The International Association for the Properties of Water and Steam

Stockholm, Sweden
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Guideline on a Virial Equation for the Fugacity of H$_2$O in Humid Air

This Guideline has been authorized by the International Association for the Properties of Water and Steam (IAPWS) at its meeting in Stockholm, Sweden, 28 June – 3 July, 2015. The members of IAPWS are: Britain and Ireland, Canada, the Czech Republic, Germany, Japan, Russia, Scandinavia (Denmark, Finland, Norway, Sweden), and the United States, plus Associate Members Argentina & Brazil, Australia, France, Greece, New Zealand, and Switzerland. The President at the time of adoption of this document is Dr. David Guzonas of Canada.

Summary

The correlation provided in this Guideline is a virial expansion for the fugacity of water vapor in humid air as a function of vapor mole fraction, temperature and pressure; details can be found in the article "Virial Approximation of the TEOS-10 Equation for the Fugacity of Water in Humid Air" by R. Feistel *et al.* [1]. This equation is consistent with the IAPWS "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" [2].

This Guideline contains 11 pages, including this cover page.

Further information about this Guideline and other documents issued by IAPWS can be obtained from the Executive Secretary of IAPWS (Dr. R.B. Dooley, bdooley@structint.com) or from http://www.iapws.org.

Contents

1 Nomenclature

Symbol	Physical quantity	Unit
A_{55}, A_{56}	Coefficients of the virial coefficients B^{WW}, C^{WWW}, Table 2	
$a_0 \dots a_4$	Coefficients of the third virial coefficient C^{AAW}, Table 3	
a_{55}, a_{56}	Coefficients of the virial coefficients B^{WW}, C^{WWW}, Table 2	
B_{55}, B_{56}	Coefficients of the virial coefficients B^{WW}, C^{WWW}, Table 2	
B^{AA}, B^{AW}, B^{WW}	Second virial coefficients, Eqs. (5), (7), (10)	$\mathrm{m^3\,mol^{-1}}$
$b_0 \dots b_3$	Coefficients of the third virial coefficient C^{AWW}, Table 3	
b_{55}, b_{56}	Coefficients of the virial coefficients B^{WW}, C^{WWW}, Table 2	
$b*$	Reducing factor, $b* = 10^{-6}\,\mathrm{m^3\,mol^{-1}}$	$\mathrm{m^3\,mol^{-1}}$
C_{55}, C_{56}	Coefficients of the virial coefficients B^{WW}, C^{WWW}, Table 2	
$C^{AAA}, C^{AAW},$ C^{AAW}, C^{WWW}	Third virial coefficients, Eqs. (6), (8), (9), (11)	$\mathrm{m^6\,mol^{-2}}$
$c_1 \dots c_3$	Coefficients of the second virial coefficient B^{AW}, Table 3	
$c*$	Reducing factor, $c* = 10^{-6}\,\mathrm{m^6\,mol^{-2}}$	$\mathrm{m^6\,mol^{-2}}$
D_{55}, D_{56}	Coefficients of the virial coefficients B^{WW}, C^{WWW}, Table 2	
$d_1 \dots d_3$	Coefficients of the second virial coefficient B^{AW}, Table 3	
f_V	Fugacity of water vapor in humid air, Eqs. (1), (2)	Pa
i	Summation index	
$j_1 \dots j_{18}$	Coefficients of the virial coefficients B^{AA}, C^{AAA}, Table 4	
k	Uncertainty coverage factor	
M_W	Molar mass of water, $M_W = 0.018\ 015\ 268\ \mathrm{kg\,mol^{-1}}$	$\mathrm{kg\,mol^{-1}}$

Symbol	Physical quantity	Unit
$n_1...n_{18}$	Coefficients of the virial coefficients B^{AA}, C^{AAA}, Table 4	
$n_1...n_{56}$	Coefficients of the virial coefficients B^{WW}, C^{WWW}, Tables 1, 2	
p	Absolute pressure	Pa
R	Molar gas constant, $R = 8.314\,4621$ J mol^{-1} K^{-1}	J mol^{-1} K^{-1}
S_{BA}, S_{BW}, S_{CW}	Sets of summation indices, Eqs. (5), (6), (10)	
T	Absolute temperature (ITS-90)	K
$\bar{T}$	Reduced temperature, $\bar{T} = T/(100\,\text{K})$	
T_a	Reducing temperature, $T_\text{a} = 132.6312$ K	K
T_c	Critical temperature of water, $T_\text{c} = 647.096$ K	K
$t_1...t_{26}$	Coefficients of the virial coefficients B^{WW}, C^{WWW}, Tables 1, 2	
U	Expanded uncertainty, coverage factor $k = 2$	
x	Mole fraction of water vapor in humid air	mol mol^{-1}
x^{sat}	Mole fraction of water vapor in saturated humid air	mol mol^{-1}
β	Auxiliary function, Eqs. (2), (3)	m^3 mol^{-1}
β_{55}, β_{56}	Coefficients of the virial coefficients B^{WW}, C^{WWW}, Table 2	
γ	Auxiliary function, Eqs. (2), (4)	m^6 mol^{-2}
θ_{55}, θ_{56}	Auxiliary functions, $\theta_i \equiv A_i + 1 - \tau$, Eqs. (5), (6), (8)	
μ_W	Chemical potential of water in humid air	J mol^{-1}
μ_W^{id}	Chemical potential of water in humid air, ideal-gas part	J mol^{-1}
ρ_a	Reducing molar density of air, $\rho_\text{a} = 10.4477$ mol dm^{-3}	mol dm^{-3}
ρ_c	Critical mass density of water, $\rho_\text{c} = 322$ kg m^{-3}	kg m^{-3}
τ	Reduced reciprocal temperature, $\tau = T_\text{c}/T$, Eqs. (5), (6)	
τ	Reduced reciprocal temperature, $\tau = T_\text{a}/T$, Eqs. (10), (11)	

2 Introductory Remarks

The equation of state for humid air described in the IAPWS Guideline [2] is in the form of the specific Helmholtz energy as a function of mass density, temperature, and mass fraction of dry air. It only indirectly permits the calculation of the mole-based chemical potential of water in humid air, μ_W, and its ideal-gas limit, μ_W^{id}, as functions of the mole fraction of water vapor, x, pressure, p, and temperature, T. The fugacity of water vapor in humid air, f_V, expresses the residual part of that chemical potential,

$$\mu_\text{W} = \mu_\text{W}^{\text{id}} + RT \ln \frac{f_\text{V}}{xp}, \tag{1}$$

where R is the molar gas constant. In this Guideline, consistent with Eq. (1), a virial expansion is provided as an explicit analytical approximation formula for a more convenient evaluation of f_V at a given x between zero and saturation, T between −80 °C and 200 °C, and p up to 5 MPa. The correlation equations reported here for the required second and third virial coefficients for water-water, water-air, and air-air interactions are extracted from the IAPWS Guideline [2].

The Guideline is intended to be used for the description of humid air in geophysical, industrial, or metrological applications.

3 The Fugacity Equation

The fugacity equation is given here as a truncated series expansion with respect to the pressure, in terms of the second and third virial and cross virial coefficients of humid air. It is expressed as a function of water-vapor mole fraction x, temperature T, and pressure p. The temperature values are based on the temperature scale ITS-90 [3]. The fugacity of water vapor in humid air, f_V, takes the form

$$f_V(x,T,p) = xp \exp\left\{ \beta(x,T)\frac{p}{RT} + \frac{1}{2}\gamma(x,T)\left(\frac{p}{RT}\right)^2 \right\}. \tag{2}$$

The molar gas constant has the value $R = 8.314\ 462\ 1$ J mol^{-1} K^{-1} [4,5]. The auxiliary functions $\beta(x,T)$ and $\gamma(x,T)$ represent certain combinations of virial coefficients [1] and are defined by

$$\beta(x,T) \equiv x(2-x)B^{WW}(T) + (1-x)^2\left[2B^{AW}(T) - B^{AA}(T)\right] \tag{3}$$

and

$$\begin{aligned}
\gamma(x,T) \equiv\ & x^2(3-2x)C^{WWW}(T) \\
& + (1-x)^2\left[6xC^{AWW}(T) + 3(1-2x)C^{AAW}(T) - 2(1-x)C^{AAA}(T)\right] \\
& + \left[x^2B^{WW}(T) + 2x(1-x)B^{AW}(T) + (1-x)^2 B^{AA}(T)\right] \\
& \times \left[x(3x-4)B^{WW}(T) + 2(1-x)(3x-2)B^{AW}(T) + 3(1-x)^2 B^{AA}(T)\right].
\end{aligned} \tag{4}$$

Equation (2) is a mathematically rigorous expression in terms of second and third virial and cross virial coefficients of humid air. The formulation given by Eqs. (2)-(4) remains valid for D$_2$O or other isotopic compositions of water when the virial coefficients are chosen accordingly. With appropriate changes in virial coefficients, it can also be applied for different chemical and isotopic compositions of dry air, and for water in any humid gas.

4 Equations for Virial Coefficients

The equations given in this section for the virial coefficients appearing in Eqs. (2)-(4) are taken from Ref. [2] in order to be consistent with that IAPWS Guideline. If improved functions

are developed in the future for any of the coefficients, they may be substituted without changing the remainder of the calculation.

TABLE 1 Coefficients of the virial coefficients $B^{WW}(T)$ and $C^{WWW}(T)$ of water, Eqs. (5), (6)

i	t_i	n_i
1	−0.5	$0.125\ 335\ 479\ 355\ 23 \times 10^{-1}$
2	0.875	$0.789\ 576\ 347\ 228\ 28 \times 10$
3	1	$-0.878\ 032\ 033\ 035\ 61 \times 10$
4	0.5	$0.318\ 025\ 093\ 454\ 18$
5	0.75	$-0.261\ 455\ 338\ 593\ 58$
8	4	$-0.668\ 565\ 723\ 079\ 65$
9	6	$0.204\ 338\ 109\ 509\ 65$
10	12	$-0.662\ 126\ 050\ 396\ 87 \times 10^{-4}$
11	1	$-0.192\ 327\ 211\ 560\ 02$
12	5	$-0.257\ 090\ 430\ 034\ 38$
23	7	$-0.107\ 936\ 009\ 089\ 32$
24	1	$0.176\ 114\ 910\ 087\ 52 \times 10^{-1}$
25	9	$0.221\ 322\ 951\ 675\ 46$
26	10	$-0.402\ 476\ 697\ 635\ 28$

TABLE 2 Coefficients of the virial coefficients $B^{WW}(T)$ and $C^{WWW}(T)$ of water, Eqs. (5), (6)

i	a_i	b_i	B_i	n_i	C_i	D_i	A_i	β_i
55	3.5	0.85	0.2	$-0.148\ 746\ 408\ 567\ 24$	28	700	0.32	0.3
56	3.5	0.95	0.2	$0.318\ 061\ 108\ 784\ 44$	32	800	0.32	0.3

The second virial coefficient of water, $B^{\mathrm{WW}}(T)$,

$$B^{\mathrm{WW}} = \frac{M_{\mathrm{W}}}{\rho_{\mathrm{c}}}\left\{\sum_{i \in S_{\mathrm{BW}}} n_i \tau^{t_i} + \sum_{i=55}^{56} n_i\left[\theta_i^2 + B_i\right]^{b_i} \exp\left[-C_i - D_i(\tau-1)^2\right]\right\},$$ (5)

and the third virial coefficient of water, $C^{\mathrm{WWW}}(T)$,

$$C^{\mathrm{WWW}} = 2\left(\frac{M_{\mathrm{W}}}{\rho_{\mathrm{c}}}\right)^2\left\{\sum_{i \in S_{\mathrm{CW}}} n_i \tau^{t_i} - \sum_{i=8}^{10} n_i \tau^{t_i}\right.$$
$$\left. + 2\sum_{i=55}^{56} n_i\left[C_i\left(\theta_i^2 + B_i\right) - b_i\left(\frac{A_i \theta_i}{\beta_i} + B_i a_i\right)\right]\left(\theta_i^2 + B_i\right)^{b_i-1} \exp\left[-C_i - D_i(\tau-1)^2\right]\right\},$$ (6)

of IAPWS-95 [6] are given in [1] as analytical expressions. Here, $M_{\mathrm{W}} = 0.018\,015\,268$ kg mol^{-1} is the molar mass of water [4], the critical mass density is $\rho_{\mathrm{c}} = 322$ kg m^{-3}, the reduced reciprocal temperature is $\tau = T_{\mathrm{c}}/T$, and the critical temperature is $T_{\mathrm{c}} = 647.096$ K. The sets of indices over which the first sums in Eq. (5) and Eq. (6) run, respectively, are $S_{\mathrm{BW}} = \{1,2,3,8,9,10,23\}$ and $S_{\mathrm{CW}} = \{4,5,11,12,24,25,26\}$; they relate to the original coefficients in [6] and in Table 1. As an abbreviation, $\theta_i \equiv A_i + 1 - \tau$ is used. The coefficients A_i, a_i, B_i, b_i, C_i, D_i, n_i, t_i, and β_i of Eqs. (5) and (6) are given in Tables 1 and 2.

TABLE 3 Coefficients of the cross virial coefficients $B^{\mathrm{AW}}(T)$, $C^{\mathrm{AAW}}(T)$ and $C^{\mathrm{AWW}}(T)$, Eqs. (7)-(9)

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	$-0.319\,317 \times 10^{-1}$			

The second air-water cross virial coefficient, $B^{\mathrm{AW}}(T)$, is given by [7] as

$$B^{\mathrm{AW}}(T) = b*\sum_{i=1}^{3} c_i \bar{T}^{d_i} .$$ (7)

The coefficients of Eq. (7) are given in Table 3. The reducing factor is $b* = 10^{-6}\,\mathrm{m}^3\,\mathrm{mol}^{-1}$; the reduced temperature is $\bar{T} = T/(100\,\mathrm{K})$.

The third air-water cross virial coefficients $C^{\mathrm{AAW}}(T)$ and $C^{\mathrm{AWW}}(T)$ are estimated in [8], in the form

$$C^{\mathrm{AAW}}(T) = c * \sum_{i=0}^{4} a_i \overline{T}^{-i} \tag{8}$$

$$C^{\mathrm{AWW}}(T) = -c * \exp\left\{\sum_{i=0}^{3} b_i \overline{T}^{-i}\right\}. \tag{9}$$

The coefficients of Eqs. (8) and (9) are given in Table 3. The reducing factor is $c* = 10^{-6}\,\mathrm{m}^6\,\mathrm{mol}^{-2}$; the reduced temperature is $\overline{T} = T / (100\,\mathrm{K})$.

The second virial coefficient of dry air, $B^{\mathrm{AA}}(T)$,

$$B^{\mathrm{AA}} = \frac{1}{\rho_a} \sum_{i \in S_{\mathrm{BA}}} n_i \tau^{j_i}, \tag{10}$$

and the third virial coefficient of dry air, $C^{\mathrm{AAA}}(T)$,

$$C^{\mathrm{AAA}} = \frac{2}{\rho_a^2}\left(n_4 - n_{11}\tau^{j_{11}}\right), \tag{11}$$

are given in [1]. Here, the reducing molar density is $\rho_a = 10.4477\,\mathrm{mol\,dm}^{-3}$, the reduced reciprocal temperature is $\tau = T_a/T$, and the reducing temperature is $T_a = 132.6312\,\mathrm{K}$. In Eq. (10), the set of indices over which the sum is executed is $S_{\mathrm{BA}} = \{1,2,3,11,15,18\}$ and relates to the coefficients in the IAPWS Guideline [2] and in Table 4, where the coefficients j_i and n_i of Eqs. (10) and (11) are given.

TABLE 4 Coefficients of the virial coefficients $B^{\mathrm{AA}}(T)$ and $C^{\mathrm{AAA}}(T)$ of dry air, Eqs. (10), (11)

i	j_i	n_i
1	0	0.118 160 747 229
2	0.33	0.713 116 392 079
3	1.01	−0.161 824 192 067 × 10
4	0	0.714 140 178 971 × 10^{-1}
11	1.6	−0.101 365 037 912
15	3.6	−0.146 629 609 713
18	3.5	0.148 287 891 978 × 10^{-1}

5 Range of Validity and Brief Discussion

The fugacity equation, Eq. (2), with the virial coefficients given in Section 4 is valid for humid air within the temperature and pressure ranges

$$193 \text{ K} \le T \le 473 \text{ K and } 0 < p \le 5 \text{ MPa},$$

where the temperature range results exclusively from the equations for the virial coefficients given in Section 4. All validity intervals of the virial coefficients combined in Eq. (2) overlap only in this range. The separate ranges of validity of the individual virial coefficients are wider, for some of them significantly, as given in Table 5. Therefore, Eq. (2) will also provide reasonable results outside of the temperature range given above if some virial coefficients dominate numerically in Eq. (2) and are evaluated within their particular ranges of validity. This applies for instance to low-pressure conditions under which the third virial coefficients are negligible. The pressure range given above is derived from the truncation error of the virial approximation [1] employed in this Guideline and may differ if more accurate virial coefficients, or virial coefficients for other compositions of the humid gas, are used to evaluate Eq. (2).

The water-vapor mole fraction x can take any value between 0 and its saturation value, i.e.,

$$0 \le x \le x^{\text{sat}}(T, p).$$

If saturation is impossible at the given (T, p), then the range of validity is $0 \le x \le 1$. Equation (2) also gives reasonable results when extrapolated to values of x somewhat above the saturation value, provided that the temperature and pressure are within the ranges given above.

The exact value of the water vapor fraction $x^{\text{sat}}(T, p)$ of saturated humid air is determined by the equilibrium condition of equality of fugacities (or, equivalently, of chemical potentials) between water in the vapor phase and in the condensed phase (liquid if the temperature is above the freezing point or ice if the temperature is below the freezing point), as described in [2].

TABLE 5 Estimated ranges of validity of the virial coefficients

Coeff.	Validity Range	Ref.
B^{AA}	60–2000 K	[1]
B^{AW}	130–2000 K	[6]
B^{WW}	130–1273 K	[1]
C^{AAA}	60–2000 K	[1]
C^{AAW}	193–493 K	[7]
C^{AWW}	173–473 K	[7]
C^{WWW}	130–1273 K	[1]

6 Estimates of Uncertainty

Here, estimated expanded uncertainties U, coverage factor $k = 2$, are reported, corresponding to a 95 % confidence level [9]. Uncertainty estimates available for each of the virial coefficients are given in Table 6 as functions of the temperature [1]. Uncertainty estimates for the fugacity equation, Eq. (2), are obtained from uncertainty propagation of values reported in Table 6 and are displayed in Figure 1. The uncertainty budget of Eq. (2) is dominated by the uncertainties estimated for B^{WW} at low pressures and for B^{AW} at higher pressures [1].

TABLE 6 Estimated expanded uncertainties U of the virial coefficients

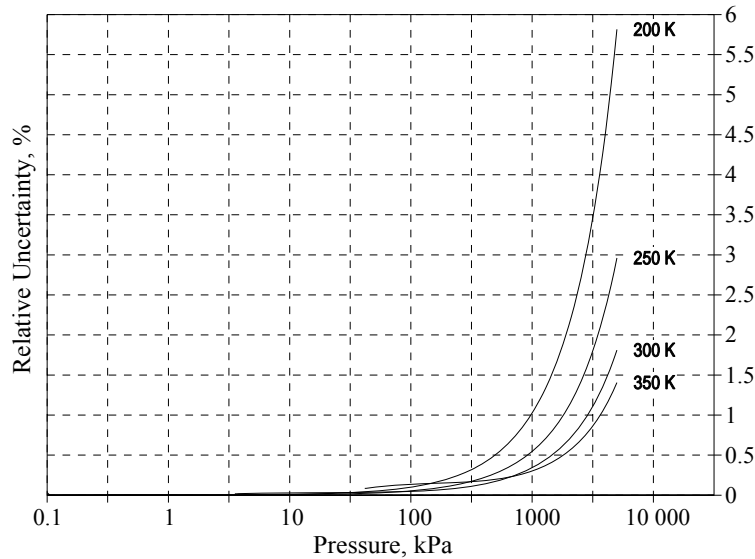| T	B^{AA}	B^{AW}	B^{WW}	C^{AAA}	C^{AAW}	C^{AWW}	C^{WWW}
K	cm^3 mol^{-1}			cm^6 mol^{-2}			
150	1	15	-	-	-	-	-
200	1	8.3	5600	680	1100	7.0×10^6	-
250	1	5.6	710	590	920	8.9×10^5	-
300	1	4.2	120	540	800	2.3×10^5	8.2×10^6
350	1	3.4	58	510	720	8.6×10^4	5.3×10^5
400	1	2.8	5	490	670	4.0×10^4	-
450	1	2.4	5	470	640	2.2×10^4	-
500	1	2.1	5	460	620	-	-

Fig. 1 Expanded (k=2) uncertainties of the fugacity equation, Eq. (2), for saturated humid air at 200 K and 250 K with respect to ice Ih, and at 300 K and 350 K with respect to liquid water, from propagation of uncertainties of Table 6, as functions of the total pressure [1]. Curves at 200 K and 250 K are valid under the weak restriction that the unknown uncertainties $U(C^{WWW})$ at those temperatures are less than 10^{15} cm^6 mol^{-2} and 10^{10} cm^6 mol^{-2}, respectively. Shown are relative uncertainties, $U(f_v)/f_v$, in percent.

7 Computer-Program Verification

To assist the user in computer-program verification, Tables 7 and 8 with test values are given for specified parameter values of humid air. They contain values for the seven virial coefficients, Eqs. (5)-(11), as well as the fugacity f_V, Eq. (2), and its auxiliary functions $\beta(x, T)$ and $\gamma(x, T)$, Eqs. (3)-(4).

TABLE 7 Numerical check values for the second virial coefficients, B^{AA}, B^{AW}, B^{WW}, and for the third virial coefficients, C^{AAA}, C^{AAW}, C^{AWW}, C^{WWW}, Eqs. (5)-(11), of humid air at the temperatures 200 K, 300 K, and 400 K.

Quantity	Value	Value	Value	Unit
T	200	300	400	K
B^{AA}	$-0.392\ 722\ 567 \times 10^{-4}$	$-0.776\ 210\ 977 \times 10^{-5}$	$0.603\ 953\ 176 \times 10^{-5}$	$m^3\ mol^{-1}$
B^{AW}	$-0.784\ 874\ 278 \times 10^{-4}$	$-0.295\ 672\ 747 \times 10^{-4}$	$-0.100\ 804\ 610 \times 10^{-4}$	$m^3\ mol^{-1}$
B^{WW}	$-0.186\ 282\ 737 \times 10^{-1}$	$-0.120\ 129\ 928 \times 10^{-2}$	$-0.348\ 784\ 166 \times 10^{-3}$	$m^3\ mol^{-1}$
C^{AAA}	$0.227\ 113\ 063 \times 10^{-8}$	$0.181\ 166\ 638 \times 10^{-8}$	$0.162\ 604\ 635 \times 10^{-8}$	$m^6\ mol^{-2}$
C^{AAW}	$0.105\ 493\ 575 \times 10^{-8}$	$0.801\ 977\ 741 \times 10^{-9}$	$0.672\ 018\ 172 \times 10^{-9}$	$m^6\ mol^{-2}$
C^{AWW}	$-0.349\ 872\ 634 \times 10^{-5}$	$-0.115\ 552\ 784 \times 10^{-6}$	$-0.200\ 806\ 021 \times 10^{-7}$	$m^6\ mol^{-2}$
C^{WWW}	$-0.263\ 959\ 706 \times 10^{-3}$	$-0.420\ 419\ 196 \times 10^{-5}$	$-0.217\ 733\ 298 \times 10^{-6}$	$m^6\ mol^{-2}$

TABLE 8 Numerical check values for the auxiliary functions, β, γ, Eqs. (3)-(4), and for the fugacity, f_V, Eq. (2), at the temperature 300 K, at mole fractions x of 0.1 and 0.9, and at pressures p of 10, 100, and 1000 kPa. Note that the values of x used here do not necessarily correspond to thermodynamically stable states of humid air.

Quantity	p / Pa	$x = 0.1$	$x = 0.9$	Unit
β		$-0.269\ 858\ 540 \times 10^{-3}$	$-0.118\ 980\ 001 \times 10^{-2}$	$m^3\ mol^{-1}$
γ		$-0.187\ 149\ 793 \times 10^{-6}$	$-0.546\ 369\ 346 \times 10^{-5}$	$m^6\ mol^{-2}$
f_V	0.1×10^5	$0.998\ 917\ 199 \times 10^3$	$0.895\ 677\ 892 \times 10^4$	Pa
f_V	0.1×10^6	$0.989\ 090\ 701 \times 10^4$	$0.854\ 318\ 372 \times 10^5$	Pa
f_V	0.1×10^7	$0.884\ 061\ 686 \times 10^5$	$0.360\ 075\ 128 \times 10^6$	Pa

8 References

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