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Revised Release on the Pressure along the Melting and Sublimation Curves of Ordinary Water Substance

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In 1993, IAPWS issued a “Release on the Pressure along the Melting and Sublimation Curves of Ordinary Water Substance.” The empirical equations presented were fitted to relatively old experimental data for the several sections of the melting curve and the sublimation curve. Thus, these equations are not thermodynamically consistent with the subsequently developed IAPWS equations of state for fluid and solid H₂O. These equations are “The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use” [1, 2] and “The Equation of State of H₂O Ice Ih” [3, 4]. In order to make the equations for the melting and sublimation pressures consistent with the IAPWS-95 formulation and the ice Ih equation of state, new equations for the melting pressure and sublimation pressure of ice Ih were developed. In addition, the melting-pressure equation of ice III was slightly modified to make it consistent with the melting-pressure equation of ice Ih at the triple point “ice Ih – ice III – liquid”, see Fig. 1. The melting-pressure equations for ice V, ice VI, and ice VII are unchanged. In 2011, the estimate for the uncertainty in ice Ih sublimation pressure was revised.

Further details about the newly developed equations and the estimation of the uncertainties in sublimation pressure presented in this release can be found in the article by W. Wagner *et al.* [5].

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>.

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1 Nomenclature

Thermodynamic quantities

p	Pressure
T	Temperature
θ	Reduced temperature, $\theta = T/T^*$
π	Reduced pressure, $\pi = p_{\text{melt}}/p^*$ and $\pi = p_{\text{subl}}/p^*$, respectively

Superscript

*	Reducing quantity
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Subscripts

melt	Value on the melting curve
subl	Value on the sublimation curve
t	Value at a triple point
calc	Calculated value
data	Input data used to develop the equations
exp	Experimental value

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

2 Introduction

Figure 1 shows the phase-boundary curves of water in a p - T diagram. In the context of this release, the phase boundaries between fluid water (gas and liquid) and solid water (ice) are of interest. These are the sublimation curve and the melting curves of the various phases of ice (ice Ih, ice III, ice V, ice VI, and ice VII).

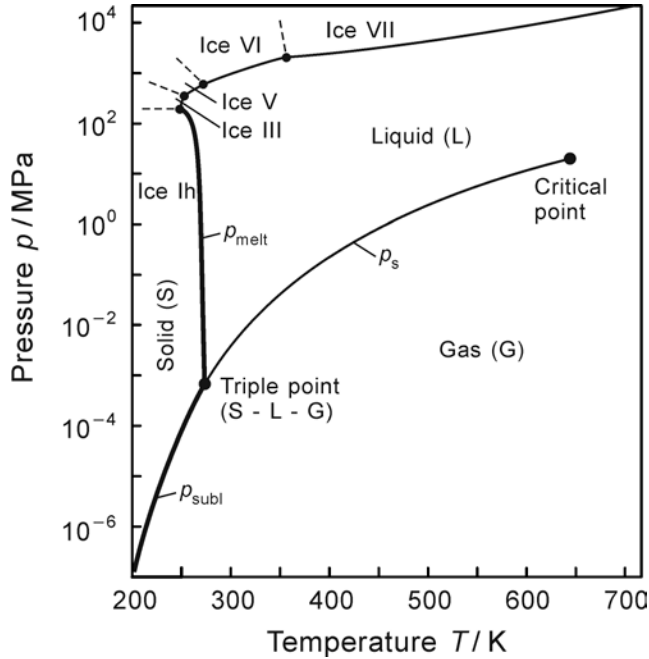


Fig. 1 Phase-boundary curves of water in a p - T diagram.

In the previous release of 1993 on this matter (see the Appendix of [6]), equations were presented that had been fitted to experimental p - T data along all of these phase-boundary curves. However, these relatively old data [6] are subject to larger uncertainties and scatter, and the sublimation-pressure data cover the sublimation curve only down to about 190 K.

In the meantime, equations of state for fluid water (IAPWS-95 formulation [1, 2]) and solid water (ice Ih equation [3, 4]) have been developed. With these equations and application of the phase-equilibrium condition, more accurate T - p values can be determined that are consistent with the properties of fluid water and ice Ih. For the sublimation curve, these data cover a temperature range from 130 K to 273.16 K and the entire ice Ih melting curve (251.165 K to 273.16 K). For the temperature range between 30 K and 130 K, sublimation pressures were calculated from a recently developed physical model [7]. The T - p values determined in this way were used to establish new equations for the melting pressure of ice Ih, Eq. (1), and for the sublimation pressure, Eq. (6). These two-phase boundaries are shown in Fig. 1 in bold. The melting-pressure equation of ice III was slightly modified to make it consistent with the ice Ih equation at the triple point ice Ih – ice III–liquid ($T = 251.165$ K).

3 Melting Pressure

3.1 Melting pressure of ice Ih (temperature range from 273.16 K to 251.165 K)

$$\pi = 1 + \sum_{i=1}^3 a_i (1 - \theta^{b_i}), \quad (1)$$

where $\pi = p_{\text{melt}}/p^*$ and $\theta = T/T^*$ with $T^* = T_t = 273.16$ K and $p^* = p_t = 611.657$ Pa; T_t and p_t are the values of the “normal” triple point (S–L–G). The coefficients a_i and exponents b_i are given by the values

$$\begin{aligned} a_1 &= 0.119\,539\,337 \times 10^7 & b_1 &= 0.300\,000 \times 10^1 \\ a_2 &= 0.808\,183\,159 \times 10^5 & b_2 &= 0.257\,500 \times 10^2 \\ a_3 &= 0.333\,826\,860 \times 10^4 & b_3 &= 0.103\,750 \times 10^3. \end{aligned}$$

3.2 Melting pressure of ice III (temperature range from 251.165 K to 256.164 K)

$$\pi = 1 - 0.299\,948 (1 - \theta^{60}), \quad (2)$$

where $\pi = p_{\text{melt}}/p^*$ and $\theta = T/T^*$ with $T^* = 251.165$ K and $p^* = 208.566$ MPa.

3.3 Melting pressure of ice V (temperature range from 256.164 K to 273.31 K)

$$\pi = 1 - 1.187\,21 (1 - \theta^8), \quad (3)$$

where $\pi = p_{\text{melt}}/p^*$ and $\theta = T/T^*$ with $T^* = 256.164$ K and $p^* = 350.1$ MPa.

3.4 Melting pressure of ice VI (temperature range from 273.31 K to 355 K)

$$\pi = 1 - 1.074\,76 (1 - \theta^{4.6}), \quad (4)$$

where $\pi = p_{\text{melt}}/p^*$ and $\theta = T/T^*$ with $T^* = 273.31$ K and $p^* = 632.4$ MPa.

3.5 Melting pressure of ice VII (temperature range from 355 K to 715 K)

$$\ln \pi = 0.173\,683 \times 10^1 (1 - \theta^{-1}) - 0.544\,606 \times 10^{-1} (1 - \theta^5) + 0.806\,106 \times 10^{-7} (1 - \theta^{22}), \quad (5)$$

where $\pi = p_{\text{melt}}/p^*$ and $\theta = T/T^*$ with $T^* = 355$ K and $p^* = 2216$ MPa.

Note: The upper value of the temperature range of Eq. (5) corresponds to the highest temperature for which measurements exist and not the end of the melting curve of ice VII.

Equations (2) to (5) are constrained to fit the experimental values T_t and p_t of the relevant triple points given in Table 1.

Table 1 Values for the triple points of the solid phases which coexist with the liquid

Coexisting phases	T_t/K	p_t/MPa
ice Ih – ice III – liquid	251.165	208.566 ^a
ice III – ice V – liquid	256.164	350.1
ice V – ice VI – liquid	273.31	632.4
ice VI – ice VII – liquid	355	2216

^a This is not the experimental triple-point pressure $p_{t,\text{exp}}$, but was calculated to make Eqs. (1) and (2) consistent with each other at this triple point. The difference ($p_{t,\text{exp}} - p_{t,\text{calc}}$) is 0.64% of the triple-point pressure, which is clearly within the 3% uncertainty of the experimentally determined triple-point pressure.

4 Sublimation Pressure

$$\ln \pi = \theta^{-1} \sum_{i=1}^3 a_i \theta^{b_i}, \quad (6)$$

where $\pi = p_{\text{subl}}/p^*$ and $\theta = T/T^*$ with $T^* = T_t = 273.16 \text{ K}$ and $p^* = p_t = 611.657 \text{ Pa}$; T_t and p_t are the values of the “normal” triple point (S–L–G). The coefficients a_i and exponents b_i are given by the values

$$\begin{aligned} a_1 &= -0.212\,144\,006 \times 10^2 & b_1 &= 0.333\,333\,333 \times 10^{-2} \\ a_2 &= 0.273\,203\,819 \times 10^2 & b_2 &= 0.120\,666\,667 \times 10^1 \\ a_3 &= -0.610\,598\,130 \times 10^1 & b_3 &= 0.170\,333\,333 \times 10^1. \end{aligned}$$

Note: Equation (6) is valid from 50 K to 273.16 K.

5 Range of Validity of the Equations

IAPWS endorses the validity of the equations presented in this release for each of the saturation lines. Equations (1) to (4) are valid for the entire range of the solid-liquid equilibrium. Equations (5) and (6) only cover the ranges of the solid-liquid or solid-vapor equilibrium, respectively, as indicated.

6 Estimates of Uncertainty

The estimated uncertainties of the melting and sublimation pressures calculated from Eqs. (1) to (6) are listed in Table 2. Based on the relatively high uncertainties of the experimental melting pressures, the derivatives of Eqs. (2) to (5) could be subject to larger errors.

Table 2 Estimated uncertainties of the calculated pressures

Equation	Equilibrium	Uncertainty
(1)	ice Ih – liquid	2%
(2)	ice III – liquid	3%
(3)	ice V – liquid	3%
(4)	ice VI – liquid	3%
(5)	ice VII – liquid	7%
(6)	ice Ih – gas	see Fig. 2 and Eqs. (7a) and (7b)

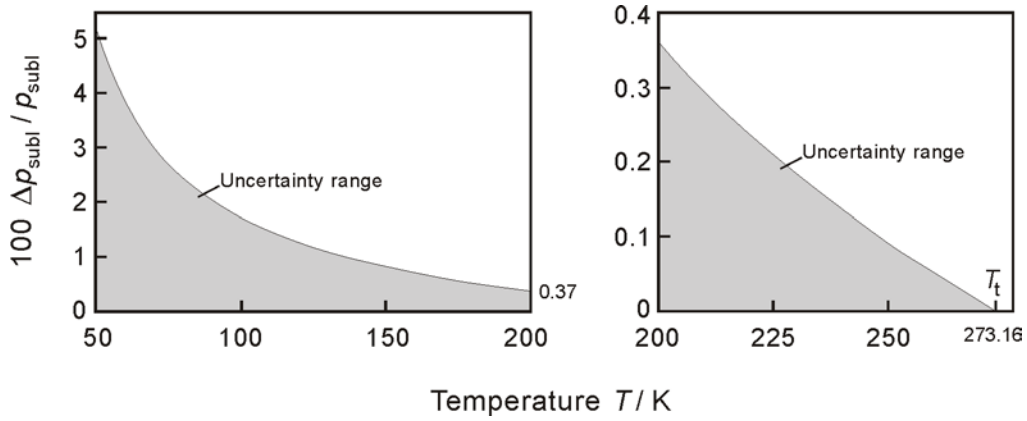


Fig. 2 Percentage uncertainties in pressure for the sublimation-pressure equation, Eq. (6). The uncertainties correspond to the expanded uncertainty with coverage factor $k = 2$. The estimate for the uncertainty at the triple-point temperature is 0.0011%.

The expanded uncertainty in sublimation pressure [Eq. (6)] was estimated from the following equations: For temperatures above 130 K

$$\left[\frac{U(p_{\text{subl}})}{p_{\text{subl}}} \right]^2 \approx (1.1 \times 10^{-5})^2 + \left[1 \times 10^{-2} \left(\frac{T_t}{T} - 1 \right) \right]^2 + \left[4 \times 10^{-4} \left(\frac{T_t}{T} - 1 - \ln \frac{T_t}{T} \right) \right]^2 \quad (7a)$$

and between 50 K and 130 K

$$\left[\frac{U(p_{\text{subl}})}{p_{\text{subl}}} \right]^2 \approx (1.1 \times 10^{-5})^2 + \left[1 \times 10^{-2} \left(\frac{T_t}{T} - 1 \right) \right]^2 + \left[1.4 \times 10^{-4} + 0.4 \times 10^{-1} \left(\frac{130 \text{ K}}{T} - 1 - \ln \frac{130 \text{ K}}{T} \right) \right]^2. \quad (7b)$$

Figure 2 is the graphical illustration of the results from Eqs. (7a) and (7b). The article by W. Wagner *et al.* [5] shows the derivation of these equations.

7 Computer-Program Verification

To assist the user in computer-program verification, Table 3 lists values for the pressures calculated from each of the six equations at one temperature within the range of validity.

Table 3 Pressures calculated from Eqs. (1) to (6) for selected temperatures

Equation	Equilibrium	T/K	p/MPa
(1)	ice Ih – liquid	260.0	138.268
(2)	ice III – liquid	254.0	268.685
(3)	ice V – liquid	265.0	479.640
(4)	ice VI – liquid	320.0	1356.76
(5)	ice VII – liquid	550.0	6308.71
(6)	ice Ih – gas	230.0	$8.947\,35 \times 10^{-6}$

8 References

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