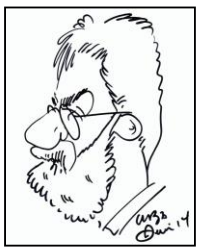
Defining Relative Humidity in Terms of Water Activity



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Article in press at Metrologia

IOP Publishing | Bureau International des Poids et Mesures Metrologia

Metrologia **00** (2017) 1–11 UNCORRECTED PROOF

Defining relative humidity in terms of water activity. Part 1: definition

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Received 2 March 2017, revised 27 April 2017
Accepted for publication 2 May 2017
Published

Abstract

Relative humidity (RH) is a quantity widely used in various fields such as metrology, meteorology, climatology or engineering. However, RH is neither uniformly defined, nor do some definitions properly account for deviations from ideal-gas properties, nor is the application range of interest fully covered. In this paper, a new full-range definition of RH is proposed that is based on the thermodynamics of activities in order to include deviations from real-gas behaviour. Below the critical point of pure water, at pressures $p < 22.064$ MPa and temperatures $T < 657$ K, RH is rigorously defined as the relative activity (or relative fugacity) of water in humid air. For this purpose, reference states of the relative activity are specified appropriately. Asymptotically, the ideal-gas limit of the new definition is consistent with *de-facto* standard RH definitions published previously and recommended internationally. Virial approximations are reported for estimating small corrections to the ideal-gas equations.

Keywords: humid air, relative humidity, relative activity, fugacity, virial coefficients

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

IOP Publishing | Bureau International des Poids et Mesures Metrologia
Metrologia **53** (2016) R40–R59 doi:10.1088/0026-1394/53/1/R40

Review

Background:

Joint 2016 Article of

CCT WG Hu & IAPWS

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

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Received 28 May 2015, revised 8 July 2015
Accepted for publication 13 July 2015
Published 15 December 2015

CrossMark

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.

Ambiguity of existing RH definitions

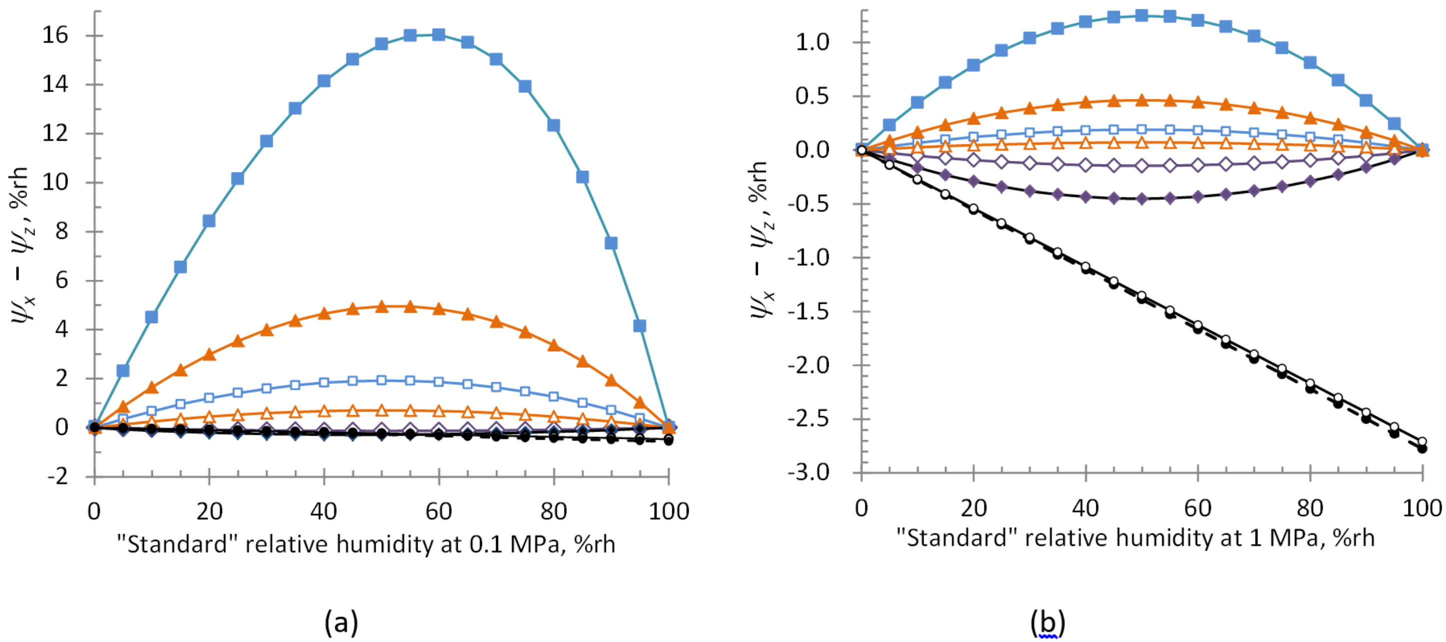


Figure 4: Differences between the standard definition ψ_x and four non-standard definitions at 40 °C (hollow symbols) and 80 °C (filled symbols) for pressures *p* = 0.1 MPa, panel (a), and p = 1 MPa, panel (b). Three non-standard definitions are of the form ψ_z, where the humidity quantity *z* is the 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).

From: Lovell-Smith et al. (2016)

Aim: Contribute to discussion on possible SI definition of RH

New RH definition should:

- Possess clear physical justification
- Allow for non-ideal gas effects
- Cover the „extended range“ $p < e$ (or, $T > T_{boil}$)
- Properly express thermodynamic non-equilibrium forces
- Include some current definitions as ideal-gas limits
- Allow for dissolution of air in water
- Be rigorously continuous and unambiguous across water phases
- Envisage application to humid gases other than air

Activity and Fugacity

Activity is a „real-gas equivalent“ of the mole fraction / concentration:

$$\mu(\boldsymbol{x},T,p)=\mu_0(T,p)+RT\ln a(\boldsymbol{x},T,p)$$

Standard or *reference state* μ_0 where a = 1, independent of x

Fugacity is a „real-gas equivalent“ of the partial pressure:

$$\mu_{\mathrm{V}}^{\mathrm{AV}}(x,T,p)=\mu_{\mathrm{V}}^{\mathrm{AV,id}}(x,T,p)+RT\ln\frac{f_{\mathrm{V}}}{xp}$$

Activity – fugacity conversion:

$$\ln a_{\mathrm{V}}^{\mathrm{AV}}(x,T,p)=\ln\frac{f_{\mathrm{V}}(x,T,p)}{f_{\mathrm{V}}^{0}(T)}-\frac{\mu_0(T,p)}{RT}$$

$$xp\exp\left\{-\frac{\mu_{\mathrm{V}}^{\mathrm{AV,id}}(x,T,p)}{RT}\right\}\equiv f_{\mathrm{V}}^{0}(T)$$

Phase equilibria: equal activities / fugacities
(not partial pressures or so)

Relative Humidity

De-facto standard RH definition of WMO, ASHRAE, etc:

$$\psi_x(x,T,p) = \frac{x}{x^{\text{sat}}} = \frac{p_V(x,T,p)}{p_V(x^{\text{sat}},T,p)}$$

Substitute x, p_V by their „real-gas equivalents": **Relative Fugacity**

$$\boxed{\psi_f(x,T,p) = \frac{a}{a^{\text{sat}}} = \frac{f_V(x,T,p)}{f_V(x^{\text{sat}},T,p)}}$$

Define activity reference state μ_0 by the saturation state:

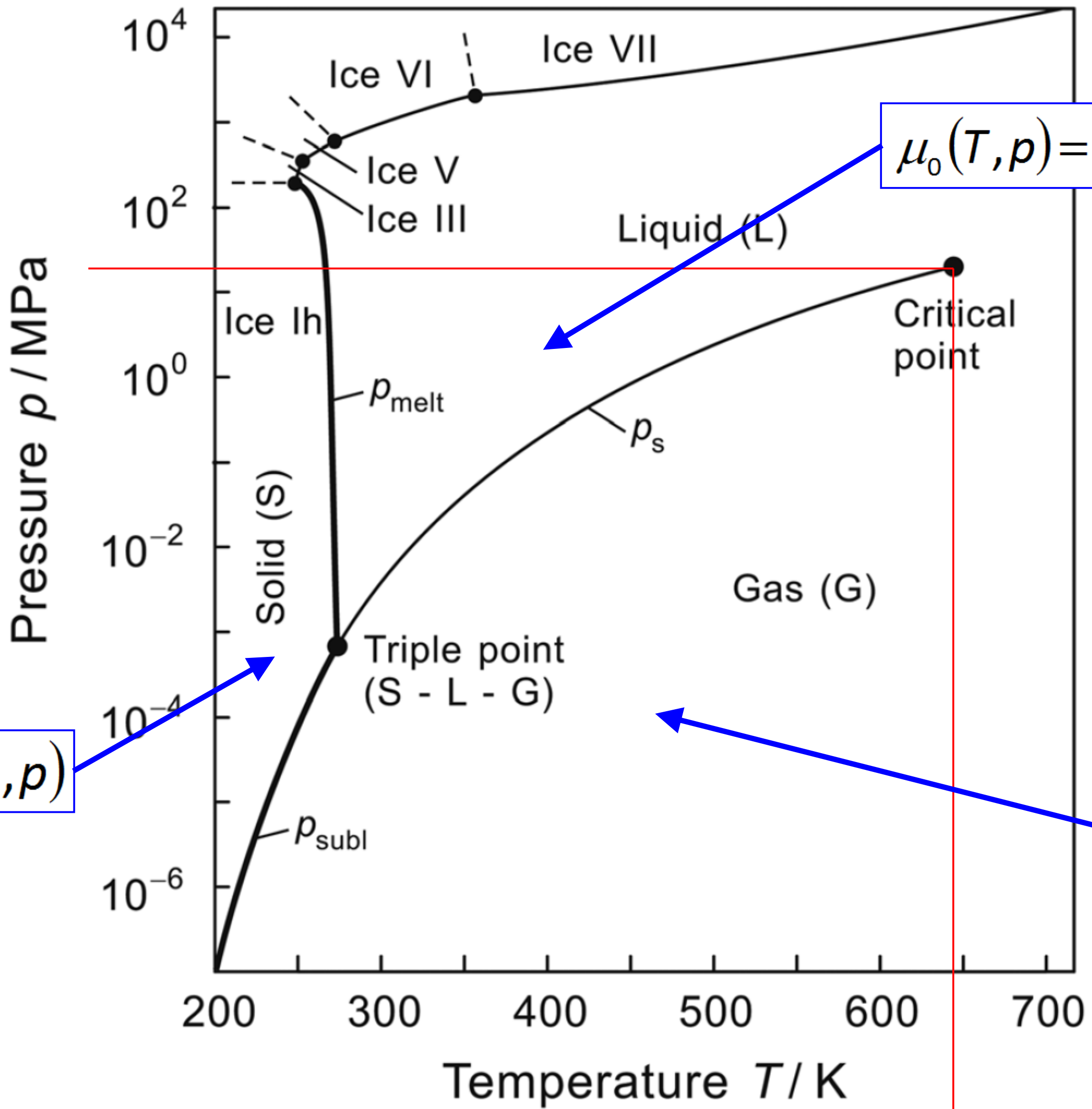
$$a(x^{\text{sat}},T,p) = 1$$

$$\boxed{RT\ln\psi_f(x,T,p) = RT\ln a_V^{AV}(x,T,p) = \mu_V^{AV}(x,T,p) - \mu_0(T,p)}$$

Definition ?

Available from IAPWS

IAPWS: *T – p* Phase Diagram of Water



$$\mu_0(T,p) = \mu_W^{AW}(x_W(T,p),T,p)$$

$$\mu_0(T,p) = g^{Ih}(T,p)$$

„Extended Range“

$$\mu_0(T,p) = ?$$

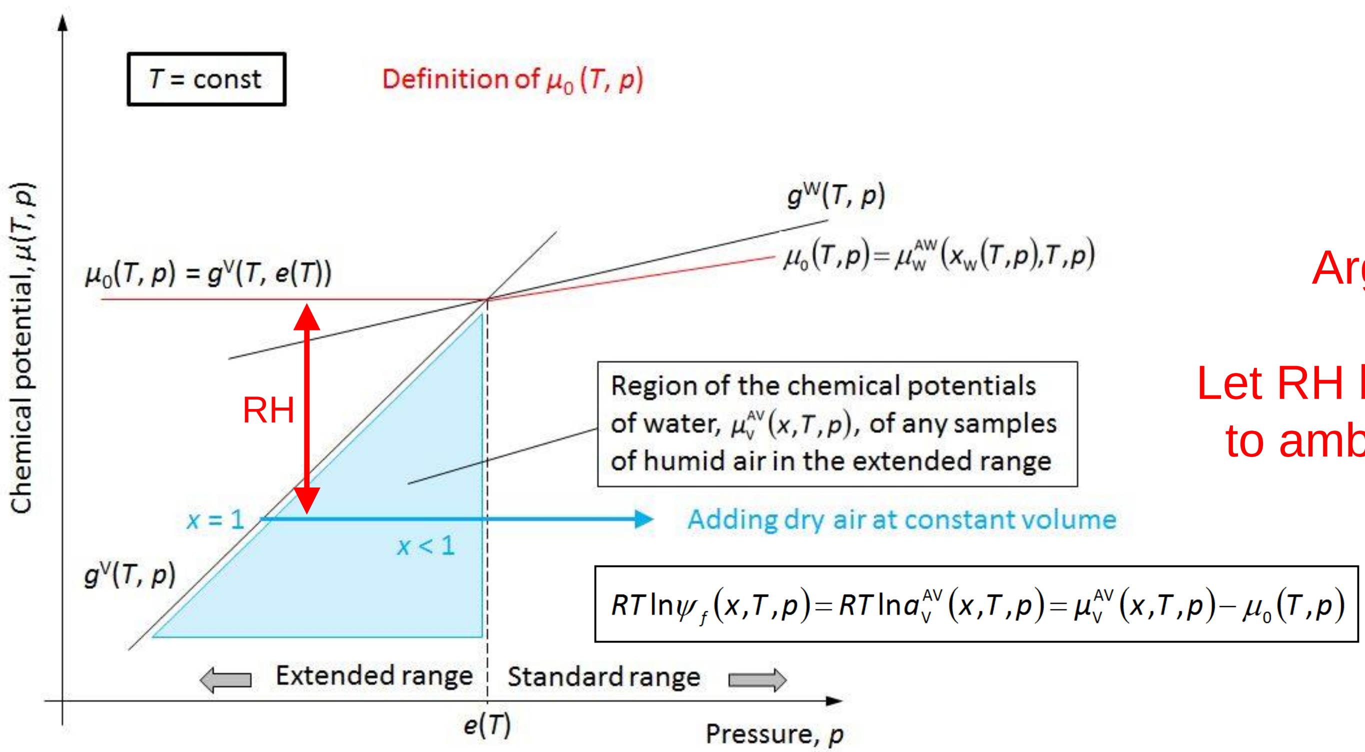
New Full Range of RH

Extended-Range Definition of RH

Problem: No saturation state of humid air if $p < e$. How to specify $a = 1$?

Approach: Onsager force remains valid also in (G):

$$E = \ln a_W^{SW}(x_W, T, p) - \ln a_V^{AV}(x, T, p) = \ln a_W^{SW}(x_W, T, p) - \ln \psi_f$$



Argument:

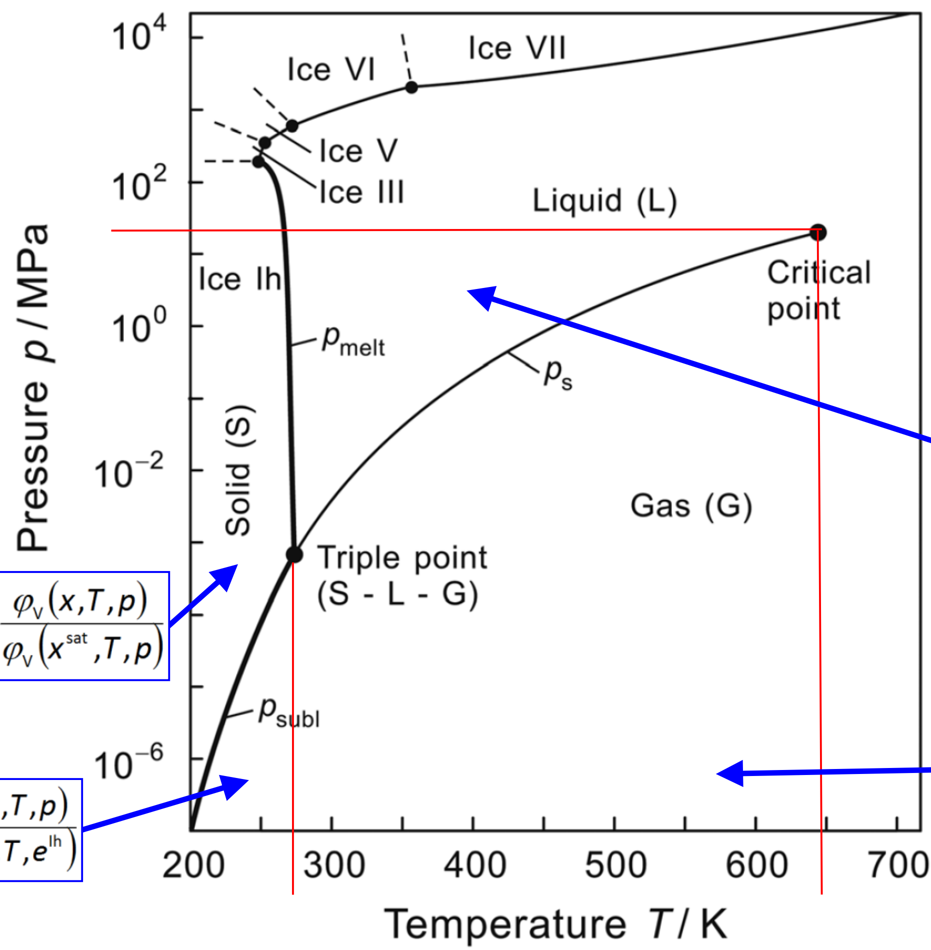
Let RH be insensitive to ambient dry gas

Virial Equations

Virial approximation of the fugacity coefficient:

$$\varphi_V(x,T,p) = \frac{f_V}{xp} = \exp\left\{\frac{p}{RT}\left(\beta(x,T) + \gamma(x,T)\frac{p}{2RT}\right)\right\}$$

Available from IAPWS



$$\psi_f = \frac{f_V(x,T,p)}{f_V(x^{sat},T,p)} = \frac{x}{x^{sat}(T,p)}\frac{\varphi_V(x,T,p)}{\varphi_V(x^{sat},T,p)}$$

$$\psi_f = \frac{f_V(x,T,p)}{f_V(x^{sat},T,p)} = \frac{x}{x^{sat}(T,p)}\frac{\varphi_V(x,T,p)}{\varphi_V(x^{sat},T,p)}$$

$$\psi_f = \frac{f_V(x,T,p)}{f_V(1,T,e^{W})} = \frac{xp}{e^{W}(T)}\frac{\varphi_V(x,T,p)}{\varphi_V(1,T,e^{W})}$$

$$\psi_f = \frac{f_V(x,T,p)}{f_V(1,T,e^{Ih})} = \frac{xp}{e^{Ih}(T)}\frac{\varphi_V(x,T,p)}{\varphi_V(1,T,e^{Ih})}$$

Outlook

Open tasks and problems:

- Measurement procedures and references
- Standard equations for RF calculation from measurands
- Standard equations for converting legacy data
- Uncertainties
- Metastable phases
- Discussion of pros, cons and potential alternatives
- Independent verification and recommendation ?
- Official „blessing“ of RH by CCT ?

IAPWS-BIPM Humidity Workshop at the 17th ICPWS in Prague 2018:

www.icpws2018.com