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Metrological challenges for measurements of key climatological observables. Part 4: atmospheric relative humidity

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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. In this paper, we examine the climatologically relevant atmospheric relative humidity, noting fundamental deficiencies in the definition of this key observable. The metrological history of this quantity is reviewed, problems with its current definition and measurement practice 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, such as are suggested here, for what are long-standing metrological problems.

Keywords: relative humidity, meteorology, metrology, IAPWS, BIPM, definitions, climate

(Some figures may appear in colour only in the online journal)
1. Introduction

As part of a series of papers examining metrological challenges for measurements of key climatological observables (Feistel et al. 2016, Pawlowicz et al. 2016, Dickson et al. 2016), in this paper we examine 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, \( \mu \), of each component is the same in all coexisting phases. The vapour-phase water mole fraction, \( x_n = n_w / (n_w + n_A) \), where \( n_w \) and \( n_A \) respectively, are the numbers of water and air molecules, at equilibrium depends primarily on the temperature, \( T \), 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 on the total pressure, \( p \). If at equilibrium the condensed phase—either 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 at saturation.

In general, the relative humidity (RH), \( \psi \), of humid air\(^8\) is the ratio of some non-negative humidity quantity, \( z \), to the same quantity at saturation, \( z_{sat} \), at the same temperature, i.e.,

\[
\psi = \frac{z}{z_{sat}} = \frac{z(x, T, p)}{z(x_{sat}, T, p_{sat})},
\]

where the superscript ‘(s)’ indicates that the conditions at saturation need be specified as an additional relation imposed on the independent quantities \( x_{sat} \) and \( p_{sat} \). Choices for \( z \) have included the water-vapour mole fraction, \( x \), the mixing ratio, \( r = M_w / M_A \), the specific humidity, \( q = M_w / (M_w + M_A) \), the pure water vapour pressure, \( e \), the water-vapour partial pressure, \( p_v = x p \), and the fugacity of water vapour, \( f_v \). Here, \( M_w \) and \( M_A \) represent the masses of water vapour and dry air, respectively, in a unit volume. A preferred choice for \( s \) has been \( p = p_{sat} \), i.e., saturation is established via an isobaric process in contrast to, say, isothermal compression or vapour injection at constant volume. The subscript \( V \) is used here to distinguish fugacity from the common symbol \( f \) for the water-vapour enhancement factor. When expressing RH in percent, the unit symbol \%rh will be used in this paper.

Note, however, that equation (1) requires the specification of a saturated gas phase in order to calculate \( z(x_{sat}, T, p_{sat}) \); this condition is not trivially obeyed under any practical circumstances and essentially constricts the possibility of possible RH definitions by the form of equation (1). To date, the most important definition has set \( z = x \), with which \( \psi = p / p_{sat} \) is equivalent to \( z = p_v \). This de facto standard definition (as it will be referred to in this paper) has been authorized by the WMO\(^9\) since 1950 and by many other organizations (see section 3.2). However, the standard definition is valid only over a limited range, and attempts to create full-range definitions have lacked both clear theoretical basis and official sanction. Finally, a variety of other non-standard definitions (e.g., with \( z = q \) and \( z = r \)) continue to propagate in particular in climatological and meteorological textbooks or research articles.

We present in section 2 a brief review of the importance of relative humidity in climate dynamics, and emphasize the related need for its unambiguous definition and consistent measurement, traceable to the International System of Units, the SI. Apparently self-evident, this requirement is by no means a metrologically well-settled subject, as is evident from the history reviewed in section 3. In sections 4 and 5, the core of this paper provides an analysis of the various inconsistent definitions in use for relative humidity, especially in geophysical and climate research (Katsaros 2001), which neither cover the complete range of reasonable applicability (Böse and Mitter 2004, Lovell-Smith and Pearson 2006) nor represent physically rigorous measures of the thermodynamic driving force to equilibrium. To provide a consistent solution to these long-standing problems, we suggest in section 6 an axiomatic approach based on equations of state for humid air, liquid water and ice that are parts of TEOS-10, the Thermodynamic Equation of Seawater 2010 (IOC et al. 2010). This approach

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\(^8\) Although this section primarily concerns humid air and water vapour, much of the discussion can be generalized to apply to any humid gas or to different samples of humid air of varied composition.

is supported by an explicit example specified in appendix D in the supplement of the part 1 companion paper (Feistel et al. 2016).

2. Climatological relevance

Hypothetically, our early ancestors developed sweating for effective cooling in the hot but arid African savannah, likely more than a million years ago (Rantala 2007). At least since then, the spatially and temporally widely varying amounts of water vapour in the air of the terrestrial climate zones from deserts to jungles have influenced our social evolution, our living conditions, agriculture, technology, ways of life and even our spoken language (Everett et al. 2015). As a result of this variety, humidity problems are investigated today in various branches of science and engineering, from air conditioning to weather forecast.

Water is a key player in terrestrial climate dynamics; Heinrich Hertz in 1885 was perhaps the first who painted the physical picture of climate as a ‘gigantic steam engine’ (Mulligan and Hertz 1997, p. 41). Related knowledge is still insufficient because processes involving water in the atmosphere are very complex, theoretically and observationally demanding, and subject to significant uncertainties (Chahine 1992, Schneider et al. 2010, Randall 2012, Gimeno 2013, Josey et al. 2013). In contrast to the greenhouse effect, the hydrological cycle has received only marginal attention in the recent public debates on global warming related to carbon dioxide (CO₂) emissions. For example, the observed seasonal cycle of ocean temperatures cannot be explained by merely the radiation balance without latent heat export which, similar to that of the sweaty human skin, is controlled by ambient RH (Kraus 1972, Feistel and Ebeling 2011, Pierce et al. 2011).

2.1. Greenhouse feedback of water-vapour amount

Water vapour is the Earth’s main greenhouse gas—and usefully so. Without it, average temperatures would be uncomfortably colder (Le Treut et al. 2007). But unlike human-made CO₂ emissions, water-vapour emissions generally cannot be controlled: surface water evaporates everywhere, in amounts governed mostly by temperature, wind and humidity. Atmospheric water vapour forms clouds and falls as rain, when temperature, pressure and air movements dictate. To the terrestrial greenhouse effect, i.e., to the atmospheric absorption of outgoing thermal radiation, CO₂ actually contributes only one quarter while the major part comes mainly from water vapour and from clouds (Abbot and Fowle 1908, Emden 1913, Trenberth et al. 2007, Lacin et al. 2010, Schmidt et al. 2010).

On average per surface area, liquid water in clouds amounts to about 0.11 kg m⁻² (Greenwald and Stephens 1995), a fraction slightly less than 0.5 % of the total water mass of about 25 kg m⁻² contained in the vertically integrated air column. About twice as much water as in clouds resides in the stratosphere above the ‘cold trap’ tropopause (Seidel 2002), while about 98 % constitutes moisture confined to the troposphere below, where it strongly absorbs and emits infrared radiation (Sugiyama et al. 2005). The increasing amount of tropospheric water, which is assumed to result from global warming, in turn amplifies the temperature rise via a positive feedback loop (Komabayasi 1967, Ingersoll 1969, 2013, Dessler et al. 2008, Dessler 2010, Ingram 2010, Pierrehumbert 2010, Soares 2010). About 80 % to 90 % of global evaporation originates from the ocean (Reid and Valdés 2011, Durack et al. 2013). The moisture content of the air column over the ocean has increased by 0.41 kg m⁻² or 1.6 % per decade since 1988 (Santer et al. 2007), in accord with a mean warming rate of 13 mK yr⁻¹ of the marine atmosphere (Trenberth et al. 2007). Along with the increase in precipitable water, atmospheric circulation seems to be slowing down (Counou et al. 2015, Laliberté et al. 2015).

2.2. Relative fugacity driving the hydrological cycle

On the annual average, 72 % of the Earth’s cross section exposed to sunlight is covered by the ocean (Feistel 2013) where about 60 % of the solar energy is absorbed (Macdonald and Baringer 2013) and subsequently exported to the atmosphere by radiation, by sensible heat flux and by latent heat of evaporation controlled by RH. Largely unaffected by tropospheric CO₂ levels, latent heat energy is carried by water vapour across the dense layers of the atmosphere before it is released in clouds and radiated to the cold cosmic background. The dominant role of this transport route in the global energy balance is not always clearly emphasized in climatological literature; the following estimates regarding the three mechanisms of oceanic heat loss may underpin this role and in turn that of RH.

Estimates for the latent-heat fraction of ocean-atmosphere energy exchange vary between 45 % (Emery et al. 2006) and 90 % (Wells 2012). The mean oceanic evaporation of about 1200 mm yr⁻¹ (Baumgartner and Reichel 1975, Peixoto and Oort 1992) corresponds to a latent heat export rate of approximately 100 W m⁻², or to roughly 2/3 of the solar irradiation absorbed in the water column (Feistel and Ebeling 2011, Pierce et al. 2011). On land, the latent heat flux is dominated by transpiration that amounts to 33 W m⁻² (Jasechko et al. 2013), or to about 1/2 of the irradiation absorbed there (Trenberth et al. 2009). Thus, driven by atmospheric subsaturation measured in terms of RH, evaporation is the dominant process of oceanic energy export (Pierrehumbert 1996). In contrast, even if any greenhouse effect is ignored, black-body radiation from the ocean surface is too slow to explain the observed oceanic thermal relaxation time of only 2–3 months (Prescott and Collins 1951, Schwartz 2007, Feistel and Ebeling 2011) and may not dominate ocean cooling. Finally, sensible heat flow is driven by the sea–air temperature difference such as from the warm water to the colder air above. However, this difference is generally small (Kara et al. 2007), and in addition, when a turbulent isentropic greenhouse atmosphere is in radiation balance with the ocean, the air temperature at the sea surface appears even slightly higher than that of the emitting water underneath, as a result of the adiabatic vertical temperature gradient (Feistel 2011a), which suggests that the average sensible heat transfer in such a conceptual model is instead
downwards from the air to the sea. Also, the cool oceanic skin caused by evaporation (Saunders 1967, Schlüssel et al 1990) counteracts sensible heat export. Compared to the former two processes, sensible heat exchange plays only a minor role in sea–air interaction.

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). Climate processes are driven by such gradients that are built up by uneven absorption of solar energy and its subsequent conversion and self-organized redistribution by radiation, phase transitions and global circulation. 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 digital supplement of part 1 of this series, i.e., Feistel et al (2016)) of water vapour in the atmosphere, which is one of the options for defining RH. To a reasonable approximation, see section 5, the spatial distribution of the relative fugacity of water vapour can be described by that of the RH in the standard definition (Erikson 1965, Kraus 1972, Hansen and Takahashi 1984, IOC et al 2010, Feistel et al 2010b, 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, RH immediately above the sea surface essentially controls the latent heat export from the ocean. Similar to the variety of empirical equations in use for estimating RH, the driving forces for the mass transfer of water across phase boundaries are parameterized by differences of various alternative humidity quantities (Erikson 1965, Kusuda 1965, Liu and Nielsen 1990, Katsaros 2001, Schneider et al 2010), motivated mainly by practical convenience rather than by physical rigour.

After averaging over diurnal cycles and weather fluctuations, RH over the oceans is rather constant at values of about 80 %rh, almost independent of region, season, or atmospheric warming (Albrecht 1940, Gill 1982, Mitchell 1989, Peixoto and Oort 1996, Allen and Ingram 2002, Dai 2006, Pierrehumbert 2010), in contrast to RH in the upper troposphere (Paltridge et al 2009, Falušlo and Trenberth 2012). Mean sea-surface RH is slightly higher (up to 85 %rh) in the tropics and slightly lower (down to 75 %rh) in the trade-wind belt. A global climatological atlas of ocean-surface RH was published by Wright (1988). A spurious ‘decline in marine relative humidity around 1982’ in climate data was caused by ‘a change in reporting practice for dew-point temperature’ (IPCC 2013, section 2.5.4, ‘Surface Humidity’, p 206). While the approximate constancy of RH is well-known from observations and models, its fundamental physical causes remain elusive (Ingram 2010, Pierrehumbert 2010, Held and Shell 2012). A simple hypothesis is that slightly deviating values of RH may drive the global energy fluxes out of balance and the resulting deviations of ocean temperature, hydrological cycle and cloudiness will quickly return RH to its observed value (Feistel 2013).

Climatological sensitivity, planetary albedo and changes in cloudiness are closely linked to changes of RH (Smagorinsky 1960, Hansen and Takahashi 1984, Falušlo and Trenberth 2012, Quaas 2012, Feistel 2013, Lea 2015, Martínez-Boit et al 2015). No significant trend for the land-ocean average of the total cloud cover was found for the period 1971–96 (Warren et al 2007). Also, no significant change in cloud albedo has yet been detected (Wielicki et al 2005); certain trends found in remotely sensed cloudiness may suffer from monitoring inadequacies (Dai et al 2006). While surface RH drives the ocean’s cooling, clouds and albedo control its heating by sunlight in such a way that, on the global average, gain and loss are almost perfectly balanced by a stable feedback loop. Thus, small long-term trends possibly observed in surface RH are key indicators for fundamental changes in the climate system and may offer insights in, for example, the effects of volcanic eruptions or solar activity, in the variability of the global albedo or cloudiness, and in regional acceleration of the water cycle (Durack et al 2012, Falušlo and Trenberth 2012, Held and Shell 2012, Josey et al 2013, Gimeno 2013, Bintanja and Selten 2014, Yu and Luo 2014). Cloud-climate interaction is poorly understood in general, in particular how humid air is lifted into the atmosphere and drives cloud formation and rainfall (Bony et al 2015, Schiermeier 2015). Solar dimming measures of ‘geo-engineering’ occasionally discussed to counteract global warming may substantially modify the atmospheric RH as a risky side-effect (Schmidt et al 2012).

All the above estimates suffer from considerable uncertainties; monitoring and modelling the latent heat flux and the related evaporative cooling still poses a challenge (Kleeman and Power 1995, Pierrehumbert 1996, 2010, Josey et al 1999, 2013, Worley et al 2005, van Hooijdonk and Huber 2009). Based on the best measurements, closing the global ocean energy budget still fails by as much as about 20 %, or 30 W m−2, likely due to poor knowledge of the latent heat flux (Chahine 1992, Katsaros 2001, Stephens et al 2012, Josey et al 2013). For comparison, natural albedo fluctuations typically change solar irradiation by only about 1 % (Wielicki et al 2005), while a tiny systematic imbalance on the order of 0.003 %, or 0.005 W m−2, of the terrestrial heat flux is large enough to raise the atmospheric temperature at the observed rate of 2 K per century (Hansen et al 2006). Theoretically, under otherwise unaltered conditions, a minor systematic offset of 1 %rh (an uncertainty typical for meteorological observation, see section 4.3) in mean sea-surface RH would suffice to cause a significant oceanic latent heat-flux difference of almost 6 W m−2 (Feistel and Ebeling 2011). Thus, the heat-flux deviation to be monitored for global warming is about three orders of magnitude less than the uncertainty of oceanic latent-heat export estimates.

The recent pause (‘hiatus’) in global surface warming (Kosaka and Xie 2013, Li et al 2013, Chen and Tung 2014, Clement and DiNezio 2014, Tollefson 2014) indicates that heat-flux fluctuations of a magnitude typical for global warming, likely caused by ocean-atmosphere interaction, may well occur on climatic time scales. Possibly related global fluctuations of RH are unclear. The disputed hiatus may be just an insignificant spurious effect within data uncertainty.

2.3. Importance of atmospheric humidity to salinity and climate variability

Local and temporal changes of atmospheric humidity significantly influence the sea-surface salinity, the hydrological cycle and the climatic variability (Dai 2006, Santer et al 2007, Durack and Wijffels 2010, Durack et al 2012, Pierce et al 2012), see also Pawlowicz et al (2016). As an example, after the closing of the Isthmus of Panama about 3.5 million years ago (Coates 1997), the increasing humidity over the North Atlantic is considered responsible for the subsequent Arctic glaciation (Haug and Tiedemann 1998, Haug et al 2005). The somewhat later polar warming of between 8 K and 19 K cannot be explained by the CO₂ levels that were similar to the present ones, however, uncertain additional feedbacks, in particular related to water vapour, may grow stronger in warmer climates (Lea 2015, Martínez-Boti et al 2015). Moisture dynamics also governs, e.g., the anomalies of rainy seasons in the African Sahel zone (Poan et al 2013), the yields in the US Corn Belt (Ott and Long 2014), and the climate sensitivity to CO₂ (Wang et al 2014). Also, atmospheric water vapour affects almost any radiation-based measurements from space. Measurement and numerical simulation of global atmospheric humidity distributions and their changes on the long-term scale are therefore fundamental for understanding and monitoring climatic change. The global water cycle is expected to become a major focus for climate research in the coming years (Sherwood et al 2010, Reid and Valdés 2011, Tollielsen 2012, Fasullo and Trenberth 2012, IPCC 2013, Stevens and Bony 2013).

3. Brief history

The scientific concept of relative humidity arose with the development of instruments (hygrometers) to measure humidity (Molyneux 1685, Arderon 1746, Gatley 2013). De Luc provided what is possibly the first formal definition of relative humidity and recognition of an underlying physical reality, noting that many natural fibre-based materials, including hygrometer sensing fibres, were observed to respond to the ‘degree of saturation’ (i.e., to the ratio of the actual quantity of steam to the maximum possible at that temperature) rather than to the absolute quantity of water vapour (de Luc 1792, pp 412–13). Gilbert (1803) is credited with the first use of the term ‘relative humidity’ although a variety of ratios (e.g., density and vapour tension) and terms (e.g., ‘fraction of saturation’, ‘degrees of saturation’, ‘relative degree of humidity’, ‘degree of moisture’ and ‘percentage humidity’) were used throughout the 19th century (Regnault 1845, Miller 1851, Guyot 1859, Shaw 1889).

Detailed reviews of the history of atmospheric humidity measurements were published by Sonntag (1966), Moller (2008), Holland and Stöhr (2011) and Gatley (2013). The beginning of quasi-regular meteorological measurements of RH can be dated to 1873, when OMI/IMO10 was established to coordinate the collection and international exchange of meteorological data and information11. Since its invention in 1887 (Sprung 1888), Assmann’s psychrometer has proven to be a robust instrument for practical meteorological observations of RH (WMO 2008). Diurnal and seasonal cycles as well as spatial variability of RH were already known at certain locations before 1873 (Brewster 1832, Forbes and Mahlmann 1836). For example, records between 1849 and 1868 of dry-bulb and wet-bulb thermometers at the Royal Observatory at Greenwich were analysed by Ellis (1878), and at the German weather station Hohenpeissenberg, where continuous RH records began in 1879 (DWD 2012), different hygrometers and a psychrometer (in 1841) had been used since 178112. Nevertheless, long-term series of RH comparable in length and quality to historical records of temperature and precipitation are ‘almost not available’ (Hocke et al 2013) for modern climate research.

3.1. Vapour pressure, partial pressure, fugacity and the enhancement factor

Relative-humidity definitions based on vapour pressure are not equivalent to those based on vapour density since, as was noted by Regnault (1845), the partial density of saturated water vapour in moist air is greater than the density of pure saturated vapour at the same temperature. In other words, the saturation partial pressure of water vapour in humid air, \( p_v^\text{sat} \), is greater than the pressure of pure saturated water vapour, \( e^\text{sat} \), at the same temperature. By the end of the 19th century, this enhancement of the partial pressure above \( e^\text{sat} \) was recognized to be a combination of three thermodynamic phenomena, whereby the ‘effective’ water-vapour pressure (and hence evaporative flux), associated with the condensed phase, increases due to the applied pressure (Poynting effect) and decreases due to dissolved gas (colligative or Raoul effect), and whereby the ‘effective’ water-vapour pressure (and hence condensing flux) in the gas phase is reduced due to interactions among air and water molecules (Van der Waals 1873, Maxwell 1874, Poynting 1881, Lewis 1900, 1901a, 1901b, McDonald 1963, Hyland 1975, Wisniak 2001).

Consequently, for humid air the ‘effective’ vapour pressure driving water transport towards equilibrium is identified with neither \( e \) nor \( p_v \), but with the fugacity, \( f_v \), of water vapour relative to the fugacity of water in the other phases. The concept of fugacity, which is related to the free energy and chemical potential, was introduced in 1900 by Lewis as the tendency of a molecular species to escape from the phase it is in, such that at equilibrium the fugacities (and chemical potentials) of...
the species in each phase are equal. With units of pressure, the value of $f_{W}$ is smaller than $p_{V}$ but approaches $p_{V}$ in the ideal-gas limit (Lewis 1900, p 54, 1901a, 1901b, p 48, and see appendices A–C in the digital supplement of part 1 of this series). The ratio $f_{W}/p_{V}$ is known as the fugacity coefficient, $\varphi_{V}(x, T, p)$.

The ratio $p_{V}^{\text{sat}}/e^{\text{sat}}$ is known as the water-vapour enhancement factor, $f(T, p)$. Thermodynamically-based equations for the enhancement factor in air were developed by Goff and Gratch (1945) for ASHVE\textsuperscript{13} and revised by Wexler and Hyland (1983), whose work for ASHRAE was most recently updated by Herrmann et al (2009) using the latest virial coefficients and the IAPWS equations for $e^{\text{sat}}(T)$ over water and ice (IAPWS 1992, 2011, Wagner and Pruss 1993, Wagner et al 2011).

The expression for the enhancement factor is based on the equality at equilibrium of the chemical potential of water in the gas and condensed phases (and hence of the respective fugacities) and is a product of terms accounting for the Raoult, the gas and condensed phases (and hence of the respective equality at equilibrium of the chemical potential of water in accordance to part 1 of this series),

\[ f = x_{W} \pi(T, p) \varphi_{V}(1, T, e^{\text{sat}}) / \varphi_{V}(x^{\text{sat}}, T; p). \]  

(2)

This equation is equivalent to the complex formula given by Herrmann et al (2009) if the mole fraction of liquid water, $x_{W}$, is expressed by Henry’s law for dissolved air, the Poynting factor of liquid water, $\pi(T, p)$, is estimated by assuming a linear pressure dependence of specific volume, and a virial approximation of the fugacity coefficient (IAPWS 2015, Feistel et al 2015a, 2015b) and; equation C.19 in appendix C of the digital supplement to part 1 of this series).

Figure 1 shows how the partial pressure, $x_{W} \pi(T, p)$, would increase, were dry air to be added to a system at temperature, $T = 300 K$ initially containing saturated vapour above a pool of water in a sealed box, for which the fugacities of the liquid water, $f_{W}$, and the saturated water vapour, $f_{V}^{\text{sat}}$, are equal. The curves marked with ‘A’, ‘+’ and ‘□’ represent the results of multiplying the pure vapour pressure, $e^{\text{sat}}$ (dashed line) by the Raoult, Poynting and gas-phase interaction factors, respectively. Initially, the total pressure, $p$, in the container is due to the water vapour, $x = 1$ and the partial pressure $x_{W} \pi(x, T, p)$ at this stage, $f_{W}^{\text{sat}}$ is slightly less than $e^{\text{sat}}$ because of interactions between vapour-phase water molecules. As dry air is added, the small amount of air dissolving causes a slight decrease in $f_{W}$. At the same time, the increase in total pressure exerted on the liquid causes a substantial increase in $f_{W}$. These phenomena, respectively, contribute a slight decrease and increase in partial pressure. The dominant contributor to the increase in partial pressure is the gas-phase interaction amongst water and air molecules, which acts to lower the fugacity of water in the vapour phase and thus to increase the net evaporation until $f_{W}^{\text{sat}} = f_{W}$.

3.2. Formal definition by the WMO

In 1953, the newly formed WMO adopted the definition that had been proposed in the first of two resolutions issued earlier by the International Joint Committee on Psychrometric Data (IJCPTD) as reported by List (1951), which in turn followed a dominant historic practice in the meteorological community of defining relative humidity as the ratio of vapour pressures. The WMO definition sets $z = x$ in equation (1) which, with the condition that saturation is defined at the same pressure, i.e., $s = p^{\text{sat}} = p$, is equivalent to also setting $z = p_{V}$; so that in this paper’s notation,

\[ \varphi_{V}(x^{\text{sat}}, T; p) = \frac{p_{V}}{p^{\text{sat}}(s)}, s = p^{\text{sat}} = p, \]  

(WMO 2008, p 1.4–27). However, in the limit of pure water vapour the choice $z = x$ does not provide a suitable measure of sub-saturation, in contrast to $z = p_{V}$. Note that to indicate saturation with respect to liquid water or hexagonal ice $I$, subscripts ‘W’ and ‘Ih’, respectively, will be used where relevant and omitted otherwise. Also, superscript ‘s’ will be omitted for simplicity. The WMO has continued to recommend this definition through seven editions of ‘The WMO Guide to Meteorological Instruments and Methods of Observation (CIMO Guide)’ from 1954 to 2008\textsuperscript{14} (WMO 2008). The definition is also promoted by many other influential organizations\textsuperscript{15} and standards publications (ASHRAE 1994, NF X 15–110 1994, IMC 1996, BS 1339–1 2002, ASTM 2014) and as the de facto standard is referred to here also as the standard definition. It is widely accepted, extremely useful and can be accurately calculated from other humidity quantities using reference equations for pure-water saturation vapour pressure, $e^{\text{sat}}(T)$, and for the humid-air water-vapour enhancement factor, $f(T, p)$.

The WMO definition does not apply to moist air when the pressure $p$ is less than the saturation water-vapour pressure [$e^{\text{sat}}(T)$] at temperature $T$ (WMO 2008, p 1.4–27). To illustrate, the range of possible states of humid air defined by the triple, $(x, T, p)$, for $T = 300 K$ is shown in figure 2. The thick solid curve represents the pressure at which the humid gas becomes saturated as a function of $x$. While from any point below the curve (e.g., A, B or C), saturation is possible, the WMO definition was only intended to cover that part above the horizontal dashed line, $p \geq e^{\text{sat}}$, of the range where, as in most meteorological conditions, saturation could be achieved at constant pressure (i.e., isobaric saturation $s : p^{\text{sat}} = p$ represented by a horizontal arrow from A to the state $(x^{\text{sat}}, T, p)$) on the saturation curve.

\textsuperscript{13} ASHVE: American Society of Heating and Ventilation Engineers, a forerunner of ASHRAE.

\textsuperscript{14} Although the 1953 definition included a note that relative humidity at temperatures less than 0 °C is to be evaluated with respect to liquid water, it now allows evaluation with respect to ice and requires appropriate identification to avoid ambiguity.

The second resolution issued by the IJCPD (List 1951) defined an extended form of equation (3) to the effect that when barometric pressure and temperature … [conditions were] … such that saturation was impossible, relative humidity is the ratio of the partial pressure of water vapour in the mixture or sample to the saturation pressure of pure water \( e_{\text{sat}} \) at the given temperature’ (List 1951, Goff 1960). In the notation used here, the extension is

\[
\varphi_{\text{ext}} = \frac{p_y}{e_{\text{sat}}} \quad s : p^{\text{sat}} = e_{\text{sat}},
\]  

(4)

Figure 1. This chart shows, for saturated humid air at 300 K, the theoretical water-vapour partial pressures as functions of pressure, \( p \), that would arise where each of the Raoult, Poynting or interaction contributions to act alone in the enhancement of the full partial pressure (thick curve without marks) above the pure saturation vapour pressure (dashed line). The curves marked with ‘Δ’, ‘+’ and ‘□’ represent theoretical partial pressures obtained by multiplying the Raoult, Poynting and gas-phase interaction factors (extracted from the enhancement-factor equation given in Herrmann et al 2009) by the pure vapour pressure, \( e_{\text{sat}} \) (dashed line). Also shown for comparison is the water-vapour fugacity (‘●’), which was calculated using TEOS-10 functions (Wright et al 2010, Feistel et al 2010a). Note that for pure saturated vapour at 300 K (‘■’), \( p^{\text{sat}} = e_{\text{sat}} = 3537 \) Pa and \( f_{\text{N}}^{\text{sat}} \approx e_{\text{sat}} - 6 \) Pa because of water-water gas-phase interaction. See text for details.

Figure 2. The saturation-pressure curve, \( p = p^{\text{sat}}(x, T) \), and unsaturated states for humid air at 300 K at pressure \( p \), as a function of \( x \). The saturation curve is found from \( x = e^{\text{sat}}(T, f(T, p)/p) \), and is represented by the thick solid line. Humid air can exist at 300 K at any state represented by a point below the saturation curve. The horizontal dashed line indicates the saturation vapour pressure for pure water at 300 K. Circles represent particular humid-air or vapour states and the arrows indicate potential paths to saturation including isobaric (from A and B) and isocompositional (from A, B and C). See text for details.
and is indicated by the dashed arrow from B in figure 2. The resolution was issued subject to verification, but no further action was taken. Worrall (1965) proposed the same definition, emphasizing that here $e^{\text{sat}}$ is used ‘as a reference only’. In his definitive work, Harrison (1965) published a definition for unsaturated pure vapour,

$$\psi_{\text{vap}}^{(s)} = \frac{p}{e^{\text{sat}}}, \quad s : p^{\text{sat}} = e^{\text{sat}},$$

(5)

which is a special case of $\psi_{\text{sat}}$ for which $x = 1$ so that $p_{v} = p$ (vertical arrow from C), but omitted an extended-range definition. The issue was further addressed by Böse and Mitter (2004), who called $p^{\text{sat}}$ the ‘virtual’ saturation pressure, and by Lovell-Smith and Pearson (2006). In 2007, an extended-range definition was included in the German Standard VDI/VDE 3514 (2007), where saturation occurs at a ‘hypothetical’ system pressure equal to $e^{\text{sat}}$.

3.3. Relative fugacity and water activity

Lewis (1901a, p 55) wrote that the ‘great utility of this new quantity [fugacity] … [lies] in the fact that the approximate equations containing the vapor pressure and developed rigorously except for the assumption that the vapor pressure obeys the [ideal] gas law, may be replaced by exact equations of the same form or of equal simplicity containing the fugacity instead of the vapor pressure’ (see also Gavroglu and Simões 2012). While the fugacity of water is equilibrated across phases at saturation, the relative fugacity of water, $\psi_{f}$, (also known as the water activity, $a_{w}$, see appendices B and C in the supplement of the part 1 companion paper) has been defined with reference to pure water under pressures $p$ at the same temperature rather than to water containing some dissolved air when $p > e^{\text{sat}}$ (Lewis and Randall 1923, p 349, 1961, p 243). However, in practice difficulties in measurement of $f_{v}$, and the close approximation of $f_{v}$ to $p_{v}$ over much of the range, have meant that the water activity $a_{w}$ has usually been approximated by the ratio of vapour pressures $\psi_{v}$ measured directly (Robinson and Sinclair 1934, Scott 1958) or by $\psi_{f}$ determined using RH sensors (Schiraldi et al 2012).

4. Current definition and measurement practice

4.1. Current definitions

We can identify four major usages of RH definitions in contemporary publications.

(1) The WMO or standard definition, equation (3),

$$\psi = \frac{x}{x^{\text{sat}}} = \frac{p_{v}}{p_{v}^{\text{sat}}}, \quad s : p^{\text{sat}} = e^{\text{sat}},$$

(6)

is valid over most (but not all) of the range addressed by industry and by the meteorological, domestic and commercial air-conditioning communities. Over the valid range, the metrological community provides traceability to the SI for standard RH via calibration (see section 4.2).

(2) Full-range definition: In the absence of official sanction (apart from the comparatively recent standard VDI/VDE 3514 (2007)), those who need to calculate, measure or calibrate in the subsaturation pressure region have generally developed a pragmatic solution based on $z = p_{v}$ rather than $z = x$. Since $f(T, p) = 1$ when $p = e^{\text{sat}}$, the ‘pragmatic’ full-range definition is

$$\psi_{\text{full}}(x, T, p) = \frac{p_{v}(x, p)}{e^{\text{sat}}(T, p)} = \frac{p_{v}(x, p)}{e^{\text{sat}}(T, f(T, p))}$$

(7)

where $p^{\text{sat}} = p$ if $e^{\text{sat}} \leq p$.

Nevertheless, with many major manufacturers of RH sensors extending the range well above 100 °C and as high as 180 °C, the need for widespread sanction of a definition covering the full range is clear. For example, this definition is recommended by a major manufacturer of humidity sensors and instruments.16,17

(3) Other non-standard definitions: Beside the predominant standard definition, several other RH definitions such as $\psi_{f}$ and $\psi_{q}$ continue to be used and to propagate on-line and in print. For example, the OMI (1951) definition $\psi_{q}$,

$$\psi_{q} = \frac{r}{q^{\text{sat}}}, \quad s : p^{\text{sat}} = p,$$

(8)

is occasionally mistakenly referred to as the WMO definition. The mistake possibly originated in a WMO training manual (Retallick 1973) and continues to propagate (Gill 1982, Rogers and Yau 1989, Pruppacher and Klett 1997, Katsaros 2001, Jacobson 2005, Dai 2006, Pierrehumbert 2010), including in some background articles of TEOS-10 (Feistel et al 2010a, 2010b) and online. On the other hand, ASHRAE (1994) and BS 1339-1 (2002) identify the ratio of mixing ratios, $r/l^{\text{sat}}$, as the ‘degree of saturation’ and ‘percentage saturation’, respectively, thus clearly distinguishing it from the standard definition. Again, several papers define RH in terms of specific humidity as

$$\psi_{q} = \frac{q}{q^{\text{sat}}}, \quad s : p^{\text{sat}} = p,$$

(9)


17. Certain commercial products are identified in this paper, but only in order to foster understanding. Such identification neither constitutes nor implies recommendation or endorsement by any of the organizations represented by the authors.

18. For example, the on-line ‘Glossary of Meteorology’ of the American Meteorological Society (AMS) incorrectly states that relative humidity ‘is alternatively defined by the World Meteorological Organization as the ratio of the mixing ratio to the saturation mixing ratio’ (http://glossary.ametsoc.org/wiki/Relative humidity retrieved 17 April 2015).
\[ \psi_{\text{IUPAC}} = \frac{p_v}{e^{\psi_v}}, \]  

(10)

which is problematic because it does not yield exactly 100 %rh at saturation of humid air.

(4) Water-vapour relative fugacity (see appendix C in the supplement of the part 1 companion paper):

(a) For unsaturated humid air specified by \((x, T, p)\) in the presence of a bulk condensed phase, the thermodynamic driving force for net flux of water molecules is the difference between the (mass-based) chemical potentials \(\mu_W^A(x, T, p)\) and \(\mu_W(W, T, p)\) of water in the gas and condensed phases, respectively. This difference can be expressed in terms of the ratio of the fugacity, \(f_v\) (or equivalently the absolute activity, \(a_v\), see appendices B and C in the supplement of the part 1 companion paper), of water in the gas phase to that in the condensed phase, i.e., in terms of the relative fugacity, \(\psi_f\), or water activity, \(a_W\), of the unsaturated air,

\[ \psi_f = \exp \left( \frac{\mu_W^A(x, T, p) - \mu_W(W, T, p)}{R_W T} \right) = \frac{f_v}{f_v^{\text{sat}}} = a_W, \]

\[ s : p^{\text{sat}} = p, \]  

(11)

where \(R_W\) is the specific gas constant of water (see appendix D in the supplement of the part 1 companion paper). This ratio characterizes unsaturated humid air with reference to a theoretical bulk condensed phase, and also arises in thermodynamic derivations of the Kelvin equation for non-planar interfaces and of the vapour-pressure modifications associated with solutions (see also IOC et al 2010, Feistel 2012). This thermodynamic definition is widely referred to in food and solution chemistry, but its use in practice is limited, see entry (b) below. Consistent with TEOS-10, a virial equation for the calculation of the fugacity of water vapour in humid air has recently been published (IAPWS 2015, Feistel et al 2015a, 2015b). Note that the definition (11) is preliminary as it refers to pure liquid water as the condensed phase rather than to air-saturated water, i.e., the Raoult effect is neglected (see appendix C in the supplement of the part 1 companion paper for more details).

(b) For many physical chemists, climate modellers and chemical and food engineers, the water-vapour partial pressure is viewed as a convenient ideal-gas approximation to the fugacity, and the standard definition (3) is used as a convenient approximation to the relative fugacity, i.e.,

\[ \psi_f = a_W = \frac{f_v}{f_v^{\text{sat}}} \approx \frac{p_v}{p_v^{\text{sat}}} = \psi_v, \]

\[ s : p^{\text{sat}} = p, \]  

(12)


4.2. Measurement practice, use and calculation of relative humidity

Whilst there are many methods of measuring individual quantities from which the RH could be calculated when \(T\) and \(p\) are known, metrology-type applications favour chilled-mirror dew-point meters, since these offer the most reliability and precision over the greatest range, and because dew-point temperature \(T_d\) is often the quantity realized at the primary standard level.

For most industrial applications and for ground-based meteorology, RH is measured using the electrical response of thin-film humidity sensors and, less frequently, using wet- and dry-bulb psychrometers and chilled-mirror hygrometers. Satellite and airborne remote-sensing applications tend to use electromagnetic absorption methods yielding a volumetric concentration. Good overviews of current and historical meteorological practice including calibration are given in WMO (2008) and Kämpfer (2013). Although all humidity sensors require calibration, those measuring RH require more frequent calibration because of processes associated with drift, ageing and contamination of the sensitive material.

Calibration implies comparison against a traceable reference and assumes appropriate propagation of the associated measurement uncertainty (VIM 2012). SI-traceability is disseminated through a chain of calibrations via a primary humidity standard. Currently, the primary humidity generator19 (HG) is the most common ultimate source of traceability in humidity measurements, and a typical traceability chain for RH is presented in figure 3. In most such generators, a continuously flowing gas is brought to saturation at a known temperature, \(T_1\), and pressure, \(p_1\). In so-called twopressure and two-temperature humidity generators, the saturated gas passes through an expansion valve and/or heater to flow as an unsaturated humid gas without changing its vapour mole fraction, \(x\), provided no condensation takes place. This now unsaturated mole fraction, \(x\), can be calculated as

\[ x = \frac{e^{\text{sat}}(T_1)(T_1, p_1)}{p_1} = \frac{F(T_1; a)F(T_1; p_1; b)}{p_1}, \]  

(13)

Here, \(F(T_1; a)\) and \(F(T_1; p_1; b)\) represent reference functions that allow the calculation at \(T_1\) of the saturation water-vapour pressure \(e^{\text{sat}}\) and at \(T_1\) and \(p_1\) of the water-vapour enhancement factor, \(f\), respectively, and \(a\) and \(b\) are vectors of fitted parameters for the respective reference functions (see Lovell-Smith 2009, 2012). In other generators, the input gas may be humidified directly to a non-saturated level—using partial saturation, diffusion or blending approaches—that is, definitively characterized in terms of mass, volume or amount of

19 Occasionally gravimetric hygrometers are used as additional confirmation of generator performance; however, it is rare for this to be the main route of traceability to the SI.

Once the mole fraction, $x$, is known, by whatever method, the measurement of other parameters at the device under calibration (DUC) such as the gas temperature, $T_2$, and pressure, $p_2$, enables calculation of other unknown quantities such as dew-point temperature, RH or others. The standard RH at the DUC is, from equations (3) and (13),

$$
\psi_k = \frac{x}{x_{sat}(T_2; p_2)} = \frac{e_{sat}(T_2)p_2}{e_{sat}(T_k)p_1},
$$
in general, and for the two-pressure humidity generator, by solving

$$
\frac{e_{sat}(T_2)f(T_2; p_2)}{p_2} = \frac{e_{sat}(T_k)f(T_k; p_1)}{p_1}.
$$

The output from a saturator may be fed directly to a hygrometer with minimal reduction in pressure, such that $p_2 \approx p_1$ and $T_2 \approx T_1$. This is the principle of the single-pressure humidity generator. In practice, for greater accuracy, the pressure difference $\Delta p = p_1 - p_2$ is measured and a correction $-(\partial f/\partial p)\Delta p$ added (Lovell-Smith 2009).

Note the necessity to calculate $e_{sat}(T)$ and $f(T, p)$ in equations (14) and (16) above, and in most calculations. The most up-to-date versions of $e_{sat}$ reference equations are reported by IAPWS (1992, 2011), and the most up-to-date version of the $f(T, p)$ reference function is given in Herrmann et al. (2009). However, a wide variety of reference functions continue to be used. For example, the WMO CIMO Guide (WMO 2008) recommends the so-called Magnus equations (IMC 1996) for calculating $e_{sat}$ above ice and water for meteorological conditions, and a simple equation to calculate $f(T, p)$ as a function of $p$ only when the pressure is around 100 kPa. For values of $f(T, p)$ over a wider pressure and temperature range, WMO recommends International Meteorological Tables of 1966 (WMO 1966), which were calculated using the original Goff and Gratch equations (Goff 1949).

Figure 3. Typical traceability chains for RH based on a primary humidity generator (HG) conditioning air to a known water-vapour mole fraction $x$ which is calculated as a function of the saturation temperature and pressure ($T_1$ and $p_1$, respectively, see equation (13)) and the humidity reference functions for the vapour pressure $e_{sat}(T)$ and enhancement factor $f(T, p)$. The quantity $x$ can be used to calibrate a cavity-ring-down spectrometer (CRDS), for example. A further pressure and temperature measurement allows $T_d(x, p_2)$ using equation (16) and $\psi(x, p_2, T_2)$ using equations (3) and (14) to be calculated for calibration of chilled-mirror hygrometers (CMH) and RH hygrometers as secondary standards, respectively. When using a generator as a non-traceable stable source, the secondary standards can be used to measure $x$, $T_d$ or $\psi$ of conditioned air for calibration of a ‘device under calibration’ (DUC), including, as illustrated, a RH hygrometer.
Under the axiomatic framework of TEOS-10, the calculation of the standard RH requires solving for $x$ and $x_{\text{ref}}$, respectively, the implicit equations

$$
\mu_{w}^{\text{AV}}(x, T_1, p_1) = \mu_{w}^{T}(T_1, p_1) \quad \text{and} \quad \mu_{w}^{\text{AV}}(x, T_2, p_2) = \mu_{w}^{T}(T_2, p_2),
$$

which replace equations (13) and (14). Similarly, calculation of the dew-point temperature, $T_d$, requires the equations

$$
\mu_{w}^{\text{AV}}(x, T_1, p_1) = \mu_{w}^{T}(T_1, p_1) \quad \text{and} \quad \mu_{w}^{\text{AV}}(x, T_2, p_2) = \mu_{w}^{T}(T_2, p_2),
$$

to be solved for $x$ and $T_d$, respectively. Equations (18) and (19) may equivalently be expressed in terms of fugacities substituting the corresponding chemical potentials, see equation (C.1) in the digital supplement of part 1 of this series. Note that including the dissolution of air in liquid water will require a future extension of TEOS-10.

### 4.3. Meteorological uncertainty requirements

The spatiotemporal patterns of atmospheric water-vapour fields result from the superposition of contributions from microscopic to macroscopic length and time scales. The length, period and amplitude of the smallest scales that need to be resolved depend on the question of interest and may strongly differ between uses in

(i) applied meteorology (e.g., agriculture and forest meteorology, hydrology, environmental and technical meteorology),

(ii) numerical meteorology (e.g., numerical weather prediction, general circulation and climate modelling) and

(iii) monitoring tasks (e.g., regional and global climate monitoring).

Atmospheric water-vapour observation is based on both in situ and remote-sensing measurement techniques with different measurement uncertainties, collocation and representativeness errors (Peixoto and Oort 1996, Randel et al 1996, Miloshevich et al 2006, Kämpfer 2013). For applications in synoptic, aeronautical, agricultural and marine meteorology, hydrology and climatology, the WMO CIMO Guide recommends target uncertainties for surface humidity of 1 %rh and 5 %rh at high-range and mid-range RH, respectively, with a reporting resolution of 1 %rh (WMO 2008, table 4.1, p I.4-2 and annex 1.B), whilst recognizing that these can be difficult to achieve in practice. The monitoring of the current increase in stratospheric water by approximately 0.5 μmol mol⁻¹ per decade (Kley et al 2000, Rosenlof et al 2001, Leiterer et al 2005), as well as the quantification of the water-vapour transport from the troposphere to the stratosphere (Hintsa et al 1999), requires very high accuracies of humidity measurements in the upper troposphere/lower stratosphere and at the hygropause (Kley et al 1979). The latter is characterized by joint occurrences of low temperatures down to 190 K and low water-vapour mole ratios (see section 2) down to $(2 \pm 1) \text{ mol mol}^{-1}$ at an altitude of 17 km in the tropics (Teitelbaum et al 2000). Best-performing state-of-the-art radiosondes with application of sophisticated correction schemes were demonstrated to achieve a mean relative uncertainty, $u(y)/y$, of about 1 % in the lower and middle troposphere (where RH >10 %rh) and of about 2 % in the upper troposphere under mostly night-time conditions (Miloshevich et al 2006, table 3 therein). By application of the method of standardized frequencies to a research radiosonde, Nagel et al (2001) and Leiterer et al (2005) exceptionally reported an achievable repeatability of 0.01 %rh and a standard uncertainty of 1 %rh for RH determination in the temperature region down to $-70$ °C. This accuracy is comparable with the accuracy of the traditional aspiration method of meteorology and close to the uncertainty requirement of better than 1 %rh for climatological research (Leiterer et al 2005). However, in view of the multitude of different radiosonde types and correction schemes in use, the required accuracy for climate research is still very difficult to realize in the operational radiosounding service (Miloshevich et al 2001, Antikainen et al 2002, Ovarlez et al 2002, Tompkins et al 2007). Forward simulation of atmospheric dynamics from an initial state, such as boundary-layer turbulence-forced moist convection, also poses very high requirements on the observation (and initialization) of humidity fields (Crook 1996). The very high sensitivity of predicted convective rainwater to the initial specific humidity at the surface suggests a required uncertainty below 1 %rh for surface RH in order to fulfil hydrological demands with respect to flood prediction in the course of severe weather events.

Given that RH is a non-linear function of temperature, pressure and vapour mole fraction, the current fixed meteorological uncertainty requirement of 1 %rh for RH measurements is already demanding at both high relative humidities and low temperatures, yet might still be too large a tolerance with respect to uncertainty propagation in the derivation of climatological long-term statistics including higher-order statistical moments and cross correlations. The consideration of uncertainties in the analysis of meteorological time series is beginning (Willett et al 2013), but is not yet common practice as can be seen from the comparatively small number of dedicated studies on uncertainty analysis. Continued dialog and collaboration between the meteorological and metrological communities will enable the best use of resources to maintain and improve (i) strict and unified metrological requirements for RH in the operational observation service and for data processing (inclusive protocol standards), and (ii) SI-traceability of humidity measurements.

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20 This uncertainty is equal to the width of the interval in which the true value lies with a probability level of 95 %, corresponding to the 2σ level for a Gaussian distribution of the variable (WMO 2008, Annex 1.B).

5. Problems and deficiencies

For a number of reasons, the definition of RH requires attention. A good definition should have a firm thermodynamic foundation, it should be unambiguous, complete and internally consistent, and tailored subset definitions should be derivable to meet more limited applications. While meeting these requirements, it must also be possible to relate any definition to achievable practical realizations, so that the definition can be connected with disseminated traceable calibrations will be based on the standard definition \( \psi_x \), and the incorrect assumption by some users that the hygrometer (triangles), and the fugacity, \( f_x \) (squares), the specific humidity, \( q \) (triangles), and the fugacity, \( f_x \) (diamonds). The fourth non-standard definition is \( \psi_{\text{IUPAC}} \) (circles). For each value of \( \psi_x (T, p) \), \( x \) and \( x^{\text{sat}} \) are calculated and substituted into equation (20), which is rearranged to give each of the differences, \( \psi_i - \psi_x \).

\[
\psi_x = \psi_{x^{\text{sat}}} = \frac{1}{1-x^{\text{sat}}} \psi_{l} = \frac{x\omega + (1-x)}{x^{\text{sat}}\omega + (1-x^{\text{sat}})} \psi_{l} = \frac{q_x(x^{\text{sat}}, T, p)}{q_x(x, T, p)} \psi_{l} = \frac{1}{f(T, p)} \psi_{\text{IUPAC}}.
\]

Here, \( \omega \) is the ratio of the molar masses of water and dry air, and \( \psi_{l} \) is the fugacity coefficient of water in the gas phase (see appendices C and D in the supplement of the part I companion paper).

(2) The ‘full-range’ definition lacks official sanction and theoretical justification. The full-range definition \( \psi_{\text{full}} \), equation (7), has been a common-sense but informal choice by those needing to measure outside the standard range. Although proposed by the IJCPD in 1950, until the publication of the German Standard VDI/VDE 3514 (2007), the full definition had no official sanction, and to date no other authorities have provided recognition. Note that to achieve saturation, in figure 2 any number of paths could be chosen from an unsaturated state such as B to the saturation curve. The definition of a ‘theoretical’ saturation state such that \( p^{\text{sat}} = e^{\text{sat}} \) provides continuity and consistency with the standard definition, yet theoretical justification is lacking. Nor is it clear in what sense the saturation state for the pure-vapour definition is ‘theoretical’.

(3) The reference saturation phase is not fully specified. The key to a definition of the relative humidity of unsaturated humid air (or water vapour) at \( T \) and \( p \) is the specification of the nature of the reference condensed phase. Under the standard definition, the reference phase is fully specified over the limited range \( p \geq e^{\text{sat}} \), through the isobaric condition defining the total pressure \( s : p^{\text{sat}} = p \), and through the water-vapour enhancement-factor reference function that implicitly defines the associated dissolution of air in the condensed phase. For a full definition, the saturation phase cannot be so defined. From a typical unsaturated state in the

Figure 4. Differences between the standard definition \( \psi_x \) and four non-standard definitions at 40 °C (hollow symbols) and 80 °C (filled symbols) for pressures \( p = 0.1 \text{MPa} \) (a) and \( p = 1 \text{MPa} \) (b). Three non-standard definitions are of the form \( \psi_x \), where the humidity quantity \( z \) is the mixing ratio, \( x \) (squares), the specific humidity, \( q \) (triangles), and the fugacity, \( f_x \) (diamonds). The fourth non-standard definition is \( \psi_{\text{IUPAC}} \) (circles). For each value of \( \psi_x (T, p) \), \( x \) and \( x^{\text{sat}} \) are calculated and substituted into equation (20), which is rearranged to give each of the differences, \( \psi_i - \psi_x \).
extended range, (e.g., state B in figure 2), saturation is not possible unless \( p^\text{sat} > p \) and here the isobaric condition must be replaced by another constraint such as on \( x^\text{sat} \) (e.g., \( x^\text{sat} = 1 \)) or \( p^\text{sat} \) (e.g., \( p^\text{sat} = e^\text{sat} \)) in order to specify a unique condensed-phase state.

(4) Standard approaches are lacking for gas compositions different from standard air.

The water-vapor enhancement factor for humid air (e.g., Herrmann et al 2009) is specified for air of a standard composition. However, the composition of air is neither uniform nor invariable. Under meteorological conditions, such non-uniformity and variability is practically irrelevant, but for industrial applications (such as for flue gases, carbon sequestration or fuel cells) the conditions and composition may be sufficiently different as to require a new or modified enhancement-factor reference function (or at least allowance for differing composition in the uncertainty budget). For example, the enhancement factor of \( \text{H}_2\text{O} \) in \( \text{CO}_2 \) differs greatly from that in air (Meyer and Harvey 2015). From equation (2), the requirements for modification of the enhancement factor to allow for variation in composition are evident. While the Poynting factor and the fugacity coefficient for pure saturated water vapour are independent of dry-gas species, the fugacity coefficient describing non-ideality due to interactions in the gas-phase mixture will strongly depend on gas composition. The equilibrium mole fraction of liquid water will also change due to different solubility of the gas compared to standard air, the gas-phase mixture will strongly depend on gas composition. For example, for specific humidity the correct wording is ‘water in air at a mass fraction of 0.05’ or ‘water in air at a mass fraction of 50 g kg\(^{-1}\)’. However, widespread preferred usage is to express relative humidity as a percentage, usually with an associated text qualifier giving for example ‘%rh’ rather than %.

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(5) Most RH definitions do not directly represent thermodynamic driving forces.

The main relative-humidity definitions reported here, i.e., equations (6)–(11), can be calculated and realized with equal traceability to the SI. But none of the quantities \( x^\text{sat}, p^\text{sat}, q^\text{sat} \) and \( e^\text{sat} \) has a related quantity in the condensed phase to which it may become equilibrated. Rather, these quantities represent gas-phase properties at the outcome of a saturation process. The saturated state itself occurs at equilibrium when the chemical potentials of species existing in two or more phases are equilibrated, and the fugacity of water can be used to quantify the saturated state. Significantly, the driving force towards the saturated state of any particular unsaturated humid-air or pure-vapour state is the difference in chemical potential of water in each phase, and this difference can be expressed equivalently as the relative fugacity of water, which seems, therefore, to provide a suitable thermodynamic basis for the definition of RH.

(6) There is no internationally agreed unit symbol for RH, nor an agreed method for scaling of the dimensionless unit.

By its definition, equation (1), RH is a non-negative quantity of dimension one (commonly referred to as ‘dimensionless’) with values ranging from 0 for dry gas to 1 for saturated gas and higher for supersaturated states common in upper-air meteorology (Peter et al 2006) or in transient states of technical processes. According to the SI (BIPM 2006), the expressions \( \psi = 0.5 \) and \( \psi = 50 \% \) are equivalent. The SI suggests that dimensionless numbers should be specified in terms of the entities, so that the vapour mole fraction \( x = 2.5 \times 10^{-3} \) may also be written as \( x = 2.5 \text{ mmol mol}^{-1} \). For example, for specific humidity the correct wording is ‘water in air at a mass fraction of 0.05’ or ‘water in air at a mass fraction of 50 g kg\(^{-1}\)’. However, widespread preferred usage is to express relative humidity as a percentage, usually with an associated text qualifier giving for example ‘%rh’ rather than %. The qualifier allows a clear distinction to be made between RH ‘percentage units’ and intervals expressed as ‘percent of value’, in particular when different values of RH are compared or uncertainties reported. The unit symbol %rh is in some cases standardized nationally (BS 1339-1 2002) but not universally, and some language variations exist. Although the SI Brochure stipulates that ‘Phrases such as ‘percentage by mass’, ‘percentage by volume’, or ‘percentage by amount of substance’ should not be used’, the use of the symbol %rh is consistent with the recommendation that ‘extra information on the quantity should instead be conveyed in the description of the measurand and the name and symbol for the unit’ (BIPM 2006, p 134).

As a rule, the form (1) of the various RH definitions ensures that at saturation, \( \psi = 100 \% \)rh, however, where a different form is used, such as for relative fugacity, saturation should occur at 100%rh. This should be spelled out, since at least one relatively authoritative definition, \( \psi_{\text{IUPAC}} \), is a ratio of two different humidity quantities: vapour partial pressure and pure-water saturation vapour pressure. This definition does apply over the extended range; however, within the standard range, where \( e^\text{sat} < p \) and \( p^\text{sat} > e^\text{sat} \), condition (10) will always give \( \psi_{\text{IUPAC}} > 100 \% \text{rh} \) at saturation (e.g., see figure 4).

(7) Reference-equation uncertainty is incompletely specified.

Currently, in meteorological articles and manuals, equations and data used for the evaluation of the RH are often not accompanied by reasonable uncertainty estimates. Similarly, approximations such as using \( \psi_r \) for \( \psi_e \) are sometimes given, but uncertainty associated with the approximation is not. While conventional uncertainty propagation rules sum over all positive contributions, a procedure that ignores uncertainty covariances may produce estimated uncertainties that are much too large for the case of equation (16). To account for this effect, covariance coefficients need to be included appropriately (Lovell-Smith 2006, 2012, BIPM et al 2008, Feistel 2011b).

6. Suggested tasks

A number of problems and deficiencies in or associated with the definition of RH have been raised. We recommend that the BIPM in cooperation with IAPWS, and with other international organizations and institutions, develop and support state-of-the-art solutions for what are long-standing metrological issues, and in this section outline potential tasks. The immediate task seems to be to provide a framework within
which existing definitions fit (or are excluded) and from there to explore the thermodynamic basis and the potential usefulness of the different definitions, and hence also to provide means to calculate and compare the definitions.

6.1. Framework

The framework can be straightforward. For example, the standard definition, where \( p \geq e^aq \) and \( x < 1 \), and the pure-vapour definition, where \( p = e^aq \) and \( x = 1 \), are each a special case of the full-range definition. Saturation is attained isobarically and isocompositionally, respectively. The full-range definition with its ‘hypothetical’ saturation can be viewed as an approximation to a relative-fugacity definition in the same way that the ITS-90 temperature scale acts as a useful, consistent and SI-traceable approximation to the thermodynamic temperature.

The relative-fugacity definition can, at least initially, take on the same extended range and justification as the full-range RH definition, as the starting point to explore the underlying theoretical basis. The relative-fugacity definition will need some qualifier to distinguish it from the more general term of theoretical basis. The relative-fugacity definition will need a firm thermodynamic basis for defining the reference state must be provided. This basis for a relative-humidity definition, a firm thermodynamic basis for defining the reference state must be provided.

On the basis of the framework, thermodynamic basis and the means to calculate, further main tasks can be identified:

Technical developments:

(a) Investigate the need to account for departure from standard air composition, including isotopic and chemical variation and chemical reactions associated with the gas and condensed phases.

(b) Develop reference equations (such as for the virial expression for fugacity, the enhancement factor and vapour-pressure reference functions, and for larger systems such as TEOS-10) with uncertainty expressed in the form of fitted parameter covariance.

(c) Consider other humid gases besides standard air for which real-gas properties are available to derive corresponding fugacity equations.

Conceptual framework:

(d) Develop an ‘axiomatic’ approach to humidity. TEOS-10 has demonstrated the possibility and value of a rigorous axiomatic foundation of the description of seawater–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 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 of the digital supplement to part 1 of this series. The enhanced subset of TEOS-10-based functions will also include tailored standalone functions (such as for saturation vapour pressure, the enhancement factor and fugacity, Feistel et al 2015a, 2015b) where less computational complexity is desired, while maintaining consistency with TEOS-10 within a specified tolerance.

(e) Develop a mise en pratique (BIPM 2006) for RH to provide guidance for practitioners to realize RH according to its definition, as well as guidance for calculating the quantities and their associated uncertainties. The mise en pratique will be informed by the definition hierarchy, and will link to similar mises en pratique for other humidity quantities and also to TEOS-10 as outlined in (d).

(f) Develop standardized nomenclature and units. This activity would be integrated with (e). Note that the definition of a physical quantity is independent of the particular unit in which the measured values may be expressed.

International harmonisation:

(g) Encourage official sanction of the framework and associated thermodynamic basis. Encourage the reporting of applied RH definition in calibration reports and in journal articles.

(h) Identify non-standard definitions and publicize alternative names. Identify incorrect attribution to WMO or other sources. Provide documentation of terms and definitions on websites such as WMO (where it already exists) and IAPWS, AMS23, IUPAC, etc., and also Wikipedia.

(i) Continue to dialogue with organizations representative of users of the alternative definitions of RH, to increase the level of harmonization, where possible.

7. Conclusion

A thermodynamically founded definition of relative humidity could be formulated in terms of water-vapour fugacity. Other definitions currently in widespread use, such as the relative partial pressure, can be understood as practical proxies to the fugacity definition, consistent within the uncertainty of routine measurements in industry or meteorology. As a preferred SI-traceable surrogate measurand, dew-point temperature is adopted for its realizability and low measurement uncertainty. Calculation of relative fugacity from dew-point temperature, and conversion between alternative RH definitions, is possible using TEOS-10 equations, with an extension to dissolved air and conversion between alternative RH definitions, is possible. Unambiguous nomenclature may be developed and recommended by the international committees governing the SI. In order to ensure their most widespread acceptance and use, it is important that the solutions for these long-standing metrological issues be addressed by a wide range of international organizations and institutions beginning with the BIPM in cooperation with IAPWS.

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