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Development of thermodynamic potentials for fluid water, ice and seawater: a new standard for oceanography

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Abstract

A new seawater standard has been developed for oceanographic and engineering applications that consists of three independent thermodynamic potential functions, derived from extended distinct sets of very accurate experimental data. The results have been formulated as Releases of the International Association for the Properties of Water and Steam, IAPWS (1996, 2006, 2008) and are to be adopted internationally by other organizations in subsequent years. In order to successfully perform computations such as phase equilibria from combinations of these potential functions, mutual compatibility and consistency of these independent mathematical functions must be ensured. In this article, a brief review of their separate development and ranges of validity is given. We analyse background details on the conditions specified at their reference states, the triple point and the standard ocean state, to ensure the mutual consistency of the different formulations, and we consider the necessity and possibility of numerically evaluating metastable states of liquid water. Computed from this formulation in quadruple precision (128 bit floating point numbers), tables of numerical reference values are provided as anchor points for the consistent incorporation of additional potential functions in the future, and as unambiguous benchmarks to be used in the determination of numerical uncertainty estimates of double-precision implementations on different platforms that may be customized for special purposes.

1 Introduction

The International Equation of State of Seawater (EOS-80, Fofonoff and Millard, 1983) has successfully served the needs of oceanographers for three decades. Challenged by climate change, equipped with more powerful computers and confronted with new and more accurate standards in neighboring fields of science and technology, the SCOR/IAPSO Working Group 127 (WG127) was established and charged with developing a new seawater standard for oceanography.

The very accurate mathematical description of liquid water and vapor, IAPWS-95, issued by the International Association for the Properties of Water and Steam in the form of a Helmholtz potential (Wagner and Pruß, 2002) has provided the foundation for the cooperative development of a common seawater formulation for both oceanographic and engineering applications worldwide. To complement the Helmholtz potential for pure water, an equation of state for salt-free ice was developed in the form of a Gibbs potential function (Feistel and Wagner, 2006), presented at the 14th International Conference on the Properties of Water and Steam (ICPWS) in Kyoto in 2004, and approved by IAPWS as a Release in 2006. Together, the Helmholtz and the Gibbs potentials cover all three stable phases of pure water found under ambient conditions in a consistent, comprehensive and precise way. To use the IAPWS-95 formulation over the required application range for seawater, the implementations of IAPWS-95 must be able to provide results for metastable states of liquid water; i.e. to conditions of temperature and pressure under which seawater is a stable liquid, but pure water is already transformed into ice or vapor. A discussion of this work is presented in Sect. 4.

The presence of sea salt in water changes its thermodynamic properties. The saline part of a Gibbs potential of seawater (i.e. the addition to the Gibbs potential of pure water required to represent seawater) has now been determined for the quantitative description of these deviations (Feistel, 2003, 2008). For its application to seawater under extreme natural conditions or in technical systems like desalination plants, the range of validity of the saline Gibbs function has been extended to 80°C and covers salinities extending from 0 to 120 g/kg, for which experimental data of adequate accuracy are available. The required salinity range extends beyond the currently valid Practical Salinity Scale of 1978, PSS-78, at both low and high values. This problem is circumvented by using a new salinity scale termed Reference-Composition Salinity that was developed by WG127 (Millero et al., 2008). Saturation conditions for particular components of sea salt are discussed by Marion et al. (2008).

The combination of the Helmholtz function for pure water, the Gibbs potential for salt-free ice and the saline part of the Gibbs potential provide the foundation for the computation of the thermodynamic properties of pure water and seawater within a new, unified and fully consistent framework.

Our approach to construct a new seawater standard explicitly from three distinct thermodynamic potential functions is unprecedented and has not been discussed in the scientific literature before. We discuss the conditions that need to be met to realize this novel approach as well as the solutions found to overcome the problems encountered. The ambiguities of different triple point definitions and their implications for the formulation of seawater thermodynamics are analysed in Sect. 3. Revising earlier definitions (Feistel, 1993, 2003; Feistel and Hagen, 1995), the new WG127 specification of the seawater reference point is given and its properties are considered in detail in the same section.

In Appendix A, highly accurate numerical values for the properties at the reference states of water and seawater are provided. In particular, we have recomputed in this paper the numerical check values published in the Releases IAPWS-95 for fluid water, IAPWS-06 for ice and IAPWS-08 for seawater, using quadruple precision calculations and these are presented to 20 significant figures. These results provide unambiguous benchmarks against which double-precision implementations of the new seawater standard on different platforms can be validated.

In this paper, formula symbols are used which in some cases deviate from the common symbols used in oceanography. In particular, p is absolute pressure (in Pa, MPa etc.) rather than sea pressure (relative to 101 325 Pa), and w is sound speed (in m/s). S_A is used to represent Absolute Salinity which we note is not accurately represented by Practical Salinity. For the relation between Absolute and Practical Salinity, see Millero et al. (2008).

2 Development of the formulations

In 1984, what was then called the International Association for the Properties of Steam, adopted the Helmholtz potential developed by Haar et al. (1982, 1984) as the international standard sometimes referred to as IAPS-84. At its 1990 meeting in Buenos Aires, IAPWS agreed on the need for a replacement of IAPS-84 which should be based on the temperature scale ITS-90, represent a wider range of data, and improve the representation of the critical and the metastable regions. This led to the approval of the Helmholtz function developed by Pruß and Wagner (1995) as the formulation IAPWS-95, which was adopted in its final form by IAPWS (1996) in Fredericia, Denmark, and is described in detail by Wagner and Pruß (2002). Its validity range in temperature and pressure is shown in Fig. 1. Fortran source code of an implementation is available from the digital supplement of Feistel et al. (2008b).

Ice Ih is the ice phase I that occurs under normal pressure and temperature conditions, in contrast to the ices II, III etc. which exist at very high pressures or low temperatures. Ice Ih possesses a stable hexagonal crystal lattice rather than a cubic one (termed ice Ic). The possibility of constructing Gibbs functions for the different high-pressure ice phases (>200 MPa) is discussed by Tchijov et al. (2008).

The first Gibbs functions for ice Ih were proposed by Feistel and Hagen (1995, 1998), Tillner-Roth (1998) and Feistel (2003). They were each derived from only a few experimental data sets, restricted in validity to the vicinity of the melting curve, and possessed significant uncertainties, in particular in compressibility. In a subsequent, more comprehensive approach, the entire region of existence of ice Ih was covered by a new Gibbs function developed by Feistel and Wagner (2005). Its source code was published by Feistel et al. (2005) in the digital supplement. An improved version including additional data, in particular for the absolute entropy at the melting point (Feistel and Wagner, 2006), was adopted by IAPWS (2006) in Witney, UK. The range of validity of this formulation, which we will refer to as IAPWS-06, is shown in Fig. 2. Its source code with the updated coefficients is available from Feistel et al. (2008b).

The possibility of an extension in the form of a Gibbs function for vapor below 130 K has recently been discussed by Feistel and Wagner (2007) and Riethmann et al. (2008) and will be implemented in a forthcoming source code library (Feistel et al., 2008a[1]).

More as a theoretical concept than a practical algorithm, a Gibbs function for seawater was described by Fofonoff (1962). During the development of the International Equation of State of Seawater (EOS-80), apparently no attempt was made to combine the theoretical concept with the available data to build such a thermodynamic potential, even though all necessary properties were quantitatively available before 1980. Separate correlation equations for the density, heat capacity, sound speed and freezing temperature were derived and adopted as the new standard for oceanography (Fofonoff and Millard, 1983), and they still remain as the international standard after nearly three decades.

Additional thermal and colligative properties published by Millero and Leung (1976) were used in combination with the EOS-80 equations for the construction of the first Gibbs function of seawater (Feistel, 1993). Feistel and Hagen (1995) improved this function by including additional data, e.g. for the sound speed and the temperatures of maximum density, and conversion to ITS-90. Properties like entropy and enthalpy that are available from this formulation in a consistent form are of growing interest for more accurate ocean models (McDougall, 2003; McDougall et al., 2003, 2008[2]; Griffies et al., 2005; Jackett et al., 2006; Tailleux, 2008[3]).

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After the appearance of the fundamental paper of Wagner and Pruß (2002), a systematic improvement of the Gibbs function of seawater proved possible by replacing pure-water properties of the Gibbs function of Feistel and Hagen (1995) by those computed from IAPWS-95 (Feistel, 2003). The related source code for seawater can be found in the digital supplement of Feistel (2005), and with the same mathematical structure but improved coefficients in Feistel et al. (2008b). The extension of this formulation to high salinity and temperature for thermal and colligative properties, which became possible with the introduction of the new Reference-Composition Salinity Scale, is to be adopted as a new international standard to replace EOS-80 (Millero et al., 2008; Feistel, 2008; McDougall et al., 2008[2]; IAPWS, 2008), in conjunction with IAPWS-95 for fluid water and IAPWS-06 for ice. This is the first formulation developed cooperatively by IAPWS for general applications and by the SCOR/IAPSO Working Group 127 for oceanography, being fully consistent in its pure water properties. The range of validity of the IAPWS-08 formulation on seawater is shown in Fig. 3. A publication of a source code library including this latest version is in preparation (Feistel et al., 2008a[1]).

The range of validity shown in Fig. 3 is additionally constrained by precipitation or degassing of sea salt constituents from the solution. The related boundaries as functions of temperature, pressure and salinity are insufficiently known yet; for selected components of sea salt they are reviewed by Marion et al. (2008).

The three individual thermodynamic potentials for fluid water, for ice, and for the saline contribution for seawater were constructed from separate and independent experimental data sets. The integrity of this comprehensive new formulation, consisting of three independent potential functions, is higher than that of the former EOS-80 in two important ways. First, individual correlation equations for particular properties of water, ice and seawater have been consistently combined into compact functions, the thermodynamic potentials. Second, these independent potential functions can, in turn, be combined consistently providing not only the properties of the particular phases/components, but also of their mutual combinations and transitions. This family of thermodynamic potentials is conveniently structured in such a way that it obeys three general conditions that are highly desirable for proper axiomatic systems. It is consistent, i.e. the possibility of deducing two different formulas for the same property is excluded, independent, i.e. no formula can be deduced from other ones, and complete, i.e. a formula is provided for every thermodynamic property.

Since thermodynamic experiments can reveal only changes of entropy or energy, the values of the absolute energy and the absolute entropy for each component, including water in liquid, gas or solid phase as well as sea salt, are freely adjustable (Fofonoff, 1962). To achieve consistency between the potential functions, both the absolute energy and entropy of each substance must take the same values independent of the particular phase or mixture of this substance; this requires their proper adjustment among the potential functions. This is commonly achieved by specifying reference state conditions, as described in the following section.

3 Reference states

For fluid water, the traditional reference state condition is vanishing entropy and internal energy of the liquid phase at the solid-liquid-gas triple point of pure water. To unambiguously implement this condition in the numerical models, the triple point itself must be exactly defined by mathematical equations. In implementations of IAPWS-95 and IAPWS-06, this had not always been done sufficiently rigorously or consistently, and thus requires a meticulous reconsideration, as discussed below.

First, note that the *ITS-90* scale defines the Kelvin temperature unit by setting the temperature value at the *triple point* of water to be exactly 273.16 K (Preston-Thomas, 1990).

The common *physical triple point* of water is the thermodynamic equilibrium state between liquid water, water vapor and ice. The standard definition of pure water is Vienna Standard Mean Ocean Water, VSMOW, consisting of several isotopes of hydrogen and oxygen as found under ambient conditions (IAPWS, 2005). If the particular liquid, gaseous and solid phases possess mutually different isotope ratios, equilibrium temperatures can vary over an interval that has been estimated to be of approximately 40 μK width, rather than being confined to a single, unique "point". Different isotope fractionations between liquid, gas and ice correspond to different equilibrium temperatures between those phases (Nicholas et al., 1996; White et al., 2003; Chialvo and Horita, 2003; Feistel and Wagner, 2006; Polyakov et al., 2007). Consequently, the uncertainty of any ITS-90-calibrated thermometer cannot be smaller than 40 μK, even if its precision in resolving temperature differences may be smaller, unless the isotopic ratios of all phases are rigorously specified in the temperature scale definition, and carefully established in the laboratory.

The *experimental triple point* pressure, i.e. the vapor pressure of pure water at 273.16 K, was determined by Guildner et al. (1976) as p_t=611.657(10) Pa. The number given in brackets is the uncertainty of the last two digits.

The *numerical IAPWS-95 triple point* is defined mathematically by equal chemical potentials and pressures of liquid water and vapor at exactly 273.16 K.

The *numerical IAPWS-95/06 triple point* can be defined mathematically by equal chemical potentials of liquid water, water vapor and ice Ih, where liquid and vapor are described by IAPWS-95 and ice is described by IAPWS-06.

In this paper, the above defined numerical triple points will be computed. Before doing this, we mention two problems that have arisen with the implementation of IAPWS-95:

1. In order that the defined reference values of vanishing internal energy and entropy in the liquid phase at the triple point are accurately reproduced, it has been recommended that the parameters n_1° and n_2° specified in the formulation of IAPWS-95 are individually adjusted for the particular software implementation and hardware configuration. While such a procedure is essentially correct, its application was often either overlooked or ignored. Recent tests have suggested that this adjustment phase is not essential if IAPWS-95 is implemented as given in the Release but with modified values of n_1° and n_2° as given below.

2. Implementations should refrain from rounding of coefficients and employ the full accuracy of the official formulation that has parameters given to 14 significant figures, in conjunction with the values of n_1° and n_2° given in the footnote added in September 2008 to Table 4 of IAPWS (1996). For applications considered in this article, the values of n_1° and n_2° given below should be used.

The properties of the numerical IAPWS-95 triple point have been computed from two different quadruple-precision (128 bit) implementations of IAPWS-95 made independently by two of us. One result for the numerical IAPWS-95 triple point was based on code, referred to as the Wagner and Pruß code, made available to our group by W. Wagner, recently published in Feistel et al. (2008b). The numerical precision of the code was increased to 128 bit accuracy using the double-double precision system developed and made available by Bailey et al. (2008). Error tolerances of numerical iteration procedures were reduced to the point that further reductions made no difference to our results. All coefficients were expressed to the full accuracy given in IAPWS (1996). In this implementation, the coefficients n_1° and n_2° of the IAPWS-95 formulation were adjusted to the reference-point conditions of vanishing entropy and internal energy of the liquid phase at the triple point determined by an iterative routine available in the original code obtained from W. Wagner. The results are given in Table 1.

The second version of the code, referred to as the NIST code, was independently implemented at the National Institute of Standards and Technology. Compiler options available in the Lahey/Fujitsu Fortran 95 compiler[4] were used to promote all 64 bit real variables to 128 bit real variables and convergence tolerances were reduced until no change was observed to the desired number of digits. The quadruple-precision values of coefficients n_1° and n_2° determined from the Wagner and Pruß code (Table 1) were used.

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[4] Certain commercial products are identified in this paper, but only in order to adequately specify the procedure. Such identification neither constitutes nor implies recommendation or endorsement by any of the organizations represented by the authors.

Properties at the IAPWS-95 triple point, determined using the quadruple precision codes described above, are given in Table 2 to the number of digits that the two implementations agree.

The properties of the numerical IAPWS-95/06 triple point have also been computed from a quadruple-precision implementation of IAPWS-95 and IAPWS-06 as discussed below.

If (T, p) is a good initial approximation to the numerical IAPWS-95/06 triple point (e.g. T=273.16 K, p=611.655 Pa as reported in IAPWS-95), an iterative improvement can be obtained using the linearized equations

$$g^{\mathrm{Ih}} - s^{\mathrm{Ih}}\Delta T + v^{\mathrm{Ih}}\Delta p = g^{\mathrm{W}} - s^{\mathrm{W}}\Delta T + v^{\mathrm{W}}\Delta p \qquad (1a)$$

$$g^{\mathrm{Ih}} - s^{\mathrm{Ih}}\Delta T + v^{\mathrm{Ih}}\Delta p = g^{\mathrm{Vap}} - s^{\mathrm{Vap}}\Delta T + v^{\mathrm{Vap}}\Delta p \quad , \qquad (1b)$$

that have the solution

$$\Delta T = \frac{\left(g^{\mathrm{Ih}} - g^{\mathrm{W}}\right)\left(v^{\mathrm{Vap}} - v^{\mathrm{Ih}}\right) - \left(g^{\mathrm{Ih}} - g^{\mathrm{Vap}}\right)\left(v^{\mathrm{W}} - v^{\mathrm{Ih}}\right)}{\left(s^{\mathrm{Ih}} - s^{\mathrm{W}}\right)\left(v^{\mathrm{Vap}} - v^{\mathrm{Ih}}\right) - \left(s^{\mathrm{Ih}} - s^{\mathrm{Vap}}\right)\left(v^{\mathrm{W}} - v^{\mathrm{Ih}}\right)} \qquad (2a)$$

$$\Delta p = \frac{\left(s^{\mathrm{Ih}} - s^{\mathrm{W}}\right)\left(g^{\mathrm{Ih}} - g^{\mathrm{Vap}}\right) - \left(s^{\mathrm{Ih}} - s^{\mathrm{Vap}}\right)\left(g^{\mathrm{Ih}} - g^{\mathrm{W}}\right)}{\left(s^{\mathrm{Ih}} - s^{\mathrm{W}}\right)\left(v^{\mathrm{Vap}} - v^{\mathrm{Ih}}\right) - \left(s^{\mathrm{Ih}} - s^{\mathrm{Vap}}\right)\left(v^{\mathrm{W}} - v^{\mathrm{Ih}}\right)} \quad . \qquad (2b)$$

Here, g is the specific Gibbs energy, s the specific entropy and v the specific volume of ice (superscript Ih), liquid water (W) and vapor (Vap). Using this iterative approach to determine successive improvements allows one to determine the numerical triple point temperature and pressure values corresponding to the parameter values listed in the Releases. When this is done using quadruple precision calculations, we find that T_{t}=273.160000930708556675161234 K and p_{t}=611.654775144545131192098 52×10^{-6} MPa.

The deviation of the above estimate of the triple point temperature from 273.16 K shows that a small modification of the adjustable coefficient g_{00} of the ice formulation IAPWS-06 is required for consistency with the ITS-90 temperature scale at this level of precision. Starting again with $T=273.16$ K, and using Eq. (1a, b) to iteratively adjust Δp and g^{Ih} with $\Delta T=0$, we find that the value $g_{00}=-0.632020233449497\times10^{6}\,\mathrm{J\,kg^{-1}}$ published for the Gibbs function of ice (Feistel and Wagner, 2006; IAPWS, 2006), must be adjusted to $g_{00}=-0.632020233335886\times10^{6}\,\mathrm{J\,kg^{-1}}$ to correct the numerical IAPWS-95/06 triple-point temperature from the value given above to $T=273.160000000000$ K in all 15 digits. The more precise quadruple precision estimate of g_{00} is given in Table 1.

The triple point properties of all three water phases were computed in quadruple precision after the adjustment of the coefficient g_{00} and are reported in Table 3. These results are given to the full precision that stable results between iterations are obtained on one particular platform. Slight differences may occur on other platforms. Note that we use the full quadruple precision coefficients in Table 3 and in all of the tables presented in Appendix A. The values presented are thus our best estimates of the true solutions, but will not be precisely reproduced by double precision implementations. Shading has thus been used in Tables 3–11 to indicate the digits that are not expected to be reproduced by double precision implementations. A discussion of the methods used to estimate what precision is achievable with double precision implementations is given in Appendix A.

From a practical point of view, all triple-point definitions discussed above and in related IAPWS publications are consistent with each other within their experimental uncertainties and natural physical fluctuations. Numerically, however, the related values are slightly different. In this paper, the numerical IAPWS-95 triple point results were used as the definite reference point required for the consistent adjustment of free parameters in the other formulations.

In the seawater formulation (Feistel, 2008; IAPWS, 2008), the Gibbs function, g, of seawater is expressed as a sum of a water part, g^{W}, derived from the IAPWS-95

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Helmholtz potential, and a saline part, g^{S}, as,

$$g(S_{\mathrm{A}},T,p) = g^{\mathrm{W}}(T,p) + g^{\mathrm{S}}(S_{\mathrm{A}},T,p). \tag{3a}$$

The function $g^{\mathrm{W}}(T, p)$ is related to the Helmholtz potential $f^{\mathrm{W}}(T, \rho^{\mathrm{W}})$ by the relation

$$g^{\mathrm{W}}(T,p) = f^{\mathrm{W}}(T,\rho^{\mathrm{W}}) + \rho^{\mathrm{W}}(T,P) \times f^{\mathrm{W}}_{\rho}(T,\rho^{\mathrm{W}}), \tag{3b}$$

where the subscript ρ on f^{W} indicates partial differentiation with T constant and

$$\rho^{\mathrm{W}}(T,p) = \rho(S_{\mathrm{A}} = 0,T,p). \tag{3c}$$

The salinity argument of the Gibbs function in Eq. (3) is the Absolute Salinity S_{A} which is the mass of dissolved material in seawater per unit mass of solution. For seawater of Reference Composition, Absolute Salinity is the same as the Reference-Composition Salinity (Millero et al., 2008).

It is convenient to adjust the free parameters determining the reference levels of absolute energy and absolute entropy of sea salt such that entropy and enthalpy of seawater vanish for the standard ocean state (p_{SO}=101 325 Pa, T_{SO}=273.15 K, S_{SO}=35.16504 g kg^{-1}). The related adjustable coefficients of the Gibbs function of seawater are g_{200} and g_{210}, i.e. its terms proportional to salinity and to the powers 0 and 1 in temperature (Fofonoff, 1962; Feistel, 2003; IAPWS, 2008).

At its meeting in Warnemünde, Germany, in May 2006, WG127 chose to specify the arbitrary constants corresponding to the saline specific entropy, s^{S}, and the saline specific enthalpy, h^{S}, at the standard ocean state as

$$s^{\mathrm{S}}(S_{\mathrm{SO}},T_{\mathrm{SO}},p_{\mathrm{SO}}) = s^{\mathrm{W}}(T_{\mathrm{t}},p_{\mathrm{t}}) - s^{\mathrm{W}}(T_{\mathrm{SO}},p_{\mathrm{SO}}) \tag{4a}$$

$$h^{\mathrm{S}}(S_{\mathrm{SO}},T_{\mathrm{SO}},p_{\mathrm{SO}}) = u^{\mathrm{W}}(T_{\mathrm{t}},p_{\mathrm{t}}) - h^{\mathrm{W}}(T_{\mathrm{SO}},p_{\mathrm{SO}}). \tag{4b}$$

Here, u^{W}, h^{W} and s^{W} are the specific internal energy, enthalpy and entropy of liquid water of the IAPWS-95 formulation, respectively, and (T_{t}, p_{t}) refers to the numerical

IAPWS-95 triple point as in Table 2. Numerical values of the quantities referred to in Eq. (4a), (4b) are reported in Appendix A.

The definitions (4a, b) have the following properties:

1. the free constants of the saline Gibbs energy, g^S, are being specified, rather than those of the complete Gibbs energy, g, of seawater,
2. the reference state definitions (4a, b) do not impose any conditions on the IAPWS-95 formulation,
3. the definitions (4a, b) do not require any additional explicit numerical values to be given,
4. the right sides of (4a, b) are independent of the choice of the two free constants within IAPWS-95, and so are the saline quantities $s^S(S_{SO}, T_{SO}, p_{SO})$ and $h^S(S_{SO}, T_{SO}, p_{SO})$. In other words, the IAPWS reference state definition does not impose any conditions onto the formulation, $g^S(S, T, p)$,
5. the definitions are different from the ones given in Feistel (2003) only by the tiny misfit of $g(0, T_{SO}, p_{SO})$ from Feistel (2003) to $g^W(T_{SO}, p_{SO})$ from IAPWS-95, thus being comfortably consistent for oceanographers, and
6. the numerical absolute values of $s(S_{SO}, T_{SO}, p_{SO})$ and $h(S_{SO}, T_{SO}, p_{SO})$ for seawater do depend on the IAPWS-95 reference state in the same way as do $s^W(T_t, p_t)$ and $u^W(T_t, p_t)$ from IAPWS-95.

The properties of liquid water, ice and seawater at the standard ocean state were computed in quadruple precision and are reported to an accuracy of 20 significant figures in Table 11 of Appendix A.

We note that in all of our tables, we have reported results to much higher precision than could be justified by the constraints available from experimental data. To explain why we have done this, it is necessary to clearly distinguish between mathematical formulations, practical implementations and the representation of experimental data. Formulations like IAPWS-96, IAPWS-06 or IAPWS-08 are mathematical models of the reality that provide precise descriptions of all thermodynamic properties in their particular scope. Although the agreement with reality is required only to the uncertainty of the experimental data, the mathematical models used to approximate the data are precisely defined constructs. Implementations, on the other hand, possess numerical uncertainties depending on the hardware and software of the implementation platform, on the way the program flow is organized in the code, the syntax permitted by the programming language, and on the way this code is executed by compilers or interpreters. There can of course be different implementations of the same mathematical model. They are all only approximations of the precise mathematical models that they represent, but their numerical errors should be negligibly small compared to the uncertainties of the experimental data.

Things become more complicated when more than one formulation is considered and mutual consistency is required, as in the case of fluid water, ice and seawater. Although the mathematical models may be formulated to be exactly consistent, if the reference point properties of ice are determined from an arbitrary implementation of fluid water properties and used as part of the mathematical model, then the theoretical formulation for ice becomes implementation-dependent rather than mathematically exact. If further formulations are integrated this way into a family of formulations, this procedure may eventually lead to significant inconsistencies within that family. Whether or not these inconsistencies are significant will depend on the accuracy used to determine all parameters that are determined based on consistency requirements.

To consider a simple example as an illustration, we imagine the following situation. Given is the Gibbs function $g(T, p)$ of liquid water (e.g. computed from IAPWS-95). To obtain a fast implementation, we develop separate correlation equations (i.e. mathematical models in our terminology) for each of its partial derivatives g, g_t, g_P, g_{TT}, g_{TP} and g_{PP}. We only require that these correlation equations agree with the original formulation within the experimental uncertainty of entropy, density etc. Using this approach, we will very probably arrive at a situation where our simplified separate equations in their combination no longer reproduce, say, the sound speed of the original formulation within its uncertainty.

The conclusion from this consideration is that the consistency between different but related formulations should always be as precise as possible, in the ideal case mathematically exact. If this consistency can be specified only numerically, then the required relations should be computed with the highest achievable accuracy rather than within experimental uncertainty only. In particular, the fundamental mutual anchor points that impose consistency between the formulations should be very precisely determined in order to avoid unpredictable consequences for quantities derived from arbitrary combinations of those formulations.

There are two different methods whereby this requirement for rigorous consistency can be realized: the static and the dynamic definition of the adjustable coefficients. In the static method, the coefficients are computed based on the reference state conditions with a high precision in advance and the result of this computation is given as an explicit numerical value for each coefficient. The advantage of this method is that all implementations will use an identical set of coefficients, and the algorithms for fluid water, ice, and the saline part of seawater can be implemented as modules independent of each other.

In the dynamic way, the adjustable coefficients are defined by the reference state conditions in the form of equations rather than their solutions. These equations will be solved numerically during the run-time initialization of each particular implementation, leading to slightly implementation-dependent values of the adjustable coefficients which most accurately obey the conditions on the given platform.

For the quadruple-precision implementation used to compute the tables in Appendix A, we have applied the dynamic method. However, we recommend that the static values with 15 significant figures, obtained by rounding the coefficients given in Table 1, be used in future work with double precision code. This is already the recommendation for the Releases IAPWS-06 and IAPWS-08. We recommend that this approach also be taken for IAPWS-95 with coefficients determined from Table 1. This approach will be taken in the forthcoming source-code library (Feistel et al., 2008a[1]) where we will take all coefficients to be consistent with Table 1, including g_{00} which is not currently planned to be officially updated by IAPWS. This approach provides the most accurate coefficients currently available, the best possible consistency at the reference states obtainable with static values of all coefficients and it will ensure that any inconsistencies between the results from different implementations are due to the details of the implementation or the platform used to do the calculations, and not due to differences in the specification of coefficients. Tests reveal that differences between results on different platforms obtained using static coefficients should be entirely negligible from a practical point of view.

Finally, we note that the mutually consistent family of formulations for water, ice and seawater will likely grow further in the future. Possible candidates are descriptions of aqueous sodium chloride solutions, of solid sea salt components and their saturation and precipitation from seawater, properties of humid air or gases dissolved in water, and the surface tension and refractive index of seawater. There will certainly be a demand to consistently link such formulations to the existing family. This will require highly accurate reference state properties to be used for the determination of the coefficients of the added formulations. For this purpose, we provide in this paper tables of highly accurate reference values.

As an example, one may wish to consider components of sea salt like NaCl or CO_2 in order to describe their individual properties in a solid or gas state or aqueous solution. Their absolute energies and entropies can conveniently be specified then from the absolute energy and entropy of seawater at the standard ocean state, using the Reference-Composition model (Millero et al., 2008). For components which contribute only, say, a fraction of 0.01% to the total mass of sea salt, their absolute internal energy may be defined with precision reduced by the same fraction. If the total internal energy of sea salt is available now with 15 correct digits, only 11 accurate digits will be available for such a component, since all fractions need to sum up to give exactly 1.

Thus, providing 19 digits for sea salt will permit a consistent specification of those components with 15 valid digits. For the same reason the Reference Composition of sea salt itself was defined with more valid digits than required by the experimental uncertainties of its measurements, for example, to guarantee mathematically exact electrical neutrality of the resulting electrolyte model.

4 Metastable liquid water

When sea salt is dissolved in water, the triple point defined by the equilibrium between seawater, ice and vapor is displaced from its pure-water locus along the sublimation line of pure water to lower pressures and temperatures (Fig. 4). As a consequence, stable liquid seawater is found at temperatures and pressures where pure water is a metastable liquid, either subcooled or superheated. Thus, to determine seawater properties as a sum of pure water plus saline contributions, the properties of water in the metastable regimes are needed.

A rough estimate of the amount by which the vapor pressure and the freezing temperature are lowered due to dissolved sea salt can be determined from the thermodynamic equilibrium conditions in the form of the first terms of the related series expansions with respect to salinity, commonly known as Raoult's laws.

The equilibrium between ice and seawater requires equal temperatures, pressures and chemical potentials of the water component in both phases, i.e.

$$g^{\mathrm{Ih}} = g^{\mathrm{W}} + g^{\mathrm{S}} - S_{\mathrm{A}} \left(\frac{\partial g^{\mathrm{S}}}{\partial S_{\mathrm{A}}} \right)_{T,p} . \tag{5}$$

For a small depression value, $\Delta T/T$, expanding Eq. (5) in a power series in ΔT and S, we obtain approximately

$$\frac{\Delta T}{T} \approx -\frac{R_{\mathrm{S}} T}{h^{\mathrm{W}} - h^{\mathrm{Ih}}} \times S_{\mathrm{A}} \approx -0.22 \times S_{\mathrm{A}} \tag{6}$$

Here, $R_S = R/M_S = 264.7599\,\mathrm{J\,kg^{-1}\,K^{-1}}$ is the specific gas constant of sea salt, R is the molar gas constant, $M_S = 31.40382\,\mathrm{g\,mol^{-1}}$ is the molar mass of sea salt (Millero et al., 2008), and $h^W - h^{Ih} \approx 333\,\mathrm{kJ\,kg^{-1}}$ is the melting enthalpy of ice.

Similarly, from the equilibrium condition between vapor and seawater,

$$g^{Vap} = g^W + g^S - S_A \left(\frac{\partial g^S}{\partial S_A} \right)_{T,p}, \tag{7}$$

we get the analogous approximation for the vapor pressure lowering, as

$$\frac{\Delta p}{p} \approx -\frac{M_W}{M_S} \times S_A \approx -0.57 \times S_A. \tag{8}$$

Here, $M_W = 18.015268\,\mathrm{g\,mol^{-1}}$ is the molar mass of water (IAPWS, 2005).

It is evident that for our purposes the mathematical function $g^W(T, p)$ in Eq. (3) must produce reasonable values over the entire range of validity of $g^S(S_A, T, p)$. Some documentation of reasonable metastable behaviour of IAPWS-95 was provided by Wagner and Pruß (2002), but an IAPWS task group was formed to investigate this issue more thoroughly and concluded in its report given at the 2007 meeting in Lucerne that:

1. the investigations established conclusively that IAPWS-95 behaves reasonably in the subcooled liquid range down to temperatures as low as 240 K,
2. IAPWS-95 functions are visually and numerically smooth in the subcooled region even at high pressures,
3. an extensive literature research made in 2005 did not reveal any evidence for any new data in the subcooled region not already mentioned in the Wagner and Pruß (2002) paper,
4. IAPWS-95 is in satisfactory agreement with existing experimental data for subcooled water (density, heat capacity, speed of sound) at normal pressure,

5. there are no data for subcooled water at high pressures (The values discussed in some papers are exclusively computed from models or extrapolation.), and
6. there is no better option than IAPWS-95 as the pure water reference for the seawater formulation.

As is evident from Fig. 4, the metastable liquid range required for use in the determination of seawater properties using the form (3), extends to pressures and temperatures that are well below those corresponding to the triple point of pure water. For seawater applications, code implementing IAPWS-95 should allow consideration of the full range of property values indicated in Fig. 4, rather than being restricted to the region of the stable liquid phase. (Such an application of IAPWS-95 corresponds to an extrapolation of this formulation.) A new version of the code that allows consideration of the full range of seawater conditions of interest will be made available in Feistel et al. (2008a)[1].

5 Discussion

The SCOR/IAPSO Working Group 127 (WG127) was formed in 2005 and charged with developing a new seawater standard for oceanography to replace the International Equation of State of Seawater (EOS-80; Fofonoff and Millard, 1983) that has served the needs of oceanographers for nearly three decades. The general approach taken by WG127 has been to develop a Gibbs function formulation that can be applied over the full range of conditions of interest including pure water, seawater and sea ice.

The IAPWS-95 Helmholtz potential function (Wagner and Pruß, 2002) has served as the starting point from which the Gibbs function for pure water has been determined. This was complemented by Feistel and Wagner (2006) by the introduction of a Gibbs potential for salt-free ice, thus completing the required set of Gibbs functions for pure water, including solid, liquid and vapor phases.

The solid-liquid-gas triple point plays a special role in Gibbs function (and other) formulations of the thermodynamic properties of seawater. In particular, it serves as a reference point at which entropy and internal energy of the liquid water phase are commonly set to zero to determine two free parameters in the formulation. Once these two free parameters for the liquid phase are set, an additional free parameter that enters the formulation of the Gibbs potential for the solid phase must be chosen consistent with the definition of the ITS-90 temperature scale for which the value 273.16 K is defined by the triple point. A consequence of this fact is that any change in the Gibbs function for pure water that results in a change in the value of the Gibbs potential for liquid and vapor at the triple point will require an adjustment of the free parameter in the Gibbs function for the solid phase in order to retain the property that the temperature is exactly 273.16 K at this point.

Unfortunately, the numerical implementation of the code used by Feistel and Wagner (2006) had its parameters rounded off to give slightly lower precision than those listed in the IAPWS-95 release, thus resulting in a very small but non-zero deviation from the strict IAPWS-95 definition of the Helmholtz function. While this difference results in changes that are well within measurement uncertainties, the adjustment to achieve strict consistency with IAPWS-95 results in a small inconsistency between the physical definition of the triple point and the requirement that the temperature at the triple point is 273.16 K on the ITS-90 temperature scale. In Sect. 3, we have thus adjusted the free parameter g_{00} to very precisely satisfy this condition. To achieve highly accurate results (and much more accurate than required for consistency with observations), we have used quadruple precision numerical code in this exercise, resulting in the adjusted value $g_{00}=-0.632020233335886\times10^{6}\,\mathrm{J\,kg^{-1}}$ when rounded to double precision.

With code in precise agreement with IAPWS-95 and properly adjusted to the reference state conditions, and the correction of the parameter g_{00} as required to maintain consistency with the ITS-90 temperature scale, Table 1, the Gibbs function formulation for pure water is complete and fully consistent.

To complete the Gibbs function formulation for seawater, the Gibbs potential associated with salinity effects has been determined by Feistel (2008) and added to the Gibbs potential for pure water as in Eq. (3). Use of this form for the Gibbs function of seawater ensures consistency with the Helmholtz formulation for pure water, but requires some special considerations for its application. In particular, to use Eq. (3) over the desired application range for seawater, it has been necessary to extend the range of application of the Gibbs function for pure water to temperature and pressure values for which seawater is a stable liquid, but the stable phase of pure water is ice Ih or vapor. Thus metastable states of liquid water have been examined as discussed in Sect. 4.

An important feature of the formulation of Feistel (2008) is its applicability to thermal and colligative properties for temperatures up to 80°C and for salinities extending from 0 to 120 g/kg at atmospheric pressure. This salinity range extends beyond the currently valid salinity scale PSS-78 at both low and high values. A review of the development of different salinity scales is given in Millero et al. (2008), in which a new salinity scale termed Reference-Composition Salinity is defined that does not suffer from these limitations of the PSS-78 salinity scale. This new scale is used in the Gibbs function formulation of Feistel (2008).

The combination of the Helmholtz function for pure water, the Gibbs potential for salt-free ice and the saline part of the Gibbs potential for seawater provides a unified and fully consistent foundation for the consideration of the thermodynamic properties of pure water and seawater.

Mathematically, the combination of a Helmholtz function for the pure water part with a Gibbs function for the saline part requires a proper use of theoretical thermodynamic methods and is not always a trivial exercise. For convenience of application, WG127 is implementing the new set of thermodynamic functions for liquid water, water vapor, ice, and seawater, as well as their mutual phase equilibria, in a comprehensive source code library for oceanographers and other scientists and engineers who deal with seawater (Feistel et al., 2008a[1]). In addition to the precise implementations of the relations discussed herein, efficient and accurate approximations for some quantities that require computationally efficient implementations will also be provided. Quantities like entropy and enthalpy of seawater, which were not available from EOS-80, result naturally from the Gibbs function formalism and the WG127 source code will include these quantities.

Appendix A

In this Appendix the tables with numerical check values published in the Releases IAPWS-95, IAPWS-06 and IAPWS-08 are recomputed in quadruple precision. The original numerical check tables that IAPWS provides along with its Releases are intended to assist the user in verifying and debugging particular implementations of the formulation. For the easy detection of coding errors, these tables report numbers with more digits than required by the experimental accuracy. They report fewer digits than available from a typical 64-bit floating point number and suppress the part which very likely varies between different implementations, since those digits may be more confusing than helpful for the examination of the code's correctness. Thus, with respect to these published check values, all correct and well-organised implementations are considered equally good.

For certain applications of the Releases, as e.g. for the development of a source code library for seawater, it is important to estimate the implementation errors, i.e. the deviations from the mathematical formulations. This is of interest when speed-optimized code is required for circulation models or other time-critical applications, to monitor the precision costs of certain accelerating modifications or simplifications. This is also of interest to see the effects of reorganising internal details of the code, the sequence of execution, the grouping into procedures etc.

For these reasons, we are publishing alternative versions of the IAPWS tables with numerical check values for fluid water, ice and seawater with very high accuracy, typically 20 valid digits.

In addition to these tables with numerical check values we report in this Appendix properties of water, vapor, ice and seawater at the reference states explained in Sect. 3.

Shading in all tables (including Table 3 in the text as well as those in this Appendix) shows the digits that double precision implementations of the fluid, ice and seawater potential functions are not able to reliably reproduce from the more accurate quadruple precision results. This was achieved using two independent techniques. The first method is based on a manual comparison of double and quadruple precision results and the observation that different implementations of the potential functions in double precision arithmetic give the same agreement with the quadruple precision table entries to within one digit. We compared two different implementations in two different languages on different machines and operating systems. The second technique is based on calculating the relative condition numbers (Dahlquist et al., 1974) of the evaluations of the table entries. These condition numbers measure the sensitivities of the computations to small perturbations of input variables and the number of digits lost in the computation of a given quantity is given by the logarithm to the base 10 of the corresponding relative condition number. In all but a few of the comparisons between the two accuracy estimates the estimate from condition number is smaller, in terms of number of digits of accuracy, than the agreement between the double and quadruple precision results. The differences between estimates arise primarily because condition number is real and requires rounding or truncating to give its integer estimate. Also, the precision of computations on a given platform may be slightly better than 15 significant figures as assumed in the condition number estimate. The lack of shading presented in the tables is made on the conservative side in that it reports the minimum of these three numbers (the two double precision estimates and the condition number estimate) as the number of digits that we believe double precision code should be able to reproduce the more accurate results obtained with quadruple precision calculations.

Formulas for the computation of thermodynamic properties from the potentials f and g are summarized in Table 12.

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Table 1. The precise values of the adjustable coefficients of IAPWS-95 (pure fluid water), IAPWS-06 (pure ice) and IAPWS-08 (saline component of seawater) obtained from quadruple precision code implementations. The coefficients for ice and seawater are determined by the reference conditions (1) and (4) as discussed in Sect. 3.

Coefficient	Value
Pure Water	
n_1°	−8.3204464837496930225479768045 26
n_2°	6.6832105275932258525679019290 71
Ice	
g_{00}	−632 020.233335885558300326500234 8
Seawater	
g_{200}	1416.2764848419698523628625630 56
g_{210}	168.07240831154488636625918926 66

Table 2. Numerical results for properties at the IAPWS-95 triple point obtained from quadruple precision implementations. Here, g is the specific Gibbs energy and ρ the density of water (superscript W) and vapor (Vap). The different shadings for p^{W} and p^{Vap} correspond to the results obtained by determining these quantities from the corresponding density estimates (at $T = 273.16$ K) and comparing these to the full quadruple precision result.

Property	Value	Unit
T	273.16	K
p^{W}	611.654771007894426444 2598 E-6	MPa
p^{Vap}	611.6547710078944264442598 E-6	MPa
g^{W}	0.611781703456382623667 3	$\mathrm{J\,kg^{-1}}$
g^{Vap}	0.6117817034563826236673	$\mathrm{J\,kg^{-1}}$
ρ^{W}	999.792520031620646603898354735	$\mathrm{kg\,m^{-3}}$
ρ^{Vap}	4.854575724778588417176210 E-3	$\mathrm{kg\,m^{-3}}$

Table 3. Quadruple-precision results for the properties of water, vapor and ice at the quadruple precision estimate of the IAPWS-95 triple point given in Table 2 (T=273.16 K, p=611.654771007894426442598$\times 10^{-6}$ MPa), computed with the coefficients given in Table 1 of this paper.

Property	Property of water	Property of vapor	Property of ice	Unit
g	6.1178170345638262367E-1	6.1178170345638262367E-1	6.1178170345638262367E-1	J kg^{-1}
$(\partial g/\partial T)_p$	−2.E-27[b], 3.E-11[b]	−9.1554934092985614572E3	1.2206943393964807369E3	J kg^{-1} K^{-1}
$(\partial g/\partial p)_T$	1.0002075230252500703E-3	2.0599122491710824907E2	1.0908581273666870118E-3	m^3 kg^{-1}
$(\partial^2 g/\partial T^2)_p$	−1.5448497277676153768E1	−6.8983454098615831310	−7.6760298587519086996	J kg^{-1} K^{-2}
$(\partial^2 g/\partial T\,\partial p)$	−6.7979215180919329145E-8	7.5819292780093068933E-1	1.7438796470007613398E-7	m^3 kg^{-1} K^{-1}
$(\partial^2 g/\partial p^2)_T$	−5.0906231711021898838E-13	−3.3699243312745608812E-1	−1.2849594157169302559E-13	m^3 kg^{-1} Pa^{-1}
h	6.1178170345638262367E-1	2.5009151914656985040E6	−3.3344425396783922172E5	J kg^{-1}
f	4.E-26 [b], 3.E-9 [b]	−1.2599490372460606626E5	−5.5446874640188852815E-2	J kg^{-1}
u	7.E-25 [b], −6.E-9 [b]	2.3749196759593889814E6	−3.3344492119641731829E5	J kg^{-1}
s	2.E-27[b], −3.E-11[b]	9.1554934092985614572E3	−1.2206943393964807369E3	J kg^{-1} K^{-1}
ρ	9.9979252003162064660E2	4.8545757247785884172E-3	9.1670949219948795011E2	kg m^{-3}
c_p	4.2199115163700181633E3	1.8843520321577900481E3	2.0967843162166713804E3	J kg^{-1} K^{-1}
α	−6.7965110855503138742E-5	3.6807049820012030606E-3	1.5986310256590902275E-4	K^{-1}
κ_T	5.0895669687676183977E-10	1.6359552852946201284E-3	1.1779344934788178705E-10	Pa^{-1}
κ_s	5.0865762475261953085E-10	1.2314112503314651356E-3	1.1416159777876331107E-10	Pa^{-1}

[b] Each of these numbers is identically zero in the theoretical model. The numbers shown here give the roundoff errors corresponding to quadruple and double precision implementations, respectively.

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Table 4. Quadruple-precision values corresponding to results published in Table 6 of IAPWS-95 with the coefficients given in Table 1 of this paper. The ideal-gas part ϕ^o and for the residual part ϕ^r of the dimensionless Helmholtz free energy together with the corresponding derivatives[a] are shown for T=500 K and ρ=838.025 kg m^{-3}.

ϕ^o	2.04797733479597767929658675670 1	ϕ^r	−3.42693205681559284894224359995 2
ϕ^o_δ	0.38423674711374958980937322872 23	ϕ^r_δ	−0.36436665036388172980348797250 24
$\phi^o_{\delta\delta}$	−0.14763787783255553734814808208 1	$\phi^r_{\delta\delta}$	0.85606370097461138236330811285 60
ϕ^o_τ	9.04611106175242203902133714815 6	ϕ^r_τ	−5.81403435238416925802879424636 1
$\phi^o_{\tau\tau}$	−1.93249185013052032623179717858 1	$\phi^r_{\tau\tau}$	−2.23440736884336375579666201923 2
$\phi^r_{\delta\tau}$	0	$\phi^r_{\delta\tau}$	−1.12176914670306188890214708781 7

[a] For the abbreviated notation of the derivatives of ϕ^o and ϕ^r see the footnotes of Tables 4 and 5 of IAPWS-95, respectively.

Table 5. Quadruple-precision results for water properties in the single-phase region at the selected values of T and ρ published in Table 7 of IAPWS-95 with the coefficients given in Table 1 of this paper.

T K	ρ kg m^{-3}	p MPa	c_v J kg^{-1} K^{-1}	w m s^{-1}	s J kg^{-1} K^{-1}
300	996.5560	9.9241835181379651094E-2	4.1301811158584960765E3	1.5015191380813064465E3	0.39306264288077403467E3
	1005.308	2.0002251528132528836E1	4.0679834708858382510E3	1.5349250109621962916E3	0.38740540099921296375E3
	1188.202	7.0000470354978172066E2	3.4613558020377671029E3	2.4435799167401894386E3	0.13260961642075693598E3
500	0.435000	9.9967942317602231789E-2	1.5081754139110436746E3	5.4831425265432771044E2	7.9448827136464213826E3
	4.532000	9.9993812483991278912E-1	1.6699102452455069490E3	5.3573900134521477951E2	6.8250272527689584303E3
	838.0250	1.0000385800922118506E1	3.2210621867405833518E3	1.2712844091476324779E3	2.5669091854222539144E3
	1084.564	7.0000040549458516645E2	3.0743769300454436204E3	2.4120087657446758352E3	2.0323750919066389535E3
647	358.0000	2.2038475570652149984E1	6.1831572766683092166E3	2.5214507827000715938E2	4.3209230667550033099E3
900	0.241000	1.0006255868266188154E-1	1.7589065704448138520E3	7.2402714652918938252E2	9.1665319385523842681E3
	52.61500	2.0000069037214614551E1	1.9351052551262241493E3	6.9844567383679534276E2	6.5907022485101277853E3
	870.7690	7.0000000575565402666E2	2.6642234977936996739E3	2.0193360824868338741E3	4.1722380158463258117E3

Table 6. Quadruple-precision results for property values in the two-phase region at the selected values of temperature published in Table 8 of IAPWS-95 with the coefficients given in Table 1 of this paper[a]. The different shadings for p^{W} and p^{Vap} correspond to the results obtained by determining these quantities from the corresponding density estimates (at T=273.16 K) and comparing these to the full quadruple precision result.

Property	T=275 K	T=450 K	T=625 K	Unit
p^{W}	6.98451166700084935279E-4	9.3220356362820145516E-1	1.69082693185784409807E1	MPa
p^{Vap}	6.98451166700084935279E-4	9.3220356362820145516E-1	1.69082693185784409807E1	MPa
ρ'	9.9988740611984984069E2	8.9034124976167258553E2	5.6709038514635254862E2	kg m^{-3}
ρ''	5.50664918504122780 79E-3	4.8120036012567123262	1.1829028045115688596E2	kg m^{-3}
h^{W}	7.7597220155398177939E3	7.4916158501216908622E5	1.6862697594697419575E6	J kg^{-1}
h^{Vap}	2.5042899500405145942E6	2.7744107798896210429E6	2.5507162456234704801E6	J kg^{-1}
s^{W}	2.8309466959519726149E1	2.1086584468844730194E3	3.8019468301114322634E3	J kg^{-1} K^{-1}
s^{Vap}	9.1066012052321552768E3	6.6092122132788107010E3	5.1850612079573978994E3	J kg^{-1} K^{-1}

[a] Each of these test values was calculated from the Helmholtz free energy by applying the phase-equilibrium condition (Maxwell criterion).

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Table 7. Quadruple-precision results for the properties of pure ice at the triple point, the normal pressure melting point and at $T=100\,\mathrm{K}$, $p=100\,\mathrm{MPa}$. Results correspond to Table 6 of IAPWS-06 with the corrected coefficient g_{00} of ice given in Table 1.

Property	Value at $T=T_t=273.16\,\mathrm{K}$ $p=p_t=611.657\times10^{-6}\,\mathrm{MPa}$	Value at $T=273.152519\,\mathrm{K}$ $p=0.101325\,\mathrm{MPa}$	Value at $T=100\,\mathrm{K}$ $p=100\,\mathrm{MPa}$	Unit
g	6.11784134970536682445E-1	1.01342740687800954 92E2	−2.22296513087615583787E5	$\mathrm{J\,kg^{-1}}$
$(\partial g/\partial p)_T$	1.09085812736640059 54E-3	1.09084388214311034 31E-3	1.06193389259649146 71E-3	$\mathrm{m^3\,kg^{-1}}$
$(\partial g/\partial T)_p$	1.22069433939686944 63E3	1.22076932549695584 10E3	2.61195122588784941 94E3	$\mathrm{J\,kg^{-1}\,K^{-1}}$
$(\partial^2 g/\partial p^2)_T$	−1.28495941571494444 77E-13	−1.28485364928455470 78E-13	−9.41807981760913989 70E-14	$\mathrm{m^3\,kg^{-1}\,Pa^{-1}}$
$\partial^2 g/\partial p\partial T$	1.74387964699598040 34E-7	1.74362219972159070 57E-7	2.74505162488107677 55E-8	$\mathrm{m^3\,kg^{-1}\,K^{-1}}$
$(\partial^2 g/\partial T^2)_p$	−7.67602985875067425 65	−7.67598233364797668 51	−8.66333195516833785 37	$\mathrm{J\,kg^{-1}\,K^{-2}}$
h	−3.33444253965513887 43E5	−3.33354873636736613 84E5	−4.83491635676400779 81E5	$\mathrm{J\,kg^{-1}}$
f	−5.54468746400136645 15E-2	−9.18701567034970059 30	−3.28489902347264984 58E5	$\mathrm{J\,kg^{-1}}$
u	−3.33444921196523497 98E5	−3.33465403393094764 49E5	−5.89685024936049926 51E5	$\mathrm{J\,kg^{-1}}$
s	−1.22069433939686944 63E3	−1.22076932549695584 10E3	−2.61195122588784941 94E3	$\mathrm{J\,kg^{-1}\,K^{-1}}$
c_p	2.09678431621633417 99E3	2.09671391023544329 08E3	8.66333195516833785 37E2	$\mathrm{J\,kg^{-1}\,K^{-1}}$
ρ	9.16709492199728641 96E2	9.16721463419096003 00E2	9.41678203296572991 39E2	$\mathrm{kg\,m^{-3}}$
α	1.59863102565512723 53E-4	1.59841589457879991 91E-4	2.58495528207435063 86E-5	$\mathrm{K^{-1}}$
β	1.35714764658593923 67E6	1.35705899321101058 76E6	2.91466166993892774 80E5	$\mathrm{Pa\,K^{-1}}$
κ_T	1.17793449347730674 05E-10	1.17785291765150292 39E-10	8.86880048114989071 93E-11	$\mathrm{Pa^{-1}}$
κ_s	1.14161597778630574 25E-10	1.14154442556498041 60E-10	8.86060982686811647 48E-11	$\mathrm{Pa^{-1}}$

Table 8. Quadruple-precision results for the water part, saline part and total properties published in Table 8a of IAPWS-08 with the coefficients given in Table 1 of this paper. Properties at $S_A=S_n=0.03516504\,\text{kg}\,\text{kg}^{-1}$, $T=T_0=273.15\,\text{K}$, $p=p_0=0.101325\,\text{MPa}$. g_0, g_{200} and g_{210} are as given in Table 1.

Property	Water part	Saline part	Property of seawater	Unit
g	1.01342741729390628 82E2	−1.01342741729390628 82E2	−2.E-29[b], 1.E-8[b]	$\text{J}\,\text{kg}^{-1}$
$(\partial g/\partial S_A)_{T,p}$	0.0	6.39974067312299045 27E4	6.39974067312299045 27E4	$\text{J}\,\text{kg}^{-1}$
$(\partial g/\partial T)_{S,p}$	1.47643376346252665 31E-1	−1.47643376346252665 31E-1	7.E-32[b], −5.E-11[b]	$\text{J}\,\text{kg}^{-1}\,\text{K}^{-1}$
$(\partial g/\partial p)_{S,T}$	1.00015693912169263 47E-3	−2.74957224268432874 57E-5	9.72661216694849347 29E-4	$\text{m}^3\,\text{kg}^{-1}$
$(\partial^2 g/\partial S_A \partial p)_T$	0.0	−7.59615411515308894 45E-4	−7.59615411515308894 45E-4	$\text{m}^3\,\text{kg}^{-1}$
$(\partial^2 g/\partial T^2)_{S,p}$	−1.54473542319772893 39E1	8.52861151175922510 26E-1	−1.45944930808013668 29E1	$\text{J}\,\text{kg}^{-1}\,\text{K}^{-2}$
$(\partial^2 g/\partial T \partial p)_S$	−6.77700317865582657 55E-8	1.19286787413957641 32E-7	5.15167556273993755 63E-8	$\text{m}^3\,\text{kg}^{-1}\,\text{K}^{-1}$
$(\partial^2 g/\partial p^2)_{S,T}$	−5.08928894643490172 38E-13	5.81535172332882249 27E-14	−4.50775377410201947 45E-13	$\text{m}^3\,\text{kg}^{-1}\,\text{Pa}^{-1}$
h	6.10139534804117132 95E1	−6.10139534804117132 95E1	−4.E-29[b], 3.E-8[b]	$\text{J}\,\text{kg}^{-1}$
f	1.83987288512260878 38E-3	−9.85567376544907327 23E1	−9.85548977816056101 14E1	$\text{J}\,\text{kg}^{-1}$
u	−4.03269483760937929 20E1	−5.82279494055118171 94E1	−9.85548977816056101 14E1	$\text{J}\,\text{kg}^{-1}$
s	−1.47643376346252665 30E-1	1.47643376346252665 31E-1	−7.E-32[b], 5.E-11[b]	$\text{J}\,\text{kg}^{-1}\,\text{K}^{-1}$
ρ	9.99843085504330496 47E2	–[a]	1.02810719995400781 27E3	$\text{kg}\,\text{m}^{-3}$
c_p	4.21944480846459658 31E3	−2.32959023443703233 68E2	3.98648578502089334 94E3	$\text{J}\,\text{kg}^{-1}\,\text{K}^{-1}$
w	1.40238253108822626 06E3	–[a]	1.44900246362148362 06E3	$\text{m}\,\text{s}^{-1}$
μ_W	1.01342741729390628 82E2	−2.35181410932935947 07E3	−2.25047136759996884 19E3	$\text{J}\,\text{kg}^{-1}$

[a] The quantities ρ and w are nonlinear in g and hence cannot be computed from g^S alone.

[b] Each of these numbers is identically zero in the theoretical model. The numbers shown here give the roundoff errors corresponding to quadruple and double precision implementations, respectively.

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Table 9. Quadruple-precision results for the water part, saline part and total seawater properties published in Table 8b of IAPWS-08 with the coefficients given in Table 1 of this paper. Properties at S_A=0.1 kg kg^{-1}=100 g kg^{-1}, T=353 K, p=p_0=0.101325 MPa. This point is located in the regions with restricted validity.

Property	Water part	Saline part	Property of seawater	Unit
g	−4.4611496899569225658E4	1.50871740037052741 97E4	−2.95243228958639514 62E4	J kg^{-1}
$(\partial g/\partial S_A)_{T,p}$	0.0	2.5195727585141284916E5	2.5195727585141284916E5	J kg^{-1}
$(\partial g/\partial T)_{S,p}$	−1.07375993188745491 94E3	1.5623090740429099119E2	−9.1752902448316392819E2	J kg^{-1} K^{-1}
$(\partial g/\partial p)_{S,T}$	1.02892955635611007 00E-3	−5.7922728577125827635E-5	9.7100682777898424241E-4	m^3 kg^{-1}
$(\partial^2 g/\partial S_A \partial p)_T$	0.0	−3.0595780244233918005E-4	−3.0595780244233918005E-4	m^3 kg^{-1}
$(\partial^2 g/\partial T^2)_{S,p}$	−1.1888500004754679683E1	1.2792264931550738238E0	−1.0609273511599605860E1	J kg^{-1} K^{-2}
$(\partial^2 g/\partial T \partial p)_S$	6.5905155233936161134E-7	8.0306159575153091195E-7	1.4621131480908925233E-6	m^3 kg^{-1} K^{-1}
$(\partial^2 g/\partial p^2)_{S,T}$	−4.7467281936106728585E-13	2.1308615424374026844E-13	−2.6158666511732701741E-13	m^3 kg^{-1} Pa^{-1}
h	3.3442575905670236088E5	−4.0062336310009445692E4	2.9436342274669291 52E5	J kg^{-1}
f	−4.4715753186867008511E4	1.5093043024178351471E4	−2.9622710162688657 04E4	J kg^{-1}
u	3.3432150276940457803E5	−4.0056467289536368418E4	2.9426503547986820961E5	J kg^{-1}
s	1.0737599318874549194E3	−1.5623090740429099119E2	9.1752902448316392819E2	J kg^{-1} K^{-1}
ρ	9.7188383191307839206E2	–[a]	1.0298588757479005489E3	kg m^{-3}
c_p	4.1966405016784019283E3	−4.5156695208374105981E2	3.7450735495946608685E3	J kg^{-1} K^{-1}
w	1.5544629665347162190E3	–[a]	3.9612783529250024954E3	m s^{-1}
μ_W	−4.46114968995692256 58E4	−1.0108553581436010719E4	−5.4720050481005236377E4	J kg^{-1}

[a] The quantities ρ and w are nonlinear in g and hence cannot be computed from g^S alone.

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Table 10. Quadruple-precision results for the water part, saline part and total seawater properties published in Table 8c of IAPWS-08 with the coefficients given in Table 1 of this paper. Properties at S_A=0.03516504 kg kg^{-1}, T=T_0=273.15 K, p=100 MPa.

Property	Water part	Saline part	Property of seawater	Unit
g	9.7730386219537338734E4	−2.6009305073063660852E3	9.5129455712230972649E4	J kg^{-1}
$(\partial g/\partial S_A)_{T,p}$	0.0	−5.4586158064879659787E3	−5.4586158064879659787E3	J kg^{-1}
$(\partial g/\partial T)_{S,p}$	8.5146650206262343669E0	7.5404568488116539426E0	1.6055121869437888309E1	J kg^{-1} K^{-1}
$(\partial g/\partial p)_{S,T}$	9.5668332915350911569E-4	−2.2912384179113101721E-5	9.3377094497439601397E-4	m^3 kg^{-1}
$(\partial^2 g/\partial S_A \partial p)_T$	0.0	−6.4075761854574757172E-4	−6.4075761854574757172E-4	m^3 kg^{-1}
$(\partial^2 g/\partial T^2)_{S,p}$	−1.4296987338759055994E1	4.8807697394225122581E-1	−1.3808910364816804768E1	J kg^{-1} K^{-2}
$(\partial^2 g/\partial T \partial p)_S$	1.9907957080315389517E-7	4.6628441224121312517E-8	2.4570801202727520769E-7	m^3 kg^{-1} K^{-1}
$(\partial^2 g/\partial p^2)_{S,T}$	−3.7153088942341756981E-13	3.5734573584532666554E-14	−3.3579631583888490325E-13	m^3 kg^{-1} Pa^{-1}
h	9.5404605469153282817E4	−4.6606062955592693597E3	9.0743999173594013457E4	J kg^{-1}
f	2.0620533041864271652E3	−3.0969208939505591314E2	1.7523612147913712521E3	J kg^{-1}
u	−2.6372744619762875211E2	−2.3693678776479591876E3	−2.6330953238455879397E3	J kg^{-1}
s	−8.5146650206262343669E0	−7.5404568488116539426E0	−1.6055121869437888309E1	J kg^{-1} K^{-1}
ρ	1.0452779613969214514E3	–[a]	1.0709264465574263352E3	kg m^{-3}
c_p	3.9052220915820361447E3	−1.3331822543232592233E2	3.7719038661497102223E3	J kg^{-1} K^{-1}
w	1.5754223984859303496E3	–[a]	1.621989976498$\underline{7}$563752E3	m s^{-1}
μ_W	9.7730386219537338734E4	−2.4089780641265845021E3	9.5321408155410754232E4	J kg^{-1}

[a] The quantities ρ and w are nonlinear in g and hence cannot be computed from g^S alone.

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Table 11. Quadruple-precision results for the properties of water, ice and seawater at the standard ocean state, computed with all coefficients as given in Table 1 of this paper. T=273.15 K, p=0.101325 MPa and S_A=0.03516504 for seawater.

Property	Property of water	Property of ice	Property of seawater	Unit
g	1.0134274172939062882E2	9.8267598403431717064E1	−2.E-29[b], 1.E-8[b]	$\mathrm{J\,kg^{-1}}$
$(\partial g/\partial S_A)_{T,p}$	0.0	0.0	6.39974067312229904527E4	$\mathrm{J\,kg^{-1}}$
$(\partial g/\partial T)_{Sp}$	1.4764337634625266531E-1	1.2207886612999530642E3	7.E-32[b], -5E-11[b]	$\mathrm{J\,kg^{-1}\,K^{-1}}$
$(\partial g/\partial p)_{S,T}$	1.0001569391216926347E-3	1.09084344292643352467E-3	9.7266121669484934729E-4	$\mathrm{m^3\,kg^{-1}}$
$(\partial^2 g/\partial S_A \partial p)_T$	0.0	0.0	−7.5961541151530889445E-4	$\mathrm{m^3\,kg^{-1}}$
$(\partial^2 g/\partial T^2)_{S,p}$	−1.5447354231977289339E1	−7.6759851115667509185E0	−1.4594493080801366829E1	$\mathrm{J\,kg^{-1}\,K^{-2}}$
$(\partial^2 g/\partial T \partial p)_S$	−6.7770031786558265755E-8	1.7436082496084962410E-7	5.1516755627399375563E-8	$\mathrm{m^3\,kg^{-1}\,K^{-1}}$
$(\partial^2 g/\partial p^2)_{S,T}$	−5.0892889464349017238E-13	−1.2848482463976179327E-13	−4.5077537741020194745E-13	$\mathrm{m^3\,kg^{-1}\,Pa^{-1}}$
h	6.1013953480411713295E1	−3.3336015523567874778E5	−4.E-29[b], 3.E-8[b]	$\mathrm{J\,kg^{-1}}$
f	1.8398728851226087838E-3	−1.2262113451089334305E1	−9.8554897781605610114E1	$\mathrm{J\,kg^{-1}}$
u	−4.0326948376093792920E1	−3.3347068494753326883E5	−9.8554897781605610114E1	$\mathrm{J\,kg^{-1}}$
s	−1.4764337634625266531E-1	−1.2207886612999530642E3	−7.E-32[b], 5E-11[b]	$\mathrm{J\,kg^{-1}\,K^{-1}}$
ρ	9.9984308550433049647E2	9.1672183252738167257E2	1.02810719995400078127E3	$\mathrm{kg\,m^{-3}}$
c_p	4.2194448084645965831E3	2.0966953332244580134E3	3.9864857850208933494E3	$\mathrm{J\,kg^{-1}\,K^{-1}}$
α	−6.7759397686198971741E-5	1.5984037497909609918E-4	5.2964747378800447017E-5	$\mathrm{K^{-1}}$
κ_T	5.0884903632265555122E-10	1.1778484389572171289E-10	4.6344541107741383004E-10	$\mathrm{Pa^{-1}}$
κ_s	5.0855176492808069170E-10	1.1415405263722770087E-10	4.6325845206948706884E-10	$\mathrm{Pa^{-1}}$
μ_W	1.0134274172939062882E2	9.8267598403431717064E1	−2.2504713675999688419E3	$\mathrm{J\,kg^{-1}}$

[b] Each of these numbers is identically zero in the theoretical model. The numbers shown here give the roundoff errors corresponding to quadruple and double precision implementations, respectively.

Table 12. Formulas for properties reported in Tables 5–12, expressed in terms of partial derivatives of the Helmholtz function $f(T, \rho)$ of fluid water and the Gibbs functions $g(T, p)$ of ice and $g(S_\mathrm{A}, T, p)$ seawater.

Property	Expression in $g\ (S, T, p)$ of seawater	Expression in $g\ (T, p)$ of ice	Expression in $f\ (T, \rho)$ of fluid water	Comment
g	g	g	$f+\rho f_\rho$	specific Gibbs energy
$(\partial g/\partial S_\mathrm{A})_{T,p}$	g_S	0	0	
$(\partial g/\partial T)_{S,p}$	g_T	g_T	f_T	
$(\partial g/\partial p)_{S,T}$	g_p	g_p	ρ^{-1}	
$(\partial^2 g/\partial S_\mathrm{A}\partial p)_T$	g_{Sp}	0	0	
$(\partial^2 g/\partial T^2)_{S,p}$	g_{TT}	g_{TT}	$f_{TT}-\rho f_{\rho T}^2/\left(2f_\rho+\rho f_{\rho\rho}\right)$	
$(\partial^2 g/\partial T\partial p)_\mathrm{S}$	g_{Tp}	g_{Tp}	$f_{\rho T}/\left(2\rho f_\rho+\rho^2 f_{\rho\rho}\right)$	
$(\partial^2 g/\partial p^2)_{S,T}$	g_{pp}	g_{pp}	$-1/\left\{\rho^3\left(2f_\rho+\rho f_{\rho\rho}\right)\right\}$	
h	$g-Tg_T$	$g-Tg_T$	$f-T f_T+\rho f_\rho$	specific enthalpy
f	$g-pg_p$	$g-p g_p$	f	specific Helmholtz energy
u	$g-Tg_T-pg_p$	$g-Tg_T-pg_p$	$f-T f_T$	specific internal energy
s	$-g_T$	$-g_T$	$-f_T$	specific entropy
p	p	p	$\rho^2 f_\rho$	pressure
ρ	$1/g_p$	$1/g_p$	ρ	density
c_p	$-Tg_{TT}$	$-Tg_{TT}$	$T\left\{\rho f_{T\rho}^2\left(2f_\rho+\rho f_{\rho\rho}\right)-f_{TT}\right\}$	specific isobaric heat capacity
α	g_{Tp}/g_p	g_{Tp}/g_p	$f_{T\rho}/\left(2f_\rho+\rho f_{\rho\rho}\right)$	thermal expansion
κ_T	$-g_{pp}/g_p$	$-g_{pp}/g_p$	$1/\left\{\rho^2\left(2f_\rho+\rho f_{\rho\rho}\right)\right\}$	isothermal compressibility
κ_s	$\left(g_{tp}^2-g_{tt}\,g_{pp}\right)/\left(g_p\,g_{tt}\right)$	$\left(g_{tp}^2-g_{tt}\,g_{pp}\right)/\left(g_p\,g_{tt}\right)$	$f_{TT}/\left\{\rho^2 f_{TT}\left(2f_\rho+\rho f_{\rho\rho}\right)-\rho^3 f_{T\rho}^2\right\}$	isentropic compressibility
w	$g_p\sqrt{g_{tt}/\left(g_{tp}^2-g_{tt}g_{pp}\right)}$	–[a]	$\sqrt{\rho^2\left(f_{TT}f_{\rho\rho}-f_{\rho T}^2\right)/f_{TT}+2\rho f_\rho}$	sound speed
μ_W	$g-S_\mathrm{A}g_\mathrm{S}$	g	$f+\rho f_\rho$	chemical potential of water
β	–	$-g_{Tp}/g_{pp}$	–	pressure coefficient for ice

[a] Sound speeds in solid crystals cannot be computed from volume compressibility

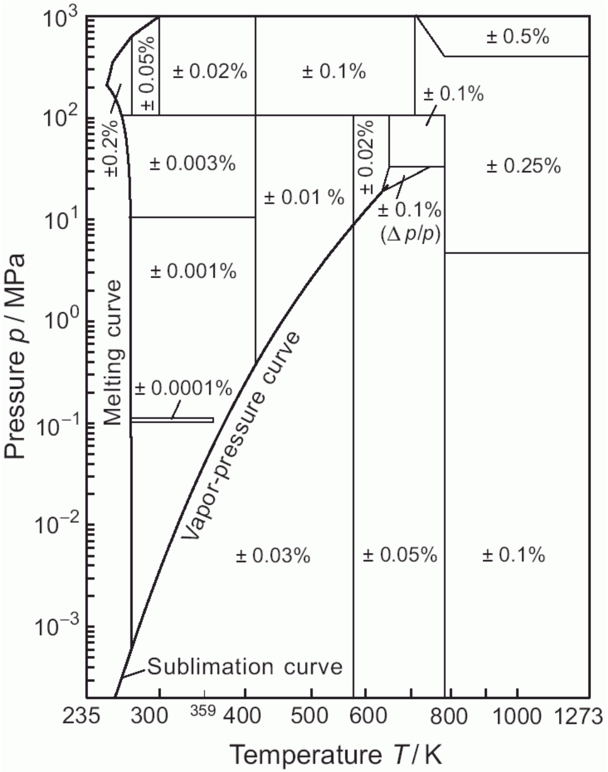

Fig. 1. Range of validity (excluding the ice phases at the left border line) and uncertainty of water density in the IAPWS-95 formulation.

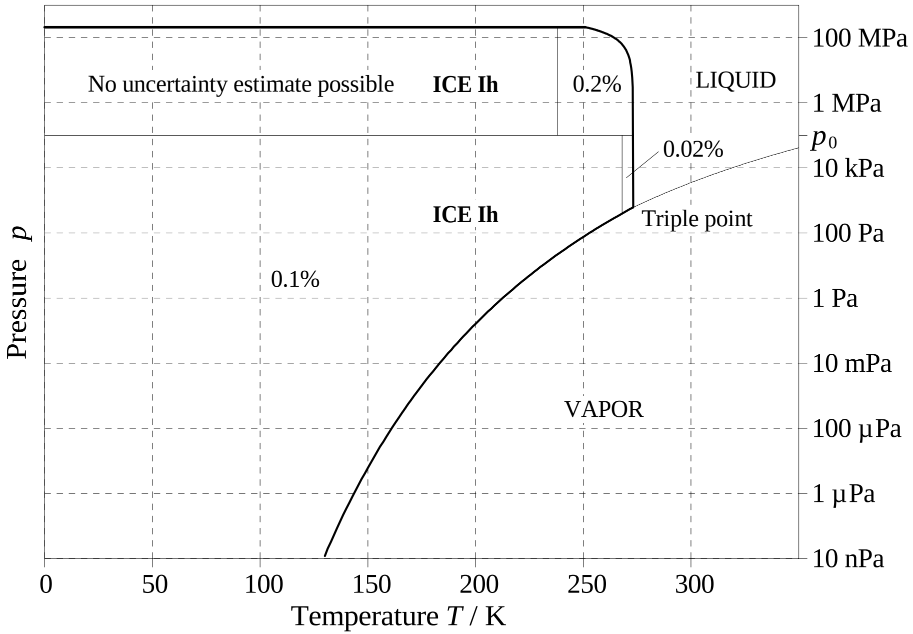

Fig. 2. Range of validity, shown in bold, and uncertainty of ice density in the IAPWS-06 formulation. The Gibbs function of ice remains valid at pressures even below the range shown here (it can be extrapolated to negative pressures to represent the effects of tensile stress), but the validity of IAPWS-95 for water vapor ends at T=130 K and hence does not extend below p=10 nPa.

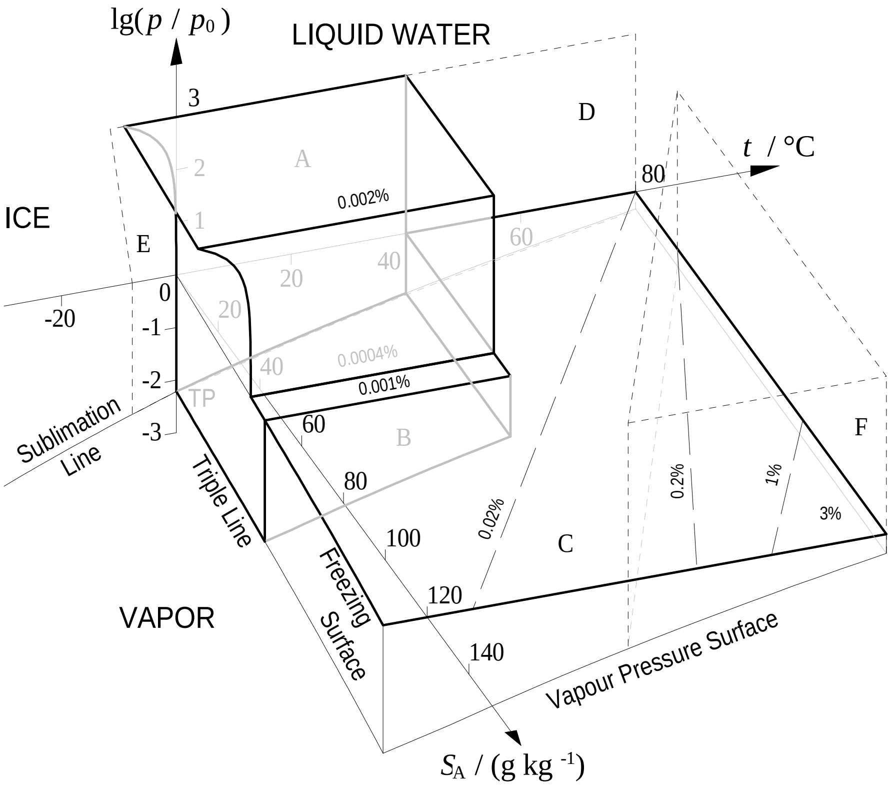

Fig. 3. Range of validity, shown in bold, and uncertainty of seawater density in the IAPWS formulation on seawater planned for adoption in 2008. The indicated regions are A: oceanographic standard range, B: extension to higher salinity at low pressure, C: extension to concentrated and hot brines at atmospheric pressure, D: IAPWS-95 pure water part, E: extension of IAPWS-95 to the metastable liquid, F: Range of unreliable extrapolated density derivatives. The plane S_A=0 is shown in Figs. 1 and 2 with more details.

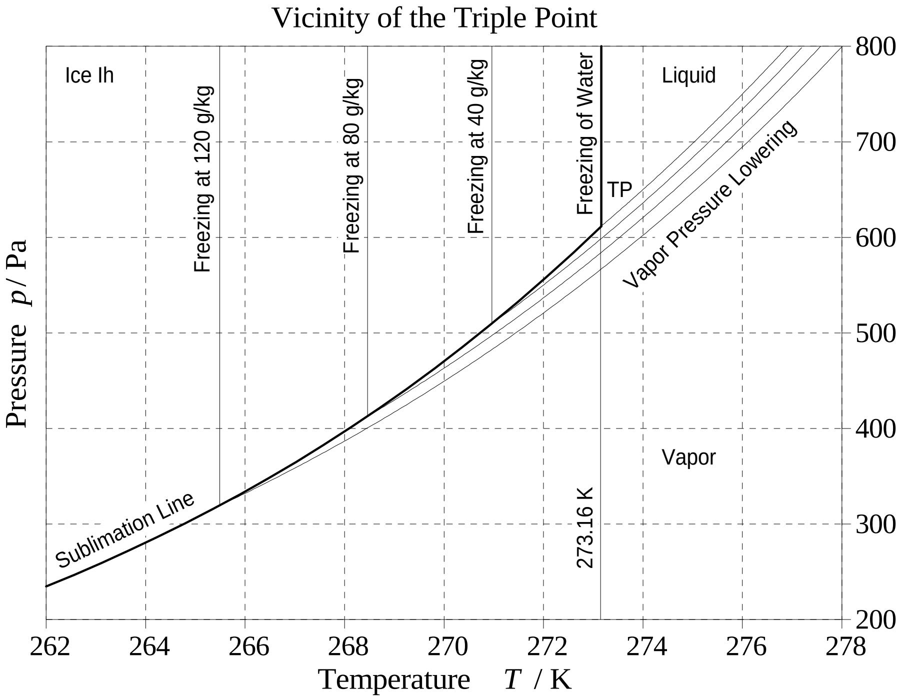

Fig. 4. Lowering of vapor pressure and of freezing temperature of seawater as a function of salinity in the vicinity of the pure-water triple point (TP). The four curves correspond to the four values of absolute salinity for which freezing temperatures are indicated on the diagram, with higher salinity values resulting in lowering of the vapor pressure for a given temperature. For non-zero salinities, the stable seawater phase occurs at temperature and salinity values for which the pure water liquid phase is metastable. This figure is a magnified projection of Fig. 3 along the salinity axis.