The International Association for the Properties of Water and Steam

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Guideline on Thermodynamic Properties of Supercooled Water

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Summary

The equation of state for cold and supercooled liquid H_2O (ordinary water substance) provided in this guideline is a fundamental equation for the Gibbs energy as a function of temperature and pressure; details of the equation can be found in Ref. [1].

This guideline contains 10 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 or from http://www.iapws.org.

Contents

1 Nomenclature

Thermodynamic quantities

c_p	Specific isobaric heat capacity
c_v	Specific isochoric heat capacity
g	Specific Gibbs energy
p	Pressure
R	Specific gas constant
s	Specific entropy
T	Absolute temperature (ITS-90)
u	Specific internal energy
v	Specific volume
w	Speed of sound
α_p	Thermal expansion coefficient, $\alpha_p = -(1/\rho)(\partial\rho/\partial T)_p$
κ_T	Isothermal compressibility, $\kappa_T = (1/\rho)(\partial\rho/\partial p)_T$
π	Reduced pressure, $\pi = p/(\rho_0 R T_{\mathrm{LL}})$
ρ	Mass density
τ	Reduced temperature, $\tau = (T/T_{\mathrm{LL}}) - 1$
ψ	Reduced Gibbs energy, $\psi = g/(R T_{\mathrm{LL}})$

Other dimensionless quantities

L	Ordering field
x	Mole fraction of low-density structure
ϕ	Order parameter
χ	Scaling susceptibility
ω	Interaction parameter

Subscripts

0	Reference quantity
LL	Liquid–liquid critical point
H	Homogeneous ice nucleation limit
t	Ice I–liquid–vapor triple point
π	Partial derivative with respect to π
τ	Partial derivative with respect to τ

Superscripts

r	Regular background contribution

2 Equation of State

The equation of state presented here is in the form of the dimensionless Gibbs energy $\psi = g/(RT_{\mathrm{LL}})$ as a function of temperature and pressure, corresponding to a Gibbs potential function. The expression for the Gibbs energy is based on a two-state model, in which water is considered as a mixture of a high-density structure and a low-density structure,

$$\psi(T,P) = \psi^{\mathrm{r}}(\tau,\pi) + (\tau+1)\left[xL(\tau,\pi) + x\ln x + (1-x)\ln(1-x) + \omega(\pi)x(1-x)\right], \tag{1}$$

where the reduced temperature τ and the reduced pressure π are defined as

$$\tau = \frac{T}{T_{\mathrm{LL}}} - 1, \qquad \pi = \frac{p}{\rho_0 R T_{\mathrm{LL}}}. \tag{2}$$

The values of reference parameters T_{LL} and ρ_0 and the specific gas constant R are given in Table 1. The dimensionless background Gibbs energy ψ^{r} is given by

$$\psi^{\mathrm{r}}(\tau,\pi) = \sum_{i=1}^{20} c_i(\tau+1)^{a_i}(\pi+\pi_0)^{b_i}\,\mathrm{e}^{-d_i(\pi+\pi_0)}. \tag{3}$$

The reference parameter π_0 is given in Table 1, and the coefficients a_i, b_i, and c_i are listed in Table 2. The field $L(\tau,\pi)$ has the form

$$L(\tau,\pi) = L_0\frac{K_2}{2k_1k_2}\left[1 + k_0k_2 + k_1(\pi + k_2\tau) - K_1\right], \tag{4}$$

where the values of L_0, k_0, k_1, and k_2 are given in Table 1, and K_1 and K_2 are given by

$$\begin{aligned} K_1 &= \left\{\left[1 + k_0k_2 + k_1(\pi - k_2\tau)\right]^2 - 4k_0k_1k_2(\pi - k_2\tau)\right\}^{1/2}, \\ K_2 &= (1+k_2^2)^{1/2}. \end{aligned} \tag{5}$$

The interaction parameter ω has a linear pressure dependence,

$$\omega(\pi) = 2 + \omega_0\pi, \tag{6}$$

with ω_0 given in Table 1. The mole fraction x of the low-density structure depends on pressure and temperature, and is found by minimizing the Gibbs energy as a function of x at constant temperature and pressure,

$$\left(\frac{\partial\psi}{\partial x}\right)_{T,p} = 0, \tag{7}$$

which corresponds to the condition

$$L(\tau,\pi) + \ln\frac{x}{1-x} + \omega(\pi)(1-2x) = 0\,. \tag{8}$$

This equation cannot be solved analytically for x, so the solution must be found numerically. Further information on solving this equation is given in Sec. 6.

Table 1. Parameter values for the equation of state

Parameter	Value	Parameter	Value	Unit
ω_0	0.521 226 9	T_{LL}	228.2	K
L_0	0.763 179 54	ρ_0	1081.648 2	kg m^{-3}
k_0	0.072 158 686	R	461.523 087	J kg^{-1} K^{-1}
k_1	−0.315 692 32			
k_2	5.299 260 8			
π_0	$\dfrac{300\times10^6\ \mathrm{Pa}}{\rho_0 R T_{\mathrm{LL}}}$			

Table 2. Parameter values for Eq. (3)

i	c_i	a_i	b_i	d_i
1	−8.157 068 138 165 5	0	0	0
2	1.287 503 2	0	1	0
3	7.090 167 359 801 2	1	0	0
4	$-3.277\,916\,1 \times 10^{-2}$	−0.2555	2.1051	−0.0016
5	$7.370\,394\,9 \times 10^{-1}$	1.5762	1.1422	0.6894
6	$-2.162\,862\,2 \times 10^{-1}$	1.6400	0.9510	0.0130
7	−5.178 247 9	3.6385	0	0.0002
8	$4.229\,351\,7 \times 10^{-4}$	−0.3828	3.6402	0.0435
9	$2.359\,210\,9 \times 10^{-2}$	1.6219	2.0760	0.0500
10	4.377 375 4	4.3287	−0.0016	0.0004
11	$-2.996\,777\,0 \times 10^{-3}$	3.4763	2.2769	0.0528
12	$-9.655\,801\,8 \times 10^{-1}$	5.1556	0.0008	0.0147
13	3.759 528 6	−0.3593	0.3706	0.8584
14	1.263 244 1	5.0361	−0.3975	0.9924
15	$2.854\,269\,7 \times 10^{-1}$	2.9786	2.9730	1.0041
16	$-8.599\,494\,7 \times 10^{-1}$	6.2373	−0.3180	1.0961
17	$-3.291\,615\,3 \times 10^{-1}$	4.0460	2.9805	1.0228
18	$9.001\,961\,6 \times 10^{-2}$	5.3558	2.9265	1.0303
19	$8.114\,972\,6 \times 10^{-2}$	9.0157	0.4456	1.6180
20	−3.278 821 3	1.2194	0.1298	0.5213

The values of the coefficients c_1 and c_3 in Table 2 do not affect measurable properties of liquid water. The values of these coefficients have been chosen such that values of the specific entropy and the specific Gibbs energy at the triple point satisfy the following conditions. The zero point of the specific entropy s has been chosen in accordance with the IAPWS convention that the specific entropy of liquid water is zero at the triple point,

$$s(T_\mathrm{t}, p_\mathrm{t}) = 0, \tag{9}$$

where T_t and p_t are the temperature and pressure at the ice Ih–liquid–vapor triple point [3,4],

$$\begin{aligned} T_\mathrm{t} &= 273.16\ \mathrm{K}, \\ p_\mathrm{t} &= 611.654\,771\,007\,894\ \mathrm{Pa}. \end{aligned} \tag{10}$$

The value for the triple-point pressure given here is not the experimental value, but was calculated [4] from the IAPWS-95 formulation and the equation of state of ice Ih. The calculated value agrees with the experimental value of (611.657 ± 0.010) Pa. In accordance with IAPWS convention, in the IAPWS-95 formulation [2] the internal energy u of liquid water is set to zero at the triple point given by Eq. (10). In the present formulation, the specific internal energy of liquid water at the triple point slightly deviates from zero and it is defined by the condition that the specific Gibbs energy g at the ice Ih–liquid–vapor triple point equals the specific Gibbs energy calculated from the IAPWS-95 formulation $g_{\mathrm{IAPWS\text{-}95}}$ [2],

$$g(T_\mathrm{t}, p_\mathrm{t}) = u(T_\mathrm{t}, p_\mathrm{t}) - T_\mathrm{t} s(T_\mathrm{t}, p_\mathrm{t}) + p_\mathrm{t} v(T_\mathrm{t}, p_\mathrm{t}) = g_{\mathrm{IAPWS\text{-}95}}(T_\mathrm{t}, p_\mathrm{t}). \tag{11}$$

By this choice, it is ensured that the temperature and pressure at the triple point computed from the present formulation for the liquid, the formulation IAPWS-95 [2] for the vapor, and the 2006 formulation for ice Ih [3], are equal to the values in Eq. (10) within the numerical precision.

3 Thermodynamic Properties

All thermodynamic properties can be derived from Eq. (1) by using the derivatives of the dimensionless Gibbs energy with respect to temperature and pressure. It is convenient to express the thermodynamic properties in terms of the order parameter ϕ and susceptibility χ, defined as

$$\phi = 2x - 1, \qquad \chi = \left(\frac{2}{1-\phi^2} - \omega \right)^{-1}. \tag{12}$$

The specific volume v is given by

$$v = \frac{1}{\rho_0}\left\{\frac{\tau+1}{2}\left[\frac{\omega_0}{2}(1-\phi^2) + L_\pi(\phi+1)\right] + \psi_\pi^{\mathrm{r}}\right\}, \tag{13}$$

and the mass density ρ is found from $\rho = 1/v$. In Eq. (13) and in the following equations, subscripts τ and π indicate partial derivatives with respect to the subscripted quantities. Expressions for the derivatives of L and ψ^{r} with respect to τ and π are given in Table 3.

The specific entropy s is given by

$$s = -R\left\{\frac{(\tau+1)L_\tau}{2}(\phi+1) + \left[xL + x\ln x + (1-x)\ln(1-x) + \omega x(1-x)\right] + \psi_\tau^{\mathrm{r}}\right\}. \tag{14}$$

The isothermal compressibility κ_T, thermal expansion coefficient α_p, and specific isobaric heat capacity c_p are given by

$$\begin{aligned}
\kappa_T &= \frac{\rho}{\rho_0^2 R T_{\mathrm{LL}}}\left\{\frac{\tau+1}{2}\left[\chi(L_\pi - \omega_0\phi)^2 - (\phi+1)L_{\pi\pi}\right] - \psi_{\pi\pi}^{\mathrm{r}}\right\}, \\
\alpha_p &= \frac{\rho}{\rho_0 T_{\mathrm{LL}}}\left\{\frac{L_{\tau\pi}}{2}(\tau+1)(\phi+1) + \frac{1}{2}\left[\frac{\omega_0(1-\phi^2)}{2} + L_\pi(\phi+1)\right] - \frac{(\tau+1)L_\tau}{2}\chi(L_\pi - \omega_0\phi) + \psi_{\tau\pi}^{\mathrm{r}}\right\}, \\
c_p &= -R(\tau+1)\left\{L_\tau(\phi+1) + \tfrac{1}{2}(\tau+1)\left[L_{\tau\tau}(\phi+1) - L_\tau^2\chi\right] + \psi_{\tau\tau}^{\mathrm{r}}\right\}.
\end{aligned} \tag{15}$$

The specific isochoric heat capacity c_v is found from the thermodynamic relation

$$c_v = c_p - \frac{T\alpha_p^2}{\rho\kappa_T}, \tag{16}$$

and the speed of sound w is found from

$$w = \left(\rho\kappa_T \frac{c_v}{c_p}\right)^{-1/2} = \left(\rho\kappa_T - \frac{T\alpha_p^2}{c_p}\right)^{-1/2}. \tag{17}$$

Table 3. Derivatives of L and ψ^{r}

Derivatives of L	Derivatives of ψ^{r} (see Note)
$L_\tau = \frac{L_0 K_2}{2}\left(1 + \frac{1 - k_0 k_2 + k_1(\pi - k_2\tau)}{K_1}\right)$	$\psi^{\mathrm{r}}_\tau = \sum_{i=1}^{20} c_i a_i \bar{\tau}^{a_i - 1} \bar{\pi}^{b_i} \mathrm{e}^{-d_i \bar{\pi}}$
$L_\pi = \frac{L_0 K_2 (K_1 + k_0 k_2 - k_1 \pi + k_1 k_2 \tau - 1)}{2 k_2 K_1}$	$\psi^{\mathrm{r}}_\pi = \sum_{i=1}^{20} c_i \bar{\tau}^{a_i} \bar{\pi}^{b_i - 1} (b_i - d_i \bar{\pi}) \mathrm{e}^{-d_i \bar{\pi}}$
$L_{\tau\tau} = -\frac{2 L_0 K_2 k_0 k_1 k_2^2}{K_1^3}$	$\psi^{\mathrm{r}}_{\tau\tau} = \sum_{i=1}^{20} c_i a_i (a_i - 1) \bar{\tau}^{a_i - 2} \bar{\pi}^{b_i} \mathrm{e}^{-d_i \bar{\pi}}$
$L_{\tau\pi} = \frac{2 L_0 K_2 k_0 k_1 k_2}{K_1^3}$	$\psi^{\mathrm{r}}_{\tau\pi} = \sum_{i=1}^{20} c_i a_i \bar{\tau}^{a_i - 1} \bar{\pi}^{b_i - 1} (b_i - d_i \bar{\pi}) \mathrm{e}^{-d_i \bar{\pi}}$
$L_{\pi\pi} = -\frac{2 L_0 K_2 k_0 k_1}{K_1^3}$	$\psi^{\mathrm{r}}_{\pi\pi} = \sum_{i=1}^{20} c_i \bar{\tau}^{a_i} \bar{\pi}^{b_i - 2} \left[(d_i \bar{\pi} - b_i)^2 - b_i\right] \mathrm{e}^{-d_i \bar{\pi}}$

Note: to simplify the expressions, the following shorthand definitions are used: $\bar{\tau} = \tau + 1$ and $\bar{\pi} = \pi + \pi_0$.

4 Range of Validity

The equation of state is recommended for the metastable liquid from the homogeneous ice nucleation temperature to the melting temperature at pressures from 0 MPa to 400 MPa. The equation is also valid for stable liquid states up to 300 K in the same pressure range, where IAPWS-95 remains the recommended formulation. In this latter region, calculated properties agree with those from IAPWS-95 within their mutual uncertainties. The equation of state behaves reasonably when extrapolated to 1000 MPa.

The homogeneous ice nucleation curve can be approximated by the fits given in Eqs. (18) and (19) [1]. There is a discontinuity in the slope of the homogeneous ice nucleation curve at approximately 181.4 K and 198.9 MPa, where Eqs. (18) and (19) intersect. Equation (18) is to be used at pressures below the discontinuity, and Eq. (19) at pressures above it.

For pressures in the range of 0 MPa to 198.9 MPa:

$$p_{\mathrm{H}} / \mathrm{MPa} = 0.1 + 228.27(1 - \theta^{6.243}) + 15.724(1 - \theta^{79.81}), \quad \text{with } \theta = T/(235.15\ \mathrm{K}). \tag{18}$$

For pressures in the range of 198.9 MPa to 1500 MPa:

$$T_{\mathrm{H}} / \mathrm{K} = 172.82 + 0.03718(p/\mathrm{MPa}) + 3.403\times10^{-5}(p/\mathrm{MPa})^2 - 1.573\times10^{-8}(p/\mathrm{MPa})^3. \tag{19}$$

Here T_{H} and p_{H} are the temperature and pressure on the homogeneous ice nucleation curve.

5 Estimates of Uncertainty

Estimates have been made of the uncertainty of the density and speed of sound when calculated from the equation of state. These estimates, shown in Figs. 1 and 2, were derived from comparisons with the various sets of experimental data.

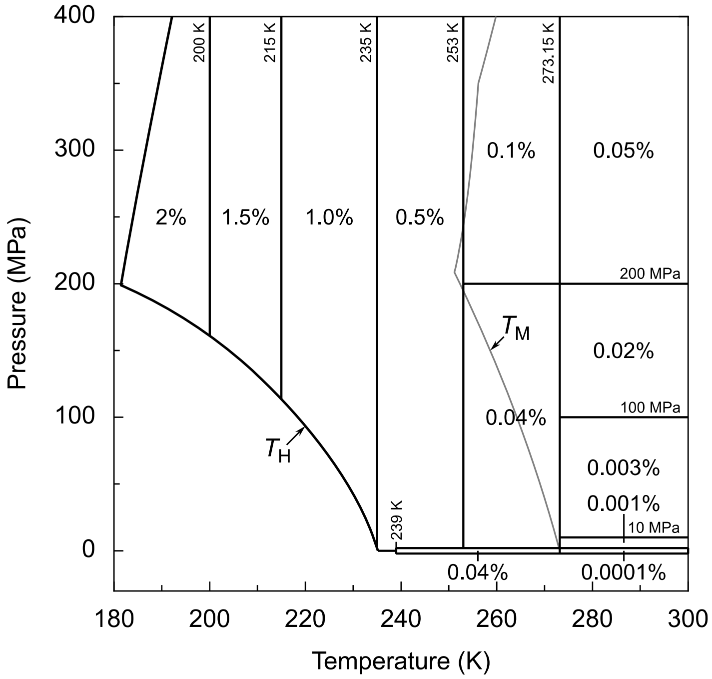

Fig. 1. Uncertainties in density estimated for Eq. (1). The thin rectangles around zero pressure refer to pressures near atmospheric ($0.09 \text{ MPa} < p < 0.11 \text{ MPa}$). T_M indicates the melting temperature [5] and T_H the homogeneous nucleation temperature (Sec. 4). The melting curve does not separate uncertainty regions.

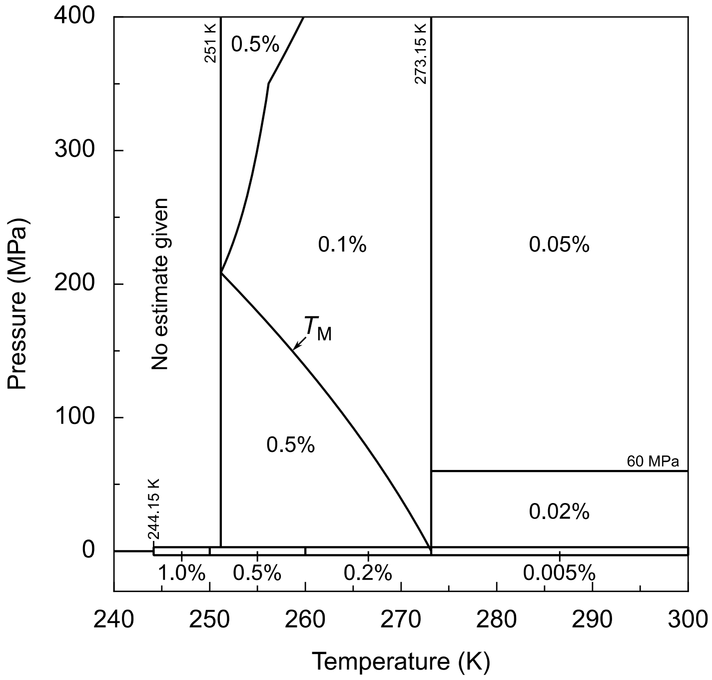

Fig. 2. Uncertainties in speed of sound estimated for Eq. (1). The thin rectangles around zero pressure refer to pressures near atmospheric ($0.09 \text{ MPa} < p < 0.11 \text{ MPa}$). T_M indicates the melting temperature [5]. In the region labeled "No estimate given", there are no experimental data for the speed of sound; this region extends down to the homogeneous nucleation temperature.

6 Solving Eq. (8)

To find x, Eq. (8) must be solved numerically. For some implementations, it is helpful or necessary to know the interval in which the solution is located. Table 4 provides several of these intervals for x, depending on the values of L and ω.

Table 4. Intervals in which x, the solution of Eq. (8), is located

Values of L and ω	Interval for x, containing the solution of Eq. (8)	
	Lower bound	Upper bound
$\omega < (10/9)\,[\ln(19) - L]$	0.049	0.5
$(10/9)\,[\ln(19) - L] \le \omega < (50/49)\,[\ln(99) - L]$	0.0099	0.051
$\omega \ge (50/49)\,[\ln(99) - L]$	$0.99\exp[-(50/49)L - \omega]$	$\min(1.1\exp(-L - \omega), 0.0101)$ [a]

[a] the "min" function returns the smallest of its arguments

7 Computer-Program Verification

For the verification of computer programs, Table 5 lists calculated values for several properties as well as values of x and L. To reproduce the values in Table 5 to the number of digits given, the solution for the fraction x should be accurate to 10^{-10}.

Table 5. Values for computer program verification

$\frac{T}{\mathrm{K}}$	$\frac{p}{\mathrm{MPa}}$	$\frac{\rho}{\mathrm{kg\,m^{-3}}}$	$\frac{\alpha_p}{10^{-4}\,\mathrm{K^{-1}}}$	$\frac{\kappa_T}{10^{-4}\,\mathrm{MPa^{-1}}}$	$\frac{c_p}{\mathrm{J\,kg^{-1}\,K^{-1}}}$	$\frac{w}{\mathrm{m\,s^{-1}}}$	x	L
273.15	0.101325	999.842 29	−0.683 042	5.088 499	4 218.300 2	1 402.388 6	0.096 654 715 5	0.621 204 74
235.15	0.101325	968.099 99	−29.633 816	11.580 785	5 997.563 2	1 134.585 5	0.255 102 858 7	0.091 763 68
250	200	1090.456 77	3.267 768	3.361 311	3 708.390 2	1 668.202 0	0.030 429 266 7	0.723 770 81
200	400	1185.028 00	6.716 009	2.567 237	3 338.525 0	1 899.329 4	0.007 170 080 9	1.155 396 5
250	400	1151.715 17	4.929 927	2.277 029	3 757.214 4	2 015.878 2	0.005 358 836 6	1.434 514 5

8 References

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