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Defining relative humidity in terms of water activity: III. Relations to dew-point and frost-point temperatures

Rainer Feistel^{1,2,*} , Olaf Hellmuth^{2,3} and Jeremy Lovell-Smith⁴ 

¹ Leibniz Institute for Baltic Sea Research (IOW), 18119 Warnemünde, Germany

² Leibniz-Sozietät der Wissenschaften zu Berlin e. V., 10117 Berlin, Germany

³ Leibniz Institute for Tropospheric Research (TROPOS), 04318 Leipzig, Germany

⁴ Measurement Standards Laboratory (MSL), PO Box 31-310, Lower Hutt, New Zealand

E-mail: rainer.feistel@io-warnemuende.de

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Abstract

Relative humidity (RH) is a fundamental quantity used in many fields of engineering and science, and in particular in meteorology and climate research. Relative fugacity (RF) and, equivalently, relative activity of water vapour in humid air have recently been proposed as a physically well-founded, unambiguous common metrological reference quantity for several conventional but mutually inconsistent definitions of RH. The RF definition is valid under real-gas conditions and above boiling and sublimation temperatures. While differences between RH and RF mostly remain within uncertainties of typical present-day RH measurements, such systematic discrepancies are expected to be of substantial climatological relevance. Consequently, interdisciplinary harmonisation of RH definitions is overdue within the SI framework. Dew-point and frost-point temperatures are preferred measurands in humidity metrology using, for example, chilled-mirror hygrometers. Here, relations are presented for estimating RF from those temperatures, based on equations of state of the 2011 IUGG⁵ standard TEOS-10, the ‘international thermodynamic equation of seawater—2010’. Recommendations are given for numerically computing RF using the open-source TEOS-10 SIA library⁶. The asymptotic limiting laws of RF for nearly saturated humid air exhibit the familiar form of Clausius–Clapeyron-like equations, despite departing from ideal-gas assumptions. Under various practical conditions, these simple equations may cover the full humidity range with only minor residuals compared to the full numerical TEOS-10 solution for RF.

Keywords: humid air, metrology, hygrometry, dewpoint, relative humidity, fugacity, TEOS-10

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

1. Introduction

Relative humidity (RH) is an important thermodynamic quantity in various branches of science and technology, such

as meteorology, climatology, air-conditioning, wood drying and ceramics industries, that is subject to advancing metrology [1–8]. However, conventional RH is not uniformly defined, and the definitions available typically do not cover the full range of potential applicability [9, 10]. In its latest strategy document, the Consultative Committee for Thermometry of the CIPM [11]: pp 2–17 has described the unsatisfactory present metrological situation by declaring that ‘the

* Author to whom any correspondence should be addressed.

⁵ IUGG: International Union of Geodesy and Geophysics, <https://iugg.org/>.

⁶ SIA Library: Sea-Ice-Air Library of TEOS-10, <http://teos-10.org>

expression of RH is not yet standardised' and its engagement to 'continue development of relative fugacity (RF) as a real-gas alternative for the conventional RH definition, together with options for realization within the SI'. Related work is ongoing in cooperation between the BIPM⁷ and IAPWS⁸ under the umbrellas of the CCT⁹ and JCS¹⁰.

For these reasons, a new, physically rigorous definition of RH has been developed [12] in the form of RF, or equivalently, of relative activity of water vapour in humid air, which covers the entire subcritical temperature-pressure range of pure water (see figure 10 and table 2). RF allows for deviations from ideal-gas approximations and can be computed from highly accurate equations which form the international thermodynamic standard TEOS-10 for seawater, ice and humid air [13–18]. For example, estimates for the effects of RH changes on the global climatic energy balance indicate that real-gas effects or differences between different current RH definitions are of similar magnitude as the observed global warming [19, 20]. Typically, practical atmospheric RH measurements possess uncertainties that prevent resolving such differences, and more accurate measurement methods are highly desirable [21]. A definition of RF in the framework of the SI may serve as a uniform common reference quantity for the several RH definitions currently in widespread practical use in various fields of science and technology.

The advantages of RF over the several conventional RH definitions result mainly from the fact that the partial pressure of water vapour, which appears in ideal-gas approximations of humidity equations, for non-ideal gases needs to be substituted by the fugacity of water vapour, or equivalently, by its activity or chemical potential, as explained in detail in the part 1 companion paper [12]. In particular, the RF definition reflects the physics of thermodynamic equilibrium—that for each composition species, at equilibrium its chemical potential (and hence the fugacity or activity) is equal across phases. The difference in the chemical potentials of water vapour (and equivalently, the ratio of the fugacities) across phases is the driver to equilibrium. This is not true of the partial pressure or any of the other humidity quantities mentioned in equation (1) below, since it does not make sense to say that there is an equality of these quantities across phases at thermodynamic equilibrium.

For the measurement of RF, osmotic methods are theoretically possible, which require only pressure and temperature measurements, both traceable to the SI [22]. A metrological standard method for practical RH measurement is the determination of dew-point and frost-point temperatures; in this paper equations are presented that permit the calculation of RF from those measurements. Conventionally, a suitable equation of state of humid air is requisite for this purpose, such as for the evaluation of conventional RH measures [23], but is, by

contrast, not necessary for the osmotic method of measuring RF [22].

In this paper it is assumed that by metrological devices such as chilled-mirror hygrometers [10], a given sample of humid air is isobarically cooled down to the condensation point at which liquid water or ice precipitates from the moist gas; this process may happen under atmospheric conditions but is to be distinguished from condensation during adiabatic expansion such as in cloud formation by forced and free convection. This paper addresses explicitly also the so-called 'extended pressure range' in which the pressure of humid air at a given temperature is below the vapour pressure of liquid water or the sublimation pressure of ambient hexagonal ice (ice Ih). Such conditions, under which condensed water phases do not stably exist, are mainly of metrological and technical interest but are not typically encountered in meteorology, except perhaps in the vicinity of geothermal vents, volcanic eruptions, impacts of meteorites, or lightning.

In section 2, equations are derived for the computation of RF from dew-point or frost-point temperatures, as conventionally measured by chilled-mirror hygrometers. In addition to thermodynamically rigorous expressions in terms of properties such as chemical potentials available from TEOS-10, also simplified, Clausius–Clapeyron-type formulas are derived for the limiting case of weakly subsaturated humid air, the water-vapour content of which is only slightly below its saturation value. The use of similar approximations is widespread in the humidity literature; for example, the driving force for evaporation is often estimated by a linearisation of the proper water activity term, $-\ln(\text{RF}) \approx (1 - \text{RH})$, which is valid sufficiently close to saturation [21, 24].

Section 3 is a summary of the new equations suggested in this paper. Appendix A, for easy reference, repeats briefly the original definition of RF, appendix B provides details on the derivation of approximate equations for RF in the limit of weak subsaturation, appendix C reports selected mathematical relations describing saturation properties, that is, equilibria between humid air and either liquid water or ice Ih, which are relevant for this paper, appendix D explains corrections for the case that the solubility of air in liquid water is to be included, appendix E suggests a collection of helpful calls to the TEOS-10 source code library for computing RF, and appendix F provides a source-code example for computing RF in the context of the open-source TEOS-10 SIA Library. Finally, a list of symbols used in this paper is collected in appendix G. This article refrains from comprehensively reporting uncertainty estimates; this task is intended to be the key topic of a subsequent companion paper on the RF.

In the fundamental mathematical functions of TEOS-10, various thermodynamic properties are given as specific quantities, expressed per unit of mass, while humidity calculations are otherwise usually done with molar quantities. Accordingly, while the amount of substance (informally, the mole fraction) of water vapour, x , the specific humidity, q , or the humidity (or mass-mixing) ratio, $r = q/(1 - q)$, are conventionally used in humidity calculations as composition variables, TEOS-10 functions are mostly expressed in terms of the dry air mass

⁷ BIPM: Bureau International des Poids et Mesures, <http://bipm.org>.

⁸ IAPWS: International Association for the Properties of Water and Steam, <http://iapws.org>.

⁹ CCT: Consultative Committee for Thermometry, <https://bipm.org/en/committees/cc/cct>.

¹⁰ JCS: IAPSO/SCOR/IAPWS Joint Committee on the Properties of Seawater, <http://teos-10.org>.

fraction, $A = 1 - q$, of humid air. The reason for this decision was that water in its different phases is present in the hydrosphere, atmosphere and cryosphere, admixed with sea salt in the ocean or with dry air in the atmosphere, both being described similarly by the solute mass fractions of the latter ones, either of dissolved salt ('absolute salinity'), S , or of dry air, A , and water as the solvent of the fluid mixtures. Given here for convenience, the humidity concentration variables A , q , r and x convert mutually by the molar masses of dry air and water, M_A and M_W , respectively, via the equation

$$\left(\frac{1}{A} - 1\right)^{-1} = \frac{1}{q} - 1 = \frac{1}{r} = \frac{M_A}{M_W} \left(\frac{1}{x} - 1\right). \quad (1)$$

In TEOS-10, temperatures are exclusively expressed on the International Temperature Scale of 1990, ITS-90 [25]. In this text and figures, numerical values of RH, including RF, are expressed in the unit %rh, so that saturation corresponds to an RF of 100 %rh = 1.

2. Relative fugacity from dew-point or frost-point temperature

A homogeneous sample of humid air can be characterised by three independent thermodynamic variables, namely temperature, T , pressure, p , and a humidity concentration variable such as the mole fraction of water vapour, x , the mass fraction of dry air, A , or the specific humidity, $q = 1 - A$ (see equation (1)). Pressure p is occasionally regarded here as the *total pressure* in contrast to the *partial pressure*, $xp = f(T,p)e(T)$, of water vapour in humid air. Here, $e(T)$ is the water-vapour saturation (or sublimation) pressure which is a function of T , and $f(T,p)$ is the water vapour enhancement factor which is a function of T and p . A humid-air sample is represented by a point in a 3D thermodynamic state space spanned by the three variables (x, T, p) or (A, T, p) (see figure 1).

Humid air in thermodynamic equilibrium with either liquid water or ice Ih beyond a planar interface is termed *saturated*. Although, in theory, relative fugacity could encompass pressures above the critical pressure and frost points could be determined corresponding to the adjacent phases, ice phases other than Ih are beyond the scope of this paper. The saturation state of a sample of humid air is uniquely defined by a function, $x = x^{\text{sat}}(T, p)$, or equivalently, $A = A^{\text{sat}}(T, p)$, and is represented by a related 2D surface in the 3D state space. Upon isobaric ($p = \text{const.}$) and iso-compositional ($x = \text{const.}$) cooling, the thermodynamic state point characterising an unsaturated air sample at (T, p) is displaced along a straight 1D trajectory, $(x, p) = \text{const.}$, until it intersects the saturation surface $x = x^{\text{sat}}(T, p)$ at the condensation temperature $T = T_{\text{cp}}(x, p)$, so that the identities

$$T \equiv T_{\text{cp}}(x^{\text{sat}}(T, p), p) \quad (2)$$

and

$$x \equiv x^{\text{sat}}(T_{\text{cp}}(x, p), p) \quad (3)$$

hold. The special case of a saturated humid air sample consisting of pure water vapour, $x = x^{\text{sat}}(T, p) = 1$ (or

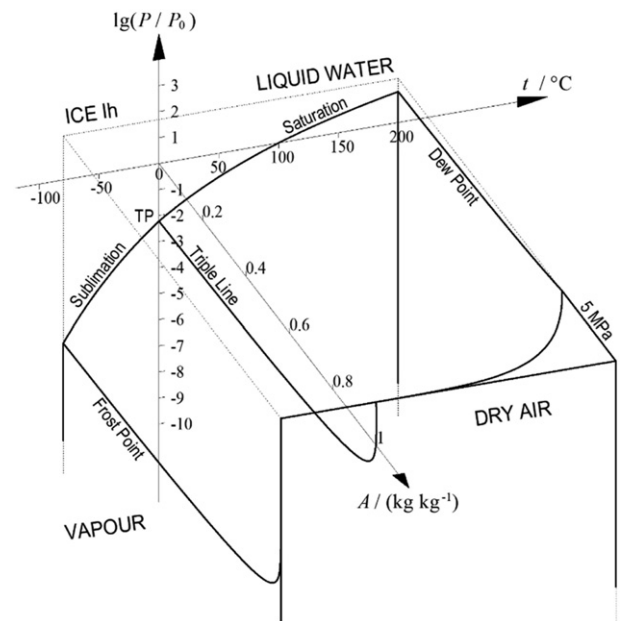


Figure 1. 3D phase diagram (A, T, p) of humid air. As separately shown in figures 2 and 10, the T - p plane in the back at $A = 0$ is the phase diagram of pure water with the solid (S) phase of 'ice Ih' above the 1D 'sublimation' curve, the liquid (L) phase of 'water' above the 1D 'saturation' curve, and the gas (G) phase of 'vapour' below those two curves. Starting at the triple point of water (TP), the 1D melting curve (not shown) separates 'ice Ih' from 'liquid water' in the plane $A = 0$. Presence of dry air, $A > 0$, extrudes the 1D 'sublimation' and 'saturation' curves to form 2D surfaces of frost points and dew points, respectively, along which humid air is saturated, $A = A^{\text{sat}}(T, p)$. Those surfaces are spanned here by the curves denoted as 'Frost Point' and 'Dew Point', together with the 1D 'Triple Line' along which they intersect each other at the melting temperature of ice Ih. Stable humid air exists below those 2D surfaces; states above are supersaturated and metastable or unstable. The reference pressure of the vertical axis is $P_0 = 101\,325$ Pa; 'lg' denotes the decadic logarithm. The pressure of '5 MPa' indicated at the top plane is the upper validity limit of the TEOS-10 formulation of humid air [14, 15, 26, 27]. The vertical plane $A = 1$ in front belongs to pure 'dry air'. Reprinted from [27], Copyright (2012), with permission from Elsevier.

equivalently, $A = 0$), defines the 1D water-vapour saturation (or sublimation) pressure curve given by $p = e(T)$ as a function of temperature in the 2D T - p diagram of water:

$$x^{\text{sat}}(T, e(T)) \equiv 1. \quad (4)$$

On this background, the RF of an unsaturated humid-air sample with the temperature T and the total pressure p is defined separately in four different T - p regions projected onto the phase diagram of pure water, as defined in the part 1 companion paper [12] and repeated briefly here for convenience in appendix A. The reason for this multiple definition is that RF, depending on its particular given T - p condition, needs to be referenced to an appropriate condensed phase of water at T which varies discontinuously with changing conditions as laid out by the phase diagram.

In this paper, for a given T , we define the *standard pressure range* as that range where $p \geq e(T)$, and define the *extended pressure range* as that range where $p < e(T)$ and no condensed water phase stably exists.

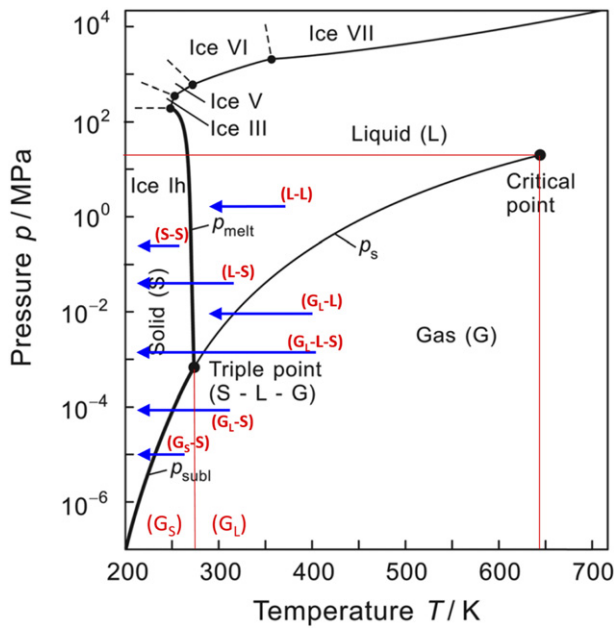


Figure 2. Temperature-pressure phase diagram of pure water, annotated with horizontal arrows indicating isobaric cooling processes of humid air samples. Arrows begin at (T, p) of the given sample and end at the saturated chilled-mirror state, either at the dew point, (T_{dp}, p) , or at the frost point, (T_{fp}, p) . Here, original arrows embedded at $A > 0$ in the 3D phase space displayed in figure 1 are shown as projections onto the boundary plane $A = 0$. The upper three cases, (L-L) to (L-S), belong to samples in the standard pressure range of RH, the lower four cases, (G_L-L) to (G_S-S) , to the extended pressure range, starting in the gas-phase region (G). In the original 3D space, figure 1, all those arrows start in the gaseous region below the saturation surface and end where they intersect that surface. Cases (L-L) and (G_L-L) lead to dew-point temperatures in the liquid region (L), the remaining ones to frost points in the solid region (S). G_S and G_L , respectively, denote the vapour-phase regions of (G) below and above the triple point temperature. Reprinted from [28].

A given sample of humid air with the properties (x, T, p) or (A, T, p) is represented in one of those regions by a point of known values of T and p , but with RF yet to be determined. To measure the humidity, quantitatively expressed by x , A or RF, the sample is cooled down isobarically to the dew point or frost point, that is, to a temperature at which condensation occurs, as either dew or frost respectively.

In the 2D phase diagram of pure water, figure 2, the saturation and sublimation curves, respectively, represent the loci of dew points and frost points of air-free water vapour. By contrast, rather than referring to pure water vapour, the arrows shown in the diagram refer to isobaric cooling of samples of unsaturated humid air with the same (T, p) values. Upon isobaric cooling, those samples have their dew points and frost points where the related arrows end.

Depending on the possibly different stable water phases at the sample's initial and final T - p conditions, this 'chilling' process may proceed in several qualitatively different ways, cases (L-L) to (G_S-S) , as indicated by horizontal arrows in the phase diagram of figure 2. Arrows begin at (T, p) of the given sample, characterised by its initial-state triple (A, T, p) with unknown A , and end at the chilled-mirror state,

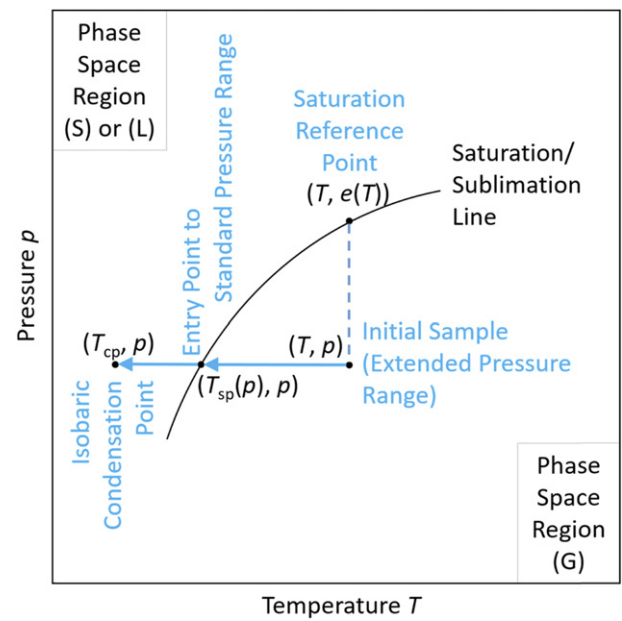


Figure 3. Schematic of isobaric cooling in the extended pressure range. RF of the initial sample at (T, p) is defined relative to saturated pure water vapour at the same temperature $(T, e(T))$. Upon isobaric cooling, condensation is thermodynamically impossible before crossing the saturation or sublimation curve, i.e., before entering the standard-pressure region at $(T_{sp}(p), p)$. The temperature difference between this entry point and the actual condensation point of the humid-air sample, $T_{sp} - T_{cp}$, determines the partial subsaturation at the entry point (T_{sp}, p) in addition to the remaining partial subsaturation resulting from the initial pressure insufficiency, $e(T) - p$.

characterised by the final-state triple at the condensation point (subscript 'cp'), (A, T_{cp}, p) , either at the dew point (subscript 'dp'), (T_{dp}, p) , or at the frost point (subscript 'fp'), (T_{fp}, p) . The arrows displayed in the 2D space of figure 2 actually constitute projections onto the p - T plane $A = 0$ of the horizontal isobaric and iso-compositional cooling trajectory, $A = \text{const.}$, $p = \text{const.}$, in the 3D space of figure 1 from a point at (A, T, p) below the saturation surface to the intersection point (A, T_{cp}, p) with the saturation surface, $A = A^{\text{sat}}(T_{cp}, p)$. Simple equations, consistent with TEOS-10, for evaluating the saturation-, sublimation- and melting-pressure curves of the pure-water phases involved are provided in appendix A.

If the initial sample is under (T, p) conditions of the extended pressure range, the isobaric cooling process down to condensation must first cross the saturation or sublimation curve of pure water vapour to enter the standard-pressure range, subscript 'sp', at (T_{sp}, p) , a curve being defined by condensation of pure vapour at the given pressure, $e(T_{sp}) = p$, see figure 3, which is independent of the humidity of the initial sample. Further cooling, then depending on that initial humidity, results in condensation of humid air at the condensation-point temperature, subscript 'cp', (T_{cp}, p) within the standard pressure range. With regard to an approximation formula of RF for weakly subsaturated samples, mathematics similar to that of the standard pressure range can be applied to the second cooling step, while the first step requires alternative considerations.

Next, the seven different possible routes to condensation, as indicated in figure 2, are analysed in turn. The qualitatively different cases are symbolically indicated by ‘(X–Y)’, where X is placeholder for the pure water phase, either ‘L’, ‘S’, or ‘G’, at the initial T – p conditions before chilling, and Y is that at the final condensation point after chilling, (T_{cp}, p) . The gas phase ‘G’ of X is additionally separated in ‘G_S’ below the triple-point temperature and ‘G_L’ above it, while Y may only take the actual values ‘L’ or ‘S’. For each of those cases, a full analytical expression for RF is given as well as a simplified formula as an approximation in the limit of weak subsaturation. The full formulas depend only on the phase space regions of the initial and the final state of the cooling process, while the approximations depend also on different conditions possibly passed in between and require detailed mathematical manipulations as carried out in appendix B.

2.1. Case (L–L): standard range with respect to water, dew-point condensation

In the standard pressure range and with respect to liquid water, RF, ψ_f , in the region (L) is defined by equations (A.4) and (A.5) of appendix A, namely by

$$R_W T \ln \psi_f = \mu_V^{AV}(A, T, p) - g^W(T, p). \quad (5)$$

Here, R_W is the specific gas constant of water, μ_V^{AV} is the chemical potential of water vapour (subscript ‘V’) in humid air (superscript ‘AV’) and g^W is the chemical potential of pure liquid water (superscript ‘W’), which equals its specific Gibbs energy. In equation (5), the dry-air fraction A of the initial sample is still the same as its saturation value after chilling,

$$A = A^{\text{sat}}(T_{dp}, p), \quad (6)$$

associated with the dew-point temperature T_{dp} at the same pressure, which obeys the equilibrium condition between the two chemical potentials,

$$\mu_V^{AV}(A^{\text{sat}}(T_{dp}, p), T_{dp}, p) = g^W(T_{dp}, p). \quad (7)$$

Similarly, the saturation value $A^{\text{sat}}(T, p)$ at any temperature T associated with the initial sample conditions can be computed from the equilibrium equation

$$\mu_V^{AV}(A^{\text{sat}}(T, p), T, p) = g^W(T, p). \quad (8)$$

A physically reasonable such solution can be assumed to exist because the T – p conditions belong to the region (L). As an aside, it may be noted that the ratio

$$\psi_q = \frac{1 - A^{\text{sat}}(T_{dp}, p)}{1 - A^{\text{sat}}(T, p)} \quad (9)$$

is the RH ψ_q of the given sample in the conventional climatological RH definition [10, 21].

From equations (5) and (8), the sample’s RF can be computed from the measured dew-point temperature by

$$R_W T \ln \psi_f = \mu_V^{AV}(A^{\text{sat}}(T_{dp}, p), T, p) - \mu_V^{AV}(A^{\text{sat}}(T, p), T, p). \quad (10)$$

The chemical potential μ_V^{AV} of water vapour in humid air is numerically available from the TEOS-10 Gibbs function, g^{AV} , of humid air, by the thermodynamic relation [15, 29]

$$\mu_V^{AV} = g^{AV} - A \left(\frac{\partial g^{AV}}{\partial A} \right)_{T, p}. \quad (11)$$

As an alternative to the numerical implementation of the thermodynamically rigorous equation (10), this formula also permits a derivation of an approximate, simplified mathematical expression by power series expansion about T , including exactly all linear terms in δT ,

$$R_W T \ln \psi_f = \mu_V^{AV}(A^{\text{sat}}(T - \delta T, p), T, p) - \mu_V^{AV}(A^{\text{sat}}(T, p), T, p), \quad (12)$$

for the case that the subsaturation expressed by the temperature depression, $\delta T \equiv T - T_{dp}$, of the given sample of humid air is only weak, i.e.,

$$|\delta T/T| \ll 1. \quad (13)$$

The result of this calculation, as outlined in detail in appendix B.1, is a limiting formula for the RF, equation (B.7), similar to the Clausius–Clapeyron approximation for ideal gases,

$$\psi_f = \exp \left\{ \frac{L_L(T_{dp}, p)}{R_W} \left(\frac{1}{T} - \frac{1}{T_{dp}} \right) \right\} + O \left(\left| \frac{\delta T}{T} \right|^2 \right). \quad (14)$$

Note that the specific enthalpy, $L_L(T_{dp}, p)$, of evaporation of water vapour from liquid water to humid air is well-defined only along the 2D phase boundary in the 3D state space spanned by (A, T, p) , figure 1, namely on the saturation surface, $A = A^{\text{sat}}(T, p)$, and depends on only two independent variables such as, say, $L_L(T, p)$. This applies similarly also to the sublimation enthalpy, $L_S(T, p)$, considered later. Both, L_S and L_L , denote the latent heats released by condensation of water vapour from humid air to either the solid (subscript ‘S’) or the liquid condensed phase (subscript ‘L’), respectively.

In figure 4, the deviation of equation (14) from (10) is evaluated numerically for some typical meteorological situations. Down to below 75%rh, the residuals remain well within 0.1%rh.

Computed from TEOS-10, as a numerical example comparing equations (10) and (14), at given $p = 101325$ Pa, $T = 300$ K and RH of $x/x^{\text{sat}}(T, p) = 80\%$ rh, the sample’s water-vapour mole fraction is $x = 2.804746\%$, the dew point is at $T_{dp} = 296.259246$ K, RF from equation (10) is 80.053534%rh and RF from equation (14) is 80.023785%rh, calculated with the evaporation enthalpy value of $L_L(T_{dp}, p) = 2443589.2$ J kg^{−1}. Note that the Clausius–Clapeyron approximation, equation (14), of RF is slightly closer to conventional RH than to the exact RF, equation (10). In appendix F, further check values for RF are given.

2.2. Case (S–S): standard range with respect to ice, frost-point condensation

In the standard pressure range and with respect to ice Ih, RF in the region (S) is defined in appendix A by equations (A.4) and (A.5) as

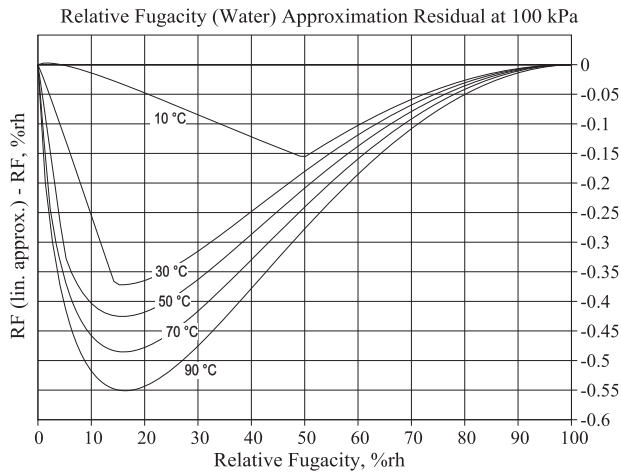


Figure 4. Cases (L–L) and (L–S). Deviation in %rh of the linear weak-subsaturation approximation of RF (14) from the full numerical result (10) at atmospheric pressure and initial temperatures between 10 °C and 90 °C as indicated near the curves. Abscissa value is the RF of the initial sample before chilling; weakly subsaturated samples take values near 100%rh. To the left of the pronounced minimum, condensation appears at the frost point (case L–S) rather than at the dew point (case L–L), and the responsible approximation equation becomes (26) instead of (14). For the typical marine troposphere about 80%rh, the approximation error remains below 0.1%rh, significantly less than the typical uncertainty of routine meteorological hygrometers of 1–5%rh [30, 31]. Note that the abscissa covers the full range from dry air (at 0% rh) to saturation (at 100%rh) of RF, which is possible only in the standard pressure range.

$$R_W T \ln \psi_f = \mu_V^{AV}(A, T, p) - g^{lh}(T, p). \quad (15)$$

The calculations of section 2.1 can be repeated here quite similarly for ice rather than liquid water. Then, equation (10) turns into the rigorous equation for RF in terms of the frost-point temperature, T_{fp} ,

$$R_W T \ln \psi_f = \mu_V^{AV}(A^{sat}(T_{fp}, p), T, p) - \mu_V^{AV}(A^{sat}(T, p), T, p), \quad (16)$$

and its approximation at weak subsaturation, equation (14), as derived in appendix B.2, consequently becomes

$$\psi_f = \exp \left\{ \frac{L_S(T_{fp}, p)}{R_W} \left(\frac{1}{T} - \frac{1}{T_{fp}} \right) \right\} + O \left(\left| \frac{\delta T}{T} \right|^2 \right). \quad (17)$$

Here, $L_S(T_{fp}, p)$ is the specific sublimation enthalpy of ice Ih in humid air at the frost-point temperature, defining the saturation state $A = A^{sat}(T_{fp}, p)$. As an illustration, the deviation of this equation (17) from the rigorous formula (16) is displayed in figure 5 for some meteorological conditions.

2.3. Case (L–S): standard range with respect to water, frost-point condensation

In the standard pressure range and with respect to liquid water, RF in the region (L) is defined by equations (A.4) and (A.5) as

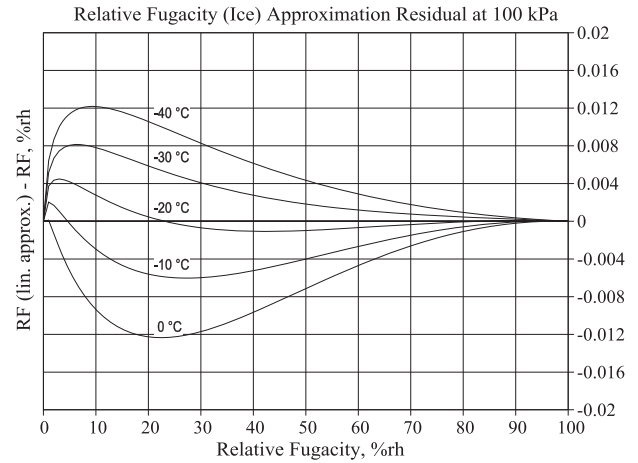


Figure 5. Case (S–S). Deviation in %rh of the linear weak-subsaturation approximation of RF (17) with respect to ice Ih from the full numerical result (16) at atmospheric pressure and initial temperatures between 0 °C and –40 °C as indicated near the curves. Abscissa value is the RF of the initial sample before chilling; weakly subsaturated samples take values near 100%rh. The approximation error remains well below 0.1%rh even for strongly subsaturated air, significantly less than the typical uncertainty of routine meteorological hygrometers of 1–5%rh [30, 31].

$$R_W T \ln \psi_f = \mu_V^{AV}(A, T, p) - g^W(T, p) \quad (18)$$

The dry-air fraction A of the given sample is available as the saturation value from the frost-point temperature T_{fp} at the same pressure,

$$A = A^{sat}(T_{fp}, p), \quad (19)$$

which obeys the equilibrium condition

$$\mu_V^{AV}(A^{sat}(T_{fp}, p), T_{fp}, p) = g^{lh}(T_{fp}, p). \quad (20)$$

Similarly, the reference saturation value $A^{sat}(T, p)$ associated with the given initial sample conditions can be computed from the equilibrium equation at the related dew point, $T = T_{dp}$,

$$\mu_V^{AV}(A^{sat}(T, p), T, p) = g^W(T, p). \quad (21)$$

The rigorous formula for RF then is equivalent to equation (16):

$$R_W T \ln \psi_f = \mu_V^{AV}(A^{sat}(T_{fp}, p), T, p) - \mu_V^{AV}(A^{sat}(T, p), T, p). \quad (22)$$

In this case (L–S), the melting point, $T_{mp}(p)$, of ice Ih is located between the initial and final temperatures of the chilling process,

$$T_{fp}(A, p) < T_{mp}(p) < T. \quad (23)$$

At this melting point, the derivative $(\partial A^{sat} / \partial T)_p$ of the 2D saturation surface $A^{sat}(T, p)$ in figure 1, as derived analytically in appendix C, exhibits a discontinuity,

$$A^{\text{sat}}(T, p) \left(\frac{\partial^2 g^{\text{AV}}}{\partial A^2} \right)_{T,p} \left(\frac{\partial A^{\text{sat}}}{\partial T} \right)_p = \begin{cases} -L_L(T, p)/T & \text{if } T \geq T_{\text{mp}}(p) \\ -L_S(T, p)/T & \text{if } T \leq T_{\text{mp}}(p) \end{cases}, \quad (24)$$

with the difference

$$L_S(T_{\text{mp}}(p), p) - L_L(T_{\text{mp}}(p), p) = L_M(p) \quad (25)$$

being the melting enthalpy of ice. Note that in the 3D state space spanned by (A, T, p) , the functions L_S and L_L are defined on the 2D saturation surfaces of humid air with respect to ice and liquid water, respectively, and carry two independent arguments, while L_M is defined on the 1D melting curve of ice, independent of air, and depends on one independent variable only.

For an approximation formula of equation (22) valid at weak subsaturation, the series expansion with respect to the temperature lowering, $\delta T \equiv T - T_{\text{fp}}$, is carried out in appendix B.3. The resulting final approximation formula for RF in the case (L–S) is, equation (B.23),

$$\psi_f \approx \exp \left\{ \frac{L_L(T_{\text{mp}}, p)}{R_W} \left(\frac{1}{T} - \frac{1}{T_{\text{mp}}} \right) + \frac{L_S(T_{\text{mp}}, p)}{R_W} \left(\frac{1}{T_{\text{mp}}} - \frac{1}{T_{\text{fp}}} \right) \right\}, \quad (26)$$

or, equivalently,

$$\psi_f = \exp \left\{ \frac{L_S(T_{\text{mp}}, p)}{R_W} \left(\frac{1}{T} - \frac{1}{T_{\text{fp}}} \right) - \frac{L_M(p)}{R_W} \left(\frac{1}{T} - \frac{1}{T_{\text{mp}}} \right) \right\} + O \left(\left| \frac{\delta T}{T} \right|^2 \right). \quad (27)$$

In the limit $T_{\text{fp}} \rightarrow T_{\text{mp}}$, equation (26) is consistent with equation (14) of case (L–L), and similarly with equation (17) of case (S–S) in the limit $T \rightarrow T_{\text{mp}}$. As an illustration, the deviation of equation (26) from the rigorous formula (22) is displayed in figure 4 under some selected conditions.

2.4. Case (G_L –L): extended range with respect to water, dew-point condensation

According to equations (A.4) and (A.5), in the region G_L of figure 2 the RF is defined as

$$R_W T \ln \psi_f = \mu_V^{\text{AV}}(A, T, p) - g^V(T, e^W(T)) = \mu_V^{\text{AV}}(A, T, p) - \mu_V^{\text{AV}}(0, T, e^W(T)). \quad (28)$$

The air fraction A is obtained from saturation at the dew point, T_{dp} ,

$$A = A^{\text{sat}}(T_{\text{dp}}, p), \quad (29)$$

so that

$$R_W T \ln \psi_f = \mu_V^{\text{AV}}(A^{\text{sat}}(T_{\text{dp}}, p), T, p) - \mu_V^{\text{AV}}(0, T, e^W(T)). \quad (30)$$

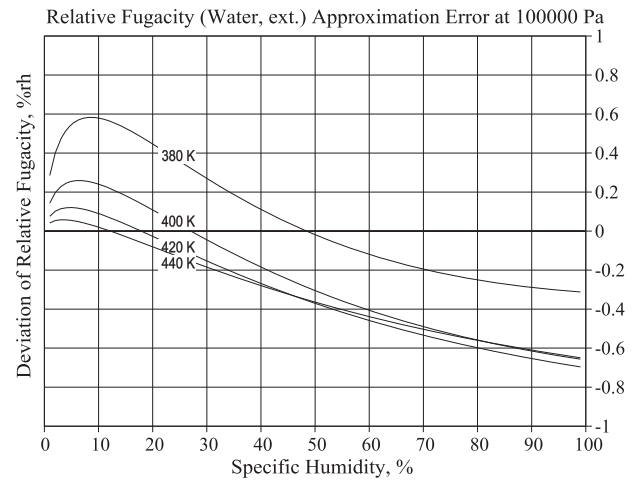


Figure 6. Case (G_L –L). Deviation of approximate RF, equation (32), from full RF, equation (31), in the extended pressure range at 100 kPa as a function of specific humidity $q = 1 - A$ expressed as a percentage, at several initial sample temperatures as indicated near the curves. The residual visible at $q = 100\%$ results from the ideal-gas approximation used for deriving the pre-factor $p/e^W(T)$ in equation (32). Note that the abscissa covers the full range from dry air (at 0%) to pure water vapour (at 100%) of specific humidity, which is possible only in the extended pressure range.

Making use of TEOS-10 library functions, the calculation of the RF $\psi_f(A, T, p)$ of the given sample requires (i) evaluation of the saturation pressure of liquid water, $e^W(T)$, (ii) evaluation of the saturation dry-air fraction $A^{\text{sat}}(T_{\text{dp}}, p)$ at the measured dew point, and finally (iii) computing

$$\psi_f = \exp \left\{ \frac{\mu_V^{\text{AV}}(A^{\text{sat}}(T_{\text{dp}}, p), T, p) - g^V(T, e^W(T))}{R_W T} \right\}. \quad (31)$$

During the chilling process, the sample passes from the extended pressure range to the standard pressure range (subscript ‘sp’) at the point (T_{sp}, p) , where T_{sp} is the boiling temperature of pure water at the pressure p , as shown in figure 3.

For weakly subsaturated humid air, the formula (31) may be approximated by a simpler expression, as derived in appendix B.4. The linear approximation of equation (31) for the RF, in the case of weak subsaturation, is consistent with the Clausius–Clapeyron-like formula,

$$\psi_f \approx \frac{p}{e^W(T)} \exp \left\{ \frac{L_L(p)}{R_W} \left(\frac{1}{T_{\text{sp}}} - \frac{1}{T_{\text{dp}}} \right) \right\}. \quad (32)$$

The residual of the approximation equation (32) in comparison to the full numerical expression (31) is displayed in figure 6 for some typical cases, remaining well below 1%rh.

2.5. Case (G_L –L–S): extended range with respect to water, frost-point condensation

Similar to section 2.4, according to equations (A.4) and (A.5), in the region G_L of figure 2 the RF is defined as

$$\begin{aligned} R_W T \ln \psi_f &= \mu_V^{\text{AV}}(A, T, p) - g^V(T, e^W(T)) \\ &= \mu_V^{\text{AV}}(A, T, p) - \mu_V^{\text{AV}}(0, T, e^W(T)). \end{aligned} \quad (33)$$

The air fraction A is obtained from saturation at the frost point,

$$A = A^{\text{sat}}(T_{\text{fp}}, p), \quad (34)$$

so that

$$R_W T \ln \psi_f = \mu_V^{\text{AV}}(A^{\text{sat}}(T_{\text{fp}}, p), T, p) - \mu_V^{\text{AV}}(0, T, e^W(T)). \quad (35)$$

Making use of TEOS-10 library functions, the calculation of the RF $\psi_f(A, T, p)$ of the given sample requires (i) evaluation of the saturation pressure of liquid water, $e^W(T)$, (ii) evaluation of the saturation dry-air fraction $A^{\text{sat}}(T_{\text{fp}}, p)$ at the measured frost point, and finally (iii) computing

$$\psi_f = \exp \left\{ \frac{\mu_V^{\text{AV}}(A^{\text{sat}}(T_{\text{fp}}, p), T, p) - g^V(T, e^W(T))}{R_W T} \right\}. \quad (36)$$

For weakly subsaturated humid air, this formula may be approximated by a simpler expression which requires considering the details of the cooling path rather than just its endpoints at T and T_{fp} . In contrast to section 2.4, after entering the standard pressure range, see figure 3, the cooling process additionally crosses the melting temperature T_{mp} before condensation occurs at the frost point, see figure 2.

The associated linearisation is explicitly carried out in appendix B.5, with the result rearranged in Clausius–Clapeyron form

$$\begin{aligned} \psi_f &\approx \frac{p}{e^W(T)} \exp \left\{ \frac{L_L(T_{\text{mp}}, p)}{R_W} \left(\frac{1}{T_{\text{sp}}} - \frac{1}{T_{\text{mp}}} \right) \right. \\ &\quad \left. + \frac{L_S(T_{\text{mp}}, p)}{R_W} \left(\frac{1}{T_{\text{mp}}} - \frac{1}{T_{\text{fp}}} \right) \right\}. \end{aligned} \quad (37)$$

This is the intended linear approximation formula for the RF at weak subsaturation in the case (G_L – L – S). The residual of the approximation equation (37) in comparison to the full numerical expression (36) is displayed in figure 7 for some typical cases, remaining well below 0.2%rh.

2.6. Case (G_L – S): extended range with respect to water, frost-point condensation

This case (G_L – S) can be treated similarly to the case (G_L – L) in section 2.4 by formally substituting the dew point by the frost point. According to equations (A.4) and (A.5), in the region G_L of figure 2 the RF is defined as

$$\begin{aligned} R_W T \ln \psi_f &= \mu_V^{\text{AV}}(A, T, p) - g^V(T, e^W(T)) \\ &= \mu_V^{\text{AV}}(A, T, p) - \mu_V^{\text{AV}}(0, T, e^W(T)). \end{aligned} \quad (38)$$

The air fraction A is obtained from saturation at the frost point,

$$A = A^{\text{sat}}(T_{\text{fp}}, p), \quad (39)$$

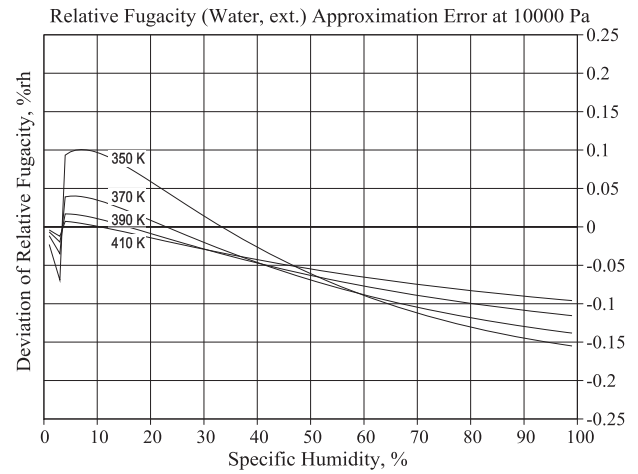


Figure 7. Cases (G_L – L) and (G_L – L – S). Deviation of approximate RF, equations (37) and (32), from full RF, equations (36) and (31), respectively, in the extended pressure range at 10 kPa as a function of specific humidity $q = 1 - A$ expressed as a percentage, at several initial sample temperatures as indicated near the curves. On the left of the minimum, condensation happens at the dew point in region (L), equation (e2.52) relative to (31), while at lower humidities condensation occurs at lower temperatures in the ice region (S), equation (e2.67) relative to (36). The residual visible at $q = 100\%$ results from the ideal-gas approximation used for deriving the pre-factor $p/e^W(T)$ in equation (37).

so that

$$R_W T \ln \psi_f = \mu_V^{\text{AV}}(A^{\text{sat}}(T_{\text{fp}}, p), T, p) - \mu_V^{\text{AV}}(0, T, e^W(T)). \quad (40)$$

Making use of TEOS-10 library functions, the calculation of the RF $\psi_f(A, T, p)$ of the given sample requires (i) evaluation of the saturation pressure of liquid water, $e^W(T)$, (ii) evaluation of the saturation dry-air fraction $A^{\text{sat}}(T_{\text{fp}}, p)$ at the measured frost point, and finally (iii) computing

$$\psi_f = \exp \left\{ \frac{\mu_V^{\text{AV}}(A^{\text{sat}}(T_{\text{fp}}, p), T, p) - g^V(T, e^W(T))}{R_W T} \right\}. \quad (41)$$

For weakly subsaturated humid air, this formula may be approximated by a simpler expression, as derived in appendix B.6. The resulting linear approximation of equation (41) for the RF in the case of weak subsaturation is therefore, up to quadratic terms in the perturbation series, the simple Clausius–Clapeyron-like formula

$$\psi_f \approx \frac{p}{e^W(T)} \exp \left\{ \frac{L_S(p)}{R_W} \left(\frac{1}{T_{\text{sp}}} - \frac{1}{T_{\text{fp}}} \right) \right\}. \quad (42)$$

Here, $T_{\text{sp}}(p)$ is the sublimation temperature of ice with respect to pure water vapour, at which the isobaric cooling process enters the standard pressure range, and $L_S(p)$ is the sublimation enthalpy of ice Ih with respect to pure water vapour at this point. The residual of the approximation equation (42) in comparison to the full numerical expression (41) is displayed in figure 8 for some typical cases, remaining well below 0.001%rh.

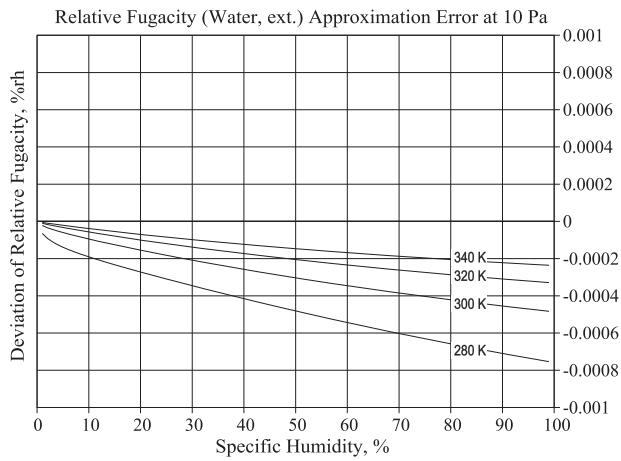


Figure 8. Case (G_L-S). Deviation of approximate RF, equation (42), from full RF, equation (41), in the extended pressure range at 10 Pa as a function of specific humidity $q = 1 - A$ expressed as a percentage, at several initial sample temperatures as indicated near the curves. The residual visible at $q = 100\%$ results from the ideal-gas approximation used for deriving the pre-factor $p/e^W(T)$ in equation (42).

2.7. Case (G_S-S): extended range with respect to ice, frost-point condensation

This case (G_S-S) can be treated similarly to the case (G_L-S) in section 2.6 by formally substituting the saturation pressure $e^W(T)$ by the sublimation pressure $e^{lh}(T)$. According to equations (A.4) and (A.5), in the region G_S of figure 2 the RF is defined as

$$\begin{aligned} R_W T \ln \psi_f &= \mu_V^{AV}(A, T, p) - g^V(T, e^{lh}(T)) \\ &= \mu_V^{AV}(A, T, p) - \mu_V^{AV}(0, T, e^{lh}(T)). \end{aligned} \quad (43)$$

The air fraction A is obtained from saturation at the frost point,

$$A = A^{\text{sat}}(T_{fp}, p), \quad (44)$$

so that

$$R_W T \ln \psi_f = \mu_V^{AV}(A^{\text{sat}}(T_{fp}, p), T, p) - \mu_V^{AV}(0, T, e^{lh}(T)). \quad (45)$$

Making use of TEOS-10 library functions, the calculation of the RF $\psi_f(A, T, p)$ of the given sample requires (i) evaluation of the sublimation pressure of ice, $e^{lh}(T)$, (ii) evaluation of the saturation dry-air fraction $A^{\text{sat}}(T_{fp}, p)$ at the measured frost point, and finally (iii) computing

$$\psi_f = \exp \left\{ \frac{\mu_V^{AV}(A^{\text{sat}}(T_{fp}, p), T, p) - g^V(T, e^{lh}(T))}{R_W T} \right\}. \quad (46)$$

For weakly subsaturated humid air, this formula may be approximated by a simpler expression, as outlined in appendix B.7. The linear approximation of equation (46) for the RF

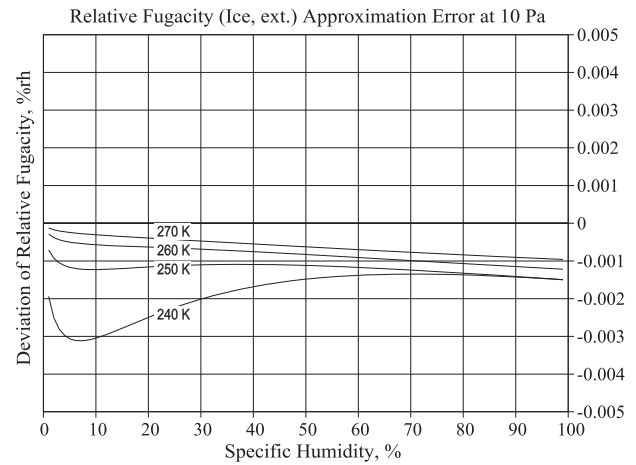


Figure 9. Case (G_S-S). Deviation of approximate RF, equation (47), from full RF, equation (46), in the extended pressure range at 10 Pa as a function of specific humidity $q = 1 - A$ expressed as a percentage, at several initial sample temperatures as indicated near the curves. The residual visible at $q = 100\%$ results from the ideal-gas approximation used for deriving the pre-factor $p/e^{lh}(T)$ in equation (47).

in cases of weak subsaturation is therefore, up to quadratic correction terms, the simple Clausius–Clapeyron-like formula

$$\psi_f \approx \frac{p}{e^{lh}(T)} \exp \left\{ \frac{L_S(p)}{R_W} \left(\frac{1}{T_{sp}} - \frac{1}{T_{fp}} \right) \right\}. \quad (47)$$

Here, $T_{sp}(p)$ is the sublimation temperature of ice with respect to pure water vapour, at which the isobaric cooling process enters the standard pressure range, and $L_S(p)$ is the sublimation enthalpy of ice Ih with respect to pure water vapour at this point. The residual of the approximation equation (47) in comparison to the full numerical expression (46) is displayed in figure 9 for some typical cases, remaining well below 0.01%rh.

3. Summary

For a variety of mutually inconsistent versions of RH currently in practical use, as a thermodynamically well-founded, unambiguous reference quantity, RF has been suggested [15]: equation (10.10) [10], and rigorously defined mathematically [12] in the context of TEOS-10. In this paper, equations are provided for the calculation of RF from measurands well-established in RH metrology and meteorology.

In table 1, equations for the computation of RF from measured dew-point and frost-point temperatures are summarised as derived in this paper. The rigorous thermodynamic expressions are given as differences of chemical potentials which are numerically available from TEOS-10 equations as provided in the open source code SIA library by function calls explained in appendix E. If TEOS-10 equations are unavailable, alternative estimates are given in table 1 as approximations in the limit of weak subsaturation, possibly being evaluated by means of other empirical equations required only for latent heats and vapour pressures.

Table 1. Summary of equations for the calculation of RF, $\psi_f(A, T, p)$, from dew-point and frost-point temperatures. Formula symbols are summarised in appendix G.

Case	$\ln \psi_f(A, T, p) =$	Equation	Range
(L–L)	$\frac{\mu_V^{AV}(A^{sat}(T_{dp}, p), T, p) - \mu_V^{AV}(A^{sat}(T, p), T, p)}{R_W T}$	(10)	Standard pressure range $p \geq e(T)$
	$\approx \left(\frac{1}{T} - \frac{1}{T_{dp}}\right) \frac{L_L(T_{dp}, p)}{R_W}$	(14)	
(S–S)	$\frac{\mu_V^{AV}(A^{sat}(T_{fp}, p), T, p) - \mu_V^{AV}(A^{sat}(T, p), T, p)}{R_W T}$	(16)	
	$\approx \left(\frac{1}{T} - \frac{1}{T_{fp}}\right) \frac{L_S(T_{fp}, p)}{R_W}$	(17)	
(L–S)	$\frac{\mu_V^{AV}(A^{sat}(T_{fp}, p), T, p) - \mu_V^{AV}(A^{sat}(T, p), T, p)}{R_W T}$	(22)	
	$\approx \left(\frac{1}{T} - \frac{1}{T_{mp}}\right) \frac{L_L(T_{mp}, p)}{R_W} + \left(\frac{1}{T_{mp}} - \frac{1}{T_{fp}}\right) \frac{L_S(T_{mp}, p)}{R_W}$	(26)	
(G _L –L)	$\frac{\mu_V^{AV}(A^{sat}(T_{dp}, p), T, p) - g^V(T, e^W(T))}{R_W T}$	(31)	Extended pressure range $p < e(T)$
	$\approx \left(\frac{1}{T_{sp}} - \frac{1}{T_{dp}}\right) \frac{L_L(p)}{R_W} + \ln \frac{p}{e^W(T)}$	(32)	
(G _L –L–S)	$\frac{\mu_V^{AV}(A^{sat}(T_{fp}, p), T, p) - g^V(T, e^W(T))}{R_W T}$	(36)	
	$\approx \left(\frac{1}{T_{sp}} - \frac{1}{T_{mp}}\right) \frac{L_L(T_{mp}, p)}{R_W} + \left(\frac{1}{T_{mp}} - \frac{1}{T_{fp}}\right) \frac{L_S(T_{mp}, p)}{R_W} + \ln \frac{p}{e^W(T)}$	(37)	
(G _L –S)	$\frac{\mu_V^{AV}(A^{sat}(T_{fp}, p), T, p) - g^V(T, e^W(T))}{R_W T}$	(41)	
	$\approx \left(\frac{1}{T_{sp}} - \frac{1}{T_{fp}}\right) \frac{L_S(p)}{R_W} + \ln \frac{p}{e^W(T)}$	(42)	
(G _S –S)	$\frac{\mu_V^{AV}(A^{sat}(T_{fp}, p), T, p) - g^V(T, e^{lh}(T))}{R_W T}$	(46)	
	$\approx \left(\frac{1}{T_{sp}} - \frac{1}{T_{fp}}\right) \frac{L_S(p)}{R_W} + \ln \frac{p}{e^{lh}(T)}$	(47)	

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Author contributions

RF: manuscript idea and concept, elaboration of the thermodynamic theory, execution of the calculations, manuscript draft; OH, JLS: verification of the theory, recalculation of all figures, manuscript discussion and revision.

Appendix A. Brief definition of relative fugacity/relative activity

For convenience, in this appendix the definition of RF and, equivalently, relative activity of water in humid air, as provided in detail in the part 1 companion paper [12], is repeated in a brief, compact form.

Above the freezing point, at pressures p exceeding the vapour pressure of liquid water, e^W , or, at a temperature T

below the freezing point, with p exceeding the sublimation pressure of ambient hexagonal ice Ih, e^{lh} , the RF is defined by

$$\psi_f = \frac{f_V(x, T, p)}{f_V(x^{sat}, T, p)}. \quad (A.1)$$

Here, x is the water-vapour mole fraction, and x^{sat} is its value at saturation, either with respect to liquid water or to ice. At lower pressures, in the so-called ‘extended range’, $p < e$, where stable condensed states are thermodynamically impossible, RF is defined relative to pure water vapour at saturation pressure, e ,

$$\psi_f = \frac{f_V(x, T, p)}{f_V(1, T, e)}. \quad (A.2)$$

Here, $e = e^{lh}$ below the triple-point temperature and $e = e^W$ otherwise. The regions of the four separate RF definitions, ψ_f^{lh} , ψ_f^{AW} , $\psi_f^{V, lh}$, $\psi_f^{V, W}$, are specified in figure 10 and in table 2.

RF is defined at temperatures below the critical temperature, $T < T_c = 647.096$ K, and pressures below the critical pressure, $p < p_c = 22.064$ MPa, of water. It is understood that these definitions apply only to gaseous humid air; liquid air may form below $T_{liq} = 132.6$ K [32]. In TEOS-10, the dissolution of air in liquid water is neglected; this will also apply here. Rather than the mole fraction x of water vapour, TEOS-10 uses

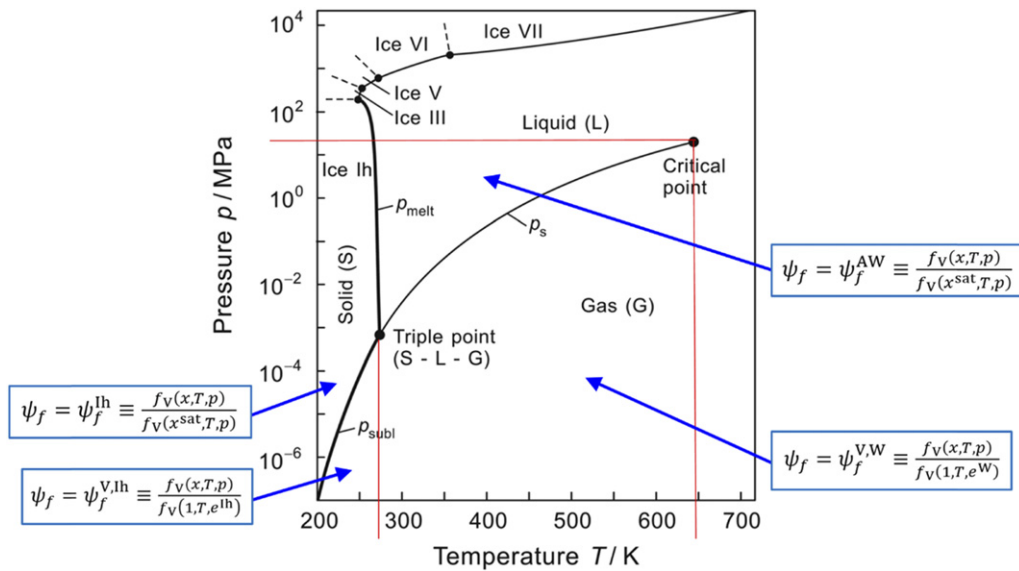


Figure 10. Regions of definition of RF in the temperature-pressure diagram of water from [18]. The curves indicate phase transitions between stable gaseous (G), liquid (L) and solid (S) states of air-free water; p_{melt} indicates the melting line of ambient hexagonal ice Ih, p_{subl} its sublimation line (sublimation pressure denoted by e^{lh} in this article), and p_s the saturation line (saturation pressure denoted by e^{W} in this article), or boiling line. In terms of water-vapour fugacity, f_v , the RF, ψ_f , is defined differently in four regions of the phase space, as indicated by the arrows, see equations (A.4) and (A.5). Reproduced from [18]. © 2018 BIPM & IOP Publishing Ltd. All rights reserved.

Table 2. RF of humid air, ψ_f , has been defined in four separate but continuous and mutually consistent ways [12], depending on temperature, T , and pressure, p , as displayed in figure 10. Here, f_v and x , respectively, are the fugacity and the mole fraction of water vapour in humid air, x^{sat} is the mole fraction at saturation, and e is the sublimation pressure of ice Ih, $e = e^{\text{lh}}$ (T), or the saturation vapour pressure of pure liquid water, $e = e^{\text{W}}$ (T).

RF with respect to	Ice Ih	Liquid water
Normal range $p \geq e$ (T)	$\psi_f^{\text{lh}} = \frac{f_v(x, T, p)}{f_v(x^{\text{sat}}, T, p)}$	$\psi_f^{\text{AW}} = \frac{f_v(x, T, p)}{f_v(x^{\text{sat}}, T, p)}$
Extended range $p \leq e$ (T)	$\psi_f^{\text{v, lh}} = \frac{f_v(x, T, p)}{f_v(1, T, e^{\text{lh}})}$	$\psi_f^{\text{v, W}} = \frac{f_v(x, T, p)}{f_v(1, T, e^{\text{W}})}$

the mass fraction A of dry air, equation (1),

$$A = \left\{ 1 + \frac{xM_{\text{W}}}{(1-x)M_{\text{A}}} \right\}^{-1} \quad (\text{A.3})$$

In TEOS-10, the molar masses of water and dry air, respectively, take the values of $M_{\text{W}} = 0.018015268 \text{ kg mol}^{-1}$ and $M_{\text{A}} = 0.02896546 \text{ kg mol}^{-1}$.

Fugacity is defined relative to the ideal-gas state of the given substance, in our case, of water. However, ideal-gas formulas are theoretical expressions which are not explicitly provided by routines of the TEOS-10 code. Therefore, it is more convenient to implement the activity definition of RF as specified in equations (49) and (50) of the part 1 companion paper, in terms of the chemical potential, $\mu_{\text{V}}^{\text{AV}}$, of water vapour in humid air:

$$R_{\text{W}}T \ln \psi_f = \mu_{\text{V}}^{\text{AV}}(A, T, p) - \mu_0(T, p) \quad (\text{A.4})$$

Here, $R_{\text{W}} = 461.51805 \text{ J kg}^{-1} \text{ K}^{-1}$ is the specific gas constant of water as specified in TEOS-10. The reference function $\mu_0(T, p)$ of the chemical potential is defined separately in each

of the four different regions of figure 10:

$$\mu_0(T, p) = \begin{cases} g^{\text{W}}(T, p) & \text{in region (L) at } p < p_c \\ g^{\text{lh}}(T, p) & \text{in region (S) at } p < p_c \\ g^{\text{V}}(T, e^{\text{lh}}(T)) & \text{in region (G}_S) \text{ at } T_{\text{liq}} < T \leq T_t \\ g^{\text{V}}(T, e^{\text{W}}(T)) & \text{in region (G}_L) \text{ at } T_t < T < T_c \\ \text{undefined otherwise} \end{cases} \quad (\text{A.5})$$

Here, (S), (L) and (G), respectively, indicate the stable solid, liquid and gas phases of pure liquid water (see figure 10). At the triple-point temperature, $T_t = 273.16 \text{ K}$, the gas region (G) is divided in two parts in which RF is separately defined with respect to either the solid (G_S) or the liquid (G_L) condensed phase. The specific Gibbs energies of liquid water, ice Ih and water vapour are g^{W} , g^{lh} and g^{V} , respectively. Compared to the original definition [12], equation (A.4) is simplified due to neglecting the dissolution of air in the liquid phase. Note that for RF evaluated from equations (A.4) and (A.5), the determination of saturation states is not required, in contrast to what equation (A.1) and table 2 may virtually be suggesting.

When a measurement of the dew- or frost point is carried out, a sample of humid air at given temperature T and pressure p is cooled down isobarically to the respective condensation point, T_{cp} and p . Here, ‘condensation point’ (cp) may suitably refer to either the dew point (dp) or the frost point (fp). From figure 10, the initial state (T, p) may be located anywhere below the critical ITS-90 temperature, $T_c = 647.096 \text{ K}$, and the critical pressure, $p_c = 22.064 \text{ MPa}$. The target state (T_{cp}, p) needs to be at conditions where a condensed state may emerge; that is, in either the region (L) or the region (S) of figure 10. Because of the different definitions of RF in the different regions of the phase space, in section 2 the normal range

Table 3. Coefficients a_i and exponents b_i of the saturation-pressure equation, equation (A.6).

i	a_i	b_i
1	$-0.785\,951\,783 \times 10^1$	1
2	$0.184\,408\,259 \times 10^1$	1.5
3	$-0.117\,866\,497 \times 10^2$	3
4	$0.226\,807\,411 \times 10^2$	3.5
5	$-0.159\,618\,719 \times 10^2$	4
6	$0.180\,122\,502 \times 10^1$	7.5

Table 4. Coefficients a_i and exponents b_i of the sublimation-pressure equation, equation (A.7).

i	a_i	b_i
1	$-0.212\,144\,006 \times 10^2$	$0.333\,333\,333 \times 10^{-2}$
2	$0.273\,203\,819 \times 10^2$	$0.120\,666\,667 \times 10^1$
3	$-0.610\,598\,130 \times 10^1$	$0.170\,333\,333 \times 10^1$

with (T, p) in either (L) or (S) will be considered separately from the extended range with (T, p) in (G). For simplicity, the dissolution of air in liquid water is neglected there and treated as a small subsequent correction in appendix D.

In order to practically decide to which region of (A.5) a measured point (T, p) belongs, convenient equations, consistent with TEOS-10, are available for $e^W(T)$, $e^{lh}(T)$ and for the melting pressure $p_{\text{melt}}(T)$ of the pure-water phases [28, 33–35]. In the environment of the TEOS-10 SIA library, this decision can be made by simply calling the routine `aux_water_phase(T, p)` given in appendix F.

The IAPWS equation of the saturation pressure is [33]

$$e^W(T) = p_c \exp \left\{ \frac{T_c}{T} \sum_{i=1}^6 a_i \left(1 - \frac{T}{T_c} \right)^{b_i} \right\}, \quad (\text{A.6})$$

with $T_c = 647.096$ K and $p_c = 22.064$ MPa. The other coefficients are given in table 3.

The IAPWS equation of the sublimation pressure is [28]

$$e^{lh}(T) = p_t \exp \left\{ \sum_{i=1}^3 a_i \left(\frac{T}{T_t} \right)^{b_i-1} \right\}, \quad (\text{A.7})$$

with $T_t = 273.16$ K and $p_t = 611.657$ Pa. The other coefficients are given in table 4.

The IAPWS equation of the melting pressure is [28]

$$p_{\text{melt}}(T) = p_t \left\{ 1 + \sum_{i=1}^3 a_i \left[1 - \left(\frac{T}{T_t} \right)^{b_i} \right] \right\} \quad (\text{A.8})$$

with $T_t = 273.16$ K and $p_t = 611.657$ Pa. The other coefficients are given in table 5.

Table 5. Coefficients a_i and exponents b_i of the melting-pressure equation, equation (A.8).

i	a_i	b_i
1	$0.119\,539\,337 \times 10^7$	$0.300\,000 \times 10^1$
2	$0.808\,183\,159 \times 10^5$	$0.257\,500 \times 10^2$
3	$0.333\,826\,860 \times 10^4$	$0.103\,750 \times 10^3$

Appendix B. Derivation of approximation equations for RF at weak subsaturation

B.1. Case (L–L): standard range with respect to water, dew-point condensation

As an alternative to the numerical implementation of the thermodynamically rigorous equation (10), this formula also permits a derivation of an approximate, simplified mathematical expression by power-series expansion about T ,

$$R_W T \ln \psi_f = \mu_V^{\text{AV}}(A^{\text{sat}}(T - \delta T, p), T, p) - \mu_V^{\text{AV}}(A^{\text{sat}}(T, p), T, p), \quad (\text{B.1})$$

for the case that the subsaturation, $\delta T \equiv T - T_{\text{dp}} \geq 0$, of the given sample of humid air is only weak, i.e.,

$$\begin{aligned} \delta A &= A^{\text{sat}}(T - \delta T, p) - A^{\text{sat}}(T, p) \\ &= - \left(\frac{\partial A^{\text{sat}}}{\partial T} \right)_p \delta T + O \left(\left| \frac{\delta T}{T} \right|^2 \right) \ll 1. \end{aligned} \quad (\text{B.2})$$

Expanding equation (12) up to linear terms with respect to a small chilling depression δT reads

$$R_W T \ln \psi_f = - \left(\frac{\partial \mu_V^{\text{AV}}}{\partial A} \right)_{T,p} \left(\frac{\partial A^{\text{sat}}}{\partial T} \right)_p \delta T + O \left(\left| \frac{\delta T}{T} \right|^2 \right). \quad (\text{B.3})$$

In terms of the specific Gibbs energy of humid air, g^{AV} , the derivative of the chemical potential of water vapour in humid air, equation (11), is

$$\left(\frac{\partial \mu_V^{\text{AV}}}{\partial A} \right)_{T,p} = -A \left(\frac{\partial^2 g^{\text{AV}}}{\partial A^2} \right)_{T,p}. \quad (\text{B.4})$$

At the saturation conditions of $A = A^{\text{sat}}(T, p)$, the specific evaporation enthalpy, $L_L(T_{\text{dp}}, p)$, of liquid water at the dew point, $T = T_{\text{dp}}$, into humid air can be expressed by the thermodynamic relation

$$\frac{L_L(T, p)}{T} = -A^{\text{sat}}(T, p) \left(\frac{\partial^2 g^{\text{AV}}}{\partial A^2} \right)_{T,p} \left(\frac{\partial A^{\text{sat}}}{\partial T} \right)_p \quad (\text{B.5})$$

(see equation (C.6) of appendix C, and [15]). Combining equations (B.3)–(B.5), at weak subsaturation a suitable

approximation formula for RF in the region (L) in terms of the dew-point temperature is obtained as

$$R_W T \ln \psi_f \approx -L_L(T, p) \frac{\delta T}{T} \approx L_L(T, p) \left(1 - \frac{T}{T_{dp}}\right) \approx L_L(T_{dp}, p) \left(1 - \frac{T}{T_{dp}}\right). \quad (\text{B.6})$$

All these expressions, by virtue of equation (13), are equivalent estimates as they deviate from one another only by terms $O(\delta T^2)$. Here, the third option of equation (B.6),

$$\psi_f \approx \exp \left\{ \frac{L_L(T_{dp}, p)}{R_W} \left(\frac{1}{T} - \frac{1}{T_{dp}} \right) \right\}, \quad (\text{B.7})$$

is preferred for its similarity to the common Clausius–Clapeyron formula for the saturation pressure of pure water vapour in the ideal-gas approximation. In contrast to that, equation (B.7) for RF holds for weakly subsaturated real gases regardless of ideal-gas assumptions.

B.2. Case (S–S): standard range with respect to ice, frost-point condensation

The calculation steps of appendix B.1 apply similarly to the case (S–S) if the properties of liquid water are replaced by those of ice Ih, and accordingly, dew point by frost point, and saturation by sublimation.

At the saturation conditions of $A = A^{\text{sat}}(T, p)$ with respect to ice Ih, the specific sublimation enthalpy, L_S , in humid air can be expressed by the thermodynamic identity

$$\frac{L_S(T, p)}{T} = -A^{\text{sat}}(T, p) \left(\frac{\partial^2 g^{\text{AV}}}{\partial A^2} \right)_{T, p} \left(\frac{\partial A^{\text{sat}}}{\partial T} \right)_p. \quad (\text{B.8})$$

(see equation (C.6) of appendix C, and [15]). Here, $L_S(T_{fp}, p)$ is the specific sublimation enthalpy from ice Ih to humid air at the frost point. At weak subsaturation, an appropriate approximation formula for RF in the region (S) in terms of the frost-point temperature is

$$R_W T \ln \psi_f \approx -L_S(T, p) \frac{\delta T}{T} \approx L_S(T, p) \left(1 - \frac{T}{T_{fp}}\right) \approx L_S(T_{fp}, p) \left(1 - \frac{T}{T_{fp}}\right). \quad (\text{B.9})$$

All these expressions are mutually equivalent estimates, by virtue of equation (13), as they deviate from one another only by terms $O(\delta T^2)$. Here, the last option of equation (B.9),

$$\psi_f \approx \exp \left\{ \frac{L_S(T_{fp}, p)}{R_W} \left(\frac{1}{T} - \frac{1}{T_{fp}} \right) \right\}, \quad (\text{B.10})$$

is favourable for its similarity to the familiar Clausius–Clapeyron approximation for the sublimation pressure of pure water vapour in the ideal-gas approximation. By contrast, equation (B.10) for RF holds for weakly subsaturated real gases without ideal-gas assumptions.

B.3. Case (L–S): standard range with respect to water, frost-point condensation

For an approximation formula of equation (22) valid at weak subsaturation, the series expansion with respect to the temperature lowering, $\delta T \equiv T - T_{fp}$, needs to be split at the melting point in two intervals,

$$R_W T \ln \psi_f = \Delta \mu_{fp} + \Delta \mu_{mp}. \quad (\text{B.11})$$

The two contributions are

$$\Delta \mu_{fp} \equiv \mu_V^{\text{AV}}(A^{\text{sat}}(T_{fp}, p), T, p) - \mu_V^{\text{AV}}(A^{\text{sat}}(T_{mp}, p), T, p) \quad (\text{B.12})$$

and

$$\Delta \mu_{mp} \equiv \mu_V^{\text{AV}}(A^{\text{sat}}(T_{mp}, p), T, p) - \mu_V^{\text{AV}}(A^{\text{sat}}(T, p), T, p), \quad (\text{B.13})$$

specified by $T = T_{mp} + \delta T_L$ and $T_{fp} = T_{mp} - \delta T_S$, corresponding to the two partial lengths of the arrow of isobaric cooling within the phase regions (L) and (S), respectively:

$$\Delta \mu_{fp} = \mu_V^{\text{AV}}(A^{\text{sat}}(T_{mp} - \delta T_S, p), T, p) - \mu_V^{\text{AV}}(A^{\text{sat}}(T_{mp}, p), T, p), \quad (\text{B.14})$$

$$\Delta \mu_{mp} = \mu_V^{\text{AV}}(A^{\text{sat}}(T_{mp}, p), T, p) - \mu_V^{\text{AV}}(A^{\text{sat}}(T_{mp} + \delta T_L, p), T, p). \quad (\text{B.15})$$

Expanding A^{sat} with respect to those temperature differences gives

$$\Delta \mu_{fp} \approx \mu_V^{\text{AV}}(A^{\text{sat}}(T_{mp}, p) - \delta A_S, T, p) - \mu_V^{\text{AV}}(A^{\text{sat}}(T_{mp}, p), T, p), \quad (\text{B.16})$$

$$\Delta \mu_{mp} \approx \mu_V^{\text{AV}}(A^{\text{sat}}(T_{mp}, p), T, p) - \mu_V^{\text{AV}}(A^{\text{sat}}(T_{mp}, p) + \delta A_L, T, p), \quad (\text{B.17})$$

where

$$\delta A_S = \lim_{\varepsilon \rightarrow 0} \left(\frac{\partial A^{\text{sat}}(T_{mp} - \varepsilon, p)}{\partial T} \right)_p \quad (\text{B.18})$$

$$\delta T_S = - \frac{L_S(T_{mp}, p) \delta T_S}{T_{mp} A^{\text{sat}}(T_{mp}, p) \left(\frac{\partial^2 g^{\text{AV}}}{\partial A^2} \right)_{T, p}}$$

and

$$\delta A_L = \lim_{\varepsilon \rightarrow 0} \left(\frac{\partial A^{\text{sat}}(T_{mp} + \varepsilon, p)}{\partial T} \right)_p \quad (\text{B.19})$$

$$\delta T_L = - \frac{L_L(T_{mp}, p) \delta T_L}{T_{mp} A^{\text{sat}}(T_{mp}, p) \left(\frac{\partial^2 g^{\text{AV}}}{\partial A^2} \right)_{T, p}}$$

Expanding in turn equation (B.10) with respect to δA_S and δA_L results in

$$R_W T \ln \psi_f = - \left(\frac{\partial \mu_V^{\text{AV}}(A^{\text{sat}}(T_{mp}, p), T, p)}{\partial A} \right)_{T, p} (\delta A_S + \delta A_L). \quad (\text{B.20})$$

Up to terms $O(\delta T^2)$, this may be rewritten as

$$R_W \ln \psi_f \approx - \left(\frac{\partial \mu_V^{\text{AV}} (A^{\text{sat}}(T_{\text{mp}}, p), T_{\text{mp}}, p)}{\partial A} \right)_{T,p} \times \left(\frac{\delta A_S}{T_{\text{fp}}} + \frac{\delta A_L}{T} \right). \quad (\text{B.21})$$

Next, exploiting equations (B.4), (B.18) and (B.19) yields

$$R_W \ln \psi_f = \frac{L_S(T_{\text{mp}}, p)}{T_{\text{mp}} T_{\text{fp}}} (T_{\text{fp}} - T_{\text{mp}}) - \frac{L_L(T_{\text{mp}}, p)}{T_{\text{mp}} T} (T - T_{\text{mp}}) + O\left(\left|\frac{\delta T}{T}\right|^2\right). \quad (\text{B.22})$$

The resulting final approximation formula for RF in the case (L–S) is

$$\psi_f = \exp \left\{ \frac{L_S(T_{\text{mp}}, p)}{R_W} \left(\frac{1}{T_{\text{mp}}} - \frac{1}{T_{\text{fp}}} \right) + \frac{L_L(T_{\text{mp}}, p)}{R_W} \left(\frac{1}{T} - \frac{1}{T_{\text{mp}}} \right) \right\} + O\left(\left|\frac{\delta T}{T}\right|^2\right). \quad (\text{B.23})$$

In the limit $T_{\text{fp}} \rightarrow T_{\text{mp}}$, equation (B.23) is consistent with equation (14) of case (L–L), and similarly with equation (17) of case (S–S) in the limit $T \rightarrow T_{\text{mp}}$. Exploiting equation (25), an alternative form of equation (B.23) is

$$\psi_f = \exp \left\{ \frac{L_S(T_{\text{mp}}, p)}{R_W} \left(\frac{1}{T} - \frac{1}{T_{\text{fp}}} \right) - \frac{L_M(p)}{R_W} \left(\frac{1}{T} - \frac{1}{T_{\text{mp}}} \right) \right\} + O\left(\left|\frac{\delta T}{T}\right|^2\right), \quad (\text{B.24})$$

where $L_M(p) = L_S(T_{\text{mp}}, p) - L_L(T_{\text{mp}}, p)$ is the specific melting enthalpy of ice Ih.

B.4. Case (G_L–L): extended range with respect to water, dew-point condensation

For weakly subsaturated humid air, the formula (31) may be approximated by a simpler expression. For this purpose, the entry point (T_{sp}, p) from the extended pressure range to the standard pressure range (subscript ‘sp’, see figure 3) can be introduced to formally split equation (30) in two different contributions:

$$R_W T \ln \psi_f = \Delta \mu_{\text{dp}} + \Delta \mu_{\text{sp}}. \quad (\text{B.25})$$

where the first term,

$$\Delta \mu_{\text{dp}} \equiv \mu_V^{\text{AV}}(A^{\text{sat}}(T_{\text{dp}}, p), T, p) - \mu_V^{\text{AV}}(A^{\text{sat}}(T_{\text{sp}}, p), T, p), \quad (\text{B.26})$$

describes the chilling within the standard pressure range from the entry point to the dew point, and the second term,

$$\Delta \mu_{\text{sp}} \equiv \mu_V^{\text{AV}}(A^{\text{sat}}(T_{\text{sp}}, p), T, p) - \mu_V^{\text{AV}}(0, T, e^W(T)), \quad (\text{B.27})$$

covers the cooling process across the extended pressure range. Note that the second term of equation (B.26) and the first term of equation (B.27) cancel one another in the sum (B.25); these identical terms are chosen quite arbitrarily in a way that renders $\Delta \mu_{\text{sp}}$ a function of pure-water properties alone, independent of the humidity of the chilled sample.

With respect to a small temperature lowering, $\delta T \equiv (T - T_{\text{dp}})$, the first difference may be linearised about the entry point,

$$\Delta \mu_{\text{dp}} \approx \left(\frac{\partial \mu_V^{\text{AV}}(A^{\text{sat}}(T_{\text{sp}}, p), T, p)}{\partial A} \right)_{T,p} \times \left(\frac{\partial A^{\text{sat}}(T_{\text{sp}}, p)}{\partial T} \right)_p (T_{\text{dp}} - T_{\text{sp}}). \quad (\text{B.28})$$

Up to terms $O(\delta T^2)$, this is the same as

$$\begin{aligned} \Delta \mu_{\text{dp}} &\approx \left(\frac{\partial \mu_V^{\text{AV}}(A^{\text{sat}}(T_{\text{sp}}, p), T_{\text{sp}}, p)}{\partial A} \right)_{T,p} \times \left(\frac{\partial A^{\text{sat}}(T_{\text{sp}}, p)}{\partial T} \right)_p (T_{\text{dp}} - T_{\text{sp}}) \\ &= \left(\frac{T_{\text{dp}}}{T_{\text{sp}}} - 1 \right) L_L(p) \end{aligned} \quad (\text{B.29})$$

Here, equations (B.4) and (B.5) have been applied, and $L_L(p)$ is the evaporation enthalpy of pure water vapour at the boiling point, $(T_{\text{sp}}(p), p)$. At this point, accordingly, the property

$$A^{\text{sat}}(T_{\text{sp}}, p) = 0 \quad (\text{B.30})$$

defines implicitly the boiling temperature $T_{\text{sp}}(p)$, so that the latent heat $L_L(p)$ depends on a single parameter only.

The second difference in equation (B.25) occurs only with respect to the pressure:

$$\begin{aligned} \Delta \mu_{\text{sp}} &= \mu_V^{\text{AV}}(0, T, p) - \mu_V^{\text{AV}}(0, T, e^W(T)) \\ &= g^V(T, p) - g^V(T, e^W(T)). \end{aligned} \quad (\text{B.31})$$

This difference is independent of the measured condensation point and of the sample’s humidity. It may be calculated from the vapour density equation

$$g^V(T, p) - g^V(T, e^W(T)) = \int_{e^W}^p \frac{1}{\rho^V(T, p')} dp'. \quad (\text{B.32})$$

At low pressure in the extended range, an ideal-gas approximation of the water-vapour density, ρ^V , may be assumed as a sufficiently accurate estimate for the pressure dependence, so that

$$\Delta \mu_{\text{sp}} \approx R_W T \ln \frac{p}{e^W(T)}. \quad (\text{B.33})$$

If required for higher accuracy, the density formula of (B.32) may still be improved using virial corrections available from TEOS-10 [16, 20, 36].

The linear approximation of equation (31) for the RF in the case of weak subsaturation is therefore the simple formula

$$\psi_f = \exp \left\{ \frac{\Delta\mu_{dp} + \Delta\mu_{sp}}{R_W T} \right\} \approx \frac{p}{e^W(T)} \exp \left\{ \frac{L_L(p)}{R_W T} \left(\frac{T_{dp}}{T_{sp}} - 1 \right) \right\}. \quad (\text{B.34})$$

To within the linear perturbation order, by virtue of equation (13), this may be converted into a Clausius–Clapeyron-like form,

$$\psi_f \approx \frac{p}{e^W(T)} \exp \left\{ \frac{L_L(p)}{R_W} \left(\frac{1}{T_{sp}} - \frac{1}{T_{dp}} \right) \right\}. \quad (\text{B.35})$$

B.5. Case (G_L – L – S): extended range with respect to water, frost-point condensation

For weakly subsaturated humid air, this formula may be approximated by a simpler expression which requires considering the details of the cooling path rather than just its endpoints at T and T_{fp} . In contrast to section 2.4, after entering the standard pressure range (see figure 3), the cooling process additionally passes the melting temperature T_{mp} before condensation occurs at the frost point, see figure 2. The difference (35) is formally split in three related parts:

$$R_W T \ln \psi_f = \Delta\mu_{fp} + \Delta\mu_{mp} + \Delta\mu_{sp}. \quad (\text{B.36})$$

Here,

$$\Delta\mu_{fp} \equiv \mu_V^{AV}(A^{\text{sat}}(T_{fp}, p), T, p) - \mu_V^{AV}(A^{\text{sat}}(T_{mp}, p), T, p) \quad (\text{B.37})$$

covers the process between frost point, T_{fp} , and melting point, T_{mp} , in the region (S),

$$\Delta\mu_{mp} \equiv \mu_V^{AV}(A^{\text{sat}}(T_{mp}, p), T, p) - \mu_V^{AV}(A^{\text{sat}}(T_{sp}, p), T, p) \quad (\text{B.38})$$

is the contribution to RF from crossing the liquid region (L), entering the standard-pressure range at T_{sp} , and finally,

$$\Delta\mu_{sp} \equiv \mu_V^{AV}(A^{\text{sat}}(T_{sp}, p), T, p) - \mu_V^{AV}(0, T, e^W(T)) \quad (\text{B.39})$$

describes the cooling process within the extended pressure range (G) up to the exit at T_{sp} . Note that the second term of (B.38) and the first term of (B.39) are specified arbitrarily in a useful manner and cancel mutually in the sum (B.36).

Only the part $\Delta\mu_{fp}$ depends on the measured frost point, the remaining two follow from (T, p) of the given sample and general thermodynamic properties. Linearisation of equation (B.37) about T_{mp} yields

$$\begin{aligned} \Delta\mu_{fp} &\approx \left(\frac{\partial \mu_V^{AV}(A^{\text{sat}}(T_{mp}, p), T, p)}{\partial A} \right)_{T,p} \\ &\times \left(\frac{\partial A^{\text{sat}}(T_{mp}, p)}{\partial T} \right)_p (T_{fp} - T_{mp}) \\ &\approx \left(\frac{T_{fp}}{T_{mp}} - 1 \right) L_S(T_{mp}, p). \end{aligned} \quad (\text{B.40})$$

Here, equations (B.4) and (B.5) have been applied, $L_S(T_{mp}, p)$ is the specific sublimation enthalpy at the melting temperature, and the chemical potential estimate applied,

$$\mu_V^{AV}(A^{\text{sat}}(T_{mp}, p), T, p) \approx \mu_V^{AV}(A^{\text{sat}}(T_{mp}, p), T_{mp}, p), \quad (\text{B.41})$$

neglects the deviation involved as a quadratic term in subsaturation. Similarly to (B.40),

$$\begin{aligned} \Delta\mu_{mp} &\approx \left(\frac{\partial \mu_V^{AV}(A^{\text{sat}}(T_{mp}, p), T, p)}{\partial A} \right)_{T,p} \\ &\times \left(\frac{\partial A^{\text{sat}}(T_{mp}, p)}{\partial T} \right)_p (T_{mp} - T_{sp}) \\ &\approx \left(1 - \frac{T_{sp}}{T_{mp}} \right) L_L(T_{mp}, p), \end{aligned} \quad (\text{B.42})$$

with $L_L(T_{mp}, p)$ being the specific evaporation enthalpy of humid air at the melting temperature $T_{mp}(p)$ of ice Ih. Third, as in equation (B.31), the difference between the Gibbs energies of pure water vapour

$$\begin{aligned} \Delta\mu_{sp} &= \mu_V^{AV}(0, T, p) - \mu_V^{AV}(0, T, e^W(T)) \\ &= g^V(T, p) - g^V(T, e^W(T)), \end{aligned} \quad (\text{B.43})$$

is expressed in ideal-gas approximation,

$$\Delta\mu_{sp} \approx R_W T \ln \frac{p}{e^W(T)}. \quad (\text{B.44})$$

If required for higher accuracy, the difference of g^V in equation (B.43) may still be improved using virial corrections available from TEOS-10 [16, 20, 36].

The sum (B.36) of the above three terms,

$$\begin{aligned} \psi_f &= \exp \left\{ \frac{\Delta\mu_{fp} + \Delta\mu_{mp} + \Delta\mu_{sp}}{R_W T} \right\} \\ &\approx \frac{p}{e^W(T)} \exp \left\{ \frac{L_S(T_{mp}, p)}{R_W T} \left(\frac{T_{fp}}{T_{mp}} - 1 \right) \right. \\ &\quad \left. + \frac{L_L(T_{mp}, p)}{R_W T} \left(1 - \frac{T_{sp}}{T_{mp}} \right) \right\}, \end{aligned} \quad (\text{B.45})$$

is the intended linear approximation formula for the RF at weak subsaturation. Up to quadratic terms in the temperature lowering, by virtue of equation (13),

$$\frac{1}{T} \left(\frac{T_{fp}}{T_{mp}} - 1 \right) = \frac{1}{T_{fp}} \left(\frac{T_{fp}}{T_{mp}} - 1 \right) + O(|T - T_{fp}|^2) \quad (\text{B.46})$$

and

$$\frac{1}{T} \left(1 - \frac{T_{sp}}{T_{mp}} \right) = \frac{1}{T_{sp}} \left(1 - \frac{T_{sp}}{T_{mp}} \right) + O(|T - T_{fp}|^2), \quad (\text{B.47})$$

the expression (B.45) may also be rewritten in simpler Clausius–Clapeyron form,

$$\begin{aligned} \psi_f \approx \frac{p}{e^w(T)} \exp \left\{ \frac{L_S(T_{mp}, p)}{R_W} \left(\frac{1}{T_{mp}} - \frac{1}{T_{fp}} \right) \right. \\ \left. + \frac{L_L(T_{mp}, p)}{R_W} \left(\frac{1}{T_{sp}} - \frac{1}{T_{mp}} \right) \right\}. \end{aligned} \quad (\text{B.48})$$

B.6. Case (G_L –S): extended range with respect to water, frost-point condensation

For weakly subsaturated humid air, formula (41) may be approximated by a simpler expression. For this purpose, the entry point (T_{sp}, p) to the standard pressure range, as shown in figure 3, can be introduced formally in equation (30):

$$R_W T \ln \psi_f = \Delta\mu_{fp} + \Delta\mu_{sp}, \quad (\text{B.49})$$

where the first term is

$$\Delta\mu_{fp} \equiv \mu_V^{AV}(A^{\text{sat}}(T_{fp}, p), T, p) - \mu_V^{AV}(A^{\text{sat}}(T_{sp}, p), T, p) \quad (\text{B.50})$$

and the second one is

$$\Delta\mu_{sp} \equiv \mu_V^{AV}(A^{\text{sat}}(T_{sp}, p), T, p) - \mu_V^{AV}(0, T, e^w(T)). \quad (\text{B.51})$$

Here, T_{sp} equals the sublimation temperature of ice at the pressure p . Note that the second term of (B.50) and the first term of (B.51) are specified arbitrarily in a useful manner and cancel mutually in the sum (B.49). With respect to a small temperature lowering, ($T_{fp} - T_{sp}$), the first difference may be linearised about that sublimation point,

$$\begin{aligned} \Delta\mu_{fp} &\approx \left(\frac{\partial \mu_V^{AV}(A^{\text{sat}}(T_{sp}, p), T, p)}{\partial A} \right)_{T,p} \\ &\quad \times \left(\frac{\partial A^{\text{sat}}(T_{sp}, p)}{\partial T} \right)_p (T_{fp} - T_{sp}) \\ &\approx \left(\frac{T_{fp}}{T_{sp}} - 1 \right) L_S(p). \end{aligned} \quad (\text{B.52})$$

Here, equations (B.4) and (B.5) have been applied, and $L_S(p)$ is the specific sublimation enthalpy of ice to pure water vapour at the point, (T_{sp}, p), at which, accordingly,

$$A^{\text{sat}}(T_{sp}, p) = 0. \quad (\text{B.53})$$

The second difference in equation (B.49) occurs only with respect to the pressure:

$$\begin{aligned} \Delta\mu_{sp} &= \mu_V^{AV}(0, T, p) - \mu_V^{AV}(0, T, e^w(T)) = g^v(T, p) \\ &\quad - g^v(T, e^w(T)). \end{aligned} \quad (\text{B.54})$$

This difference is independent of the measured condensation point and of the sample's humidity. It may be calculated from the vapour density equation

$$g^v(T, p) - g^v(T, e^w(T)) = \int_{e^w}^p \frac{1}{\rho^v(T, p')} dp'. \quad (\text{B.55})$$

At low pressure in the extended range, an ideal-gas approximation of the water-vapour density may be assumed as a sufficiently accurate estimate for the pressure dependence, so that

$$\Delta\mu_{sp} \approx R_W T \ln \frac{p}{e^w(T)}. \quad (\text{B.56})$$

If required for higher accuracy, the density formula of (B.55) may still be improved using virial corrections available from TEOS-10 [16, 20, 36].

The resulting linear approximation of equation (41) for the RF in case of weak subsaturation is, therefore, the simple formula

$$\begin{aligned} \psi_f &= \exp \left\{ \frac{\Delta\mu_{fp} + \Delta\mu_{sp}}{R_W T} \right\} \\ &\approx \frac{p}{e^w(T)} \exp \left\{ \frac{L_S(p)}{R_W T} \left(\frac{T_{fp}}{T_{sp}} - 1 \right) \right\}. \end{aligned} \quad (\text{B.57})$$

Up to quadratic terms in the perturbation series, by virtue of equation (13), this formula equals the simpler Clausius–Clapeyron expression

$$\psi_f \approx \frac{p}{e^w(T)} \exp \left\{ \frac{L_S(p)}{R_W} \left(\frac{1}{T_{sp}} - \frac{1}{T_{fp}} \right) \right\}. \quad (\text{B.58})$$

B.7. Case (G_S –S): extended range with respect to ice, frost-point condensation

For weakly subsaturated humid air, formula (46) may be approximated by a simpler expression. For this purpose, the standard-pressure entry point (T_{sp}, p), as shown in figure 3, can be introduced into equation (30):

$$R_W T \ln \psi_f = \Delta\mu_{fp} + \Delta\mu_{sp}. \quad (\text{B.59})$$

Here, the standard-pressure range contributes to RF by

$$\Delta\mu_{fp} \equiv \mu_V^{AV}(A^{\text{sat}}(T_{fp}, p), T, p) - \mu_V^{AV}(A^{\text{sat}}(T_{sp}, p), T, p) \quad (\text{B.60})$$

and the extended-pressure range by

$$\Delta\mu_{sp} \equiv \mu_V^{AV}(A^{\text{sat}}(T_{sp}, p), T, p) - \mu_V^{AV}(0, T, e^{\text{lh}}(T)). \quad (\text{B.61})$$

Here, T_{sp} equals the sublimation temperature of ice at the pressure p . The second term of (B.60) and the first term of (B.61) are specified arbitrarily and cancel mutually in the sum (B.59). With respect to a small temperature lowering,

$(T_{\text{fp}} - T_{\text{sp}})$, the first difference may be linearised about the saturation point,

$$\begin{aligned} \Delta\mu_{\text{fp}} &\approx \left(\frac{\partial\mu_{\text{V}}^{\text{AV}}(A^{\text{sat}}(T_{\text{sp}}, p), T, p)}{\partial A} \right)_{T,p} \\ &\quad \times \left(\frac{\partial A^{\text{sat}}(T_{\text{sp}}, p)}{\partial T} \right)_p (T_{\text{fp}} - T_{\text{sp}}) \\ &\approx \left(\frac{T_{\text{fp}}}{T_{\text{sp}}} - 1 \right) L_{\text{S}}(p). \end{aligned} \quad (\text{B.62})$$

Here, equations (B.4) and (B.5) have been applied, and $L_{\text{S}}(T_{\text{sp}}, p)$ is the specific sublimation enthalpy of ice at the point, (T_{sp}, p) , at which, accordingly,

$$A^{\text{sat}}(T_{\text{sp}}, p) = 0. \quad (\text{B.63})$$

The second difference in equation (B.49) is for pure water vapour and exists only with respect to the pressure:

$$\begin{aligned} \Delta\mu_{\text{sp}} &= \mu_{\text{V}}^{\text{AV}}(0, T, p) - \mu_{\text{V}}^{\text{AV}}(0, T, e^{\text{lh}}(T)) = g^{\text{V}}(T, p) \\ &\quad - g^{\text{V}}(T, e^{\text{lh}}(T)). \end{aligned} \quad (\text{B.64})$$

At low pressure, an ideal-gas approximation of the water-vapour density may be assumed as a sufficiently accurate estimate, so that

$$\Delta\mu_{\text{sp}} \approx R_{\text{W}}T \ln \frac{p}{e^{\text{lh}}(T)}. \quad (\text{B.65})$$

If required for higher accuracy, the difference of g^{V} in equation (B.64) may still be improved using virial corrections available from TEOS-10 [16, 20, 36].

The linear approximation of equation (41) for the RF in case of weak subsaturation is therefore the simple formula

$$\begin{aligned} \psi_{\text{f}} &= \exp \left\{ \frac{\Delta\mu_{\text{fp}} + \Delta\mu_{\text{sp}}}{R_{\text{W}}T} \right\} \\ &\approx \frac{p}{e^{\text{lh}}(T)} \exp \left\{ \frac{L_{\text{S}}(p)}{R_{\text{W}}T} \left(\frac{T_{\text{fp}}}{T_{\text{sp}}} - 1 \right) \right\}. \end{aligned} \quad (\text{B.66})$$

Up to quadratic correction terms, by virtue of equation (13), this is equivalent to the Clausius–Clapeyron form

$$\psi_{\text{f}} \approx \frac{p}{e^{\text{lh}}(T)} \exp \left\{ \frac{L_{\text{S}}(p)}{R_{\text{W}}} \left(\frac{1}{T_{\text{sp}}} - \frac{1}{T_{\text{fp}}} \right) \right\}. \quad (\text{B.67})$$

Appendix C. Thermodynamic relations of humid-air equilibria with liquid water or ice Ih

In this appendix, selected thermodynamic relations are briefly summarised from [15], and are valid for ‘wet air’ and ‘ice air’, that is, for two-phase composites at equilibrium between humid air and either liquid water or ice Ih, respectively.

The equilibrium between humid air and liquid water requires equality of the chemical potentials of water in humid air, equation (11) (see also [29]: equation (5.10.6) therein),

$$\mu_{\text{V}}^{\text{AV}} \equiv g^{\text{AV}} - A \left(\frac{\partial g^{\text{AV}}}{\partial A} \right)_{T,p}, \quad (\text{C.1})$$

with that of water, $\mu^{\text{W}} \equiv g^{\text{W}}$, i.e.,

$$\Delta\mu \equiv g^{\text{AV}}(A^{\text{sat}}, T, p) - A^{\text{sat}} \left(\frac{\partial g^{\text{AV}}}{\partial A} \right)_{T,p} - g^{\text{W}}(T, p) = 0. \quad (\text{C.2})$$

If the temperature is changing at constant pressure, maintaining the equilibrium implies that $\Delta\mu$ remains zero by appropriately adjusting A^{sat}

$$\begin{aligned} \left(\frac{\partial}{\partial T} \right)_p \Delta\mu = 0 &= \left(\frac{\partial g^{\text{AV}}}{\partial T} \right)_{A,p} \\ &\quad - A^{\text{sat}} \left(\frac{\partial^2 g^{\text{AV}}}{\partial A^2} \right)_{T,p} \left(\frac{\partial A^{\text{sat}}}{\partial T} \right)_p \\ &\quad - A^{\text{sat}} \left(\frac{\partial^2 g^{\text{AV}}}{\partial A \partial T} \right)_{T,p} - \left(\frac{\partial g^{\text{W}}}{\partial T} \right)_p \end{aligned} \quad (\text{C.3})$$

Introducing entropy $s = -(\partial g / \partial T)_p$ for each phase, s^{AV} and s^{W} , leads to

$$s^{\text{AV}} - A^{\text{sat}} \left(\frac{\partial s^{\text{AV}}}{\partial A} \right)_{A,p} - s^{\text{W}} = -A^{\text{sat}} \left(\frac{\partial^2 g^{\text{AV}}}{\partial A^2} \right)_{T,p} \left(\frac{\partial A^{\text{sat}}}{\partial T} \right)_p. \quad (\text{C.4})$$

Up to a factor of T , the left-hand side of this equation is just the isobaric evaporation enthalpy (see equation (C.13)),

$$L_{\text{L}} \equiv T \left[s^{\text{AV}} - A^{\text{sat}} \left(\frac{\partial s^{\text{AV}}}{\partial A} \right)_{A,p} - s^{\text{W}} \right], \quad (\text{C.5})$$

of liquid water in contact with humid air, so that there exists the thermodynamically rigorous relation

$$\frac{L_{\text{L}}}{T} = -A^{\text{sat}} \left(\frac{\partial^2 g^{\text{AV}}}{\partial A^2} \right)_{T,p} \left(\frac{\partial A^{\text{sat}}}{\partial T} \right)_p. \quad (\text{C.6})$$

After replacing the Gibbs function of liquid water, g^{W} , by that of ice Ih, g^{lh} , a similar calculation may be repeated and will result in a similar expression for the isobaric sublimation enthalpy, L_{S} , of ice in contact with humid air

$$\frac{L_{\text{S}}}{T} = -A^{\text{sat}} \left(\frac{\partial^2 g^{\text{AV}}}{\partial A^2} \right)_{T,p} \left(\frac{\partial A^{\text{sat}}}{\partial T} \right)_p. \quad (\text{C.7})$$

At the melting temperature of ice, i.e., along the ‘triple line’ in figure 1, L_{S} and L_{L} differ by the melting enthalpy of ice Ih, L_{M} ; therefore the derivative $(\partial A^{\text{sat}} / \partial T)_p$ of humid air is discontinuous at this temperature. Geometrically, in figure 1, this means that the slopes of the sublimation and saturation surfaces differ across their mutual intersection curve.

For completeness, we briefly report here also the thermodynamic expressions for the latent heats of phase transitions, as derived in more detail by [14, 15].

Let an equilibrium two-phase composite contain the masses m^{W} , m^{V} and m^{A} , respectively, of liquid water, water vapour and dry air. By definition, the equilibrium fraction of dry air in humid air is

$$A^{\text{sat}} = \frac{m^{\text{A}}}{m^{\text{A}} + m^{\text{V}}}. \quad (\text{C.8})$$

Table 6. Procedures of the TEOS-10 SIA Library to be used for evaluating reference values that appear in the approximation formulas for RF at weak subsaturation.

Quantity	Evaluated from SIA procedure	Appearing in equations
T_{dp}	<code>liq_air_dewpoint_si(a, p)</code>	(14) and (32)
T_{fp}	<code>ice_air_frostpoint_si(a, p)</code>	(17), (26), (27), (37), (42) and (47)
T_{mp}	<code>ice_liq_meltingtemperature_si(p)</code>	(26), (27) and (37)
T_{sp}	<code>liq_vap_boilingtemperature_si(p)</code>	(32) and (37)
T_{sp}	<code>ice_vap_sublimationtemp_si(p)</code>	(42) and (47)
$L_L(p)$	<code>liq_vap_enthalpy_evap_si</code> () after having executed <code>set_liq_vap_eq_at_p(p)</code>	(32)
$L_L(T, p)$	<code>liq_air_enthalpy_evap_si</code> () after having executed <code>set_liq_air_eq_at_t_p(t, p)</code>	(14) and (26) and (37)
$L_S(p)$	<code>ice_vap_enthalpy_subl_si</code> () after having executed <code>set_ice_vap_eq_at_p(p)</code>	(42) and (47)
$L_S(T, p)$	<code>ice_air_enthalpy_subl_si</code> () after having executed <code>set_ice_air_eq_at_t_p(t, p)</code>	(17) and (26) and (27), (37)
$L_M(p)$	<code>ice_liq_enthalpy_melt_si</code> after having executed <code>set_ice_liq_eq_at_p(p)</code>	(27)
$e^W(T)$	<code>liq_vap_vapourpressure_si(t)</code>	(32) and (37) and (42)
$e^{th}(T)$	<code>ice_vap_sublimationpressure_si(t)</code>	(47)

The sample's total enthalpy is the mass-weighted sum,

$$H^{W+AV}(T, p) = m^W h^W + (m^A + m^V) h^{AV}, \quad (C.9)$$

of the specific enthalpies of liquid water and humid air, h^W and h^{AV} , respectively. At constant masses of dry air, $m^A = \text{const.}$, and of total water, $m^{H_2O} \equiv m^W + m^V = \text{const.}$, the change of this enthalpy with temperature defines the specific isobaric evaporation enthalpy, L_L , as the coefficient of the water-mass evaporation rate, $\partial m^V / \partial T = -\partial m^W / \partial T$, of an associated excess term expected to additionally appear in the mass-weighted sum,

$$\left(\frac{\partial H^{W+AV}}{\partial T} \right)_{p, m^A, m^{H_2O}} = m^W c_p^W + (m^A + m^V) c_p^{AV} + \frac{\partial m^V}{\partial T} L_L, \quad (C.10)$$

of the specific isobaric heat capacities $c_p^W = (\partial h^W / \partial T)_p$ and $c_p^{AV} = (\partial h^{AV} / \partial T)_{A, p}$ of liquid water and humid air, respectively. Equation (C.10) describes the warming up of a system consisting of liquid water and humid air at equilibrium. Some heat is required to warm up the water phase (first term), some to warm up the moist air (second term), and finally some

heat is absorbed for the transfer process of water from the liquid to the gas phase (last term), known as ‘latent heat’ [15]: equation (7.16) therein. Taking the temperature derivative of equation (C.9) at constant masses of dry air and of total water, leads to an equation of the form (C.10), namely to

$$\begin{aligned} \left(\frac{\partial H^{W+AV}}{\partial T} \right)_{p, m^A, m^{H_2O}} &= m^W \left(\frac{\partial h^W}{\partial T} \right)_p + \frac{\partial m^W}{\partial T} h^W \\ &+ (m^A + m^V) \left[\left(\frac{\partial h^{AV}}{\partial T} \right)_{A,p} \right. \\ &\left. + \left(\frac{\partial h^{AV}}{\partial A} \right)_{T,p} \left(\frac{\partial A^{sat}}{\partial T} \right)_p \right] + \frac{\partial m^V}{\partial T} h^{AV}. \end{aligned} \quad (C.11)$$

Exploiting the derivative of (C.8),

$$\left(\frac{\partial A^{sat}}{\partial T} \right)_{p, m^A} = - \frac{m^A}{(m^A + m^V)^2} \frac{\partial m^V}{\partial T} = \frac{A^{sat}}{(m^A + m^V)} \frac{\partial m^W}{\partial T}, \quad (C.12)$$

and comparing (C.10) with (C.11), the final result for the latent heat of evaporation is ([15]: equation (7.22) therein)

$$L_L = h^{AV} - A^{sat} \left(\frac{\partial h^{AV}}{\partial A} \right)_{T,p} - h^W. \quad (C.13)$$

Applying the enthalpy definition $h = g + Ts$ to each phase and considering the equilibrium condition (C.2),

$$0 = g^{AV} - A^{sat} \left(\frac{\partial g^{AV}}{\partial A} \right)_{T,p} - g^W, \quad (C.14)$$

the equation (C.5) for the evaporation entropy is readily obtained from (C.13).

If in the former derivation the properties of liquid water are substituted by those of ice Ih, the latent heat of sublimation is obtained in a similar way as

$$L_S = h^{AV} - A^{sat} \left(\frac{\partial h^{AV}}{\partial A} \right)_{T,p} - h^{lh}. \quad (C.15)$$

From the TEOS-10 SIA library [37], the phase transition enthalpies L_L and L_S , respectively, are numerically available from the function calls `liq_air_enthalpy_evap_si()` and `ice_air_enthalpy_subl_si()`, see also table 6.

Appendix D. Dissolution of air in water

D.1. General correction for dissolved air

In the region (L) of figure 10, RF ψ_f^{AW} is defined with respect to the equilibrium state between humid air and liquid water, at which air is saturated with water vapour and the liquid is saturated with dissolved air ([12]: equation (49) therein),

$$RT \ln \psi_f^{AW} = \hat{\mu}_V^{AV}(x, T, p) - \hat{\mu}_W^{AW}(x_W, T, p). \quad (D.1)$$

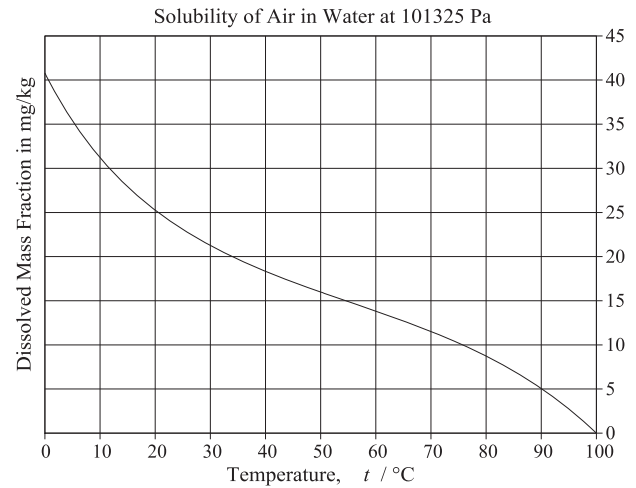


Figure 11. Solubility of air in liquid water at ambient pressure of 101 325 Pa [39], equation (D.4), given as the mass fraction, A , of dissolved air in parts per million (ppm). Note that composition and mean molar mass of dissolved air deviate from those of the ambient gas phase.

Here, $\hat{\mu}_W^{AW}$ is the molar chemical potential of water in air-saturated liquid water, and x_W is the molar fraction of that solvent. The concentration of dissolved air is small and the chemical potential of water can be approximated by the Lewis fugacity rule [12, 38]: equation (19) therein:

$$\hat{\mu}_W^{AW}(x_W, T, p) \approx \hat{\mu}_W(T, p) + RT \ln x_W. \quad (D.2)$$

Comparison of equation (D.1) with (A.4) results in the simple correction formula of the RF for dissolved air,

$$\psi_f^{AW} = \frac{\psi_f}{x_W}. \quad (D.3)$$

Dissolved air is mostly neglected in TEOS-10 and its function libraries, so that x_W needs to be estimated from external sources. [39]: equation (108) therein provide for the saturated mole fraction $x_A(T, p) = (1 - x_W)$ of dissolved air in liquid water at $p = p_0 = 101\,325$ Pa the formula

$$\begin{aligned} \ln x_A(T, p_0) &= -104.208 + 137.296 \left(\frac{100\,K}{T} \right) \\ &+ 58.7394 \ln \left(\frac{T}{100\,K} \right) - 5.7669 \left(\frac{T}{100\,K} \right) \end{aligned} \quad (D.4)$$

between 0 and 100 °C, see figure 11, with an estimated uncertainty of 0.24% in x_A . The underlying experimental data were originally published in 1901. No conversion of the obsolete temperature scale is reported by those authors.

According to Henry’s law, the solubility at other pressures can be calculated by correction with the Poynting factor of liquid water [38], in the form of the Krichevsky–Kasarnovsky equation [40]

$$\ln x_A(T, p) = \ln x_A(T, p_0) + \frac{1}{RT} \int_{p_0}^p v_A(T, p') dp'. \quad (D.5)$$

Here, v_A is the molar volume of dissolved air with a different chemical composition than in the gas phase, and depending on temperature and pressure [41].

D.2. Dew-point-temperature correction for dissolved air

Equation (D.1) considers a correction of the RF for the effect of dissolved air for $x_W < 1$,

$$RT \ln \psi_f^{AW} = \hat{\mu}_W^{AV}(x, T, p) - \hat{\mu}_W^{AW}(x_W, T, p), \quad (D.6)$$

if the sample composition x is known from some measurement unaffected by or corrected for dissolved air. If, however, x is determined from a measured dew point, T_{dp} , as an estimate x^W by exploiting equations that ignore the effects of dissolved air, the final estimate for the RF is given by equation (A.4),

$$RT \ln \psi_f^W = \hat{\mu}_W^{AV}(x^W, T, p) - \hat{\mu}_W(T, p). \quad (D.7)$$

The result x^W of this pure-water determination needs also to be corrected, $x^W = x + \Delta x$, from the estimate equation (5) for x^W ,

$$\hat{\mu}_W^{AV}(x^W, T_{dp}, p) - \hat{\mu}_W(T_{dp}, p) = 0, \quad (D.8)$$

and the correct equation for x ,

$$\hat{\mu}_W^{AV}(x, T_{dp}, p) - \hat{\mu}_W^{AW}(x_W, T_{dp}, p) = 0. \quad (D.9)$$

The difference between these two equations gives, after linearisation in Δx ,

$$\Delta x \approx -\frac{RT_{dp} \ln x_W(T_{dp})}{\partial \hat{\mu}_W^{AV}(T_{dp}) / \partial x} \quad (D.10)$$

Also linearised in Δx , the uncorrected estimate (D.7) for the RF is

$$RT \ln \psi_f^W \approx \hat{\mu}_W^{AV}(x, T, p) + \frac{\partial \hat{\mu}_W^{AV}(T)}{\partial x} \Delta x - \hat{\mu}_W(T, p). \quad (D.11)$$

Comparison with equation (D.6) by virtue of (D.2) and (D.10) provides the correction factor

$$\ln \frac{\psi_f^{AW}}{\psi_f^W} = \frac{\partial \hat{\mu}_W^{AV}(T) / \partial x}{\partial \hat{\mu}_W^{AV}(T_{dp}) / \partial x} \frac{T_{dp}}{T} \ln x_W(T_{dp}) - \ln x_W(T). \quad (D.12)$$

This small second-order correction to the already small correction for dissolved air may be neglected under most circumstances, so that

$$\psi_f^{AW} \approx \psi_f^W \quad (D.13)$$

holds for the correction of dew-point-determined RF with respect to dissolved air. In other words, equations (10) and (22) remain valid in the presence of dissolved air without any explicit allowance for it, obtained from the uncorrected TEOS-10 equations.

Appendix E. TEOS-10 functions for relative fugacity

On its website (www.teos-10.org), TEOS-10 provides open source code of two libraries, the Seawater-Ice-Air (SIA)

library and the Gibbs-Seawater (GSW) library. While GSW is tailored for application in ocean models, SIA is a general library for thermodynamic properties of liquid water, water vapour, ice, seawater and humid air, including their mutual phase equilibria. No such library is available yet, unfortunately, designed specifically for atmospheric applications. In particular, no code has been developed explicitly for the computation of water fugacity or water activity in humid air. The official SIA code is written in two languages, in VBA (for use in Excel) and in Fortran-90 (for inclusion in user code), both versions with identical names of routines and parameters. In this appendix, selected SIA routines available for evaluating fugacity and RF are reviewed.

A complete list of SIA modules with the related TEOS-10 routines and their parameters is reported in the paper of [37] and its digital supplement. The equations implemented in those routines are explained by [14]. Thermodynamic derivations of those equations are presented in [13] and [15]. Throughout the SIA library, the suffix `_si` on function or variable names indicates that the quantity carries the basic SI unit at output or input, such as `t_si` for T in K, `p_si` for p in Pa, or `a_si` for A in kg kg^{-1} . All numerical non-integer values are implemented as 64-bit floating-point numbers.

E.1. Rigorous numerical TEOS-10 routines

With respect to the definition (A.4) and (A.5), the TEOS-10 SIA library provides, scattered over some modules, all necessary functions for the computation of RF. These are

- The chemical potential of water vapour in humid air, $\mu_V^{AV}(A, T, p)$, is available from calling `air_g_chempot_vap_si(a_si, t_si, p_si)` of the module `Air_3b`,
- The Gibbs function of liquid water, $g^W(T, p)$, is available from calling `liq_gibbs_energy_si(t_si, p_si)` of the module `Flu_3b`,
- The Gibbs function of ice Ih, $g^{lh}(T, p)$, is available from calling `ice_chempot_si(t_si, p_si)` of the module `Ice_2`,
- The Gibbs function of water vapour, $g^V(T, p)$, is available from calling `vap_gibbs_energy_si(t_si, p_si)` of the module `Flu_3b`,
- The sublimation pressure, $e^{lh}(T)$, is available from calling `ice_vap_sublimationpressure_si(t_si)` of the module `Ice_Vap_4`,
- The saturation pressure, $e^W(T)$, is available from calling `liq_vap_vapourpressure_si(t_si)` of the module `LiQ_Vap_4`.

A new explicit code example for computing RF from these functions is given in appendix F as the additional function `air_relative_fugacity_vap_si(a_si, t_si, p_si)`.

From the SIA Library, various other properties are available for equilibria between humid air and ice Ih or liquid water, in particular also the saturation mass fraction of dry air, $A^{\text{sat}}(T, p)$, from calling `ice_air_massfraction_air_si`

(t_{si} , p_{si}) of the module `Ice_Air_4a` and `liq_air_massfraction_air_si` (t_{si} , p_{si}) of `Liq_Air_4a`, respectively. The mass fraction A^{sat} can easily be converted to the mole fraction x^{sat} of water vapour by calling `air_molfraction_vap_si` (a_{si}) of the module `Convert_0`. From x^{sat} , in turn, the enhancement factor is available in combination with the evaluation of the saturation or sublimation pressure, either from `liq_vap_vapourpressure_si` (t_{si}) or from `ice_vap_sublimationpressure_si` (t_{si}), respectively.

E.2. Approximations for weak subsaturation

The simple limiting laws approximating RF asymptotically in cases of weak subsaturation require the knowledge of certain familiar thermodynamic properties of liquid water and ice, as well as of their equilibria with humid air. Various empirical equations for these properties are available in the humidity literature, being more or less consistent with TEOS-10. In order to check this consistency and to estimate errors possibly involved, table 6 reports for convenience the necessary functions implemented in the TEOS-10 SIA library [14, 37] which return the requisite numerical values. For example, at atmospheric pressure, $p = 101\,325$ Pa, the TEOS-10 value for the boiling temperature is $T_{\text{sp}} = 373.124\,296$ K, the evaporation enthalpy is $L_{\text{L}} = 2256\,471.59$ J kg⁻¹, the (air-free) melting point is $T_{\text{mp}} = 273.152\,519$ K, and the melting enthalpy is $L_{\text{M}} = 333\,426.517$ J kg⁻¹.

Appendix F. Source-code extension of the TEOS-10 SIA library

The Sea-Ice-Air (SIA) library is available on the web at www.teos-10.org as freely accessible open source code equivalently in either Fortran 90 or in VBA for spreadsheet calculations. The numerous thermodynamic properties available for computation from SIA are documented in the companion papers of [14] and [37]. However, SIA does not provide explicit routines for computing the RF of water vapour in humid air. Required VBA code is newly provided in this appendix and can directly be executed within the SIA environment. The code consists of three routines:

- RF, $\psi_{\text{f}}(A, T, p)$, as defined in appendix A, is implemented here as the procedure `air_relative_fugacity_vap_si`(a_{si} , t_{si} , p_{si}).
- RF, $\psi_{\text{f}}(T, p, T_{\text{cp}})$, as defined in equations (10), (16), (22), (30) and (35) is implemented here as the procedure `air_rf_from_cond_temp_si`(t_{si} , p_{si} , $t_{\text{cp_si}}$).
- As an auxiliary function, the procedure `aux_water_phase`(t_{si} , p_{si}) returns the phase of pure water as 'S', 'L' or 'G' of the position of the point (T, p) in the phase diagram, figure 2.

Note that throughout the SIA library, as well as here, the suffix `_si` of variable names indicates that the unit in which the quantity value is expressed is exclusively the associated basic SI unit, such as K, Pa, kg kg⁻¹ etc.

```

'=====
Public Function air_relative_fugacity_vap_si(ByVal a_si As Double, _
                                           ByVal t_si As Double, _
                                           ByVal p_si As Double) As Double

'implemented 03 Mar 2021 R.Feistel

'this function computes the relative fugacity of water vapour in humid air
'(dissolution of air in liquid water is neglected)
'covering both standard and extended pressure range as defined in the article:
'
'Feistel R and Lovell-Smith J W 2017
'Defining relative humidity in terms of water activity. Part 1: definition
'Metrologia 54 566-76, https://doi.org/10.1088/1681-7575/aa7083
'
'returns air_relative_fugacity_vap_si as a fraction of unity (in Pa/Pa)

'input:
'a_si    mass fraction of dry air in kg/kg
't_si    ITS-90 temperature in K
'p_si    absolute pressure in Pa

'check values:
'air_relative_fugacity_vap_si(0.99, 300, 1E5) = 0.450709619903812
'air_relative_fugacity_vap_si(0.99, 300, 100) = 4.52622523782885E-04
'air_relative_fugacity_vap_si(0.9999, 250, 1E5) = 0.210549531582716
'air_relative_fugacity_vap_si(0.9999, 250, 100) = 2.11521774640382E-04

Dim mu As Double, mu0 As Double, e As Double, pm As Double

Const Tc# = CP_temperature_si      '647.096 K, critical temperature
Const Tt# = TP_temperature_si      '273.16 K, triple point temperature
Const tl# = 132.6                  'K, max. boiling temperature of liquid dry air
Const pc# = CP_pressure_si         '22064000 Pa, critical pressure
Const RW# = Gas_constant_H2O_IAPWS95 '461.51805 J kg-1 K-1, consistent with IAPWS-95

air_relative_fugacity_vap_si = ErrorReturn      '9.99999999E+98

If t_si >= Tc Then Exit Function
If t_si <= tl Then Exit Function
If p_si >= pc Then Exit Function

mu = air_g_chempot_vap_si(a_si, t_si, p_si)
If mu = ErrorReturn Then Exit Function

mu0 = ErrorReturn
Select Case aux_water_phase(t_si, p_si)
    Case "S": mu0 = ice_chempot_si(t_si, p_si)
    Case "L": mu0 = liq_gibbs_energy_si(t_si, p_si)
    Case "G":
        If t_si < Tt Then
            e = ice_vap_sublimationpressure_si(t_si)
        Else
            e = liq_vap_vapourpressure_si(t_si)
        End If
        If e = ErrorReturn Then Exit Function
        mu0 = vap_gibbs_energy_si(t_si, e)
End Select
If mu0 = ErrorReturn Then Exit Function

air_relative_fugacity_vap_si = Exp((mu - mu0) / (RW * t_si))

End Function

```

```

'=====
Public Function air_rf_from_cond_temp_si(ByVal t_si As Double, _
                                       ByVal p_si As Double, _
                                       ByVal tcp_si As Double) As Double

'implemented 01 Mar 2021 R.Feistel

'this function computes the relative fugacity of water vapour in humid air
'from the isobaric condensation temperature (such as chilled-mirror reading)
'
'returns air_rf_from_cond_temp_si as a fraction of unity (in Pa/Pa)

't_si      ITS-90 temperature in K of the given sample
'p_si      absolute pressure in Pa of the given sample
'tcp_si     ITS-90 condensation-point temperature in K (frost or dew point)

'check values:
'air_rf_from_cond_temp_si(300, 1E5, 280) = 0.281019158950085      'standard pressure range
'air_rf_from_cond_temp_si(250, 100, 240) = 0.358757713737742      'standard pressure range
'air_rf_from_cond_temp_si(280, 1E5, 240) = 2.75633614746615E-02    'standard pressure range
'air_rf_from_cond_temp_si(270, 100, 250) = 0.161781869608256      'extended pressure range
'air_rf_from_cond_temp_si(280, 100, 250) = 7.66984606766766E-02    'extended pressure range
'air_rf_from_cond_temp_si(400, 1E5, 300) = 1.48234413183474E-02    'extended pressure range
'air_rf_from_cond_temp_si(400, 1E5, 250) = 3.18921884464612E-04    'extended pressure range

Dim a As Double, e As Double, mu As Double, mu0 As Double

Const Tt# = TP_temperature_si      '273.16 K, triple point temperature
Const tl# = 132.6                  'K, max. boiling temperature of liquid dry air
                                   '(Lemmon et al., 2000)
Const RW# = Gas_constant_H2O_IAPWS95 '461.51805 J kg-1 K-1, consistent with IAPWS-95

air_rf_from_cond_temp_si = ErrorReturn      '9.99999999E+98

If t_si <= tl Then Exit Function      'rf undefined
If tcp_si <= tl Then Exit Function    'rf undefined
If tcp_si > t_si Then Exit Function    'condensation must happen at lowered temperature

If tcp_si = t_si Then                 'sample is already saturated
    air_rf_from_cond_temp_si = 1
    Exit Function
End If

a = ErrorReturn
Select Case aux_water_phase(tcp_si, p_si) 'final sample
    Case "S": a = ice_air_massfraction_air_si(tcp_si, p_si)
    Case "L": a = liq_air_massfraction_air_si(tcp_si, p_si)
End Select
If a = ErrorReturn Then Exit Function

mu0 = ErrorReturn
Select Case aux_water_phase(t_si, p_si) 'initial sample
    Case "S": mu0 = ice_chempot_si(t_si, p_si)
    Case "L": mu0 = liq_gibbs_energy_si(t_si, p_si)
    Case "G":
        If t_si < Tt Then                'region GS
            e = ice_vap_sublimationpressure_si(t_si)
        Else                             'region GL
            e = liq_vap_vapourpressure_si(t_si)
        End If
        If e = ErrorReturn Then Exit Function
        mu0 = vap_gibbs_energy_si(t_si, e)
End Select

If mu0 = ErrorReturn Then Exit Function

mu = air_g_chempot_vap_si(a, t_si, p_si)
If mu = ErrorReturn Then Exit Function

air_rf_from_cond_temp_si = Exp((mu - mu0) / (RW * t_si))

End Function

```

```

'=====
Public Function aux_water_phase(ByVal t_si As Double, _
                               ByVal p_si As Double) As String

'Function returns "S", "L", "G" or "" indicating the (t, p) region
'of the subcritical pure-water phase diagram

'input:
't_si:    ITS-90 temperature in K
'p_si:    absolute pressure in Pa

Dim ts As Double, tm As Double, tb As Double

Const Pt# = TP_pressure_IAPWS95_si '611.654771007894 Pa, triple point pressure
Const Tc# = CP_temperature_si      '647.096 K, critical temperature
Const pc# = CP_pressure_si         '22064000 Pa, critical pressure

aux_water_phase = "" 'out of specified region (or other unspecified error)

If t_si >= Tc Then Exit Function 'supercritical T
If p_si >= pc Then Exit Function 'supercritical p

If p_si <= Pt Then

    ts = ice_vap_sublimationtemp_si(p_si)
    If ts = ErrorReturn Then Exit Function

    If t_si <= ts Then
        aux_water_phase = "S"
    Else
        aux_water_phase = "G"
    End If

Else

    tb = liq_vap_boilingtemperature_si(p_si)
    If tb = ErrorReturn Then Exit Function

    If t_si > tb Then
        aux_water_phase = "G"
    Else
        tm = ice_liq_meltingtemperature_si(p_si)
        If tm = ErrorReturn Then Exit Function

        If t_si > tm Then
            aux_water_phase = "L"
        Else
            aux_water_phase = "S"
        End If
    End If

End If

End Function

```

Appendix G. List of symbols

Symbol	Explanation	Reference	Equation
A	Mass fraction of dry air in humid air		(1)
A^{sat}	Mass fraction of dry air at saturation		
c_p^{AV}	Specific isobaric heat capacity of humid air		(C.10)
c_p^{W}	Specific isobaric heat capacity of liquid water		(C.10)
e	Vapour pressure of liquid water or ice Ih		(4)
e^{Ih}	Vapour pressure of ice Ih		(43)
e^{W}	Vapour pressure of liquid water		(28)
f_{V}	Fugacity of water vapour in humid air		(A.1)
g^{AV}	Specific Gibbs energy of humid air		(11)
g^{Ih}	Specific Gibbs energy of ice Ih		(15)
g^{V}	Specific Gibbs energy of water vapour		(28)
g^{W}	Specific Gibbs energy of liquid water		(5)
h^{AV}	Specific enthalpy of humid air		(C.9)
h^{Ih}	Specific enthalpy of ice Ih		(C.15)
h^{W}	Specific enthalpy of liquid water		(C.9)
$H^{\text{W+AV}}$	Enthalpy of liquid water plus humid air		(C.9)
L_{L}	Specific evaporation enthalpy of liquid water		(14)
L_{M}	Specific melting enthalpy of ice Ih		(25)
L_{S}	Specific evaporation enthalpy of ice Ih		(17)
M_{A}	Molar mass of dry air, 28.965 46 g mol ⁻¹	[26]	(1)
m^{A}	Mass of dry air		(C.8)
$m^{\text{H}_2\text{O}}$	Mass of liquid water plus water vapour		(C.10)
m^{V}	Mass of water vapour		(C.8)
m^{W}	Mass of liquid water		(C.9)
M_{W}	Molar mass of water, 18.015 268 g mol ⁻¹	[26]	(1)
p	Pressure		(2)
p_0, p_0	Atmospheric pressure, 101 325 Pa		
p_{c}	Critical pressure, 22.064 MPa	[42]	(A.5)
p_{melt}	Melting pressure of ice Ih		(A.8)
p_{t}	Triple-point pressure, 611.657 Pa	[42]	
q	Specific humidity		(1)
r	Humidity ratio		(1)
R	Molar gas constant, 8.314 4626 ... J mol ⁻¹ K ⁻¹	[43]	(D.1)
R_{W}	Specific gas constant of water, 461.518 05 J kg ⁻¹ K ⁻¹	[42]	(5)
s^{AV}	Specific entropy of humid air		(C.4)
s^{W}	Specific entropy of liquid water		(C.4)
T	Absolute temperature (ITS-90)		(2)
T_{c}	Critical temperature, 647.096 K	[42]	(A.5)
T_{cp}	Condensation-point temperature		(2)
T_{dp}	Dew-point temperature		(6)
T_{fp}	Frost-point temperature		(16)
T_{liq}	Maxcondentherm temperature of air, 132.6 K	[32]	
T_{mp}	Melting temperature of ice Ih		(23)
T_{sp}	Sublimation or boiling temperature		
T_{t}	Triple-point temperature, 273.16 K	[42]	(A.5)
v_{A}	Molar volume of air dissolved in water		(D.5)
x	Mole fraction of water vapour in humid air		(1)
x_{A}	Mole fraction of air dissolved in water		(D.4)
x^{sat}	Saturation mole fraction of water vapour		(2)
x_{W}	Mole fraction of water in air-saturated liquid water		(D.1)
δT	Temperature depression		(12)
μ_0	Reference chemical potential		(A.5)

Symbol	Explanation	Reference	Equation
μ_V^{AV}	Chemical potential of water vapour in humid air		(5)
$\hat{\mu}_V^{\text{AV}}$	Molar chemical potential of water vapour in humid air		(D.1)
$\hat{\mu}_W^{\text{AW}}$	Molar chemical potential of water in air-saturated liquid water		(D.1)
$\hat{\mu}_W$	Molar chemical potential of pure liquid water		(D.2)
ρ^V	Mass density of water vapour		(B.55)
ψ_f	RF of water in humid air		(5)
ψ_f^{AW}	RF relative to liquid water		Table 2
ψ_f^{Ih}	RF relative to ice Ih		Table 2
$\psi_f^{\text{V,Ih}}$	RF (extended range) relative to ice Ih		Table 2
$\psi_f^{\text{V,W}}$	RF (extended range) relative to water		Table 2
ψ_q	RH (climatological definition)		(9)

ORCID iDs

Rainer Feistel  <https://orcid.org/0000-0003-0665-7532>

Jeremy Lovell-Smith  <https://orcid.org/0000-0001-6429-005X>

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