

# **The International Association for the Properties of Water and Steam**

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## **Guideline on an Equation of State for Humid Air in Contact with Seawater and Ice, Consistent with the IAPWS Formulation 2008 for the Thermodynamic Properties of Seawater**

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This Guideline contains 21 pages, including this cover page.

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The equation of state provided in this Guideline is a fundamental equation for the specific Helmholtz energy as a function of air mass fraction, temperature and density; details can be found in the article “Thermodynamic Properties of Sea Air” by R. Feistel *et al.* [1]. This equation is rigorously consistent with the IAPWS Releases on fluid water, ice and seawater [2, 3, 4] and can be used for the computation of the properties of arbitrary mutual phase transitions and composites thereof.

Further information about this Guideline and other documents issued by IAPWS can be obtained from the Executive Secretary of IAPWS or from <http://www.iapws.org>.

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### 1 Nomenclature

Symbol	Physical quantity	Unit
$A$	Mass fraction of dry air in humid air	$\text{kg kg}^{-1}$
$A^{\text{sat}}$	Mass fraction of dry air in saturated humid air, Eqs. (12), (13)	$\text{kg kg}^{-1}$
$A^{\text{cond}}$	Mass fraction of dry air in humid air at the condensation point in contact with seawater, Eq. (14)	$\text{kg kg}^{-1}$
$a_0 \dots a_4$	Coefficients of the third cross-virial coefficient $C^{\text{AAW}}$ , Table 4	
$b_0 \dots b_3$	Coefficients of the third cross-virial coefficient $C^{\text{AWW}}$ , Table 4	
$b^*$	Reducing factor, $b^* = 10^{-6} \text{ m}^3 \text{ mol}^{-1}$	$\text{m}^3 \text{ mol}^{-1}$
$B^{\text{AW}}$	Second cross-virial coefficient, Eq. (9)	$\text{m}^3 \text{ mol}^{-1}$
$c_1 \dots c_3$	Coefficients of the second cross-virial coefficient $B^{\text{AW}}$ , Table 4	
$c^*$	Reducing factor, $c^* = 10^{-6} \text{ m}^6 \text{ mol}^{-2}$	$\text{m}^6 \text{ mol}^{-2}$
$C^{\text{AAW}}, C^{\text{AWW}}$	Third cross-virial coefficients, Eqs. (10), (11)	$\text{m}^6 \text{ mol}^{-2}$
$c_p$	Specific isobaric heat capacity of humid air, Eq. (T3)	$\text{J kg}^{-1} \text{ K}^{-1}$
$c_v$	Specific isochoric heat capacity	$\text{J kg}^{-1} \text{ K}^{-1}$
$d_1 \dots d_3$	Coefficients of the second cross-virial coefficient $B^{\text{AW}}$ , Table 4	
$f^{\text{A}}$	Specific Helmholtz energy of dry air, Eq. (3)	$\text{J kg}^{-1}$
$f^{\text{AV}}$	Specific Helmholtz energy of humid air, Eq. (1)	$\text{J kg}^{-1}$
$f^{\text{IAPWS-95}}$	IAPWS-95 Helmholtz function of fluid water	$\text{J kg}^{-1}$
$f^{\text{mix}}$	Specific Helmholtz energy of air-water interaction, Eq. (8)	$\text{J kg}^{-1}$
$f^{\text{V}}$	Specific Helmholtz energy of water vapor, Eq. (2)	$\text{J kg}^{-1}$

Symbol	Physical quantity	Unit
$g$	Specific Gibbs energy of humid air, Eq. (T5)	$\text{J kg}^{-1}$
$g^{\text{lh}}$	Specific Gibbs energy of ice Ih	$\text{J kg}^{-1}$
$g^{\text{liq}}$	Specific Gibbs energy of liquid water	$\text{J kg}^{-1}$
$h$	Specific enthalpy of humid air, Eq. (T4)	$\text{J kg}^{-1}$
$h^{\text{A}}$	Specific enthalpy of dry air	$\text{J kg}^{-1}$
$i_1 \dots i_{19}$	Coefficients of the residual part of dry air, Table 3	
$j_1 \dots j_{19}$	Coefficients of the residual part of dry air, Table 3	
$k$	Uncertainty coverage factor, and dummy summation index	
$l_1 \dots l_{19}$	Coefficients of the residual part of dry air, Table 3	
$M_{\text{A}}$	Molar mass of dry air, $M_{\text{A}} = 0.028\,965\,46 \text{ kg mol}^{-1}$	$\text{kg mol}^{-1}$
$M_{\text{W}}$	Molar mass of pure water, $M_{\text{W}} = 0.018\,015\,268 \text{ kg mol}^{-1}$	$\text{kg mol}^{-1}$
$n_1 \dots n_{19}$	Coefficients of the residual part of dry air, Table 3	
$n_1^0 \dots n_{13}^0$	Coefficients of the ideal-gas part of dry air, Table 2	
$p$	Absolute pressure, Eq. (T1)	Pa
$p_0$	Normal pressure, $p_0 = 101\,325 \text{ Pa}$	Pa
$p^{\text{sat}}$	Saturation pressure of liquid water	Pa
$p^{\text{subl}}$	Sublimation pressure of ice	Pa
$p^{\text{vap}}$	Partial pressure of water in humid air, Eq. (T68)	Pa
$p^{\text{vap,sat}}$	Partial pressure of water in saturated humid air	Pa
$R$	Molar gas constant, $R = 8.314\,472 \text{ J mol}^{-1} \text{ K}^{-1}$	$\text{J mol}^{-1} \text{ K}^{-1}$
$R^{\text{L}}$	Molar gas constant [5], $R^{\text{L}} = 8.314\,51 \text{ J mol}^{-1} \text{ K}^{-1}$	$\text{J mol}^{-1} \text{ K}^{-1}$
$RH$	Relative humidity, Eq. (T67)	
$S$	Absolute salinity of seawater	$\text{kg kg}^{-1}$
$s$	Specific entropy of humid air, Eq. (T2)	$\text{J kg}^{-1} \text{ K}^{-1}$
$s^{\text{A}}$	Specific entropy of dry air	$\text{J kg}^{-1} \text{ K}^{-1}$
$T$	Absolute temperature (ITS-90)	K
$T_0$	Celsius zero temperature point, $T_0 = 273.15 \text{ K}$	K
$T_{\text{A}}^*$	Reducing temperature, $T_{\text{A}}^* = 132.6312 \text{ K}$	K
$\bar{T}$	Reduced temperature (virial coefficients), $\bar{T} = T / (100 \text{ K})$	
$U$	Expanded uncertainty	
$u_{\text{c}}$	Combined standard uncertainty	
$w$	Speed of sound in humid air, Eq. (T10)	$\text{m s}^{-1}$
$x_{\text{A}}$	Mole fraction of dry air in humid air, Eq. (T72)	$\text{mol mol}^{-1}$
$\alpha$	Thermal expansion coefficient of humid air, Eq. (T6)	$\text{K}^{-1}$
$\alpha^{\text{id}}$	Ideal-gas part of the Helmholtz function of dry air, Eq. (4)	

<b>Symbol</b>	<b>Physical quantity</b>	<b>Unit</b>
$\alpha^{\text{res}}$	Residual part of the Helmholtz function of dry air, Eq. (5)	
$\beta_s$	Isentropic temperature-pressure coefficient of humid air, adiabatic lapse rate, Eq. (T7)	K Pa <sup>-1</sup>
$\delta$	Reduced density, $\delta = \rho^A / \rho_A^*$	
$\kappa_s$	Isentropic compressibility of humid air, Eq. (T9)	Pa <sup>-1</sup>
$\kappa_T$	Isothermal compressibility of humid air, Eq. (T8)	Pa <sup>-1</sup>
$\mu$	Relative chemical potential of humid air, Eq. (T64)	J kg <sup>-1</sup>
$\mu_W^{\text{sw}}$	Chemical potential of water in seawater	J kg <sup>-1</sup>
$\mu_W$	Chemical potential of water in humid air, Eq. (T65)	J kg <sup>-1</sup>
$\rho$	Mass density of humid air	kg m <sup>-3</sup>
$\rho^A$	Mass density of dry air	kg m <sup>-3</sup>
$\rho_A^*$	Reducing density, $\rho_A^* = 10\,447.7 \text{ mol m}^{-3} \times M_A$	kg m <sup>-3</sup>
$\rho^V$	Mass density of water vapor	kg m <sup>-3</sup>
$\tau$	Reduced reciprocal temperature (dry air), $\tau = T_A^* / T$	

## 2 Introductory Remarks and Special Constants

The ‘‘Release on the IAPWS Formulation 2008 for the Thermodynamic Properties of Seawater’’ [4] describes the specific Gibbs energy of seawater relative to liquid pure water. At given temperature and pressure, the liquid-water part is computed from the Helmholtz function provided by the IAPWS-95 formulation [2]. Similarly, the IAPWS-95 Helmholtz function gives the water-vapor part in the equation of state for humid air described in this Guideline. The mass fraction  $A$  of dry air is used to describe the mixing mass ratio of water vapor with air, which is modeled by the form of the ambient mixture of nitrogen, oxygen and argon at fixed mutual ratios as described in [5]. The mass fraction of water vapor is  $(1 - A)$ . The interaction between water and air is accounted for in the form of the second [6] and the third [7] cross-virial coefficients [1].

The Guideline is primarily intended to be used for geophysical applications in oceanography and meteorology, as well as for technical systems such as desalination plants, in particular for the computation of phase equilibrium properties between humid air and liquid water, ice or seawater [1].

**TABLE 1** Special constants and values used in this Guideline

Quantity	Symbol	Value	Unit	Reference
Molar gas constant	$R$	8.314 472	$\text{J mol}^{-1} \text{K}^{-1}$	[8]
Molar gas constant <sup>a</sup>	$R^L$	8.314 51	$\text{J mol}^{-1} \text{K}^{-1}$	[5]
Molar mass of dry air	$M_A$	0.028 965 46	$\text{kg mol}^{-1}$	[10]
Molar mass of water	$M_W$	0.018 015 268	$\text{kg mol}^{-1}$	[8]
Celsius zero temperature point	$T_0$	273.15	K	[9]
Normal pressure	$p_0$	101 325	Pa	[11]

<sup>a</sup>Value used by Lemmon *et al.* [5] in the formulation for dry air; used in Eq. (3) for consistency

## 3 The Equation of State

The equation of state is represented here in terms of the specific Helmholtz energy of humid air,  $f^{AV}$ , expressed as a function of dry-air mass fraction  $A$ , temperature  $T$  and humid-air mass density  $\rho$ . The temperatures are based on the temperature scale ITS-90 [9]. The Helmholtz function takes the form

$$f^{AV}(A, T, \rho) = (1 - A)f^V(T, \rho^V) + Af^A(T, \rho^A) + f^{\text{mix}}(A, T, \rho). \quad (1)$$

The water-vapor part is given by the IAPWS-95 Helmholtz function for fluid water,

$$f^V(T, \rho^V) \equiv f^{\text{IAPWS-95}}(T, \rho^V), \quad (2)$$

which is defined in [2], and is computed at the partial density of water vapor,  $\rho^V = (1 - A)\rho$ . The dry-air part,  $f^A(T, \rho^A)$ , is defined by Eq. (3) and is computed at the partial density of dry air,

$\rho^A = A\rho$ . The air-water cross-virial part  $f^{\text{mix}}$  is defined by Eq. (8). In the special cases of dry air,  $A = 1$ , or pure water vapor,  $A = 0$ , Eq. (1) must be replaced by its mathematical limits,  $f^{\text{AV}} = f^A$  or  $f^{\text{AV}} = f^V$ , respectively.

The specific Helmholtz energy for dry air is [5]

$$f^A(T, \rho^A) = \frac{R^L T}{M_A} [\alpha^{\text{id}}(\tau, \delta) + \alpha^{\text{res}}(\tau, \delta)]. \quad (3)$$

The values to be used for molar mass,  $M_A$ , of dry air, and for the molar gas constant,  $R^L$ , are given in Table 1. The function  $\alpha^{\text{id}}(\tau, \delta)$  is the ideal-gas part,

$$\begin{aligned} \alpha^{\text{id}}(\tau, \delta) = \ln \delta + \sum_{i=1}^5 n_i^0 \tau^{i-4} + n_6^0 \tau^{1.5} + n_7^0 \ln \tau + n_8^0 \ln[1 - \exp(-n_{11}^0 \tau)] \\ + n_9^0 \ln[1 - \exp(-n_{12}^0 \tau)] + n_{10}^0 \ln[2/3 + \exp(n_{13}^0 \tau)] \end{aligned} \quad (4)$$

and  $\alpha^{\text{res}}(\tau, \delta)$  is the residual part,

$$\alpha^{\text{res}}(\tau, \delta) = \sum_{k=1}^{10} n_k \delta^{i_k} \tau^{j_k} + \sum_{k=11}^{19} n_k \delta^{i_k} \tau^{j_k} \exp(-\delta^{l_k}). \quad (5)$$

The reduced variables in Eqs. (3)-(5) are  $\tau = T_A^*/T$  with the reducing temperature  $T_A^* = 132.6312$  K, and  $\delta = \rho^A / \rho_A^*$  with the reducing density  $\rho_A^* = 10447.7 \text{ mol m}^{-3} \times M_A$ . The value of  $M_A$  is given in Table 1. The coefficients of Eqs. (4) and (5) are given in Tables 2 and 3.

**TABLE 2** Dimensionless coefficients and exponents for the ideal-gas part, Eq. (4), for dry air [5]. In this release, the coefficients  $n_4^0$  and  $n_5^0$  are re-adjusted to the reference state conditions, Eqs. (6) and (7), and consequently differ from the originally published values [5].

$i$	$n_i^0$	$i$	$n_i^0$
1	$0.605\ 719\ 400\ 000\ 000 \times 10^{-7}$	8	$0.791\ 309\ 509\ 000\ 000$
2	$-0.210\ 274\ 769\ 000\ 000 \times 10^{-4}$	9	$0.212\ 236\ 768\ 000\ 000$
3	$-0.158\ 860\ 716\ 000\ 000 \times 10^{-3}$	10	$-0.197\ 938\ 904\ 000\ 000$
4	$0.974\ 502\ 517\ 439\ 480 \times 10$	11	$0.253\ 636\ 500\ 000\ 000 \times 10^2$
5	$0.100\ 986\ 147\ 428\ 912 \times 10^2$	12	$0.169\ 074\ 100\ 000\ 000 \times 10^2$
6	$-0.195\ 363\ 420\ 000\ 000 \times 10^{-3}$	13	$0.873\ 127\ 900\ 000\ 000 \times 10^2$
7	$0.249\ 088\ 803\ 200\ 000 \times 10$		

**TABLE 3** Coefficients and exponents for the residual part, Eq. (5), for dry air [5]

$k$	$i_k$	$j_k$	$l_k$	$n_k$
1	1	0	0	0.118 160 747 229
2	1	0.33	0	0.713 116 392 079
3	1	1.01	0	$-0.161\ 824\ 192\ 067 \times 10$
4	2	0	0	$0.714\ 140\ 178\ 971 \times 10^{-1}$
5	3	0	0	$-0.865\ 421\ 396\ 646 \times 10^{-1}$
6	3	0.15	0	0.134 211 176 704
7	4	0	0	$0.112\ 626\ 704\ 218 \times 10^{-1}$
8	4	0.2	0	$-0.420\ 533\ 228\ 842 \times 10^{-1}$
9	4	0.35	0	$0.349\ 008\ 431\ 982 \times 10^{-1}$
10	6	1.35	0	$0.164\ 957\ 183\ 186 \times 10^{-3}$
11	1	1.6	1	$-0.101\ 365\ 037\ 912$
12	3	0.8	1	$-0.173\ 813\ 690\ 970$
13	5	0.95	1	$-0.472\ 103\ 183\ 731 \times 10^{-1}$
14	6	1.25	1	$-0.122\ 523\ 554\ 253 \times 10^{-1}$
15	1	3.6	2	$-0.146\ 629\ 609\ 713$
16	3	6	2	$-0.316\ 055\ 879\ 821 \times 10^{-1}$
17	11	3.25	2	$0.233\ 594\ 806\ 142 \times 10^{-3}$
18	1	3.5	3	$0.148\ 287\ 891\ 978 \times 10^{-1}$
19	3	15	3	$-0.938\ 782\ 884\ 667 \times 10^{-2}$

The parameters  $n_4^0$  and  $n_5^0$  listed in Table 2 are arbitrary and are computed here from the reference-state conditions of zero specific entropy,  $s^A$ , and specific enthalpy,  $h^A$ , of dry air at the temperature  $T_0$  and the normal pressure  $p_0$ , as given in Table 1,

$$s^A(T_0, p_0) = 0, \quad (6)$$

$$h^A(T_0, p_0) = 0. \quad (7)$$

The Helmholtz function  $f^{\text{mix}}$  in Eq. (1) describes the water-air interaction and is defined by

$$f^{\text{mix}}(A, T, \rho) = \frac{2A(1-A)\rho RT}{M_A M_W} \left\{ B^{\text{AW}}(T) + \frac{3}{4} \rho \left[ \frac{A}{M_A} C^{\text{AAW}}(T) + \frac{(1-A)}{M_W} C^{\text{AWW}}(T) \right] \right\}. \quad (8)$$

The values used for the molar gas constant  $R$ , the molar mass of dry air,  $M_A$ , and the molar mass of water,  $M_W$ , are given in Table 1.

The second cross-virial coefficient,  $B^{\text{AW}}(T)$ , is given by [6] as

$$B^{\text{AW}}(T) = b^* \sum_{i=1}^3 c_i \bar{T}^{d_i} . \quad (9)$$

The coefficients of Eq. (9) are given in Table 4. The reducing factor is  $b^* = 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ ; the reduced temperature is  $\bar{T} = T / (100 \text{ K})$ .

The third cross-virial coefficients  $C^{\text{AAW}}(T)$  and  $C^{\text{AWW}}(T)$  are defined in [7], in the form

$$C^{\text{AAW}}(T) = c^* \sum_{i=0}^4 a_i \bar{T}^{-i} \quad (10)$$

$$C^{\text{AWW}}(T) = -c^* \exp \left\{ \sum_{i=0}^3 b_i \bar{T}^{-i} \right\} . \quad (11)$$

The coefficients of Eqs. (10) and (11) are given in Table 4. The reducing factor is  $c^* = 10^{-6} \text{ m}^6 \text{ mol}^{-2}$ ; the reduced temperature is  $\bar{T} = T / (100 \text{ K})$ .

**TABLE 4** Coefficients of the cross-virial coefficients  $B^{\text{AW}}(T)$ ,  $C^{\text{AAW}}(T)$  and  $C^{\text{AWW}}(T)$ , Eqs. (9)-(11)

$i$	$a_i$	$b_i$	$c_i$	$d_i$
0	$0.482\,737 \times 10^{-3}$	$-0.107\,288\,76 \times 10^2$		
1	$0.105\,678 \times 10^{-2}$	$0.347\,802\,00 \times 10^2$	$0.665\,687 \times 10^2$	-0.237
2	$-0.656\,394 \times 10^{-2}$	$-0.383\,383\,00 \times 10^2$	$-0.238\,834 \times 10^3$	-1.048
3	$0.294\,442 \times 10^{-1}$	$0.334\,060\,00 \times 10^2$	$-0.176\,755 \times 10^3$	-3.183
4	$-0.319\,317 \times 10^{-1}$			

#### 4 Relations of the Thermodynamic Properties to the Specific Helmholtz Energy

The thermodynamic properties of humid air can be derived from Eq.(1) by using the appropriate combinations of the specific Helmholtz energy and its derivatives. Relations between thermodynamic properties and  $f^{\text{AV}}(A, T, \rho)$  and its derivatives with respect to  $A$ ,  $T$  and  $\rho$  are summarized in Table 5. All required derivatives of the specific Helmholtz energy are given in Table 6.

**TABLE 5** Relations of the thermodynamic properties to the Helmholtz energy of humid air, Eq. (1), and its  $T$ - $p$  derivatives<sup>a</sup>

Property	Relation	Unit	Eq.
Pressure			
$p(A, T, \rho) = -(\partial f^{\text{AV}} / \partial v)_{A, T}$	$p = \rho^2 f_{\rho}^{\text{AV}}$	Pa	(T1)
Specific entropy			
$s(A, T, \rho) = -(\partial f^{\text{AV}} / \partial T)_{A, \rho}$	$s = -f_T^{\text{AV}}$	J kg <sup>-1</sup> K <sup>-1</sup>	(T2)
Specific isobaric heat capacity			
$c_p(A, T, \rho) = T(\partial s / \partial T)_{A, p}$	$c_p = -Tf_{TT}^{\text{AV}} + \frac{T\rho(f_{T\rho}^{\text{AV}})^2}{(2f_{\rho}^{\text{AV}} + \rho f_{\rho\rho}^{\text{AV}})}$	J kg <sup>-1</sup> K <sup>-1</sup>	(T3)
Specific enthalpy			
$h(A, T, \rho) = f^{\text{AV}} + Ts + p / \rho$	$h = f^{\text{AV}} - Tf_T^{\text{AV}} + \rho f_{\rho}^{\text{AV}}$	J kg <sup>-1</sup>	(T4)
Specific Gibbs energy			
$g(A, T, \rho) = f^{\text{AV}} + p / \rho$	$g = f^{\text{AV}} + \rho f_{\rho}^{\text{AV}}$	J kg <sup>-1</sup>	(T5)
Thermal expansion coefficient			
$\alpha(A, T, \rho) = v^{-1}(\partial v / \partial T)_{A, p}$	$\alpha = f_{T\rho}^{\text{AV}} / (2f_{\rho}^{\text{AV}} + \rho f_{\rho\rho}^{\text{AV}})$	K <sup>-1</sup>	(T6)
Isentropic temperature-pressure coefficient, adiabatic lapse rate			
$\beta_s(A, T, \rho) = (\partial T / \partial p)_{A, s}$	$\beta_s = \frac{f_{T\rho}^{\text{AV}} / \rho}{\rho(f_{T\rho}^{\text{AV}})^2 - f_{TT}^{\text{AV}}(2f_{\rho}^{\text{AV}} + \rho f_{\rho\rho}^{\text{AV}})}$	K Pa <sup>-1</sup>	(T7)
Isothermal compressibility			
$\kappa_T(A, T, \rho) = -v^{-1}(\partial v / \partial p)_{A, T}$	$\kappa_T = [\rho^2(2f_{\rho}^{\text{AV}} + \rho f_{\rho\rho}^{\text{AV}})]^{-1}$	Pa <sup>-1</sup>	(T8)
Isentropic compressibility			
$\kappa_s(A, T, \rho) = -v^{-1}(\partial v / \partial p)_{A, s}$	$\kappa_s = \frac{f_{TT}^{\text{AV}} / \rho^2}{f_{TT}^{\text{AV}}(2f_{\rho}^{\text{AV}} + \rho f_{\rho\rho}^{\text{AV}}) - \rho(f_{T\rho}^{\text{AV}})^2}$	Pa <sup>-1</sup>	(T9)
Speed of sound			
$w(A, T, \rho) = \sqrt{(\partial p / \partial \rho)_{A, s}}$	$w = \sqrt{\rho^2 \frac{f_{TT}^{\text{AV}} f_{\rho\rho}^{\text{AV}} - (f_{T\rho}^{\text{AV}})^2}{f_{TT}^{\text{AV}}} + 2\rho f_{\rho}^{\text{AV}}}$	m s <sup>-1</sup>	(T10)

<sup>a</sup>  $f_T^{\text{AV}} \equiv \left( \frac{\partial f^{\text{AV}}}{\partial T} \right)_{A, \rho}$ ,  $f_{\rho}^{\text{AV}} \equiv \left( \frac{\partial f^{\text{AV}}}{\partial \rho} \right)_{A, T}$ ,  $f_{TT}^{\text{AV}} \equiv \left( \frac{\partial^2 f^{\text{AV}}}{\partial T^2} \right)_{A, \rho}$ ,  $f_{T\rho}^{\text{AV}} \equiv \left( \frac{\partial^2 f^{\text{AV}}}{\partial T \partial \rho} \right)_A$ ,  $f_{\rho\rho}^{\text{AV}} \equiv \left( \frac{\partial^2 f^{\text{AV}}}{\partial \rho^2} \right)_{A, T}$

**TABLE 6** Equations for the Helmholtz energy, Eq. (1), and its derivatives<sup>a</sup>. The required derivatives of the Helmholtz function of water vapor,  $f^V$ , Eq. (2), are given in Table 7 in terms of properties available from the IAPWS-95 Release [2]. The required derivatives of the Helmholtz function of dry air,  $f^A$ , Eq. (3), are given in Table 8. The required derivatives of the cross-virial part,  $f^{\text{mix}}$ , Eq. (8), are given in Table 10.

Equation	Unit	Eq.
$f^{\text{AV}} = (1-A)f^V + Af^A + f^{\text{mix}}$	$\text{J kg}^{-1}$	(T11)
$f_A^{\text{AV}} = -f^V - \rho^V f_{\rho^V}^V + f^A + \rho^A f_{\rho^A}^A + f_A^{\text{mix}}$	$\text{J kg}^{-1}$	(T12)
$f_T^{\text{AV}} = (1-A)f_T^V + Af_T^A + f_T^{\text{mix}}$	$\text{J kg}^{-1} \text{K}^{-1}$	(T13)
$f_{\rho}^{\text{AV}} = (1-A)^2 f_{\rho^V}^V + A^2 f_{\rho^A}^A + f_{\rho}^{\text{mix}}$	$\text{J m}^3 \text{kg}^{-2}$	(T14)
$f_{AA}^{\text{AV}} = \rho(2f_{\rho^V}^V + \rho^V f_{\rho^V \rho^V}^V + 2f_{\rho^A}^A + \rho^A f_{\rho^A \rho^A}^A) + f_{AA}^{\text{mix}}$	$\text{J kg}^{-1}$	(T15)
$f_{AT}^{\text{AV}} = -f_T^V - \rho^V f_{T\rho^V}^V + f_T^A + \rho^A f_{T\rho^A}^A + f_{AT}^{\text{mix}}$	$\text{J kg}^{-1} \text{K}^{-1}$	(T16)
$f_{A\rho}^{\text{AV}} = -(1-A)(2f_{\rho^V}^V + \rho^V f_{\rho^V \rho^V}^V) + A(2f_{\rho^A}^A + \rho^A f_{\rho^A \rho^A}^A) + f_{A\rho}^{\text{mix}}$	$\text{J m}^3 \text{kg}^{-2}$	(T17)
$f_{TT}^{\text{AV}} = (1-A)f_{TT}^V + Af_{TT}^A + f_{TT}^{\text{mix}}$	$\text{J kg}^{-1} \text{K}^{-2}$	(T18)
$f_{T\rho}^{\text{AV}} = (1-A)^2 f_{T\rho^V}^V + A^2 f_{T\rho^A}^A + f_{T\rho}^{\text{mix}}$	$\text{J m}^3 \text{kg}^{-2} \text{K}^{-1}$	(T19)
$f_{\rho\rho}^{\text{AV}} = (1-A)^3 f_{\rho^V \rho^V}^V + A^3 f_{\rho^A \rho^A}^A + f_{\rho\rho}^{\text{mix}}$	$\text{J m}^6 \text{kg}^{-3}$	(T20)

$$^a f_A^{\text{AV}} \equiv \left( \frac{\partial f^{\text{AV}}}{\partial A} \right)_{T,\rho}, \quad f_T^{\text{AV}} \equiv \left( \frac{\partial f^{\text{AV}}}{\partial T} \right)_{A,\rho}, \quad f_{\rho}^{\text{AV}} \equiv \left( \frac{\partial f^{\text{AV}}}{\partial \rho} \right)_{A,T},$$

$$f_{AA}^{\text{AV}} \equiv \left( \frac{\partial^2 f^{\text{AV}}}{\partial A^2} \right)_{T,\rho}, \quad f_{AT}^{\text{AV}} \equiv \left( \frac{\partial^2 f^{\text{AV}}}{\partial A \partial T} \right)_{\rho}, \quad f_{A\rho}^{\text{AV}} \equiv \left( \frac{\partial^2 f^{\text{AV}}}{\partial A \partial \rho} \right)_{T},$$

$$f_{TT}^{\text{AV}} \equiv \left( \frac{\partial^2 f^{\text{AV}}}{\partial T^2} \right)_{A,\rho}, \quad f_{T\rho}^{\text{AV}} \equiv \left( \frac{\partial^2 f^{\text{AV}}}{\partial T \partial \rho} \right)_{A}, \quad f_{\rho\rho}^{\text{AV}} \equiv \left( \frac{\partial^2 f^{\text{AV}}}{\partial \rho^2} \right)_{A,T}$$

**TABLE 7** The partial derivatives of the Helmholtz function of water vapor,  $f^v(T, \rho^v)$ , expressed in terms of thermodynamic coefficients provided in IAPWS-95 [2], calculated at  $\rho = \rho^v$ . The IAPWS-95 properties refer to water vapor; superscripts are omitted here for consistency with [2].

Derivative of $f^v(T, \rho^v)$	IAPWS-95 property	Unit	Eq.
$f^v(T, \rho^v)$	$f$	$\text{J kg}^{-1}$	(T21)
$f_T^v(T, \rho^v)$	$-s$	$\text{J kg}^{-1} \text{K}^{-1}$	(T22)
$f_{\rho^v}^v(T, \rho^v)$	$\frac{p}{\rho^2}$	$\text{J m}^3 \text{kg}^{-2}$	(T23)
$f_{TT}^v(T, \rho^v)$	$-\frac{c_v}{T}$	$\text{J kg}^{-1} \text{K}^{-2}$	(T24)
$f_{T\rho^v}^v(T, \rho^v)$	$\frac{\alpha}{\rho^2 \kappa_T}$	$\text{J m}^3 \text{kg}^{-2} \text{K}^{-1}$	(T25)
$f_{\rho^v \rho^v}^v(T, \rho^v)$	$\frac{1}{\rho^3} \left( \frac{1}{\kappa_T} - 2p \right)$	$\text{J m}^6 \text{kg}^{-3}$	(T26)

## 5 Colligative Properties

For the computation of equilibria between humid air and the different phases of H<sub>2</sub>O, or seawater, the required thermodynamic condition is equality of the chemical potential  $\mu_w$  of H<sub>2</sub>O in humid air, Table 12, Eq. (T65), with the chemical potential of H<sub>2</sub>O in that particular phase. In this work, chemical potentials are expressed on a mass basis, which is the usual (molar) chemical potential divided by molar mass. Conversion formulas relating mole fractions to mass fractions are given in Table 12 together with other relevant quantities. The chemical potential of a pure phase equals its specific Gibbs energy.

At the saturation point of humid air, the air fraction  $A = A^{\text{sat}}$ , the condensation temperature  $T$ , and the total pressure  $p$  obey the equilibrium condition between humid air and liquid water,

$$\mu_w(A^{\text{sat}}, T, p) = g^{\text{liq}}(T, p), \quad (12)$$

or, below the freezing temperature, the equilibrium condition between humid air and ice [1],

$$\mu_w(A^{\text{sat}}, T, p) = g^{\text{lh}}(T, p). \quad (13)$$

Here,  $g^{\text{liq}}$  is the specific Gibbs energy of liquid water, available from IAPWS-95 [2], and  $g^{\text{lh}}$  is the specific Gibbs energy of ice Ih, available from the IAPWS Release on ice [3]. The solution  $A^{\text{sat}}$  of Eqs. (12) or (13) is required for the computation of the relative humidity, Eq. (T67).

The equilibrium between humid air and seawater obeys the condition [1],

$$\mu_{\text{W}}(A^{\text{cond}}, T, p) = \mu_{\text{W}}^{\text{SW}}(S, T, p). \quad (14)$$

Here,  $A^{\text{cond}}$  is the air fraction at the condensation point in contact with seawater,  $S$  is the absolute salinity and  $\mu_{\text{W}}^{\text{SW}}$  is the chemical potential of water in seawater, available from the IAPWS Release on seawater [4]. Humid air in equilibrium with seawater,  $S > 0$ , is always subsaturated,  $A^{\text{cond}} > A^{\text{sat}}$ , if no ice is present, i.e., if the temperature is higher than the freezing temperature of seawater.

In Eqs. (12) and (14), the dissolution of the constituents of air in the liquid phase is neglected.

**TABLE 8** The partial derivatives of the Helmholtz function of dry air,  $f^{\text{A}}(T, \rho^{\text{A}})$ , Eq. (3), expressed in terms of derivatives of the dimensionless quantities,  $\alpha^{\text{id}}(\tau, \delta)$  and  $\alpha^{\text{res}}(\tau, \delta)$ , with respect to the reduced variables,  $\tau = T_{\text{A}}^*/T$ ,  $\delta = \rho^{\text{A}}/\rho_{\text{A}}^*$ , as given in Table 9. The reducing temperature is  $T_{\text{A}}^* = 132.6312$  K, and the reducing density is  $\rho_{\text{A}}^* = 10.4477 \text{ mol dm}^{-3} \times M_{\text{A}}$ , where  $M_{\text{A}}$  is given in Table 1.

Derivative of $f^{\text{A}}(T, \rho^{\text{A}})$	Expression in terms of reduced quantities	Unit	Eq.
$f^{\text{A}}(T, \rho^{\text{A}})$	$f^{\text{A}} = \frac{R^{\text{L}}T}{M_{\text{A}}} [\alpha^{\text{id}} + \alpha^{\text{res}}]$	$\text{J kg}^{-1}$	(T27)
$f_T^{\text{A}}(T, \rho^{\text{A}})$	$\frac{R^{\text{L}}}{M_{\text{A}}} [\alpha^{\text{id}} + \alpha^{\text{res}} - (\alpha_{\tau}^{\text{id}} + \alpha_{\tau}^{\text{res}}) \tau]$	$\text{J kg}^{-1} \text{K}^{-1}$	(T28)
$f_{\rho^{\text{A}}}^{\text{A}}(T, \rho^{\text{A}})$	$\frac{R^{\text{L}}T}{M_{\text{A}}\rho_{\text{A}}^*} (\alpha_{\delta}^{\text{id}} + \alpha_{\delta}^{\text{res}})$	$\text{J m}^3 \text{kg}^{-2}$	(T29)
$f_{TT}^{\text{A}}(T, \rho^{\text{A}})$	$\frac{R^{\text{L}}\tau^2}{M_{\text{A}}T} (\alpha_{\tau\tau}^{\text{id}} + \alpha_{\tau\tau}^{\text{res}})$	$\text{J kg}^{-1} \text{K}^{-2}$	(T30)
$f_{T\rho^{\text{A}}}^{\text{A}}(T, \rho^{\text{A}})$	$\frac{R^{\text{L}}}{M_{\text{A}}\rho_{\text{A}}^*} [\alpha_{\delta}^{\text{id}} + \alpha_{\delta}^{\text{res}} - \alpha_{\tau\delta}^{\text{res}} \tau]$	$\text{J m}^3 \text{kg}^{-2} \text{K}^{-1}$	(T31)
$f_{\rho^{\text{A}}\rho^{\text{A}}}^{\text{A}}(T, \rho^{\text{A}})$	$\frac{R^{\text{L}}T}{M_{\text{A}}(\rho_{\text{A}}^*)^2} (\alpha_{\delta\delta}^{\text{id}} + \alpha_{\delta\delta}^{\text{res}})$	$\text{J m}^6 \text{kg}^{-3}$	(T32)

**TABLE 9** The partial derivatives of the ideal-gas part,  $\alpha^{\text{id}}$ , and the residual part,  $\alpha^{\text{res}}$ , of the Helmholtz function of dry air,  $f^{\text{A}}(T, \rho^{\text{A}})$ , Eq. (3). The coefficients are given in Tables 2 and 3.

Formula for the derivative	Eq.
$\alpha^{\text{id}} = \ln \delta + \sum_{i=1}^5 n_i^0 \tau^{i-4} + n_6^0 \tau^{1.5} + n_7^0 \ln \tau + n_8^0 \ln [1 - \exp(-n_{11}^0 \tau)]$ $+ n_9^0 \ln [1 - \exp(-n_{12}^0 \tau)] + n_{10}^0 \ln [2/3 + \exp(n_{13}^0 \tau)]$	(T33)
$\alpha_{\tau}^{\text{id}} = \sum_{i=1}^3 (i-4)n_i^0 \tau^{i-5} + n_5^0 + 1.5n_6^0 \tau^{0.5} + n_7^0 \tau^{-1} + n_8^0 n_{11}^0 [\exp(n_{11}^0 \tau) - 1]^{-1}$ $+ n_9^0 n_{12}^0 [\exp(n_{12}^0 \tau) - 1]^{-1} + n_{10}^0 n_{13}^0 [2 \exp(-n_{13}^0 \tau) / 3 + 1]^{-1}$	(T34)
$\alpha_{\delta}^{\text{id}} = 1 / \delta$	(T35)
$\alpha_{\tau\tau}^{\text{id}} = \sum_{i=1}^3 (i-4)(i-5)n_i^0 \tau^{i-6} + 0.75n_6^0 \tau^{-0.5} - n_7^0 \tau^{-2} - n_8^0 (n_{11}^0)^2 [\exp(n_{11}^0 \tau) - 1]^{-2} \exp(n_{11}^0 \tau)$ $- n_9^0 (n_{12}^0)^2 [\exp(n_{12}^0 \tau) - 1]^{-2} \exp(n_{12}^0 \tau) + 2n_{10}^0 (n_{13}^0)^2 [2 \exp(-n_{13}^0 \tau) / 3 + 1]^{-2} \exp(-n_{13}^0 \tau) / 3$	(T36)
$\alpha_{\tau\delta}^{\text{id}} = 0$	(T37)
$\alpha_{\delta\delta}^{\text{id}} = -1 / \delta^2$	(T38)
$\alpha^{\text{res}} = \sum_{k=1}^{10} n_k \delta^{i_k} \tau^{j_k} + \sum_{k=11}^{19} n_k \delta^{i_k} \tau^{j_k} \exp(-\delta^{l_k})$	(T39)
$\alpha_{\tau}^{\text{res}} = \sum_{k=1}^{10} j_k n_k \delta^{i_k} \tau^{j_k-1} + \sum_{k=11}^{19} j_k n_k \delta^{i_k} \tau^{j_k-1} \exp(-\delta^{l_k})$	(T40)
$\alpha_{\delta}^{\text{res}} = \sum_{k=1}^{10} i_k n_k \delta^{i_k-1} \tau^{j_k} + \sum_{k=11}^{19} n_k \delta^{i_k-1} (i_k - l_k \delta^{l_k}) \tau^{j_k} \exp(-\delta^{l_k})$	(T41)
$\alpha_{\tau\tau}^{\text{res}} = \sum_{k=1}^{10} j_k (j_k - 1) n_k \delta^{i_k} \tau^{j_k-2} + \sum_{k=11}^{19} j_k (j_k - 1) n_k \delta^{i_k} \tau^{j_k-2} \exp(-\delta^{l_k})$	(T42)
$\alpha_{\tau\delta}^{\text{res}} = \sum_{k=1}^{10} i_k j_k n_k \delta^{i_k-1} \tau^{j_k-1} + \sum_{k=11}^{19} j_k n_k \delta^{i_k-1} (i_k - l_k \delta^{l_k}) \tau^{j_k-1} \exp(-\delta^{l_k})$	(T43)
$\alpha_{\delta\delta}^{\text{res}} = \sum_{k=1}^{10} i_k (i_k - 1) n_k \delta^{i_k-2} \tau^{j_k}$ $+ \sum_{k=11}^{19} n_k \delta^{i_k-2} [i_k (i_k - 1) - (l_k + 2i_k - 1) l_k \delta^{l_k} + (l_k \delta^{l_k})^2] \tau^{j_k} \exp(-\delta^{l_k})$	(T44)

**TABLE 10** The cross-virial part  $f^{\text{mix}}(A, T, \rho)$ , Eq. (8), of the Helmholtz function of humid air, and its partial derivatives. The virial coefficients  $B^{\text{AW}}(T)$ ,  $C^{\text{AAW}}(T)$  and  $C^{\text{AWW}}(T)$  and their derivatives are given in Table 11.

	Formula for the derivative	Eq.
	$f^{\text{mix}} = \frac{2A(1-A)\rho RT}{M_A M_W} \left\{ B^{\text{AW}} + \frac{3\rho}{4} \left[ \frac{A}{M_A} C^{\text{AAW}} + \frac{(1-A)}{M_W} C^{\text{AWW}} \right] \right\}$	(T45)
	$f_A^{\text{mix}} = \frac{2\rho RT}{M_A M_W} \left\{ (1-2A)B^{\text{AW}} + \frac{3\rho}{4} \left[ \frac{A(2-3A)}{M_A} C^{\text{AAW}} + \frac{(1-A)(1-3A)}{M_W} C^{\text{AWW}} \right] \right\}$	(T46)
	$f_T^{\text{mix}} = \frac{2A(1-A)\rho R}{M_A M_W} \times \left\{ B^{\text{AW}} + TB_T^{\text{AW}} + \frac{3\rho}{4} \left[ \frac{A}{M_A} (C^{\text{AAW}} + TC_T^{\text{AAW}}) + \frac{(1-A)}{M_W} (C^{\text{AWW}} + TC_T^{\text{AWW}}) \right] \right\}$	(T47)
	$f_\rho^{\text{mix}} = \frac{A(1-A)RT}{M_A M_W} \left\{ 2B^{\text{AW}} + 3\rho \left[ \frac{A}{M_A} C^{\text{AAW}} + \frac{(1-A)}{M_W} C^{\text{AWW}} \right] \right\}$	(T48)
	$f_{AA}^{\text{mix}} = \frac{\rho RT}{M_A M_W} \left\{ -4B^{\text{AW}} + 3\rho \left[ \frac{(1-3A)}{M_A} C^{\text{AAW}} - \frac{(2-3A)}{M_W} C^{\text{AWW}} \right] \right\}$	(T49)
	$f_{AT}^{\text{mix}} = \frac{2\rho R}{M_A M_W} (1-2A)(B^{\text{AW}} + TB_T^{\text{AW}}) + \frac{3\rho^2 R}{2M_A M_W} \left[ \frac{A(2-3A)}{M_A} (C^{\text{AAW}} + TC_T^{\text{AAW}}) + \frac{(1-A)(1-3A)}{M_W} (C^{\text{AWW}} + TC_T^{\text{AWW}}) \right]$	(T50)
	$f_{A\rho}^{\text{mix}} = \frac{2RT}{M_A M_W} \left\{ (1-2A)B^{\text{AW}} + \frac{3}{2}\rho \left[ \frac{A(2-3A)}{M_A} C^{\text{AAW}} + \frac{(1-A)(1-3A)}{M_W} C^{\text{AWW}} \right] \right\}$	(T51)
	$f_{TT}^{\text{mix}} = \frac{2A(1-A)\rho R}{M_A M_W} \times \left\{ 2B_T^{\text{AW}} + TB_{TT}^{\text{AW}} + \frac{3\rho}{4} \left[ \frac{A}{M_A} (2C_T^{\text{AAW}} + TC_{TT}^{\text{AAW}}) + \frac{(1-A)}{M_W} (2C_T^{\text{AWW}} + TC_{TT}^{\text{AWW}}) \right] \right\}$	(T52)
	$f_{T\rho}^{\text{mix}} = \frac{2A(1-A)R}{M_A M_W} \times \left\{ B^{\text{AW}} + TB_T^{\text{AW}} + \frac{3\rho}{2} \left[ \frac{A}{M_A} (C^{\text{AAW}} + TC_T^{\text{AAW}}) + \frac{(1-A)}{M_W} (C^{\text{AWW}} + TC_T^{\text{AWW}}) \right] \right\}$	(T53)
	$f_{\rho\rho}^{\text{mix}} = \frac{3A(1-A)RT}{M_A M_W} \left[ \frac{A}{M_A} C^{\text{AAW}} + \frac{(1-A)}{M_W} C^{\text{AWW}} \right]$	(T54)

**TABLE 11** Definition of the cross-virial coefficients  $B^{\text{AW}}(T)$ ,  $C^{\text{AAW}}(T)$  and  $C^{\text{AWW}}(T)$  and their derivatives used in Table 10. The reducing factors are  $b^* = 10^{-6} \text{ m}^3 \text{ mol}^{-1}$  and  $c^* = 10^{-6} \text{ m}^6 \text{ mol}^{-2}$ . The reduced temperature is  $\bar{T} = T / (100 \text{ K})$  and the values of the coefficients  $a_i$ ,  $b_i$  and  $c_i$  are given in Table 4.

Derivative	Expression	Eq.
$B^{\text{AW}}$	$b^* \sum_{i=1}^3 c_i \bar{T}^{d_i}$	(T55)
$B_T^{\text{AW}} \equiv \frac{dB^{\text{AW}}}{dT}$	$b^* \frac{\bar{T}}{T} \sum_{i=1}^3 c_i d_i \bar{T}^{d_i-1}$	(T56)
$B_{TT}^{\text{AW}} \equiv \frac{d^2 B^{\text{AW}}}{dT^2}$	$b^* \frac{\bar{T}^2}{T^2} \sum_{i=1}^3 c_i d_i (d_i - 1) \bar{T}^{d_i-2}$	(T57)
$C^{\text{AAW}}$	$c^* \sum_{i=0}^4 a_i \bar{T}^{-i}$	(T58)
$C_T^{\text{AAW}} \equiv \frac{dC^{\text{AAW}}}{dT}$	$-c^* \frac{\bar{T}}{T} \sum_{i=1}^4 i a_i \bar{T}^{-i-1}$	(T59)
$C_{TT}^{\text{AAW}} \equiv \frac{d^2 C^{\text{AAW}}}{dT^2}$	$c^* \frac{\bar{T}^2}{T^2} \sum_{i=1}^4 i(i+1) a_i \bar{T}^{-i-2}$	(T60)
$C^{\text{AWW}}$	$-c^* \exp \left\{ \sum_{i=0}^3 b_i \bar{T}^{-i} \right\}$	(T61)
$C_T^{\text{AWW}} \equiv \frac{dC^{\text{AWW}}}{dT}$	$c^* \frac{\bar{T}}{T} \left( \sum_{i=1}^3 i b_i \bar{T}^{-i-1} \right) \exp \left\{ \sum_{i=0}^3 b_i \bar{T}^{-i} \right\}$	(T62)
$C_{TT}^{\text{AWW}} \equiv \frac{d^2 C^{\text{AWW}}}{dT^2}$	$-c^* \frac{\bar{T}^2}{T^2} \left\{ \left[ \sum_{i=1}^3 i(i+1) b_i \bar{T}^{-i-2} \right] + \left( \sum_{i=1}^3 i b_i \bar{T}^{-i-1} \right)^2 \right\} \exp \left\{ \sum_{i=0}^3 b_i \bar{T}^{-i} \right\}$	(T63)

**TABLE 12** Relations of the thermodynamic properties to the equation for the Helmholtz energy of humid air, Eq. (1), and its  $A$  derivative<sup>a</sup>, and conversion formulas related to the mole fraction,  $x_A$ , and the mass fraction,  $A$ , of dry air in humid air. The molar masses of air,  $M_A$ , and of water,  $M_W$ , are given in Table 1.

Property	Relation	Unit	Eq.
Relative chemical potential $\mu(A, T, \rho) = (\partial f^{\text{AV}} / \partial A)_{T, \rho}$	$\mu = f_A^{\text{AV}}$	$\text{J kg}^{-1}$	(T64)
Chemical potential of H <sub>2</sub> O $\mu_w(A, T, \rho) = g - A\mu$	$\mu_w = f^{\text{AV}} + \rho f_\rho^{\text{AV}} - A f_A^{\text{AV}}$	$\text{J kg}^{-1}$	(T65)
Humidity ratio	$(1/A) - 1$		(T66)
Relative humidity <sup>b, c</sup>	$RH = \frac{1 - x_A}{1 - x_A^{\text{sat}}}$		(T67)
Partial pressure of water	$p^{\text{vap}} = (1 - x_A)p$	Pa	(T68)
Molar mass of humid air	$\frac{1}{[(1 - A)/M_w] + (A/M_A)}$	$\text{kg mol}^{-1}$	(T69)
Mass fraction of dry air	$A = \frac{x_A}{1 - (1 - x_A)[1 - (M_w/M_A)]}$		(T70)
Mass fraction of water	$1 - A = \frac{1 - x_A}{1 - x_A[1 - (M_A/M_w)]}$		(T71)
Mole fraction of dry air	$x_A = \frac{A(M_w/M_A)}{1 - A[1 - (M_w/M_A)]}$		(T72)
Mole fraction of water	$1 - x_A = \frac{1 - A}{1 - A[1 - (M_w/M_A)]}$		(T73)

$$^a f_A^{\text{AV}} \equiv \left[ \frac{\partial f^{\text{AV}}}{\partial A} \right]_{T, \rho}, f_\rho^{\text{AV}} \equiv \left[ \frac{\partial f^{\text{AV}}}{\partial \rho} \right]_{A, T}$$

<sup>b</sup> standard definition of relative humidity as adopted for example by the World Meteorological Organization (WMO) [*Guide to Meteorological Instruments and Methods of Observation*, 7th ed. (WMO, Geneva, 2008), p. I.4-27]. Other definitions are sometimes used which result in slightly different values.

<sup>c</sup>  $1 - x_A^{\text{sat}}$  is computed from Eq. (T73) at  $A = A^{\text{sat}}$

## 6 Range of Validity and Brief Discussion

The equation of state, Eq. (1), is valid for humid air within the temperature and pressure range

$$193 \text{ K} \leq T \leq 473 \text{ K} \text{ and } 0 < p \leq 5 \text{ MPa.}$$

The pressure is computed from Eq. (T1). All validity regions of the formulas combined in Eq. (1), including the Helmholtz functions of water vapor and dry air, as well as the cross-virial coefficients, overlap only in this range. The separate ranges of validity of the individual components are wider, for some of them significantly. Therefore, Eq. (1) will also provide reasonable results outside of the  $T$ - $p$  range given above if one component dominates numerically in Eq. (1) and is evaluated within its particular range of validity.

The air fraction  $A$  can take any value between 0 and 1 provided that the partial pressure of water,  $p^{\text{vap}}$ , Eq. (T68), does not exceed its saturation value, i.e.,

$$0 < A < 1 \text{ and } A^{\text{sat}}(T, p) \leq A.$$

The exact value of the air fraction  $A^{\text{sat}}(T, p)$  of saturated humid air is given by equal chemical potentials of water in humid air and of either liquid water, Eq. (12), if the temperature is above the freezing point, or of ice, Eq. (13), if the temperature is below the freezing point. At low density, the partial pressure  $p^{\text{vap, sat}}$  of saturated humid air can be estimated by either the correlation function for the vapor pressure,  $p^{\text{sat}}(T)$ , of liquid water [12], or for the sublimation pressure,  $p^{\text{subl}}(T)$ , of ice [13], to obtain  $A^{\text{sat}}(T, p) = (p - p^{\text{vap, sat}}) / [p - p^{\text{vap, sat}}(1 - M_{\text{w}} / M_{\text{A}})]$ , from Eq. (T70) as a sufficient practical approximation.

This formulation for the thermodynamic properties of humid air was developed in cooperation with the SCOR/IAPSO Working Group 127 on Thermodynamics and Equation of State of Seawater.

## 7 Estimates of Uncertainty

Here, estimated combined standard uncertainties  $u_c$  [14] are reported, from which expanded uncertainties  $U = k u_c$  can be obtained by multiplying with the coverage factor  $k = 2$ , corresponding to a 95% confidence level. The term ‘‘uncertainty’’ used in the following refers to combined standard uncertainties or to relative combined standard uncertainties.

Uncertainty estimates are not directly available for the full Helmholtz function of humid air, Eq. (1), or the properties derived from it. Rather, comprehensive uncertainty estimates are available only for the formulations of its parts, dry air [5] and water vapor [2]. In the range considered here, the dry-air uncertainty of the density is 0.1%, of the sound speed is 0.2% and of the heat capacity is 1%.

The uncertainties of the second cross-virial coefficient  $B^{\text{AW}}(T)$  and of its enthalpy coefficient,  $B^{\text{AW}} - T dB^{\text{AW}}/dT$ , as functions of the temperature are tabulated in [6]. They decrease monotonically from about 8 and 24  $\text{cm}^3 \text{ mol}^{-1}$  at 150 K, to 2 and 5  $\text{cm}^3 \text{ mol}^{-1}$  at 300 K, and to 0.3 and 0.5  $\text{cm}^3 \text{ mol}^{-1}$ , respectively, at 2000 K. The agreement of values computed from Eq. (T68) with experimental data for the partial pressure of water in saturated air is better than 0.5% up to densities of 50  $\text{kg m}^{-3}$  and about 1% at 100  $\text{kg m}^{-3}$  [1].

## 8 Computer-Program Verification

To assist the user in computer-program verification, Tables 13, 14 and 15 with test values are given for specified parameter values of saturated air. They contain values for the specific Helmholtz energy,  $f^{AV}(A, T, \rho)$ , and its parts together with their first and second derivatives, as well as some thermodynamic properties.

## 9 References

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**TABLE 13** Numerical check values for the Helmholtz function  $f^{\text{AV}}$  and its derivatives, Table 6, for saturated air,  $A = A^{\text{sat}}$ , with respect to ice at 200 K, and with respect to liquid water at 300 and 400 K. The numerical functions evaluated here at given points  $(A, T, \rho)$  are defined in Tables 5, 6 and 12.

Quantity	Value	Value	Value	Unit
$A$	0.892 247 719	0.977 605 798	0.825 565 291	$\text{kg kg}^{-1}$
$T$	200	300	400	K
$\rho$	$0.163\,479\,657 \times 10^{-4}$	$0.114\,614\,216 \times 10$	$0.793\,354\,063 \times 10$	$\text{kg m}^{-3}$
$p$	0.999 999 998	$0.100\,000\,000 \times 10^6$	$0.100\,000\,000 \times 10^7$	Pa
$f^{\text{AV}}$	$-0.682\,093\,392 \times 10^6$	$-0.927\,718\,178 \times 10^5$	$0.240\,345\,570 \times 10^5$	$\text{J kg}^{-1}$
$(\partial f^{\text{AV}}/\partial A)_{T,\rho}$	$-0.572\,680\,404 \times 10^6$	$-0.263\,453\,864 \times 10^3$	$0.311\,096\,733 \times 10^6$	$\text{J kg}^{-1}$
$(\partial f^{\text{AV}}/\partial T)_{A,\rho}$	$-0.405\,317\,966 \times 10^4$	$-0.296\,711\,481 \times 10^3$	$-0.106\,891\,931 \times 10^4$	$\text{J kg}^{-1} \text{K}^{-1}$
$(\partial f^{\text{AV}}/\partial \rho)_{A,T}$	$0.374\,173\,101 \times 10^{10}$	$0.761\,242\,496 \times 10^5$	$0.158\,878\,781 \times 10^5$	$\text{J m}^3 \text{kg}^{-2}$
$(\partial^2 f^{\text{AV}}/\partial A^2)_{T,\rho}$	$0.920\,967\,684 \times 10^6$	$0.624\,886\,233 \times 10^7$	$0.113\,786\,423 \times 10^7$	$\text{J kg}^{-1}$
$(\partial^2 f^{\text{AV}}/\partial A \partial T)_{\rho}$	$0.915\,653\,743 \times 10^4$	$0.822\,733\,446 \times 10^4$	$0.702\,631\,471 \times 10^4$	$\text{J kg}^{-1} \text{K}^{-1}$
$(\partial^2 f^{\text{AV}}/\partial A \partial \rho)_{T,\rho}$	$-0.213\,442\,099 \times 10^{10}$	$-0.450\,004\,399 \times 10^5$	$-0.727\,972\,651 \times 10^4$	$\text{J m}^3 \text{kg}^{-2}$
$(\partial^2 f^{\text{AV}}/\partial T^2)_{A,\rho}$	$-0.394\,011\,921 \times 10$	$-0.244\,742\,952 \times 10$	$-0.222\,449\,294 \times 10$	$\text{J kg}^{-1} \text{K}^{-2}$
$(\partial^2 f^{\text{AV}}/\partial T \partial \rho)_{A,\rho}$	$0.187\,087\,034 \times 10^8$	$0.254\,456\,302 \times 10^3$	$0.414\,350\,772 \times 10^2$	$\text{J m}^3 \text{kg}^{-2} \text{K}^{-1}$
$(\partial^2 f^{\text{AV}}/\partial \rho^2)_{A,T}$	$-0.228\,880\,603 \times 10^{15}$	$-0.664\,465\,525 \times 10^5$	$-0.201\,886\,184 \times 10^4$	$\text{J m}^6 \text{kg}^{-3}$
$h$	$0.189\,712\,231 \times 10^6$	$0.834\,908\,383 \times 10^5$	$0.577\,649\,408 \times 10^6$	$\text{J kg}^{-1}$
$g$	$-0.620\,923\,701 \times 10^6$	$-0.552\,260\,595 \times 10^4$	$0.150\,081\,684 \times 10^6$	$\text{J kg}^{-1}$
$s$	$0.405\,317\,966 \times 10^4$	$0.296\,711\,481 \times 10^3$	$0.106\,891\,931 \times 10^4$	$\text{J kg}^{-1} \text{K}^{-1}$
$\mu_{\text{w}}$	$-0.109\,950\,917 \times 10^6$	$-0.526\,505\,193 \times 10^4$	$-0.106\,748\,981 \times 10^6$	$\text{J kg}^{-1}$
$c_p$	$0.109\,387\,397 \times 10^4$	$0.102\,681\,324 \times 10^4$	$0.123\,552\,454 \times 10^4$	$\text{J kg}^{-1} \text{K}^{-1}$
$w$	$0.291\,394\,959 \times 10^3$	$0.349\,234\,196 \times 10^3$	$0.416\,656\,820 \times 10^3$	$\text{m s}^{-1}$

**TABLE 14** Numerical check values for the dry-air part,  $f^A$ , and the water-vapor part,  $f^V$ , of the Helmholtz function  $f^{AV}$  and its derivatives, Table 6, for saturated air,  $A = A^{\text{sat}}$ , with respect to ice at 200 K, and with respect to liquid water at 300 and 400 K, corresponding to Table 13. The numerical functions evaluated here at given points  $(A, T, \rho)$  are defined in Tables 7 and 8.

Quantity	Value	Value	Value	Unit
$A$	0.892 247 719	0.977 605 798	0.825 565 291	$\text{kg kg}^{-1}$
$T$	200	300	400	K
$\rho$	$0.163\,479\,657 \times 10^{-4}$	$0.114\,614\,216 \times 10$	$0.793\,354\,063 \times 10$	$\text{kg m}^{-3}$
$\rho^A = A \rho$	$0.145\,864\,351 \times 10^{-4}$	$0.112\,047\,522 \times 10$	$0.654\,965\,578 \times 10$	$\text{kg m}^{-3}$
$f^A$	$-0.740\,041\,144 \times 10^6$	$-0.916\,103\,453 \times 10^5$	$0.895\,561\,286 \times 10^5$	$\text{J kg}^{-1}$
$(\partial f^A / \partial T)_{\rho^A}$	$-0.304\,774\,177 \times 10^4$	$-0.108\,476\,220 \times 10^3$	$0.193\,271\,394 \times 10^3$	$\text{J kg}^{-1} \text{K}^{-1}$
$(\partial f^A / \partial \rho^A)_T$	$0.393\,583\,654 \times 10^{10}$	$0.768\,326\,795 \times 10^5$	$0.175\,560\,114 \times 10^5$	$\text{J m}^3 \text{kg}^{-2}$
$(\partial^2 f^A / \partial T^2)_{\rho^A}$	$-0.357\,677\,878 \times 10$	$-0.239\,319\,940 \times 10$	$-0.181\,809\,877 \times 10$	$\text{J kg}^{-1} \text{K}^{-2}$
$\partial^2 f^A / \partial T \partial \rho^A$	$0.196\,791\,837 \times 10^8$	$0.256\,683\,306 \times 10^3$	$0.442\,769\,673 \times 10^2$	$\text{J m}^3 \text{kg}^{-2} \text{K}^{-1}$
$[\partial^2 f^A / \partial (\rho^A)^2]_T$	$-0.269\,828\,549 \times 10^{15}$	$-0.685\,917\,373 \times 10^5$	$-0.267\,635\,928 \times 10^4$	$\text{J m}^6 \text{kg}^{-3}$
$\rho^V = (1 - A) \rho$	$0.176\,153\,059 \times 10^{-5}$	$0.256\,669\,391 \times 10^{-1}$	$0.138\,388\,485 \times 10$	$\text{kg m}^{-3}$
$f^V$	$-0.202\,254\,351 \times 10^6$	$-0.143\,157\,426 \times 10^6$	$-0.285\,137\,534 \times 10^6$	$\text{J kg}^{-1}$
$(\partial f^V / \partial T)_{\rho^V}$	$-0.123\,787\,544 \times 10^5$	$-0.851\,598\,213 \times 10^4$	$-0.705\,288\,048 \times 10^4$	$\text{J kg}^{-1} \text{K}^{-1}$
$(\partial f^V / \partial \rho^V)_T$	$0.523\,995\,674 \times 10^{11}$	$0.538\,480\,619 \times 10^7$	$0.129\,645\,039 \times 10^6$	$\text{J m}^3 \text{kg}^{-2}$
$(\partial^2 f^V / \partial T^2)_{\rho^V}$	$-0.694\,877\,601 \times 10$	$-0.480\,817\,011 \times 10$	$-0.411\,710\,659 \times 10$	$\text{J kg}^{-1} \text{K}^{-2}$
$\partial^2 f^V / \partial T \partial \rho^V$	$0.262\,001\,885 \times 10^9$	$0.181\,489\,502 \times 10^5$	$0.361\,784\,086 \times 10^3$	$\text{J m}^3 \text{kg}^{-2} \text{K}^{-1}$
$[\partial^2 f^V / \partial (\rho^V)^2]_T$	$-0.297\,466\,671 \times 10^{17}$	$-0.210\,184\,992 \times 10^9$	$-0.965\,539\,462 \times 10^5$	$\text{J m}^6 \text{kg}^{-3}$

**TABLE 15** Numerical check values for the cross-virial part,  $f^{\text{mix}}$ , and the cross-virial coefficients,  $B^{\text{AW}}$ ,  $C^{\text{AAW}}$ ,  $C^{\text{AWW}}$ , of the Helmholtz function  $f^{\text{AV}}$  and its derivatives, Table 6, for saturated air,  $A = A^{\text{sat}}$ , with respect to ice at 200 K, and with respect to liquid water at 300 and 400 K, corresponding to Table 13. The numerical functions evaluated here at given points  $(A, T, \rho)$  are defined in Tables 10 and 11.

Quantity	Value	Value	Value	Unit
$A$	0.892 247 719	0.977 605 798	0.825 565 291	$\text{kg kg}^{-1}$
$T$	200	300	400	K
$\rho$	$0.163\ 479\ 657 \times 10^{-4}$	$0.114\ 614\ 216 \times 10$	$0.793\ 354\ 063 \times 10$	$\text{kg m}^{-3}$
$f^{\text{mix}}$	$-0.786\ 231\ 899 \times 10^{-3}$	$-0.711\ 677\ 596 \times 10$	$-0.161\ 991\ 543 \times 10^3$	$\text{J kg}^{-1}$
$(\partial f^{\text{mix}}/\partial A)_{T,\rho}$	$0.641\ 550\ 398 \times 10^{-2}$	$0.311\ 844\ 020 \times 10^3$	$0.831\ 044\ 354 \times 10^3$	$\text{J kg}^{-1}$
$(\partial f^{\text{mix}}/\partial T)_{A,\rho}$	$0.456\ 438\ 658 \times 10^{-5}$	$0.441\ 247\ 962 \times 10^{-1}$	$0.178\ 968\ 942 \times 10$	$\text{J kg}^{-1} \text{K}^{-1}$
$(\partial f^{\text{mix}}/\partial \rho)_{A,T}$	$-0.480\ 937\ 188 \times 10^2$	$-0.623\ 030\ 392 \times 10$	$-0.223\ 330\ 257 \times 10^2$	$\text{J m}^3 \text{kg}^{-2}$
$(\partial^2 f^{\text{mix}}/\partial A^2)_{T,\rho}$	$0.163\ 552\ 956 \times 10^{-1}$	$0.534\ 234\ 669 \times 10^3$	$0.135\ 814\ 949 \times 10^4$	$\text{J kg}^{-1}$
$(\partial^2 f^{\text{mix}}/\partial A \partial T)_{\rho}$	$-0.372\ 455\ 576 \times 10^{-4}$	$-0.195\ 073\ 372 \times 10$	$-0.916\ 854\ 756 \times 10$	$\text{J kg}^{-1} \text{K}^{-1}$
$(\partial^2 f^{\text{mix}}/\partial A \partial \rho)_T$	$0.392\ 437\ 132 \times 10^3$	$0.274\ 155\ 508 \times 10^3$	$0.125\ 834\ 930 \times 10^3$	$\text{J m}^3 \text{kg}^{-2}$
$(\partial^2 f^{\text{mix}}/\partial T^2)_{A,\rho}$	$-0.378\ 875\ 706 \times 10^{-7}$	$-0.148\ 783\ 177 \times 10^{-3}$	$-0.536\ 741\ 578 \times 10^{-2}$	$\text{J kg}^{-1} \text{K}^{-2}$
$(\partial^2 f^{\text{mix}}/\partial T \partial \rho)_A$	0.279 209 778	$0.390\ 012\ 443 \times 10^{-1}$	0.249 580 143	$\text{J m}^3 \text{kg}^{-2} \text{K}^{-1}$
$(\partial^2 f^{\text{mix}}/\partial \rho^2)_{A,T}$	$-0.192\ 042\ 557 \times 10^2$	$-0.365\ 975\ 429 \times 10^{-1}$	-0.482 623 664	$\text{J m}^6 \text{kg}^{-3}$
$B^{\text{AW}}$	$-0.784\ 874\ 278 \times 10^{-4}$	$-0.295\ 672\ 747 \times 10^{-4}$	$-0.100\ 804\ 610 \times 10^{-4}$	$\text{m}^3 \text{mol}^{-1}$
$dB^{\text{AW}}/dT$	$0.848\ 076\ 624 \times 10^{-6}$	$0.280\ 097\ 360 \times 10^{-6}$	$0.135\ 021\ 228 \times 10^{-6}$	$\text{m}^3 \text{mol}^{-1} \text{K}^{-1}$
$d^2 B^{\text{AW}}/dT^2$	$-0.122\ 622\ 146 \times 10^{-7}$	$-0.242\ 599\ 241 \times 10^{-8}$	$-0.839\ 901\ 729 \times 10^{-9}$	$\text{m}^3 \text{mol}^{-1} \text{K}^{-2}$
$C^{\text{AAW}}$	$0.105\ 493\ 575 \times 10^{-8}$	$0.801\ 977\ 741 \times 10^{-9}$	$0.672\ 018\ 172 \times 10^{-9}$	$\text{m}^6 \text{mol}^{-2}$
$dC^{\text{AAW}}/dT$	$-0.152\ 535\ 000 \times 10^{-11}$	$-0.196\ 103\ 457 \times 10^{-11}$	$-0.812\ 416\ 406 \times 10^{-12}$	$\text{m}^6 \text{mol}^{-2} \text{K}^{-1}$
$d^2 C^{\text{AAW}}/dT^2$	$-0.113\ 436\ 375 \times 10^{-12}$	$0.170\ 055\ 638 \times 10^{-13}$	$0.683\ 147\ 461 \times 10^{-14}$	$\text{m}^6 \text{mol}^{-2} \text{K}^{-2}$
$C^{\text{AWW}}$	$-0.349\ 872\ 634 \times 10^{-5}$	$-0.115\ 552\ 784 \times 10^{-6}$	$-0.200\ 806\ 021 \times 10^{-7}$	$\text{m}^6 \text{mol}^{-2}$
$dC^{\text{AWW}}/dT$	$0.188\ 025\ 052 \times 10^{-6}$	$0.261\ 363\ 278 \times 10^{-8}$	$0.274\ 535\ 403 \times 10^{-9}$	$\text{m}^6 \text{mol}^{-2} \text{K}^{-1}$
$d^2 C^{\text{AWW}}/dT^2$	$-0.124\ 996\ 856 \times 10^{-7}$	$-0.751\ 334\ 582 \times 10^{-10}$	$-0.491\ 763\ 910 \times 10^{-11}$	$\text{m}^6 \text{mol}^{-2} \text{K}^{-2}$