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Metrological Aspects of Humidity: State of Discussion on Common Positions, Challenges, and Needs by

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This report is based on the humidity related part of a joint BIPM and IAPWS position and review paper (inclusive previous drafts)

Metrological challenges for measurements of key climatological observables: Oceanic salinity and pH, and atmospheric humidity by

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submitted to Metrologia, 06 February 2015 (hereafter cited as Feistel et al., 2015), the presentations and discussion during the workshop, and comments by J W Lovell-Smith (08 November 2013), M Heinonen (10 and 27 November 2013), and R Feistel (11 November 2013).

The main contribution to the present draft has been provided by R Feistel and J W Lovell-Smith. The compilation of the material presented here has been performed by O Hellmuth and J Kalova.

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⁶ Consultative Committee for Thermometry

⁷ Consultative Committee for Amount of Substance – Metrology in Chemistry

⁸ Joint Committee on Seawater, established by SCOR and IAPWS

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Rationale

Observational data of relative humidity need to be globally comparable within requisite uncertainties over time spans of centuries. This increasingly urgent and long-pending goal can only be achieved by proper metrological traceability to the International System of Units (SI). Consistent with such SI-based definitions, state-of-the-art correlation equations for thermophysical properties of water, seawater, ice and humid air should be developed and adopted as joint international standards for all branches of climate research, in oceanography, meteorology and glaciology for data analysis and numerical models. The IAPWS-SCOR Joint Committee on Seawater JCS is targeting at these aims in cooperation with BIPM, WMO and other international bodies.

There is consensus among the workshop participants regarding

- (i) the need for SI-traceable, world-wide uniform and long-term stable international standard for humidity definition,
- (ii) an increasing demand for standardised, consistent and uniform correlation equations to be used for the calculation of humid air in the climate system, and
- (iii) resulting requirements in estimating robust and comprehensive uncertainties related to such equations.

Aim of the present document is (i) to identify key problems in current definitions of relative humidity, and (ii) to provide a notional basis ('lingua franca') to support the further discussion within IAPWS between metrologists, meteorologists, oceanographers, and engineers from different disciplines faced with 'humid air'.

The importance of humidity measures for climatological purposes, especially a SI compatible definition of relative humidity, is discussed in detail in Feistel et al. (2015) and will therefore not be discussed here. In contrast to this, the metrological aspects of relative humidity definition will be presented as detailed as currently possible to allow full traceability of argumentation by the workshop participants.

1 Survey of Available Relative Humidity Definitions

1.1 Basic Notions

(a) Humidity and Moisture

The term ‘humidity’ indicates water vapour, normally admixed with air or other dry gas. In contrast to this, the term ‘moisture’ is preferably used to indicate water adsorbed or absorbed in solid or liquid materials. 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 . In the subsequent sections the condensed phase, either pure liquid water or ice, is considered to be a bulk phase having a planar interface with the vapour phase. Hence, ‘pre-bulk’ states such as water clusters of confined water are excluded from consideration.

(b) Pure Water Vapour Pressure and Water Vapour Partial Pressure

Pure water vapour with pressure e is called to be ‘saturated’, when it coexists in stable thermodynamic equilibrium with a plane surface of the condensed phase of pure water, which can either be liquid water or ice. At the interface, both temperature and pressure in both coexisting phases are equal. If the liquid water is in supercooled state, then the thermodynamic equilibrium is not stable, but metastable. The pressure of pure water vapour at saturation is called the ‘saturation vapour pressure’, denoted with symbol e^{sat} . The saturation vapour pressure of pure water vapour is only a function of temperature. Depending on whether the condensed phase is liquid water or ice, the subscript “w” or “lh” is added from case to case to the symbol e^{sat} .

Humid air is a mixture of dry air and water vapour. According to Dalton’s law of partial pressures for ideal gases, the water-vapour partial pressure in the gas mixture is given by $p_V = xp$, where x is the previously introduced water-vapour mole fraction), and p is the total pressure of the mixture. Analogously to saturation of pure vapour, water vapour with partial pressure p_V in humid air is called to be ‘saturated’, when it coexists in stable thermodynamic equilibrium with a plane surface of the condensed phase of water. The density of saturated water vapour in humid air is greater than that of pure saturated vapour at the same temperature. Equivalently, the saturation partial pressure, $p_V^{\text{sat}} = x^{\text{sat}}p$, is greater than the pressure of pure saturated vapour, e^{sat} , at the same temperature.

(c) Water Vapour-Pressure Enhancement Factor

The enhancement factor, \hat{f} , is defined as the ratio of the saturation vapour pressure of moist air to that of pure water vapour:

$$\hat{f}_w(T,p) = \frac{p_{V,w}^{\text{sat}}}{e_w^{\text{sat}}} > 1, \quad \hat{f}_{lh}(T,p) = \frac{p_{V,lh}^{\text{sat}}}{e_{lh}^{\text{sat}}} > 1.$$

Here, $p_{V,W}^{\text{sat}}$ and $p_{V,ih}^{\text{sat}}$ denote the water-vapour partial pressures of saturated moist air with respect to water (second superscript w) and hexagonal ice (second superscript ih) ('saturation partial pressure of water vapour in humid air'), and e_W^{sat} and e_{ih}^{sat} are the corresponding saturation pressures of the pure (water) vapour.

The fact that $p_{V,*}^{\text{sat}}$ is larger than e_*^{sat} at the same temperature is caused by a combination of three thermodynamic parts, which, in parts, counteract each other: (i) increase of the water vapour pressure associated with the condensed phase due to the applied pressure (Poynting effect), (ii) decreases of the water vapour pressure associated with the condensed phase due to dissolved gas (colligative or Raoult effect), and (iii) decrease of the water-vapour partial pressure in the mixture due to interaction between air and water molecules in the gas phase. The water vapour partial pressure p_V is defined as the vapour pressure of humid air at ambient temperature T , or saturation vapour pressure at its dew-point or frost-point temperatures, T_D and T_F , respectively. The relationships among the above terms are given by the following expressions:

$$\begin{aligned} p_{V,W}^{\text{sat}} &= e_W^{\text{sat}}(T) \hat{f}_W(T, p) \quad \text{with respect to water,} \\ p_{V,ih}^{\text{sat}} &= e_{ih}^{\text{sat}}(T) \hat{f}_{ih}(T, p) \quad \text{with respect to ice,} \\ p_V &= e_W^{\text{sat}}(T_D) \hat{f}_W(T_D, p) \quad \text{with respect to water,} \\ p_V &= e_{ih}^{\text{sat}}(T_F) \hat{f}_{ih}(T_F, p) \quad \text{with respect to ice.} \end{aligned}$$

(d) Fugacity

Lewis' concept of fugacity (symbol f_V), a thermodynamic property with dimension of a pressure¹⁰, can explain the phenomenon that the thermodynamic activity of saturated pure

¹⁰ The chemical potential of a virtual gas consisting of noninteracting point particles undergoing Brownian motion is a function of temperature and mechanical gas pressure. For a real gas, however, in which intermolecular forces and molecular size are important, the mechanical pressure has to be replaced by a fictitious 'effective pressure', introduced by Gilbert N. Lewis in (1901) as 'fugacity'. It can be formally defined as the mechanical pressure of an ideal gas, which would have the same chemical potential as a nonideal gas. Owing to the action of intermolecular attractive forces, the fugacity is lower than the mechanical pressure, motivating the interpretation of fugacity as the tendency to 'flee or escape'. The deviation of fugacity from the mechanical gas pressure reflects the degree of nonideality. The concept of fugacity also applies to mixtures of real gases.

With respect to applications such as (a) psychrometric process calculations, (b) meteorological analysis, (c) drying process calculations, and (d) evaporation from liquid water and ice surfaces one might ask why to introduce or use the notion 'fugacity'? Fugacity is the chemical potential of a substance expressed in the form of a pressure. This form is more convenient for many users than a chemical potential, and fugacity has the advantage that it does not need reference states to specify certain arbitrary constants. From the thermodynamic perspective, fugacities and chemical potentials are equivalent quantities. As such, they control any equilibria between different phases and mixtures, as already worked out by J. W. Gibbs. In the ideal-gas limit, fugacity equals partial pressure. This has led scientists and engineers before Gibbs to believe that partial pressures control equilibria, but in fact partial pressures do it only in that very special case and have no thermodynamic relevance for real gases, liquids, solids, food, rocks, alloys etc., in contrast to fugacity and chemical potential which apply universally. An interesting feature of fugacity is that relative fugacity can seamlessly be extended into T -regions where saturation states of relative humidity do not stably exist, which is very useful in metrology. A plausible reason for preferring partial pressure over fugacity is that it is easy to measure and to calculate. To promote application of fugacity by practitioners a user-friendly precept for its easy calculation (e.g., fixed in an IAPWS guideline) is desirable.

water vapour is greater than that of humid air with the same water vapour density. For a nonideal humid gas, the fugacity of water in humid air (subscript V), $f_V(x, T, p)$, is equal to the partial pressure of water vapour, $p_V = xp$, multiplied by the fugacity coefficient $\phi(T, p) = \lambda_V / \lambda_V^{\text{id}}$ i.e.,

$$f_V = p_V \phi = xp \phi.$$

Here, λ_V and λ_V^{id} denote the absolute activities of the real and ideal gases, respectively (see Appendix A for full derivation). In the ideal-gas limit, $\phi = 1$, and the fugacity is equal to the partial vapour pressure. Using the semi-empirical theory of Lewis, thermodynamic properties of real-gas mixtures can be found by replacing, in formulas for ideal-gas mixtures, the partial pressure p_V by the fugacity f_V . The fugacity can be directly calculated from a virial equation, or iteratively calculated from the equation of state of humid air (e.g., TEOS-10). At equilibrium, the fugacity of water vapour equals the fugacity of water in the condensed phase. For humid air the fugacity can be considered as the 'effective' water vapour pressure (neither $p_{V,*}^{\text{sat}}$ nor e_*^{sat}) driving water transport toward equilibrium.

The fugacity coefficient at saturation reads:

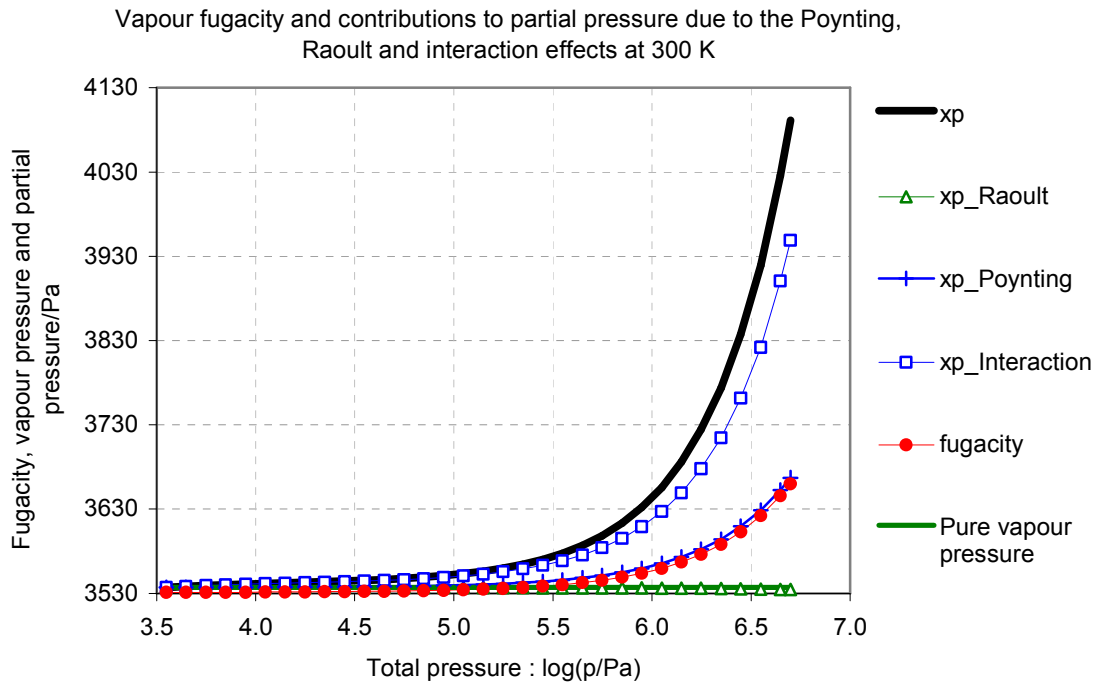
$$\phi^{\text{sat}}(T, p) \equiv \phi(x^{\text{sat}}, T, p) = \frac{f_V(x, T, p)}{p_V^{\text{sat}}(T, p)} = \frac{f_V^{\text{sat}}(T, p)}{\hat{f}(T, p) e^{\text{sat}}(T)}.$$

To illustrate the relationship between the fugacity and partial pressure let us consider an equilibrium of liquid water with pure vapour in a closed volume. When dry air is introduced into the container the total pressure, i.e., the sum of the partial water-vapour pressure and the partial dry-air pressure, will rise. The higher pressure exerted on the liquid will tend to enhance evaporation (Poynting effect, see Appendix B), which is only negligibly lowered by the introduced presence of dissolved air (Raoult effect). The resulting evaporation further increases the total pressure as well as the vapour density. The effective pressure, or 'escaping tendency' from the liquid phase is the liquid-water fugacity (subscript W), f_W , which is at equilibrium balanced by the fugacity of water in the vapour phase, f_V . At very low pressures and hence low densities corresponding to the ideal-gas limit, the vapour fugacity is equal to the vapour partial pressure. However, in a real-gas mixture attractive interaction forces between water and air molecules in the gas phase reduce the vapour fugacity below $p_V = xp$ in proportion to the vapour density, so more water must evaporate to balance f_W . Consequently, at equilibrium the partial pressure of vapour in humid air will be higher than the pressure of saturated pure vapour, expressed in the previously introduced water-vapour pressure enhancement factor (see Appendix B for rigorous definition of $\hat{f}(p, T)$ in terms of fugacity).

Let us recall an isothermal system (at $T=300$ K), which initially contains saturated vapour above a pool of water in a sealed box at equilibrium between the fugacity of the saturated water vapour and the fugacity of the liquid water, $f_V^{\text{sat}} = f_W$. Upon addition of dry air the system behaves as depicted in **Figure 1.1**, which shows the pure vapour pressure e , the fugacity f_V , and the single contributions to the partial vapour pressure $p_V = xp$ as function of the decadic logarithm of the total (mixed-air) pressure. In the initially state (corresponding to the lower left part of the diagram in Fig. 1.1a) the partial pressure p_V (black solid line) exactly equals the pure saturation vapour pressure (which is kept fixed, depicted as the green solid

line), $p_v = xp = e^{\text{sat}}(T)$, as no air is present. Upon increasing the total pressure by adding dry air, the small amount of air dissolving causes a slight decrease in f_w (in Fig. 1.1 denoted as 'xp_Raoult'). At the same time, the increase in total pressure exerted on the liquid causes a substantial increase in f_w (in Fig. 1.1 denoted as 'xp_Poynting'). The partial water vapour pressure will rise as does the fugacity, rather more slowly. The three contributions to the partial water vapour pressure are also depicted in Fig. 1.1, showing the interaction effect (in Fig. 1.1 denoted as 'xp_Interaction') dominating the total pressure dependence followed by the Poynting effect, and the Raoult effect exerting a small decrease in partial pressure. In the gas phase, the interaction amongst water and air molecules acts to lower the fugacity in the vapour phase, and the resulting net evaporation until $f_v^{\text{sat}} = f_w$ is the dominant contributor ('xp_Interaction' line). In Fig 1.1b the ordinate scale is stretched to see more details.

(a)



(b)

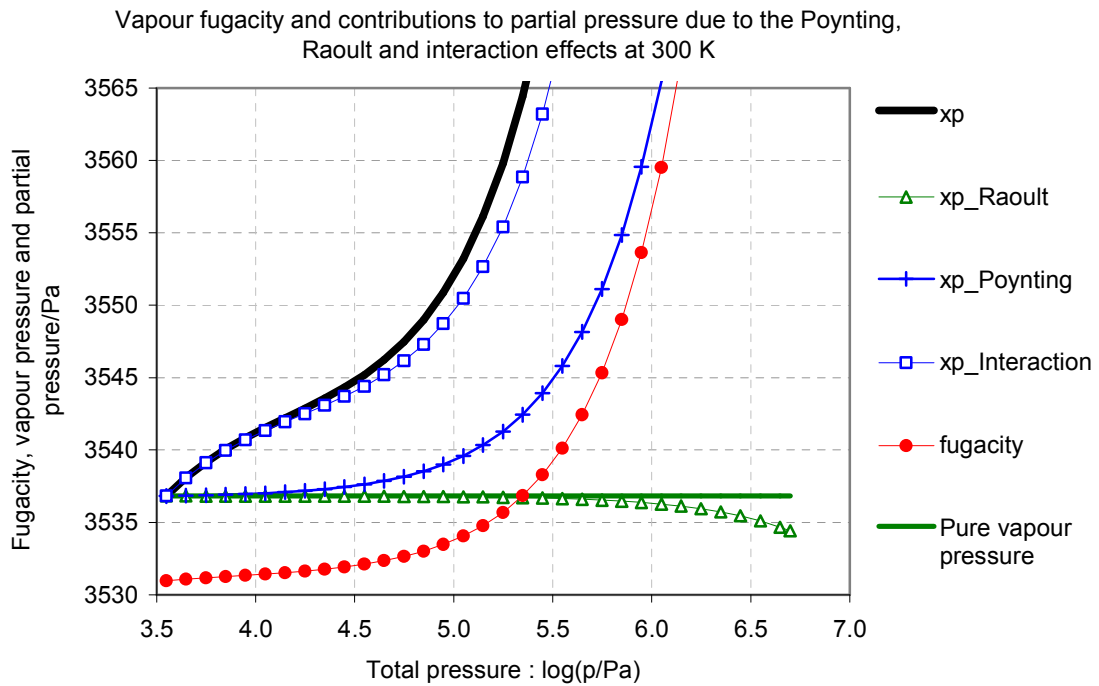


Fig. 1.1: Saturated water-vapour fugacity, pressure of pure water vapour, and partial water-vapour pressure as function of the decadic logarithm of the total (mixed air) pressure p . (a) Pure vapour pressure e , fugacity f_v , and contributions of Raoult, Poynting, and interaction effects, respectively, to the partial vapour pressure $p_v = xp$. (b) As in panel (a), but for stretched ordinate scale to see details. The fugacity for pure vapour is about 6 Pa less than the pure vapour pressure, $f_v^{\text{sat}} \approx e^{\text{sat}} - 6 \text{ hPa}$, because pure saturated vapour is not an ideal gas and interactions between water molecules reduce the total fugacity.

(e) Pro's and Con's for the Choice of a Certain Humidity Measure

Note that while the vapour amount fraction and the related 'partial pressure' may describe a humid gas physically in one way, the transport and chemical activity properties of the water vapour may be better described by the fugacity. For some applications, such as the study of the greenhouse effect, the physically important variable is the actual amount of water (mass or moles) in the phase. For other applications, such as the evaporation from seawater, it is the chemical potential or fugacity that is important. Therefore, any particular definition of relative humidity will be sub-optimal for somebody. To the chemist, a definition based on a ratio of partial pressures may seem to merely approximate real behaviour of moist air (better expressed by the fugacity) by substituting the properties of a mixture of ideal gases. For the heating and refrigeration engineer, wanting to calculate the moisture load in a room, a relative humidity definition based on the mixing ratio r is best. Similarly, x and r are important for meteorologists, and because for most purposes the moist gas is air without significant contaminant, the deeper thermodynamic theory of Lewis was unnecessary and neglected. In a rigorous approach, the practically very similar quantities must conceptually be well distinguished. Any of the humidity quantities can be calculated from any others if sufficient information is given to uniquely specify the moisture state and particular definitions used.

1.2 Common Definitions of Relative Humidity

Any humidity quantity z describing a sample of humid gas (or pure vapour), at a given temperature T and pressure p may be written as a function of the triple (x, T, p) of independent variables representing the 'actual' state, i.e., $z = z(x, T, p)$. Then, all available definitions of relative humidity, ψ , can be expressed in the general form

$$\psi_z^{(s)} = \frac{z}{z^{\text{sat}}} = \frac{z(x, T, p)}{z(x^{\text{sat}}, T, p^{\text{sat}})}, \quad (1.1)$$

The value z^{sat} denotes the chosen humidity quantity at saturation, i.e., when the gas is brought to equilibrium with a plane surface of water or ice. We identify with superscript 'sat' those independent variables which have changed at saturation from their original values. The superscript "s" to the quantity ψ is an indicator for the particular way the saturation state is defined. The specification of the saturation state at given system temperature T requires an additional relation imposed on the independent quantities x^{sat} and p^{sat} . Pure vapour can be treated as a particular case of humid air where $x = 1$. A preferred choice to define the pathway s has been $p = p^{\text{sat}}$, i.e., saturation is established via an isobaric process in contrast to, e.g., isothermal compression or vapor injection at constant volume. The

functional dependence in form of a triple given by Eq. (1.1) is a direct consequence of Gibbs phase rule. If there are n types of particle in a system and ϕ phases, then the number of degrees of freedom (i.e., independent variables to describe the system) is given by $n + 2 - \phi$. Here, dry air is treated as one type of particle and water as another, i.e., $n = 2$. Unsaturated humid air ($\phi = 1$) requires $2 + 2 - 1 = 3$ independent quantities (such as x , T , and p) to specify the state. Saturated moist air is in contact with the condensed phase ($\phi = 2$), thus one needs only $2 + 2 - 2 = 2$ quantities as does unsaturated vapour ($1 + 2 - 1 = 2$) (where by definition $A = 0$). Water vapour, water and ice at equilibrium have $1 + 2 - 3 = 0$ independent quantities, hence A , T , and p are completely specified at the water triple point. A selection of published definitions of relative humidity is presented in **Table 1.1**. In the following the definition of the saturation state and some peculiarities of the relative-humidity definitions presented in Table 1.1 will be discussed.

Table 1.1: Common definitions of relative humidity (RH) in use (see explanations of symbols below).

Definition name and quantity $z(A, T, p)$	Condition	Equation $\psi_z^{(s)}$
(1) “Standard” (WMO, ASHRAE, VDI/VDE):		
Vapour amount fraction: $x = \frac{1 - A}{1 - A - \omega A}$	Isobaric saturation $s: p = p^{\text{sat}} \geq e^{\text{sat}}(T)$	$\psi_x = \frac{x}{x^{\text{sat}}} = \frac{p_v}{p_v^{\text{sat}}(T, p)}$
Partial vapour pressure: $p_v = xp$		
(2) Obsolete WMO:		
Mixing ratio: $r = (1 - A)/A$	“ ”	$\psi_r = \frac{r}{r^{\text{sat}}}$
(3) Miscellaneous:		
Specific humidity: $q = 1 - A$	“ ”	$\psi_q = \frac{q}{q^{\text{sat}}}$
(4) IOC:		
Fugacity: $f_v(A, T, p)$	“ ”	$\psi_{\lambda/F} = \frac{\lambda_v}{\lambda_v^{\text{sat}}} = \frac{f_v}{f_v^{\text{sat}}}$
Absolute activity: $\lambda_v = \exp\left(\frac{\mu_W^{\text{AV}}}{RT}\right)$		
(5) Miscellaneous:		
Pure vapour pressure: e	Non-isobaric saturation $s: p^{\text{sat}} = e^{\text{sat}}(T) \geq p$	$\psi_e = \frac{e}{e^{\text{sat}}(T)}$
(6) ‘Extended range’ definition:		
Partial vapour pressure: $p_v = xp$	“ ”	$\psi_{\text{EXT}} = \frac{p_v}{e^{\text{sat}}(T)}$
(7) IUPAC:		
$p_v = xp = e\hat{f}$	Undefined saturation state	$\psi_{\text{IUPAC}} = \frac{p_v}{e^{\text{sat}}(T)}$

Symbols: A := dry-air mass fraction; e := pure water vapour pressure; \hat{f} := water-vapour pressure enhancement factor; f_V := fugacity of water vapour in humid air; m_A := total mass of air molecules; m_V := total mass of water vapour molecules; M_A := molar mass of dry air; M_W := molar mass of water; n_A := mole number of dry-air molecules; n_V := mole number of water vapour molecules; p := total air pressure; p_V := partial water vapour pressure in humid air; $q := m_V / (m_A + m_V)$:= specific humidity; $r = m_V / m_A$:= water vapour mixing ratio; R := universal gas constant; T := temperature; $x = n_V / (n_A + n_V)$:= water vapour amount fraction; ψ := relative humidity; μ_W^{AV} := molar chemical potential of water in humid air; λ_V := activity of water in humid air $\omega = M_W / M_A$:= molar mass ratio.

1.3 Characterisation of the Saturation State

(a) Definition of the Saturation State

Humid air is said to be saturated if the chemical potential of water in humid air, μ_W^{AV} , equals that of water in the condensed liquid phase, μ^W ,

$$\mu_W^{AV}(x^{\text{sat}}, T, p) = \mu^W(T, p), \quad (1.2)$$

or similarly, that of condensed water in the form of hexagonal ice I, μ^{lh} . For a given temperature $T = \text{const.}$, the solution of the chemical equilibrium condition, Eq. (1.2), delivers the function $p^{\text{sat}} = p^{\text{sat}}(x) = p(x^{\text{sat}})$, shown as the black solid line in Fig. 1.2 for $T = 300 \text{ K}$.

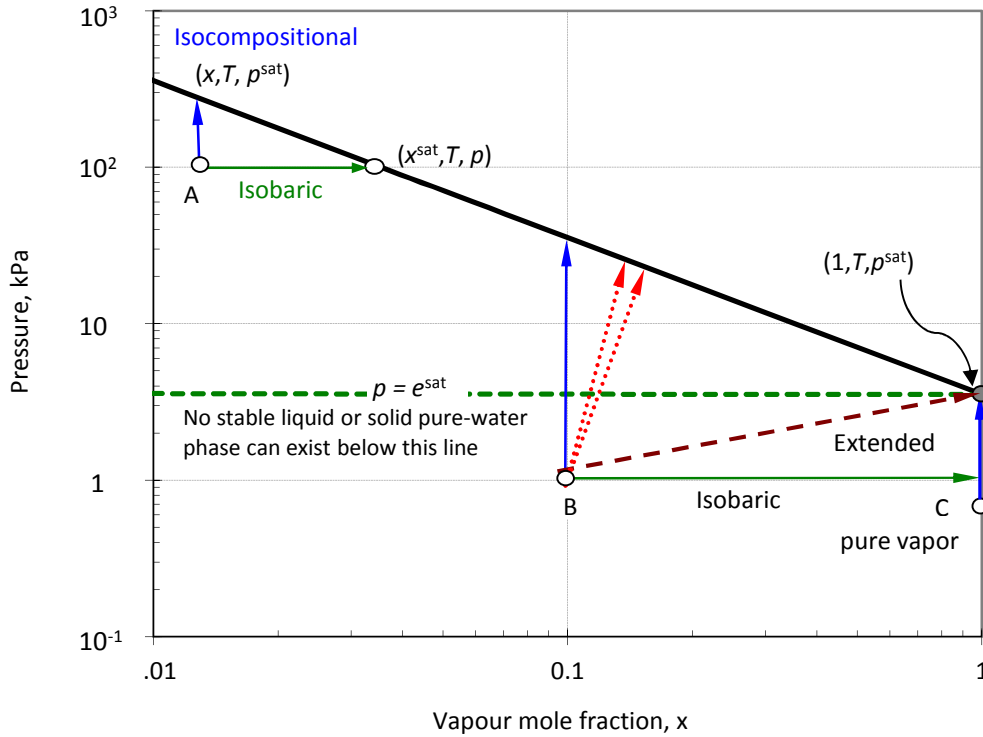


Fig. 1.2: The saturation-pressure curve, $p = p^{\text{sat}}(x, T)$, and unsaturated states for humid air at 300 K at pressure p , as a function of x . The saturation curve is found from $x = e^{\text{sat}}(T) \hat{f}(T, p) / p$, and is represented by the thick solid line. Humid air can exist at 300 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.

For any air sample A-c placed in this diagram, there are different pathways to achieve the saturation curve, whereat the specific pathway depends on the definition of the relative humidity according to Table 1.1. Two useful such saturation functions, isobaric saturation, $s: p^{\text{sat}} - p = 0$, and isocompositional compression, $s: x^{\text{sat}} - x = 0$, are represented by the horizontal and vertical arrows, respectively, in Fig. 1.2.

(b) Saturation due to Isobaric Evaporation

The WMO relative humidity definition (**entry (1) in Table 1.1**) employs the isobaric saturation condition, which constraints the validity of the standard definition by the following inequality at saturation:

$$\psi_x = 1 = \frac{x^{\text{sat}} p}{\hat{f}_w(T, p) e_w^{\text{sat}}(T)} \rightarrow \frac{e_w^{\text{sat}}(T)}{p} = \frac{x^{\text{sat}}}{\hat{f}_w(T, p)},$$

$$x^{\text{sat}} \leq 1, \hat{f}_w(T, p) \geq 1 \rightarrow e_w^{\text{sat}}(T) \leq p.$$

This constraint of the validity of the WMO definition corresponds to the pressure range below the saturation pressure line (black solid line) and above the pressure of the pure saturated water vapour (green dashed line $p = e_w^{\text{sat}}(T)$) in Fig. 1.2. In other words: The WMO definition does not apply to moist air when the pressure p is less than the saturation vapour pressure $e_w^{\text{sat}}(T)$ at temperature T .

For subsaturated samples A and B of air being located in this range, the saturation condition (1.2) can be realised by **isobaric evaporation** of water into the sample (associated with displacement of dry air) until $p(x^{\text{sat}})$ is reached. This pathway is represented by the green horizontal arrows starting at sample locations A and B. Again, the WMO is not applicable to the pressure range $p \leq e_w^{\text{sat}}$.

(c) Saturation due to Isocompositional Compression

For any subsaturated state $(x \leq 1, T, p)$ including pure water vapour $(x = 1, T, p)$, saturation can be also achieved by **isocompositional¹¹ compression** of the air sample until the $p^{\text{sat}}(x, T)$ curve is reached, i.e., $p \rightarrow p^{\text{sat}}$ for $x = x^{\text{sat}} = \text{const.}$ This pathway is represented by the blue vertical arrows starting at locations of the samples A-C in Fig. 1.2. For pure water vapour, saturation via isocompositional compression may be reached by adding vapour. However, for any other state of humid air merely adding water vapour will both change the composition (increasing of x) and increase the total air pressure p .

In practice, the realisation of the saturated state via isocompositional compression has been used as relative-humidity reference state only for defining relative humidity for a sample of pure unsaturated vapour (**entry (5) in Table 1.1**). Here $z = e$ (i.e., the pure-phase vapour pressure), and the saturation condition requires $p^{\text{sat}} = e^{\text{sat}}$ and $x = x^{\text{sat}} = 1$.

The corresponding RH definition can be written as follows:

$$\psi_e^{(s)} = \frac{e}{e^{\text{sat}}}, \quad s : p^{\text{sat}} = e^{\text{sat}} \quad (1.3)$$

(d) Unachievable Saturation: ‘Subsaturated Pressure’ Condition

The air sample B in Fig. 1.2 is characterised by the triple, at which the pressure of the pure water vapour at saturation, e^{sat} , exceeds the total air pressure of the air sample, p . This means, that the number of water molecules exerting the pressure $p_v = xp$ in that humid-air

¹¹ We prefer the notion ‘isocompositional’ instead of ‘isohumid’ because only compositional measures of humidity (e.g. x and A , q and r) are constant under compression. The dew point, wet-bulb temperature, relative humidity and vapour pressure all increase.

sample, can never reach the number of molecules at saturation determined by the saturation pressure of the pure vapour, e^{sat} . Here, this state will be called ‘subsaturated pressure condition’. It is practically realised in

- (a) superheated (i.e., metastable) water, when the temperature of liquid pure water exceeds the pressure-dependent boiling point temperature, or
- (b) when the total air pressure decreases below the saturation vapour pressure and the liquid water starts to boil.

As indicated by the dotted arrows leading from sample B in the figure, in theory, any point on the solid saturation line in Fig. 1.2, is a potential saturation state for any subsaturated state represented by the given triple $(x, T, p \leq e^{\text{sat}})$. However, the saturation state for sample B is inaccessible by isobaric evaporation.

2. The Standard Definition of Relative Humidity

According to the standard definition given by **entry (1) in Table 1.1**, the relative humidity is defined as the ratio of the actual water-vapour mole fraction in humid air to the water-vapour vapour mole fraction at saturation, which is equivalent to the ratio of the actual partial vapour pressure to the saturation partial vapour pressure, given the condition that saturation be achieved at the same temperature and pressure. This definition is adopted by many authorities (including WMO, ASRAE, IMC, ISO 80000-5, VDI/VDE), and is widely accepted as *the* definition of relative humidity. Departures from this definition are, to the same extent, regarded as non-standard. The standard definition is very useful in many humidity calculations and has wide but not universal adherence. However, entry (1) is subject to several shortcomings:

- (a) The definition suffers from lack of a rigorous physical basis (e.g., lack of reconcilability with the notion of chemical potential).
- (b) It describes the drive to equilibrium at which the chemical potential (or, equivalently, the fugacity) of each component is the same in all coexisting phases only in an approximative way. The equality of the partial pressure of water vapour in the coexisting phases does not correspond to the thermodynamic equilibrium state of the system.
- (c) The definition does not apply to the ‘subsaturated pressure’ condition, i.e., air or vapour at a temperature above the saturation temperature of water at given pressure, or equivalently to air or vapour at a pressure below the saturation pressure of pure water at given temperature. This is a disadvantage because relative-humidity sensors and materials apparently sensitive to relative humidity respond also in the pure unsaturated vapour and superheated humid-air ranges as if there is a reference saturation state, which must be at a higher pressure.
- (d) The saturation state is incompletely defined.

3 Non-Standard Definitions of Relative Humidity

Three ‘non-standard’ definitions, given by **entries (2), (3), and (4) in Table 1.1**, retain the ‘isobaric saturation’ condition over the standard range $(e^{\text{sat}}(T) \leq p)$, but choose different humidity quantities z such as:

- the mixing ratio $r = x\omega/(1-x)$, where $\omega = M_W/M_A$ is the ratio of the molar masses of water and dry air:

$$\psi_r^{(s)} = \frac{r}{r^{\text{sat}}} , \quad s : p = p^{\text{sat}} \geq e^{\text{sat}}(T) \quad (3.1)$$

- the specific humidity $q = x\omega/(x\omega - x + 1)$:

$$\psi_q^{(s)} = \frac{q}{q^{\text{sat}}} , \quad s : p = p^{\text{sat}} \geq e^{\text{sat}}(T) \quad (3.2)$$

- the fugacity $f_V(x, T, p) \equiv f_V^0(T) \lambda_V(x, T, p)$ where $\lambda_V = \exp(\mu_W^{\text{AV}}/RT)$ is the absolute activity, $\mu_W^{\text{AV}}(x, T, p)$ and $\mu_W^{\text{W}}(T, p)$ are the mass-based chemical potentials of water in the gas and condensed phases, respectively:

$$\psi_F^{(s)} = \frac{f_V}{f_V^{\text{sat}}} = \frac{\lambda_V}{\lambda_V^{\text{sat}}} = \exp \left\{ \frac{\mu_W^{\text{AV}}(x, T, p) - \mu_W^{\text{W}}(T, p)}{R_W T} \right\} , \quad s : p = p^{\text{sat}} \quad (3.3)$$

While Eqs. (3.1) and (3.2) are used in meteorology, the relative fugacity, Eq. (3.3), is used in chemistry and in particular in food science. Since $f_V^0(T)$ cancels, the relative fugacity is also known as the activity (with suppression of ‘relative’) or water activity a_W . Note that in many applications, standard relative humidity (known as equilibrium relative humidity or ERH) is either identified with or seen as a good approximation to the water activity. Furthermore, water activity is measured with a relative humidity sensor calibrated for standard relative humidity. The definition of relative humidity according to Eq. (3.3) is reconcilable with the constraint of vanishing thermodynamic driving force at equality of the chemical potentials in the coexisting phases, i. e., an interface-crossing molecule flux equal to zero. Hence, the relative fugacity is a suitable metric for the thermodynamic driving force controlling the latent heat export from the ocean. The apparent approximate invariance of atmospheric relative humidity with respect to global warming probably reflects the constancy of cloudiness and solar heating driving the water flux of the global hydrological cycle. Long-term trends in fugacity are key indicators for fundamental changes in the climate system and may offer insights in, e.g., the effects of volcanic eruptions, in the variability of the global albedo or cloudiness, and in regional acceleration of the water cycle. A prerequisite for application of Eq. (3.3) is the determination of the chemical potentials of the coexisting phases (water vapour/liquid water and water vapour/ice), which are available from the new oceanographic standard Thermodynamic Equation of Seawater 2010, TEOS-10, satisfying the need for accurate, consistent and comprehensive descriptions of the thermodynamic properties of seawater and its equilibria in contact with ice and humid air.

A non-standard definition for ‘subsaturated pressure’ conditions ($p \leq e^{\text{sat}}(T)$) is given by **entry (5) in Table 1.1**, according to which the relative humidity is the ratio of the pure vapour pressure to the saturated pure vapour pressure at the same temperature. This definition, however, does not cover the case of humid air under subsaturated pressure conditions.

The relative humidity of humid air under subsaturated pressure conditions ($p \leq e^{\text{sat}}(T)$) is defined by **entry (6) in Table 1.1**, called ‘extended range’ definition, indicated by the dashed brown arrow from B in Fig. 1.2 (label ‘Extended’). The extended definition can be written in the ‘full’ form as:

$$\psi_{\text{EXT}} = \frac{p_V(x,p)}{p_V^{\text{ref}}(T,p)} = \frac{p_V(x,p)}{e^{\text{sat}}(T) \hat{f}(T,p)} \quad \text{with} \quad \hat{f}(T,p) = 1 \quad \text{for} \quad e^{\text{sat}}(T) > p.$$

Finally, in the IUPAC definition of relative humidity given by **entry (7) in Table 1.1**,

$$\psi_{\text{IUPAC}} = \frac{p_V}{e^{\text{sat}}(T)} = \frac{p_V \hat{f}(T, p_V^{\text{sat}})}{p_V^{\text{sat}}}, \quad (3.4)$$

the saturation state is not defined. It can be seen that for slightly unsaturated humid air, i.e., for $p_V = p_V^{\text{sat}} / \hat{f}(T, p_V^{\text{sat}}) < p_V^{\text{sat}}$, this definition will give a relative humidity of 100%rh, and for saturated humid, $p_V = p_V^{\text{sat}}$ a value >100%rh.

4 Sensor Calibration and Traceability to SI Standards

The relative humidity can be measured directly using sensors that are sensitive to the ratio of some humidity measure to its maximum value corresponding to the given temperature, such as defined in Table 1.1. As the response of any such sensor depends on highly variable and (in general) non-controllable macro- and micro-structural features, all relative humidity sensors require frequent calibration against a traceable reference.

Methods of measuring humidity quantities that are based on more easily controlled physical phenomena are considered more fundamental. Basic hygrometric methods are:

- Gravimetric hygrometry: direct measurement of the mass or amount fraction without need of an empirical reference equation;
- Cavity-ring-down-spectroscopy (CRDS): direct measurement of the water vapour mixing ratio r and related quantities by monitoring the absorption of electromagnetic radiation by water molecules;
- Chilled-mirror hygrometer (CMH): direct measurement of the dew-point temperature T_D by active cooling of a mirror to bring a sample into equilibrium with a saturated state (condensation);
- Psychrometer: direct measurement of the wet-bulb temperature T_W by evaporative cooling of a wetted wick-covered thermometer down to T_W .

In principle, corresponding reference hygrometers of these types can be used to provide humidity measurements traceable to the SI without reference to other humidity standards and thus may serve as primary humidity standards. But in practice, difficulties associated with providing well-controlled reference conditions for hygrometry and in characterising and validating instrumental performance mean that only a very few such instruments can provide SI traceability only by evidence on the equivalence with other primary humidity standards and without direct calibration in terms of a humidity quantity.

In calibration, a measuring instrument is compared against a reference (i.e., measurement standard), and a relation between the two is determined with associated measurement uncertainty. Today most often humidity traceability chains are linked to the SI with **primary humidity generators**¹² in which a gas is (a) saturated under well defined conditions, or (b)

¹² Occasionally gravimetric hygrometers are used as additional confirmation of generator performance; however, it is rare for such a hygrometer to be claimed as the direct path to the SI. Indeed most national measurement institutes (NMIs) claim traceability to the SI for their humidity standard via the NMI's primary humidity generators, or through a chilled mirror hygrometer calibrated at another NMI.

humidified through adding known amounts of water vapour. The conditioned gas of known humidity quantity value is passed to a **secondary standard** (usually a CMH or an electromagnetic absorption hygrometer). These may then be used to calibrate other reference standards by comparison under well-controlled conditions, e.g., in a climatic chamber or humidity calibrators.

For example, the calibration of a measurement device, i.e., hereafter ‘device under calibration’ (DUC), can be realised against a primary standard as follows. At first, a ‘two-pressure’ (2- p) humidity generator is used to condition the air (or nitrogen) by saturation at a well characterised temperature, T_1 , and pressure, p_1 . Secondly, the saturated air sample passes through an expansion valve and then flowing as an unsaturated humid gas into a temperature-controlled chamber at a somewhat lower pressure, $p_2 < p_1$, where the DUC is held at air temperature T_2 . Assuming no condensation or evaporation taking place between the saturator and the DUC, the water vapour amount fraction (vapour mole fraction) at the DUC is the same as at the saturator exit and calculated as:

$$x_1^{\text{sat}} = \frac{F_e(T_1; \mathbf{a}) F_f(T_1, p_1; \mathbf{b})}{p_1} = \frac{e^{\text{sat}}(T_1) \hat{f}(T_1, p_1)}{p_1}. \quad (4.1)$$

Here, $F_e(T; \mathbf{a})$ and $F_f(T, p; \mathbf{b})$ are reference functions used to calculate the pure-phase water vapour pressure and the water vapour enhancement factor respectively, and \mathbf{a} and \mathbf{b} are vectors of fitted parameters. The function $F_e(T; \mathbf{a})$ has the dimension of a pressure and represents the reference saturation vapour pressure of the pure vapour. Analogously, $F_f(T, p; \mathbf{b})$ is a dimensionless function and represents the reference enhancement factor. Equation (4.1) can be formally obtained by evaluating the standard relative humidity definition (entry (1) in Table 1.1) at saturation at the saturator exit, $\psi_x = 1$, employing reference functions for the saturation vapour pressure and the enhancement factor.

Some relationships between various humidity quantities are illustrated in **Fig. 4.1**. Note that the reference functions are required whenever transforming between mass or mole-based measures and saturation-temperature based measures and for many humidity calculations in general.

Thus for example, the water-vapour mole fraction x_1 may be calculated from any relative humidity measured at T_1 and p_1 using

$$x_1 = x_1^{\text{sat}} \psi_x = \frac{F_e(T_1; \mathbf{a}) F_f(T_1, p_1; \mathbf{b})}{p_1} \psi_x. \quad (4.2)$$

From Eq. (4.1) and equations given in Fig. 4.1 any other humidity quantity at the DUC can be calculated such as the mixing ratio r , specific humidity q , the dew-point temperature T_D and the relative humidity ψ .

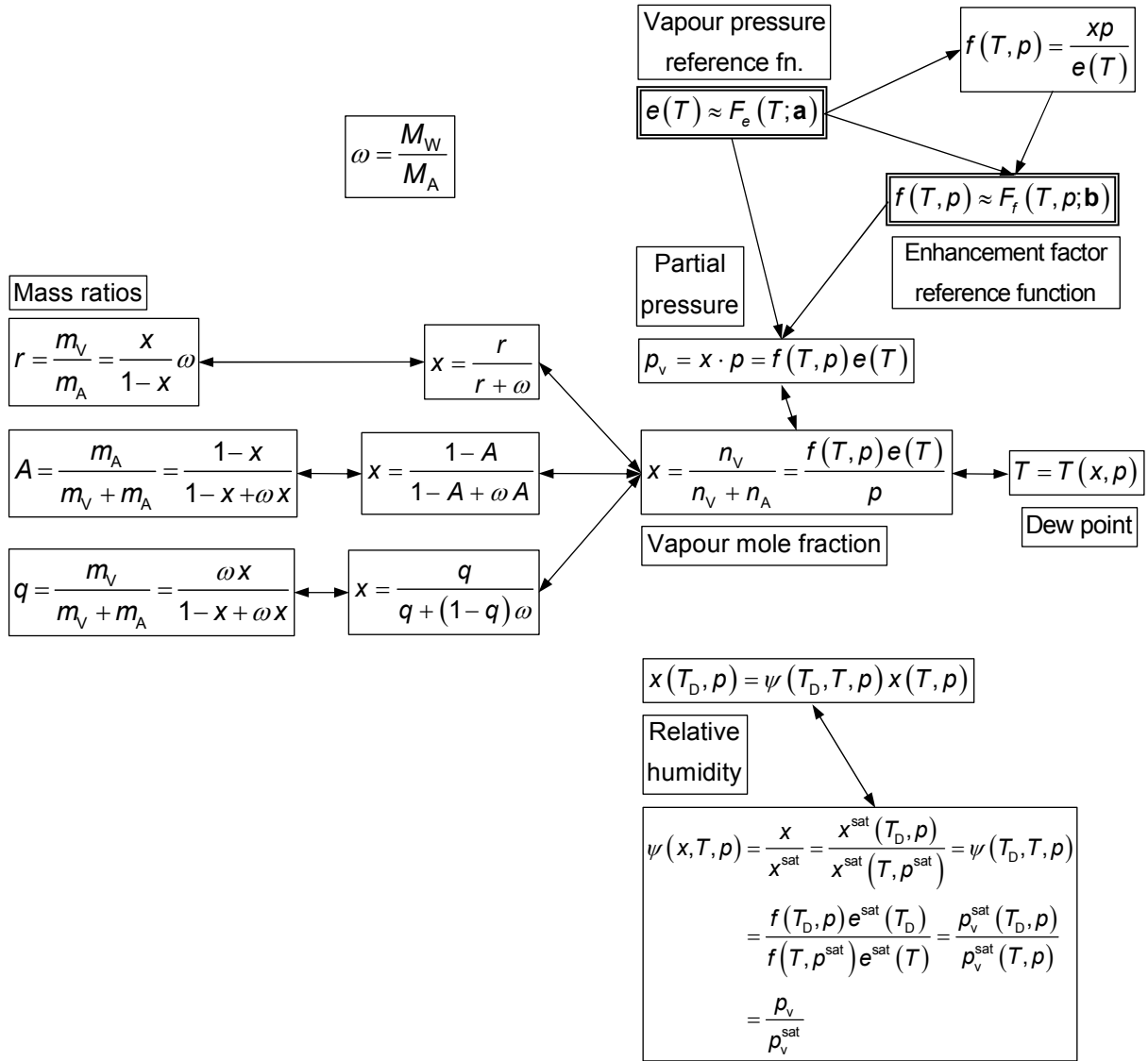


Figure 4.1: Relationships between common humidity quantities.

The relative humidity at the DUC is given by $\psi_x = x_1^{\text{sat}} / x_2^{\text{sat}}$ with x_1^{sat} given by Eq. (4.1), and the saturation amount fraction at the DUC

$$x_2^{\text{sat}} = \frac{F_e(T_2; \mathbf{a}) F_f(T_2, p_2; \mathbf{b})}{p_2}. \quad (4.3)$$

The dew-point temperature T_D at the DUC is found by isobaric cooling down the air sample, assumed to be in a closed thermodynamic system, from temperature T_2 to T_D at pressure p_2 until the equality

$$x_1^{\text{sat}} = \frac{F_e(T_1; \mathbf{a}) F_f(T_1, p_1; \mathbf{b})}{p_1} = \frac{F_e(T_D; \mathbf{a}) F_f(T_D, p_2; \mathbf{b})}{p_2} = x_2^{\text{sat}} \quad (4.4)$$

is satisfied.

For most industrial applications and for ground-based meteorology, relative humidity is measured directly using the electrical response of thin-film humidity sensors and, less frequently, using wet and dry-bulb psychrometers. Satellite and airborne remote-sensing applications tend to use electromagnetic absorption methods yielding a mass-based quantity. Metrology-type applications favour the chilled mirror dew-point meters since these offer most reliability and precision over the greatest range. In these cases, the actual amount fraction,

x , is measured and the reference state x^{sat} evaluated using Eq. (4.3).

Figure 4.2. gives a summary of the typical traceability chains for humidity.

5 Problems and Deficiencies

Despite the seemingly widespread acceptance of the standard definition, a number of ‘non-standard’ relative humidity definitions listed above continue to be used and reported. The range of relative humidity definitions used reflects the (a) variety of purpose and required uncertainty, (b) variety of definitions historically and recently reported in particular fields, (c) approximate equivalence of many relative humidity definitions, (d) occasional need to measure under conditions not covered by the standard definition, and the (e) lack of firm physical basis for a particular definition.

5.1 Differences among Available Definitions

For a particular sample of humid air taken to saturation under isobaric conditions, the standard relative humidity according to entry (1) in Table 1.1 may be expressed by virtue of Eqs. (3.1)-(3.3) and by choice of pure-vapour pressure e for the humidity variable z , $\psi_e^{(s)} = e/e^{\text{sat}}(T)$,

$$\psi_x = \psi_{p_v} = \frac{1-x}{1-x^{\text{sat}}} \psi_r = \frac{x\omega + (1-x)}{x^{\text{sat}}\omega + (1-x^{\text{sat}})} \psi_q = \frac{\varphi(x^{\text{sat}}, T, p)}{\varphi(x, T, p)} \psi_F = \frac{\hat{f}(T, p)}{\hat{f}(T, p^{\text{sat}})} \psi_e, \quad (5.1)$$

where $\varphi(x, T, p) = f_v(x, T, p)/(xp)$ is the fugacity coefficient. The differences between the definitions evaluated using the same values of x , T , and p can be significant (see **Fig. 5.1**). The use in publications and data storage of several different definitions leads to confusion and error, and considerable work in recalculation, especially if incorrect assumptions are made regarding the definition used. Further confusion and error may arise if databases do not store the definition with the data.

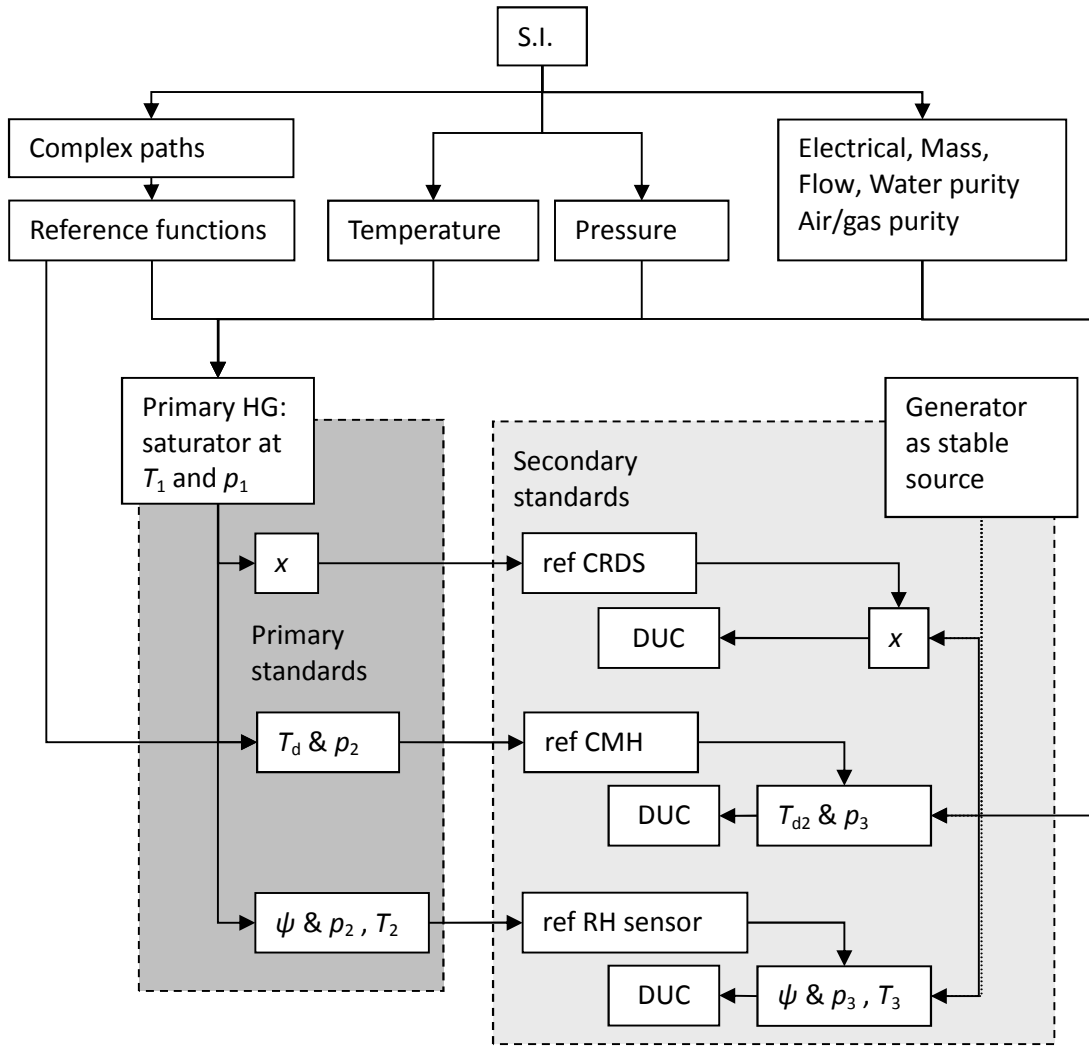


Figure 4.2 Typical traceability chains for humidity. A primary humidity generator (HG) saturates air to a well-defined vapour amount fraction $x = x_1^{\text{sat}}$, which is calculated as a function of the saturation temperature and pressure (T_1 and p_1 respectively) and the humidity reference functions for the vapour pressure and enhancement factor according to Eq. (4.1). The value x_1^{sat} can be used to calibrate, for example, cavity-ring-down-spectrometers (CRDSs). Further pressure and temperature measurements allow the dew point temperature $T_D(x_1^{\text{sat}}, p_2)$ from Eq. (4.4) and the relative humidity $\psi(x_1^{\text{sat}}, T_2, p_2)$ to be determined, so as to calibrate chilled mirror hygrometers (CMH) and relative humidity hygrometers as secondary standards. The secondary standards can be used to measure x_1^{sat} , T_D , or ψ of the conditioned air in a generator acting as a stable source or environment, so as to calibrate other hygrometers.

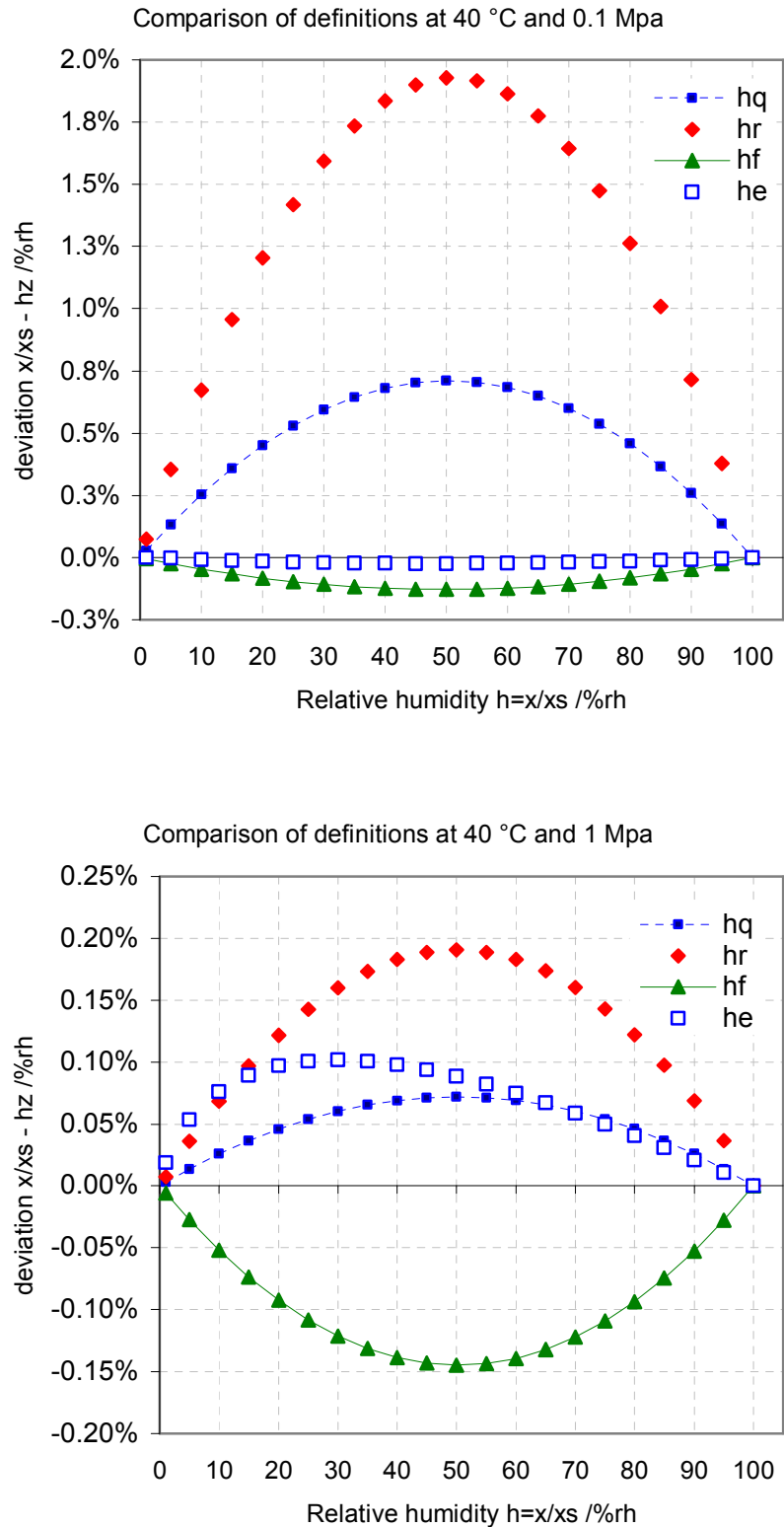


Fig. 5.1: Differences between the standard definition of relative humidity (ψ_x) based on $z = x$, and the non-standard isobaric definitions (ψ_q, ψ_r, ψ_F) based on $z = q, r, F$, and the pure vapour definition (ψ_e) based on $z = e$, for 0.1 MPa (top) and 1 MPa (bottom). **Abscissa:** standard definition of RH. **Ordinate:** standard 'minus' non-standard definition of RH. Generally the differences increase with increasing temperature and decreasing pressure.

5.2 Ill-defined Physical Basis

The ‘standard’ definition arose as a useful compromise between competing definitions. The decision, however, is arbitrary in that there was no physical basis established for choosing one definition over another even though the candidate definitions are numerically equivalent only at the limiting values of 0 %rh and 100 %rh.

5.3 Limited Range of Validity

There are various practical conditions that are not or only insufficiently covered by the existing set of definitions. None of the usual isobaric formulas reported in Table 1.1 (definitions (1)–(4)) considers constant composition as saturation condition (isocompositional evaporation, see Section 1.3), $s: x^{\text{sat}} - x = 0$, as would be required to describe, e. g., subsaturated pure water vapour with $x = 1$ and $p < p^{\text{sat}}$. Also in this case, several measures z Table 1.1 are inappropriate because for pure vapour $x = q = 1$ equally holds for both saturated and subsaturated states. We also note that the isobaric condition, $s: p^{\text{sat}} - p = 0$, is inappropriate to suitably define saturation states at low pressures such as ‘sample B’ shown in Fig. 1.2.

The ‘standard’ and other isobaric definitions do not apply to unsaturated water vapour or to subsaturation pressure of moist air ($p \leq e^{\text{sat}}(T)$), yet it is reasonable to consider their ‘closeness to saturation’. **Figure 5.1** shows the experimental setup of the measurement chamber (top panel) and the corresponding sensor behaviour (bottom panel) for the case of **unsaturated pure water vapour** ($e < e^{\text{sat}}(T) \leq p$). Relative-humidity sensors performs well, showing a linear dependence of the calibrated sensor reading on the relative humidity, defined by $\psi_e^{(s)} = e/e^{\text{sat}}(T)$. **Figure 5.2** shows the same kind of information but for the case of **unsaturated moist air** ($p \leq e^{\text{sat}}(T)$), where the saturated state cannot be reached without changing the pressure. The time series of the calibrated sensor reading in dependence of the mixing state of a humid-air sample at isothermal conditions, shown in the bottom panel of Fig. 5.2 is separated in to three time intervals: **(1) Time 2.5–2.9 h**: At the initial time the experimental chamber is filled with pure water vapour with pressure $e \approx 1400$ Pa corresponding to a sensor reading of about 53.4 %rh. **(b) Time 2.9–3.2 h**: By adding dry air to the pure water vapour, the total pressure of the humid air will rise, but still remaining below the saturation pressure of the pure water vapour, i.e., $p < e^{\text{sat}}(T) \approx 2500$ Pa. **(c) Time >3.2 h**: Addition of further dry air to the chamber will further increase of the total air pressure, but which will now exceed the saturation pressure of the pure water vapour, i.e., $p > e^{\text{sat}}(T) \approx 2500$ Pa. Over the whole time period, the sensor reading appeared to be nearly independent on the mixing state of the humid air sample (approx. 53.4 %rh) and behaves likewise the sensor reading in a isothermal sample of unsaturated pure water vapour, i.e., according to $\psi_e^{(s)} = e/e^{\text{sat}}(T)$ (see Fig. 5.1). As temperature and the pressure of the pure water vapour has not been changed during the experiment, the relative humidity remained nearly constant.

Experimental setup for pure unsaturated water vapour ($e < e^{\text{sat}}(T) \leq p$)

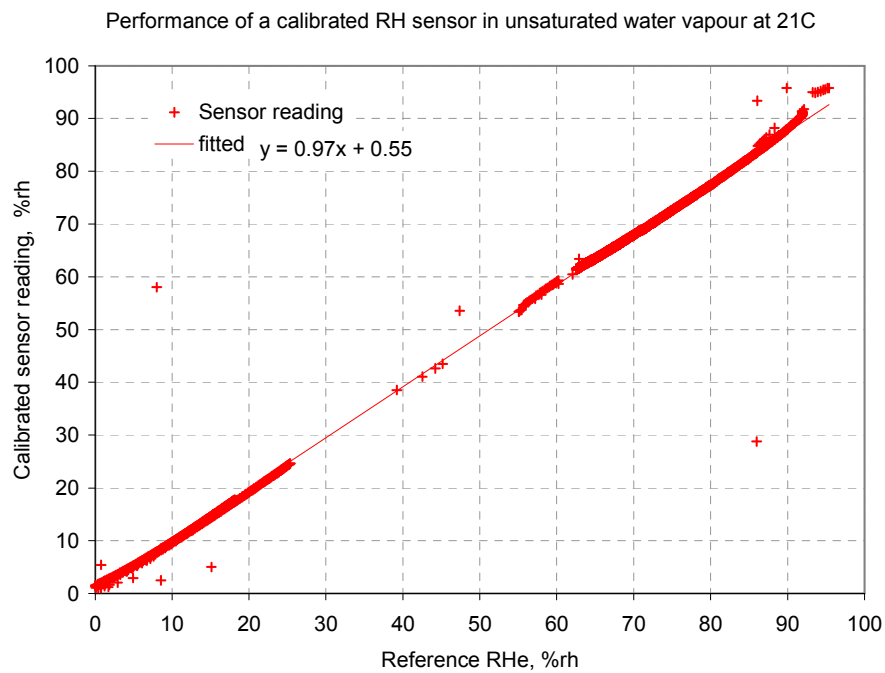
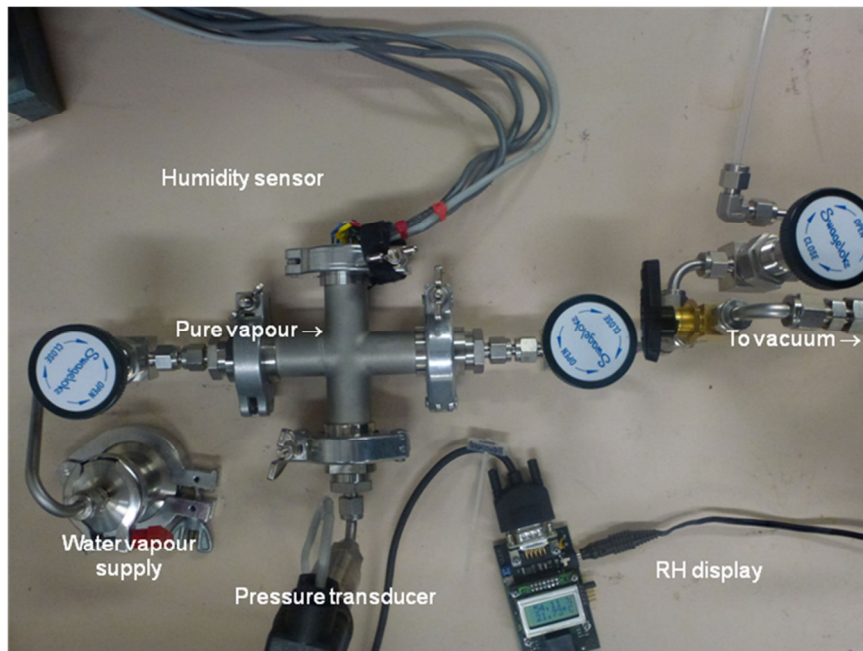


Fig. 5.1 Experimental setup (top) and calibrated sensor reading vs. relative humidity (bottom, defined as $\psi_e^{(s)} = e/e^{\text{sat}}(T)$), in unsaturated pure water vapour. The relative-humidity sensor behaves well, showing a linear response to the relative humidity.

Experimental setup for unsaturated moist air ($p < e^{\text{sat}}(T)$)

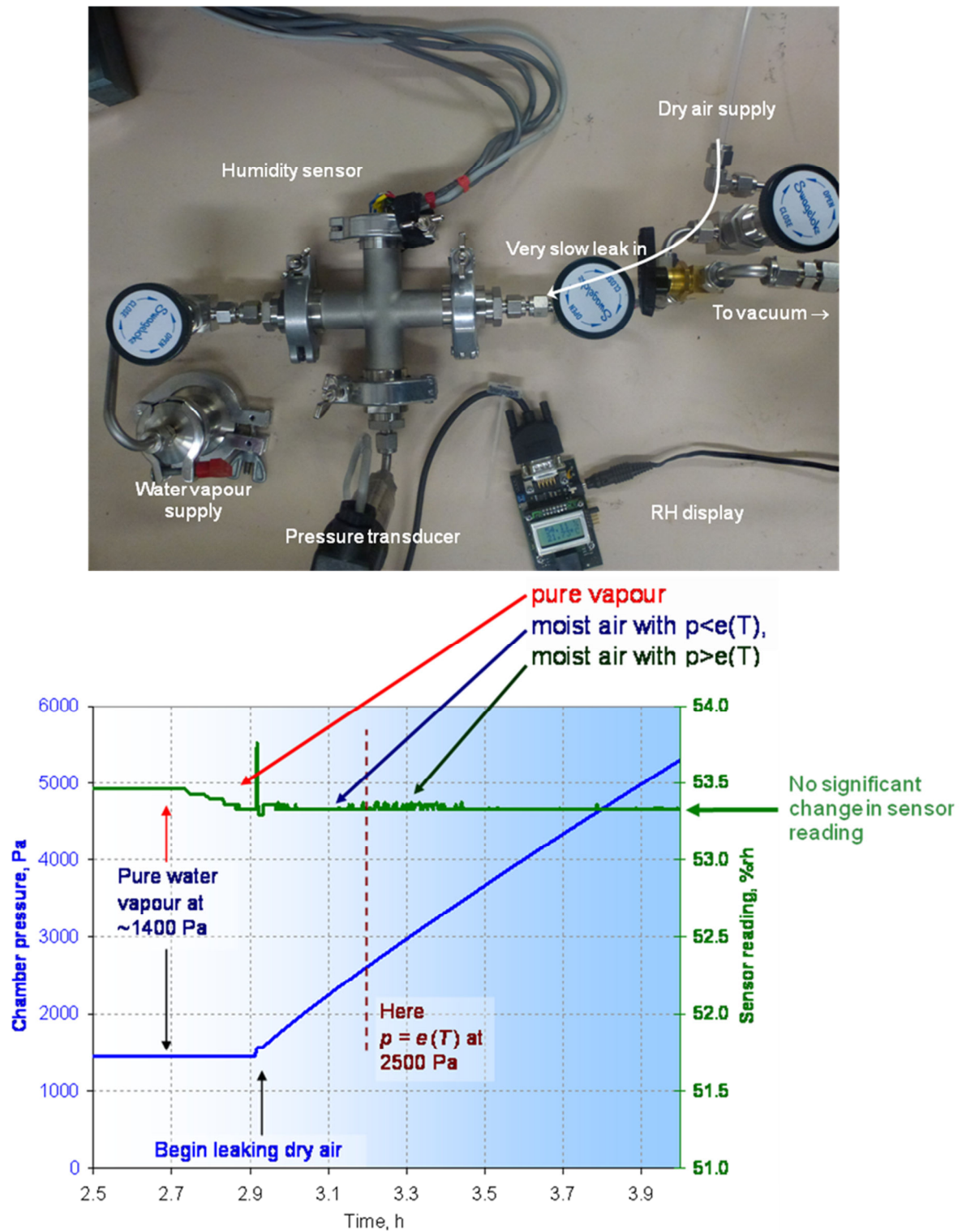


Fig. 5.2 As in Fig. 5.1 but for unsaturated moist air. The time series of the calibrated sensor reading in dependence of the mixing state of a humid-air sample at isothermal conditions is separated in to three time intervals, the characterisation of which is given in the text.

In this context, the following questions deserve further consideration:

- (i) What is the reference state for pure vapour and humid air at ‘subsaturation pressure’ conditions?
- (ii) How does the reference state for pure vapour differ, if at all, from the saturation state of humid air in the normal range?
- (ii) Can studying the response of humidity sensors and humidity sensitive materials point to a non-arbitrary physical basis for relative humidity?

From the plethora of possible paths to saturation from ‘subsaturation pressure’ states such as air sample B in Fig. 1.2, extended range definitions have all chosen a pure-vapour saturation state.

This reference state seems to follow naturally from a combination of two measures: (a) the isobaric replacement of air molecules with water leading to the ‘standard’ saturation states, (b) the addition of water required to saturate pure vapour. However, so far no rigorous physical basis has been provided for such extended definitions, although the extended definition provides an apparently seamless transition from the standard to ‘subsaturation pressure’ conditions.

Figure 5.3 shows the partial vapour pressure as a function of dry-air mass fraction (left ordinate vs. abscissa), $p_v = x(A) \cdot p = p(1 - A)/(1 - \omega A)$, at $T = 300$ K for different values of total pressure p (‘isobars’, sloped solid lines). The red solid line refers to the case $p = e^{\text{sat}}(T)$. The standard definition does not apply when $p < e^{\text{sat}}(T) = 3537$ Pa, i.e., left and below the solid red line, respectively. The figure displays also the dependence $p_v = p_v(A) = \psi_x \hat{f}(T, p^{\text{sat}}) e^{\text{sat}}(T)$ for different relative humidities $\psi_x = 20, 40, \dots, 100$ %rh (‘isohumids’, quasi-horizontal dotted lines) as defined according to the standard definition.

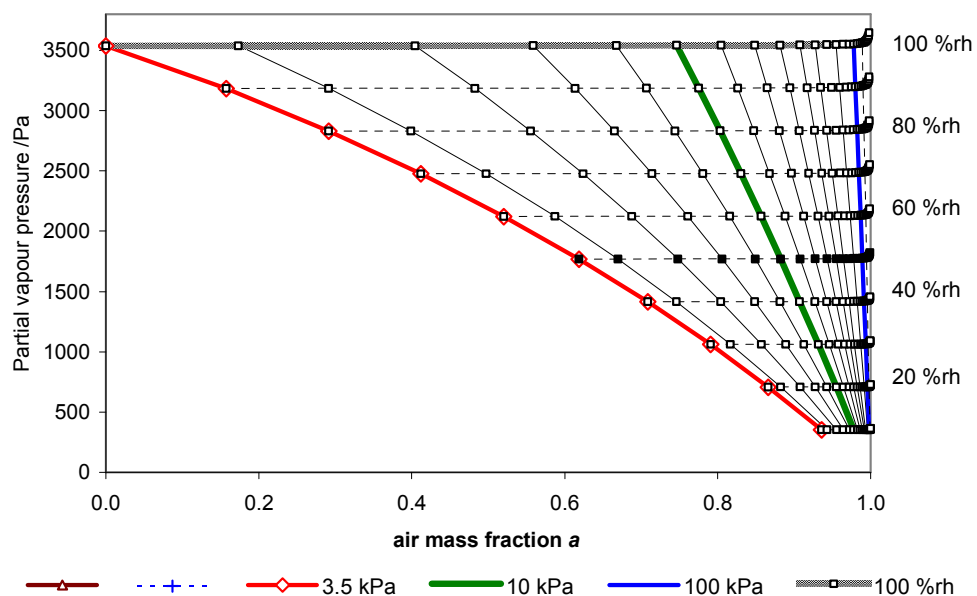


Fig 5.3: Partial vapour pressure as a function of dry-air mass fraction (left ordinate vs. abscissa), $p_v = x(A) \cdot p$, at $T = 300$ K for different for different values of total pressure p (‘isobars’, sloped solid lines). The red solid line refers to the case $p = e^{\text{sat}}(T)$. The standard definition does not apply when $p < e^{\text{sat}}(T) = 3537$ Pa,

i.e., left and below the solid red line, respectively. The figures displays also the dependence $p_v = p_v(A) = \psi_x \hat{f}(T, p^{\text{sat}}(A)) e^{\text{sat}}(T)$ at different relative humidities $\psi_x = 20\text{ \%rh}, 40\text{ \%rh}, \dots, 100\text{ \%rh}$ ('isohumids', quasi-horizontal dotted lines) as defined according to the standard definition.

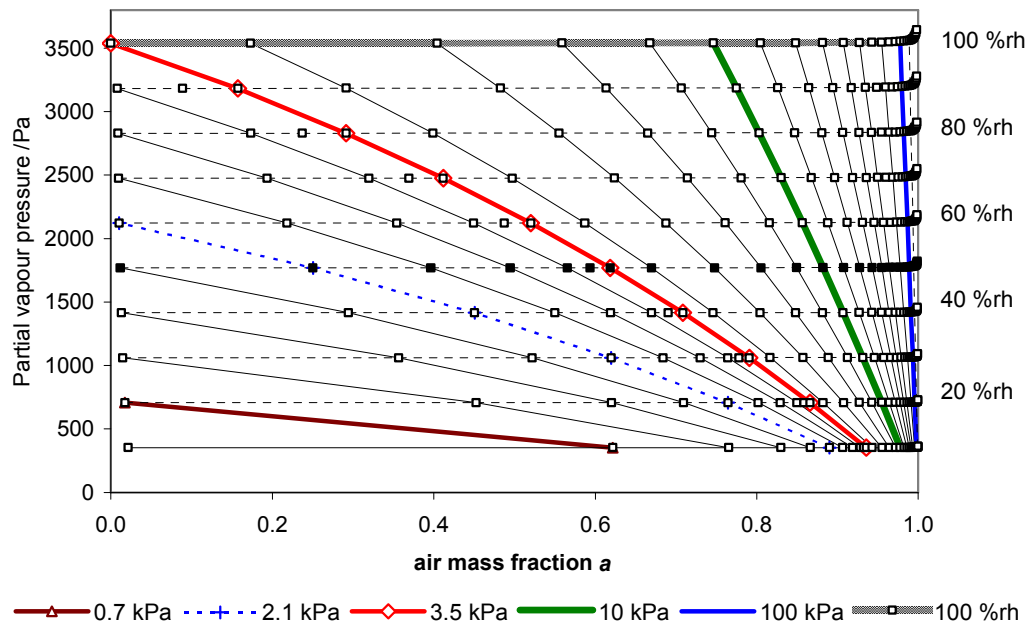


Fig. 5.4: As in Fig. 5.3, but here showing both the standard and extended definition of relative humidity (to the right and left of the solid red line respectively).

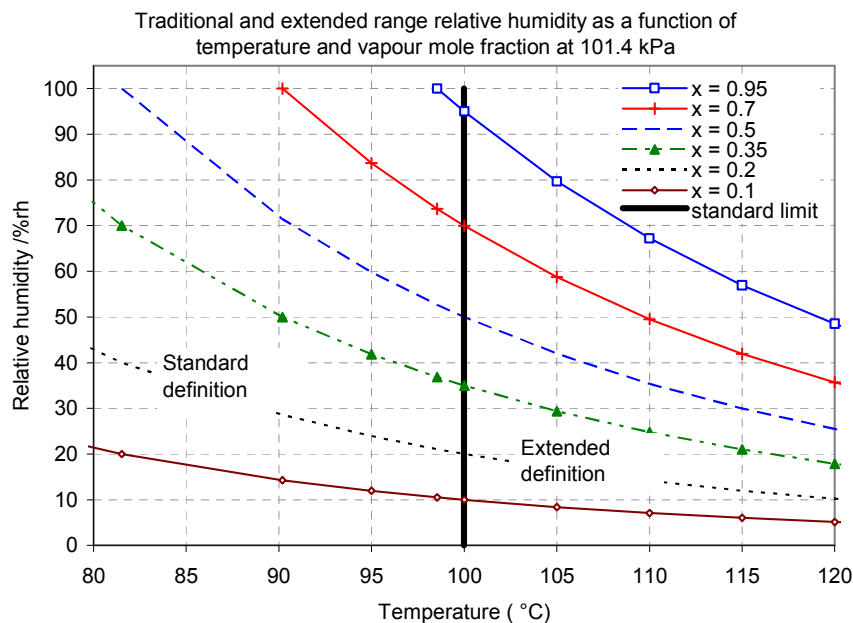


Fig. 5.5: Standard and 'extended range' relative humidity as a function of temperature for different values of the vapour amount fraction x ('isohumids') at total pressure $p = 101.4\text{ kPa}$. Note that the standard limit (at 100 °C) and other values will change with pressure.

Figure 5.4 shows the same dependencies as in Fig. 5.3, but for both the standard and

‘extended range’ definitions, i.e., including also the range $p < e^{\text{sat}}(T) = 3537 \text{ Pa}$. Finally, **Fig. 5.5** displays the standard and ‘extended range’ relative humidity as a function of temperature for different values of the vapour amount fraction x (‘isocompositionals’) at total pressure $p = 101.4 \text{ kPa}$.

5.4 Reference Equations and the Standard Equation of State

There is no single, generally recognised standard equation of state yet that is agreed upon for the evaluation of saturation properties and transformation between ‘composition-type’ measures of humidity such as mass fraction, molar fraction or partial density, and ‘thermodynamic-type’ measures such as vapour pressure, dew-point temperature or fugacity. The use of different correlation equations may create spurious trends in the analysis of meteorological long-term series. Consistency with other properties, range of validity or uncertainty of published reference equations are not always clearly stated or are even unknown. Similar to the current metrological practice in using temperature scales, changes in definitions and standards of relative humidity should be well documented and recommended conversion formulas should be available.

As techniques for the generation and measurement of humidity generation improve, currently insignificant differences or inconsistencies between variants of reference equations and their associated uncertainty become of increasing significance.

5.5 Incompleteness of Current Reference Equations

While enhancement factors and saturation vapour pressures can be derived from chemical potentials, the opposite is not true, i.e., the reference equations used for the ‘traditional’ descriptions of relative humidity are incomplete in this sense. This deficiency is apparent when equilibria between subsaturated humid air and other moist substances, such as seawater, are to be calculated. In contrast to conventional use of a variety of possibly independently derived reference functions, the humidity quantities can be calculated directly and self-consistently from TEOS-10.

5.6 Definition of the Reference Phase

Current definitions allow saturation to be defined with respect to liquid pure water or to ice Ih, in both cases under the condition of a planar interface between the gas and the condensed phase. At this stage the isotopic composition of the condensed phase is not specified, although the observed isotopic fractionation between water phases is of increasing importance for the understanding of the global hydrological cycle. In the temperature range between the freezing point of liquid water and the onset of ice nucleation in clouds, supercooled liquid water is frequently observed and a related definition of relative humidity with respect to a metastable liquid phase is useful. Equilibria between humid air and water droplets or ocean water also differ from conventional saturation states and deserve special consideration.

5.7 Chemical Reactions in Gas Phase

In order to measure the composition of a moist gas such as humid air, the sample is often transferred to other temperature-pressure conditions under the silent assumption that the molar or mass fraction of water is conservative and that the measured value equivalently applies to the original gas mixture. However, chemical reactions between water and dry-gas components may violate that assumption¹⁴. For uniqueness it is preferred to define certain reference conditions under which a given composition is assumed to be valid within a given uncertainty.

5.8 Inconsistency

The IUPAC definition is inconsistent in allowing the subsaturated sample having a higher vapour density than the reference saturated state. That is, the reference saturated state is 'drier' than the subsaturated sample. In addition, any definition of relative humidity should always produce the value 0 for dry air, and the value 1 for saturated air. As an example, for ambient air at 300 K and 101325 Pa, $\varphi_{\text{IUPAC}} = 100\%$ rh when the dew point temperature is just 299.925 K and $\varphi_{\text{IUPAC}} = 100.44\%$ rh at saturation.

5.9 Nomenclature and Units

While the limitations of the predominant WMO/ASHRAE definitions have been explored, the continual publication and propagation of different and inconsistent definitions of relative humidity is confusing and leads to ill-defined reporting. Furthermore, there is no internationally agreed symbol for relative humidity, nor for the expression of the dimensionless unit.

5.10 Units

By its definition, relative humidity is a dimensionless quantity and is expressed by non-negative values, 0 for dry gas and 1 for saturated gas, however, or by multiples thereof such as % or ppm. Several current definitions given in the literature require a specific unit such as % to be used, however, the definition of a physical quantity should be independent of the particular unit in which the measured values may be expressed.

5.11 Uncertainty

Currently, in meteorological articles and manuals, equations and data used for the evaluation of the relative humidity are not accompanied by reasonable uncertainty estimates. Similarly, approximations such as φ_e to standard relative humidity φ_x are sometimes given, but uncertainty associated with the approximation is not. While usual uncertainty propagation rules sum up over all positive contributions, such a procedure that ignores correlations may

¹⁴ For example, a gas mixture containing O₂, CO₂ and H₂O, will always have chemical reactions such as $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$ and $2\text{H}_2\text{O} + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}_2$ adjusting to equilibrium, as temperature, pressure and density change. Under ambient conditions of air-conditioning or meteorology, such reactions are practically irrelevant, but in industrial applications at high pressures and temperatures (such as flue gases), such processes can be significant, and the non-conservative water vapour fraction may need to be determined via a relative humidity-like measurement.

produce significantly overestimated results for the case of Eq. (1.1). To account for this effect, covariance coefficients need to be included appropriately.

6 Suggested Advancements

(1) Refine the physical basis for concept of relative humidity:

(1.1) Define saturation, the driving forces toward saturation, and appropriate paths to saturation for all physically realistic conditions.

(1.2) Study the behaviour of sensors and other materials and surfaces in unsaturated vapour and 'subsaturated pressure' moist air.

(2) Propose a fundamental definition of relative humidity that applies over the whole range and if necessary redefine the standard definition in terms of this with known correction. To ensure harmonisation, either a single, generally recognised standard definition could supersede the existing variety, or the term "relative humidity" and its formula symbol could be employed for a whole family of related quantities and must then always be used in combination with additional specifiers, such as "WMO 2008 relative humidity", to unambiguously represent a measurable quantity:

(2.1) Relative fugacity:

Work to date suggests that relative fugacity provides a natural and fundamental basis for relative humidity. At equilibrium the chemical potentials of water in each phase are equal. Equivalently, the fugacities of water in each phase are equal. If the liquid phase is a plane surface of *near* pure water, then at equilibrium the vapour phase is saturated with respect to water. It is not true to say that the vapour pressures or vapour amount fractions etc are equal.

(2.2) The relative fugacity applies across the whole range. Note that at equilibrium, the chemical potential of water vapour is equal to the chemical potential of pure water containing a small amount of dissolved air depending on the pressure and vapour amount fraction.

(2.3) Units: By its definition, relative humidity is a dimensionless quantity and is expressed by non-negative values, 0 for dry gas and 1 for saturated gas, however, or by multiples thereof if more convenient units such as %, %rh or ppm are preferred. Several current definitions given in the literature require a specific unit such as % to be used, however, the definition of a physical quantity should be independent of the particular unit in which the measured values may be expressed.

(3) The work toward a universally acceptable and accepted definition of relative humidity, has highlighted other weaknesses in the measurement and calculation of humidity quantities. To ensure world-wide uniformity and long-term comparability of measurement results, it is important (a) that BIPM CCT-WG6 works with IAPWS to jointly recommend TEOS-10 (or references equations derived from it such as IAPWS 2011 for sublimation pressure of water), and (b) work together to develop useful methods of propagating the associated uncertainty.

It is most important to achieve agreement within the wider humidity community. The suggested activities include

- (i) consistent "axiomatic" definition and nomenclature of humidity quantities as derived from a small set of empirical fundamental equations, similar to the approach of TEOS-10
- (ii) formal endorsement of the IAPWS reference equations (and associated uncertainty) as CCT reference equations,
- (iii) definition of standard chemical and isotopic composition models for dry air and for water based on previous CIPM and IAPWS specifications,
- (iv) discussion of parameter covariance when calculating uncertainty (and hence presentation of parameter covariance or equivalent when publishing the equations),
- (v) updating the "Greenspan equation" for the enhancement factor to reflect values (and uncertainty) obtained from TEOS-10 (or an improved successor thereof),
- (vi) updating air-water virial coefficients exploiting most recent measurements, and the related IAPWS formulations,
- (vii) possible revision of TEOS-10 to more systematically include uncertainty and covariance, and effects caused by the dissolution of air in water, as well as extension to supercooled liquid water.

7 An Axiomatic Approach to Define Humid-Air Properties

7.1 Primary Quantities (Axioms)

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

Here is first the basic set of quantities considered as known a priori or defined externally (the "axioms"). This set is axiomatic in the sense that it is

- a) *independent* in that none of its elements can in part or in toto be derived from other elements of the set,
- b) *consistent* in that it is impossible to derive from the set alternative, different results for the same derived quantity, and
- c) *complete* in that exclusively all quantities defined in a second step can/must be mathematically rigorously specified in terms of the "axioms" exclusively.

The axiomatic set of **nine basic quantities** suggested here is:

1. **Pressure p** : absolute, total, in-situ pressure to which the actual sample of humid air, liquid water or ice is exposed.
2. **Temperature T** : absolute, in-situ, dry-bulb temperature the actual sample of humid air, liquid water or ice has. T is assumed here to be given on ITS-90.
3. **Dry air fraction A** : mass fraction of dry air in the actual sample of humid air.
4. **Gibbs function $g^{AV}(A, T, p)$** : Gibbs energy of humid air expressed in terms of the independent variables A, T, p . As a thermodynamic potential, g^{AV} provides all thermodynamic properties of humid air from algebraic combinations of its partial derivatives.
5. **Gibbs function $g^W(T, p)$** : Gibbs energy of liquid water expressed in terms of the independent variables T, p . As a thermodynamic potential, g^W provides all thermodynamic properties of liquid water from algebraic combinations of its partial derivatives. The freely adjustable parameters of g^W must be specified consistently with those of g^{AV} .
6. **Gibbs function $g^{lh}(T, p)$** : Gibbs energy of ice Ih expressed in terms of the independent variables T, p . As a thermodynamic potential, g^{lh} provides all thermodynamic properties of ice Ih from algebraic combinations of its partial derivatives. The freely adjustable parameters of g^{lh} must be specified consistently with those of g^{AV} .
7. **Molar mass M_W** : The molar mass of water is $M_W = 0.018\,015\,268\text{ kg mol}^{-1}$.
8. **Molar mass M_A** : The molar mass of dry air is $M_A = 0.028\,965\,46\text{ kg mol}^{-1}$.
9. **Molar gas constant R** : The CODATA 2010 value is $R = 8.314\,4621\text{ J K}^{-1}\text{ mol}^{-1}$.

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

7.2 Secondary Quantities

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

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

4. **Chemical potential of ice Ih** $\mu^{\text{lh}}: \mu^{\text{lh}}(T, p)$ is computed from the Gibbs function of ice Ih by the relation $\mu^{\text{lh}} = g^{\text{lh}}$.
5. **Triple point solid-liquid-gas of water (T_t, p_t):** Temperature and pressure of the common triple point of water are defined by the equations $\mu^{\text{lh}}(T_t, p_t) = \mu^{\text{w}}(T_t, p_t) = \mu^{\text{v}}(T_t, p_t)$.
6. **Specific gas constants R_W, R_A :** From the basic quantities 7, 8 and 9, the specific gas constants $R_W \equiv R/M_W$ of water and $R_A \equiv R/M_A$ of dry air are specified for convenience.
7. **Amount ("mole") fraction x_A :** Using the basic quantities 3, 7 and 8, the amount fraction of dry air in humid air is computed from $x_A = AM_W / (M_A - AM_A + AM_W)$.
8. **Amount ("mole") fraction x_V :** Using the basic quantities 3, 7 and 8, the amount fraction of water vapour in humid air is computed from $x_V = (1 - A)M_A / (M_A - AM_A + AM_W)$.
9. **Specific gas constant of humid air R_{AV} :** The molar gas constant, divided by the mass of one mole of humid air, is a linear function of the mass fraction A of dry air, in the form $R_{AV}(A) = R / (x_A M_A + x_V M_W) \equiv AR_A + (1 - A)R_W$.
10. **Gibbs function $g^{\text{AV,id}}(A, T, p)$:** Gibbs energy of ideal-gas humid air expressed in terms of the independent variables A, T, p . As a thermodynamic potential, $g^{\text{AV, id}}$ provides all thermodynamic properties of ideal-gas humid air from algebraic combinations of its partial derivatives. $g^{\text{AV, id}}$ is the mathematical low-pressure limit of g^{AV} , obtained from the basic quantity 4 and the derived quantity 9, in the form

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

The triple-point pressure p_t is defined in (5) and is used here only to make the argument of the logarithm dimensionless.
11. **Chemical potential of water vapour in humid air $\mu_W^{\text{AV}}: \mu_W^{\text{AV}}(A, T, p)$** is computed from the Gibbs function of humid air by the relation

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

$$\mu_W^{\text{AV,id}} = g^{\text{AV,id}} - Ag_A^{\text{AV,id}} \equiv g^{\text{AV,id}} - A \left(\partial g^{\text{AV,id}} / \partial A \right)_{T,p}.$$
13. **Freezing temperature of water T_{frz} :** $T_{\text{frz}}(p)$ is computed implicitly from the equation for the phase equilibrium between liquid water and ice, $\mu^{\text{w}}(T_{\text{frz}}, p) = \mu^{\text{lh}}(T_{\text{frz}}, p)$.
14. **Saturated vapour pressure of water¹⁵ e_W^{sat} :** e_W^{sat} is computed implicitly from the equation for the phase equilibrium between liquid water and water vapour, $\mu^{\text{w}}(T, e_W^{\text{sat}}) = \mu^{\text{v}}(T, e_W^{\text{sat}})$.

¹⁵ Here, we use symbol e to denote the pure vapour pressure and e^{sat} for the saturation vapour pressure. If distinction need be made as to the temperature then we may need to use $e^{\text{sat}}(T)$ as appropriate. If distinction need be made as to condensate phase then we may need to use respective $e_W^{\text{sat}}(T)$ and $e_{\text{lh}}^{\text{sat}}(T)$ as appropriate.

15. **Sublimation pressure of ice e_{lh}^{sat}** : e_{lh}^{sat} is computed implicitly from the equation for the phase equilibrium between ice lh and water vapour, $\mu^{lh}(T, e_{lh}^{sat}) = \mu^v(T, e_{lh}^{sat})$.
 16. **Specific humidity q** : Specific humidity, or the mass fraction of water vapour in humid air, is computed by $q = 1 - A$.
 17. **Partial pressure of water vapour p_v** : The partial pressure of water vapour in humid air is defined as $p_v = x_v p$.
 18. **Dew-point temperature T_D** : The dew-point temperature $T_D(A, p)$ associated with the actual humid-air sample is defined as the temperature at which a sample with the same pressure and composition is in equilibrium with liquid water, $\mu_W^{AV}(A, T_D, p) = \mu^W(T_D, p)$.
 19. **Frost-point temperature T_F** : The frost-point temperature $T_F(A, p)$ associated with the actual humid-air sample is defined as the temperature at which a sample with the same pressure and composition is in equilibrium with ice, $\mu_W^{AV}(A, T_F, p) = \mu^{lh}(T_F, p)$.
 20. **Saturated air mass fraction A^{sat}** : At the air mass fraction A^{sat} , replacing dry air by water vapour at constant T and p approaches saturation with respect to liquid water at the air fraction A^{sat} , $\mu_W^{AV}(A^{sat}, T, p) = \mu^W(T, p)$.
 21. **Saturated air mass fraction A^{sat}** : At the air mass fraction A^{sat} , replacing dry air by water vapour at constant T and p approaches saturation with respect to ice at the air fraction A^{sat} , $\mu_W^{AV}(A^{sat}, T, p) = \mu^{lh}(T, p)$.
 22. **(a) Enhancement factor of saturated humid air with respect to liquid water \hat{f}_w** :
At given composition, A and x_v , the enhancement factor $\hat{f}_w(T, p)$ is computed implicitly from the equation for the phase equilibrium between liquid water and humid air, $\mu^W(T, \hat{f}_w e_w^{sat} / x_v^{sat}) = \mu_W^{AV}(A^{sat}, T, \hat{f}_w e_w^{sat} / x_v^{sat})$.
(b) Or alternatively: At given pressure, p , the enhancement factor $\hat{f}_w(T, p)$ is computed by solving for A^{sat} the equation for the phase equilibrium between liquid water and humid air, $\mu^W(T, p) = \mu_W^{AV}(A^{sat}, T, p)$, finding x_v^{sat} using item (8) and then finding $\hat{f}_w(T, p) = x_v^{sat} p / e_w^{sat}$. Mathematically, (a) and (b) provide identical results.
 23. **(a) Enhancement factor of saturated humid air with respect to ice lh, \hat{f}_{lh}** : At given composition, A and x_v , the enhancement factor $\hat{f}_{lh}(T, p)$ is computed implicitly from the equation for the phase equilibrium between ice lh and humid air:
 $\mu^{lh}(T, \hat{f}_{lh} e_{lh}^{sat} / x_v^{sat}) = \mu_W^{AV}(A^{sat}, T, \hat{f}_{lh} e_{lh}^{sat} / x_v^{sat})$
(b) Or alternatively: At given pressure, p , the enhancement factor $\hat{f}_{lh}(T, p)$ is computed by solving for $A(T, p)$ the equation for the phase equilibrium between ice lh and humid air, $\mu^{lh}(T, p) = \mu_W^{AV}(A, T, p)$, find $x_v(T, p)$ using item (8) and then finding $\hat{f}_{lh}(T, p) = x_v^{sat} p / e_{lh}^{sat}(T)$. Mathematically, (a) and (b) provide identical results.
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24. **(a) Fugacity of water vapour in humid air f^{AV}** : In the real gas, the role of the partial pressure p_v is played by the fugacity:

$$f^{\text{AV}}(A, T, p) = x_v p \exp \left\{ \frac{\mu_w^{\text{AV}}(A, T, p) - \mu_w^{\text{AV}, \text{id}}(A, T, p)}{R_w T} \right\}.$$

- (b) Fugacity of pure water vapour f^{AV} ($A = 0$)**: In the absence of dry air, the limit $A \rightarrow 0$ can readily be carried out for the fugacity of vapour, as

$$f^{\text{AV}}(0, T, p) = p \exp \left\{ \frac{\mu_w^{\text{AV}}(0, T, p) - \mu_w^{\text{AV}, \text{id}}(0, T, p)}{R_w T} \right\} \equiv p \exp \left\{ \frac{\mu^v(T, p) - \mu^{v, \text{id}}(T, p)}{R_w T} \right\}$$

25. **Fugacity coefficient of water vapour in humid air ϕ** : The deviation of the fugacity from the partial pressure of water vapour, caused by non-ideal effects, is the fugacity coefficient:

$$\phi(A, T, p) = \frac{f^{\text{AV}}(A, T, p)}{x_v p} \equiv \exp \left\{ \frac{\mu_w^{\text{AV}}(A, T, p) - \mu_w^{\text{AV}, \text{id}}(A, T, p)}{R_w T} \right\}$$

26. **Relative fugacity of humid air relative to liquid water and to hexagonal ice, $\psi_{f, \text{W}}$ and $\psi_{f, \text{lh}}$** : The relative fugacities of humid air with respect to liquid water and ice are defined as follows:

$$\psi_{f, \text{W}}(A, T, p) \equiv \frac{f_w^{\text{AV}}(A, T, p)}{f_w^{\text{AV}}(A^{\text{sat}}, T, p)} = \exp \left\{ \frac{\mu_w^{\text{AV}}(A, T, p) - \mu^{\text{W}}(T, p)}{R_w T} \right\}.$$

$$\psi_{f, \text{lh}}(A, T, p) \equiv \frac{f_{\text{lh}}^{\text{AV}}(A, T, p)}{f_{\text{lh}}^{\text{AV}}(A^{\text{sat}}, T, p)} = \exp \left\{ \frac{\mu_w^{\text{AV}}(A, T, p) - \mu^{\text{lh}}(T, p)}{R_w T} \right\}.$$

27. **Relative fugacity of pure water vapour, $p = e$, with respect to liquid water and hexagonal ice, $\psi_{f, \bullet}$** : The relative fugacity of pure water vapour with respect to either of the two possible condensed phases corresponds to the limiting case of vanishing air, $A=0$:

$$\psi_{f, \text{W}}(T, e) = \exp \left\{ \frac{\mu^v(T, e) - \mu^{\text{W}}(T, e^{\text{sat}})}{R_w T} \right\},$$

$$\psi_{f, \text{lh}}(T, e) = \exp \left\{ \frac{\mu^v(T, e) - \mu^{\text{lh}}(T, e^{\text{sat}})}{R_w T} \right\}.$$

28. **Extended, non-isobaric relative fugacity of humid air $\psi_{f, \text{W}}^{\text{EXT}}$ and $\psi_{f, \text{lh}}^{\text{EXT}}$** : The relative fugacity expressions given in items 26 and 27 include also the special case where moist air is at subsaturated pressure ('extended range'). Thus, there is no further need for a special, extended range definition of relative humidity.

29. **Relative humidity ψ** : One option to define relative humidity is:

$$\psi(A, T, p) = (x_v p) / [\hat{f}(T, p) e^{\text{sat}}(T)].$$

30. **Extended, non-isobaric relative humidity (extended) ψ_{EXT} :** One option (of many possible) for an “extended” definition of relative humidity to cover the case where moist air is at subsaturated pressure is:

$$\psi_{\text{EXT}} = \begin{cases} p_V / p_V^{\text{sat}} & \text{when } p > e^{\text{sat}} \\ p_V / e^{\text{sat}} & \text{when } p \leq e^{\text{sat}} \end{cases}, \text{ or equivalently}$$

$$\psi_{\text{EXT}}(A, T, p) = \frac{e^{\text{sat}}(T_D) \hat{f}(A, T_D, p)}{e^{\text{sat}}(T) \hat{f}(A^{\text{sat}}, T, p')} \text{ where } p' = \begin{cases} p & \text{for } e^{\text{sat}}(T) \leq p \\ e^{\text{sat}}(T) & \text{for } e^{\text{sat}}(T) > p \\ \text{[i.e. choosing } A^{\text{sat}} = 0 \text{]} \end{cases}$$

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

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

Appendix A: Definition of Fugacity and Relative Fugacity

The *fugacity*, f_v , the "escaping tendency" of a substance (here water vapour) in a gaseous mixture (here humid air), is defined as:

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

where x is the amount fraction of water vapour in humid air, μ_W^{AV} the mole-based chemical potential of humid air, and R is the molar gas constant. The reference fugacity, $f_v^0(T)$, is a function of the temperature alone and is chosen to be

$$f_v^0(T) = xp \exp \left\{ -\frac{\mu_W^{AV, id}(x, T, p)}{RT} \right\}, \quad (\text{A.2})$$

where $\mu_W^{AV, id}$ is the chemical potential of humid air in the ideal-gas limit, i.e.,

$$\mu_W^{AV, id}(x, T, p) = RT \ln \frac{p}{p_0} + \lim_{p \rightarrow 0} \left\{ \mu_W^{AV}(x, T, p) - RT \ln \frac{p}{p_0} \right\}. \quad (\text{A.3})$$

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

$$\mu_W^{AV, id}(x, T, p) = g_0 + \int_{T_0}^T \left(1 - \frac{T}{T'} \right) \cdot c_p^{id}(T') dT' + RT \ln \frac{xp}{p_0}, \quad (\text{A.3a})$$

where $c_p^{id}(T)$ is the molar isobaric heat capacity, and g_0 , T_0 , p_0 are arbitrary constants, usually specified by reference-state conditions.

Making use of Eq. (A.3a), Eq. (A.2) leads to the expression

$$f_v^0(T) = p_0 \exp \left\{ -\frac{g_0}{RT} - \frac{1}{R} \int_{T_0}^T \left(\frac{1}{T} - \frac{1}{T'} \right) \cdot c_p^{id}(T') dT' \right\} \quad (\text{A.3b})$$

In Eq. (A.1) the factor, λ_v ,

$$\lambda_v(x, T, p) = \exp \left\{ \frac{\mu_W^{AV}(x, T, p)}{RT} \right\} \quad (\text{A.4})$$

is termed the (*absolute*) *activity* of the substance in the mixture and has the ideal-gas limit

$$\lambda_v^{id}(x, T, p) = \exp \left\{ \frac{\mu_W^{AV, id}(x, T, p)}{RT} \right\} = \frac{xp}{f_v^0(T)}. \quad (\text{A.4a})$$

Note that only differences of chemical potentials, rather than their absolute values, are physically relevant and measurable. Hence, while different activity definitions exist in dependence on certain additional conventions, fugacities are unambiguous.

The fugacity of a substance in a liquid or solid mixture is defined to equal the fugacity of that substance in a gaseous mixture which is in equilibrium with the given condensed phase.

The *fugacity coefficient*, $\varphi = \lambda_v / \lambda_v^{id}$, is used to quantify the deviation of the fugacity from the partial pressure, in the form

$$f_v(x, T, p) = xp \varphi(x, T, p), \quad (\text{A.5})$$

with the limiting property,

$$\lim_{p \rightarrow 0} \varphi(x, T, p) = 1. \quad (\text{A.6})$$

The *relative fugacity*, ψ_f , of a substance in a gaseous mixture is defined as the fugacity of that substance divided by the saturation fugacity, f_v^{sat} ,

$$\psi_f(x, T, p) = \frac{f_v}{f_v^{\text{sat}}} \equiv \frac{f_v(x, T, p)}{f_v(x^{\text{sat}}, T, p)} = \frac{\lambda_v(x, T, p)}{\lambda_v(x^{\text{sat}}, T, p)}. \quad (\text{A.7})$$

Here, x^{sat} is the amount ("mole") fraction of the substance in the gas mixture when it is in equilibrium with a liquid or solid reference phase at the same T and p , and λ_v and f_v are given in Eqs. (A.4) and (A.1), respectively.

Finally, we express the relative fugacity of the gas phase in terms of the chemical potential of water in an aqueous solution that is in equilibrium with humid air. From (A.4) and (A.7) we get

$$\psi_f(x, T, p) = \frac{\lambda_v(x, T, p)}{\lambda_v(x^{\text{sat}}, T, p)} = \exp \left\{ \frac{\mu_W^{\text{AV}}(x, T, p) - \mu_W^{\text{AV}}(x^{\text{sat}}, T, p)}{RT} \right\}. \quad (\text{A.8})$$

Equilibrium between gas and liquid is characterised by equal chemical potentials of water in both phases. This applies to the equilibrium between the given humid-air sample and a solution of appropriate molality, m ,

$$\mu_W^{\text{AV}}(x, T, p) = \mu^{\text{W}}(m, T, p), \quad (\text{A.9})$$

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

$$\mu_W^{\text{AV}}(x^{\text{sat}}, T, p) = \mu^{\text{W}}(m = 0, T, p). \quad (\text{A.10})$$

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

$$\psi_f(x, T, p) = \exp \left\{ \frac{\mu^{\text{W}}(m, T, p) - \mu^{\text{W}}(m = 0, T, p)}{RT} \right\} = a_w(m, T, p) \quad (\text{A.11})$$

where the reference state of the activity of water, a_w , is chosen as the pure solvent. We see that, *when water vapour or humid air is in equilibrium with an aqueous solution, the relative fugacity of the gas phase is equal to the (relative) activity of water in the liquid phase*, independent of the presence or absence of air.

Relative fugacity is used for the description of moist solids. The relative fugacity of water vapour in humid air with respect to liquid water or ice as the reference substances is usually also termed "relative humidity".

Appendix B: Representation of Water Vapour Pressure Enhancement Factor in Terms of the Fugacity Coefficient

The fugacity coefficient $\varphi(x, T, p)$, introduced by Eq. (A.5), can also be used to express the enhancement factor $\hat{f}(T, p)$. Evaluating Eq. (A.10) for pure water vapour and denoting the saturation pressure by $e^{\text{sat}}(T)$, we have

$$\mu_W^{\text{AV}}(x=1, T, e^{\text{sat}}) = \mu^{\text{W}}(m=0, T, e^{\text{sat}}) \quad (\text{B.1})$$

Subtracting Eq. (B.1) from Eq. (A.10) yields:

$$\mu_W^{\text{AV}}(x^{\text{sat}}, T, p) - \mu_W^{\text{AV}}(x=1, T, e^{\text{sat}}) = \mu^{\text{W}}(m=0, T, p) - \mu^{\text{W}}(m=0, T, e^{\text{sat}}). \quad (\text{B.2})$$

The left-hand side of Eq. (B.2) can be rewritten in terms of fugacity $f_v(x, T, p)$ according to Eq. (A.1), and the right-hand side of Eq. (B.2) can be expressed in terms of the Poynting correction factor of liquid water, $\pi(T, p)$:

$$\begin{aligned} \pi(T, p) &\equiv \exp \left\{ \frac{\mu_W(0, T, p) - \mu_W(0, T, e^{\text{sat}})}{RT} \right\} \\ &= \frac{\lambda_W(T, p)}{\lambda_W(T, e^{\text{sat}})} = \exp \left\{ \frac{1}{RT} \int_{e^{\text{sat}}(T)}^p \nu_W(T, p') dp' \right\}, \end{aligned} \quad (\text{B.3})$$

In Eq. (B.3) $\lambda_W(T, p)$ denotes the (absolute) activity of liquid water, and ν_W its molar volume. Therewith one obtains:

$$RT \ln \frac{f_v(x^{\text{sat}}, T, p)}{f_v(x=1, T, e^{\text{sat}})} = RT \ln \pi(T, p). \quad (\text{B.4})$$

By virtue of Eq. (A.5), Eq. (B.4) reads:

$$\frac{f^{\text{AV}}(x^{\text{sat}}, T, p)}{f^{\text{AV}}(x=1, T, e^{\text{sat}})} = \frac{x^{\text{sat}} p \cdot \varphi(x^{\text{sat}}, T, p)}{e^{\text{sat}} \cdot \varphi(x=1, T, e^{\text{sat}})} = \pi(T, p). \quad (\text{B.5})$$

Finally, considering the definition of the water-vapour pressure enhancement factor, we arrive at the following general relation:

$$\hat{f}(x^{\text{sat}}, T, p) = \frac{p_v^{\text{sat}}}{e^{\text{sat}}} = \frac{\varphi(x=1, T, e^{\text{sat}})}{\varphi(x^{\text{sat}}, T, p)} \pi(T, p). \quad (\text{B.6})$$

Appendix C: TEOS-10 based Determination of the Saturation State

The saturation vapour amount fraction, x^{sat} , and hence the saturation partial vapour pressure, $p_v^{\text{sat}} = x^{\text{sat}} p$, are determined by balancing of vapour and water fugacities. To physically explain the control of the vapour partial pressure by the fugacity, we consider a vacuum in which liquid water is added. The water will evaporate until the vapour fugacity equals the water fugacity, i.e., the vapour fugacity is controlled by the water fugacity. As air is added, the pressure will rise and cause the following effects:

- Air dissolves in water and will reduce the water fugacity (Raoult effect).
- The increased pressure acting on water will raise the water fugacity (Poynting effect).
- Air-water interaction will reduce the vapour fugacity (interaction affect).

As a net effect, more water is needed in the vapour phase to balance the water fugacity, which leads to an increase of the partial vapour pressure.

Figure C.1 depicts the way of determination of the saturation state on the base of TEOS-10.

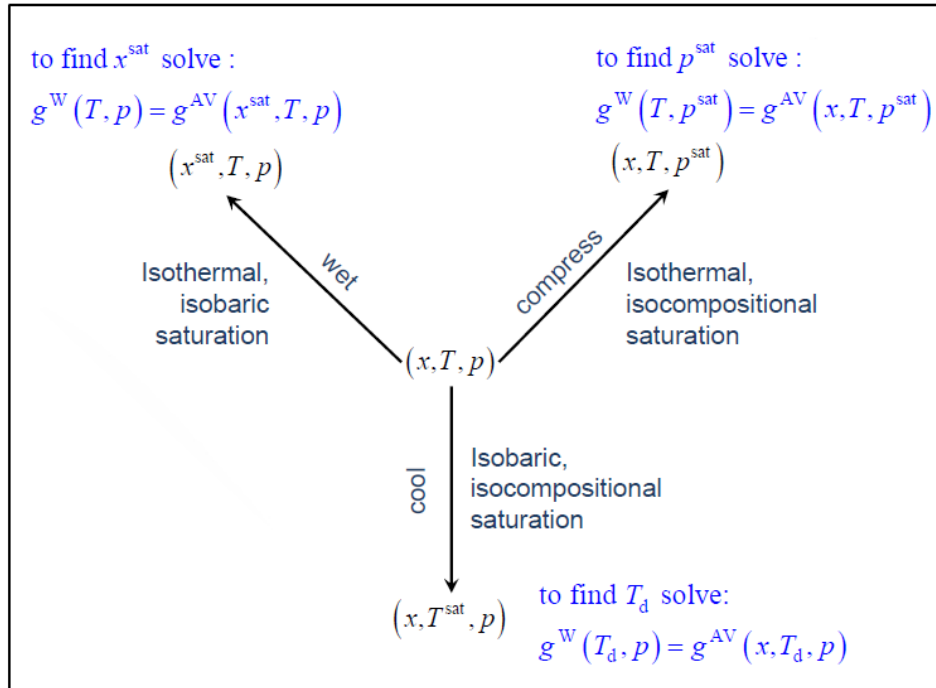


Fig. C.1 TEOS-10 based approach to uniquely determine the saturation state $(x^{\text{sat}}, T^{\text{sat}}, p^{\text{sat}})$ of an humid air sample characterised by the triple (x, T, p)

The enhancement factor $\hat{f}(T, p)$ can be determined by sequential numerical solution of the following thermodynamic equilibria:

$$g^w(T, p) = g^{AV}(x, T, p) \quad \text{to determine } x,$$

$$g^w(T, e) = g^{AV}(x = 1, T, e) \quad \text{to determine } e,$$

$$g^w(T, p) = g^{AV}(x, T, \hat{f} e / x) \quad \text{to determine } \hat{f}.$$