Improved and Always Improving: Reference Formulations for Thermophysical Properties of Water

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This article reviews the state of knowledge of the thermophysical properties of water in all its phases and the reference formulations that provide standardized, recommended values for these properties for use in science and industry. The main focus is the standard formulations adopted by the International Association for the Properties of Water and Steam (IAPWS), but some properties are covered for which IAPWS has not yet adopted recommendations. It is emphasized that, despite many advances over the last 100 years, there is room for further improvement, and current weaknesses and opportunities for advancing knowledge are discussed. Particular attention is given to the formulation for thermodynamic properties of fluid water known as IAPWS-95, which is planned to be replaced in the coming years. Additional topics include properties of heavy water and seawater, and the growing ability of molecular modeling to provide properties at conditions where experimental measurements are difficult or inaccurate.

Key words: D₂O; H₂O; heavy water; IAPWS; ice; molecular modeling; seawater; steam; thermodynamic properties; transport properties; water

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1. Introduction

Water is arguably the most important chemical compound on Earth, especially for living creatures like humans. It may also be the most thoroughly studied. For more than 100 years, skilled experimenters have measured the thermophysical properties of water and steam, and for most of that time people have worked to develop accurate tabulations and correlations of those properties. One might think that, by this point, there would be nothing left to do.

In reality, for a substance as important as water, there is always room for improvement. Both industrial and scientific users continue to demand better property formulations, although "better" may mean different things in different contexts.

The original impetus (over a century ago) for standardized properties for water and steam came from the steam power industry. The resulting "steam tables" have been improved and extended in range several times over the years, and the thermodynamic properties in such tables (saturation pressure, enthalpy, entropy, specific volume) are now known accurately enough for most uses in that industry. However, needs exist for improved consistency and for formulations that allow fast calculation in computer-intensive applications such as computational fluid dynamics (CFD). In addition, other properties of interest in some industrial settings (such as thermal conductivity and self-ionization constant) are in need of improved data.

In scientific settings, water has long served as an important reference. The original definition of the gram depended on the density of water, and before the SI redefinition in 2019 the thermodynamic temperature scale was anchored to water's triple point. Water is used as a calibration fluid for a wide variety of experiments, making it necessary to know its properties as accurately as possible so that the properties of the reference fluid do not add uncertainty to the resulting measurements. While the knowledge of water properties at room-temperature liquid conditions is sufficient for most purposes, there are still gaps in knowledge for regions such as the metastable supercooled liquid and the fluid near the vapor-liquid critical point. Improvement is also needed at high temperatures and/or pressures. Because of the many scientific uses for water, and the variety of physical processes where properties of water are essential to modeling, there will always be a demand for improved reference formulations.

This review describes the history and the state of the art of reference formulations for thermophysical properties of water (and heavy water), focusing on those adopted by the International Association for the Properties of Water and Steam (IAPWS). While IAPWS also works in the area of aqueous mixtures, we will not cover those efforts here, with the exception of formulations for seawater and humid air. More information about the activities of IAPWS, including its guidance for power-cycle chemistry, can be found at www.iapws.org.

Secondarily, we will include some properties of water for which IAPWS has not yet developed formulations. In some of these cases, sufficient data exist to provide a useful reference. Experiments for measuring properties of water are outside the scope of this review, although some



FIG. 1. Differences in saturated steam enthalpy of early steam tables, as illustrated in a 1925 article in *Mechanical Engineering*.⁴ Used with permission of ASME.

experimental work will be noted as contributing to existing and future formulations.

2. Background

2.1. The need for standardization

In the early 1900s, the use of steam power was expanding rapidly, particularly for electricity generation. Engineers based design and performance calculations on "steam tables," tabulated values of thermodynamic properties of water and steam based on the knowledge of the time. Widely used early steam tables included those of Marks and Davis in the United States,¹ Callendar in the United Kingdom,² and Mollier in Germany.³ However, the various tables in use disagreed with each other. While possible inaccuracy of tables was a concern, the bigger problem was their inconsistency, because use of different steam tables could make comparison of equipment specification and performance in commerce nearly impossible. Figure 1, taken from a 1925 article,⁴ illustrates saturated steam enthalpy from different steam tables; these differences were of large economic significance at higher saturation pressures.

Recognizing this untenable situation, in 1921 the American Society of Mechanical Engineers (ASME) began efforts both to improve the available experimental data and to produce standardized and self-consistent tables.⁵ Parallel efforts were started in the UK⁶ and in other countries. Because of the increasingly international nature of the power industry, it was logical for the different national efforts to cooperate with the goal of international standardization.

2.2. The evolution of IAPWS

The first step toward international standardization was the International Steam-Table Conference, held in London in 1929. This was followed by similar conferences in 1930 (Berlin) and 1934 (New York). At the 1934 meeting, agreement was reached on a set of "skeleton tables" that gave values of specific enthalpy and specific volume, along with estimated uncertainties expressed as "tolerances," at fixed points on the vapor-liquid saturation boundary and for single-phase vapor and liquid states. While it did not exactly adopt the 1934 values, the 1936 steam tables book of Keenan and Keyes⁷ was based on the same data and became a *de facto* standard for many years. The 1934 tables were also the basis of several other important steam tables published around the world.^{8–11}

After the Second World War, plants began to be built at pressures and temperatures exceeding the limits of the 1934 tables. This led to renewed interest in steam property research and standardization,¹² beginning with conferences in 1954 (Philadelphia), 1956 (London), and 1963 (New York). During this time, interests expanded to include other properties of water and steam, notably transport properties. The 7th International Conference on the Properties of Steam (Tokyo, 1968) was organized as a scientific conference, with research presentations in addition to the working sessions; this format has continued for subsequent conferences.

As it became clear that a more formal organization was necessary to maintain steam property standards, the International Association for the Properties of Steam (IAPS) was established in 1971. The name was changed in 1989 to the International Association for the Properties of Water and Steam (IAPWS); the added word reflected increased interest in properties of water and aqueous solutions in contexts beyond the steam power industry.

IAPWS holds working meetings annually and larger conferences roughly every five years. One of its main functions is to promulgate standards for various properties of water, steam, and aqueous solutions, not only for the steam power industry but for all areas of science and engineering. The main products are called Releases; other categories of documents (all available at www.iapws.org) include Supplementary Releases, Guidelines, and Advisory Notes. IAPWS standards are developed and evaluated by Working Groups with international membership, voted on by an Executive Committee representing IAPWS member countries, and supported by publications in archival journals. In most cases, we will cite both the IAPWS document and the journal article when discussing IAPWS reference formulations.

3. Preliminary Details

3.1. Units of measure

IAPWS formulations use the International System of Units (SI).¹³ While the underlying definitions of the SI underwent a significant revision in 2019 in order to base the system entirely on fundamental physics rather than on physical artifacts,¹⁴ this change was largely invisible to the scientists and engineers who use the system. The SI remains a standard, self-consistent, and rational system for expressing physical quantities.

For historical and practical reasons, some work uses non-SI units such as the cubic foot, the calorie, and the British thermal unit (Btu). Conversions between these units and those of the SI can be easily found, but caution is required since some sources may use rounded or obsolete values. Reliable information is given in a NIST publication.¹⁵

The use of non-SI energy units (calories, Btus) for water and steam is especially problematic. Historically, these were defined as the amount of heat needed to raise the temperature of a mass of liquid water (a gram for the calorie; a pound for the Btu) by one degree (Celsius for the calorie, Fahrenheit for the Btu) at atmospheric pressure. However, this amount depends on the temperature of the experiment; this ultimately led to the definition of the calorie as a fixed number of joules (and a corresponding definition of the Btu from the conversion between the gram and the pound and between the Celsius and Fahrenheit degrees). Unfortunately, two definitions are in common use. Most scientific work uses the "thermochemical" calorie defined by 1 cal_{th} = 4.184 J. However, the Fifth International Conference on the Properties of Steam (London, 1956) defined the "International Table" calorie by 1 cal_{IT} = 4.1868 J (the corresponding Btu_{IT} is approximately 1055.056 J), and this is the value used in steam tables and the steam power industry. Those who use non-SI units need to be clear about which conversion is being used; it can become especially tricky if water is mixed with other compounds where the thermochemical definition may be used.

Many properties may be given on a per-mass or per-mole basis; for example, a density may be given in kg m⁻³ or mol m⁻³. Some IAPWS formulations are stated in terms of mass (sometimes called "specific" properties) and some are in molar units; conversion between mass and molar units should use the molar mass given in Sec. 4.1 unless more specific information is available about the isotopic composition of the sample in question.

3.2. Temperature scale

Rigorous measurement of the thermodynamic temperature is difficult. Practical temperature measurement therefore uses defined scales, calibrated to match the true thermodynamic temperature as well as possible at the time of adoption of the scale.¹⁶ The current standard is the International Temperature Scale of 1990 (ITS-90).¹⁷ Current IAPWS formulations are developed on ITS-90; if input data were reported on other scales, they are converted before fitting the formulations.

There is a subtle point regarding the use of ITS-90 in IAPWS formulations. Some formulations make use of quantities calculated from molecular theory. This is the case for the ideal-gas heat capacity that is a part of the thermodynamic equation of state (see Secs. 5.2.3 and 7.1.2) and the low-density limit of the transport properties (Secs. 6 and 7.2). These refer to the thermodynamic temperature, not to ITS-90. IAPWS has decided that the errors introduced by the small [on the

order of 10 mK (Refs. 18 and 19)] differences between ITS-90 and the thermodynamic temperature are negligible in the context of the current formulations.

3.3. Gas constant and other fundamental constants

Thermophysical property formulations typically use some fundamental physical constants, such as the molar gas constant *R*, the Boltzmann constant *k*, and the Avogadro constant N_A . The recommended values of these quantities, along with their estimated uncertainties, are maintained by the Committee on Data (CODATA) of the International Science Council. The latest version is the 2018 evaluation.^{20,21} Notably, as a part of the latest SI revision,^{13,14} the Boltzmann and Avogadro constants now are fixed exactly at 1.380649 × 10⁻²³ JK⁻¹ and 6.02214076 × 10²³ mol⁻¹, respectively. The means that the molar gas constant is also exact, since $R = N_A k$.

Because most IAPWS formulations were developed prior to the latest CODATA revision, they may contain values of R and other constants slightly different from their current values. Because the older values were used in the fitting of experimental data, it is important to use the values exactly as given in the formulation to avoid distorting the calculated results.

4. The Water Molecule

4.1. Isotopic composition and molar mass

A water molecule consists of two hydrogen atoms and one oxygen atom. Different stable isotopes exist for these elements. Hydrogen can have a single proton (¹H) or a proton plus a neutron (²H, commonly called deuterium and written as D). Oxygen has three stable isotopes: ¹⁶O, ¹⁷O, and ¹⁸O. If we ignore unstable isotopes such as ³H and ¹⁵O, there are nine possible water molecules (H₂O, HDO, and D₂O, each with three possible oxygen isotopes).

Most hydrogen on Earth is ¹H (which we will normally write as just H) and most oxygen is ¹⁶O. Because of isotopic fractionation in chemical reactions, diffusion, and phase equilibria, the isotopic composition of water reflects its environment and history; these variations are used in the study of hydrological cycles over both short-term and geologic time scales.^{22,23} The usual reference for water's isotopic composition is ocean water below the surface well away from freshwater sources, which is remarkably constant across the globe. This led to the definition of Vienna Standard Mean Ocean Water (VSMOW) as a standard composition.^{24,25} Because of exhaustion of the original VSMOW sample, a new standard called VSMOW2, with composition identical to the original VSMOW to within measurement uncertainty, has been prepared.²⁶ The isotopic composition of VSMOW is 0.015 574(5) atom percent D of the total hydrogen, with the minor oxygen isotopes ¹⁷O and ¹⁸O at 0.037 90(9) and 0.200 04(5) atom percent, respectively.²⁵ The number in parentheses indicates the standard uncertainty in the last digit.

IAPWS standards for ordinary water (sometimes the older term "ordinary water substance" is used) by definition refer to the isotopic composition of VSMOW.²⁷ For most properties, the

exact isotopic composition is not a significant concern, but for precisely measured properties such as the liquid density at room temperature it can be significant at the level of uncertainty of the best measurements. In these cases, knowledge of the true isotopic composition and molar mass is essential. The relative molar mass of VSMOW is obtained by combining the isotopic composition with the accepted atomic masses of each isotope;²⁸ the result is 18.015 268, with an uncertainty of no greater than two in the last digit.

IAPWS also produces formulations for heavy water, which is defined^{27,29} as water whose hydrogen isotopic content is 100% D and whose oxygen isotopes are in the same proportions as in VSMOW. A similar calculation to that for ordinary water yields a relative molar mass of 20.027 508, with an uncertainty of no more than two in the last digit. However, the oxygen isotopic composition of real heavy water may differ significantly from that of VSMOW depending on the process by which it is made, and typical heavy water is only about 99.9% isotopically pure in terms of D, so isotopic analysis is necessary if a scientific application requires accurate knowledge of the molar mass.

4.2. Molecular quantities

4.2.1. Geometry

The geometry of the water molecule can be characterized by the O-H bondlengths and the H-O-H angle. However, in a rigorous description we cannot assume a single fixed geometry. Even if we restrict our attention to the ground vibrational and rotational state, the zero-point quantum vibrations of the molecule mean that the geometric parameters are described by a probability distribution. Within this distribution, two special geometries are often discussed. The first is the *equilibrium* geometry, which is the global minimum of the single-molecule potential-energy surface. The second is the vibrationally averaged geometry, which is the expectation value of the geometry averaged over the ground-state wavefunction. Because experiments at finite temperatures necessarily sample states in addition to the ground state, the most accurate values of the groundstate geometry are obtained from *ab initio* quantum calculations. The equilibrium O-H distance is 0.095 785 nm, while the equilibrium H-O-H angle is 104.500°.³⁰ The respective vibrationally averaged values for the ground state are 0.097 565 nm and 104.430°.³¹ For D₂O, the equilibrium values are 0.095 783 nm and 104.490°, while the vibrationally averaged ground-state values are 0.097 077 nm and 104.408°.³¹ Czakó et al.³¹ provided vibrationally averaged rotationless values for several of the lowest-lying excited vibrational states, and performed Boltzmann-weighted averaging over vibration and rotation to calculate expectation values of geometric parameters as a function of temperature. Such vibrationally averaged calculations require a potential-energy surface for the molecule; a recent high-quality surface is that of Mizus *et al.*³²

The above discussion was for an isolated water molecule. Interactions with other molecules cause the average geometry to be different in liquid water and in ice. Information can be obtained

from neutron diffraction, but interpretation of the data is difficult due to the distribution of geometric parameters, disorder in the liquid phase, and disorder of the hydrogens within ice Ih. For ice Ih, the average intramolecular O-H bond distance is near 0.0986 nm,^{33,34} slightly larger than the gas-phase value, and the average H-O-H bond angle is approximately 107° ,³³ somewhat closer to the tetrahedral angle of 109° . The liquid is more difficult to study, but the O-H distance appears to be similar to that in ice.³⁵ As in the gas phase, the average O-D bond lengths for D₂O in the solid and liquid phases are about 0.0005 nm shorter.^{33,35}

4.2.2. Multipole moments and polarizability

As with the geometry, the electric multipole moments of the water molecule (dipole, quadrupole, etc.) are quantum mechanical averages over the molecular wavefunction, which depend on the rotational and vibrational state of the molecule. The same is true for the polarizability, which has the additional complication of wavelength dependence.

The dipole moment of the isolated H₂O molecule in its ground state was accurately measured by Shostak *et al.*,³⁶ who used molecular beam electric resonance spectroscopy to obtain a value (in the traditional debye units) of 1.854 98(9) D. Since 1 D \approx 3.335641 × 10⁻³⁰ Cm, the value in SI units is 6.1875(3) × 10⁻³⁰ Cm. For D₂O, the ground-state dipole moment was measured with a similar technique by Dyke and Muenter³⁷ as 1.8545(4) D. There is a small temperature dependence of the dipole moment, because the excited rovibrational states populated at higher temperatures have slightly different moments from the ground state. The temperature dependence of the dipole moment has been calculated theoretically by Garberoglio *et al.*³⁸

Verhoeven and Dymanus used maser spectroscopy of the Zeeman effect to derive the quadrupole tensors of both H_2O and D_2O .³⁹ Higher multipole moments (octupole, hexadecapole, etc.) have not been measured experimentally; estimates for these moments can be obtained from *ab initio* quantum mechanical calculations.^{40–42}

In condensed phases (liquid and solid), the charge distribution is different from that of the isolated molecule. The molecules polarize one another such that the average dipole moment is significantly enhanced. This effect is not directly measurable, but with reasonable assumptions an average moment can be estimated from x-ray measurements in liquid water⁴³ and from theoretical approaches including *ab initio* molecular dynamics simulation.^{40,44–49} These studies suggest that the average dipole moment in the liquid is roughly 60% larger than for the isolated molecule, with a slightly greater increase for ice.

For a molecule such as H_2O , there are two distinct contributions to the polarizability. The *electronic* polarizability reflects the response of the electrons to an electric field. This depends on the direction of the field relative to the molecular axes, but the quantity of most interest is the mean polarizability, which can be derived from measurements of the refractive index for water vapor; the most precise study,⁵⁰ when its results at optical frequency are extrapolated to the static limit with the dipole oscillator strength sums of Zeiss and Meath,⁵¹ yields a static electronic polarizability

of 1.453×10^{-24} cm³. The best *ab initio* calculations yield a value about 0.3% larger for the vibrationally averaged ground state.⁵² A recent, somewhat less precise, refractivity measurement⁵³ is consistent within mutual uncertainties with both the experimental⁵⁰ and *ab initio*⁵² results. At low frequencies, there is also a *pure vibrational* contribution caused by the electric field acting differentially on the positive and negative parts of the molecule. This effect adds approximately an extra 3% to the polarizability in the static limit;⁵⁴ the temperature dependence of this vibrational contribution has been calculated.³⁸ The polarizability is frequency-dependent; the small dispersion effect on the electronic polarizability is described at optical frequencies by Schödel *et al.*⁵⁰

4.2.3. Molecular partition function

The partition function of the canonical ensemble in statistical mechanics is a Boltzmannweighted sum over all possible energy levels; thermodynamic properties can be obtained from mathematical operations on the sum. For a single molecule, the internal partition function is only a function of temperature, and derived thermodynamic properties correspond to those of the ideal gas.

In the past, partition functions of molecules like water were typically computed by assuming the molecule to be a rigid rotor with harmonic vibrations at frequencies obtained by spectroscopy. More advanced methods added corrections for anharmonicity and rotation-vibration coupling. The most thorough such calculations for water were performed by Woolley,^{55,56} who also derived ideal-gas thermodynamic properties.

More recently, for molecules that are well-studied both spectroscopically and theoretically, it has become possible to compute more accurate partition functions by direct summation over molecular energy levels. Modern spectroscopy can yield highly accurate energy levels, and *ab initio* calculations can fill in gaps (typically at highly excited states) where measurements are lacking. For $H_2^{16}O$, which is the most abundant water isotopologue, this approach was used by Furtenbacher *et al.*,⁵⁷ who derived the partition function and ideal-gas thermodynamic properties at temperatures up to 6000 K. Similar calculations were performed by Simkó *et al.*⁵⁸ for the three isotopologues comprising heavy water ($D_2^{16}O$, $D_2^{17}O$, and $D_2^{18}O$). In both cases, the first and second moments of the partition function (related to its temperature derivatives and needed for thermodynamic computations) were given along with their uncertainties.

A similar approach has been used by Gamache *et al.*,⁵⁹ who calculated the molecular partition functions (which they call Total Internal Partition Sums) for a number of common molecules, including the nine stable isotopologues of water. Their partition functions are in good agreement with those mentioned in the previous paragraph^{57,58} for $H_2^{16}O$, $D_2^{16}O$, $D_2^{17}O$, and $D_2^{18}O$, and provide the best current partition functions for the other five isotopologues.

The ideal-gas thermodynamic properties resulting from the partition function of the water molecule are discussed further in Sec. 11.2.1.

5. Thermodynamics of Ordinary Water

5.1. History of formulations

As mentioned in Sec. 2.2, a consensus set of "skeleton tables" was agreed upon at the Third International Steam Tables Conference in 1934. These tables covered, in a coarse grid, temperatures up to 550 °C and pressures up to approximately 30 MPa, with values of specific enthalpy and specific volume at each grid point and estimated uncertainties for each point. There was also a table for the vapor-liquid saturation boundary. The 1936 steam tables book of Keenan and Keyes,⁷ which was consistent with the 1934 tables although not strictly based on them, was widely used for over 30 years.

The next generation of formulations, incorporating improved data and extending to higher temperatures and pressures, was developed in the 1960s by an International Formulation Committee (IFC) that was authorized at the steam-table conferences. The IFC made use of critical evaluations of experimental data and formulations for various regions developed by teams within several countries. By far the most used formulation of that generation was the IFC-67 formulation "for industrial use."⁶⁰ IFC-67 covered temperatures up to 800 °C and pressures up to 100 MPa, enough to satisfy contemporary and anticipated needs of the steam power industry. Importantly, it was provided as a set of equations (dividing pressure/temperature space into six regions, each with its own sub-formulation) suitable for computer programming, enabling routine use of computers in engineering calculations. IFC-67 was used to tabulate values in steam-tables books,^{61–65} but the standard was the equations, not the printed tables. In 1968, a modification "for scientific and general use" was issued, which contained some additional equations to improve the behavior near water's critical point.^{66,67} This formulation, known as IFC-68, was not widely used.

While it was not an IAPS standard, a notable development was the 1969 formulation of Keenan *et al.*,⁶⁸ which was the first to derive all thermodynamic properties from a single equation for the Helmholtz energy as a function of temperature and density. This eliminates the discontinuities between regions that are inevitable in piecewise formulations such as IFC-67, and allows thermodynamic properties to be obtained by differentiation and vapor-liquid equilibrium to be obtained by solving the Maxwell criteria. This approach was followed for subsequent IAPS/IAPWS formulations.

In 1984, IAPS adopted a new "Formulation for Scientific and General Use" that was, for the first time in an IAPS standard, a single equation of state for entire fluid region.^{69,70} While IAPS-84 was a significant step forward, some shortcomings became evident after its adoption; several of these are discussed by Wagner and Pruß.⁷¹ Some derivative properties, such as the isothermal compressibility, were not well-behaved in the liquid region. Special terms that had been added in an attempt to better describe the critical region led to unphysical oscillations. Extrapolation to the metastable subcooled liquid and to high temperatures and pressures was not good.

In addition to these shortcomings, the adoption of the ITS-90 temperature scale¹⁷ led IAPWS

to seek a new formulation that would use modern equation-of-state technology to ensure correct behavior of derivatives and correct extrapolation while using ITS-90. The result of several years of development and testing was the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use, which has become known as IAPWS-95.^{71,72} IAPWS-95 remains the standard for thermodynamic properties of water and steam.

5.2. IAPWS-95 formulation for general and scientific use

5.2.1. Structure of formulation

The IAPWS-95 formulation, like all modern reference equations of state, is an expression for the Helmholtz energy as a function of temperature T and density ρ , from which other properties can be computed by differentiation and combination of terms. The relationships for calculating properties and vapor-liquid equilibria are given in the IAPWS document⁷² and in the IAPWS-95 journal article.⁷¹ The Helmholtz energy a is on a specific (per unit mass) basis, and ρ is the mass density. The function is written as the sum of an ideal-gas term and a residual term, both in dimensionless form,

$$\frac{a(\boldsymbol{\rho},T)}{R_{\rm w}T} \equiv \phi(\boldsymbol{\delta},\tau) = \phi^{\circ}(\boldsymbol{\delta},\tau) + \phi^{\rm r}(\boldsymbol{\delta},\tau), \tag{1}$$

where the reduced density is $\delta = \rho/\rho_c$, the reduced reciprocal temperature is $\tau = T_c/T$, and the subscripts c denote the critical parameters that are given in Sec. 5.2.2. The ϕ° term is the dimensionless Helmholtz energy of an ideal gas, which only requires knowledge of the ideal-gas heat capacity. The ϕ^r term accounts for all intermolecular interactions, and contains adjustable parameters fitted to experimental data.

Since the formulation is mass-based, R_w in Eq. (1) is a substance-specific gas constant obtained by dividing the molar gas constant by the molar mass of water. Because of obsolete values of these quantities used in the development of IAPWS-95, the value used ($R_w = 0.46151805 \text{ kJ kg}^{-1} \text{ K}^{-1}$) is not what would be obtained from their current values (or even the best known values in 1995); see Sec. 6.1 of Ref. 71 for more details.

 ϕ^{r} contains 56 terms of various types, which were selected in an optimization process (described in detail in Ref. 71) to best represent the experimental data. The form of ϕ^{r} is

$$\phi^{\mathbf{r}}(\delta,\tau) = \sum_{i=1}^{7} n_i \delta^{d_i} \tau^{t_i} + \sum_{i=8}^{51} n_i \delta^{d_i} \tau^{t_i} \exp(-\delta^{c_i}) + \sum_{i=52}^{54} n_i \delta^{d_i} \tau^{t_i} \exp[-\alpha_i (\delta - \varepsilon_i)^2 - \beta_i (\tau - \gamma_i)^2] + \sum_{i=55}^{56} n_i \Delta^{b_i} \delta \psi, \qquad (2)$$

where the symbols with subscript *i* are adjustable parameters (although most of them except for n_i are restricted to positive integer values) and the functions Δ and ψ are defined elsewhere.^{71,72} The first two sums are polynomial terms and polynomial-exponential terms that are used in most

TADIE 1	Critical	noromatara	of	ordinom	and	hoorn	water 7	14
IABLE I.	Critical	parameters	OI	ordinary	and	neavy	water.	•

Parameter	Ordinary water	Heavy water
T _c /K	$647.096 + \delta_1$	$643.847 + \delta_2$
	$\delta_1=0.000\pm0.100$	$\delta_2 = 0.000 \pm 0.200$
<i>p</i> _c /MPa	$22.064 + 0.27\delta_1 \pm 0.005$	$21.671 + 0.27\delta_1 \pm 0.010$
$\rho_{\rm c}/({\rm kg}~{\rm m}^{-3})$	322 ± 3	356 ± 5

modern reference equations of state. The third sum consists of three "Gaussian bell-shaped" functions; these improve the representation of properties near the critical point. Finally, the fourth sum consists of two "nonanalytic" terms intended to mimic the limiting behavior of fluids very near the critical point.

5.2.2. Critical point, triple point, and reference state

The state parameters at the critical point not only provide reducing parameters for the equation of state; they fix the endpoint of the vapor-liquid saturation boundary. They are therefore key quantities in any equation of state. Levelt Sengers *et al.*⁷³ examined all the available data and recommended values for the critical temperature, pressure, and density of both ordinary and heavy water. Those recommendations, converted to the ITS-90 temperature scale, are given in an IAPWS Release⁷⁴ and reproduced in Table 1. The unusual manner of writing the uncertainty in the critical temperature and pressure reflects the fact that their uncertainties are coupled; because the vapor-pressure relationship with temperature is known accurately, an error in T_c will produce an error in p_c in the same direction. Despite the fact that it has been almost 40 years since the evaluation described in Ref. 73, we are not aware of any new data for the critical parameters.

The other endpoint of the vapor-liquid saturation boundary is the triple point, where vapor, liquid, and solid phases exist in equilibrium. Prior to 2019, the thermodynamic temperature scale was defined by fixing the value 273.16 K at the triple point of water (more precisely, water with the isotopic composition of VSMOW as discussed in Sec. 4.1; see Refs. 75–77 for the effect of isotopic composition on the triple-point temperature). While this is no longer the case in the "new SI," 273.16 K is still the best estimate of the thermodynamic temperature of the triple point, which now has a relative standard uncertainty of 3.7×10^{-7} ,¹³ and is still the value fixed in the ITS-90 scale.¹⁷ The pressure at the triple point was measured accurately by Guildner *et al.*;⁷⁸ the result is 611.657 Pa with an expanded uncertainty (99% confidence interval) of 0.010 Pa. This not only provides an accurate point on the vapor-pressure curve (which IAPWS-95 reproduces within its uncertainty), but also anchors the melting and sublimation curves discussed in Sec. 8.3.

In an equation of state, thermodynamic calculations are invariant with respect to arbitrary constant shifts in the enthalpy and the entropy. This makes it necessary to select a reference state in order to fix the numerical values of enthalpy- and entropy-related quantities. For water, the longstanding convention is that the internal energy and the entropy of the saturated liquid are defined to be zero at the triple point.

5.2.3. Ideal-gas term

The ideal-gas term ϕ° in Eq. (1) is obtained by integrating the expression for water's idealgas specific isobaric heat capacity given by Cooper,⁷⁹ which was obtained as a fit to the values calculated by Woolley⁵⁵ from statistical mechanics. The equation of Cooper covered temperatures from 130 K to 2000 K. Water vapor at even lower temperatures, down to 50 K, can be described in the IAPWS-95 framework with an extension of the ideal-gas Helmholtz function.^{80,81}

Two constants in the representation of ϕ° are arbitrary because of the arbitrary zeros of energy and enthalpy. These are fixed in accordance with the choice of reference state discussed in Sec. 5.2.2.

5.2.4. Key data sources

The archival paper documenting IAPWS-95 contains a thorough discussion of the experimental data sources used.⁷¹ The foundation for this effort was an IAPWS project that collected and organized available experimental thermodynamic data for water and steam.⁸² Here, we briefly review the sources that were most important for constraining the thermodynamic formulation. See Sec. 11.1 for discussion of new sources of data since the development of IAPWS-95 and of needs for additional data.

For many purposes, notably in the steam power industry, the most important properties are those corresponding to vapor-liquid equilibrium. This is not only the vapor-pressure curve $p_{\sigma}(T)$, but also the densities and enthalpies of the saturated vapor and liquid and the enthalpy of vaporization (latent heat). The vapor-pressure curve is anchored at the low-temperature end by a measurement of the pressure at the triple point (273.16 K).⁷⁸ At the high-temperature end, it is constrained by the critical point discussed in Sec. 5.2.2. Between these extremes, the vapor-pressure curve is largely determined by measurements at the U.S. National Bureau of Standards (NBS, now the National Institute of Standards and Technology, NIST) from 25–100 °C (Ref. 83) and from 100 °C to near T_c ,⁸⁴ and also data by Kell *et al.*⁸⁵ at the National Research Council of Canada from 423 K to 623 K.

For properties along the saturation boundary, much of our knowledge comes from thorough calorimeteric measurements performed in the 1930s by Osborne and coworkers at NBS. Separate but similar apparatus were used for measurements up to 100 °C (Ref. 86) and from 100 °C to the critical point.⁸⁷ Depending on apparatus configuration, these experiments yielded three quantities at saturation, which they denoted by $\Delta \alpha$, β , and γ . $\Delta \alpha$ is closely related to the internal energy of vaporization, while $\beta = Tv'dp_{\sigma}/dT$ and $\gamma = Tv''dp_{\sigma}/dT$, where v' and v'' are the saturated liquid and saturated vapor specific volumes, respectively. Both β and γ can also be related to the specific enthalpy of vaporization through the Clapeyron equation. More information about relating

these quantities in a consistent way to thermodynamic properties at saturation is given by Saul and Wagner.⁸⁸ Additional accurate densities for the saturated liquid were reported by Kell *et al.*⁸⁵

For the pressure–density–temperature ($p\rho T$) behavior, the gas phase is covered up to 773 K by the data of Kell *et al.*⁸⁹ At higher temperatures, the formulation primarily depends on the somewhat more uncertain data of Vukalovich *et al.*⁹⁰ The compressed liquid up to 423 K and 100 MPa is covered by the data of Kell and Whalley,⁹¹ while Grindley and Lind⁹² reported data at higher pressures to 800 MPa. Unfortunately, there is an unexplained offset between these two data sets where they overlap; the developers of IAPWS-95 resolved the inconsistency by reducing the densities of Grindley and Lind by 0.02%.⁷¹ At even higher pressures, up to 3500 MPa, older data are available from Bridgman.^{93,94} At temperatures above 423 K, liquid densities are given by Kell *et al.*⁹⁵ up to 100 MPa and by Hilbert *et al.*⁹⁶ up to 400 MPa. Some additional papers, mostly from the Soviet Union in the 1960s, provided $p\rho T$ data near the critical point; see Wagner and Pruß⁷¹ for citations and details. Additional highly accurate data for the liquid density near atmospheric pressure are discussed in Sec. 5.5.

For the liquid near atmospheric pressure, the high-precision sound-speed data of Del Grosso and Mader⁹⁷ and of Fujii and Masui⁹⁸ are in good agreement, giving us high confidence in this region. At higher pressures, the only high-accuracy data were the liquid-phase data of Fujii⁹⁹ that extend to 200 MPa from 303 K to 323 K.

Most of the data used for the isobaric heat capacity c_p come from a series of papers reporting work done in the 1950s and 1960s in the group of Sirota in the Soviet Union; see Ref. 71 for references and details. Many of these data are in the critical region where c_p diverges. Closely related are measurements of enthalpy differences for a finite temperature interval at constant pressure. The liquid-phase data of Castro-Gomez *et al.*¹⁰⁰ cover the range up to 455 K and 11.9 MPa with 1% uncertainty. The enthalpy increments of Philippi¹⁰¹ are somewhat more uncertain, but extend to 670 K at pressures from 20 MPa to 50 MPa.

5.2.5. Range of validity and extrapolation

The range of validity of IAPWS-95 is all stable fluid states from the melting and sublimation curves (see Sec. 8.3) up to 1273 K at pressures to 1000 MPa. When extrapolated in pressure and temperature, the behavior is physically reasonable up to 100 GPa and 5000 K; however, it should be noted that dissociation of the water molecule significantly affects the thermodynamics above roughly 2000 K, and is not taken into account in IAPWS-95.

While IAPWS-95 agrees with available experimental data for thermodynamic properties near the vapor-liquid critical point, it does not reproduce the asymptotic critical exponents given by the modern theory of critical phenomena. It therefore cannot be used to study the "nonclassical" behavior in the vicinity of the critical point. Methods for describing the crossover from IAPWS-95 to the asymptotic critical behavior were presented by Kiselev and Friend¹⁰² and by Kostrowicka Wyczalkowska *et al.*¹⁰³ In addition, the IAPWS-95 values for some properties that depend on

second derivatives of the Helmholtz energy, such as the isothermal compressibility and isochoric heat capacity, have unphysical slopes and oscillations at some conditions very close to the critical point; see Refs. 71, 72, and 103 for details.

IAPWS-95 may also be extrapolated to metastable states. For the superheated liquid (where the stable phase would be a vapor), the behavior agrees with the very limited data available. For the supercooled vapor (where the stable phase would be a liquid), no experimental data are available; the behavior is believed to be accurate near the saturation boundary, but not at large degrees of supercooling; see Ref. 71 for details. For the supercooled liquid (where the stable phase would be a solid), more experimental data are available. The extrapolation is physically reasonable, but is inferior to a formulation that has been developed especially for this region.^{104,105} The supercooled liquid will be discussed further in Sec. 5.6.

5.2.6. Uncertainty

The uncertainty of IAPWS-95 is primarily determined by the uncertainty of the underlying experimental data and the degree to which the formulation reproduces those data. Most of the relevant comparisons are given by Wagner and Pruß;⁷¹ additional analysis was later performed by Wagner and Thol.¹⁰⁶ In some cases, the uncertainty can be further constrained by theoretical considerations. While IAPWS does not attach precise statistical significance to these values, it is reasonable to consider them as expanded uncertainties with coverage factor k = 2, roughly corresponding to a 95% confidence interval. It should be noted that in some cases the uncertainty estimates in IAPWS-95 have been updated since the initial publication,⁷¹ so uncertainty information should be obtained from the latest version of the IAPWS Release.⁷²

Figure 2 shows the IAPWS uncertainty diagrams for the saturation vapor pressure and the saturated vapor and liquid densities, where there is only one independent variable (here, temperature) along the saturation boundary. The vapor pressure is constrained at the low-temperature end by an accurate measurement at the triple point.⁷⁸ At high temperatures, the uncertainty is determined by the uncertainty of the critical parameters as given in Table 1. In this and subsequent uncertainty figures, the positions of the divisions between different uncertainty regions should be considered approximate.

The uncertainty in density of IAPWS-95 is shown in Fig. 3 as a function of temperature and pressure. Because the density near the critical point is very sensitive to small changes in temperature or pressure, a density uncertainty is not meaningful in that region, and a relative uncertainty in the calculated pressure (as a function of temperature and density), $\Delta p/p$, is given instead in a triangular region encompassing the critical point. The narrow region in Fig. 3 with 0.0001% uncertainty reflects the highly accurate measurements of the liquid near atmospheric pressure discussed in Sec. 5.5. At low pressures for the vapor, the uncertainties become smaller than those indicated on Fig. 3, because the behavior must approach that of an ideal gas, which is known with very small uncertainty.



FIG. 2. Expanded uncertainty in vapor pressure p_{σ} , saturated liquid density ρ' , and saturated vapor density ρ'' from the IAPWS-95 formulation.⁷²



FIG. 3. Expanded uncertainty in density from the IAPWS-95 formulation.⁷² In the enlarged critical region (triangle), the uncertainty is given as relative uncertainty in pressure. This region is bordered by the two isochores 527 kgm^{-3} and 144 kgm^{-3} and by the 30 MPa isobar. At low pressures for the vapor, the uncertainties become much smaller than indicated because the vapor is nearly an ideal gas.



FIG. 4. Expanded uncertainty in sound speed from the IAPWS-95 formulation.⁷² The triangle around the critical point is defined in the Fig. 3 caption. At low pressures for the vapor, the uncertainties become much smaller than indicated because the vapor is nearly an ideal gas.

The uncertainty of the speed of sound was reanalyzed in 2015 by Wagner and Thol.¹⁰⁶ They considered several new sources of data that had become available since the development of IAPWS-95, most notably the measurements of Lin and Trusler¹⁰⁷ that extend from 253 K to 473 K at pressures to 400 MPa with uncertainties of only 0.03–0.04%. Wagner and Thol also made use of the correlation of Holten *et al.*;¹⁰⁴ that work is based on the data of Lin and Trusler and other reliable sources at pressures up to 400 MPa at temperatures below 300 K. As a result of this analysis, the stated uncertainty of IAPWS-95 could be reduced in several regions and uncertainty estimates could be given at some conditions where no estimate was previously possible. The updated IAPWS-95 uncertainty diagram for sound speed is shown in Fig. 4.

Wagner and Thol¹⁰⁶ also reanalyzed the uncertainty of the isobaric heat capacity, c_p . Their



FIG. 5. Expanded uncertainty in isobaric heat capacity from the IAPWS-95 formulation.⁷² The triangle around the critical point is defined in the Fig. 3 caption. The uncertainty values in the shaded area are given in the lower diagram, where the uncertainty in the region between two lines should be conservatively given by the larger of the two corresponding values. Above the 18% line, the estimated uncertainty is 20%. The uncertainty in the vapor phase at low pressures approaches the uncertainty of the ideal-gas heat capacity, which is less than 0.1%.

analysis made use of the work of Trusler and Lemmon,¹⁰⁸ who derived c_p from the experimental sound speeds of Lin and Trusler.¹⁰⁷ The equation of Holten *et al.*¹⁰⁴ was also used to aid the analysis. The new data showed systematic deviations from IAPWS-95 above 100 MPa, where previously there had been no c_p data to compare with. As a result of this analysis, IAPWS adopted a new uncertainty diagram for the isobaric heat capacity, with estimates large enough to encompass this deviation in the region where previously there were no uncertainty estimates. The new diagram is reproduced in Fig. 5.

While the uncertainty of enthalpy is of interest in engineering contexts, it is not a straightforward concept because enthalpy is not a measurable quantity (only enthalpy differences between states can be measured) and because it is defined relative to an arbitrary reference state (see Sec. 5.2.2). IAPWS examined the uncertainty of input data and their representation by several equations of state to develop recommended uncertainties as a function of temperature and pressure for the enthalpy relative to the IAPWS reference state; these are given in an Advisory Note.¹⁰⁹ The same document recommends relative uncertainties in enthalpy differences taken along isobaric (constant pressure) and adiabatic reversible (constant entropy) paths. The absolute uncertainty of the enthalpy of vaporization is also given as a function of temperature.

5.3. 1997 formulation for industrial use (IAPWS-IF97)

As mentioned in Sec. 2, the original impetus for the work of IAPWS came from the steam power industry. For some applications in that industry, an alternative to the rather complex IAPWS-95 formulation is needed, for two reasons. First, some calculations require greater computational speed than can be obtained with IAPWS-95. Second, the IAPWS "scientific" formulation may be updated when better information becomes available, but changes in formulations complicate industrial design and guarantee calculations, because it is necessary to use the same steam tables that were used in the original contract and because some applications use empirical correction factors that would have to be reevaluated when switching to a different formulation. A formulation for industrial use needs to be stable for decades.

In the 1990s, IAPWS decided to produce a new industrial formulation to replace the IFC-67 standard that had been in place since 1967. Criteria for the new formulation (based on input from industrial users) included increased computing speed compared to IFC-67 and improved consistency at boundaries between regions. The result of this effort was the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam, abbreviated as IAPWS-IF97.^{110,111} IAPWS-IF97 was fitted within tight tolerances to values calculated from IAPWS-95, with functional forms chosen to optimize computing speed. It contains four regions in addition to the vapor-liquid saturation boundary; these are the normal vapor and liquid regions, a region for supercritical conditions and states around the critical point, and a special high-temperature region (extending to 2000 °C) intended for calculations involving combustion turbines. It is supplemented by some "backward" equations to facilitate calculations where a dependent variable in the formulation is used as input, such as T(p,h) and T(p,s) (temperature as a function of pressure and enthalpy or pressure and entropy). Additional "backward" formulations were later developed by IAPWS and may be found at www.iapws.org.

Because IAPWS-IF97 is a specialized industrial formulation rather than the reference data that is the subject of this review, we will not consider it further here. More information can be found in the IAPWS document,¹¹⁰ the archival journal article,¹¹¹ steam tables books,^{112,113} and at www.iapws.org.

i	a_i
1	-7.85951783
2	1.84408259
3	-11.7866497
4	22.6807411
5	-15.9618719
6	1.80122502

TABLE 2. Coefficients of IAPWS vapor-pressure correlation for H₂O, Eq. (3).^{114,115}

For some applications, notably computational fluid dynamics (CFD), even greater calculational speed than that of IAPWS-IF97 is needed. Approaches for faster calculations, along with prospects for future industrial formulations, will be discussed in Sec. 11.3.

5.4. Simpler formulations for special conditions

The comprehensive IAPWS-95 formulation is by necessity complicated in its functional form. Implementing it requires a major programming effort, or obtaining software that somebody else has programmed. It is desirable to have simpler and less computationally demanding correlations that cover commonly used subsets of the state space, for example for use within a spreadsheet.

One common set of conditions is the vapor-liquid saturation boundary. The saturation pressure (vapor pressure) as a function of temperature is a foundational quantity, and many processes operate at or near saturation so that engineering calculations can use properties such as enthalpy of the saturated vapor and/or liquid. In 1986, IAPS adopted correlations for the saturation pressure and for the density, specific enthalpy, and specific entropy of the saturated vapor and liquid as functions of temperature for the entire saturation boundary.⁸⁸ These were slightly modified later to correspond to the ITS-90 temperature scale.^{114,115} These auxiliary formulations agree with values calculated from the full IAPWS-95 formulation to less than the uncertainties of the calculated quantities. Because of the importance of the vapor-pressure curve, we reproduce that formulation here:^{114,115}

$$\ln\left(\frac{p_{\sigma}}{p_{c}}\right) = \frac{T_{c}}{T} \left[a_{1}\tau + a_{2}\tau^{1.5} + a_{3}\tau^{3} + a_{4}\tau^{3.5} + a_{5}\tau^{4} + a_{6}\tau^{7.5} \right],$$
(3)

where p_c and T_c are the critical pressure and critical temperature given in Table 1, $\tau = 1 - T/T_c$, and the coefficients a_i are given in Table 2.

Simple formulas are also desirable for liquid water at pressures near atmospheric, where accurate properties are needed for calibrations and for everyday scientific and engineering use. For some properties (particularly density), the precision of instruments may be such that small variations in pressure can affect the property at a measurable level. Pátek *et al.*¹¹⁶ produced correlations as a function of temperature for the specific Gibbs energy, specific volume, and $(\partial v/\partial p)_T$ (isothermal pressure derivative of specific volume), all at 0.1 MPa. Appropriate differentiation and combination of these equations allows calculation of all thermodynamic properties not only at 0.1 MPa, but at any pressure from saturation up to 0.3 MPa. The equations were fitted to IAPWS-95, with the requirement that the difference between calculated quantities and IAPWS-95 be at least an order of magnitude smaller than the uncertainty of IAPWS-95. The formulation, adopted as a Supplementary Release by IAPWS,¹¹⁷ is valid from 253.15 K to 383.15 K, which includes some metastable liquid states.

The same IAPWS project^{116,117} also developed equations for the viscosity, thermal conductivity, and static dielectric constant of the liquid at 0.1 MPa. No pressure dependence was included, because the effect of small variations in pressure on these quantities is much smaller than their uncertainty. For viscosity and thermal conductivity, the equations were fitted to the IAPWS formulations (see Secs. 6.2 and 6.3). For the dielectric constant, the newer high-accuracy data of Hamelin *et al.*¹¹⁸ (see Sec. 10.2) were used.

5.5. Liquid density near atmospheric pressure

The density of liquid water at ambient temperature and pressure, particularly the value at its density maximum near 4 °C, has long been of interest as a reference standard; during the early 1900s this density was even used as part of the definition of the liter. For metrology, it is desirable to know this quantity with a relative uncertainty of 10^{-6} (1 ppm) or better. Early measurements (see Ref. 119 for a summary) were highly precise, but they were made before the discovery of isotopes and therefore have additional uncertainty due to lack of knowledge of isotopic composition of the water used.

The first modern high-accuracy density measurements of liquid water were those of Takenaka and Masui,¹²⁰ who reported the ratio of the density to that at the maximum between 0 °C and 85 °C. Masui *et al.* supplemented these relative measurements with a painstaking determination of the absolute density at 16 °C and 0.101 325 MPa.¹²¹ Watanabe reported measurements of similarly low uncertainty at temperatures from 0 °C to 44 °C; unfortunately the paper only reported a smoothing equation and not the underlying data.¹²² Finally, Patterson and Morris reported absolute densities from 1 °C to 40 °C.¹²³ All of the absolute measurements were made by a hydrostatic method that measured the buoyancy of a sphere or cylinder of accurately known dimensions, and all of them were reported (with small corrections as necessary) for the isotopic composition of VSMOW.

These data were evaluated by Tanaka *et al.*,¹¹⁹ who produced a recommended table and equation between 0 °C and 40 °C. This recommendation was adopted in 2001 by the International Committee for Weights and Measures (Comité international des poids et mesures, CIPM).

Since both IAPWS-95^{71,72} and the CIPM formulation¹¹⁹ provide accurate densities for liquid water, the question naturally arises as to when it is appropriate to use each formulation. This question was considered by a joint Task Group between the two organizations; their recommendations^{124,125} can be summarized as:

1. The CIPM formula is preferred for use in metrology within its recommended range, from

0 °C to 40 °C near atmospheric pressure. It should not be extrapolated outside this range.

- 2. In the range where both formulations are valid, their densities are consistent within mutual uncertainties. Outside the CIPM region of validity, IAPWS-95 is the preferred method for calculating water densities.
- 3. For uses covering a range of conditions, some of which are inside the range of validity of the CIPM standard and some of which are not, it is generally preferable to use the IAPWS-95 formulation for the entire calculation in order to avoid discontinuities.

Another option for high-accuracy calculation of liquid water density is to use the simple IAPWS correlation described in Sec. 5.4 for the liquid near atmospheric pressure.

When it is necessary to worry about uncertainties in liquid water density at the ppm level, two minor effects must be considered. First, it makes a difference whether the water is degassed or is saturated (or partly saturated) with atmospheric air. At standard atmospheric pressure, dissolved air at saturation makes water less dense by roughly 0.0003% (3 ppm) at 20 °C; the effect varies with temperature. The CIPM recommendation¹¹⁹ included a correction by Bignell for dissolved air,¹²⁶ which was developed for the range 0 °C to 25 °C. Since then, Harvey *et al.*¹²⁷ performed a detailed calculation of the effect along the lines pioneered by Kell,²⁹ with uncertainty analysis, for temperatures from 0 °C to 50 °C. It agrees well with the Bignell correction in its range of validity. Second, the isotopic composition can affect the density; for example, typical fresh water is depleted in heavy isotopes compared to ocean water so that it is a few ppm less dense than VSMOW. This means that any density determination with relative uncertainty on the order of 10^{-6} requires knowing the isotopic composition of the water. Corrections to convert between VSMOW liquid densities and those corresponding to other isotopic compositions are given by Girard and Menaché.¹²⁸

5.6. Thermodynamic properties of supercooled liquid water

Water can exist as a metastable liquid at temperatures well below the equilibrium freezing temperature. Most work on supercooled liquid water has focused on the behavior near standard atmospheric pressure, where its properties are of interest in meteorological and climate studies. There has been some work at higher pressures, where food processing is a relevant application.

Beginning in the 1970s, it was recognized that some properties of the supercooled liquid, such as the isothermal compressibility and the heat capacity, seemed to be diverging (or at least increasing rapidly) at increasing degrees of supercooling. This early work was summarized by Angell.¹²⁹ The apparent divergence resembles what might be expected if a critical point were being approached, although the physical limit of supercooling is reached before the hypothetical critical point.

Since then, there have been numerous experimental and theoretical studies focusing on the possible existence of a liquid-liquid critical point in supercooled water. Much of this work is

covered in two reviews of Gallo *et al.*^{130,131} A liquid-liquid transition has been observed in computer simulation of molecular models approximating water,^{132–135} and experimental evidence of this transition has been presented.^{136–138} The study of stretched (negative pressure) water has also contributed to understanding.^{139–141}

Since our focus is on thermophysical properties, we leave aside the details and controversies of this possible phase separation. The most fruitful models for thermodynamics of the supercooled liquid are "two-state" models that treat the liquid as a mixture of two types of molecules related by a reaction equilibrium. One state represents a low-density structure like that of ice, while the other represents water that is more closely packed. Such models are, of course, unphysical in the sense that the molecules in real water sample a continuous range of local configurations and densities. However, they seem to capture enough physics to provide a successful representation of experimental data.

Holten *et al.*¹⁰⁴ examined the available data for the supercooled liquid and developed a twostate model that reproduced the data significantly better than extrapolation of the IAPWS-95 equation of state. The model is designed to match IAPWS-95 closely in the stable liquid phase up to 325 K so that switching from one formulation to the other does not introduce large discontinuities. This formulation was adopted as an IAPWS Guideline in 2015.¹⁰⁵ IAPWS states its range of validity as pressures up to 400 MPa at temperatures from the homogenous ice nucleation temperature up to 300 K, and it can be extrapolated reasonably up to 1000 MPa.

Since the publication of Ref. 104, adiabatic calorimetry has provided improved values for the isobaric heat capacity of supercooled water at atmospheric pressure.¹⁴² These new data suggest that the heat capacity at temperatures below about 260 K should be slightly higher than that in the formulation of Holten *et al.* The even more recent data of Pathak *et al.*,¹⁴³ obtained with a novel ultrafast pulse heating technique, extend to lower temperatures and suggest a higher heat capacity that may go through a maximum near 229 K. Additional new data for both density and sound speed, many of which extend to high pressures, are discussed in Sec. 11.1.2.

The saturated vapor pressure of supercooled water is an important quantity in atmospheric science. It can be calculated by equating the Gibbs energy of the supercooled liquid from the formulation of Holten *et al.* with that given for the vapor by IAPWS-95. This quantity has also been measured with good accuracy down to 252 K by Beltramino *et al.*;¹⁴⁴ the results are consistent with the supercooled liquid model of Ref. 104.

6. Transport Properties of Ordinary Water

6.1. History of formulations

It was recognized by the 1950s that, in addition to thermodynamic properties, industry needed reliable data for the viscosity and thermal conductivity of water and steam.¹² In 1964, the Sixth International Conference on the Properties of Steam issued a set of tables accompanied by region-

dependent interpolating equations for each property.¹⁴⁵ Both properties were described at temperatures to 700 °C; the upper pressure limit was 80 MPa for the viscosity and 50 MPa for the thermal conductivity.

New high-quality data for both properties were published in the 1960s and 1970s, leading IAPS to undertake an effort to replace the 1964 tables with more accurate formulations that would be in equation form to facilitate computer calculations. The 1964 tables also failed to account for the enhancement of the thermal conductivity in a wide region around the critical point, which was demonstrated for steam in the early 1970s.^{146,147} A new viscosity formulation, covering temperatures to 800 °C and pressures to 100 MPa, was adopted in 1975 and documented by Nagashima.¹⁴⁸ A new thermal conductivity formulation, covering the same range of conditions, was adopted in 1977 and described by Sengers *et al.*¹⁴⁹ Both of these used temperature and density as independent variables, and were based on use of the IFC-68 formulation for thermodynamic properties to convert between those variables and the combination of temperature and pressure corresponding to most experimental data. When IFC-68 was replaced by the IAPS-84 thermodynamic formulation, it was verified that the transport formulations could continue to be used in conjunction with the new thermodynamic equation of state.^{149,150}

The next generation of transport property formulations was adopted in 1985. The viscosity formulation incorporated a significantly improved functional form originally developed by Watson *et al.*,¹⁵¹ and for the first time included a term for the weak near-critical enhancement of the viscosity. The range of validity was extended to 900 °C and 300 MPa; pressures up to 500 MPa were included at lower temperatures. The thermal conductivity was essentially the same as the 1977 formulation, updated to reflect the new viscosity formulation. Both 1985 standards were described by Sengers and Watson.¹⁵²

After adoption of the IAPWS-95 thermodynamic formulation, IAPWS appointed a Task Group to revise the transport property formulations so that they would be consistent with IAPWS-95 and with the latest experimental and theoretical knowledge. It was desired that they cover the expanded range of applicability of IAPWS-95 to the extent possible. The first step was the collection and evaluation of literature data for the viscosity and thermal conductivity, as reported by Assael *et al.*¹⁵³ This provided the foundation for the formulations described in Secs. 6.2 and 6.3.

6.2. 2008 formulation for viscosity

In 2008, IAPWS adopted the IAPWS Formulation 2008 for the Viscosity of Ordinary Water Substance.¹⁵⁴ The formulation and underlying data were described by Huber *et al.*¹⁵⁵ As suggested by theory, the viscosity μ is written (in reduced form) as a product of three terms:

$$\overline{\mu} = \overline{\mu}_0(\overline{T}) \times \overline{\mu}_1(\overline{T}, \overline{\rho}) \times \overline{\mu}_2(\overline{T}, \overline{\rho}), \tag{4}$$

where $\overline{\mu} = \mu/(1 \times 10^{-6} \text{ Pas})$ and \overline{T} and $\overline{\rho}$ are the temperature and density, respectively, reduced by their critical values as given in Table 1.

 $\overline{\mu}_0$ is the low-density limit of the viscosity, which is only a function of temperature. Input data for this function were obtained by extrapolating data on isotherms to zero density, covering temperatures up to 1345 K. The data of Teske *et al.*¹⁵⁶ were particularly important in constraining the low-density behavior below 440 K. The functional form of $\overline{\mu}_0(\overline{T})$ is suggested by the kinetic theory of gases, and is dominated by a term proportional to the square root of the absolute temperature. Subsequently, Hellmann and Vogel¹⁵⁷ reported additional experimental data and also values calculated from a high-quality pair potential. They suggested an improved zero-density function based on their results, but the differences from the IAPWS function within its range of validity are less than 0.5% except at very low temperatures.

 $\overline{\mu}_1$ is an entirely empirical term, reflecting all finite-density effects on the viscosity (except for the critical enhancement $\overline{\mu}_2$ discussed below). $\overline{\mu}_1$ was fitted to the entire dataset; a temperature-dependent linear-in-density component of $\overline{\mu}_1$ was simultaneously fitted to values of

$$\mu^{(1)} = \lim_{\rho \to 0} \left(\frac{\partial \mu}{\partial \rho} \right)_T \tag{5}$$

derived during the isotherm analysis used to produce zero-density values for $\overline{\mu}_0$.

 $\overline{\mu}_2$ accounts for the divergence of the viscosity that occurs near the critical point. The theoretical framework for describing this divergence was given by Bhattacharjee and coworkers;^{158,159} it consists of a multiplicative term acting on the "background" viscosity $\mu_b \equiv \mu_0 \times \mu_1$. $\overline{\mu}_2$ depends on the isothermal compressibility, which approaches infinity at the critical point. Details can be found in Ref. 155. Because the critical enhancement of the viscosity is only significant in a very small region around the critical point, IAPWS states that the $\overline{\mu}_2$ term in Eq. (4) may be ignored (set to 1) for simplified industrial use.¹⁵⁴

The range of validity of Eq. (4) extends from the melting curve up to 1173.15 K and 300 MPa, with the pressure range extending to 350 MPa below 873.15 K, 500 MPa below 433.15 K, and 1000 MPa below 373.15 K. The extrapolation behavior is physically reasonable down to at least 250 K for both the vapor and the metastable supercooled liquid; recent experiments in the supercooled liquid¹⁶⁰ agree with the extrapolated IAPWS formulation within roughly 2% down to 250 K, with deviations increasing to 8–10% near 240 K. At high temperatures and pressures, Eq. (4) extrapolates reasonably at conditions where IAPWS-95 is valid (up to 1273 K and 1000 MPa), and the high-temperature extrapolation of the dilute-gas term should be reasonable to at least 2500 K. It should not be extrapolated to pressures above 1000 MPa.

The uncertainty of the formulation is determined by the uncertainty of the experimental data and the degree to which the formulation reproduces the data. This varies from region to region; the expanded uncertainty (coverage factor k = 2, roughly comparable to a 95% confidence interval) is summarized as a function of temperature and pressure in Fig. 6.



FIG. 6. Expanded (k = 2) uncertainty of 2008 IAPWS viscosity formulation.¹⁵⁴

6.3. 2011 formulation for thermal conductivity

In 2011, IAPWS adopted the IAPWS Formulation 2011 for the Thermal Conductivity of Ordinary Water Substance.¹⁶¹ The formulation and underlying data were described by Huber *et al.*¹⁶² The form for the thermal conductivity λ is similar to that for the viscosity, except that the critical enhancement is additive instead of multiplicative:

$$\overline{\lambda} = \overline{\lambda}_0(\overline{T}) \times \overline{\lambda}_1(\overline{T}, \overline{\rho}) + \overline{\lambda}_2(\overline{T}, \overline{\rho}), \tag{6}$$

where $\overline{\lambda} = \lambda/(1\,mW\,m^{-1}\,K^{-1}).$

As with the viscosity, input data for the zero-density term $\overline{\lambda}_0(\overline{T})$ were obtained by grouping low-density data into isotherms and evaluating their zero-density limit. These results were supplemented at the low and high ends of the temperature range with theoretical values derived from a high-accuracy pair potential.¹⁶³ Unlike with the viscosity, there was some disagreement between the experimental and theoretical results at temperatures above roughly 500 K. Since no reason was found to prefer one over the other, the uncertainties assigned to the experimental points were increased to encompass the theoretical results. [A later theoretical study,¹⁶⁴ with an improved method for calculating thermal conductivity from the intermolecular potential, achieved better agreement with experiment.] A correlation for $\overline{\lambda}_0(\overline{T})$, with a leading term proportional to the



FIG. 7. Magnitude of thermal conductivity critical enhancement for H_2O .¹⁶² The curves are contours of the specified percent enhancement relative to the background.

square root of temperature as suggested by kinetic theory, was fitted to the zero-density values from 250 K to 1100 K.

The residual term $\overline{\lambda}_1$ is an empirical function of reduced temperature and reduced density; it was fitted to the experimental database and contains a total of 28 terms.

The critical enhancement $\overline{\lambda}_2$ is, unlike the viscosity critical enhancement, significant over a wide range of temperature and pressure around the critical point. Its representation is based on the crossover model of Olchowy and Sengers.¹⁶⁵ The critical enhancement for the thermal conductivity depends not only upon the isothermal compressibility, but also on the isobaric and isochoric heat capacities (obtained from IAPWS-95) and the viscosity [calculated from Eq. (4)]. The magnitude of the enhancement is shown in Fig. 7, where contours of the relative contribution of $\overline{\lambda}_2$ to the thermal conductivity are plotted.

The range of validity of Eq. (6) is the stable fluid up to 1173.15 K at pressures up to 100 MPa. The upper pressure limit is extended to 250 MPa at temperatures below 874 K, 687 MPa below 573 K, 785 MPa below 403 K, and 1000 MPa below 348 K. At higher pressures, it extrapolates well at least up to 4 GPa, as shown by comparison with the data of Abramson *et al.*¹⁶⁶ At high temperatures and low densities, the extrapolation of $\overline{\lambda}_0(\overline{T})$ is reasonable, although above roughly 1500 K the thermal conductivity of real water is affected by dissociation (see Sec. 11.7), which is not accounted for in the formulation. Extrapolation to stable fluid regions outside the range of validity of Eq. (6) but within the range of validity of IAPWS-95.

The uncertainty of Eq. (6) has been estimated in the regions of temperature and pressure where data are available; these expanded uncertainties are summarized in Fig. 8.

Because the critical enhancement of the thermal conductivity is significant over a wide range



FIG. 8. Expanded (k = 2) uncertainty of 2011 IAPWS thermal conductivity formulation.¹⁶¹

of conditions, it cannot be neglected for simplified industrial use. Instead, IAPWS approved a simplified procedure for estimating $\overline{\lambda}_2(\overline{T},\overline{\rho})$ for industrial use.^{161,162}

6.4. Self-diffusion coefficient

The self-diffusion coefficient of water is less studied than the other transport properties, but it is of interest in the modeling of processes in water and steam. Its values, if accurately known, can also be used to test molecular models for water, since it can be derived relatively easily from a molecular dynamics computer simulation.

Like the other transport properties, the self-diffusion coefficient (more properly, the product of the self-diffusion coefficient and the molar density) has a low-density limit that is a function of temperature only, based on the interaction of two molecules. This has been calculated by Hellmann *et al.* from a high-accuracy pair potential;¹⁶³ the values change slightly if the newer collision calculations of Hellmann and Vogel¹⁵⁷ are used instead. For liquid water near room temperature, the experimental results of Mills¹⁶⁷ are widely accepted as the most accurate, and data for the liquid over a wider temperature range have been given by Easteal *et al.*¹⁶⁸ At high temperatures, including supercritical conditions, results have been obtained by nuclear magnetic resonance (NMR) methods by Yoshida and coworkers^{169,170} and by Lamb *et al.*¹⁷¹ An IAPWS Task Group is working on a formulation for the self-diffusion coefficient based on these and other data.

7. Properties of Heavy Water

7.1. Thermodynamic properties of heavy water

7.1.1 Background

Heavy water (D₂O), defined in Sec. 4.1, is used in a variety of scientific and medical applications. Its largest industrial use is in nuclear reactors, where its relative transparency to neutrons can provide advantages over ordinary water. Because of the use of heavy water in Canadian reactors, accurate density data for the vapor and liquid phases at temperatures up to 773 K were taken by Kell and coworkers at the National Research Council of Canada.^{89,172} Based on these and other data, a comprehensive equation of state was developed by Hill *et al.* at the University of British Columbia;¹⁷³ this was adopted as an IAPS standard in 1984.

Since 1984, additional high-quality experimental data became available,^{89,174,175} along with theoretical data for the second virial coefficient based on an accurate molecular model.¹⁷⁶ There have also been many improvements in the methodology for developing equations of state. Consequently, IAPWS undertook a project to replace the Hill equation, resulting in a new standard formulation from the work of Herrig *et al.*^{177,178} This formulation is valid at temperatures up to 825 K and pressures up to 1200 MPa, and extrapolates reasonably to higher temperatures and pressures and also in the supercooled liquid region. The basic structure of the formulation is the same as that described for ordinary water in Sec. 5.2.1.

7.1.2. Ideal-gas term

In the Hill equation of state, the ideal-gas contribution was fitted to the 1954 work of Friedman and Haar,¹⁷⁹ which was based on a relatively simple molecular model. In 2017, Simkó *et al.* published a thorough analysis of the partition function of the D₂O molecule (with all three oxygen isotopes) and used it to derive the ideal-gas heat capacity of heavy water.⁵⁸ The results, which are accurate to within 0.01%, are a significant improvement over the values of Friedman and Haar, especially at temperatures above 500 K. These data were fitted to a functional form for use in the equation of state, and two constants in the function were fixed in accordance with the triple-point reference state defined in Sec. 5.2.2.

7.1.3. New reference equation of state

The equation of state has the same structure as Eq. (1), with the dimensionless Helmholtz energy as the sum of an ideal-gas term and a residual term. The residual term has the functional form shown in Eq. (2), except that no "nonanalytic" critical terms are used. In all, 24 terms were used for the residual part.

Detailed information about the uncertainties and the improved representation of experimental data can be found in the journal article;¹⁷⁷ uncertainty information is also in the IAPWS Release.¹⁷⁸ In brief, the expanded (k = 2) uncertainty in vapor pressure is 0.05% or less, except for a region between 300–350 K where it is 0.1% due to scatter in the available experimental data. The expanded uncertainty in liquid density is less than 0.1% at most conditions up to 100 MPa, while somewhat larger uncertainties (0.1% or 0.5%, depending on the temperature) are obtained for vapor densities. The sound speed in the liquid has an expanded uncertainty of 0.015% in the region covered by the data of Wegge *et al.*,¹⁷⁴ and 0.1% at most other conditions. The data situation for the heat capacity is less satisfactory, with expanded uncertainties of 1% for the liquid. While there are few experimental data in the vapor phase for comparison, the fact that both the ideal-gas heat capacity and second virial coefficient are known with good accuracy means that vapor-phase properties should be represented well as long as the density is not too high.

As is the case with any analytical equation of state, uncertainties are larger in the vicinity of the critical point, and the formulation is not able to reproduce the nonclassical exponents that characterize the asymptotic behavior as the critical point is approached. Nevertheless, as discussed in Ref. 177, the limited experimental data in the critical region are mostly reproduced within their uncertainties.

7.2. Transport properties of heavy water

7.2.1. History of heavy water transport formulations

The development of the equation of state of Hill *et al.* in the early 1980s¹⁷³ made it feasible to develop formulations for the viscosity and thermal conductivity of heavy water. The experimental database and correlating equations were described by Matsunaga and Nagashima,¹⁸⁰ and the formulations were adopted by IAPS in 1984. Both incorporated a zero-density term as a function of temperature, supplemented with a residual term for finite-density effects. Divergence at the critical point was not included for either property; this necessitated the exclusion of a region around the critical point from the range of validity of the thermal conductivity formulation.

The development of a new equation of state for heavy water,^{177,178} as described in Sec. 7.1.3, in addition to some improved data, led to an IAPWS project to produce new reference formulations for the viscosity and thermal conductivity of heavy water.

7.2.2. Viscosity

The new formulation for the viscosity of heavy water was adopted by IAPWS in 2020.¹⁸¹ The formulation and underlying data are described by Assael *et al.*¹⁸²

The formulation has the same general form as that for ordinary water given by Eq. (4). The viscosity in the zero-density limit is based on theoretical values by Hellmann and Bich,¹⁸³ which were calculated by classical kinetic theory with an accurate *ab initio* pair potential and have an expanded (k = 2) uncertainty of 2%. The formulation represents these data within 0.05% and behaves in a physically reasonable manner down to 250 K and up to at least 2500 K. The en-

hancement of the viscosity in the critical region is accounted for by the model of Battacharjee and coworkers.^{158,159} For simplified industrial use, the critical enhancement may be neglected as in the formulation for ordinary water.

The range of validity extends from the melting curve up to 775 K, with pressures up to 960 MPa below 373 K, up to 200 MPa between 373 K and 473 K, and up to 100 MPa between 473 K and 775 K. For stable fluid states outside the range of validity, but within the range of validity of the thermodynamic equation of state, it extrapolates in a physically reasonable way. It also extrapolates reasonably into the metastable subcooled liquid region at atmospheric pressure down to 242 K; agreement with recent experimental data in this region¹⁶⁰ is within 5% down to roughly 250 K, but deviations become on the order of 15% near 245 K.

The uncertainty is mainly determined by the uncertainty of the experimental data and the degree to which the formulation reproduces the data. It is 1% in the liquid region between the melting curve and 473 K up to 100 MPa, and increases to 2% between 100 MPa and 200 MPa. Between the melting curve and 373 K at pressures between 200 MPa and 400 MPa, it is 2% and increases to 5% at pressures between 400 MPa and 960 MPa. In the gas region, the liquid region between 473 K and the critical temperature up to 100 MPa, and in the supercritical region up to 775 K with pressures up to 100 MPa, it is 2%. In the near-critical region, the uncertainty is larger than 2%.

7.2.3. Thermal Conductivity

The new formulation for the thermal conductivity of heavy water was approved by IAPWS in $2021.^{184}$ The formulation and underlying data are described by Huber *et al.*¹⁸⁵

The formulation has the same form as that for ordinary water given by Eq. (6). The thermal conductivity in the zero-density limit is based on theoretical values that have an expanded (k = 2) uncertainty of 2% below 600 K, 3% from 600 K to 1500 K, and 4% above 1500 K. These data are updates of the values of Hellmann and Bich.¹⁸³ In the update, ideal-gas heat capacities from the new equation of state for heavy water,¹⁷⁸ which are based on the values of Simkó *et al.*,⁵⁸ were used. The formulation represents the calculated data within 0.05% and behaves in a physically reasonable manner down to 250 K and up to at least 2500 K. In contrast to the 1984 IAPS Formulation, the new formulation accounts for the critical enhancement of the thermal conductivity, based on the crossover model of Olchowy and Sengers.¹⁶⁵

The range of validity of the formulation extends from the melting curve up to 825 K with pressures up to 250 MPa. For stable fluid states outside this range, but within the range of validity of the thermodynamic equation of state,¹⁷⁸ the extrapolation behavior is physically reasonable.

The uncertainty of the formulation has been estimated in the regions of temperature and pressure where data are available. The expanded uncertainty varies from 2% in the zero-density limit and 1.5% in the liquid region at low temperature up to 6% at pressures between 100 MPa and 250 MPa.



FIG. 9. Phase diagram of water showing different ice forms that coexist with fluid water.¹⁸⁹ Reproduced from W. Wagner, T. Riethmann, R. Feistel, and A.H. Harvey, *J. Phys. Chem. Ref. Data* **40**, 043103 (2011).

8. Properties of Ice

The most familiar and well-studied form of solid water is the hexagonal ice Ih that is in equilibrium with liquid water at atmospheric pressure near 0 °C. However, there are many other stable crystal forms, some of which (ice III, ice V, ice VI, ice VII) can exist in equilibrium with liquid water at high pressures and some of which are only in equilibrium with other ice forms. We refer readers elsewhere for more details on the solid phase diagram of water.^{186–188} In this section, we primarily focus on ice Ih, and secondarily on other ices that coexist with liquid water. A diagram of the phases considered here is shown in Fig. 9.¹⁸⁹

8.1. Thermodynamics of ice Ih

In a similar manner to the equation of state for fluid water discussed in Sec. 5.2, the equation of state for ice can be described as a thermodynamic potential from which properties are calculated by appropriate derivatives and combination of terms. For a solid phase where the ideal-gas limit is not relevant, it is convenient to express this as the Gibbs energy as a function of temperature and pressure. Feistel and Wagner evaluated available thermodynamic data for ice Ih over a wide range of conditions and published a Gibbs potential in 2005.¹⁹⁰ An improved version was published in 2006 (Ref. 191) and was adopted by IAPWS.¹⁹² A slight modification was later made to improve
consistency with the IAPWS-95 equation of state so that properties like enthalpy and entropy would be consistent at the triple point and other states where the solid and fluid coexist.¹⁹³

Data sources used in development of the equation of state are summarized in Ref. 191. The key sources include measurements of density,^{194,195} thermal expansion coefficient,¹⁹⁶ isentropic compressibility,^{197,198} and isobaric heat capacity.^{199–202} The relationship to the fluid equation of state is constrained by accurate measurements of the enthalpy of melting at atmospheric pressure.^{199,202,203} In addition, the theoretically correct low-temperature behavior of the heat capacity and the entropy was ensured.

The range of validity of the formulation is for stable ice Ih at temperatures from 0 K to the melting (or sublimation) curve at pressures up to 210 MPa. Uncertainties of the computed properties are discussed by Feistel and Wagner¹⁹¹ and given in the IAPWS document;¹⁹² they are primarily determined by the uncertainties of the underlying experimental data.

8.2. Other ice phases

While the high-pressure phases of ice do not occur naturally on Earth, they are of interest in planetary science and in high-pressure freezing applications. Given sufficient data, the thermodynamics of other ice forms can be represented in a similar manner to ice Ih. While IAPWS has not adopted formulations for other ice forms, Journaux *et al.*¹⁸⁸ recently presented Gibbs energy equations of state for ice II, ice III, ice V, and ice VI, based in part on their experimental volumetric measurements and on statistical physics calculations of lattice vibrations.

8.3. Melting and sublimation curves

The melting and sublimation curves for water are both anchored by the triple point, as shown on Fig. 9. As discussed in Sec. 5.2.2, the pressure at the triple point is known very accurately from the measurement of Guildner *et al.*⁷⁸

Accurate measurements of the sublimation curve are difficult. Bielska *et al.*²⁰⁴ used cavity ringdown spectroscopy to measure the ratio of the vapor pressure of ice to that at the triple point with a relative standard uncertainty near 0.5% at temperatures down to 175 K; their paper summarizes previous experimental work. Somewhat smaller uncertainties can be obtained by equating the fugacity of ice Ih calculated from the equation of state discussed in Sec. 8.1 with that of the vapor calculated from IAPWS-95; the results of this method (which is equivalent to a thermodynamic integration of the Clapeyron equation along the sublimation curve) are consistent with the experimental data within mutual uncertainties. This calculation is described by Wagner *et al.*,¹⁸⁹ who report a correlation for the sublimation pressure as a function of temperature that was adopted by IAPWS in 2008.²⁰⁵ The 2005 formula of Murphy and Koop²⁰⁶ for the sublimation curve, widely used in atmospheric science, gives results almost identical to the IAPWS formulation.

Wagner et al.¹⁸⁹ made similar use of the ice Ih equation of state to calculate the melting curve

from the solid–liquid–vapor triple point at low pressure to the triple point near 251 K and 209 MPa where liquid, ice Ih, and ice III coexist (see Fig. 9). For the melting curves of ice III, ice V, ice VI, and ice VII, earlier work by Wagner *et al.*²⁰⁷ fitted simple correlations constrained by reported triple points and some limited data for the melting curves. These have been adopted by IAPWS,²⁰⁵ with a slight adjustment of the ice III curve to meet the triple point corresponding to the ice Ih correlation of Wagner *et al.*¹⁸⁹ Most of the high-pressure data used were taken by Bridgman in the early 1900s.^{94,208,209} It should be noted that, as pointed out by Babb,²¹⁰ Bridgman's pressures should be multiplied by a constant factor to account for his use in calibration of a now-obsolete value for the melting pressure of mercury at 0 °C. Based on current data for mercury,²¹¹ this factor is 1.0102.

Unfortunately, for ice III the work of Wagner et al.²⁰⁷ on which the current IAPWS standard is based used only the 1912 data of Bridgman.²⁰⁸ There have been several newer studies that better constrain the ice III melting curve. The triple point for the liquid with ices Ih and III was measured very accurately (especially in pressure) by Bignell and Bean,²¹² who obtained a pressure about 1 MPa lower than that of Bridgman and a temperature about 0.2 K lower. This is in good agreement with the less precise measurement of Kell and Whalley.²¹³ At the other end of the ice III melting curve, the coordinates of the triple point between the liquid and ices III and V were reported by Engelhardt and Whalley,²¹⁴ who agreed with the pressure reported by Bridgman but obtained a triple-point temperature about 0.5 K lower. Engelhardt and Whalley also reported an equation representing their points on the ice III melting curve, showing a similar offset in temperature from the points of Bridgman. Engelhardt and Whalley reported equations for the melting curve of ice V and part of the ice VI melting curve, along with the triple point of the liquid with ices V and VI; that triple point is in good agreement with that of Bridgman and their ice V and ice VI equations are in fair agreement with the IAPWS formulations.^{189,205} Based on these additional data, the melting curve of ice III could be significantly improved, and that of ice V could be somewhat improved, based on improved knowledge of the relevant triple points and on some experimental data that were not previously considered.

For ice VII, the IAPWS formulation was only fitted up to 19.9 GPa and 715 K, the limit of available data at the time.²⁰⁷ Work in diamond-anvil cells has extended the range over which the ice VII melting curve has been measured.^{215–223} These studies exhibit some disagreement at higher pressures, and additional ice forms may be present, so expert analysis would be needed to develop a new recommended ice VII melting equation.

The stronger hydrogen bonding in heavy water causes the stability range of D_2O ice Ih to extend to higher temperatures than for ordinary water; for example, the freezing point at standard atmospheric pressure is near 3.8 °C. Formulations for the melting and sublimation curves of heavy water, based on limited experimental data, are given by Herrig *et al.*¹⁷⁷

8.4. Other ice properties

Experimental data for the thermal conductivity of ice Ih were reviewed by $Slack^{224}$ (whose recommended results were later put in equation form²²⁵) and also by Fukusako.²²⁶ It appears that this property is known to within roughly 5–10% over a wide temperature range. In principle, the thermal conductivity depends on the direction of heat conduction relative to the crystalline structure of the ice, but this anisotropy is believed to be less than 5%.²²⁴

The static dielectric constant of ice is not easy to measure, but it appears to be somewhat higher than that of liquid water near the freezing point, ranging from around 95 near 273 K to 190 near 135 K. Johari and Whalley²²⁷ report measurements over this temperature range and cite several previous experimental studies. Unfortunately, none of the experimental papers reports the original data points, so it is necessary to rely on a smoothing equation or graphical representation of data. A thorough study of the refractive index and optical absorption of ice Ih over a wide range of wavelengths was presented by Warren and Brandt.²²⁸

9. Properties of Seawater

9.1. Background

While this review focuses on properties of pure water, we make an exception for one important and abundant aqueous solution: seawater. The Earth's oceans are central to the climate and vital ecosystems. In physical oceanography, understanding material and energy flows in the ocean requires knowledge of the variation of properties such as density and heat capacity with temperature, pressure, and salinity. Industrially, knowledge of the properties of seawater is needed in order to design desalination systems and for use of seawater as a cooling fluid.

The properties of seawater are directly affected by its salt content, and knowledge of these properties has generally advanced in conjunction with techniques to estimate the salinity to high precision. Because of the complex mixture of ions in seawater, these developments have mostly been confined to the specialized oceanographic community. Aspects of this history are described by several authors.^{229–232}

In the 19th Century, it was recognized that the dominant chloride anion in seawater could be measured accurately by titration with silver nitrate, leading ocean scientists to use a mass fraction variable called "chlorinity." In all the ocean (except some marginal seas like the Baltic), the ratios of all relevant solutes to chloride are very nearly the same. As a consequence, properties of seawater can be practically described by only three parameters: temperature, pressure, and chlorinity. A description in terms of three parameters still provides the basis for the latest standard, the 2010 Thermodynamic Equation of Seawater (TEOS-10). The total mass fraction of dissolved salt in seawater is termed "absolute salinity"; this quantity is difficult to determine accurately.^{233,234}

In the 1960s, electrical conductivity measurements became a convenient and accurate alterna-

tive to the demanding titration procedure required to determine the chlorinity of a seawater sample. However, different methods led to slightly inconsistent results and in turn to spurious spatial density differences. This confusing situation led several international organizations to form a Joint Panel on Oceanographic Tables and Standards (JPOTS) to bring order to the situation. The result was a Practical Salinity Scale, known as PSS-78, based on electrical conductance,²³⁵ and the International Equation of State 1980 for seawater density, known as EOS-80.^{236,237} Equations for additional thermodynamic properties were developed at roughly the same time, and were often considered part of EOS-80.²³⁸

One weakness of EOS-80 was that, because it contained several independent equations, it was not fully thermodynamically consistent. It also lacked a means for calculating some properties that are needed in certain contexts, such as the specific enthalpy and specific entropy of seawater and the chemical potentials that drive evaporation rates. It addition, its pure-water limits differed from the best knowledge. A more subtle problem was its use of a salinity variable ("Practical Salinity") that was deduced from a conductivity measurement rather than the actual amount of dissolved salts; this for example resulted in salinity not being strictly conserved in calculations.²³⁹

Recognition of these issues led to an international effort to develop a new standard. This involved cooperation of IAPWS with SCOR (Scientific Committee on Oceanic Research) and IAPSO (International Association for the Physical Sciences of the Oceans), resulting in the seawater standard TEOS-10,²⁴⁰ discussed in Sec. 9.2. This cooperation continues through an IAPSO/SCOR/IAPWS Joint Committee on the Properties of Seawater.^{239,241}

9.2. Thermodynamics of seawater

While in principle the modeling of properties of seawater is quite complex due to the many different ions present, major simplification is possible in practice because the relative proportions of the different ionic species are very nearly constant throughout the world's oceans. With the introduction of TEOS-10, seawater standards are defined in terms of a *reference composition* that represents typical seawater as given by IAPSO Standard Seawater (SSW), a reference material that has been produced from seawater regularly collected from the North Atlantic since 1901. With that reference composition, the salt content is represented by a single variable called "Reference-Composition Salinity" to distinguish it from other salinity-related variables used in the past. The development of the Reference Composition and the associated salinity scale, along with its relationship to previous salinity scales, is documented by Millero *et al.*²³³

The equation of state of seawater adopted in the international standard TEOS-10 (Ref. 240) writes the specific Gibbs energy of seawater, g^{SW} , as a function of temperature *T*, pressure *p*, and salinity *S*. The Gibbs energy, with pressure as an independent variable, is used in preference to the Helmholtz energy (and density) because oceanographic instruments routinely measure temperature and pressure. The specific Gibbs energy is obtained by adding a salinity correction to the

IAPWS-95 equation of state for pure water (Sec. 5.2), as

$$g^{SW}(S,T,p) = g^{W}(T,p) + g^{S}(S,T,p),$$
(7)

The g^{W} term is simply the specific Gibbs energy of pure water as computed from IAPWS-95.

The salinity-dependent part of Eq. (7) was fitted to a large amount of experimental data for the thermodynamic properties of seawater. The resulting Gibbs function $g^{S}(S,T,p)$ is given by Feistel,²⁴² who also documents the quality of the fit to the various data. In the low-salinity limit, $g^{S}(S,T,p)$ obeys the Debye limiting law and the logarithmic term of Planck's theory of ideal solutions. In addition to the IAPWS-95 reference state of the pure-water part at the triple point, the reference state for the salt part is given by vanishing entropy and enthalpy of seawater at the standard ocean state, $S = 35.16504 \text{ gkg}^{-1}$, T = 273.15 K, $p = 101325 \text{ Pa}.^{193,241,243}$ While this specification does not affect any measurable properties, it is relevant for the absolute values of potential enthalpy used for the TEOS-10 definition of Conservative Temperature, an important quantity in ocean modeling.²⁴⁴ Additional information about using the seawater formulation in calculations, including its use with the IAPWS formulation for thermodynamic properties of ice described in Sec. 8.1, is given by Feistel *et al.*¹⁹³

The range of validity of Eq. (7) results from the range of available data. It is rather complex because three variables are involved, but it includes the range of conditions encountered in the ocean, covering temperatures from the freezing temperature to 313 K and pressures up to 100 MPa at salinities up to 42 g kg^{-1} . At standard atmospheric pressure, the range extends to 353 K and a salinity of 120 g kg^{-1} .²⁴³

The IAPWS-95 formulation for pure-water thermodynamics is computationally demanding, and because it is a fundamental equation in the Helmholtz energy its conversion to Gibbs energy for use in Eq. (7) is not trivial. For convenience in oceanographic use, a simplified approximation to IAPWS-95 was developed (and adopted as an IAPWS Supplementary Release) that is explicit in the Gibbs energy and whose thermodynamic properties for liquid water differ from those computed with IAPWS-95 by less than the uncertainties of IAPWS-95.^{245,246} While not officially adopted by IAPWS or as a part of TEOS-10, computationally fast polynomial approximations for seawater density and specific volume have been developed that are useful in some oceanographic modeling.²⁴⁷

In addition to the IAPWS documents,^{243,246} information (and software) concerning these formulations for the thermodynamic properties of seawater can be found at the TEOS-10 website, www.teos-10.org.

9.3. Electrical conductivity

Extensive attention has been given to precise measurement of the electrical conductivity of seawater over a wide range of temperature, pressure, and composition, because the conductivity

is used as a proxy for salinity, and therefore for density. Small changes in density, on the order of 10 ppm, may cause vertical displacement of vast amounts of ocean water, carrying thermal energy, CO_2 , etc. to a different depth. It is necessary to be able to resolve salinity differences with five significant digits, roughly to 0.002 gkg^{-1} .^{235,238,248}

Conductivity is measurable with a typical absolute accuracy on the order of 1% (maybe as accurately as 100 ppm in some metrology laboratories), but oceanography requires knowledge of even smaller variations.^{249,250} This can be achieved by measuring conductance in an instrument relative to a standard reference such as a carefully prepared KCl solution or certified standard seawater, at the cost, however, of not knowing the absolute conductivity to the same accuracy. This causes no problem in oceanography, however, if all conductance sensors refer to the identical absolute standard reference value, as specified in PSS-78. For this reason, experimental seawater conductance data used for preparing PSS-78 are reported as ratios rather than absolute numbers.²³⁵

The PSS-78 conductivity equation²³⁸ has successfully served the needs of ocean science for more than 40 years and is still in use in the context of TEOS-10. It is valid for salinities between 2 g kg⁻¹ and 42 g kg⁻¹, temperatures from $-2 \,^{\circ}$ C to 35 $^{\circ}$ C, and pressures up to 100 MPa at 35 g kg⁻¹ and below 0 $^{\circ}$ C, but otherwise mostly up to about 20 MPa.²³⁸ It takes temperature values on the obsolete IPTS-68 temperature scale, and returns values of Practical Salinity that need to be converted to Reference-Composition Salinity before being used in TEOS-10 thermodynamic formulas. The pressure variable is relative to the nominal ocean surface (101 325 Pa) rather than to 0 Pa. The PSS-78 conductivity equation has not been expressed as an IAPWS document. Extensions of the equation are available to lower salinities²⁵¹ and to higher salinities.^{252,253}

9.4. Other thermophysical properties of seawater

Other thermophysical properties of seawater are of interest, particularly in industrial contexts such as desalination. IAPWS has adopted a Guideline on the surface tension of seawater as a function of temperature and salinity;²⁵⁴ this is based on the work of Nayar *et al.*²⁵⁵ and provides a salinity-dependent correction, valid up to 92 °C, to the surface tension of pure water. The formulation's validity for supercooled states has been confirmed by Vinš *et al.*²⁵⁶

An IAPWS Guideline was developed for the thermal conductivity of seawater,²⁵⁷ based on the work of Wang and Anderko.²⁵⁸ The pure-water limit is provided by the IAPWS formulation for the thermal conductivity of water,¹⁶¹ and the range of validity extends up to 140 MPa, 523.15 K, and a salinity of 170 gkg^{-1} . In principle, a similar approach could be applied for the viscosity, based on a model such as that of Lencka *et al.*²⁵⁹ and using as a boundary condition the IAPWS viscosity formulation for pure water;¹⁵⁴ this is in the future plans for IAPWS. Some experimental data and empirical correlations for the viscosity of seawater are summarized by Sharqawy *et al.*²⁶⁰

A property of major interest is the pH, which is a central parameter in modeling oceanic chemistry. Some fundamental gaps exist in definitions and measurement standardization, although progress is being made.^{261,262} The index of refraction is also of interest as a route for determining salinity and/or density.^{263–265}

10. Miscellaneous Properties of Water

10.1. Surface tension

The surface tension is important for capillary phenomena, liquid flow in narrow ducts and on surfaces, and phase transition processes including condensation, boiling, and cavitation. The surface tension of water is particularly important for power cycles and for atmospheric processes such as formation of cloud droplets. Surface tension can be interpreted either as the tension of an imaginary membrane stretched parallel to the interface, with units Nm^{-1} , or as energy per area (more properly the surface excess grand potential), with units Jm^{-2} . The surface tension of ordinary water is relatively high (72.7 mNm⁻¹ at 20 °C) and common impurities, especially surface active compounds, reduce it dramatically even at minute concentrations. On the other hand, dissolved salts usually increase the surface tension. Surface tension is often measured for water in contact with air or another gas. Due to the adsorption of gas molecules on the liquid surface, the surface tension slightly decreases. Here we consider only the surface tension of the interface between pure water and pure steam, sometimes called the *orthobaric* surface tension.

In 1975, IAPS critically examined the experimental data for the surface tension of ordinary water and recommended a set of surface tension values and uncertainties associated with each value.²⁶⁶ In 1976, IAPS issued a Release on the Surface Tension of Ordinary Water Substance²⁶⁷ summarizing these results. Background information was given by Vargaftik *et al.*²⁶⁸ A minor revision of the 1976 Release was adopted in 1994 to provide adjusted values corresponding to temperatures (including the critical temperature) on the ITS-90 scale. IAPWS recommends an equation for the surface tension σ between the triple point and the critical point,

$$\sigma = B\tau^{\mu} \left(1 + b\tau \right) \,, \tag{8}$$

where $\tau = 1 - T/T_c$, T_c is the critical temperature given in Table 1, *B* and *b* are parameters fitted to experimental data, and the exponent $\mu = 1.256$. Equation (8) has the form of a universal critical scaling law corrected by a linear term for temperatures far below the critical point. The current accepted value of the critical exponent is $\mu = 2\nu = 1.260$,¹⁰³ but the 1.256 in the IAPWS formulation is close enough that the difference is not significant.

In 2016, Pátek *et al.*²⁶⁹ published a thorough assessment of experimental data and developed a table of recommended values of surface tension including 95% confidence intervals. Their recommended values are within the uncertainties given in the IAPWS Release²⁶⁷ and the confidence intervals are narrower than the IAPWS uncertainties. Pátek *et al.* also refitted Eq. (8).

Recently, there has been a significant interest in the surface tension of supercooled water. Vinš *et al.*^{270,271} confirmed that Eq. (8) can be extrapolated at least down to -25 °C. There is an ongo-

ing discussion about the existence of a second inflection point of $\sigma(T)$ located in the supercooled region (the first inflection point is in the high-temperature region). While it has been shown that a strong change of slope of $\sigma(T)$ seen in some older data was an artifact,²⁷² it appears that the function $\sigma(T)$ loses curvature below the triple-point temperature, thus indicating a weak inflection in the supercooled region.^{273,274} In 2022, Kalova and Mareš critically analyzed experimental data, including the supercooled region, and proposed a new correlation from 240 K to the critical point.²⁷⁵

The IAPWS Release²⁶⁷ provides a satisfactory representation of experimental data on the surface tension of ordinary water, although minor improvements are possible. Data coverage is highly nonuniform: while dozens of quality data sets are available near room temperature, only sparse data exist between the normal boiling point and the critical point. Accurate measurements above 350 K could considerably improve the data situation.

The surface tension of heavy water was considered by IAPWS in 1983, and an equation of the form of Eq. (8) was developed.²⁷⁶ In 1994, the IAPWS Release on Surface Tension of Heavy Water Substance was issued,²⁷⁷ in which the table of recommended values and correlating equation were adjusted to the ITS-90 temperature scale. Compared to ordinary water, the amount of data for the surface tension of heavy water is much smaller; only one data set approaches the critical temperature.

10.2. Dielectric constant

The static dielectric constant (also called the relative permittivity) measures the extent to which a medium reduces the electric field between charges relative to a vacuum. It is important for understanding and modeling the behavior of charged and polar species in solution. A major application arises in models for aqueous electrolyte solutions, where the dielectric constant appears in the Debye-Hückel limiting law that describes the thermodynamics at low ion concentrations. While most interest in this property is for the liquid at ambient temperatures, it is desirable to know it over a wider range of conditions for applications such as geochemistry, atmospheric chemistry, and reactions in supercritical water.

The first representation of the static dielectric constant adopted by IAPS was that of Uematsu and Franck.²⁷⁸ This was a simple empirical fit of several data sources, extending from 0 °C to 550 °C at pressures up to 500 MPa. It was recognized at the time that more work was needed to accurately capture the details of the physical behavior.

A correlation with a better physical basis and covering a wider range of conditions, combining a simple density dependence with a fitted function of temperature and pressure, was proposed by Archer and Wang in 1990.²⁷⁹ The Archer-Wang formulation still finds some use, although it was never adopted by IAPWS. One disadvantage is that it was based on volumetric properties of water derived from the equation of state of Hill,²⁸⁰ which is not widely used.

A sustained effort of data collection and evaluation culminated in the adoption of a new for-

mulation by IAPWS in 1997,²⁸¹ based on the work of Fernández *et al.*²⁸² This formulation covers temperatures from 238 K to 873 K at pressures up to 1200 MPa; it can also be used to calculate derivatives of the dielectric constant with respect to pressure and temperature and the related Debye-Hückel slopes that appear in thermodynamic quantities such as enthalpies of solution. The IAPWS-95 formulation was used to convert input data reported as a function of temperature and pressure to the variables (temperature, density) used in the correlation, and is also used when calculating derivatives and Debye-Hückel slopes.

Fernández *et al.* used a physically based functional form in which the static dielectric constant ε is related to the mean polarizability α and dipole moment μ of the water molecule:

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{3\varepsilon} = \frac{n}{\varepsilon_0} \left(\alpha + \frac{g\mu^2}{3kT} \right),\tag{9}$$

where α is the molecular polarizability, μ is the molecular dipole moment, *n* is the number density (*N*_A times the molar density), and ε_0 is the permittivity of the vacuum. This relationship defines the quantity *g*, which was introduced by Kirkwood²⁸³ as a measure of the degree to which the orientations of neighboring molecules are correlated. Various relationships between *g* and ε have been proposed; that in Eq. (9) is due to Harris and Alder.²⁸⁴ The formulation is developed as a correlation for $g(T, \rho)$, with the physical boundary conditions that $g \rightarrow 1$ as the density approaches zero and also as the temperature approaches infinity. Fernández *et al.*²⁸² present extensive comparisons with experimental data, most of which are represented within their uncertainties.

Since its adoption in 1997, weaknesses in the IAPWS formulation have been identified that suggest it should be replaced. For the important liquid region, there was some discrepancy among available data sources. In 1998, Hamelin et al.¹¹⁸ published radio-frequency resonance measurements of the static dielectric constant of liquid water at saturation up to 418 K with very small uncertainties (on the order of 0.01 in ε). These data suggest that the 1997 formulation, while accurate near 300 K, is in error by up to 0.3 for the liquid near 400 K. New data have also been published for the pressure dependence of the liquid dielectric constant up to 13 MPa.²⁸⁵ Also, the 1997 formulation diverges to infinity at a temperature of 228 K; this was intended to reproduce a divergence that was believed to exist at a hypothesized low-temperature critical point in supercooled liquid water. While the existence of such a critical point is still a matter of controversy (see Sec. 5.6), theory suggests²⁸⁶ that the static dielectric constant would not diverge to infinity. In addition, this divergence in the formulation at 228 K happens at all densities, which is unphysical for vapor states. The formulation also uses a value for the dipole moment that is about 1% too low compared to the best experimental value given in Sec. 4.2.2, which means that its dilute-gas results are slightly in error and that values of g at higher densities must be distorted by about 2% to make up for the discrepancy.

Another area for future work is the dielectric constant of heavy water, of interest in part due to the use of D_2O (often in comparison with H_2O) in solution chemistry studies. Only a few

sources of experimental data exist, but they include saturated vapor and liquid states²⁸⁷ and the compressed liquid to 300 MPa.²⁸⁸ The better-known behavior of ordinary water could be used to guide the behavior of a formulation in regions where no experimental data exist.

The frequency-dependent dielectric behavior is also of interest to physical chemists, because it can give insight into structural and relaxation phenomena. That topic is outside the scope of this review; we point readers to two reviews^{289,290} of the data situation for liquid water.

10.3. Refractive index

The refractive index *n* is more difficult to describe than other properties because an additional variable is involved; it depends on the wavelength of the light. In 1990, Schiebener *et al.* published a correlation of the refractive index of water as a function of temperature, density, and wavelength.²⁹¹ This was modified in 1998 by Harvey *et al.*,²⁹² based on essentially the same data but using the IAPWS-95 equation of state and the ITS-90 temperature scale. The 1998 work is the current IAPWS formulation,²⁹³ which has a range of validity from -12 °C to 500 °C at densities up to 1060 kg m⁻³ and wavelengths from 200 nm to 1100 nm. This covers the range of visible light and some distance into the UV and the IR. It has been shown²⁹² that extrapolation further into the IR is accurate to 1900 nm, and Burnett and Kaplan²⁹⁴ showed that extrapolation slightly further into the UV (190 nm) is also reasonable. Recent experiments in supercooled liquid water^{295,296} agree well with extrapolation of the IAPWS formulation in that region.

The correlation has the functional form suggested by the Lorentz-Lorenz equation:

$$\frac{n^2 - 1}{n^2 + 2} = \rho f(T, \rho, \lambda), \tag{10}$$

where f is a weak function of temperature T, molar density ρ , and wavelength λ . In the lowdensity limit, f is proportional to the mean polarizability of the molecule at the wavelength of interest, although the polarizability was not explicitly used in the formulation. The function f consists of eight terms with combinations of temperature, density, and wavelength; parameters in two of the terms describe the influence of absorption in the UV and the IR.

Because the functional form of Eq. (10) is relatively simple, the IAPWS formulation does not describe the refractive index of ambient liquid water to the accuracy with which it is known. Its expanded uncertainty in this region is given as 1.5×10^{-5} . The best reference values come from the work of Tilton and Taylor,²⁹⁷ who measured the refractive index between 0 °C and 60 °C at 13 visible wavelengths from 404 nm to 707 nm with a precision near 2×10^{-6} . When using the data of Tilton and Taylor,²⁹⁷ three caveats should be kept in mind. First, their results are not absolute indices, but are relative to dry air at standard atmospheric pressure (101.325 kPa) at the reported temperature. Conversion to absolute indices requires a formula for the refractive index of dry air, such as that of Birch and Downs.²⁹⁸ Second, the Tilton and Taylor data were reported on the International Temperature Scale of 1927 (ITS-27); because the difference made by the deviation of

ITS-27 from ITS-90 is of similar magnitude to the precision of the measurements, the temperature scale must be carefully considered if that level of accuracy is required. Third, it has been shown¹²⁷ that the reasoning Tilton and Taylor used to dismiss the effect of dissolved air on the refractive index was faulty. Since the level of air saturation of their data is unknown, they must be considered to have an extra expanded uncertainty of roughly 5×10^{-6} in *n*.

10.4. Magnetic susceptibility

Water is diamagnetic; its susceptibility is relevant for NMR applications and for testing theories and simulations of magnetism in the liquid state.

The magnetic susceptibility of liquid water near 20 °C has been measured several times. Most data are mutually consistent within 0.5%,^{299–303} with a volume magnetic susceptibility (in the SI, as opposed to the cgs electromagnetic units used in older literature) of -9.05×10^{-6} . The resulting molar susceptibility is -1.633×10^{-10} m³ mol⁻¹. The small variation of the molar susceptibility with temperature for liquid water has also been studied.^{304,305} The molar susceptibility of liquid heavy water (not, of course, the mass susceptibility) is almost identical to that of ordinary water.^{306,307} The molar susceptibility of ice appears to be a few percent smaller than that of liquid water near the freezing point.^{308,309}

The magnetic susceptibility of an isolated molecule can be obtained from *ab initio* quantum calculations. The computed susceptibility per molecule is approximately 10% larger than the measured values for the liquid.³¹⁰ There do not appear to be any experimental measurements in the vapor phase to verify this difference, although it is qualitatively consistent with the small increase in the liquid phase when the density is lowered by increasing the temperature.^{304,305}

10.5. Self-ionization constant

The self-ionization constant of water, K_w , is essential for understanding phenomena in aqueous solutions where charged species are involved. K_w is defined as the equilibrium constant for the reaction

$$H_2O \rightleftharpoons H^+ + OH^-,$$

or, equivalently under the convention that the activity of H_3O^+ equals the product of the activities of H_2O and H^+ ,

$$2H_2O \rightleftharpoons H_3O^+ + OH^-,$$

where the standard state used is the hypothetical infinitely dilute state at unit molality.

The first IAPWS formulation for this quantity was based on the work of Marshall and Franck,³¹¹ who fitted an empirical function to experimental data that included not only normal liquid conditions but also supercritical temperatures and pressures. A weakness of this formulation, as noted by Pitzer,³¹² was the failure to extrapolate to the correct low-density limit.

Bandura and Lvov³¹³ developed a molecular model for ion hydration and combined it with the low-density limit obtained from the properties of the isolated species given in the JANAF tables.³¹⁴ Their formulation was adopted as an IAPWS Release in 2007,³¹⁵ valid for temperatures up to 800 °C and densities from 0 to 1.25 g cm⁻³.

Recently, new values of K_w were given by Arcis *et al.*,³¹⁶ derived from measurements of the electrical conductivity of very pure water in flow-through apparatus up to 674 K and 31 MPa. These data are the most accurate available at elevated temperatures near the critical point. They are consistent with the formulation of Bandura and Lvov at most conditions, but significant disagreement is observed at conditions near water's critical point, where Bandura and Lvov had no data to fit. Incorporation of the data of Ref. 316 in a new model that retains the correct low-density behavior would provide an improved formulation for K_w .

10.6. Electrical conductivity

The electrical conductivity of pure water is a function of the self-ionization constant K_w and the limiting conductances of the hydrogen and hydroxide ions. In 1990, IAPWS adopted a Guideline for this quantity³¹⁷ based on the work of Marshall.³¹⁸ Marshall made use of semiempirical relationships for ion conductances and several sources of high-temperature data; K_w in the formulation was from the 1981 work of Marshall and Franck.³¹¹ This Guideline could be updated to take advantage of the new knowledge of K_w and pure-water conductivity discussed in Sec. 10.5.

10.7. Isotopic fractionation

The minor isotopic species in water, particularly D and ¹⁸O, are used as tracers in modeling weather, climate, and other geophysical processes.^{22,23,319} A key factor in these studies is *isotopic fractionation*, where the minor species distributes unevenly between two phases, for example during evaporation or precipitation. The important quantity in most processes is the equilibrium fractionation, which is typically expressed as the concentration ratio of D/H (or ¹⁸O/¹⁶O) in one phase to that in the other. For example, in vapor–liquid equilibrium at 20 °C, the vapor phase is roughly 8% depleted in D compared to the liquid phase.

The equilibrium vapor–liquid fractionation of water isotopes has been extensively studied and is known with relatively low uncertainty. While the main interest is at conditions present in Earth's atmosphere, higher temperatures are sometimes of interest in geochemical modeling. Comprehensive equations for the equilibrium vapor–liquid fractionation of D and of ¹⁸O were given by Japas *et al.*³²⁰ for temperatures from 0 °C to T_c . These were largely based on the wide-ranging experimental work of Horita and Wesolowski,³²¹ which should be consulted for references to other experimental data.

The equilibrium vapor-solid and solid-liquid fractionations have not been studied as thoroughly. For vapor-solid fractionation of D, the experimental sources do not agree very well, particularly at low temperatures.^{322–324} For ¹⁸O, the solid–vapor fractionation data are in fairly good agreement.^{323,325,326} Solid–liquid fractionation is, for the most part, only of interest near 0 °C. Both D and ¹⁸O fractionation were measured at this temperature by Lehmann and Siegenthaler.³²⁷ A clever indirect route to these quantities was taken by Wang and Meijer,³²⁸ who made use of the well-studied effects of isotopic variation on the triple-point temperature of water. They obtained results that agreed with those of Lehmann and Siegenthaler, but with a smaller uncertainty.

The three-phase equilibrium at the triple point provides a consistency check, since at that point only two of the ratios are independent for each isotope. The two experimentally best-known factors (vapor–liquid and solid–liquid) can be combined to yield the vapor–solid fractionation factor. For ¹⁸O, the existing vapor–solid data sources are reasonably consistent with the vapor–liquid and solid–liquid values. For D, there may be a small discrepancy, but that is unclear since none of the experimental vapor–solid sources made measurements closer than about 5 K below the triple point.

In some situations, isotopic fractionation depends on an additional kinetic effect, determined by the relative diffusivities of the isotopic species in air. Kinetic fractionation is beyond the scope of this review, but we note a recent study³²⁹ that used molecular modeling to calculate these diffusivity ratios in air, providing values over a wide range of temperatures in contrast to the scattered experimental data.

11. Future Directions and Needs

11.1. Replacement of IAPWS-95

IAPWS-95 has served scientists and engineers well for over 25 years, but it has become apparent that there is room for improvement. Certain properties in some regions exhibit problematic behavior, and many improved data have become available. Here, we discuss the shortcomings of IAPWS-95 and ways it might be improved in a future formulation for general and scientific use.

11.1.1. Known deficiencies

As mentioned in Sec. 5.2.1, an obsolete value was used for the water-specific gas constant. The IAPWS-95 value of R_w is roughly 0.0011% larger than the value that would be obtained by combining the current (exact) value of R with the molar mass given in Sec. 5.2.2. This means that the density in the dilute-gas limit is systematically low by 11 ppm.

As mentioned in Sec. 5.2.5, certain derivative properties such as the heat capacities and the isothermal compressibility exhibit unphysical behavior near the saturation boundaries in the vicinity of the critical point. This is believed to be due to the "nonanalytic" terms in Eq. (2); such terms are no longer used in reference equations of state.

The extrapolation of IAPWS-95 into the metastable supercooled liquid region, while physically reasonable, does not match the best available data, especially at high pressures. This is described

by Holten *et al.*¹⁰⁴ in the context of an improved model for the supercooled liquid; further analysis is given by Wagner and Thol.¹⁰⁶ The extrapolation behavior of IAPWS-95 can also cause problems in mixture calculations, where the formulation may be evaluated at temperatures outside its range of validity. Modern equation-of-state technology can minimize these problems.

It was discovered that the virial expansion of IAPWS-95 behaves in an unphysical way below about 300 K, meaning that virial expansions of properties for low-temperature vapors do not converge as expected.³³⁰ Also, the second virial coefficient B(T) unphysically diverges to infinity in the high-temperature limit. Again, equation-of-state developers now know how to prevent such problems.

11.1.2. New experimental data

In this subsection, we review new experimental data. It is not our intent to list all data on water published since the completion of IAPWS-95; instead we describe selected sources that expand existing data coverage, provide reduced uncertainty compared to previous work, or contribute to resolving disagreements among data sources.

Several new studies of the speed of sound in the compressed liquid are expected to significantly improve the representation of that region. Lin and Trusler¹⁰⁷ reported highly accurate sound speeds (expanded uncertainty 0.03–0.04%) at pressures up to 400 MPa and temperatures from 253 K to 473 K. This includes the high-pressure liquid where, due to the negative initial slope of water's melting curve, stable liquid exists below 273.15 K; few measurements exist in this region. These are complemented by data of Benedetto *et al.*³³¹ with uncertainty of 0.05% up to 394 K and 90 MPa, Meier and Kabelac³³² with uncertainties on the order of 0.01% at 303–323 K at pressures up to 100 MPa, El Hawary and Meier³³³ with uncertainties on the order of 0.007% at 274–368 K at pressures up to 100 MPa, and Fehres³³⁴ with uncertainties on the order of 0.005% at 273–323 K at pressures up to 60 MPa. At even higher pressures, sound-speed data were published by Bollengier *et al.*³³⁵ up to 700 MPa at temperatures from the melting curve to 353 K. There is good agreement among these sources where their data overlap, and they show some systematic deviations from IAPWS-95.

Troncoso³³⁶ reported the isobaric heat capacity at pressures up to 500 MPa at temperatures from 255 K to 313 K. These data have a scatter of roughly 1%, but that is an improvement over existing high-pressure data that are of higher uncertainty and are completely lacking in some of this region. Additional caloric information at high pressures was reported by Dzhavadov *et al.*,³³⁷ who measured the isentropic variation of temperature with pressure, $\left(\frac{\partial T}{\partial p}\right)_s$, from 273 K to 473 K at pressures up to 1200 MPa.

The supercooled liquid, both at atmospheric pressure and at high pressure, has been a subject of extensive study; some of the data are reviewed by Holten *et al.*¹⁰⁴ and by Wagner and Thol.¹⁰⁶ A few of the sound-speed data of Lin and Trusler¹⁰⁷ extend into the supercooled region. Romeo *et al.*³³⁸ reported densities up to 400 MPa at temperatures from 243 K to 283 K. Blahut *et al.*³³⁹

measured densities to 200 MPa in the supercooled and stable liquid up to 303.15 K. Wagner and Pru β^{71} noted discrepancies among available experimental data sources for the isobaric heat capacity of the supercooled liquid at atmospheric pressure that hindered the evaluation of the formulation in that region. Recently, more clarity has been obtained with the adiabatic calorimetry measurements of Voronov *et al.*,¹⁴² which confirm the data of Tombari *et al.*³⁴⁰ while disagreeing with some other sources. The heat-capacity measurements of Pathak *et al.*¹⁴³ used a novel method and extend to lower temperatures, but with considerable scatter. Beltramino *et al.*¹⁴⁴ measured the vapor pressure of supercooled water at temperatures down to 252 K, although calculation from a thermodynamic model anchored to the well-known triple point¹⁰⁴ may have smaller uncertainties.

As was the case for IAPWS-95, the development of a new formulation will not be a simple matter of adding these points to existing data and performing a regression on the many thousands of available data points. Expert judgment is needed to identify the most accurate measurements to play a primary role in constraining the equation of state. Important tasks in this critical evaluation include examining the uncertainty of reported data (including whether uncertainties reported by authors are realistic) and evaluating the consistency among sources. Consistency issues arise not only in different measurements for the same property, but also among different types of data because of the thermodynamic relationships among properties (for example, the speed of sound is related to the heat capacity and derivatives of the density). Developing the equation of state as a single Helmholtz energy formulation facilitates this work by allowing all types of data to be fitted simultaneously.

11.1.3. Measurement needs

In 2019, IAPWS analyzed the data situation for the thermodynamics of water and issued an IAPWS Certified Research Need (ICRN) describing data that would be particularly helpful for reducing the uncertainties of a new reference equation of state.³⁴¹ The following needs for experimental measurement are extracted from Ref. 341; the uncertainties mentioned should be interpreted as expanded (k = 2) uncertainties including uncertainties of the independent experimental variables.

- Accurate measurements of saturation vapor pressure above 373 K. The uncertainty of the measurements should be at most 0.02%, but preferably less than 0.01%. Similarly accurate measurements below 373 K are also welcome to check the validity of existing data.
- Liquid densities at high temperatures (above approximately 400 K), especially near or at the vapor-liquid saturation boundary. These should preferably have uncertainties of 0.01% or better.
- Vapor densities at high temperatures (above approximately 500 K), especially near or at the vapor-liquid saturation boundary. These should preferably have uncertainties of 0.03% or

better.

- Density, heat capacity, and/or sound-speed data for the metastable subcooled vapor. Data should be more accurate than extrapolation based on a truncated virial equation using quantum-mechanical values of the second virial coefficient.
- Density data at temperatures above 800 K.
- Density data at pressures above 100 MPa.
- Density data near the vapor-liquid critical point, preferably with overall uncertainty expressed in terms of pressure not exceeding 0.03% for given temperature and density.
- Sound speeds above 473 K in the vapor, liquid, and supercritical regions, preferably of similar accuracy to the measurements of Ref. 107 whose expanded relative uncertainty is 0.03–0.04%.
- Heat capacities (either isobaric or isochoric), especially in the liquid phase (with uncertainty of 0.1% or better) and near the critical point.

11.1.4. Guidance from molecular calculations

For most states and properties of interest, the accuracy of state-of-the-art experiments far exceeds that attainable from molecular modeling techniques. However, in a few cases, notably the properties of the dilute gas that serve as boundary conditions for property formulations, the best molecular calculations can now produce lower uncertainties than experiment. In addition, such calculations can guide extrapolation of the equation of state in regions that are difficult to study experimentally. The present and potential future contributions from molecular theory are discussed in Sec. 11.2.

11.2. Properties from molecular theory

Advances in *ab initio* quantum calculations, along with advances in theory and in computing power, continue to improve the ability to calculate certain properties of water with an accuracy that is competitive with, or in some cases superior to, the accuracy of experiments. This is an active area of research, so it is likely that data from molecular theory (in some cases combined with spectroscopy) will play an increasingly important role in the future. These data are not only useful as input to reference-quality thermophysical property formulations; they can also be of direct scientific interest. In addition, comparison of calculated properties to accurate experimental data can provide a test of theoretical methods and molecular models not only for pure water but for use in modeling aqueous mixtures.

We can divide properties from molecular theory into three categories based on the number of molecules considered in the calculation. The first category is properties (such as the ideal-gas heat capacity or the molecular polarizability) that are calculated for one isolated molecule. Second, some important properties depend only on the interaction between two molecules; examples include the low-density limit of the transport properties and the second virial coefficient that characterizes the initial departure from ideal-gas behavior. Also in this category would be properties that depend on interactions among only a few molecules, such as the third virial coefficient that is a property of three molecules. The third category is bulk properties, such as typical experimentally measured quantities (density, heat capacity, viscosity, etc.). Calculating these properties typically involves simulation of a large number of molecules interacting at once. In order to be tractable, such simulations require more approximations than calculations involving only a few molecules.

11.2.1. Ideal-gas heat capacity

As mentioned in Sec. 4.2.3, a combination of modern spectroscopy and *ab initio* calculations enables the calculation of the molecular partition function, and thence the ideal-gas heat capacity required for equation-of-state development, with unprecedented accuracy. The calculation of heat capacity requires not only the partition function but also its first and second moments, but the calculation of these moments adds no extra complication when the sum-over-states method is used for the partition function. High-accuracy calculations of the partition function and idealgas heat capacity have been published for the dominant $H_2^{16}O$ isotopologue⁵⁷ and for the three isotopologues present in $D_2O.^{58}$ If similar results can be provided for the other five water isotopologues, the resulting improved ideal-gas heat capacity for ordinary water would provide a sound foundation for the equation of state, especially at high temperatures.

It should be noted that these molecular calculations produce a maximum in the calculated heat capacity between 4000 K and 5000 K. This is an artifact of the approach, in which only molecular water is considered and the number of high-energy states is limited. In reality, water undergoes significant dissociation at high temperatures, so that the addition of heat also goes to dissociating the molecule, but this calculation does not consider that pathway. This point is discussed by Simkó *et al.*⁵⁸

11.2.2. Intermolecular potential-energy surfaces

The literature on intermolecular potential-energy surfaces for water is voluminous and growing, so we will only summarize key aspects related to the prediction of thermophysical properties. More detailed reviews are given by Cisneros *et al.*³⁴² and Demerdash *et al.*³⁴³

The simplest and most widely used models consider only pairwise interactions of rigid molecules comprised of a small number of point charges and sites for nonelectrostatic interactions (typically modeled by the venerable Lennard-Jones potential). A popular model is the three-site SPC/E potential introduced in 1987,³⁴⁴ which consists of partial charges on the oxygen and hydrogen sites, a Lennard-Jones interaction between oxygen sites, and the intramolecular angle set at its tetrahedral value of 109.47°. Similar in form is the TIP family of potentials, whose most widely used representative is the TIP4P model introduced in 1983,³⁴⁵ which is similar to SPC/E except that the negative charge is displaced from the oxygen atom, making it a four-site model. A review of rigid, nonpolarizable models, with particular attention to the reproduction of bulk properties, was given by Vega and Abascal;³⁴⁶ see also Vega³⁴⁷ on describing the dielectric constant. The parameters in these potentials are optimized to fit thermodynamic, dielectric, and structural data of real water. Different models result from emphasizing different properties; for example, there is a modified version of TIP4P optimized for describing ice.³⁴⁸ These pair potentials are useful for modeling aqueous solutions, particularly in biochemical contexts where thousands of water molecules may be needed and use of a more rigorous model would be prohibitive.

When assessing the ability to predict properties, it must be recognized that these simple models are only *effective* potentials, attempting to describe water (usually liquid water) in a way that approximately accounts for the physics that is left out of the models. The most important omission is the fact that multibody effects (beyond the approximation of pairwise interactions) are large in liquid (and solid) water. The interaction between a pair of molecules is significantly affected by other nearby molecules; the multibody effects have a strong directional nature associated with hydrogen bonding. As noted in Sec. 4.2.2, the mutual polarization of the molecules is enough to increase the average molecular dipole moment in the liquid by roughly 60%; the pairwise models typically have a dipole moment larger than the real isolated water molecule. Because of these unphysical aspects, effective pair potentials are inadequate for quantitative prediction of thermophysical properties of real water.

For properties that depend only on the pair interaction, the difficulty of multibody interactions can be bypassed, and physically realistic pair potentials can be developed from *ab initio* calculations. This can now be done at a high level of theory with large basis sets; the functional forms typically combine theoretical guidance with empiricism. Examples include pair potentials known as CCpol-8s,³⁴⁹ WHBB,³⁵⁰ and MB-pol.³⁵¹ The latter two potentials include intramolecular flexibility, while CCpol-8s is rigid; flexibility has been superimposed on CCpol-8s in a potential known as CCpol-8sf.³⁵² These realistic pair potentials produce much more accurate values for quantities such as the second virial coefficient and dilute-gas viscosity than effective potentials such as SPC/E whose pair interaction is distorted to make up for missing multibody effects.

Realistic modeling of multibody effects can involve superimposing polarization (for example in the form of fluctuating charges or induced multipole moments) on a simpler model, or an explicit three-body potential fitted to high-level *ab initio* calculations, or a combination of these. Many such models have been proposed for water; we refer the reader to a review.³⁴² For quantitative prediction of thermophysical properties (such as the third virial coefficient that depends on interactions among three molecules), the most promising approaches build upon state-of-the-art

two-body potentials. Quantitatively accurate three-body potentials are incorporated in the models WHBB,³⁵⁰ CCpol3 (related to the CCpol-8s two-body potential),³⁵³ and MB-pol.³⁵⁴ In principle, accurate three-body potentials should allow the prediction of the third virial coefficient; we discuss such calculations in Sec. 11.2.3. It appears that effects beyond three-body forces are significant in water; a four-body potential has recently been presented.³⁵⁵

Another omission in most molecular modeling of water is nuclear quantum effects.^{356,357} Typical simulations use classical mechanics, ignoring the quantization of translation, rotation, and intramolecular vibration. It is clear that these effects are not negligible, because D_2O (which has less of a quantum nature due to the larger mass of D) has somewhat different properties from H₂O. Potentials used in classical simulations and fitted to experimental data can be thought of as incorporating quantum effects in an effective way, but this must introduce error since the quantum effects are temperature-dependent while the effective potentials are not. Quantitative prediction of water properties should therefore combine realistic potentials with a calculation procedure that incorporates nuclear quantum effects. Such procedures are discussed further for virial coefficients in Sec. 11.2.3. For low-density transport properties (see Sec. 11.2.4), it has not been possible so far to move beyond classical calculations for water molecules. For condensed phases, thermophysical properties can be obtained by simulating realistic potentials while accounting for the quantum effects with path-integral or other techniques,^{356,358–362} although this is more computationally expensive than classical simulations.

A different approach to simulation bypasses the intermolecular potential-energy surface altogether. In *ab initio* molecular dynamics (AIMD), the electronic structure is solved "on the fly" during the simulation, usually with a density functional theory (DFT) approximation, so that the forces acting on the nuclei at each time step result from the evolving distribution of electron density. In principle, AIMD could provide rigorous properties for systems of many molecules. In practice, the DFT approximations needed to make the calculations tractable limit the accuracy. Since it does not appear that AIMD will be able to supplant experimental data and conventional simulations in the foreseeable future for prediction of thermophysical properties at experimentally accessible conditions, we merely point readers to some references for AIMD simulations of liquid water.^{49,363–366} However, see Sec. 11.7 for discussion of AIMD for calculating properties at extreme temperatures and pressures.

11.2.3. Virial coefficients

A promising area for molecular theory is the prediction of virial coefficients. The virial expansion provides a rigorous series of corrections to the ideal-gas law:

$$\frac{p}{\rho RT} = 1 + B(T)\rho + C(T)\rho^2 + \dots,$$
 (11)

where the second virial coefficient *B* is rigorously related to the pair potential, the third virial coefficient *C* depends on the interactions among three molecules, etc. These coefficients are useful in their own right for describing the low-density behavior of water vapor and its mixtures, but they can also provide boundary conditions for fitting a reference equation of state, as has been done with B(T) in the case of heavy water.¹⁷⁷

For ordinary water, the available experimental information for the second virial coefficient has been evaluated by Harvey and Lemmon.³⁶⁷ B(T) is well determined by experiment from 350 K to 773 K, leaving significant room for improvement at low and high temperatures. The data for C(T) are more sparse, but results of fair accuracy are available from roughly 500 K to 773 K.^{89,368,369}

The calculation of virial coefficients from molecular theory is complicated by nuclear quantum effects, which are most significant at low temperatures. Because of the small moment of inertia of the water molecule, the quantum effects on B(T) for water amount to roughly 25% at 300 K, and remain significant up to at least 1000 K.¹⁷⁶ While no exact solution is known for the quantum virial coefficients of nonspherical molecules, these effects can be rigorously included by the path-integral Monte Carlo (PIMC) method, as first demonstrated for rigid molecules by Schenter³⁷⁰ and extended to flexible potentials by Garberoglio and collaborators.^{176,371}

The performance of state-of-the-art pair potentials for B(T) was studied by Garberoglio *et al.*¹⁷⁶ They used PIMC to calculate B(T) for the flexible potentials WHBB,³⁵⁰ MB-pol,³⁵¹ and CCpol-8sf,³⁵² along with rigid versions of the same potentials fixed at the vibrationally averaged groundstate geometry. The results are shown in Fig. 10, where several reliable sources of experimental data are shown in black (with their error bars where available) and the calculated results are shown in red. The effect of flexibility cannot be neglected for quantitative results, as it accounts for several percent of the value of B(T) at most temperatures. The existence of accurate second virial coefficients from experiment over a limited temperature range allows comparison of the different potentials. CCpol-8sf agrees with experiment over the entire range. WHBB also shows good agreement, although it begins to deviate from experiment at low temperatures. MB-pol performs somewhat worse; it yields B(T) higher (less negative) than experiment throughout the range the deviations are not large, but clearly exceed the uncertainties of the experimental data. We therefore conclude that second virial coefficients from the CCpol-8sf potential will also be reliable at temperatures where accurate experimental data are lacking.

Garberoglio *et al.*¹⁷⁶ were unsuccessful in their effort to establish similar benchmark results for the third virial coefficient. They performed calculations not only with two-body and three-body potentials from one group (e.g., MB-pol), but also combinations like the CCpol-8sf pair potential with the MB-pol three-body term. The computational expense of PIMC for C(T), especially for flexible models, is substantial, but they obtained results at 300 K, 500 K, 600 K, 700 K, and 1000 K. Unfortunately, while the three-body potentials tested^{350,353,354} all gave qualitatively accurate results, none of them was able to match the experimental C(T). The CCpol3 potential³⁵³ gave the best agreement with experiment, but systematic differences remained.



FIG. 10. Second virial coefficients calculated from high-accuracy pair potentials and compared to experimental data for H_2O . The baseline for the plot is the correlation of Ref. 367. Black symbols are experimental data. Red symbols are calculated values: open for rigid models and filled for flexible models. Reproduced from Ref. 176 with permission from the Royal Society of Chemistry.

Two needs stand out for the prediction of virial coefficients. The first is a better three-body potential to enable quantitative prediction of C(T). The second is the development of a more complete flexible two-body potential. While CCpol-8sf is excellent for the most part, it gives unphysical behavior when extrapolated to molecular geometries beyond the range of deformations to which the flexible contribution to the potential was fit. Because these distorted geometries are sampled occasionally in PIMC calculations, Garberoglio et al.¹⁷⁶ had to set their energy to the value at the edge of the fitted range. An improved potential would describe the full range of geometries. It would also be desirable to estimate the uncertainty of the virial coefficients, which can be computed from the uncertainty in the potential as has been done for other systems.^{371,372} Analysis of convergence of the quantum calculations, and of the goodness of the fit of the potential function, should make this possible for the pair potential; uncertainty estimates for a three-body potential would be much more difficult. Finally, similar methods could yield higher coefficients, such as the fourth virial coefficient D(T), for which no experimental information is available. It may be sufficient to neglect higher-order effects and use only two-body and three-body potentials, especially since even qualitative results would be an improvement over existing knowledge. This is currently computationally prohibitive for realistic models, but could be feasible with advances in computing power.

11.2.4. Transport properties in the zero-density limit

Transport properties, i.e., viscosity, thermal conductivity, and diffusion coefficients, can be predicted accurately in the zero-density limit because, like the second virial coefficient, they can be rigorously related to the pair potential. The basic equation of kinetic theory is the Boltzmann equation, which is a nonlinear integro-differential equation that describes the spatial and temporal evolution of the one-particle distribution function. In its original form, it is only valid for gases of spherical particles without internal degrees of freedom. The corresponding quantum-mechanical equation was derived by Uehling and Uhlenbeck.³⁷³ Later, the Boltzmann equation was general-ized for polyatomic molecules, resulting in the classical Curtiss-Kagan-Maksimov equation^{374–377} and, in the quantum-mechanical case, the Waldmann-Snider equation.^{378–381}

No general solution of the Boltzmann equation for non-equilibrium states has been obtained. In order to develop a formalism for calculating transport properties, Chapman³⁸² and Enskog³⁸³ independently derived an approximate solution for monatomic gases. They assumed that the disturbance from equilibrium is small so that the Boltzmann equation can be linearized. Since the resulting expressions for the transport properties are not suitable for practical calculations, the solution is approximated by a finite number of basis functions. With these basis functions, generalized scattering cross sections are defined that can be determined by classical or quantum-mechanical collision trajectory calculations. The transport properties are formulated as functions of these cross sections. Different orders of approximations result, depending on the number of cross sections used. An exact solution requires an infinitely large basis set. For further details, the reader is referred to the literature.^{384–387}

For polyatomic gases, the generalized Boltzmann equations can be solved analogously, and the solutions approximated by orthogonal basis functions, from which generalized cross sections result. This formalism is much more complex than for monatomic gases. The relations for classical generalized scattering cross sections were derived by Curtiss for rigid linear molecules³⁸⁸ and extended to nonlinear molecules by Dickinson *et al.*³⁸⁹ The theory was applied by Hellmann *et al.*¹⁶³ to calculate the viscosity, thermal conductivity, and self-diffusion coefficient of H₂O in the low-density limit using the CC-pol potential.³⁹⁰ The theory for the thermal conductivity of polyatomic molecules was later improved by Hellmann and Bich¹⁶⁴ and applied to H₂O and D₂O. These calculations were used in the development of the IAPWS transport property formulations for ordinary water described in Sec. 6 and for heavy water described in Sec. 7.2.

The complete quantum-mechanical calculation of transport properties of polyatomic gases has so far not been possible because of the mathematical complexity and large computational requirements. For collisions between a helium atom and a nitrogen molecule, scattering cross sections were calculated quantum-mechanically and compared to the corresponding classical values.^{391,392} The comparison showed that quantum effects are small except at low temperatures, and that they should be negligible for most applications. Quantum-mechanical calculations of dilute-gas transport properties for hydrogen atoms with water molecules³⁹³ have also been carried out.

11.2.5. Thermodynamic and transport properties from molecular simulation

Thermodynamic properties at arbitrary states can be calculated by molecular-dynamics or Monte Carlo simulations.³⁹⁴ Both techniques are based on the ensemble theory of statistical mechanics. Various ensembles are available, each of which is characterized by three independent variables, a thermodynamic potential, from which all thermodynamic properties can be obtained as combinations of derivatives of the potential with respect to the independent variables, and a weight factor, with which the systems are distributed in the ensemble. Graben and Ray³⁹⁵ summarized the fundamentals of the eight basic ensembles of statistical mechanics, which are related to one another by a Laplace-Legendre transformation scheme.

Although the microcanonical ensemble is the starting point for the theoretical formulation of statistical mechanics and is the natural basis for molecular-dynamics simulations, the exact expressions for calculating thermodynamic properties were not known until 1985, when Pearson et al.³⁹⁶ introduced a Laplace transform technique to evaluate the integrals over the momenta of the particles in the microcanonical partition function. This was key for the development of the theory of the microcanonical ensemble and the molecular-dynamics ensemble, in which the total momentum vector of the particles \mathbf{P}^{397} and a further vectorial quantity \mathbf{G}^{398} , which is related to the initial position of the center of mass of the system, yield six additional constants of motion. Based on the works of Pearson et al.³⁹⁶ and Çağin and Ray,^{397,399} Lustig developed a rigorous methodology to derive expressions for thermodynamic properties, such as the isochoric and isobaric heat capacities, isothermal compressibility, thermal pressure coefficient, and speed of sound, in the microcanonical,⁴⁰⁰ molecular-dynamics,⁴⁰¹⁻⁴⁰⁴ and canonical ensembles.^{405,406} By introducing phase-space functions to represent derivatives of the partition functions with respect to the independent variables, Lustig systematically obtained expressions for thermodynamic properties in terms of the kinetic energy, potential energy, and volume derivatives of the potential energy of the system. With this methodology, essentially exact expressions for all thermodynamic properties and derivatives of arbitrary order of the thermodynamic potential can be derived in any ensemble. Recently, Meier and co-workers applied Lustig's methodology to derive expressions for thermodynamic properties and derivatives of the thermodynamic potential of arbitrary order in the NpT ensemble,⁴⁰⁷ in the grand canonical ensemble,⁴⁰⁸ and in the less-known NpH,⁴⁰⁹ μVL ,⁴¹⁰ and $\mu p R^{410}$ ensembles. A unique result is that the calculation of thermodynamic properties in those ensembles in which the pressure is an independent variable does not require volume derivatives of the potential energy. This is particularly advantageous in simulations when the interactions are described by very accurate *ab initio* pair and three-body potentials.

Transport properties can be calculated by equilibrium or nonequilibrium molecular-dynamics simulations.³⁹⁴ In equilibrium simulations, they are obtained as integrals of the time-correlation functions of the corresponding thermodynamic fluxes⁴¹¹ or as slopes of generalized mean-squared displacements in the long-time limit.⁴¹² For example, the viscosity is determined by the time inte-

gral of the shear stress autocorrelation function or the mean-squared displacement of the center of momentum. The time-correlation function formalism and generalized mean-squared displacement approach have the advantage that all transport properties can be determined by a single simulation run, but usually very long simulations are required to obtain accurate results.

In contrast, nonequilibrium simulations mimic experimental measurements of transport properties. Gradients of the thermodynamic force are imposed on the simulated systems to induce a flux that corresponds to the transport property to be determined. This is then calculated as the ratio of time averages of the flux induced by the thermodynamic force. For example, by imposing a linear velocity profile on a system by the Lees-Edwards periodic boundary conditions, planar Couette flow is simulated, and the viscosity is obtained by the ratio of the time average of the resulting shear stress and the imposed velocity gradient. Thermostating mechanisms must be applied to remove the dissipated energy from the system and retain the steady state. Usually, only one transport property can be determined by a particular algorithm. Since the simulated systems are small, the applied gradients are much larger than those in experiments. Therefore, several simulations with different gradients must be performed, and the results extrapolated to the low-gradient limit to obtain a value representative of a macroscopic system. Nonequilibrium simulation techniques are described in several monographs^{394,413} and review articles.^{414–417} The theory of nonequilibrium simulations is described in the book of Evans *et al.*⁴¹⁸

When these techniques are combined with highly accurate potentials, accurate values for all thermodynamic and transport properties can be calculated. Molecular simulations can be useful to explore regions of the phase diagram of a fluid that are inaccessible or difficult to study experimentally, e.g., metastable regions, such as the supercooled or superheated liquid, or extreme pressures and temperatures. They also enable calculating properties that are difficult to measure accurately, e.g., the Joule–Thomson coefficient, the isothermal compressibility, or the isobaric expansion coefficient. Furthermore, the structure of liquids can be investigated.

In simulations of water, typically simpler potentials are applied than the accurate models that have been used for calculating virial coefficients and transport properties in the low-density limit, limiting the accuracy and predictive power of the results. A few studies used accurate *ab initio* potentials. For example, Bukowski *et al.*⁴¹⁹ performed molecular-dynamics simulations of liquid water with the CC-pol pair potential and the three-body potential of Mas *et al.*⁴²⁰ to calculate the structure, internal energy, coordination number, and self-diffusion. Muniz *et al.*⁴²¹ applied the MB-pol many-body potential to investigate the vapor–liquid equilibrium of water. Due to the strong quantum effects at low temperature, the flexibility of the water molecule, and nonadditivity of the interactions beyond three-body effects, classical simulations even with semi-empirical quantum corrections cannot provide results for thermophysical properties of water with uncertainties comparable to those of the best experiments. On the other hand, they can provide insights that are difficult to obtain by other means. A notable example is the prediction of a liquid–liquid phase transition with a second critical point at low temperature in the subcooled liquid region, which

was first observed by Poole *et al.*¹³² in molecular-dynamics simulations and has been discussed controversially ever since.¹³⁰

11.2.6. Molecular calculations for dielectric and optical properties

As is apparent in Eq. (9), the molecular polarizability and dipole moment are an essential part of the description of the static dielectric constant, providing the boundary condition for its behavior at low density. The polarizability at optical frequency is similarly important for the refractive index. All of these properties have a small temperature dependence (negligible for most purposes), because the population of rovibrational states varies with temperature and each state has a different dipole moment and polarizability. Good theoretical surfaces now exist for the dependence of the electronic polarizability⁵² and dipole moment⁴²² on molecular geometry; these can be used to calculate the expectation value for each rovibrational state and then combined with Boltzmann weighting to calculate the temperature dependence of the property not only for H₂O but also D₂O, HDO, etc.³⁸

This low-density boundary condition for the dielectric constant is also complicated by the quantization of rotation, which results in a small correction factor for the dipolar contribution.^{423,424} Recent work by Garberoglio *et al.*³⁸ for the first time computed this effect rigorously for water, finding that it reduces the first dielectric virial coefficient by roughly 3% at room temperature.

Above the low-density limit, the dielectric constant of a gas (or its refractive index, which is closely related) can be described with a virial expansion, in which the second dielectric (or refractivity) virial coefficient is determined by interactions between two molecules, the third coefficient involves three molecules, etc. While the second dielectric virial coefficient has been calculated accurately from first principles for noble gases,⁴²⁵ the complex manner in which multipolar molecules affect each other's charge distribution makes such calculations difficult for molecules like water. The temperature-dependent second dielectric virial coefficient has been calculated for the fixed-charge TIP4P water model by Yang *et al.*⁴²⁶ and for two models with distributed polarizable multipoles by Stone *et al.*⁴²⁷ While both studies yielded positive coefficients, their magnitudes and temperature dependences are quite different. These were classical calculations, but quantum effects would probably be significant as is the case for the density virial coefficients discussed in Sec. 11.2.3.

The second refractivity virial coefficient can be calculated with a similar approach, requiring the multidimensional surface of the difference between the electronic polarizability of the twobody system and the sum of the polarizabilities of the isolated molecules. To our knowledge, no such calculation has been performed for water. The magnitude of water's second refractivity virial coefficient is probably small, since no nonzero value can be discerned in the accurate vapor-phase refractivity measurements of Schödel *et al.*⁵⁰

While it is now commonplace to compute the dielectric constant of water from molecular simulation, the complexity of the interactions is such that simulation is not close to matching the accuracy of experiment. In the medium term, the only role for simulation in providing data for the dielectric constant of water is likely to be at experimentally inaccessible conditions. For example, AIMD has been used to estimate the dielectric constant of water at 1000 K and 2000 K at pressures of a few GPa, representing conditions in the Earth's mantle.⁴²⁸

11.3. Future of industrial calculations

For some industrial uses, and in some areas of research, a comprehensive equation of state such as IAPWS-95 (or its eventual replacement) will be too computationally slow to be useful. For a significant increase in speed, IAPWS already has the formulation for industrial use IAPWS-IF97 as mentioned in Sec. 5.3.

However, there are cases where even the simpler equations in IAPWS-IF97 are too slow, or where greater speed would be desirable to improve the level of detail attainable in modeling. Chief among these is computational fluid dynamics (CFD). For applications such as steam turbine analysis, simple models such as the ideal gas or cubic equations of state are inadequate to model the phenomena of interest and thermodynamic properties closely approximating the real values are needed.

This speedup can be accomplished by pre-generating a table of points (perhaps also including derivatives) and interpolating within the table during calculations. However, some interpolation schemes can result in loss of thermodynamic consistency between related calculations (for example, enthalpy as a function of temperature and pressure compared to temperature as a function of pressure and enthalpy). Furthermore, some properties change much faster in some regions of the phase diagram (such as near the critical point) than in other regions; this means that a simple grid may not be optimal.

Researchers working with IAPWS have developed two table interpolation approaches. The first was the Tabular Taylor Series Expansion (TTSE) of Miyagawa and Hill,^{429,430} which was adopted as an IAPWS Guideline in 2003.⁴³¹ The TTSE method uses a six-term Taylor series expansion around grid points in a plane of independent variables.

The second table interpolation approach, which by construction eliminates internal inconsistencies, is the Spline-Based Table Lookup (SBTL) developed by Kunick⁴³² and adopted as an IAPWS Guideline in 2015.⁴³³ The SBTL method has been applied in several simulation tools, for example in modeling the thermal and hydraulic behavior of nuclear power plants⁴³⁴ and in CFD modeling of steam turbines.⁴³⁵ A somewhat similar approach, using b-splines for fast interpolation, has been proposed by Brown.⁴³⁶

As mentioned in Sec. 5.3, the electric power industry needs a formulation that is not only fast, but that is stable for decades to be used in equipment performance and guarantee calculations. This need is currently met by the IAPWS-IF97 formulation; several paths could be envisioned for the future. It could be decided that IAPWS-IF97 is adequate for future needs, so that it would not be replaced even after a new formulation replaces IAPWS-95. Alternatively, a similar indus-

trial formulation, taking advantage of lessons learned from IAPWS-IF97 and perhaps with tighter constraints on internal consistency, could be fitted to the new reference formulation. Finally, a spline-based interpolation method such as SBTL, applied to a new reference formulation, could be specified as a new industrial standard. Since one requirement for this use is consistent results for all users, this would require exact specification of the grids to be used; perhaps IAPWS could pre-compute and distribute the necessary tables of spline coefficients.

Another possibility is that the next "scientific" standard (the replacement for IAPWS-95) could be specified as the industrial standard for the purpose of contracting and performance guarantees. For those limited purposes, the relatively slow speed of a comprehensive formulation should not be a problem. Then, for other more computationally demanding uses of water/steam properties (heatcycle optimization, CFD, etc.), users would be free to adopt an appropriate faster approximation, which could be tailored to the accuracy and speed requirements of the specific application.

11.4. Extension of range for seawater

While the standard formulation for thermodynamic properties of seawater described in Sec. 9.2 covers the range of conditions found in the Earth's oceans, it does not include all conditions encountered for industrial use of seawater such as thermal desalination or the use of seawater as a cooling fluid for power plants. While some formulations extending to other conditions have been developed,^{437–439} additional data have been reported in recent years that could provide a more complete foundation for extensions in temperature, pressure, and salinity.

New data that have become available include densities at high salinities extending to 468 K and 140 MPa,^{440,441} sound speeds extending to 368 K at atmospheric pressure over a range of salinities,⁴⁴² and sound speeds at temperatures up to 313 K extending up to 70 MPa in one study⁴⁴³ and up to 60 MPa in another.³³⁴ It should be possible to use these data, along with those used for the existing seawater formulation, to develop an equation of state that covers a wider, industrially relevant, range of conditions. The more abundant thermodynamic data for NaCl in H₂O might be used to guide such a formulation in regions where no data exist.

Additionally, there is evidence, both from oceanographic measurements^{444–446} and from work in metrology laboratories,^{447,448} that there may be a systematic bias on the order of 5 ppm in the density computed by TEOS-10 for salinities near that of typical ocean water. This would be barely significant compared to the uncertainty of the formulation.²⁴³ If this discrepancy is confirmed, it could be an area for future improvement.

Thermophysical properties of other natural waters, such as lakes, rivers, and subsurface brines, are of interest in various contexts. In the case of freshwater lakes and rivers, the properties can be taken as those of pure water for most practical purposes. Direct use of a seawater formulation to calculate the effect of impurities on the properties of other waters will introduce error, because their relative proportions of dissolved salts can differ significantly from those in seawater. For surface waters, relatively simple modifications to TEOS-10 have been presented that significantly

reduce this error.449

11.5. Humid air

An important water-containing mixture is humid air. Its properties are central to humidity metrology, heating and air conditioning, and atmospheric science. Most interest is for pressures near atmospheric, but there are some applications, such as compressed air energy storage,^{450,451} where higher pressures are relevant. While high-accuracy reference formulations exist for the thermodynamic properties of pure water (IAPWS-95) and for air,⁴⁵² the development of models for their mixture has thus far been relatively *ad hoc*.

In many contexts, the key quantity is the *saturation* condition, where a humid vapor is in equilibrium with liquid water or solid ice or an aqueous solution such as seawater. For example, this provides a baseline for the relative humidity, which expresses how close the water vapor concentration is to saturation. Thermodynamically, saturation is described by equating the fugacity of water in the vapor phase to that in the condensed phase at temperature T and pressure p:

$$x_{\rm w}\gamma_{\rm w}f_{\rm w}(T,p) = y_{\rm w}\phi_{\rm w}p. \tag{12}$$

In Eq. (12), x_w is the mole fraction of water in the condensed phase, which is unity for ice and close to unity for liquid water unless the pressure is quite high. γ_w is the activity coefficient of water in the condensed phase, which can be assumed to be unity if $x_w \approx 1$. $f_w(T, p)$ is the fugacity of pure water at the temperature and pressure of the equilibrium. y_w is the vapor-phase mole fraction of water, and ϕ_w is the fugacity coefficient of water in the gas phase, which is unity for an ideal gas but is typically slightly less in real atmospheric systems.

Solution of Eq. (12) is iterative, because the fugacity coefficients depend on T, p, and composition and the liquid mole fraction x_w depends on the vapor fugacities. This has led people to develop approximations to the full phase-equilibrium solution, but the level of error introduced by the approximations is often poorly understood. With modern computers, there is no excuse not to solve the full problem, as least as a baseline against which approximations can be judged.

On the left side of Eq. (12), x_w can be computed from Henry's law if the fugacity of air is known in the vapor phase. If the calculations model air as a mixture, Henry's constants from the IAPWS Guideline can be used.^{453,454} Often it is more convenient to model dry air as a pseudo-pure component, in which case the Henry's constants for individual air components can be weighted to produce an effective value for air. The fugacity of pure water $f_w(T, p)$ can be computed rigorously from a thermodynamic potential such as IAPWS-95 (or, if the condensed phase is ice, the IAPWS formulation discussed in Sec. 8.1), but simplifications are possible. $f_w(T, p)$ can be obtained by starting with the well-known vapor pressure of pure water or ice, making a small correction for its fugacity coefficient at saturation, and applying a Poynting correction for the effect of pressure on the fugacity. Rigorous calculation of the Poynting correction requires the thermodynamic potential, but simple approximations exist whose accuracy for water and ice has been studied.⁴⁵⁵

The key quantity on the right side of Eq. (12) is the fugacity coefficient. Calculating fugacity coefficients requires a mixture model, but since most applications of humid air are near atmospheric pressure, it is usually sufficient to represent the gas-phase properties by the virial expansion (see Sec. 11.2.3), which for standard atmospheric pressure can usually be truncated after the second virial coefficient. The most important quantity is B_{aw} , the cross second virial coefficient between air and water. While there are some experimental data for B_{aw} , the best values now come from molecular calculations.⁴⁵⁶ At higher pressures, third virial coefficients become important (the airair-water and air-water-water interactions), but there is little information about these quantities. Thermodynamics of humid air at the level of the third virial coefficient has been described by Herrmann *et al.*⁴⁵⁷ and Feistel *et al.*⁴⁵⁸

It is also possible to develop a mixture equation of state that combines IAPWS-95 and the reference equation of state for air. Mixture virial coefficients like B_{aw} can provide a boundary condition for such models. This approach was taken in the humid-air portion of the seawater standard TEOS-10.^{80,459} Calculations for water–air mixtures were also demonstrated by Bell *et al.*⁴⁶⁰ A challenge in equation-of-state calculations of water with nonpolar gases is that it is difficult to find mixing schemes that simultaneously represent the very different environments of the vapor and liquid phases. The formulation in TEOS-10 avoids this problem by ignoring the solubility of air in liquid water, which is a reasonable approximation for many purposes.

These thermodynamic models can also be used to calculate properties in single-phase systems. An important example is the density of moist air, which is needed for buoyancy corrections in mass metrology. The CIPM has adopted a standard formulation, based on a virial expansion, for the density of moist air near normal atmospheric conditions.⁴⁶¹ Several formulations for humid air density, including some valid over a wider range of conditions than the CIPM formula, were reviewed and compared by Hellmuth *et al.*⁴⁶²

The transport properties of moist air are also of interest. At typical atmospheric conditions, these properties are not much different from those of dry air because the mole fraction of water is small, but the effect of moisture is significant at higher temperatures and/or pressures where the water content can be higher. Mixture models for calculating the viscosity and thermal conductivity of humid air have been presented by Herrmann *et al.*⁴⁶³

There are a variety of future needs for the thermodynamics of humid air, but perhaps the most important are in the area of definition and standardization. There are inconsistencies among definitions of relative humidity, and there are parts of the phase diagram where some definitions are not applicable. Lovell-Smith *et al.*⁴⁶⁴ discuss these issues, with particular attention to climate and atmospheric studies.

It has been proposed that the "relative fugacity" (or, equivalently, activity) may be a more useful physical quantity than the relative humidity.^{465,466} A good case can be made for a fugacity-based definition when the properties of interest are related to phase equilibria, for which water fugacity

is the rigorous physical variable. Examples would include dew and frost points, evaporation, and supersaturation. On the other hand, for applications where the relevant quantity is the actual number or density of water molecules (such as absorption of radiation in the atmosphere), the relative fugacity measure would take one further away from the physics of interest. Thus, there may be no single measure that is best in all circumstances, but some standardization of the current array of inconsistent definitions is needed in any event.

On the data side, it would be helpful to have accurate third virial coefficients characterizing water–air interactions. Computational chemistry has reached the point where it should be feasible to calculate three-body interactions such as $N_2-N_2-H_2O$ with enough accuracy to improve on current knowledge. The development of better mixture equation-of-state models, capable of describing both phases of gas-water systems, is also needed. Finally, calculations for humid gases other than air are needed for some applications. Most of the tools for water–air calculations would still be applicable; one could for example substitute for B_{aw} first-principles cross second virial coefficients for water with hydrogen⁴⁶⁷ or with carbon dioxide.⁴⁶⁸

11.6. More rigorous uncertainty analysis

Statements of estimated uncertainty are part of IAPWS Releases and similar documents. The estimates are based on observed scatter of experimental data, on differences between data sets by various laboratories, and when available on information about experimental uncertainties. Typically, extremely accurate experimental data exist for the liquid close to atmospheric pressure, both because of their practical importance and because accurate experimental techniques are available. At high pressures, or high or low temperatures, fewer data exist and the experimental uncertainties are often orders of magnitude larger. Because the coverage of data is highly non-uniform over the broad ranges of property formulations, diagrams are often provided showing different uncertainties in various subdomains of the pressure–temperature (possibly also salinity) space. In newer IAPWS documents, the uncertainties are stated to be expanded uncertainties with coverage factor k = 2. In earlier work, the statistical meaning of the uncertainties is not provided; however, the estimates are conservative and they can be understood as a proxy for k = 2 expanded uncertainties.

In applications where the uncertainty of values computed from thermophysical property formulations is critical, one might be interested not only in uncertainties of a computed quantity at a given state, but also a covariance of the property computed for two states. The covariance plays a role, e.g., when the uncertainty of a difference or a ratio of a quantity at different states is to be evaluated. Another interesting question arises for thermodynamic formulations, which allow computation of quantities that were not determined experimentally but follow from identities that relate different derivatives of the thermodynamic potential, and therefore different properties. As a simple example, the Clapeyron equation can be used to extrapolate the saturation vapor pressure down to temperatures where the vapor pressure is too low to be measured accurately. The uncertainty is then related to the uncertainties of saturation densities and heat capacities used in the computation. These interrelationships can in general provide uncertainty information on properties that were not measured, but taking advantage of them is not trivial.

Although the concepts of uncertainty evaluation are known,^{469,470} their application to thermophysical property formulations has not yet been fully developed. The uncertainties of values computed from these formulations can be thought of as arising from two sources. The first is the uncertainty of the underlying experimental data, which projects into the uncertainty of parameters of equations constituting the thermophysical property formulations. The uncertainty of parameters then projects into the uncertainty of values computed with these equations. The second source is the error of the model. While models are constructed such that known laws (such as the ideal gas equation) are satisfied in limiting cases, they are predominantly empirical equations fitted to experimental data (and sometimes to quantum mechanical results). Infinitely many variants with different mathematical structures could be constructed that fit the available data. For example, scattered data might be fitted by a parabola or by an exponential. Although both fits appear satisfactory, the computed values will be somewhat different and extrapolations will diverge. Evaluating this kind of uncertainty might require constructing a representative ensemble of different surfaces that fit the data at a similar level of likelihood. The error of the model could then be quantified in a quasi-statistical approach based on observed scatter of computed values for the ensemble of models. The error of the model is especially critical in regions poorly supported by data, in cases where derivatives need to be computed, and for extrapolation. Significant progress has been achieved in reducing the number of terms and improving the extrapolation behavior.¹⁷⁷ Alternative approaches that at least partly eliminate the error of model imperfection can be based on piecewise polynomials or non-parametric regression.²⁶⁹ However, such approaches require a very dense data coverage and they do not appear suitable to formulations covering broad ranges of temperatures and pressures, where the supporting data are highly heterogeneous.

We focus now on the uncertainties of the underlying data and on the way they affect values computed from a model based on these data. This problem has received substantial attention in IAPWS. A discussion was initiated by Feistel,⁴⁷¹ who rigorously applied the analysis of error propagation to complex regression models such as IAPWS-95. However, the experimental errors were assumed to be random and mutually uncorrelated, which led to unrealistically small uncertainties of computed values. Later it was recognized that systematic errors cause covariances in the experimental data.⁴⁷² By introducing estimated systematic errors in the data and constructing a corresponding covariance matrix, confidence bands for the saturation vapor pressure of water were constructed that resembled the published empirical bands. Feistel *et al.*⁴⁷³ applied generalized regression to IAPWS-95 and studied the effect of correlation coefficients of data. Lovell-Smith *et al.*⁴⁷⁴ showed that high correlation coefficients (up to 0.9) need to be assumed in order for the predicted uncertainty for isobaric heat capacities computed from IAPWS-95 to be comparable with expert estimates.

The quoted studies show that the uncertainties and covariances of quantities computed from

thermophysical property formulations can, in principle, be estimated using a mathematical apparatus of generalized regression. In practice, application of this approach is hindered primarily by the absence of knowledge of the covariance matrix of experimental data (and among different data sets). Although modern publications of data contain information on uncertainties, almost no sources provide a covariance matrix; estimating this covariance in experimental work is difficult at best. We note that only providing an estimate of type A and type B uncertainty is not sufficient to reconstruct the covariance matrix. For multivariate problems (with temperature, density, composition as independent variables), the systematic errors might have the nature of a systematic offset, a systematic relative error, or something else. Even if such information is provided, it should be remembered that uncertainties provided in original publications are based on known sources of error ("known unknowns"). In addition, unidentified sources of errors may exist ("unknown unknowns"). Consequently, it often happens that error bars of different data sets do not overlap, and it remains to the data evaluator to cope with such inconsistencies.

There have been some attempts to develop methods for determining the uncertainty of derived quantities from a reference equation of state. If one makes the simplifying assumption of ignoring uncertainty due to the structure of the formulation, in principle this is straightforward mathematics if the uncertainties of the input data are known along with the correlations among the data, so that a covariance matrix of the formulation parameters can be developed along with the uncertainties of the parameters. However, the first such attempt,⁴⁷³ applied to the IAPWS-95 formulation with some additional simplifying assumptions, produced uncertainty estimates that were unrealistically small for some quantities (such as the third virial coefficient at low temperatures where no reliable vapor data existed at the time IAPWS-95 was developed). Another attempt,⁴⁷⁵ applied to the reference equation of state of propane and also with some simplifying assumptions due to lack of complete data, produced uncertainty estimates that were much too large for some quantities (such as the vapor pressure in the range where it is well known). The reasons for these poor outcomes are not understood as far as we are aware.

Comprehensive evaluation of the uncertainty of thermophysical property formulations thus remains a challenging task. Progress will depend on a better accounting of correlations among the input data for the formulations, on proper accounting of the covariance of model parameters, and on the development of a good way to estimate the structural uncertainty due to the choice of model. These advances will require cooperation between experts in statistics and data fitting and experts in thermophysical properties.

11.7. Going to extremes

IAPWS formulations are normally limited to the range of temperature and pressure where experimental data exist, although they are constructed so that the predicted properties are reasonable for extrapolations that are not too large. Extremely high temperatures and/or pressures, beyond the range of experimental data, may be encountered in rocketry and in shock waves, and also in modeling the interior of Earth and other planets. In addition, the behavior at extreme conditions may be scientifically interesting; an example is the many phases of ice that can exist at high pressure (see Sec. 8).

At temperatures above roughly 1500 K (above the range of validity of existing IAPWS formulations), the dissociation of water begins to become significant. This pressure-dependent effect can be estimated if the thermochemistry of the various species is known from a source such as the JANAF tables.³¹⁴ Calculations of the dissociation have been performed by Kessel'man *et al.*⁴⁷⁶ The mole fraction of undissociated water at 0.1 MPa pressure is 0.9895 at 2000 K, 0.0303 at 4000 K, and essentially zero at 6000 K. High pressure suppresses dissociation, so the mole fraction of H₂O at 100 MPa is 0.9991 at 2000 K, 0.7957 at 4000 K, and 0.1947 at 6000 K. Initially, the dominant dissociation products are H₂ and O₂, but at higher temperatures (especially at low pressures) the radicals OH, H, and O become dominant.

The effect of dissociation on thermodynamic properties was examined by Kessel'man *et al.*,⁴⁷⁶ and tabulations of properties with incorporation of dissociation were presented by Vargaftik *et al.*⁴⁷⁷ For some properties, such as density, dissociation does not have a major effect. Because the sound speed is largely determined by the molar mass, it is increased by dissociation into lighter species. The heat capacity is significantly increased by dissociation, because some of the energy that would otherwise go into raising the temperature is taken up by the energy of the dissociation reaction. The effect of dissociation on the viscosity and thermal conductivity has also been examined.^{477,478} The effect on the viscosity is modest, resulting from the larger number of lighter species. However, there is a large increase in the thermal conductivity at conditions where dissociation is large; this is due to the additional path for energy transfer provided by the dissociation reactions.⁴⁷⁹

In planetary science, particularly in modeling the interiors of giant planets, pressures of interest can be on the order of 1000 GPa, with temperatures of thousands of kelvins and densities an order of magnitude greater than that of normal liquid water. A rich variety of behavior is believed to exist, including a partially dissociated plasma-like state and a superionic state where the oxygen atoms are in a crystalline lattice but the hydrogen atoms are mobile like a liquid.

Water and ice can be studied up to tens of GPa using diamond-anvil cells, but for the most part these studies are not conducive to accurate thermophysical property measurements. There have been a few experimental studies of properties, mainly the sound speed,^{480–486} but also including thermal diffusion¹⁶⁶ and viscosity.^{487,488}

At even higher pressures, especially at the temperatures relevant to planetary interiors, molecular simulation is the only available tool. Because molecules distort and dissociate at these conditions, the typical intermolecular potentials used to study room-temperature water are not applicable; instead, the AIMD method discussed in Sec. 11.2.2 is used. While these simulations are computationally intensive and imperfect in their treatment of forces, at least semiquantitative accuracy can be attained. This active area of research is beyond the scope of this review, but we cite a few such studies of thermodynamic^{489–491} and transport^{492–494} properties.

12. Conclusions

Our knowledge of the thermophysical properties of water and steam has come a long way since the first coordinated "steam tables" efforts a century ago. We now have a consistent formulation for the thermodynamic properties of water and steam up to 1000 °C and 1000 MPa that reproduces most experimental data within their uncertainties. We also have formulations for the viscosity and thermal conductivity that cover most of that range, obeying necessary boundary conditions for the dilute gas and exhibiting the correct divergence at the critical point. Reference formulations have been developed for a variety of other properties, including properties of heavy water and of seawater.

While the progress in the last 100 years is impressive, the ongoing pursuit of further improvement is a worthwhile task. Several current formulations have weaknesses in their mathematical form and/or their extrapolation behavior. New experimental data (and, increasingly, data from molecular theory) continue to appear that reduce the uncertainty of our knowledge of properties, or that extend knowledge into regions where no data previously existed. The existing formulations are good enough for many purposes, but the importance of water as a reference fluid for scientific and industrial applications is such that additional reduction in uncertainty or expansion of the range of validity is always welcome. New technologies (such as advanced combustion systems in power generation) and new areas of scientific study (such as study of planetary interiors) may require properties at new conditions.

As mentioned in Sec. 2, much of the work on defining reference data for thermophysical properties of water is performed under the auspices of the International Association for the Properties of Water and Steam. The work of IAPWS is open to all interested parties; more information is available at www.iapws.org. The organization would be happy to have more scientists and engineers join the continuing quest for better reference data for this essential substance.

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13. Author Declarations

13.1. Conflict of interest

The authors have no conflicts to disclose.

14. Data Availability

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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