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TEOS-10: A New International Oceanographic Standard for Seawater, Ice, Fluid Water, and Humid Air

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Abstract Very accurate empirical thermodynamic potential functions are available for fluid water, ice, seawater, and humid air covering wide ranges of temperature and pressure conditions, including those of the terrestrial hydrosphere and atmosphere. These potential functions are formulated as international standards endorsed by the International Association for the Properties of Water and Steam (IAPWS). A related seawater standard referred to as the International Thermodynamic Equation of Seawater 2010 (TEOS-10) was adopted in 2009 by UNESCO for oceanography. Here, the formulations available from TEOS-10 for the description of the vapor pressure of ice and for thermodynamic properties of humid air, in particular, the relative humidity, are reviewed. It is concluded that the IAPWS formulation for the sublimation pressure is superior in uncertainty and range of validity over other available correlation equations, and that relative fugacity is a physically reasonable generalization of relative humidity for the case of non-ideal gases or equilibria with moist substances.

Keywords Equation of state · Fugacity · Humid air · Ice · Relative humidity · Sublimation · Thermodynamics · Uncertainty · Vapor pressure

1 Introduction

More than a century ago, Josiah Willard Gibbs [1] discovered that "an equation giving internal energy in terms of entropy and specific volume, or more generally any finite equation between internal energy, entropy and specific volume, for a definite quantity of any fluid, may be considered as the fundamental thermodynamic equation of that fluid, as from it … may be derived all the thermodynamic properties of the fluid (so

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far as reversible processes are concerned).” With the increasing availability of faster computers, the previously rather theoretical option of constructing thermodynamic potentials, or synonymously, fundamental thermodynamic equations, turned soon into the most accurate and consistent practical method of representing measured thermodynamic properties of fluid and solid pure substances, or of mixtures or phase equilibria thereof. This approach is fundamental to the formulations released by the International Association for the Properties of Water and Steam (IAPWS). In the new International Thermodynamic Equation of Seawater 2010 (TEOS-10) which was adopted in 2009 by UNESCO-IOC[1] for oceanography, four empirical thermodynamic potentials replace a large variety of available correlation functions for properties of liquid water, water vapor, ice, seawater, and humid air [2–4]. The sea–ice–air (SIA) source-code library was developed to support the use of TEOS-10 and is freely available [5–7]. TEOS-10 offers significant improvements in accuracy, consistency, completeness, and range of validity over its predecessors. While the current humid-air formulation of TEOS-10 is well suited for applications in oceanography and other geosciences, certain properties may be improved in a subsequent version. For example, the density of humid air computed from TEOS-10 is not as accurate as the metrological CIPM-2007 equation [8].

The modular architecture of TEOS-10 and its supporting SIA library reflect three different layers, referred to as the Primary, the Secondary, and the Tertiary TEOS-10 Standard. The Primary Standard consists of four IAPWS documents and is guided by the axiomatic principles of consistency, independence, and completeness. Virtually unlimited sets of property equations for the geophysical substances and their mutual phase equilibria can be derived from the Primary Standard by rigorous thermodynamic relations and their numerical implementation, without additional empirical constants or correlation equations. Those derived functions form the Secondary Standard; they are no longer independent of each other. The set of derived quantities is easily and arbitrarily extendible to provide additional required properties without modification of the Primary Standard. Alternatively, the modular semi-order structure in combination with the mutual independence of the Primary Standard modules permits the separation of smaller, self-contained sub-libraries from TEOS-10 that are restricted to special tasks, such as properties of humid air, on which we will focus in this article. For application in restricted parameter ranges, or for high computation-speed requirements, additional simple correlation equations or look-up tables can be derived from data points compiled from the Secondary Standard. That layer with a reduced range of validity and/or reduced accuracy contains additional empirical constants and is regarded as the Tertiary Standard. For example, the Gibbs function for liquid water [9] and the Gibbs-SeaWater (GSW) library [10] are parts of the Tertiary Standard. All information contained in the secondary and tertiary layers is numerically extracted from the Primary TEOS-10 Standard.

In Sect. 2, the structure of TEOS-10 is briefly outlined. In Sect. 3, the equation used for the sublimation pressure is explained. Uncertainty estimates for the sublimation pressure equation used in TEOS-10 are compared with those of available experimental

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[1] IOC: Intergovernmental Oceanographic Commission, http://ioc-unesco.org.

data in Sect. 4. Section 5 provides the TEOS-10 equation of state for humid air and its range of validity. Section 6 briefly discusses different definitions of the relative humidity implemented in the SIA library.

2 TEOS-10: A Combination of Mutually Consistent Thermodynamic Potentials

TEOS-10, the International Thermodynamic Equation of Seawater 2010, as well as its sea–ice–air (SIA) library of properties consists of various modules that form a hierarchical structure and is organized in columns and levels (Fig. 1). Even though TEOS-10 was developed primarily for properties of seawater, other self-contained sub-libraries can also be extracted from it. In this article, we will focus on the SIA sub-library available for the vapor pressure of ice and for properties of humid air.

TEOS-10 was developed by the SCOR[2]/IAPSO[3] Working Group 127 (WG127) in cooperation with IAPWS and is described in a document published by IOC et al. [5] which is available online at www.teos-10.org. The four columns of the SIA library are two pure substances, fluid (liquid or gaseous) water, and hexagonal ice, as well as two additives in the form of the natural mixtures "sea salt" and "dry air" with fixed molar compositions [4,8,11].

At the SIA level 1, these four columns represent the *Primary TEOS-10 Standard* in the form of empirical thermodynamic potentials described in the documents IAPWS-95 for fluid water [12,13], IAPWS-06 for ice Ih [14,15], IAPWS-10 for humid air [4,16], and IAPWS-08 for seawater [17–19]. Note that regarding the shorthand notation of those four documents, only "IAPWS-95" is an official term of IAPWS. Endorsed IAPWS documents are available online at www.iapws.org. Mutual consistency requirements for the four potential functions are discussed by Feistel et al. [3,4], in particular, the reference state conditions that are defined for a unique specification of the absolute entropies and energies of water, sea salt, and dry air which cannot be determined by means of thermodynamic measurements.

All empirical constants of the SIA library are contained in the modules at level 1. Thus, exclusively the four thermodynamic potentials represent in a very compact and highly accurate form the entire extensive experimental evidence on which TEOS-10 is based. The Primary TEOS-10 Standard obeys the axiomatic principles of *consistency*, *independence*, and *completeness*. Consistency implies that it is impossible to derive from the Primary Standard two different results for the same property. Independence means that it is impossible to derive the same property from two different parts of the Primary Standard. Finally, completeness expresses the fact that all equilibrium properties of the four substances, their composites, and mutual phase transitions can be computed from the thermodynamic potentials or combinations thereof by purely mathematical operations.

The Primary Standard is defined in terms of mathematical functions described in the related IAPWS documents [13,15,16,19]. For convenience of their use, the formulations were implemented by WG127 as open source code in Fortran 90 and Visual

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[2] SCOR: Scientific Committee on Oceanic Research, http://www.scor-int.org.

[3] IAPSO: International Association for the Physical Sciences of the Oceans, http://iapso.sweweb.net.

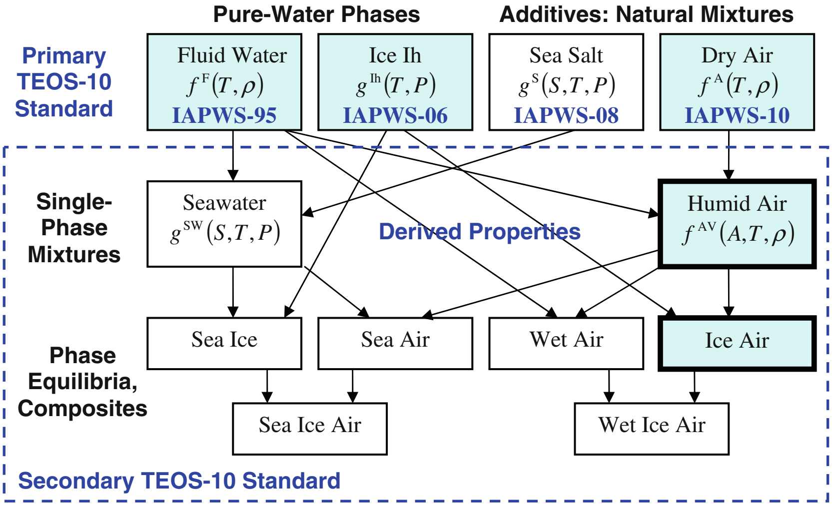

Fig. 1 Selected components of the TEOS-10 sea–ice–air (SIA) library. As a part of the Secondary Standard, humid air and ice air represent a self-contained subset of the properties derived from three of the Primary TEOS-10 Standards: for fluid water (IAPWS-95), for ice (IAPWS-06), and for air (IAPWS-10). The sub-library for humid air and its equilibria with ice is emphasized (adapted from [20])

Basic 6. Version 1.0 of the SIA library is freely available as the digital supplement of Wright et al. [20], and the implemented mathematical relations are described by Feistel et al. [21]. The updated version 1.1 is available from Wright et al. [7], and the corresponding formulas are given by Feistel et al. [6]. The two versions differ only by the molar mass of dry air used to convert the molar formulation of Lemmon et al. [22] to a mass-based equation. Version 1.0 is consistent with the description of the formulation given by Feistel et al. [4], using the molar mass of air published by Lemmon et al. [22], $M_{\mathrm{A}} = 28.9586\ \mathrm{g \cdot mol^{-1}}$. Version 1.1 is consistent with the description of the formulation given by IAPWS [16], using the molar mass of air published by Picard et al. [8], $M_{\mathrm{A}} = 28.96546\ \mathrm{g \cdot mol^{-1}}$. Various alternative formulations for humid air were recently reviewed by Herrmann et al. [23].

Level 2 of the SIA library provides various properties that can be computed from direct evaluation of the functions of level 1. In particular, these functions are expressed in terms of the independent variables of the thermodynamic potentials. These variables are temperature T and density ρ in the case of fluid water, temperature, and pressure P in the case of ice, and temperature, density, and dry-air mass fraction A in the case of humid air. Except for numerical roundoff, the functions of level 2 are exactly consistent with those of level 1, but level 2 functions no longer adhere to the principles of independence and completeness.

Level 3 of the SIA library uses numerical iteration procedures to solve implicit equations, thus sacrificing exact consistency with level 1. For instance, properties of water or of humid air in terms of temperature and pressure are made available at this level, but also properties at a given entropy for an easy application to adiabatic processes.

While the previous levels covered single-phase properties, level 4 of the SIA library provides phase-equilibrium properties such as the sublimation pressure of ice or the relative humidity of air. As a rule, these properties are determined by numerically solving implicit systems of equations.

3 Sublimation Pressure of Ice

Feistel and Wagner [24] published the first Gibbs function for ice that covered the entire region of existence of hexagonal ice I and that was significantly more accurate than its less comprehensive predecessors [25–27]. For example, in conjunction with IAPWS-95 the 2005 Gibbs function predicted the ice point of air-free water to an estimated uncertainty of only 2 µK, provided that the triple-point temperature is exactly 273.16 K. Version 2 of this Gibbs function [14] was improved by additional data, in particular, the CODATA entropy of water [28]. A minor correction applied to the conversion of obsolete units displaced the calculated ice point by 1 µK to the recent value of 273.152 519(2) K. The remarkably small uncertainty is inferred from ice density measurements of Ginnings and Corruccini [29]. Another minor correction was applied in the revised formulation of IAPWS [15] that resulted from a tiny mismatch of the triple-point pressure used for the ice formulation in comparison to the numerical value computed from IAPWS-95, as described by Feistel et al. [3].

The first IAPWS document on the sublimation pressure, i.e., the vapor pressure of ice, was based on the correlation of vapor-pressure data by Wagner et al. [30]. After the Gibbs function for ice [14] was endorsed by IAPWS, the sublimation pressure of ice could be computed from the chemical potentials of ice and of vapor. The estimated uncertainty of this derived property is significantly smaller than those of vapor-pressure measurements at low temperatures; therefore, the revised document [31] provides a correlation with respect to computed data rather than measurements of the sublimation pressure. As well, the sublimation-pressure equation could be extended below 130 K [32], which is the lower bound for the validity of IAPWS-95. Water vapor cannot reasonably be expected to exist below temperatures of about 50 K [32]. Another revision of the IAPWS document on the sublimation pressure is in the final stage of the formal adoption procedure and is expected to be released in September 2011 [33]. It will provide a more accurate estimate of the uncertainty; in particular, in the vicinity of the triple point the uncertainty is significantly less than previously estimated by Feistel and Wagner [14,32] from the measurements of Jancso et al. [34]; see the following section.

In TEOS-10, the sublimation equilibrium is determined from solving numerically the condition of equal chemical potentials of vapor and ice, in the form,

$$g^{\mathrm{Ih}} = f^{\mathrm{F}} + \rho f^{\mathrm{F}}_{\rho}. \tag{1}$$

The vapor pressure of ice at a given temperature can be computed from Eq. 1 by means of the function `ice_vap_sublimationpressure_si` implemented in the SIA library [20], including the extension down to 50 K [4,21]. Alternatively, if the pressure is given, the sublimation temperature is available from the function call ice_vap_sublimationtemp_si.

4 Uncertainty of Sublimation Pressure

Information on the uncertainty of selected properties computed from the Primary Standard of TEOS-10 is available from the related IAPWS documents. For future implementations of the SIA library, it is intended to provide an uncertainty estimate along with any computed property value. To date, the theoretical and practical methods available to satisfy this metrological requirement are immature yet and under development.

The triple-point pressure calculated from TEOS-10, $P_\mathrm{t} = 611.654\,771$ Pa, is well within the uncertainty of the measurement of Guildner et al. [35], $P_\mathrm{t} = 611.657(10)$ Pa. The vapor pressure of ice at lower temperatures, and the uncertainties of experimental data and of correlation equations derived thereof [36–40], were recently reviewed by Lovell-Smith.[4] Uncertainties of vapor-pressure measurements are significantly larger than those of the theoretical prediction, Eqs. 1 and 2, available from TEOS-10 [14,31–33] which is consistent with extended sets of other thermodynamic properties available for vapor and ice. Between the triple-point temperature and 150 K, the equations of Sonntag [36] and of Wagner et al. [30] agree with TEOS-10 within its uncertainty, Fig. 2.

The solution of Eq. 1 is mathematically equivalent to the Clausius–Clapeyron formula,

$$P^{\mathrm{subl}}(T) = P_\mathrm{t} + \int_{T_\mathrm{t}}^{T} \frac{\Delta s}{\Delta v} \mathrm{d}T', \tag{2}$$

where P^{subl} is the vapor pressure of ice, P_t and T_t are the triple-point pressure and temperature, respectively, Δs is the sublimation entropy, and Δv is the difference between the specific volumes of the two phases. Uncertainties of Δs and Δv can be estimated from determinations of the entropies of ice [41] and water vapor [28], of the sublimation enthalpy, of the heat capacities of vapor and ice, and of the density of ice and the second virial coefficient of water [42]. The uncertainties of the ice density and of the virial coefficient are very small when compared to the ideal-gas volume of vapor. Except for some vicinity of the triple point, the dominating contribution to the uncertainty of the integral (Eq. 2) results from the sublimation entropy (or sublimation enthalpy). The uncertainty of the sublimation-pressure values computed from TEOS-10 is typically one order of magnitude less than the scatter of vapor-pressure measurements, Fig. 2. It is obvious that correlation equations derived from those measurements are expected to be less accurate than predictions derived indirectly from other measureable thermodynamic properties. New optical measurements of the vapor

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[4] J. Lovell-Smith, *Proposed programme for addressing issues concerning the humidity reference functions*, BIPM CCT-WG6, Discussion paper, June 2010.

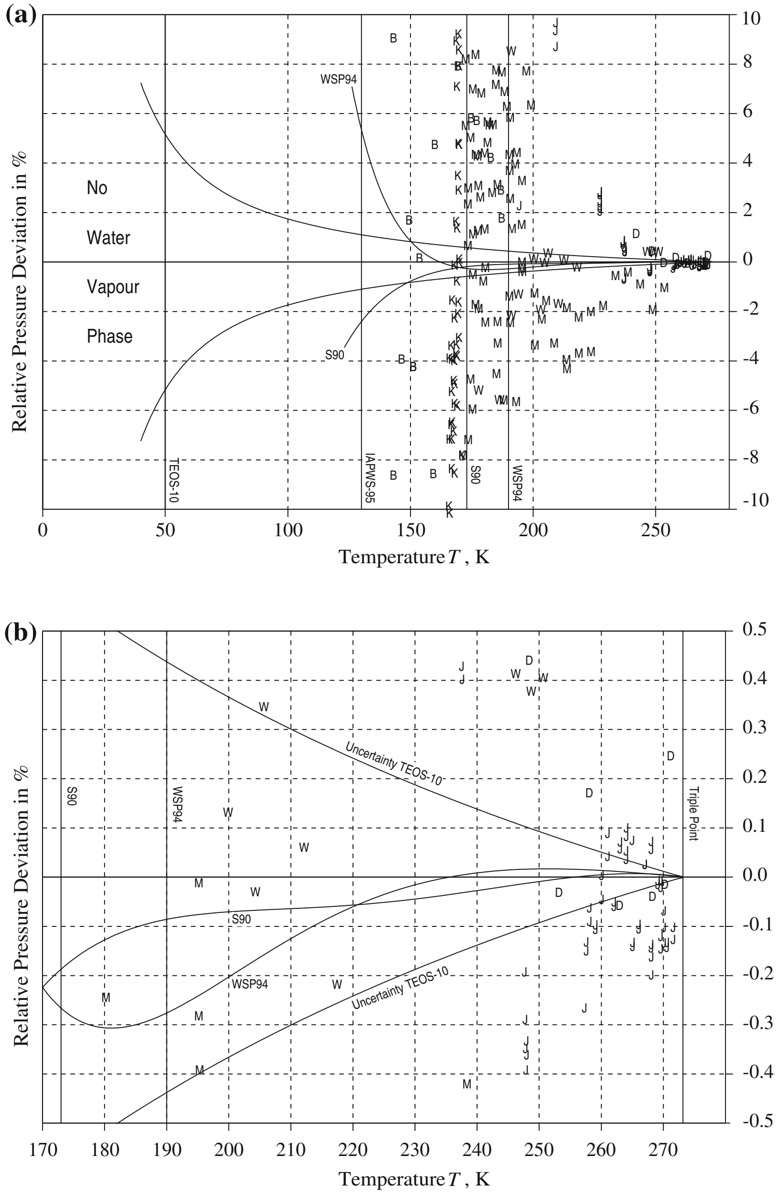

Fig. 2 Comparison between experimental data for the sublimation pressure with the TEOS-10 prediction: panel (a) full range of validity, panel (b) vicinity of the triple point, magnified. The "trumpet"-shaped curves describe the ($k = 2$) uncertainty estimate $U(P^{\text{subl}})$ of the values calculated from TEOS-10 [33,42]. This equation is valid down to 130 K using IAPWS-95, indicated by a *vertical line* and, using the TEOS-10 extension given by Feistel et al. [4], down to 50 K, indicated by another *vertical line* in panel (a). Below 50 K, water vapor cannot reasonably be assumed to exist [32]. "WSP94" indicates the correlation equation of Wagner et al. [30] which is valid above 190 K, as indicated by a *vertical line*, and "S90" the equation of Sonntag [36], valid above 173 K, as indicated by a *vertical line*. Experimental data points are *B* Bryson et al. [65], *D* Douslin and Osborn [66], *J* Jancso et al. [34], *K* Mauersberger and Krankowsky [39], *M* Marti and Mauersberger [38], and *W* Weber [67]

pressure are expected to possess a reduced uncertainty [43]. The author is not aware of any existing vapor-pressure measurements at temperatures below 130 K which correspond to sublimation pressures <10 nPa [32] and to a molar volume of vapor that exceeds 100 $\mathrm{km}^3 \cdot \mathrm{mol}^{-1}$. At low temperatures, the vapor pressure of metastable ice phases such as ice Ic or ice Ias may deviate significantly from that of ice Ih considered here [44].

An improved uncertainty estimate for the sublimation pressure, in particular, for the vicinity of the triple point, is intended to be endorsed by IAPWS [33], as shown in Fig. 2. The derivation of uncertainties for quantities computed from combinations of thermodynamic potentials such as TEOS-10 is not a trivial exercise and usually requires significant efforts of experienced humans [14,32,42].

Better suitable for automatic processing, a more general and more systematic approach has recently been suggested [45]. It takes into account the covariance between the regression coefficients [46] which is particularly important to prevent substantial overestimates when some hundred regression coefficients may be involved. For the sublimation pressure, the general equation for the uncertainty in the new formalism reads

$$u_\mathrm{c}(P^\mathrm{subl}(T))^2 = \frac{1}{(\Delta v)^2}\left(\frac{\partial g^\mathrm{Ih}}{\partial \mathbf{c}} - \frac{\partial f^\mathrm{F}}{\partial \mathbf{c}}\right)\mathbf{C}\left(\frac{\partial g^\mathrm{Ih}}{\partial \mathbf{c}} - \frac{\partial f^\mathrm{F}}{\partial \mathbf{c}}\right). \tag{3}$$

Here, $\mathbf{c}$ is the joint vector of adjusted coefficients of the thermodynamic potentials for ice, g^Ih, and fluid water, f^F, and $\mathbf{C}$ is the covariance matrix of those coefficients. All terms except for $\mathbf{C}$ depend on the temperature at which the sublimation pressure is evaluated. In contrast, $\mathbf{C}$ consists of constant numbers computed from the measurements from which g^Ih and f^F were derived. Rigorous expressions similar to Eq. 3 can be obtained for all the properties available from TEOS-10, based on the same covariance matrix. This method may allow in the future an automatic and systematic calculation of uncertainties for arbitrary quantities evaluated from the SIA library.

5 Humid-Air Formulation

The empirical Helmholtz function for humid air, f^AV, adopted in 2010 by IAPWS [16] is a combination of the IAPWS-95 Helmholtz function for water vapor, f^F, the Helmholtz function for dry air, f^A, of Lemmon et al. [22] converted from a molar to a mass basis, the molar second cross-virial coefficient $B_\mathrm{AW}(T)$ of Harvey and Huang [47], and the molar third cross-virial coefficients $C_\mathrm{AAW}(T)$ and $C_\mathrm{AWW}(T)$ of Hyland and Wexler [48]:

$$\begin{aligned} f^\mathrm{AV}(A,T,\rho) = {} & (1-A)f^\mathrm{F}(T,(1-A)\rho) + Af^\mathrm{A}(T,A\rho) \\ & + \frac{2A(1-A)\rho RT}{M^\mathrm{A}M^\mathrm{W}}\left\{B_\mathrm{AW}(T) + \frac{3}{4}\rho\left[\frac{A}{M^\mathrm{A}}C_\mathrm{AAW}(T)\right.\right. \\ & \left.\left. + \frac{(1-A)}{M^\mathrm{W}}C_\mathrm{AWW}(T)\right]\right\}. \end{aligned} \tag{4}$$

Here, R is the molar gas constant, M^{A} and M^{W} are the molar masses of dry air and water, respectively, ρ is the mass density of humid air, and A is the mass fraction of dry air in humid air, which is related to the specific humidity, $q = (1 - A)$, and to the mixing ratio, $r = (1 - A)/A$. Similar to the salinity of seawater, TEOS-10 uses A rather than q to describe the concentration of the natural mixture "air" added to fluid water. The reference state conditions for the dry-air part of Eq. 4 are specified in TEOS-10 more conveniently for geophysical applications than the conditions applied originally by Lemmon et al. [22], as discussed by Feistel et al. [4].

The range of validity of Eq. 4 is $193\ K \leq T \leq 473$ K and $0 < P \leq 5$ MPa. The air fraction A can take any value between 0 and 1 provided that the partial pressure of water vapor does not exceed its saturation value, i.e., $0 < A < 1$ and $A^{\mathrm{sat}}(T, P) \leq A$, as shown in Fig. 3. If the third cross-virial coefficients are negligible for the intended application, the valid temperature range is significantly larger [4,20,21]. The relevance of those third virial coefficients can be inferred from Fig. 4; at densities higher than $100\ \mathrm{kg} \cdot \mathrm{m}^{-3}$, they cut the deviation in half from the experimental data.

At the saturation point of humid air, the air fraction $A = A^{\mathrm{sat}}$, the condensation temperature T, and the total pressure P obey the equilibrium condition of equal chemical potentials of liquid water, g^{liq}, and of water vapor in humid air, μ_{W},

$$\mu_{\mathrm{W}}\left(A^{\mathrm{sat}}, T, P\right) = g^{\mathrm{liq}}(T, P), \tag{5}$$

or, below the freezing temperature, the related equilibrium condition between humid air and ice,

$$\mu_{\mathrm{W}}(A^{\mathrm{sat}}, T, P) = g^{\mathrm{Ih}}(T, P). \tag{6}$$

Here, g^{liq} is the specific Gibbs energy of liquid water, available from IAPWS-95, and g^{Ih} is the specific Gibbs energy of ice Ih, available from the IAPWS-06. The chemical potential of water in humid air, μ_{W}, is calculated from Eq. 4 in the form,

$$\mu_{\mathrm{W}} = f^{\mathrm{AV}} + \rho f^{\mathrm{AV}}_{\rho} - A f^{\mathrm{AV}}_{\mathrm{A}}, \tag{7}$$

where the subscripts of f^{AV} indicate partial derivatives. The solution $A^{\mathrm{sat}}(T, P)$ of Eq. 5 or 6 is required for the computation of the relative humidity, as described in the next section.

6 Relative Humidity

In the SIA library of TEOS-10, three different measures for the relative humidity of air are implemented. According to Jacobson [49], the World Meteorological Organisation (WMO) defines the relative humidity as

$$RH_{\mathrm{WMO}} = \frac{r}{r^{\mathrm{sat}}} = \frac{(1/A) - 1}{\left(1/A^{\mathrm{sat}}\right) - 1}, \tag{8}$$

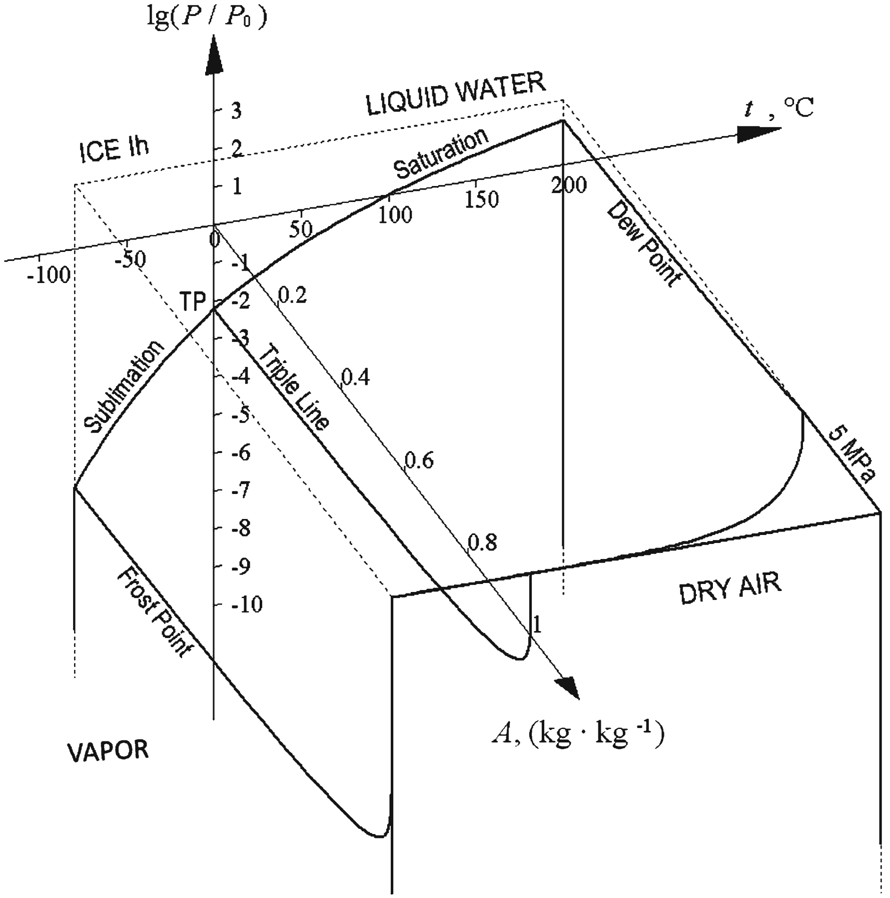

Fig. 3 Validity range of the humid-air formulation [16], indicated by *bold lines* in the diagram. The temperature is restricted to the interval between −80 °C and +200 °C, the upper bound of pressure is 5 MPa. At a given T and P, the mass fraction of dry air in humid air, A, may take any value between 1 (dry air) and either 0 (pure water vapor) or saturation, $A^{\mathrm{sat}}(T, P)$, which is given by the condition (Eq. 6) with respect to ice ("sublimation", "frost point") or to liquid water ("saturation", "dew point"), Eq. 5. "TP" is the common triple point of water; the "triple line" is its extension in the presence of air. $P_0 = 101\,325$ Pa is the standard atmospheric pressure

where $r = (1 - A)/A$ is the humidity ratio, and r^{sat} is its value at saturation. This definition is also given by other sources such as Gill [50]. Alternatively, internal discussion documents of BIPM CCT-WG6 (Lovell-Smith, priv. comm.) consider as a suitable option for the definition of relative humidity the commonly used formula

$$RH_{\mathrm{CCT}} = \frac{x_{\mathrm{V}}^{\mathrm{AV}}}{x_{\mathrm{V}}^{\mathrm{AV,sat}}}. \tag{9}$$

Here, $x_{\mathrm{V}}^{\mathrm{AV}}$ is the molar fraction of water vapor in humid air, and $x_{\mathrm{V}}^{\mathrm{AV,sat}}$ is the value at saturation. This definition is also recommended in a recent document of WMO [51], in

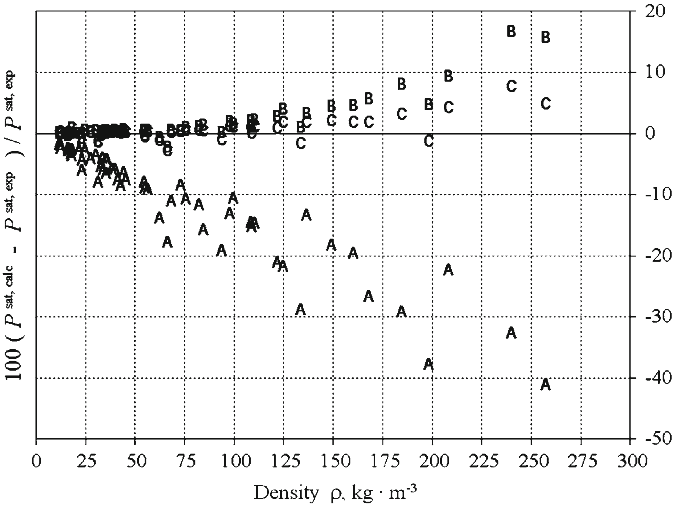

Fig. 4 Experimental data for the saturated vapor pressure of humid air at different pressures and temperatures of Pollitzer and Strebel [68], Webster [69], Hyland and Wexler [70], Hyland [71], and Wylie and Fisher [72], in comparison to values computed from Eq. 4. Symbol *A* Eq. 4 without cross-virial coefficients, *B* formula (Eq. 4) with the second cross-virial coefficient $B_{\mathrm{AW}}(T)$, *C* formula (Eq. 4) with the second and third cross-virial coefficients $B_{\mathrm{AW}}(T)$, $C_{\mathrm{AAW}}(T)$, and $C_{\mathrm{AWW}}(T)$. The improvement realized by including the *C* coefficients is effective mainly at densities higher than 100 kg · m^{-3} (adapted from [21])

contrast to Eq. 8. The definition of relative humidity given by the International Union of Pure and Applied Chemistry, IUPAC [52] is very similar to Eq. 9 but uses the ratio of the partial pressure of water vapor in humid air to the pressure of saturated, air-free vapor. An obvious deficiency of the IUPAC definition is that is does not exactly equal unity at saturation. In the SIA library, Eqs. 8 and 9 are separately implemented for optional use, and both in turn separately for saturation with respect to liquid water and to ice.

In the semi-empirical theory of Lewis [53,54], non-ideal properties of solutions are described by chemical potentials in the form $\mu = \mu^0(T, P) + RT \ln a$, where μ^0 is some concentration-independent function, and R is the gas constant. Here, the activity of the solute, a, formally replaces the concentration, x, of the related formula in the limit of infinite dilution, $\mu^{\mathrm{id}} = \mu^0(T, P) + RT \ln x$. Consequently, formulas for phase equilibria, for the mass-action law or for the pH value of non-ideal solutions can be written in the same way as for very dilute, ideal solutions if only the concentrations are formally substituted by activities [55]. The ratio $\gamma = a/x$ is the activity coefficient which approaches unity in the limit of infinite dilution, $\mu - \mu^{\mathrm{id}} = RT \ln \gamma$.

A similar approach is used for mixtures of non-ideal gases [52,56,57]. In that case the activity, a_{X}, of a certain component, X, multiplied by the total pressure, P, is termed the fugacity of X, $f_{\mathrm{X}} = a_{\mathrm{X}}P$, which in the ideal-gas limit approaches the partial pressure, $e_{\mathrm{X}} = x_{\mathrm{X}}P$. The activity coefficient of X, $\gamma_{\mathrm{X}} = a_{\mathrm{X}}/x_{\mathrm{X}}$, is termed here the fugacity coefficient, $\phi_{\mathrm{X}} = f_{\mathrm{X}}/e_{\mathrm{X}}$, which approaches unity in the ideal-gas limit. Thus, formulas for colligative properties of ideal-gas mixtures remain valid also for real gases if the partial pressure, e_{X}, is formally substituted therein by the fugacity, f_{X}.

In humid air, the water vapor is in equilibrium with liquid water in a solution or in a moist substance if the chemical potentials of water in the two phases are the same. If the chemical potential is expressed in terms of fugacities, equilibrium requires that the fugacity (or the activity) of water is the same in the gas and in the condensed phase. Saturated air is defined by the condition that the condensed phase is either pure liquid water or ice. Consequently, the fugacity of water in a solution or in a moist substance in comparison to the fugacity of pure liquid water is a measure for the subsaturation of humid air which is in equilibrium with the solution or the moist substance considered. In the ideal-gas limit, this measure approaches the relative humidity, Eq. 9.

Fugacity is a directly measurable quantity because the chemical potential, rather than the molar fraction or the ideal-gas partial pressure, physically controls equilibrium states and non-equilibrium flux rates between humid air and reference substances. Only in the ideal-gas limit, the chemical potential depends merely on the combination of pressure P and molar fraction x in the form of their product, (xP). For a non-ideal gas, the chemical potential depends separately on x and on P in the form of the fugacity. As an example, the partial pressure of atmospheric carbon dioxide at the ocean surface is routinely reported in terms of the measured fugacity [58–60].

The flux of water between ocean and atmosphere, and along with it the exchange of latent heat, is driven by the difference of the chemical potentials of water in seawater and in humid air. In terms of fugacities, the oceanic evaporation rate is controlled by the relative fugacity rather than the relative humidity [4,5]. Similar arguments hold for technical systems such as desalination plants.

With respect to seawater (or to any other solution or moist substances such as meat [61]), the relative fugacity of water vapor [4],

$$\varphi = \frac{f_{\mathrm{V}}}{f_{\mathrm{V}}^{\mathrm{sat}}}, \tag{10}$$

is a physically reasonable and convenient measure for the relative humidity at higher densities since at equilibrium it equals the activity of water in seawater [6]. The ratio (Eq. 10) is sometimes also regarded as the relative humidity [62] because it coincides with Eq. 9 in the ideal-gas limit. The fugacity of water vapor in humid air, f_{V}, is defined as [52]

$$f_{\mathrm{V}}(A, T, P) = f_{\mathrm{V}}^{0}(T) \exp\left\{\frac{\mu_{\mathrm{W}}(A, T, P)}{R_{\mathrm{W}} T}\right\}. \tag{11}$$

Here, μ_{W} is the mass-based chemical potential of water vapor in humid air, Eq. 7, and R_{W} is the specific gas constant of water. The reference fugacity, $f_{\mathrm{V}}^{0}(T)$, is chosen as

$$f_{\mathrm{V}}^{0}(T) = x_{\mathrm{V}}^{\mathrm{AV}} P \exp\left\{-\frac{\mu_{\mathrm{W}}^{\mathrm{id}}(A, T, P)}{R_{\mathrm{W}} T}\right\}, \tag{12}$$

where μ_W^{id} is the chemical potential of vapor in humid air in the ideal-gas limit. Therefore, the fugacity f_V approaches the partial pressure of vapor in the ideal-gas limit of infinite dilution [56,57],

$$\lim_{P\to 0} f_V(A, T, P) = x_V^{AV} P. \tag{13}$$

Thus, the fugacity can be written as a product of the partial pressure, $e = x_V^{AV} P$, with an "absolute" enhancement factor of real-gas humid air, the fugacity coefficient,

$$\phi(A, T, P) = \frac{f_V}{x_V^{AV} P} = \exp\left\{\frac{\mu_W(A, T, P) - \mu_W^{id}(A, T, P)}{R_W T}\right\}. \tag{14}$$

This factor is different from the common enhancement factor, f, which relates the vapor pressure of saturated humid air to that of pure water vapor [63].

Due to the mathematical form of μ_W^{id}, the function $f_V^0(T)$ does not depend on x_V^{AV} or P [4]. The function $f_V^0(T)$ takes the same value for saturated and for subsaturated humid air at the same temperature and cancels in the ratio (Eq. 10). If humid air is saturated over ice, the chemical potentials of water in humid air and of ice satisfy the equilibrium condition (Eq. 6), and the relative fugacity takes the form,

$$\varphi = \exp\left\{\frac{\mu_W(A, T, P) - g^{Ih}(T, P)}{R_W T}\right\}. \tag{15}$$

In the ideal-gas limit, φ equals the relative humidity, Eq. 9, i.e.,

$$\frac{x_V^{AV}}{x_V^{AV,sat}} = \exp\left\{\frac{\mu_W^{id}(A, T, P) - \mu_W^{id}\left(A^{sat}, T, P\right)}{R_W T}\right\}. \tag{16}$$

It follows that the relative fugacity is related to the relative humidity by the "absolute" enhancement factors, Eq. 14, in the form,

$$\varphi = \frac{x_V^{AV}}{x_V^{AV,sat}} \frac{\phi(A, T, P)}{\phi\left(A^{sat}, T, P\right)}. \tag{17}$$

Thus, the three quantities, Eqs. 9, 8, and 10, coincide in the ideal-gas limit but evaluate to different values for the real gas.

Similar to Eq. 15 for ice, in the case of saturation with respect to liquid water, Eq. 5, the relative fugacity takes the form [4],

$$\varphi = \exp\left\{\frac{\mu_W(A, T, P) - g^{liq}(T, P)}{R_W T}\right\}. \tag{18}$$

A comparison between the relative humidity, Eq. 9, and the relative fugacity, Eq. 18, is shown in Fig. 5. At atmospheric pressure and different temperatures, the deviations remain well below 0.5 %.

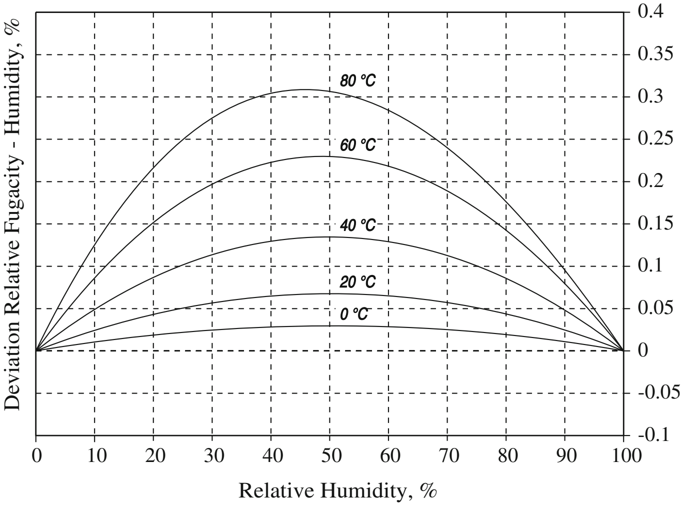

Fig. 5 Deviation between relative humidity, Eq. 9, in %, and relative fugacity, Eq. 18, in %, at different temperatures at atmospheric pressure, 101 325 Pa. Values of 0 % refer to dry air, of 100 % to saturation of humid air with respect to liquid water

From the SIA library, the *RH* values are available as functions of the mass fraction A, temperature and pressure by the function calls liq_air_rh_cct_from_a_si and liq_air_rh_wmo_from_a_si, respectively, with respect to liquid water, and by ice_air_rh_cct_from_a_si and ice_air_rh_wmo_from_a_si with respect to ice. Vice versa, to compute A from *RH*, the inverse functions liq_air_a_from_rh_cct_si, liq_air_a_from_rh_wmo_si, ice_air_a_from_rh_cct_si, and ice_air_a_from_rh_wmo_si are implemented.

The relative fugacity is currently implemented in compact form only for equilibria with seawater, function sea_air_chempot_evap_si, but can in general be computed from Eqs. 15 and 18 for given mass fractions A by calling the library functions air_g_chempot_vap_si to get μ_W, liq_gibbs_energy_si to get g^{liq}, and ice_chempot_si to get g^{Ih}. The curves of Fig. 5 were calculated this way.

For humid air in equilibrium with seawater, the dry-air mass fraction A is available from the SIA function call sea_air_massfraction_air_si for a given salinity, temperature, and pressure. From the result for A, the relative humidity can be calculated as described above.

7 Conclusion and Discussion

TEOS-10 is a new international standard for oceanography that provides all thermodynamic properties of seawater, liquid water, water vapor, ice, and humid air, as well as of their mutual phase transitions and composites, with high accuracy, perfect intrinsic consistency, and over a wide range of conditions. The TEOS-10 Manual is available from http://www.teos-10.org. Its Primary TEOS-10 Standard is formulated in IAPWS documents, available at http://www.iapws.org. A supporting "Sea-Ice-Air"

(SIA) source-code library, its description and background articles are available from the Special Issue "Thermophysical Properties of Seawater" published in Ocean Science under an open-access Creative Commons License, http://www.ocean-sci-discuss.net/special_issue23.html.

Because of its small uncertainty, the extended range of validity and evident consistency with virtually all available measurements of ice and water-vapor properties, the TEOS-10 values for the sublimation pressure of ice represent preferred reference data in favor of various separate correlation equations found in the literature. To further increase the reliability of vapor-pressure values at very low temperatures, precision determinations of the temperature dependence of the sublimation enthalpy or entropy appear to be a more promising metrological approach than, e.g., direct pressure measurements.

Similarly, the computation of humid-air properties from a suitable thermodynamic potential, consistent with related formulations for liquid water, water vapor and ice, results in more complete, more accurate, and more reliable data than from selected independent correlation equations of uncertain mutual consistency for particular quantities. A new, general, and systematic theoretical method for the estimation of uncertainties for arbitrary properties computed from empirical thermodynamic potentials, based on covariance matrices derived from the experimental evidence, is currently under consideration as a future addition to the SIA library.

As was emphasized recently [64], it is highly desirable that international bodies such as CCT, IAPWS, IUPAC, or WMO agree on joint sets of thermodynamic reference equations for fluid water, ice, seawater, and humid air, and in particular on unambiguous definitions and nomenclature of oceanic salinity, relative humidity, and related measures, for the key role those properties and substances play in technical devices and in the climate system.

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