

## Review

# Metrological challenges for measurements of key climatological observables: oceanic salinity and pH, and atmospheric humidity. Part 1: overview

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## Abstract

Water in its three ambient phases plays the central thermodynamic role in the terrestrial climate system. Clouds control Earth's radiation balance, atmospheric water vapour is the strongest 'greenhouse' gas, and non-equilibrium relative humidity at the air–sea interface drives evaporation and latent heat export from the ocean. On climatic time scales, melting ice caps and regional deviations of the hydrological cycle result in changes of seawater salinity, which in turn may modify the global circulation of the oceans and their ability to store heat and to buffer anthropogenically produced carbon dioxide. In this paper, together with three companion articles, we examine the climatologically relevant quantities ocean salinity, seawater pH and atmospheric relative humidity, noting fundamental deficiencies in the definitions of those key observables, and their lack of secure foundation on the International System of Units, the SI. The metrological histories of those three quantities are reviewed,

problems with their current definitions and measurement practices are analysed, and options for future improvements are discussed in conjunction with the recent seawater standard TEOS-10. It is concluded that the International Bureau of Weights and Measures, BIPM, in cooperation with the International Association for the Properties of Water and Steam, IAPWS, along with other international organizations and institutions, can make significant contributions by developing and recommending state-of-the-art solutions for these long standing metrological problems in climatology.

Keywords: seawater salinity, seawater pH, relative humidity, traceability

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So wäre es zu wünschen, daß man zukünftig bei der Bestimmung ... immer von denselben Voraussetzungen ausgeht, oder jedenfalls daß die Grundlage des angewandten Verfahrens scharf pointiert wird.

[It is desirable that future estimates ... be always based on the same assumptions, or at least that the method applied be precisely described.]

S.P.L. Sørensen, S. Palitzsch, 1910

## 1. Introduction

Climate research is a special scientific task that inherently requires close world-wide cooperation over many human generations. Observational data, be they measured directly or derived from equations that transform the original input values, need to be rigorously defined, consistent and comparable between groups that work at distant locations or times. The impossibility of repeating real-time climatological measurements largely prevents correcting erratic or suspicious readings made in the past. Data measured today will likely be exploited in the future and should be unambiguous and reliable to the highest standards currently available. The preferred and most advanced metrological basis to be employed is the International System of Units, the SI (BIPM 2006). The requisite traceability to the SI of environmental measurement results was only gradually established in recent years, and in several fields this traceability still poses a serious challenge (BIPM 2010), as will also be emphasized in this paper and its companions (Pawlowicz *et al* 2015, Dickson *et al* 2016, Lovell-Smith *et al* 2015). Solving these metrological problems in geosciences demands joint efforts of international organizations and institutions that develop and implement definitions, equations and measurement standards based on the SI.

Water in its three ambient phases is the unrivalled key substance in the complex dynamic terrestrial climate system. Water vapour in the atmosphere accounts for 50 % to 60 % of the terrestrial greenhouse effect, in contrast to 20 % to 25 % due to carbon dioxide, CO<sub>2</sub> (Trenberth *et al* 2007, Schmidt *et al* 2010). Water in the atmosphere not only controls the Earth's radiation balance but also the oceanic export of latent heat and entropy as well as the formation and distribution of clouds (Baumgartner and Reichel 1975, Clement *et al* 2009, Dessler 2010, Feistel and Ebeling 2011, Wells

2012, Tollefsen 2012, Fasullo and Trenberth 2012, Hellmuth *et al* 2013); the latter may contribute another 10 % to 25 % to greenhouse warming (Lacis *et al* 2010, Schmidt *et al* 2010). Melting polar glaciers raise the sea level and influence the surface salinity distribution, and in turn may affect the large-scale vertical and horizontal circulations in the oceans which continuously store, release or displace huge amounts of heat and dissolved gases (Peixoto and Oort 1992, Barker *et al* 2011, Rayner *et al* 2011, Reid and Valdés 2011, Marotzke 2012, Stocker 2013, Otto-Bliesner *et al* 2014, Schmidtko *et al* 2014, Böhm *et al* 2015). Trends in global distributions of humidity, latent heat flux, evaporation and precipitation are closely connected with small but precisely measurable systematic shifts and anomalies in sea-surface salinities (Boyer *et al* 2005, Stott *et al* 2008, Durack and Wijffels 2010, Durack *et al* 2012, 2013, Pierce *et al* 2012). Seawater is the largest buffer for anthropogenically produced CO<sub>2</sub>, a fact that highlights the risk of ocean acidification and potential damage to the marine ecosystem (Caldeira and Wickett 2003, Raven *et al* 2005, Marion *et al* 2009, Kerr 2010, Le Quéré 2010, Le Quéré *et al* 2015). Seawater pH is an important parameter associated with the distribution of inorganic carbon in the ocean.

It is evident from climatology and geosciences that atmospheric relative humidity, ocean salinity and seawater pH are key parameters for observing, modelling and analysing the increasing effects of global warming on ecosystems and society. However, despite their widespread use and relevance, the metrological underpinning of these parameters is inadequate, relies on century-old provisional concepts, lacks traceability to the SI, or suffers from ambiguities and deficiencies of definitions, conventions and measurement techniques. The recent introduction of the international standard TEOS-10, the Thermodynamic Equation of Seawater 2010 (IOC *et al* 2010), has raised new awareness of these long standing and increasingly urgent problems, and has at the same time offered new perspectives for overcoming them.

The definition of relative humidity stands out from that of salinity and pH in that a widely accepted and authorized definition, clearly traceable to the SI, and acting as a *de facto* standard, has been established and promulgated by the WMO<sup>18</sup> since 1950. Nevertheless, the definition does not cover the full range of conditions possible under both industrial and extreme

<sup>18</sup> WMO: World Meteorological Organization, [www.wmo.int](http://www.wmo.int)

natural conditions, and a number of non-standard definitions continue to propagate. The challenge is to provide a definition of relative humidity with a sound thermodynamic basis consistent with the WMO definition yet covering the full range.

TEOS-10 was adopted by the IOC<sup>19</sup> in 2009 (UNESCO 2009) for oceanography with respect to thermodynamic properties of seawater and ice, and by the IUGG<sup>20</sup> in 2011 (IUGG 2011) for marine sciences by a resolution that also recommends the use of the TEOS-10 equation for humid air. While TEOS-10 supersedes the previous oceanographic Equation of State of 1980 (EOS-80, see Unesco 1981), its relation to atmospheric standard equations recommended by JCOMM<sup>21</sup> and WMO (2008) is left unsettled (JCOMM 2014). The formulation and successful international adoption of TEOS-10 was the result of close cooperation between the SCOR<sup>22</sup>/IAPSO<sup>23</sup> Working Group 127 and IAPWS<sup>24</sup> in the years 2006 to 2011, until WG 127 was disbanded in accordance with the rules governing SCOR/IAPSO Working Groups (Pawlowicz *et al* 2012). In order to address metrological problems beyond TEOS-10, the standing Joint Committee on the Properties of Seawater, JCS, was established by SCOR, IAPSO and IAPWS in 2012. In this context, the plan for this position paper arose during meetings held at the BIPM<sup>25</sup> at Sèvres in August 2011 and February 2012, and became definite during a joint meeting of JCS with representatives of CIPM<sup>26</sup>–CCT<sup>27</sup> and CIPM–CCQM<sup>28</sup> at the 16th International Conference on the Properties of Water and Steam in Greenwich, London, UK, in September 2013 (Feistel 2013, IAPWS 2013, Hellmuth *et al* 2014, Pawlowicz *et al* 2014). Under the umbrella of JCS, cooperation commenced between the IAPWS, the international standards developing organization for properties of water and aqueous systems, and the BIPM, the organization that ensures and promotes the global comparability of measurements and provides the coherent International System of units (SI), as defined by the CIPM and described by BIPM (2006). The BIPM-IAPWS cooperation was confirmed at the 2012 and 2014 meetings of CCQM and CCT (BIPM 2012, 2014).

The recent standard for the thermodynamic properties of seawater, TEOS-10, is introduced in the next section. Sections 3–5, respectively, briefly introduce the metrological challenges of ocean salinity, seawater pH and atmospheric relative humidity which are then analysed in greater depth

in the subsequent parts 2 (Pawlowicz *et al* 2015), 3 (Dickson *et al* 2016) and 4 (Lovell-Smith *et al* 2015), respectively, of this series of articles. Those companion papers review the scientific histories of definition and measurement of seawater salinity, seawater pH and atmospheric relative humidity, explain the key roles of those quantities in the climate system, consider the problems of their current definitions and measurement techniques, and provide options for future improvements. In appendices A, B and C in the digital supplement ([stacks.iop.org/MET/53/R1/mmedia](http://stacks.iop.org/MET/53/R1/mmedia)) of this paper, for easy reference, some relevant thermodynamic definitions and properties of chemical potentials, activities and fugacities are summarized from a metrological perspective. Based on TEOS-10, appendix D in the supplement ([stacks.iop.org/MET/53/R1/mmedia](http://stacks.iop.org/MET/53/R1/mmedia)) provides an example for an axiomatic approach to define humidity quantities in a mutually consistent manner.

The authors of the present series of articles are specialists in the different fields of research and technology involved; they are active in several National Metrological Institutes (NMIs) as well as in national and international organizations and institutions such as ASHRAE<sup>29</sup>, BIPM, IAPSO, IAPWS, IUPAC<sup>30</sup>, JCOMM, OSIL<sup>31</sup>, SCOR or WMO. Despite this, it is understood that the perspectives and opinions expressed in these papers do not necessarily reflect official policies of those organizations.

## 2. Thermodynamic Equation of Seawater—2010 (TEOS-10)

The need for accurate, consistent and comprehensive descriptions of the thermodynamic properties of seawater and its equilibria in contact with ice and humid air led to the development of the new oceanographic standard TEOS-10, the Thermodynamic Equation of Seawater 2010 (IOC *et al* 2010). At the core of TEOS-10 are four empirical thermodynamic potentials, officially adopted as IAPWS formulations,

- (i) the specific Helmholtz energy of pure fluid water,  $f^F(T, \rho)$ , as a function of ITS-90 temperature,  $T$ , and mass density,  $\rho$ , commonly known as the IAPWS-95 formulation (Wagner and Pruß 2002, IAPWS 2014),
- (ii) the specific Gibbs energy of hexagonal ice I,  $g^{\text{Ih}}(T, p)$ , as a function of temperature and pressure,  $p$  (Feistel and Wagner 2006, IAPWS 2009b),
- (iii) the specific Gibbs energy of IAPSO Standard Seawater,  $g^{\text{SW}}(S_A, T, p)$ , as a function of Absolute Salinity,  $S_A$ , temperature and pressure (Feistel 2008, IAPWS 2008), and
- (iv) the specific Helmholtz energy of humid air,  $f^{\text{AV}}(A, T, \rho)$ , as a function of dry-air mass fraction,  $A$ , temperature and mass density (Feistel *et al* 2010a, IAPWS 2010).

By design, the identity  $f^{\text{AV}}(0, T, \rho) \equiv f^F(T, \rho)$  holds for humid air in the limiting case of air-free water vapour, and similarly  $g^{\text{SW}}(0, T, p) \equiv f^F(T, \rho) + p/\rho$  is obeyed in the zero-salinity limit of pure liquid water. The four thermodynamic

<sup>19</sup> IOC: Intergovernmental Oceanographic Commission of UNESCO, <http://ioc-unesco.org>

<sup>20</sup> IUGG: International Union of Geodesy and Geophysics, [www.iugg.org](http://www.iugg.org)

<sup>21</sup> JCOMM: Joint Technical Commission for Oceanography and Marine Meteorology, [www.jcomm.info/](http://www.jcomm.info/)

<sup>22</sup> SCOR: Scientific Committee on Oceanic Research, <http://www.scor-int.org>

<sup>23</sup> IAPSO: International Association for the Physical Sciences of the Oceans, <http://iapso.iugg.org/>

<sup>24</sup> IAPWS: International Association for the Properties of Water and Steam, [www.iapws.org](http://www.iapws.org)

<sup>25</sup> BIPM: International Bureau for Weights and Measures, [www.bipm.org/en/about-us/](http://www.bipm.org/en/about-us/)

<sup>26</sup> CIPM: Comité International des Poids et Mesures, [www.bipm.org/en/committees/cipm/](http://www.bipm.org/en/committees/cipm/)

<sup>27</sup> CCT: Consultative Committee on Thermometry, [www.bipm.org/en/committees/cc/cct/](http://www.bipm.org/en/committees/cc/cct/)

<sup>28</sup> CCQM: Consultative Committee for Amount of Substance, [www.bipm.org/en/committees/cc/ccqm/](http://www.bipm.org/en/committees/cc/ccqm/)

<sup>29</sup> ASHRAE: American Society of Heating, Refrigerating and Air-Conditioning Engineers, [www.ashrae.org/](http://www.ashrae.org/)

<sup>30</sup> IUPAC: International Union of Pure and Applied Chemistry, [www.iupac.org](http://www.iupac.org)

<sup>31</sup> OSIL: Ocean Scientific International Ltd., <http://www.osil.co.uk>

potentials of TEOS-10 therefore satisfy axiomatic conditions of *completeness*, *consistency* and *independence*. Here, completeness means that all thermodynamic properties of the pure phases, their phase equilibria and composites can be computed from algebraic combinations of partial derivatives of the potentials (Feistel *et al* 2008, 2010b, IOC *et al* 2010). Consistency means the impossibility of deriving from the potentials two different results for the same quantity. Finally, independence excludes the possibility of deriving the same quantity alternatively from different parts of the four potentials. This rigorous axiomatic approach distinguishes TEOS-10 from earlier collections of empirical correlations for thermodynamic properties of aqueous geophysical systems, such as those recommended by JPOTS<sup>32</sup> in the context of the 1980 Equation of State of Seawater, EOS-80 (Unesco 1981, 1983, Millero 2010, Pawlowicz *et al* 2012), or those recommended by WMO (2008) for the atmosphere.

A rigorous axiomatic approach has many advantages. Special thermodynamic quantities such as fugacity coefficients or enhancement factors of humid air (WMO 2008, Feistel 2012) are sometimes introduced in textbooks on a merely empirical basis in terms of selected correlation equations. In contrast, as a consequence of consistency, independence and completeness, not only can such quantities be computed from TEOS-10 (or its improved successors) in a way that is consistent with virtually any other measured thermodynamic property of the related substances, such quantities can also be defined unambiguously in terms of the corresponding thermodynamic potentials and their independent variables, see appendix D in the digital supplement ([stacks.iop.org/MET/53/R1/mmedia](http://stacks.iop.org/MET/53/R1/mmedia)). Such a uniform method of formally defining and representing all thermodynamic properties with respect to a minimum common set of basic functions may avoid confusion, may more easily permit identification and quantification of differences between seemingly equivalent quantities such as various alternative available definitions of relative humidity, and may establish solid thermodynamic links between quantities that were originally introduced separately and independently, such as correlations for the heat capacity and for the sublimation pressure of ice.

TEOS-10 is also highly accurate. For example, within their common ranges of validity, TEOS-10 is consistent within mutual uncertainties with the CIPM-2001 equation for the density of liquid water (Tanaka *et al* 2001, Harvey *et al* 2009, IAPWS 2009c) and with the CIPM-2007 equation for the density of humid air (Picard *et al* 2008), which are recommended for metrology by the International Committee for Weights and Measures (CIPM).

However, the advantages of TEOS-10 over other collections of equations are not without some computational cost. For convenience of use, easier numerical implementation and increased computation speed, IAPWS has released tailored ‘supplementary’ correlation equations for selected properties that are consistent (within small tolerances) with the four

‘primary’ potential functions of TEOS-10 but are not independent of the latter. Those fits to data points computed from the original equations may possess smaller ranges of validity, or larger uncertainties, or may be expressed in terms of more convenient independent variables. Available, for example, are a Gibbs function of liquid water for oceanographic use (Feistel 2003, IAPWS 2009a), a description of water properties at pressures in the vicinity of 0.1 MPa (Pátek *et al* 2009, IAPWS 2011a), and simple equations for the melting and sublimation curves of pure ice in the  $p$ - $T$  diagram (Wagner *et al* 2011, IAPWS 2011b). The Gibbs-Seawater (GSW) library is a collection of tailored equations for high-speed oceanographic applications, derived from the four basic formulations of TEOS-10 (McDougall and Barker 2011).

Possible future applications of TEOS-10 and IAPWS equations to the atmosphere may be supported additionally by low-temperature extensions for water vapour below 130 K (IAPWS 2012) and for supercooled liquid water (Holten *et al* 2014). While IAPWS-95 describes air-free liquid water, equations for Henry’s constants and partial molar volumes are available for the calculation of properties of dilute aqueous solutions of gases (Fernández-Prini *et al* 2003, IAPWS 2004, Harvey *et al* 2005) whose effects exceed the measurement uncertainty in particular for colligative properties. For example, due to the dissolution of air, the very accurate TEOS-10 pure-water freezing point of 273.152519 K at 101 325 Pa (with an uncertainty of only 2  $\mu$ K because the triple point is at exactly 273.16 K by definition, Feistel and Wagner 2006) is lowered to the common ice point of 273.150019 K (with an estimated uncertainty of 5  $\mu$ K, Harvey *et al* 2013). In contrast, effects of dissolved air on the humid-air saturation pressure, even though of similar magnitude (relative saturation-pressure change of about  $2 \times 10^{-5}$  at standard ocean surface conditions, McDonald 1963), are irrelevant in practice (Harvey *et al* 2005).

### 3. Seawater salinity

Salinity, or more precisely, *Absolute Salinity* (Wright *et al* 2011), is a term used to quantify the total mass of substances dissolved in pure water to form a given mass of seawater. Seawater salinity changes as a result of mixing processes in the water column and, more dramatically, by precipitation and evaporation at the surface, by freezing and melting of sea ice, and by freshwater discharge from rivers and glaciers. In the form of latent heat, the oceans export 50 % to 90 % of the absorbed solar energy to the atmosphere by evaporating water (Josey *et al* 1999, 2013, Emery *et al* 2006, Pierrehumbert 2010, Feistel and Ebeling 2011, Wells 2012). The related global hydrological cycle is reflected in the distribution of sea-surface salinities; arid regions in the trade-wind belts show higher, and humid regions at the equator and at mid-latitudes lower salinities than the global average. While observations of latent heat fluxes are technically demanding and subject to large uncertainties on the order of 20 %, or 30 W m<sup>-2</sup> (Katsaros 2001, Josey *et al* 2013), local long-term trends in salinity are precisely measurable indicators for climatic

<sup>32</sup> JPOTS: Unesco/SCOR/ICES/IAPSO Joint Panel on Oceanographic Tables and Standards (until 1990, Pawlowicz *et al* 2012).

changes in the terrestrial water cycle (Durack and Wijffels 2010, Durack *et al* 2012, 2013, Pierce *et al* 2012). Salinity deviations, in turn, affect the density gradients in the ocean and in this way modify the world-wide marine ‘conveyor belt’ of heat transports. Along with temperature and pressure as key parameters for ocean modelling and observation, salinity significantly influences almost every property of seawater, including its heat capacity, sound speed, refractive index and viscosity (IOC *et al* 2010).

However, the demonstrated usefulness of salinity in oceanography is in striking contrast to the practical inability to directly measure it (Lewis 1980, Millero *et al* 2008). During the last century, only two methods of measuring this total dissolved mass were successfully exploited to establish salinity scales that were officially adopted by oceanography, namely by drying a sample and weighing the residue (Forch *et al* 1902), or by carrying out a complete chemical analysis of the sample’s composition and adding up the constituent masses (Millero *et al* 2008). Neither method is appropriate for the frequent regular measurements required in oceanographic studies, nor are they mutually consistent with one another within requisite accuracy. In practice, oceanographers, for many years, have used the fast, reliable and robust technique described by the Practical Salinity Scale of 1978 (PSS-78; see Unesco 1981) to approximate these other methods. This *Practical Salinity* is defined by using proxy measurements of electrical conductivity relative to that of a bottled standard, natural seawater, reference material called *IAPSO Standard Seawater* (SSW), commercially provided by OSIL<sup>33</sup>. Use of this proxy measurement is possible because the chemical composition of seawater is largely ionic, and the relative proportions of the different ions are almost constant.

An uncertainty level of  $0.002 \text{ g kg}^{-1}$  in dissolved mass fraction (i.e. a relative uncertainty of  $6 \times 10^{-5}$  for typical seawater with a dissolved mass fraction of about  $35 \text{ g kg}^{-1}$ ) is required for routine research and monitoring purposes (SUN 1985, Seitz *et al* 2011). Significant efforts have been made to ensure consistency of salinity measurements to this level over the past century; unfortunately, no robust link has yet been established between any of the salinity definitions and the International System of Units (SI) despite the fact that Practical Salinity was recommended for oceanography in the context of SI units (SUN 1985, Siedler 1998).

As part of the development of TEOS-10, a first step was taken to move away from reliance on the electrical conductivity of SSW as an artefact reference material used to define other seawater properties. Instead, the best available stoichiometric data for the composition of SSW was used to define a *Reference Composition* of seawater. The resulting salinity measure was termed *Reference-Composition Salinity* (Millero *et al* 2008). Although the new TEOS-10 Reference-Composition Salinity Scale has many advantages, there still remain two fundamental problems with the current definition and measurement technology of seawater salinity: (i) a lack

of traceability of salinity measurement results to the SI at the uncertainty required, and (ii) an incomplete knowledge of methods to handle small deviations in the chemical composition of the dissolved salts from the Reference Composition, which regionally occur in the oceans and marginal seas and may have relevant effects on seawater properties.

A proposed new concept that takes advantage of currently available density measurement technology and at the same time leaves established oceanographic practice largely unaffected is a combination of conductivity and SI-traceable density measurement (Seitz *et al* 2011). In this concept, the salinity of SSW samples can be additionally certified (or at least checked) by density measurements in combination with the TEOS-10 equation of state. Implementing a degree of traceability to the SI will significantly improve the reliability of long-term comparisons of observational data, and this may be possible by making additional measurements of density.

A more thorough review of the climatological relevance of seawater salinity, its measurement history, current definition and practice, related problems and deficiencies as well as suggestions for overcoming them are given in the part 2 companion paper (Pawlowicz *et al* 2015).

#### 4. Seawater pH

Seawater pH is a critical parameter for characterizing many important processes in the ocean, and is in turn affected by these processes. In particular, the ocean carbon dioxide ( $\text{CO}_2$ ) system is central to a wide variety of biological processes in the ocean, with  $\text{CO}_2$  being taken up by photosynthetic organisms and remineralized by a variety of respiration processes. Furthermore, a wide variety of calcifying organisms rely on their ability to form calcium carbonate ( $\text{CaCO}_3$ ) for shells or skeletons from the surrounding seawater (Bednaršek *et al* 2012, Smith *et al* 2012). All of these processes affect and are affected by seawater pH, which can exhibit pronounced diurnal and seasonal cycles as well as strong irregular fluctuations related to local mixing and many other factors (Buch 1945, Hofmann *et al* 2011, Doney 2013, Omstedt *et al* 2014).

Over the past two centuries, the release of  $\text{CO}_2$  from human industrial and agricultural practices has resulted in atmospheric  $\text{CO}_2$  levels that are now higher than has been experienced on the Earth for at least the last 800 000 years (Lüthi *et al* 2008). During this period, the oceans have taken up about 30 % of the total amount of  $\text{CO}_2$  produced by human activities (Khaliwala *et al* 2013, IPCC 2013). This addition of anthropogenic  $\text{CO}_2$  to the ocean has reduced the surface ocean pH by about 0.13 to date and is expected to reduce pH by a further 0.3 by the end of this century (Feely *et al* 2004).

The concept of pH was introduced by Sørensen (Sørensen 1909) in terms of a logarithmic function of the hydrogen-ion concentration,  $\text{pH} = -\lg[c(\text{H}^+)/(\text{1 mol L}^{-1})]$ , later replaced by the reduced practical activity (as defined by equation (B.11) in appendix B in the supplement) ([stacks.iop.org/MET/53/R1/mmedia](http://stacks.iop.org/MET/53/R1/mmedia)),

$$\text{pH} = -\lg a(\text{H}^+), \quad (1)$$

<sup>33</sup> Certain commercial products are identified in this paper, but only in order to adequately specify the procedure. Such identification neither constitutes nor implies recommendation or endorsement by any of the organisations represented by the authors.

to better account for ionic interactions in the solution (Sørensen and Linderstrøm-Lang 1924). In recent decades, because of the impossibility of measuring single-ion activities and other, more technical issues, a variety of related but different operationally defined pH-like quantities have been introduced (IUPAC 1985). However, as Bates and Popovych (1981) noted more than 30 years ago, related problems of incompatibility are inevitable. Only for a few selected calibration procedures in media of low ionic strength can the traceability hierarchy between the conceptually defined values, equation (1), and experimentally assessed pH values with inherent uncertainties be established successfully (Baucke 2002, Buck *et al* 2002).

These technical issues are particularly problematic in seawater studies. First, seawater has a high ionic strength, which causes problems when using conventional pH calibration standards. Second, some current research problems such as detection of the long-term anthropogenically driven changes in ocean carbon chemistry over multi-decadal timescales would benefit from an extremely small standard uncertainty in pH measurements such as 0.003 (Newton *et al* 2014), albeit over a fairly narrow range of pH, and this is far smaller than the differences between many of the available operationally defined ‘pH’ quantities (Marion *et al* 2011). The notation ‘pH’ in quotation marks is used to emphasize that, although commonly called pH, these various operationally defined quantities are not identical to the accepted definition, equation (1). It is the decision to define pH as the single-ion activity, equation (1), which causes additional difficulties. Such a single-ion activity is immeasurable by any thermodynamic method and requires a convention for its evaluation (Buck *et al* 2002).

As a result of critical assessments (Marion *et al* 2011) of the various concepts that have been adopted by different groups for pH of seawater, the following steps are suggested for improvement:

First, a suitable nomenclature is needed to keep pH terminology less ambiguous and to make more transparent the alternative definitions and conventions. It is the task of international bodies such as IUPAC or IOC to develop and promote such conventions.

Second, it is recommended that ocean scientists be encouraged to use the same chemical quantity, namely the free concentration or activity of the hydrogen ion, to examine the effect of pH on processes in the oceans. pH can be estimated from measurement (potentiometric, spectrophotometric) and modelling approaches. Accuracy via different definitions and conventions clearly requires consistency with respect to experimental measurements, equilibrium constants, activity coefficients, and buffer solutions that are used for specific approaches.

A third suggestion is that standard formulas be developed for the accurate and unambiguous conversion between the different pH scales that are in practical use, and that their uncertainty budgets be developed. Similar to existing standard equations for conductivity or density of seawater, future empirical correlation equations for the pH of Standard Seawater (or artificial seawater) as functions of salinity, temperature, pressure, CO<sub>2</sub> fugacity and other relevant involved

parameters, consistent with the IAPWS formulation for the dissociation constant of pure water (Bandura and Lvov 2006, IAPWS 2007), should be envisaged as helpful tools to ensure international comparability of measurement results.

Fourth, the development of appropriate numerical models should be pursued to find a suitable convention for activity of the hydrogen ion in seawater or in other aqueous solutions. With the existence of such a convention, metrological traceability to the SI can be developed.

Finally, as a related though separate issue, the development is needed of pH standard buffer solutions which can be used directly to calibrate pH electrodes in potentiometric pH measurements and also in the experimental determination of  $pK_a$  values,  $pK_a \equiv -\lg(K_a)$ , where  $K_a$  is the equilibrium constant for the acid ionization of the indicator dyes for spectrophotometric seawater pH measurements. This requires the development of an artificial seawater and its characterization under different conditions.

A more thorough review of the climatological relevance of seawater pH, its oceanographic measurement history, current definition and practice, related problems and deficiencies as well as suggestions for overcoming them are given in the part 3 companion paper (Dickson *et al* 2016).

## 5. Atmospheric relative humidity

The term *humidity* indicates water vapour, normally admixed with air or other dry gas. Above liquid water and aqueous solutions, above ice, and in pore spaces lined with adsorbed water, water vapour will be found, often with an interface-crossing net flux of molecules. The irreversible net flux only ceases at equilibrium, at which point the chemical potential of water is the same in all coexisting phases. The chemical potential depends primarily on the temperature, but also on the curvature of the interface between gas and liquid, the surface material, the gas mixture, the substances dissolved in the condensed phase and the total pressure. If at equilibrium the condensed phase—either pure liquid water or ice—has a planar interface with the vapour phase, the vapour (or more loosely, the humid gas) is said to be *saturated* and the system is said to be *at saturation*.

In general, the *relative humidity* of a humid gas is the ratio of some humidity quantity to the same quantity at saturation at the same temperature. In particular, the *de facto* standard definition, which has been authorized by the WMO since 1950 (WMO 2008, chapter 4, annex 4.a, pp 1.4–27) and by many other organizations, chooses the optional humidity quantity to be the water-vapour mole fraction. Nevertheless, a variety of alternative definitions using different ratios continue to propagate in particular in climatological and meteorological textbooks or research articles (Katsaros 2001). The problems of definition of relative humidity relate in part to the resulting ambiguity and the lack of a fundamental basis that would support one definition over another. An equally serious and related problem is the inability of the WMO definition (and of most alternative definitions) to cover the full range over which other humidity quantities apply and relative-humidity sensors respond usefully.

The state of a humid gas can be characterized by a wide variety of humidity quantities, including the mixing ratio, the specific humidity, the vapour mole fraction, the vapour pressure, the water-vapour partial pressure and the water fugacity (for details of the definitions see Feistel *et al* 2015a, the digital supplement ([stacks.iop.org/MET/53/R1/mmedia](http://stacks.iop.org/MET/53/R1/mmedia)) of this paper and the part 4 companion paper, Lovell-Smith *et al* 2015). Of these quantities, it is only the water fugacity that is equal in each phase at equilibrium and it is only the relative fugacity that constitutes the proper thermodynamic driving force to saturation.

In irreversible thermodynamics, fluxes of heat and matter result from Onsager forces which are combinations of gradients of temperature and chemical potentials (de Groot and Mazur 1962, Falkenhagen *et al* 1971, Glansdorff and Prigogine 1971, Landau and Lifschitz 1974). In the climate system, the most relevant differences of chemical potentials are those of water between ocean, ice cover and humid air, at the boundary of and within the atmosphere. These differences can be exactly expressed in terms of the relative fugacity (see appendix C in the supplement [stacks.iop.org/MET/53/R1/mmedia](http://stacks.iop.org/MET/53/R1/mmedia)) of water vapour in the atmosphere, which is one of the options for defining relative humidity. To a reasonable approximation, the spatial distribution of the relative fugacity of water vapour can be described by that of the relative humidity in the WMO definition (Erikson 1965, Kraus 1972, Hansen and Takahashi 1984, IOC *et al* 2010, Feistel *et al* 2010a, Feistel and Ebeling 2011, Li and Chylek 2012, Li *et al* 2015). At the sea surface, the thermodynamic driving force for evaporation is the difference between the chemical potentials of water in the ocean and in the atmosphere (Kraus and Businger 1994, IOC *et al* 2010). Thus, relative humidity immediately above the sea surface essentially controls the latent heat export from the ocean, which in turn constitutes the dominant energy source driving global weather and climate processes (Chahine 1992, Trenberth *et al* 2005, Schneider *et al* 2010, Pierce *et al* 2011, Josey *et al* 2013, Bony *et al* 2015, Schiermeier 2015).

TEOS-10 has demonstrated the possibility and value of a rigorous axiomatic foundation of the description of sea-water–ice–air thermodynamic properties. Using the same approach, development of a consistent ‘axiomatic’ definition and nomenclature of humidity quantities, as derived from a small set of empirical fundamental equations, will help to provide clarity and consistency within the wider humidity community. One such axiomatic approach to humidity, which uses an enhanced subset of TEOS-10, is outlined in appendix D in the supplement ([stacks.iop.org/MET/53/R1/mmedia](http://stacks.iop.org/MET/53/R1/mmedia)).

A more thorough review of the climatological relevance of relative humidity, its measurement history, current definition and practice, related problems and deficiencies as well as suggestions for overcoming them are given in the part 4 companion paper (Lovell-Smith *et al* 2015).

## 6. Discussion and conclusion

Long-term data records of meteorological and oceanographic observations covering several decades are fundamental for the detection and quantification of climatic changes and for the verification of numerical climate models developed for

the prediction of future physical and chemical conditions in the atmosphere and in the ocean. For this purpose, it is indispensable that the measurement results collected over the years from locations all over the globe are mutually comparable and free of spurious trends and discontinuities. Metrological comparability of measurement results for quantities of a given kind requires metrological traceability to the same reference (VIM 2012). It is demonstrated in detail in the articles of this review that salinity, pH and relative humidity only incompletely satisfy important conditions implied by comparability, namely

- metrological traceability to shared primary standards possessing high temporal stability, preferably to the International System of Units (SI),
- unambiguous and clearly specified definitions of the measured quantities,
- consistency of empirical equations applied for the conversion, combination or correction of different values involved in the measurement or comparison procedures, and
- provision of realistic uncertainty estimates for each measurement result and each derived quantity.

Seawater salinity, seawater pH and atmospheric relative humidity are key climatological observables whose long-term trends are known to be small but fundamental indicators for changes in the global hydrological cycle, in ocean–atmosphere interaction and in the terrestrial balances of energy and matter. With the Thermodynamic Equation of Seawater 2010 (TEOS-10), a new axiomatic set of equations has recently become available that consistently and comprehensively describes the thermodynamic properties of seawater, ice and humid air, as well as their mutual phase equilibria and composites such as sea ice or clouds. The development of TEOS-10 by the SCOR/IAPSO Working Group 127 in close cooperation with IAPWS has raised new awareness of various deficiencies in the definition and measurement practice of seawater salinity, seawater pH and atmospheric relative humidity regarding traceability to the SI or inconsistent, incomplete or ambiguous definitions or measurement techniques.

More than a century ago, Knudsen and Sørensen developed the first official international salinity scale along with the definition of standard seawater as a metrological primary reference material for oceanographic salinity measurements (Culkin and Smed 1979). At about the same time, Sørensen defined pH as a measure of acidity of solutions such as seawater (Sørensen 1909), and Lewis introduced fugacity as a real-gas substitute for the ideal-gas partial pressure of gaseous mixtures (Lewis 1900). Notwithstanding, partial pressure of water vapour has been the basis of international standards for relative humidity since 1950, and further alternative, inconsistent definitions are frequently used in textbooks, research papers or numerical models in climatology and meteorology. Seawater salinity and pH have been measured with respect to many different scales, however, none of them provided proper traceability to the SI.

The conclusion from this review is that new SI-based definitions need to be introduced or new methods must be established which uniquely link the quantities of interest to

SI-traceable measurement results. Such links may consist of equations (or ‘conventions’), such as the TEOS-10 equation for the density of standard seawater which permits the calculation of Absolute Salinity from measurements of temperature, pressure and density, all of the latter traceable to the SI (Seitz *et al* 2011). A similar approach is possible for the relative fugacity making use of the TEOS-10 equation of state of humid air (Feistel 2012, Feistel *et al* 2015a, 2015b). The development of an equation for the activity of the hydrogen ion in seawater derived from Pitzer equations has also been suggested recently (Marion *et al* 2011).

The general metrological concept of separating the definition of a quantity from the set of instructions (*‘mise en pratique’*, see BIPM 2006, or ‘operational definition’) that in practice allows its measurement at the lowest level of uncertainty is also promising for the climatological key observables seawater salinity, pH and atmospheric relative humidity. For example, the options of defining salinity in terms of the solute mass fraction, pH in terms of the hydrogen-ion activity, and relative humidity in terms of the water-vapour fugacity are theoretically well-founded and consistent with traditional use. For practical measurements, alternative quantities may be more suitable *surrogate measurands* if they are traceable to the SI and linked to the quantity in question by a robust theoretical or empirical relation. In the cases considered in this series of papers, preferred surrogate properties that obey these conditions may be seawater density, optical attenuation of an indicator dye, and dew-point temperature, which may be measured and used to calculate salinity, pH and relative fugacity, respectively, rather than measuring or realizing these quantities directly. The target quantities are then calculated from those measurands by certain, explicitly specified empirical equations (such as those of TEOS-10) that should constitute an integral part of the particular measurement standard.

Following this approach, establishing traceability to SI of salinity, pH and relative-humidity measurement results may include (Feistel 2013, 2015, Hellmuth *et al* 2014)

- (i) the rigorous theoretical definition of those key quantities in terms of thermodynamic properties of seawater and humid air, such as composition variables or chemical potentials,
- (ii) the specification of one or several surrogate properties that strongly correlate with the respective original quantity, that are traceable to the SI, and are conveniently measurable in practice to the requisite accuracy,
- (iii) the development and formal adoption of equations that relate the original quantities to their surrogates,
- (iv) the development and subsequent specification of best-practice procedures for measuring the surrogate properties, including the calibration rules that establish the links to SI units,
- (v) the estimate of uncertainties involved in steps (i) to (iv),
- (vi) the development of recommended conversion procedures between legacy data and the new quantities, and
- (vii) the release of recommendations regarding steps (i) to (vi) on an international and interdisciplinary level in the form of published resolutions, guides or manuals.

First steps in these directions have been undertaken in the cooperation between BIPM and IAPWS under the umbrella of the Joint SCOR/IAPWS/IAPSO Committee on the Properties of Seawater, JCS (BIPM 2012, 2014).

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## Digital Supplement of the 2015 Metrologia article:

### **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  $\mathbf{X} = (X_1, \dots, X_N)$  can be written in the form

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

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,  $\mu_i$ , are the *chemical potentials*,

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

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

$$\sum_{i=1}^N X_i d\mu_i(\mathbf{X}, T, p) = 0. \quad (\text{A.3})$$

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

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

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  $X_n = M_w$  is the mass of water in seawater, and  $X_i = M_i$  are the masses of the solutes,  $i = 1, \dots, N-1$ , the related mass-based chemical potential of water in seawater follows from (A.2) to be

$$\mu_w = \frac{\partial G}{\partial X_n} = g - S \frac{\partial g}{\partial S}, \quad (\text{A.5})$$

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,  $i = 1, \dots, N - 1$ , the mole-based chemical potential of water in humid air is computed from (A.2) to give

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

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  $\mu_i$  is the chemical potential of a substance  $i$ , the modified function,

$$\mu_i^*(\mathbf{X}, T, p) = \mu_i(\mathbf{X}, T, p) + A_i + B_i T, \quad (\text{A.7})$$

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 5<sup>th</sup> ICPS<sup>1</sup> 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 Pr u , 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,  $\mu_i^{\text{id}}$ , takes the asymptotic form (Planck, 1888; Guggenheim, 1949; Falkenhagen et al., 1971; Prausnitz et al., 1999)

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

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

$$\mu_i^0(T, p) = RT \lim_{x_i \rightarrow 0} \left\{ \frac{\mu_i(\mathbf{X}, T, p)}{RT} - \ln x_i \right\}. \quad (\text{A.9})$$

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

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<sup>1</sup> ICPS: International Conference on the Properties of Steam, held by a forerunner of IAPWS, [www.iapws.org](http://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*,  $\lambda_i$ , of a substance  $i$  in a mixture is defined by (Guggenheim, 1949; Harrison, 1965; Kittel, 1969)

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

where  $\mu_i$  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,  $\lambda_i$  and  $\lambda_i'$ , may differ by an arbitrary factor of the form

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

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

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

where  $\mu_i^0$  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

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

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,  $(\mu_i - \mu_i^0)/(RT)$ , of the hydrogen ion (Himmel et al., 2010),

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

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

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

with the limiting property

$$\lim_{x_i \rightarrow 0} \gamma_i(x_i, T, p) = 1. \quad (\text{B.7})$$

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)

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

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

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

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

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

where  $m^\circ$  is an arbitrary constant value, usually chosen as a standard-state molality of  $m^\circ = 1 \text{ mol kg}^{-1}$  (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),

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

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

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

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,  $\mu_w(m_i)$ , and that of the pure solvent,  $\mu_w(0)$ , as a function of the solute molality,  $m_i$ , expressed by means of the *osmotic coefficient*,  $\phi(m_i)$ ,

$$\mu_w(m_i) - \mu_w(0) = -m_i RT \phi(m_i), \quad (\text{B.13})$$

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),

$$d[m_i(1 - \phi)] + m_i d \ln \gamma_i^{(m)} = 0. \quad (\text{B.14})$$

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”,  $\psi(m_i) = 1 - \phi + \ln(\gamma_i^{(m)})$ , in the form (Feistel and Marion, 2007),

$$\phi = 1 + m_i \frac{d\psi}{dm_i}, \quad \ln \gamma_i^{(m)} = \frac{d(m_i \psi)}{dm_i}. \quad (\text{B.15})$$



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),  $G^{\text{ex}} = m_i RT \psi$ .

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

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

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  $\text{Na}^+$  plus 1 mole of the anion  $\text{Cl}^-$ . 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  $\text{MgSO}_4$ , that is, 3 total moles of “salt”, the final solution is in no way different from that obtained by dissolving 1 mole of  $\text{Na}_2\text{SO}_4$  and 1 mole of  $\text{MgCl}_2$ , 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  $m = 1.1605813 \text{ mol kg}^{-1}$  (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)

$$f_v(x, T, p) = f_v^0(T) \exp\left\{\frac{\mu_v(x, T, p)}{RT}\right\}, \quad (\text{C.1})$$

where  $x$  is the mole fraction of water vapour in the mixture,  $\mu_v$  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

$$f_v^0(T) \equiv xp \exp\left\{-\frac{\mu_v^{\text{id}}(x, T, p)}{RT}\right\}, \quad (\text{C.2})$$

where  $\mu_v^{\text{id}}$  is the chemical potential in the ideal-gas limit, i.e.,

$$\mu_v^{\text{id}}(x, T, p) \equiv RT \ln \frac{p}{p_0} + \lim_{p \rightarrow 0} \left\{ \mu_v(x, T, p) - RT \ln \frac{p}{p_0} \right\}. \quad (\text{C.3})$$

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)

$$\mu_v^{\text{id}}(x, T, p) = g_0 + \int_{T_0}^T \left(1 - \frac{T}{T'}\right) c_p^{\text{id}}(T') dT' + RT \ln \frac{xp}{p_0}, \quad (\text{C.4})$$

where  $c_p^{\text{id}}(T)$  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),  $g_0 = M^W \times 2\,501\,460.964\,842\,82 \text{ J kg}^{-1}$ ,  $T_0 = 273.16 \text{ K}$ ,  $p_0 = 253\,269\,701\,789.662 \text{ Pa}$ ,  $R = M^W \times 461.523\,64 \text{ J kg}^{-1} \text{ K}^{-1}$ , where  $M^W = 18.015\,268 \text{ g mol}^{-1}$  is the molar mass of water. The function  $c_p^{\text{id}}(T)$  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

$$f_v^0(T) = p_0 \exp\left\{-\frac{g_0}{RT} - \frac{1}{R} \int_{T_0}^T \left(\frac{1}{T} - \frac{1}{T'}\right) c_p^{\text{id}}(T') dT'\right\}. \quad (\text{C.5})$$

In eq. (C.1) the factor,  $\lambda_v$ ,

$$\lambda_v \equiv \exp\left\{\frac{\mu_v(x, T, p)}{RT}\right\} \quad (\text{C.6})$$

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

$$\lambda_v^{\text{id}}(x, T, p) = \exp\left\{\frac{\mu_v^{\text{id}}(x, T, p)}{RT}\right\} = \frac{xp}{f_v^0(T)}. \quad (\text{C.7})$$

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*,  $\varphi_v$ , is used to quantify the deviation of the fugacity from the partial pressure, in the form,

$$f_v(x, T, p) = xp\varphi_v(x, T, p); \quad (\text{C.8})$$

it equals  $\varphi_v = \lambda_v / \lambda_v^{\text{id}}$  with the limiting property,

$$\lim_{p \rightarrow 0} \varphi_v(x, T, p) = 1. \quad (\text{C.9})$$

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

$$\psi_f(x, T, p) = \frac{f_v}{f_v^{\text{sat}}} \equiv \frac{f_v(x, T, p)}{f_v(x^{\text{sat}}, T, p)} = \frac{\lambda_v(x, T, p)}{\lambda_v(x^{\text{sat}}, T, p)}. \quad (\text{C.10})$$

Here,  $x^{\text{sat}}$  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  $\lambda_v$  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)

$$\psi_f(x, T, p) = \exp\left\{\frac{\mu_v(x, T, p) - \mu_w(1, T, p)}{RT}\right\} \quad (\text{C.11})$$

where  $\mu_v$  and  $\mu_w$ , 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  $\mu_w$  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,  $\mu_w$ , in eq. (C.11) may be substituted by the chemical potential of ice,  $\mu_{\text{Ih}}$ . 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

$$\psi_f(x, T, p) = \frac{\lambda(x, T, p)}{\lambda(x^{\text{sat}}, T, p)} = \exp\left\{\frac{\mu_v(x, T, p) - \mu_v(x^{\text{sat}}, T, p)}{RT}\right\}. \quad (\text{C.12})$$

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  $x_w$ ,

$$\mu_v(x, T, p) = \mu_w(x_w, T, p), \quad (\text{C.13})$$

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

$$\mu_v(x^{\text{sat}}, T, p) = \mu_w(1, T, p). \quad (\text{C.14})$$

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

$$\psi_f(x, T, p) = \exp\left\{\frac{\mu_w(x_w, T, p) - \mu_w(1, T, p)}{RT}\right\} = a_w(m, T, p), \quad (\text{C.15})$$

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  $\varphi_v(x, T, p)$ , 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  $e^{\text{sat}}(T)$ , we have

$$\mu_v(\mathbf{1}, T, e^{\text{sat}}) = \mu_w(\mathbf{1}, T, e^{\text{sat}}). \quad (\text{C.16})$$

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

$$f(x^{\text{sat}}, T, p) = \frac{\varphi_v(\mathbf{1}, T, e^{\text{sat}})}{\varphi_v(x^{\text{sat}}, T, p)} \pi(T, p). \quad (\text{C.17})$$

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

$$\pi(T, p) \equiv \exp\left\{\frac{\mu_w(\mathbf{1}, T, p) - \mu_w(\mathbf{1}, T, e^{\text{sat}})}{RT}\right\} = \frac{\lambda_w(T, p)}{\lambda_w(T, e^{\text{sat}})} = \exp\left\{\frac{1}{RT} \int_{e^{\text{sat}}(T)}^p v_w(T, p') dp'\right\}, \quad (\text{C.18})$$

where  $\lambda_w$  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  $x^{\text{sat}}$  is specified with respect to air-saturated water, eq. (C.17) for the enhancement factor must be replaced by

$$f(x^{\text{sat}}, T, p) \equiv \frac{x^{\text{sat}} p}{e^{\text{sat}}(T)} = x_w \frac{\varphi_v(\mathbf{1}, T, e^{\text{sat}})}{\varphi_v(x^{\text{sat}}, T, p)} \pi(T, p), \quad (\text{C.19})$$

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

$$f_v^{\text{sat}}(T, p) = f_v(x^{\text{sat}}, T, p) = x^{\text{sat}} p \varphi_v(x^{\text{sat}}, T, p) = x_w e^{\text{sat}} \varphi_v(\mathbf{1}, T, e^{\text{sat}}) \pi(T, p), \quad (\text{C.20})$$

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

$$x_w = 1 - \beta(p - e^{\text{sat}}(T)). \quad (\text{C.21})$$

Here,  $\beta$  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  $e^{\text{sat}}(T)$  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  $\varphi_v$  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<sup>2</sup> 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  $g^{lh}(T, p)$** : Specific Gibbs energy of ice Ih expressed in terms of the independent variables  $T, p$ . As a thermodynamic potential,  $g^{lh}$  provides all thermodynamic properties of ice Ih from algebraic combinations of its partial derivatives. The freely adjustable parameters of  $g^{lh}$  must be specified consistently with those of  $g^{AV}$ , see App. A.
7. **Molar mass  $M^W$** : The molar mass of water is  $M^W = 0.018\ 015\ 268\ \text{kg mol}^{-1}$  (IAPWS, 2001). If the isotopic composition of water vapour in humid air is different from that of VSMOW<sup>3</sup>, 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  $M^A = 0.028\ 965\ 46\ \text{kg mol}^{-1}$  (Picard et al., 2008). If the chemical or isotopic composition of dry air in humid air may vary, such as by a changing

<sup>2</sup> also known as "dry-bulb temperature" in meteorology (WMO, 2008)

<sup>3</sup> VSMOW: Vienna Standard Mean Ocean Water (IAPWS, 2001)

fraction of CO<sub>2</sub> 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<sup>4</sup>  $R$** : The CODATA 2010 value is  $R = 8.314\,4621\text{ J K}^{-1}\text{ mol}^{-1}$  (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  $R = \frac{M^w}{T} \lim_{p \rightarrow 0} \left\{ p \frac{\partial}{\partial p} g^{AV}(0, T, p) \right\}$ , 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  $g^V(T, p)$** : The Gibbs function of water vapour is available from the Gibbs function of humid air in the limit of vanishing dry air,  $g^V(T, p) = g^{AV}(0, T, p)$ . 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  $\mu^V$** :  $\mu^V(T, p)$  is computed from the Gibbs function of water vapour by the relation  $\mu^V = g^V$ .
3. **Chemical potential of liquid water  $\mu^w$** :  $\mu^w(T, p)$  is computed from the Gibbs function of liquid water by the relation  $\mu^w = g^w$ .
4. **Chemical potential of ice Ih  $\mu^{lh}$** :  $\mu^{lh}(T, p)$  is computed from the Gibbs function of ice Ih by the relation  $\mu^{lh} = g^{lh}$ .
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  $\mu^{lh}(T_t, p_t) = \mu^w(T_t, p_t) = \mu^V(T_t, p_t)$ .
6. **Specific gas constants  $R_w, R_A$** : From the basic quantities (7), (8) and (9), the specific gas constants  $R_w \equiv R/M^w$  of water and  $R_A \equiv R/M^A$  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

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



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

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

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

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

$$R_{AV}(A) = R/(x_A M^A + x M^W) \equiv A R_A + (1-A) R_W$$

10. **Gibbs function  $g^{AV,id}(A, T, p)$ :** Specific Gibbs energy of ideal-gas humid air expressed in terms of the independent variables  $A, T, p$ . As a thermodynamic potential,  $g^{AV,id}$  provides all thermodynamic properties of ideal-gas humid air from algebraic combinations of its partial derivatives.  $g^{AV,id}$  is the mathematical low-pressure limit of  $g^{AV}$ , obtained from the basic quantity (4) and the derived quantity (9), in the form

$$g^{AV,id}(A, T, p) = R_{AV} T \ln \frac{p}{p_0} + \lim_{p \rightarrow 0} \left\{ g^{AV}(A, T, p) - R_{AV} T \ln \frac{p}{p_0} \right\}.$$

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  $\mu_W^{AV}$ :**  $\mu_W^{AV}(x, T, p)$  is computed from the Gibbs function of humid air by the relation  $\mu_W^{AV} = g^{AV} - A g_A^{AV} \equiv g^{AV} - A(\partial g^{AV} / \partial A)_{T,p}$  and from (8).
12. **Chemical potential of ideal-gas water vapour in humid air  $\mu_W^{AV,id}$ :**  $\mu_W^{AV,id}(x, T, p)$  is computed from the Gibbs function of ideal-gas humid air (10) by the relation  $\mu_W^{AV,id} = g^{AV,id} - A g_A^{AV,id} \equiv g^{AV,id} - A(\partial g^{AV,id} / \partial A)_{T,p}$  and from (8).
13. **Freezing temperature of water  $T_{frz}$ :**  $T_{frz}(p)$  is computed implicitly from the equation for the phase equilibrium between liquid water and ice,  $\mu^W(T_{frz}, p) = \mu^{lh}(T_{frz}, p)$ .
14. **Saturated vapour pressure of water  $e^{sat}$ :**  $e^{sat}(T)$  is computed implicitly from the equation for the phase equilibrium between liquid water and water vapour,  $\mu^W(T, e^{sat}) = \mu^V(T, e^{sat})$ .
15. **Sublimation pressure of ice  $e^{subl}$ :**  $e^{subl}(T)$  is computed implicitly from the equation for the phase equilibrium between ice lh and water vapour,  $\mu^{lh}(T, e^{subl}) = \mu^V(T, e^{subl})$ .
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  $p_V = x p$ .
18. **Dew-point temperature  $T_d$ :** The dew-point temperature  $T_d(x, p)$  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,  $\mu_W^{AV}(x, T_d, p) = \mu^W(T_d, p)$ .

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,  $\mu_w^{AV}(x, T_f, p) = \mu^{lh}(T_f, p)$ .

20. **Saturated water-vapour mole fraction  $x^{\text{sat}}$** : The saturated water-vapour mole fraction  $x^{\text{sat}}(T, p)$ , with respect to liquid water or ice, is found by solving the equation for the phase equilibrium between humid air and liquid water,  $\mu_w^{AV}(x^{\text{sat}}, T, p) = \mu^w(T, p)$ , or the equation for the phase equilibrium between humid air and ice lh,  $\mu_w^{AV}(x^{\text{sat}}, T, p) = \mu^{lh}(T, p)$ , 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  $f(T, p) = x^{\text{sat}} p / e^{\text{sat}}(T)$  or  $f(T, p) = x^{\text{sat}} p / e^{\text{subl}}(T)$ , respectively. Here  $x^{\text{sat}}$ ,  $e^{\text{sat}}$  and  $e^{\text{subl}}$  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  $x^{\text{sat}}$  and  $T$  are known, is computed implicitly from the equation for the phase equilibrium between liquid water and humid air,  $\mu^w(T, f e^{\text{sat}} / x^{\text{sat}}) = \mu_w^{AV}(x^{\text{sat}}, T, f e^{\text{sat}} / x^{\text{sat}})$ , or the equation for the phase equilibrium between ice lh and humid air,  $\mu^{lh}(T, f e^{\text{subl}} / x^{\text{sat}}) = \mu_w^{AV}(x^{\text{sat}}, T, f e^{\text{subl}} / x^{\text{sat}})$ , respectively. Here  $e^{\text{sat}}(T)$  and  $e^{\text{subl}}(T)$  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  $f_v(x, T, p) = x p \exp\left\{\frac{\mu_w^{AV}(x, T, p) - \mu_w^{AV, id}(x, T, p)}{R_w T}\right\}$ .

**(b) Fugacity of pure water vapour  $f_v$** : For the absence of dry air, the limit  $x \rightarrow 1$  can readily be carried out for the fugacity of water vapour, as

$$f_v(1, T, p) = p \exp\left\{\frac{\mu_w^{AV}(1, T, p) - \mu_w^{AV, id}(1, T, p)}{R_w T}\right\} \equiv p \exp\left\{\frac{\mu^v(T, p) - \mu^{v, id}(T, p)}{R_w T}\right\}.$$

23. **Fugacity coefficient of water vapour in humid air  $\varphi_v$** : The deviation of the fugacity from the partial pressure of water vapour, caused by non-ideal effects, is represented by the fugacity coefficient  $\varphi_v(x, T, p) = \frac{f_v(x, T, p)}{x p} \equiv \exp\left\{\frac{\mu_w^{AV}(x, T, p) - \mu_w^{AV, id}(x, T, p)}{R_w T}\right\}$

24. **Relative fugacity of humid air  $\psi_f$** : The relative fugacity of water vapour in humid air is

$$\text{defined as } \psi_f(x, T, p) = \exp\left\{\frac{\mu_w^{AV}(x, T, p) - \mu^w(T, p)}{R_w T}\right\} \equiv \frac{f_v(x, T, p)}{f_v(x^{\text{sat}}, T, p)} \text{ with respect to liquid}$$

$$\text{water and } \psi_f(x, T, p) = \exp\left\{\frac{\mu_w^{AV}(x, T, p) - \mu^{lh}(T, p)}{R_w T}\right\} \equiv \frac{f_v(x, T, p)}{f_v(x^{\text{sat}}, T, p)} \text{ with respect to ice.}$$

25. **Relative fugacity of water vapour  $\psi_f$** : In the limit of vanishing air, the relative fugacity of

$$\text{water vapour is } \psi_f(1, T, p) = \exp\left\{\frac{\mu^v(T, p) - \mu^w(T, p)}{R_w T}\right\} \text{ with respect to liquid water, and}$$

$$\psi_f(1, T, p) = \exp\left\{\frac{\mu^v(T, p) - \mu^{lh}(T, p)}{R_w T}\right\} \text{ with respect to ice.}$$

26. **Full-range relative humidity  $\psi_{full}$** : The relative humidity of moist air or water vapour is

$$\text{defined as } \psi_{full}(x, T, p) = \frac{p_v(x, p)}{p_v^{ref}(T, p)} = \frac{p_v(x, p)}{e^{sat}(T)f(T, p)} \text{ where } f(T, p) = 1 \text{ for } e^{sat}(T) > p.$$

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
$A^{\text{sat}}$	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
$c_p^{\text{id}}$	ideal-gas molar isobaric heat capacity	App C
$e^{\text{sat}}$	water-vapour pressure at saturation	Pure water
$e^{\text{subl}}$	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
$f_V^{\text{sat}}$	fugacity of water in vapour phase at saturation	
$G$	Gibbs energy	App A
$G^{\text{ex}}$	excess Gibbs free energy	App B
$g_0$	arbitrary constant molar energy	App C
$g^{\text{AV}}$	specific Gibbs energy of humid air	App D
$g^{\text{Ih}}$	specific Gibbs energy of hexagonal ice I	
$g^{\text{V}}$	specific Gibbs energy of water vapour	App D
$g^{\text{W}}$	specific Gibbs energy of liquid water	App D
$g^{(m)}$	molar Gibbs energy	App A
$M$	sample mass	App A
$M^{\text{A}}$	molar mass of dry air	App D $M^{\text{A}} = 0.028\,965\,46\text{ kg mol}^{-1}$
$M_i$	mass of solute molecules	App A
$M^{\text{W}}$	molar mass of water	App A, D $M^{\text{W}} = 0.018\,015\,268\text{ kg mol}^{-1}$
$M_{\text{W}}$	mass of water molecules in solution	App A
$m$	solute molality (with subscripts)	
$m^0$	standard-state molality	$m^0 = 1\text{ mol kg}^{-1}$
$N$	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 <sup>5</sup>	$R = 8.314\,4621\text{ J K}^{-1}\text{ mol}^{-1}$
$R_{\text{A}}$	specific gas constant of dry air	$R_{\text{A}} = R / M^{\text{A}}$ , App D
$R_{\text{AV}}$	specific gas constant of humid air	App D
$R_{\text{W}}$	specific gas constant of water	$R_{\text{W}} = R / M^{\text{W}}$
$S$	solute mass fraction	App A

<sup>5</sup> The CODATA 2010 value reported here has recently been updated to  $R = 8.314\,4598\text{ J K}^{-1}\text{ mol}^{-1}$ , <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
$T_{\text{frz}}$	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
$x^{\text{sat}}$	mole fraction at saturation	
$x_w$	mole fraction of liquid water	App C
$\beta$	reciprocal Henry's constant of dry air	App C
$\varphi_v$	fugacity coefficient of water vapour	
$\phi$	osmotic coefficient	App B, C
$\gamma$	molal activity coefficient (with subscripts)	
$\gamma^{(m)}$	practical activity coefficient	App B
$\lambda$	absolute activity	App B
$\mu$	chemical potential (with super/subscripts)	
$\pi$	Poynting correction factor of liquid water	App C
$\psi$	activity potential	App B
$\psi$	relative humidity (with super/subscripts)	
$\psi_{\text{full}}$	relative humidity in the extended range, $e^{\text{sat}} > p$	App D