The International Association for the Properties of Water and Steam

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Guideline on a Low-Temperature Extension of the IAPWS-95 Formulation for Water Vapor

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This Guideline contains 5 pages, including this cover page.

This Guideline has been authorized by the International Association for the Properties of Water and Steam (IAPWS) at its meeting in Boulder, Colorado, USA, 30 September - 05 October, 2012, for issue by its Secretariat. The members of IAPWS are: Britain and Ireland, Canada, the Czech Republic, Germany, Japan, Russia, Scandinavia (Denmark, Finland, Norway, Sweden), and the United States, and associate members Argentina & Brazil, Australia, France, Greece, Italy, New Zealand, and Switzerland.

The equation of state provided in this Guideline is a low-temperature extension of the ideal-gas part of the IAPWS-95 formulation [1] for the specific Helmholtz energy of water as a function of temperature in the range between 50 K and 130 K; details can be found in the article “Thermodynamic Properties of Sea Air” by R. Feistel *et al.* [2]. This equation is numerically and thermodynamically consistent with the IAPWS Releases on ice Ih and on its sublimation pressure [3, 4]; it permits the computation of all thermodynamic properties of water vapor down to 50 K, and in particular the calculation of the sublimation pressure from the thermodynamic equilibrium condition between water vapor and ice Ih over the entire temperature range of validity of the IAPWS Revised Release [4].

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

Symbol	Physical quantity	Unit
c_p^{id}	Specific isobaric ideal-gas heat capacity, Eq. (6)	J kg^{-1} K^{-1}
E	Extension coefficient, Table 1	
f	IAPWS-95 specific Helmholtz free energy of fluid water	J kg^{-1}
k	Uncertainty coverage factor	
R^{95}	Specific gas constant of water, R^{95} = 461.51805 J kg^{-1} K^{-1}	J kg^{-1} K^{-1}
T	Absolute temperature (ITS-90)	K
T_c	Critical temperature of water, T_c = 647.096 K	K
T_E	Extension temperature, T_E = 130 K	K
δ	Reduced density, $\delta = \rho / \rho_\mathrm{c}$	
ε	Inverse reduced extension temperature, $\varepsilon = T_\mathrm{c} / T_\mathrm{E}$	
ϕ^r	Residual part of the IAPWS-95 formulation [1]	
ϕ^o	Ideal-gas part of the IAPWS-95 formulation [1]	
ϕ^ex	Extension part of the IAPWS-95 formulation, Eq. (2)	
ρ	Density of water	kg m^{-3}
ρ_c	Critical density of water, ρ_c = 322 kg m^{-3}	kg m^{-3}
τ	Inverse reduced temperature, $\tau = T_\mathrm{c} / T$	

2 Introductory Remarks and Special Constants

The “Revised Release on the Pressure along the Melting and Sublimation Curves of Ordinary Water Substance” [4] describes the sublimation curve of ice Ih in the temperature range between 50 K and 273.16 K. While the “Revised Release on the Equation of State 2006 for H_2O Ice Ih” [3] is valid over this range, the validity of the IAPWS-95 formulation [1] is restricted to temperatures above 130 K [5] as a result of the invalidity of the ideal-gas heat-capacity formula of water vapor [6] below that temperature. The modification described in this Guideline extends the validity of this heat-capacity equation down to 50 K and permits the computation of the gas-phase properties also in this low-temperature range.

TABLE 1 Special constants and values used in this Guideline

Quantity	Symbol	Value	Unit	Ref.
Specific gas constant of water[a]	R^{95}	461.51805	J kg^{-1} K^{-1}	[1]
Critical temperature of water	T_c	647.096	K	[1]
Critical density of water	ρ_c	322	kg m^{-3}	[1]
Extension temperature	T_E	130	K	[2]
Extension coefficient	E	0.278 296 458 178 592	-	[2]

[a]Value used in the IAPWS-95 formulation for water

3 The Extended Equation of State

The equation of state is represented here in terms of the specific Helmholtz energy of fluid water, f , expressed as a function of temperature T and density ρ. The temperatures are based on the temperature scale ITS-90 [7]. The Helmholtz function takes the form

$$f(T,\rho) = R^{95}T\left[\phi^{\mathrm{r}}(\tau,\delta) + \phi^{\mathrm{o}}(\tau,\delta) + \phi^{\mathrm{ex}}(\tau)\right] . \tag{1}$$

Here, R^{95} is the specific gas constant of water, given in Table 1, and ϕ^{r}, ϕ^{o}, respectively, are the residual and the ideal-gas part of the IAPWS-95 formulation [1]. The inverse reduced temperature and reduced density variables are defined as $\tau = T_c / T$ and $\delta = \rho / \rho_c$, respectively, with the values of T_c and ρ_c given in Table 1. The low-temperature extension $\phi^{\mathrm{ex}}(\tau)$ in the range $50\ \mathrm{K} \le T \le 130\ \mathrm{K}$ is given by

$$\phi^{\mathrm{ex}}(\tau) = E\left[-\frac{1}{2\tau} - \frac{3}{\varepsilon^2}(\tau+\varepsilon)\ln\frac{\tau}{\varepsilon} - \frac{9}{2\varepsilon} + \frac{9\tau}{2\varepsilon^2} + \frac{\tau^2}{2\varepsilon^3}\right], \tag{2}$$

and by $\phi^{\mathrm{ex}}(\tau) \equiv 0$ otherwise. Here, the inverse reduced extension temperature is $\varepsilon = T_c / T_E$ and the values of T_E and E are given in Table 1. The derivatives of $\phi^{\mathrm{ex}}(\tau)$ are given in Table 2.

TABLE 2 The derivatives of the extension of the Helmholtz function of fluid water, $\phi^{\mathrm{ex}}(\tau)$, Eq. (2), expressed in terms of derivatives of the dimensionless quantities with respect to the inverse reduced temperature, $\tau = T_{\mathrm{c}}/T$. The reducing temperature is T_{c} = 647.096 K, and the inverse reduced extension temperature is $\varepsilon = T_{\mathrm{c}}/T_{\mathrm{E}}$, where the values of T_{E} and E are given in Table 1.

Derivative of $\phi^{\mathrm{ex}}(\tau)$	Expression	Eq.
$\phi^{\mathrm{ex}}(\tau)$	$E\left[-\frac{1}{2\tau}-\frac{3}{\varepsilon^2}(\tau+\varepsilon)\ln\frac{\tau}{\varepsilon}-\frac{9}{2\varepsilon}+\frac{9\tau}{2\varepsilon^2}+\frac{\tau^2}{2\varepsilon^3}\right]$	(3)
$\phi_{\tau}^{\mathrm{ex}}(\tau) \equiv \frac{\mathrm{d}\phi^{\mathrm{ex}}}{\mathrm{d}\tau}$	$E\left(\frac{1}{2\tau^2}-\frac{3}{\tau\varepsilon}-\frac{3}{\varepsilon^2}\ln\frac{\tau}{\varepsilon}+\frac{3}{2\varepsilon^2}+\frac{\tau}{\varepsilon^3}\right)$	(4)
$\phi_{\tau\tau}^{\mathrm{ex}}(\tau) \equiv \frac{\mathrm{d}^2\phi^{\mathrm{ex}}}{\mathrm{d}\tau^2}$	$E\left(-\frac{1}{\tau}+\frac{1}{\varepsilon}\right)^3$	(5)

4 Range of Validity and Estimates of Uncertainty

The modification of the IAPWS-95 formulation, Eq. (2), is valid within the temperature range

$$50\ \mathrm{K} \le T \le 130\ \mathrm{K}.$$

In this range, the specific isobaric ideal-gas heat capacity computed from Eq. (1),

$$\frac{c_p^{\mathrm{id}}}{R^{95}} = 1-\tau^2\left(\frac{\mathrm{d}^2\phi^{\mathrm{o}}}{\mathrm{d}\tau^2}+\phi_{\tau\tau}^{\mathrm{ex}}\right) \qquad (6)$$

shows a root-mean-square deviation of 0.013 % from the data points reported by Woolley [8]. Assuming for those data the expanded (k = 2) uncertainty of 0.01 % that was estimated for c_p^{id} above 130 K [9], the expanded uncertainty of c_p between 50 K and 130 K can be estimated as $\sqrt{(2\times 0.013\%)^2+(0.01\%)^2} \approx 0.03\%$.

In the temperature range of this extension, the contribution of the residual part of IAPWS-95 to the thermodynamic properties of water vapor is negligible.

5 Computer-Program Verification

To assist the user in computer-program verification, Table 3 gives check values for specified temperatures. It contains values for the extension function $\phi^{\mathrm{ex}}(\tau)$ together with its first and second derivatives.

TABLE 3 Numerical check values for the extension function $\phi^{\mathrm{ex}}(\tau)$, Eq. (2), and its derivatives as given in Table 2, as well as for the ideal-gas heat capacity, Eq. (6), at the temperatures of 50 and 100 K

Quantity	T = 50 K	T = 100 K
ϕ^{ex}	$0.381\,124\,912 \times 10^{-2}$	$0.398\,019\,838 \times 10^{-5}$
$\phi^{\mathrm{ex}}_{\tau}$	$0.172\,505\,502 \times 10^{-2}$	$0.120\,506\,637 \times 10^{-4}$
$\phi^{\mathrm{ex}}_{\tau\tau}$	$0.525\,861\,643 \times 10^{-3}$	$0.277\,309\,851 \times 10^{-4}$
$c_p^{\mathrm{id}} / R^{95}$	$0.391\,824\,190 \times 10$	$0.400\,536\,708 \times 10$

6 References

[1] IAPWS, Revised Release on the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use (2009). Available from http://www.iapws.org

[2] Feistel, R., Wright, D. G., Kretzschmar, H.-J., Hagen, E., Herrmann, S., and Span, R., Thermodynamic Properties of Sea Air. *Ocean Sci.* **6**, 91-141 (2010). Available at http://www.ocean-sci.net/6/91/2010/

[3] IAPWS, Revised Release on the Equation of State 2006 for H_2O Ice Ih (2009). Available from http://www.iapws.org

[4] IAPWS, Revised Release on the Pressure along the Melting and Sublimation Curves of Ordinary Water Substance (2011). Available from http://www.iapws.org

[5] 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).

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

[7] Preston-Thomas, H., The International Temperature Scale of 1990 (ITS-90). *Metrologia* **27**, 3-10 (1990).

[8] Woolley, H. W., Thermodynamic Properties for H_2O in the Ideal Gas State, in: Straub, J., and Scheffler, K. (Eds.), *Water and Steam, Proceedings of the 9th International Conference on the Properties of Steam*, München, 1979. (Pergamon Press, Oxford, 1980), pp.166-175.

[9] Wagner, W., Riethmann, T., Feistel, R., and Harvey, A. H., New Equations for the Sublimation Pressure and Melting Pressure of H_2O Ice Ih. *J. Phys. Chem. Ref. Data* **40**, 043103 (2011).