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Metrological challenges for measurements of key climatological observables: Oceanic salinity and pH, and atmospheric humidity. Part 1: Overview

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This supplement is also related to the companion articles

- **Metrological challenges for measurements of key climatological observables. Part 2: Oceanic salinity**

- **Metrological challenges for measurements of key climatological observables. Part 3: Seawater pH**

- **Metrological challenges for measurements of key climatological observables. Part 4: Atmospheric relative humidity**

Appendix A: Chemical potentials and reference states

Chemical potentials were defined by Gibbs (1873) for the thermodynamic description of equilibria of multi-component and/or heterogeneous systems, and are closely linked to activity coefficients and fugacities. The statement of Kittel (1971) that "a vague discomfort at the thought of the chemical potential is still characteristic of a physics education" and that "this intellectual gap is due to the obscurity of the writings of J. Willard Gibbs who discovered and understood the matter 100 years ago" is still true even more than four decades later. In this Appendix, emphasis is put on some freedom available in the definition of chemical potentials, an aspect that is often only marginally touched in textbooks, but which is relevant here for the question of whether a certain mathematical expression in terms of chemical potentials may represent a measurable quantity or not.

The Gibbs energy, G, of a mixture of N substances with the composition $\boldsymbol{X} = (X_1, .., X_N)$ can be written in the form

$$G(\boldsymbol{X},T,p)=\sum_{i=1}^{N}\mu_i(\boldsymbol{X},T,p)X_i \ . \tag{A.1}$$

Typically, the extensive variables X_i may be the mass, the particle number or the mole number of constituent i. Conjugate to the chosen X_i, the partial Gibbs energies, μ_i, are the *chemical potentials*,

$$\mu_i=\left(\frac{\partial G}{\partial X_i}\right)_{X_{j\neq i},T,p} \ . \tag{A.2}$$

For theoretical reasons, at constant temperature and pressure, the set of chemical potentials of any given mixture always fulfils the Gibbs-Duhem differential equation,

$$\sum_{i=1}^{N}X_i\mathrm{d}\mu_i(\boldsymbol{X},T,p)=0 \ . \tag{A.3}$$

If $\boldsymbol{X}$ and $\boldsymbol{X}'$ are two alternative sets of composition variables describing the same mixture, their conjugate chemical potentials are converted into each other by the linear transformation,

$$\mu_i'=\left(\frac{\partial G}{\partial X_i'}\right)_{X_{j\neq i},T,p}=\sum_{j=1}^{N}\frac{\partial X_j}{\partial X_i'}\mu_j \ . \tag{A.4}$$

While this transformation is used to convert between mass-based and mole-based chemical potentials, it is commonly not applied if mass fractions or mole fractions are introduced as composition variables. For example, if $X_n = M_\mathrm{W}$ is the mass of water in seawater, and $X_i = M_i$ are the masses of the solutes, $i = 1, \ldots, N-1$, the related mass-based chemical potential of water in seawater follows from (A.2) to be

$$\mu_\mathrm{W}=\frac{\partial G}{\partial X_N}=g-S\frac{\partial g}{\partial S}, \tag{A.5}$$

where $g = G/M$ is the specific Gibbs energy of seawater, $S=\sum_{i=1}^{N-1}M_i/M$ is the mass fraction of dissolved salt, and $M=\sum_{i=1}^{N}X_i$ is the mass of the sample.

Similarly, if $X_N = n_W$ is the number of moles of water vapour in a sample of humid air, and $X_i = n_i$ are the mole numbers of the dry-air constituents, $i = 1, \ldots, N-1$, the mole-based chemical potential of water in humid air is computed from (A.2) to give

$$\mu_W^{(m)} = \frac{\partial G}{\partial X_N} = g^{(m)} + (1-x)\frac{\partial g^{(m)}}{\partial x}, \tag{A.6}$$

where $g^{(m)} = G/n$ is the molar Gibbs energy of humid air, $x = n_W / n$ the mole fraction of water vapour, and $n = \sum_{i=1}^{N} X_i$ is the number of moles contained in the sample.

In addition to the dependence of chemical potentials on the choice of the concentration variables, they are also arbitrary with respect to a linear function of temperature. If μ_i is the chemical potential of a substance i, the modified function,

$$\mu_i'(\boldsymbol{X}, T, p) = \mu_i(\boldsymbol{X}, T, p) + A_i + B_i T, \tag{A.7}$$

constitutes an equivalent chemical potential of that substance whatever constant values we may choose for A_i and B_i, provided that mutually consistent values are chosen for the same substance in each phase or mixture in the given system. The two undefined constants represent the partial absolute energy and the partial absolute entropy of the substance, which cannot be measured experimentally. Consequently, individual chemical potentials cannot be measured either.

A convenient way to fix those arbitrary constants is the formulation of reference-state conditions (Hamer and Wu, 1972). For water, in 1956 at the 5th ICPS[1] it was decided to set the entropy and the internal energy of liquid water to zero at the liquid-solid-gas triple point (Wagner and Pruß, 2002). Consistency requires that the same choice must also be applied for ice, for water in seawater and for water vapour in humid air (Feistel et al., 2008). Similar reference-state conditions were specified in TEOS-10 for sea salt and for dry air (IOC et al., 2010), but not separately for each chemical constituent of those mixtures. Because the composition of dissolved air in water deviates from that of dry air in the gas phase and depends on temperature and pressure, the current TEOS-10 specifications will be insufficient if the dissolution of air is no longer neglected. In general it is recommended that reference states be chosen at conditions where the correlation equations used are known with high accuracy, rather than at extreme states such as at zero absolute temperature.

The mole-based chemical potential of a solute at infinite (ideal) dilution, μ_i^{id}, takes the asymptotic form (Planck, 1888; Guggenheim, 1949; Falkenhagen et al., 1971; Prausnitz et al., 1999)

$$\mu_i^{id}(\boldsymbol{X}, T, p) = \mu_i^0(T, p) + RT \ln x_i, \tag{A.8}$$

where x_i is the mole fraction of the solute, and the reference chemical potential μ_i^0 is defined by the mathematical limit,

$$\mu_i^0(T, p) = RT \lim_{x_i \to 0} \left\{ \frac{\mu_i(\boldsymbol{X}, T, p)}{RT} - \ln x_i \right\}. \tag{A.9}$$

Note that the arbitrary constants in the definition of chemical potentials remain in the limit of infinite dilution, so that the difference $\mu_i(\boldsymbol{X}, T, p) - \mu_i^{id}(\boldsymbol{X}, T, p)$ is independent of the free constants in (A.7).

[1] ICPS: International Conference on the Properties of Steam, held by a forerunner of IAPWS, www.iapws.org

Appendix B: Definition of activity, activity coefficient and osmotic coefficient

Activities, instead of composition variables, were introduced by Lewis (1907) for the empirical description of solutions whose behaviour deviates from ideality.

The *absolute activity*, λ_i, of a substance *i* in a mixture is defined by (Guggenheim, 1949; Harrison, 1965; Kittel, 1969)

$$\lambda_i = \exp\left(\frac{\mu_i}{RT}\right), \tag{B.1}$$

where μ_i is the mole-based chemical potential of the substance. As an example, in TEOS-10 (IOC et al., 2010) the activity of water in seawater is defined by eq. (B.1).

For simplicity, a single solute is considered in the following. Because of the ambiguity (A.7) of the chemical potential, physically equivalent absolute activities, λ_i and λ_i', may differ by an arbitrary factor of the form

$$\lambda_i' = \exp\left(\frac{\mu_i'}{RT}\right) = \lambda_i \exp\left(\frac{A_i}{RT} + \frac{B_i}{R}\right). \tag{B.2}$$

Avoiding the ambiguity of the absolute activity, *relative activities* (or simply activities) can be defined by

$$a_i = \exp\left(\frac{\mu_i - \mu_i^0}{RT}\right) \equiv \frac{\lambda_i}{\lambda_i^0}, \tag{B.3}$$

where μ_i^0 is given by eq. (A.9), or by an alternative convention specifying some reference state that is assigned a relative activity of $a_i = 1$. Writing eq. (B.3) in the form

$$\mu_i(x_i, T, p) = \mu_i^0(T, p) + RT \ln a_i, \tag{B.4}$$

comparison with eq. (A.8) shows that for a concentrated solution the activity, a_i, formally takes over the role of the mole fraction, x_i, of a dilute solution.

Note that, up to a constant factor, the pH of a solution (see Part 3 of the companion articles) equals the excess chemical potential, $\left(\mu_i - \mu_i^0\right)/(RT)$, of the hydrogen ion (Himmel et al., 2010),

$$\mathrm{pH} = -\frac{\mu_{\mathrm{H}^+}\left(x_{\mathrm{H}^+}, T, p\right) - \mu_{\mathrm{H}^+}^0(T, p)}{RT \ln 10}. \tag{B.5}$$

To quantify the deviation of the activity from the mole fraction, the *activity coefficient*, γ_i, is used in the form

$$a_i(x_i, T, p) = x_i \gamma_i(x_i, T, p), \tag{B.6}$$

with the limiting property

$$\lim_{x_i \to 0} \gamma_i(x_i, T, p) = 1. \tag{B.7}$$

The activity coefficient (B.6) is sometimes termed “rational” in contrast to measured *practical activity coefficients*, $\gamma_i^{(m)}$, defined by (Lewis and Randall, 1921; Falkenhagen et al., 1971; Hamer and Wu, 1972)

$$a_i^{(m)}(m_i,T,p)=m_i\gamma_i^{(m)}(m_i,T,p), \tag{B.8}$$

where m_i is the molality of the solute. The molar activity, $a_i^{(m)}$, has the limiting property

$$\lim_{m_i\to 0}\frac{a_i^{(m)}(m_i,T,p)}{m_i}=1. \tag{B.9}$$

Since the molar activity is not dimensionless, eq. (B.4) is replaced by

$$\mu_i(m_i,T,p)=\mu_i^{(m),0}(T,p)+RT\ln\frac{a_i^{(m)}}{m^0}, \tag{B.10}$$

where m° is an arbitrary constant value, usually chosen as a standard-state molality of $m^\circ=1\,\mathrm{mol\,kg^{-1}}$ (Covington et al., 1985). Writing eq. (B.10) more conveniently, a *reduced practical activity* "referenced to Henry's law" is defined by (McGlashan, 1971; Buck et al., 2002; p. 59 in IUPAC, 2007),

$$a_{m,i}(m_i,T,p)=\frac{a_i^{(m)}}{m^\circ}=\frac{m_i}{m^\circ}\gamma_i^{(m)}(m_i,T,p), \tag{B.11}$$

where $a_i^{(m)}$ is given by eq. (B.8) and $m^\circ=1\,\mathrm{mol\,kg^{-1}}$. This reduced practical activity has the limiting property

$$\lim_{m_i\to 0}\frac{a_{m,i}(m_i,T,p)}{m_i}=\frac{1}{m^\circ}. \tag{B.12}$$

Experimentally, activity coefficients of solutes may be determined from their effects on colligative properties of the solution, such as the related lowering of the vapour pressure or of the freezing point. Those properties are described by the difference between the chemical potential of the solvent (e.g., water) in the solution, $\mu_\mathrm{W}(m_i)$, and that of the pure solvent, $\mu_\mathrm{W}(0)$, as a function of the solute molality, m_i, expressed by means of the *osmotic coefficient*, $\phi(m_i)$,

$$\mu_\mathrm{W}(m_i)-\mu_\mathrm{W}(0)=-m_iRT\phi(m_i), \tag{B.13}$$

which was introduced by Bjerrum (1918).

Making use of the definitions (B.10) and (B.13), the Gibbs-Duhem equation (A.3) relates the osmotic coefficient to the solute's activity coefficient, $\gamma_i^{(m)}$, by the Bjerrum differential equation (Bjerrum, 1919; Lewis and Randall, 1961; Millero and Leung, 1976; Blandamer et al., 2005; Feistel and Marion, 2007),

$$\mathrm{d}\left[m_i(1-\phi)\right]+m_i\,\mathrm{d}\ln\gamma_i^{(m)}=0. \tag{B.14}$$

If $\phi(m_i)$ is determined experimentally, the solution of this equation provides $\gamma_i^{(m)}(m_i)$ only up to an arbitrary integration constant that may be normalised by the condition (B.9). Note that eq. (B.14) is obeyed if $\phi(m_i)$ and $\gamma_i^{(m)}(m_i)$ are derived from a joint "activity potential", $\psi(m_i)=1-\phi+\ln\left(\gamma_i^{(m)}\right)$, in the form (Feistel and Marion, 2007),

$$\phi=1+m_i\frac{\mathrm{d}\psi}{\mathrm{d}m_i}, \qquad \ln\gamma^{(m)}=\frac{\mathrm{d}(m_i\psi)}{\mathrm{d}m_i}. \tag{B.15}$$

The function $\psi(m_i)$ may possess an arbitrary constant offset and is related to the excess Gibbs free energy of the solution per mass of solvent (Friedman, 1972; Hamer and Wu, 1972; Prausnitz et al., 1999), $G^{\mathrm{ex}} = m_i RT\psi$.

If the solute is a mixture itself, the Bjerrum relation (B.14) applies to the *mean activity coefficient*,

$$\ln\gamma^{(m)} = \frac{1}{m}\sum_i m_i \ln\gamma_i^{(m)} , \qquad \text{(B.16)}$$

where the sum is extended over all constituents of the solute, $m = \sum m_i$ is the total molality, and m_i and $\gamma_i^{(m)}$, respectively, are the molalities and the activity coefficients of the individual solutes. In such calculations, it is important to remember that for example the "total molality" of binary symmetric electrolytes is actually twice as large as the numerical value typically reported as the "molality" of the solution. This is because it is (another) convention to count only dissolved molecules rather than dissociated ions.

In the case of electrolyte solutions, additional ambiguities are encountered. First, the molality of multi-component, multi-valent electrolyte solutions is ambiguous. The solution of 1 mole of NaCl contains 2 moles of dissociated solute, 1 mole of the cation Na^+ plus 1 mole of the anion Cl^-. Such a solution is usually described as 1-molal (1 mol / (kg solvent)), referring to the salt originally dissolved (analytical concentration) as well as to the concentration of each of the two ionic species found in the solution. However, if 2 moles of NaCl are dissolved together with 1 mole of $MgSO_4$, that is, 3 total moles of "salt", the final solution is in no way different from that obtained by dissolving 1 mole of Na_2SO_4 and 1 mole of $MgCl_2$, that is, of 2 total moles of "salt". Unless the definition (B.13) and the Bjerrum relation (B.14) are specifically modified to compensate for the particular molality convention, the ambiguity of *m* may result in many different related osmotic coefficients for the same mixture, and may in turn also affect the results obtained for the mean activity coefficients.

Ambiguity in specifying the moles of solute in seawater with given salinity has led to very different molalities being reported in the literature (Feistel and Marion, 2007). In the TEOS-10 standard, the ambiguity of seawater molality is tentatively resolved by a convention based on the ions and molecules of the sea-salt Reference Composition. The related standard-ocean molality is *m* = 1.1605813 mol kg^{-1} (Millero et al., 2008).

A more critical problem in multi-component systems arises due to the electroneutrality of the solution. That is, when the solute consists of at least two ionic species (one cation and one anion), only their mean activity coefficient (B.16) can be determined from experiments. Problems in measuring single-ion activities are discussed by Bjerrum (1919) and Guggenheim (1949). Single-ion activities cannot unambiguously be inferred from mean chemical potentials of electrically neutral combinations of ions. To overcome this problem, as in particular required for the calculation of pH, eq. (B.5), auxiliary assumptions are sometimes applied, such as equating the activities of the cations and the anions of a particular solute, as suggested for KCl by Lewis and Randall (1923). Such arbitrary practical "conventions" may reasonably be applied as long as they do not conflict with experimental evidence. On the other hand, the Debye-Hückel limiting law predicts that the ion activity is a well-defined function of the ionic strength of very dilute electrolytes. Theoretical relations of this kind between activities and other measurable quantities (such as concentrations), for example, equations for single-ion activities derived from Pitzer equations, are in conflict with the putative arbitrariness of those conventions.

In contrast to empirical thermodynamics, single-ion activities are well-defined quantities in the theoretical framework of statistical thermodynamics (Falkenhagen and Ebeling, 1971; Ebeling and Scherwinski, 1983; Prausnitz et al., 1999), but related analytical expressions such as the Debye-Hückel limiting laws are available only for dilute solutions. At higher concentrations, microscopic

details of ion-ion and ion-solvent interactions become relevant. However, these are not precisely known and can only approximately be accounted for mathematically (Ebeling and Scherwinski, 1983). One practical way out of this situation is the use of so-called Pitzer equations, i.e., by approximating single-ion activities as series expansions with respect to the ion concentrations and to adjust the unknown empirical coefficients to measured data, such as to chemical mass-action laws (Nesbitt, 1980; Marion and Grant, 1994; Prausnitz et al., 1999; Marion and Kargel, 2008; Marion et al., 2011). Of the best currently known Pitzer equations of seawater ions, consistency is excellent with respect to colligative properties while other properties such as sound speed may not yet be represented within experimental uncertainty (Feistel and Marion, 2007; Feistel, 2008; Sharp et al., 2015).

Appendix C: Definition of fugacity and relative fugacity for water in humid air

Fugacity, f_V, the "escaping tendency" (Lewis, 1901a, b) of water vapour in a gaseous mixture, is defined as (Prausnitz et al., 1999; Zeebe and Wolf-Gladrow, 2005; IUPAC, 2006)

$$f_V(x,T,p) = f_V^0(T)\exp\left\{\frac{\mu_V(x,T,p)}{RT}\right\}, \tag{C.1}$$

where x is the mole fraction of water vapour in the mixture, μ_V is its mole-based chemical potential, and R is the molar gas constant. The fugacity has dimensions of pressure, eq. (C.2), and may be thought of as an "effective partial pressure" which deviates from the partial pressure, xp, at states away from the ideal-gas limit; see eq. (C.8) below. Although fugacity is a concept valid for arbitrary substances, here for water vapour the subscript V is used in order to distinguish the symbol for fugacity from that of the water-vapour enhancement factor, f. Also, for simplicity of the equations, the mole fraction is used here as the composition variable, in contrast to the mass fraction chosen in Appendix D. The conversion between the two is given by entry #8 of the derived quantities in that Appendix.

The reference fugacity in eq. (C.1), $f_V^0(T)$, is a function of the temperature alone and is chosen to be

$$f_V^0(T) \equiv xp\exp\left\{-\frac{\mu_V^{id}(x,T,p)}{RT}\right\}, \tag{C.2}$$

where μ_V^{id} is the chemical potential in the ideal-gas limit, i.e.,

$$\mu_V^{id}(x,T,p) \equiv RT\ln\frac{p}{p_0} + \lim_{p\to 0}\left\{\mu_V(x,T,p) - RT\ln\frac{p}{p_0}\right\}. \tag{C.3}$$

Here, p_0 is an arbitrary constant pressure value. By definition, fugacities take only non-negative values. In explicit terms, the chemical potential of ideal-gas water vapour can be written in the mathematical form (Feistel et al., 2010)

$$\mu_V^{id}(x,T,p) = g_0 + \int_{T_0}^{T}\left(1-\frac{T}{T'}\right)c_p^{id}(T')\mathrm{d}T' + RT\ln\frac{xp}{p_0}, \tag{C.4}$$

where $c_p^{id}(T)$ is the (pressure-independent) ideal-gas molar isobaric heat capacity of water vapour, and g_0, T_0, p_0 are arbitrary constants, usually specified by reference-state conditions, see Appendix A. For example, in TEOS-10 the constants used for water vapour take the values (Feistel et al., 2010), $g_0 = M^W \times 2\,501\,460.964\,842\,82$ J kg^{-1}, $T_0 = 273.16$ K, $p_0 = 253\,269\,701\,789.662$ Pa, $R = M^W \times 461.523\,64$ J kg^{-1} K^{-1}, where $M^W = 18.015\,268$ g mol^{-1} is the molar mass of water. The function $c_p^{id}(T)$ is available from Cooper (1982) with an extension down to 50 K (IAPWS, 2012).

Making use of eq. (C.4), eq. (C.2) leads to the expression

$$f_V^0(T) = p_0\exp\left\{-\frac{g_0}{RT} - \frac{1}{R}\int_{T_0}^{T}\left(\frac{1}{T}-\frac{1}{T'}\right)c_P^{id}(T')\mathrm{d}T'\right\}. \tag{C.5}$$

In eq. (C.1) the factor, λ_V,

$$\lambda_{\mathrm{v}} \equiv \exp\left\{\frac{\mu_{\mathrm{v}}(x,T,p)}{RT}\right\} \tag{C.6}$$

is termed the *(absolute) activity* of water vapour in the mixture (Guggenheim, 1949, Kittel, 1969; see eq. (B.1)), and has the ideal-gas limit

$$\lambda_{\mathrm{v}}^{\mathrm{id}}(x,T,p) = \exp\left\{\frac{\mu_{\mathrm{v}}^{\mathrm{id}}(x,T,p)}{RT}\right\} = \frac{xp}{f_{\mathrm{v}}^{0}(T)}\,. \tag{C.7}$$

Note that only differences of chemical potentials, rather than their absolute values, are physically relevant and measurable. Hence, while different activity definitions exist depending on additional conventions, fugacities are unambiguous. Up to moderate pressures, the fugacity of water in humid air can conveniently be calculated from a virial equation (Feistel et al., 2015; IAPWS, 2015) that is free of any arbitrary constants or reference states.

The fugacity of a substance in a liquid or solid mixture is equal to the fugacity of that substance in a gaseous mixture which is in equilibrium with the given condensed phase (Guggenheim, 1949, §4.51). This approach is practically useful for substances such as ice for which the meaning of the zero-pressure limit (C.3) is not obvious (Feistel and Wagner, 2007).

The *fugacity coefficient,* φ_{v}, is used to quantify the deviation of the fugacity from the partial pressure, in the form,

$$f_{\mathrm{v}}(x,T,p) = xp\varphi_{\mathrm{v}}(x,T,p); \tag{C.8}$$

it equals $\varphi_{\mathrm{v}} = \lambda_{\mathrm{v}} / \lambda_{\mathrm{v}}^{\mathrm{id}}$ with the limiting property,

$$\lim_{p\to 0}\varphi_{\mathrm{v}}(x,T,p) = 1\,. \tag{C.9}$$

The *relative fugacity*, ψ_f, of water vapour in a gaseous mixture is defined as the fugacity of water vapour divided by the saturation fugacity, $f_{\mathrm{v}}^{\mathrm{sat}}$, (IOC et al., 2010; Feistel et al., 2010; Feistel, 2012),

$$\psi_f(x,T,p) = \frac{f_{\mathrm{v}}}{f_{\mathrm{v}}^{\mathrm{sat}}} \equiv \frac{f_{\mathrm{v}}(x,T,p)}{f_{\mathrm{v}}\left(x^{\mathrm{sat}},T,p\right)} = \frac{\lambda_{\mathrm{v}}(x,T,p)}{\lambda_{\mathrm{v}}\left(x^{\mathrm{sat}},T,p\right)}\,. \tag{C.10}$$

Here, x^{sat} is the mole fraction of water vapour in the gas mixture when it is in equilibrium with a liquid or solid reference phase at the same T and p, and λ_{v} and f_{v} are given in eqs. (C.6) and (C.1), respectively. Note that solutions such as seawater are not used as reference phases; humid air in equilibrium with seawater is considered as subsaturated.

Since at saturation the chemical potential of water in humid air equals that in the condensed phase, liquid or ice Ih, the relative fugacity of humid air with respect to liquid water can be written in the form (Feistel et al., 2010, IOC et al., 2010; Feistel, 2012; see also Appendix D)

$$\psi_f(x,T,p) = \exp\left\{\frac{\mu_{\mathrm{v}}(x,T,p) - \mu_{\mathrm{w}}(1,T,p)}{RT}\right\} \tag{C.11}$$

where μ_{v} and μ_{w}, respectively, are the chemical potentials of water in humid air and of pure liquid water. Note that here, for formal consistency with the vapour-phase notation, the argument "1" of μ_{w} represents the mole fraction of water in the liquid mixture, in contrast to Appendix B where often the solute molality, m, is the preferred composition variable, as common in solution chemistry. Below the freezing point, the chemical potential of liquid water, μ_{w}, in eq. (C.11) may be substituted by the chemical potential of ice, μ_{Ih}. It is important that in the form of eq. (C.11), the relative fugacity

does not require an explicit definition of a gaseous saturation state and can reasonably be extended to conditions under which no stable saturation state of liquid water or ice exists, such as in contact with stable solutions at temperatures below the pure-phase freezing point or above the pure-water boiling point. For example, the vapour pressure of a saturated lithium chloride solution at 25 °C is 353 Pa (Acheson, 1965), which is much smaller than the saturation vapour pressure of 3172 Pa below which no stable liquid pure-water phase exists at this temperature. If the vapour over this solution is admixed with dry air, the relative fugacity, eq. (C.11), of water in this mixture takes continuous values of 11.1 %rh over the whole pressure range from 353 Pa total pressure to atmospheric pressure (Wylie, 1965), smoothly crossing over the formal threshold at 3172 Pa below which the conventional definition of relative humidity ceases to exist. When expressing relative humidity in percent, the unit symbol %rh is preferably used here and in the Part 4 companion paper.

Finally, we express the relative fugacity of water in the gas phase in terms of the chemical potential of water in an aqueous solution that is in equilibrium with humid air. From (C.6) and (C.10) we get

$$\psi_f(x,T,p) = \frac{\lambda(x,T,p)}{\lambda\left(x^{\mathrm{sat}},T,p\right)} = \exp\left\{\frac{\mu_{\mathrm{v}}(x,T,p) - \mu_{\mathrm{v}}\left(x^{\mathrm{sat}},T,p\right)}{RT}\right\}. \tag{C.12}$$

Equilibrium between gas and liquid is characterised by equal chemical potentials of all species in both phases. This applies to water in equilibrium between the given humid-air sample and a solution with the solvent mole fraction x_{W},

$$\mu_{\mathrm{v}}(x,T,p) = \mu_{\mathrm{w}}(x_{\mathrm{w}},T,p), \tag{C.13}$$

and similarly, by definition of saturation, to that between saturated gas and liquid pure water,

$$\mu_{\mathrm{v}}\left(x^{\mathrm{sat}},T,p\right) = \mu_{\mathrm{w}}(1,T,p). \tag{C.14}$$

So we get for the relative fugacity of water in the gas phase,

$$\psi_f(x,T,p) = \exp\left\{\frac{\mu_{\mathrm{w}}(x_{\mathrm{w}},T,p) - \mu_{\mathrm{w}}(1,T,p)}{RT}\right\} = a_{\mathrm{w}}(m,T,p), \tag{C.15}$$

where the pure solvent is chosen as the reference state for the activity of water, a_{W}, eq. (B.3), in a solution with solute molality m, and for the relative fugacity, eq. (C.14). We see that, *when water vapour or humid air is in equilibrium with an aqueous solution, the relative fugacity of water in the gas phase is equal to the (relative) activity of water in the liquid phase*, independent of the presence or absence of air, and of the nature of the solute (Hamer and Wu, 1972, eq. (3.1) therein; Feistel et al., 2010, eq. (10.14) therein; IOC et al., 2010, eq. 3.40.11 therein). Equation (C.15) may be used to produce reference materials of certified relative fugacity (Wylie, 1965; Acheson, 1965; Hamer and Wu, 1972; Greenspan, 1977), by e.g. the isopiestic method (Robinson, 1954).

Relative fugacity is used for the description of moist solids (Ott, 1943; Kollmann and Côté, 1984; Köfinger et al., 2009). The relative fugacity of water vapour in humid air with respect to liquid water or ice as the reference substances is usually also termed "relative humidity" (Wylie, 1965; Kraus, 1972; Greenspan, 1977; Kraus and Businger, 1994; Li and Chylek, 2012).

The fugacity coefficient $\varphi_{\mathrm{v}}(x,T,p)$, eq. (C.8), can also be used to express the enhancement factor f, a frequently used humid-air property that was introduced by Goff (1949), see Appendix D. If we write eq. (C.14) for pure water vapour and denote the saturation pressure by $e^{\mathrm{sat}}(T)$, we have

$$\mu_{\mathrm{V}}\left(1,T,e^{\mathrm{sat}}\right)=\mu_{\mathrm{W}}\left(1,T,e^{\mathrm{sat}}\right). \tag{C.16}$$

By subtracting this equation from (C.14), we obtain a general relation between the enhancement factor and the fugacity coefficient

$$f\left(x^{\mathrm{sat}},T,p\right)=\frac{\varphi_{\mathrm{V}}\left(1,T,e^{\mathrm{sat}}\right)}{\varphi_{\mathrm{V}}\left(x^{\mathrm{sat}},T,p\right)}\pi(T,p). \tag{C.17}$$

Here, $\pi(T,p)$ is the Poynting correction factor of liquid water (Prausnitz et al., 1999),

$$\pi(T,p)\equiv\exp\left\{\frac{\mu_{\mathrm{W}}(1,T,p)-\mu_{\mathrm{W}}\left(1,T,e^{\mathrm{sat}}\right)}{RT}\right\}=\frac{\lambda_{\mathrm{W}}(T,p)}{\lambda_{\mathrm{W}}\left(T,e^{\mathrm{sat}}\right)}=\exp\left\{\frac{1}{RT}\int_{e^{\mathrm{sat}}(T)}^{p}v_{\mathrm{W}}(T,p')\mathrm{d}p'\right\}, \tag{C.18}$$

where λ_{W} is the (absolute) activity of liquid water, eq. (B.1), and v_{W} is its molar volume.

Eq. (C.17) does not account for the dissolution of air in water; if x^{sat} is specified with respect to air-saturated water, eq. (C.17) for the enhancement factor must be replaced by

$$f\left(x^{\mathrm{sat}},T,p\right)\equiv\frac{x^{\mathrm{sat}}p}{e^{\mathrm{sat}}(T)}=x_{\mathrm{W}}\frac{\varphi_{\mathrm{V}}\left(1,T,e^{\mathrm{sat}}\right)}{\varphi_{\mathrm{V}}\left(x^{\mathrm{sat}},T,p\right)}\pi(T,p), \tag{C.19}$$

where x_{W} is the solvent mole fraction in ideal-solution approximation (Feistel et al., 2015). Here, x_{W} describes the Raoult effect, $\pi(T,p)$ the Poynting effect, and the ratio of the fugacity coefficients represents the gas-phase interaction effect on the enhancement factor. Eq. (C.19) implies that the fugacity at saturation can be expressed by the relation

$$f_{\mathrm{V}}^{\mathrm{sat}}(T,p)=f_{\mathrm{V}}\left(x^{\mathrm{sat}},T,p\right)=x^{\mathrm{sat}}p\varphi_{\mathrm{V}}\left(x^{\mathrm{sat}},T,p\right)=x_{\mathrm{W}}e^{\mathrm{sat}}\varphi_{\mathrm{V}}\left(1,T,e^{\mathrm{sat}}\right)\pi(T,p), \tag{C.20}$$

and can be evaluated without explicit knowledge of the value of x^{sat} if x_{W} is set to unity or, if $p > e^{\mathrm{sat}}(T)$, is estimated by Henry's law using ideal-solution and ideal-gas approximations,

$$x_{\mathrm{W}}=1-\beta\left(p-e^{\mathrm{sat}}(T)\right). \tag{C.21}$$

Here, β is the reciprocal Henry's constant of dry air defined by Herrmann et al. (2009).

Similarly to eq. (C.20), the relation between relative fugacity and solvent activity, eq. (C.15), may also require correction for dissolved air. For the practical evaluation of eq. (C.20), numerically convenient correlation equations are available for $e^{\mathrm{sat}}(T)$ of saturated water vapour with respect to liquid water and to ice Ih (IAPWS, 1992, 2011; Wagner and Pruß, 1993; Wagner et al., 2011) and for f_{V} and φ_{V} of humid air in the form of a virial approximation (Feistel et al., 2015; IAPWS, 2015).

Appendix D: Example of an axiomatic approach to the definition of humid-air properties

An "axiomatic" approach to relative humidity and related quantities could be based upon consistently specified thermodynamic potentials, such as those provided in IAPWS documents for liquid water, ice and humid air. Given these three empirical formulations (plus a few additional quantities such as molar masses or fundamental constants), all thermodynamic properties of humid air such as chemical potentials, vapour pressures, dew-point temperatures or relative humidities can first be formally defined and subsequently evaluated within this context, as well as subsequently evaluated quantitatively in a consistent, complete and accurate way.

First the *basic* set of quantities considered as known *a priori* or defined externally (the "axioms") are stated. This set is axiomatic in the sense that it is
a) *independent* in that none of its elements can in part or *in toto* be derived from other elements of the set,
b) *consistent* in that it is impossible to derive from the set alternative, different results for the same derived quantity, and
c) *complete* in that all quantities defined in a second step can/must be mathematically rigorously specified exclusively in terms of the "axioms".

The axiomatic set of nine basic quantities suggested here is:

1. **Pressure p**: absolute, total, *in-situ* pressure to which the actual sample of humid air, aqueous liquid phase or ice is exposed.

2. **Temperature T**: absolute, *in-situ* temperature[2] of the actual sample of humid air, liquid water or ice. T is assumed here to be given on ITS-90.

3. **Air mass fraction A**: mass fraction of dry air in the actual sample of humid air.

4. **Gibbs function $g^{AV}(A, T, p)$**: Specific Gibbs energy of humid air expressed in terms of the independent variables A, T, p. As a thermodynamic potential, g^{AV} provides all thermodynamic properties of humid air from algebraic combinations of its partial derivatives.

5. **Gibbs function $g^{W}(T, p)$**: Specific Gibbs energy of liquid water expressed in terms of the independent variables T, p. As a thermodynamic potential, g^{W} provides all thermodynamic properties of liquid water from algebraic combinations of its partial derivatives. The freely adjustable parameters of g^{W} must be specified consistently with those of g^{AV}, see App. A.

6. **Gibbs function $g^{Ih}(T, p)$**: Specific Gibbs energy of ice Ih expressed in terms of the independent variables T, p. As a thermodynamic potential, g^{Ih} provides all thermodynamic properties of ice Ih from algebraic combinations of its partial derivatives. The freely adjustable parameters of g^{Ih} must be specified consistently with those of g^{AV}, see App. A.

7. **Molar mass M^{W}**: The molar mass of water is M^{W} = 0.018 015 268 kg mol^{-1} (IAPWS, 2001). If the isotopic composition of water vapour in humid air is different from that of VSMOW[3], such as by fractionation in evaporation (Jasechko et al., 2013), the composition must be specified rather than a single value for the molar mass.

8. **Molar mass M^{A}**: The molar mass of dry air is M^{A} = 0.028 965 46 kg mol^{-1} (Picard et al., 2008). If the chemical or isotopic composition of dry air in humid air may vary, such as by a changing

[2] also known as "dry-bulb temperature" in meteorology (WMO, 2008)
[3] VSMOW: Vienna Standard Mean Ocean Water (IAPWS, 2001)

fraction of CO_2 or by dissolution of air in water, the composition must be specified rather than a single value for the molar mass (Picard et al., 2008).

9. **Molar gas constant**[4] ***R***: The CODATA 2010 value is R = 8.314 4621 J K^{-1} mol^{-1} (Mohr et al., 2012).
   Note that in the successively adopted IAPWS formulations used for TEOS-10, several slightly different, now obsolete values for R are specified. In principle, the value of R is not independent of the former basic quantities and can be obtained from the ideal-gas equation of state in the form of the mathematical limit $R = \frac{M^{\mathrm{W}}}{T} \lim_{p \to 0} \left\{ p \frac{\partial}{\partial p} g^{\mathrm{AV}}(0, T, p) \right\}$, but this result will not exactly provide the most recent CODATA value if the TEOS-10 formula for g^{AV} is used. Therefore, the R value of 2010 is introduced here additionally as an independent "exact" constant, consistent with the former basic quantities only within reasonable uncertainty.

Note that there are various alternative possibilities of defining the axiomatic set, such as by using the IAPWS-95 Helmholtz function for fluid water (as a function of temperature and density) rather than by separate Gibbs function for liquid water (here, as basic item (5)) and for water vapour (here, as derived item #1, below). The actual choice made is a matter of convenience and purpose.

The list of quantities that can be derived from the quantities (1) - (9) still obeys consistency but is no longer subject to requirements of independence or completeness. The list is extendable as required and is potentially unlimited. Provided the set of basic ("primary") quantities is complete in the sense described above, *derived* ("secondary") properties do not introduce any new empirical coefficients or correlations; they inherit their equations exclusively from those of the basic quantities.

1. **Gibbs function $g^{\mathrm{V}}(T, p)$**: The Gibbs function of water vapour is available from the Gibbs function of humid air in the limit of vanishing dry air, $g^{\mathrm{V}}(T, p) = g^{\mathrm{AV}}(0, T, p)$. As a thermodynamic potential, g^{V} provides all thermodynamic properties of water vapour from algebraic combinations of its partial derivatives.

2. **Chemical potential of water vapour** μ^{V}: $\mu^{\mathrm{V}}(T, p)$ is computed from the Gibbs function of water vapour by the relation $\mu^{\mathrm{V}} = g^{\mathrm{V}}$.

3. **Chemical potential of liquid water** μ^{W}: $\mu^{\mathrm{W}}(T, p)$ is computed from the Gibbs function of liquid water by the relation $\mu^{\mathrm{W}} = g^{\mathrm{W}}$.

4. **Chemical potential of ice Ih** μ^{Ih}: $\mu^{\mathrm{Ih}}(T, p)$ is computed from the Gibbs function of ice Ih by the relation $\mu^{\mathrm{Ih}} = g^{\mathrm{Ih}}$.

5. **Triple point solid-liquid-gas of water (T_{t}, p_{t})**: Temperature and pressure of the common triple point of water are defined by the equations
   $\mu^{\mathrm{Ih}}(T_{\mathrm{t}}, p_{\mathrm{t}}) = \mu^{\mathrm{W}}(T_{\mathrm{t}}, p_{\mathrm{t}}) = \mu^{\mathrm{V}}(T_{\mathrm{t}}, p_{\mathrm{t}})$.

6. **Specific gas constants R_{W}, R_{A}**: From the basic quantities (7), (8) and (9), the specific gas constants $R_{\mathrm{W}} \equiv R / M^{\mathrm{W}}$ of water and $R_{\mathrm{A}} \equiv R / M^{\mathrm{A}}$ of dry air are specified for convenience.

7. **Mole fraction x_{A}**: Using the basic quantities (3), (7) and (8), the mole fraction of dry air in humid air is computed from

[4] The CODATA 2010 value reported here has recently been updated to R = 8.314 4598 J K^{-1} mol^{-1}, http://physics.nist.gov/cgi-bin/cuu/Value?r

$$x_{\mathrm{A}} = \frac{A/M^{\mathrm{A}}}{(1-A)/M^{\mathrm{W}} + A/M^{\mathrm{A}}}.$$

8. **Mole fraction *x***: Using the basic quantities (3), (7) and (8), the mole fraction of water vapour in humid air is computed from

$$x = \frac{(1-A)/M^{\mathrm{W}}}{(1-A)/M^{\mathrm{W}} + A/M^{\mathrm{A}}}.$$

9. **Specific gas constant of humid air R_{AV}**: The molar gas constant, divided by the mass of one mole of humid air, is a linear function of the mass fraction A of dry air, in the form $R_{\mathrm{AV}}(A) = R/\left(x_{\mathrm{A}}M^{\mathrm{A}} + xM^{\mathrm{W}}\right) \equiv AR_{\mathrm{A}} + (1-A)R_{\mathrm{W}}$

10. **Gibbs function $g^{\mathrm{AV,id}}(A, T, p)$**: Specific Gibbs energy of ideal-gas humid air expressed in terms of the independent variables A, T, p. As a thermodynamic potential, $g^{\mathrm{AV,\,id}}$ provides all thermodynamic properties of ideal-gas humid air from algebraic combinations of its partial derivatives. $g^{\mathrm{AV,\,id}}$ is the mathematical low-pressure limit of g^{AV}, obtained from the basic quantity (4) and the derived quantity (9), in the form
$$g^{\mathrm{AV,id}}(A,T,p) = R_{\mathrm{AV}}\,T\ln\frac{p}{p_0} + \lim_{p\to 0}\left\{g^{\mathrm{AV}}(A,T,p) - R_{\mathrm{AV}}\,T\ln\frac{p}{p_0}\right\}.$$
Here, p_0 is an arbitrary constant pressure, such as $p_0 = 1$ Pa, and is used here only to make the argument of the logarithm dimensionless.

11. **Chemical potential of water vapour in humid air $\mu_{\mathrm{W}}^{\mathrm{AV}}$**: $\mu_{\mathrm{W}}^{\mathrm{AV}}(x,T,p)$ is computed from the Gibbs function of humid air by the relation $\mu_{\mathrm{W}}^{\mathrm{AV}} = g^{\mathrm{AV}} - Ag_A^{\mathrm{AV}} \equiv g^{\mathrm{AV}} - A\left(\partial g^{\mathrm{AV}}/\partial A\right)_{T,p}$ and from (8).

12. **Chemical potential of ideal-gas water vapour in humid air $\mu_{\mathrm{W}}^{\mathrm{AV,id}}$**: $\mu_{\mathrm{W}}^{\mathrm{AV,id}}(x,T,p)$ is computed from the Gibbs function of ideal-gas humid air (10) by the relation $\mu_{\mathrm{W}}^{\mathrm{AV,id}} = g^{\mathrm{AV,id}} - Ag_A^{\mathrm{AV,id}} \equiv g^{\mathrm{AV,id}} - A\left(\partial g^{\mathrm{AV,id}}/\partial A\right)_{T,p}$ and from (8).

13. **Freezing temperature of water T_{frz}**: $T_{\mathrm{frz}}(p)$ is computed implicitly from the equation for the phase equilibrium between liquid water and ice, $\mu^{\mathrm{W}}(T_{\mathrm{frz}},p) = \mu^{\mathrm{Ih}}(T_{\mathrm{frz}},p)$.

14. **Saturated vapour pressure of water e^{sat}**: $e^{\mathrm{sat}}(T)$ is computed implicitly from the equation for the phase equilibrium between liquid water and water vapour, $\mu^{\mathrm{W}}(T,e^{\mathrm{sat}}) = \mu^{\mathrm{V}}(T,e^{\mathrm{sat}})$.

15. **Sublimation pressure of ice e^{subl}**: $e^{\mathrm{subl}}(T)$ is computed implicitly from the equation for the phase equilibrium between ice Ih and water vapour, $\mu^{\mathrm{Ih}}(T,e^{\mathrm{subl}}) = \mu^{\mathrm{V}}(T,e^{\mathrm{subl}})$.

16. **Specific humidity *q***: Specific humidity, or the mass fraction of water vapour in humid air, is computed by $q = 1 - A$.

17. **Partial pressure of water vapour p_{V}**: The partial pressure of water vapour in humid air is defined as $p_{\mathrm{V}} = x\,p$.

18. **Dew-point temperature T_{d}**: The dew-point temperature $T_{\mathrm{d}}(x, p)$ associated with the actual humid-air sample is defined as the temperature at which a sample with the same pressure and composition is in equilibrium with liquid water, $\mu_{\mathrm{W}}^{\mathrm{AV}}(x,T_{\mathrm{d}},p) = \mu^{\mathrm{W}}(T_{\mathrm{d}},p)$.

19. **Frost-point temperature T_f**: The frost-point temperature $T_f(x, p)$ associated with the actual humid-air sample is defined as the temperature at which a sample with the same pressure and composition is in equilibrium with ice, $\mu_W^{AV}(x, T_f, p) = \mu^{Ih}(T_f, p)$.

20. **Saturated water-vapour mole fraction x^{sat}**: The saturated water-vapour mole fraction $x^{sat}(T, p)$, with respect to liquid water or ice, is found by solving the equation for the phase equilibrium between humid air and liquid water, $\mu_W^{AV}(x^{sat}, T, p) = \mu^{W}(T, p)$, or the equation for the phase equilibrium between humid air and ice Ih, $\mu_W^{AV}(x^{sat}, T, p) = \mu^{Ih}(T, p)$, respectively.

21. **(a) Enhancement factor of saturated humid air f**: The enhancement factor f of saturated humid air with respect to liquid water or ice, if T and p are known, is found by calculating $f(T, p) = x^{sat} p / e^{sat}(T)$ or $f(T, p) = x^{sat} p / e^{subl}(T)$, respectively. Here x^{sat}, e^{sat} and e^{subl} are determined using items (20), (14) and (15), respectively.

    (b) Enhancement factor of saturated humid air f: The enhancement factor f of saturated humid air with respect to liquid water or ice, if x^{sat} and T are known, is computed implicitly from the equation for the phase equilibrium between liquid water and humid air, $\mu^{W}(T, fe^{sat}/x^{sat}) = \mu_W^{AV}(x^{sat}, T, fe^{sat}/x^{sat})$, or the equation for the phase equilibrium between ice Ih and humid air, $\mu^{Ih}(T, fe^{subl}/x^{sat}) = \mu_W^{AV}(x^{sat}, T, fe^{subl}/x^{sat})$, respectively. Here $e^{sat}(T)$ and $e^{subl}(T)$ are determined using items (14) and (15), respectively.

22. **(a) Fugacity of water vapour in humid air f_V**: In the real gas, the role of the partial pressure p_V is played by the fugacity $f_V(x, T, p) = xp \exp\left\{\dfrac{\mu_W^{AV}(x, T, p) - \mu_W^{AV,id}(x, T, p)}{R_W T}\right\}$.

    (b) Fugacity of pure water vapour f_V: For the absence of dry air, the limit $x \to 1$ can readily be carried out for the fugacity of water vapour, as
    $f_V(1, T, p) = p \exp\left\{\dfrac{\mu_W^{AV}(1, T, p) - \mu_W^{AV,id}(1, T, p)}{R_W T}\right\} \equiv p \exp\left\{\dfrac{\mu^{V}(T, p) - \mu^{V,id}(T, p)}{R_W T}\right\}$.

23. **Fugacity coefficient of water vapour in humid air φ_V :** The deviation of the fugacity from the partial pressure of water vapour, caused by non-ideal effects, is represented by the fugacity coefficient $\varphi_V(x, T, p) = \dfrac{f_V(x, T, p)}{xp} \equiv \exp\left\{\dfrac{\mu_W^{AV}(x, T, p) - \mu_W^{AV,id}(x, T, p)}{R_W T}\right\}$

24. **Relative fugacity of humid air ψ_f** : The relative fugacity of water vapour in humid air is defined as $\psi_f(x, T, p) = \exp\left\{\dfrac{\mu_W^{AV}(x, T, p) - \mu^{W}(T, p)}{R_W T}\right\} \equiv \dfrac{f_V(x, T, p)}{f_V(x^{sat}, T, p)}$ with respect to liquid water and $\psi_f(x, T, p) = \exp\left\{\dfrac{\mu_W^{AV}(x, T, p) - \mu^{Ih}(T, p)}{R_W T}\right\} \equiv \dfrac{f_V(x, T, p)}{f_V(x^{sat}, T, p)}$ with respect to ice.

25. **Relative fugacity of water vapour ψ_f** : In the limit of vanishing air, the relative fugacity of water vapour is $\psi_f(1, T, p) = \exp\left\{\dfrac{\mu^{V}(T, p) - \mu^{W}(T, p)}{R_W T}\right\}$ with respect to liquid water, and $\psi_f(1, T, p) = \exp\left\{\dfrac{\mu^{V}(T, p) - \mu^{Ih}(T, p)}{R_W T}\right\}$ with respect to ice.

26. **Full-range relative humidity ψ_{full}:** The relative humidity of moist air or water vapour is defined as $\psi_{\text{full}}(x,T,p) = \frac{p_{\text{v}}(x,p)}{p_{\text{v}}^{\text{ref}}(T,p)} = \frac{p_{\text{v}}(x,p)}{e^{\text{sat}}(T) f(T,p)}$ where $f(T, p) = 1$ for $e^{\text{sat}}(T) > p$.

In this list, if no arguments are reported explicitly, the actual (*in-situ*) arguments (x, T, p) are meant rather than those of any associated reference states, etc.

The numerical values of derived, "secondary" quantities can be used to calculate arbitrary data tables to which suitable "tertiary" functions may be fitted for more convenient use, with well-known ranges of validity and consistency.

While it is metrologically mandatory that any value computed for one of the above quantities, be it basic or derived, has to be accompanied by an uncertainty estimate, there is not yet any systematic method for adding the requisite information to the basic “axiomatic” quantities, and for extracting the uncertainty of a desired quantity from that basic information. It has been argued that it is necessary and sufficient to add to the basic correlation equations a set of covariance coefficients (Saunders, 2003; Cox and Harris, 2006; Lovell-Smith, 2009; Feistel, 2011; Strutz, 2011) along with the set of empirical coefficients. Considering the experimental uncertainties related to the original background data from which the basic equations were constructed (typically by numerical regression) is no longer necessary as soon as the covariance coefficients have been determined. In the special case of small uncertainties, the generation and algebraic manipulation of covariance matrices is consistent with methods recommended by BIPM et al. (2008a, b) and GUM (2011). More thorough investigation of this approach is warranted.

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List of symbols used in the supplement

Symbol	Quantity	Remarks
A	dry-air mass fraction of humid air	
A	arbitrary constant (with subscripts)	App A, B
A^{sat}	dry-air mass fraction of saturated humid air	App D
a	relative activity (with subscripts)	
a	reduced practical activity	
$a^{(m)}$	molar activity	App B
B	arbitrary constant (with subscripts)	App A, B
c_p^{id}	ideal-gas molar isobaric heat capacity	App C
e^{sat}	water-vapour pressure at saturation	Pure water
e^{subl}	sublimation pressure of ice Ih	App D
f	water-vapour enhancement factor	App D
f_{V}	fugacity of water in vapour phase	
f_{V}^0	reference fugacity	App C
$f_{\mathrm{V}}^{\mathrm{sat}}$	fugacity of water in vapour phase at saturation	
G	Gibbs energy	App A
G^{ex}	excess Gibbs free energy	App B
g_0	arbitrary constant molar energy	App C
g^{AV}	specific Gibbs energy of humid air	App D
g^{Ih}	specific Gibbs energy of hexagonal ice I	
g^{V}	specific Gibbs energy of water vapour	App D
g^{W}	specific Gibbs energy of liquid water	App D
$g^{(\mathrm{m})}$	molar Gibbs energy	App A
M	sample mass	App A
M^{A}	molar mass of dry air	App D $M^{\mathrm{A}} = 0.028\,965\,46$ kg mol^{-1}
M_i	mass of solute molecules	App A
M^{W}	molar mass of water	App A, D $M^{\mathrm{W}} = 0.018\,015\,268$ kg mol^{-1}
M_{W}	mass of water molecules in solution	App A
m	solute molality (with subscripts)	
m^{o}	standard-state molality	$m^{\mathrm{o}} = 1$ mol kg^{-1}
N	number of substances	
n	number of moles (with subscripts)	
p	absolute pressure	
p_0	arbitrary constant pressure	App C, D
pH	pH value	
p_{t}	triple-point pressure	App D
p_{V}	water-vapour partial pressure	App D
q	specific humidity	
R	molar gas constant[5]	$R = 8.314\,4621$ J K^{-1} mol^{-1}
R_{A}	specific gas constant of dry air	$R_{\mathrm{A}} = R / M^{\mathrm{A}}$, App D
R_{AV}	specific gas constant of humid air	App D
R_{W}	specific gas constant of water	$R_{\mathrm{W}} = R / M^{\mathrm{W}}$
S	solute mass fraction	App A

[5] The CODATA 2010 value reported here has recently been updated to $R = 8.314\,4598$ J K^{-1} mol^{-1}, http://physics.nist.gov/cgi-bin/cuu/Value?r

T	absolute temperature, ITS-90	
T_0	arbitrary constant temperature	App C
T_d	dew-point temperature	App D
T_f	frost-point temperature	App D
T_{frz}	freezing temperature	App D
T_t	triple-point temperature	App D
v_W	molar volume of liquid water	App C
X	composition variable (with subscripts)	App A
x	mole fraction of water vapour	
x_A	mole fraction of dry air	App D
x^{sat}	mole fraction at saturation	
x_W	mole fraction of liquid water	App C
β	reciprocal Henry's constant of dry air	App C
φ_v	fugacity coefficient of water vapour	
ϕ	osmotic coefficient	App B, C
γ	molal activity coefficient (with subscripts)	
$\gamma^{(m)}$	practical activity coefficient	App B
λ	absolute activity	App B
μ	chemical potential (with super/subscripts)	
π	Poynting correction factor of liquid water	App C
ψ	activity potential	App B
ψ	relative humidity (with super/subscripts)	
ψ_{full}	relative humidity in the extended range, $e^{sat} > p$	App D