The International Association for the Properties of Water and Steam

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Revised Release on the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use

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This revised release replaces the corresponding release of 1996 and contains 18 pages, including this cover page.

This release has been authorized by the International Association for the Properties of Water and Steam (IAPWS) at its meeting in Doorwerth, The Netherlands, 6-11 September, 2009, for issue by its Secretariat. The members of IAPWS are: Britain and Ireland, Canada, the Czech Republic, Denmark, France, Germany, Greece, Japan, Russia, and the United States of America, and associate members Argentina and Brazil, Italy, and Switzerland.

The formulation provided in this release is recommended for general and scientific use; further details about the formulation can be found in an article "The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use" by W. Wagner and A. Pruß [1]. This formulation provides the most accurate representation of the thermodynamic properties of the fluid phases of water substance over a wide range of conditions available at the time this release was prepared.

IAPWS also has a formulation intended for industrial use.

This revised release is identical to the original release issued by IAPWS in 1996, except for inclusion of the calculated triple-point pressure, improved values for the coefficients n_1^o and n_2^o in Table 1 to match more accurately the arbitrary conventions for the zeros of energy and entropy. The improved coefficients produce slight changes in the numerical values of u, s, h, f, and g; other properties (and all measurable differences in properties) are unchanged. Minor editorial corrections have also been made, including corrections in the last digits of a few calculated values in Tables 6-8 and updates to references. In 2010, a reference for estimated uncertainties in enthalpy was added.

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

The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use

1 Nomenclature

Thermodynamic quantities:

B	Second virial coefficient
c_p	Specific isobaric heat capacity
c_v	Specific isochoric heat capacity
f	Specific Helmholtz free energy
h	Specific enthalpy
M	Molar mass
p	Pressure
R	Specific gas constant
R_m	Molar gas constant
s	Specific entropy
T	Absolute temperature
u	Specific internal energy
w	Speed of sound
β_s	Isentropic throttling coefficient
δ	Reduced density, $\delta = \rho/\rho_\mathrm{c}$
δ_T	Isothermal throttling coefficient
ϕ	Dimensionless Helmholtz free energy, $\phi = f/(RT)$
κ_T	Isothermal compressibility
μ	Joule-Thomson coefficient
ρ	Mass density
τ	Inverse reduced temperature, $\tau = T_\mathrm{c}/T$

Superscripts

o	Ideal-gas property
r	Residual
′	Saturated liquid state
″	Saturated vapor state

Subscripts

c	critical point
σ	saturation
t	triple point

Note: T denotes absolute temperature on the International Temperature Scale of 1990.

2 Reference Constants

$$T_c = 647.096 \text{ K} \tag{1}$$

$$\rho_c = 322 \text{ kg m}^{-3} \tag{2}$$

$$R = 0.461\,518\,05 \text{ kJ kg}^{-1} \text{ K}^{-1} \tag{3}$$

The numerical values for the critical temperature T_c and critical density ρ_c are identical to those given in the IAPWS revised release on the critical parameters of ordinary water substance [2]. The value of the specific gas constant R is derived from values of the molar gas constant R_m [3] and the molar mass M [4], which differ slightly from the accepted values of these quantities at the time this release was prepared. The use of the more recent values would yield a specific gas constant which is greater than the value given in Eq. (3) by about 1 part in 60 000. Since the value of R in Eq. (3) has been used in obtaining the coefficients in the residual part ϕ^r, Eq. (6), then this value of R must be used in obtaining property values from the formulation, Eq. (4).

Due to the use of the *specific* gas constant, Eq. (4) corresponds to a mass-based formulation. In order to convert values of specific properties to molar properties, an appropriate value for the molar mass should be used (see [5]).

3 The Formulation

The formulation is a fundamental equation for the specific Helmholtz free energy *f*. This equation is expressed in dimensionless form, $\phi = f/(RT)$, and is separated into two parts, an ideal-gas part ϕ^o and a residual part ϕ^r, so that :

$$\frac{f(\rho,T)}{RT} = \phi(\delta, \tau) = \phi^o(\delta, \tau) + \phi^r(\delta, \tau), \tag{4}$$

where $\delta = \rho/\rho_c$ and $\tau = T_c/T$ with ρ_c, T_c and R given by Eqs. (2), (1) and (3).

The ideal-gas part ϕ^o of the dimensionless Helmholtz free energy is obtained from an equation for the specific isobaric heat capacity in the ideal-gas state developed by Cooper [6] and reads:

$$\phi^o = \ln\delta + n_1^o + n_2^o\tau + n_3^o\ln\tau + \sum_{i=4}^{8} n_i^o \ln\left[1 - e^{-\gamma_i^o\tau}\right], \tag{5}$$

where $\delta = \rho/\rho_c$ and $\tau = T_c/T$ with ρ_c and T_c according to Eqs. (2) and (1). Table 1 contains the coefficients and parameters of Eq. (5).

The form of the residual part ϕ^{r} of the dimensionless Helmholtz free energy is as follows:

$$\phi^{\mathrm{r}} = \sum_{i=1}^{7} n_i \delta^{d_i} \tau^{t_i} + \sum_{i=8}^{51} n_i \delta^{d_i} \tau^{t_i} \mathrm{e}^{-\delta^{c_i}} + \sum_{i=52}^{54} n_i \delta^{d_i} \tau^{t_i} \mathrm{e}^{-\alpha_i(\delta-\varepsilon_i)^2 - \beta_i(\tau-\gamma_i)^2} + \sum_{i=55}^{56} n_i \Delta^{b_i} \delta \psi \qquad (6)$$

$$\text{with} \quad \Delta = \theta^2 + B_i \left[(\delta-1)^2 \right]^{a_i}$$

$$\theta = (1-\tau) + A_i \left[(\delta-1)^2 \right]^{\frac{1}{2\beta_i}}$$

$$\psi = \mathrm{e}^{-C_i(\delta-1)^2 - D_i(\tau-1)^2} \quad,$$

where $\delta = \rho/\rho_{\mathrm{c}}$ and $\tau = T_{\mathrm{c}}/T$ with ρ_{c} and T_{c} according to Eqs. (2) and (1). The coefficients and parameters of Eq. (6) are listed in Table 2.

Since the 5th International Conference on the Properties of Steam in London in 1956, the specific internal energy and the specific entropy of the saturated liquid at the triple point have been set equal to zero. Thus, at the triple-point[1] temperature $T_{\mathrm{t}} = 273.16$ K,

$$u_{\mathrm{t}}' = 0, \quad s_{\mathrm{t}}' = 0. \qquad (7)$$

In order to meet this condition, the coefficients n_1^{o} and n_2^{o} in Eq. (5) have been adjusted accordingly. As a consequence, after calculating for T_{t} the saturated liquid density ρ_{t}' via the phase-equilibrium condition (see Table 3), Eq. (4) yields for the specific enthalpy of the saturated liquid at the triple point:

$$h_{\mathrm{t}}' = 0.611782 \text{ J kg}^{-1}. \qquad (8)$$

In the liquid-water region, small changes in density along an isotherm cause large changes in pressure. For this reason, due to an accumulation of small errors, a particular computer code may fail to return the zeros in Eq. (7) for the saturated liquid density at the triple-point temperature. If a user wants to reproduce the zeros of Eq. (7) more precisely, the constants n_1^{o} and n_2^{o} in Eq. (5) may be readjusted by imposing the condition $u_{\mathrm{t}}' = 0,\ s_{\mathrm{t}}' = 0$ with the desired accuracy.

4 Relations of Thermodynamic Properties to the Dimensionless Helmholtz Free Energy

All thermodynamic properties can be derived from Eq. (4) by using the appropriate combinations of the ideal-gas part ϕ^{o}, Eq. (5), and the residual part ϕ^{r}, Eq. (6), of the dimensionless Helmholtz free energy and their derivatives. Relations between thermodynamic

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[1] The calculation of the triple-point pressure p_{t} from Eq. (4) yields $p_{\mathrm{t}} = 611.654\ 771$ Pa.

properties and ϕ^{o} and ϕ^{r} and their derivatives are summarized in Table 3. All required derivatives of the ideal-gas part and of the residual part of the Helmholtz free energy are explicitly given in Table 4 and Table 5, respectively.

Besides the single-phase region, the formulation also covers the liquid-vapor saturation curve. For given saturation temperature and solving simultaneously the three equations of the phase-equilibrium condition (see Table 3) by iteration, Eq. (6) yields the thermal saturation properties p_σ, ρ' and ρ''. Then, all the other properties can be derived from Eq. (4). In this way, the properties calculated on the saturation curve are thermodynamically consistent with the properties of the single-phase region.

Note: IAPWS has issued the Supplementary Release on *Saturation Properties of Ordinary Water Substance* [7] containing a set of simple equations which yield values for the vapor pressure as well as the density, specific enthalpy and specific entropy of the saturated vapor and liquid. The values calculated from these equations are not identical with the corresponding values derived from Eq. (4), but agree with them within the uncertainties of the simple equations for the saturation properties.

5 Range of Validity

IAPWS has tested the formulation and endorses its validity in the following way:

(1) The formulation is valid in the entire stable fluid region of H_2O from the melting-pressure curve [8] to 1273 K at pressures up to 1000 MPa; the lowest temperature on the melting-pressure curve is 251.165 K (at 208.566 MPa) [8], see Fig. 1.

In this entire region, Eq. (4) represents the experimental data available at the time the release was prepared (except for very few data points) to within their uncertainties.

Although Eq. (4) is also in satisfactory agreement with the experimental data in the critical region, the equation has some unsatisfactory features in the immediate vicinity of the critical point. These features involve second order and higher derivatives of the dimensionless Helmholtz free energy and properties obtained from them. Specifically, the isothermal compressibility κ_T $\left(\kappa_T = \rho^{-1}(\partial\rho/\partial p)_T\right)$ and the specific isobaric heat capacity c_p exhibit unphysical behavior which occurs in a region from T_c to 5 K above T_c for densities ± 0.5 % from ρ_c. In addition, within a temperature range from 20 mK below T_c up to T_c, the isochoric heat capacity c_v exhibits a maximum and the speed of sound w exhibits a minimum not at the saturation temperature T_σ of the corresponding isochore (as it should be) but in the single-phase region up to 2.5 mK above T_σ.

(2) In the stable fluid region, the formulation can also be extrapolated beyond the limits given under item (1).

Tests show that Eq. (4) behaves reasonably when extrapolated to pressures up to about

100 GPa and temperatures up to about 5000 K. This holds at least for the density and enthalpy of undissociated H_2O.

In the gas region at pressures below the triple-point pressure, Eq. (4) behaves reasonably when extrapolated to the sublimation-pressure curve [8] for temperatures down to 200 K. Due to the extremely low densities in this region which go down to about 10^{-6} kg m^{-3}, attention must be paid to numerical problems.

(3) As far as can be tested with experimental data, the formulation behaves reasonably when extrapolated into the metastable regions. Equation (4) represents the currently available experimental data of the subcooled liquid (solid-liquid metastable region) and of the superheated liquid (liquid-gas metastable region) to within the experimental uncertainty. In the case of the subcooled gas (gas-liquid metastable region), no experimental data are available. In this region, for pressures below 10 MPa, Eq. (4) produces reasonable values close to the saturation line. For calculations further away from the saturation line, an alternative equation (the so-called gas equation) is given in reference [1].

For further details see reference [1].

6 Estimates of Uncertainty

Estimates have been made of the uncertainty of the density, speed of sound, and isobaric heat capacity when calculated from the formulation, Eq. (4). These estimates were derived from comparisons with the various sets of experimental data together with the judgement of the Working Group on Thermophysical Properties of Water and Steam of IAPWS.

For the single-phase region, these tolerances are indicated in Figs. 1 to 3, which give the estimated uncertainties in various areas. As used here, "tolerance" means the range of possible values as judged by IAPWS, and no statistical significance can be attached to it. With regard to the uncertainty for the speed of sound and the specific isobaric heat capacity, see Figs. 2 and 3, it should be noted that the uncertainties for these properties increase drastically when approaching the critical point. The statement "no definitive uncertainty estimates possible" for the high-pressure region in Figs. 2 and 3 is based on the lack of experimental data in this region.

For the saturation properties, the estimates of the uncertainties of vapor pressure, saturated liquid density, and saturated vapor density are shown in Fig. 4.

Estimated uncertainties in enthalpy, in enthalpy differences in the single-phase region, and in the enthalpy of vaporization are given in IAPWS Advisory Note No. 1 [9].

7 Computer-Program Verification

To assist the user in computer-program verification, three tables with test values are given. Table 6 contains values of the ideal-gas part ϕ^{o} and the residual part ϕ^{r} of the dimensionless Helmholtz free energy together with the corresponding derivatives. Table 7 lists values for the pressure p, the specific isochoric heat capacity c_v, the speed of sound w, and the specific entropy s calculated at selected values of temperature T and density ρ. Table 8 gives values for the vapor pressure p_σ, values for the density ρ', specific enthalpy h' and specific entropy s' for the saturated liquid, and values for the density ρ'', specific enthalpy h'' and specific entropy s'' for the saturated vapor. All these saturation values have been calculated with Eq. (4) by using the phase-equilibrium condition (see the corresponding comment in Section 4).

8 References

[1] Wagner, W., and Pruß, A., The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use, *J. Phys. Chem. Ref. Data* **31**, 387-535 (2002).

[2] IAPWS, *Release on the Values of Temperature, Pressure, and Density of Ordinary and Heavy Water Substances at Their Respective Critical Points* (1992). Available from http://www.iapws.org.

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[4] Kell, G. S., Effects of Isotopic Composition, Temperature, Pressure, and Dissolved Gases on the Density of Liquid Water, *J. Phys. Chem. Ref. Data* **6**, 1109-1131 (1977).

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[6] Cooper, J. R., Representation of the Ideal-Gas Thermodynamic Properties of Water, *Int. J. Thermophys.* **3**, 35-43 (1982).

[7] IAPWS, *Revised Supplementary Release on Saturation Properties of Ordinary Water Substance* (1992). Available from http://www.iapws.org. See also Wagner, W., and Pruß, A., International Equations for the Saturation Properties of Ordinary Water Substance – Revised According to the International Temperature Scale of 1990. *J. Phys. Chem. Ref. Data* **22**, 783-787 (1993).

[8] IAPWS, *Revised Release on the Pressure along the Melting and Sublimation Curves of Ordinary Water Substance* (2008). Available from http://www.iapws.org. See also Wagner, W., Riethmann, T., Feistel, R., and Harvey, A. H., to be submitted to *J. Phys. Chem. Ref. Data*.

[9] IAPWS Advisory Note No. 1: *Uncertainties in Enthalpy for the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use (IAPWS-95) and the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam (IAPWS-IF97)* (2003). Available from http://www.iapws.org

Table 1. Numerical values of the coefficients and parameters of the ideal-gas part of the dimensionless Helmholtz free energy, Eq. (5)

i	n_i^{o}	γ_i^{o}	i	n_i^{o}	γ_i^{o}
1	−8.320 446 483 749 7	–	5	0.973 15	3.537 342 22
2	6.683 210 527 593 2	–	6	1.279 50	7.740 737 08
3	3.006 32	–	7	0.969 56	9.244 377 96
4	0.012 436	1.287 289 67	8	0.248 73	27.507 510 5

Table 2. Numerical values of the coefficients and parameters of the residual part of the dimensionless Helmholtz free energy, Eq. (6)

i	c_i	d_i	t_i	n_i
1	–	1	–0.5	$0.125\ 335\ 479\ 355\ 23 \times 10^{-1}$
2	–	1	0.875	$0.789\ 576\ 347\ 228\ 28 \times 10^{1}$
3	–	1	1	$-0.878\ 032\ 033\ 035\ 61 \times 10^{1}$
4	–	2	0.5	$0.318\ 025\ 093\ 454\ 18$
5	–	2	0.75	$-0.261\ 455\ 338\ 593\ 58$
6	–	3	0.375	$-0.781\ 997\ 516\ 879\ 81 \times 10^{-2}$
7	–	4	1	$0.880\ 894\ 931\ 021\ 34 \times 10^{-2}$
8	1	1	4	$-0.668\ 565\ 723\ 079\ 65$
9	1	1	6	$0.204\ 338\ 109\ 509\ 65$
10	1	1	12	$-0.662\ 126\ 050\ 396\ 87 \times 10^{-4}$
11	1	2	1	$-0.192\ 327\ 211\ 560\ 02$
12	1	2	5	$-0.257\ 090\ 430\ 034\ 38$
13	1	3	4	$0.160\ 748\ 684\ 862\ 51$
14	1	4	2	$-0.400\ 928\ 289\ 258\ 07 \times 10^{-1}$
15	1	4	13	$0.393\ 434\ 226\ 032\ 54 \times 10^{-6}$
16	1	5	9	$-0.759\ 413\ 770\ 881\ 44 \times 10^{-5}$
17	1	7	3	$0.562\ 509\ 793\ 518\ 88 \times 10^{-3}$
18	1	9	4	$-0.156\ 086\ 522\ 571\ 35 \times 10^{-4}$
19	1	10	11	$0.115\ 379\ 964\ 229\ 51 \times 10^{-8}$
20	1	11	4	$0.365\ 821\ 651\ 442\ 04 \times 10^{-6}$
21	1	13	13	$-0.132\ 511\ 800\ 746\ 68 \times 10^{-11}$
22	1	15	1	$-0.626\ 395\ 869\ 124\ 54 \times 10^{-9}$
23	2	1	7	$-0.107\ 936\ 009\ 089\ 32$
24	2	2	1	$0.176\ 114\ 910\ 087\ 52 \times 10^{-1}$
25	2	2	9	$0.221\ 322\ 951\ 675\ 46$
26	2	2	10	$-0.402\ 476\ 697\ 635\ 28$
27	2	3	10	$0.580\ 833\ 999\ 857\ 59$
28	2	4	3	$0.499\ 691\ 469\ 908\ 06 \times 10^{-2}$
29	2	4	7	$-0.313\ 587\ 007\ 125\ 49 \times 10^{-1}$
30	2	4	10	$-0.743\ 159\ 297\ 103\ 41$
31	2	5	10	$0.478\ 073\ 299\ 154\ 80$
32	2	6	6	$0.205\ 279\ 408\ 959\ 48 \times 10^{-1}$
33	2	6	10	$-0.136\ 364\ 351\ 103\ 43$
34	2	7	10	$0.141\ 806\ 344\ 006\ 17 \times 10^{-1}$
35	2	9	1	$0.833\ 265\ 048\ 807\ 13 \times 10^{-2}$
36	2	9	2	$-0.290\ 523\ 360\ 095\ 85 \times 10^{-1}$
37	2	9	3	$0.386\ 150\ 855\ 742\ 06 \times 10^{-1}$
38	2	9	4	$-0.203\ 934\ 865\ 137\ 04 \times 10^{-1}$
39	2	9	8	$-0.165\ 540\ 500\ 637\ 34 \times 10^{-2}$
40	2	10	6	$0.199\ 555\ 719\ 795\ 41 \times 10^{-2}$
41	2	10	9	$0.158\ 703\ 083\ 241\ 57 \times 10^{-3}$
42	2	12	8	$-0.163\ 885\ 683\ 425\ 30 \times 10^{-4}$
43	3	3	16	$0.436\ 136\ 157\ 238\ 11 \times 10^{-1}$
44	3	4	22	$0.349\ 940\ 054\ 637\ 65 \times 10^{-1}$
45	3	4	23	$-0.767\ 881\ 978\ 446\ 21 \times 10^{-1}$
46	3	5	23	$0.224\ 462\ 773\ 320\ 06 \times 10^{-1}$
47	4	14	10	$-0.626\ 897\ 104\ 146\ 85 \times 10^{-4}$
48	6	3	50	$-0.557\ 111\ 185\ 656\ 45 \times 10^{-9}$
49	6	6	44	$-0.199\ 057\ 183\ 544\ 08$
50	6	6	46	$0.317\ 774\ 973\ 307\ 38$
51	6	6	50	$-0.118\ 411\ 824\ 259\ 81$

i	c_i	d_i	t_i	n_i	α_i	β_i	γ_i	ε_i
52	–	3	0	$-0.313\ 062\ 603\ 234\ 35 \times 10^{2}$	20	150	1.21	1
53	–	3	1	$0.315\ 461\ 402\ 377\ 81 \times 10^{2}$	20	150	1.21	1
54	–	3	4	$-0.252\ 131\ 543\ 416\ 95 \times 10^{4}$	20	250	1.25	1

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

Table 3. Relations of thermodynamic properties to the ideal-gas part ϕ^{o} and the residual part ϕ^{r} of the dimensionless Helmholtz free energy and their derivatives[a]

Property	Relation
Pressure $p = \rho^2 \left(\partial f / \partial \rho \right)_T$	$\dfrac{p(\delta,\tau)}{\rho RT} = 1 + \delta \phi_\delta^{\mathrm{r}}$
Internal energy $u = f - T\left(\partial f / \partial T \right)_\rho$	$\dfrac{u(\delta,\tau)}{RT} = \tau\left(\phi_\tau^{\mathrm{o}} + \phi_\tau^{\mathrm{r}} \right)$
Entropy $s = -\left(\partial f / \partial T \right)_\rho$	$\dfrac{s(\delta,\tau)}{R} = \tau\left(\phi_\tau^{\mathrm{o}} + \phi_\tau^{\mathrm{r}} \right) - \phi^{\mathrm{o}} - \phi^{\mathrm{r}}$
Enthalpy $h = f - T\left(\partial f / \partial T \right)_\rho + \rho\left(\partial f / \partial \rho \right)_T$	$\dfrac{h(\delta,\tau)}{RT} = 1 + \tau\left(\phi_\tau^{\mathrm{o}} + \phi_\tau^{\mathrm{r}} \right) + \delta \phi_\delta^{\mathrm{r}}$
Isochoric heat capacity $c_v = \left(\partial u / \partial T \right)_\rho$	$\dfrac{c_v(\delta,\tau)}{R} = -\tau^2 \left(\phi_{\tau\tau}^{\mathrm{o}} + \phi_{\tau\tau}^{\mathrm{r}} \right)$
Isobaric heat capacity $c_p = \left(\partial h / \partial T \right)_p$	$\dfrac{c_p(\delta,\tau)}{R} = -\tau^2 \left(\phi_{\tau\tau}^{\mathrm{o}} + \phi_{\tau\tau}^{\mathrm{r}} \right) + \dfrac{\left(1 + \delta\phi_\delta^{\mathrm{r}} - \delta\tau\phi_{\delta\tau}^{\mathrm{r}} \right)^2}{1 + 2\delta\phi_\delta^{\mathrm{r}} + \delta^2 \phi_{\delta\delta}^{\mathrm{r}}}$
Speed of sound $w = \left(\partial p / \partial \rho \right)_s^{1/2}$	$\dfrac{w^2(\delta,\tau)}{RT} = 1 + 2\delta\phi_\delta^{\mathrm{r}} + \delta^2 \phi_{\delta\delta}^{\mathrm{r}} - \dfrac{\left(1 + \delta\phi_\delta^{\mathrm{r}} - \delta\tau\phi_{\delta\tau}^{\mathrm{r}} \right)^2}{\tau^2 \left(\phi_{\tau\tau}^{\mathrm{o}} + \phi_{\tau\tau}^{\mathrm{r}} \right)}$
Joule-Thomson coefficient $\mu = \left(\partial T / \partial p \right)_h$	$\mu R \rho = \dfrac{-\left(\delta\phi_\delta^{\mathrm{r}} + \delta^2 \phi_{\delta\delta}^{\mathrm{r}} + \delta\tau\phi_{\delta\tau}^{\mathrm{r}} \right)}{\left(1 + \delta\phi_\delta^{\mathrm{r}} - \delta\tau\phi_{\delta\tau}^{\mathrm{r}} \right)^2 - \tau^2 \left(\phi_{\tau\tau}^{\mathrm{o}} + \phi_{\tau\tau}^{\mathrm{r}} \right)\left(1 + 2\delta\phi_\delta^{\mathrm{r}} + \delta^2 \phi_{\delta\delta}^{\mathrm{r}} \right)}$
Isothermal throttling coefficient $\delta_T = \left(\partial h / \partial p \right)_T$	$\delta_T \rho = 1 - \dfrac{1 + \delta\phi_\delta^{\mathrm{r}} - \delta\tau\phi_{\delta\tau}^{\mathrm{r}}}{1 + 2\delta\phi_\delta^{\mathrm{r}} + \delta^2 \phi_{\delta\delta}^{\mathrm{r}}}$
Isentropic temperature-pressure coefficient $\beta_s = \left(\partial T / \partial p \right)_s$	$\beta_s \rho R = \dfrac{1 + \delta\phi_\delta^{\mathrm{r}} - \delta\tau\phi_{\delta\tau}^{\mathrm{r}}}{\left(1 + \delta\phi_\delta^{\mathrm{r}} - \delta\tau\phi_{\delta\tau}^{\mathrm{r}} \right)^2 - \tau^2 \left(\phi_{\tau\tau}^{\mathrm{o}} + \phi_{\tau\tau}^{\mathrm{r}} \right)\left(1 + 2\delta\phi_\delta^{\mathrm{r}} + \delta^2 \phi_{\delta\delta}^{\mathrm{r}} \right)}$
Second virial coefficient $B(T) = \lim\limits_{\rho \to 0} \left(\partial\left(p/(\rho RT) \right) / \partial\rho \right)_T$	$B(\tau)\rho_{\mathrm{c}} = \lim\limits_{\delta \to 0} \phi_\delta^{\mathrm{r}}(\delta,\tau)$
Third virial coefficient $C(T) = \lim\limits_{\rho \to 0} \left[\dfrac{1}{2}\left(\partial^2\left(p/(\rho RT) \right) / \partial\rho^2 \right)_T \right]$	$C(\tau)\rho_{\mathrm{c}}^2 = \lim\limits_{\delta \to 0} \phi_{\delta\delta}^{\mathrm{r}}(\delta,\tau)$
Phase-equilibrium condition (Maxwell criterion)	$\dfrac{p_\sigma}{RT\rho'} = 1 + \delta'\phi_\delta^{\mathrm{r}}(\delta',\tau) \quad ; \quad \dfrac{p_\sigma}{RT\rho''} = 1 + \delta''\phi_\delta^{\mathrm{r}}(\delta'',\tau)$ $\dfrac{p_\sigma}{RT}\left(\dfrac{1}{\rho''} - \dfrac{1}{\rho'} \right) - \ln\left(\dfrac{\rho'}{\rho''} \right) = \phi^{\mathrm{r}}(\delta',\tau) - \phi^{\mathrm{r}}(\delta'',\tau)$

[a] $\phi_\delta^{\mathrm{r}} = \left[\dfrac{\partial\phi^{\mathrm{r}}}{\partial\delta} \right]_\tau , \ \phi_{\delta\delta}^{\mathrm{r}} = \left[\dfrac{\partial^2\phi^{\mathrm{r}}}{\partial\delta^2} \right]_\tau , \ \phi_\tau^{\mathrm{r}} = \left[\dfrac{\partial\phi^{\mathrm{r}}}{\partial\tau} \right]_\delta , \ \phi_{\tau\tau}^{\mathrm{r}} = \left[\dfrac{\partial^2\phi^{\mathrm{r}}}{\partial\tau^2} \right]_\delta , \ \phi_{\delta\tau}^{\mathrm{r}} = \left[\dfrac{\partial^2\phi^{\mathrm{r}}}{\partial\delta\partial\tau} \right] , \ \phi_\tau^{\mathrm{o}} = \left[\dfrac{\partial\phi^{\mathrm{o}}}{\partial\tau} \right]_\delta , \ \phi_{\tau\tau}^{\mathrm{o}} = \left[\dfrac{\partial^2\phi^{\mathrm{o}}}{\partial\tau^2} \right]_\delta .$

Table 4. The ideal-gas part ϕ^o of the dimensionless Helmholtz free energy and its derivatives[a]

$$\phi^\text{o} = \ln\delta + n_1^\text{o} + n_2^\text{o}\tau + n_3^\text{o}\ln\tau + \sum_{i=4}^{8} n_i^\text{o}\ln\left(1-e^{-\gamma_i^\text{o}\tau}\right)$$

$$\phi_\delta^\text{o} = 1/\delta + 0 + 0 + 0 + 0$$

$$\phi_{\delta\delta}^\text{o} = -1/\delta^2 + 0 + 0 + 0 + 0$$

$$\phi_\tau^\text{o} = 0 + 0 + n_2^\text{o} + n_3^\text{o}/\tau + \sum_{i=4}^{8} n_i^\text{o}\gamma_i^\text{o}\left[\left(1-e^{-\gamma_i^\text{o}\tau}\right)^{-1}-1\right]$$

$$\phi_{\tau\tau}^\text{o} = 0 + 0 + 0 - n_3^\text{o}/\tau^2 - \sum_{i=4}^{8} n_i^\text{o}\left(\gamma_i^\text{o}\right)^2 e^{-\gamma_i^\text{o}\tau}\left(1-e^{-\gamma_i^\text{o}\tau}\right)^{-2}$$

$$\phi_{\delta\tau}^\text{o} = 0 + 0 + 0 + 0 + 0$$

a $\phi_\delta^\text{o}=\left[\dfrac{\partial\phi^\text{o}}{\partial\delta}\right]_\tau$, $\phi_{\delta\delta}^\text{o}=\left[\dfrac{\partial^2\phi^\text{o}}{\partial\delta^2}\right]_\tau$, $\phi_\tau^\text{o}=\left[\dfrac{\partial\phi^\text{o}}{\partial\tau}\right]_\delta$, $\phi_{\tau\tau}^\text{o}=\left[\dfrac{\partial^2\phi^\text{o}}{\partial\tau^2}\right]_\delta$, $\phi_{\delta\tau}^\text{o}=\left[\dfrac{\partial^2\phi^\text{o}}{\partial\delta\partial\tau}\right]$.

Table 5. The residual part ϕ^{r} of the dimensionless Helmholtz free energy and its derivatives[a]

$$\phi^{\mathrm{r}} = \sum_{i=1}^{7} n_i \delta^{d_i} \tau^{t_i} + \sum_{i=8}^{51} n_i \delta^{d_i} \tau^{t_i} \mathrm{e}^{-\delta^{c_i}} + \sum_{i=52}^{54} n_i \delta^{d_i} \tau^{t_i} \mathrm{e}^{-\alpha_i(\delta-\varepsilon_i)^2 - \beta_i(\tau-\gamma_i)^2} + \sum_{i=55}^{56} n_i \Delta^{b_i} \delta \psi$$

with $\Delta = \theta^2 + B_i \left[(\delta-1)^2 \right]^{a_i}$

$$\theta = (1-\tau) + A_i \left[(\delta-1)^2 \right]^{\frac{1}{2\beta_i}}$$

$$\psi = \mathrm{e}^{-C_i(\delta-1)^2 - D_i(\tau-1)^2}$$

$$\phi_\delta^{\mathrm{r}} = \sum_{i=1}^{7} n_i d_i \delta^{d_i-1} \tau^{t_i} + \sum_{i=8}^{51} n_i \mathrm{e}^{-\delta^{c_i}} \left[\delta^{d_i-1} \tau^{t_i} \left(d_i - c_i \delta^{c_i} \right) \right] + \sum_{i=52}^{54} n_i \delta^{d_i} \tau^{t_i} \mathrm{e}^{-\alpha_i(\delta-\varepsilon_i)^2 - \beta_i(\tau-\gamma_i)^2} \left[\frac{d_i}{\delta} - 2\alpha_i(\delta-\varepsilon_i) \right] + \sum_{i=55}^{56} n_i \left[\Delta^{b_i} \left(\psi + \delta \frac{\partial \psi}{\partial \delta} \right) + \frac{\partial \Delta^{b_i}}{\partial \delta} \delta \psi \right]$$

$$\phi_{\delta\delta}^{\mathrm{r}} = \sum_{i=1}^{7} n_i d_i (d_i-1) \delta^{d_i-2} \tau^{t_i} + \sum_{i=8}^{51} n_i \mathrm{e}^{-\delta^{c_i}} \left[\delta^{d_i-2} \tau^{t_i} \left(\left(d_i - c_i \delta^{c_i} \right) \left(d_i - 1 - c_i \delta^{c_i} \right) - c_i^2 \delta^{c_i} \right) \right] + \sum_{i=52}^{54} n_i \tau^{t_i} \mathrm{e}^{-\alpha_i(\delta-\varepsilon_i)^2 - \beta_i(\tau-\gamma_i)^2}$$

$$\cdot \left[-2\alpha_i \delta^{d_i} + 4\alpha_i^2 \delta^{d_i} (\delta-\varepsilon_i)^2 - 4 d_i \alpha_i \delta^{d_i-1} (\delta-\varepsilon_i) + d_i (d_i-1) \delta^{d_i-2} \right] + \sum_{i=55}^{56} n_i \left[\Delta^{b_i} \left(2 \frac{\partial \psi}{\partial \delta} + \delta \frac{\partial^2 \psi}{\partial \delta^2} \right) + 2 \frac{\partial \Delta^{b_i}}{\partial \delta} \left(\psi + \delta \frac{\partial \psi}{\partial \delta} \right) + \frac{\partial^2 \Delta^{b_i}}{\partial \delta^2} \delta \psi \right]$$

$$\phi_\tau^{\mathrm{r}} = \sum_{i=1}^{7} n_i t_i \delta^{d_i} \tau^{t_i-1} + \sum_{i=8}^{51} n_i t_i \delta^{d_i} \tau^{t_i-1} \mathrm{e}^{-\delta^{c_i}} + \sum_{i=52}^{54} n_i \delta^{d_i} \tau^{t_i} \mathrm{e}^{-\alpha_i(\delta-\varepsilon_i)^2 - \beta_i(\tau-\gamma_i)^2} \left[\frac{t_i}{\tau} - 2\beta_i(\tau-\gamma_i) \right] + \sum_{i=55}^{56} n_i \delta \left[\frac{\partial \Delta^{b_i}}{\partial \tau} \psi + \Delta^{b_i} \frac{\partial \psi}{\partial \tau} \right]$$

$$\phi_{\tau\tau}^{\mathrm{r}} = \sum_{i=1}^{7} n_i t_i (t_i-1) \delta^{d_i} \tau^{t_i-2} + \sum_{i=8}^{51} n_i t_i (t_i-1) \delta^{d_i} \tau^{t_i-2} \mathrm{e}^{-\delta^{c_i}} + \sum_{i=52}^{54} n_i \delta^{d_i} \tau^{t_i} \mathrm{e}^{-\alpha_i(\delta-\varepsilon_i)^2 - \beta_i(\tau-\gamma_i)^2} \left[\left(\frac{t_i}{\tau} - 2\beta_i(\tau-\gamma_i) \right)^2 - \frac{t_i}{\tau^2} - 2\beta_i \right]$$

$$+ \sum_{i=55}^{56} n_i \delta \left[\frac{\partial^2 \Delta^{b_i}}{\partial \tau^2} \psi + 2 \frac{\partial \Delta^{b_i}}{\partial \tau} \frac{\partial \psi}{\partial \tau} + \Delta^{b_i} \frac{\partial^2 \psi}{\partial \tau^2} \right]$$

$$\phi_{\delta\tau}^{\mathrm{r}} = \sum_{i=1}^{7} n_i d_i t_i \delta^{d_i-1} \tau^{t_i-1} + \sum_{i=8}^{51} n_i t_i \delta^{d_i-1} \tau^{t_i-1} \left(d_i - c_i \delta^{c_i} \right) \mathrm{e}^{-\delta^{c_i}} + \sum_{i=52}^{54} n_i \delta^{d_i} \tau^{t_i} \mathrm{e}^{-\alpha_i(\delta-\varepsilon_i)^2 - \beta_i(\tau-\gamma_i)^2} \left[\frac{d_i}{\delta} - 2\alpha_i(\delta-\varepsilon_i) \right] \left[\frac{t_i}{\tau} - 2\beta_i(\tau-\gamma_i) \right]$$

$$+ \sum_{i=55}^{56} n_i \left[\Delta^{b_i} \left(\frac{\partial \psi}{\partial \tau} + \delta \frac{\partial^2 \psi}{\partial \delta \partial \tau} \right) + \delta \frac{\partial \Delta^{b_i}}{\partial \delta} \frac{\partial \psi}{\partial \tau} + \frac{\partial \Delta^{b_i}}{\partial \tau} \left(\psi + \delta \frac{\partial \psi}{\partial \delta} \right) + \frac{\partial^2 \Delta^{b_i}}{\partial \delta \partial \tau} \delta \psi \right]$$

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Table 5. Continued

Derivatives of the distance function Δ^{b_i}:

$$\frac{\partial \Delta^{b_i}}{\partial \delta} = b_i \Delta^{b_i-1} \frac{\partial \Delta}{\partial \delta}$$

$$\frac{\partial^2 \Delta^{b_i}}{\partial \delta^2} = b_i \left\{ \Delta^{b_i-1} \frac{\partial^2 \Delta}{\partial \delta^2} + (b_i - 1) \Delta^{b_i-2} \left(\frac{\partial \Delta}{\partial \delta} \right)^2 \right\}$$

$$\frac{\partial \Delta^{b_i}}{\partial \tau} = -2\theta b_i \Delta^{b_i-1}$$

$$\frac{\partial^2 \Delta^{b_i}}{\partial \tau^2} = 2 b_i \Delta^{b_i-1} + 4\theta^2 b_i (b_i - 1) \Delta^{b_i-2}$$

$$\frac{\partial^2 \Delta^{b_i}}{\partial \delta \partial \tau} = -A_i b_i \frac{2}{\beta_i} \Delta^{b_i-1} (\delta-1) \left[(\delta-1)^2 \right]^{\frac{1}{2\beta_i}-1} - 2\theta b_i (b_i-1) \Delta^{b_i-2} \frac{\partial \Delta}{\partial \delta}$$

with

$$\frac{\partial \Delta}{\partial \delta} = (\delta-1) \left\{ A_i \theta \frac{2}{\beta_i} \left[(\delta-1)^2 \right]^{\frac{1}{2\beta_i}-1} + 2 B_i a_i \left[(\delta-1)^2 \right]^{a_i-1} \right\}$$

$$\frac{\partial^2 \Delta}{\partial \delta^2} = \frac{1}{(\delta-1)} \frac{\partial \Delta}{\partial \delta} + (\delta-1)^2 \left\{ 4 B_i a_i (a_i-1) \left[(\delta-1)^2 \right]^{a_i-2} + 2 A_i^2 \left(\frac{1}{\beta_i} \right)^2 \left\{ \left[(\delta-1)^2 \right]^{\frac{1}{2\beta_i}-1} \right\}^2 \right.$$

$$\left. + A_i \theta \frac{4}{\beta_i} \left(\frac{1}{2\beta_i} - 1 \right) \left[(\delta-1)^2 \right]^{\frac{1}{2\beta_i}-2} \right\}$$

Derivatives of the exponential function ψ :

$$\frac{\partial \psi}{\partial \delta} = -2 C_i (\delta-1) \psi$$

$$\frac{\partial^2 \psi}{\partial \delta^2} = \left\{ 2 C_i (\delta-1)^2 - 1 \right\} 2 C_i \psi$$

$$\frac{\partial \psi}{\partial \tau} = -2 D_i (\tau-1) \psi$$

$$\frac{\partial^2 \psi}{\partial \tau^2} = \left\{ 2 D_i (\tau-1)^2 - 1 \right\} 2 D_i \psi$$

$$\frac{\partial^2 \psi}{\partial \delta \partial \tau} = 4 C_i D_i (\delta-1)(\tau-1) \psi$$

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[a] $\phi_\delta^r = \left[\dfrac{\partial \phi^r}{\partial \delta} \right]_\tau$, $\phi_{\delta\delta}^r = \left[\dfrac{\partial^2 \phi^r}{\partial \delta^2} \right]_\tau$, $\phi_\tau^r = \left[\dfrac{\partial \phi^r}{\partial \tau} \right]_\delta$, $\phi_{\tau\tau}^r = \left[\dfrac{\partial^2 \phi^r}{\partial \tau^2} \right]_\delta$, $\phi_{\delta\tau}^r = \left[\dfrac{\partial^2 \phi^r}{\partial \delta \partial \tau} \right]$.

Table 6. Values for the ideal-gas part ϕ^{o}, Eq. (5), and for the residual part ϕ^{r}, Eq. (6), of the dimensionless Helmholtz free energy together with the corresponding derivatives[a] for $T = 500$ K and $\rho = 838.025$ kg m^{-3}

ϕ^{o}	$= 0.204\ 797\ 733 \times 10^{1}$	ϕ^{r}	$= -0.342\ 693\ 206 \times 10^{1}$
$\phi^{\mathrm{o}}_{\delta}$	$= 0.384\ 236\ 747$	$\phi^{\mathrm{r}}_{\delta}$	$= -0.364\ 366\ 650$
$\phi^{\mathrm{o}}_{\delta\delta}$	$= -0.147\ 637\ 878$	$\phi^{\mathrm{r}}_{\delta\delta}$	$= 0.856\ 063\ 701$
ϕ^{o}_{τ}	$= 0.904\ 611\ 106 \times 10^{1}$	ϕ^{r}_{τ}	$= -0.581\ 403\ 435 \times 10^{1}$
$\phi^{\mathrm{o}}_{\tau\tau}$	$= -0.193\ 249\ 185 \times 10^{1}$	$\phi^{\mathrm{r}}_{\tau\tau}$	$= -0.223\ 440\ 737 \times 10^{1}$
$\phi^{\mathrm{o}}_{\delta\tau}$	$= 0$	$\phi^{\mathrm{r}}_{\delta\tau}$	$= -0.112\ 176\ 915 \times 10^{1}$

[a] For the abbreviated notation of the derivatives of ϕ^{o} and ϕ^{r} see the footnotes of Tables 4 and 5, respectively.

Table 7. Thermodynamic property values in the single-phase region for selected values of T and ρ

T/K	$\rho/$ (kg m^{-3})	p/MPa	$c_v /$(kJ kg^{-1} K^{-1})	$w/$(m s^{-1})	$s/$(kJ kg^{-1} K^{-1})
300	$0.996\ 556\ 0 \times 10^{3}$	$0.992\ 418\ 352 \times 10^{-1}$[a]	$0.413\ 018\ 112 \times 10^{1}$	$0.150\ 151\ 914 \times 10^{4}$	$0.393\ 062\ 643$
	$0.100\ 530\ 8 \times 10^{4}$	$0.200\ 022\ 515 \times 10^{2}$	$0.406\ 798\ 347 \times 10^{1}$	$0.153\ 492\ 501 \times 10^{4}$	$0.387\ 405\ 401$
	$0.118\ 820\ 2 \times 10^{4}$	$0.700\ 004\ 704 \times 10^{3}$	$0.346\ 135\ 580 \times 10^{1}$	$0.244\ 357\ 992 \times 10^{4}$	$0.132\ 609\ 616$
500	$0.435\ 000\ 0$	$0.999\ 679\ 423 \times 10^{-1}$	$0.150\ 817\ 541 \times 10^{1}$	$0.548\ 314\ 253 \times 10^{3}$	$0.794\ 488\ 271 \times 10^{1}$
	$0.453\ 200\ 0 \times 10^{1}$	$0.999\ 938\ 125$	$0.166\ 991\ 025 \times 10^{1}$	$0.535\ 739\ 001 \times 10^{3}$	$0.682\ 502\ 725 \times 10^{1}$
	$0.838\ 025\ 0 \times 10^{3}$	$0.100\ 003\ 858 \times 10^{2}$	$0.322\ 106\ 219 \times 10^{1}$	$0.127\ 128\ 441 \times 10^{4}$	$0.256\ 690\ 919 \times 10^{1}$
	$0.108\ 456\ 4 \times 10^{4}$	$0.700\ 000\ 405 \times 10^{3}$	$0.307\ 437\ 693 \times 10^{1}$	$0.241\ 200\ 877 \times 10^{4}$	$0.203\ 237\ 509 \times 10^{1}$
647	$0.358\ 000\ 0 \times 10^{3}$	$0.220\ 384\ 756 \times 10^{2}$	$0.618\ 315\ 728 \times 10^{1}$	$0.252\ 145\ 078 \times 10^{3}$	$0.432\ 092\ 307 \times 10^{1}$
900	$0.241\ 000\ 0$	$0.100\ 062\ 559$	$0.175\ 890\ 657 \times 10^{1}$	$0.724\ 027\ 147 \times 10^{3}$	$0.916\ 653\ 194 \times 10^{1}$
	$0.526\ 150\ 0 \times 10^{2}$	$0.200\ 000\ 690 \times 10^{2}$	$0.193\ 510\ 526 \times 10^{1}$	$0.698\ 445\ 674 \times 10^{3}$	$0.659\ 070\ 225 \times 10^{1}$
	$0.870\ 769\ 0 \times 10^{3}$	$0.700\ 000\ 006 \times 10^{3}$	$0.266\ 422\ 350 \times 10^{1}$	$0.201\ 933\ 608 \times 10^{4}$	$0.417\ 223\ 802 \times 10^{1}$

[a] In the liquid-water region at low pressures small changes in density along an isotherm cause large changes in pressure. For this reason, due to an accumulation of small errors, a particular computer code or a particular PC may fail to reproduce the pressure value with nine significant figures.

Table 8. Thermodynamic property values in the two-phase region for selected values of temperature[a]

	$T = 275$ K	$T = 450$ K	$T = 625$ K
p_σ/MPa	$0.698\ 451\ 167 \times 10^{-3}$	$0.932\ 203\ 564$	$0.169\ 082\ 693 \times 10^{2}$
$\rho'/$(kg m^{-3})	$0.999\ 887\ 406 \times 10^{3}$	$0.890\ 341\ 250 \times 10^{3}$	$0.567\ 090\ 385 \times 10^{3}$
$\rho''/$(kg m^{-3})	$0.550\ 664\ 919 \times 10^{-2}$	$0.481\ 200\ 360 \times 10^{1}$	$0.118\ 290\ 280 \times 10^{3}$
$h'/$(kJ kg^{-1})	$0.775\ 972\ 202 \times 10^{1}$	$0.749\ 161\ 585 \times 10^{3}$	$0.168\ 626\ 976 \times 10^{4}$
$h''/$(kJ kg^{-1})	$0.250\ 428\ 995 \times 10^{4}$	$0.277\ 441\ 078 \times 10^{4}$	$0.255\ 071\ 625 \times 10^{4}$
$s'/$(kJ kg^{-1} K^{-1})	$0.283\ 094\ 670 \times 10^{-1}$	$0.210\ 865\ 845 \times 10^{1}$	$0.380\ 194\ 683 \times 10^{1}$
$s''/$(kJ kg^{-1} K^{-1})	$0.910\ 660\ 121 \times 10^{1}$	$0.660\ 921\ 221 \times 10^{1}$	$0.518\ 506\ 121 \times 10^{1}$

[a] All these test values were calculated from the Helmholtz free energy, Eq. (4), by applying the phase-equilibrium condition (Maxwell criterion).
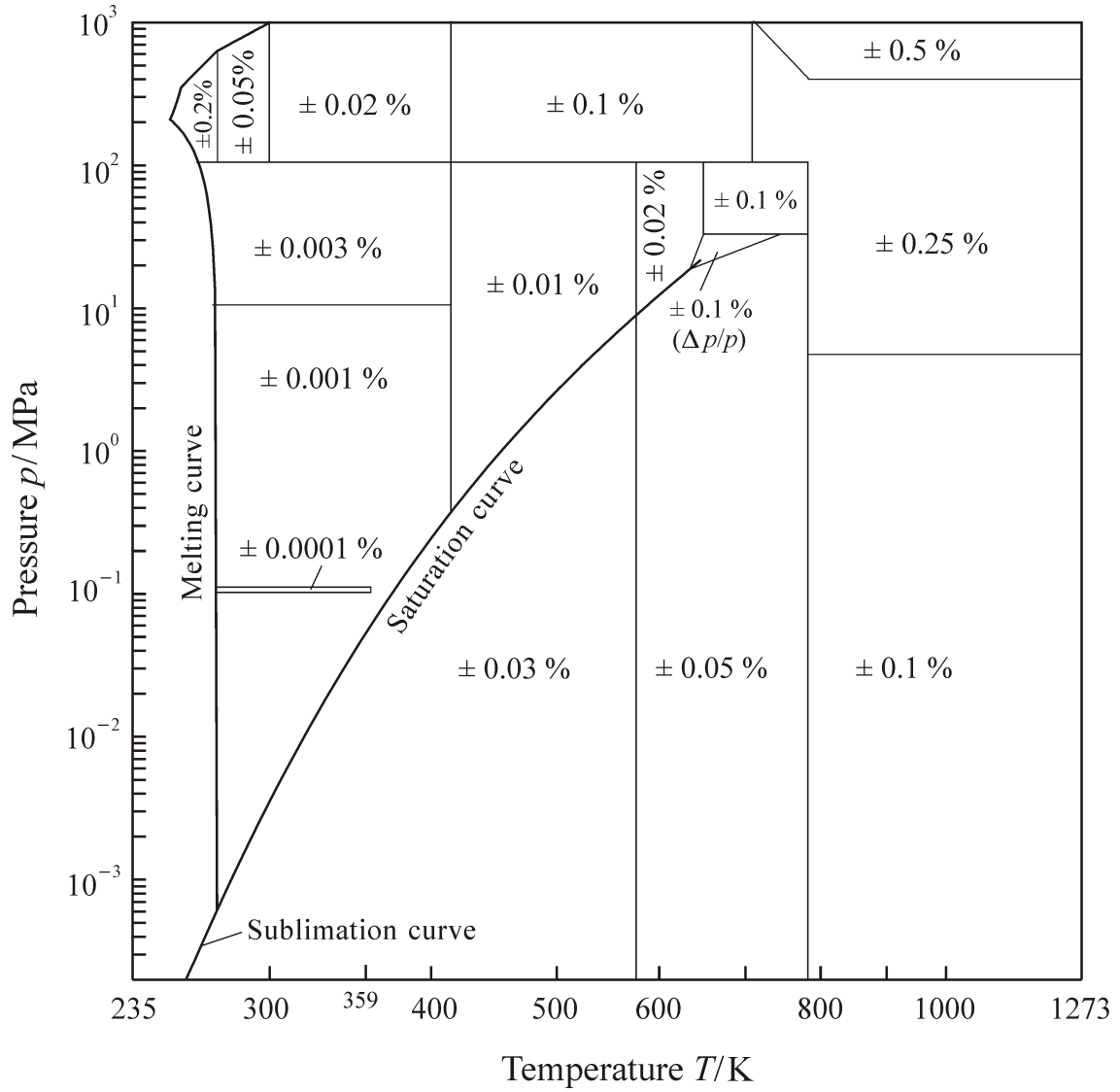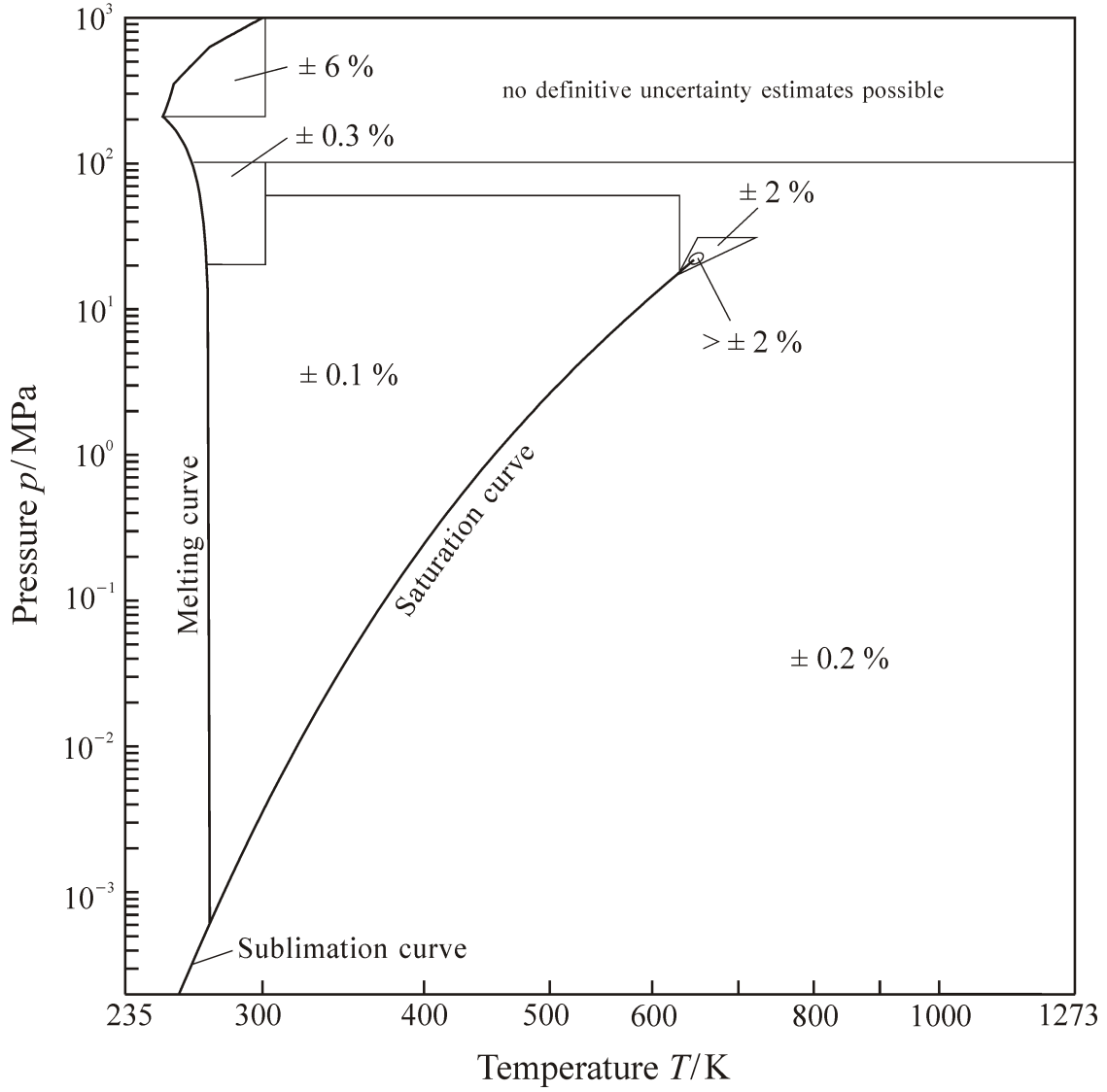
Fig. 1. Uncertainties in density, $\Delta\rho/\rho$, estimated for Eq. (4). In the enlarged critical region (triangle), the uncertainty is given as percentage uncertainty in pressure, $\Delta p/p$. This region is bordered by the two isochores 527 kg m^{-3} and 144 kg m^{-3} and by the 30 MPa isobar. The positions of the lines separating the uncertainty regions are approximate.
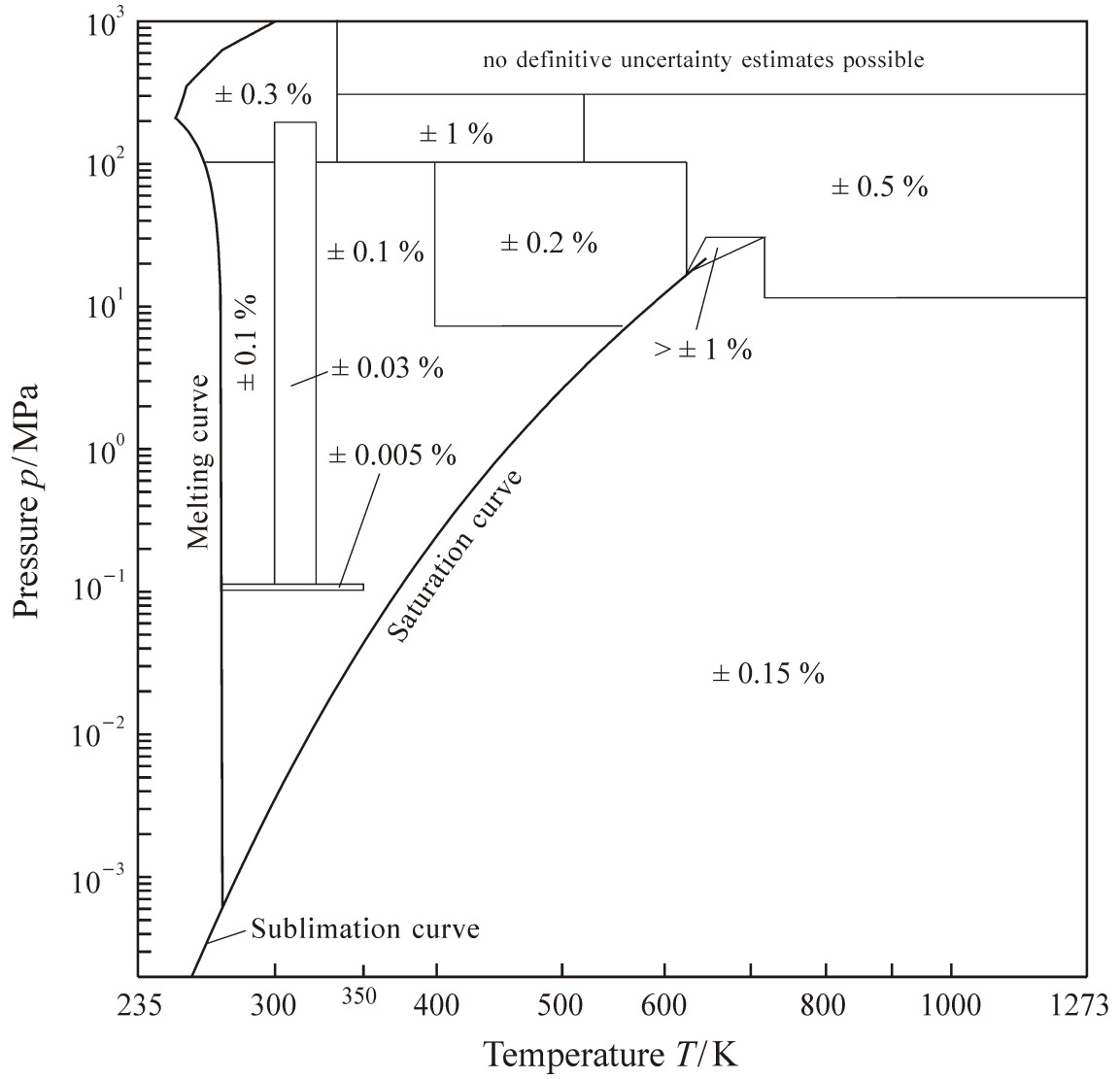
Fig. 2. Uncertainties in speed of sound, $\Delta w/w$, estimated for Eq. (4). For the uncertainty in the triangle around the critical point, see the remark in Section 6; for the definition of this region, see Fig. 1. The positions of the lines separating the uncertainty regions are approximate.

Fig. 3. Uncertainties in specific isobaric heat capacity, $\Delta c_p/c_p$, estimated for Eq. (4). For the uncertainty in the immediate vicinity of the critical point, see the remark in Section 6; for the definition of the triangle around the critical point, see Fig. 1. The positions of the lines separating the uncertainty regions are approximate.
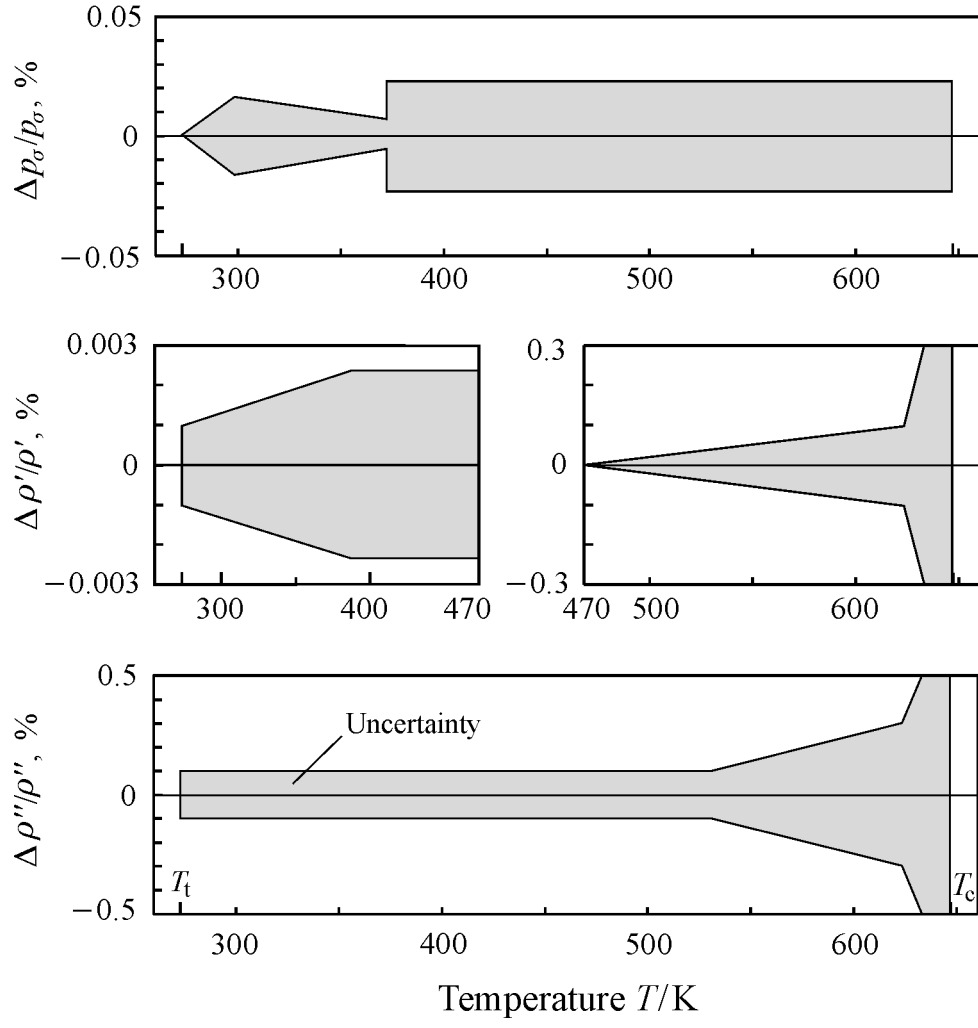
Fig. 4. Uncertainties in vapor pressure, $\Delta p_\sigma/p_\sigma$, in saturated liquid density, $\Delta\rho'/\rho'$, and in saturated vapor density, $\Delta\rho''/\rho''$, estimated for Eq. (4).