International Equations for the Pressure Along the Melting and Along the Sublimation Curve of Ordinary Water Substance

Cite as: Journal of Physical and Chemical Reference Data 23, 515 (1994); https://doi.org/10.1063/1.555947
Submitted: 10 October 1992. Published Online: 15 October 2009

Wolfgang Wagner, A. Saul, and A. Pruss

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International Equations for the Pressure along the Melting and along the Sublimation Curve of Ordinary Water Substance

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Received October 10, 1992; revised manuscript received November 12, 1993

In order to define the phase boundary between the solid phase (ice) and the fluid phase (liquid and gas) of ordinary (light) water substance in pressure-temperature coordinates, correlation equations for the pressure along the melting curve of the various modifications of ice as well as for the pressure along the sublimation curve are presented. The five equations for the melting pressure of the ice phases ice I, ice III, ice V, ice VI, and ice VII, which only contain one to three fitted coefficients, cover the pressure range from the "normal" triple point to 20000 MPa. In this entire range the equations represent the selected measurements of the melting pressure within their experimental uncertainty. The 2-coefficient equation for the sublimation pressure covers the temperature range from 190 K to the triple point (273.16 K). The equations correspond to the new International Temperature Scale of 1990 (ITS-90). All these equations form the basis of the revised release on the pressure along the melting and sublimation curves of ordinary water substance. A verbatim copy of this release is presented in the Appendix of this paper.

Key words: correlation equations; melting line; sublimation line; water.

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Nomenclature

Symbol | Description
--- | ---
\( a \) | Adjustable coefficient
\( \varepsilon_p \) | Isobaric specific heat capacity
\( G \) | Gas
\( h \) | Specific enthalpy
\( i \) | Serial number
\( I \) | Maximum number of terms in an equation
\( L \) | Liquid
\( n \) | Exponent
\( p \) | Pressure
\( S \) | Solid
\( t \) | Exponent
\( T \) | Absolute temperature
\( v \) | Specific volume

Greek

\( \pi \) | Reduced pressure (\( \pi = p/p_0 \))
\( \theta \) | Reduced temperature (\( \theta = T/T_0 \))

Superscripts

\( + \) | Denotes the state of the solid phase on the melting-pressure curve and on the sublimation-pressure curve, respectively.
\( ' \) | Denotes the state of the liquid phase on the vapor-pressure curve.
\( '' \) | Denotes the state of the gas phase on the vapor-pressure curve and on the sublimation-pressure curve, respectively.
\( \text{gen} \) | General; full bank of terms.

Subscripts

calc | Calculated
expt | Experimental
\( i \) | Index
\( m \) | Denotes the melting pressure
\( n \) | Denotes a quantity used to normalize another quantity, e.g., \( \pi = p_m/p_0 \)
\( s \) | Denotes the vapor pressure
subl | Denotes the sublimation pressure
\( t \) | At a triple point

1. Introduction

The International Association for the Properties of Water and Steam (IAPWS) provides internationally accepted formulations for the properties of light and heavy steam, water and selected aqueous solutions for scientific and industrial applications. Besides publications on other properties there are the IAPWS approved equation of state, called IAPS-84,\(^1\) covering the fluid range of ordinary water substance (H\(_2\)O), and special correlation equations for the gas-liquid saturation properties of ordinary water substance.\(^2,3\)

In this context, it is the purpose of this paper to define the locus of the phase boundary in pressure-temperature coordinates between the fluid phases of water (liquid and gas) and solid water (ice). Based on the available data sources correlation equations for the sublimation pressure as well as for the melting pressures of the various modifications of ice (ice I, ice III, ice V, ice VI, and ice VII) are presented.

Figure 1 shows the phase-boundary curves of water in a p-\( T \) diagram. The curves for which correlation equations are given in this paper are drawn by bold lines. The equation for the vapor pressure \( p_v \) is described in the paper of Wagner et al.\(^2\) (ITS-90) which is a revision of the article of Saul and Wagner\(^1\) (IPTS-68) with regard to the temperature scale.

2. Melting Curves

One of the anomalies of water substance is the variety of modifications of the solid. Experimental melting-pressure data exist for the species ice I, ice III, ice V to ice VII along the solid-liquid phase boundaries. There is no set of equations which allows the calculation of the melting pressure for the whole phase boundary covered by experimental data. There are only correlation equations developed by Pistorius et al.\(^4\) and Mishima and Endo\(^5\) for the part of the melting curve where ice VII coexists with the liquid. Both authors use the Simon equation as well as a correlation equation in the form of a power series for the phase transition ice VII-liquid. The Simon equation

\[
\frac{p_m}{p_v} = 1 + a \left[ 1 - \left( \frac{T}{T_v} \right)^\gamma \right]
\]

is characterized by its simplicity; temperature can be obtained directly for a given pressure and it is very suitable for extrapolation purposes. However, neither Pistorius et al.\(^4\) nor Mishima and Endo\(^5\) were able to correlate their own measurements within the experimental uncertainty by the Simon equation. To yield a satisfactory representation of the experimental data both authors fitted power series to their own data.

The triple-point temperatures and the corresponding pressures where two solid phases coexist with the liquid are given in Table 1.

The melting curve is mainly described by the measurements of Bridgman\(^8\) obtained in the period 1912 to 1942. As the reference points for the calibration of pressure indicators were changed after Bridgman had taken his measurements, we corrected all pressures in accordance with the advice given by Babb.\(^7\) Moreover, all temperature values of the measurements were converted into the 1990 International Temperature Scale (ITS-90).\(^9,10\)

Besides the Bridgman data, Table 2 lists the selected data sets for the melting curve of water. The recalculated data of Mishima and Endo\(^5\) for the melting pressure of ice VII were not used because they are considered to be inconsistent with the data of the other authors.

Based on the selected data we have developed equations for the melting pressure of the phase transitions ice I-L, ice III-L, ice V-L, ice VI-L, and ice VII-L (ice II and ice IV are modifications of ice I) thermodynamic consistency with respect to the melting pressure of the various ice phases together with the exception of Eq. (2.8), which was derived from a general functional form of the equation and at the upper triple point was determined by the Clausius-Clapeyron equation. The following two expressions formed the bank of terms for all correlation equations of the melting pressure:

\[
\begin{align*}
\frac{P_{m}^{\text{gen}}}{P_n} &= 1 + \sum_{i=1}^{l} a_i \left[ 1 - \left( \frac{T}{T_n} \right)^q \right] \\
\ln \left( \frac{E_{m}^{\text{gen}}}{P_n} \right) &= \sum_{i=1}^{l} a_i \left[ 1 - \left( \frac{T}{T_n} \right)^q \right]
\end{align*}
\] (2.2)

where \( p_n \) and \( T_n \) are suitably chosen normalizing values for pressure and temperatures; see below. Eq. (2.2) corresponds to a general bank of terms of the Simon type. It was found that this type of equation provides a suitable formalism for the melting-pressure equations of ice I, ice III, ice V, and ice VI. The new equations (2.4) to (2.7) (see Table 3) represent all the experimental data within the estimated experimental uncertainty. Equations which were established on the basis of Eq. (2.3) behaved quite similarly (except for ice I) but did not improve the representation of the experimental data. For the ice VII region, however, the new general functional form defined by Eq. (2.3) is superior to the Simon equation and allowed the development of a melting-pressure equation for ice VII that represents all selected data within the experimental uncertainty given in Table 2. However, within the experimental uncertainty, the data of Holzapfel and Franck \( ^{14} \) and of Pistorius et al. \( ^{16} \) show systematic deviations of about -4%. The reason for this behavior is based on the fact that, just for fitting the equation, we shifted these data by about +4% to bring them into agreement with the more accurate data of Bridgman \( ^{7,8} \) and of Bendeliani and Vereschagin \( ^{15} \) for temperatures below 475 K. This "manipulation" was to stabilize the fitting process; of course, the comparison shown in Fig. 2 was carried out with the original, unshifted data.

To yield thermodynamic consistency at the triple points, with the exception of Eq. (2.8), each of the melting-pressure equations was fixed at the lower triple point (that one which corresponds to the lower pressure, see Table 1) by the choice of the functional form of the equation and at the upper triple point by a constraint. However, since, for phase equilibrium ice VII-liquid only one triple point is known, Eq. (2.8) was only fixed at the triple point ice VI-ice VII-L.

At the "normal" triple point solid-liquid-gas (S-L-G, S = ice I) thermodynamic consistency with respect to the internationally recommended vapor-pressure equation \( ^{12} [p_v(T) = P_v(T)] \) was achieved by calculating the reduced pressure \( \pi \) of the melting-pressure equation (2.4) with the \( p_v \) value obtained from the vapor-pressure equation at the triple point, namely \( P_v(T_0) = 611.657 \) Pa. Furthermore, the slope of the melting-pressure equation for ice I at the S-L-G triple point was fitted to the value determined as follows: At the S-L-G triple point the volume difference between the saturated liquid and the melting solid, \( \nu_L - \nu_m = -0.090 \text{ cm}^3/\text{g} \), is known from the measurements of Bridgman. \( ^{4} \) If one uses the value 333.66 \text{ J/g} calculated by Jancso et al. \( ^{16} \) for the enthalpy of melting namely, \( h_L - h_m = 333.66 \text{ J/g} \), the slope of the melting curve ice I-L at the triple point S-L-G can be determined from the Clausius-Clapeyron equation as \( dP_m/dT = -13.57 \text{ MPa/K} \).

3. Sublimation Curves

Several correlation equations for the sublimation pressure are known. The two latest versions are the five-coefficient equation of Jancso et al. \( ^{16} \) and the six-coefficient equation of Wexler, \( ^{18} \) which are based on temperatures according to the IPTS-68. These two equations cover the temperature range between 173 K and 273 K.

There are only a few experimental studies of the sublimation pressure of water. Information about the two data sets of Jancso et al. \( ^{16} \) and of Douslin and Osborn \( ^{19} \) is summarized in Table 4. The values of the experimental sublimation pressures given in the paper of Jancso et al. \( ^{16} \) had to be corrected because the capacitance manometer was calibrated by measuring the known pressure on the sublimation curve at 273.15 K which corresponded to a pressure at the triple point (273.16 K) of 611.283 Pa. Since, however, this value differs from the triple-point pressure which is internationally accepted at present, namely 611.657 Pa measured by Guildner et al., \( ^{17} \) we corrected the sublimation pressures of Jancso et al. \( ^{16} \) correspondingly.

To ensure thermodynamic consistency at the ice I-L-G triple point with respect to the vapor-pressure equation and to the melting-pressure equation for ice I \( [p_v(T) = P_{v1}(T) = p_1(T)] \), we fixed the sublimation-pressure equation at the triple-point pressure of 611.657 Pa by the choice of the functional structure. The slope of the sublimation pressure curve at the triple point was determined by the Clausius-Clapeyron equation

\[
\frac{dP_{subl}}{dT} = \frac{1}{T} \frac{h'' - h^*}{\nu'' - \nu^*}
\] (3.1)

In order to evaluate this equation at the ice I-L-G triple point, it can be written in the following form:

\[
\frac{dP_{subl}}{dT} = \frac{1}{T} \frac{(h'' - h^*)+(h'-h^*)}{(\nu'' - \nu^*+(\nu' - \nu^*)}.
\] (3.1a)
The values for the enthalpy of vaporization $h'' - h' = 2500.3$ kJ/kg and for the difference between the volume of the saturated vapor and liquid $v'' - v' = 206.030$ m$^3$/kg were obtained from the internationally recommended equations for the saturation line.\textsuperscript{21} The values for $h'' - h'$ as well as for $v'' - v'$ have already been given in Sec. 2. The resulting slope of the sublimation-pressure curve at the ice I-L-G triple point is determined as:

$$\frac{dP_{subl}}{dT} = 50.36 \text{ Pa} \quad \frac{K}{T=273.16 \text{ K}} \quad (3.2)$$

Based on a bank of terms similar to Eq. (2.3) and taking into account the selected data and the determined slope of the sublimation pressure at the triple point, the optimization procedure of Setzmann and Wagner\textsuperscript{15} yielded the following equation:

$$\ln \left[ \frac{P_{subl}}{P_i} \right] = a_1(1 - \theta^{-1}) + a_2(1 - \theta^0) + a_3(1 - \theta^2) \quad (3.3)$$

with $\theta = T/T_i, \ T_i = 273.16 \text{ K},$ and $P_i = 611.657 \text{ Pa}.$ The coefficients $a_1$ to $a_3$ are not given for the following reason. Although Fig. 3 shows that Eq. (3.3) represents the measured sublimation pressures (see Table 4) in the entire temperature range $190 \text{ K} \leq T \leq 273.16 \text{ K}$ within the scattering of the data, Eq. (3.3) yields values for the derivatives which are not sufficiently accurate. The good representation of the experimental sublimation pressures, especially at temperatures below $240 \text{ K},$ leads to incorrect derivatives $dP_{subl}/dT$ and $d^2P_{subl}/dT^2.$ Rabinovitch\textsuperscript{20} found this out when calculating the molar isobaric heat capacity $c_p^s$ of the solid ice I on the sublimation-pressure curve from the relation

$$c_p^s = c_p^s - T \frac{d^2P_{subl}}{dT^2} (v'' - v')$$

$$- 2T \frac{dP_{subl}}{dT} \left[ \left( \frac{\partial v''}{\partial T} \right)_p - \left( \frac{\partial v'}{\partial T} \right)_p \right]$$

$$- T \left( \frac{dP_{subl}}{dT} \right)^2 \left[ \left( \frac{\partial v''}{\partial p} \right)_T - \left( \frac{\partial v'}{\partial p} \right)_T \right], \quad (3.4)$$

which can be derived from Eq. (3.1). When Rabinovitch determined the needed derivatives of the sublimation pressure from the IPTS-68 version of Eq. (3.3),\textsuperscript{21} he obtained physically unreasonable values for $c_p^s$ and for $T \leq 240 \text{ K}$ he found even negative values. The reason for this misguided behavior is not based on incorrect values for $c_p^s,$ $v'',$ $v'$, and the derivatives of $v$ and $v''$ (there are correlation equations in literature which are sufficiently accurate) but on the values of the derivatives $dP_{subl}/dT$ and $d^2P_{subl}/dT^2,$\textsuperscript{2} which were not sufficiently accurate.

The reason for obtaining incorrect derivatives from Eq. (3.3) is that the experimental sublimation pressures especially at lower temperatures must have much larger experimental uncertainties than estimated by Jancso et al.\textsuperscript{16} and by Doussin and Osborn,\textsuperscript{18} see Table 4.

Thus, the new sublimation-pressure equation could not be developed by using the experimental sublimation pressures as the only input data. In order to extend the data base for the new sublimation-pressure equation, we calculated $dP_{subl}/dT$ and $d^2P_{subl}/dT^2$ from Eq. (3.1) where the enthalpy of sublimation $(h'' - h')$ and the specific volume $v''$ of the gas on the desublimation line were determined from correlation equations given by Wexler.\textsuperscript{18} Then, based on the bank of terms similar to Eq. (2.3) and taking into account the experimental sublimation pressures with a low weight and the calculated derivatives $dP_{subl}/dT$ and $d^2P_{subl}/dT^2$ with relatively high weights, the optimization procedure of Setzmann and Wagner\textsuperscript{15} iteratively used in combination with a nonlinear least-squares procedure yielded the following equation:

$$\ln \left( \frac{P_{subl}}{P_i} \right) = a_1(1 - \theta^{-1.2}) + a_2(1 - \theta^{-1.2}) \quad (3.5)$$

with $\theta = T/T_i, \ T_i = 273.16 \text{ K}, \ P_i = 611.657 \text{ Pa}, \ a_1 = -13.9281690,$ and $a_2 = 34.7078238.$ Eq. (3.5) is valid for the temperature range $190 \text{ K} \leq T \leq 273.16 \text{ K}.$ Fig. 4 shows that for temperatures above $245 \text{ K},$ Eq. (3.5) represents the experimental sublimation pressures within their scattering. The lower, absolute deviation diagram of Fig. 4 illustrates the systematic deviations between the experimental data and the values calculated from Eq. (3.5); these deviations are "necessary" to obtain the correct derivatives from Eq. (3.5). The very good agreement between Eq. (3.5) and Wexler's six-coefficient equation is not surprising because a part of the input data (the derivatives) used to establish Eq. (3.5) were calculated from Wexler's auxiliary equations given in Ref. 18. In this way, Eq. (3.5) is partly based on Wexler's concept to establish a sublimation-pressure equation based on theoretical considerations. We mainly used Wexler's "physically correct" derivatives of the sublimation pressure instead of adhering too closely to uncertain experimental data. As well as Wexler's equation,\textsuperscript{18} Eq. (3.5) also yields physically meaningful $c_p^s$ values when applying Eq. (3.4).

All in all, Eq. (3.5) represents the sublimation pressure and the corresponding derivatives of the sublimation-pressure curve of water as well as Wexler's six-coefficient equation but this quality is achieved with only two fitted coefficients and Eq. (3.5) corresponds to ITS-90.

4. Estimates of Uncertainties and Computer-program Verification

The estimated uncertainties of the melting and sublimation pressures calculated from Eqs. (2.4) to (2.8) and (3.5) are listed in Table 5. Based on the relatively high uncertainties of the experimental melting pressures, the derivatives of Eqs. (2.4) to (2.8) could be subject to larger errors.

To assist the user in computer-program verification, Table 6 lists values for the pressures calculated from each of the six equations at one temperature within the range of validity.
PRESSURE ALONG MELTING AND SUBLIMATION CURVES OF WATER

Table 1. Values for the triple points of the solid phases which coexist with the liquid (L)

<table>
<thead>
<tr>
<th>Coexisting phases</th>
<th>$T_i/K$</th>
<th>$p_i/\text{MPa}$</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>ice I – ice III – L</td>
<td>251.165</td>
<td>209.9</td>
<td>Bridgman$^6$</td>
</tr>
<tr>
<td>ice III – ice V – L</td>
<td>256.164</td>
<td>350.1</td>
<td>Bridgman$^6$</td>
</tr>
<tr>
<td>ice V – ice VI – L</td>
<td>273.31</td>
<td>632.4</td>
<td>Bridgman$^6$</td>
</tr>
<tr>
<td>ice VI – ice VII – L</td>
<td>355</td>
<td>2216</td>
<td>Bridgman$^7$</td>
</tr>
</tbody>
</table>

Table 2. Selected data sets for the melting pressure $p_m$ and estimated total experimental uncertainties in pressure

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Temp. range $T/K$</th>
<th>Number of data$^a$</th>
<th>Ice phase</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bridgman$^6$</td>
<td>1912</td>
<td>251 – 273</td>
<td>5</td>
<td>I</td>
<td>± 3% MPa</td>
</tr>
<tr>
<td>Henderson &amp; Speedy$^{12}$</td>
<td>1987</td>
<td>258 – 274</td>
<td>9 (10)</td>
<td>I</td>
<td>± 0.5 MPa</td>
</tr>
<tr>
<td>Bridgman$^6$</td>
<td>1912</td>
<td>251 – 256</td>
<td>4</td>
<td>III</td>
<td>± 3% MPa</td>
</tr>
<tr>
<td>Bridgman$^6$</td>
<td>1912</td>
<td>256 – 273</td>
<td>7</td>
<td>V</td>
<td>± 3% MPa</td>
</tr>
<tr>
<td>Bridgman$^6$</td>
<td>1912</td>
<td>200 – 334</td>
<td>13</td>
<td></td>
<td>± 3% MPa</td>
</tr>
<tr>
<td>Bridgman$^6$</td>
<td>1937</td>
<td>325 – 355</td>
<td>6</td>
<td>VI</td>
<td>± 3% MPa</td>
</tr>
<tr>
<td>Bridgman$^7$</td>
<td>1942</td>
<td>298</td>
<td>1</td>
<td></td>
<td>± 3% MPa</td>
</tr>
<tr>
<td>Bendeliani &amp; Vereschagin$^{13}$</td>
<td>1969</td>
<td>298 + 331</td>
<td>1 (2)</td>
<td></td>
<td>± 3% MPa</td>
</tr>
<tr>
<td>Bridgman$^7$</td>
<td>1937</td>
<td>355 – 465</td>
<td>10</td>
<td></td>
<td>± 3% MPa</td>
</tr>
<tr>
<td>Bridgman$^8$</td>
<td>1942</td>
<td>355 – 448</td>
<td>3</td>
<td></td>
<td>± 3% MPa</td>
</tr>
<tr>
<td>Holzapfel &amp; Franck$^{14}$</td>
<td>1969</td>
<td>350 – 620</td>
<td>20</td>
<td>VII</td>
<td>± 10% MPa</td>
</tr>
<tr>
<td>Pistorius et al.$^7$</td>
<td>1963</td>
<td>473 – 700</td>
<td>14</td>
<td></td>
<td>± 10% MPa</td>
</tr>
<tr>
<td>Bendeliani &amp; Vereschagin$^{13}$</td>
<td>1969</td>
<td>378 – 619</td>
<td>7</td>
<td></td>
<td>± 5% MPa</td>
</tr>
</tbody>
</table>

$^a$If the number of selected data does not correspond to the total number of data, the latter is given in brackets.

Table 3. Equations for the melting pressure of the various ice phases of ordinary water ($\theta=TI/T_i$ and $\pi=p_i/p_i$)

<table>
<thead>
<tr>
<th>Ice phase</th>
<th>Temp. range $T/K$</th>
<th>Pressure range $p/\text{MPa}$</th>
<th>$T_i/K$</th>
<th>$p_i/\text{MPa}$</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>273.16 – 251.165</td>
<td>0.000611657</td>
<td>273.16</td>
<td>0.000611657</td>
<td>$\pi=1.055177 \times 10^6 (1-\theta^{-3})$ (2.4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-209.9$</td>
<td></td>
<td></td>
<td>$+0.197135 \times 10^6 (1-\theta^{-15})$ (2.5)</td>
</tr>
<tr>
<td>III</td>
<td>251.165 – 256.164</td>
<td>209.9 – 350.1</td>
<td>251.165</td>
<td>209.9</td>
<td>$\pi=1.059025 \times 10^6 (1-\theta^0)$ (2.6)</td>
</tr>
<tr>
<td>V</td>
<td>256.164 – 273.31</td>
<td>350.1 – 632.4</td>
<td>256.164</td>
<td>350.1</td>
<td>$\pi=1.18721 (1-\theta^0)$ (2.7)</td>
</tr>
<tr>
<td>VI</td>
<td>273.31 – 355</td>
<td>632.4 – 2216</td>
<td>273.31</td>
<td>632.4</td>
<td>$\pi=1.07476 (1-\theta^0)$ (2.8)</td>
</tr>
<tr>
<td>VII</td>
<td>355 – 715$^d$</td>
<td>2216 – 19910$^d$</td>
<td>355</td>
<td>2216</td>
<td>$\ln (\pi)=0.173683 \times 10^1 (1-\theta^{-1})$ (2.9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$-0.544606 \times 10^1 (1-\theta^0)$ (2.10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$+0.806106 \times 10^1 (1-\theta^0)$ (2.11)</td>
</tr>
</tbody>
</table>

$^d$These values do not characterize the end of the melting curve for ice VII but correspond to the highest temperature and pressure for which measurements exist.
Table 4. Selected data sets for the sublimation pressure $P_{\text{subl}}$ and their estimated total experimental uncertainties in pressure

<table>
<thead>
<tr>
<th>Authors</th>
<th>Temp.range $T$/K</th>
<th>Number of data</th>
<th>Uncertainty$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doussin &amp; Osborn$^9$</td>
<td>242 - 271</td>
<td>8</td>
<td>$\pm 3 \times 10^{-3}p$ ($\pm 3 \times 10^{-4}p$)</td>
</tr>
<tr>
<td>Janca et al.$^{16}$</td>
<td>194 - 271</td>
<td>77</td>
<td>$T \geq 230$ K: $\pm 5 \times 10^{-5}p$ ($\pm (3-4) \times 10^{-4}$ Pa)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$T &lt; 230$ K: $\pm 0.2$ Pa ($\pm (3-4) \times 10^{-3}$ Pa)</td>
</tr>
</tbody>
</table>

$^a$Uncertainty values given in brackets were estimated by ourselves.

Table 5. Estimated uncertainties of the calculated melting pressures, Eqs. (2.4 to 2.8), and the sublimation pressure, Eq. (3.3). For a comment on the uncertainty of the derivatives of the Eqs. (2.4) to (2.8) see Sec. 4.

<table>
<thead>
<tr>
<th>Equation</th>
<th>Equilibrium</th>
<th>Percentage uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2.4)</td>
<td>ice I - liquid</td>
<td>$\leq \pm 3$</td>
</tr>
<tr>
<td>(2.5)</td>
<td>ice III - liquid</td>
<td>$\leq \pm 3$</td>
</tr>
<tr>
<td>(2.6)</td>
<td>ice V - liquid</td>
<td>$\leq \pm 3$</td>
</tr>
<tr>
<td>(2.7)</td>
<td>ice VI - liquid</td>
<td>$\leq \pm 3$</td>
</tr>
<tr>
<td>(2.8)</td>
<td>ice VII - liquid</td>
<td>$\leq \pm 7$</td>
</tr>
<tr>
<td>(3.3)</td>
<td>ice I - gas</td>
<td>$T &lt; 250$ K: $\leq \pm 0.5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T \geq 250$ K: $\leq \pm 1$</td>
</tr>
</tbody>
</table>

Table 6. Pressure values calculated from Eqs. (2.4) to (2.8) and (3.3) at a selected temperature

<table>
<thead>
<tr>
<th>Equation</th>
<th>Equilibrium</th>
<th>$T$/K</th>
<th>$p$/MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2.4)</td>
<td>ice I - liquid</td>
<td>250</td>
<td>139.382</td>
</tr>
<tr>
<td>(2.5)</td>
<td>ice III - liquid</td>
<td>250</td>
<td>269.456</td>
</tr>
<tr>
<td>(2.6)</td>
<td>ice V - liquid</td>
<td>250</td>
<td>479.640</td>
</tr>
<tr>
<td>(2.7)</td>
<td>ice VI - liquid</td>
<td>250</td>
<td>1356.76</td>
</tr>
<tr>
<td>(2.8)</td>
<td>ice VII - liquid</td>
<td>250</td>
<td>6308.71</td>
</tr>
<tr>
<td>(3.3)</td>
<td>ice I - gas</td>
<td>230</td>
<td>0.0000089465</td>
</tr>
</tbody>
</table>
Fig. 1. The phase-boundary curves of water in a $pT$ diagram.
FIG. 2. Percentage deviation of the experimental melting pressures $P_{m, expt}$ from the values $P_{m, calc}$ calculated from Eq. (2.4) for ice I, Eq. (2.5) for ice III, Eq. (2.6) for ice V, Eq. (2.7) for ice VI, and Eq. (2.8) for ice VII.

Temperature $T/K$ vs. Temperature $T/K$.
Fig. 3. Percentage deviation $\Delta P_{\text{subl}} = (P_{\text{subl,exp}} - P_{\text{subl,cld}})/P_{\text{subl,exp}}$ and absolute deviations of the experimental sublimation pressures $P_{\text{subl,exp}}$ from values $P_{\text{subl,cld}}$ calculated from Eq. (3.3); the absolute deviation diagram only covers the lower temperature range from 190 K to 240 K. Values calculated from Wexler's equation\textsuperscript{18} are plotted for comparison.
FIG. 4. Percentage deviation $\Delta p_{\text{subl}} = (p_{\text{subl,exp}} - p_{\text{subl,calc}})/p_{\text{subl,exp}}$ and absolute deviations of the experimental sublimation pressures $p_{\text{subl,exp}}$ from values $p_{\text{subl,calc}}$ calculated from Eq. (3.5); the absolute deviation diagram only covers the lower temperature range from 190 K to 240 K. Values calculated from Wexler's equation$^{18}$ are plotted for comparison.
5. Acknowledgments

The authors are grateful to the Deutsche Forschungsgemeinschaft for financial support of this project. We would also like to thank the members of the Working Group “Thermophysical Properties of Water and Steam” of IAPWS for fruitful discussions. The comments of A. A. Alexandrov, I. R. Cooper, J. M. H. Levelt Sengers, O. Sifner, H. Sato, K. Watanabe and E. Whalley had a significant impact on the final form of this paper. We would especially like to thank one of the reviewers and also Prof. V. A. Rabinovitch for their important hints with regard to the consistency test of the sublimation-pressure equation via the \( c_p \) calculation.

6. References

20. V. A. Rabinovitch, Presentation at the 1992 IAPWS meeting in St. Petersburg.
Appendix

The International Association for the Properties of Water and Steam
Milan, Italy
September 1993

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

Unrestricted publication allowed in all countries.

Issued by the
International Association for the Properties of Water and Steam

President:
J. R. Cooper
Queen Mary and Westfield College
London E1 4NS England

Executive Secretary:
Dr. R. B. Dooley
Electric Power Research Institute
Palo Alto, California 94304 USA

This release is a revision of the edition of 1989 and contains 4 numbered pages.

This release has been authorized by the International Association for the Properties of Water and Steam (IAPWS) at its meeting in Milan, Italy, 12 – 18 September 1993, for issue by its Secretariat. The members of IAPWS are: Canada, Czech Republic, Denmark, the Federal Republic of Germany, France, Japan, Russia, the United Kingdom, and the United States of America, and the associate members are: Argentina and Italy.

IAPWS issued in 1989 a Release on the Pressure along the Melting and Sublimation Curves of Ordinary Water Substance based on the IPTS-68 temperature scale. This revised release has been prepared with the temperatures of the triple points and the coefficients in the correlation equations changed to correspond to the ITS-90. To obtain the values for the new coefficients, the equations have been refitted using the same input data but with temperatures converted to ITS-90.

Compared with the IPTS-68 temperatures in the original release, one more decimal place is given here to the converted ITS-90 temperatures. This ensures that any recalculation to the original IPTS-68 temperature values produces the same figures as given in the original source after rounding to the same number of decimal places. This increase by one decimal in the converted ITS-90 temperatures does not imply that these values have been redetermined or are more accurate than previously stated on IPTS-68. In the second revision, Eq. (6) has been replaced by a simpler equation which better represents the derivatives of the sublimation pressure. Moreover, the parameter in Eq. (4) has been adjusted for a better representation of the ice VI – ice VII – liquid triple point.

Further details about the equations presented in this release can be found in an article “International Equations for the Pressure along the Melting and the Sublimation Curves of Ordinary Water Substance” by W. Wagner, A. Saul, and A. Pruß, to be published in the Journal of Physical and Chemical Reference Data.

Further information about this release and other releases issued by IAPWS can be obtained from the Executive Secretary of IAPWS.

Equations for the Pressure along the Melting and the Sublimation Curves of Ordinary Water Substance

1 Nomenclature

Thermodynamic quantities:
\[ p = \text{Pressure} \]
\[ T = \text{Temperature} \]
\[ \theta = \frac{T}{T_n} \]
\[ \pi = \frac{p_{m}}{p_{n}} \]

Subscripts:
\[ m \] Denotes a value on the melting curve
\[ n \] Denotes a quantity used to obtain a dimensionless variable
\[ \text{subl} \] Denotes a value on the sublimation curve
\[ t \] Denotes a value at a triple point

Note: \[ T \] denotes absolute Temperature on the International Temperature Scale of 1990.
2 Melting Pressure

2.1 Melting pressure of ice I (temperature range from 273.16 to 251.165 K)

\[ \pi = 1 - 0.626000 \times 10^6 (1 - \theta^3) + 0.197135 \times 10^6 (1 - \theta^{31.2}) \]  
with \( T_n = 273.16 \) K and \( p_n = 0.000611657 \) MPa.

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

\[ \pi = 1 - 0.295252 (1 - \theta^{60}) \]  
with \( T_n = 251.165 \) K and \( p_n = 209.9 \) MPa.

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

\[ \pi = 1 - 1.18721 (1 - \theta^6) \]  
with \( T_n = 256.164 \) K and \( p_n = 350.1 \) MPa.

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

\[ \pi = 1 - 1.07476 (1 - \theta^{46}) \]  
with \( T_n = 273.31 \) K and \( p_n = 632.4 \) MPa.

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

\[ \ln(\pi) = 0.173683 \times 10^4 (1 - \theta^1) - 0.544606 \times 10^{-1} (1 - \theta^2) + 0.806106 \times 10^{-7} (1 - \theta^{22}) \]  
with \( T_n = 355 \) K and \( p_n = 2216 \) MPa.

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

Eqs. (1) to (5) are constrained to fit the experimental values \( T \) and \( p \) 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

<table>
<thead>
<tr>
<th>Coexisting phases</th>
<th>( T_n / K )</th>
<th>( p_n / \text{MPa} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ice I - ice III - liquid</td>
<td>251.165</td>
<td>209.9</td>
</tr>
<tr>
<td>ice III - ice V - liquid</td>
<td>256.164</td>
<td>350.1</td>
</tr>
<tr>
<td>ice V - ice VI - liquid</td>
<td>273.31</td>
<td>632.4</td>
</tr>
<tr>
<td>ice VI - ice VII - liquid</td>
<td>355</td>
<td>2216</td>
</tr>
</tbody>
</table>

3 Sublimation pressure

\[ \ln \left( \frac{p_n}{p_t} \right) = a_1 (1 - \theta^{1.5}) + a_2 (1 - \theta^{1.25}) \]  
with \( a_1 = -13.9281690 \) and \( a_2 = 34.7078238 \).

Note: Eq. (6) is valid from 190 to 273.16 K.

4 Range of validity of the equations

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

5 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. (1) to (5) could be subjected to larger errors.

<table>
<thead>
<tr>
<th>Equation</th>
<th>Equilibrium</th>
<th>Percentage uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) ice I - liquid</td>
<td>( T &lt; 250 ) K: ( \pm 3 )</td>
<td></td>
</tr>
<tr>
<td>(2) ice III - liquid</td>
<td>( T \geq 250 ) K: ( \pm 3 )</td>
<td></td>
</tr>
<tr>
<td>(3) ice V - liquid</td>
<td>( T &lt; 250 ) K: ( \pm 3 )</td>
<td></td>
</tr>
<tr>
<td>(4) ice VI - liquid</td>
<td>( T \geq 250 ) K: ( \pm 7 )</td>
<td></td>
</tr>
<tr>
<td>(5) ice VII - liquid</td>
<td>( T \geq 250 ) K: ( \pm 7 )</td>
<td></td>
</tr>
<tr>
<td>(6) ice I - gas</td>
<td>( T &lt; 250 ) K: ( \pm 0.1 )</td>
<td></td>
</tr>
</tbody>
</table>

6 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>
<thead>
<tr>
<th>Equation</th>
<th>Equilibrium</th>
<th>( T / K )</th>
<th>( p / \text{MPa} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) ice I - liquid</td>
<td>260.0</td>
<td>139.382</td>
<td></td>
</tr>
<tr>
<td>(2) ice III - liquid</td>
<td>254.0</td>
<td>269.456</td>
<td></td>
</tr>
<tr>
<td>(3) ice V - liquid</td>
<td>265.0</td>
<td>479.640</td>
<td></td>
</tr>
<tr>
<td>(4) ice VI - liquid</td>
<td>320.0</td>
<td>1356.76</td>
<td></td>
</tr>
<tr>
<td>(5) ice VII - liquid</td>
<td>550.0</td>
<td>6308.71</td>
<td></td>
</tr>
<tr>
<td>(6) ice I - gas</td>
<td>230.0</td>
<td>0.0000089465</td>
<td></td>
</tr>
</tbody>
</table>