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Metrological challenges for measurements of key climatological observables, Part 4: Atmospheric relative humidity

J W Lovell-Smith¹, R Feistel², A H Harvey³, O Hellmuth⁴, S A Bell⁵, M Heinonen⁶, and J R Cooper⁷

¹Measurement Standards Laboratory (MSL), Lower Hutt, PO Box 31-310, New Zealand ²Leibniz Institute for Baltic Sea Research (IOW), D-18119 Warnemünde, Germany ³National Institute of Standards and Technology (NIST), Boulder, CO 80305-3337, USA ⁴Leibniz Institute for Tropospheric Research (TROPOS), D-04318 Leipzig, Germany ⁵National Physical Laboratory (NPL), Hampton Road, Teddington, Middlesex, TW11 0LW, UK ⁶MIKES Metrology, VTT Technical Research Centre of Finland Ltd, Tekniikantie 1, FI-02151 Espoo, Finland ⁷Queen Mary, University of London (QMUL), Mile End Road, London, E1 4NS, UK

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 organisations and institutions, can make significant contributions by developing and recommending state-of-the-art solutions for this long standing metrological problem, such as are suggested here.

1. Introduction

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, μ , of each component is the same in all coexisting phases. The vapour-phase water mole fraction, $x = n_V/(n_V + n_A)$, where n_V 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,

Symbol	Quantity	Remarks
$\mathbf{a}$	Vector of fitted parameters	(13)
a_W	Relative activity of water	
$\mathbf{b}$	Vector of fitted parameters	(13)
e^{sat}	Water-vapour pressure at saturation	Pure water
F_e, F_f	Saturation reference functions	(13)
f	Water-vapour enhancement factor	
f_V	Fugacity of water in vapour phase	
f_V^{sat}	Fugacity of water in vapour phase at saturation	
f_W	Fugacity of water in liquid phase	
k	Uncertainty coverage factor	
M^A	Molar mass of dry air	$M^A = 0.028\,965\,46\text{ kg mol}^{-1}$
M_A	Mass of dry-air molecules	
M^W	Molar mass of water	$M^W = 0.018\,015\,268\text{ kg mol}^{-1}$
M_V	Mass of water-vapour molecules	
p	Absolute pressure	
p^{sat}	Pressure at saturation	
p_V	Water-vapour partial pressure	
p_V^{ref}	Reference partial pressure of water vapour	
p_V^{sat}	Saturation partial pressure of water vapour	
q	Specific humidity	
q^{sat}	Specific humidity at saturation	
R	Molar gas constant	$R = 8.314\,4621\text{ J K}^{-1}\text{ mol}^{-1}$
R_W	Specific gas constant of water	$R_W = R/M^W$
r	Mixing ratio	
r^{sat}	Mixing ratio at saturation	
s	Saturation condition	
T	Absolute temperature, ITS-90	
T_d	Dew-point temperature	
x	Mole fraction of water vapour	
x^{sat}	Mole fraction at saturation	
x_W	Mole fraction of liquid water	
z	Humidity quantity (with superscripts)	
ϕ_V	Fugacity coefficient of water vapour	
λ	Absolute activity	
μ	Chemical potential (with super/subscripts)	
π	Poynting correction factor of liquid water	
ω	Ratio of molar masses of water and dry air	
ψ	Relative humidity (with super/subscripts)	
ψ_{full}	Relative humidity in the extended range, $e^{\text{sat}} > p$	

saturation.

In general, the *relative humidity* (RH), ψ , of humid air¹ is the ratio of some non-negative humidity quantity, z , to the same quantity at saturation, z^{sat} , at the same temperature, i.e.,

$$\psi_z^{(s)} = \frac{z}{z^{\text{sat}}} = \frac{z(x, T, p)}{z(x^{\text{sat}}, T, p^{\text{sat}})}, \quad (1)$$

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 vapour mole fraction, x , the mixing ratio, $r = M_V/M_A$, the specific humidity, $q = M_V/(M_V + M_A)$, the saturation vapour pressure, e^{sat} , the water-vapour partial pressure, $p_V = xp$, and the fugacity of water vapour, f_V . Here, M_V and M_A represent the mass of water and air molecules, respectively, in a unit volume. A preferred choice for s has been $p = p^{\text{sat}}$, 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 eq. (1) requires the specification of a saturated gas phase in order to calculate $z(x^{\text{sat}}, T, p^{\text{sat}})$; this condition is not trivially obeyed under any practical circumstances. To date, the most important definition has set $z = x$, which with $s: p = p^{\text{sat}}$ is equivalent to $z = p_V$. This *de facto standard definition* (as it will be referred to in this paper) has been authorised by the WMO² since 1950 and by many other organisations (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 emphasise 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

¹Although this section primarily concerns humid air and water vapour, much of the discussion can be generalised to apply to any humid gas or to different samples of humid air of varied composition.

²WMO: World Meteorological Organization, <http://www.wmo.int>

is supported by an explicit example specified in Appendix D in the supplement of the Part 1 companion paper (Feistel et al., 2015b).

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; Randal, 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 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; Pierce et al., 2011; Feistel and Ebeling, 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 man-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; Lacis 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; Soares, 2010; Pierrehumbert, 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 (Laliberté et al., 2015; Coumou 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 CO_2 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 emphasised in climatological literature; the following estimates regarding the three ways 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 (Pierce et al., 2011; Feistel and Ebeling, 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 downward from the air to the sea. Also, the cool oceanic skin caused by evaporation (Saunders, 1967; Schluessel 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; Glansdorff and Prigogine, 1971; Falkenhagen et al., 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-organised 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) of water vapour in the atmosphere, which is one of the options for defining RH. To a reasonable approximation, see Sec. 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., 2010a; Feistel and Ebeling, 2011; Li and Chylek, 2012; Li et al., 2014). 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 parameterised by differences of various alternative humidity quantities (Kusuda, 1965; Erikson, 1965; Liu and Niiler, 1990; Katsaros, 2001; Schneider et al., 2010), motivated mainly by practical convenience rather than by physical rigor.

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; Fasullo 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, 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; Fasullo and Trenberth, 2012; Quaas, 2012; Feistel, 2013; Lea, 2015; Martínez-Botí 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 (Held and Shell, 2012; Durack et al., 2012; Fasullo and Trenberth, 2012; Josey et al., 2013; Gimeno, 2013; Yu and Luo, 2014; Bintanja and Selten,

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 Hooidek 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; Tollefsen, 2014; Clement and DiNezio, 2014; Chen and Tung, 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. Perhaps, the disputed hiatus may be just an insignificant spurious effect within data uncertainty and natural fluctuations (Cowtan and Way, 2014; Kintisch, 2014; Curry, 2014; Marotzke and Forster, 2015; Steinman et al., 2015).

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 the Part 2 companion paper. 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 CO_2 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-Botí 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 (Ort and Long, 2014), and the climate sensitivity to CO_2 (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; Tollefsen, 2012; Fasullo and Trenberth, 2012; Stevens and Bony, 2013; IPCC, 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. 412–413). 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), Möller (2008), Holland and Stöhr (2011) and Gatley (2013). The beginning of quasi-regular meteorological measurements of RH can be dated to 1873, when OMI/IMO³ was established to coordinate the collection and international exchange of meteorological data and information⁴. 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 1781⁵. 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

³OMI: Organisation Météorologique Internationale, IMO: International Meteorological Organisation (1873–1951), a forerunner of WMO (founded in 1950)

⁴Donald P. Gatley, personal communication (2012)

⁵Wikipedia: Meteorologisches Observatorium Hohenpeißenberg http://de.wikipedia.org/wiki/Meteorologisches_Observatorium_Hohenpei%C3%9Fenberg#Literatur, retrieved 18 Jan. 2015

temperature. In other words, the saturation partial pressure of water vapour in humid air, $p_V^{\text{sat}} = x^{\text{sat}} p$, is greater than the pressure of pure saturated water vapour, e^{sat} , at the same temperature. By the end of the 19th century, this enhancement of the partial pressure above e^{sat} was recognised 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 Raoult 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, 1901a,b; McDonald, 1963; Hyland, 1975; Wisniak, 2001).

Consequently, for humid air the “effective” vapour pressure driving water transport toward equilibrium is identified with neither e^{sat} nor p_V^{sat} 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 1901 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_V is smaller than p_V but approaches p_V in the ideal-gas limit (Lewis, 1901a, p. 48; Lewis, 1901b, p. 54, and see Appendices A–C in the Digital Supplement of Part 1 of this series). The ratio f_V / p_V is known as the *fugacity coefficient*, $\phi_V(x, T, p)$.

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 ASHVE⁶ 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 consists of a product of terms accounting for the Raoult, Poynting and (non-ideal) gas-phase molecular interaction effects (Hyland, 1975) in the general form (Feistel et al., 2015a; see also Part 1 of this series and eq. C.19 in Appendix C of its Digital Supplement),

$$f = x_w \pi(T, p) \frac{\varphi_V(1, T, e^{\text{sat}})}{\varphi_V(x^{\text{sat}}, T, p)}. \quad (2)$$

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 (Feistel et al., 2015a) is used.

⁶ASHVE: American Society of Heating and Ventilation Engineers, a forerunner of ASHRAE

Figure 1 shows how the partial pressure, xp (solid black curve), would increase, were dry air to be added to a system at $T = 300$ 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^{sat} , are equal. The green ‘ Δ ’, blue ‘+’ and blue ‘ $\square$ ’, curves represent the results of multiplying the Raoult, Poynting and gas-phase interaction factors by the pure vapour pressure, e^{sat} (solid green line). Initially, the total pressure, p , in the container is due to the water vapour, so that the partial pressure $xp = e^{\text{sat}}$, since $x = 1$. At this stage, f_V^{sat} is slightly less than e^{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 increase the net evaporation until $f_V^{\text{sat}} = f_W$.

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 (IJCPD) (List, 1959), 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 eq. (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,

$$\psi_x^{(s)} = \frac{x}{x^{\text{sat}}} = \frac{p_V}{p_V^{\text{sat}}}, s: p^{\text{sat}} = p \quad (3)$$

(WMO, 2008, p. 1.4–27). 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 2008⁷ (WMO, 2008). The definition is also promoted by many other influential organisations⁸ and standards publications (ASHRAE, 1994; NF X 15–110, 1994; IMC, 1996; BS 1339-1, 2002; ASTM, 2006, 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, $f(T, p)$.

⁷Although 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.

⁸For example, ASHRAE: American Society of Heating, Refrigeration and Air-conditioning Engineers; AFNOR: Association Française de Normalisation; IMC: Institute of Measurement and Control; VDI/VDE: Verein Deutscher Ingenieure/Verband der Elektrotechnik, Elektronik und Informationstechnik; BSI: British Standards Institute; ASTM: American Society for Testing and Materials

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 Fig 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 green line, $p = e^{\text{sat}}$, 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 green arrow from A to the state (x^{sat}, T, p) on the saturation curve.

The second resolution issued by the IJCPD (1950) defined an extended form of eq. (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 vapor in the mixture or sample to the saturation pressure of pure water [e^{sat}] at the given temperature” (List, 1959; Goff, 1960). In the notation used here, the extension is

$$\psi_{\text{ext}} = \frac{p_v}{e^{\text{sat}}}, s: p^{\text{sat}} = e^{\text{sat}}, \quad (4)$$

and is indicated by the dashed brown arrow from B in Fig. 2. The resolution was issued subject to verification, but no further action was taken. Worrall (1965) proposed the same definition, emphasising that here e^{sat} is used “as a reference only”. In his definitive work, Harrison (1965) published a definition for unsaturated pure vapour,

$$\psi_{\text{vap}}^{(s)} = \frac{p}{e^{\text{sat}}}, s: p^{\text{sat}} = e^{\text{sat}}, \quad (5)$$

which is a special case of ψ_{ext} for which $x = 1$ so that $p_v = p$ (vertical blue arrow from C), but omitted an extended-range definition. The issue was further addressed by Böse and Mitter (2004), who called p^{sat} the “virtual” saturation pressure, and by Lovell-Smith and Pearson (2006), and 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^{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, ψ_f (also known as the water activity, a_w , see Appendix B and C in the supplement of the Part 1 companion paper) has been defined with reference to pure water under pressure 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 ψ_e measured directly (Robinson and Sinclair, 1934; Scott, 1958) or by ψ_x 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, eq. (3),

$$\psi_x = \frac{x}{x^{\text{sat}}} = \frac{p_V}{p_V^{\text{sat}}}, s: p^{\text{sat}} = p, \quad (6)$$

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

$$\psi_{\text{full}}(x, T, p) = \frac{p_V(x_V, p)}{p_V^{\text{ref}}(T, p)} = \frac{p_V(x_V, p)}{e^{\text{sat}}(T) f(T, p^{\text{sat}})} \text{ where } \begin{cases} p^{\text{sat}} = p & \text{if } e^{\text{sat}} \leq p \\ p^{\text{sat}} = e^{\text{sat}} & \text{if } e^{\text{sat}} > p \end{cases} \quad (7)$$

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^{9,10}.

3. Other non-standard definitions: Beside the predominant standard definition, several other RH definitions such as ψ_r and ψ_q continue to be used and to propagate on-line and in print. For example, the OMI (1951) definition ψ_r

$$\psi_r = \frac{r}{r^{\text{sat}}}, s: p^{\text{sat}} = p, \quad (8)$$

⁹Vaisala Humidity Calculator, <http://www.vaisala.com/en/services/technicalsupport/downloads/HumidityCalculator/Pages/default.aspx>, retrieved 17 April 2015

¹⁰Certain 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 organisations represented by the authors..

is occasionally mistakenly referred to as the WMO definition. The mistake possibly originated in a WMO training manual (Retallack, 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 online¹¹. On the other hand, ASHRAE (1994) and BS 1339-1 (2002) identify the ratio of mixing ratios, r / r^{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

$$\psi_q = \frac{q}{q^{\text{sat}}}, \quad s: p^{\text{sat}} = p \quad (9)$$

(e.g., Sundqvist, 1978; Peixoto and Oort, 1992; Katsaros, 2001; Tompkins et al., 2007; Lamquin et al., 2009; Quaas, 2012; Wells, 2012). In the category of other non-standard definitions we note that IUPAC’s online “Goldbook” (IUPAC, 2006) defines RH as

$$\psi_{\text{IUPAC}} = \frac{p_v}{e^{\text{sat}}}, \quad (10)$$

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 $\mu_{\text{w}}^{\text{AV}}(x, T, p)$ and $\mu^{\text{W}}(T, p)$ 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, λ_v , see Appendix 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, ψ_f , or water activity, a_{w} , of the unsaturated air,

$$\psi_f = \exp \left\{ \frac{\mu_{\text{w}}^{\text{AV}}(x, T, p) - \mu^{\text{W}}(T, p)}{R_{\text{w}} T} \right\} = \frac{f_v}{f_v^{\text{sat}}} = a_{\text{w}}, \quad s: p^{\text{sat}} = p, \quad (11)$$

where R_{w} is the specific gas constant of water (see Appendix D in the supplement of the Part 1 companion paper). This ratio characterises unsaturated humid air with reference to a theoretical bulk condensed phase,

¹¹For 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)

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 (Feistel et al., 2015a; IAPWS, 2015). 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 modelers 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) used as a convenient approximation to the relative fugacity, i.e.,

$$\psi_f = a_w = \frac{f_v}{f_v^{\text{sat}}} \approx \frac{p_v}{p_v^{\text{sat}}} = \psi_x, \quad s: p^{\text{sat}} = p \quad (12)$$

(Loncin et al., 1968; Hamer and Wu, 1972; Kraus, 1972; Greenspan, 1977; Mathlouthi, 2001; Blandamer et al., 2005; Choosri et al., 2009; Björklund and Wadsö, 2011; Feistel and Ebeling, 2011; Schiraldi et al., 2012; Li and Chylek, 2012).

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 realised 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, aging 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 generator¹² (HG) is the most common ultimate source of traceability in humidity measurements, and a typical traceability chain for RH is presented in Fig. 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 *two-pressure* 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 or evaporation takes place. This, now unsaturated mole fraction, x , can be calculated as

$$x = \frac{e^{\text{sat}}(T_1) f(T_1, p_1)}{p_1} = \frac{F_e(T_1; \mathbf{a}) F_f(T_1, p_1; \mathbf{b})}{p_1}. \quad (13)$$

Here, $F_e(T_1; \mathbf{a})$ and $F_f(T_1, p_1; \mathbf{b})$ represent reference functions that allow the calculation at T_1 of the saturation water vapour pressure e^{sat} and at T_1 and p_1 of the water vapour enhancement factor f respectively, and $\mathbf{a}$ and $\mathbf{b}$ 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 characterised in terms of mass, volume or amount of component substances, and that enables the mole fraction to be calculated (Hasegawa and Little, 1977; Stevens and Bell, 1992; Heinonen, 2002, Lovell-Smith, 2009; Mackrodt, 2012; Meyer et al., 2012).

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 , enable calculation of other unknown quantities such as dew-point temperature, RH or others. The standard RH at the DUC is, from eqs. (3) and (13),

$$\psi_x = \frac{x}{x^{\text{sat}}(T_2, p_2)} = \frac{x p_2}{e^{\text{sat}}(T_2) f(T_2, p_2)} \quad (14)$$

in general, and for the two-pressure humidity generator,

$$\psi_x = \frac{e^{\text{sat}}(T_1) f(T_1, p_1) p_2}{e^{\text{sat}}(T_2) f(T_2, p_2) p_1}. \quad (15)$$

Where RH traceability is required using a generator as a stable source, the reference hygrometer is usually a chilled-mirror hygrometer calibrated for dew-point temperature, T_d , which is found by solving

$$\frac{e^{\text{sat}}(T_d) f(T_d, p_2)}{p_2} = x \quad (16)$$

in general, and for the two-pressure humidity generator, by solving

¹²Occasionally 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.

$$\frac{e^{\text{sat}}(T_d) f(T_d, p_2)}{p_2} = \frac{e^{\text{sat}}(T_1) f(T_1, p_1)}{p_1}. \quad (17)$$

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 $T_d \approx T_1$. This is the principle of the single-pressure humidity generator. In practice, for greater accuracy, the pressure difference $p = p_1 - p_2$ is measured

and a correction $-\frac{\partial T_1}{\partial p_1} \Delta p$ added (Lovell-Smith, 2009).

Note the necessity to calculate $e^{\text{sat}}(T)$ and $f(T, p)$ in (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).

Under the axiomatic framework of TEOS-10, the calculation of the standard RH requires solving for x and x^{sat} , respectively, the implicit equations

$$\mu_{\text{w}}^{\text{AV}, \text{sat}}(x, T_1, p_1) = \mu^{\text{W}}(T_1, p_1) \quad \text{and} \quad \mu_{\text{w}}^{\text{AV}, \text{sat}}(x^{\text{sat}}, T_2, p_2) = \mu^{\text{W}}(T_2, p_2), \quad (18)$$

which replace eqs. (13) and (14). Eq. (18) may equivalently be expressed in terms of fugacities substituting the corresponding chemical potentials, see eq. (C.1) in the Digital Supplement of the Part 1 companion paper. Similarly, the equation

$$\mu^{\text{W}}(T_d, p_2) = \mu^{\text{W}}(T_1, p_1). \quad (19)$$

must be solved to find the dew-point temperature T_d . 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 pattern 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 modeling), 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; Randal 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 uncertainties¹³ 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 water¹⁴ by approximately $0.5 \mu\text{mol mol}^{-1}$ 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 characterised by joint occurrences of low temperatures down to 190 K and low water-vapour mole ratios¹⁵ (see Section 2) down to $(2 \pm 1) \mu\text{mol mol}^{-1}$ 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, $u(\psi)/\psi$, of about 1 % in the lower and middle troposphere (where RH > 10 %rh) and of about 2 % in the upper troposphere under mostly nighttime conditions (Miloshevich et al., 2006, Table 3 therein). By application of the method of standardised 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 realise 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 fulfill hydrological demands with respect to flood prediction in the course of severe weather events.

¹³This 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).

¹⁴Water vapour significantly contributes to the total hydrogen budget of the stratosphere (Dessler et al., 1994; Hurst et al., 1999) and plays an important role in stratospheric chemistry such as in formation of polar stratospheric clouds, the ozone hole, and photochemically reactive radicals (Brasseur and Solomon, 2005; Farman et al., 1985; Solomon, 1988; Spivakovsky et al., 2000). It may also serve as a tracer to study atmospheric circulation and the hydrological budget (Brewer, 1949; Dobson, 1956; Johnston and Solomon, 1979; Newell and Gould-Stewart, 1981; Danielsen, 1982; Hintsa et al., 1994; Webster et al., 1994; Crook, 1996; Mote et al., 1996; Dethof et al., 1999; Roms and Kuang, 2010).

¹⁵In order to be consistent with WMO (2008) and other authorities, for the quantity n_v/n_a (see Section 1) we use the term *mole ratio* rather than *mixing ratio*, which is the term used by Teitelbaum et al. (2000).

Given that RH is a nonlinear 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 error 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.

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 realisations, so that the definition can be connected with disseminated traceable measurements.

(1) The *de facto* standard definition of RH is incomplete and other non-standard definitions compete

While the standard definition, ψ_x , given by eq. (6) has widespread official sanction and use, it is defined over only part of the full range over which other humidity quantities are defined, where the concept of RH is meaningful and useful, and where RH sensors respond sensibly. The definition is restricted to humid-air states where $p < p^{\text{sat}}(T)$ and isobaric saturation is possible.

Two non-standard definitions, ψ_r , given by eq. (8), and ψ_q , given by eq. (9), share the limited range of the standard definition and continue to appear in the literature. A third non-standard definition, eq. (10) sanctioned by IUPAC, defines the saturated state with reference to pure water, but is inconsistent since it yields RH of 100 %rh before saturation is reached. Differences between the standard and non-standard definitions including also the relative fugacity eq. (11) are shown in Fig. 4. Most traceable RH calibrations will be based on the standard definition ψ_x , and the incorrect assumption by some users that the hygrometer instead reports ψ_r , ψ_q or ψ_{IUPAC} (or has been calibrated with respect to these) could lead to significant error.

The differences between different RH measures are often significant, and to prevent invisible propagation of non-standard definitions, the definition used should always be documented to allow conversion to ψ_x as in

$$\psi_x = \psi_{p_V} = \frac{1-x}{1-x^{\text{sat}}} \psi_r = \frac{x\omega + (1-x)}{x^{\text{sat}}\omega + (1-x^{\text{sat}})} \psi_q = \frac{\varphi_v(x^{\text{sat}}, T, p)}{\varphi_v(x, T, p)} \psi_f = \frac{1}{f(T, p)} \psi_{\text{IUPAC}} \quad (20)$$

Here, ω is the ratio of the molar masses of water and dry air and ϕ_v is the fugacity coefficient of water in the gas phase (see Appendix C and D in the supplement of the Part 1 companion paper).

(2) The “full-range” definition lacks official sanction and theoretical justification

The full-range definition ψ_{full} , eq. (7), has been a common-sense but informal choice by those needing to measure outside the standard range. Although proposed by the IJCPD in 1949, 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 Fig. 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 $p < e^{\text{sat}}$, 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 extended range (e.g., state B in Fig. 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^{sat} (e.g., $x^{\text{sat}} = 1$) or p^{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-vapour 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 ambient conditions of air-conditioning or meteorology, such nonuniformity and variability is irrelevant for practical purposes, 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 H_2O in 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 nonideality 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, but for sparingly soluble gases at pressures near atmospheric this difference will be negligible. For high concentrations of dissolved gases, the ideal-solution approximation used in eq. (2) may also require correction.

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

The main relative-humidity definitions reported here, i.e., eqs. (6)–(11), can be calculated and realised with equal traceability to the SI. But not one of the quantities x^{sat} , r^{sat} , q^{sat} and e^{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 toward 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.

Against this, it might be argued that the usefulness of the partial-pressure and mole-fraction RH definitions will outweigh consideration of relative fugacity in the near future. After all, in those fields such as food chemistry where water activity is used, the reference saturation state is most often defined with respect to pure water (or ice), and e^{sat} is almost inevitably used as a suitable approximation to f_v^{sat} . The problem of developing relative fugacity as the thermodynamic basis for a relative-humidity definition is tied to the problem of providing a firm thermodynamic basis for defining the reference state.

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

By its definition, eq. (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 mixing ratio 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 standardised 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 ψ_{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 $p_v^{\text{sat}} > e^{\text{sat}}$ hold, eq. (10) will always give $\psi_{\text{IUPAC}} > 100$ %rh at saturation (e.g., see Fig. 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 ψ_e for ψ_x are sometimes given, but uncertainty associated with the approximation is not. While usual uncertainty propagation rules sum over all positive contributions, a procedure that ignores uncertainty covariance’s may produce estimated uncertainties that are much too large for the case of eq. (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. 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.

(1) Framework

The framework is straightforward: the standard definition, where $p = e^{\text{sat}}$ and $x < 1$, and the pure-vapour definition, where $p = e^{\text{sat}}$ 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 relative humidity. Steps will need to be taken to determine the status of water activity and (relative) activity within the framework.

The ratios r/r^{sat} and q/q^{sat} as RH definitions will be deprecated but will retain their other assigned names of the “degree of saturation” and the “relative specific humidity”, respectively.

(2) Thermodynamic basis

For a given sample of unsaturated humid air, what are the advantages of having a definition of relative humidity directly linked to the sample’s mass-based chemical potential

$\mu_{\text{w}}^{\text{AV}}(x, T, p)$ and fugacity, as opposed to a definition directly linked to the sample’s vapour mole fraction or water vapour partial pressure? Given that it is straightforward to calculate one from the other, the advantages will probably lie in understanding and developing not only the thermodynamic basis of saturation but also the thermodynamic basis of non-saturated equilibrium such as might be found between humidity sensors and the adjacent humid air, or between industrial surfaces and conditioning gases. For example, it will be useful to derive the Kelvin equation for curved interfaces (and extensions for electric field, aqueous solutions, etc.) in terms of fugacity and relative fugacity without resorting to the ideal-gas limit.

Such investigation should also explore the nature of the equilibrium when the pressure is too low to support a bulk condensed phase, i.e., under conditions where the extended-range part of the relative-fugacity definition applies. To what extent does the clear thermodynamic basis of relative fugacity over the standard range support a single unified definition over the full range?

(3) Means to calculate

The relationship between the fugacity and partial pressure of water vapour in humid air was sketched in Section 3. TEOS-10 and the work of Feistel et al. (2015a) provide new means to calculate the fugacity and relative fugacity of water in humid air. Additional corrections for dissolved air in liquid water are required. Further work is needed to enable propagation of uncertainty from the large amount of data input to the Helmholtz and Gibbs energy equations forming the basis of TEOS-10 into those equations through to the many calculable quantities including the fugacity. Again, stand-alone virial equations for the fugacity (Feistel et al., 2015a) and for the enhancement factor (Herrmann et al., 2009) should also have associated uncertainty presented in a way that allows correct accounting for covariance’s.

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

- 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. Encourage official sanction of the framework and associated thermodynamic basis. Encourage the reporting of applied RH definition in calibration reports and in journal articles.
- c. Identify non-standard definitions and publicise 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, AMS¹⁶, IUPAC, etc., and also Wikipedia.

- d. 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.
- e. Develop a *mise en pratique* (BIPM, 2006) for RH to provide guidance for practitioners to realise 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 or some subset as outlined in Appendix D of the Digital Supplement to Part 1 of this series.
- f. 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) where less computational complexity is desired, while maintaining consistency with TEOS-10 within a specified tolerance.
- g. Develop standardised 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.
- h. Consider other humid gases besides standard air for which real-gas properties are available to derive corresponding fugacity equations.
- i. Continue to dialogue with organisations representative of users of the alternative definitions of RH, to increase the level of harmonisation, 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 realisability and low measurement uncertainty. Calculation of relative fugacity from dew-point temperature, and conversion between alternative RH definitions, is possible using TEOS-10 equations,

¹⁶AMS: American Meteorological Society, <http://www.ametsoc.org/>

with an extension to dissolved air to be specified in the future. Consistently covering also the low-pressure range where saturated humid air does not stably exist seems possible, but will require future studies. Unambiguous nomenclature may be developed and recommended by the international committees governing the SI.

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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 were each of the Raoult, Poynting or interaction contributions to act alone in the enhancement of the full partial pressure (thick black line) above the pure saturation vapour pressure (dashed green line). The theoretical partial pressures shown are calculated using the enhancement-factor equation from Herrmann et al. (2009) modified to highlight the Raoult (green ' Δ '), Poynting (blue '+') and gas-phase interaction (blue ' $\square$ ') effects individually. Also shown for comparison is the water-vapour fugacity (red ' $\bullet$ '), which was calculated using TEOS-10 functions (Feistel et al., 2010b; Wright et al., 2010). Note that for pure saturated vapour at 300 K (black ' $\blacksquare$ '), $p^{\text{sat}} = e^{\text{sat}} = 3.537 \text{ kPa}$ and $f_V^{\text{sat}} \approx e^{\text{sat}} - 6 \text{ Pa}$ 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 green 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.

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 eq. (13)) and the humidity reference functions for the vapour pressure $e^{\text{sat}}(T)$ 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 eq. (16) and $\psi(x, p_2, T_2)$ using eqs. (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 ψ of conditioned air for calibration of a “device under calibration” (DUC), including, as illustrated, a RH hygrometer.

Figure 4.

Differences between the standard definition ψ_x and four non-standard definitions at 40 °C (hollow symbols) and 80 °C (filled symbols) for pressures $p = 0.1$ MPa, panel (a), and $p = 1$ MPa, panel (b). Three non-standard definitions are of the form ψ_z , where the humidity quantity z is the mixing ratio, r (squares), the specific humidity q (triangles), and the fugacity f_V (diamonds). The fourth non-standard definition is ψ_{IUPAC} (circles).