_p) is not positive. A negative pressure is disqualifying, but one is not likely to specify a negative value for the desired pressure. Unfortunately, the lowest value of calculated Gibbs energy cannot be used to identify which of a set of numerical solutions corresponds to the desired one. There may be disqualifying factors other than those noted here, but these are the main ones that have been observed in testing H₂O I95 and they appear to be sufficient.

4.2.3. Multiple Solutions for Water at 298.15K and 0.1 MPa.

The following input file was created for finding the properties of water at 298.15K (25°C) and 0.1 MPa (1 bar), the thermochemical reference temperature and pressure. The temperature is a “low” value in relation to the saturation curve. The pressure is higher than the saturation pressure at this temperature. Stable fluid in this region would therefore be referred to as simply “liquid.” This input file specifies the density values to use as starting estimates. The file was created by making multiple runs, trying various values. The process included finding “boundary” values for obtaining specific numerical solutions, using a method perhaps described as interval-halving by hand.

```

input_rtp
# MCrtip

# Calculate results for 298.15K and 1 bar pressure,
# specifying different starting values for the density
# (rhog, kg/m3). The purpose is to examine convergence
# behavior and to check for multiple solutions.
# Here two solutions are found, one of which is the
# expected solution for liquid water. The other
# solution can be interpreted as representing metastable
# vapor, although this is technically an extrapolation
# and may not be accurate.

# The following strings are write option switches.

#showphi
#showdetails1
#showdetails2
#showdetails3

      tempk      press (MPa)      rhog (kg/m3)
298.150  1.000000000d-01  5000.
298.150  1.000000000d-01  2000.
298.150  1.000000000d-01  1000.
298.150  1.000000000d-01  900.
298.150  1.000000000d-01  894.327

      298.150  1.000000000d-01  894.326
      298.150  1.000000000d-01  800.
      298.150  1.000000000d-01  600.
      298.150  1.000000000d-01  400.
      298.150  1.000000000d-01  380.927

      298.150  1.000000000d-01  380.926
      298.150  1.000000000d-01  200.
      298.150  1.000000000d-01  100.
      298.150  1.000000000d-01  10.

```

The pertinent results are that over a range of starting density values from 10 to 5000 kg/m³, two solutions were found, each characterized by a specific range of starting values. One range was also found in which no solution was found. Starting values from 894.327 to 5000 kg/m³ led to a “high density” solution characterized by a final density of 997.047039 kg/m³. Starting values from 380.927 to 784,325 kg/m³ led to a “mid density” solution characterized by a density of 861.841021 kg/m³. Starting values from 10 to 380.926 kg/m³ did not lead to a numerical solution. In other words, no “low density” solution was found. However, it will be shown below that it does technically exist.

The mid density solution is not valid, as the derivative of pressure with respect to density is less than zero (indicating an unstable solution). Furthermore, this solution does not have a valid value for the speed of sound. The high density solution has no disqualifying characteristics and is thus the desired solution.

4.2.4. Water at 298.15K over a Wide Range of Pressure

Figure 3 shows the calculated pressure-density curve for 298.15 over the density range 0 to 1400 kg/m³ and for pressure in the range -400 to 1000 MPa. As was the case for 500K, the full range of calculated pressure cannot be shown without losing necessary detail. The pressure curve again extends beyond the boundaries of the figure. The three numerical solutions for 25 MPa (low, mid, and high density solutions) are marked on the diagram. Again, multiple runs were required to generate this figure, and the corresponding input files are not given here or included in the test case package.

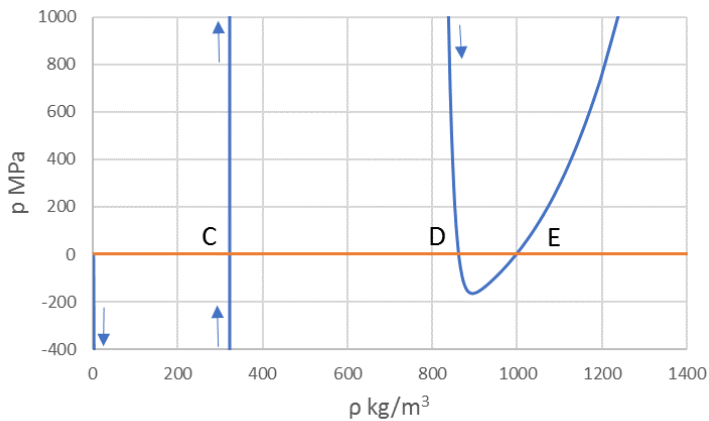


Figure 5. Pressure as a function of density (blue) at 298.15K. Arrows are shown to indicate curve direction moving across the field of view. The line for 0.1 MPa is shown in red. For this pressure, C = low density solution, D = mid density solution, and E = high density solution.

In section 4.2.3 (“MCrtp”), the iterative calculations to find numerical solutions failed to find the low density solution marked “C” in Figure 5. Additional iterative calculations were made to explore this issue. Starting with a density value of 321.999 kg/m³ produced the following results taken from the output file:

```
CALPRE: Temp (K) = 298.1500          tau    = 0.217037062E+01
          press  = 0.100000000E+00 MPa

          rhog   = 0.321999000E+03 kg/m3 (starting value)
```

This appears to be liquid.

```
CALPRE: iter= 0, px= -1.295824659E+13, sbetmx= -1.29582E+14
CALPRE: iter= 1, px= 1.408383723E+08, sbetmx= 1.40838E+09
CALPRE: iter= 2, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 3, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 4, px= -8.780838300E+01, sbetmx= -8.79084E+02
```

```
CALPRE: iter= 5, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 6, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 7, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 8, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 9, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 10, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 11, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 12, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 13, px= -8.780838300E+01, sbetmx= -8.79084E+02
```

CALPRE: ITERATION IS NOT LEADING TO IMPROVEMENT.

```
MAX NORM betamx = 8.791E+02, TOLERANCE btxtol = 1.000E-09
MAX NORM dltamx = 2.107E-17, TOLERANCE deltol = 1.000E-12
```

CALPRE: ITERATION FAILED.

The first pressure (“px”) calculated corresponds to the starting density value. This pressure value is negative with quasi-infinite magnitude. Note that the calculated pressure appears to converge to a value of about -87.8084 MPa, which is not the desired pressure of 0.1 MPa.

A seemingly similar result is obtained for a starting density value of 322.000 kg/m³. The corresponding results taken from the output file are

```
CALPRE: Temp (K) = 298.1500          tau    = 0.217037062E+01
        press    = 0.100000000E+00 MPa
        rhog     = 0.322000000E+03 kg/m3 (starting value)
```

This appears to be liquid.

```
CALPRE: iter= 0, px= 1.813767579E+09, sbetmx= 1.81377E+10
CALPRE: iter= 1, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 2, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 3, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 4, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 5, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 6, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 7, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 8, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 9, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 10, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 11, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 12, px= -8.780838300E+01, sbetmx= -8.79084E+02
CALPRE: iter= 13, px= -8.780838300E+01, sbetmx= -8.79084E+02
```

CALPRE: ITERATION IS NOT LEADING TO IMPROVEMENT.

```
MAX NORM betamx = 8.791E+02, TOLERANCE btxtol = 1.000E-09
MAX NORM dltamx = 2.107E-17, TOLERANCE deltol = 1.000E-12
```

CALPRE: ITERATION FAILED.

This resembles the results for the case shown previously. However, the first calculated pressure is now a positive number with very large, nearly quasi-infinite magnitude. The curve segment in Figure 5 associated with the problematic solution is a line with nearly infinite slope. Interestingly, the calculated pressure similarly converges to the same incorrect value. Both calculations terminate with the report that “MAX NORM dltamx = 2.107E-17”. The value reported here is the magnitude of the final Newton-Raphson correction, which about matches the machine epsilon for 64-bit arithmetic.

The problem is that 64-bit arithmetic is insufficient to obtain convergence within normal tolerances for such a steep curve. Because all starting values close to the solution converge to the same finite pressure value, any attempt to further refine the precision of the starting estimates for density, as by interval halving, would be a futile exercise, as the precision of the specified starting value would eventually run up against the machine epsilon (maximum allowed precision in the working calculations). The calculated thermodynamic (absolute) entropy in this neighborhood of density has a negative quasi-infinite value of $\sim -1.07 \times 10^{18} \text{ J mol}^{-1} \text{ K}^{-1}$. Thus, this numerical solution is non-physical.

The part of the pressure-density curve in the lower left-hand corner of Figure 5 (which is barely visible there) is shown in expanded detail in Figure 6. This figure is analogous to Figure 4, which was for 500K. Two numerical solutions are found here at the saturation pressure of $3.16992934 \times 10^{-3} \text{ MPa}$ (the previous pressure of interest of 0.1 MPa is off the scale here). The solution on the left (A) is again the valid solution for saturated vapor, while the solution on the right (B) is an unstable solution. Point E from Figure 5, adjusted to the saturation pressure, is the valid solution for saturated liquid.

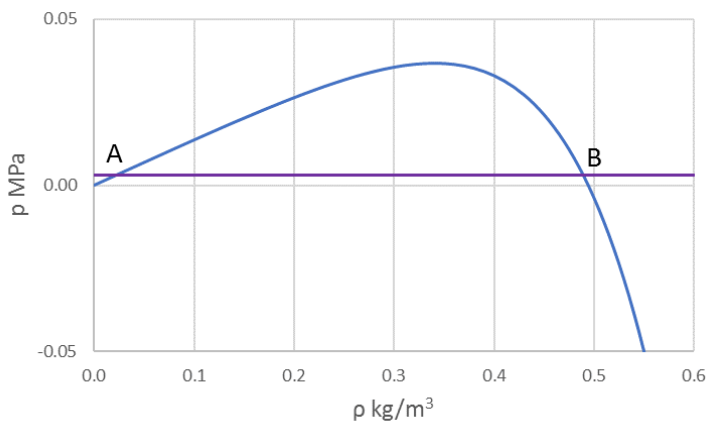


Figure 6. Pressure as a function of density (blue) and the saturation pressure (violet) at 298.15. Points A and B mark numerical solutions in this range. Point A corresponds to the physically valid solution for vapor, while Point B marks an unstable numerical solution.

4.2.5. Multiple Solutions for Water at 640K and 25 MPa

The following input file was created for finding the properties of water at 640K and 25 MPa. This temperature is several degrees below the critical temperature of 647.096K and slightly above the critical pressure of 22.064 MPa.

```
input_clf
# MCclf

# Calculate results for 640K and 25 MPa
# (in the compressed liquid field), specifying
# different starting values for the density
# (rhog, kg/m3). The purpose is to examine
# convergence behavior and check for multiple
# solutions. Here only one solution is found.
#
# The following strings are write option switches.

#showphi
#showdetails1
#showdetails2
#showdetails3

      tempk      press (MPa)      rhog (kg/m3)

# Unique density solution
640.      25.00000000d+00      10000.
640.      25.00000000d+00      5000.
640.      25.00000000d+00      2000.
640.      25.00000000d+00      1100.
640.      25.00000000d+00      1000.
640.      25.00000000d+00      900.
640.      25.00000000d+00      800.
640.      25.00000000d+00      700.
640.      25.00000000d+00      600.
640.      25.00000000d+00      500.
640.      25.00000000d+00      443.094

# No solution
640.      25.00000000d+00      443.093
640.      25.00000000d+00      400.
640.      25.00000000d+00      300.
640.      25.00000000d+00      200.
640.      25.00000000d+00      100.
640.      25.00000000d+00      10.
```

Only one numerical solution is found. Below it will be shown that there is indeed only one numerical solution (the valid one).

4.2.6 Water at 640K over a Wide Range of Pressure

Figure 7 shows a plot of pressure versus density at 640K, using the same scale as in Figures 3 and 5. Also shown is the line (red) for a pressure of 25 MPa. The pressure-density curve here (blue) appears much better behaved, nearly monotonic at this scale. It appears to fall on the 25 MPa curve over much of the left-hand side of the figure. Figure 8 presents a close-up. Now it is clear that the nearly flat region of the pressure-density curve lies below the 25 MPa curve, closer in fact to the saturation pressure of 20.2652229 MPa, crossing the 25 MPa line at a single point (C). Again, multiple runs were made to generate these figures, and the corresponding input files are not given here nor in the test case package.

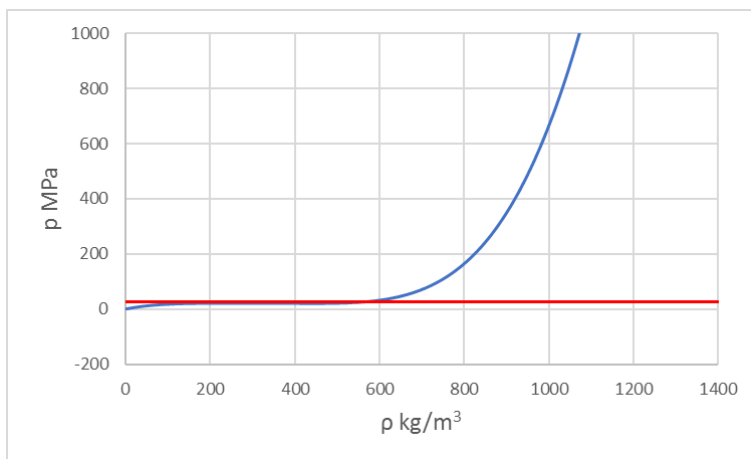


Figure 7. Pressure as a function of density (blue) at 640K. The line for 25 MPa is shown in red. No solution points are marked in this figure owing to the wide range of near overlap.

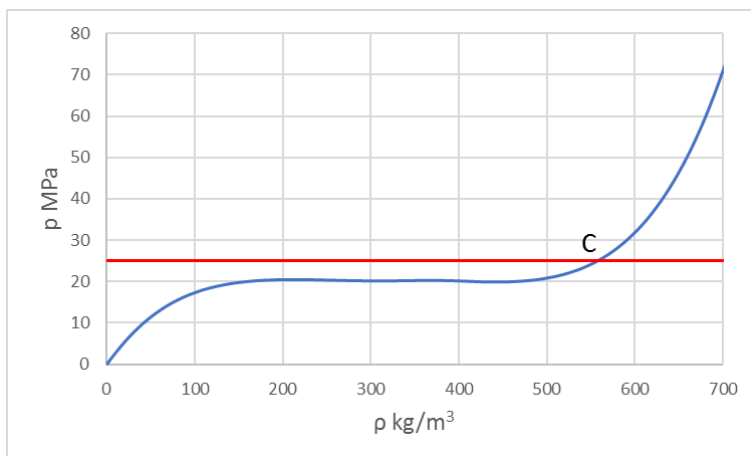


Figure 8. Pressure as a function of density (blue) at 640K, expanding the area where the area where the calculated pressure is close to 25 MPa (red line). There is a single solution point (“C”).

Figure 9 presents a much more detailed close-up (greatly reduced pressure scale). The formerly flat-appearing curve segment shows significant curvature about the saturation pressure. Three numerical solutions are shown (points A, B, and C). In addition, there is a near-solution at point X. Point A marks the solution for stable vapor and point C (the point C from Figure 8 but adjusted to the saturation pressure) marks the solution for stable liquid. The solution corresponding to point B is unstable. There is a near solution marked X. At a slightly lower pressure, say 20.2 MPa, two additional numerical solutions would appear. It can be shown that these are non-physical using the methods previously discussed.

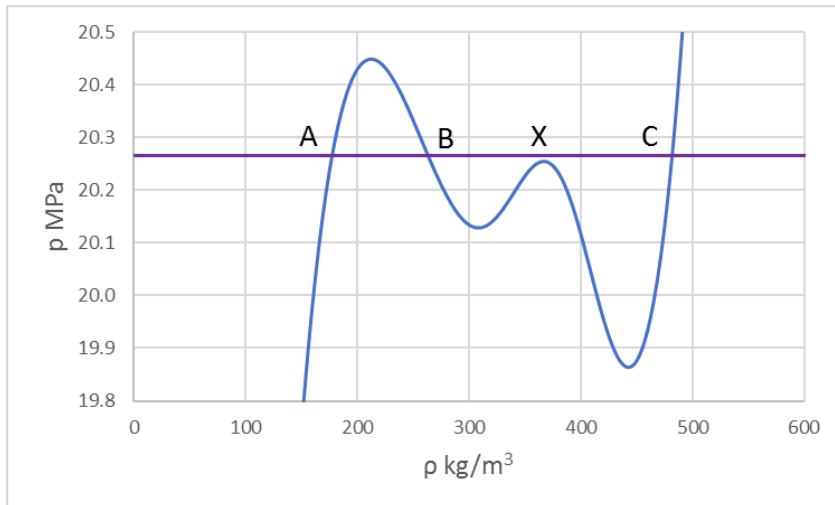


Figure 9. Pressure as a function of density (blue) at 640K, expanding the area where the curve appears nearly flat in Figure 8. On the present scale, it appears very much not flat. The violet line marks the saturation pressure. Three numerical solutions are apparent. The blue line does not touch or cross the violet line near the point marked “X”.

4.2.7. Water at 655K over a Wide Range of Pressure

Figure 10 shows a plot of pressure versus density at 655K (above the critical point), using the same scale as in Figures 3, 5, and 7. No special pressure line is shown. The pressure-density curve here (blue) appears monotonic at this scale. That was also the case for 640K, although in that case analysis showed non-monotonicity at finer scale. The curve differs significantly from that expected for ideal gas (red line, $P = \rho RT$). Figure 11 presents a close-up of the blue curve analogous to Figure 9. In this case (655K), there is clear monotonicity, implying only one numerical solution for any given pressure.

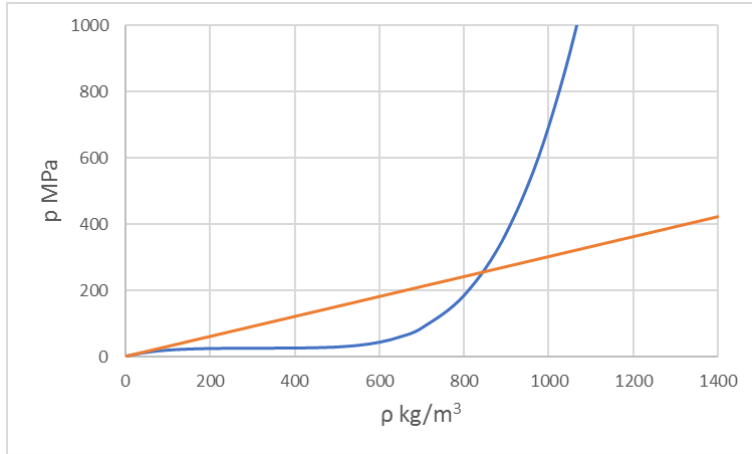


Figure 10. Pressure as a function of density (blue) at 655K. The ideal gas pressure is shown by the red line.

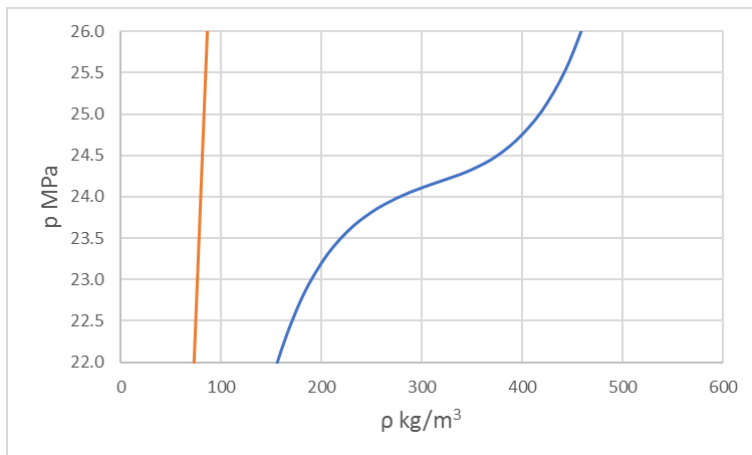


Figure 11. Pressure as a function of density (blue) at 655K, expanding the area where the curve appears nearly flat in Figure 10. The curve is clearly monotonic on this finer scale. The ideal gas pressure is shown by the red line.

It can be shown that at still higher temperature (as in the case for 800K noted below), the pressure curve remains monotonic.

4.2.8. Water at 800K over a Wide Range of Pressure

Figure 12 shows a plot of pressure versus density at 800K (well above the critical point), using the same scale as in Figures 3, 5, 7, and 10. The pressure-density curve here (blue) appears monotonic. The curve still differs significantly from the pressure expected from an ideal gas (red line). Figure 13 presents a close-up view analogous to Figures 9 and 11. This confirms monotonicity of the blue curve. The calculated behavior more clearly converges with that of ideal gas (red line) at sufficiently low pressure..

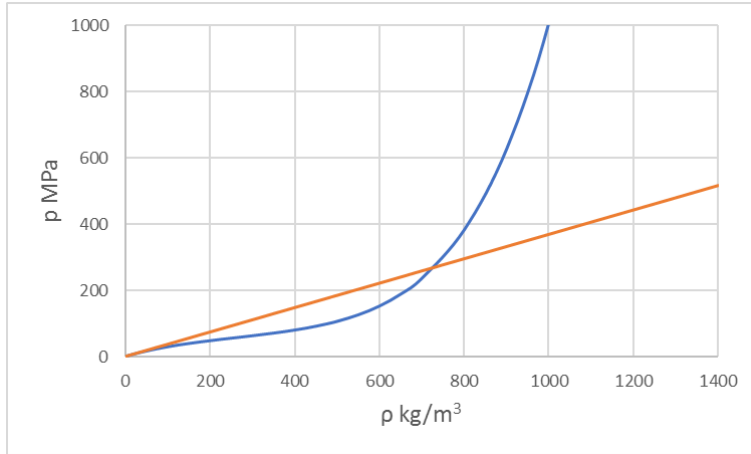


Figure 12. Pressure as a function of density (blue) at 800K. The red line shows the behavior of ideal gas.

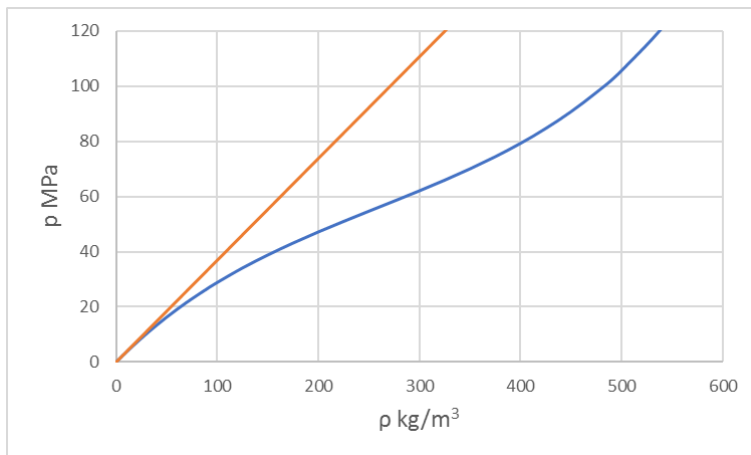


Figure 13. Pressure as a function of density (blue) at 800K, expanding the area in the lower left corner of Figure 12 (low density and low pressure). The red line again shows the behavior of ideal gas. Monotonicity of the blue curve is quite clearly apparent. Also apparent is the approach of the blue curve to ideality at very low density and pressure.

Although monotonicity is a characteristic of pressure as a function of density at temperatures above the critical temperature, ideal gas behavior is approached only at rather low pressure.

Due to the mathematical complexity of the IAPWS-95 model and the fact that the model is only calibrated in a specific range of temperature and pressure, any extrapolation outside that range (especially to higher pressure) should be done with care. Additional numerical studies would be recommended.

5. Concluding Remarks

The IAPWS-95 model (Wagner and Pruss, 2002) modified as described by IAPWS (2016) has been implemented in the program H2OI95. The program is written in simple Fortran and can be used as a basis for incorporating the IAPWS-95 model into codes such as SUPCRT92 (Johnson et al., 1992), which calculates the thermodynamic and thermochemical properties of chemical species including water over a wide range of temperature and pressure. H2OI95 calibrates the thermochemical properties to match the recommended CODATA key values (Cox et al., 1989). The implementation has been carefully validated against results given by both IAPWS (2016) and Wagner and Pruss (2002). The software is provided as both a Windows PC executable and source code. The present user interface is handled through text-based input files, and output includes a text-based output file and two .csv (comma-separated-variable) files that can be opened by a spreadsheet or plotting program. A test case library is included as part of the package. The simple Fortran source code could be easily translated into another programming language such as C/C++ or Visual Basic.

The IAPWS-95 model, like previous equation-of-state models for water, is mathematically complex and exhibits very complex (“non-cubic”) behavior below the critical temperature. The model uses reduced density and inverse reduced temperature as its primary variables. Thus for common problems of specified pressure and temperature, iteration is required to find the density matching the desired pressure. This is done using Newton-Raphson iteration. The difficulty is that below the critical temperature, there may be multiple numerical solutions, of which only one can be valid (or two, at the saturation pressure). The numerical solution found is a function of the starting estimate for the density. Some numerical solutions can be shown to be physically invalid, such as those have a negative derivative of pressure with respect to density (“unstable” solutions) or non-physical results for a physical property such as the square of the speed of sound, the heat capacity at constant pressure, or the absolute entropy. H2OI95 and other implementations of this and similar equation-of-state models for water use default starting values that are thought to generally lead to valid results. H2OI95 has been used to conduct numerical studies of the IAPWS-95 model to complement the studies made by Junglas (2008). Results of these numerical studies have been used to identify default density values that lead to valid results for problems with specified temperature and pressure.

During testing it was found that that for problems with specified temperature and pressure, there are convergence issues between the triple point temperature (273.16K) and 298.15K and between 647.082K and the critical point temperature (647.096K). It was necessary to apply looser convergence criteria in

these temperature ranges. Others including Junglas (2008) and Haar et al. (1984, for the earlier IAPS-84 equation of state model) used similar accommodations, and it is likely that this is also the case for other water equation-of-state solvers. Junglas (2008) ascribed the need for such accommodations to the highly non-cubic behavior of the IAPWS-95 model in these regions, but there is more to it. The model itself is not truly convergent in these regions, but only nearly so. The signed residual function never reaches the zero line, but only gets very close. A “solution” thus exists only for some minimum tolerance, not an arbitrarily small tolerance consistent with the 64-bit machine epsilon (smallest non-zero floating point number). The model is challenged in these circumstances, but the results are still satisfactory from a practical perspective. It is possible that some other set of model equations might avoid this problem, and this would represent at least a small improvement over the IAPWS-95 model.

Additional numerical studies are recommended if one is attempting to extrapolate the IAPWS-95 model outside its specified range of temperature and pressure. The user should remain cognizant that the model equations are complex with limited basis in theory, and that the model itself was fit to data only within the specified range of temperature and pressure.

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Appendix. Equations for Obtaining Thermochemical Results

Results obtained directly from the equation-of-state model (IAPWS-95 and similar models) are typically not consistent with standard thermochemical conventions, including those of CODATA (Cox et al., 1989). Helgeson and Kirkham (1974a) developed a translation approach to obtain thermochemical data for water in the original SUPCRT program noted earlier in this report. This program used the now outdated Keenan et al. (1969) equation-of-state model. A more straightforward translation approach is presented here. In the following discussion, lower case symbols denote quantities defined on a mass basis (e.g., units of J g^{-1} or $\text{J g}^{-1} \text{K}^{-1}$). Upper case symbols denote quantities defined on a molar basis (e.g., units of J mol^{-1} or $\text{J mol}^{-1} \text{K}^{-1}$). Symbols including the “°” sign (S° , $\Delta_f U^\circ$, $\Delta_f H^\circ$, $\Delta_f A^\circ$, $\Delta_f G^\circ$) denote quantities defined on the standard thermochemical scale. Symbols not including this denote quantities on the triple point scale.

The entropy, internal energy, and enthalpy can be treated by applying simple offset corrections along with adjustment of units using M_w (g mol^{-1}) the molecular weight of water. The requisite relations can be written as

$$S^\circ = M_w [(s - s_{triple}) + k_s] \quad (A - 1)$$

$$\Delta_f U^\circ = M_w [(u - u_{triple}) + k_u] \quad (A - 2)$$

$$\Delta_f H^\circ = M_w [(h - h_{triple}) + k_h] \quad (A - 3)$$

Here k_s , k_u , and k_h are the respective offsets for the specific entropy, specific internal energy, and specific enthalpy (k_s was introduced in the main text). Recall that u_{triple} and s_{triple} are zero by convention. Recall also that $h_{triple} = P_{triple} v_{triple}$. Although this is small, it is not zero.

For the Helmholtz and Gibbs energies, there are two offsets for each. One is associated with the entropy. This can be thought of as the “slope” correction, as it affects the temperature dependence of both energy functions. The other can be thought of as the “intercept” correction (addition of a constant). The requisite standard thermodynamic relations are $a = u - Ts$ and $g = h - Ts$. Applying the slope correction first, one would redefine the specific Helmholtz energy as $a = u - T(s + k_s)$ and the specific Gibbs energy as $g = h - T(s + k_s)$. Then one would add an appropriate constant to each to complete the scale transformation. The resulting forms are

$$\Delta_f A^\circ = M_w [u - T(s + k_s) + k_a] \quad (A - 4)$$

$$\Delta_f G^\circ = M_w [h - T(s + k_s) + k_g] \quad (A - 5)$$

Here k_a and k_g are the respective intercept corrections.

Applying equations (A-1) through (A-5) to 298.15K and 1 bar and rearranging, one may obtain:

$$k_s = \frac{S_{298.15K,1\text{ bar}}^\circ}{M_w} - (s_{298.15K,1\text{ bar}} - s_{\text{triple}}) \quad (A - 6)$$

$$k_u = \frac{\Delta_f U_{298.15K,1\text{ bar}}^\circ}{M_w} - (u_{298.15K,1\text{ bar}} - u_{\text{triple}}) \quad (A - 7)$$

$$k_h = \frac{\Delta_f H_{298.15K,1\text{ bar}}^\circ}{M_w} - (h_{298.15K,1\text{ bar}} - h_{\text{triple}}) \quad (A - 8)$$

$$k_a = \frac{\Delta_f A_{298.15K,1\text{ bar}}^\circ}{M_w} - u_{298.15K,1\text{ bar}} + 298.15(s_{298.15K,1\text{ bar}} + k_s) \quad (A - 9)$$

$$k_g = \frac{\Delta_f G_{298.15K,1\text{ bar}}^\circ}{M_w} - h_{298.15K,1\text{ bar}} + 298.15(s_{298.15K,1\text{ bar}} + k_s) \quad (A - 10)$$

Table A-1 gives the constants calculated from the IAPWS-95 model and the CODATA (Cox et al., 1989) recommendations. Slightly different results would be obtained for other equation-of-state models.

Table A- 1. Simple offset constants for the IAPWS-95 model and the CODATA (Cox et al., 1989) thermochemical recommendations.

| Constant | Value | Units |
|----------|------------|-----------------------------------|
| k_s | 3.51562 | $\text{kJ kg}^{-1} \text{K}^{-1}$ |
| k_u | -15767.194 | kJ kg^{-1} |
| k_h | -15970.895 | kJ kg^{-1} |
| k_a | -11906.844 | kJ kg^{-1} |
| k_g | -12110.528 | kJ kg^{-1} |